

INVESTIGATION OF THE PYROLYSIS OF *ACACIA MEARNsii* DE WILD. UNDER DIFFERENT ATMOSPHERE CONDITIONS

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Abstract. *The present work aimed at investigating the effects of heating rate and atmosphere nature (N₂ or air) on the efficiency and kinetics parameters of the pyrolysis of Acacia mearnsii De Wild. Wood (black wattle). The pyrolysis behavior was experimentally investigated through thermogravimetry (TGA) and differential scanning calorimetry (DSC). The kinetics parameters were obtained from the dynamic runs which were performed from room temperature to 900 °C under heating rates ranging from 2 to 50 °C.min⁻¹. The dynamically obtained data were evaluated according to the Kissinger method. The results revealed that lower heating rates and air atmospheres (that is, O₂ availability) favor the completeness of biomass decomposition. DSC analysis showed that the investigated pyrolysis process takes place exothermically with enthalpies ranging from 13 to 0.9 J, according to the heating rate and atmosphere condition. Also, the calculated activation energies for the pyrolysis under nitrogen and air resulted E=154.0 and 171.5 kJ.mol⁻¹, respectively. The values are in accordance to previously reported results. The present work has contributed to better understand biomass pyrolysis processes, in particular the A. mearnsii pyrolysis, leading to an improvement of the presently applied methods for charcoal biomass conversion.*

Keywords: *pyrolysis, thermal analysis, kinetics, acacia, DSC, TGA.*

1. INTRODUCTION

It has been a growing interest in finding alternative ways of gradually substitutes the traditional fossil fuels matrix all over the world. In this context, biomass utilization for energy production plays an important role since it comprises a renewable resource and offers a means to utilize agricultural and forestry waste residues. Charcoal is a highly reactive solid carbon material which is the resulting residue of biomass pyrolysis. Compared to fossil fuels, charcoal has virtually no sulfur or mercury, and has a very low content of nitrogen and ash, (FONTES et al, 2005; ANTAL; MORTEN, 2003).

Wood is an intrinsically complex material, composed of many components which vary from species to species, and among the same species, with many factors as for example the location of the tree, (ANTAL et al., 2000; LIN, 2006; SYRED et al., 2006). Woody biomass has most frequently been used to obtain charcoal for energy conversion in domestic and industrial applications. However, upon suitable selection of the precursor species and applying controlled carbonization processes, wood can also be used to obtain advanced carbonaceous materials for application in chemical and pharmaceutical industry. (BYRNE; NAGLE, 1997) Additionally, activated carbons derived from chemically activated wood find application as adsorption agents for solvents, vapours and pollutants.

Since, in developing countries, charcoal is mostly produced in domestic small scale kilns, despite representing advantages concerning traditional fossil fuels substitution, the use and production of charcoal can be very harmful to the environment and to the populations involved. Many condensable and non condensable products and byproducts are emitted from the kiln exhaust, being the constituents and their distribution very dependent on raw materials and carbonization parameters such as temperature, pressure, gas flow environment and raw material characteristics (size and texture, crystallinity, presence of impurities) and others, (NAKAI et al., 2007; ANTAL et al., 2000; SYRED et al., 2006). Water and carbon dioxide are the main gaseous products evolved on thermal decomposition of woody samples. Other components are organic pollutants such as furans and carbonyl derivatives. Also, alcohols, acids and aliphatic hydrocarbons are minor products. Many of these constituents, if not appropriately collected and disposed, can seriously contaminate the surrounding areas including air, water and ground pollution, (HALOUANI; FARHAT, 2003).

Acacia mearnsii de Wild., know as black wattle, is a fast-growing and short-leaved tree which contains high levels of condensed tannin in its bark (over 40 wt% - dry basis, being widely used for the production of charcoal in countries like Brazil, China, India, South Africa, and eastern Africa (Kenya and Zimbabwe). Among the advantages of black wattle cultivation is the fact that the species fixes nitrogen in the soil, making it useful in soil recovery. Also, the shape and anchoring of its radicle system make it useful in controlling erosion.

In Brazil, *Acacia mearnsii de Wild.* is mostly cultivated in the south region at an estimated area of 100,000 hectares, aiming the production of tannin for leather industry, (TONIETTO; STEIN, 1997; BYRNE; NAGLE, 1997). As a consequence, black wattle wood is used to provide cellulose, paper and charcoal, (CALDEIRA et al., 2002, 2003, 2004). Regarding the charcoal production, it is conducted by 10,000 small farmers in rudimentary (conventional) kilns,

(HIGA et al., 1998; TONIETTO; STEIN, 1997). Therefore this activity has a profound economical and social impact around the cultivated areas.

The present paper reports an experimental work aiming to investigate the effect of parameters such as pyrolysis temperature, heating rate and atmosphere on the yield and kinetics of the thermal decomposition process of *Acacia mearnsii de Wild.* (black wattle) wood harvested from the Brazilian south region farms. Experimental data were obtained via thermogravimetry and differential scanning calorimetry, performing dynamic experiments. Kinetic data were evaluated based on already described models. Isothermal runs were treated assuming first order kinetics (SFOR) and dynamic runs were obtained following the Ozawa and Kissinger methods which assume that the main decomposition reaction temperature shifts due to different heating rates at fixed conversions (MA; HILL; HENG, 1991; BIAGINI et al., 2002).. In both cases, rate constants were assumed to follow the Arrhenius law. The obtained results provide information for setting up pilot-scale combustor, optimizing traditional kilns and for designing more effective conversion systems.

2. EXPERIMENTAL

Wood from *Acacia mearnsii de Wild.* was taken from a farm and investigated as received. Samples consisted of cubes of approximately 5.3 mg ($\pm 5\%$) which were measured in a platinum crucible. Tests revealed that, within this mass range, mass transfer is not a limiting factor to be considered in the conditions used in the runs.

Thermogravimetric experiments were conducted on a Shimadzu TGA-50 equipment, under pure nitrogen or synthetic air flow rate of 75 mL.min⁻¹. Dynamic experiments were performed from room temperature to 900°C at heating rates of 2, 5, 10, 15, 20, 30 and 50°C.min⁻¹. For each set of variables, at least two reproducible experiments were considered.

Calorimetric experiments were carried out at a DSC-60 Shimadzu calorimeter, at the same rates employed in the TGA runs and at the same gas flux. Both, pure N₂ and synthetic air; were employed in order to check the influence of the ambient atmosphere on the pyrolysis behavior.

3. RESULTS AND DISCUSSION

3.1. Thermogravimetric Analysis

Typical TGA curves for the pyrolysis of black wattle wood, obtained at different heating rates, under nitrogen and air atmospheres, are given in Figs 1 and 2, respectively. Under nitrogen, the pyrolysis took place according to two clearly seen weight loss processes. The only exception was the curve at 2 °C.min⁻¹ which showed a three steps weight loss profile. On the other hand, under air, it could be observed three main step of devolatilization for all heating rates. According to what was discussed in a previous paper (RIEGEL et. al), the first weight loss step, at low temperature, can be attributed to loss of adsorbed water and the second one, at higher temperatures (250-450°C), can be imputed to the main biomass degradation. A third decomposition step could be observed at lower heating rate (2 °C.min⁻¹) under nitrogen and at all heating rates under air, leading to total biomass decomposition (total weight loss at 900°C). Under nitrogen, at other heating rates (5 to 50°C.min⁻¹) this third step manifested itself as a smooth mass decrease giving some residue at 900°C. Also, the behavior observed at 2 °C.min⁻¹ can be explained due to lower rate of diffusion process that takes place at lower heating rates.

Many authors (ÓRFÃO, 1999, 2001; ANTAL et al., 2000; SYRED et al., 2006; BYRNE, 1997) suggest that four simplified stages, based on slow heating rates, are involved on woody biomass pyrolysis: a) loss of adsorbed water, up to 150°C, b) starting of polymer decomposition (mainly hemicelluloses) with the release of some gases like carbon monoxide and carbon dioxide, and light liquids, as acetic acid and methanol, up to 300°C, c) intense chain scission or depolymerization characterized by the beginning of lignin and cellulose decomposition which dominates the weight loss process at this step that occurs around 240-400°C; d) decomposition of remaining lignin, above 400°C.

In our experiments, steps two and three, discussed above, could not be seen as distinguishable steps. Also, from Figs 1 and 2 it can be concluded that lower heating rates and air atmospheres (that is, O₂ availability) favor the completeness of biomass decomposition. Comparing Figs 3 and 4, one can conclude that higher heating rates, at the same atmosphere conditions, and air atmosphere shift the decomposition events to higher temperatures.

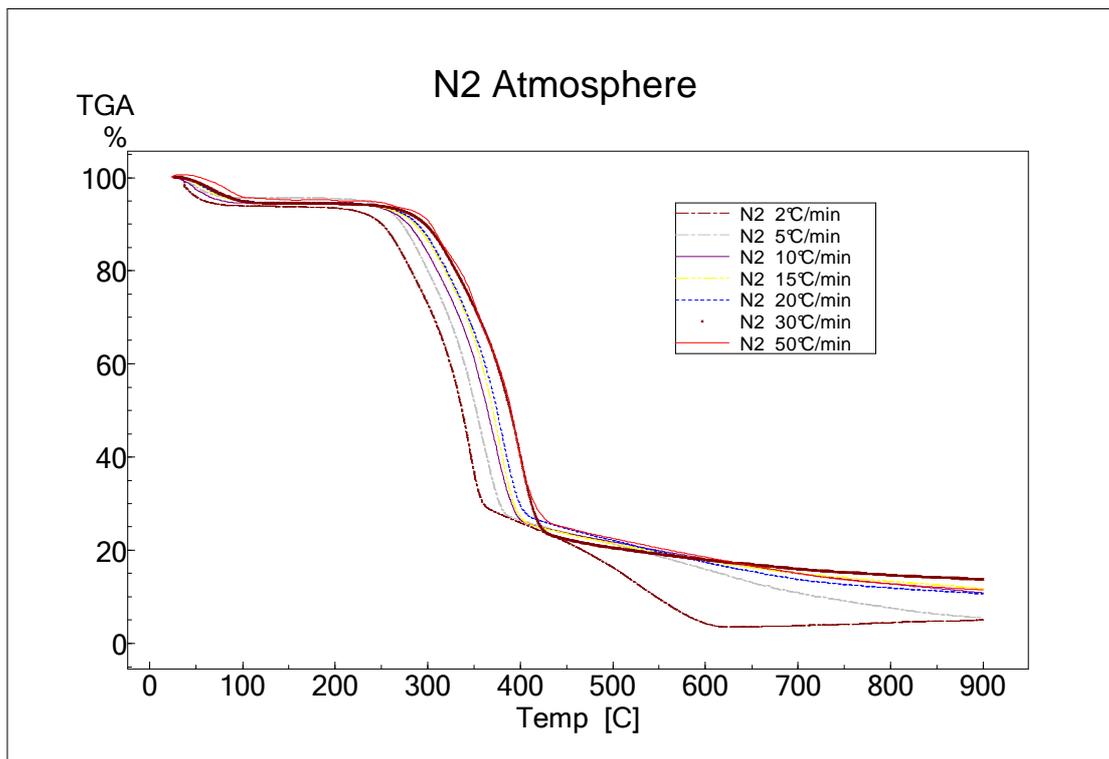


Figure 1. Mass loss profile of *Acacia mearnsii*, under N₂ atmosphere, as a function of temperature for different heating rates. Between 300 °C e 450 °C, from left to right, the curves correspond to the rates 2, 5, 10, 15, 20, 30 and 50 °C min⁻¹, respectively. (RIEGEL et. Al, 2008)

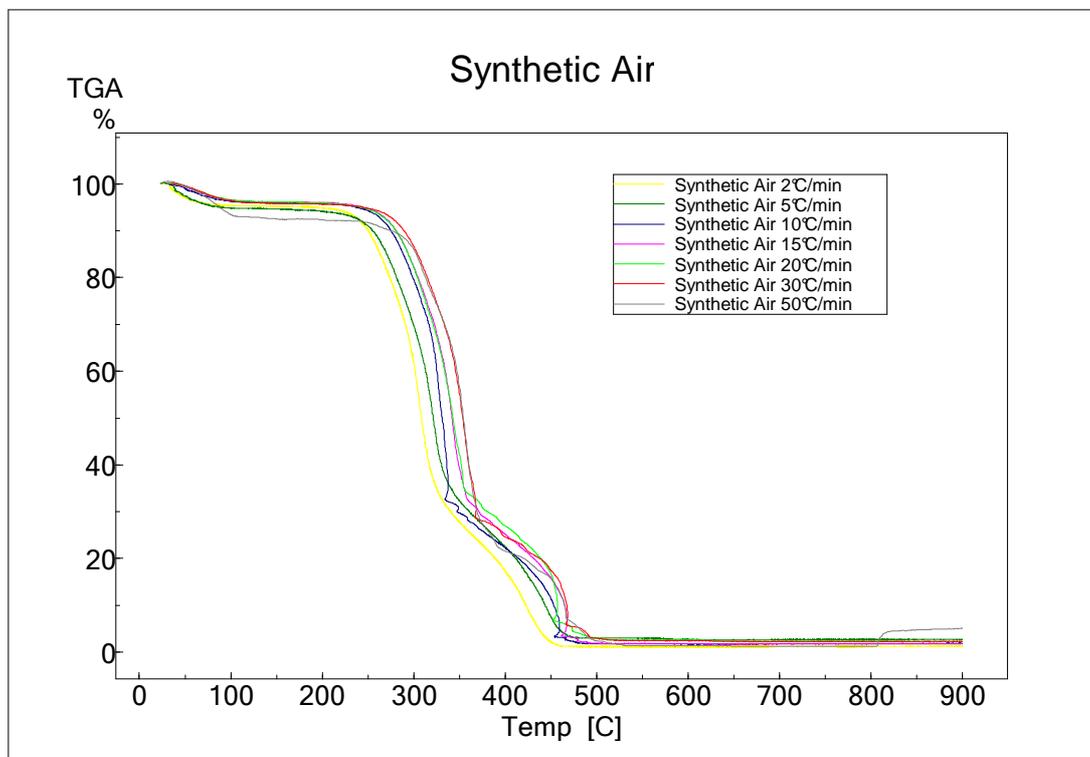


Figura 2. Mass loss profile of *Acacia mearnsii*, under synthetic air atmosphere as a function of temperature for different heating rates. Between 300 °C e 450 °C, from left to right, the curves correspond to the rates 2, 5, 10, 15, 20, 30 and 50 °C min⁻¹, respectively. (RIEGEL et. Al, 2008)

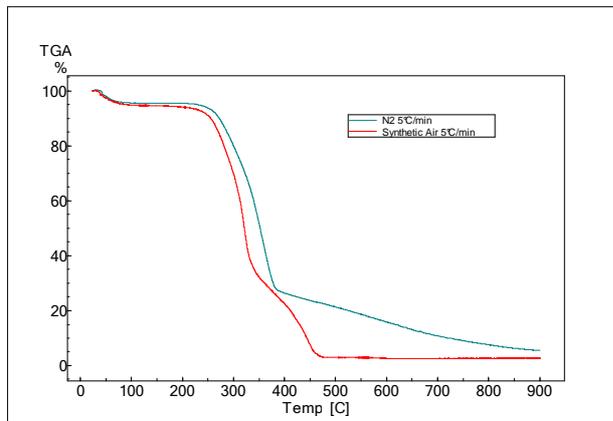


Figure 3. Mass loss profile of *Acacia mearnsii*, under N₂ and synthetic air atmospheres, at 5 °C min⁻¹.

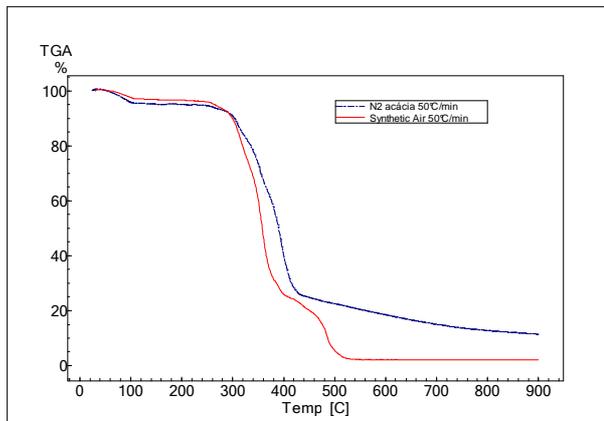


Figure 4. Mass loss profile of *Acacia mearnsii*, under N₂ and synthetic air atmospheres, at 50 °C min⁻¹.

3.2. TGA versus DSC

Differential scanning calorimetry (DSC) proved to be an effective technique for the obtainment of reliable values of the elementary heat of reaction in the absence of complicating phenomena, as heat or mass transfer limitations [KEMP; LAMPRECHT; 2000; RATH et al. 2002].

Figures 5 and 6 show the superimposed TGA and DSC curves of *Acacia mearnsii* pyrolysis under N₂ and synthetic air atmospheres, at 5 °C min⁻¹. Both DSC curves show an endothermic peak, at low temperature, attributed to the water weight loss, as can be seen by the TGA curve. At higher temperatures, two exothermic events can be observed, depicted by heat flow peaks above the baseline. Under nitrogen atmospheres, the two events can not be clearly separated. On the other hand, under synthetic air, the pyrolysis take place according to two well defined exothermic processes. Looking at the TGA curves, one can conclude that the exothermic peaks correspond to the second and third weight loss steps, in agreement to the discussion presented in Section 3.1.

The enthalpies of the pyrolysis process were calculated and demonstrated in Tables 1 and 2. The enthalpies are very low at nitrogen atmosphere; however, under synthetic air they vary from 13 to 0.9 J, decreasing with increasing heating rate.

Table1. Calculated enthalpies results of the pyrolysis process in air atmosphere.

AIR					
DSC			TGA (mass loss)		TGA (T máx)
rate (°C/min)	heat (1st event)	heat (2nd event)	1st event %	2nd event %	Tmáx (°C) 2nd event
2	11,84J	9,66J	61,676	33,824	391,55
5	10,68J	12,24J	57,343	35,224	409,24
10	8,34J	13,18J	57,494	28,837	426,24
15	4,68J	6,52J	63,373	25,482	467,33
20	2,65J	0,98995J	57,962	23,024	429,35
30	1,59J	0,12520J	60,674	18,496	0
50	0	0,96583J	63,927	29,667	468,42

Table 2. Calculated enthalpies results of the pyrolysis process in nitrogen atmosphere.

N ₂					
DSC			TGA (mass loss)		TGA (T máx)
rate (°C/min)	heat (1st event)	heat (2nd event)	1st event %	2nd event %	Tmáx (°C) 2nd event
2	0	1,74J	64,165	29,066	476,80
5	0,16759J	0,28633J	66,977	14,708	393,60
10	0,14068J	1,26J	69,430	0	0
15	0,48239J	1,26J	69,980	0	0
20	0,19103J	2,05J	68,466	0	0
30	0,32439J	1,20J	71,064	0	0
50	0,32515J	0,85091J	70,014	0	0

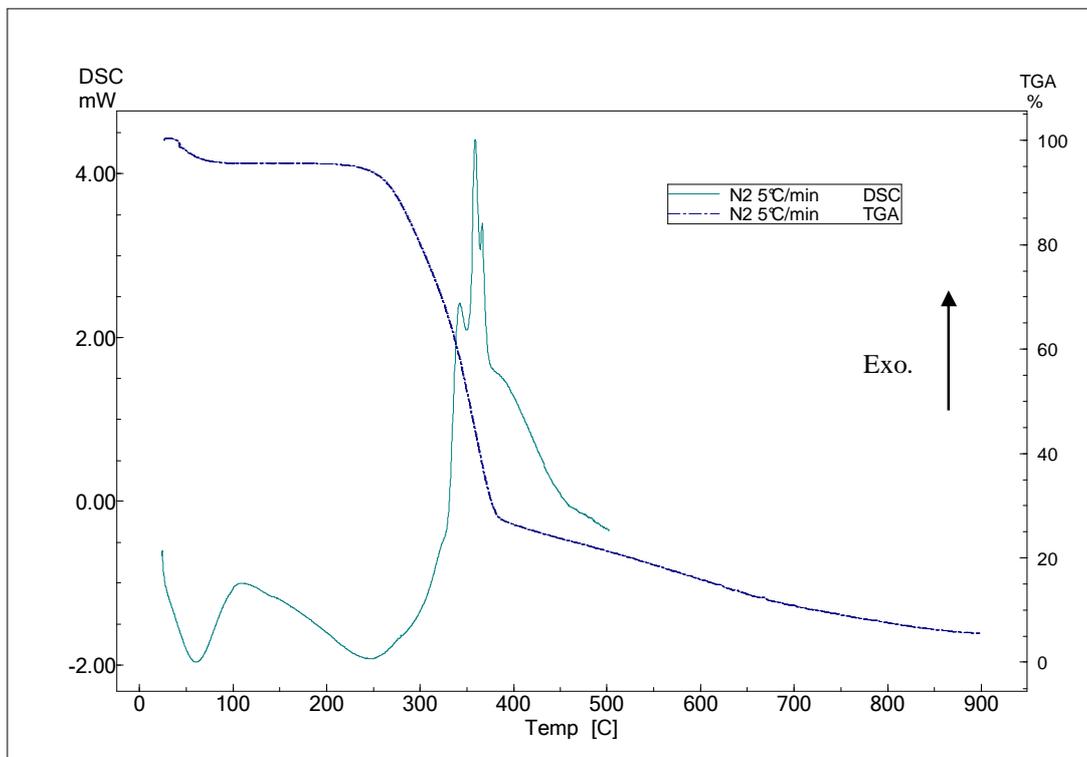


Figure 5. DSC and TGA profiles of *Acacia mearnsii* pyrolysis, under N₂ atmosphere, at 5 °C min⁻¹.

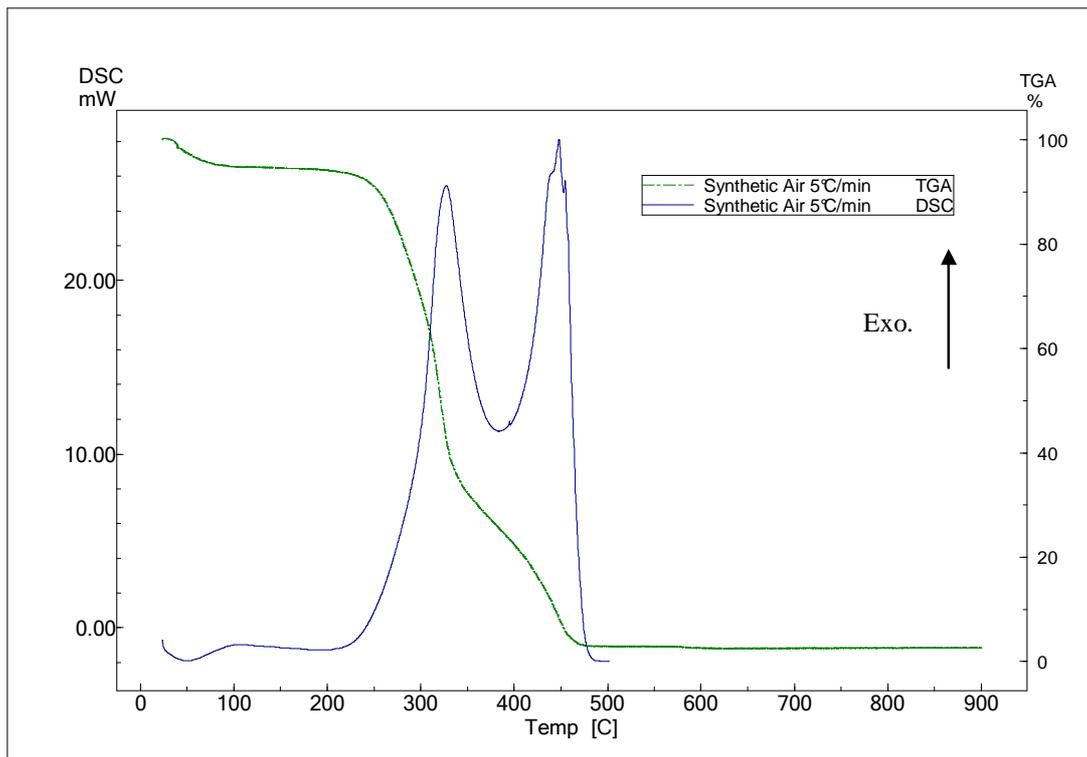


Figure 6. DSC and TGA profiles of *Acacia mearnsii* pyrolysis under synthetic air atmosphere, at 5 °C min⁻¹.

3.3. Pyrolysis kinetics based on multiple heating rate method

The use of two or more different nonisothermal curves to derive the activation energy is called multiple heating rate method and is based on the assumption that the temperature displacement between two or more curves at a point of equal conversion is a function of activation energy.

The rate of the thermal decomposition reaction of a solid can be described as a product of a temperature dependent function, $k(T)$, and a composition dependent term, $f(\alpha)$:

$$\frac{d\alpha}{dt} = k(T)f(\alpha), \quad (1)$$

where T is the absolute temperature, α expresses the degree of transformation, and $\frac{d\alpha}{dt}$ is the isothermal rate of change of the composition per unit of time, t .

According to Arrhenius relationship, the temperature dependent term is:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

The variable E is the activation energy, A is the pre-exponential factor and R is the universal gas constant. Thus, Eq. (1) can be written in the form:

$$\frac{d\alpha}{dt} = A e^{-\frac{E}{RT}} f(\alpha), \quad (3)$$

Introducing the heating rate, $\phi = \frac{dT}{dt}$, in Eq. (3) leads to the variation of the degree of transformation as a function of the temperature, this temperature being dependent of the time of heating:

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\phi} \exp\left(-\frac{E}{RT}\right) dT, \quad (4)$$

The function $f(\alpha)$ depends on the amount of solid and temperature, separately.

Due to the complexibility of the pyrolysis reaction, the form of the function can be very complicated.

Many published works has assumed that a simple n th-order kinetic relationship applies for the conversion dependent term as:

$$f(\alpha) = (1 - \alpha)^n, \quad (5)$$

Kissinger (BIAGINNI, 2002) used an approximation based on successive integration parts and then retained only the first term in a rapid converging series. The final expression, based on the maximum rate temperature (T_{peak}), is given according to the following equation:

$$\ln\left(\frac{\phi}{T_{peak}^2}\right) = \left[\ln\left(\frac{AR}{E}\right) - \ln g(\alpha) \right] - \frac{E}{RT_{peak}} \quad (6)$$

By plotting $\ln\left(\frac{\phi}{T_{peak}^2}\right)$ versus $\frac{1}{T}$, given in K^{-1} , at a constant conversion should lead to a straight line with

slope $-E/R$. The function $f(\alpha)$ is assumed as in Eq. 6. This method is valid only for a temperature range around the peak temperature.

The Kissinger analysis was applied on our results for the pyrolysis of black wattle wood, under nitrogen and synthetic air. The corresponding plots are presented in Figs 7 and 8. The correlation coefficient of the evaluated dat resulted in $R=0.989$ and 0.988 and the derived activation energies parameter were $E=154.0$ and $171.5 \text{ kJ.mol}^{-1}$, respectively.

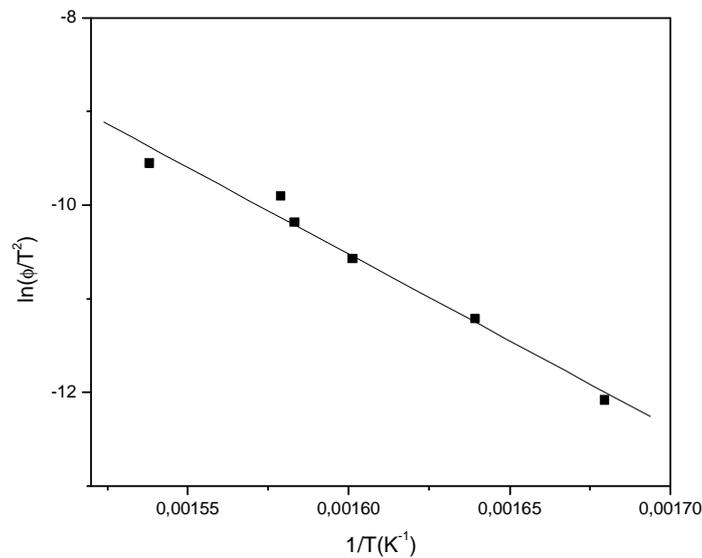


Figure 7. Kissinger plot from the data of the first weight loss event of pyrolysis of *Acacia mearnsii*, under N_2 . $R=0.989$ and $E=154.0 \text{ kJ.mol}^{-1}$.

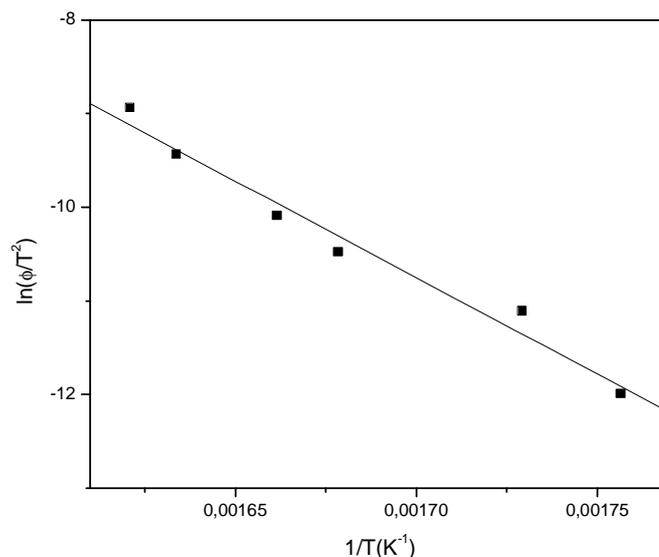


Figure 8. Kissinger plot from the data of the first weight loss event of pyrolysis of *Acacia mearnsii*, under synthetic air. $R=0.988$ and $E=171.5 \text{ kJ.mol}^{-1}$.

The obtained activation energy results falls into the range referred to in the literature for the pyrolysis of lignocellulosic materials.

4. CONCLUSIONS

The present work aimed at investigating the effects of heating rate and atmosphere nature (N_2 or air) on the efficiency and kinetics parameters of the pyrolysis of *Acacia mearnsii* De Wild. Wood (black wattle). The pyrolysis behavior was experimentally investigated through thermogravimetry (TGA) and differential scanning calorimetry (DSC). The TGA curves under nitrogen, the pyrolysis present two clearly seen weight loss processes at different heating rates, with the exception in the curve at $2 \text{ }^\circ\text{C.min}^{-1}$ which showed a three steps weight loss profile. Moreover under air, it could be observed three main step of devolatilization for all heating rates. The first weight loss step, at low temperature, can be attributed to loss of adsorbed water. The second one, at higher temperatures ($250\text{-}450^\circ\text{C}$), can be imputed to the main biomass degradation and the third decomposition step, at lower heating rate ($2 \text{ }^\circ\text{C.min}^{-1}$) under nitrogen and at all heating rates under air, leading to total biomass decomposition (total weight loss at 900°C). Under nitrogen, at other heating rates (5 to $50^\circ\text{C.min}^{-1}$) this third step manifested itself as a smooth mass decrease giving some residue at 900°C . Also, the behavior observed at $2 \text{ }^\circ\text{C.min}^{-1}$ can be explained due to lower rate of diffusion process that takes place at lower heating rates.

In our experiments, steps two and three, could not be seen as distinguishable steps. It can be concluded that lower heating rates and air atmospheres (that is, O_2 availability) favor the completeness of biomass decomposition. And also, that higher heating rates, at the same atmosphere conditions, and air atmosphere shift the decomposition events to higher temperatures.

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5. ACKNOWLEDGEMENTS

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