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An Alternative and Novel Explanation for the Formation of Toxic Carbon Monoxide from the Combustion of Methane

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Abstract: It is not only the imperfect combustion of solid materials that can lead to the formation of carbon monoxide (CO), but also the reaction of a perfectly combusted gas, methane, the presence of which unfortunately cannot be ruled out in the case of open-combustion gas-burning equipment. The main danger of this type of reaction is that the formation of CO is extremely rapid. Due to the high speed of the reactions taking place in the combustion chamber and the simultaneous appearance of CO in living spaces without CO alarm devices, it is almost impossible for people to escape. The formation of CO is possible due to several chemical reactions. In our study, the conditions of the methane - carbon dioxide - carbon monoxide reactions were examined; primarily the chemical and physical conditions that cause the sudden appearance of CO. Our results lead us to conclude that the cause of CO formation is not an oxygen-deficient environment, but rather a chemical reaction driven by a highly exothermic chain reaction mechanism. Based on the authors' research, the cause of the sudden increase in CO concentration is the chain reaction mechanisms controlling the chemical reaction speed, i.e., not only the concentration of the components but the temperature referenced in the Arrhenius equation seems to be the determining factor. Based on our conclusions, in addition to measuring the CO concentration, it is also justified to measure the CO_2 concentration at the same time. This is especially important in the case of retrofitted ventilation fans or windows when the possibility of backflow of combustion products should be expected.

Keywords: carbon monoxide, methane combustion, carbon dioxide, Arrhenius equation, critical condition

1. Introduction

The basic characteristics of combustion have been investigated in numerous studies, and the overall experience is also reflected in well-known books [1,2]. The combus-tion of methane, as one of the most basic combustible gases, has also been the subject of numerous studies, from many different aspects and under different conditions. Al-ready in the first sufficiently detailed study, by Garner and Ham (1938), we find a de-scription of how and under what conditions carbon monoxide (CO) is produced during the combustion of methane [3]. However, recent studies have focused mainly on the investigation of the combustion of gas-air mixtures under pressure, in particular to in-crease the efficiency of various engines, and therefore the CO production is only pe-ripherally addressed [4-8]. CO, an odorless gas that is highly toxic and colorless, is the cause of many unwarranted deaths [9,10]. However, the authors' finding as to why, under certain conditions, the concentration of CO in open combustion chamber changes so drastically, leading to regular deaths of occupants, has not been explained.

There are thousands of statistics available from all over the world regarding cases of unfortunate CO poisonings. Despite more and more people using CO alarms, the danger is still present in residential buildings in individual flats, where open chamber boilers with natural draft is used [11].

Research report [12] reviewed several studies, where the CO and carbon dioxide emissions of open chamber atmospheric gas boilers' operation under various circum-stances have been examined. These studies mostly explain the increased CO levels as a result of backflow of the combustion products. Our multiple reconstructive measure-ments showed that CO gas does indeed appear when combustion product backflow occurs; this is followed by a chemical reaction that, based on our observations and as-sumptions, is a consequence of the backflow, which involves a sudden, jump-like in-crease in CO concentration. The extent of this CO generation can reach lethal value in the circumstances. The formation of CO is described by several chemical reactions, but the most common is incomplete combustion, or in other words a state of oxygen defi-ciency. At first glance we may think incomplete combustion is caused by reduced air supply (oxygen deficiency). However, after careful analysis of the possible chemical reactions we hypothesize a chemical reaction controlled by a chain reaction.

Some of the co-authors of this article are firefighters who started the research based on their practical experience. The devices used for measurement (gas detectors) are also mobile devices that are used during fire inspections, but are also suitable for

detecting danger. Data from several cases of CO poisonings were analyzed to provide the background of the research. By means of reconstructive measurements carried out on location of cases involving CO poisoning, it was established that during improper operation of open chamber gas appliances, dangerous amounts of both CO and carbon dioxide develop [13].

To understand the rapid generation of CO, multiple reconstruction measurements were planned. We created measurement conditions that may realistically occur in a household during boiler operation. (e.g., kitchen extractor fan is on). The goal of the reconstructive measurements was to determine whether a rapid buildup of CO con-centration can indeed occur, and what the reaction kinetics are of such an increase (if any). As a result of the extremely rapid increase in CO concentration, the occupants may lose consciousness, and if further increase in concentration occurs, death may also be objectively expected.

Based on the available literature and our own measurements (increased CO2 and CO values), the other aim of our work was to identify, out of all possible reactions, the ones that may occur in the combustion chamber of open chamber boilers and the con-ditions under which they occur. We were also looking to answer whether the sudden increase in CO concentration is driven by an oxygen-deficient environment, or chemi-cal reaction kinetics, or some other mechanism.

The amount of these gases initially increased at a steady rate, followed by a sud-den, high intensity “explosive” increase of CO generation, result of which exceeded the maximum range of the measuring instrument in a very short time. We found that the oxygen concentration in the room has not decreased to the point of creating an oxy-gen-deficient combustion environment, not even by the end of the reconstruction measurements. Measurements taken at various locations showed values between 19.8-20.4 % v/v for oxygen. At almost all locations, some kind of depressurizing extrac-tion system (e.g., in the kitchen) was found to have been active at the time of the events. Furthermore, it was found in multiple cases that the poisoned victims did not try to escape, indicating that they had become unconscious suddenly. The progress of poisoning must have been extremely rapid.

2. Materials and Methods

2.1. The dangers of operating gas appliances

During the combustion of gas, the resulting flue gas contains low levels of both CO and sulfur dioxide. The combustion product is essentially a mixture of carbon dioxide (CO_2) and water vapor, and is expelled from the combustion chamber by gravity or ventilation. The density of CO_2 is higher than air at low temperatures

(CO_2 ρ = 1.4 kg/m³) and lower than air in flue gas (it is about ρ= 0.7 kg/m³ at 150 0C), and therefore it is able to escape from the combustion chamber through the ventilation system. Open chamber boilers ("B_{11}" type) require at least 20 m³ of air for the complete combustion of 1 m³ of methane [14].

The efficiency of the gravity-induced draft is greatly influenced by the tempera-ture difference between the outside air and the combustion products, and the height of the chimney. However, the combustion product extraction system includes more than just the chimney itself. It is the interaction of several components, and it should be examined as such. During operation, a continuous supply of air must be provided to these type of gas appliances. Furthermore, it must be ensured that use of the kitchen air extraction appliance is temporarily disabled to prevent its use at the same time as the boiler. This is in order to prevent creating a depressurized state, which would interfere with the gravity induced draft, reducing its effectiveness or terminating it entirely. The components of gravitationally induced combustion exhaust systems are [15]:

- Atmospheric gas burner with air inlet (including the combustion chamber and the heat exchanger);
- Flow switch (also known as flow regulator, deflector, or draft breaker);
- Combustion product extraction system (flue pipes and tubes, flue duct, chimney and its cleaning and connecting parts).

An important element of this system is the flow switch, also known as the deflec-tor or draft breaker, which performs several safety functions when expelling the com-bustion products. (Figure 1).

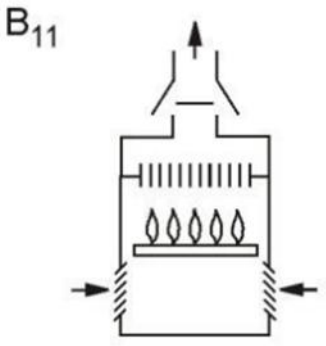


Figure 1.
Flow patterns created in open chamber boilers with natural draft ("Type B_{11}").

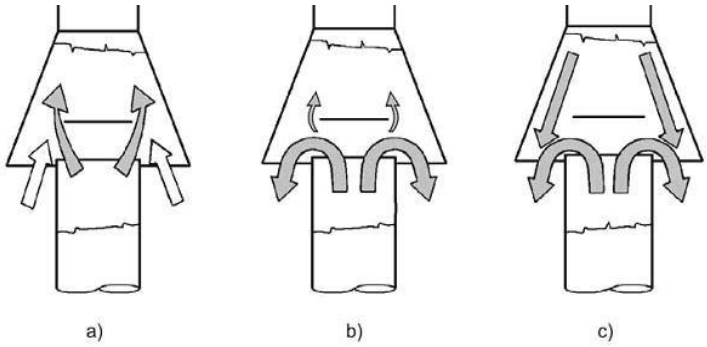


Figure 2.
Air intake of the flow switch [6].

One of the most important points is that it prevents excessive suction caused by the wind by pulling "dilution air" from the room (Figure 2, case "a"). Furthermore, if the chimney is cold, the draft may be inadequate, which may cause combustion products to flow back into the combustion chamber, resulting in the flame being extinguished. In this case the flow switch returns this initial backflow to the room (by design only for a short period of time, and resulting in a harmless amount of combustion products) (Figure 2, case "b"). In the third case, which just like the previous case may occur only for a short period of time, an overpressurized zone around the chimney top prevents the combustion products from escaping (because of strong winds). Again, the objective is to prevent the flame from being extinguished by guiding the combustion products into the room (Figure 2, case "c") [16].

The flow switch has several important functions in addition to the above. Among other things, it prevents the pilot light from being extinguished (if the appliance uses a pilot light), "mixes" air with the flue gas in order to increase the stack effect, reducing its dew point temperature, and captures water droplets falling back from the chimney. The flue gas, rich in hot water vapor entering the "cold" chimney would cause conden-sation in the chimney, but the flow switch causes the water to flow back into the drip trays and evaporate into the room [17].

Thus, it is established that the flow switch plays an important role in the safe operation of the appliance and its proper functioning must therefore be ensured. If the rules of safe operation are not followed by the users (e.g., they retrofit a kitchen extractor fan without an interlock), the undesired flow conditions create a hazardous environment, resulting in the appearance of carbon dioxide and CO.

2.2. Critical reactions of carbon dioxide, carbon monoxide and methane (hydrocarbons)

In connection with the topic discussed earlier, we also need to examine the chemical reactions between the generated combustion products. Carbon dioxide is considered an inert gas in chemistry and especially in fire protection because it does not undergo chemical reactions. This property of CO2 causes it to behave as an extinguishing gas, in particular because it extinguishes by displacement. However, this only applies at low temperatures (up to about 600 - 700 °C). If we look more closely at all of the reactions of carbon dioxide, we find that this is not always the case (CO2 is not always inert).

Generally, combustion reactions may be divided into two areas according to its mechanism:

- The chemistry of high-temperature combustion (e.g., combustion of hydrogen, CO, methane) [18-20];
- The chemistry of low-temperature combustion (e.g., long-chain hydrocarbon oxidation and the formation of nitrogen oxides during combustion) [18-20].

For combustion reactions, the temperature value of approximately 900 K is an important threshold (the exact threshold temperature depends composition and pressure of the gas mixture), below which hydrogen, CO and methane are not oxidized in a rapid chain reaction, but organic hydroperoxide and transition ether compounds are formed. Above this temperature, a branching chain reaction takes place in fuel-oxygen mixtures, which leads to an explosion in a homogeneous mixture and to flame propagation in an inhomogeneous mixture. The H˙, O˙H and O˙ radicals play a prominent role in these combustion reactions. If T is over 1000 K, the chain reaction becomes the main mechanism [18-20].

We collected from literature the possible reactions that we assume may occur during the operation of a boiler. The reactions where CO is formed, and the reaction is exothermic merit our attention. Primary reactions with a high probability of CO formation [11]:

- $CH_4 + 2O_2 = CO_2 + 2H_2O$ $\Delta H0 = -298$ kJ/mol (R1);
- $CH_4 + CO_2 \Leftrightarrow 2CO + 2H_2$ $\Delta H0 = +247.05$ kJ/mol (synth. gas formation) (R2);
- $CH_4 + H_2O = CO + 3H_2$ $\Delta H0 = +206$ kJ/mol (wet reforming) (R3);
- $CH_4 + 0.5O_2 = CO + 2H_2$ $\Delta H0 = -36$ kJ/mol (R4);
- $H_2 + 0.5O_2 \rightarrow H_2O$ $\Delta H = -286$ kJ/mol (R5);
- $C + CO_2 \Leftrightarrow 2CO$ $\Delta H = +162$ kJ/mol (boudouard reaction) (R6).

Secondary reactions with a low risk of occurrence:

- $CO + H_2O \Leftrightarrow CO_2 + H_2$ $\Delta H = -42$ kJ/mol (homogenic water-gas reaction, CO conversion) (R7);
- $CO + 3H_2 \Leftrightarrow CH_4 + H_2O$ $\Delta H = -206$ kJ/mol (metanalysis) (R8);
- $2C + O_2 \Leftrightarrow 2CO$ $\Delta H = -246$ kJ/mol (R9);
- $C + H_2O \Leftrightarrow CO + H_2$ $\Delta H = +119$ kJ/mol (R10);
- $C + 2H_2 \Leftrightarrow CH_4$ $\Delta H = -87$ kJ/mol (R11).

2.3. The complex reaction kinetics of methane combustion

Our hypothesis is that the hazardous reaction is clearly the (R2) reaction, because in this case CO and H2 are generated. This reaction is described in a large amount of technical literature, because of its importance for industrial production, but the process requires high heat input and high temperatures [21]. This radical-driven mechanism is a chain reaction formed by a series of steps. A hydrogen radical is produced at each step along the chain reaction (Ḣ, ȮH, Ȯ) [21-25], as it shown on (R12).

$$\dot{C}H_4 \rightarrow \dot{C}H_3 \rightarrow \dot{C}H_2O \rightarrow \dot{C}HO \rightarrow \dot{C}O \rightarrow CO \quad \text{(R12)}.$$

Methane reactions are classified as cold or hot reactions in the technical literature. This is important for our research because our measurement result curve graphs indicate a chain reaction mechanism, which follows the well-known conversion of methane and CO2 shown on Figure 3 [26]. Above 900 K, a chain reaction based on the high temperature reaction step $\dot{H} + O_2 = \dot{O}H + \dot{O}$ takes over the main role in the oxidation of hydrocarbons.

The authors have shown [27] how complex methane reactions are, sensitive not only to temperature but also to the presence of other reactants. The authors analyzed a product gas created by the reaction of CH4 and CO2, which mainly contains H_2, CO, CH_4, CO_2 and H_2O, for the purposes of industrial production. They approximated the composition of the product by using chemical equilibrium analysis at various CH_4/CO_2 ratios where the temperature range was ranged between 200 and 1000 °C (Figure 4). The exponential nature seems to be the common point, whichever flow or reactions we consider. This indicates the emergence of chain reactions (Figure 4. a, b, c, d). This is an other important step in proving our hypothesis.

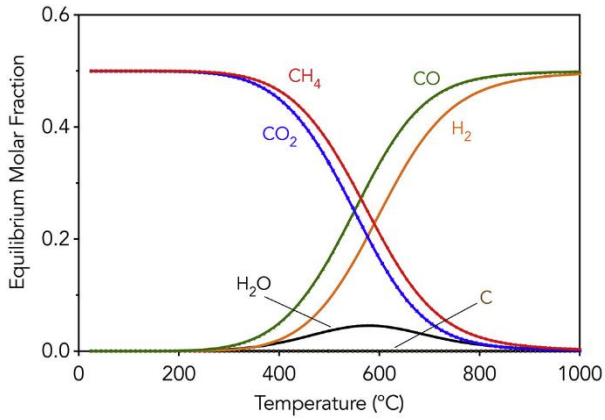


Figure 3.

Reaction equilibrium transformation curve of dry (no water vapor) CH_4 and CO_2 reactants showing the ratio of CO, H_2, H_2O and C components as a function of temperature [26].

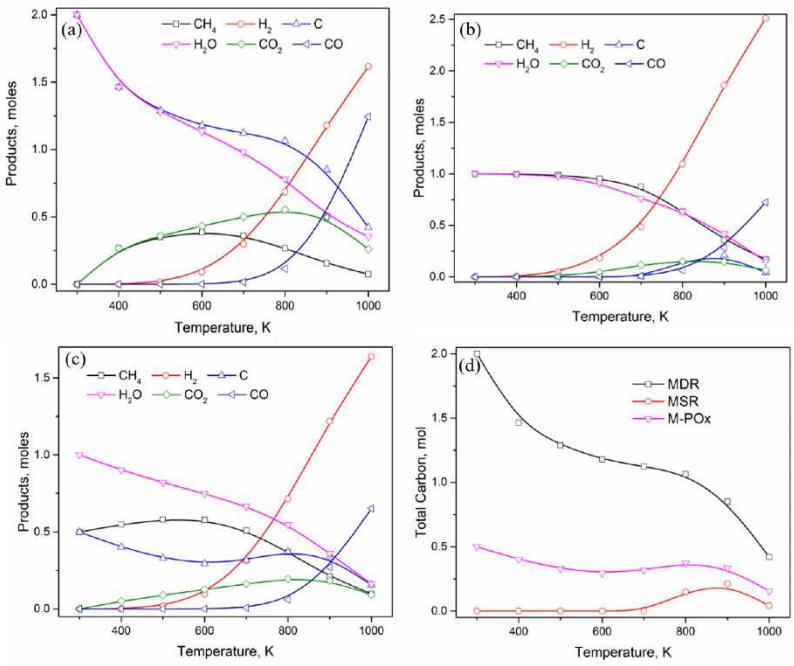


Figure 4.

Reaction product distribution (a) methane dry reformation, (b) methane vapor reformu-lation, (c) methane partial oxidation, (d) total carbon formation in all three reactions. All calculations were done at 105 Pa pressure [27].

In [27], the authors highlight that CO is not formed up to 600 K, while hydrogen starts to appear already at 400 K and both CO and H2 show an exponential concentra-tion increase as temperature rises, which indicates that higher temperature is more favorable for the formation of products (CO, H_2). Under normal conditions, the con-version of methane to carbon dioxide produces synthesis gas with a low hydrogen and CO content (R2 reaction).

In case of catalysis the optimal temperature and pressure range for CH_4 + CO_2 conversion is 700–900 °C and 2–4 MPa [28].

The CH_4/CO_2 mole ratio and the effect of temperature on the composition of the product gas are also among the most important subjects of this research [29-31]. The special behavior of methane was also modeled under explosive conditions as well, supporting our hypothesis that an explosion is actually behind the formation of CO_2 and CO [32, 33].

2.4. The design of our model experiments based on previous experience and assumptions

We formulated several hypothesis based on their previous observations, and carried out proof-of-concept model experiments to verify them. We artificially interfered with the normal process of boiler flue gas venting, while measuring the concentration of the created reaction products (CO_2 and CO).

1. Hypothesis was that severe CO poisoning during the operation of open chamber gas appliances is not caused by incomplete (oxygen-deficient) combustion, but instead it is explained by another mechanism;
2. With the endotherm reaction CH_4 + CO_2= 2 CO + $2H_2$* the rate of gas generation increases exponentially, as per the Arrhenius equation [19];
3. The high temperature reduction of the backflowing and enriched CO_2 follows the Boudouard mechanism (6);
4. The (2) and (5) reactions may explain the concurrent increase in air humidity and CO.

We were looking for an explanation of what triggers the reaction shown in Figure 3; a reaction mechanism in which the conversion increases exponentially together with the temperature. We also know from our measurements that the CO_2 layer thickness increases starting from the highest point in the room. Due to artificial intervention (such as using a kitchen extractor vent), the combustion products do not discharge through the chimney, but the CO_2-rich flue gas is returned to the room through the de-flector. Given time, it reaches the level of the boiler flame. If it reaches the critical level, we expect the R2 reaction to be triggered suddenly.

This is followed by a sudden surge in reaction products (Figure 3). Although the reaction is endothermic, the resulting hydrogen is so reactive (R5 reaction) that it is immedi-ately oxidized into water. Its temporary presence cannot be detected [34]. The emer-gence of water vapor, and its condensation on cold surfaces, which has been observed in several cases, confirms that R5 reaction may be happening. Authors' hypothesis of chain reaction is confirmed by the exponential run-up.

3. Test sites, conditions and model experiments

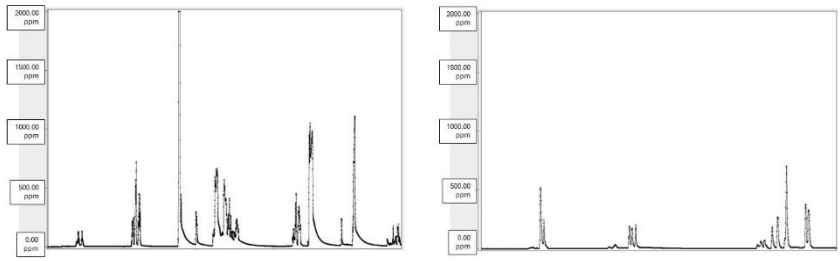
3.1. The pilot flame laboratory tests

During the pilot test we used several simple flame samples (butane, pro-pane-butane, acetylene), in an attempt to reproduce the chemical reactions that may occur in an open chamber gas boiler. For all three gases, we were able to verify the ap-pearance of CO by creating diffused and mixed flame states and introducing CO_2 into different parts of the flame and the combustible gas mixture. We were able to verify the (2) and (6) reactions at different flame temperatures (700-1250 °C), which we measured with a Cr/CrNi thermocouple (Figure 5. a). The tests were carried out in a fire laboratory at an external location where ventilation and air-movement free area was provided (Figure 5. b). CO_2, CO and ambient O_2 were measured at multiple loca-tions above the combustion chamber. In all cases, the presence of CO was immediately detectable (Figure 6.).



(a) (b)

Figure 5.
CO_2 mixed into the butane gas flame (a) and analysis of the outflowing gas at the end of the tube (b).



(a) (b)

Figure 6.

CO peaks in LPG flame (a) and butane flame (b) following the introduction of CO_2 to the flame. CO_2 added into diffused butane flame resulted in CO values greater than 200 ppm.

During tests next gas concentration measurement devices were used:

- Dräger X-am 2500 (measured gases: H_2S, CO, CH_4, O_2);
- Dräger X-am 5600 (measured gases: CO_2, CH_4,O_2, H_2S);
- Dräger X-am 2000 (measured gases: H_2S, CO, CH_4, O);
- Software: Dräger Gas Vision.

We measured flame temperatures, but these values may vary by the manufactur-ers. CO appeared at all the temperatures we measured, in other words, we could detect the presence of CO at any flame temperature we measured. Accordingly, we no longer considered the role of flame temperature to be important.

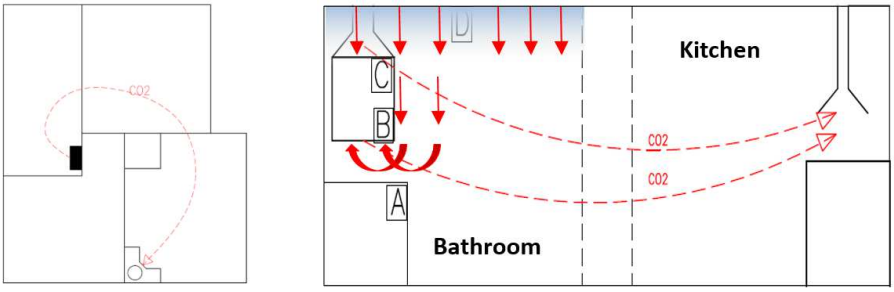
We established by the pilot flame tests that the temperature of the flames was sufficiently high for the Boudouard R6 reaction to take place, where the CO formed is a function of the temperature.

3.2. Test site and measurement points

The location of real-time measurements was an apartment. In the bathroom there was a B_{11} type open chamber boiler. There was a gravity vent in the toilet and a 100 mm diameter vent above the exhaust of the extractor hood in the kitchen (Figure 7). At the time of taking the measurement, the extractor hood in the kitchen was turned on continuously, and so was the gas boiler in the bathroom. The extraction was 5-6 meters from the location of the combustion chamber, demonstrating how easy it is to influ-ence the natural extraction of the chimney from another room, even if it is several me-ters away.

The Dräger gas detectors were placed in four locations and were relocated during the measurements several times (Figure 7.). The measurement points were chosen to obtain information on the distribution of gases at the bottom, at mid-level and in the upper air layer of the room, just below the ceiling. Locations of measurement points:

- A measurement point: 1 m high;
- B measurement point: the level of the gas burner (flame);
- C measurement point: the top of the gas boiler at about 200 cm high (flow switch/deflector);
- D measurement point: about 250 cm high.



(a) (b)

Figure 7.
Location of gas boiler and kitchen hoods (a) and measurement points (A, B, C and D) in the apartment (b).

Measurements of CO, CO_2 and O_2 concentrations started before the boiler was turned on, and were continuous during the different set-ups. A total of 4 measurement setups were used to acquire the necessary test data.

3.3. Measurement setups and results

3.3.1. Model layout 1

- A measurement point: CO (X-am 2500) approx.100 cm above floor level;
- B measurement point: —;
- C measurement point: CO (X-am 2000) top of the gas boiler at about 200 cm high;
- D measurement point: CO_2 (X-am 5600) just below the ceiling at about 250-260 cm high.

Red arrows on the graphs indicate the start of sudden CO_2 surge. The measure-ment took place between 16:25 and 16:47, after which the room was vented. The most typical measured concentrations of this setup are shown in Figure 8.

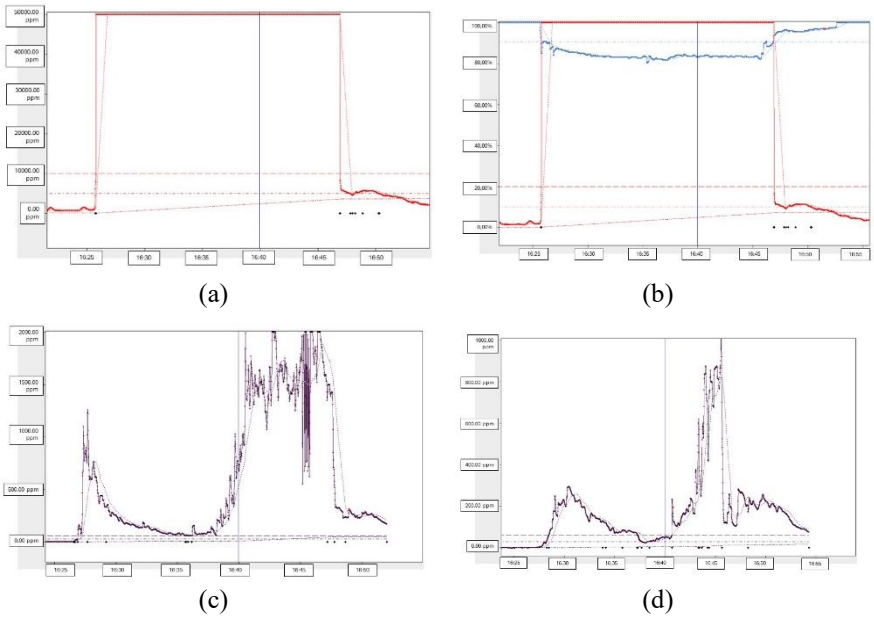


Figure 8.

Results of the measurement: measured values of CO_2 at measurement point D (a) and measured values of CO_2 and O_2 at measurement point D (b). Results of the measurement: measured ppm CO values at measurement point C (c) measured ppm CO values at measurement point A (d).

The measured values of CO_2 at measurement point D were outside the instru-ment's measurement limit (50,000 ppm). The appearance of CO_2 is shown in Figure 8 at 16:26. This is where CO_2 values appear fastest and in the highest concentrations. The decreased relative volume of oxygen is due to the displacement caused by flue gases and the hydrogen R5 reaction (Figure 8. b).

The measurement result curves are characterized by a sudden increase in CO_2 and CO concentrations. As expected, the measured CO values at measurement point C were higher (> 2000 ppm) than at measurement point A (<1000 ppm), confirming our hypothesis that CO is entering the room from the boiler combustion chamber through the flow switch (deflector). The appearance of CO was also detected sooner at meas-urement point C than at measurement point A. The sudden increase indicates a very fast chain reaction mechanism, and the decrease in oxygen does not play a significant chemical role (Figure 8 b.). The immediate combustion of CO is clearly triggered by the CO_2. The fall-off after the first CO surge during the measurement is due to the stack effect and the unsteady flow conditions.

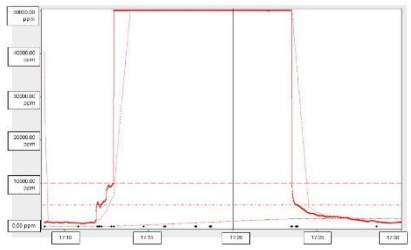
3.3.2. Model layout 2

- A measurement point: The CO measurement point (X-am 2500) is about 100 cm above the floor and 30 cm below the boiler;

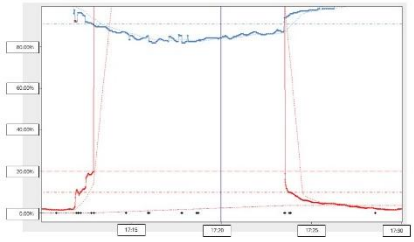
- B measurement point: —;
- C measurement point CO_2 (X-am 5600) top of the boiler unit at about 200 cm high;
- D measurement point CO (X-am 2000) below the ceiling at about 250-260 cm high.

The measurement took place between 17:11 and 17:47, after which the room was vented. The most typical measured concentrations of this setup are shown in Figure 9.

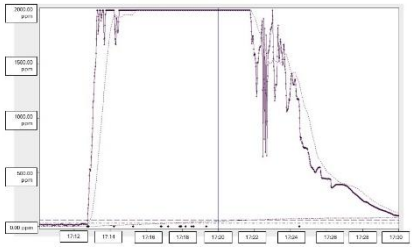
Same as in the first measurement, the CO_2 values measured at measurement point C were outside the instrument's measurement range (>50,000 ppm) (Figure 9.a). The CO creating reaction started without delay and no interference from flow effects were observed (Figure 9.c). The decreased relative volume of oxygen is due to the displace-ment caused by the created flue gases and the hydrogen reaction (R5) (Figure 9 b.) The measured values of CO at measurement point D were outside the instrument's meas-urement range (>2000 ppm). Further, it was found that CO concentration in this upper area was several times higher than at measurement point A (<800ppm), and that the dangerous levels above 2000 ppm were reached in less than 30 seconds at measure-ment point D (Figure 9 c and d).



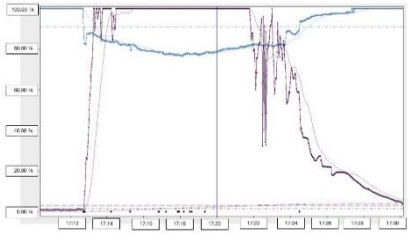
(a)



(b)



(c)



(d)

Figure 9.

Results of the measurement: measured ppm values of CO_2 at measurement point C (a) and measured percentage of CO_2 and O_2 by volume at measurement point C (b). Results of the meas-urement: measured ppm values of CO at measurement point D (c) and measured percentage by volume of CO and O_2 at measurement point D (d).

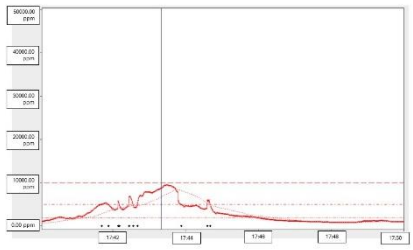
3.3.3. Model layout 3

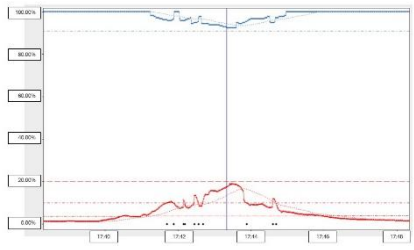
- A measurement point: —;
- B measurement point of CO_2 (X-am 5600) approx.130 cm high, at the lower part of boiler (flame carpet level);
- C measurement point CO (X-am 2500) top of the boiler unit at about 200 cm high;
- D measurement point CO (X-am 2000) below the ceiling at about 250-260 cm high.

The measurement took place between 17:38 and 17:45, after which the room was vented. The most typical measured concentrations of this setup are shown in Figure 10.

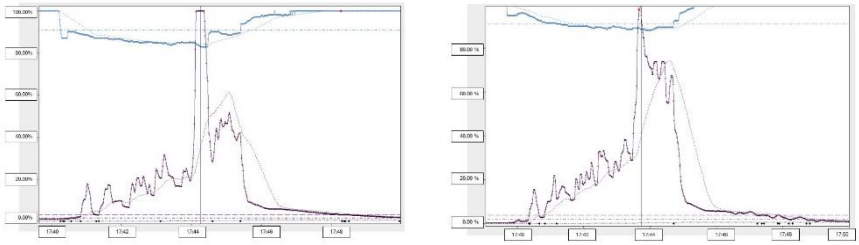
The aim of this setup was to determine at what CO_2 level measured below the combustion chamber we should expect a sharp rise in CO. We also took O_2 measurements below the boiler, at the location where combustion air flows into the boiler's combustion chamber. We have done this to negate the possibility that CO creation is caused by low O_2 levels in the air.

The CO_2 value reached a maximum of about 10,000 ppm, shortly after which a sharp rise in CO levels was observed (Figure 10. a.,c.,d.). The data taken at measurement point D at 17:43:58 was 382 ppm CO, which fluctuated before that time due to the non-uniform flow conditions discussed earlier. The CO measurement at 17:44:03 showed about 600 ppm and at 17:44:09 it exceeded the 2000 ppm measurement limit. This change is more than 1400 ppm in 6 seconds, which cannot be explained by the CO content of the returned flue gas and the lack of oxygen but can be attributed to the mechanisms described earlier (R5 reaction, Figure 10. c.). The relative volume of oxygen (shown as the blue line) was around 19 % V/V at measurement point B. Based on our previous observations, an explosive rise of CO is triggered at levels as low as about 5000 ppm CO_2. We were able to verify this using measurement setup 3.





(a) (b)



(c) (d)

Figure 10.

Results of the measurement: measured ppm values of CO_2 at measurement point B (a) measured percentage of CO_2 and O_2 by volume at measurement point B (b). Results of the meas-urement: CO and O_2 measured % by volume at measurement point D (c) and CO and O_2 measured % by volume at measurement point C (d).

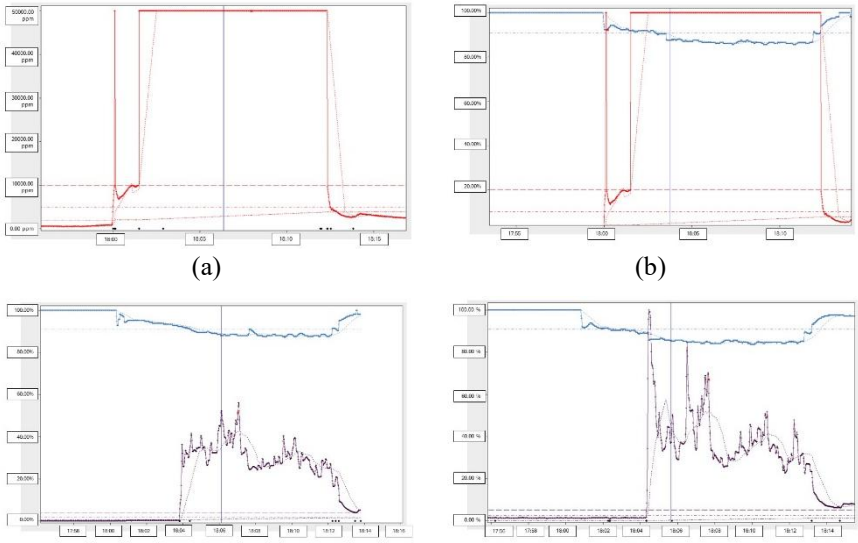
3.3.4. Model layout 4

- A measurement point:—;
- B measurement point:—;
- C measurement point CO (X-am 2500) top of the boiler unit at about 200 cm high;
- D measurement point CO_2 (X-am 5600) below the ceiling at about 250-260 cm high;
- D measurement point CO (X-am 2000) below the ceiling at about 250-260 cm high.

The measurement took place between 17:59 and 18:11, after which the room was vented. The most typical measured concentrations of this setup are shown in Figure 11.

The significance of this measurement setup was that one CO meter and the CO_2 meter were placed next to each other at the highest point in the room, while the other CO meter was on top of the boiler.

In this way, the combined CO-CO_2 change at the highest point of the room was simultaneously measured, on top of which we were able to confirm the sharp rise in CO at different heights (at the outflow point and highest point).



(a) (b)

(c) (d)

Figure 11.

Results of the measurement: measured ppm values of CO_2 at measurement point D (a) and measured percentage of CO_2 and O_2 by volume at measurement point D (b). Results of meas-ured percentage of CO and O_2 by volume at measurement point C (c) and D (d). Figure 11 c., d. shows most typically that CO_2 levels spike a few seconds before CO appears, while the oxygen content of the air does not change to an extent that would attribute CO formation to insufficient oxygen levels. At the highest measurement point that is D, the CO2 concentration of the triggering event can only be estimated from the CO2 max ppm in (a) and is estimated to be above 50000 ppm.

4. Results and Discussion

Our purpose was to study in details the conditions and causes of the rapid for-mation CO. The mechanism of the reaction was discussed in details in Chapter 2.3 „The complex reaction kinetics of methane combustion". We referred to R2 reaction in the first sentence of this subchapter

Our results are based on experimental measurements. Our goal was to determine the causes of the phenomenon of the rapid generation of CO (rapid concentration ele-vation of CO). This reaction is described by the chemical R2 reaction (Chapter 2.2.). We referred to R2 reaction in the first sentence of this subchapter. The

existence of the R2 reaction is confirmed by our observation in the real environment, according to which water vapor suddenly appears in the space around the boiler. Water as a reac-tion product can be found in R5. The resulting H2 is so reactive with the oxygen in the air that it is impossible to detect, we only perceive the result, "water vapor", high hu-midity.

The measurement data gathered during the experiments show that carbon dioxide (CO_2) levels rose significantly before the emergence of CO. The data clearly shows that the main cause is the backflow of combustion products, which release large amounts of CO_2 into the room.

Our measurements show that this CO_2 from the backflow is accumulated in the room, and reacts with CO in several phases.

1. First phase: A part of the flue gas heat generated during combustion is unable to escape the combustion chamber, and in the absence of draft accumulates above the combustion chamber of the boiler (a significant part of it flows into the room) and causes the temperature to rise inside the boiler. This increased temperature is already sufficient to trigger R2 and R6 reactions. This reaction already results in an ex-tremely high increase in CO concentration, as shown by the upward curves in Figures 8-11 c and d;

2. Second phase: After the initial reactions that have taken place, the backflow of flue gases into the room (both CO and CO_2) becomes continuous, and fills the room from the ceiling downwards. In several cases the CO level drops (Figures 8-11 c and d) which are probably due to a temporary improvement of the chimney draft.;

3. Third phase: Based on both our current measurements and previous experience, if the CO_2 level reaches 5000 ppm at the height of the boiler's combustion chamber, it causes the CO level to rise further. This is also caused by R2 and R6 reactions.

Therefore the surge in CO concentration is not caused by a decrease in oxygen, because if it was, the development of concentrations would be linear. That is according to the equation v= k [A]* [B]. Therefore [A] and [B] represent the concentrations of the reagents CH_4 and CO_2, therefore we can conclude that this is not an incomplete com-bustion [35]. The common characteristic of the measurement curves is the sudden in-crease in CO_2 and CO concentrations. At the same time, the hydrogen produced during the R2 reaction may react immediately with the oxygen in the air (R5 reaction), which may result in the appearance of water vapor that has been detected multiple times in other rooms. This phenomenon has not been observed during our model measurements.

Furthermore, the exothermic process of the water formation further increases the room's air temperature.

A positive exothermic balance increases the temperature of the reaction space, which exponentially increases the reaction rate as per the Arrheni-us equation. This results in a sudden rise in CO and CO_2 concentrations, as shown in our measurements.

5. Conclusions

The aim of our work is to identify one of the many possible mechanisms of methane reactions, which may be present in households with open chamber gas appliances and pose a risk to human life. We have observed and described a phenomenon, which sheds a different light on the emergence of such dangers. Fortunately, the in-stallation of domestic CO detectors is spreading, however detecting the increase in CO can be too late, because when the CO level starts to rise, it may already have reached dangerous irreversible levels. For life protection purposes, in addition to measuring CO, it is also necessary to measure CO_2 levels, because a rise in CO_2 levels precedes the exponential increase in CO levels that we have identified. Our study based on empiri-cal observations of more cases and letal accidents happened in the practice of fire-fighters. The main part of the study was made in an apartment where people were treated in hospital after CO poisoning. For elaborate modelling in this real situation we did not have all of the boundary conditions/parameters.

Our measurement results suggest that the formation of CO is not caused by an oxygen-deficient environment, but by a chemical reaction driven by a strongly exothermic chain reaction mechanism. The outflow of methane is continuous, so the re-turning CO_2 initiates the formation of CO (R2 reaction). This process is proven by our other observation in a real environment, that water vapor suddenly appears in the space around the boiler. Water as a reaction product can be found in R5 reaction. The resulting H_2 is so reactive with the oxygen in the air that it is impossible to detect, we only perceive the result, "water vapor". Methane burns continuously, with complete combustion (R1 reaction). This is also proven by the measured oxygen concentration. Since the oxygen level does not decrease significantly, the combustion of methane is a perfect combustion where no CO is produced. Imperfect combustion can occur at concentrations below approx. 16-17 V% oxygen. In this case the appearance of CO is not the consequence of incomplete combustion. The safety device of the boiler switches off automatically when there is no combustion. However, we did not experience the automatic switch off during our tests.

First the sudden CO_2 concentration and then the CO appears, indicating the premixed, explosive mechanism of the reaction. This is showcased by the sudden surge in the run-up curves. The reduction and reaction of CO_2 (which enters the

combustion chamber via backflow) with methane produces CO and hydrogen (R2 reaction). The presence of hydrogen is a particular source of danger. It acts as a catalyst in the combustion pro-cesses because it is highly reactive with oxygen (and is undetectable). Our measure-ments show that the sudden appearance of H2 is also confirmed by the decrease in oxygen levels as per (R5 reaction), which further confirms our previous findings. The exothermic effect of the $H2 + 0.5O_2 \rightarrow H_2O$ ($\Delta H = -286$ kJ/mol) reaction further increases the air temperature [36, 37].

The reactions that take place during two of the three phases (phases 1 and 3) cause the exponential increase in CO, which occurs both directly in the zone above the flame (1000 °C) (phase 1, (R6 reaction)) and in the reaction zone of the flame (phase 3, R2 reaction), where methane is still present. Both are triggered by elevated presence of CO_2 and increased temperature. The effect of oxygen cannot be measured, but its sudden decrease is due to the displacement effect of the flue gases and the R5 reaction. The proposed hypothesis may be further supported by kinetic studies of methane oxidation that suggest the possible occurrence of CO as an intermediate species, together with empirical observations reporting the sudden appearance of water vapour at other locations under comparable conditions [38, 39].

Because CO and CO_2 both appear suddenly, it is not the quantity but the rate of emergence that should be monitored. The creation of CO_2-rich flue gas exceeded 50,000 ppm within 1-3 minutes in multiple cases, thus there was reason to expect the for-mation of dangerous levels of CO. If no effective warning or automatic intervention occurs in the early stages of the phenomenon, the very rapid evolution of CO and the subsequent development of lethal gas concentrations will occur. Since these appliances share airspace with the living quarters, the increase in CO_2 produced by the occupants must be distinguished from the rapid CO_2 increase happening during backflow. There-fore, the rate of increase is an indication of danger. Since the CO_2 backflow from the boiler is mainly present in the upper air layers of the room, the CO_2 gas detector should also be placed here.

We also aimed to determine whether household CO sensors are sufficient to detect hazards. Our CO_2 and CO measurements showed that it is not, because the appear-ance of CO is preceded by an increase in CO2 concentration. So measuring this is more important.

Contributions

Conceptualization was performed by Sándor Rácz, János Csicsely, and Gergő Érces; methodology was developed by Sándor Rácz and János Csicsely; formal analysis and investigation were carried out by Sándor Rácz, János Csicsely, and Gergő Érces; writing – original draft preparation was completed and revised by Sándor Rácz, Katalin Kopecskó, and Barbara Elek; writing – review and editing were conducted by Katalin Kopecskó, Éva Gyöngyössy, and Barbara Elek; funding acquisition was managed by Katalin Kopecskó; resources were provided by Sándor

Rácz, Gergő Érces, and Katalin Kopecskó; supervision was carried out by Katalin Kopecskó and Barbara Elek.

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