Fire Safety Journal xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Fire Safety Journal

journal homepage: www.elsevier.com/locate/firesaf

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

S. Benkorichi[a,*], T. Fateh[a], F. Richard[b], J.-L. Consalvi[c], A. Nadjai[a]

[a] FireSERT, School of the Built Environment and the Built Environment Research Institute, Ulster University, Newtownabbey BT37 0QB, UK
[b] Institut Pprime, CNRS (UPR-3346), Université de Poitiers, ISAE-ENSMA, F86961 Futuroscope, France
[c] Aix-Marseille Université, IUSTI/UMR CNRS 7343, 5 rue E. Fermi, 13453 Marseille Cedex 13, France

ARTICLE INFO

Keywords:
Forest fires
Pine needles
Gpyro
Thermal degradation
Thermogravimetric analysis
Shuffled complex evolution (SCE)
Multi-step reaction mechanism

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.

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 "gigascopic" 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 "gigascopic" 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 volatiliza-

* Corresponding author.
E-mail address: benkorichi-S@email.ulster.ac.uk (S. Benkorichi).

http://dx.doi.org/10.1016/j.firesaf.2017.03.058
Received 14 February 2017; Accepted 15 March 2017

Nomenclature

A	Pre-exponential factor (s^{-1})
Ea	activation energy ($J.mol^{-1}$)
m	Mass (g)
p	pressure
R	Universal gas constant
t	time
T	Temperature
Y	mass fraction
z	distance
Δz	Grid size

Greek

β	Heating rate ($°C.min^{-1}$)
n	Reaction order
T	Temperature (°c)
t	Time (s)
υ	stoichiometric factor
??	density
τ	dummy variable of integration
??	porosity
$\acute{\omega}$	reaction rate

subscripts

g	gas
i	Condensed phase species i
j	Gaseous species j
f	formation
DWF	Dry wildland fuel
GA	Genetic algorithms
MLR	TGA
PP	Pinus pinaster
SCE	Shuffled complex evolution
TGA	Thermo-gravimetric analysis
WWF	Wet wildland fuel
°	At time t

tion. 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:

$$R1 : WWF \rightarrow \nu_{H2O} H2O + (1 - \nu_{H2O}) DWF \quad (1)$$

$$R2 : DWF \rightarrow \nu_1 (\alpha - Pine) + (1 - \nu_1) Gas \quad (2)$$

$$R3 : (\alpha - Pine) \rightarrow \nu_2 (\beta - Pine) + (1 - \nu_2) Gas \quad (3)$$

$$R4 : (\beta - Pine) \rightarrow \nu_3 Char + (1 - \nu_3) Gas \quad (4)$$

$$R5 : (\alpha - Pine) \rightarrow \nu_4 (\beta - Pine) + (1 - \nu_4) Gas \quad (5)$$

$$R6 : (\beta - Pine) \rightarrow \nu_5 Char + (1 - \nu_5) Gas \quad (6)$$

$$R7 : Char \rightarrow \nu_6 Ash + (1 - \nu_6) Gas \quad (7)$$

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 ± 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].

Table 1
Estimated kinetic parameters for dehydration.

Reagent	Product	Kinetic parameters values			
		Log_A (s^{-1})	E_a (kJ. mol^{-1})	n (-)	?? (-)
Wet pine	Dry pine	9.71	78.6	4.29	0.9