# Thermal Decomposition of Wildland Material: Interactions among Biomass and Shallow Soil under Nitrogen and Air Atmospheres

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## ABSTRACT

In a wildland fire, the thermal decomposition of biomass supports the burning of wildland material, while the pyrolysis of shallow soil has a considerable impact on the underground smoldering. So far, the interaction between biomass and shallow soil has been scarcely studied. This work presents an effort on this problem. The thermal behaviors of pine needle, pine bark, pine branch, shallow soil and their mixtures are investigated using a thermogravimetric analyzer under nitrogen and air atmospheres. The calculated TG curves of the forest combustible mixtures, obtained with the mixing ratios and experimental data of individual materials, agree well with the experimental data. This indicates that the interaction among biomass and shallow soil mixture is negligible under nitrogen and air atmospheres. The deviation parameter and the deviation of residue yield between the calculated and experimental curves are used to evaluate the influence of interactions on the organic and inorganic components, respectively. The calculated lower values of these parameters (<3%) confirm insignificant effect of interaction between biomass and shallow soil on pyrolysis and combustion. In addition, results further indicate that the effect of interactions on the thermal decomposition of the organic component is closely associated with the atmosphere and mixing ratio, while the effect on inorganic component has no perceptible relationship with these two factors. A kinetic model, involving $n$th-order independent parallel reactions, is applied to verify the reliability of the evaluation result. The pyrolysis rate of biomass is considered as the sum of the three pseudo-components, namely cellulose, hemicellulose, and lignin. While in the pyrolysis of shallow soil, the three pseudo-components are composed of labile, intermediate, and stable organic materials. The major mass loss of single material in combustion is interpreted as the sum of the parallel reactions of the above three pseudo-components as well as char. The theoretical TG curves of the mixtures, based on mixing ratio and kinetic parameters of individual materials, are in good agreement with experimental data, which also suggests an insignificant interaction effect on pyrolysis and combustion.

**KEYWORDS:** Thermal decomposition, wildland material, interaction, kinetic analysis.

## NOMENCLATURE

| | | | |
|---|---|---|---|
| $A$ | frequency factor (1/min) | **Greek** | |
| $E$ | activation energy (kJ/mol) | $\alpha$ | conversion |
| $f(\alpha)$ | reaction function | $\beta$ | heating rate (K/min) |
| $m$ | sample mass (mg) | **Subscripts** | |
| $n$ | reaction order | 0 | initial value |
| $r$ | fraction of component | $\infty$ | final value |
| $R$ | gas constant (8.314 J/(mol·K)) | $i$ | number of components |
| $T$ | temperature (K) | $j$ | number of experimental runs |
| $t$ | time (min) | | |

$k$     number of data points in each run

## INTRODUCTION

In a wildland fire, the thermal decomposition of biomass supports the burning of wildland material, while the pyrolysis of shallow soil has a considerable impact on the underground smoldering. So far, there have been numerous reports on the thermal decomposition of biomass or soil separately [1-4]. Niu and Liu [2] established a consistent kinetic scheme with the same proportions of three pseudo-components to simulate the pyrolytic reactions in pyrolysis and combustion of pine branch. Chen et al. [3] simulated peat pyrolysis using stages of moisture evaporation and organic matter pyrolysis (which consists of pyrolysis of hemicellulose, cellulose, and lignin), and also simulated combustion processes with a scheme containing moisture evaporation and two consecutive reactions. Kučeríka et al. [4] divided the soil organic material thermal stability into three categories: labile, intermediate, and stable, linking with contents of clay, bound water, organic carbon and nitrogen.

The major organic components of biomass include cellulose, hemicellulose, and lignin. The fraction of the inorganic ash varies from less than 1% in softwoods to 15% in herbaceous biomass and agricultural residues [5]. Soil organic matter contains carbohydrates, proteins, lipids, phenol-aromatics, protein-derived and cyclic nitrogenous compounds, and some still unknown compounds [6]. The inorganic content of duff and soil below forest ground surface increases with the increment of depth [7]. The organic composition of shallow soil is different with that of plants. At the same time, shallow soil generally contains more inorganic proportion than biomass. Shallow soil and plants are in close contact under natural conditions, which may cause interactions among them when suffering from a wildland fire. Among the limited studies, Giudicianni et al. [8] reported that the presence of inorganic elements significantly affects the pyrolysis behaviours of A. donax canes, in terms of characteristic temperatures and products yields. Yang et al. [9] detected an obvious catalytic effect of $K_2CO_3$ on the pyrolysis of palm oil wastes by analyzing the peak value of mass loss rate, while most of the other mineral additives have a negligible influence. Nevertheless, the interactions between biomass and shallow soil have been scarcely studied.

The objective of this work is to evaluate the interactions between biomass and shallow soil under nitrogen and air atmospheres by analyses of organic and inorganic components. The reliability of the evaluation method is verified by kinetic calculations and experimental data.

## EXPERIMENTAL

### Sample

The materials used in this work include pine needle (pn), pine bark (pb), pine branch (pbr), shallow soil (ss) and their equal-proportion mixtures consisting of two or three components (pn-ss, pb-ss, pbr-ss, pn-pb-ss, pn-pbr-ss, and pb-pbr-ss). The forest combustible materials were collected in the Great Khingan, northeast of China. The biomass samples (pn, pb, pbr) were obtained from living Pinus Sylvestris to prevent from being polluted or mixed with impurities. The shallow soil (ss) containing humus and black soil was collected at a depth of 0~5 cm from the ground surface. Before formal sampling, the litter above the shallow soil was removed. The raw samples were dried at 75 °C for 24 h in an electric oven. Prior to thermogravimetric tests, samples were milled to powder (less than 125 μm in size).

**Ultimate analysis**

The ultimate analysis of four single samples was performed by an Elementar vario EL cube, and the results are shown in Table 1. Before oxygen analysis of shallow soil, demineralization of shallow soil was conducted by stirring the flour in 1M HCl at room temperature for 24 h. After filtration, the sample was washed with distilled water repeatedly until the pH of the supernatant became neutral. This procedure was repeated twice, and the processed sample was dried at 75 °C for 24 h.

**Table 1. Ultimate analysis results of samples**

| Material | N (%) | C (%) | H (%) | O (%) |
|---|---|---|---|---|
| Pine needle (pn) | 1.33 | 51.30 | 7.01 | 37.51 |
| Pine bark (pb) | 0.35 | 52.44 | 6.37 | 38.13 |
| Pine branch (pbr) | 0.43 | 47.64 | 6.85 | 40.15 |
| Shallow soil (ss) | 1.30 | 28.82 | 3.84 | 26.12[a] |

[a]Demineralized.

**Pyrolysis and combustion experiments**

A Netzsch thermobalance model STA 449F3 was employed for thermogravimetric (TG) experiments. The samples were evenly distributed over the crucible with the initial mass of 7.5~8.5 mg and 2~3 mg under nitrogen and air atmospheres, respectively. Dynamic experiments were carried out at heating rates of 5, 10, 15, 20 and 30 K/min, from room temperature up to 800 °C. The flow rate of sweeping gas was 100 ml/min. Some runs were repeated to check the repeatability of the tests under the same conditions.

**Kinetic analysis**

In the present work, a multi-component model is used to simulate the thermal decomposition of the forest combustible materials. If a pseudo-component $i$ goes through an $n$-order reaction, the decomposition rate (DTG) can be expressed by

$$d\alpha_i/dT = (A_i/\beta)\exp(-E_i/RT)(1-\alpha_i)^{n_i}, \tag{1}$$

where $A$ is the pre-exponential factor, $E$ is the activation energy, $n$ is the reaction order, $\beta = dT/dt$ is the heating rate and $R$ is the gas constant. The conversion fraction $\alpha_i$ is expressed as

$$\alpha_i = (m_{i0} - m_i)/(m_{i0} - m_{i\infty}), \tag{2}$$

where the subscripts "0" and "$\infty$" respectively denote the initial and final masses of the sample.

The total conversion is thus formulated as

$$\alpha = \sum_i r_i \alpha_i, \tag{3}$$

where $r_i$ represents the fraction of component $i$ ($\sum r_i = 1$).

By using the experimental data, the genetic algorithm (GA) is applied for kinetic analysis of individual fuels. The objective function is defined as Eq. (4) to minimize the differences between experimental and theoretical mass loss rate curves.

$$Dev = 100\% \cdot \sum_j \sqrt{S_j \big/ \left(Z_j - N_j\right)} \Big/ \max\left[-\left(d\alpha/dT\right)^{Exp}\right] \Big/ j \,. \tag{4}$$

Here, $j$ is the number of experimental runs, $Z_j$ is the number of data points on the $j$-th experimental curve, $N_j$ is the number of independent parameters to be determined, and $S_j$ is expressed by

$$S_j = \sum_k \left[\left(\left(d\alpha/dT\right)^{Exp}\right)_{j,k} - \left(\left(d\alpha/dT\right)^{Cal}\right)_{j,k}\right]^2, \tag{5}$$

where $k$ is the number of data points in each run. The superscripts $Exp$ and $Cal$ denote the experimental and simulated values, respectively. Experimental data at heating rates of 5, 10, 15, 20 and 30 K/min are simultaneously applied to the optimization calculations in order to overcome the kinetic compensation effects. The GA codes in MATLAB are used to perform the search.

## RESULTS AND DISCUSSION

### Thermogravimetric analysis of individual materials

**Pyrolysis and combustion experiments:** The normalized DTG curves for individual fuel obtained at different heating rates follow similar trends under nitrogen and air atmospheres. The DTG curves at the constant heating rate of 10 K/min are shown in Fig. 1. At temperatures lower than about 373.15 K, the small mass loss of the samples is attributed to moisture evaporation. As indicated in Fig. 1(a), the pine needle starts to decompose earlier at a temperature slightly below 400 K, followed by pine bark, pine branch and shallow soil. Comparing the DTG peaks of the different samples shows that the shallow soil has the widest peak temperature range. As shown in Fig. 1(b), under oxidative atmosphere, two stages are distinguished in the DTG curves for biomass fuels. The first stage in the range of 400~650 K is caused by the combination of total decomposition of hemicellulose and cellulose and partial decomposition of lignin, and the second one in the range of 650~800 K corresponds to the decomposition of the remaining lignin and char oxidation, leaving behind only ash [14]. The mass loss rate of the shallow soil increases sharply from about 450 K, and then reaches the maximum at around 590 K. This peak temperature is close to the first peak temperature of biomass fuels. After that, the mass loss rate drops to a platform and then decreases again. As shown in Table 2, the residual proportions of biomass fuels are lower than that of shallow soil in pyrolysis and combustion.
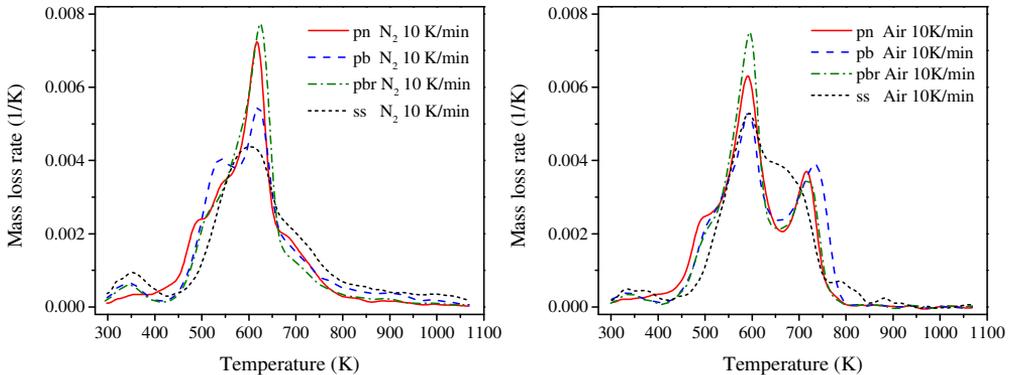
(a) (b)

**Fig. 1.** Experimental DTG curves of single materials in (a) pyrolysis and (b) combustion at the heating rate of 10 K/min.

**Table 2. Residual fraction of TG experiment under nitrogen and air atmospheres**

| Residual fraction (%) | pn | pb | pbr | ss |
|---|---|---|---|---|
| $N_2$ | 18.72±0.29 | 25.35±0.56 | 19.63 ±0.10 | 57.93±0.63 |
| Air | 2.63±0.73 | 3.58±0.13 | 2.88±0.29 | 42.56±1.00 |

**Multi-step devolatilization mechanism of single materials:** The three-step devolatilization mechanism for the volatile fractions of the pseudo-components, hemicellulose, cellulose, and lignin, is applied to describe the dynamic thermogravimetric curves of the biomass fuels under nitrogen atmosphere. For shallow soil pyrolysis, the three-step kinetic model is interpreted as the reactions of labile, intermediate and stable organic materials. The char oxidation is simulated as the fourth reaction in combustion of biomass fuels and shallow soil. The calculated kinetic parameters of the individual materials under nitrogen and air atmospheres are listed in Tables 3 and 4. Here, the char fraction under air atmosphere is expressed as

$$r_{char} = \left( residue_{nitrogen} - residue_{air} \right) / \left( 100 - residue_{air} \right) \tag{6}$$

while the other parameters are determined by the GA method. The *Dev* values lie within the range of 2.30~3.24%, suggesting good fit between the theoretical and experimental DTG data. The simulated curves of shallow soil at the heating rate of 10 K/min are presented in Fig. 2, for which the data of dehydration stage have been removed since the focus of this work is on the thermal decomposition reaction. As shown, the theoretical DTG curves are in good agreement with the experimental ones. For the figures in this work, the sub-reactions 1~4 are defined as the thermal decomposition of hemicellulose, cellulose, lignin, and char for biomass materials. While for shallow soil, the four corresponding pseudo-components are labile, intermediate, stable organic materials and char, respectively.

**Table 3. Optimal solutions of kinetic parameters in pyrolysis**

| Material | Component | $E$ (kJ/mol) | $\lg A$ [lg (min-1)] | $n$ | $r$ (%) | $Dev$ (%) |
|---|---|---|---|---|---|---|
| pn | Hemicellulose | 68.40 | 6.21 | 2.30 | 44.94 | 2.93 |
| | Cellulose | 163.33 | 13.58 | 1.19 | 32.35 | |
| | Lignin | 195.75 | 14.77 | 4.85 | 22.71 | |
| pb | Hemicellulose | 94.46 | 8.75 | 2.22 | 42.71 | 2.76 |
| | Cellulose | 187.47 | 15.51 | 2.79 | 35.88 | |
| | Lignin | 184.17 | 12.63 | 9.77 | 21.41 | |
| pbr | Hemicellulose | 92.29 | 8.40 | 2.80 | 44.99 | 2.78 |
| | Cellulose | 179.87 | 14.83 | 1.47 | 36.18 | |
| | Lignin | 191.25 | 14.16 | 9.82 | 18.83 | |
| ss | Labile organic materials | 96.09 | 8.82 | 3.48 | 33.94 | 2.93 |
| | Intermediate organic materials | 207.04 | 18.41 | 3.46 | 16.59 | |

| | | 192.13 | 15.42 | | 9.65 | 49.47 |
|---|---|---|---|---|---|---|
| | Stable organic materials | | | | | |

**Table 4. Optimal solutions of kinetic parameters in combustion**

| Sample | Component | $E$ (kJ/mol) | $\lg A$ [lg (min-1)] | $n$ | $r$ (%) | $Dev$ (%) |
|---|---|---|---|---|---|---|
| pn | Hemicellulose | 86.09 | 8.40 | 2.55 | 29.95 | 2.46 |
| | Cellulose | 147.63 | 12.77 | 1.55 | 36.13 | |
| | Lignin | 158.85 | 12.27 | 2.96 | 17.40 | |
| | Char | 196.18 | 13.90 | 1.00 | 16.52 | |
| pb | Hemicellulose | 92.32 | 8.82 | 2.79 | 30.38 | 2.46 |
| | Cellulose | 160.34 | 13.85 | 2.67 | 35.73 | |
| | Lignin | 178.74 | 13.09 | 2.23 | 11.32 | |
| | Char | 152.74 | 10.32 | 0.90 | 22.57 | |
| pbr | Hemicellulose | 85.24 | 7.96 | 2.56 | 30.13 | 2.30 |
| | Cellulose | 147.42 | 12.67 | 1.23 | 36.71 | |
| | Lignin | 161.71 | 12.32 | 2.97 | 15.92 | |
| | Char | 174.08 | 12.29 | 1.08 | 17.24 | |
| ss | Labile organic materials | 109.25 | 10.23 | 2.51 | 22.82 | 3.24 |
| | Intermediate organic materials | 162.35 | 14.04 | 2.74 | 35.01 | |
| | Stable organic materials | 165.43 | 12.85 | 2.96 | 15.41 | |
| | Char | 158.26 | 11.47 | 2.58 | 26.76 | |



(a)                    (b)
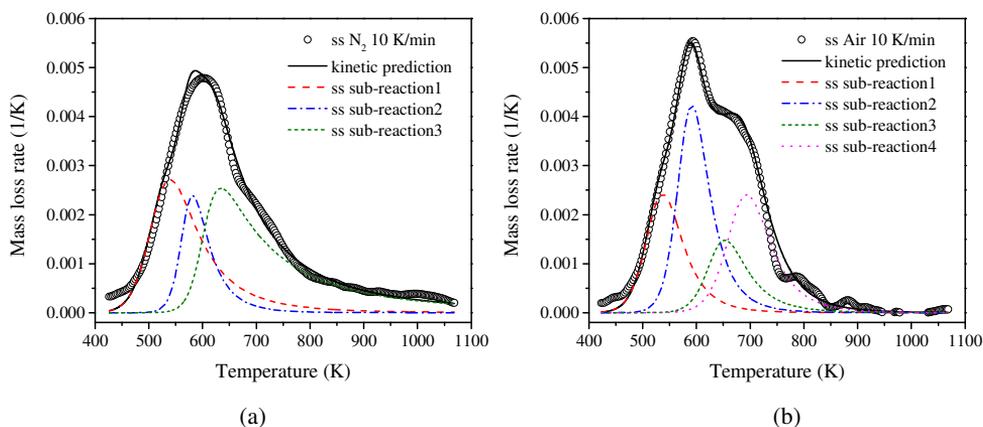
**Fig. 2.** Theoretical and experimental DTG curves of shallow soil in (a) pyrolysis and (b) combustion at the heating rate of 10 K/min.

## Thermogravimetric analysis of mixtures

**Calculated and experimental curves:** We calculate TG curves of mixtures by a weighted sum of experimental curves of individual materials and then compare the calculated curves with the experimental data in Fig. 3. The results suggest that there is no obvious interaction between biomass and shallow soil during pyrolysis and combustion. As shown in Table 5, the residual fractions of blends are in range of 32.47 ~ 41.44% for pyrolysis, and 15.67 ~ 23.94% for combustion. As

indicated, under a certain atmosphere, the residue mass fractions for two-component mixtures are higher than those for three-component mixtures. In other words, the residual mass fractions increase with the decrease of biomass proportion.



(a)

(b)

(c)

(d)
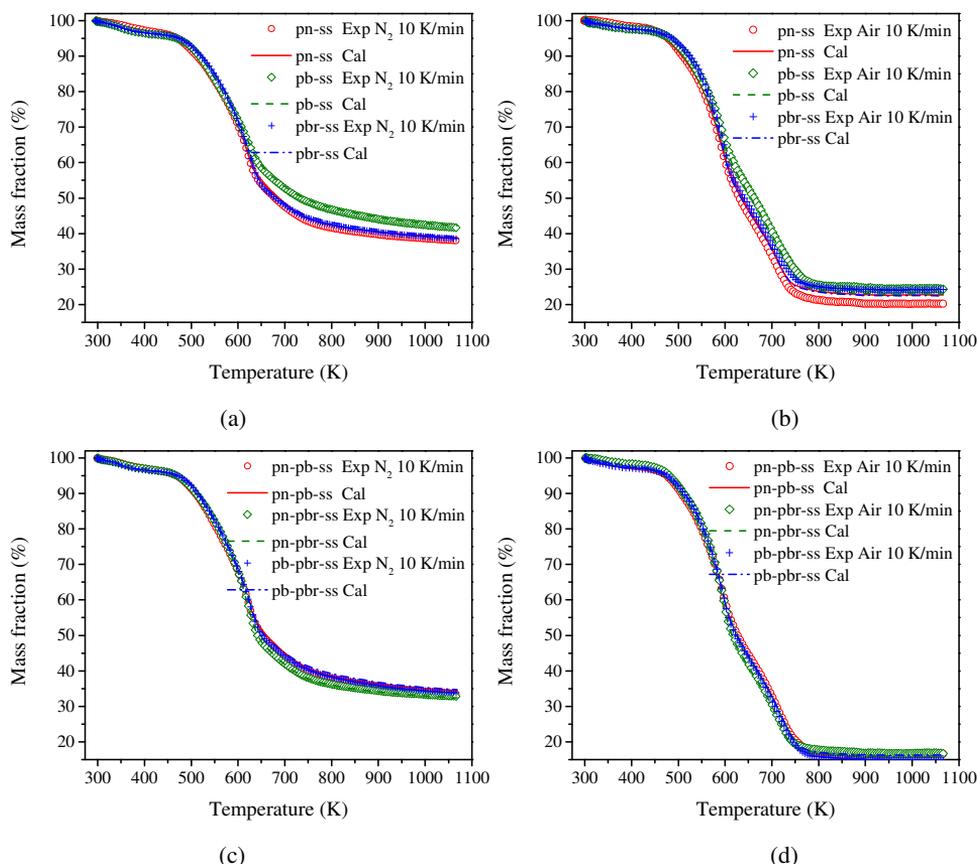
**Fig. 3.** Comparison between calculated and experimental TG curves for mixtures heated at 10 K/min in pyrolysis and combustion.

**Table 5. Residual fraction of mixtures under nitrogen and air atmospheres**

| Residual fraction (%) | pn-ss | pb-ss | pbr-ss | pn-pb-ss | pn-pbr-ss | pb-pbr-ss |
|---|---|---|---|---|---|---|
| $N_2$ | 37.88±0.23 | 41.44±0.92 | 37.78±0.77 | 33.76±0.43 | 32.47±0.57 | 33.83±0.19 |
| Air | 21.78±1.19 | 23.30±2.84 | 23.94±0.77 | 16.13±1.07 | 16.16±1.80 | 15.67±1.70 |

**Quantitative method of interaction assessment:** Usually, single-point values of TG or DTG curves (such as peak mass loss rate, peak temperatures, and product yield) were used to evaluate the influence of interactions on the thermal decomposition of mixtures [8-12]. A more reasonable quantitative method is by using a quantity that reflects the overall feature of the curves. For example, by using the root mean square (RMS) value of relative error in prediction of fractional residue, Sadhukhan et al. [13] revealed that there were no synergistic effects between coal and biomass. In this work, a similar quantitative approach is used to assess the interaction effect among mixtures. The parameter *Dev* (Eq. (4)) and the deviation of unreacted mass between the calculated

and experimental curves are used to evaluate the influence of interactions on organic and inorganic components, respectively. As shown in Fig. 4, among all the tests, a maximum *Dev* of 2.63% is reached for pb-ss under air atmosphere. For this mixture, all the calculated and experimental results are in good agreements (see Fig. 5). Besides, a maximum $|\Delta residue|$ of 1.17% is reached for pbr-ss under air atmosphere.

The calculated low parameters of *Dev* and $|\Delta residue|$ (<3%) also indicate insignificant effect of interaction between biomass and shallow soil on pyrolysis and combustion. In addition, the effect of interactions on the thermal decomposition of organic component is closely associated with the atmosphere and mixing ratio: interaction under air is more significant than that under nitrogen, and the interaction is generally enhanced with higher shallow soil content. However, there is no obvious relationship between these two factors and the effect on the inorganic component.



(a)  (b)
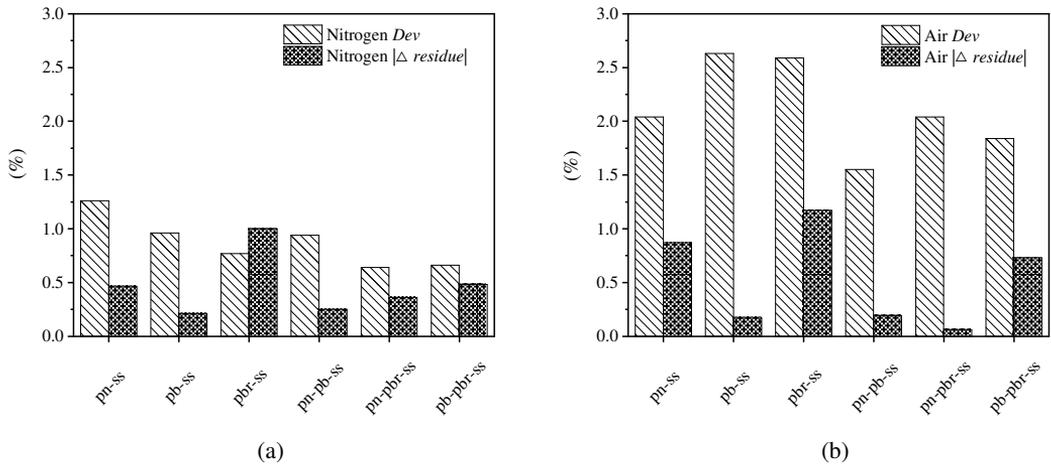
**Fig. 4.** Quantitative evaluation of interaction effect among mixtures under (a) nitrogen and (b) air atmospheres.
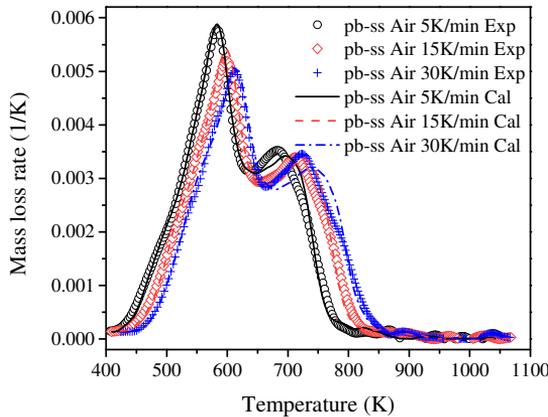


**Fig. 5.** Comparison between calculated and experimental DTG curves for pb-ss in combustion.

**Theoretical and experimental curves:** In the previous section, the multi-step devolatilization mechanism is used to obtain the kinetic parameters of single materials. Here, the theoretical curves of individual materials are summed, based on the mixing ratio, to predict the DTG curves of the mixtures. The *Dev* values of biomass-shallow soil mixture vary in the range of 2.53~3.92%, which

implies that the theoretical and experimental DTG curves have good agreement, and the materials undergo thermal decomposition independent of each other. This verifies the applicability of the model for predicting the pyrolysis and combustion behavior of the biomass-shallow soil mixture without losing any generality [13, 14].

The maximum $Dev$ of 3.92% corresponds to the combustion processes of pb-ss, for which the theoretical and experimental DTG curves of this mixture are indicated in Fig. 6. The curves for the sub-reactions of pine bark and shallow soil are also plotted. The good comparison between theoretical and experimental DTG curves also suggests an insignificant effect of the interactions on pyrolysis and combustion.
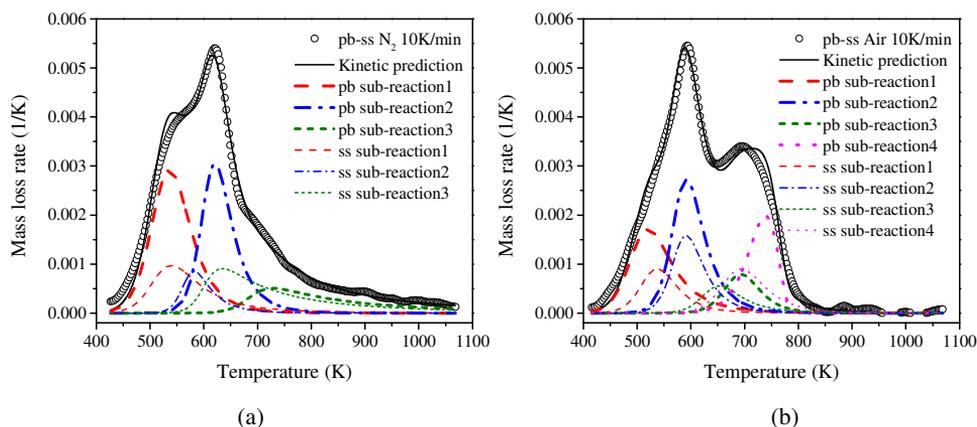


**Fig. 6.** Comparison of theoretical and experimental curves of pb-ss at the heating rate of 10 K/min under (a) nitrogen and (b) air atmospheres.

## CONCLUSIONS

In this work, the interactions between biomass and shallow soil are studied to promote the understanding of thermal decomposition of forest combustible mixtures when suffering from a wildland fire. A quantitative method is applied to compare the calculated and experimental curves, in which the parameters $Dev$ and $|\Delta residue|$ are used to evaluate the influence of mixing on organic and inorganic components, respectively. A kinetic method is used to check the reliability of this assessment method. The interaction under different conditions can be examined by using this quantitative method. The results show that the interaction between biomass and shallow soil has an insignificant effect on pyrolysis and combustion. In addition, the effect of interactions on thermal decomposition of the organic component is closely associated with the atmosphere and mixing ratio: interactions under air are stronger than that under nitrogen, and the interaction is generally enhanced with higher shallow soil content. However, the effect on thermal decomposition of the inorganic component is hardly related to these two factors. The residual fractions of blends increase with the increase of the shallow soil proportion of blend under a certain atmosphere.

## ACKNOWLEDGEMENTS

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