Rapport SGC 135

Catalytic combustion in gas stoves – Phase II

Anna-Karin Hjelm
CATATOR AB

Rapport SGC 135 • ISSN 1102-7371 • ISRN SGC-R--135-SE

SGC:s FÖRORD

FUD-projekt inom Svenskt Gastekniskt Center AB avrapporteras normalt i rapporter som är fritt tillgängliga för envar intresserad.

SGC svarar för utgivningen av rapporterna medan uppdragstagarna för respektive projekt eller rapportförfattarna svarar för rapporternas innehåll. Den som utnyttjar eventuella beskrivningar, resultat e dyl i rapporterna gör detta helt på eget ansvar. Delar av rapport får återges med angivande av källan.

En förteckning över hittills utgivna SGC-rapporter finns på SGC´s hemsida www.sgc.se.

Svenskt Gastekniskt Center AB (SGC) är ett samarbetsorgan för företag verksamma inom energigasområdet. Dess främsta uppgift är att samordna och effektivisera intressenternas insatser inom områdena forskning, utveckling och demonstration (FUD). SGC har följande delägare: Svenska Gasföreningen, Sydkraft Gas AB, Sydkraft AB, Göteborg Energi AB, Lunds Energi AB och Öresundskraft AB.

Följande parter har gjort det möjligt att genomföra detta utvecklingsprojekt:

Sydkraft Gas AB
AB Fortum Värme samägt med Stockholm Stad
Svenska Gasföreningen
Göteborg Energi AB
Nova Naturgas AB
Catator AB
IGF Energigas AB
Dansk Gasteknisk Center a/s
Statens Energimyndighet

SVENSKT GASTEKNISKT CENTER AB

Johan Rietz

Summary

Several independent studies show that gas stoves to some degree contribute to the indoor emissions of NO_x, especially in situations were the ventilation flow is poor. The peak-NO_x-concentrations can reach several hundred ppb but the integral concentration seldom exceeds about 20 – 50 ppb, which corresponds to an indoor-outdoor ratio of about 1 – 2.5. Epidemological studies indicate increasing problems with respiratory symptoms in sensitive people at concentrations as low as 15 ppb of NO_2. Consequently, the NO_x-concentration in homes where gas stoves are used is high enough to cause health effects. However, in situations where the ventilation flow is high (utilisation of ventilation hoods) the NO_x-emissions are not likely to cause any health problems.

This study has been aimed at investigating the possibilities to reduce the NO_x emissions from gas stoves by replacing the conventional flame combustion with catalytic combustion. The investigation is requested by Swedish Gas Center (SGC AB), and is a following-up work of an earlier conducted feasability study presented in April-2002. The present investigation reports on the possibility to use cheap and simple retro-fit catalytic design suggestions for traditional gas stoves. Experiments have been conducted with both natural and town gas, and parameters such as emissions of NO_x, CO and unburned fuel gas and thermal efficiency, etc, have been examined and are discussed. The results show that it is possible to reduce the NO_x emissions up to 80% by a simple retro-fit installation, without decreasing the thermal efficiency of the cooking plate. The measured source strengths correspond to indoor NO_x concentrations that are below or equal to the average outdoor concentration, implying that no additional detrimental health effects are probable. The drawback of the suggested installations is that the concentration of CO and in some cases also CH_4 are increased in the flue gases. To overcome the latter, improved aeration of the system is needed, e.g. modification of nozzle-size and/or flame port plate.

The effects of installing a retro-fit catalytic design onto the burner in the gas oven were also examined. Similar to the burners of the cooking plates, the emitted NO_x was greatly reduced, i.e. up to 90 %.

Other on-going projects using similar catalyst concepts as in this study have shown that the life-time of the catalyst, i.e. the mechanical stability and the catalytic activity, is extremely good (> 1000 h). To examine if this durability of the catalyst is limited in this specific application by deactivation caused by possible food spillage, a number of commonly used food ingredients were painted onto the catalysts and the activity of the catalyst prior to and after the "deactivation" was investigated. The results show that no ingredients of organic type (fat, milk, egg, sugar) have any significant impact on the catalytic activity. Salt however was seen to block active reaction sites of the catalyst, but the tests showed that the catalyst could in this case be easily re-activated by simply washing it in water.

Sammanfattning

Ett flertal oberoende studier visar att användning av gasspisar i viss grad bidrar till en ökad halt av NO_x inomhus, speciellt i de fall då ventilationsflödet är bristfälligt. Den maximala halten kan uppgå till flera hundra ppb men medelhalten överstiger sällan 20 – 50 ppb, vilket motsvarar ett haltförhållande mellan inomhus- och utomhusluften på 1 – 2.5. Epidemologiska undersökningar visar samtidigt att en varaktig ökning av NO_x-halten på 15 ppb medför respiratoriska symptom hos känsliga personer. Användning av gasspisar medför således en tillräckligt stor ökning av NO_x-halten för att hälsoeffekter skulle kunna uppstå. Om ventilationsflödet är tillräckligt stort (utnyttjande av spisfläkt) reduceras dock problemen i väsentlig grad och härvid förväntas hälsoeffekterna bli försumbara.

Målet med denna studie är att undersöka möjligheterna att reducera NO_x-emissioner från gasspisar med hjälp av att byta ut den konventionella flamförbränningen med katalytisk förbränning. Undersökningen är på uppdrag av Svenskt Gastekniskt Center AB (SGC AB), och är en uppföljning av en tidigare genomförd förstudie som presenterades i april-2002. Följande arbete rapporterar kring möjligheten att använda sig av billiga, enkla designlösningar för traditionella gasspisar. Experiment har utförts med både natur- och stadsgas, och parametrar såsom emissioner av NO_x, CO och oförbränd gas samt kokplattans termiska effektivitet har undersökts och diskuteras. Resultaten visar att det är möjligt att reducera NO_x-utsläppen upp till 80 %, utan att minska den termiska effektiviteten. Av dynamiska simuleringar framgår att motsvarande inomhuskoncentration är lägre än eller samma som den genomsnittliga NO_x-utomhuskoncentrationen, vilket indikerar på att man med hjälp av dessa enkla lösningar kan eliminera de hälsoproblem som i vissa studier sammankopplas med användning av gasspisar inomhus. Nackdelen med de föreslagna modifieringerna är att CO-, och i vissa fall även CH_4- koncentrationen ökar i rökgaserna. Det sistnämna problemet skulle kunna lösas med hjälp av förbättrad luftinblandning, tex modifiering av brännarens munstycke och/ eller flamportsarea.

I studien undersöktes även effekten av att installera en enkel katalysatordesign på ugnsbrännaren. I likhet med kokplattsbrännararna så var det möjligt att reducera NO_x -utsläppen väsentligt, upp till 90 %.

Andra pågående projekt som använder sig av liknande katalysatorkoncept som i denna studie har visat att katalysatorns livslängd, dvs den mekaniska stabiliteten och den katalytiska aktiviteten, är mycket bra (> 1000 timmar). För att undersöka om denna livslängd i den här specifika applikationen är begränsad av förgiftning orsakad av eventuella överkok/matspill, så penslades vanligt använda livsmedelsingredienser på katalysatorn och dess aktivitet mättes före och efter ”deaktiveringen”. Resultaten visar att organiska matingredienser har ingen signifikant inverkan på katalysatoraktiviteten. Salt däremot visade sig blockera aktiva reaktionssäten, men av testerna så framgick också att en salt-deaktiverad katalysator kan mycket enkelt reaktiveras genom sköljning i vanligt kranvatten.

List of contents

1. Introduction

The utilisation of traditional gas stoves for heating and cooking results in indoor emissions containing chemical species such as carbon monoxide (CO), unburned hydrocarbons (UHC) and nitrogen oxides (NO_x). A number of independent studies have been conducted over the years to analyse and to quantify the detrimental health effects of these emissions (references in [1]). Indeed, the results imply that indoor emissions of NO_x may cause respiratory diseases, even at very low concentrations at long-term exposure (about 15 ppb NO_2) [2].

The gas stove contribution is dependent upon several factors. The main factors include:

-source strength/emission rate of NO_x
-ventilation flow (presence/absence of ventilation hood)
-room design
-background concentration (outdoor concentration of NO_x)

It is clear from previous studies that the most important factors for the indoor concentation build-up is the source strength of NO_x and the ventilation flow. One way that has been suggested for reducing the harmful NO_x emissions is to replace the traditional burners, in which flame combustion takes place, with catalytic cooking plates.

The possibilities of using catalytic cooking plates were recently investigated by Catator AB in a feasibility study on the request of Swedish Gas Center (SGC AB). Catator AB has developed a wire-mesh catalyst suitable for retro-fit installations in atmospheric burners, which is also the type of burner that traditional gas stoves are based on. The wire-mesh catalyst is characterised by high mass- and heat transfer capacities, a high intrinsic catalytic activity and an extremely low pressure drop. In addition, the wire-mesh catalyst has a high degree of geometric flexibility, which is of importance in this application. The feasibility work suggested several design solutions for catalytic gas stove burners. The simplest types were shown to be suitable for retro-fit installation in atmospheric burners, whereas the more sophisticated types need an assisting fan for the primary air supply. Introductory experiments indicated that catalytic wire-meshes and catalytic coils installed downstream the existing flame ports of the burner have great potential for NO_x-reduction. Furthermore, in order to evaluate the consequences of the related indoor air quality, a dynamic simulation model (CSTR-approximation) was used.

This work is a following-up study of the above mentioned feasibility study. The goals of this study were threefold. First, it was aimed at carrying out comprehensive studies concerning emissions (i.e. NO_x, CO and CH_4) and thermal efficiencies for different simple catalytic retro-fit design suggestions for tradional gas stoves burners. The second aim was to investigate possible deactivation of the catalyst, caused by food spillage onto the catalyst during cooking. Experiments were conducted using both natural and town gas and the results were compared and discussed. Finally, the effect of placing a wire-mesh catalyst downstream the flame port of the burner positioned in the oven was examined.

2. Experimental

2.1. Experimental set-up

The series of results presented in this work was performed with a commercial gas stove (IGF-Noblesse). The burner investigated, adjusted for natural (20-24 mbar) and town gas (7-9 mbar), has the nominal and low output power of 1.75 and 0.32 kW, respectively. The gas compositions of the two gases used are given in Table 1.

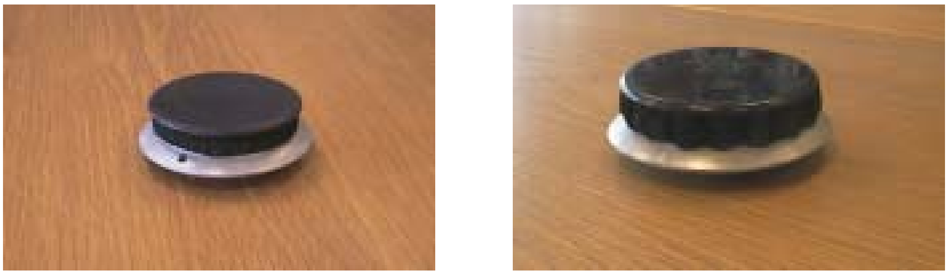
Table 1. *Gas composition of the natural and town gas used. Besides the components given herein, the natural gas contained small vol% of butane, pentane, hexane and nitrogen.*

Natural gas/vol%		*Town gas/ vol%*	
1.18	CO_2	2.6	CO
2.70	C_3H_8	13.0	CO_2
6.50	C_2H_6	30.40	CH_4
88.08	CH_4	54.0	H_2

Different retro-fit catalyst alternatives for the 1.75 kW burner were evaluated, which are summarised in Table 2. Photos of the various concepts can be seen in Fig. 1. The support material of the catalyst consisted of either a woven wire-mesh, planar or folded, of various mesh numbers (8, 12, 16 and 35), or a coil, which were all made of high temperature resistant steel. To increase the surface area of the substrate, a porous metal layer was deposit onto the material according to Catator´s technology. The substrate material was then washcoated with a ceramic layer (50/50 wt% ceria/alumina). Platinum was used as the active material. The amount of catalyst was typically between 0.2-0.3 dm^2, which corresponds to a catalyst load of about 580-875 kW/m^2 and 110-160 kW/m^2 at maximal and minimal power output, respectively. Furthermore, to examine the effect of the washcoating, uncoated wire-mesh rings (fwm25) were also tested.

Table 2. *Summary of different catalyst "retro-fit"-alternatives tested with the 1.75 kW burner.*

Notation	*Test performed*
Without mod.	Ordinary flame combustion
fcwm35	Folded catalytic wire-mesh ring downstream port plate, mesh number: 35
fwm35	Folded wire-mesh ring downstream port plate, mesh number: 35
cwm16	Catalytic wire-mesh ring downstream port plate, mesh number: 16
cwm8	Catalytic wire-mesh ring downstream port plate, mesh number: 8
cc	Catalytic coil downstream flame port plate



(a) *cwm16* ***(b)*** *fcwm35*

(c) *cc*

Fig. 1. *Photos of the different catalyst alternatives described in Table 2.*

The different catalyst alternatives were evaluated with respect to emission levels and thermal efficiency. In order to collect and to dilute the primary flue gases, a hood was placed 300 mm above the stove, Fig. 2. Analysis of emissions were performed in the exhaust pipe and the source strength of emissions (mg/kWh) could be calculated from emission data in combination with knowledge of the flow rate and the temperature of the air in the pipe. To ensure that the emissions in the flue gases were collected as good as possible in the exhaust pipe without a significant waste to the outside of the hood, insulation were attached in the open space between the hood and the stove. Experiments were conducted with and without the insulation, and the analysed emission were compared. No significant difference in result could be detected, thus, it can be established that the majority of the emissions was properly collected. NO_x (NO and NO_2) was measured by means of a chemiluminescent $NO/NO_2/NO_x$ analyzer (Model 200, Advanced Pollution Instrumentation), whereas CO and CH_4 were analysed by a photoacoustic infra-red detection method (Multi-gas Monitor Type 1302, Brüel & Kjær). Moreover, unburned hydrocarbons (UHC) were analysed by a Flame Ionizator Detector (FID). To estimate the dilution of the analysed flue gases, O_2 was also measured; in this work, by an electrochemical device. The latter instrument also enabled continous measurements of CO, whose detected value was throughout time of experiment double-checked with that value given by the infra-red technique. All the analysis instruments were prior to usage calibrated with test gases containing known concentrations of NO_x, CO and CH_4, respectively.

Fig. 2. *Gas stove with hood mounted for collecting the emissions in the flue gases.*

The thermal efficiency was estimated from tests with water heating. 1 kg of water was heated from room temperature (i.e. about 20 °C) to 100 °C. We measured the time needed to reach 100 °C at full power (i.e. 1.75 kW). By comparing the theoretical time to heat the water with the experimentally obtained time, we were able to estimate the thermal efficiency of the cooking plate. It should however be noted that the absolute value of the thermal efficiency can vary due to the choice of the cooking pate, the diameter and somewhat also due to the position of the pan. As a consequence, the estimated absolute values of the thermal efficiency given in this report should only be considered as approximate values. It is still however accurate to draw conclusions with respect to the observed variations between the different catalyst designs, since the same set-up was used throughout the whole series of measurements.

2.2. Deactivation study

In order to simulate different “worst case” food spillages onto the catalyst during cooking, various, commonly used food ingredients were painted, with a small paint-brush, onto a hot wire-mesh catalyst positioned downstream the flame port plate of the burner. The prepared solutions representing the various food spillages are displayed in Table 3. The emissions were measured prior to and after that the painting of food residues had been made. By comparing the emission data, conclusions about possible deactivation of the catalyst could be drawn.

Table 3. *Description of food spillage- ingredients.*

Food ingredient	*Prepared solution painted onto catalyst*
Salt (Cl^-)	Water solution satured with salt
Sugar	Melted sugar
Egg	Scrambled raw egg
Oil/Fat	Maize oil
Milk (Ca)	Milk (1.5 % fat)

2.3. The oven

The effect of positioning a catalyst downstream the flame port plate of the oven burner (nominal output power: 2.65 kW) was also examined. In this case, the catalyst consisted of a coated or an uncoated folded wire-mesh, see Table 4 and Fig. 3. The distance given in parenthesis in Table 3 refers to the actual distance of the air intake gap of the burner. This distance was varied in order to study the influence of primary aeration. In contrast to the experiments made with the 1.75 kW burner described above, the tests performed with the oven was solely conducted with natural gas and the performance of the catalyst was only evaluated with respect to the emissions measured in the exhaust pipe. Thus, no attention was in this case paid to possible influence on the thermal efficiency.

Table. 4. *Summary of different catalyst "retro-fit"-alternatives tested with the 2.65 kW burner in the oven. All the experiments were run at maximal setting, i.e. 240 °C.*

Notation	*Test performed*
Without mod. (4 mm)	Ordinary flame combustion, no modfication of originally set distance of air intake gap.
fcwm35 (4 mm)	Folded catalytic wire-mesh ring downstream port plate, mesh number: 35. Originally setting of air intake gap.
fwm35 (4 mm)	Folded wire-mesh ring downstream port plate, mesh number: 35. Originally setting of air intake gap.
fcwm35 (11 mm)	Folded catalytic wire-mesh ring downstream port plate, mesh number: 35. Increased primary aeration.
fcwm35 (2 mm)	Folded catalytic wire-mesh ring downstream port plate, mesh number: 35. Decreased primary aeration.

Fig. 3. *A folded catalytic wire-mesh (fcwm35) mounted downstreams the flame port plate of the burner placed in the oven. To clarify how the catalyst was attached to the burner/port plates, the photo shows the burner in an up-side down position.*

3. Results and discussion

3.1. Characterisics of the 1.75 kW burner

The photo displayed in Fig. 4 shows an example of how the combustion looked like when a wire-mesh ring was placed downstream the flame port plate of the 1.75 kW burner. At maximal power output, a mixture of flame and catalytic combustion was seen, whereas at low power output, pure catalytic combustion seemed to take place, i.e. no flames could be observed.

Fig. 4. *Example of catalytic combustion gas stove burner.*

The effect on the emissions of this simple retro-fit installation is illustrated in Fig. 5 and Fig. 6 for natural and town gas, respectively. In order to point out the characteristics of the gas stove, the emissions were measured at maximal and minimum power with and without a pan positioned above the burner. Explanations to the notations in the figures are given in Table 5. The emissions displayed in Figs. 5 and 6 are the concentrations that were measured when no further variations with time could be observed; thus these values are representing the emissions when steady-state of the burner has been reached. Experiments with ordinary flame combustion gives that the source strength of NO_x corresponds to a value of about 110 and 90 mg/kWh, for natural and town gas, respectively. These values are in fair agreement with values presented by Jensen et al. [3]. Furthermore, the results show that it is possible to reduce the NO_x-emissions up to 80 % by a simple retro-fit installation of wire-mesh ring. The drawback of this modification, compared to the unmodified flame combustion, is that the CO-emissions increased in almost all tested experimental conditions, Figs. 5b and 6b. The most drastic increase is seen when a pan is positioned above the burner at low power output. This result can be explained by the working principle of the burner. The burners of gas stoves are so called atmospheric burners, which are normally designed for a primary aeration of about 40-70 %, which means that a significant secondary aeration takes place downstream the flame port plate. By placing the catalyst downstreams directly onto the flame ports, the pressure drop over the system is increased, which decreases the degree of primary aeration. A decline in aeration degree may in turn lead to an increased extent of uncompleted combustion. This phenomenon becomes more significant at lower temperatures, which also explains why the highest CO-concentrations were obtained at low power output in combination to when the flames impinged onto a cool surface, i.e. a pan.

Table 5. *Explanations of notations used in Figs. 5 and 6.*

Notation	Test performed
max	Nominal power,1.75 kW
min	Low power, 0.32 kW
cat	With wire-mesh ring (mesh number:16) downstream flame port plate
pan	With a pan (diameter: 160 mm) placed above the burner

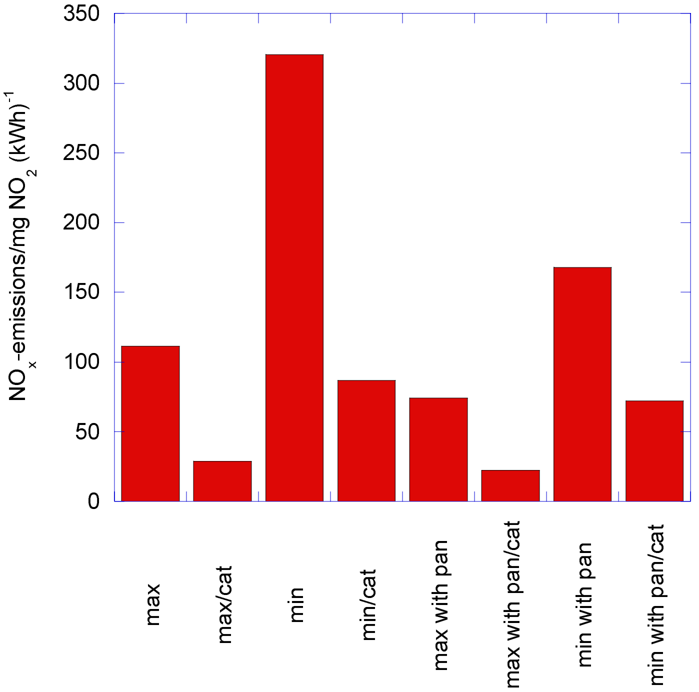


Fig. 5a.

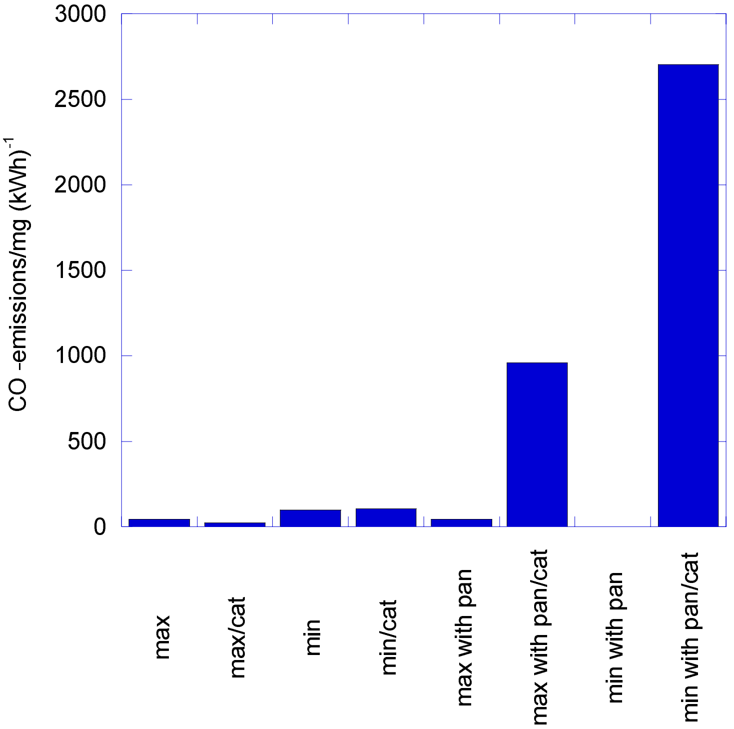


Fig. 5b.

Fig. 5. *Emissions of a) NO_x and b) CO measured under various conditions with the 1.75 kW burner with natural gas. The catalyst used was the cwm16.*

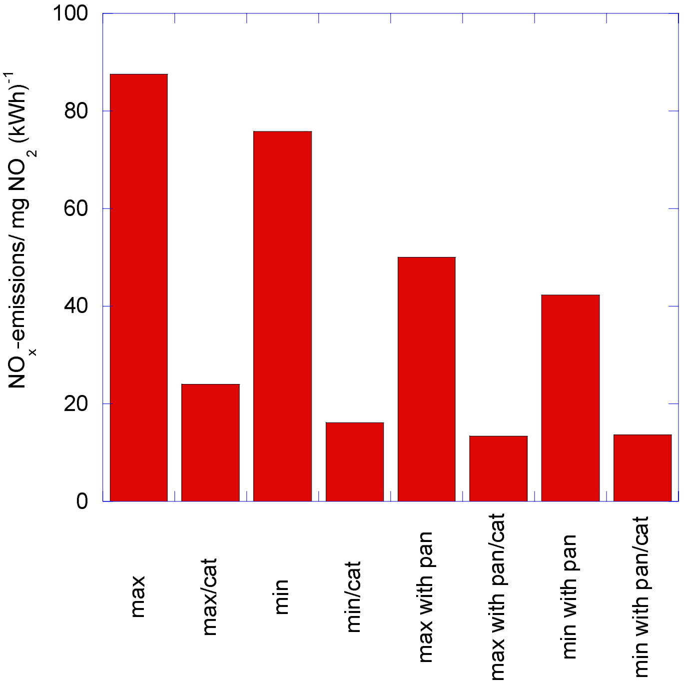


Fig. 6a.

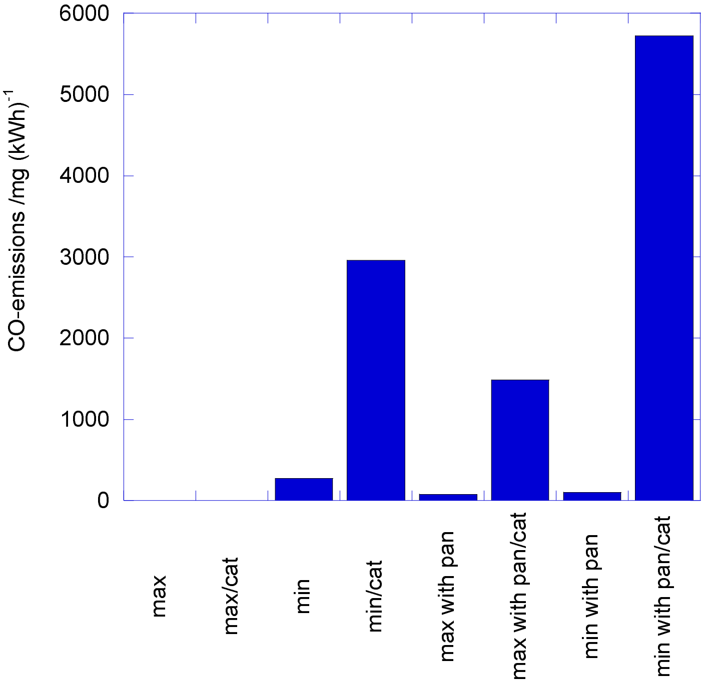


Fig. 6b.

Fig. 6. *Emissions of a) NO$_x$ and b) CO measured under various conditions with the 1.75 kW burner with town gas. The catalyst used was the cwm16.*

Even though the same trends in results were obtained with natural and town gas, there are some differences with respect to the absolute emission levels that should be mentioned. Compared to natural gas, the combustion of town gas results overall in lower NO_x-emissions, but significantly higher CO-emissions. These results may be attributed to the differences in gas composition, see Table 1. The lower concentration of methane in town gas compared to that in natural gas (30 % compared to 88%) may lead to a lower formation of prompt NO_x, which originates from radical reactions between hydrocarbons species and nitrogen. Moreover, the high emissions of CO are most probably a consequence of that the town gas, in contrast to the natural gas, contains a rather high concentration of CO (2.6 % compared to 0 %), which in turn implies that there were significant amounts of unburned gas in the flue gases at low power. Indeed, at low power, in contrast to when natural gas was used, significant amounts of unburned CH_4 (200-300 ppm at 20 % O_2) were detected in the exhaust pipe.

Similar to the majority of different burner systems, the emissions vary more or less with time during the start-up as a consequence of the time needed for reaching the desired working temperature. To get an idea of the time variations achieved with the middle size burner, typical results of emitted NO_x and CO measured as a function of time with and without a catalyst are plotted in Figs. 7a-b. Initially, the emissions of NO_x increased for both cases (i.e. with and without a catalyst), Fig. 7a. However, at about t>5 minutes, the NO_x concentration was observed to be rather constant with time for the ordinary flame combustion, whereas for the case with the catalyst present, the emission of NO_x was seen to continously decline until about t>10 minutes, when steady-state seemed to had been attained. Furthermore, with respect to the CO-emissions, the efficiency of the catalytic combustion seemed to increase significantly with time, Fig. 7b, attributed to the time to reach the desired combustion temperature of the catalyst.

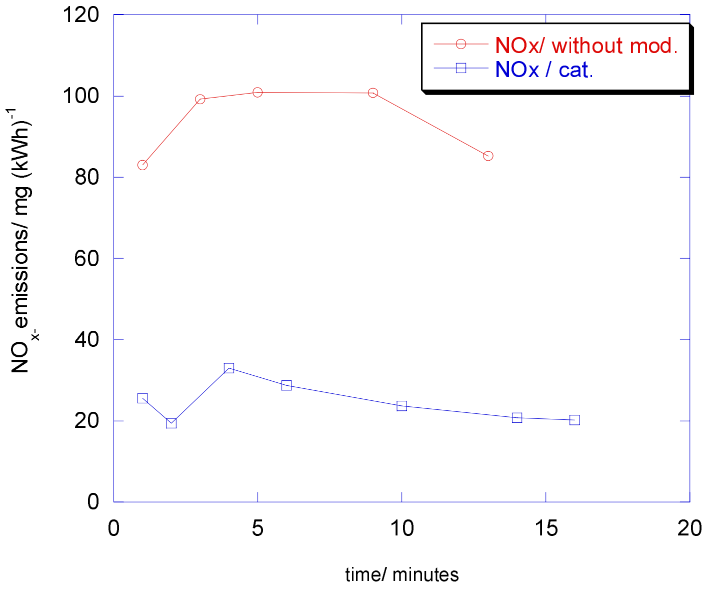


Fig. 7a.

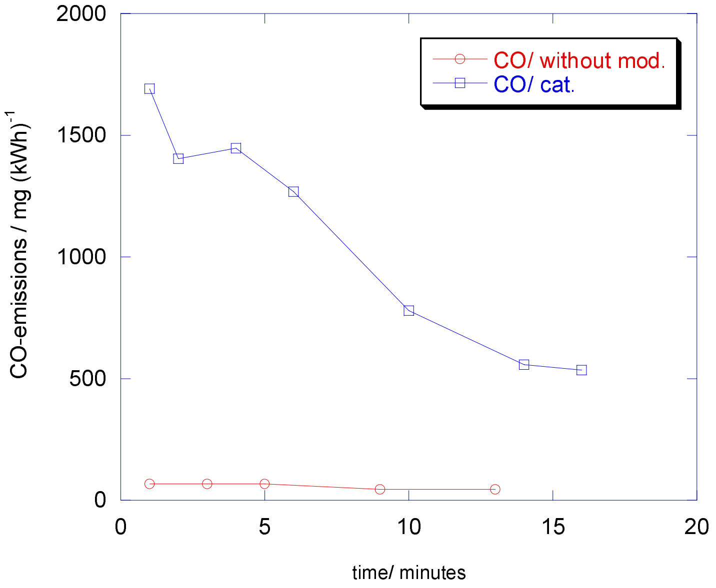


Fig. 7b.

***Fig. 7**. Emissions of a) NO$_x$ and b) CO as a function of time (i.e. t=0 is the time when the burner is switched on to maximal power output). The experiments were performed with natural gas and the catalyst used was the fcwm35.*

3.2. Different catalyst designs

In Fig. 8, the emission results measured with different catalyst alternatives (see Table 2) are summarised. Similar to the results shown in Figs. 5 and 6, the given emission levels are those detected when steady-state had been reached. With respect to the emitted NO_x, the following can be concluded:

- the wire-mesh ring seems to be a better concept than the catalytic coil.
- the mesh number of the wire-mesh ring does not play a significant role.
- the difference in emissions and hence, in activity between a coated and a uncoated catalyst is approximately 30%.

Furthermore, with respect to the CO-emissions, the differences in result between the various alternatives were more significant than with respect to the emitted NO_x-levels. In this case, the folded wire-mesh catalytic concept resulted in about 2,5 times less CO than what was measured with the other alternatives. This result is attributed to the fact that the folded wire-mesh has a larger catalytic surface area than the other concepts in combination with that the folded structure to a less extent disturbes the primary aeration. Moreover, the difference in result between the washcoated and un-washcoated is about 15 %. This small difference in activity is not surprising, since the un-washcoated wire-mesh had been coated with a porous layer of metal, see “Experimental”, section 2, which provides a certain extent of catalytic activity. Finally, except for different geometries and mesh numbers of the catalyst assembly, the effect of various washcoatings (i.e. different ceramic layers, e.g. TiO_2, ZrO_2) were also examined, but no significant difference in emission results among the different coatings applied could be detected in this investigation.

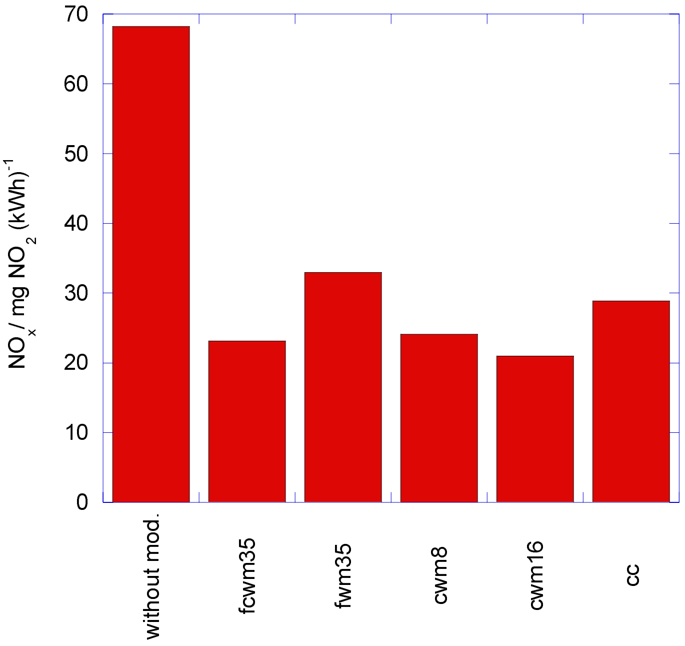


Fig. 8a.

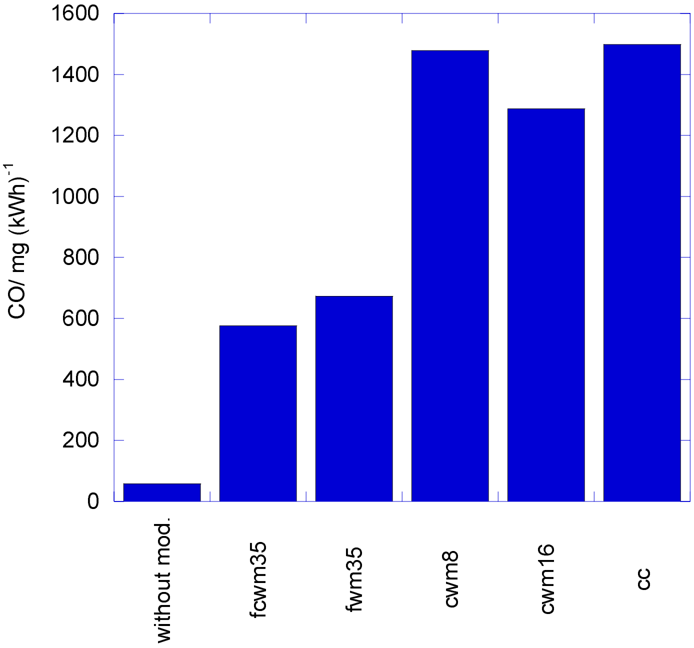


Fig. 8b.

Fig. 8. *Emissions of a) NO_x and b) CO measured with various catalyst alternatives with the 1,75 kW burner, over which a pan was positioned. The measurements were performed with natural gas.*

The thermal efficiency of the gas stove is expected to be rather low since very much of the hot gases will pass by the pan. Measurements with water heating indicated a thermal efficiency of about 35 % when no modification of the burner was made, see Fig. 9. Similar to the results obtained with the IGF Kavalkad gas stove, which are presented in the feasability report [1], all the catalytic alternatives were shown to somewhat increase the thermal efficiency, probably attributed to effects of thermal radiation.

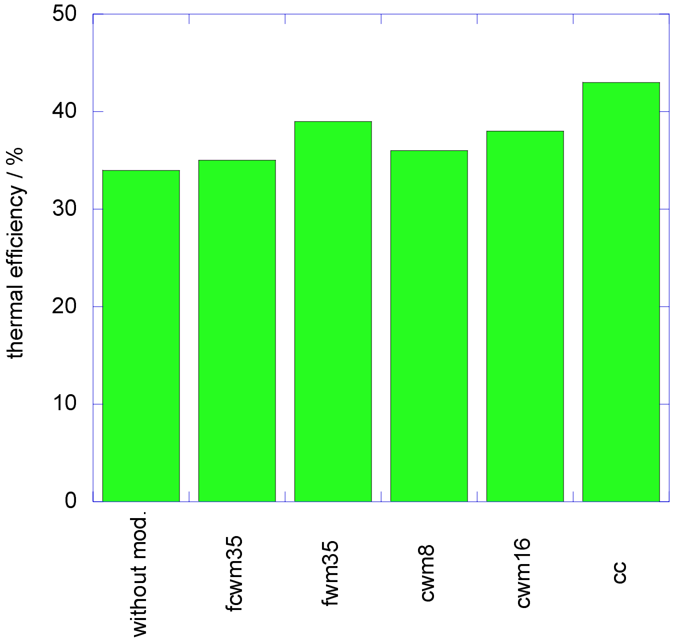


Fig. 9. *Thermal efficiency estimated by water heating for various catalyst alternatives. The measurements were performed with naural gas.*

3.3. Construction of burner

When a burner of a gas stove is evaluated with respect to emissions as is described in the previous sections, it is of interest to ask whether these results are valid for all types of conventional gas stoves or if every single type of commercial gas stove has to be investigated in order to ensure that the given conclusions are valid in a wider perspective. To get an idea of the latter, the results obtained in this investigation are compared with results obtained under the same experimental conditions (i.e. same catalyst concept, same gas composition), but with the IGF Kavalkad gas stove. The data collected with the IGF Kavalkad gas stove are the data that are presented in the feasability report [1].

Figs. 10a and b present a comparison between the emission of NO_x and CO measured when the IGF Kavalkad and IGF Noblesse gas stove were in use. As can be seen in Fig. 10a, there is no significant difference in NO_X-emissions between the two gas stoves. However, a much higher concentration of CO, i.e. up to 7 times, was detected when the IGF Kavalkad gas stove was used, Fig. 10b. It should be noted that the difference between the two stoves in emitted CO is much larger than the corresponding difference observed between the tested catalyst alternatives (section 3.2). This result points strongly to that the emissions of CO is mostly dependent on the construction of the burner, and that the catalyst concept, in this case, seems to play a more minor role.

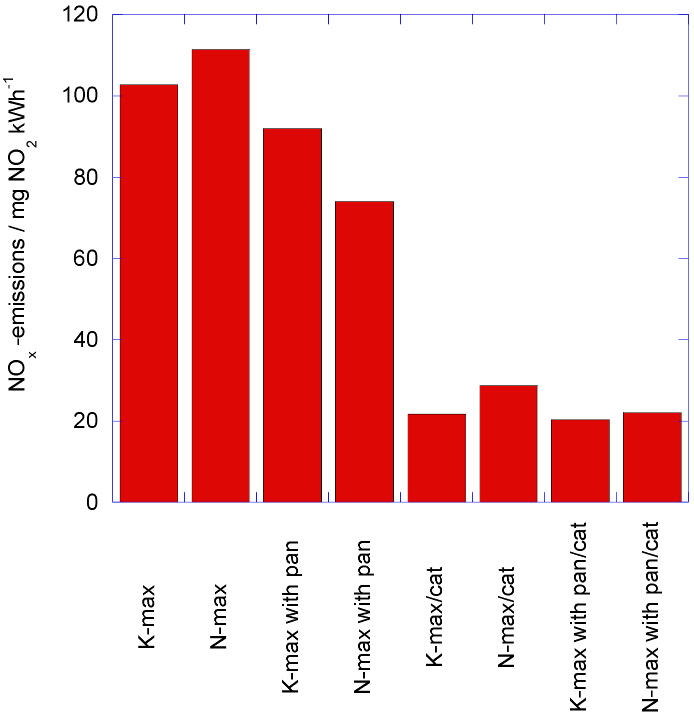


Fig. 10a.

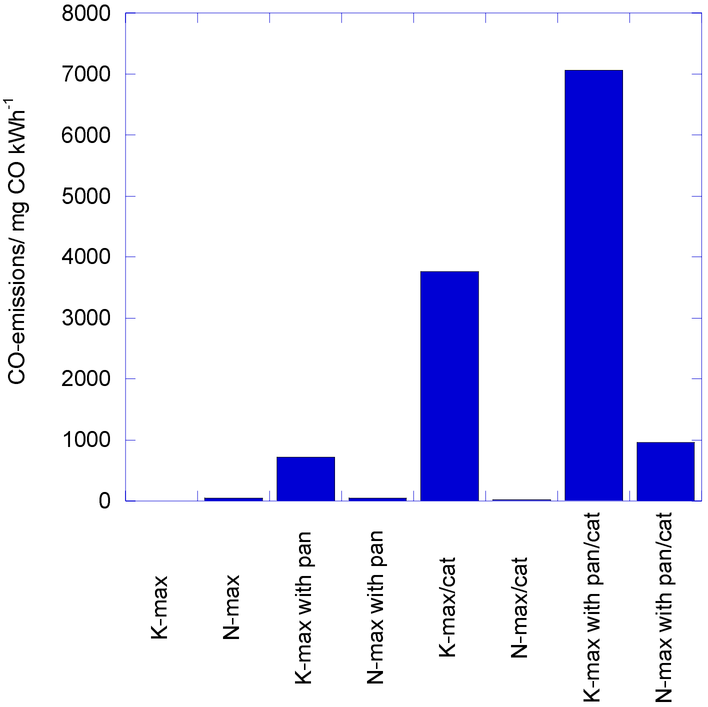


Fig. 10b.

Fig. 10. *Emissions of a) NO_x and b) CO measured under various conditions, using the middle-size burner of the IGF Kavalkad (K) and the IGF Noblesse (N) gas stove. The catalyst used was the cwm16. The experiments were performed with natural gas.*

To further illustrate the importance of the burner construction and hence, the influence of the degree of primary aeration of the combustion, the injector/nozzle adapted for the middle size burner (i.e. 0.95 mm in diameter, 1.75 kW, natural gas) was replaced with the injector adapted for the smallest burner of the gas stove (i.e. 0.70 mm in diameter, 1 kW). The measurements were performed at maximal power output with a pan placed above the burner. The results are shown in Fig. 11a and b. Even though the NO_x concentration was only slightly reduced by the installation of the smaller injector, a drastic decline of the CO emissions was obtained, i.e. about 60 %. This result can be explained by the theoretical relation shown in Fig. 12, which is valid for natural gas in conventional atmospheric burners [6]. By using a smaller nozzle diameter, the ratio between the area of the nozzle, A_0, and the area of the flame ports, A_p, will decrease, which results in an increase of the primary aeration. The same beneficial effect can thus also be achieved by increasing the flame port area. Besides the ratio A_p/A_0, Fig. 12 shows the possible flame port load at a pressure of 100 Pa. As can be seen, the flame port load decreases, as expected, with the degree of aeration.

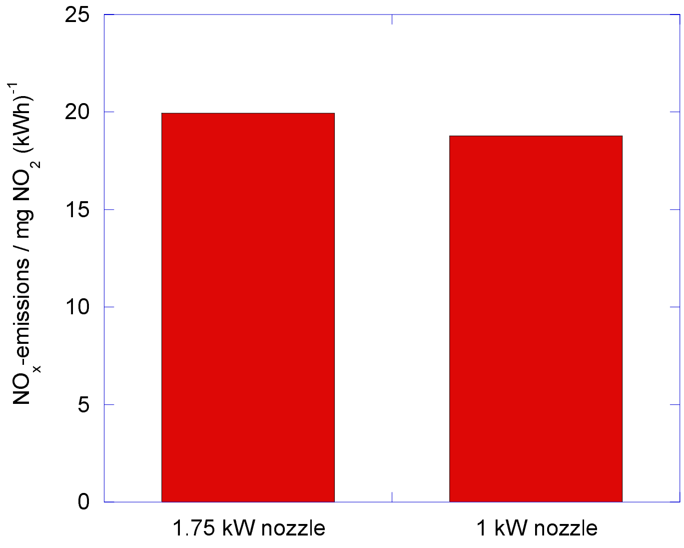


Fig. 11a.

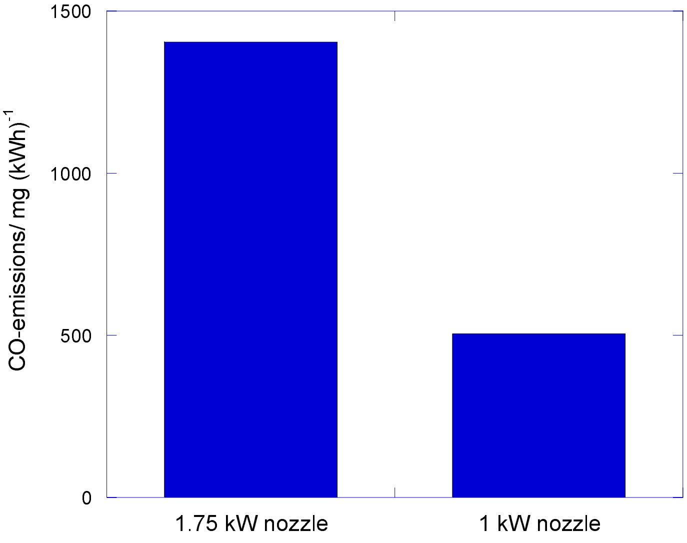


Fig. 11b.

Fig. 11. *The influence of nozzle diameter on the emissions of a) NO_x and b) CO. The measurements were performed at maximal power with the middle size burner. Natural gas was used and the catalyst concept was the cwm16.*

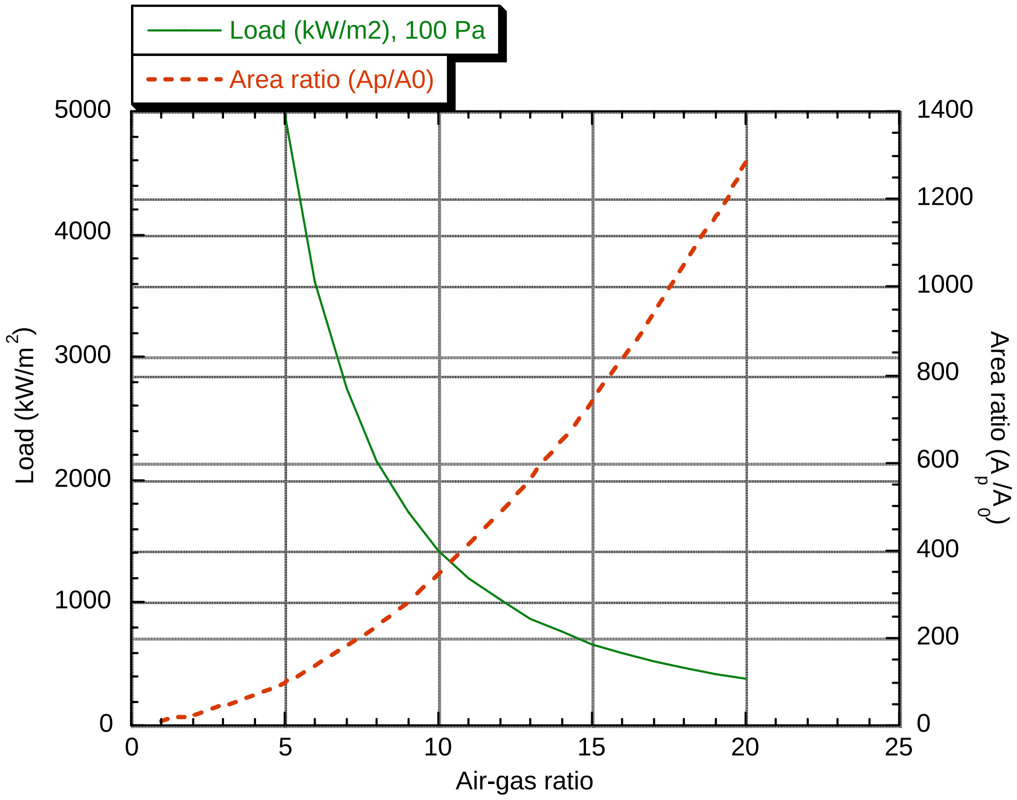


Fig. 12. *Air-gas ratio in atmospheric burners as a function of the ratio between the flame port area (A_p) and the nozzle area (A_0).*

3.4. Deactivation of catalyst

Figs. 13-14, illustrate the results of the deactivation study of the catalyst. The catalyst used in this series of experiments was the cwm16. Except for salt, no deactivation of catalyst could be detected for any of the tested food spillages. Similar results were observed for both natural and town gas. All the organic residues that were painted onto the hot catalyst burnt within a few seconds and consequently, had no significant impact on the activity of the catalyst. Salt crystals were however seen to block some parts of the catalyst, which resulted in a significant increase of ordinary flame combustion. This increased tendency for flame combustion was in particular clearly illustrated when natural gas was used. In this case, a significant raise in emitted NO_x could be measured, simultaneously as the CO concentration was seen to be reduced, Figs. 13a-b. However, in the case of town gas, the salt deactivation was instead illustrated by a significant increase of unburned fuel gas (i.e. CO and CH_4) in the flue gases, Figs. 14a-b.

Even though the salt crystals were seen to somewhat block the active sites of the catalyst, this is not, with respect to the catalyst's life-time, a serious effect. The salt could easily be eliminated by washing the catalyst in ordinary water, and after that the catalyst had been heated up again, the catalyst was observed to be fully re-activated, i.e. the same levels of emissions were detected as prior to the deactivation.

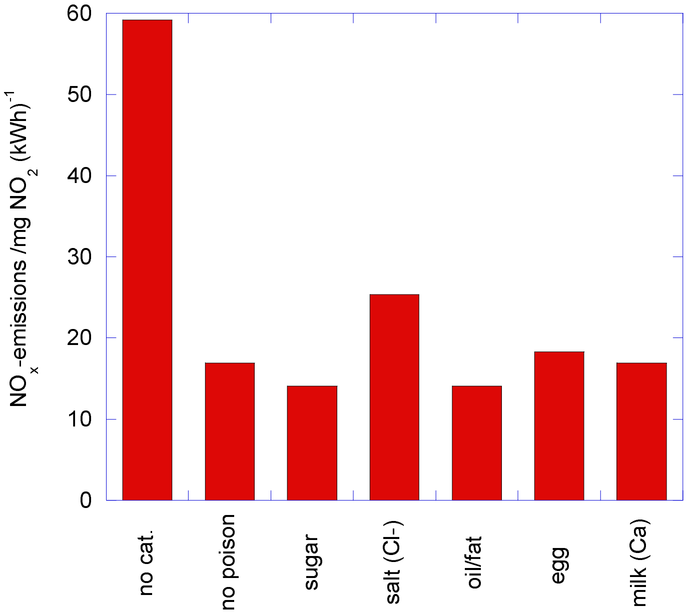


Fig. 13a.

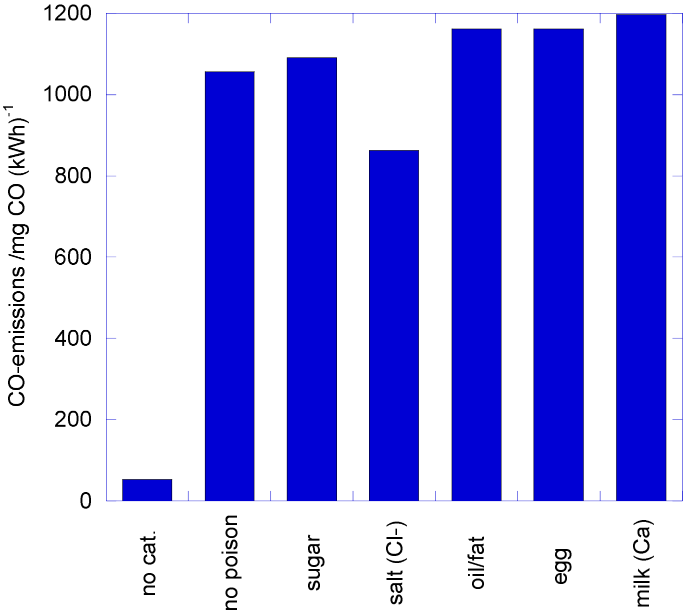


Fig. 13b.

Fig. 13. *Study of deactivation of catalyst, illustrated as emissions of a) NOx and b) CO. The measurements were performed with natural gas using the cwm16.*

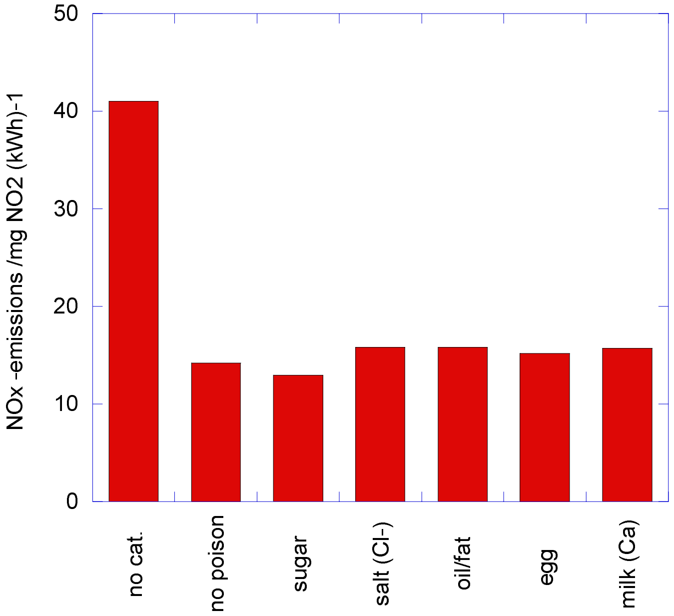


Fig. 14a.

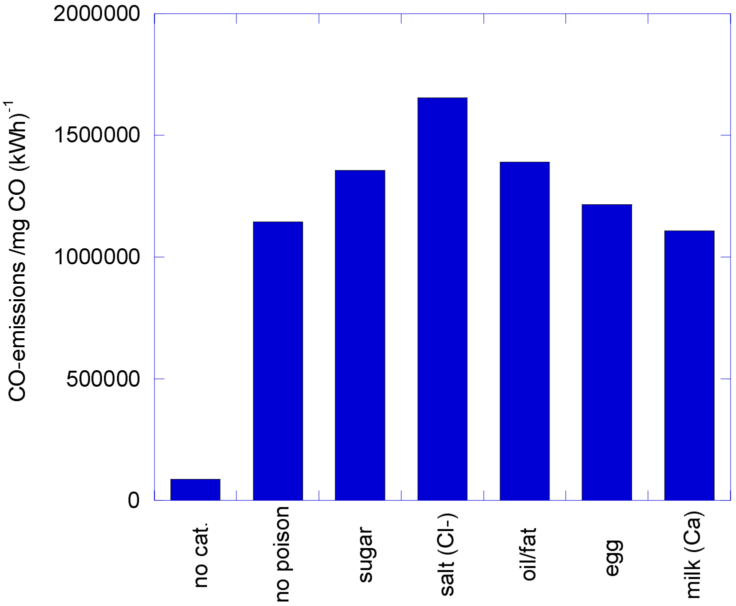


Fig. 14b.

Fig. 14. *Study of deactivation of catalyst, illustrated as emissions of a) NOx and b) CO. The measurements were performed with town gas using the cwm16.*

3.5. Characteristics of the oven

The effect of simply placing a wire-mesh catalyst downstream the flame ports of the burner positioned in the gas oven is displayed in Figs. 14a-c. The given concentrations are those values that were measured after that the oven had been on for 15-20 minutes at maximal output power, which is also the recommended preheating time, by the user guide, before food is placed inside. The evaluation with time during the preheat can be seen in Figs. 15a-c. It can be concluded that, similar to the results obtained with the 1.75 kW burner, the concentration of formed NO_x in the flue gases can be greatly reduced, up to 90 %, by a simple retro-fit catalyst installation. Furthermore, for the same reasons as was described in section 3.2, an increased concentration of CO was detected when the catalyst was used, even though this raise was not as serious as for the 1.75 kW burner, i.e. about 5 times higher than when conventional combustion takes place. In addition, rather high concentrations of CH_4 could be measured, thus pointing to that the presence of the catalyst in this case increased significantly the degree of uncompleted combustion. Surprisingly, the emissions could not be reduced to any great extent by increasing the distance of the air intake gap, Figs. 14b-c. This indicates that it might in this case be necessary to re-design the nozzle and the flame ports of the burner in order to arrive at full aeration (see Fig. 12), and thereby, arrive at low emissions of CO and CH_4.

Another aspect, except for the emissions to the atmosphere, that should be briefly discussed when examining a gas oven, are the health risks that are related to the fact that food is in direct contact with the flue gases during the time of cooking/baking. A large number of scientific studies [4,5] have reported on the risks for formation of carcinogenic nitrosamines in the food, most probabaly caused by chemical reactions between produced NO_x circulating in the oven and proteins in the food. To get an idea of eventuel health risks of this kind, NO_x were measured inside the oven during usage. At flame combustion, the concentration of NO_x was about 8 ppm (19 % O_2), while at catalytic combustion, a concentration of 1-2 ppm was detected (19 % O_2). According to the literature, no indication of nitrosamines have been observed in food (fish and bread) which have been prepared in gas ovens in which the NO_x concentration has been measured to be in the range of 3-26 ppm. It can thus be concluded that cooking/baking in this gas oven should not result in any levels of nitrosamines that may have an impact on human health.

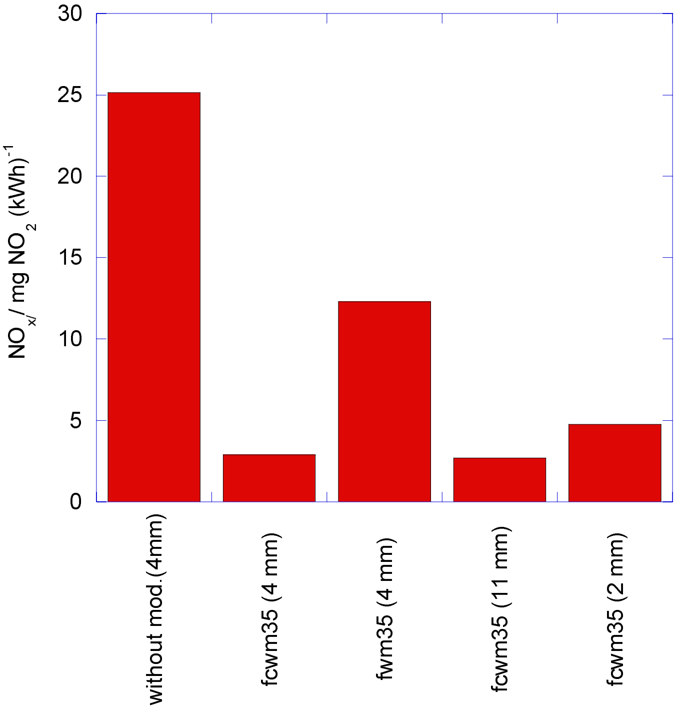


Fig. 15a.

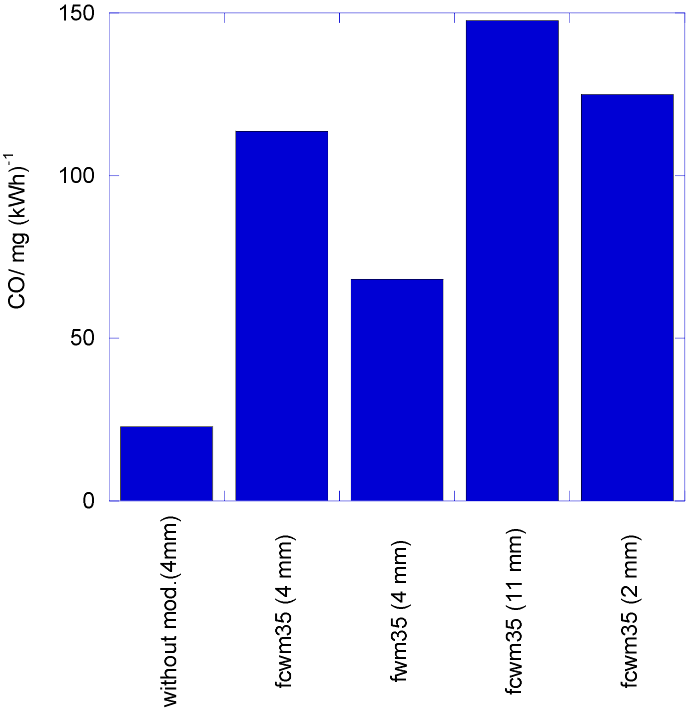


Fig. 15b.

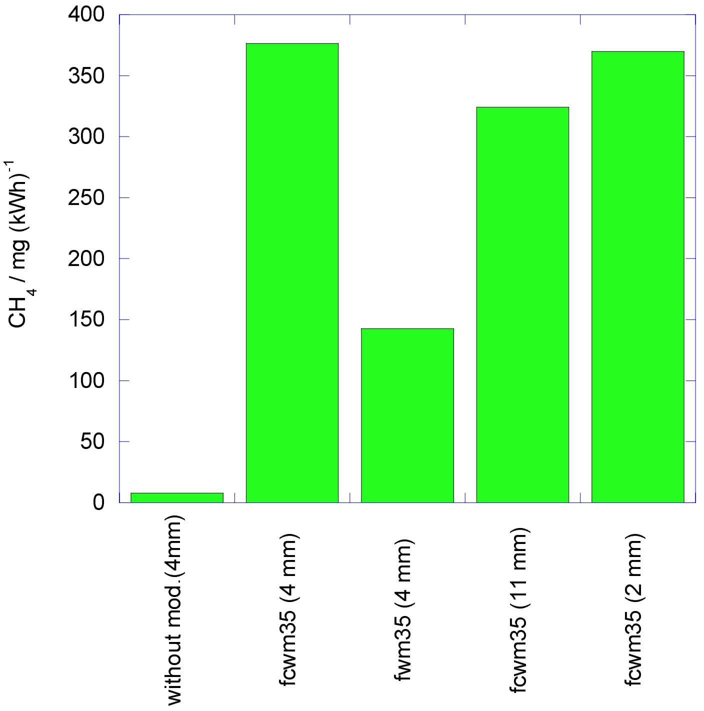


Fig. 15c.

Fig. 15. *Emissions of a) NO$_x$, b) CO and c) CH$_4$ measured in the exhaust pipe when the oven was set to its maximal power output, i.e. 240 °C. The experiments were performed with natural gas.*

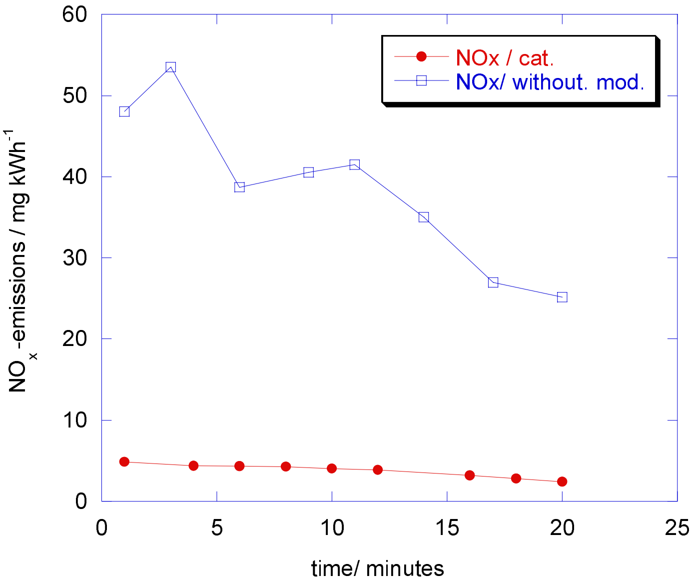


Fig. 16a.

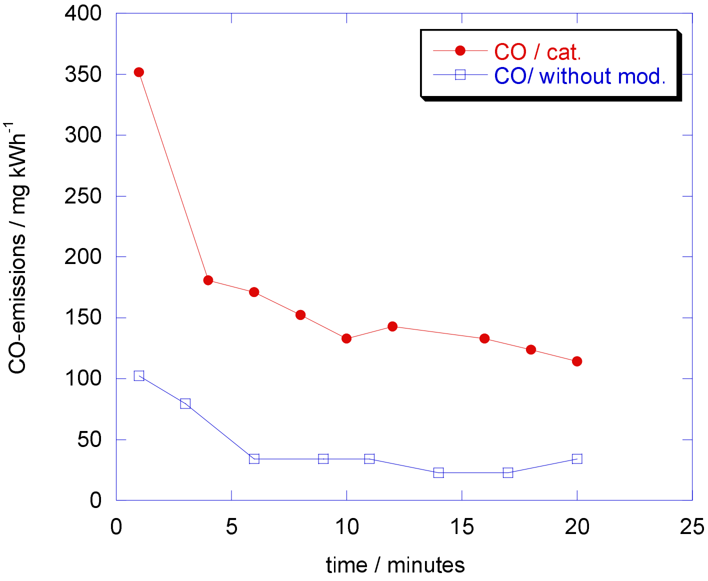


Fig. 16b.

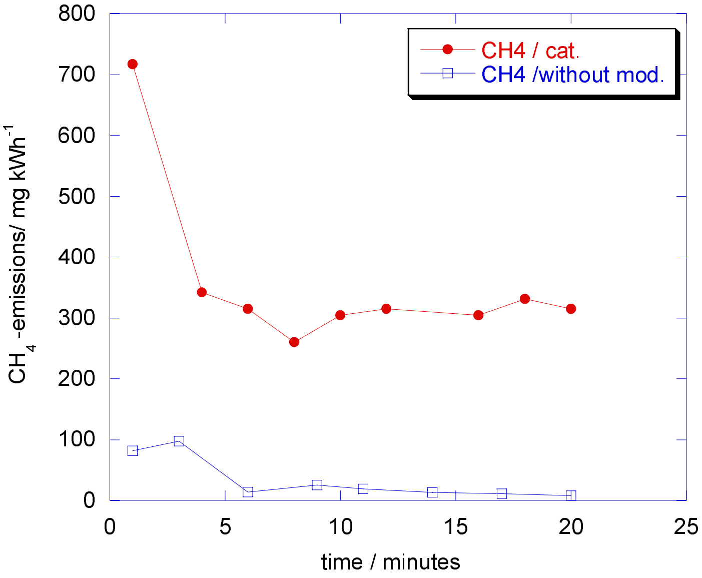


Fig. 16c.

Fig. 16. *Emissions of a) NO$_x$, b) CO and c) CH$_4$ as a function of time. The catalyst used was the fcwm35.*

4. Consequences

It is reasonable to expect a strong correlation between the source strength of the emissions (NO_x, CO) and the indoor concentrations. To get an idea of the consequences of the measured emissions on the indoor quality in this case, a dynamic simulation model, presented in the feasability report of this work [1], was used. In brief, the model assumes a room volume of 30 m^3 with an infiltration ventilation flow rate of 15 nm^3/h and that a forced ventilation flow of 200 nm^3/h is in operation when the gas stove is in use. Moreover, the capture efficiency of the hood was set to 70% and NO_2 was assumed to decay according to a first order reaction scheme with a rate of 0.5 h^{-1}. The concentration changes were simulated during a day (24 h) when the gas stove was used according to a scheme presented by Stymne [7], see Table 5 below. It should be underlined that the absolute values of the calculated concentrations given in Figs. 16-18 can only be considered as approximate, since these are strongly dependent on the assumed values of the indata parameters, e.g. capture efficiency of ventilation hood, used in the simulation. Still, these results give us an indication of the magnitudes of the indoor dosages corresponding to the measured source strengths of NO_2 and CO for the case with a conventional and catalytic cooking plate, respectively.

Table 5. *Utilisation patter of the gas stove according to Stymne [6].*

Activity	Duration (time)	Effect (kW)
Coffee	07.00 – 07.05	3
Coffee	09.30 – 09.35	3
Boiling	11.30 – 11.40	3
Boiling	11.40 – 11.50	0.5
Boiling/broiling	11.50 – 12.00	3.5
Coffee	12.15 – 12.20	3
Coffee	15.00 – 15.05	3
Boiling	17.30 – 17.35	3
Boiling	17.35 – 17.45	0.5
Broiling	17.45 – 17.50	3
Coffee	18.10 – 18.15	3
Tea	21.00 – 21.05	3

The raw emissions used as indata were those values that are displayed in Figs. 5a-b, thus, 111 and 28 mg/ kW NO_x at maximal power output at ordinary flame and catalytic combustion, respectively. Furthermore, the source strength of NO_x at maximal power when a pan was placed above the burner at catalytic combustion was 22 mg/kW. The corresponding source strengths of CO used in the simulations were 45, 21 and 960 mg/kW, respectively. Fig. 16 shows the concentration variations of NO_x during one day. As expected, the peak concentrations are for all cases obtained at lunch, i.e. about 350 $\mu g/m^3$ (0.2 ppm) and 120 $\mu g/m^3$ (0.06 ppm) at maximal power without and with catalyst. These peak concentrations are above the average outdoor concentration, i.e. 40 $\mu g/m^3$.

However, for judging whether these emissions have any detrimental health impact, the corresponding integrated (accumulated) NO_x dosages, during the 24 h, were calculated. Fig. 17 shows the integrated NO_x-ratio indoor:outdoor for conventional and catalytic combustion. As seen, the integral concentration will change much slower than the momentary concentration, as indicated in Fig. 16. For the ordinary flame combustion, the NO_x concentration will build up to levels about twice as high as the outdoor concentrion during the course of the day. For the catalytic case however, the indoor integral concentration is below or the same as the outdoor concentration. Consequently, it can be concluded that the use of catalytic cooking plates does not seem to cause any additional NO_x -related health risks.

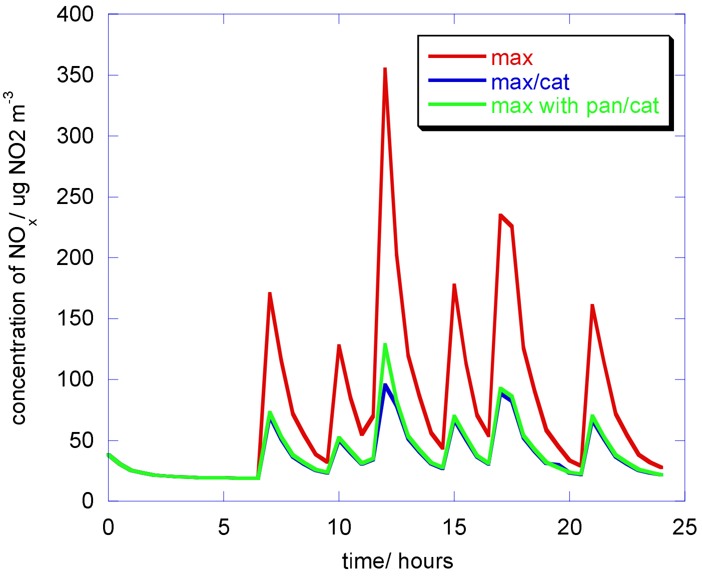


Fig. 16. *Consequences of catalytic combustion on the NO_x emissions. Outdoor level: 40 µg/m* (20 ppb). *The catalyst used was the cwm16.*

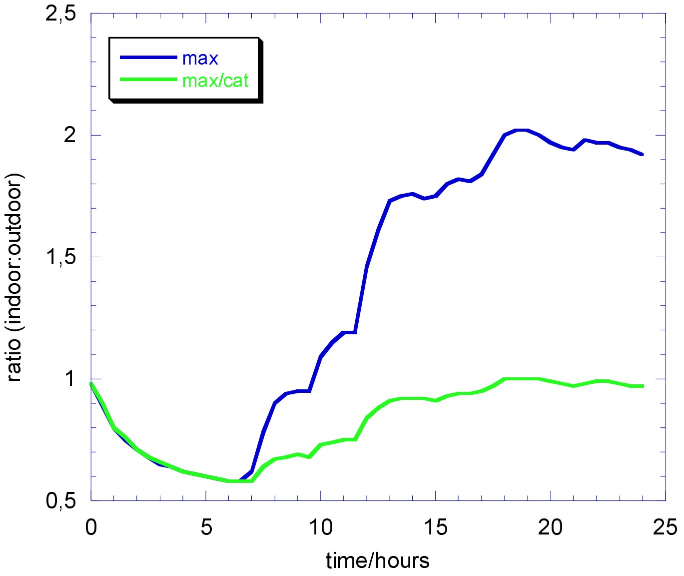


Fig. 17. *NO_x-ratio indoor:outdoor, comparison between conventional and catalytic combustion. The catalyst is was the cwm16.*

As expected, the peak concentrations of CO at catalytic combustion coincide with the peak concentrations of NO_x, Fig. 18. Even though the peak concentrations of CO (2-3 ppm) is about 10-12 times higher than those obtained for NO_x (when a pan is placed above the burner), this does not provide any additional health risks. According to reference [7], there is no danger for health effects on a person who is exposed to <35 ppm CO for < 8 h.

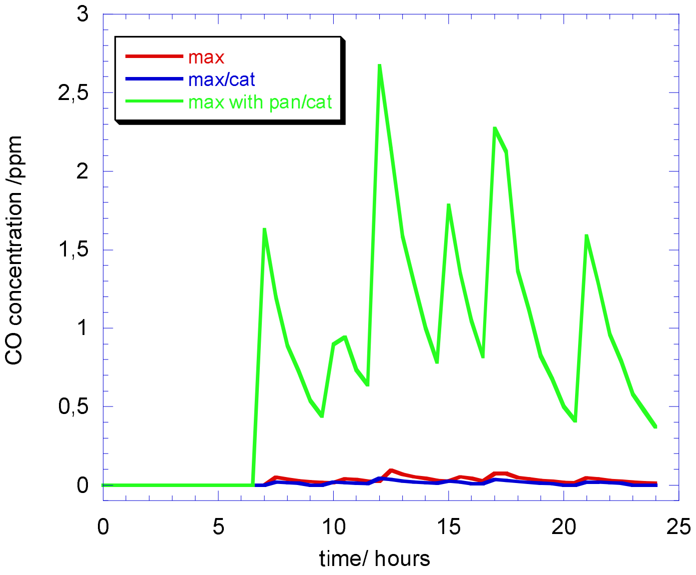


Fig. 18. *Consequences of catalytic combustion on the CO emission. The catalyst used was the cwm16.*

l

5. Conclusions

This work shows that catalytic combustion can be easily realised in existing atmospheric burners in gas stoves. The design modifications are very modest and the amount of catalyst is small, about 6-10 SEK per cooking plate.

The measurements, performed with both natural and town gas, indicate that a simple retro-fit catalytic installation can reduce the NO_x emissions up to 80% when the gas stove is in use. Under these circumstances, the indoor concentration of NO_x will be below or equal to the outdoor concentration. Consequently, no additional detrimental NO_x related health effects seem to be probable. Another advantage of the retro-fit design compared to the conventional one is that the thermal efficiency of the cooking plate seems to somewhat increase. Furthermore, the drawback of this design is that it results in rather high CO emissions and in some cases also, rather high concentrations of unburned gas. To overcome this, a re-design of the existing burners needs to be made, e.g. change of nozzle diameter or flame port plate surface area.

The effect of a simple retro-fit catalytic modification of the burner positioned in the oven was also exmined. Similar to the cooking plates, the NO_x emissions could be significantly reduced, i.e. up to 90 %.

Finally, no deactivation of the catalysts could be observed by spillage of common food ingredients such as milk, sugar, egg or oil onto the hot catalyst. In contrast to the organic spillages, salt was seen to block the active sites of the catalyst and hence, the tendency for flame combustion was increased. This was however not a serious effect, since a salt-poisoned catalyst could easily be reactivated by rinsing it in ordinary tap water.

6. References

[1] F. Silversand, Catator AB, “Catalytic combustion in gas stoves-feasability study”, Rapport SGC 1212, April 2002.
[2] V. Hasselblad, D.M. Eddy and D.J. Kotchmar, J. Of the Air & Waste Management Association, v 42 5 May 1992, p. 662-671.
[3] J. Jensen, H. Andersen, B. Schmidt and N.B. Rasmussen ”NO_2-koncentrationer i køkkener med gaskomfur”, DGC 719.26, Danskt Gastekniskt center a/s Hørsholm 1999.
[4] B.E. Jensen et al., Nitrat och nitrit i köttvaror. Statens livsmedelsinstitut, 1981.
[5] J. Gry et al., Undersökning över nitriters betydelse för kommersiell framställning av köttvaror på den danska marknaden. Statens livsmedelsinstitut, 1983.
[6] R. Pritchard, J.J. Guy and N.E. Connor, ”Industrial Gas Utilization”, British Gas Corposarion, ISBN 0-85935-059-2, 1978, p. 232.
[7] AFS, 2000:3, ”Hygieniska gränsvärden och åtgärder mot luftföroreningar”, 2003, p. 46.

SE-205 09 MALMÖ • TEL 040-24 43 10 • FAX 040-24 43 14
Hemsida www.sgc.se • epost info@sgc.se