Thermal removal of nitrogen species from wood waste containing urea formaldehyde and melamine formaldehyde resins

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Abstract

The removal of nitrogen from wood board waste through a low temperature pyrolysis (523–573 K) is investigated with two analytical methods.

The kinetic study of the thermal behaviour of wood board and of its components (wood, UF and MF resins) shows the feasibility of removing thermally nitrogen from wood board waste. Indeed, the range of temperatures associated with the degradation of wood is different from the one obtained for the degradation of UF and MF resin. Isothermal conditions enable the determination of a kinetic model for degradation of wood board and of its components and demonstrate that the thermal behaviour of wood board is not the reflection of the sum of its components' behaviour.

FTIR analysis of gas products confirms the feasibility removing nitrogen thermally and enables the evaluation of the optimum treatment conditions (temperature/duration). Elementary analysis of the treated samples and study of their low heating value (LHV) enable to quantify the efficiency of the thermal treatment in terms of nitrogen removal and of energy recovery. Results show that around 70% of the initial nitrogen can be removed from the waste, and that the temperature of treatment (between 523 K and 573 K) does not influence the efficiency in terms of nitrogen removal. Nevertheless, the ratio Residual energy/Initial energy (between 76% and 90%) is improved with the lowest temperature of treatment.
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1. Introduction

Taking onto account problems of greenhouse effect together with the decrease of fossil resources, what kind of solution can be provided by human society to satisfy its own increasing need for energy?

Biomass gasification is one of the few options which can provide a substantial part of this share in the near future. Nevertheless, the industrial development of such a biomass gasification process is slowed down by the expensive cost of wood and biomass. The idea would then be to substitute this natural feedstock by wood waste. Indeed their low or even negative cost would improve the economic efficiency of the gasification process and favour its development. We focus this work on wood waste which contains urea-formaldehyde and melamine-formaldehyde resins such as wood board or laminated flooring which represent an easily collectable feedstock and a non-

negligible resource of energy. Resins associated with this type of wood waste have a high content of nitrogen [1] (see Fig. 1) and are responsible for producing ammonia, isocyanic acid, hydrogen cyanide and nitric oxides when a classical thermo-chemical conversion (combustion or gasification) is operated [2,3].

The global process studied is a two-stage thermal treatment where in the first step the N-species are to be removed through a low temperature pyrolysis, followed by a second step where the remaining material is processed through a gasification process for heat and electricity production. The volume of polluted gases released during such a process is far lower than the one released during the only official way of disposing of wood board waste: incineration. As a result the cost of gas cleaning will be far lower. Therefore, this two-stage process may improve the economic efficiency of gasification process and of wood board waste disposal. This work is focused on the first step of the process.

We propose firstly to study the kinetics of thermal degradation of wood board and of its components in order to check the feasibility of a selective decomposition of UF and MF resins from

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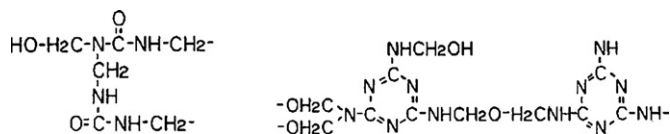E-mail address: pierre.girods@yahoo.fr (P. Girods).

Fig. 1. Typical linkages in UF and MF resin [2].

the waste. The range of temperatures associated with degradations of wood, UF and MF resins and wood board are studied to check if selective decomposition of UF and MF resin from wood board is possible. Thermal degradation of wood, UF and MF resins and wood board is then studied in order to establish numerical models and to check if the thermal behaviour of wood board can be considered as the sum of its components' thermal behaviour. Isothermal curves for weight loss, measured in an inert atmosphere for a range of temperatures for which the rate of resins thermal degradation is maximum, are used to elaborate a reaction mechanism scheme.

In a second way, thermal removal of N-species from wood board is analysed by IR spectrometry in a pyrolysis reactor to characterize the gas products, to evaluate the efficiency of the process in terms of nitrogen removal and to determine optimum duration of treatment according to the temperature of the reaction.

Finally, elementary analysis, proximate analysis and study of the low heating value (LHV) of the treated samples are realized to characterize the different treated materials and to determine the efficiency of the process in terms of nitrogen removal and of energy recovery.

Kinetics of degradation of biomass have been well studied [4–15] but no model could be clearly established because of the great variability of the resource and the operating conditions (temperature, reaction atmosphere, transfer of mass and heat). We can note however that the mechanism of biomass degradation shows the presence of several decomposition phases. A drying phase with elimination of some volatile compounds takes place at temperature up to 473 K. For a range of temperatures between 473 K and 553 K, hemicelluloses are converted essentially into gases and acetic acid. It is the phase known as torrefaction. Above 553 K, lignin and cellulose decompose to give three products: gas, tar and char. The kinetic analysis of wood carbonization, also called low temperature pyrolysis, under isothermal conditions has been carried out by several authors to represent the kinetic schemes of this process. The simplest treatment describes the process by means of a one step global reaction for degradation in which the activation energies vary toughly between 60 kJ mol^{-1} and 170 kJ mol^{-1} [5–7]. These models are not applicable for simulating wood carbonization because they assume a constant ratio of the charcoal to volatiles yield [8]. A one-step-multi-reaction kinetic mechanism for beech wood was described by [9] as a two-stage temperature process in the range of 523–673 K. Two sets of kinetic parameters (activation of energies of 17–115 kJ mol^{-1}) were needed depending on a limit temperature of 603 K. This kinetic scheme cannot be extended to systems different from the one on which is based [8]. Multi-stage, semi-global models are developed to describe the kinetic of isothermal wood degradation [10–15].

These models include the description of the primary degradation of virgin wood and the secondary degradation of primary pyrolysis products. Important differences can be observed in the reported results which means that further analysis are needed to study the multi-stage thermal degradation kinetics of wood under isothermal conditions.

Concerning wood waste degradation, several works are proposed in literature. Pyrolysis of CCA-treated wood has been well studied by [16,17]. A study of the kinetics of pyrolysis for five kinds of wood waste (forest, demolition, machines, furniture, pallets) has been carried out by [18] using models proposed by [19,20]. The works of [21,22] aim to describe degradation of creosote-treated waste. Concerning melaminated wood board which contains aminoplasts resins (urea-formaldehyde, melamine-formaldehyde), literature gives little information. Studies undertaken by [2,22] give information about the thermal field related to degradation of UF and MF resins. The UF resin pyrolysis is observed between 493 K and 563 K with three peaks at 498 K, 508 K and 523 K, the maximum being at 508 K, whereas for MF resin, the field of degradation is more extended and extends/goes from 493 K to 793 K with two maxima at 523 K and 673 K. During degradation of these resins, we can observe formation of methanol, ammonia, formaldehyde and carbon dioxide [23].

Several authors [24–27] report that during thermochemical conversion of nitrogen containing materials, fuel-nitrogen is converted to ammonia (NH_3), isocyanic acid (HNCO), hydrogen cyanide (HCN), nitric oxides (NO_x, N_2O), molecular nitrogen (N_2) and organic nitrogen. Part of fuel nitrogen remains in the char in a pyrolysis process. The distribution of fuel-nitrogen in a thermochemical conversion process is strongly influenced by the intrinsic parameters of nitrogen containing material (nitrogen content, chemical structure, volatility) [24] and by conditions of reaction (temperature, heating rate, inert or oxidative atmosphere). HCN/NH_3 and HCN/HNCO ratios were shown to increase with increasing temperature [25]. It has been shown that nitric oxides are mostly produced during combustion processes [26] and are mainly formed by oxidation of NH_3, HCN, HNCO and organic nitrogen. Low yields of NO can nevertheless be observed during pyrolysis process [25].

The work presented here will help to improve our knowledge about the thermal degradation of wood board and of its components (wood, UF and MF resins) which is needed to investigate the selective decomposition of UF and MF resin from wood board.

2. Experimental

2.1. Samples preparation

Wood, UF resin and wood board samples are provided by a wood board factory. MF resin has been formulated in our lab by addition of formalyne and water to melamine. The pH of the solution is fixed at 9.5 and the temperature is increased slowly to reach 365 K during 1 h. The pH is thus decreased to 7.2 during the time needed for water tolerance (WT) to reach 200% (WT is a characteristic of MF resins and corresponds to the quantity

Table 1
Elementary analysis of wood, wood board, UF and MF resins

	wt%			
	C	H	O	N
Wood	50.5	5.9	43.5	0.1
Wood board	47.3	5.8	43.1	5.4
UF resin	28.6	6.6	38.1	26.6
MF resin	34.5	5.6	9.5	50.2

of water which can be added to the resin without a change of phase; a WT of 200% means that the mass of water which can be added without a change of phase is twice the mass of resin). The pH is finally increased to 10.5 while the temperature decreases slowly to room temperature. The molar ratio $F/M = 1.8/1$ for the MF resin and the molar ratio $F/U = 1.5/1$ for the UF resin. The proportion of wood, UF and MF resin in the wood board isn't well known. The manufacture give us an approximation of the wt.% (on dry mass) of each component: Wood (88–90%), UF resin (10–12%), MF resin (<0.5%). The particle size for the samples which have been crushed is lower than 1 mm. For thermogravimetric study, samples were dried in an oven for 24 h at 103 °C before the experiments to be performed. In the case of a study on laboratory device, humidity of samples was about 7% (on wet basis). Table 1 shows the elementary analysis for wood, wood board, UF resin and MF resin realized in the Analysis Central Service of CNRS in France.

2.2. Apparatus description

2.2.1. Thermogravimetric analysis

Experimental work was carried out on a computerized thermobalance (Setaram Setsys 12). Thermobalance configuration gives a sensitivity of $\pm 0.4\,\mu g$ thus allowing the use of small samples (100–150 mg) which is needed to ensure isothermal conditions in samples. In order to establish an inert atmosphere during all experiments, a controlled nitrogen flow (fixed at 300 mL/min, 273 K, 1 atm) sweeps the measurement cell that is purged during 20 min before starting the heating program. During experiments, the nitrogen flow is fixed at 90 mL/min. The initial dry mass of samples is about 105 mg.

2.2.2. Study in the pyrolysis reactor

The experiment Fig. 2 consists in a quartz tubular reactor whose temperature is controlled by a regulated furnace. A quartz sample box enables the insertion of waste (a few grams maximum) in the furnace whose temperature can reach 1373 K.

The gases resulting from the reactor (mixture carrier gas/pyrolysis products) are sent, via a heated line, to the 135 mL gas cell (a 10 cm long path heated to 473 K to avoid any condensation which would damage the very sensitive windows in KBr (Potassium bromide)) of the FTIR spectrometer (Bruker Equinox 55) where there are analysed in a semi-continuous way (time of sampling: 15 s). The configuration of the FTIR spectrometer (resolution of $2\,cm^{-1}$, 5 scans per measure) allows a qualitative analysis of many compounds: carbon dioxide and monoxide, methane, light hydrocarbons (ethane, ethylene, etc.),

formaldehyde, N-compounds (ammonia, iscocyanic and cyanhydric acid, nitric oxides), methanol, formic and acetic acid.

2.3. Experimental and measurements methodology

2.3.1. Thermogravimetric analysis

2.3.1.1. Non-isothermal conditions. The experiments start with a rise in temperature at 20 K/min from room temperature to 373 K with a holding time of 5 min. Then, a heating rate of 1.5 K/min is applied to the oven in order to reach 1173 K. The low heating rate used aims at avoiding spatial gradients of temperature, diffusion factors and superposition of different steps of the degradation.

The initial mass is the one given by thermobalance after the isothermal step at 373 K.

2.3.1.2. Isothermal conditions. The kinetic parameters are determined in isothermal conditions to prevent/exclude influence of diffusion factors. The experiments start with a rise in temperature at 20 K/min from room temperature to 403 K with a holding time of 5 min to make sure that the sample be dry. Then, a heating rate of 25 K/min is applied to the oven in order to reach the fixed studied value. This methodology is used to shorten the first thermal dynamic stage. The subsequent thermal decomposition is carried out in isothermal conditions during 1 h for UF and MF resins and during 3 h for wood and wood board. The same experiment is repeated for 3 fixed temperatures 533 K, 543 K and 553 K which correspond to the range of temperatures for which thermal degradation of wood begins and for which thermal degradation of UF resin is at its maximum.

The initial mass is the one measured/reached at the end of the drying phase at 403 K. For the purpose of separating the mass loss during the dynamic stage (non-isothermal) of decomposition from the isothermal stage, the relative values of total mass before reaching the fixed temperature are not taken into account in the estimation of the kinetics parameters. The time origin at the beginning of the transformation is obtained by an exponential extrapolation of the mass values corresponding to the beginning of the experimental curves in isothermal conditions.

2.3.2. Study in the pyrolysis reactor

The temperature of the furnace is fixed at the temperature of treatment (523 K, 533 K, 543 K, 553 K, 563 K and 573 K). The reactor is fed with a nitrogen flow set at 2 NL/min (controlled by numerical flowmeters: Aalborg DFC 2600). The heating rate of samples is between 10 K/s and 20 K/s in these conditions.

A one gram sample is placed in the sample box. Once the sample has been set up, a short delay is necessary to purge the device in order to achieve a correct reference measurement with the spectrometer FTIR.

The level of ammonia in the mixture pyrolysis products/carrier gas is considered as a good indicator of the efficiency of the process in terms of nitrogen elimination. In this way, the optimum durations of treatment are determined by following this level of ammonia and by considering that treatment is no longer efficient (in terms of nitrogen elimination) when it reaches a value lower than 100 ppm. Three 20 min tests are car-
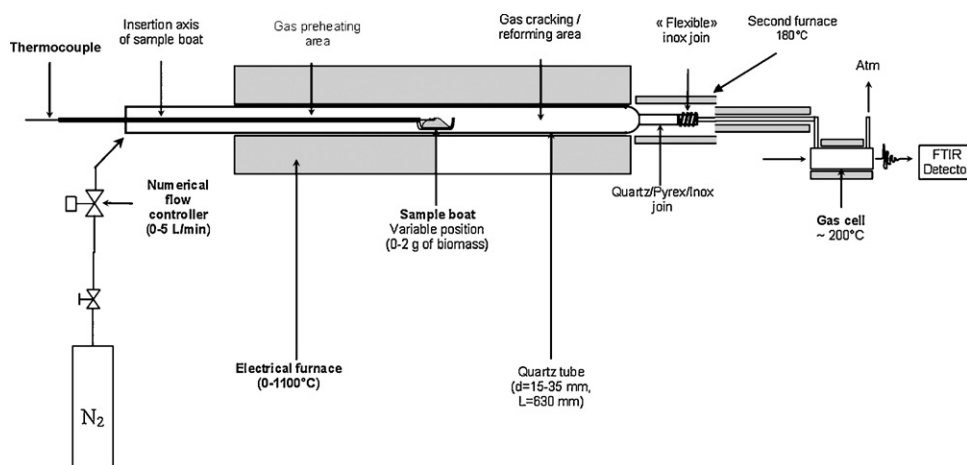
Fig. 2. Sketch of the pyrolysis reactor.

ried out for each temperature of treatment (523 K, 533 K, 543 K, 553 K, 563 K and 573 K). The 80 recorded spectra are treated by a numerical quantification method. The evolution of the level of NH_3 in the mixture pyrolysis products/carrier gas is shown on Excel graphs.

New experiments are achieved following the same methodology. The duration of experiments which was first of 20 min is now set to the optimum duration determined with the previous experiments. The treated samples are then weighed after a cooling delay.

Elementary analysis of the treated samples are then realized in the Analysis Central Service of CNRS to evaluate the efficiency of the process in terms of nitrogen elimination. Level of devolatilization of nitrogen is deduced from the results of the elementary analysis and from the level of degradation of the samples after each treatment following the Eq. (1):

$$N_{\text{removed}} = \frac{N_i \times m_i - N_T \times m_T}{N_i \times m_i} \times 100$$

with N_{removed}, the percentage of nitrogen eliminated in gases (condensable and non-condensable); N_i, the initial percentage of nitrogen in dry wood board samples; N_T, the percentage of nitrogen in the residue after treatment at the temperature T; m_i, the initial dry mass of wood board samples; m_T, the residual weight after treatment at temperature T. N_i, N_T, m_T are given in Table 5 and m_i is equal to 0.93 g.

The study of the LHV of the treated samples (in a calorimetric bomb) enables the determination of the ratio between energy retained in the residue (LHV of the residue × residual dry mass of the residue) and energy contained in the initial wet waste (16 300 kJ/kg). This ratio, which does not take into account the energy needed for the process and the one contained in gases produced (condensable and non-condensable), cannot be considered as the energy efficiency of the process. It is nevertheless a good criteria to compare the different treatments in terms of energy recovery.

3. Results and discussion

3.1. Study of the temperature ranges relative to the degradation of wood, UF and MF resins (heating rate: 1.5 K min⁻¹)

First and foremost, the results obtained/correspond with the data of the literature [2,6,13–15,22] for wood, UF and MF resins. The range of temperatures for wood degradation extends from 453 K to 923 K where we can distinguish three peaks at 490 K, 543 K and 600 K which do not necessarily correspond with the decomposition temperatures of the three main components. The maximum rate is achieved around 600 K. The range of temperatures for UF resin degradation extends from 493 K and 700 K with three peaks at 498 K, 528 K and 568 K the maximum being at 528 K. Values are a bit higher than the one presented by [2] but it can be explained by the heating rate which was 1 K/min and not 1.5 K/min as in our case. In the case of MF resin, the degradation extends from 600 K to 1000 K with two peaks at 633 K and 933 K. The maximum rate is achieved at 633 K (see Fig. 3).

These results highlight the shift between the range of temperatures for wood, UF and MF resin degradation what confirms results obtained by [22] and which may enable the selective pyrolysis. Indeed, for temperatures between 523 K and 573 K, volatilisation of UF resin should be significant while the one for wood should be limited.

In a second way, results show that the selective decomposition of MF resin from wood waste by low temperature pyrolysis will be difficult as wood is volatilised before MF resin. Nevertheless, the quantity of MF resin in wood board is so low that the main objective is to eliminate the UF resin.

The thermal behaviour of wood board is really close to the wood one as wood board contains around 90% of wood. We can note however a little difference in the range of temperatures from 470 K to 515 K where wood board rate of degradation is higher than the one for wood.
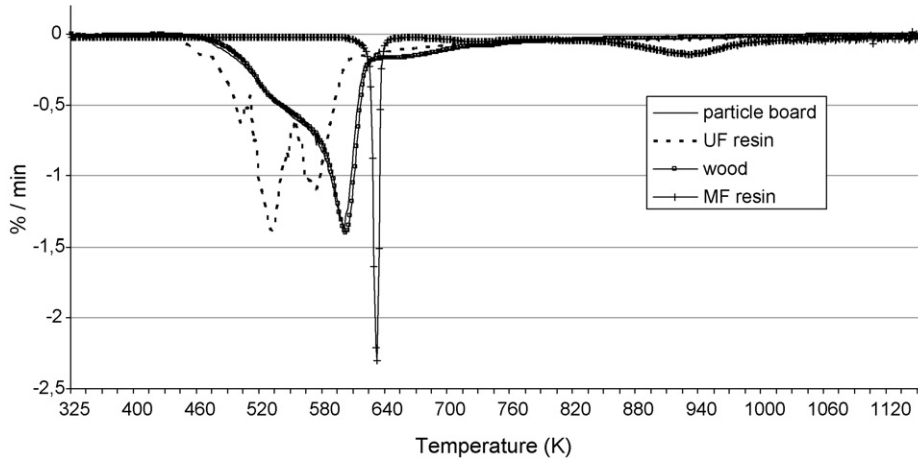
Fig. 3. DTG diagrams of wood board and of its components: wood, UF and MF resin (heating rate: 1.5 K/min; nitrogen flow: 90 mL/min).

3.2. Study of the isothermal degradation of wood board and of its components

3.2.1. Wood

Literature proposes several kinetic models of wood pyrolysis which suggest to divide the wood in three parts corresponding to the main components of wood (hemicelluloses, cellulose and lignin). However, the thermal degradation behaviour of wood cannot be considered as a reflection of the sum of the thermal response of its components [8] as some inorganic components (ashes) catalyse the conversion process in an unpredictable variety of ways.

The model used for wood is a two stage, semi global multi reaction kinetic model established for olive wood [15]. In this model, we consider three parallels and independent first order reactions with three solids, A_i which corresponds to a mass fraction α_i of the initial solid. These pseudo solids A_i cannot be considered as the main three components of wood (cellulose, hemicelluloses, lignin) since it has always been shown that this consideration does not give good results [8]. Each solid decomposes to produce a part of volatiles G_i and a part of solid residues, B and C. γ and β correspond to the proportion of solid produced by the solids A_2 and A_3, respectively. k_i is the rate coefficient which follows an Arrehnius-type law ($k_i = k_{0i} \exp(-E_{ai}/RT)$ with k_{0i}, the pre-exponential factors and E_{ai}, the apparent activation of energy.
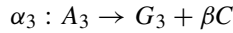
$$\alpha_1 : A_1 \rightarrow G_1$$
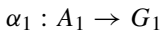
$$\frac{dm_{A_1}}{dt} = -k_1 m_{A_1} \tag{1}$$

$$\frac{dm_{A_2}}{dt} = -k_2 m_{A_2} \tag{2}$$

$$\alpha_2 : A_2 \rightarrow G_2 + \gamma B$$
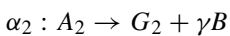
$$\frac{dm_B}{dt} = \gamma k_2 m_{A_2} = \gamma k_2 \alpha_2 m_0 \exp(-k_2 t) \tag{3}$$

$$\frac{dm_{A_3}}{dt} = -k_3 m_{A_3} \tag{4}$$

$$\alpha_3 : A_3 \rightarrow G_3 + \beta C$$

$$\frac{dm_C}{dt} = \beta k_3 m_{A_3} = \beta k_3 \alpha_3 m_0 \exp(-k_3 t) \tag{5}$$

After having integrated Eqs. (1)–(5), we obtain the following five equations:

$$m_{A_1} = \alpha_1 m_0 \exp(-k_1 t) \tag{6}$$

$$m_{A_2} = \alpha_2 m_0 \exp(-k_2 t) \tag{7}$$

$$m_{A_3} = \alpha_3 m_0 \exp(-k_3 t) \tag{8}$$

$$m_B = \gamma \alpha_2 m_0 [1 - \exp(-k_2 t)] \tag{9}$$

$$m_C = \beta \alpha_3 m_0 [1 - \exp(-k_3 t)] \tag{10}$$

Considering ($m_{(t)}/m_0$) as the sum of the mass of the five solids, we can write:

$$\frac{m_{(t)}}{m_0} = \alpha_1 \exp(-k_1 t) + \alpha_2 (1 - \gamma) \exp(-k_2 t)$$
$$+ \alpha_3 (1 - \beta) \exp(-k_3 t) + \gamma \alpha_2 + \beta \alpha_3 \tag{11}$$

The values of some parameters are given by [15]:

$$\alpha_1 + \alpha_2 = 0.4$$

$$\alpha_3 + 1 - (\alpha_1 + \alpha_2) = 0.6$$

values of α_1 and α_2 have been adjusted from 0.16 and 0.24 respectively to 0.13 and 0.27 in order to optimize the model.

$$\beta = -2.4 \times 10^{-3} T + 1.9252 \rightarrow \beta_{533} = 0.646;$$
$$\beta_{543} = 0.622; \quad \beta_{553} = 0.598$$

$$\gamma = 0.42$$

Table 2
Kinetics parameters of wood, UF and MF resin carbonization for a temperature range of 533–553 K

	T (K)	k_1 (s^{-1})	k_2 (s^{-1})	k_3 (s^{-1})	λ_1	λ_2
Wood	533	1.75E−03	1.00E−04	7.15E−06		
	543	2.69E−03	2.22E−04	9.45E-06		
	553	4.71E−03	3.82E−04	3.79E−05		
Wood [15]	523	9.50E−04	8.65E−05	8.63E−06		
	548	2.90E−03	2.25E−04	4.50E− 05		
Particleboard	533	1.52E−03	1.55E−04	5.85E−06		
	543	2.57E−03	2.52E−04	1.89E−05		
	553	4.41E−03	4.52E−04	6.99E−05		
UF resin	533	2.69E−03	3.89E−05		0.553	
	543	3.49E−03	4.88E−05		0.519	
	553	4.73E−03	6.58E−05		0.497	
MF resin	533	4.31E−03	3.39E−04		0.937	0.985
	543	5.42E−03	6.22E−04		0.935	0.982
	553	6.81E−03	9.85E−04		0.933	0.978

By minimizing an error function Er(k_1, k_2, k_3) between measured and calculated values, all parameters have been defined. They are listed in Table 2.
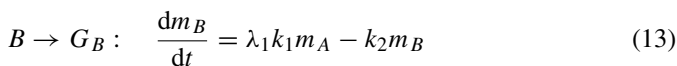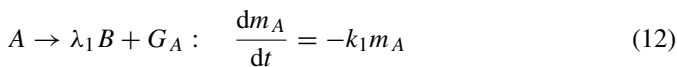
$$\mathrm{Er}(k_1, \ k_2, \ k_3) = \sum_i (X_{i\,\mathrm{calc}} - X_{i\,\exp})^2$$

with $X_{i,\mathrm{calc}}$, the calculated reduced mass of the samples at the ith points of measure and $X_{i,\exp}$, the measured reduced mass of the samples at the ith points of measure.

Fig. 4 shows that model gives a good representation of the experimental mass loss evolution. Kinetic constants are reported in Table 2. Values of rate of reactions k_1, k_2 and k_3 correspond with the literature.

3.2.2. UF resin

In the case of UF resin, we consider two dependent parallel first order reactions where a solid A decomposes to produce a part of volatiles G_A and a proportion λ_1 of a solid B which decomposes as well as A to produce volatiles G_B.

$$A \rightarrow \lambda_1 B + G_A : \quad \frac{\mathrm{d}m_A}{\mathrm{d}t} = -k_1 m_A \tag{12}$$

$$B \rightarrow G_B : \quad \frac{\mathrm{d}m_B}{\mathrm{d}t} = \lambda_1 k_1 m_A - k_2 m_B \tag{13}$$

After having integrated the Eqs. (12) and (13), we obtain the following two equations:

$$m_A = m_0 \exp(-k_1 t) \tag{14}$$

$$m_B = \frac{\lambda_1 k_1 m_0}{k_1 - k_2}[\exp(-k_2 t) - \exp(-k_1 t)] \tag{15}$$

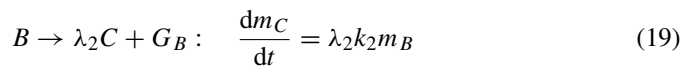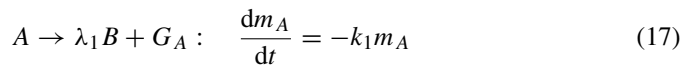Considering ($m_{(t)}/m_0$) as the sum of the mass of the two solids, we can write:

$$\frac{m_{(t)}}{m_0} = \lambda_1 + \left[1 - \frac{\lambda_1 k_1}{k_1 k_2}\right] \exp(-k_1 t) + \frac{\lambda_1 k_1}{k_1 k_2} \exp(-k_2 t) \tag{16}$$

As for wood, model gives a good representation of the experimental mass loss evolution (see Fig. 5). The parameters of

the model have been defined by minimizing an error function between measured and calculated values. They are listed in the Tables 2 and 3.

3.2.3. MF resin

In the case of MF resin, we consider two dependent parallel first order reactions where a solid A decomposes to produce a part of volatiles G_A and a proportion λ_1 of a solid B which decomposes as well as A to produce volatiles G_B and a proportion λ_2 of an indecomposable carboneous solid C.

$$A \rightarrow \lambda_1 B + G_A : \quad \frac{\mathrm{d}m_A}{\mathrm{d}t} = -k_1 m_A \tag{17}$$

$$\frac{\mathrm{d}m_B}{\mathrm{d}t} = \lambda_1 k_1 m_A - k_2 m_B \tag{18}$$

$$B \rightarrow \lambda_2 C + G_B : \quad \frac{\mathrm{d}m_C}{\mathrm{d}t} = \lambda_2 k_2 m_B \tag{19}$$

After having integrated the Eqs. (17)–(19), we obtain the following three equations:

$$m_A = m_0 \exp(-k_1 t) \tag{20}$$

$$m_B = \frac{\lambda_1 k_1 m_0}{k_1 - k_2}[\exp(-k_2 t) - \exp(-k_1 t)] \tag{21}$$

$$m_C = \frac{\lambda_1 k_2 m_0}{k_1 - k_2}[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] + \lambda_1 \lambda_2 m_0 \tag{22}$$

Considering ($m_{(t)}/m_0$) as the sum of the mass of the three solids, we can write:

$$\frac{m_{(t)}}{m_0} = \lambda_1 \lambda_2 + \left[1 - \frac{\lambda_1}{k_1 - k_2}(k_1 - k_2 \lambda_2)\right]$$
$$\exp(-k_1 t) + \frac{k_1 \lambda_1 (1 - \lambda_2)}{k_1 - k_2} \exp(-k_2 t) \tag{23}$$

As for wood, model gives a good representation of the experimental mass loss evolution (see Fig. 6). The parameters of the model have been defined by minimizing an error function
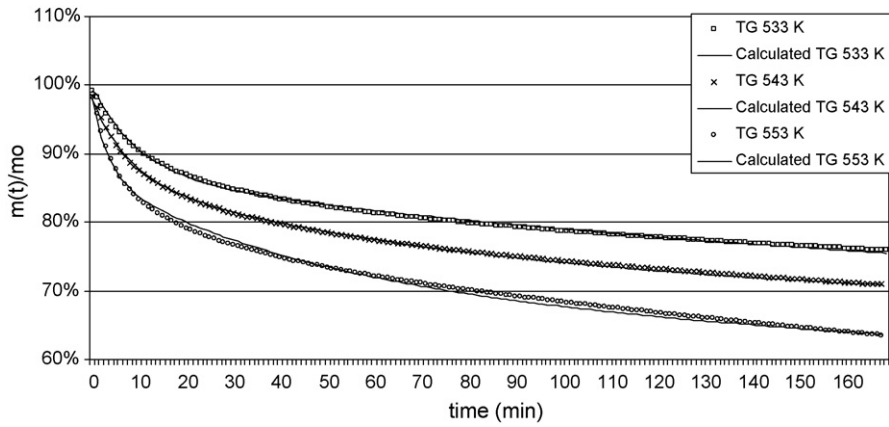
Fig. 4. TG and calculated TG diagrams of wood in isothermal conditions between 533 K and 553 K. Thin lines correspond to experimental TG curves.
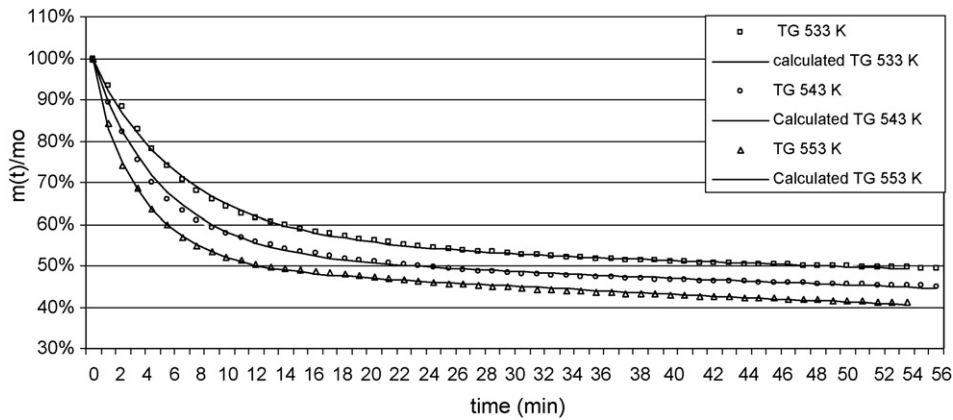

Fig. 5. TG and calculated TG diagrams of UF resin in isothermal conditions for different temperatures. Thin lines correspond to experimental TG curves.

Table 3
Kinetic constants of the different reactions

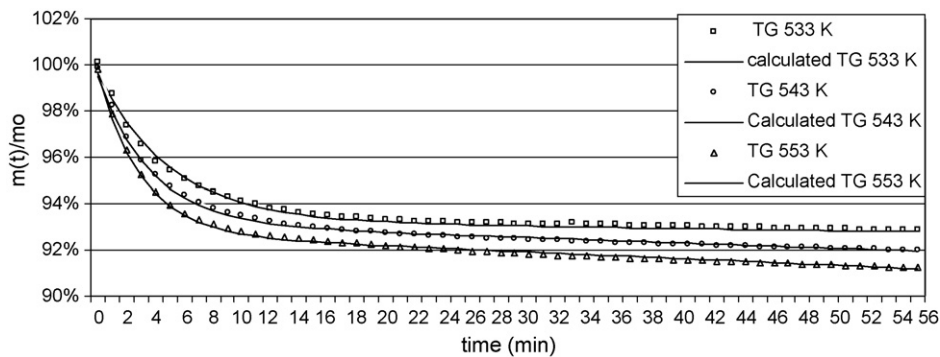|	k_{01} (s^{-1})	k_{02} (s^{-1})	k_{03} (s^{-1})	E_{a_1} (kJ/mol)	E_{a_2} (kJ/mol)	E_{a_3} (kJ/mol)
Wood	1.60E+09	1.07E+12	1.17E+01	122.18	163.67	204.39
Particleboard	9.14E+09	1.20E+09	2.84E+02	130.48	131.606	304.19
UF resin	1.61E+04	80.00		69.2	64.4	
MF resin	1.37E+03	2.18E+09		56.1	130.7	

Fig. 6. TG and calculated TG diagrams of MF resin in isothermal conditions and at different temperatures. Thin lines correspond to experimental TG curves.

between measured and calculated values. They are listed in the Tables 2 and 3.

3.2.4. Wood board

The objective of this part is not to define a numerical model in order to describe the thermal behaviour of wood board but to check if the thermal behaviour of wood board can be considered as the sum of the thermal behaviour of its components. The part of MF resin which is lower than 0.5% is neglected. The proportion of UF resin is considered equal to 10%. The numerical model is obtained as follows:

$$\frac{m_{calc.particleboard_{(t)}}}{m_0} = 0.9 \times \frac{m_{exp.wood_{(t)}}}{m_0}$$
$$+ 0.1 \times \frac{m_{exp.UFre\,sin_{(t)}}}{m_0} \quad (24)$$

The obtained experimental and calculated curves are reported in Fig. 7.

The calculated curves gives not a good representation of the experimental evolution of mass loss for the wood board samples which means that the thermal behaviour of wood board is not the reflection of the sum of the behaviour of its components. It appears that the degradation of wood board is slower than expected and that thermal properties of UF resin are influenced by the presence or not of wood during reticulation. This result does not mean that selective decomposition of UF resin from waste is impossible but that working only on the mass loss during pyrolysis is not sufficient to investigate thermal removal of N-species from waste. Further studies on the gas products and on the residues produced during this thermal treatment will help to define the accuracy of the process and to find the best conditions for the first step of the process.

However, by using a similar numerical model as for wood, good results can be obtained (see Fig. 8).

As for wood, the values of the different parameters of the model are:

$$\alpha_1 = 0.13; \quad \alpha_2 = 0.27; \quad \alpha_3 = 0.6$$

$$\beta_{533} = 0.646; \quad \beta_{543} = 0.622; \quad \beta_{553} = 0.598$$

$$\gamma = 0.42$$

Kinetic constants are reported in Table 2.

3.3. Characterization of the pyrolysis products

Breakdown products of urea-formaldehyde or melamine-formaldehyde resins at temperatures lower than 623 K are mainly N-compound such as isocyanic acid and ammonia [3,22]. Indeed, the results given by spectrometer FTIR reveal the presence of these two nitrogen containing gases. Fig. 9 shows the spectrum of pyrolysis gases after 3 min of treatment of 1 g of wood board (pyrolysis at 573 K under nitrogen (2 L/min)) where we can distinguish the peaks corresponding to ammonia and to isocyanic acid. Hydrogen cyanide, formaldehyde and nitric oxides were not observed during experiments. It is suggested that yields of hydrogen cyanide and formaldehyde are too low to be

Table 4
Optimal treatment time (min) in the temperature range between 523 K and 573 K

T (K)	Duration (min)
523	14.5
533	13
543	11
553	9.5
563	9
573	8

detected in the conditions of experiments and that nitric oxides are not produced due to the inert atmosphere. This result confirms that nitric oxides are not primary products of pyrolysis and that their formation occurs through oxidation in homogenous phase reaction.

Qualitative analysis during low temperature pyrolysis reveals the production of many compounds which can be classified as follows:

- Non-condensable gases such as CO, CO_2 and CH_4. Light hydrocarbons are not produced at this so low temperature.
- Condensable gases such as water, acetic and formic acid (coming from the degradation of cellulose and hemicelluloses [28]), methanol (coming from methoxy groups ($-OCH_3$) of the lignin) and N-compounds such as ammonia and isocyanic acid.

It is suggested that ammonia and isocyanic acid are produced by the degradation of their main precursor: urea released during the breakdown of methylene linkages in urea-formaldehyde resins, which are very sensitive to water and temperature [29]. Thermal treatment therefore leads to the removal of amide groups in the initial waste and may help to prevent the production of hydrogen cyanide during thermo-chemical conversion of the pre-treated material at higher temperature.

3.4. Determination of the optimum durations of treatment

After a numerical treatment of the different spectra recorded during each experiment, evolution of the level of NH_3 in the mixture pyrolysis products/carrier gas can be shown on graphs for different temperatures (see Fig. 10).

We can observe that the level of ammonia increases quickly in the first minutes of treatment showing the performance of the process. This level decreases almost as quickly in the following minutes to reach a value close to zero showing that the treatment is no longer efficient. Fig. 10 shows that the higher the temperature of treatment is, the shorter the time needed for the treatment is.

Treatment duration is set to the duration necessary for the ammonia level to reach a value lower than 100 ppm (0.01%). Six couples "time/temperature" of treatment are thus determined. There are reported in Table 4.
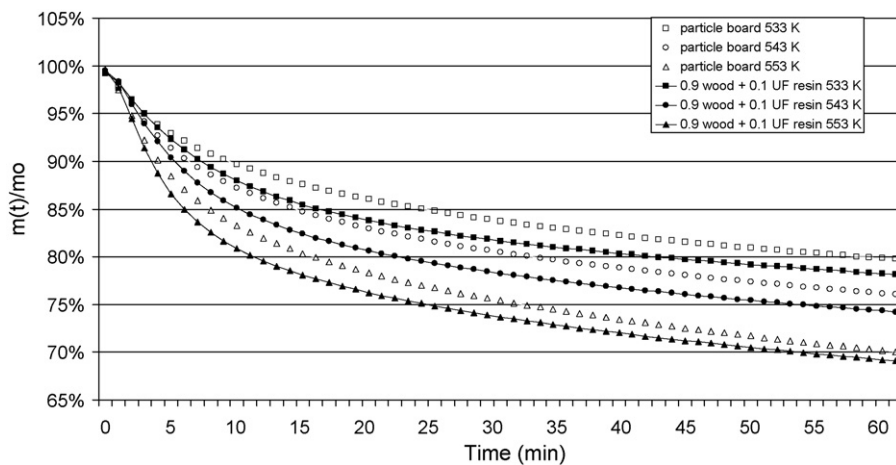
Fig. 7. TG and calculated TG diagrams of wood board in isothermal conditions and at different temperatures.
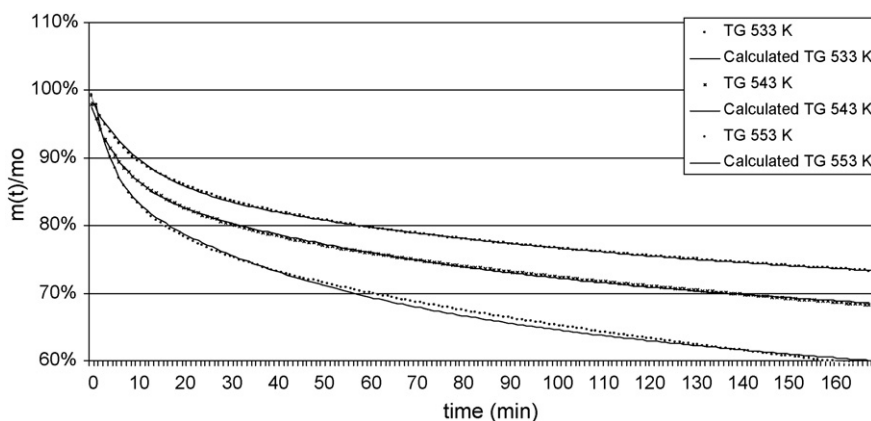

Fig. 8. TG and calculated TG diagrams of wood board in isothermal conditions for different temperatures. Thin lines correspond to experimental TG curves.

3.5. Distribution of fuel-nitrogen in the pyrolysis products

Distribution of fuel-nitrogen in the pyrolysis products is given in Table 5 for the different conditions of treatment.

Results show that the distribution of fuel-nitrogen in the pyrolysis products is not influenced by treatment conditions. In all cases, around 30% of the initial nitrogen remains in the char, 18% is removed under ammonia and the difference is converted

to isocyanic acid and organic nitrogen. It appears that a part of nitrogen is easily removed but that 30% of nitrogen is strongly linked to the residual solid.

3.6. Characterization of the different treated materials

The main characteristics of treated materials are given in Tables 6 and 7. Last column of Table 6 gives the residual mass
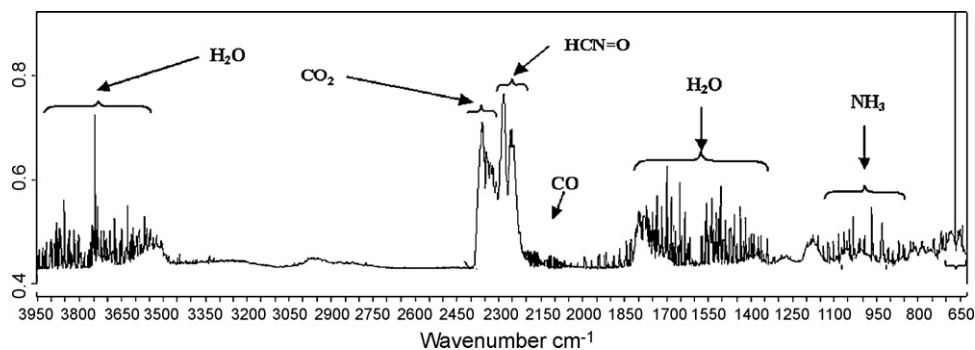

Fig. 9. IR Spectrum of the mix carrier gas/pyrolysis products after 3 min of treatment of one gram of wood board at 573 K.
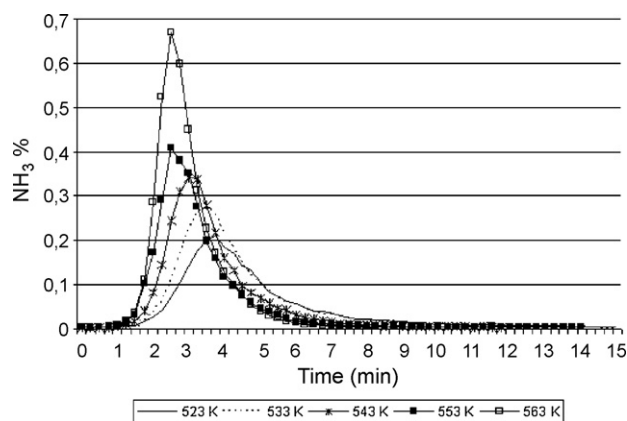
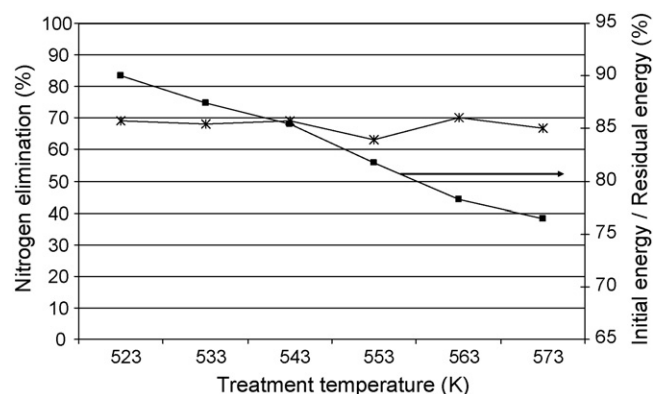Fig. 10. Evolution of NH_3 level in pyrolysis products during treatment at different temperatures.

Fig. 11. Nitrogen removal (%) and ratio residual energy/initial energy obtained for different treatments.

Table 5
Distribution of nitrogen in pyrolysis products

	%_Char	%_NH$_3$	%_(HNCO, Tar)[a]
523 K – 14.5 min	30.9	18.5	50.6
533 K – 13 min	32	20.2	47.8
543 K – 11 min	30.9	16.7	52.4
553 K – 9.5 min	36.8	17.5	45.7
563 K – 9 min	29.9	18	52.1
573 K – 8 min	33.3	19	47.7

[a] Difference between 100 and the sum of %_Char and %_NH$_3$.

Table 6
Elementary analysis of treated materials at different temperatures

	C	H	N	O	Residual dry mass (mg)
523 K – 14.5 min	53.2	5.5	2.1	38.4	750
533 K – 13 min	52.5	5.6	2.2	39.1	720
543 K – 11 min	53	5.5	2.3	37.3	690
553 K – 9.5 min	52.1	5.1	2.8	37.3	650
563 K – 9 min	54.6	5.2	2.5	36.3	610
573 K – 8 min	54.8	4.9	2.9	34.6	575

of solid after treatment; it reveals that the higher the treatment temperature, the higher the level of waste degradation, which is not expected.

Carbon content increases while oxygen and hydrogen contents decrease what it is typical in a carbonisation process. The trends noticed (Table 7) for volatile matter, fixed carbon, ash content and low heating value are also typical of a carbonisa-

Table 7
Proximate analysis of treated materials at different temperatures

	wt.% (on wet basis)			
	Moisture	Volatile matter	Fixed carbon	Ash
Wood board	7	69	23	1
523 K – 14.5 min	1.7	70	27	1.3
533 K – 13 min	0.7	68.5	29.5	1.3
543 K – 11 min	1.4	63	34	1.6
553 K – 9.5 min	1.5	64.5	32.5	1.5
563 K – 9 min	1.7	61	35.5	1.8
573 K – 8 min	1.3	61.5	35	1.7

tion process: volatile matter decreases while fixed carbon, ash content and low heating value increase with the increase of the treatment temperature. Moisture is almost stable and equal to 1.5% and nitrogen content, lower than in initial waste (5.4%), increases with the increase of the treatment temperature.

3.7. Efficiency of the process

Elementary analysis (see Table 6) enables the estimation of the efficiency of each type of treatment. Fig. 11 shows that the nitrogen removal percentage varies between 63% and 70% and that the average is about 68%. Effectiveness of the thermal treatment which aims to remove nitrogen is therefore demonstrated since the thermo-chemical conversion of the treated material will leads to a lower production of pollutants. These results show that the efficiency of the process in terms of nitrogen removal seems not to be influenced by the treatment temperature. However, it can be noticed that the ratio (residual energy/initial energy) of the samples decreases from 93% to 83% (see Fig. 11) showing that, from an energy point of view, the lowest temperature treatment gives the best results. Nevertheless, in an industrial process, the shorter treatment (higher temperature treatment) may be privileged.

3.8. Perspectives for the second step of the two-stage process

Treated waste still contains nitrogen and cannot be thus considered as "clean". Two types of thermochemical enhancement can although be considered for the treated materials:

- A gasification under water which aims to convert all the solid into combustible gases. This way will maximize the energy recovery of the step of thermo-chemical conversion but will release all the remaining nitrogen.
- A fast pyrolysis (inert atmosphere, 800 °C to 1000 °C, 50 °C/s) which aims to convert a part of the solid into combustible gases and into N-containing chars. This way, the energy recovery of the step of thermo-chemical conversion will decrease as well as the release of nitrogen. The obtained char, with a high content of nitrogen, could be used for other

applications. Indeed, some researchers such as [30] work today to produce nitrogenised activated chars useful in water treatment and more particularly, for the adsorption in liquid phase of aromatic compounds like phenol. The high added value of such a type of activated carbons (2500$/ton) [30] could highlight the economic interest of this way of enhancement.

4. Conclusion

Thermogravimetric analysis showed that UF, MF resin and wood present maximum rate of degradation at different temperatures (528 K for UF resin, 633 K for MF resin against 600 K for wood) and that, in temperature range of 533 K to 553 K, the thermal behaviour of wood board is not the reflection of the sum of the behaviour of its components. The feasibility of the selective decomposition has not been proved but remains possible. In the case of MF resin, selective pyrolysis is impossible at temperature higher than 600 K.

The devolatilisation dynamics of UF and MF resin can be well described by a simple mechanism. This consists in two parallel and dependant, first order reactions whose activation energies are 69 kJ/mol and 64 kJ/mol for UF resin and 56 kJ/mol and 130 kJ/mol for MF resin.

Concerning wood, the devolatilisation dynamics can be described by a three parallel and independent, first order reactions whose activation energies are 122 kJ/mol, 163 kJ/mol and 204 kJ/mol. Values of rate of reactions k_1, k_2 and k_3 correspond with the literature.

Concerning wood board sample, a similar reaction mechanism scheme as for wood enables a good representation. Activation energies are 130 kJ/mol, 131 kJ/mol and 304 kJ/mol.

FTIR analysis proves that UF and MF resins are responsible for the production of nitrogen compounds as ammonia and isocyanic acid but that no hydrogen cyanide is produced for temperatures between 523 K and 573 K. In this range of temperatures, the optimum times of treatment vary from 15 min to 8 min. We show that the efficiency of the process in terms of nitrogen removal is not influenced by the type of treatment. Nevertheless, temperatures of the treatment influence the level of degradation of waste and the ratio Residual energy/Initial energy which decreases from 90% to 76%, the lowest temperature treatment giving the best results.

Elementary analysis shows that this process enables to remove around 68 wt.% of the nitrogen initially present in the waste which shows the limit of this cleaning. Nevertheless, the thermo-chemical conversion (gasification or pyrolysis) of the pre-treated wood board will produce lower volumes of pollutants than virgin wood board which shows the interest of the process.

Acknowledgements

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