

Pyrolysis characteristics and global kinetics of coconut and cashew nut shells

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Abstract

Coconut and cashew nut shells are two typical biomass wastes abundant in most of the tropical countries. However, despite their enormous potential as energy sources, they are hardly studied and their thermal characteristics are still not well known. In this study, both biomasses are thermally degraded through thermogravimetry and their characteristics such as devolatilisation profiles and kinetics are analyzed, from 250 to 900 °C, in an inert atmosphere, at two different heating rates, and compared with wood pellets. The results show that their pyrolysis profiles are different from that of the commonly studied woody biomass. In fact, they present two different peaks instead of the one overlapping peak, for hemicellulose and cellulose. In addition, they present activation energies ranging from that are slightly above the commonly known maximum for biomass. At 10 and 20 °C/min the activation energy varied from about 130 to 174 and 180 to 216 kJ/mol, for cashew and coconut shells, respectively.

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1. Introduction

Biomass, defined as any hydrocarbon material mainly consisting of carbon, hydrogen, oxygen, nitrogen and some other components in small proportions [1], includes wood and its derived wastes, different organic wastes (including biodegradable MSW), agricultural and crop wastes, animal wastes, energy plantations, among others. Cashew nut (CNS) and coconut shells (CcNS) are part of this family. They are abundant in tropical countries in Latin America, Africa and Asia, occurring as biomass wastes from different agro-industrial processes. These two biomasses represent a grand potential as renewable energy sources for power generation [2–6] for different end-uses, especially for household rural energy, in the developing countries where they occur.

In biomass energy technologies, pyrolysis process is of key importance as this thermal degradation of solid fuels is present in both combustion and gasification. It has a key influence over the quality of the char that is either gasified or burned. As it is known, biomass thermo-conversion technologies are strongly

influenced by the reactivity char produced in the pyrolysis phase [7]. Therefore, for the design of any technology conversion system that suits specific characteristics of the biomass to be converted, pyrolysis process of such material is to be fully characterised. However, although many studies in biomass have already been performed in different aspects, CcNS and CNS are rarely found in such studies. In fact, in his outstanding review on biomass studies, Yaman [1] presents about two hundreds articles in biomass research studies and none of them is on CNS or CcNS. However, there are a limited number of researchers that have dedicated their investigation to these biomasses. In Raveendran et al. [5] studies of 13 different biomass samples in which CNS and CcNS are included. However, not too much attention was give particularly to these materials. In addition, Hoque and Battacharya [8] studied just the CcNS gasification product (fuel) from fluidised and spouted bed gasifiers. In both studies, the only specific characteristics that are given are proximate and/or ultimate analysis.

In the other side, lignocellulosic biomass basic components are hemicellulose, cellulose and lignin. Researchers have already confirmed that lignin starts decomposing at low temperatures (160–170 °C) and continues to decompose at low rate until approx. 900 °C. Hemicellulose is the second component to start

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decomposing, followed by cellulose, in a narrow temperature interval from about 200 to 400 °C. This is the interval in which the main decomposition takes place and accounts for the greatest decomposition in the biomass pyrolysis process consisting of degradation reactions. Beyond 400 °C, the most important reaction leads to the aromatisation process, at low mass loss rate [9].

Given the fact that biomass fuels differ extremely according to many factors [10] such as the type of biomass, species, the climate in which they are grown, the way each biomass species is cultivated (if this is the case) and other factors, the question on how different or similar the thermal characteristics of these tropical biomasses would be from the wood material that are quite well known is to be responded.

In this study, CcNS and CNS pyrolysis are investigated using thermogravimetry with the endeavour of characterising their thermal decomposition process, particularly, pyrolysis profiles and kinetics. For comparison, wood pellets are also submitted to the same analysis under identical circumstances.

Kinetics parameters were determined through the use of Coats and Redfern model, considering the pyrolysis mechanism of independent first order parallel reactions [10–13] and assuming that intra-particle heat transfer and diffusion effects are negligible, given the fine size of the sample particles used.

2. Experimental

The samples of CNS (from *Anacardium occidentale* L. tree) and CcNS (from *Coccos nucifera* L. tree) were collected in Mozambique (Africa) and were grinded to a small particle-size of less than 15 mg each (irregular size). It is important to mention that CNS were roasted beforehand as one of the cashew nut processing steps.

This study was performed using SETARAM 92 (TG), with Pt-crucible and a vertical hung-down thermobalance. Scientific argon was used as protective/inert carrier gas at 50 ml/min. The following temperature program was used:

- i. From ambient temperature to 110 °C, at a heating rate of 10 °C/min, for sample drying (moisture removal);
- ii. Isothermal drying at 110 °C, for 10 min (until constant mass is reached);
- iii. Temperature raising from 110 to 900 °C (for pyrolysis and subsequent release of volatiles) at different heating rates (5, 10, 20, 40 and 50 °C/min), and
- iv. Isothermal transformation at 900 °C for 10 min (to enhance the devolatilisation process and production of char).

From the ambient temperature to 900 °C, argon at a flow rate of 50 ml/min was used to maintain the reacting atmosphere inert. The mass loss and mass loss rate were recorded online by specific software designed by SETARAM, as functions of time and temperature.

In order to determine the pyrolysis kinetics parameters obtained through thermal analytical techniques, different methods are available [14–17], and are based in different assumptions made to simplify the complexity of the several reactions that occur during the devolatilisation process.

In this study, it is assumed that, given the smaller size of the sample particles, intra-particle heat transfer and diffusion phenomena are negligible and that a parallel first order reactions model is valid. These assumptions allow the use of Coats and Redfern method, one of the most commonly used methods and regarded as giving a good approach in thermal kinetics determination [17]. As it is required in this method, the reaction order had to be fixed in advance to allow the determination of the activation energy (E_{act}) and the pre-exponential factor (A), essential for characterising the pyrolysis kinetics.

Coats and Redfern method can be derived from the following chemical kinetics basic equations:

$$\frac{dx}{d\tau} = k(T)\Psi(x) \quad (1)$$

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

$$x = \frac{w_0 - w_\tau}{w_0 - w_f} \quad (3)$$

$$\Psi(x) = (1-x)^n \quad (4)$$

$$T = \xi\tau + T_0 \quad (5)$$

$$\xi = \frac{dT}{d\tau} \quad (6)$$

$$\int_0^x \frac{dx}{\Psi(x)} = \frac{A}{\xi} \int_0^T \exp\left(-\frac{E_{act}}{RT}\right) dT \quad (7)$$

$$F(x) = \int_0^x \frac{dx}{\Psi(x)} \approx \frac{ART^2}{\xi E_{act}} \left(1 - \frac{2RT}{E_{act}}\right) \exp\left(-\frac{E_{act}}{RT}\right) \quad (8)$$

$$\ln \frac{F(x)}{T^2} = \ln \frac{AR}{\xi E_{act}} \left(1 - \frac{2RT}{E_{act}}\right) - \frac{E_{act}}{RT} \quad (9)$$

$\Psi(x)$ is a function that depends on the reaction mechanism and the conversion rate as indicated in Eq. (4); ξ is the heating rate; k is the chemical reaction kinetics Arrhenius constant, dependent on the reaction temperature (T), as indicated in Eq. (2); w_0 , w_f and w_τ are the initial, final and actual weight of the sample being thermally decomposed; A is the Arrhenius pre-exponential factor; R is the universal gas constant; τ is the time; T is the absolute temperature that is a function of the heating rate and time [Eq. (5)]; T_0 is the initial absolute temperature; n is the order determined by the chemical reaction mechanism.

Eqs. (1)–(7) are generally derived from chemical reactions kinetics theory. Eqs. (8) and (9) are dependent on different assumption made in each specific method. Hence, in Coats and Redfern Method, the equations given below follow:

$$F(x) = -\ln(1-x) \text{ for } n = 1; \\ F(x) = \frac{-\ln[1-(1-x)^{1-n}]}{1-n} \text{ for } n \neq 1 \quad (10)$$

Table 1
Proximate and ultimate analysis of the biomass samples studied in the present work

| Biomass type | Ultimate analysis (db, % w/w) | | | | | | | Prox. analysis (db, % w/w) | | | HHV, MJ/kg | Density, kg/m ³ |
|-------------------|-------------------------------|-----|-----|-------|------|------|--------|----------------------------|-------|-----|------------|----------------------------|
| | C | H | N | O | S | Cl | Tr. El | Volat. | Fix-C | Ash | | |
| Coconut shells | 53.9 | 5.7 | 0.1 | 39.44 | 0.02 | 0.12 | 0.72 | 74.9 | 24.4 | 0.7 | 20.515 | 1090 |
| Cashew nut shells | 58.3 | 7 | 0.7 | 32.05 | 0.06 | 0.03 | 1.86 | 81.8 | 17.3 | 0.9 | 24.051 | 1012 |
| Wood pellets | 50.9 | 6.2 | 0.2 | 42.06 | 0.01 | 0.02 | 0.61 | 81.3 | 18.1 | 0.6 | 20.265 | 584 |

Since for the pyrolysis of the lignocellulosic biomasses activation energy reported in the literature is in the range of 100–250 kJ/mol [15], the approximation is made as given in Eq. (11), then Eq. (9) turns to Eq. (12).

$$\frac{RT}{E_{\text{act}}} \approx 0 \quad (11)$$

$$\ln \frac{F(x)}{T^2} = \ln \frac{AR}{\xi E_{\text{act}}} - \frac{E_{\text{act}}}{RT} \quad (12)$$

Eq. (12) is transformed into linear function, as follows:

$$F_T(X) = B - cX \quad (13)$$

Where $F_T(X) = \ln \frac{F(x)}{T^2}$, $B = \ln \frac{AR}{\xi E_{\text{act}}}$, $c = \frac{E_{\text{act}}}{R}$ and $X = \frac{1}{T}$.

Plotting thermogravimetric data by applying Eq. (13), pre-exponential (A) and activation energy (E_{act}) are determined and the Arrhenius constant obtained.

From Eq. (2), Arrhenius constant can be plotted against temperature as:

$$\ln k = \ln A - \frac{E_{\text{act}}}{R} \frac{1}{T} \quad (14)$$

This equation is used in the present study to assess the influence of temperature intervals and heating rate factors.

3. Results and discussion

3.1. Pyrolysis profiles

Table 1 presents the proximate and ultimate analysis of the three biomass samples that have been studied in this work.

The high hydrocarbons and less oxygen content are to be highlighted, together with high heating value and density of both tropical biomasses, compared to wood pellets. The carbon and hydrogen contents are a good indicative of hydrocarbons content that are to be released during pyrolysis. Additionally, it is well known that fuels that are rich in oxygen are poor in energy content (HHV). These differences play an important role in the pyrolysis of these materials and respective gases and char yields, as Figs. 1 and 2 show.

Fig. 1 shows the mass loss observed for dried samples of CNS, CcNS and wood pellets, above 100 °C, at a heating rate of 10 °C/min. The volatiles yield is greater in CNS compared to both wood pellets and CcNS. Wood pellets have comparably much volatile matter content than CcNS but lower than CNS. The char yield is inversely proportional to the volatiles yield.

The temperature interval in which each biomass sample experiences the greater mass loss is different from one to another. From the thermograms showed in Fig. 1, these intervals are 247–420, 280–415 and 260–450 °C, where about 77%, 75% and 70% of the total volatiles weight are released in CNS, CcNS and wood pellets, respectively.

Fig. 2 shows the mass loss rate (derivative thermograms) for the three samples. A clear difference between wood pellets thermogram and the other two tropical biomass samples thermograms is noticeable. In fact, the two distinct DTG peaks found in CNS and CcNS, from 250 to 450 °C, differ clearly from the typical overlapping derivative thermogram found in woody biomass and in the vast majority of biomass species in this interval. The last is found in almost all biomass thermogravimetry studies and presents a shoulder at lower temperatures and an outstanding point at higher temperatures [5,6,12,18,19].

According to the previous studies in different biomass materials, the shoulder at left hand side corresponds to the hemicellulose decomposition while the higher temperature peak in the right hand side represents the degradation of cellulose [12,14,18,20]. This difference has never attracted any special attention of any biomass researcher so far, at the knowledge of the authors of this study, although the two-peak thermogram is also presented by Siddhartha and Reed [14] for CcNS.

Based in the precedent studies of biomass pyrolysis, the first peaks in CcNS and CNS represent hemicellulose decomposition and the second pair of peaks shows the mass loss rate change during thermal degradation of cellulose. Therefore, it is to mention that the peaks for hemicellulose and cellulose are at about 340 and 395, 329 and 400, and 380¹ and 420 °C, for CNS, CcNS and wood pellets, respectively.

Although it cannot be concluded right from the thermograms, it is known that lignin decomposition is distributed along a wide range of temperature interval and its peak is not commonly distinguishable [12,18]. However, it is believed that the long flat tail observed at high temperatures is caused by lignin decomposition. Fig. 2 shows a low peak at about 500 °C for CNS which must be indicative of lignin decomposition peak. Wood pellets and CcNS lignin decomposition behave as expected, without any perceptible peak.

According to Vamvuka et al. [12] the DTG peak height is directly proportional to reactivity and the correspondent temperature is inversely proportional to this chemical activity parameter. Applying this theory, it can be concluded that reactivity of CNS is similar to that of CcNS but higher than that of wood pellets. Concerning cellulose, the wood pellets still contain the

¹ Difficult to distinguish with precision, given the peak shape.

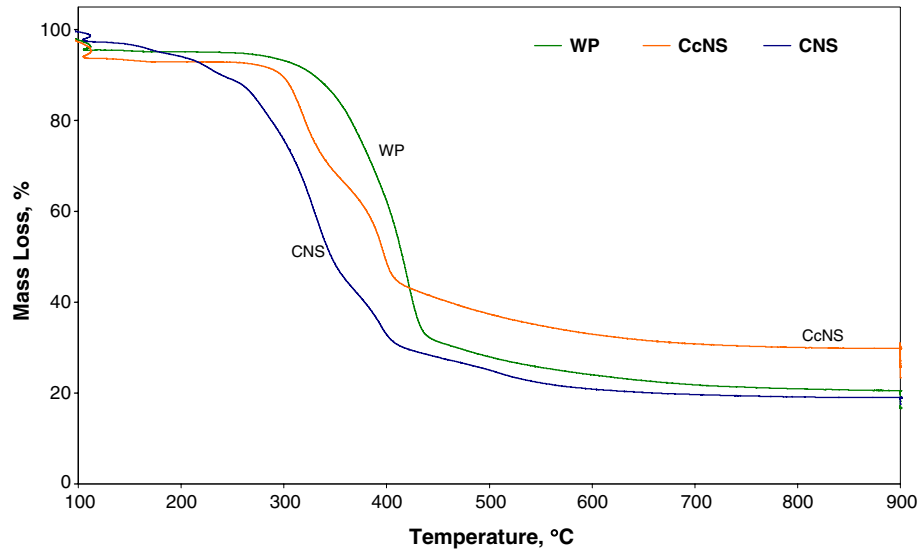


Fig. 1. Mass loss from the thermal decomposition of CNS, CcNS and wood pellets at 10 °C/min.

less reactive (high temperature) but fast reacting cellulose. CNS presents the slow reacting cellulose, despite being as reactive as that of CcNS.

3.2. Global kinetics

For kinetics parameters determination, the interval from 250 to 450 °C was used based in the fact that this is the interval in which the most pyrolysis for the three components takes place, as observed from the thermograms in Figs. 1 and 2.

As mentioned before, Coats and Redfern method is applied and first order parallel reaction mechanism is followed.

As seen in Fig. 1, the two different reactions in the temperature interval where the main pyrolysis process in both biomass species takes place, from 250 to 450 °C, are evident,

suggesting that different lignocellulosic components, first, hemicellulose and then cellulose, are degraded [14,12,21,22]. These stages are approximately from 250 to 380 °C and from 380 to 450 °C, respectively. This subdivision is observed in both biomass samples at both heating rates considered in the study. These two intervals are the main focus of the present study.

The results obtained indicate the following reactions rate equations:

For CNS, at 10 °C/min

$$\frac{dx}{d\tau} = -r_{\text{hem},10}^{\text{CNS}} = 7.18 \cdot 10^8 e^{(-15,416.8/T)} (1-x) \text{ and}$$

$$\frac{dx}{d\tau} = -r_{\text{cell},10}^{\text{CNS}} = 1.20 \cdot 10^{10} e^{(-18,694.7/T)} (1-x)$$

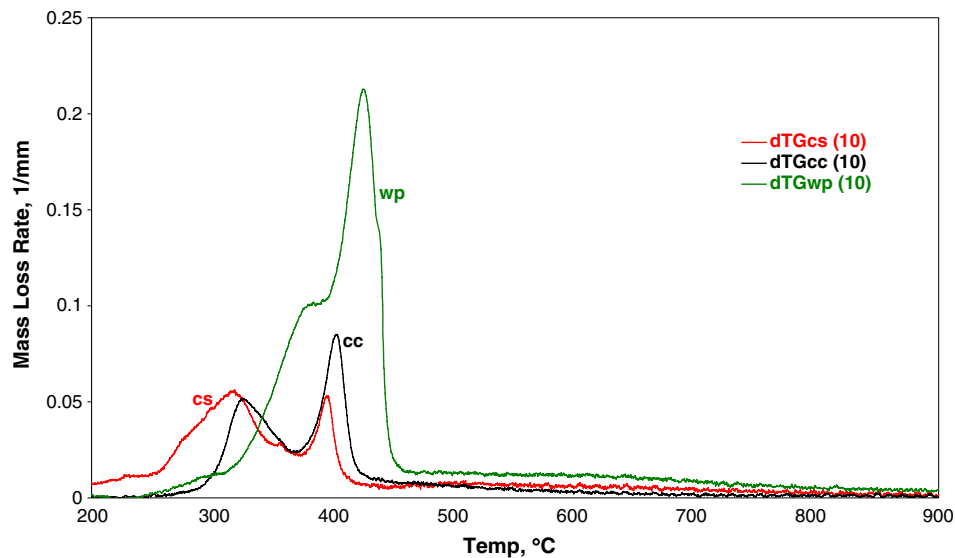


Fig. 2. Mass loss rate from the thermal decomposition of CNS, CcNS and wood pellets at 10 °C/min.

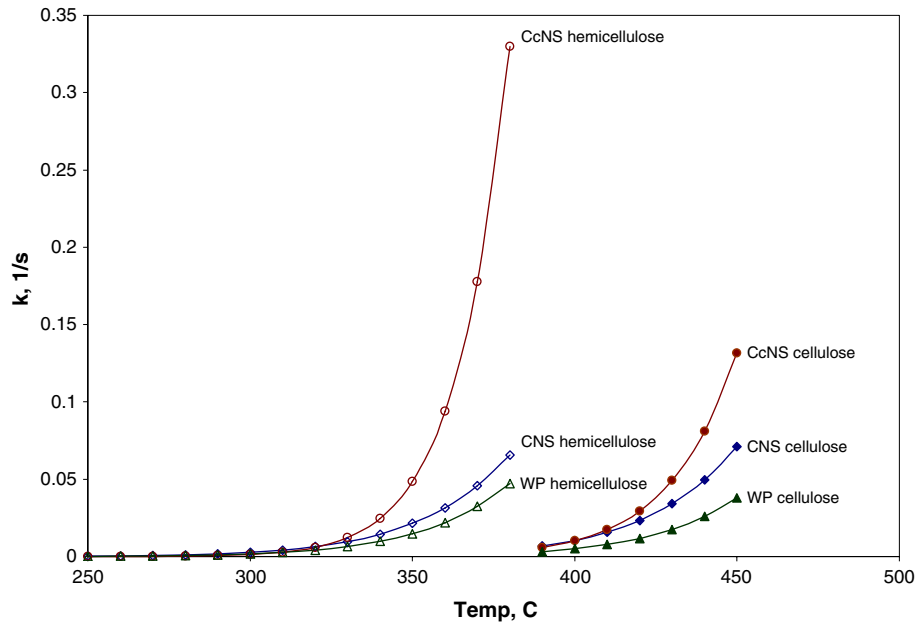


Fig. 3. Arrhenius constant vs temperature for CNS and CcNS pyrolysis at 10 °C/min.

For CNS at 20 °C/min

$$\frac{dx}{d\tau} = -r_{hem,20}^{CNS} = 4.17 \cdot 10^{09} e^{(-15,660.5/T)} (1-x) \text{ and}$$

$$\frac{dx}{d\tau} = -r_{cell,20}^{CNS} = 2.89 \cdot 10^{11} e^{(-20,396.5/T)} (1-x)$$

For CcNS at 10 °C/min

$$\frac{dx}{d\tau} = -r_{hem,10}^{CcNS} = 6.25 \cdot 10^{16} e^{(-25,985.1/T)} (1-x) \text{ and}$$

$$\frac{dx}{d\tau} = -r_{cell,10}^{CcNS} = 1.31 \cdot 10^{14} e^{(-24,973.2/T)} (1-x)$$

For CcNS at 20°C/min

$$\frac{dx}{d\tau} = -r_{hem,20}^{CcNS} = 1.15 \cdot 10^{15} e^{(-23,216.3/T)} (1-x) \text{ and}$$

$$\frac{dx}{d\tau} = -r_{cell,220}^{CcNS} = 1.54 \cdot 10^{12} e^{(-21,600.4/T)} (1-x)$$

These kinetics parameters, in each of these intervals, are expected to be mainly determined by the nature of the lignocellulosic component being degraded and, in minor proportion, of the biomass sample from which it comes, as the plot below shows.

Fig. 3 shows the influence of temperature interval (and hence of the component being decomposed) over the Arrhenius kinetics constant. Clearly the first interval, where hemicellulose thermal degradation is the most predominant, k , for all samples, changes slightly within 250 and 300 °C. Above 300 °C, CcNS hemicellulose constant shows a sharp increase, followed by CcNS. In the temperature interval where cellulose decomposition is the most important, the change is greater right from 390 °C, with CcNS showing the highest change with the temperature increase, followed by CNS. In both intervals, wood pellets showed the slowest change. Thus, it can be concluded

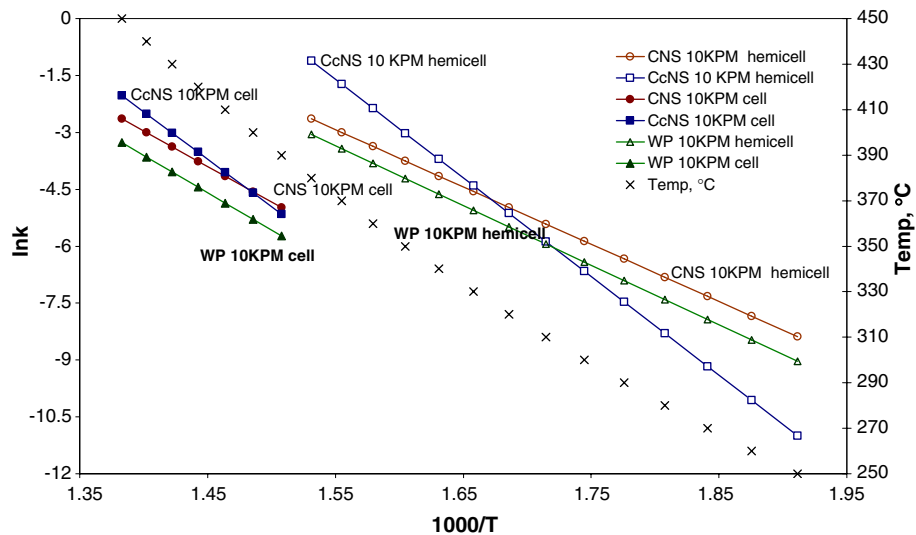


Fig. 4. The influence of the lignocellulosic component and type of biomass on the Arrhenius constant at 10 °C/min.

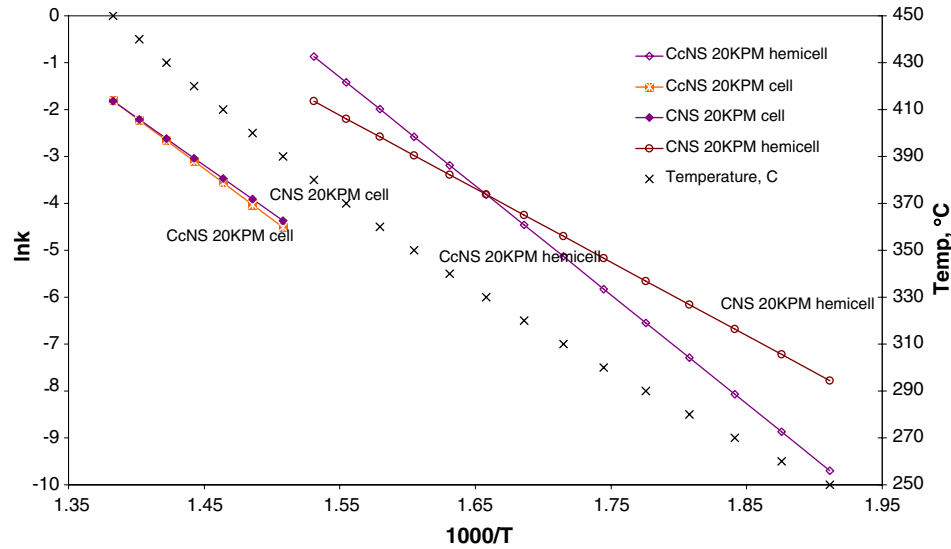


Fig. 5. The influence of the lignocellulosic component and type of biomass on the Arrhenius constant at 20 C/min.

that CNS hemicellulose and cellulose decomposition rate is greater than that of CNS.

Figs. 4 and 5 give the linearization of the relationship between kinetics constant and temperature (given in Fig. 2) based in Eq. (9) for both samples at 10 and 20 °C/min, respectively.

The heavier dependence on the component being decomposed is clearly noticeable from these two graphics. Indeed, although the biomass samples are different, Arrhenius constants are found in the same range for hemicellulose, in one hand, and for cellulose, in the other hand, for all three samples. However, there are some little differences such as the fact that CcNS constants are more sensitive to temperature change than that of CNS, as earlier noticed from Fig. 3. This is due to the global-activation energy of each reaction. The higher the activation energy, the higher is the sensitivity of Arrhenius constant to temperature. This is in line with the observed fact that activation energy changes from about 130,206 to 174,373 kJ/kmol, for CNS, and from 179,599 to

216,048 kJ/kmol, for CcNS. It is the activation energy that is high for CcNS than for CNS thermal decomposition. Such behaviour is found at both heating rates.

The influence of the heating rate can be viewed from Fig. 6, below.:

Using just one sample (CcNS) to illustrate how the Arrhenius kinetics constant is influenced by the heating rate, it can be seen that the higher the heating rate, the higher the value of the kinetic constant will be. Indeed, from Eqs. (2) and (5) it stands that the higher the heating rate, the lesser the influence of the activation energy over the kinetic constant. However, this influence tends to be smaller in cellulose than in hemicellulose decomposition. These findings were also observed in CNS pyrolysis, and wood pellets. They are in agreement with chemical kinetics reaction theory.

The figure above (Fig. 7) compares different activation energies from different studies [9,11,12,14,15,17,18,23–27],

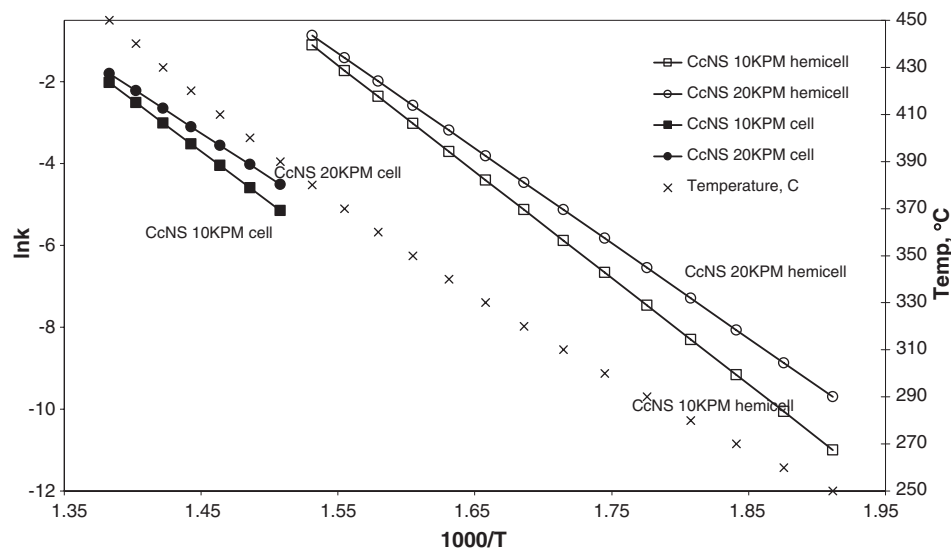


Fig. 6. The influence of the heating rate on the Arrhenius constant.

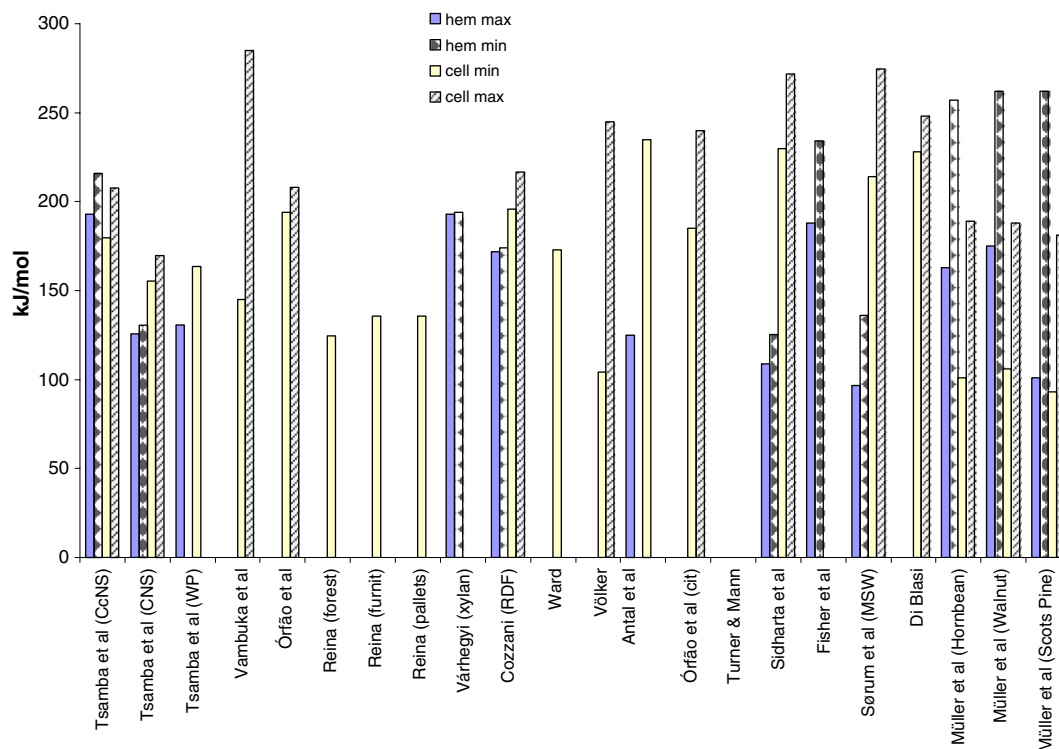


Fig. 7. Comparative activation energies results from different authors.

including from the present study. The figure clearly shows how diversified are the results, although they can be assumed to be in a fairly limited range. Excluding the results of the present study and Müller-Hagedorn et al.² [18] values, the activation energies from the other studies can be summarized as follows:

$$E_{\text{act, hem}}^{\text{min}} = 147.24 \pm 38.52 \text{ kJ/mol and}$$

$$E_{\text{act, hem}}^{\text{max}} = 172.75 \pm 39.44 \text{ kJ/mol}$$

$$E_{\text{act, cell}}^{\text{min}} = 176.92 \pm 42.41 \text{ kJ/mol and}$$

$$E_{\text{act, cell}}^{\text{max}} = 248.64 \pm 25.75 \text{ kJ/mol}$$

Results from the present study fall in the range given above for all the samples studied in the present work. Comparably, CNS and CcNS present moderate activation energies and, consequently, relatively most reactive than the average woody biomass. In fact, the higher the activation energy, the lowest will the reactivity be, according to the chemical concept of both parameters.

In general, differences are to be expected due to the different techniques, methodologies and models used as well as the nature of the samples studied. Nevertheless, the difference between the rest of the biomasses samples and coconut is manifest. This difference can only be attributed to the nature of hemicellulose and cellulose present in this kind of lignocellulosic materials. In fact, as discussed by different researchers, hemicellulose or cellulose represent different series of related macromolecular compounds that differ according to various factors as the type of biomass, the species and the geo-climatic conditions in which they are grown, among other factors. Indeed, these factors play

an important role in characteristics such as the kind of hemicellulose (*glucmannans*, *arabinogalactans* and *xylans*) as referred by Siddhartha and Reed [14], and cellulose (α and β -*glucopyranosides*), as well as in ash content which play a catalytic effect in the biomass thermal decomposition.

4. Conclusions

CNS and CcNS pyrolysis was successfully characterised. Differences and similarities between these tropical biomass wastes and wood pellets were found and discussed.

It was found that, definitely, CcNS and CNS are different from the ordinary woody biomass in some important aspects. They are richer in hydrocarbons than wood, which leads to a poor char yield. Additionally, their main pyrolysis presents clearly different and distinct peaks for hemicellulose (first) and for cellulose (second) differing from the ordinary one overlapping peak normally found in most of the woody biomass pyrolysis.

The kinetics parameters obtained for CcNS and CNS, although they can be assumed to be in conformity with the data range obtained by previous researchers, still they show some dissimilarities, compared to woody biomass, as follows:

- High hydrocarbon content in and less char CNS;
- Moderate activation energies (130 to 216 kJ/mol) which enable the respective reactivity to be high.

Symbols and abbreviations

CcNS Coconut shell
cell Cellulose

² They used a very wide range of reactions order, all different from 1 (one).

| | |
|---------------|---|
| CNS | Cashew nut shell |
| cnsl | Cashew nut shell liquid |
| daf | Dry-ash-free basis |
| db | Dry basis |
| dTG | Derivative thermogravimetry |
| hem, hemicell | Hemicellulose |
| KPM | Kelvin per minute |
| max | Maximum |
| min | Minimum |
| min | Minute |
| °C | Degrees Celsius |
| –r | Reaction rate |
| TG | Thermogravimetry (thermogravimetric analyser) |

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