# **Comparison on Generation Principle of Carbon Monoxide**

# **Concentration in Pine Combustion between Plain and Altiplano Regions**

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**Abstract:** Experiments on carbon monoxide generation principle of pine which has been widely used in the historical buildings in Tibet were conducted in a combustion cabin in high-altitude-region Lhasa and low-altitude-region Hefei respectively. Three pine samples with different sizes were adopted. The surface temperature and CO concentration under radiative heat flux of 42 kW/m<sup>2</sup> were measured. The effect of oxygen quantity and pressure on carbon monoxide production were analyzed. It was found from the experimental results that carbon monoxide generation had the same trend in both districts; it was first steadily released to a peak value, subsequently descended to a constant value, and then increased to a second value and decayed in the end. Comparing with those in Hefei, the two peak values and the steady value of carbon monoxide concentration in Lhasa were higher, and also, the time to them was much later. The main reason is that the quicker increasing temperature in lower-oxygen condition in Lhasa accelerated the incomplete oxidation of unburned hydrocarbons. Additionally, low mixing rate of volatile component and oxygen under the condition of low oxygen quantity and the ambient pressure was in favor of incomplete combustion of pine and therefore carbon monoxide production.

**Key Words :** low oxygen quantity and low ambient pressure; pyrolysis; carbon monoxide concentration; gas phase combustion; hydrocarbon oxidation

#### **1. Introductions**

Investigations showed that people's inbreathing toxic gases, especially carbon monoxide, is the main reason to casualty in fire. Therefore carbon monoxide is the most dangerous gas in fire [1-6]. Many studies have been done on the carbon monoxide releasing principles in fire. The most widely referenced work, and the basis for current predictive engineering tools for species generation, is the work of Beyler [7,8]. Beyler proposed that it might be possible to correlate the species yields and species production rates to an overall fuel-to-air ratio. The parameter proposed by Beyler is the global equivalence ratio (GER), which in his experiments is equivalent to the plume equivalence ratio (PER) during the steady-state period. Tewarson [9] performed a series of tests in the ASTME2058 fire propagation apparatus and in the Fire Research Institute's enclosure. The Fire Research Institute enclosure was a 0.022m<sup>3</sup> enclosure measuring 0.25m by 0.25m and 0.35m high. Tewarson presented

the data as a ratio of species yields for ventilation-controlled (vc) to well-ventilated (wv) fires. Tewarson concluded, from the study, that the ratios of oxygen and carbon dioxide were independent of the chemical composition of the materials, while the ratios of carbon monoxide and hydrocarbons did exhibit a dependence on the chemical structure of the materials. This agrees with the findings of Beyler [7] who reported that normalized carbon monoxide yields had a fuel dependency. The carbon monoxide releasing of fir had been investigated by Song et. al [6] on self-developed test configuration, and they mainly discussed the influence of external heat flux on carbon monoxide's generation. Some other researchers also carried out similar experiments using cone colorimeter [10]. These former studies mainly focused on the influence of fuel-air ratio, chemical elements of material and ventilation on carbon monoxide's releasing at different stages of fire, especially after flashover. Nevertheless, they all ignored the influence of oxygen quantity and atmosphere on carbon monoxide generation. But in altiplano of Tibet, the low oxygen quantity and low ambient pressure would have a certain influence on carbon monoxide for fire prevention, detection and evacuation in the special atmosphere of Tibet. The different generation principles in both districts are discussed in this article.

#### 2. Theoretical Analysis

Oxygen diffuses into the smoldering reaction region where chemical reaction occurs between raw material and oxygen and then productions overflow. The chemical reaction in the region can be described by a two-step reaction model.

(1) Thermal decomposition

Thermal decomposition is an endothermic reaction, in which combustible gases are produced. The reaction can be described as below:

$$1kgMa \to m_1Gas_1 + \lambda_1Char - Q_1 \tag{2}$$

The reaction rate is determined by temperature and material density.

$$w_1 = \frac{d\rho_s}{dt} = -\rho_s \exp(-E_1 / RT)$$
(3)

where  $\rho_s$  is material density and E<sub>1</sub> is activation energy.

(2) Thermo-oxidative decomposition

This process is an exothermic reaction, which can be described as below:

$$1kgMa + \gamma O_2 \to m_2 Gas_{prd} + \lambda_2 Char + Q_2 \tag{4}$$

The reaction rate is determined by material density, oxygen concentration and temperature as well.

$$w_{2} = \frac{d\rho_{s}}{dt} = -\rho_{s} Y_{O_{2}}^{\gamma} \exp(-E_{2} / RT)$$
(5)

where  $Y_{O_2}$  is oxygen concentration.

In fact, thermal decomposition and thermo-oxidative decomposition is a couple of competitive

reactions that occur in certain region. Assuming the proportion of material that involved in thermo-oxidative decomposition is  $\alpha$ , the proportion of materials that involved in the thermal decomposition is  $(1-\alpha)$ . Combustible gases are produced during the thermal decomposition of materials and the amounts of these gases are proportional to  $(1-\alpha)\rho_0 V_s$ . The reaction rate and the amount of combustible gases produced increased with the oxygen concentration increasing [11].

Gas phase reaction rate is determined by combustible gases concentration, oxygen concentration and temperature as well. Obviously low temperature and oxygen concentration will inhibit the reaction rate. However once they increase to reach an appropriate level, fast gas phase combustion reaction will happen and produce a flame.

In the low oxygen quantity atmosphere, the carbon monoxide production is similar to the situation under the underventilated conditions. So the carbon monoxide formation is affected by two competing mechanism (i.e., CO and hydrocarbon oxidation) [12]. Increasing gas temperature above 900 K depletes CO by accelerating the CO to  $CO_2$  conversion. However, incomplete oxidation of unburned hydrocarbons increases the CO production. Since hydrocarbon oxidation is much faster than CO oxidation, net levels increase until all available oxygen is consumed. For underventilated fires, chemical kinetics modeling indicates that higher temperature environments may result in slightly higher CO yields due to preferentially accelerated hydrocarbon oxidation compared to CO oxidation.

### 3. Test Configuration/Experimental procedure

A series of tests were carried out in the west-south altiplano regions of China Lhasa for investigating the CO production in pine combustion, comparing that of in the plain regions-Hefei city. The experimental apparatus was a 2 m (L) ×4 m (W) ×3.3 m (H) enclosure made of plasterboard. A door of  $0.7 \text{ m} \times 1.8 \text{ m}$  was closed during the experiments. There was a  $0.5 \text{ m} \times 0.5 \text{ m}$  vitreous window for observation on one side. The power of the radiation panel was 2.5kW and can produce a radiative heat flux of 42 kW/m<sup>2</sup>. Three types of pine sticks with different sizes were used: specimen No.1 of 10mm×10 mm×400 mm, specimen No.2 of 15 mm×15 mm×400 mm and specimen No.3 of 20 mm×20 mm×400 mm, and their densities were all 450kg /m<sup>3</sup>. The specimens were located above the radiation panel which is 0.4m high in the center of the enclosure. The CO concentration of plume was measured by Testo350XL Smoke Species Analyzer with a accuracy of 0.1 ppm and uncertainty of  $\pm 5\%$ . Two sampling positions are located at the 2.0m and 3.2m height of the plume, respectively. The schematic map of the experiment apparatus was shown in Figure 1.





### 4. Results and discussions

It is observed that carbon monoxide concentrations in the two positions are almost uniform, so the average values of the data measured in two positions were used which are presented in Figure 2.



Figure.2 CO concentration during the combustion of specimens

As shown in Figure 2, the pine combustion can be divided into three stages: (I) Initial stage that carbon monoxide was released when heated; (II) Steady burning stage that carbon monoxide concentration was kept at a relatively stable level; (III) Decay stage that carbon monoxide concentration would descend firstly and then reach a new maximum. The results were comply with that of cone calorimeter [10]. The experimental data in different stages were listed in Table.1. It is clear that the time of the first peak value of carbon monoxide concentration is consistent with pilot ignition time of specimen[13], which suggests that the carbon monoxide concentration reaches a peak value before ignition.

Table	1	CO	narameters	of	three	nine	specimens
Table		CO	parameters	or	unce	pine	specificits

specimen	Time to the first peak value /s	The first peak value /ppm	Steady stage duration /s	CO concentration in steady stage /ppm	Time to the second peak value /s	The second peak value /ppm
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	Lhasa	Hefei										
NO.1	924	562	72	34	166	76	46	22	1174	704	78	34
NO.2	939	585	80	49	203	112	51	24	1239	906	90	47
NO.3	982	608	99	85	231	140	66	52	1269	1152	106	94

There were significant differences on the carbon monoxide production characteristics of pine combustion between Lhasa and Hefei.

(1) At the initial stage of combustion, the first peak of carbon monoxide concentration in Lhasa was higher than that in Hefei, which suggested that the thermal decomposition period in Lhasa was longer than in Hefei. From Figure 2, it can be seen that in Lhasa region, the rate of carbon monoxide production during the initial heating stage is slow, then increased rapidly in a short time before ignition. According to the literature [11], it is suggested that the low oxygen quantity in Lhasa inhibits the reaction rate and decreases the amounts of combustible gases produced.

(2) It is also found that the period of early stage and the duration of carbon monoxide concentration kept stable in Lhasa are longer than those in Hefei. Furthermore, the stable value of carbon monoxide concentration is also higher. This can be attributed to pine's incomplete combustion and large amount of carbon monoxide in the low oxygen quantity atmosphere in Lhasa.

(3) In stage III, the remaining char begin burning and produced a large amount of carbon monoxide and the concentration value reaches a new maximum. In Hefei, the carbon monoxide concentration in stage III increased slowly while it increases rapidly in Lhasa. The second peak value of carbon monoxide concentration is little higher than the first one in both districts, respectively.



Figure.3 Surface temperature and CO concentration of specimen No.1



Figure.4 Surface temperature and CO concentration of specimen No.2



Figure.5 Surface temperature and CO concentration of specimen No.3

The surface temperature and carbon monoxide concentration of three specimens in both district are shown in Fig.3~5. The period of stage II that carbon monoxide concentration kept stable is consistent with the steady burning stage from the surface temperature curve in Hefei. However, it covers the steady burning stage and early stage of decay in the stage II in Lhasa. It is suggested that in Lhasa the oxygen near the burning specimen is consumed in a short time, which promoted the combustion of pine decays rapidly. As a result, more raw material and volatile components are remained, which continue to burn and produce carbon monoxide steadily.

Comparing the carbon monoxide concentration and surface temperature of specimens in different stages, the combustion process of pine can be distinguished: (1) Vaporization of moisture content stage that slow thermal decomposition and thermo-oxidative decomposition happen, and this process corresponds to region A of Fig.3~5. In this stage, moisture content is evaporated, yet the chemical component of specimen is preserve. Surface temperature of specimen in Lhasa is 30~60°C higher than that in Hefei in this period. (2) Pre-charring stage that is corresponding to region B of Fig.3~5. The decomposition reaction rates of specimens are accelerated and volatile components are produced. From Fig.3~5, it can be seen that the surface temperature of specimens in Lhasa is about  $30 \sim 40^{\circ}$ C higher than that in Hefei. The prior two stages are corresponding to stage I of carbon monoxide concentration. (3) Charring stage that is corresponding to region C of Figure 3 to Figure 5. In this stage, fast gas combustion happens and produce amounts of production after decomposition which forms a steady value of carbon monoxide concentration as shown in stage II of Figure 2. (4) Charred remains' combustion that is corresponding to region D of Figure 3 to Figure 5. In this stage, carbon monoxide increases once more until reaching a new maximum concentration because of charred remains' combustion. The temperature in of three pine specimens in different stages is listed in Table 2, from which it can be deduced that the carbon monoxide produced in Lhasa has a higher temperature than that in Hefei.

Table 2 Temperature of three pine samples in different stages

specimen	Stage	I	Stage II		
	Stage 1/°C	Stage 2/°C	Stage 3/°C		

	Lhasa	Hefei	Lhasa	Hefei	Lhasa	Hefei
NO.1	$\sim$ 258	$\sim$ 223	$258{\sim}468$	223~427	468~497	427~490
NO.2	$\sim$ 302	$\sim 250$	302~524	250~498	$524 \sim 580$	498~561
NO.3	$\sim$ 318	$\sim$ 262	318~570	$262 \sim 528$	570~636	528~622

At the beginning of stage I, less carbon monoxide is produced in Lhasa than in Hefei because low oxygen quantity and partial pressure in Lhasa makes it difficult for oxygen diffusing into specimen internal, which decreased the thermal decomposition rate. In stage II and stage II more carbon monoxide are produced in Lhasa than in Hefei. One reason is the incomplete combustion of specimen in Lhasa, another reason is that the low mixing rate of volatile component and oxygen under the condition of low oxygen quantity and the pressure is in favor of carbon monoxide production; the third reason, also the most significant reason, is that the quicker increasing temperature in under-oxygen condition accelerates the incomplete oxidation of unburned hydrocarbons.

Studies on carbon monoxide production are important for early fire detection and evacuation. The low oxygen quantity and low pressure environment in Lhasa can promote the carbon monoxide production and aggravate the toxicity of carbon monoxide according to experimental results on animals[14] in altiplano region.

#### 5. Conclusions

Experiments for investigating the carbon monoxide production in the combustion of pine, widely used in the historical buildings in Tibet, have been performed in Lhasa and Hefei.

The burning of specimens in Lhasa and Hefei have similar process and tendency for carbon monoxide production. The concentrations of carbon monoxide produced during the combustion of pine in both regions have two peak values. Between the two peak values, the carbon monoxide concentration kept a relatively stable value but lower.

The two peak values of carbon monoxide concentration during pine combustion in Lhasa are higher than that in Hefei. Also, the time that the peak values reached is much later. This may delay gas detector's response to fire, thus dally over time which can be used for evacuation and property protection.

The low oxygen concentration and low pressure atmosphere in Tibet is in favor of producing more high temperature carbon monoxide and aggravates the toxicity of CO. So the fire in Tibet is more harmful to occupant.

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