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Comprehensive Characterization of Pyrolysis and Combustion of Genista Salzmannii Needles (GSN) for Fire Hazard Analysis

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Abstract

This article presents a first attempt of implementation of a lab-scale methodology proposed to describe the thermal decomposition behavior, and evolved volatile analysis of vegetative fuels using the TG-FTIR technique. Experiments within this method include testing the usual grinded form of samples compared to the intact form, which can render reliable and useful information to improve the understanding of the ignitability and combustibility of forest fuels. Moreover, slow (20 and 40 °C/min) and quasi-fast (60, 80 and 100 °C/min) heating rates were chosen to get close from the actual conditions of wildland fires (preheating/smoldering and flame region, respectively). In this work, we report the thermal decomposition behavior under inert (N2) and oxidative (air) atmospheres of Genista Salzmannii Needles (GSN) involved in high-intensity fires of Mediterranean forests. The results showed that the intact GSN were characterized by a higher mass loss rate compared to the grinded GSN. Furthermore, TG analyses were performed to assess thermal reactivity and combustion indices (ignition, devolatilization, combustion and burnout indices) of grinded and cut GSN samples at fives heating rates. The used set of the thermal indices are important properties to be determined when talking about efficient wildland fire management. As the heating rate increases, reactivity and combustion indices increase linearly. At low heating rates (20 and 40 °C/min), these parameters were quite similar for both samples, while the gap becomes more and more significant at elevated heating rates (60, 80 and 100 °C/min). High correlation coefficients (R2 > 0.96) were obtained, which indicate a good degree of fitting reliability between combustion characteristics and the tested heating rates. The determined slope can be used to compare and classify ignitability and combustibility of vegetative fuels related to fire risk potential. Based on the 3D-FTIR spectra, the dominant gases released during pyrolysis were CO2, C=O bond, C-H and C-O bond and H2O, while during combustion, CO2 and H2O were the major products. For kinetic investigations, activation energy (Ea) was calculated by means of two iso-conversional methods. The variation of Ea with the conversion rate has exhibited a quite similar behavior during the whole pyrolysis and combustion process. Char formation, at the end of an intense devolatilization, was the most complex process. The oxidation of the remaining char was characterized by a significant decrease of Ea and thus it was not considered as a major event in the combustion process.

1. Introduction

Due to the worrying climatic conditions and the high sensitivity of Mediterranean forests to fires, the evaluation of fuel hazard and fire risk gets more and more attention. The thermal decomposition of forest fuels is considered as the initial step of the forest fire process. Moreover, the determination of kinetic parameters of thermal degradation provides the necessary data for the development of realistic models *(Cancellieri et al. 2013)*. In studying forest fires, thermogravimetric analysis (TGA) was commonly used to investigate the thermal behavior and kinetics data of the decomposition process of vegetative fuels *(Leroy et al. 2006, 2010)*. Moreover, *Shu et al. (2021)* analyzed the combustibility and pyrolysis kinetics of forest combustibles and demonstrated their importance for fuels managing and forest fires prediction. However, few reliable experimental and modelling studies have examined the effect of different heating rate and sample sizes on the pyrolytic and combustion behavior and kinetics of forest fuels using TG-FTIR.

Genista Salzmannii is considered as an important vegetative fuel involved in fires of Mediterranean forests. This species is characterized by a very strong homogeneity and a 90% cover (Leroy-Cancellieri, 2014). Moreover, in a recent paper focus on an experimental and numerical investigation of prescribed fire on *Genista* *salzmannii*, Fayad et al. (2022) highlight the high-intensity of wildland fire generate by this vegetation specie. As it has been demonstrated that only small fuel particles with diameter less than 6 mm, were supposed to contribute actively to fire spread *(Burrows, 2001)*, this study is focused on *Genista Salzmannii* Needles (GSN) which constitute the most of this plant.

So far, to authors knowledge, there has been no detailed investigation on the solid-phase thermal degradation behavior and kinetic analysis of GSN to support wildland fire research. This work is in this purpose. It was first focused on the investigation of thermal decomposition behavior and the evolved gas component during pyrolysis and combustion by TG-FTIR. Both grinded and cut GSN were investigated, and the effect of heating rate on thermal reactivity and combustion indices (ignition, devolatilization, combustion and burnout indices) was studied. Then, kinetic analyses were performed using two model-free methods at five heating rates of 20, 40, 60, 80 and 100 °C/min. Finally, the followed methodology and the obtained data were used to establish a database of forest fuels and will provide basic information for forest fuels management and fire modellings.

1.1. Test sample

The plant material under study, representing *Genista salzmannii*, was collected from the mountain forest in Letia region, France. The raw *Genista Salzmannii Needles* (GSN) were prepared (cut and grinded samples, see Figure 1) and dried in a forced air convection oven with a temperature of 60 °C to remove the external moisture part before the thermogravimetric tests. The grinded sample (< 600 μm) was selected for proximate analysis. Moisture (M), volatile matter (VM) and ash (A) content were determined according to EN14774-3:2009: E, EN15148:2009: E and EN14775:2009: E standards, respectively. The fixed carbon content was calculated by difference: FC (%) = 100% - (M+A+VM). The moisture content was 1.28 and 5.7% for grinded and cut sample, respectively. The result of proximate analysis, on a dry basis, was volatile (77.95%), fixed carbon (20.11) and ash (1.94%). The GSN has lower moisture and higher content of VM. The flaming zone could be the major step during combustion process. In addition, the ash content of GSN was very low. Ash in vegetative fuels retards flaming combustion and reduces the rate of VM release, which result in poor combustion performance and enhanced fire resistance *(Cai et al. 2017)*.

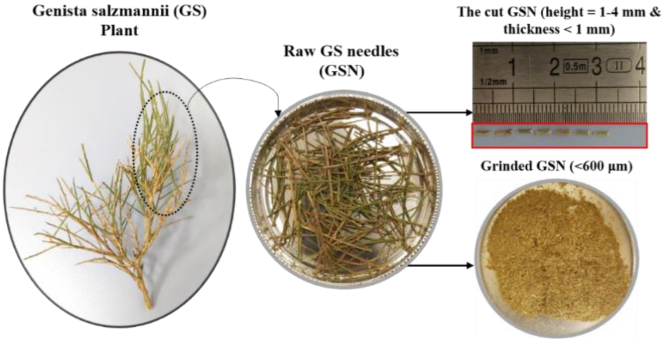

Figure 1- Grinded and cut GSN samples.

1.2. TG-FTIR analysis

Thermal decomposition behavior of grinded (< 600 μm) and cut (3-4 mm) samples of GSN was investigated by using a Perkin Elmer TGA 8000 analyzer. Air and N_2 atmospheres were used as the carrier gas with a flow rate of 30 ml/min. The gases evolved during pyrolysis and combustion were qualitatively monitored in real-time by coupling the TG instruments with a Fourier Transform Infrared (FTIR) spectrometer (Frontier, PerkinElmer, USA). The non-isothermal TG experiments with mass of about 15 ± 0.5 mg, placed in a ceramic crucible, were conducted from 35 to 1200 °C at different heating rates of 20, 40, 60, 80, 100 °C/min. During wildland fires, slow pyrolysis exists during preheating and/or smoldering combustion of vegetative fuels, while fast pyrolysis occurs in the flame zone. The selected heating rates conform to those adopted in the slow (20 and 40 °/min) and fast (60, 80 and 100 °C/min) pyrolysis *(Safdari et al. 2019)*.

1.3. Combustion characteristic indices

On the basis of TG-DTG data, characteristic parameters of thermal decomposition of vegetative fuel including the initial decomposition temperature (T_{id}), the ignition temperature (T_{ig}), the maximum mass loss rate temperature ($T_{DTG\text{-}max}$), the burnout temperature (T_b), their corresponding time (t_{id}, t_{ig}, $t_{DTG\text{-}max}$ and t_b, respectively), the maximum and average mass loss rate (DTG_{max} and DTG_{mean}), and temperature and time interval at the half value of DTG_{max} in the descending and the rising part of the peak (ΔT and Δt, respectively) were determined. These parameters can be used to quantitatively evaluate the thermal reactivity (R) and combustion indices namely ignition characteristic index (ICI), devolatilization index (DI), combustion characteristic index (CCI) and burnout characteristic index (BCI) *(Xie et al. 2020; Liu et al. 2021; Wnorowska et al. 2021)*. The used equations were listed in Table. 1.

Table. 1-Thermal reactivity and combustion indices formulas.

$R = 100 * \sum \frac{\lVert DTG_{max} \rVert}{T_{DTG_{max}}}$	$ICI = \frac{\lVert DTG_{max} \rVert}{t_{peak} * t_{DTG_{max}}}$	$DI = \frac{\lVert DTG_{max} \rVert * \lVert DTG_{mean} \rVert}{T_{DTG_{max}} * T_i * \Delta T_{1/2}}$
$CCI = \frac{\lVert DTG_{max} \rVert * \lVert DTG_{mean} \rVert}{T_i^2 * T_b}$	$BCI = \frac{\lVert DTG_{max} \rVert}{\Delta t_{1/2} * t_{DTG_{max}} * t_b}$	

1.4. Kinetic theory

The kinetic parameters provide required information to better understand the mechanisms controlling the thermal decomposition of vegetative fuels and for fire risk assessment. The kinetic analysis of GSN was carried out by using non-isothermal iso-conversional methods *(Álvarez et al. 2016)*. According to Arrhenius theory, the rate equation in terms of conversion (α) was represented as:

$$\frac{d\alpha}{dt} = Ae^{\frac{-E_a}{R.T}} f(\alpha)$$

where, α is the conversion degree ($\alpha = (m_0 - m_t)/(m_0 - m_f)$), A is the pre-exponential factor, E_a is the activation energy and f(α) is the reaction model. The model-free method as Flynn-Wall-Ozawa (FWO) was used to estimate the activation energy as follows:

$$\ln(\beta) = \ln\left(\frac{A.E_a}{R.G(\alpha)}\right) - 5.331 - 1.052\left(\frac{E_a}{R.T}\right)$$

A straight line was obtained by plotting log(β) versus 1/T and E_a can be estimated from the slope for each conversion $\left(slope = -1.052\left(\frac{E_a}{R.T}\right)\right)$. Another iso-conversional integral model-free method is Kissinger-Akahira-Sunose (KAS), which gives more accuracy or gives exact values of activation energy as compared with FWO. It was represented as follows.

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{A.R}{E_a.G(\alpha)}\right) - \left(\frac{E_a}{R.T}\right)$$

Here, E_a can be estimated by plotting $\log(\beta/T^2)$ versus 1/T.

2. Results and discussion

2.1. Thermal decomposition of GSN

Figure 2 and 3 shows the TG-DTG profiles and a typical 3D-FTIR spectra of gas products from pyrolysis and combustion of grinded (a, b) and cut (c, d) GSN at different heating rates. It can be seen that pyrolysis process of both sizes can be divided into three stages constituting two peaks and one flat line. The first stage (< 180°C), corresponds to GSN self-rehydration and the release of light volatiles. The second stage (major mass loss) include the next peak (200-600 °C) was dominated by the degradation of hemicellulose, cellulose and partly by that of lignin (rapid pyrolysis). The last stage (> 600 °C) indicates the carbonization, where a small quantity of char (unreacted fixed carbon and ash particles) was remaining. Based on the different peaks wavenumbers, the prominent pyrolytic products were CO_2, carbonyl groups (C=O), aromatic rings (C=C), H_2O, CH_4, and C-H or C-O bond contained organics. The evolved gases were principally emitted between 200 and 600 °C, which was in agreement with TG data. In case of combustion, it was observed that after residual moisture removal the mass loss takes place in two steps: the first one corresponds to the devolatilization (oxidative pyrolysis), and the second one relates to the oxidation of char. The dominant gases released during oxidative pyrolysis zone (100-

400 °C) were CO_2, C=O, H_2O and C=C. The peak of aliphatic C-H was very low. At higher temperature (above 550 °C), char oxidation produces a large amount of CO_2 while the absorbance bands of C=O and C=C decreased. In addition, the absorbance peak of CH_4 appeared at 500 °C while the saturated C-H declined gradually. Overall, the char combustion process produces CO_2, H_2O, CH_4 and a small amount of CO.

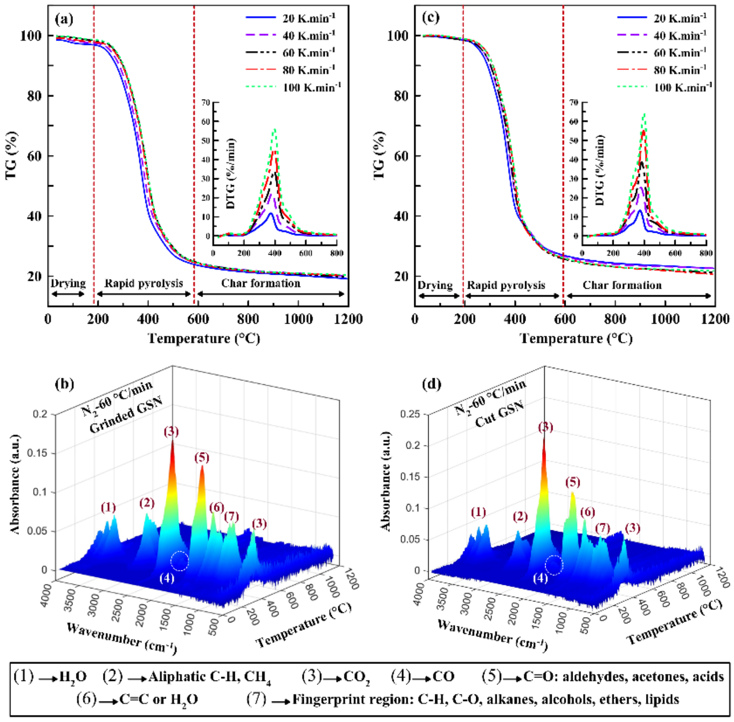

Figure 2-TG-DTG profiles and typical 3D-FTIR spectrum of the evolved volatile products from the pyrolysis of grinded (a, b) and cut (c, d) GSN.

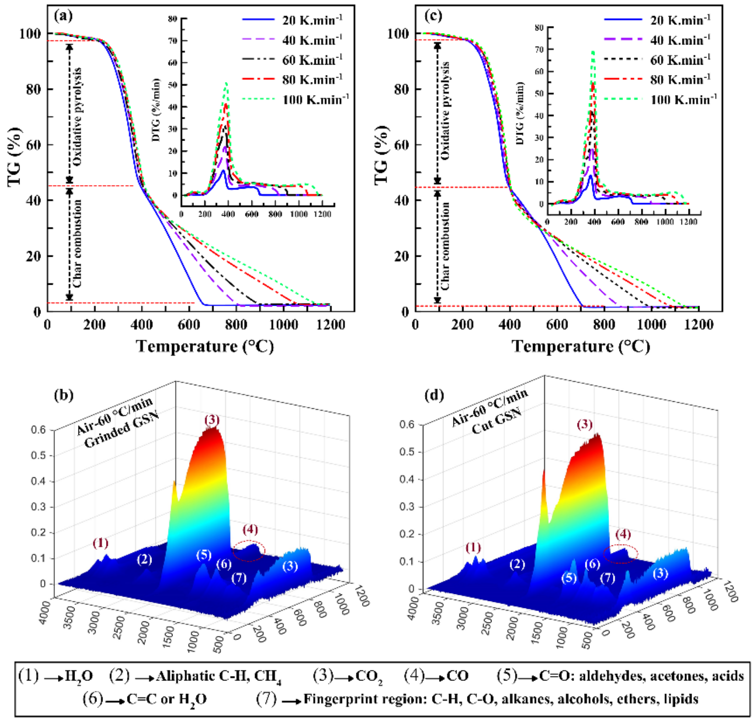

Figure 3- TG-DTG profiles and typical 3D-FTIR spectrum of the evolved volatile products from the combustion of grinded (a, b) and cut (c, d) GSN.

When the heating rate increased, the TG curves move towards high temperature region because of the limited heat transfer throughout and between particles *(Parthasarathy et al. 2021)*. Moreover, it can be observed from the DTG curves that the width and the height of peaks were increasing with increasing heating rate. On the other hand, the observed thermal behavior of grinded and cut samples of GSN was compared. The difference of DTG peaks between grinded and cut samples was increasing with increasing heating rate. This can be explained by the control of heat and mass transfer limitations, which leads to improving the weight loss rate of cut samples. Moreover, the residence time of combustion at high heating rate was short, which often leads to ineffective heat and mass transfer within and among particles. Furthermore, the rapid pyrolysis zone of both samples become more homogenous at height heating rates (80 and 100 °C/min) because of the simultaneous degradation of some components, which effecting an overlapping of peaks/shoulders.

Figure 4 demonstrates the evolution of thermal reactivity (R) and the four combustion parameters (ICI, DI, CCI and BCI) as a function of heating rates. Correlation coefficients (R^2) were all greater than 0.96, indicating a high degree of fitting reliability between combustion parameters and the tested heating rates for grinded and cut samples of GSN. As the heating rate increases, all the calculated parameters increase linearly. At low heating rates (20 and 40 °C/min), the combustion indices values for grinded and cut GSN were quite similar. The gap becomes more and more significant at high heating rates (60, 80 and 100 °C/min). This can be explained by the fact that during the heating of the cut GSN (at higher heating rate), the limitations of heat transfer leads to inefficient heat flux transmission within the sample, and thus their accumulation on the open surfaces of the sample. This leads in turns to a very short ignition and combustion times, which improves ignition and combustion indices compared to grinded GSN.

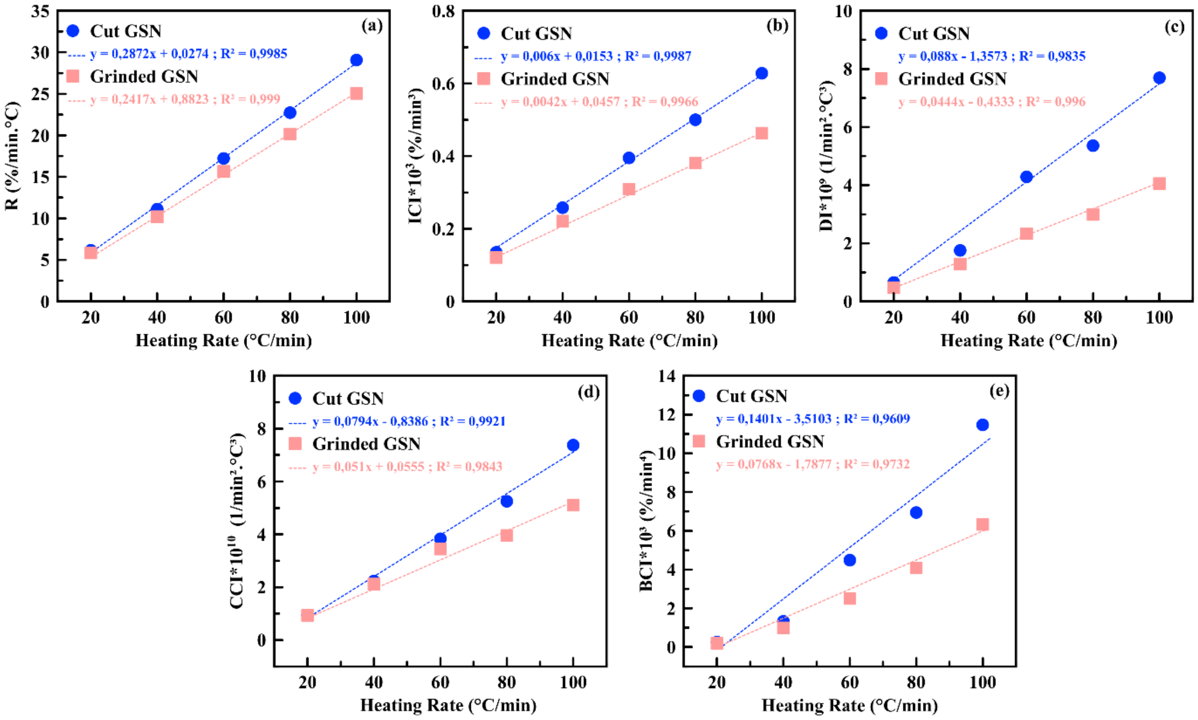

Figure 4- The relationship between R (a) ICI (b), DI (c), CCI (d) and BCI (e) and heating rates.

2.2. Kinetic analysis by model free methods

Understanding the thermal behavior and kinetics of vegetative fuels is very important for managing these resource materials and predicting forest fires. In the present study, the FWO and KAS models were used to evaluate the apparent activation energy (E_a) during pyrolysis and combustion of grinded and cut GSN samples at five heating rates. Figure 5 exhibits the E_a values for pyrolysis (a, b) and combustion (c, d) at different conversion degree. During pyrolysis (Figure 5a-b), it was observed that the E_a values for the cut GSN samples were higher as compared with grinded samples. The increased E_a in the conversion range of 0.05-0.35 was mainly caused by the hemicellulose decomposition. At α = 0.35, the E_a values show a slight change until α = 0.75 and represent the degradation of active cellulose. It is likely that pyrolysis reaction at $0.35<\alpha<0.75$ follow the same mechanism. Thereafter, a significant increase in the E_a values (especially for cut sample) was observed at the high conversion rate (0.8-0.9), followed by a rapid decrease at α = 0.95. This can be explained by the fact that after the rapid pyrolysis reaction, solid char was formed gradually. A further volatilization of this material (with low reaction activity) resulted in a remarkable activation energy increase (Chen et al. 2013). Moreover, the differences in the inherent structures of the produced char of grinded and cut GSN possibly account for the different pyrolysis behaviors at high conversion rates ($\alpha > 0.8$). Figure 5c shows the same behavior of E_a values at $0.05 < \alpha < 0.65$ during combustion of the grinded sample. A significant decrease of E_a at $\alpha > 0.65$ was due to the oxidation of remaining char, which was not considered as a major event (Rahib et al. 2020). Combustion of the cut sample (Figure 5d) at $0.55 < \alpha < 0.75$ displays a complex mechanism with negative E_a values, which indicates that devolatilization process was completed and the char was formed (Bhattacharyya et al. 2021). The reason behind this fact was probably due to the slow rate of degradation taking place at this juncture as indicated by the change of the TG curves slope in Figure 5d (see also Figure 3c). Moreover, the calculated correlation coefficients (R^2) at this region were very low, which means that the obtained E_a values were not reliable.

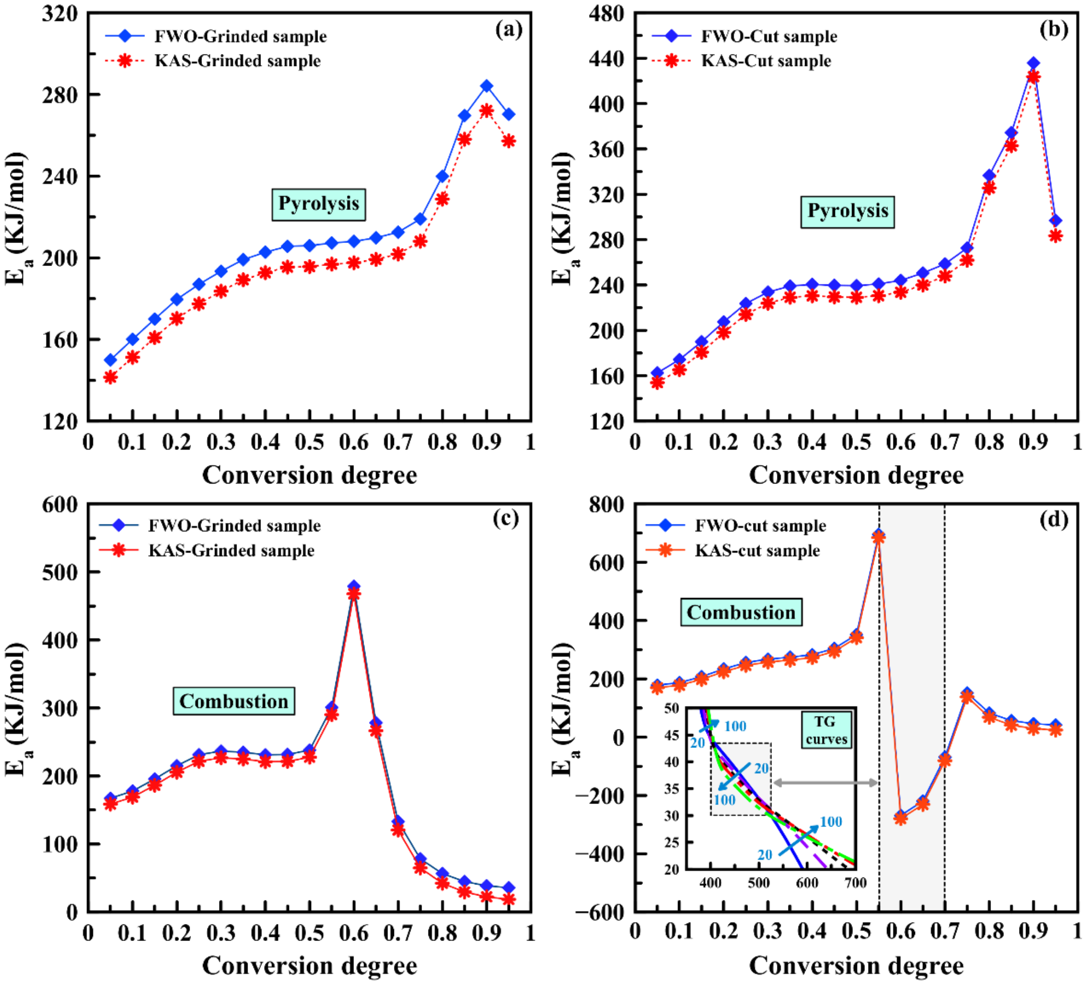

Figure 5- Estimation of E_a values according to FWO and KAS methods.

Generally, the verification of the whole chemical kinetics, controlling the thermal decomposition of forest fuel, is critical to ensure that the obtained parameters can be used in modelling the wildfire behavior. In perspective, the activation energy boundary obtained in this study by FWO and KAS methods will be compared with that obtained by model-fitting method to predict the most probable reaction mechanism. To go further into the improvement of kinetics analysis, a numerical optimization procedure will be applied in order to determine the adequate kinetic triplet.

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