

RELATION BETWEEN FOREST FUELS COMPOSITION AND ENERGY EMITTED DURING THEIR THERMAL DEGRADATION

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In this work, calorimetric experiments were performed in order to study the thermal oxidative degradation of rockrose, heather, strawberry tree and pine. Firstly, lignin, holocellulose and cellulose were extracted from the fuels and their contents were calculated according to normalized chemical methods. Then, Differential Scanning Calorimetry was used under air sweeping with dynamic mode on the temperature range [400–900 K] in order to obtain reaction enthalpy. Finally, a simple enthalpy model was developed based on the enthalpy of the thermal degradation of each biopolymer with their respective proportions in the fuels. The results showed that the model agreed satisfactorily to experimental data.

Keywords: DSC, lignocellulosic fuels, thermal degradation, wildland fire

Introduction

Every year, thousands hectares of forest do burn in southern Europe. The Mediterranean area is especially affected during the dry season. Nevertheless, in spite of considerable efforts in fire research, our ability to predict the impact of a fire is still limited, and this is partly due to the great variability of fire behaviour in different plant communities [1]. The combustion of forest fuels is partially governed by their thermal behaviour since this step produces a flammable gas mixture. Therefore, the analysis of the thermal degradation of lignocellulosic fuels is decisive for wildland fire modelling and fuel hazard studies [2–4]. We propose in this work to focus on the thermal degradation of different forest fuels and their main components. Following a literature survey, we noticed that there is a lack in the description of the thermal degradation of forest fuels concerned by wildland fires [5–8]. Even if these models are very different, it's well known that the energy emitted remains a crucial data. Classic approaches are based on the consideration of the low heat content value obtained by bomb calorimeter [9–11]. The experiments are led in constant volume what bring about a strong temperature raising, and with an excess of pure oxygen. These conditions are far from those met during a wildfire at atmospheric pressure in the air. DSC seems to be a convenient tool in order to follow the thermal degradation at the laboratory [12].

The degradation of forest fuels begins with the pyrolysis process from 373 to 773 K [13–16].

Non-combustible products, such as carbon dioxide, traces of organic compounds and water vapour, are emitted between 373 and 473 K. Above 473 K, the pyrolysis breaks down the fuels components into low molecular mass gases (volatiles), and carbonaceous char. Around 773 K all the volatiles are gone; the remaining char is oxidized in a glowing combustion [17].

Wood is a complex organic material, composed of cellulose (40 to 45% for coniferous trees and 38 to 50% for leafy trees), lignin (26 to 34% for coniferous trees and 23 to 30% for leafy trees), hemicellulose (7 to 15% for coniferous trees and 19 to 26% for leafy trees), extractives (<15%), ashes (<1%) water and mineral matter [18, 19]. The chemical composition varies from species to species and within the same variety it varies with the botanical origin, age and location in the tree (trunk, branches, crown and roots). In general, previous works refer to different commercial biopolymers (cellulose, xylan to represent hemicellulose...) whose structure is quite different from the native one [20–23]. To have a realistic representation of biopolymer behaviour, it is essential to extract it directly from its source and to perform the analysis on the extracted matter.

Similarly to other authors [20, 21, 24, 25], we made the assumption (H) that the principal components of the fuel contributes to the thermal behaviour of the whole fuel itself and we showed in the present work that the enthalpy reaction of the thermal degradation follows this law.

(H): $\langle \text{Biomass} \rangle = \alpha \langle \text{cellulose} \rangle + \beta \langle \text{lignin} \rangle + \gamma \langle \text{hemi-cellulose} \rangle$; where $\langle \rangle$ refers to the thermal behaviour,

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α , β and γ are the percentages of cellulose, lignin and hemicellulose in the biomass.

The aim of this work was to quantify the participation of the principal components of the fuel to the reaction enthalpy of thermal degradation of the fuel. In a first time we have developed and used an analytical procedure in order to determine the content of each component in the forest fuels. In a second time, we have used DSC to record the enthalpy of the thermal degradation of the fuels and their components (previously extracted) under air sweeping. Then, calculated reaction enthalpy and experimental ones are compared.

Experimental

Samples

We chose to study the thermal degradation of rockrose (*Cistus monspeliensis*: CM), heather (*Erica arborea*: EA), strawberry tree (*Arbutus unedo*: AU) and pine (*Pinus pinaster*: PP) which are representative species of the Corsican vegetation concerned by wildland fires. Naturally, the methodology developed hereafter is applicable to every lignocellulosic fuel.

Plant materials were collected from a natural Mediterranean ecosystem situated away from urban areas in order to prevent any pollution on the samples. Small particles (<6 mm) are considered in governing the dynamic of fire spread [26–28]. So we sampled the foliage and aerial parts of previously cited species. For each species, a bulk sample from six individual plants was collected in order to minimize interspecies differences. Current year, mature leaves were selected, excluding newly developed tissues at the top of the twigs. About 500 g of each species were brought to the laboratory, washed with deionised water and oven-dried for 12 h at 333 K [29]. Dry samples were then grounded and sieved to pass through a 600 μm mesh, then kept to the desiccator. The sieved powdery sample was stored in airtight plastic containers for future use. All the analysis (chemical and thermal) were performed on these powders. The moisture content coming from self-rehydration was about 4% for all the samples before the analysis.

Table 1 Elemental analysis of the fuels

	Carbon/%	Hydrogen/%	Oxygen/%	N, mineral matter/%
AU	48.24	6.15	40.33	5.28
EA	52.43	6.98	35.92	4.63
CM	46.58	6.22	37.68	9.52
PP	50.64	6.76	41.53	1.70

The elemental analysis was carried out at the SCA (Service Central d'Analyse) USR 59 CNRS, and the results are shown in Table 1.

Methods

Several analytical methods are available for the determination of lignocellulosic components. We used 2 kinds of techniques: one for the determination of the plant composition (quantitative analysis) and the other for the extraction of native constituents of the fuel (qualitative analysis).

Lignocellulosic materials were determined by different gravimetric methods, according to normalized or published methods. Figure 1 shows the experimental procedure performed on every fuel.

The extraction methods are summarized below. The extraction process was a multi-stage one excepted for cellulose 1. First of all, the extractives were determined by Soxhlet extractions with dichloromethane for six hours. Then, the sample was washed with distilled water and oven-dried [30]. From the extraction residue, we determined the lignin, the holocelluloses 1, 2 and the cellulose 2. The lignin 'Klason' content was obtained by gravimetric analysis after a sulphuric acid attack [31]. Holocellulose (i.e cellulose+hemicellulose) content was also obtained by gravimetric analysis after reaction of the extraction residue with sodium chlorite in acetate buffer; this step is called delignification. The difference between delignification 'a' and 'b' comes from the concentrations of reagent used and

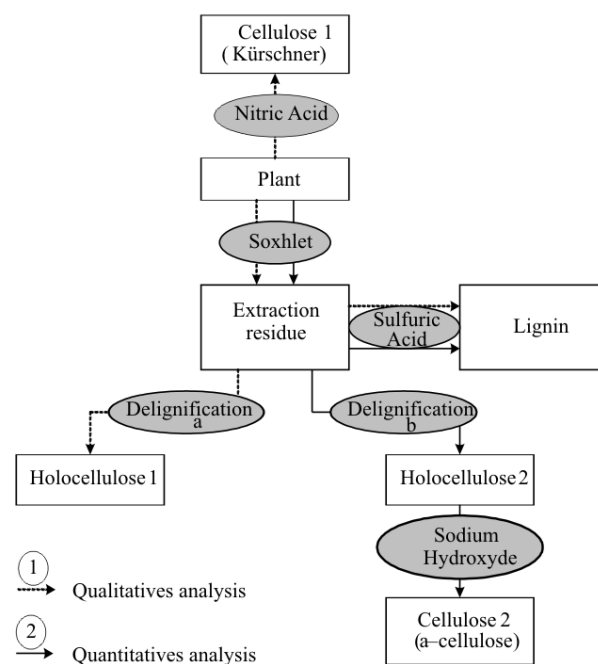


Fig. 1 Principle of extractions

time of stoking [32, 33]. The action of hydroxyl sodium on holocellulose 2 allowed obtaining cellulose 2. The cellulose 1 content was determined according to the Kürschner method [34, 35] directly on the powders by a gravimetric analysis after reaction with nitric acid.

As the chemical structure of hemicellulose and cellulose is very similar, there is no way to extract the native hemicellulose from the plant. That is why the proportions and the thermogram of this biopolymer were deducted from the difference between holocellulose and cellulose.

Thermal process

There are only a few DSC studies in the literature concerning the thermal decomposition of lignocellulosic materials which is preferably studied by TGA [36–42]. We recorded the emitted heat flow *vs.* temperature with a power compensated DSC (Perkin Elmer[®]. Pyris[®] 1). Thermal degradation was investigated in the range 400–900 K under dry air (80% N₂/20% O₂) with a gas flow of 30 mL min⁻¹, measured at ambient temperature and atmospheric pressure.

We adapted the DSC for thermal degradation studies by adding an exhaust cover disposed on the measuring cell (degradation gases escape and pressure do not increase in the furnaces). The furnaces temperature was programmed for a linear heating from 400 to 900 K and we chose an intermediate heating rate $\beta=20$ K min⁻¹ allowing very reproducible experiments. Open aluminium crucibles were used for both the sample and the reference (constituted of an empty crucible) [43]. In every experiment, the powders were uniformly disposed on the bottom of the sample crucible. Samples consisted of about 5.0 ± 0.1 mg for all the experiments. The DSC calibration was performed at 20 K min⁻¹ and verified every 5 runs using the melting point reference temperature and enthalpy reference of pure indium and zinc ($T_{\text{melt}}(\text{In})=429.8$ K. $\Delta H_{\text{melt}}(\text{In})=28.5$ J g⁻¹. $T_{\text{melt}}(\text{Zn})=692.8$ K. $\Delta H_{\text{melt}}(\text{Zn})=107.5$ J g⁻¹). The four species and their components were thermally analysed according to this procedure. Data of interest were the enthalpy values obtained by numeric integration of the DSC signal and peak top temperatures visualised on the thermogram. The uncertainty caused by weighting gave an error of 2–3% on the experimental values of enthalpy reactions. The pc-DSC allowed the measurement of very repeatable heat flows thanks to the micro furnaces. The energy measured in those experiments corresponds to the oxidation of vegetative fuels in an open atmosphere, of course this are not the same values obtained with calorimetric bombs, but the study with an adapted pc-DSC (with the exhaust cover) is more representative of forest fire conditions.

Results and discussion

For all the results, measurements (chemical and thermal analysis) were repeated at least three times.

Chemical analysis

All the results were expressed as a percentage on the dry matter (%DM). The amount of Soxhlet extract (Extracted Matter: EM) was calculated according to Eq. (1).

$$\begin{aligned} \text{Extracted Matter}(\%DM) &= \\ &= \frac{\text{finalsamplemass}(g)}{\text{initialsamplemass}(g)} 100 \end{aligned} \quad (1)$$

Holocellulose content was calculated according to Eq. (2):

$$\begin{aligned} \text{Holocellulose}(\%DM) &= \\ &= \left[\frac{\text{finalsamplemass}(g) \frac{100-EM}{100}}{\text{initialsamplemass}(g)} \right] 100 \end{aligned} \quad (2)$$

Where EM refers to the percentage of Extracted Matter. Lignin content was obtained according to Eq. (3):

$$\begin{aligned} \text{Lignin}(\%DM) &= \\ &= \left[\frac{\text{finalsamplemass}(g) \frac{100-EM}{100}}{\text{initialsamplemass}(g)} \right] 100 \end{aligned} \quad (3)$$

Finally, cellulose 1 was given by (4):

$$\begin{aligned} \text{Cellulose1}(\%DM) &= \\ &= \frac{\text{finalsamplemass}(g)}{\text{initialsamplemass}(g)} 100 \end{aligned} \quad (4)$$

And cellulose 2 by (5):

$$\begin{aligned} \text{Cellulose2}(\%DM) &= \\ &= \left[\frac{\text{finalsamplemass}(g) \text{ holocellulose}}{\text{initialsamplemass}(g) 100} \right] 100 \end{aligned} \quad (5)$$

Table 2 presents the results obtained from the analytical process and the previous equations for the species studied herein. The presented results are averages, calculated from several attempts on the same sample.

The measured total does not reach 100%, because extractions are in series and there is a small amount of nitrogenous compounds, tannins and free sugars non extracted. For these fuels two dominants components were identified: lignin and cellulose.

Thermal analysis

The results from the thermal analysis of the four species and their components are shown in the present

Table 2 Lignocellulosic analysis of the fuels

	Cellulose/%	Lignin/%	Holo-cellulose/%	Hemi-cellulose/%	Extractives/%	Total/%
AU	38.0±0.4	41.6±0.4	43.2±0.4	5.2±0.1	12.9±0.2	97.9±1.0
EA	40.7±0.4	39.7±0.4	54.3±0.5	13.6±0.2	5.8±0.1	99.8±1.0
CM	39.4±0.4	34.4±0.3	52.0±0.5	12.6±0.2	9.2±0.1	95.6±1.0
PP	38.3±0.4	38.9±0.4	43.4±0.4	5.1±0.1	13.1±0.2	95.2±1.0

Table 3 Enthalpy values and peak top temperatures for the fuels

	$\Delta_r H^\circ / \text{J g}^{-1}$	Peak 1/K	Peak 2/K
AU	-11410±342	641	791
EA	-12540±376	646	787
CM	-11070±332	630	776
PP	-10885±327	643	756

Table 4 Enthalpy values and peak top temperatures for the extracted cellulose

	$\Delta H_{\text{exp}} / \text{J g}^{-1}$	$T_{\text{exo}} 1/\text{K}$	$T_{\text{exo}} 2/\text{K}$
AU	-6935±208	623	766
EA	-7179±215	627	803
CM	-6581±197	623	778
PP	-6871±206	628	799

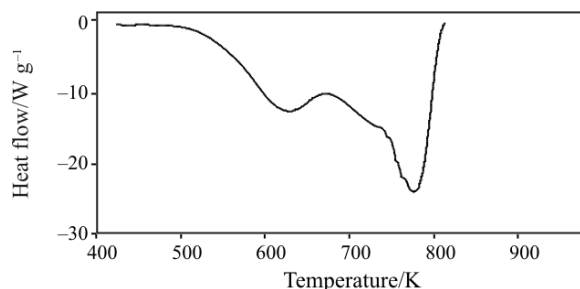
section; we chose to present only the curves of CM samples. This plant is known to have a high flammability in wildland fires.

Forest fuels

Table 3 presents the reaction enthalpy and the peak top temperatures obtained from the DSC data on every fuel. Values of enthalpies are expressed for one gram of the fuel used for each experiment.

The enthalpy reaction (numeric integration of DSC signal) is varying between -10885 J g^{-1} to -12540 J g^{-1} for these different fuels. *EA* fuel was found to be the most energetic one and *PP* fuel was found to be the less energetic one. As the sample preparation and the experimental conditions were constant for all the fuels, the differences observed on the enthalpy values should come from the chemical composition of each fuel.

Figure 2 shows the thermal behavior of *CM* sample. For all the fuels the DSC curves exhibit a similar profile with two overlapped exothermic events. Two maxima were recorded around 630 and 775 K; in a previous work we ascribed these thermal events [44] corresponding to the oxidation of volatiles and chars. The behavior is similar and reproducible for all the species since we have triplicate experiments for all the species.

**Fig. 2** DSC curve for *CM* fuel at 20 K min^{-1} under air sweeping

Cellulose

Following the extraction, the cellulose from each fuel was thermally studied and Table 4 presents the results obtained from the DSC data. Values of enthalpies are expressed for one gram of the cellulose used for each experiment.

It is important to note the strong resemblances of the thermal characteristics of the cellulose extracted from the various species. The values of enthalpy of the thermal degradation of cellulose are relatively constant for four plants (mean value: $\Delta_r H^\circ = -6892 \pm 213 \text{ J g}^{-1}$) assuming that the cellulose extracted from these plants possesses a very close structure. Ours experiments show that cellulose is the lowest energetic component of the fuels.

Figure 3 shows the thermal behavior of *CM* cellulose.

For all the fuels the DSC curves exhibit a similar profile with two overlapped exothermic events, the thermal behaviour of the cellulose extracted from the various species is similar to that of fuel. However, existing energetic interactions between the components are shown by comparing the curves of the fuel and the cellulose: the offset temperature is higher for the cellulose. In the modeling work we have neglected these interactions.

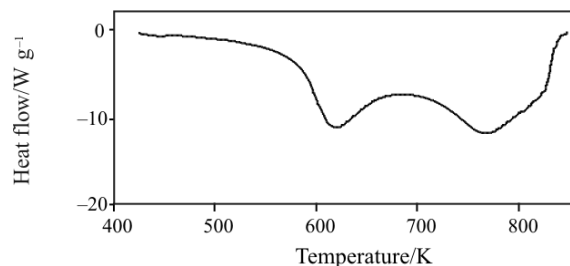
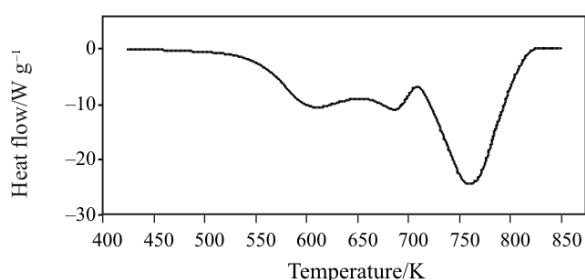
**Fig. 3** DSC curves for *CM* cellulose at 20 K min^{-1} under air sweeping

Table 5 Enthalpy values and peak top temperatures for the extracted holocellulose

	$\Delta_r H^\circ / \text{J g}^{-1}$	Peak 1/K	Peak 2'/K	Peak 2/K
AU	-10565±317	626	687	786
EA	-10891±327	609	687	759
CM	-8974 ±269	615	684	767
PP	-9789 ±294	625	697	754

**Fig. 4** DSC curve for CM holocellulose at 20 K min⁻¹ under air sweeping

Holocellulose

Following the extraction, the holocellulose from each fuel was thermally studied and Table 5 presents the results obtained from the DSC data. Values of enthalpies are expressed for one gram of the holocellulose used for each experiment.

Values of enthalpies are globally higher for the holocellulose than the cellulose; this component can be considered as highly energetic in regard to the fuels. We noted a global trend similar to that of the plant, except the appearance of a supplementary phenomenon (peak 2') between both processes already shown on the fuels. This additional step is probably coming from the thermal degradation of hemicellulose mixed with cellulose in this component; unfortunately, we did not have the possibility to isolate hemicellulose from holocellulose. Figure 4 shows the thermal behavior of CM holocellulose obtained following the previously described method.

This biopolymer showed a degradation process more complex than the other constituents. These observations are coherent as the holocellulose is a mixture of polysaccharides.

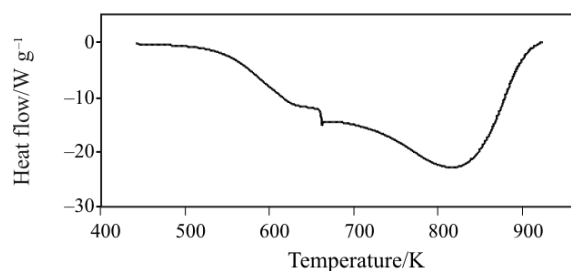
Lignin

Following the extraction, the lignin from each fuel was thermally studied and Table 6 presents the results obtained from the DSC data. Values of enthalpies are expressed for one gram of the lignin used for each experiment.

For all the species, we recorded a more marked difference between extracted lignin and the fuel. In

Table 6 Enthalpy values and peak top temperatures for the extracted lignin

	$\Delta_r H^\circ / \text{J g}^{-1}$	Peak 1/K	Peak 2/K
AU	-16278±488	653	846
EA	-16853±505	668	831
CM	-15172±455	662	815
PP	-17012±510	682	799

**Fig. 5** DSC curve for CM lignin at 20 K min⁻¹ under air sweeping

regard with others biopolymers the value of reaction enthalpy is much higher and the major part of the exotherm is shifted toward high temperatures. Lignin is the highest energetic component of the fuel with a mean value of reaction enthalpy higher than the fuel itself.

As shown on the example of Fig. 5, DSC curves present an important amplitude for the peak 2 and a peak 1 almost flooded by the second. As for the cellulose, lignin curves show existing energetic interactions between the components. Comparing the curves of the fuel and the cellulose we saw that the temperature of the end of reaction is higher for the lignin. In the modeling work we have neglected these interactions.

All the thermograms also present an artefact owed to a condensation of products during the acidic extraction of lignin. This thermal behaviour agrees with previous studies [45] indicating an only important peak for temperatures superior to 773 K.

Mean values of reaction enthalpies are presented in the following Table 7 and were calculated from the data presented in Tables 4, 5 and 6. The standard deviation was determined according to Eq. 7.

$$\sigma_x = \sqrt{\frac{\sum (\Delta_r H_x^\circ - \overline{\Delta_r H_x^\circ})^2}{n}} \quad (7)$$

where $\overline{\Delta_r H^\circ}$ is average of $\Delta_r H^\circ$, x is a component and n is the number of values.

The enthalpy variations of the various constituents are relatively constant and close to mean values. The relative error for every constituent is lower than 9%, except for the extractives (25%) which constitute a complex mixture of various chemicals. This result is however coherent, as far as the nature of compounds

Table 7 Mean values of enthalpy reaction of the components in the 4 species

	Cellulose	Lignin	Hemicellulose	Extractives
$\Delta_r H^\circ / J g^{-1}$	-6892	-16329	-15109	-8176
σ	245.9	833.1	1318.7	2031.0
$\frac{\sigma}{\Delta_r H^\circ} \times 100$	3.6%	5.1%	8.9%	24.8%

contained in the extracted matters varies according to the species (wax quantities, tannins, essential oil and colouring agents differ strongly according to the species).

Modelling and discussion

According to assumption (H) presented in the introduction section, in this work the thermal degradation of forest fuels is viewed as the thermal degradation of the components of the fuel as shown in Fig. 6.

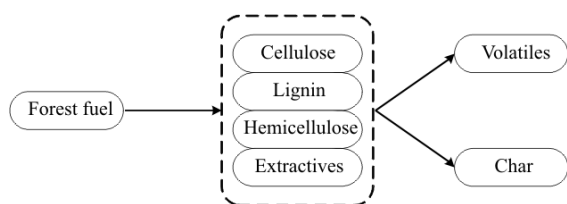


Fig. 6 Simplistic thermal degradation of a forest fuel used for the model

Compared to others studies, [20, 21, 24, 25] we added the thermal behaviour of the extractives components which play an important role in wildland fires spread [46–48].

The calculated reaction enthalpy can then be expressed as a combination of reaction enthalpy of each component of the fuel:

$$\Delta_r H_{cal}^\circ = a\Delta_r H^\circ(\text{cellulose}) + b\Delta_r H^\circ(\text{lignine}) + c\Delta_r H^\circ(\text{hemicellulose}) + d\Delta_r H^\circ(\text{extractives}) \quad (6)$$

where: *a*, *b*, *c* and *d* are the percentages of cellulose, lignin, hemicellulose and extractives respectively in the fuel.

This model is applicable and sturdy only if the enthalpy reaction of every constituent is constant for all the species. We thus made the following hypotheses of modelling which are valid in regard to the experimental results presented in Table 7.

$$\Delta_r H^\circ(\text{cellulose})_{EA} \approx \Delta_r H^\circ(\text{cellulose})_{AU} \approx \Delta_r H^\circ(\text{cellulose})_{CM} \approx \Delta_r H^\circ(\text{cellulose})_{PP} \quad H1$$

$$\Delta_r H^\circ(\text{lignin})_{EA} \approx \Delta_r H^\circ(\text{lignin})_{AU} \approx \Delta_r H^\circ(\text{lignin})_{CM} \approx \Delta_r H^\circ(\text{lignin})_{PP} \quad H2$$

$$\Delta_r H^\circ(\text{hemi.})_{EA} \approx \Delta_r H^\circ(\text{hemi.})_{AU} \approx \Delta_r H^\circ(\text{hemi.})_{CM} \approx \Delta_r H^\circ(\text{hemi.})_{PP} \quad H3$$

However it was impossible to study the thermal behaviour of extractives (too unstable and giving very noisy DSC curves). Their enthalpy reaction was deduced by subtraction between the enthalpy reaction of the fuel and the enthalpy reaction of the residue from the solvent extraction. We thus made the following assumption:

$$\Delta_r H^\circ(\text{extra.})_{EA} \approx \Delta_r H^\circ(\text{extra.})_{AU} \approx \Delta_r H^\circ(\text{extra.})_{CM} \approx \Delta_r H^\circ(\text{extra.})_{PP} \quad H4$$

Equation 6 gave calculated enthalpies of reactions ($\Delta_r H_{cal}^\circ$) for the four species according to their chemical composition.

Figure 7 shows the experimental enthalpy ($\Delta_r H_{exp}^\circ$) of thermal degradation of the fuels versus the results of calculated enthalpy. This figure clearly shows that according to its high enthalpy of reaction and its high content in the four species, lignin contributes strongly to the reaction enthalpy of the fuel. Compared to lignin, the low value of enthalpy of reaction of cellulose implies a weak contribution to the reaction enthalpy of the fuel for this component though cellulose content is as important as lignin. Our model takes into account the extractives percentage in the fuel; even if their content is low, these components are highly energetic and they should not be omitted in regard to the thermal behaviour of the fuels.

As shown in Fig. 7, the calculated enthalpy values get very close to the experimental values recorded from the thermal degradation of dry forest fuels.

The small difference between the model and experiments results indicates that energetic interactions between the various constituents of the plant can be neglected. Regarding to the fuels: EA fuel was found to be the most energetic with the higher hemicellulose

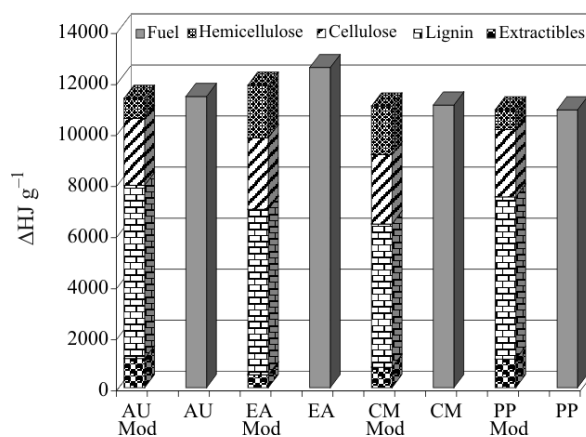


Fig. 7 Comparison between $\Delta_r H_{cal}^\circ$ and $\Delta_r H_{exp}^\circ$

content and the lowest extractives content whereas PP fuel was found to be the less energetic fuel with the lowest hemicellulose content and the higher extractives content.

This approach is interesting since the reaction enthalpy of the thermal degradation can be calculated with the knowledge of the composition of the fuel. The reaction enthalpy of the thermal degradation is an important data in the field wildland fire modelling. In a future work we will study others fuels with a final objective to get an energetic profile of the forest fuels according to their chemical composition.

Conclusion

In wildland fire modelling and forest fuel hazard studies, the thermal degradation of the solid is a fundamental stage. Two ways are suitable: the first one considers the thermal degradation of the whole fuel giving a complex mixture of gas, tars and chars; the second one considers the thermal degradation as the sum of the contributions from the principal components of the fuel. Our aim was to verify the validity of the second approach. DSC analyses were performed in order to get the enthalpy reaction of the thermal degradation under air for four forest fuels and their components. With the assumption of constant enthalpies values for each component, we calculated the enthalpy reaction of the thermal degradation.

Calculated enthalpy was compared to the experimental data and we showed a good agreement. Thus, we can say that the reaction enthalpy of the fuels can be viewed as the sum of the reaction enthalpy of each component (taking into account their percentages in the fuel). The present study shows only a weak influence of interactions between the components in the fuel on the reaction enthalpy of thermal degradation.

This approach seems very interesting in order to get the enthalpy reaction of a forest fuel when its composition is available. This data is important for modelling purpose since the rate of consumption of fuels could be calculated from the energy emitted by gram of fuel when the power of the fire is available. Although this approach is attractive by its simplicity, the attempt to reproduce the complete thermal behaviour of a fuel turns out to be a delicate spot at the moment. We are now working on thermogravimetric data in order to get kinetic data of the thermal degradation of the components and the vegetative fuel.

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