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The effect of vitiation on trace pollutants from domestic gas appliances

The effect of vitiation on the generation of carbon monoxide and nitrogen oxides from various types of domestic appliances has been studied quantitatively. Special features noted were the large increase in carbon monoxide generation with higher levels of vitiation by certain types of appliances and the unusual conversion of nitrogen dioxide to nitric oxide in room environments

This short practical paper describes what has been considered worthy of attention in everyday practice. Publications and Conferences Committee will welcome short, practical papers on other topics to consider for publication.

1. Introduction

Unflued gas appliances have for some time been recognized as a source of indoor pollution.[1–5] They are not unique in this regard and other sources,[6] particularly kerosine heaters[5,7–10] and sidestream cigarette smoke[4,5,11] have been investigated.

Concern about gas appliances seems to have centred on cookers[1,2,5,12] although, with the 'tightening' of buildings[4,6,8,10] as an energy conservation measure, some emphasis has been placed on unflued (unvented) space heaters.[3,11]

In this study tests were conducted on unflued space-heaters, cooking ranges, sink heaters (water heaters) and a gas refrigerator. It was found that in all cases measurable quantities of pollutants (nitrogen oxides and/or carbon monoxide) were produced when the appliance operated in fresh air.

When the air was allowed to vitiate (caused by partial recirculation of combustion products, which results in a decrease in the oxygen content and a corresponding increase in the levels of nitrogen, carbon dioxide and water vapour), it was found that the concentration of carbon monoxide in the exit combustion gases increased appreciably. In the case of water heaters large increases in carbon monoxide production occurred with higher levels of vitiation. These circumstances have resulted in cases of fatal poisoning in Western Australia and elsewhere. As noted in the authors' previous paper,[13] vitiation was found to have a profound effect on the nature of the nitrogen oxides produced by certain types of appliances, changing it from a predominance of nitric oxide over nitrogen dioxide when the appliance operated in fresh air to the reverse under highly vitiated conditions.

It was also found that the two principal oxides of nitrogen behaved in an unexpected manner in the vitiation test room, with the apparent formation of nitric oxide from nitrogen dioxide on standing.

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2. Experimental

2.1. Gas appliances

2.1.1. Natural-gas-fired domestic radiant (infra-red) heaters

Radiant heaters of the front-vented and top-vented type were used. Typical results from one of each class are reported in this paper. The relevant data for these two heaters are presented in Table 1. It may be noted that the higher input per unit tile area and less circuitous path of the exit gases in the case of the top-vented heater results in much higher discharge temperatures.

A discussion on the mechanism of radiant burners can be found in ref 14.

2.1.2. Natural gas cooking ranges

The ranges used in these tests had the following burners:

2.1.2.1. Cooker A

(*a*) Top boiling burners of this appliance were not used in these tests.
(*b*) Griller—radiant type with a metal mesh burner of 15 MJ/h maximum setting.
(*c*) Oven—11 MJ/h maximum setting.

2.1.2.2. Cooker B

(*a*) Top boiling burners—two front of 10.5 MJ/h each and two back of 7.5 MJ/h each.
(*b*) Griller—radiant type (similar to cooker A) of 14 MJ/h maximum setting.
(*c*) Oven—13 MJ/h maximum setting.

2.1.3. Natural gas sink heater (water heater)

This was unflued, typical of the heaters used in flats. Nominal thermal input of 37.5 MJ/h.

2.1.4. Liquefied petroleum gas refrigerator

This unit is typical of the type of appliances used in caravans and motor-homes. It had a thermal input of approximately 0.85 MJ/h.

2.2. Monitoring equipment and test facilities

In addition to the monitoring and test facilities described in the authors' previous paper,[13] a higher range chemiluminescence (for nitrogen oxides) and a second infra-red

TABLE 1 Comparison of typical top-vented and front-vented unflued space-heaters

					Exit gases					
		Thermal input	Burner loading	Discharge temperature	CO	CO_2	NO	NO_2	Ratios × 10^4	
Heater type	Fan setting	MJ/h	kW/m²	°C	(ppm)	(%)	(ppm)	(ppm)	NO/CO_2	NO_2/CO_2
Front-vented	On	18	125	≈200	29	0.45	0.05	0.7	0.1	1.6
Front-vented	Off	18	125	≈200	53	0.94	0.05	1.4	0.05	1.5
Top-vented	No fan	11	160	≈500	8	1.56	0.45	1.3	0.3	0.8

analyser (for carbon oxides) were used. The second CO/CO_2 analyser was a lower precision instrument and, for this reason, results obtained with it are quoted to less significant figures. An oxygen meter was also used. As before,[13] vitiation tests were conducted in a 19 m³ sealed room.

All concentrations are on a volume/volume basis and the CO, CO_2 and oxygen concentrations are 'dry'.

3. Results and discussion

3.1. Space-heaters

In a previous publication,[13] it was shown that the nitrogen oxides (NO_x) generated by a convective space-heater consisted largely of nitric oxide (NO), while radiant space-heaters generated mostly nitrogen dioxide (NO_2). These results are essentially similar to those of Leaderer[8] and Traynor *et al*[3] for kerosine heaters.

3.1.1. Radiant heaters

Table 1 summarizes the results of operating typical front-vented and top-vented radiant heaters in fresh air at nominal gassing rates. It is seen that the proportion of NO_x present as NO is higher in the top-vented design. In the front-vented design, the NO_x is seen to be almost entirely NO_2. These results appear to be consistent with the view that cooler flames, such as occur in radiant heaters,[14,15] especially front-vented designs, are conducive to the generation of hydroperoxyl radicals[16,17] that oxidize much of the NO to NO_2.

The effects of gas input rates above and below nominal on the top-vented heater are shown in Fig. 1. It is seen that a decrease in the NO_x/CO_2 ratio occurred with increased thermal input. (This decrease was the net result of a small increase in the NO/CO_2 ratio and a large decrease in the NO_2/CO_2 ratio.) A decrease in the NO_x generation with increasing thermal input is the opposite of what might be expected if all the NO_x was formed by the highly temperature-sensitive Zeldovich mechanism[15,18,19] and suggests that the main route of NO_x formation in radiant heaters is the much less temperature-sensitive prompt mechanism.[20,21,22] Leaderer[8] has reported relatively greater rates of NO_x (mainly NO_2) formation at lower settings with radiant kerosine heaters.

Table 2 shows the results of running the front-vented heater in the vitiation room. The result for the top-

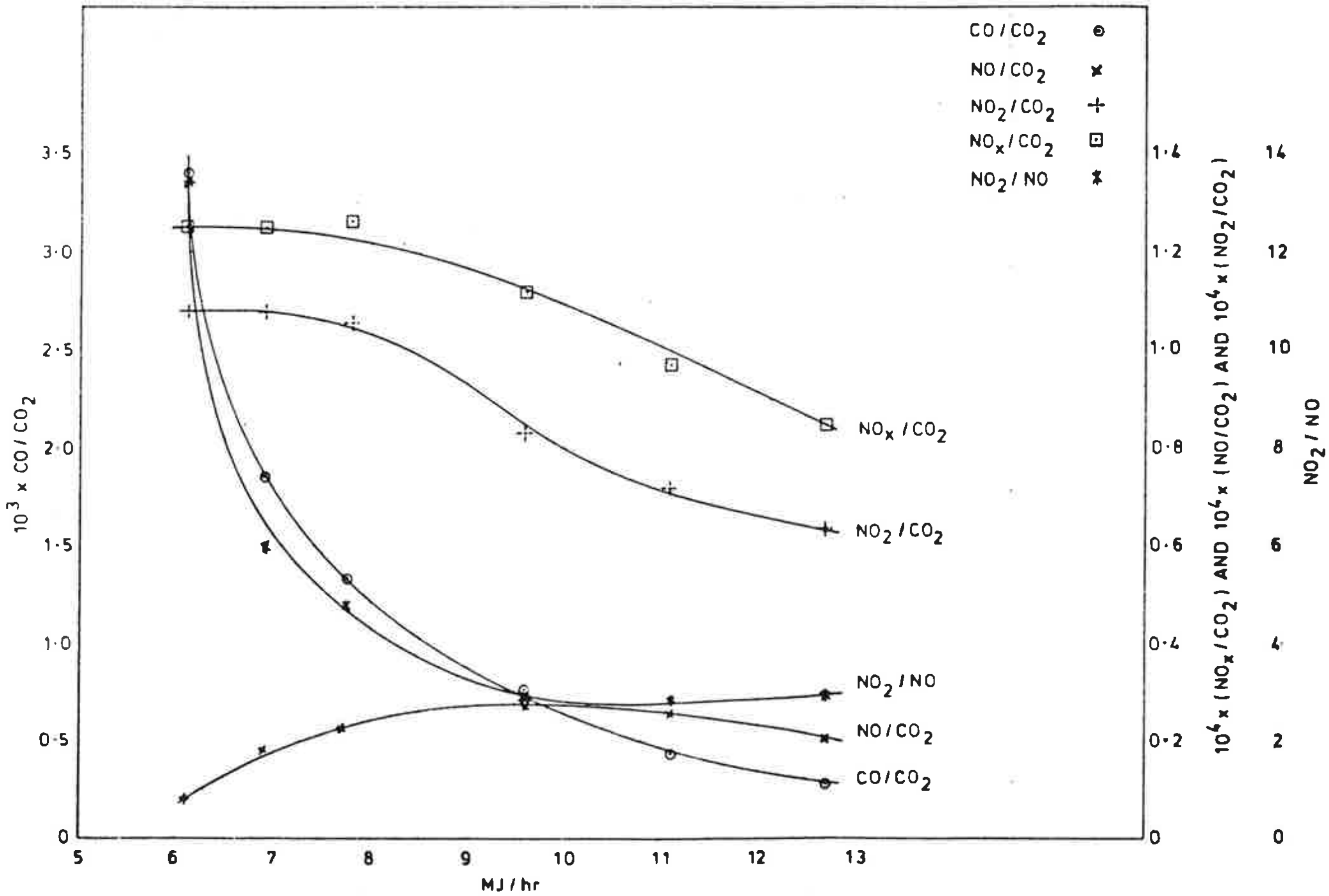

FIG. 1 Effect of gassing rate on pollutant generation—top-vented unflued radiant heater of nominal input 11 MJ/h

TABLE 2 Front-vented radiant space-heater (18 MJ/h)
Heater ran to extinction in vitiation room. Room left sealed and atmosphere monitored for approximately 24 hours

Time from ignition	Exit gases						Room atmosphere					
	NO	NO_2	CO	CO_2	Ratios × 10^4		NO	NO_2	CO	CO_2	Ratios × 10^4	
(min)	(ppm)	(ppm)	(ppm)	(%)	NO/CO_2	NO_2/CO_2	(ppm)	(ppm)	(ppm)	(%)	NO/CO_2	NO_2/CO_2
15	0.11	1.75	105	1.33	0.08	1.3						
20							0.10	0.74	61	0.93	0.11	0.80
25	0.15	2.40	142	1.90	0.08	1.3						
30							0.12	1.15	82	1.23	0.10	0.93
35	0.16	2.75	175	2 28	0.07	1.2						
40							0.16	1.65	114	1.65	0.10	1.00
45	0.19	3.15	234	2.72	0.07	1.2						
50							0.20	2.07	155	2.10	0.10	0.99
55	0.21	3.45	320	3.17	0.07	1.1						
60							0.21	2.60	213	2.52	0.08	1.03
65	0.23	3.75	462	3.59	0.06	1.0						
70							0.24	2.85	286	2.95	0.08	0.97
75	0.25	3.95	1000	3.96	0.06	1.0						
80							0.26	3.15	440	3.37	0.08	0.93
85	0.35	4.00	1610	4.16	0.08	1.0						
Heater self extinguished												
90							0.27	3.20	630	3.54	0.08	0.90
150							0.38	2.20	560	3.19	0.12	0.69
195							0.46	1.61	560	3.12	0.15	0.52
265							0.61	1.08	550	3.09	0.20	0.35
300							0.64	0.90	540	3.06	0.21	0.29
340							0.66	0.74	530	3.02	0.22	0.25
630							0.82	0.10	550	2.96	0.28	0.03
645							0.83	0.11	550	2.96	0.28	0.04
1260							0.82	0.0	510	2.63	0.31	0.0
1275							0.82	0.0	510	2.63	0.31	0.0
1290							0.82	0.0	500	2.59	0.32	0.0
1350							0.76	0.0	480	2.52	0.30	0.0
1380							0.74	0.0	480	2.48	0.30	0.0
1410							0.73	0.0	460	2.45	0.30	0.0
1440							0.70	0.0	460	2.44	0.29	0.0
1470							0.70	0.0	450	2.41	0.29	0.0
1490							0.69	0.0	450	2.40	0.29	0.0
1520							0.68	0.0	440	2.38	0.29	0.0

vented model is given in Table 3. It is seen that NO accounted for a higher proportion of the NO_x throughout the test with this heater than it did with the front-vented design. It is also evident that the relative proportion of the NO_x produced as NO by the top-vented heater fell as the level of vitiation increased. This change was, however, much smaller than the transition from mostly NO to mostly NO_2 which was observed when a convective heater operated under conditions of increasing vitiation.[13] It appears that the top-vented radiant heater, which operates at a higher temperature than the front-vented model, performs in a manner that is intermediate between those of the front-vented and convective heaters.

A surprising aspect which is shown in Table 2 is that after the heater extinguished itself (and the gas was turned off), the NO_2 concentration fell rapidly (by an almost exactly first order process) while the NO/CO_2 ratio rose by a factor of four. This result, which is also shown graphically in Fig. 2, represents a reversal of the widely accepted oxidation of NO to NO_2. This effect has been reproduced many times (on some occasions with different analytical instruments) in the vitiation room and another room, in which an unflued space-heater is installed. Generally, after extinction the NO/CO_2 ratio was found to increase until the NO_2 had all been consumed and then to fall away very slowly. Wade *et al*[1] found NO to be far more stable in a domestic room situation than NO_2 but did not report the formation of NO from NO_2. This effect (conversion of NO_2 to NO) was also found to occur in the vitiation room when the NO_2 was injected as a 2% NO_2 in a N_2 mixture (as distinct from being produced by an operating space-heater). All tests involving NO_2 were conducted in rooms in which unflued heaters had been used at some former time.

In general, unflued radiant space-heaters were found to be significant sources of NO_2, which is in agreement with the findings of Palmes *et al.*[3] As noted by Ryan *et al*,[10] in discussing kerosine heaters, gas stoves are incorrectly considered the major indoor source of NO_2. In fact, kerosine and unflued gas heaters usually run for longer periods and NO_2 exposure from such a source can easily exceed that from a gas stove.

TABLE 3 Top-vented radiant unflued space-heater (11 MJ/h); ran to extinction in vitiation room

Time from ignition	Exit gases						Room atmosphere					
	NO	NO_2	CO	CO_2	Ratios × 10^4		NO	NO_2	CO	CO_2	Ratios × 10^4	
(min)	(ppm)	(ppm)	(ppm)	(%)	NO/CO_2	NO_2/CO_2	(ppm)	(ppm)	(ppm)	(%)	NO/CO_2	NO_2/CO_2
5							0.37	0.30	10	0.18	2.1	1.7
10	0.75	0.88	30	0.6	1.3	1.5	0.43	0.44	20	0.30	1.4	1.5
40	0.82	1.89	40	1.5	0.55	1.3	0.57	1.10	30	1.15	0.50	0.90
50							0.78	1.40	40	1.55	0.50	0.90
55	0.96	1.82	40	1.9	0.51	1.3						
60							0.85	1.54	40	1.70	0.50	0.91
70	1.15	1.98	50	2.5	0.46	0.79	0.99	1.75	40	1.95	0.51	0.90
95	1.53	2.62	60	3.2	0.48	0.82	1.26	2.39	60	2.50	0.50	0.96
120	1.71	3.56	100	3.6	0.48	0.99	1.51	3.00	70	3.15	0.48	0.95
150							1.76	3.74	100	4.10	0.43	0.91
155							1.72	3.95	110	4.35	0.40	0.91
Heater self extinguished												

From Tables 2 and 3 it is seen that, for both the top- and front-vented heaters, the carbon monoxide to carbon dioxide ratio (CO/CO_2) in the exit gases increased appreciably with increasing levels of vitiation (the measure of the latter being the CO_2 content in the room atmosphere.[23]) The results indicate that the particular front-vented heater was more susceptible to CO generation under vitiation conditions than the top-vented model. However, no general conclusion concerning CO production by the two types of heaters is made, as the front-vented unit was of an older design. While the time-integrated concentrations reached were not likely to be lethal[24] to a healthy individual, they were in excess of what is considered by some authors[6,7] to be acceptable in a domestic situation.

In the authors' test series, high levels of CO resulted only with extreme levels of vitiation. However, concern about the safety of unflued heaters (CO generation and oxygen depletion) resulted in an attempt to have them banned in the United States.[25] At least sixty-five deaths were attributed to this type of appliance in the USA over a five-year period.[25] The proposal was, however, later withdrawn.[26]

3.1.2. Convective space-heaters

The results of tests on this type of heater can be found in the authors' previous paper.[13] It was found that these tended to produce more NO_x than radiant heaters and the NO_x was mostly NO in fresh air operation. Under conditions of increasing vitiation, however, a progressive transition from NO to NO_2 generation occurred.[13]

Testing with a recent model convective heater gave a NO_2/NO ratio of 0.19 when operating in fresh air, which supported the previous findings.[13]

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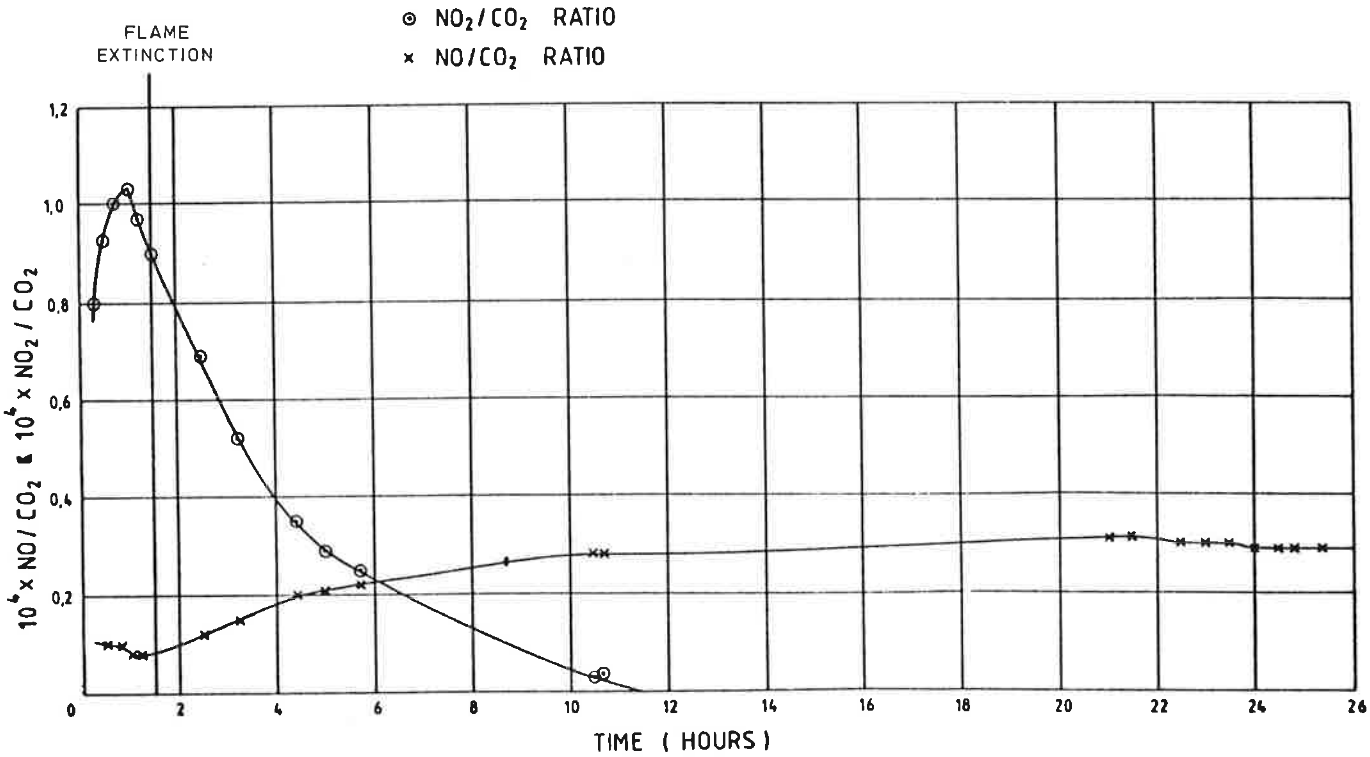

FIG. 2 Front-vented radiant heater in sealed vitiation room

TABLE 4 Effect on combustion products of operating both front burners of cooker B in vitiation room (burners were unloaded; exit gases sampled from collection hood)

Time from ignition	Exit gases							Room atmosphere			
	NO	NO_2	CO	CO_2	Ratios × 10^4			NO	NO_2	CO	CO_2
(min)	(ppm)	(ppm)	(ppm)	(%)	NO/CO_2	NO_2/CO_2	CO/CO_2	(ppm)	(ppm)	(ppm)	(%)
5	7.9	2.3	≈20	1.65	4.8	1.4	≈10	1.9	1.3	10	0.45
10	9.2	3.1	≈20	2.15	4.3	1.4	≈10				
15	10.0	4.3	≈20	2.4	4.2	1.8	≈10				
20	10.3	4.9	≈20	2.7	3.8	1.8	≈10	6.2	3.7	20	1.65
25	10.4	5.3	30	3.0	3.5	1.8	10				
30	9.4	6.1	40	3.2	2.9	1.9	13	6.8	4.8	20	2.75
35	8.0	7.2	80	3.5	2.3	2.1	23				
40	5.4	9.0	100	3.8	1.4	2.4	26	7.5	6.0	50	2.75
45	1.8	11.2	320	4.0	0.45	2.8	80	5.5	7.6	80	3.0
50	1.2	11.2	560	4.1	0.29	2.7	140	3.6	9.1	210	3.35

TABLE 5 Operation of radiant grillers in fresh air

Stove	Setting	Time from ignition (min)	Exit gases NO (ppm)	NO_2 (ppm)	CO (ppm)	CO_2 (%)	Ratios × 10^4 NO/CO_2	NO_2/CO_2	CO/CO_2
A	High	5	1.92	2.85	100	5.0	0.38	0.57	20
A	High	10	2.29	3.33	90	4.8	0.48	0.69	19
A	High	15	2.47	3.60	90	4.8	0.51	0.75	19
A	High	20	2.87	3.50	80	5.0	0.57	0.70	16
A	Low	5	0.50	2.62	350	4.2	0.12	0.62	83
A	Low	10	0.85	2.92	220	4.3	0.20	0.68	51
A	Low	15	0.77	2.70	220	4.0	0.19	0.68	55
A	Low	20	0.73	2.44	240	3.8	0.19	0.64	63
B	High	5	0.35	1.05	100	1.50	0.23	0.70	67
B	High	10	0.31	1.27	80	1.35	0.23	0.94	59
B	High	15	0.37	1.44	80	1.25	0.30	1.15	64
B	High	20	0.40	1.46	80	1.10	0.36	1.33	72

3.2. Cookers

3.2.1. Boiling burners

Tests obtained with boiling burners were in general consistent with the following principles:

1. Unloaded burners (free-standing flames) favour the generation of NO, rather than NO_2 and low levels of CO.
2. Loaded burners (with a pot containing water, for example) favour the generation of relatively greater proportions of NO_2 and CO.
3. Vitiated conditions also favour relatively greater proportions of NO_2 and CO.

These results are consistent with investigations carried out using an experimental burner and heat exchanger.[27]

A transition, from NO_x composed mainly of NO to mostly NO_2, was found to occur when boiling burners were allowed to operate under conditions of progressively increasing vitiation. This result, which is similar to that found with convective space-heaters,[13] is given in Table 4. The CO is also seen to increase with the onset of higher levels of vitiation.

Further work is to be conducted on pollutant generation by boiling burners under different sets of conditions.

3.2.2. Radiant griller

Table 5 shows that these grillers produce a NO_x which is mainly NO_2, especially when operating on low setting. This concurs with previous results which showed radiant space-heaters to produce large proportions of NO_2. Although the structure of the Schwank burners used in space-heaters is different from most types of radiant grillers, both types emit a considerable proportion of the available energy as radiation and so give rise to cooler flame gases. It is therefore not surprising that these comparable combustion processes result in similar types of NO_x emissions.

3.2.3. Ovens

Tables 6 and 7 show the results of running cooker ovens in fresh air and in vitiation conditions respectively. It is seen from Table 6 that lower oven flames tended to favour higher NO_2/NO ratios. Similarly, Table 7 shows that higher levels of vitiation also result in higher NO_2/NO ratios.

3.3. Gas refrigerators

Only one appliance was tested. This was a liquefied

TABLE 6 Cooker ovens operating in fresh air

Cooker	Thermostat setting	Time for ignition (min)	Exit gases NO (ppm)	NO_2 (ppm)	CO (ppm)	CO_2 (%)	Ratios × 10^4 NO/CO_2	NO_2/CO_2	CO/CO_2
A	High	5	6.57	3.30	200	3.0	2.2	1.10	67
A	High	10	7.67	3.20	110	2.6	3.0	1.2	42
A	High	15	7.65	2.61	60	2.3	3.3	1.1	26
A	High	20	7.62	2.05	40	1.8	4.2	1.1	22
B	High	5	7.92	6.80	$<$20	2.45	3.2	2.8	
B	High	10	6.92	5.80	$<$20	2.00	3.4	2.9	
B	High	15	5.10	3.61	$<$20	1.32	3.9	2.7	
B	High	20	4.97	3.61	$<$20	1.20	4.1	3.0	CO levels low for cooker B
B	High	25	4.45	3.33	$<$20	1.10	4.1	3.0	
B	Low	30	0.92	2.36	$<$20	0.32	2.9	7.4	
B	Low	35	0.86	3.33	$<$20	0.32	2.7	10.4	
B	Low	40	1.21	3.01	$<$20	0.32	3.8	9.4	
B	Low	45	1.64	3.04	$<$20	0.50	3.3	6.1	

TABLE 7 Cooker B oven operating under conditions of vitiation

Time from ignition (min)	Exit gases NO (ppm)	NO_2 (ppm)	CO (ppm)	CO_2 (%)	Ratios × 10^4 NO/CO_2	NO_2/CO_2	Room atmosphere NO (ppm)	NO_2 (ppm)	CO (ppm)	CO_2 (%)	Ratios × 10^4 NO/CO_2	NO_2/CO_2
15	3.04	2.14	$\approx$20	1.32	2.3	1.6						
35	3.17	2.29	$\approx$20	1.60	2.0	1.4						
55	3.40	2.66	$\approx$20	1.92	1.7	1.4						
75	3.65	3.03	$\approx$20	2.22	1.6	1.4						
95	3.89	3.63	30	2.55	1.5	1.4	3.2	3.0	20	2.0	1.6	1.5
115	3.90	4.88	30	2.88	1.4	1.7	3.2	4.3	20	2.2	1.5	2.0
125	4.00	4.45	40	3.00	1.3	1.5	3.1	5.1	30	2.4	1.3	2.1
145	3.80	6.29	40	3.30	1.2	1.9	3.4	4.9	30	2.7	1.3	1.8

petroleum gas unit which was the actual appliance involved in a dual fatality by carbon monoxide poisoning in a camper van.[28]

Unfortunately, only limited testing was possible with the unit but it can be seen from Fig. 3 that the rate of CO generation increased rapidly with vitiation. The test was not carried out to flame extinction and it follows that higher levels of CO may have resulted if the test had been continued for a longer period.

No tests of nitrogen oxides generation were carried out on the refrigerator.

3.4. Sink (water) heaters

Since the introduction of natural gas to the Perth metropolitan region in Western Australia in December 1971, there have been a number of cases of fatal carbon monoxide poisoning involving unflued sink heaters and this has led to a recent decision to ban them completely in the State. Vitiation is believed to have been a major factor in most of these fatalities.

Sink heaters are also reported to have been involved in a number of fatal CO poisonings in the Netherlands.[4]

Fig. 4 shows the effect of vitiation on the CO generation of several makes, models and modifications of sink heaters. It is evident that vitiation results in a marked increase in CO production in all cases.

Tables 8 and 9 show the results of running a sink heater in fresh air and under conditions of vitiation, respectively. It is evident that there was a large increase in the generation of carbon monoxide in the latter case. Vitiation also resulted in a considerable reduction of the NO, while the NO_2 was little changed. Both the increase in CO generation and reduction in NO appear to be attributable to quenching[29,30] of gas phase reactions as a result of flame impingement on the relatively cool heat exchanger.

When a sink heater burner with the heat exchanger removed (thus making it effectively into an unloaded burner) was operated to extinction in the vitiation room, the maximum CO/CO_2 ratio in the combustion gases was only 69×10^{-4}, as seen in Table 10, compared with 430×10^{-4} for the appliance with the heat exchanger (see Table 9). A comparison of Tables 4 and 10 shows that the unloaded cooker burners and the water heater minus its heat exchanger performed in quite a similar manner, under conditions of increasing vitiation.

From the results presented, it is apparent that vitiation contributes to carbon monoxide generation in at least two ways:

1. The reduced oxygen concentration (and accompanying increase in inerts) results in slower burning at reduced temperature; this is a direct effect of vitiation.
2. The increased flame length which results from the slower burning of (1) allows incompletely reacted gases to impinge on the relatively cool heat

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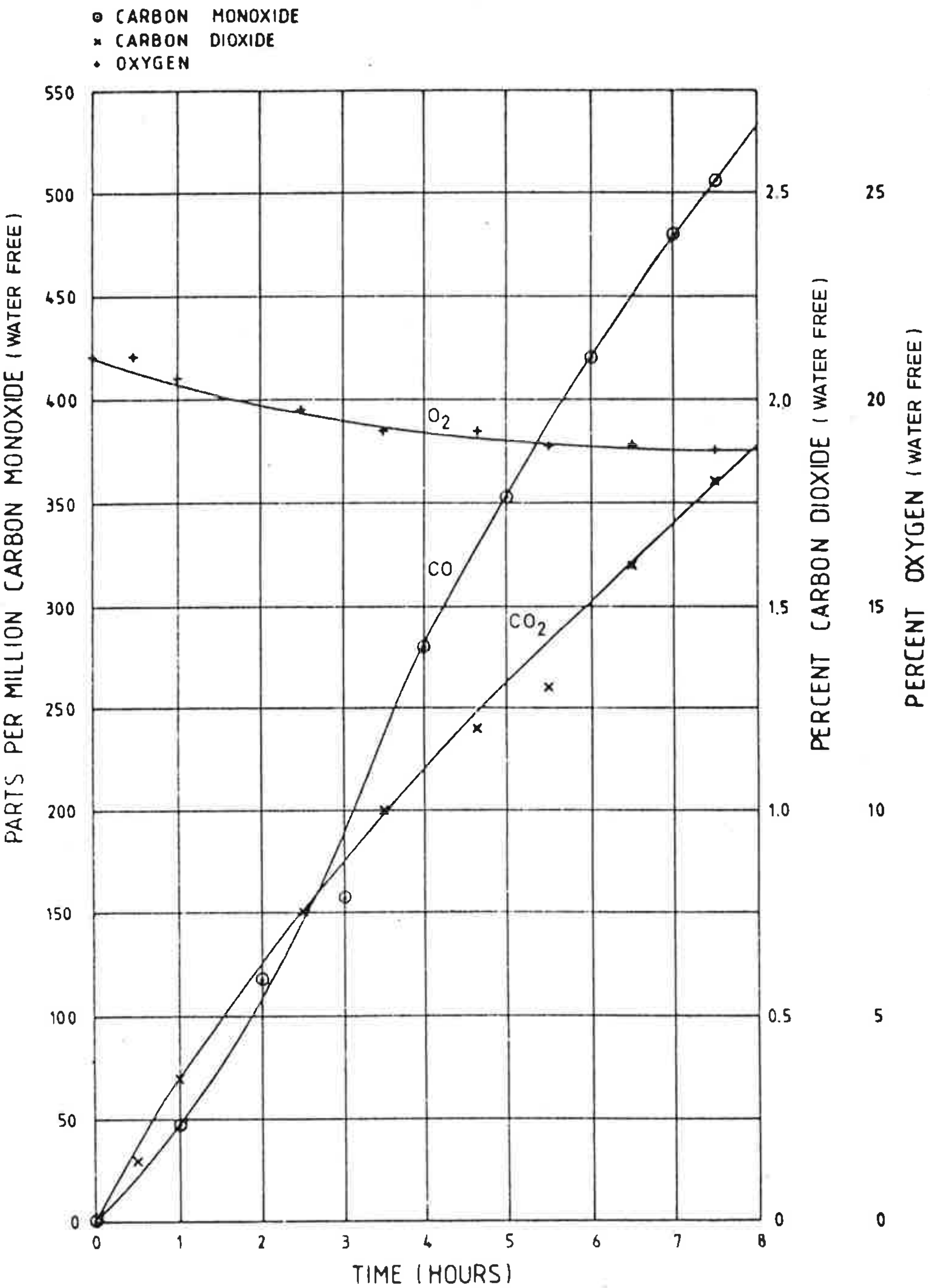

FIG. 3 Camper van atmosphere with refrigerator allowed to operate under conditions of vitiation

exchanger which largely quenches the CO burn. This (indirect) effect generally appears to be of greater magnitude than the direct effect of (1) above.

It is widely reported[19,22,31–34] that, in hydrocarbon combustion, all reactions other than CO oxidation are essentially complete immediately downstream from the flame front, producing 68% of the total heat release in the case of methane.[34] Numerous equations have been advanced[15,19,31,32] to describe the kinetics of the CO burn, which produces the remainder of the heat.

An attempt to quantify the relationship between CO generation and vitiation with one particular type of heater was partially successful in quantitative terms using the CO oxidation equations of Harris *et al.*[15] The semi-empirical equations were formulated to describe the carbon monoxide oxidation in the after-flame relatively far downstream from the flame front. Attempts to utilize equations derived from reaction data taken close to the flame front[31,32] invariably gave oxidation rates which were far greater than observed (sometimes by orders of (*continued on p 196*)

TABLE 8 Unflued sink heater operating in fresh air

Time from ignition	Exit gases			
	NO	NO_2	CO	CO_2
(min)	(ppm)	(ppm)	(ppm)	(%)
5	36.7	8.0	150	7.6
10	36.9	7.3	110	7.2
15	36.2	8.5	110	6.8
20	36.1	8.0	120	6.6
25	35.6	8.1	120	6.5
30	36.3	8.2	130	6.5

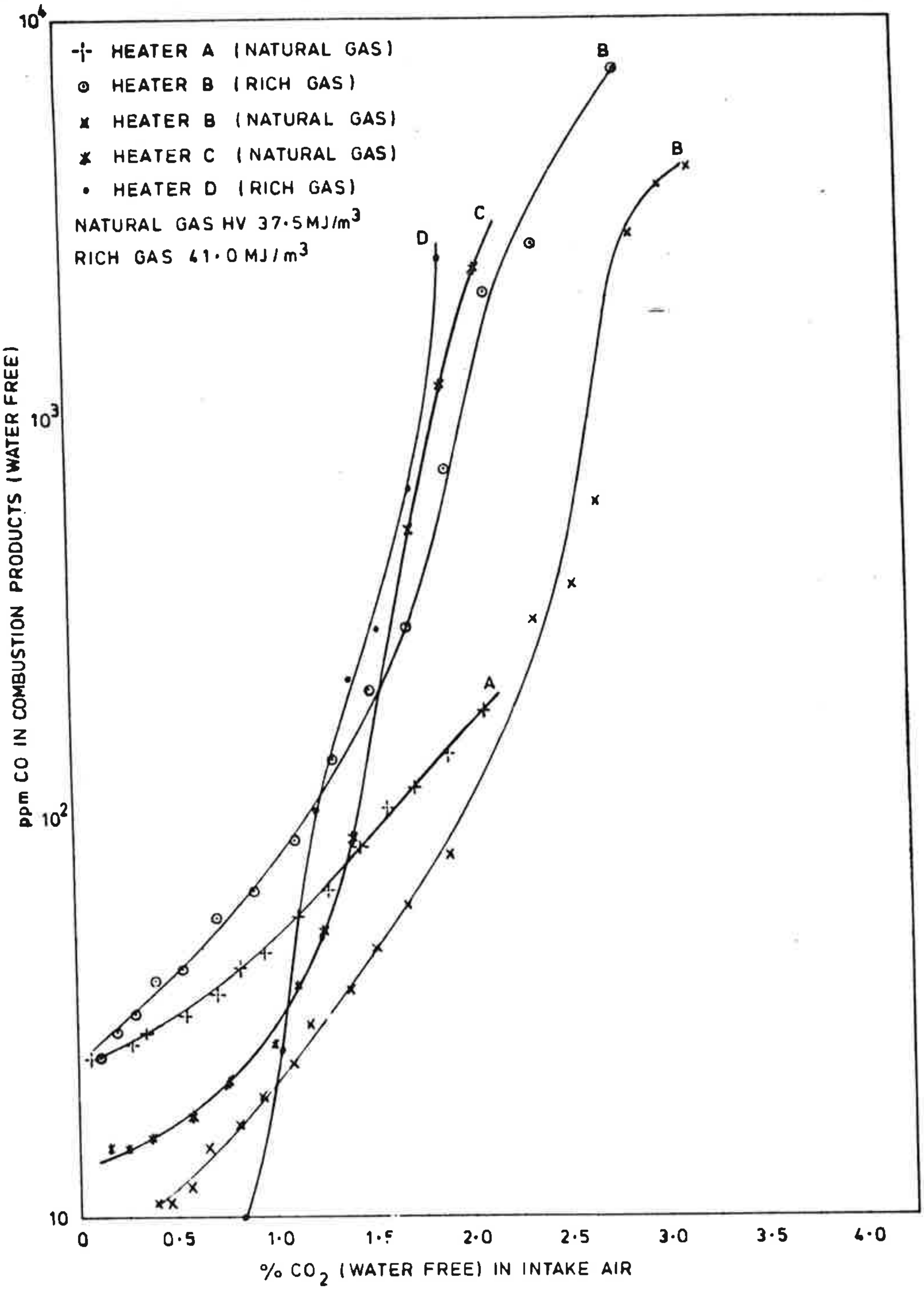

FIG. 4 Comparison of vitiation behaviour of several types of sink heater

TABLE 9 Vitiation test on unflued sink heater

Time from ignition	Intake air	Exit gases				Ratios × 10^4			Ratio
	CO_2	NO	NO_2	CO	CO_2	NO/CO_2	NO_2/CO_2	CO/CO_2	NO_2/NO
(min)	(%)	(ppm)	(ppm)	(ppm)	(%)				
5		38.1	7.7	200	7.5	5.1	1.0	27	0.20
10	0.5	33.1	8.5	200	7.6	4.4	1.1	26	0.26
15	1.3	27.8	6.6	800	8.5	3.3	0.8	94	0.24
20	1.7	22.1	7.2	2000	9.2	2.4	0.8	220	0.33
25	2.1	18.9	6.4	3200	9.8	1.9	0.7	340	0.34
30*	2.6	8.8	6.3	3000	7.0	1.3	0.9	430	0.72
Heater self extinguished									

*Note appreciable 'lifting' and escape of unburned hydrocarbon at 30-min reading.

TABLE 10 Vitiation test on unflued sink heater with heat exchanger removed

Time from ignition (min)	Intake air CO_2 (%)	Exit gases NO (ppm)	NO_2 (ppm)	CO (ppm)	CO_2 (%)	Ratios × 10^4 NO/CO_2	NO_2/CO_2	CO/CO_2	Ratio NO_2/NO
5	0.2	34	4.3	≈10	4.4	7.7	0.98	≈2	0.13
10	0.5	31	5.4	≈10	4.7	6.7	1.2	≈2	0.17
15	0.8	28	6.1	≈10	5.2	5.4	1.2	≈2	0.22
20	1.1	25	6.7	20	5.8	4.2	1.2	3.4	0.27
25	1.6	19	9.4	40	6.2	3.0	1.5	6.5	0.50
30	2.2	9.3	16	120	6.8	1.4	2.4	18	1.7
35	2.75	3.8	19	400	7.5	.51	2.5	53	5.0
40	3.5	4.8	19	600	8.7	.55	2.2	69	3.9
43	Heater self extinguished								

magnitude). Predictions based on such equations indicate a much more rapid CO 'clean-up' than was actually observed. This is explained by the quenching of the CO oxidation, which occurs as the gases cool downstream from the flame front.[30]

4. Conclusion

Further evidence has been presented which shows that radiant heaters and other cool burning combustors tend to produce a NO_x which comprises mostly NO_2. The NO_2 so produced was found to be much less stable in the test room environment than the NO in the cases tested and it appeared that up to one-quarter of the NO_2 was converted to NO.

Vitiation was shown to give rise to CO generation, especially in appliances (notably sink heaters) where flame impingement can occur.

The results emphasize the importance of maintaining acceptable levels of ventilation where gas appliances (especially unflued ones) are in use.

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6. References

1. WADE W A, COTE W A and YOCOM J E. A study of indoor air quality. *J Air Pollut Control Assoc*, 1975, **25**, 933–939.
2. TRAYNOR G W, ANTHON D W and HOLLOWELL C D. Technique for determining pollutant emissions from a gas-fired range. *Atmos Environ*, 1982, **16**, 2979–2987.
3. PALMES E D, TOMCZYK C and MARCH A W. Relationship of indoor NO_2 concentrations to use of unvented gas appliances. *J Air Pollut Control Assoc*, 1979, **29**, 392–393.
4. YOCOM J E. Indoor-outdoor air quality relationships—a critical reivew. *J Air Pollut Control Assoc*, 1982, **32**, 904–919.
5. Proposed reaffirmation of the national ambient air quality standards for nitrogen dioxide. Environmental Protection Agency, Fed Reg 49(37), 6866, 1984 (23 Feb).
6. LAO Y J, SMITH R W, RICH T L and DAVIS T G. Carbon monoxide in homes with fuel-burning space-heaters. *J Environ Health*, 1982, **44**, 180–182.
7. Are kerosine heaters safe? *Consumer Reports*, 1982, **47**, 499–507.
8. LEADERER B P. Air pollutant emissions from kerosine space-heaters. *Science*, 1982, **218**, 1113–1115.
9. TRAYNOR G W, ALLEN J R, APTE M G, GIRMAN J R and HOLLOWELL C D. Pollutant emissions from portable kerosine-fired space-heaters. *Environ Sci Technol*, 1983, **17**, 369–371.
10. RYAN B P, SPENGLER J D and LETZ R. The effects of kerosine heaters on indoor pollutant concentrations: a monitoring and modelling study. *Atmos Environ*, 1983, **17**, 1339–1345.
11. GIRMAN J R, APTE M G, TRAYNOR G W, ALLEN J R and HOLLOWELL C D. Pollutant emission rates from indoor combustion appliances and sidestream cigarette smoke. *Environ Int*, 1982, **8**, 213–221.
12. SMITH I. Nitrogen oxides from coal combustion—environmental effects. Report No ICTIS/TR10, 1980 (Oct). IEA Coal Research, London.
13. BROMLY J H, BARNES F J, JOHNSTON R C R and LITTLE L H. Nitrogen oxide emissions from unflued space-heaters. *J Inst Energy*, 1984, **57**, 411–415.
14. KILHAM J K and LANIGAN E P. A study of the mechanism of radiant burners. *J Inst Gas E*, 1970, **10**, 700–719.
15. HARRIS M E, ROWE V R, COOK E B and GRUMER J. Reduction of air pollutants from gas burner flames. US Bur Mines, Bull 653, 1970.
16. JOHNSON G M, SMITH M Y and MULCAHY M R F. The presence of NO_2 in premixed flames. Seventeenth symp (int) on *Combustion*. Combustion Institute, Pittsburgh, 1979, p 647.
17. HARDGRAVES K J A, HARVEY R, ROPER F G and SMITH D B. Formation of NO_2 in laminar flames Eighteenth symp (int) on *Combustion*. Combustion Institute, Pittsburgh, 1981, p 133.
18. WESTENBERG A A. Kinetics of NO and CO in lean, premixed hydrocarbon—air flames. *Combust Sci Technol*, 1971, **4**, 59–64.
19. BOWMAN C T. Kinetics of pollutant formation and destruction in combustion. *Prog Energy Combust Sci*, 1975, **1**, 33–45.
20. FENIMORE C P. Formation of nitric oxide in premixed hydrocarbon flames. Thirteenth symp (int) on *Combustion*. Combustion Institute, Pittsburgh, 1971, p 373.
21. HAYHURST A N and VINCE I M. Nitric acid formation from N_2 in flames: the importance of 'prompt' NO. *Prog Energy Combust Sci*, 1980, **6**, 35–51.
22. GLASSMAN I. Combustion. Academic Press, New York, 1977.
23. REED S B and WAKEFIELD R P. Vitiation of combustion air. *J Inst Gas E*, 1970, **10**, 77–92.
24. FULLGRABE E and DEGENHARD G. Continuous monitoring of work areas exposed to gas hazards by means of automatic Dräger CO measuring and warning systems in a smelting plant. *Dräger Rev*, 1972, No 28, pp 12–17.
25. Unvented gas-fired space-heaters. Proposal to ban. Consumer Product Safety Commission, Fed Reg 43(31), 6235, 1978 (14 Feb).
26. Unvented gas-fired space-heaters. Proposed withdrawal of proposed rule. Consumer Product Safety Commission, Fed Reg 43(230), 55772, 1978 (29 Nov).
27. BROMLY J H, BARNES F J, JOHNSTON R C R and LITTLE L H. Unpublished work.
28. *The West Australian* newspaper, 1983 (1 Sept), p 3.
29. FENIMORE C P and MOORE J. Quenched carbon monoxide in fuel-lean flame gas. *Combust Flame*, 1974, **22**, 343–351.
30. PALMER H B. Combustion technology: some modern developments (Howard B Palmer and J M Beér eds.). Academic Press, 1974.
31. SINGH T and SAWYER R F. CO reactions in the afterflame region of ethylene/oxygen and ethane/oxygen flames. Thirteenth symp (int) on *Combustion*. Combustion Institute, Pittsburgh, 1971.
32. SCHEFER R W and SAWYER R F. Lean premixed recirculating flow combustion for control of oxides of nitrogen. Sixteenth symp (int) on *Combustion*. Combustion Institute, Pittsburgh, 1977.
33. EDWARDS J B. Combustion formation and emission of trace species. Ann Arbor Science, Ann Arbor, 1974.
34. CREIGHTON J R. Some general principles obtained from numerical studies of methane combustion. *J Phys Chem*, 1977, **81**, 2520–2526.

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