

# Thermal Degradation Kinetics and Flammability Assessment of Forest Fuels

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## ABSTRACT

The thermal degradation kinetics and flammability of three forest fuels (pine needle, pine bark, and pine branch) were studied by thermogravimetric analysis (TGA). Friedman method and Flynn-Wall-Ozawa method were used to determine the conversion dependence of apparent activation energy ( $E$ ) for degradation of the fuels. The flammability of the three forest fuels were evaluated by the TGA results combined with the distribution of activation energies. Results indicate that pine needle is easier to release volatiles than pine branch and pine bark when heated. Pine branch involves the highest combustibility and pine bark shows the highest sustainability in fires.

**Keywords:** flammability, forest fuel, thermogravimetric analysis, model-free method

## 1. INTRODUCTION

Forest fire is a natural part of the earth's phenomenological pattern and the flammability assessment of forest fuels has been an active topic in the ecological and fire safety studies. Study on the flammability of forest fuels helps to recognize the behaviors and risks of forest fires in forms of crown fires, surface fires, fire whirls and so on [1,2]. According to the study of Anderson [3] and Liodakis [4], the flammability of forest species can be evaluated by three components: ignitability, combustibility and sustainability. Generally, the ignitability refers to how easily the fuel can be ignited, combustibility is the rate of combustion after ignition, and sustainability is related with the duration of thermal oxidative reactions.

Some searchers have investigated the flammability of various forest fuels in labs. Susott et al. [5] were the first to measure the combustion of organic materials using linear programmed heating in an inert atmosphere. Based on the various experimental tools, lots of studies

on the flammability of fuels in wildland fires were conducted. Liodakis et al. [6] measured the ignitability of five Mediterranean forest species with a specifically designed apparatus. Simeoni et al. [7] studied the ignitability of pine needles and solid polymers with Fire Propagation Apparatus (FPA). These studies created experimental conditions in labs similar with practical fires, and focused on the phenomenological fire behaviors of fuels. However, the contribution of kinetics of reactions to the flammability assessment has been scarcely discussed.

Additionally, there is little studies on comparing flammability of different parts (such as leaves, branch and bark) from the same tree. Since the ignition and spread of forest fires are closely related with the part of fuels, for example, crown fires with branches, spot fires with leaves, lighting fires with barks, thus it is meaningful to compare the flammability of different parts of the same plant. This work attempts to study the flammability of three typical forest fuels (pine needle, pine branch, and pine bark) by methods of thermogravimetric analysis and kinetic analysis.

## 2. EXPERIMENTAL

### 2.1 Materials

Materials used in this work were pine needle (PN), pine branch (PBr), and pine bark (PB) of *Pinus Sylvestris* (shown in Fig. 1) collected in the Great Khingan, northeast of China. Before tests, the samples were kept in a blast-type electric oven for 48 hours, with a constant temperature of 85 °C. A mill (brand: RRHP-100) was used for grinding of materials. Dimensions of particles can be controlled by operation time. After grinding, sieves were used to classify the particles of different dimensions into 5 groups, the smallest being under 75-100  $\mu\text{m}$  and the largest being larger than 450  $\mu\text{m}$ .



Figure 1. Forest fuels used in this study

## 2.2 Thermal Analysis Experiments

A thermobalance (model: SDTQ600) was used for thermogravimetric tests. The samples were evenly distributed over the sample pan with the initial mass kept to be  $10 \pm 0.5$  mg. Dynamic experiments were carried out at different heating rates of 5, 10, 15, 20, 30 °C/min, from room temperature up to 700 °C when the mass loss rate was very low. Air was used as sweeping gas for thermal oxidative degradation experiments, and the gas flow rate was 50 ml/min.

## 3. THEORIES

The dynamic thermogravimetry analysis holds great promise as a tool for the investigation of the physical and chemical mechanisms of thermal degradation. According to the mass loss information obtained from TG curves, conversion  $\alpha$  can be defined as:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (1)$$

where  $m_0$ ,  $m$ , and  $m_\infty$  are the initial, actual, and final mass of the sample, respectively.

The fundamental kinetic equation for non-isothermal TG experimental data is usually expressed as

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT(t)}\right) f(\alpha) \quad (2)$$

where  $t$  (min) is the time,  $\alpha$  ( $0 < \alpha < 1$ ) the conversion,  $A$  ( $\text{min}^{-1}$ ) the pre-exponential factor,  $E$  ( $\text{kJ}\cdot\text{mol}^{-1}$ ) the activation energy,  $T$  (K) the absolute temperature, and  $R$  is the gas constant,  $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . The function  $f(\alpha)$  is the so-called "model function" which relates to the reaction mechanism.

The integral of Eq. (2) yields,

$$g(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)} d\alpha = A \int_0^t \exp\left(-\frac{E}{RT}\right) dt \quad (3)$$

For a linear heating program, assume  $\beta$  is heating rate,  $^\circ\text{C}\cdot\text{min}^{-1}$ , there is  $\beta = dT/dt$ , and Eq.(3) leads to

$$g(\alpha) = \frac{A}{\beta} \int_0^T \left(-\frac{E}{RT}\right) dT = \frac{AE}{\beta R} \int_x^\infty \frac{e^{-x}}{x^2} dx = \frac{AE}{\beta R} p(x) \quad (4)$$

Where  $x = E/RT$ ,  $p(x)$  is the temperature integral which has no analytical solution but many approximations.

Model-fitting methods attempt to fit one single curve using the model functions and the one that fits the experimental data the best was considered the correct

model. Coats-Redfern method [8] is one of the most widely accepted model-fitting methods. However, model-fitting methods is problematic. For one thing, there is possibility that several model functions fit well with experimental data simultaneously; for another thing, kinetic compensation effect (KCE) exists between  $A$  and  $E$  [9].

Since the above-mentioned shortcomings of model-fitting methods, attentions of scientists turn to model-free methods, which give information of  $E$  by fitting with several curves simultaneously. Friedman method [10] is a differential method. Take  $\beta = dT/dt$  into Eq.(2) leads to

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (5)$$

Taking logarithm of both sides, yields

$$\ln \frac{d\alpha}{dT} = \ln \frac{A}{\beta} + \ln f(\alpha) - \frac{E}{RT} \quad (6)$$

Take linear regression analysis of Eq.(6), the value of activation energy  $E$  can be calculated from slope and pre-exponential factor from the intercept.

OFW method [11] is an integral method. Taking logarithm of both sides of Eq.(3) leads to

$$\ln g(\alpha) = \ln \frac{AE}{R} - \ln \beta + p(x) \quad (7)$$

Doyle approximation [12] is

$$\ln p(x) = -5.3305 + 1.052 \frac{E}{RT} \quad (8)$$

Thus

$$\ln \beta = \ln \frac{AE}{R} - \ln g(\alpha) - 5.3305 + 1.052 \frac{E}{RT} \quad (9)$$

Taking linear regression of logarithm of  $\beta$  versus reciprocal of  $T$ , the value of  $E$  can also be obtained from slope, which is similar with Friedman method.

In this study, Friedman and OFW method will be employed to calculate conversion dependence of activation energies for the thermal degradation of three forest fuels.

## 4. RESULTS AND DISCUSSION

### 4.1 Controlling Regime of Particles

Thermal oxidative degradation of forest fuels involves complex physical and chemical reactions. It is known that "thermally thin" and "thermally thick" solid fuels are controlled by kinetics and heat transfer processes, respectively. Pyle [13] developed a theory to define the regime controlling the thermal degradation process of single particles. According to this theory, controlling regime can be determined from the *Biot* number and one of two pyrolysis numbers  $P_y$  or  $P_y'$ . The result for the particles used in this study is listed in Table 1. Since particles are under kinetics control, it allows to conduct kinetic analysis for the thermal oxidative degradation of the three forest fuels.

Table 1. Dimensionless parameters of largest particles

Diameter ( $\mu\text{m}$ )	$Bi$	$P_y$	$P_y'$	Regime
75-100 $\mu\text{m}$	0.0017		58.9	Kinetics

However, even under the kinetics control, thermal degradation of particles of different dimensions still involves variable kinetic parameters due to the variation of chemical composition of particles [14]. The particles used in this study were of the same particle size (75-100  $\mu\text{m}$ ) to minimize the effects of particle size.

#### 4.2 Thermal Stability

TG and DTG curves of three forest fuels under heating rates of 10  $^{\circ}\text{C}/\text{min}$  in air were shown in Figure 2. Several thermal properties related with the oxidative thermal degradation were listed in Table 2, including initial decomposition temperatures  $T_{ini}$ , peak temperatures  $T_{peak}$ , peak values of mass loss rates  $-d\alpha/dt_{peak}$ , heat of reaction  $\Delta H$ , and the fraction of residue. Three forest fuels undergo complete thermal degradation below temperature of 600  $^{\circ}\text{C}$ , and only a little residue (approximately 2%) was left.

It can be observed that thermal oxidative decomposition of PN, PBr, and PB show two sequential stages under air flow, mainly corresponding to the pyrolytic reactions and oxidation of chars. Figure 2 show that initially, PN decomposed ahead of PBr and PB, which agrees with the lowest  $T_{ini}$  of PN. It indicates that, PN are more prone to release volatiles when heated and consequently easier to be ignited. Subsequently, when the mass loss exceeds 50%, the decomposition conversion of PBr was superior of that of PN and PB, which is due to the highest mass loss rates of the

volatilization and oxidation stages. Since the highest burning rate, PBr is considered as involving higher combustibility than other two fuels. Another observation is that the heat released during the thermal oxidative degradation of PBr is lowest, which is possibly due to the different of chemical composition for the three forest fuels. It should be noticed that the second stage (oxidation) of thermal degradation of PB involves a wide temperature range (see Figure 2a) although the process of conversion is obviously lower than PN and PBr (see Figure 2b). Correspondingly, the heat released for combustion of PB was larger than the other two fuels. Since the oxidation of PB sustains in a wide temperature range, it is considered more sustainable than PN and PBr.

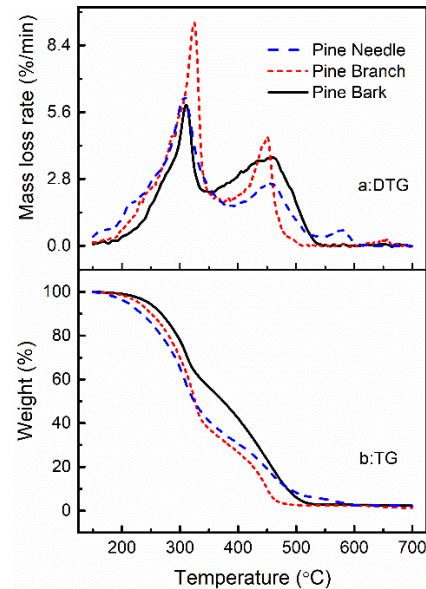


Figure 2. TG and DTG curves of oxidative thermal degradation of three fuels

Table 2 Characteristic parameters of the TG-DTG curves of forest fuels in air

Samples	$\beta$ ( $^{\circ}\text{C}/\text{min}$ )	$T_{ini}$ ( $^{\circ}\text{C}$ )	$T_{peak1}$ ( $^{\circ}\text{C}$ )	$T_{peak2}$ ( $^{\circ}\text{C}$ )	$-d\alpha/dt_{peak1}$ (%/min)	$-d\alpha/dt_{peak2}$ (%/min)	$-\Delta H$ kJ/g	Residue (%)
PN	10	256.3	308.6	460.4	6.25	2.62	12.85	2.340
PBr	10	274.8	326.1	457.9	9.35	4.54	10.86	4.366
PB	10	267.4	310.7	459.9	5.89	3.70	13.12	2.306

#### 4.3 Flammability of Different Forest Fuels

TG curves of three forest fuels under five heating rates, 5, 10, 15, 20, 30  $^{\circ}\text{C}/\text{min}$ , were used to evaluate the kinetic parameters. The Friedman method was firstly used adapted to calculate the variable activation energy. Equation (6) was used to obtain the activation energy  $E$ , which can be calculated from the slope of the straight line of  $\ln(d\alpha/dT)$  versus  $1/T$ . The values of  $E$  for the thermal oxidative degradation of three forest fuels were

plotted in Figure 3. Then, another iso-conversional method, OFW method was used in this work to calculate the activation energy. By linear fitting of  $\ln\beta$  and  $1/T$  at a given conversion  $\alpha$ , the variation of  $E$  with  $\alpha$  were obtained for conversion from 0.02 to 0.98, and the results were shown in Figure 3. By comparison, the Friedman method and the OFW method present similar trend of the  $E$  values of thermal oxidative degradation of PN, PBr and PB.

First of all, the activation energy of PN presents a different shape with that of PBr and PB, independent of the method used. With the increasing of conversion, the  $E$  values of PN increased from about 200 kJ/mol to 360 kJ/mol, and then decreased to 180 kJ/mol ignoring the errors at the beginning and end of conversion. The low values of  $E$  in the initial stage maybe correspond to superior volatilization ability of PN at low temperatures. On the other hand, high  $E$  values (larger than 300 kJ/mol) involved in the reactions between two peaks of DTG curves, which suppressed the occurrence of oxidation of chars. The smallest value of  $-d\alpha/dt_{\text{peak2}}$  (2.62%/min) of PN (see Table 2) coincides with the observation of  $E$ .

Comparatively, the  $E$  values of PBr and PB did not present sharp variations during the whole process. Activation energies of PBr were the lowest among the three fuels, which indicates that PBr particles involve higher intensities of volatilization and oxidation. Consequently, the thermal degradation of PBr cannot sustain in a wide temperature range. On the other hand, the activation energy of PB was at least 40 kJ/mol higher than that of PBr. Thus, the sustainability of PB is the highest among the three fuels.

Despite the experimental conditions of thermal oxidative degradation reactions are far from the actual conditions of forest fires, these methods can be helpful to illustrate the difference of thermal behaviors and flammability of various forest fuels.

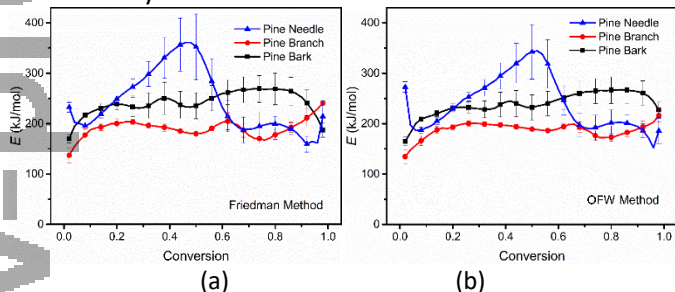


Figure 3. Conversion dependence of activation energy calculated by Friedman(a) and OFW method (b)

## 5. CONCLUSIONS

The thermal behavior and the thermal oxidative degradation kinetics of pine needle, pine branch, and pine bark of *Pinus Sylvestris* were investigated using the thermogravimetric analyzer to assess the flammability.

- The conversion dependence of activation energy was calculated by Friedman and OFW method which give similar results.
- Pine needle involves highest ignitability.
- Pine branch involves the highest combustibility.

- Pine bark particles sustain in a wide temperature range and high activation energy for the whole process indicated the highest sustainability.

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## REFERENCE

- [1] Niu H, Liu N and Ji D. Effect of atmospheric oxygen on the kinetic parameters of thermal degradation of pine branch particles. *Fire Saf. J.* 2020; 103028
- [2] Niu H and Liu N. Thermal decomposition of pine branch: Unified kinetic model on pyrolytic reactions in pyrolysis and combustion. *Fuel* 2015; 160: 339-345
- [3] Anderson HE. Forest fuel ignitability. *Fire Technol.* 1970; 6: 312-319
- [4] Lioudakis S, Vorisis D and Agiovlatis IP. A method for measuring the relative particle fire hazard properties of forest species. *Thermochim. Acta* 2005; 437: 150-157
- [5] Susott RA, Shafizadeh F and Aanerud TW. Quantitative thermal analysis technique for combustible gas detection. *Journal of Fire & Flammability* 1979; 10: 94-104
- [6] Lioudakis S, Bakirtzis D and Dimitrakopoulos A. Ignition characteristics of forest species in relation to thermal analysis data. *Thermochim. Acta* 2002; 390: 83-91
- [7] Simeoni A, Thomas JC, Bartoli P *et al.* Flammability studies for wildland and Wildland-Urban Interface fires applied to Pine Needles and solid polymers. *Fire Saf. J.* 2012; 54: 203-217
- [8] Coats AW and Redfern JP. Kinetic parameters from thermogravimetric data. *Nature* 1964; 201: 68-69
- [9] Agrawal RK. Compensation Effect in the Pyrolysis of Cellulosic Materials. *Thermochim. Acta* 1985; 90: 347-351
- [10] Friedman HL. Kinetics of Thermal Degradation of Char-forming Plastics from Thermogravimetry. Application to a Phenolic Plastic. *J Polym Sci Polym Symp* 1964; 6: 183-195
- [11] Flynn JH and Wall LA. A quick, direct method for the determination of activation energy from thermogravimetric data. *J. Polym. Sci., Part B: Polym. Lett.* 1966; 4: 323-328
- [12] Doyle CD. Kinetic Analysis of Thermogravimetric Data. *J. Appl. Polym. Sci.* 1961; 5: 285-292
- [13] Pyle DL and Zaror CA. Heat transfer and kinetics in the low temperature pyrolysis of solids. *Chem. Eng. Sci.* 1984; 39: 147-158
- [14] Niu H and Liu N. Effect of Particle Size on Pyrolysis Kinetics of Forest Fuels in Nitrogen. *Fire Safety Science* 2014; 11: 8