

Experimental determination of the effect of temperature and oxygen concentration on the production of birch wood main fire emissions

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Abstract The combustion process (efficiency and toxicity of combustion generated emissions) depends on the chemical composition and physical characteristics of materials, the oxidizing agents, and the temperature. This article will determine the influence of temperature (450 and 600 °C) and the volume of oxygen concentration (9, 15, and 21%) in an oxidizing atmosphere on the main emissions of burning White Birch wood (*Betula verrucosa* Ehrh.) The examined samples weighed 3 ± 0.05 g; the average density was 540 kg/m^3 ; and the absolute humidity was 8%. The samples were thermally loaded in a Setchkin furnace specially modified to enable the thermal sample in an atmosphere with an adjustable oxygen concentration and the withdrawal of fire emissions by means of UniGas C440 analyzer probes and BERNATH ATOMIC Modell 3006 analyzers. At 450 °C, the concentration of oxygen in the oxidation mixture did not significantly influence the

maximum concentration of carbon monoxide (CO) and the total organic carbon (TOC) in the fire emissions. At 600 °C, the decrease of the oxygen concentration in the oxidation atmosphere caused a significant increase of the maximum concentration of CO and TOC in the fire emissions. However, the generally accepted presumption of a maximum concentration increase of CO in the emissions as a result of the oxygen (O_2) concentration decrease in the oxidation atmosphere has not been confirmed. The highest concentration of CO and TOC were measured in the initiation phase or closely after it.

Keywords Combustion · Fire emissions · Fire dynamics · Thermal decomposition of materials · Temperature · Oxygen concentration

Introduction

Fire emissions from smoke are the cause of death for more than 80% of all fire victims [1]. The quality and quantity of generating fire emissions depend on the combustion temperature, material, and oxidizing agent (its chemical composition and physical properties). The combustion temperature of a specific fuel depends retroactively on the oxidizing agent and the thermal–technical properties of the location of the combustion.

Under the industrial combustion conditions, the selection of fuel, air inlets, and thermal–technical conditions of the burning area must be set so that the emission limits determined by legislation are followed. However, burning materials of variable chemical compositions and physical properties occurs under fire conditions in areas which are not designed for burning. The development of an internal fire is mostly determined by the access of air. After

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initiating fire in the internal space, the consumption of air oxygen for combustion occurs and subsequently its dilution by the generated fire emissions occurs. In the majority of internal fires, the consumption of oxygen is partly compensated by an inlet of clean air from the exterior. In most cases, the arriving air is not sufficient to maintain an oxygen concentration with 20.95% by volume in the area affected by fire. The result of this fact is that most internal fires are in an atmosphere with a reduced oxygen concentration.

Final products of the oxidation of carbon, hydrogen, and possible oxygen materials are carbon dioxide (CO₂) and water (H₂O). The mentioned compounds are the substances with the least toxicity which may emerge during combustion. When the oxygen concentration in the atmosphere of an internal fire decreases, the oxidizing agent is not sufficient for the full oxidation of fuel into CO₂ and H₂O. As a result, various intermediate products with high toxicity arise under the oxygen shortage that occurs during combustion. The carbon monoxide (CO) is the most significantly toxic substance present. To assess the influence of air access on the process of combustion and fire emissions, relatively extensive scientific research has been performed. The influence of the equivalent ratio on the concentration of main fire emissions to the majority of wide-spread organic polymers has been examined in the fire engineering field. This procedure is mainly typical at the National Institute of Standards and Technology in the USA. A different approach was selected in the power engineering field, where the influence of air access or the oxygen concentration on combustion efficiency and rising fire emissions were examined.

The equivalent ratio is defined as the ratio of gas fuel weight (from the thermal decomposition of solid material) and the weight of available oxygen for its combustion, divided by a stoichiometric coefficient. The stoichiometric coefficient is defined as the weight of complete fuel combustion which needs a per unit mass of oxygen. The equivalent ratio may be defined simply as a coefficient reciprocal value of the air surplus. If the equivalent ratio is lower than 1, the combustion is happening because of the surplus of oxygen. Well-vented fires or fires managed by the surface of fuel are characterized by this state. If the equivalent ratio is higher than 1, the combustion is happening because of a shortage of oxygen and a surplus of gas fuel. This state is used for ventilated fire simulation. Under the equivalent ratio 1, the combustion should theoretically go on under stoichiometric conditions. This is valid, however, only in special reactors used for modeling the influence of external conditions on the process of combustion, for example, NIST WSR/PFR experimental facility, which is described in detail in Stroud et al. [2]. Owing to the inhomogeneity of the flammable mixture (fuel and oxidizing agent) under industrial combustion conditions, the perfect burn will continue only with the

equivalent ratio of 0.8–0.9. In perfect conditions, the fire's burn will not take place with unrestricted air access.

Tewarson [3–5] determined by the Fire Propagation Apparatus according to ASTM E 2058 the influence of the equivalent ratio of the CO concentration in fire emissions of polyethylene, polypropylene, polystyrene, wood, polymethylmetacrylate, nylon, and polyvinylchloride. The results cited by the author show that a significant increase of CO concentration in fire emissions occurs from the approximate equivalent ratio of 0.8. This ratio should, however, be regarded as informative only, as it shows some degree of variability depending on the particular type of material. Tewarson [3–5] came to similar results also when determining the influence of the equivalent ratio on the concentration of unreacted fuel in fire emissions. In this case, the concentration of unreacted fuel began to sharply increase from the equivalent ratio of 1.

Gottuk and Roby [6] examined the influence of the equivalent ratio on CO extracted from fire emissions of methanol, ethanol, isopropanol, propane, and acetone. Based on their results, we may state that CO extracted from fire emissions of the mentioned materials increases rapidly from an equivalent ratio of 0.5. The extract of total organic carbon (TOC) in the fire emissions of propane begins to increase only from the equivalent ratio of 1.

In addition to the equivalent ratio, the concentration of the oxidizing agent also significantly influences the concentration or the extract of fire emissions. Hu et al. [7] determined the simultaneous influence of temperature, equivalent ratio, and oxygen concentration on the concentration of nitrogen oxides (NO_x) in the fire emissions of coal. The presented results show that the highest concentration of NO_x is in the emissions of coal combustion at equivalent ratio from 0.6 to 1 and increases with the increasing oxygen concentration in the oxidation mixtures, as well as with the increasing temperatures in the combustion space.

Ladomerský [8] determined the dependence of CO concentration on O₂ in fire emissions in the combustion of wooden waste under almost perfect burn conditions. Obtained results indicate that NO_x concentration in the burn emissions decreases with an increased concentration of O₂. However, this trend is only valid in almost perfect burn conditions.

Heat release rate has close relationship with CO concentration in fire effluents [9, 10].

Experimental

Description of tested samples

Samples of white birch wood (*Betula verrucosa* Ehrh.) weighing 3 ± 0.05 g, with a density of 540 kg/m^3 and

absolute humidity of 8% were used for the research. The samples used were in the form of joists with the dimensions $2 \times 2 \times 0.72$ cm. Elementary composition of the tested wood was as follows: carbon, 48.92% of weight; oxygen, 44.70% of weight; hydrogen, 6.07% of weight; and nitrogen, 0.08% of weight. The remaining 0.23% of weight was ash. The main components were as follows: hemicelluloses, 40.11% of weight; cellulose, 33.86% of weight; and lignin, 25.77% of weight. The remaining 0.26% of weight was ash.

Experimental description

The influence of oxygen concentration and the temperature of the main fire emissions of birch wood (CO, NO_x, and TOC) were determined in a specially modified Setchkin furnace. The adjustment of the Setchkin furnace lay in the addition of both a regulating part and a chamber extension. The regulator enabled setting the flow of oxidizing atmosphere streaming into the furnace and the concentration of oxygen in it. The chamber extension allowed the withdrawal of fire emissions by gas sounds of used analyzing devices before air dilution. Martinka [11] mentions a detailed description of the testing equipment used. The fire emissions analyzer UniGas C440 was used to determine the concentrations of CO, NO_x, and O₂ in fire emissions. The analyzer BERNATH ATOMIC Model 3006 was used to determine TOC concentration. The analyzers used measured the concentration of fire emissions in ppm units, which were calculated to mg/m³ at standard state conditions. TOC concentrations were calculated as propane equivalents.

Concentrations of main fire emissions were determined for the birch wood samples at (450 and 600 °C). Oxygen concentration in the oxidation mixture was 9, 15, and 21% by volume and the oxidation mixture flow was 6 l/min. At 450 °C, the samples were thermally loaded for 15 min and at 600 °C, for 10 min.

Test results and discussion

Figures 1 through 3 show the measured weight concentrations (ρ in mg/m³) of CO, NO_x, TOC, and volume percentage (φ in volume %) of O₂ in birch wood fire emissions depending on the concentration of O₂ in the oxidation mixture. The unit t represents time in seconds (s).

The rapid increase of CO and TOC (Fig. 1a) was observed in the birch wood ignition phase. After igniting and during the flame burn phase, (the ignition occurred at approximately the 350th second) the concentrations of CO and TOC began to decrease. Nearly a zero concentration of NO_x proves a relatively low flame temperature.

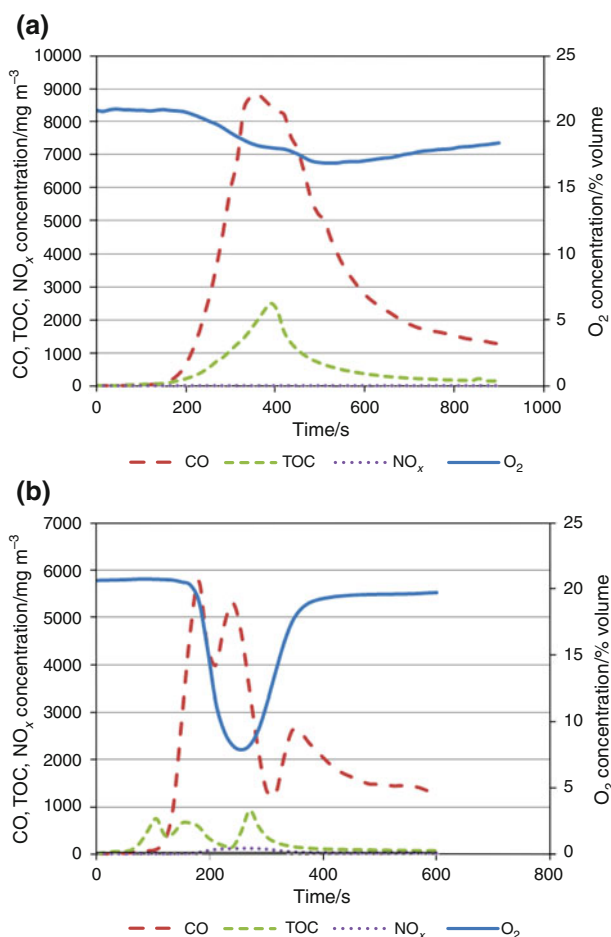


Fig. 1 Time dependences of concentrations of CO, TOC, NO_x, and O₂ in birch wood fire emissions at the concentration of oxygen in an oxidizing atmosphere of 21% by volume and the temperature: **a** 450 °C; **b** 600 °C

There are three local maxima at the time dependence of the CO concentration (Fig. 1b). The first local maximum took place in the initiation phase, which proves a time lap with the rapid decrease of oxygen concentration. The second local maximum of CO concentration was observed as the flame burning under a minimum oxygen concentration. This local maximum is due to the lack of oxygen for complete product burn arising from thermal decomposition. The third local maximum was observed during flameless burn (glow) of carbon residue. This conclusion is fully consistent with the results of Balog [12], wherein the burning speed of CO and oxygen mixtures is a monotonous function of hydrogen or hydrogen containing compounds. The concentrations of TOC and CO were similar. Local maxima of TOC, however, fell behind the local maxima of CO by about 60 s. This was probably due to a delay of the UniGas analyzer in comparison to the BERNATH ATOMIC analyzer. A slight increase of NO_x at a minimal oxygen concentration confirms the higher flame temperature than the oxidation mixture temperature of 450 °C.

There are two local maxima on the time dependences of CO and TOC (Fig. 2a). The first represents the initial phase. The second local maximum was due to the lack of oxygen in the oxidation mixture of a perfect burn.

Time dependences of CO, TOC, NO_x, and O₂ concentrations at 600 °C and concentration of oxygen in an oxidizing mixture of 15% by volume (Fig. 2b) had a very similar course as the time dependences of concentrations of the mentioned fire emissions at the same temperature, and the oxygen concentration in an oxidizing mixture with 21% by volume (Fig. 1b). The mentioned courses, however, significantly differed in absolute values. Maximum concentration of CO in the oxidizing mixture with an oxygen concentration of 21% by volume was 5,301 mg/m³. On the other hand, the maximum concentration of CO in the oxidizing mixture with an oxygen concentration of 15% by volume was as much as 21 295 mg/m³. In concentrations of TOC, a contrary trend was observed. The concentration of TOC in the fire emissions decreased with the decrease of oxygen concentration. This course may be explained by a

slower initiation of the sample in an atmosphere with a reduced concentration of oxygen because, according to Ladomerský et al. [13], the highest concentration of CO in the fire emissions of wooden materials is usually observed in the initiation phase. The influence of the oxygen concentration in the oxidizing mixture at the time of initiation coincides with the statement of Balog [12], who contends that the presence of oxygen approximately reduces the activation energy of the polymer ignition by 150 kJ/mol.

Concentrations of CO, TOC, and O₂ in the fire emissions of birch wood at 450 °C and the oxygen concentration in an oxidizing atmosphere of 9% by volume are shown in Fig. 3a.

At 450 °C and with the oxygen concentration in the oxidizing mixture of 9% by volume, only the thermal decomposition of the sample without flame burning or glowing was observed. This conclusion was drawn based on visual observation as well as by analyzing the fire emissions. The oxygen concentration in the oxidizing mixture was 9% by volume, and the minimum oxygen concentration in the oxidizing mixture

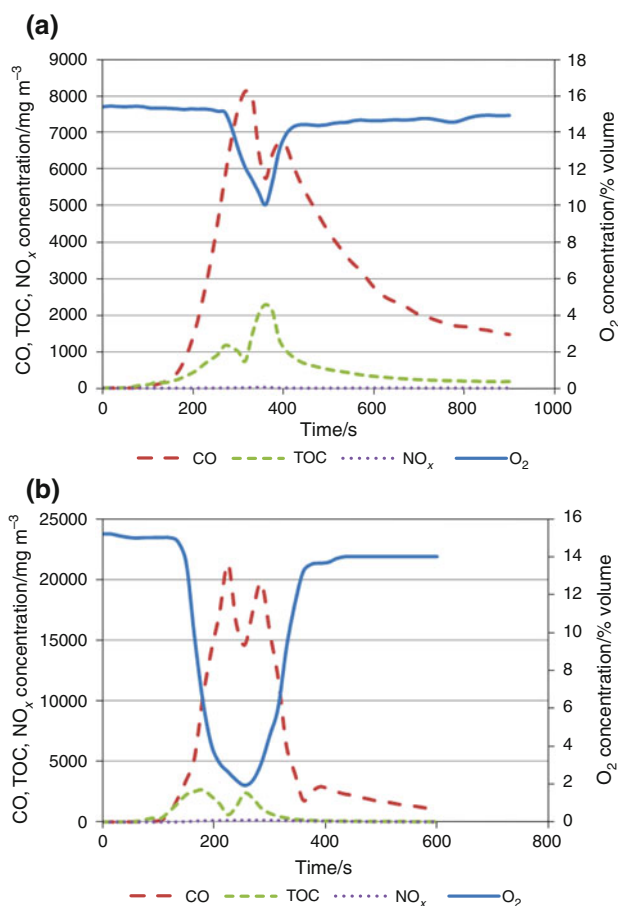


Fig. 2 Time dependences of concentrations of CO, TOC, NO_x, and O₂ in birch wood fire emissions at the concentration of oxygen in an oxidizing atmosphere of 15% by volume and the temperature: **a** 450 °C; **b** 600 °C

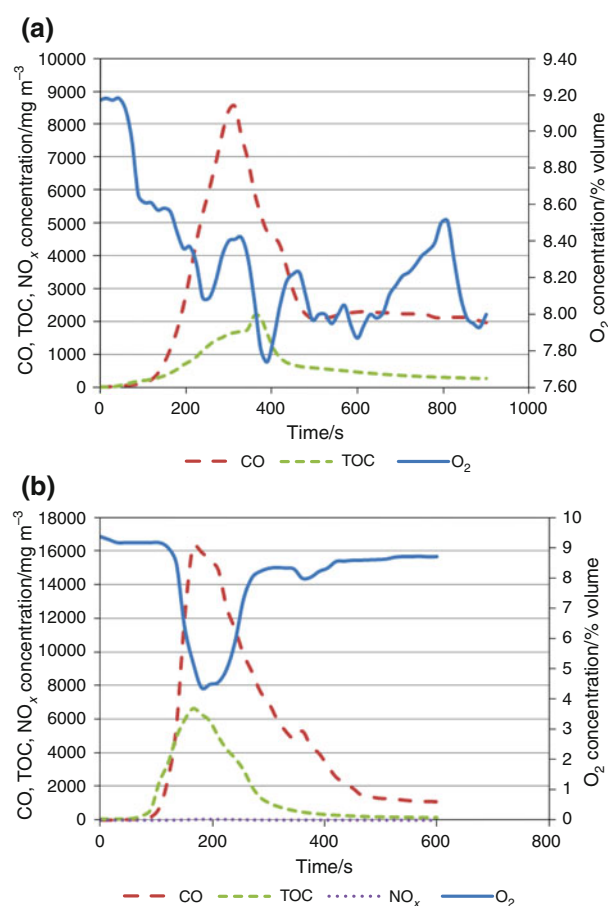


Fig. 3 Time dependences of concentrations of CO, TOC, NO_x, and O₂ in birch wood fire emissions at the concentration of oxygen in an oxidizing atmosphere of 9% by volume and the temperature: **a** 450 °C; **b** 600 °C

was 7.74% by volume. The consumption of 1.26% of the oxygen volume from the oxidizing atmosphere was sufficient for the initiation and maintenance of flame burning. The fact that under the given conditions the flame burn did not occur is also supported by an immeasurably low concentration of NO_x .

At 600 °C and with an oxygen concentration of 9% by volume, the flame burning of the sample was again observed. The time dependences of the measured fire emission concentrations are shown in Fig. 3b. The concentrations of the measured fire emissions take a very similar course as the concentrations of the determined fire emissions at 450 °C and with an oxygen concentration of 21% by volume (Fig. 1a).

These obtained results point to the need for revising the research of the influence of oxygen concentration, or the equivalent ratio on the extract of main fire emissions for the needs of fire engineering. Fire Propagation Apparatus, according to ASTM E 2058, is used in fire engineering for the purpose of determining the influence of oxygen concentration (or the equivalent ratio) on the extract of main fire emissions. This procedure was selected, for example, by Tewarson [3–5], as well as Gottuk and Roby [6], who examined the influence of the equivalent ratio on the extract of CO and TOC from the fire emissions of multiple organic materials. The cited authors' results suggest that from the equivalent ratio of 0.5–0.8, the rapid increase of CO extract occurs. The extract of TOC increases from the equivalent ratio of 1. The test in Fire Propagation Apparatus, according to ASTM E 2058, is performed under quasi-static conditions so that the equivalent ratio required in the test will be achieved. These conditions are, however, vastly different from conditions of a real fire. In a real fire, a certain part of the materials are in the whole pre-flashover phase practically right from the initiation phase. The results obtained indicate that the maximum production of CO and TOC will occur right at the stage of introducing the wooden material. Ladomerský et al. [13] concluded similar results. They contend that under industrial combustion conditions in the phase of the flaming of fuel, the concentrations of CO observed in fire emissions are raised by as much as two orders higher than the concentration of CO in a stable state.

In addition, under the conditions of a real fire, the weight reduction speed of the flammable materials and thereby also the equivalent ratio depend on the temperature and oxygen concentration of the fire cell. The main fire emissions calculation under fire conditions is therefore substantially simpler when determined by the concentration of main fire emissions at variable temperatures and oxygen concentrations rather than by measuring the extract of fire emissions under various equivalent ratios.

The presented results suggest that the effect of oxygen concentration on the oxidation mixture with the maximum

concentrations of CO and TOC in the fire emissions increases with increasing temperature. Maximum concentrations of CO and TOC at 450 °C were examined in oxygen concentrations as follows:

- For 21% by volume of O_2 in an oxidizing atmosphere, the maximum measured concentration of CO was 8,841 mg/m^3 , and that of TOC was 2,503 mg/m^3 ,
- For 15% by volume of O_2 in an oxidizing atmosphere, the maximum measured concentration of CO was 8,138 mg/m^3 , and that of TOC was 2,297 mg/m^3 ,
- For 9% by volume of O_2 in an oxidizing atmosphere, the maximum measured concentration of CO was 8,542 mg/m^3 and that of TOC was 2,181 mg/m^3 .

Maximum concentrations of CO and TOC at 600 °C were examined in oxygen concentrations as follows:

- 21% by volume of O_2 in an oxidizing atmosphere, the maximum measured concentration of CO was 5,301 mg/m^3 and that of TOC was 931 mg/m^3 ,
- 15% by volume of O_2 in an oxidizing atmosphere, the maximum measured concentration of CO was 21,295 mg/m^3 and that of TOC was 2,663 mg/m^3 ,
- 9% by volume of O_2 in an oxidizing atmosphere, the maximum measured concentration of CO was 16,294 mg/m^3 and that of TOC was 6,638 mg/m^3 .

The above mentioned values prove that the oxygen concentration at 450 °C does not significantly influence the maximum concentration of CO and TOC. On the contrary, the significant influence of oxygen concentration on the maximum concentration of CO and TOC became evident. The trend of the increase in CO concentration in the fire emissions and the decrease of O_2 concentration in the oxidation mixture were not confirmed, however. This was probably caused by the dependence on the speed of the reduction of the weight of the organic polymers during the burning of the O_2 concentration in the oxidation mixture. Also the speed of release of the decomposing products into the burn zone increases with an increasing speed of fuel weight. As a result, the oxygen concentration in the burn zone is decreased, which will be evident by an increase in equivalent ratio.

The highest concentrations of NO_x were observed at 600 °C and the oxygen concentration in the oxidation mixture of 21% by volume under the conditions of the highest temperature flame. The above results are fully aligned with results presented by Horbaj [14].

Conclusions

In this article, the influence of temperature and oxygen concentration on the concentration of main fire emissions of birch wood has been determined. The acquired results

indicate that the reduced concentration of O₂ will become evident in the increased production of CO only at temperatures over 450 °C. This means that the main contribution to the sphere of fire modeling, which is mainly used in calculating the concentrations of main fire emissions, depends on the temperature and concentration of oxygen in the fire cell. Further research must first be focused on determining the influence of not only the temperature and concentration of oxygen, but also the flow of the oxidation atmosphere on the concentration of main fire emissions. Subsequently, it is necessary to examine other widely used polymeric materials. In the last step, it will be necessary to verify the acquired data with data measured in big fire tests and to propose a modification of the testing procedure based on a results comparison. In addition to the temperature and oxygen concentration, it will also be necessary to examine the influence of thermal flow density, burn retardants, and the form of material (compact form, dust, and pressed dust). The reader may find more information about this issue in the study of Filbakk et al. [15].

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