Contribution of Gas-phase Reaction on Heat Output from Smoldering Packed-bed of Dried Leaves

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Abstract

The heat generation from gas-phase reactions in vacant spaces inside a smoldering packed-bed is evaluated experimentally. The bed is a pile of cut leaves of dried plants, having a bulk density of 0.22 g/cm^3, in a thermally-insulated vertical quartz tube of 17 mm inner diameter and 150 mm height. Its top is ignited so that the smoldering progresses vertically downward. Air is supplied from the bottom of the tube against the smoldering direction at a fixed flow rate of 30 mm/s. The temperature in the packed-bed is measured and concentrations of exhaust gas components are analyzed by means of gas chromatography, results of both which confirm that the smoldering process reaches a quasi-steady state. The smoldering is assumed to consist of three reactions: the pyrolysis of unburned leave generating char and pyrolysis gas, the surface combustion of the char generating exhaust gas and residue, and the gas-phase combustion of the pyrolysis gas also generating exhaust gas. The amount of heat generated from each of these reactions is evaluated from the balance of enthalpies between reactants and products in the reaction. Enthalpies of unburned leaves, the char, and the residue are measured by means of bomb calorimetry after those samples are collected from the corresponding regions in the tube. The exhaust gas is collected in a gas bag, and concentrations of oxygen, carbon dioxide, carbon monoxide and methane are measured by gas chromatography with thermal conductivity detection. Particulates in the exhaust gas are collected by a glass fiber filter, and its enthalpy is measured by means of bomb calorimetry. The pyrolysis gas, on the other hand, is simulated by a gas that is generated from unburned leaves while those are heated from room temperature to 400 ℃ in air, and is collected and analyzed in the same way as the exhaust gas. The heat generated in the gas phase in vacant spaces in the bed is estimated at 8.1 J/s, which is about 40% of the total heat output of 20.1 J/s from the smoldering of the packed-bed.

Introduction

Smoldering is a slow, low-temperature, flameless and self-sustaining combustion[1]; it can occur through variety of materials such as wood[2][3], sawdust[4], flexible foam[5][6], and other biomass combustibles[7][8]. It includes a variety of chemical reactions and heat and mass transports in gas and solid phases, and it emits various combustible gases [7][8].

Smoldering of a biomass combustible generally involves two stages of chemical reactions: pyrolysis (thermal decomposition) and char oxidation [6]. In order for the smoldering to continue, sufficient heat must be transferred from the region of exothermic reactions to the adjacent unburned material so that the temperature becomes high enough to initiate the oxidation of the material [1]. Thus, oxidation reactions play an important role in the propagation of smoldering.

One of typical self-propagating forms is the opposed downward smoldering, in which the reaction front propagates in the direction opposite to the oxidant flow. Under this condition, oxidant gas flows into the fresh part of the combustible material. The fresh material is heated and dried owing to conductive and radiative heat transfers from the downstream, and then is thermally decomposed under the presence of oxygen. Oxidation reactions follow depleting oxygen in the flow while it passes through the region of char and residue and heat is generated there[9] [10]. As it is noted in the review[11] of the previous studies, reactions have

been regarded as two overall reactions are assumed representing two stages, namely:

1. Pyrolysis under oxidative atmosphere producing char and gas, and
2. Oxidation of the char.

Ohlemiller and Lucca[12] have examined their reaction model for polymer and cellulosic material and have found that the first stage is predominant. This assumption can simplify it to a one-step reaction model.

$$\text{Solid Fuel} + O_2 \rightarrow \text{Solid Product} + \text{Gaseous Product} + \text{Heat} \qquad (1)$$
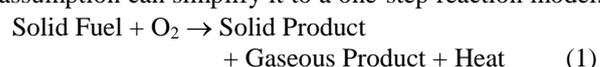
They concluded that the propagation rate of the smoldering is dependent on the heat transfer of both conduction and radiation, and that the intensity, or the rate of heat output, is dominated not only by oxygen supply but also by the reactivity of the fuel. Dasanjh et al.[13] also have adopted this one-step reaction scheme to formulate an opposed smoldering model. They pointed out that solid products are reactive and oxidation of those may vary depending on its pyrolysis reaction hysteresis. The rate of smoldering propagation is calculated by the model with consideration taken into the detail oxidation reaction of solid products. However, the intensity of smoldering measured experimentally is not always in good agreement with that calculated theoretically [8]. Further information about oxidation reactions will be required for improving the theoretical understanding of the biomass smoldering. While oxidation reactions on the solid surface have been examined considerably, those in the gas phase have been paid little attention even though it may occur in vacant spaces in the bulk of the biomass. There is a possibility that the discrepancy between

experiment and theory narrows if the gas-phase reactions are added into the theory. Thus, in this study, the contribution of gas-phase reactions on the heat generation from the smoldering of a packed bed of a biomass combustible is investigated.

Reaction model and estimation of heat output

The reaction model adopted in this work is schematically shown in Fig.1. It consists of three processes: the pyrolysis of unburnt solid, the char oxidation, and the partial combustion of the pyrolysis gas. The pyrolysis process generates gas species such as CO, CO_2, H_2, and CH_4[14][15][16]. The generated gas from this process containing these species is referred to as a "pyrolysis gas" in this paper. Although pyrolysis reactions are commonly endothermic, this process may be exothermic since oxygen is present in the atmosphere and the process may include oxidation reactions. Subsequent to that, in the gas phase, the pyrolysis gas is oxidized partially into the combustion gas like CO_2 and H_2O before it is discharged. The char left in the solid phase also undergoes oxidation due to surface combustion. The total heat output ΔH_t is written as follows:

$$\Delta H_t = \Delta H_1 + \Delta H_2 + \Delta H_3 \qquad (2)$$

where subscripts 1, 2, and 3 are for processes of the pyrolysis of unburnt solid, the char oxidation, and the partial combustion of the pyrolysis gas, respectively.

The amount of heat generated from each reaction is evaluated on the basis of the balance of enthalpies of the reactant and the product of the reaction. Some of those products are sampled directly from the smoldering test, and others are done from a simulating test before enthalpies of those are measured using a bomb calorimeter (Shimadzu CA-4AJ) or evaluated on the basis of the ingredient analysis by GC-TCD (INFICON 3000 micro GC).

Estimation of heat generated from solid and gas phase oxidation

The heat generated from the pyrolysis process is calculated as follows:

$$\Delta H_1 = H_s - (Y_c H_c + Y_p H_p), \qquad (3)$$

The heat generated from char oxidation is also calculated by using the equation.

$$\Delta H_2 = Y_c H_c - (Y_r H_r + 0) \qquad (4)$$

The heat generated from gas-phase oxidation is estimated by the following equation.

$$\Delta H_3 = \Delta H_t - (\Delta H_1 + \Delta H_2) \qquad (5)$$

where H and Y are the enthalpy and the yield, respectively, and subscripts s, c, p, and r correspond to the unburnt biomass, the char, the pyrolysis gas, and the residue respectively. Each yield is the mass ratio of each product to the unburnt biomass. The enthalpy of each substance is regarded as the thermal energy generated from its complete combustion:
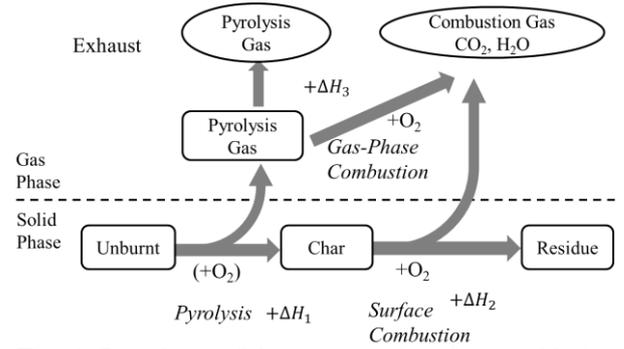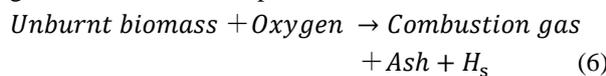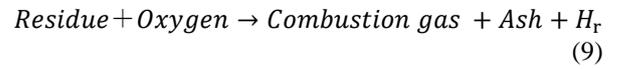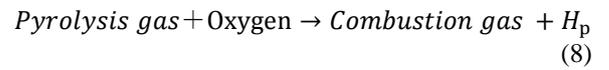
$$Unburnt\ biomass + Oxygen \rightarrow Combustion\ gas$$
$$+ Ash + H_s \qquad (6)$$

Fig 1 Reactions of heat generation for smoldering biomass

$$Char + Oxygen \rightarrow Combustion\ gas + Ash + H_c \qquad (7)$$

$$Pyrolysis\ gas + Oxygen \rightarrow Combustion\ gas + H_p \qquad (8)$$

$$Residue + Oxygen \rightarrow Combustion\ gas + Ash + H_r \qquad (9)$$
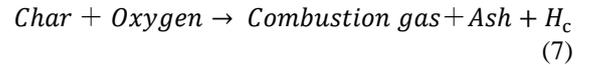
Experimental

Sample Material

The sample combustible adopted in this work is a packed bed of dried and cut leaves. An average size of a cut leaf is 1.0 mm in width, 10 mm in length and 0.1mm in thickness. Table 1 shows some properties of the sample; mass fractions of elements are measured by an elemental analyzer (SCAS Sumigraph NC-220F) and the apparent density of the sample by a porosimeter (Quanta chrome Pore Master GT60).

Table 1 Properties of dried leaves

Elemental analysis	
C (wt. %)	44.8
H (wt. %)	6.3
N (wt. %)	4.8
Apparent density	0.6 g/cm³

Smoldering Test

Smoldering experiments are conducted in a room with an air conditioning facility that controls the air to the standard ambient temperature and pressure (SATP). Figure 2 shows a schematic of the experimental setup. Cut leaves of dried plants are filled in a quartz tube of 17 mm inner diameter, which is covered with a heat-insulator composed of activated carbon fibers.

Pieces of leaves are packed in the tube such that longitudinal directions of those pieces are parallel to the axial direction of the tube. The bed of those pieces has the bulk density at 0.22 g/cm³, the void fraction at 0.8, and the height at 150 mm.

The bed is ignited at the top by means of an electrically-heated nichrome wire. The combustion propagates towards vertically-downward in countercurrent contact with the air flow, the velocity of which is about 30 mm/s. This is the lowest value to prevent the combustion from extinguishing.

Temperatures on the radial center of the test tube are measured at the heights of 90, 95, and 100 mm from the bottom with thermocouples of 0.5 mm in diameter. Data are collected by a data logger at 1.0 s intervals.

Simulating Test

With regard to the pyrolysis gas, direct in-situ sampling is not possible because gas-phase reactions are supposed to occur in this work; the pyrolysis gas generated from the solid may be oxidized in the gas phase of vacant spaces inside the smoldering packed-bed before it is collected. Therefore, the pyrolysis gas is simulated by a gas generated from 1 g of sample in the atmosphere of dry air while it is heated by an infrared image furnace (ULVAC image furnace RHL-E25) from ambient temperature to 400 ℃, below at which oxidation reactions are not supposed to react shown in fig.3. The pyrolysis test is conducted using the same tube as smoldering test and the collection regime is the same as the smoldering test.

Sampling of Products

Char and residue are collected after the smoldering bed is extinguished by supplying nitrogen gas into the tube. A typical temperature distribution and sampling regions are shown in Fig.3. The material in the pyrolysis region, where the temperature is about 400 ℃ is collected as the char. The residue is collected from the region where the temperature once raised over 400 ℃ and then went down below 400 ℃.

The exhaust gas containing particulate matter is collected directly while the smoldering is taking place. The particulate matter is captured by a glass fiber filter and its enthalpy is measured by means of bomb calorimetry. The filtered gas, on the other hand, is collected into a gas bag and its ingredients are directly analyzed by means of gas chromatography with thermal conductivity detection.

Measurement of Enthalpies

The enthalpies of solid materials; sample (H_s), char (H_c), residue (H_r) are measured using a bomb calorimeter (Shimadzu CA-4AJ). The enthalpies of pyrolysis gases (H_p) are the sum of the enthalpies of gaseous materials and particulate matter. The enthalpies of gaseous materials are estimated as the sum of the enthalpy of their components (CO, CH4). The enthalpy of particulate matter is collected by a glass filter pad and measured by a bomb calorimeter.

The enthalpies of these materials per unit weight of original sample are calculated by multiplying the each enthalpy of materials and recovery coefficient of each material per unit weight of original sample.

The recovery coefficient is calculated by the following equation.

$$Y_i = g_i / g_{unburnt} \quad (i = s, c, \text{ and } r) \quad (11)$$

Where, g_i is a weight of each sampling material per unit length of the combustion tube after extinguish. $g_{unburnt}$ indicates a weight of unburnt material per length of the tube before ignition. The subscripts s, c,
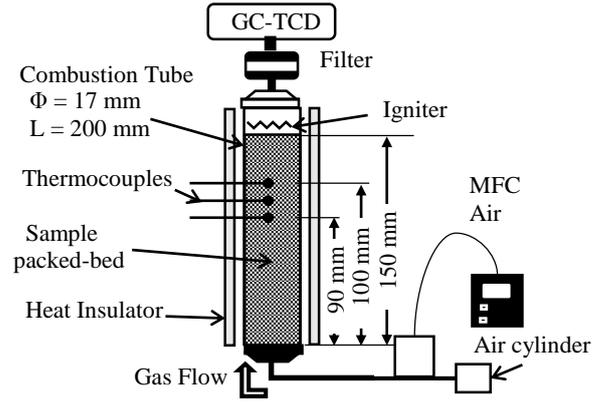

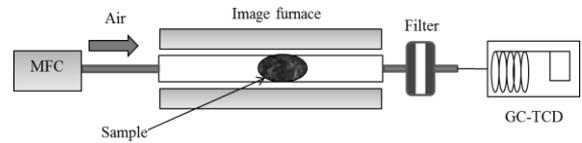**Fig 2** Schematic of experimental apparatus (smoldering test)

Fig 3 Schematic of experimental apparatus (simulating test)
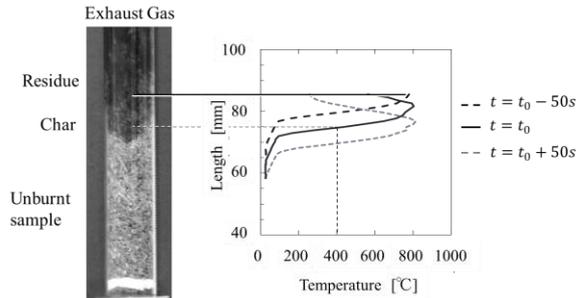

Fig 4 A typical result of temperature distribution in the tube and sampling region based on it

and r mean the sample, the char, and the residue, respectively.

Estimation of total heat output

Total heat output (ΔH_t [J/g-unburnt]) is calculated by the same method as a cone calorimeter as followings[17].

$$\Delta H_t = \frac{13100(C_0 - C)}{1.105 - 1.5C} V_{air} A M_o t \quad (12)$$

here C_0 [-] is the initial oxygen concentration of inlet gas, C [-] is the oxygen concentration of exhaust gas, V_{air} [cm/s] is the air flow rate, $A = 2.27$ cm^2 is the cross-sectional area of the tube, $M_o = 1.43 \times 10^{-3}$ g/cm^3 is the oxygen density, $t = 236$ s is the combustion duration time consumed until unburnt sample 1g burns out.

Results

Temperature Distribution

The typical temperature distribution in the tube is shown in Fig.4. As shown, these three temperature curves at three different positions are similar to each other. That means the smoldering has progressed in

quasi-steady state. The smoldering propagation rate V_s is estimated to be 9.3×10^{-3} cm/s based on this measurement.

Gas Concentration in Exhaust Gas

Figure 5 shows the variations of each gas concentration in exhaust gas. The concentration of each component becomes to be stable after 240 sec. from ignition. Due to the stability of each gas concentration, we obtain the quasi-state gas concentration for the smoldering bed. The exhaust gas is contained in a concentration of almost 0% oxygen during quasi-state smoldering.

Heat of combustion

The heats of combustion and yields of unburnt, char, residue and pyrolysis gas are shown in table 2. The heat output from each reaction per second (Δh) is calculated by using following equation;

$$\Delta h_i = \Delta H_i \times V_s \times A \times \rho \qquad (13)$$

V_s is the smoldering propagation rate, A is the cross-sectional area of the tube, ρ is the apparent density of unburnt in the bed.

The heats of combustion of CO and CH_4 are obtained by reference to the literatures[18]. Table3 shows the heats output from the reactions calculated by using the equations as described previously. The total heat output from the smoldering bed, from pyrolysis reaction, from oxidation reaction on surface of char, and the heat generated in the gas phase are estimated at 20.1 J/s, 4.7J/s, 7.4J/s, and 8.0 J/s. The contribution of gas-phase reaction on heat output from the smoldering packed-bed is about 40 % of the total heat output from the smoldering.

Table 2 heat of combustion and yield for each material

Material	Component	Yield g/g-unburnt	Heat of combustion J/g
Unburnt		1	5251
Char		0.41	5720
Residue		0.11	5620
Pyrolysis compound	CO	0.11	10100
	CH_4	0.005	55640
	Particle	0.089	4510

Table 3 Heat generation from reactions

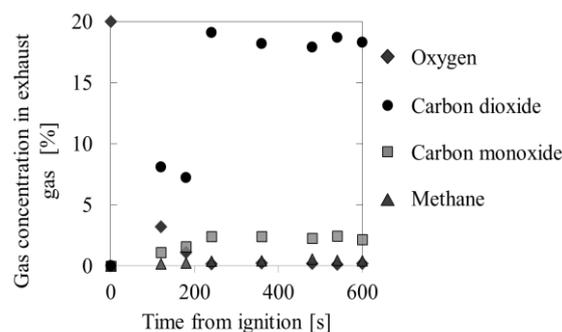| Reaction	Heat output J/g-sample	Heat output J/s
Total heat output	4741	20.1
Pyrolysis	1115	4.7
Surface combustion	1747	7.4
Gas-phase combustion	1879	8.0

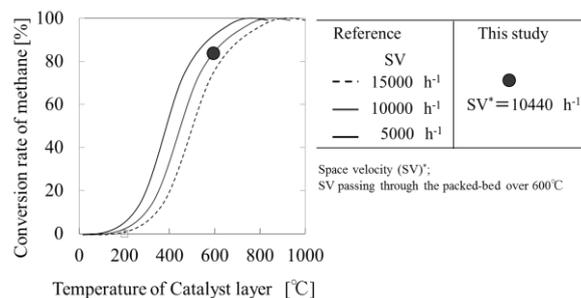**Fig 5** Concentration profile of each component in exhaust gas analyzed by GC-TCD

Fig 6 Conversion rate of methane for catalyst layer at various temperatures of catalyst layer and space velocities.

Discussion

The result, which is the heat generated in the gas phase is about 40% of the total heat output, is indicated that the oxidation of pyrolysis gases occurs in gas-phase at comparatively low temperature to flame type processes which is famous for oxidation of flammable gas in gas-phase.

Naganuma et al. [19] investigate the conversion rate of methane through catalyst layer under mixed gas of 3 % methane helium balance. The conversion rate of methane is increasing with increasing temperature of the catalyst layer or with decreasing space velocity shown in Figure 6. In our study, the length of region at over 600 ℃ is 10mm based on temperature distribution. Therefore, the space velocity through the region over 600 ℃ is estimated to be 10440 h^{-1} on our packed-bed. At the same as temperature and space velocity as our study (plotted in Figure 6), the conversion rate is estimated to be about 80%. The metal salts, which are comprised of biomass materials, sometimes show catalytic activities of oxidation reactions at smoldering process[20], this means, the oxidation of pyrolysis gas, such as carbon monoxide and hydrocarbons, which are the main byproducts of biomass smoldering combustion, may occur at the temperature in smoldering biomass process.

This result and estimation imply that gas-phase reactions should be taken into account for an accurate prediction of heat output from a smoldering packed-bed.

Conclusion

Previous studies focus on the heat generated from surface oxidation in solid-phase for smoldering processes. In this study, we evaluate the heat generation from gas-phase reactions in vacant spaces inside a smoldering packed-bed experimentally. Dried plant leaves are filled in a quartz tube of 17 mm inner diameter with a bulk density of 0.2 g/cm^3. The air is supplied against the smoldering direction at a fixed flow rate of 30 mm/s. The heat of combustion of gas-phase reactions is estimated from the balance of enthalpies of materials picked from the tube. The heat generated in the gas phase is estimated at 8.1 J/s, which is about 40% of the total heat output of 20.1 J/s from the smoldering.

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