

# Investigation of thermal degradation of pine needles using multi-step reaction mechanisms

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## ABSTRACT

The objective of this study is to assess the relevance of several multi-step reaction mechanisms to describe the mass loss and the mass loss rate of pine needles in TGA at different heating rates in inert and oxidative atmospheres. The kinetic parameters of the different reactions were optimized using the Shuffled complex evolution (SCE) technique. Model results show that both mass loss and mass loss rate should be considered in order to evaluate properly the mechanism. The drying process is described accurately by a single reaction with a well-established set of kinetic parameters. The conversion of dry pine into char requires a five-step reaction mechanism that is combined of three reactions to describe the pyrolysis under inert atmosphere and another two reactions to describe the oxidative process. Less detailed mechanisms were found to be unable to reproduce the mass loss rate. In particular, the one-step reaction mechanism, widely used to model the pyrolysis process in wildland fire simulations, should be used with care. Finally, the char oxidation process can be described with a single step-reaction mechanism. The final complex mechanism is comprised of one reaction for drying, five reactions for the conversion of dry pine into char, and one reaction for the char oxidation, is promising. Further studies are required for its validation in large-scale experiments.

**KEYWORDS:** Forest fires; pine needles, Gpyro, Thermal degradation, Thermogravimetric analysis, Shuffled complex evolution (SCE), Multi-step reaction mechanism.

## NOMENCLATURE LISTING

$A$	Pre-exponential factor ( $s^{-1}$ )	$\rho$	density
$E_a$	activation energy ( $J.mol^{-1}$ )	$\tau$	dummy variable of integration
$m$	Mass (g)	$\Psi$	porosity
$p$	pressure	$\dot{\omega}''$	reaction rate
$R$	Universal gas constant	<b>subscripts</b>	
$t$	time	$g$	gas
$T$	Temperature	$i$	Condensed phase species i
$Y$	mass fraction	$j$	Gaseous species j
$z$	distance	$f$	formation
$\Delta z$	Grid size	$DWF$	Dry wildland fuel
		$GA$	Genetic algorithms
<b>Greek</b>		$MLR$	TGA
$\beta$	Heating rate ( $^{\circ}C.min^{-1}$ )	$PP$	Pinus Pinaster
$n$	Reaction order	$SCE$	Shuffled complex evolution
$T$	Temperature ( $^{\circ}C$ )	$TGA$	Thermo-gravimetric analysis
$t$	Time (s)	$WWF$	Wet wildland fuel
$\nu$	stoichiometric factor	$\circ$	At time t

## 1. INTRODUCTION

Forest fire represents a major environmental threat to the Mediterranean region. The statistics showed that more than 50,000 fires occur per year [1-2]. An average of 600,000-800,000 ha, is being burnt annually.

Ignition and propagation of forest fires are complex phenomena involving several scales whose ranges go from micrometer to several kilometers. Using the scales nomenclature of Séro-Guillaume and Margerit [3], four scales can be defined from the smallest to the largest: 1) the microscopic scale. This scale is that a vegetation particle, and the main physical effects involved at this scale are the drying and the thermal degradation. 2) The mesoscopic scale where all the elements of vegetation and air form a porous medium. 3) The macroscopic scale where the forest fuel is considered as a locally homogeneous medium composed of vegetal and air. This scale is the first relevant scale to develop a fire spread model. 4) The “gigascope” scale where the vegetation appears as a boundary layer and the flame front as a line. Wildland fire spread models can be divided into three classes, namely statistical, semi-empirical and physical [4]. The two first classes of models operate generally at the “gigascope” scale whereas the latter is developed at the macroscopic scale. Physically-based models, initiated by Grishin [5], differ from statistical and empirical models in what they account for each mechanism of heat transfer individually and predicts not only the spread rate of the fire but also its complete behavior. The thermal degradation of the solid phase as well as the combustion of the gaseous pyrolysis products are described, requiring the development of specific kinetic models for the vegetation fuels. Most of the physically-based models have considered a simplified three-step reaction mechanism for the thermal degradation of wildland fuel [6-11]. The first reaction is related to the drying process with the wet wildland fuel (WWF) being converted into dry wildland fuel (DWF) and water vapor, the second reaction is related to the pyrolysis process with the DWF being converted into char and gaseous pyrolysis product while the third reaction is related to the char oxidation. The degradation model implemented in Wildland Urban Interface Fire Dynamics Simulator (WFDS) [12] is also based on a simplified degradation mechanism with a two stage endothermic decomposition process including water evaporation followed by solid fuel volatilization. On the other hand, FIRETEC [13] does not consider explicitly a degradation model. FIRETEC was initially dedicated to simulate wildfires at relative large scale, requiring relatively coarse grids. As a consequence, pyrolysis and gas-phase combustion were assumed to take place at the same location and a single-step reaction accounting for the two processes was developed.

The validity of this simple description as well as the development of more complex kinetic mechanisms for the wildland fuel is challenging due to the complexity of the fuel composition. One way to develop and calibrate kinetic mechanism for wildland fuel is to use Thermogravimetric Analysis (TGA) [14-18]. The concept of TGA is that it measures the amount of weight change of a material, either as a function of increasing temperature, or isothermally as a function of time, in an atmosphere of nitrogen, helium, air, other gas, or in vacuum. Examples of kinetic models on pyrolysis and combustion of pine needles and cones were introduced [15, 17] Many works used thermogravimetric analysis to determine the kinetic of thermal decomposition of fuel beds [16, 19]. Most of the previous studies focus only on one single step reaction mechanism to determine the thermal degradation process of wildland fuels [19-20], which lacks a detailed description of the thermal degradation of the wildland fuels. Therefore, in this work, several multi-step reaction mechanisms will be used to derive a detailed description of the thermal degradation of wildland fuels. In a recent study, TGA data, obtained at an inert and oxidative atmosphere, were coupled to a genetic Algorithm to determine the kinetic of degradation of pine needles [18]. A complex mechanism was established and the corresponding kinetic parameter providing the best fit between data and model results were determined. This model includes the following reactions:



Reactions (R5) to (R7) were found to complement reactions (R2) to (R4) under oxidative atmosphere.

Due to their detailed description of the fire phenomena, physically based models require a large amount of computational resources and removing the widely used three step mechanism by a complex mechanism to describe the thermal degradation of the vegetal fuel will add to the complexity. The aim of this study is then to assess the capability of different thermal degradation models, ranging from the simplest to the more complex. The corresponding kinetic parameters will be determined from TGA data obtained by considering several heating rates under both inert and oxidative atmospheres.

The Shuffled Complex Evolution (SCE) optimization algorithm [21], which is similar to the Genetic Algorithm [22-26], is used to optimize these kinetic parameters. Different optimization tools are available in literature such genetic algorithm (GA), shuffled complex evolution (SCE), and stochastic hill climber SHC. GA is widely used [22-26], it can be also coupled with nonlinear fitting algorithm as in [27] to obtain rapid convergence. However, according to a study done on optimization tools [14, 28] while using Gpyro, it was found that SCE technique is more suitable to be used since it is capable of reproducing material pyrolysis properties within approximately 1% of the actual data value. Therefore, in this work, the parameters optimization has been carried out using Shuffled complex evolution (SCE) technique [28].

## 2. METHODS

### 2.1. Experimental Setup

The experiments were conducted on pine needles with type of *Pinus pinaster* collected from the Mediterranean basin in Marseille city located in France. The experimental data generated from TA-Instrument TGA Q50 apparatus, its sample masses varies between  $5 \pm 1$  mg. Two atmosphere air conditions (nitrogen and air) were used while conducting the experiments. The experiments were conducted at different heating rates (5, 10, 15 and 20 °C/min) with temperature range of room temperature to 1000°C. More details about the experiment setup and the building of the 7-steps chemical mechanism can be found elsewhere [18].

### 2.2. Numerical Model

In this work, Gpyro [29-34] version 0.8 was used to examine thoroughly the thermal degradation of pine needles under multi-step reaction mechanisms. In 0D simulation that is used in this study where quantities of particle temperature and mass vary only temporally but not spatially. Gpyro is able to solve 0D transient equations [33] that represent the mass and species evolution of a “lumped” particle having negligible gradients of temperature species as occurs in idealized thermal analysis experiments. For the applied equations in 0D are presented elsewhere [33]. It is also worth noting that the governing equations presented in [33] of 0D can be used to estimate differential thermogravimetric curves ( $d/dt(m/m_0)$ ) and thermogravimetric curves ( $m/m_0$ ). A differential thermogravimetric curve is calculated as:

$$\frac{d}{dt} \left( \frac{m''}{m_0''} \right) = - \frac{\dot{\omega}_{fg}'' \Delta z}{m_0''} = - \frac{\dot{\omega}_{fg}'' \Delta z}{(\bar{\rho} \Delta z)_{t=0}} \quad (8)$$

Integrating the differential thermogravimetric curve gives the thermogravimetric curve:

$$\frac{m''}{m_0''}(t) = 1 - \frac{1}{m_0''} \int_0^t \dot{\omega}_{fg}''(\tau) \Delta z(\tau) d\tau \quad (9)$$

## 3. RESULTS AND DISCUSSIONS

### 3.1. Drying process

The drying process is represented by reaction 1 in the introduction. For a given reaction, the reaction rate is given by:

$$\dot{\omega}_i'' = A \exp(-E_a/RT) m_i^n \quad (10)$$

Where A is the pre-exponential factor,  $E_a$  the activation energy, n the reaction order, and  $m_i$  the mass of the reactant (here WWF). The optimized kinetic parameters are provided in Table 1.

Table 1. Estimated kinetic parameters for Dehydration.

Reagent	Product	Kinetic parameters values			
		$\text{Log}_A(\text{s}^{-1})$	$E_a(\text{kJ}\cdot\text{mol}^{-1})$	$n(-)$	$\nu(-)$
Wet pine	Dry pine	9.71	78.6	4.29	0.9

In the following, the focus will now be only on reactions that occur after dehydration under different atmosphere conditions ( $\text{N}_2$  and air), and the kinetic parameters reported in Table 1 will be used to model the drying process. Figure 1 depicts both experimental and predicted evolution of the mass loss (a) and mass loss rate (MLR) (b) as a function of the temperature at four different heating rates (5, 10, 15 and 20  $^\circ\text{C}/\text{min}$ ).

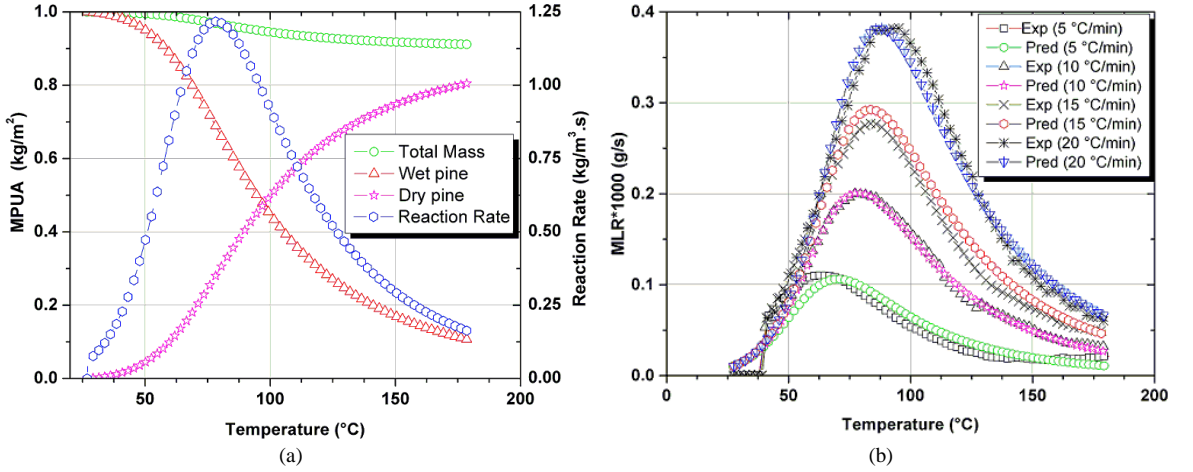


Figure 1: Evolution of the mass loss (a) and mass loss rate (b) as a function of temperature for dehydration at four different heating rates.

The total mass decreases as a function of temperature when water is released from pine needles. The mass of the wet wildland fuel decrease gradually whereas the mass of the dry wildland fuel increases. It should be noted that at a temperature of 100  $^\circ\text{C}$  about one-half of the wet pine has been converted into dry pine and water vapor. At the end of the drying process, the mass of the sample has been reduced of approximately 10%wt, indicating that the initial moisture content was approximately 10%wt (see Fig. 1a). Figure 1b shows that the MLR increases with the heating rate. The prediction using the optimized kinetic parameters appears to be in very good agreement with the experimental data.

### 3.2. Results under inert atmosphere

In this section, several kinetic mechanisms, with increased level of complexity, are assessed to determine their capability to describe the pyrolysis process under inert atmosphere.

#### a. One-step reaction mechanism

The one-step reaction mechanism where DWF is converted into char and gaseous pyrolysis products is first considered. As mentioned in the introduction, this mechanism is currently used in physically based models of wildland fires.



Where the coefficient  $\nu$  (-) [29] is estimated based on the bulk density ratio as:

$$\nu_{char} = \rho_{char} / \rho_{DWF} \quad (12)$$

After the drying process, the first reaction under nitrogen occurs, converting dry pine into char and gaseous pyrolysis products as shown in Fig. 2. As an attempt to study the influence of the reaction's order, the

parameter  $n$  was either fixed to  $n=1$  or to let free in the optimization process. The results are depicted in (Fig. 2a, Fig. 3a and Fig. 3b) and (Fig. 2b, Fig. 3c and Fig 3d) respectively. The optimized values of the kinetic parameters are summarized in Table 2 in the case where  $n$  is fixed to 1 and when  $n$  is let free in the optimization process. Figure 2 displays the numerical mass loss of condensed species as a function of temperature under a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . Figure 2a presents the results in the case  $n = 1$  whereas Fig. 2b presents the results for an optimized order of reaction.

Figure 2a and Fig. 2b show that, in both cases, the mass loss of the material is decreasing to around  $370\text{ }^\circ\text{C}$ . In the case where  $n = 1$ (see Fig 2a), the decrease stops at this temperature whereas it keeps on slowly in the case of the non-fixed order of reaction where  $n = 5$ (see Fig. 2b). Another remarkable difference is related to the char formation. In the case where  $n = 1$ (see Fig 2a), all the dry pine is converted to char, whereas in case where  $n = 5$ (see Fig 2a), the char formation keeps on increasing. More insight concerning the differences between these two approaches is given in Fig. 3 that shows the cumulative mass loss and mass loss rate for the two cases. It can be clearly observed that mass loss is in good agreement with the experimental data in the case of the optimized reaction order (Fig. 3c), whereas with the fixed reaction order noticeable discrepancies are noticed (Fig 3a). Figure 3 indicates that the mass loss alone cannot be used to assess the quality of the fit as it was presented in other study as main factor in fire modeling [16]. In the case of the optimized reaction order, the kinetic mechanism with the set of parameters in Table 2 reproduces well the mass loss but is unable to reproduce accurately the mass loss rate (see Fig 3c and Fig 3d respectively). Therefore, in this case of pine needles thermal degradation, it seems that the pyrolysis process is not a first order reaction.

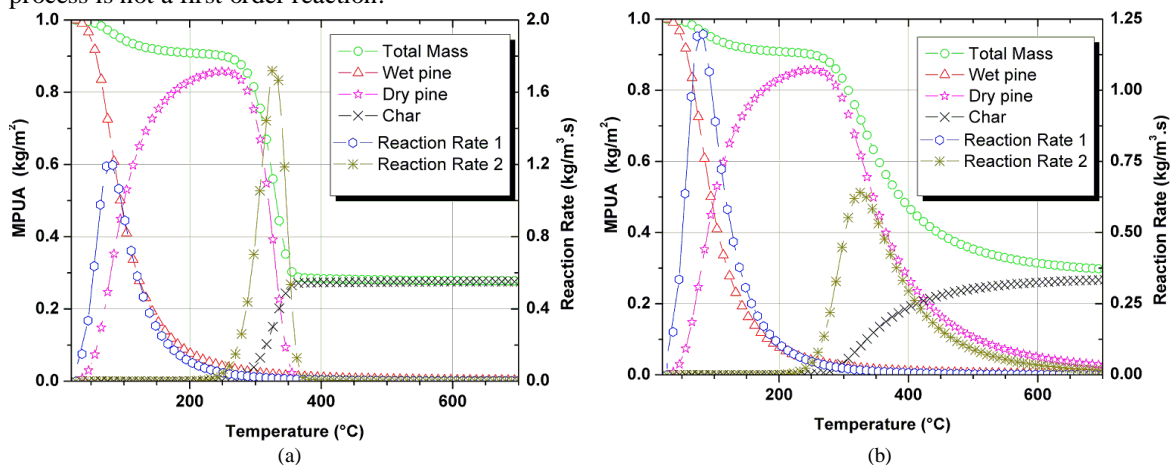


Figure 2: Numerical mass loss of condensed species as function of temperature ( $^\circ\text{C}$ ) under a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  for one-step reaction mechanism under nitrogen (a) fixed reaction order ( $n=1$ ) and (b) for an optimized reaction order.

Indeed, a first order reaction model is unable to capture correctly the right increase rate and decay rate of the total mass loss rate. Otherwise, when the reaction order is greater than 1, the decay rate of the mass loss rate at the higher temperature is quite well capture but the increase rate of the mass loss rate at lower temperatures is still not well captured. Therefore, as it can be observed from Fig. 3, the single step reaction mechanism failed to reproduce the experimental mass loss rate. Hence, mechanism that is more detailed will be introduced.

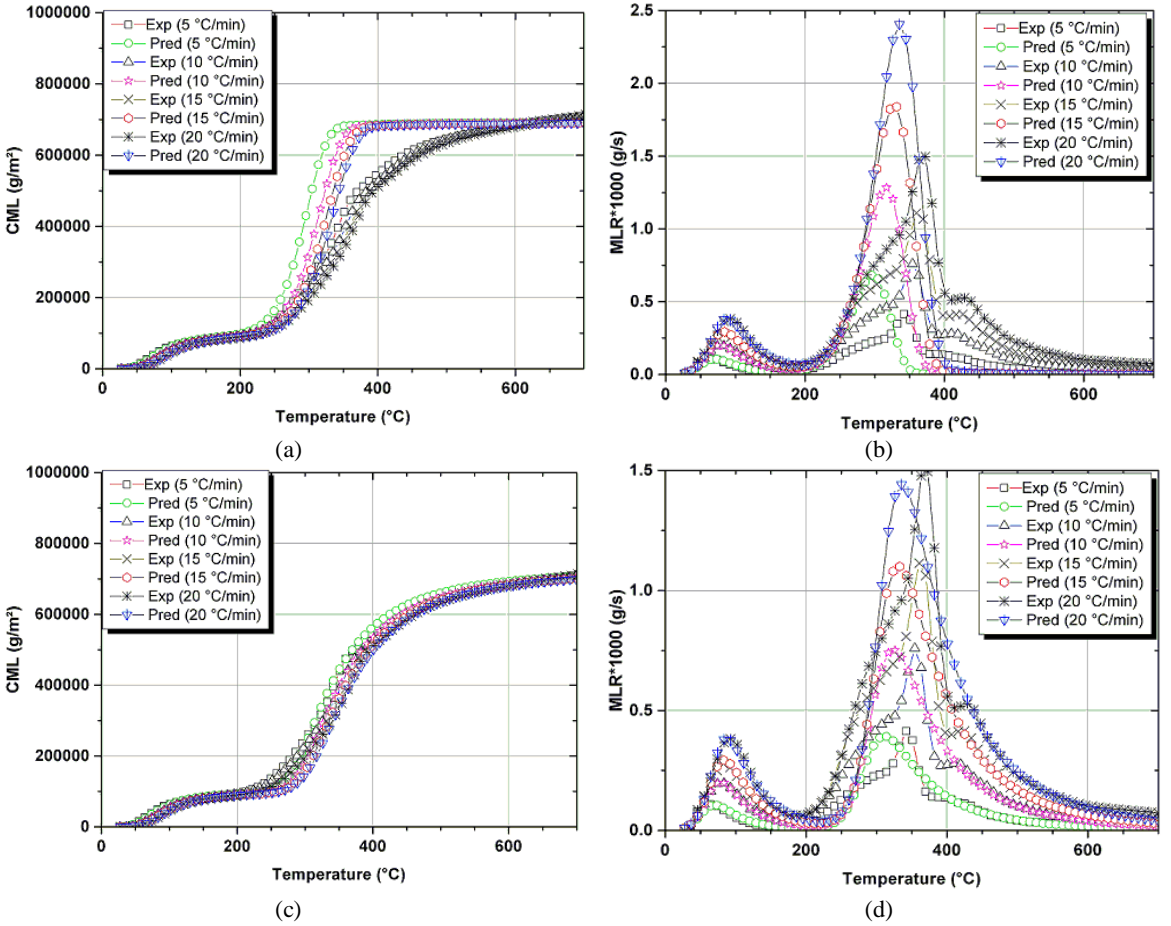
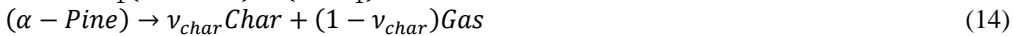


Figure 3: Evolution of cumulative mass loss and mass loss rate of one-step reaction mechanism under nitrogen (a and b) for fixed reaction order ( $n=1$ ) and (c and d) for the optimized reaction order at four different heating rates.

### b. Two-step reaction mechanism

After demonstrating that single-step mechanism cannot be sufficient to represent the thermal degradation of pine needles under inert atmosphere, a two-step reaction mechanism is introduced.



The first reaction concerns the conversion of Dry-Pine into  $\alpha$ -Pine and gaseous pyrolysis products. Next, the  $\alpha$ -Pine condensed specie is converted into char. The values of estimated kinetic parameters are presented in Table 2. Figure 4 displays the numerical mass loss of condensed species as a function of temperature under heating rate of 10 °C/min. Between 250-450 °C the total mass decreases tremendously around 60% after the dry pine needles is formed from wet pine needles to result in char formation. The cumulative Mass Loss (a) and mass loss rate (b) are depicted in Fig. 5. It can be clearly observed that mass loss (see Fig. 5a) is in good agreement with the experimental data. In an opposite way, Fig. 5b shows that the peaks of MLR are not well reproduced. In this case, the production of alpha Pine around 200°C allows to reduce the increase rate of the total mass loss rate. Indeed, for the low temperatures, the mass lost is less important in case of two pyrolysis reactions that in the case there is only one pyrolysis reaction. If we look at the reaction rates of the two pyrolysis reactions on Fig. 4, the first reaction converting dry pine into alpha pine begins around 200°C and the one converting alpha pine into char begins around 300°C.

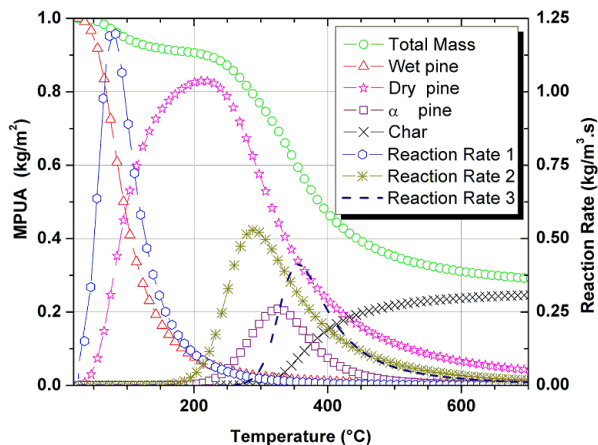


Figure 4: Numerical mass loss of condensed species as function of temperature ( $^{\circ}\text{C}$ ) under a heating rate of  $10(^{\circ}\text{C}/\text{min})$  for two-step reaction mechanism under nitrogen.

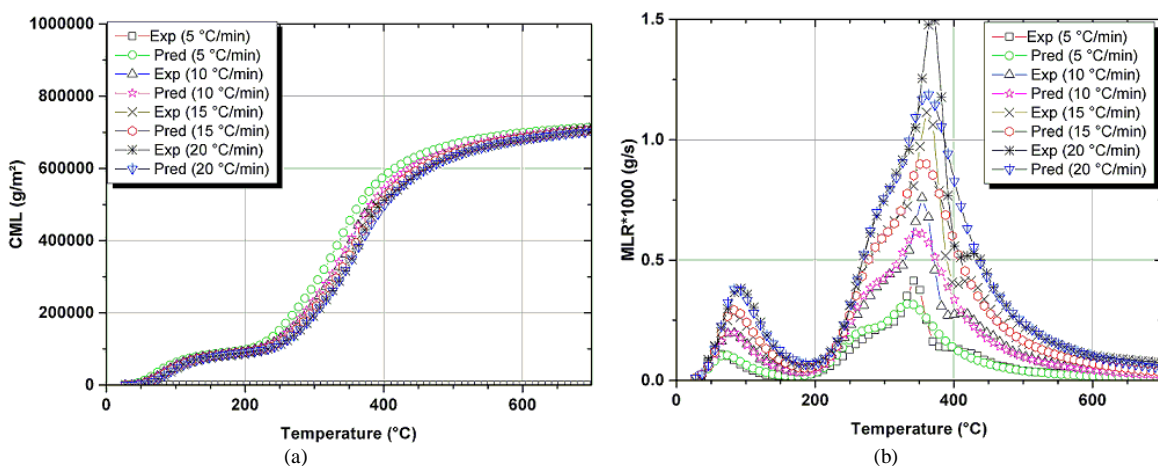


Figure 5: Evolution of the cumulative mass loss (a) and mass loss rate (b) of two-step reaction mechanism under nitrogen at four different heating rates.

The intensity of the reaction rates peaks and the delay between the beginnings of the two reactions are due to the set of kinetic parameters of the two reactions optimized. The set of kinetic parameters is also the reason that more than the good prediction of the increase rate of the mass loss rate, the two stages (the two first peaks) of the total mass loss rate occurring around  $280$  and  $350^{\circ}\text{C}$  are also quite well captured. Nonetheless, the combination of these two reactions does not allow capturing the correct intensity of the second peak (at around  $350^{\circ}\text{C}$ ) of the total mass loss rate (see Fig. 5b). At the end of the mass loss rate evolution, even if the global decay rate is well captured, the stage (peak) around  $400^{\circ}\text{C}$  is not properly captured. More complex mechanism on thermal degradation of pine needles is then investigated in following section to reproduce the right intensity of the biggest peak of the total mass loss rate, and also to capture the last stage of the total mass loss rate occurring around  $400^{\circ}\text{C}$ .

### c. Three-step reaction mechanism

This mechanism is based on the reaction 2 to 4 in the introduction. The first step reaction is related to the conversion of the Dry-Pine into  $\alpha$ -Pine and gaseous pyrolysis products. Next, another reaction converts  $\alpha$ -Pine to  $\beta$ -Pine. Finally, the  $\beta$ -Pine goes into final reaction to form char. The values of estimated kinetic parameters are presented in Table 2. Figure 6 displays the numerical mass loss of condensed species as a function of temperature under heating rate of  $10 (^{\circ}\text{C}/\text{min})$ . The formation  $\alpha$ -Pine starts around a

temperature of 200 °C. This reaction induces a significant reduction in the total mass to peak at around 300 °C where  $\alpha$ -Pine starts decreasing leading to the appearance of the  $\beta$ -Pine. These two products decrease afterward enabling the formation of char.

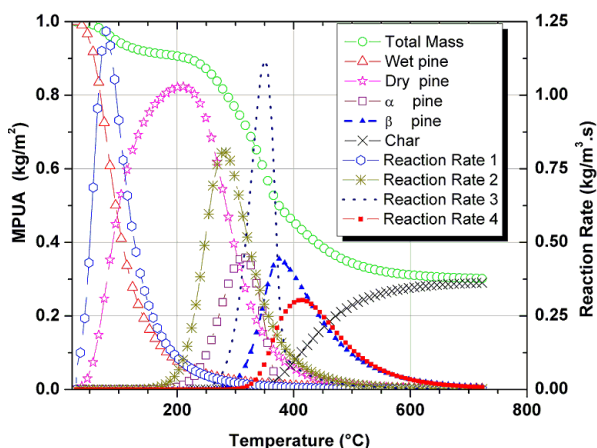


Figure 6: Numerical mass loss of condensed species as function of temperature (°C) under a heating rate of 10(°C/min) for three-step reaction mechanism under nitrogen.

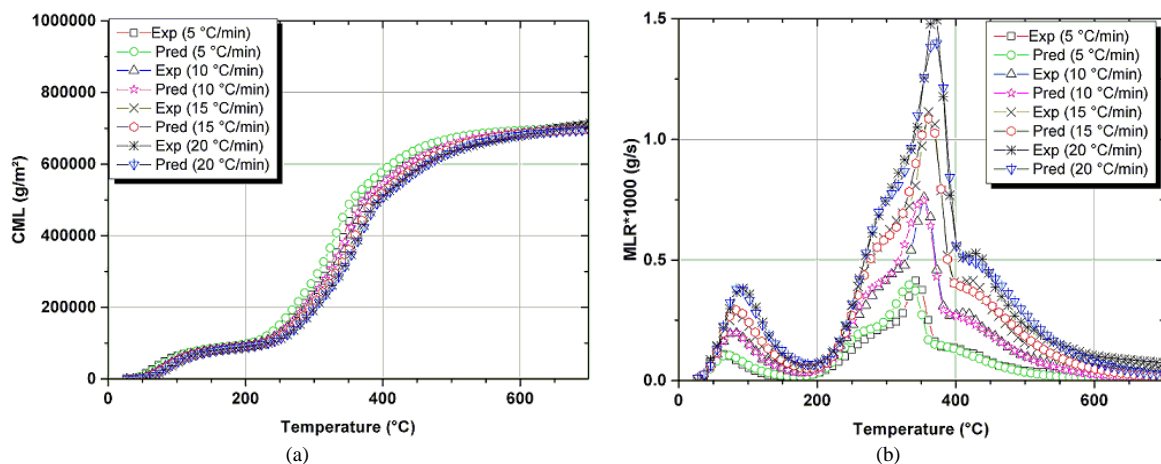


Figure 7: Evolution of the cumulative mass loss (a) and mass loss rate (b) of three-step reaction mechanism under nitrogen at four different heating rates.

The cumulative mass loss (a) and mass loss rate (b) are depicted in Fig. 7. It can be clearly observed that mass loss is in good agreement with the experimental data. Moreover, the mass loss rate Fig. 7b is also in good agreement with the experimental data under the different heating rates. This three-step mechanism was shown to be more accurate in predicting the pyrolysis process under inert atmospheres. If we look at the reaction rate (Fig. 6) the third reaction converts alpha pine into beta pine, the intensity of this reaction rate is quite large comparing to other reaction rate. The consequence of this high reaction rate results in the good prediction of the highest peak of the total mass loss rate. Moreover, the last reaction that converts beta pine into char allows capturing the last peak of the total mass loss rate occurring around 400°C.

Table 2. Estimated kinetic parameters of different mechanisms under nitrogen.

mechanism	Atmosphere	Reagent	Product	Kinetic parameters values			
				$\text{Log}_A(\text{s}^{-1})$	$E_a(\text{kJ} \cdot \text{mol}^{-1})$	$n(-)$	$\nu(-)$
One single reaction mechanism Fixed $n=1$	N2	Dry pine	Char	6.08	94	1	0.34
One-step reaction mechanism Optimized reaction order	N2	Dry pine	Char	11.2	153	5	0.3



Two-step reaction mechanism	N2	Dry pine	$\alpha$ -Pine	7.68	107	4.83	0.53
	N2	$\alpha$ -Pine	Char	12	167	2.38	0.5
Three reaction mechanism	N2	Dry pine	$\alpha$ -Pine	8	108	2.8	0.69
	N2	$\alpha$ -Pine	$\beta$ - Pine	7.6	116	0.692	0.70
	N2	$\beta$ - Pine	Char	5.04	98.3	2.5	0.64

### 3.3. Results under oxidative atmosphere

In this section, TGA experiments are performed under air. The same approach is used as in the previous approach under nitrogen, considering a simple mechanism, an intermediate mechanism and the more complex mechanism described in the introduction.

#### a. Simple mechanism

This mechanism is the thermal degradation mechanism used in wildland fire simulations. The first step reaction considers the conversion of Dry-Pine into char and gaseous pyrolysis products (Eq. 11). Then, the char is oxidized to form ash and  $\text{CO}_2$ .

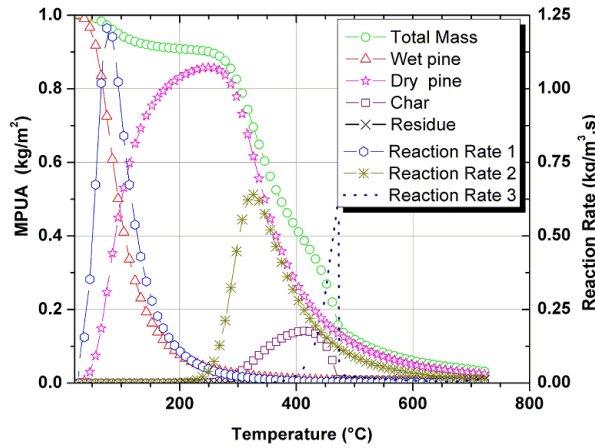


Figure 8: Numerical mass loss of condensed species as function of temperature under 10(°C/min) for simple mechanism (1 reaction under nitrogen and the other under air).

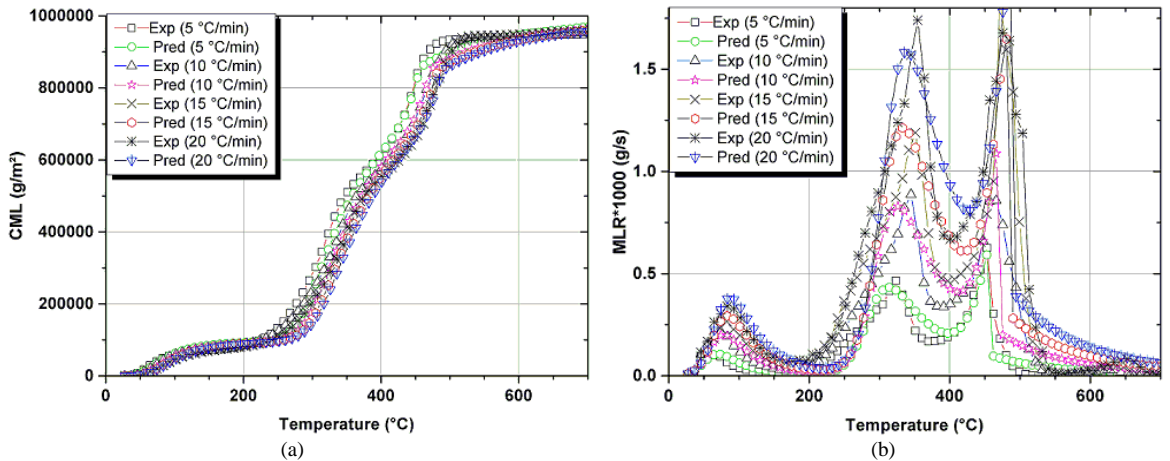


Figure 9: Evolution of the cumulative mass loss (a) and mass loss rate (b) of simple reaction mechanism (one reaction under nitrogen and the other under air) at four different heating rates.

Table 3 summarizes the values of the estimated kinetic parameters under oxidative atmosphere conditions. Figure 8 displays the numerical mass loss of condensed species as a function of temperature under a heating rate of 10°C/min. Notice that between 300-475 °C, the dry pine begins to convert to char resulting in 80% of the total mass loss. The remaining quantity of the char turns into a residue leaving around 2% from the total mass. Cumulative mass loss (a) and mass loss rate (b) are depicted in Fig. 9. It can be clearly seen that mass loss Fig. 9a is in good agreement with the experimental data. On the contrary, the mass loss rate does not reproduce well the experimental data under different heating rates. Modeling the oxidation process by only one reaction seems to give an unrealistic reaction. Indeed, the decay rate of the reaction rate of char oxidation is very abrupt that is questionable in term of physical meaning concerning solid oxidation. More complex mechanism on thermal degradation of pine needles is investigated in this following section in order to see if such oxidation reaction is characteristic to oxidation process of pine needles or if it could be a bias of the inverse modeling technique.

*b. More detailed mechanism*

The implementation of the mechanism developed in Ref. [30] was tested. The mechanism is based on the following reactions:



The first step reaction is about the conversion of Dry-Pine to char under nitrogen. The second reaction concerns the oxidative pyrolysis where the dry wildland fuel is converted into char and gaseous products. Finally, the char passes by final reaction to form the residue. Table 3 summaries the values of the estimated kinetic parameters at air condition. Figure 10 presents the numerical mass loss of condensed species as a function of temperature under a heating rate of 10 °C/min. At 200 °C, the total mass of the dry pine is around 90%. Around 300 °C dry pine decreases tremendously causing an instant increase in the mass of the char, which will turn, into residue around 500 °C. The cumulative mass loss (a) and mass loss rate (b) are depicted in Fig. 11. As it can be seen, the predicted mass loss (see Fig. 11a) is in good agreement with the experimental data. However, the experimental mass loss rate (see Fig. 11b) is not well reproduced by the model. However, the addition of 2 reactions, the first produced char through oxidation of dry pine and the second oxidized the char produced allows to match better the decay rate of the second peak of the total mass loss rate.

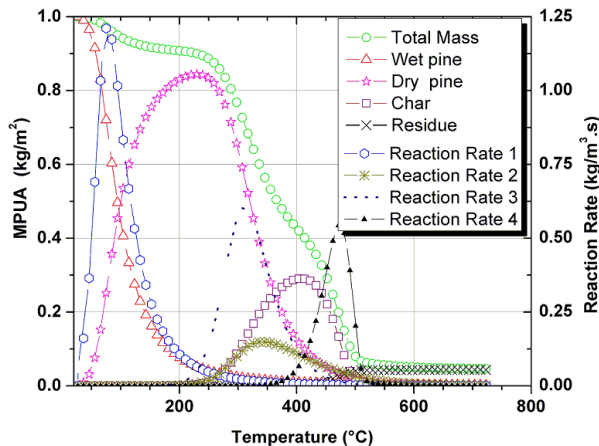


Figure 10: Numerical mass loss of condensed species as function of temperature under 10(°C/min) for more detailed mechanism (1 reaction under nitrogen and two under air).

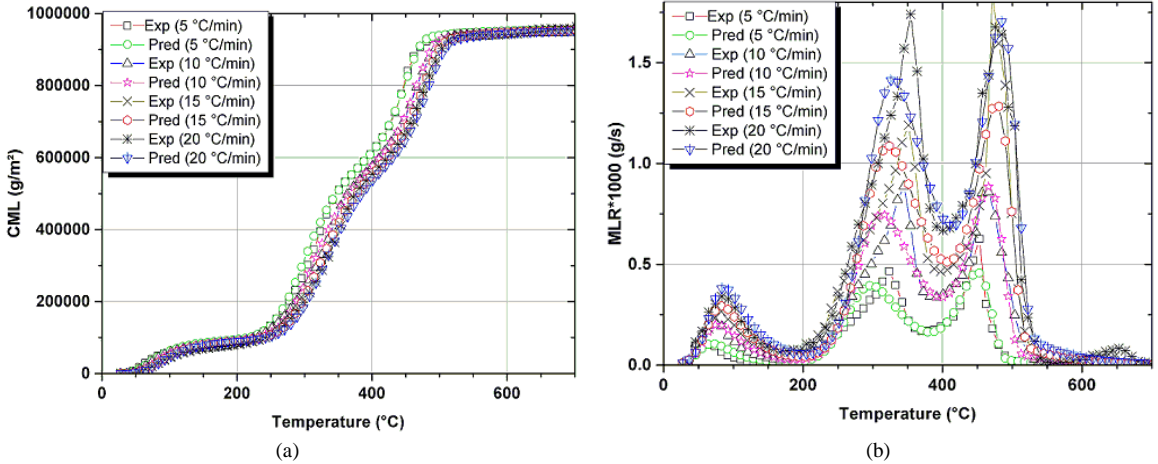


Figure 11: Evolution of the cumulative mass loss (a) and mass loss rate (b) of more detailed reaction mechanism (1 reaction under nitrogen and two under air) at four different heating rates.

### c. Complex mechanism

The complex mechanism was developed [18] based on the analysis of the gases emissions that was recorded after coupling the outlet of TGA apparatus with the FTIR spectrometer (Thermo-Nicolet 6700 equipped with a MCT-A detector). The basis of this reaction mechanism includes the drying process (R1) and the three-step mechanism established for the pyrolysis of dry pine under inert atmosphere (R2 to R4). Three reactions have been added to account for the effects of the oxygen: R5 and R6 to model the oxidative pyrolysis and R7 to model the char oxidation. The values of the estimated kinetic parameters under atmosphere conditions are presented in Table 3. Figure 12 displays the numerical mass loss of condensed species as a function of temperature under heating rate of 10  $^{\circ}\text{C}/\text{min}$ . It should be pointed out that the mass of the dry pine decreases along with the total mass to form the  $\alpha$ -Pine, which will cast the formation of the  $\beta$ -Pine to get reduced afterword by the appearance of the char and residue. It is recommended that a sensitivity analysis should be carried out to investigate the effect of the presence of the oxygen in the mechanisms of thermal degradation. Cumulative Mass Loss (a) and mass loss rate (b) are depicted in Fig. 13. It can be clearly seen that the predicted mass loss (see Fig. 13a) is in good agreement with the experimental data. In addition, the predicted mass loss rate (see Fig. 13b) is also in good agreement with the experimental data. Therefore, the complex mechanism was found to be the more reliable mechanism among all different investigated mechanisms under different atmosphere conditions ( $\text{N}_2$  and air).

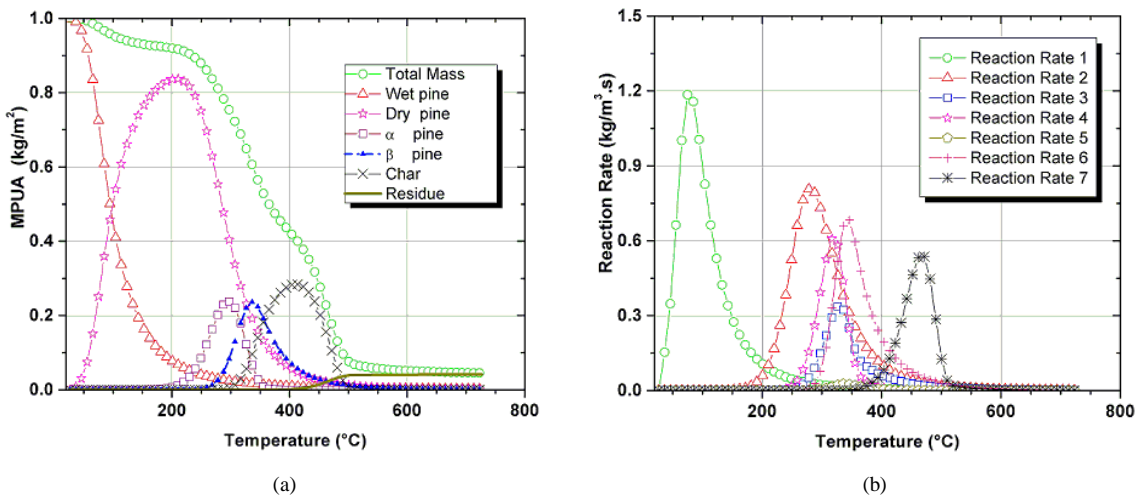


Figure12 Numerical mass loss of condensed species as function of temperature under 10( $^{\circ}\text{C}/\text{min}$ ) for complex mechanism (3 reactions under nitrogen and three under air).

Table 3. Estimated kinetic parameters of different mechanisms (under nitrogen and air).

mechanism	Atmosphere	Reagent	Product	Kinetic parameters values				
				$\text{Log}_A(\text{s}^{-1})$	$E_a(\text{kJ. mol}^{-1})$	$n(-)$	$n\text{O}_2(-)$	$\nu(-)$
Simple Mechanism	N2	Dry pine	Char	11.2	153	5	-	0.23
	Air	Char	Residue	11.6	189	0.1	1.48	0.04
Detailed mechanism	N2	Dry pine	Char	6.99	114	2.15	-	0.39
	Air	Dry pine	Char	8.06	114	3.12	2.37	0.39
	Air	Char	Residue	10	171	0.851	2.64	0.12
Complex mechanism	N2	Dry pine	$\alpha$ -Pine	8	108	2.8	-	0.69
	N2	$\alpha$ -Pine	$\beta$ - Pine	7.6	116	0.692	-	0.92
	Air	$\alpha$ -Pine	$\beta$ - Pine	7.53	104	1	1.18	0.92
	N2	$\beta$ - Pine	Char	5.04	98.3	2.5	-	0.63
	Air	$\beta$ - Pine	Char	10.3	136	2.7	1.10	0.63
	Air	Char	Residue	10.5	172	0.926	1.24	0.11

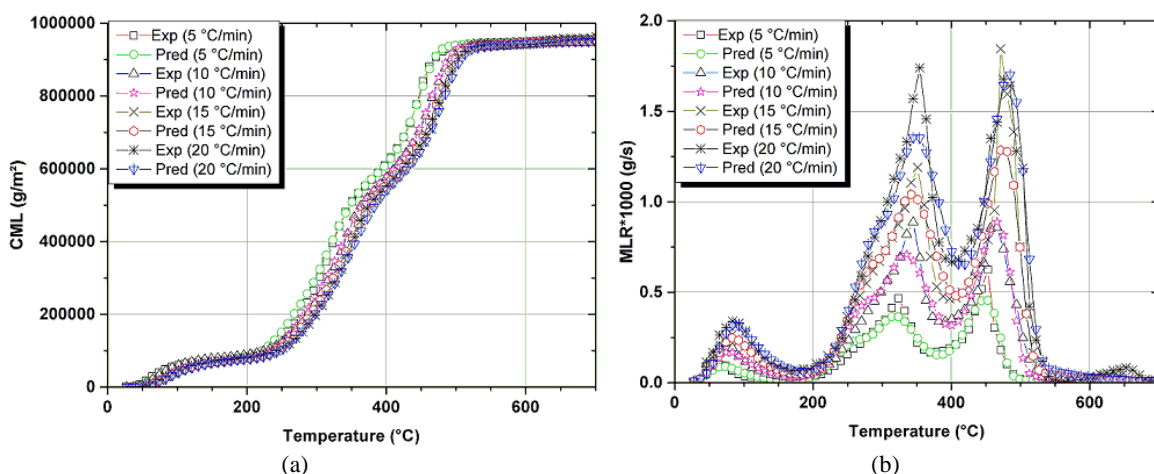


Figure13: Evolution of the cumulative mass loss (a) and mass loss rate (b) of complex reaction mechanism (3 reactions under nitrogen and three under air) under at four different heating rates.

#### 4. CONCLUSIONS

The thermal degradation of pine needles was investigation under different heating rates with two different atmosphere conditions ( $\text{N}_2$  and Air). Several mechanisms by increasing level of complexity have been assessed. The following conclusions can be drawn:

- 1) The mass loss is often used as an indicator to assess the quality of a mechanism. This study shows that this quantity alone is not sufficient and that the mass loss rate should also be considered.
- 2) The drying process can be described by a single-step reaction with well-established kinetic parameter.
- 3) The description of the pyrolysis of dry pine by a single-step mechanism, as usually done in wildland fire simulators, can reproduce only the mass loss but is unable to reproduce accurately the mass loss rate. Consequently, this simplified mechanism should be considered with care in future works.
- 4) A complex mechanism with 3 reactions to describe the pyrolysis under inert atmosphere and 2 other reactions to describe the oxidative pyrolysis, is required to reproduce the conversion of dry pine into char. Less detailed mechanisms are unable to capture accurately the mass loss rate.
- 5) The char oxidation can be described by a single-step mechanism.

Further validation of the final complex mechanism on large scale experiments is required before application in wildland fire simulator.

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