# *Influence of Alkali and alkaline earth metallic (AAEM) species on pyrolysis process of Cypress sawdust*

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## *Abstract*

The purpose of this study was to investigate the effect of demineralization process and addition of Alkali and alkaline earth metallic (AAEM) species (KCl, NaCl, $MgCl_2$, and $CaCl_2$) on the thermal degradation of Cypress sawdust using thermogravimetric analysis. Analysis of lignocellulosic composition of cypress wood sawdust showed that the addition of the inorganic salts accelerated significantly the degradation of hemicellulose. Furthermore, TG and DTG analyses showed that the AAEM species affected significantly the char yield and characteristic parameters such as the maximum weight loss rate and the corresponding peak temperatures.In particular, there was an increase in the yield of char residues with the addition of four inorganic salts.The DTG curves shift to the left, indicating a decrease in the peak corresponding to cellulose in response to the presence of potassium and sodium minerals. However no significant effect has been detected for magnesium and calcium. A decrease in the maximumdegradation ratewas observed for the cellulose fraction with addition of magnesium. Calcium affected slightly the decomposition of hemicelluloses. The results showed that Alkali and alkaline earth metallic (AAEM) species may promote the thermal degradation of cypress wood sawdust. .

**Keywords:** *Cypress sawdust,* inorganic salts, thermogravimetric analysis, thermal degradation.

## *Introduction*

The development of alternative energy processes has become imperative due to concerns about the increase of greenhouse gaseous emissions and the depletion of petroleum resources [1]. Lignocellulosic biomass is an abundant and renewable source that can be converted into fuel and chemical feedstocks [1,2]. Processes such as combustion, gasification and pyrolysis have been identified as possible routes for energy and transport fuel production [3].Combustion technology is the most widely applied on industrial scale. However, biomass gasification and pyrolysis processes are still in an early stage of development and need to overcome a number of technical and economical barriers to compete with traditional fossil fuel based technologies [4-5]. Therefore, there are extensive research motivations for achieving in-depth the understanding of biomass pyrolysis in order to ensure thetechnology development and optimization [6]. Biomass pyrolysis is very complex depending on varieties of biomass feedstock and reaction conditions, and currently it is still a way from a full unraveling [6]. Lignocellulosic biomass consists principally of cellulose, hemicellulose and lignin and contains smaller amounts of extractives and ashes [7]. These latters include considerable amounts of alkali and alkaline earth metallic species (AAEMs) such as sodium, potassium, calcium, magnesium which are the integral nutrient constituents of biomass [7].Minerals are generally considered as an important factor in biomass pyrolysis.

Several investigations have examined the effect of inorganic elements on the pyrolysis process [8-13]. These investigations indicated that minerals concentration in the raw biomass is a key factor affecting the thermal degradation kinetic during biomass thermo chemical conversion .Khelfa et al. [8] compared the effect of $MgCl_2$ and the $NiCl_2$ on the thermogravimetric data and the products composition during the birch wood pyrolysis. Authors reported that the $MgCl_2$ had a more significant effect by decreasing the maximum pyrolysis temperature and increasing the char residue. This effect was recently confirmed by Carvalho et al. [9] during the examination of sweet sorghum bagasse pyrolysis in presence of $MgCl_2$ and $ZnCl_2$. Authors have noted a decrease in the maximum degradation rate for both hemicellulose and cellulose fractions in presence of $ZnCl_2$ while a significant decrease in the peak temprature corresponding to hemicellulose was detected during the addition of $MgCl_2$.The effect of potassium on the pyrolysis of lignocellulosic biomass was also investigated in the literature. Zhou et al. [10] examined the pyrolysis of pine wood biomass impregnated with different potassium contents. Authors found that the char fraction of the impregnated samples increased significantly and the maximum degradation rate shifted to lower temperature. This catalytic effect due to the presence of potassium was previously observed during the pyrolysis of short rotation willow coppice [11]. Authors found that the average apparent first-order activation energy decreased by up to 50 kJ/mol during the catalyzed potassium pyrolysis. Eom et al. [12] studied the effect of major inorganic elements (K, Mg and Ca) on the thermal degradation mechanism of poplar wood. Authors found that potassium had a notable catalytic effect promoting the formation of low molecular weight compounds and suppressing the formation of levoglucosan. Wang et al. had examined the influence of alkali and alkaline earth metallic species on the pyrolytic products yields during the pyrolysis of red oak [13]. Authors found that the addition of these inorganic elements reduced significantly the yields of hydrocarbons followed the order: K > Na > Ca> Mg [13]. In addition to the main inorganic elements, recent investigations examined the effect of other metals impregnation (Fe, Ni) on the pyrolysis mechanism of cellulose, xylan (hemicellulose) and lignin [14]. The analysis of the pyrolysis products showed the both metals catalyzed dehydration and decarboxylation reactions which promoted the formation of char and inhibited the depolymerization of cellulose. For the lignin, both metals favored the rearrangement of the aromatic rings, which resulted in a significant decrease in the concentration of the aromatic compounds in the tar fraction. However, the results obtained from the impregnated xylan pyrolysis showed different effect since the depolymerization of xylan was inhibited in presence of iron and catalyzed in presence of nickel [14].Despite the significant amount of studies dealing with the effect of inorganic elements on biomass pyrolysis, it is clearly shown that their effect differs on the various studied biomass. In addition, few studies examined the effect of minerals on the pyrolysis kinetics which is crucial for the design of pyrolytic reactor.

Lignocellulosic biomass, contains inorganic elements (mainly K, Mg, Ca and Na) and their amounts vary depending on the source. Determination of the effects of inorganic elments on the thermal degradation is important because of theirunique impacts. Biomass leaching is an effective method to investigate the role of intrinsic or added inorganic compounds in biomass on thermal behvior. Therefore different demineralization methods using different agents such water, hydrofluoric acid, and sulfuric acid have been conducted. Jian et al.[15]studiedthe potential impact of different agents during demineralization process. The results revealed that acid leaching exhibited high removal efficiency of minerals and introduced non negligible impact on physico-chemical structure biomass comparing to water leaching.Although demineralization of biomass is widely adopted in the literature to observe the effect of inorganic elements on thermal degradation of biomass also on removal of some organic composition there is a diffuclty how to assess the indivudal influences in consequence of both mineral matter and inorganic composition varied. To the best of our knowledge, there were no studies reported in literature regarding the correlation of alkali and alkaline earth metallic (AAEM) species of thermal degradation of cypress wood sawdust and their effect on organic matter.

This work aims to evaluate the effect of the mineral species on the sawdust pyrolysis behvior and its organic matter. Hence, the effect of potassium, calcium, sodium and magnesiumon the thermal degradation of Cypress sawdust is examined using thermo gravimetric analysis in order to achieve the understanding of the decomposition of each consituent in the process of pyrolysis.

## *2. Materials and Methods*

### *2.1. Biomass collection*

The lignocellulosic raw material used in this study is constituted by Cypress wood sawdust(CWS) collected from a carpentry manufactory located in the region of Menzel Bouzelfa (North East of Tunisia).Cypress wood type "Cupressussempervirens" is one of the most abundant biomass in Tunisia which is largely used as windbreaks and ornamentals [16]. It is commonly used for household furniture and house wares and therefore generated significant quantities of Cypress sawdust wastes during transformation processes. The CWS feedstock was firstly air-dried for 10 days until constant weight and sieved for a particle size below to 400µm.

### *2.2. Preparation of impregnated biomass sample*

During this investigation, different samples containing different concentrations of inorganic elements (KCl, NaCl, $CaCl_{2,}$ and $MgCl_2$) were prepared. Control sample was prepared by water washing and serve as a reference containing a quite low amount of minerals. The impregnation of CWS with the different inorganic elements was prepared in a biosorption process. During the impregnation procedure, 5 g of samples were immersed into 50 ml solutions containing different concentration. The resulting mixture was slowly stirred (400tr/min) at room temperature during 24 h.After impregnation; the samples were separated by filtering with filter paper and washed with distilled water until neutral conductivity. Finally, the impregnated samples were dried in oven at 105°C for a period of 24h to remove residual moisture.

### *2.3. Biomass characterization*

Different analytical techniques were used to determine the physico-chemical characteristics of the different prepared sample.Proximate and ultimate analyses of the cypress wood sawdust were conducted and the fundamental lignocellulosic compositions were also determined. Proximate analysis (C, H, N and S) were measured by CHNS analyzer type« Flash EA 112 Series » of Thermo Scientific. The percentage of oxygen content was estimated by difference as follows: O (%) = 100 - (C + H + N +S+ ash). For ultimate analyses, the moisture content of the feedstock was estimated by measuring the weight loss after drying the fresh samples at 105 °C for 24 h in an oven untilobtaining a constant mass according to the EN 14774-1 standard.Ashvalue is obtained after sample combustion (about 1 g, wb) in a muffle furnace during 3h at two temperatures 550°C and

815°Caccording to EN 14775 and DIN 51719 standards, respectively.The mineral contents of the different chars were measured by an XRF (X-ray fluorescence) spectrophotometer (Philips PW2540) equipped with a rhodium target X-ray tube and a 4 kW generator. The analysis of the main fractions (cellulose, hemicelluloses and lignin) was carried out using a NKOM 2000 Fiber Analyzer. A national standard method was used to determine the main components in the different samples used in this study. This method is widely applied to determine the fiber constituents in various lignocellulosic biomasses. In this method, a biomass is divided into three main components,hemicellulose, cellulose, and lignin. The main procedures aredescribed by Shi et al. [17]

## *2.3. Thermogravimetric analysis*

The thermogravimetricanalysisof the control and impregnated biomass sample was performed using Mettler-Toledo TGA/DSC$^{3+}$. Before each experiment,sample with weight about 10 mg was put in an alumina crucible .TGA experiments were performedunder a gas flow of 100/ml at heating rates of 5°C/min from room temperature to 800°C.The mass loss (TG) and differential weight loss (DTG) were obtained using the analyzer software. These datawere calculated from mass, time and measured temperature.

## *2.4 Kinetic approaches*

The evolution with temperature of weight loss (TG) and the weight loss rate (DTG) were obtained for pyrolysis. Primarily, data from TG and DTG curves were used to determine the kinetic parameters by indicating the temperature range in which thermal degradation occurs. The Coats–Redfern model was adopted to describe the conversion processes from raw material to char and volatiles, and determiningthe kinetic parameters of the thermal degradation of the differentsamples [18]. Hence, various kineticmodels adapted for the biomass decomposition (Table 1) were applied to analyse TG and DTG da

**Table 1**. Algebraic expressions of functions used for biomass thermal degradation.

| N° | Mechanism | f(α) | g(α) = $\int_0^\alpha d\alpha / f(\alpha)$ | Symb |
|---|---|---|---|---|
| *Chemical reaction* | | | | |
| 1 | First order | $1-\alpha$ | $-Ln(1-\alpha)$ | F1 |
| 2 | Second order | $(1-\alpha)^2$ | $\left[1/(1-\alpha)\right]-1$ | F2 |
| 3 | Third order | $(1-\alpha)^3$ | (1/2)($\left[1/(1-\alpha)^2\right]-1$) | F3 |
| *Diffusion* | | | | |
| 4 | One-way transport | $1/(2\alpha)$ | $\alpha^2$ | D1 |
| 5 | Two-way transport | $\left[-Ln(1-\alpha)\right]^{-1}$ | $(1-\alpha)\ Ln(1-\alpha)+\alpha$ | D2 |
| 6 | Three-way transport | $3/2(1-\alpha)^{2/3}\left[1-(1-\alpha)^{1/3}\right]^{-1}$ | $\left[1-(1-\alpha)^{1/3}\right]^2$ | D3 |

In fact, previous investigations showed that the biomass degradation process is governed by transport (diffusion) phenomena and chemical reactions [19-20, 21] which could be expressed by the following equation (1).

$$C_{solide} = C_{solid} + D_{gas} \qquad (1)$$

where B solid is the initial biomass, and C solid and D gas are the different products during the degradation of B solid.

Global kinetics of devolatilization reaction model for a kinetic process can be written as:

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (2)$$

whereα is the fraction of solid material decomposed at time t. The conversion rate parameter a can be expressed according to the measured weight loss at the various reaction times such as:

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \qquad (3)$$

Where $m_t$ refers to the sample mass at a specified time, the subscripts, i and f, represent the initial and final of the reaction, respectively. And f(α) function is related with order of reaction as:

$$f(\alpha) = (1-\alpha)^n \qquad (4)$$

The constant rate k(T) is given by the Arrhenius equation:

$$k_i = k_{0i}\left(\frac{-E_{ai}}{RT}\right) \qquad (5)$$

where $k_{0i}$ is the pre-exponential factor (time$^{-1}$), Ea is the activation energy (kJ mol$^{-1}$), T is the temperature (°C) and R (J K$^{-1}$ mol$^{-1}$) is the universal gas constant.

In the case of a constant heating rate (β):

$$\beta = \frac{dT}{dt} \qquad (6)$$

Therefore, a combination of given equations and some change is:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta_0}\int_0^{T} \exp(-\frac{E}{RT})dT \qquad (7)$$

The right hand side of Eq. (5)has no exact analytical solution, but production of some variable switches and applying Cauchy's rule the expression can be solved to give:

$$g(\alpha) = \frac{ART^2}{\beta E}(1-\frac{2RT}{E})\exp(-\frac{E}{RT}) \qquad (8)$$

$$\ln g(\alpha)/T^2 = \ln\frac{AR}{\beta E}(1-\frac{2RT}{E}) - \frac{E}{RT} \qquad (9)$$

In general, the term 2RT/E can be neglected since it is much less than unity for the thermal decomposition of lignocellulosic materials [22]. Hence, plotting ln[g(α) ⁄ $T^2$] versus 1/T gives a straight line with a slope −E/R since ln(AR ⁄ βE) is almost constant. f(α) and g(α) expressions depend on the mathematicalmodel of each conversion mechanism. If the suitable g(α) is applied, ln[g(α) ⁄ $T^2$] versus 1/T plot is linear with high correlation coefficient ($R^2$) of the regression analysis. The latter allows extracting the activation energy and pre-exponential factor values.

## 3. Result and discussion

### *3.1. Basic characteritics of the sample*

### *3.1.1. Composition of inorganic elements*

The inorganic contents of raw, control and impregnated sampleswere determined by X-ray fluorescence analyses. Fig.1 shows the contents of AAEM species in the Cypress sawdustbefore and after impregnation.

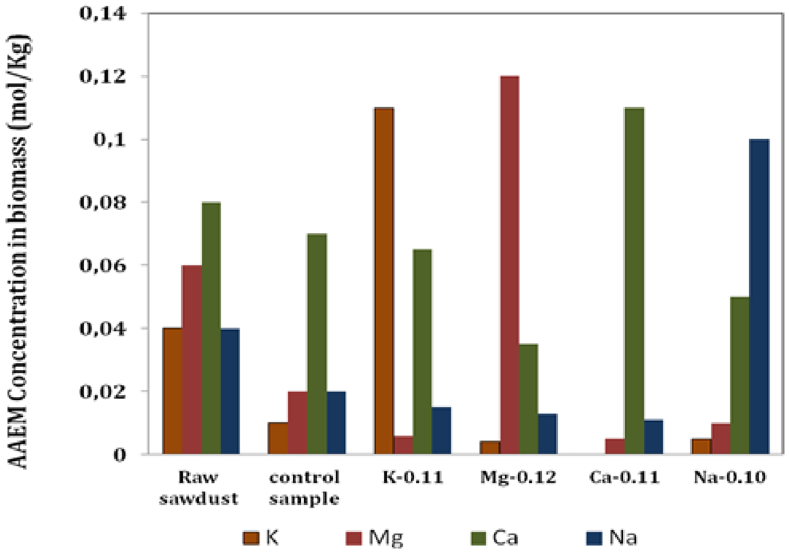

**Fig.1.** Contents of inorganic elments in biomass sample.

The main metal constituents of the samples were alkali and alkaline earth metals such as magnesium (Mg), calcium (Ca), potassium (K), and sodium (Na). Calcium was by far the most abundant elment species in the cypress wood sawdust. Water wasching treatements was generally quite successuful at removing large fraction of the AAEM species, with observed reductions of 20 to 50%. After waterleaching most of potassium and sodium were removed comparing to calcium and magnesium, which suggests that the majority of potassium and sodium were present in the form of water-soluble salts [15]. In contrast calcium could not be completely removed through washing with water. Mourant et al.[23] showed that washing biomass with dilute acid was clearly the most effective in removing the AAEM species and 4% of the initial calcium left after washing with acid. However leaching with acid might create a negative impact on physicochemical structure of the sample. Hence the water and salts-pretreatments were preferred in this present study for the removal of the aforementiend elements.

### *3.1.2. Ultimate and proximate analysis*

Ultimate and proximate analyses of raw, control and impregnated samples are shown in table2. As shown in table 2 comparing to the raw sample, the ash content of control sample decreased from 0.9% to 0.3%

and the ash contents of impregnated samples increased from 0.3 to 0.61-0.74%.. Concerning the ultimate analysis, the main constituents contents of the two materials were very similar. They were mainly formed by carbon,hydrogen and oxygen with a total percentage around 95%. Note the absence of nitrogen for control and K-impregnated sample could be attributed to the small values out of the apparatus detection limit. For raw sawdust, these results are comparable to those reported in the literature for lignocellulosic materials [24].The molecular mass of C is much heavier than H, thus C/H mass ratio reflects variance of amount of hydrocarbons. As shown in Table 1, the C/H ratioof control and impregnated samples fluctuates between 8.25 and 7.59, and the C/H ratio decreased slightly after impregnation process, which illustrates that a fraction of organic components were removed from samples during the impregnation process.

**Table2**. ultimate and proximate analysis of raw, control and impregnated sample

| | ***Raw sawdust*** | ***Control sample*** | ***K-0.11*** | ***Mg-0.12*** | ***Ca-0.11*** | ***Na-0.10*** |
|---|---|---|---|---|---|---|
| ***Proximate analysis (wt%, air dried basis )*** | | | | | | |
| ***Ash*** | 0.90 | 0.3 | 0.74 | 0.72 | 0.61 | 0.68 |
| ***Moisture*** | 6.4 | 2.5 | 1.1 | 3.39 | 2.9 | 3.54 |
| ***Ultimate analysis (wt%, air dried basis )*** | | | | | | |
| ***C*** | 52.65 | 47.67 | 40.4 | 44.11 | 46.65 | 43.80 |
| ***H*** | 6.47 | 5.72 | 4.97 | 5.81 | 5.85 | 5.56 |
| ***O*** | 39.87 | 46.78 | 53.87 | 49.5 | 46.79 | 49.17 |
| ***N*** | 0.09 | - | - | 0.09 | 0.08 | 0.19 |
| ***S*** | 0.02 | 0.02 | 0.018 | 0.02 | 0.02 | 0.018 |
| ***C/H mass ratio*** | 8.14 | 8.25 | 8.13 | 7.59 | 7.98 | 8.02 |

### *3.1.3. Effect of alkali and alkaline earth metallic species (AAEMs) on lignocellulosic composition*

In order to compare their effect on lignocellulosic composition, the analyses have been performed with the methods described previously (see Section 2).Fig.2 summarizes the data onthe pretreatment of cypress sawdust with the different salts solutions. Hemicellulose was slightly present in cypress sawdust similar in its content quote from the literature [24].The data indicated that $MgCl_2$ and KCl having the highest capacity generated as high as 60% hemicellulose removal comparing with only about 24% for $CaCl_2$and NaCl and 2.6% for control sample was washing with distilled water.All of the inorganic salts used in this study increased the hemicellulose decomposition. This degradation process were accelerated in the following order $MgCl_2$>KCl > $CaCl_2$ > NaCl. Yu et al [25] reported that the aibilities of metal salts to accept electrons and the ionic radii of metalions are different.

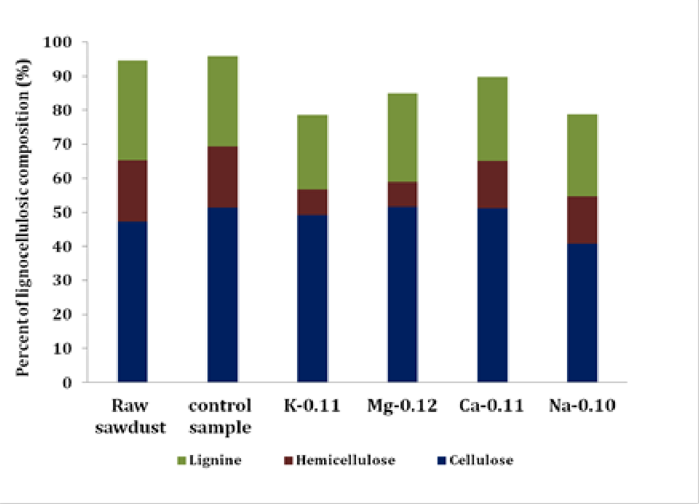

**Fig.2.** Contents of three major polymers in biomass sample

Liu et al [24]reported that the salts with weaker ability could not break the complex structure to further decompose hemicellulose.Moreover, Cellulose degradation was more difficult than hemicellulose due to their difficultstructures small amount of lignin was removed. In our results, KCl had a strong effect on hemicellulose degradation comparing to $CaCl_2$which was inconsistent with previous studies [24, 25]. These latters reported that divalent salts had a strong effect than monovalentsalts. The resultcan be explained by the difference in optimum reaction condition of lignocellulosic decomposition. Researchershave combined reagent concentration, prereatement temprature with time as a severity to observe the effect of pretreatement conditions on the hemicellulose, cellulose and lignin degradation.

### *3.2. Thermogravimetric analysis*

Thermogravimetric tests in inert atmosphere ($N_2$) at 5°C/min heating rate and were achieved to evaluate the pyrolytic behaviour of the biomass. The TGA curves obtained in Ar are plotted in Fig. 3-4. TG and DTG results demonstrated that the four inorganic salts have a significant effecton the biomass pyrolysis. This effect is evidenced by the changes in the char yield and characteristic parameters such as the maximum weight loss rate and the corresponding peak temperatures.

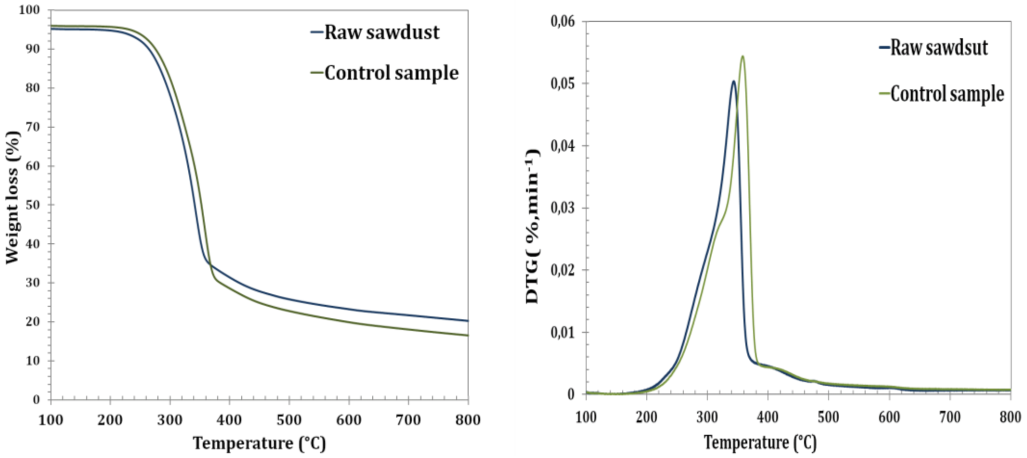

**Fig.3.** TG and DTG curves of raw and control samples in $N_2$ at heating rate of 5°C/min.

Fig. 3shows DTG curves for theraw and controlsamples. As shown in Fig. 3,in theDTG curve of the control sample, an unresolved shoulder and peak were observedat near 300°C and 360°Crespectively. In contrast, the peak at 300°C disappeared in the raw sample. It is well known that the peak at 300°C resulted from degradation of hemicellulose and that the other peak around 365°C originated from cellulose degradation [26]. The temperature at the maximum degradation rate was clearly shifted from 358°C for the control to 342°C for rawcontrol. The maxiumun degradation rate of raw sawdust was slightly lower than the control sample. This difference may be associated with the modification of the cellulose crystallinity during leaching water process[27].It can be seen also in Fig 3 that other pyrolysis feature after demineralization was a decrease in char yield. The char yield of raw sawdust sample was 20.25%. However, after demineralization of the biomass char yield decreased to 16.5%. Demineralization leads to the emissions of more volatiles during thermal degradation precess. Thus we can specule that inorganics salts promote decompostion of cellulose and hemicelluose at relatively low tempratures. In other hand the enrichment of alkali and alkaline earth metallic (AAEM) in Cypress wood sawdust apeared to have a propensity towards the deposition of more char via the catalytic cross-linking reactions.

The obtained TG and DTG curves for the impregnated samples are presented in Fig 4. In general, the pyrolysis process could be divided into two stages: main devolatilization (active pyrolysis) and continuous slight devolatilization (passive pyrolysis. In the main devolatilization, the thermal decomposition of the major lignocellulosicbimass (cellulose, hemicelluloses) occured with a large mass loss of 80%. The continuous slight devolatilization stage occured above 432°C whichcorrespondsthe degradation of ligninand the formation of the residual char[28].It has been proved previously that the major decomposition of lignocellulosic biomass mainly refers to firstly hemicellulose decomposition at the temprature of 200-300°C followed by cellulose decomposition at a higher temprature 320-420°C. The difference of thedegradation processbetween the different samples could be clearlyobserved in both TG and DTG curves. TG and DTG results demonstrated that the four inorganic salts (KCl, MgCl2, NaCl, and KCl)have a significant effect on the biomass pyrolysis. This effect is evidenced by the changes in the char yield and in the TGparameters such as the maximum degradation rate and theircorresponding peak temperatures. In Fig4, it can be seen that the alkali metal (KCl, NaCl) species can decreased the $T_{onset}$ by approximately, 10-15°C which means that the addition of alkaline earth andalkali metal compounds may catalyze the initial thermal degradation of cypress sawdust. The yield of char remaining after thermal degradation significantly increased with the impregnation of K and Na contents from 16.50 wt. % in the control sample to 21.54 wt. % and 21.24 wt. %, respectively in the K-0.11 and Na-0.10 samples. As shown in the DTG curves, two clearly resolved peaks at 30 °C and 358°C in the control sample became one unresolved peak as the two inorganic minerals contents increased. The shoulder at 300°C is attributed to the decomposition of hemicelluloses, and the other peak at 359 °C is a result of cellulose decomposition.The temperature at the maximum degradation was clearly shifted from 365°C for the control sample to 342°C for the Na-0.10 sample, and to 343°C the for K-0.11 sample. The DTG curves indicate that decomposition of hemicelluloses and cellulose was affected by the addition of K, and Na which resulted in the two separate peaks becoming one unresolved peak. The DTG curves samples indicate that the maximum degradation rate decreased with the addition of K and Na. These differing thermal degradation behaviors may result from alterations in the degradation mechanism that is specific to each of the two inorganic minerals [27]. Wang et al [29] reported that sodium and potassium ions are very small and it canspenetrate into the biomass texture and break the intermolecular hydrogn bridges under swelling or heating.The addition of $MgCl_2$ led to a significant change in the sample degradation profile, indicating an increase in the maximum degradation rate from 0.05%.min$^{-1}$for the control sample to about 0.057 %.min$^{-1}$ with addition of Mg-012. In addition the global decomposition range shifted to lower temperatures due the catalytic effects of magnesium.The maximum decomposition temperature of control sample was 358°C and it slightly decreased to 353°C for Mg-0.12.

Previous studies reported that the magnesium in biomass would combine to the oxygen containing functional groups and linkages at the surface molecules, and this could facilitate the decomposition ofbiomass. Furthermore $MgCl_2$ has an effect on the degradation of cellulose, with a negligible effect on the degradation of hemicelluloses.The yield of char remaining was clearly increased with the impregnation of Mg content from 16.50 wt. % in the control sample to 17.39 wt. %. When impregnated with calcium salt, the valuesof the characteristic parameters, such as the mass loss and the maximum mass loss rate exhibited approximately the same tendencyto the control sample. But a respectable distinction still exists between the two samples. The DTG curve indicates that only the decomposition of hemicelluloses was affected withthe calcium addition which resulted in decreasing of the maximum degradation temprature of hemecellulose. Thermal degradation mechanisms are specific to each of four tested salts which implies that the yield of pyrolytic compounds could differ according to the inorganic salt.

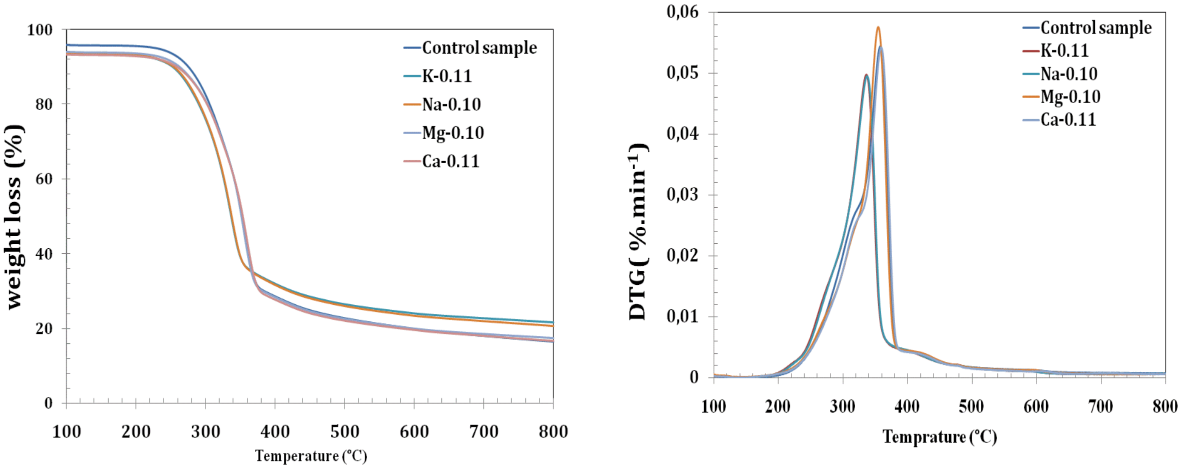

**Fig.4.** TG and DTG curves of raw and impregnated samples in N2 at heating rate of 5°C/min.

### *3.2. Kinetic parameters*

The kinetic parameters such as pre-exponential factor, activation energy and order of reaction for all three zones of the samples are determined by multiple-linear regression method in Microsoft- Excel. All the samples exhibited three reaction zones. The temperature range of zones (moisture, primary pyrolysis and secondary pyrolysis) is identified from the peaks of TG-DTG curve. The values –ln [(1/$w_i$-$w_f$) (dw/dt)], 1/RT and ln (w-$w_f$/$w_i$-$w_f$) which corresponds to y, x and z of equation (9) in the manuscript are calculated for each zones of temperature range. Microsoft –Excel is applied to determine the constants A and E which corresponds to pre-exponential factor, and activation energy. The TG data for the different samples were examined using chemical reaction and diffusion mechanisms (Table3)

**Table3** Activation energies of the thermal degradation of different samples.

| **Sample** | **Temperature *range*** | **Activation energy *(kJ·mol⁻¹)*** | **$R^2$** | **f(α)** |
|---|---|---|---|---|
| Control Sample | 236-375 | 102 | 0,9945 | D1 |
| | 236-375 | 109 | 0,9918 | D2 |
| | 375-620 | 17,6 | 0,9912 | F2 |
| | 375-620 | 47,9 | 0,9941 | F3 |
| K-0.11 | 240-360 | 90,9 | 0,9937 | D1 |
| | 240-360 | 99,4 | 0,9908 | D2 |
| | 360-620 | 21,8 | 0,9943 | F2 |
| | 360-620 | 56,1 | 0,9951 | F3 |
| Na-0.10 | 240-360 | 93,9 | 0,9950 | D1 |
| | 240-360 | 102,6 | 0,9921 | D2 |
| | 360-620 | 20,3 | 0,9946 | F2 |
| | 360-620 | 53,1 | 0,9958 | F3 |
| Mg-0.10 | 258-375 | 93 | 0,9903 | D1 |
| | 258-375 | 101,9 | 0,9840 | D2 |
| | 375-595 | 21,4 | 0,9970 | F2 |
| | 375-595 | 55,2 | 0,9978 | F3 |
| Ca-0.11 | 258-375 | 88,6 | 0,9909 | D1 |
| | 258-375 | 101,4 | 0,9906 | D2 |
| | 375-595 | 18,7 | 0,9973 | F2 |
| | 375-595 | 49,9 | 0,9986 | F3 |

Kinetic parameters analysis of the three samples shows that the best fit was obtained with a one way transport model (D1) for the devolatilization region. However, the third order chemical reaction (F3) was the most reasonable for the thermal degradation during the char formation region. In literature, these kinetic models were the most suitable for describing the thermal degradation of lignocellulosic materials. The first devolatilization stage, ranging from 236 to 375°C is well described by one way transport model (D1). The activation energy is ranging between 88.6 and 102 kJ/mol. Activation energy for the impregnated samples is slightly lower than the control sample during the devolatilization step. Such results may indicate the catalytic effect on the different minerals on the thermal degradation of cellulose and hemicellulose. In contrast, no significant effect on the energy activation is observed during the char formation zone.

The comparison between the activation energy of the different impregnated samples did not give a clear tendancy. Therefore, other kinetic models should be applied in order to identify the effect of each minerals on the thermal degradation of Cypress sawdust

## *Conclusion*

In the current experimental study, the impregnation of Cypress sawdust with Alkali and alkaline earth metallic (AAEM) species (KCl, NaCl, $MgCl_2$, and $CaCl_2$) seems to have a significant effecton its thermochemical degradation process. The observed effects of inorganic metals on thermal degradation can be summarized as follows: Char formation significantly increased for all used inorganic salts while temperatures. Maximum degradation rate was decreased with addition of potassium and sodium content. Maximum degradation rates for the K and Na impregnated samples did not significantly change, but were slightly lower than that of the control. The addition of Mg led to a significant change in the sample degradation profile, indicating an increase in the maximum degradation rate.The DTG curve indicates that only the decomposition of hemicelluloses was affected withthe calcium addition which resulted in decreasing of the maximum degradation temperature of hemicellulose. All four inorganic metals catalyzed the degradation of Cypress sawdust, as evidenced by the changes in peak shapes in the DTG curves. no significant effect on the energy activation is observed during the char formation zone.

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