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PERFORMANCE OF PORTABLE LPG DOMESTIC SPACE HEATERS IN OXYGEN DEFICIENT ATMOSPHERES

by

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SUMMARY

The performance of radiant and catalytic heaters fuelled by liquefied petroleum gas (LPG) in a sealed room has been evaluated.

Vitiation of the atmosphere by radiant heaters produced toxic conditions by the generation of carbon monoxide. Catalytic heaters did not produce enough carbon monoxide for a toxic level to exist before the formation of carbon dioxide and depletion of oxygen produced hazards.

Although the heaters did not create explosive atmospheres during the reported tests, and are unlikely to do so when operated in a room of a volume commensurate with the output of the heaters, the situation could be changed for catalytic heaters if their efficiency of combustion was seriously impaired, for example, by damage or deterioration after prolonged use.

Heaters when operated in badly ventilated spaces can produce a risk to life. This risk can be avoided if the heater is equipped with a device which will shut down the heater when the carbon dioxide in the atmosphere reaches a specific but low concentration. Such devices should also reduce the possibility of explosive atmospheres being formed.

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Department of the Environment Fire Research Station of the Building Research Establishment PERFORMANCE OF PORTABLE LPG DOMESTIC SPACE HEATERS IN OXYGEN DEFICIENT ATMOSPHERES

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INTRODUCTION

There is little published data on the performance in oxygen deficient atmospheres of portable fuel burning appliances. Perhaps because of the absence of such data, UK standards and regulations for such appliances do not specify requirements for acceptable performance in poorly ventilated spaces. The use of such appliances is increasing and with modern methods of draught prevention in rooms, oxygen deficient atmospheres may be easily created, and therefore the specification of limits of performance in such conditions is desirable. If the supply of air to a heated room is inadequate, all flueless appliances will ultimately create toxic atmospheres unless they are extinguished in time. It is also desirable that carbon dioxide is preferentially produced by combustion and the formation of carbon monoxide is minimised to reduce the toxicity of combustion products.

APPARATUS AND MATERIALS

Heaters

Three radiant - and three catalytic - liquefied petroleum gas (LPG) heaters were examined. They were all of foreign manufacture and were purchased either by mail order or from approved distributors in the UK. All heaters were provided with a compartment at the rear to contain the 14.5 kg (32 lb) LPT cylinder and regulator.

Heater A

Heater A, was purchased from an approved dealer. A label giving brief operating instructions was attached to the body of the heater and leaflets were enclosed with the heater giving detailed operating instructions, and advice on the safe use of LPG cylinders and regulators.

The heater had three radiant panels positioned side by side, and one, two, or three of these could be brought into use by pressing an appropriate button controlling the flow of butane to the panels. The maximum heat output was stated to be 3.8 kW (12970 Btu/h) when using butane at 11 in. water gauge pressure. The heater was brought into use after the main cylinder valve had been turned on, by pressing a spring-loaded button which admitted fuel to the pilot flame and the radiant panels and which by repeated pressing operated a piezoelectric device, producing sparks to ignite the fuel jet. The pilot jet in turn heated a thermocouple which, when sufficiently hot, held open the main fuel valve. Release of the starting button cut off the starting supply of fuel.

The thermocouple performed two functions. If the heated panels cooled excessively, the cooling of the thermocouple cut off the main fuel supply; also, if carbon dioxide in excess of 1 per cent was present in the atmosphere, the lift-off of the pilot flame resulted in the cooling of the thermocouple and so cut off the fuel supply.

Heater B

Heater B, advertised in the national press, was purchased by mail order. The only operating instructions provided were on a label attached to the body of the heater.

The radiant panel of the heater was horizontal and the output could be reduced by turning a knob, reducing the flow of butane. The maximum output was stated to be 2.5 kW (8530 Btu/h).

The heater was brought into use by depressing a button which allowed fuel to flow to the burners which were lit with a small flame such as a match. When the burners ignited, they in turn ignited a group of four pilot flames and continued depression of the actuating button for a further 15 to 20 seconds.actuated a snap action diaphragm which opened the main fuel valve, when the button could be released.

The snap action device was also claimed to shut down the fuel supply when the concentration of carbon dioxide in the ambient atmosphere reached a certain but unspecified value.

<u>Heater C</u>

Heater C ,had the same flame failure and starting device as Heater A, but no igniting device. It had a continuously variable output up to a maximum of 3 kW (10240 Btu/h). The heater was lit from a small flame such as a match when the combustion of the gas took place on a row of jets producing small flat diffusion flames.

Heater D

Heater D, was purchased from an approved dealer. It was received with coupling hose and regulator for the gas cylinder. The catalytic bed of the heater was made from lightly compressed platinised asbestos fibre mounted in a shallow enamelled steel case with its exposed surface protected by wire mesh. A thermocouple was fitted with a shut-down device which operated when the temperature of the asbestos bed near the thermocouple junction dropped below a certain level. The maximum output of this heater was stated to be 2.8 kW (9550 Btu/h). A valve allowed two lower thermal outputs to be selected. The heater was brought into use by depressing a spring-loaded button which overrode the flame failure device and admitted fuel to a pilot jet which heated the above thermocouple. When the temperature of the thermocouple had risen sufficiently to hold the fuel valve open, the interlock button could be released.

Heater E

Heater E, was of similar construction to Heater D, but the catalytic bed was made from platinised rockwool. Their thermal output of this heater was continuously variable up to a stated maximum of 3.5 kW (11940 Btu/h). A thermocouple combustion failure device similar to that of Heater D, was fitted. The procedure for bringing the heater into operation was similar to that for Heater D.

Heater F

Heater F, was a smaller version of Heater D, constructed from similar components but with a maximum output of 2.15 kW (8000 Btu/h).

GAS SAMPLING AND GAS ANALYSIS

The combustion products from each heater were collected in a hood fitted with a flue conforming to British Standard 1756 : 1971. A non-helical and symmetrical flow of gases within the hood was obtained by the use of gauze and honeycomb inserts so that the gas mixture in the flue was homogeneous.

TEST ROOM. VITIATED ATMOSPHERES

To test the effects of vitiated atmospheres on the performance of heaters, a 9.3 m³ cubical leakproof chamber was used. The chamber was tested for leaks by filling with air containing 1 per cent carbon dioxide (CO_2) and measuring the loss of CO_2 from the sealed room over a period of time. After 1 hour 1 per cent of the introduced CO_2 was lost. The atmosphere within the chamber was stirred by a fan throughout each test. Samples of gas for the analysis of carbon monoxide (CO) and carbon dioxide (CO_2) content were withdrawn by a small pump as required. The atmosphere was circulated through analysers for the determination of CO and CO_2 content, and samples for the determination of unburnt hydrocarbons were withdrawn from this loop. Non-dispersive infra-red analysers were used to determine CO and CO_2 , and unburnt hydrocarbons were determined by gas chromatography. The limits of resolution were 0.0001, 0.001 and 0.00005 per cent by volume respectively for CO, CO, and hydrocarbons.

The temperature of the atmosphere in the chamber was monitored during each test by a thermocouple.

RESULTS

The performance of heaters in normal atmospheres

The heaters were operated under a hood in accordance with BS 1756 : 1971. The measured CO and CO₂ concentrations are plotted as a ratio on Fig 1 for radiant heaters A, B and C. Although heaters A, B and C during the first 30 secs of the warming up period attained the maximum ratios of 0.0082,0.02 and 0.0042 respectively after three minutes burning the ratios reached equilibrium values of 0.001 for heaters A and C, and 0.002 for heater B. Fig 2 shows similar curves for catalytic heaters. Heaters D, E and F gave the maximum ratios of 0.0075, 0.0042 and 0.0146 respectively initially, but soon reached equilibrium when the CO/CO₂ ratio was less than 0.0005 for all three heaters. Tables 1 and 2 show the concentrations of unburned gases during these tests for both radiant and catalytic heaters. During the first 20 mins after ignition all heaters had lower efficiencies; however after this period they all attained equilibrium. Radiant heaters at equilibrium worked at a combustion efficiency of 99.8 per cent and catalytic heaters at combustion efficiencies ranging from 97.7 - 95.5 per cent.

Performance of the shut-down devices triggered by CO,

These tests were carried out in the leakproof chamber, with the CO and CO_2 concentrations monitored throughout the test, until shut down took place. The heaters were tested at the maximum and minimum heat outputs. Fig 3 shows the increase of CO_2 concentration in the chamber with time for each radiant heater until such time as shut down took place. The shut down devices operated within the range of CO_2 concentration of 1.0 - 2.1 per cent in all tests. It was noted that these devices showed greater sensitivity when heaters were operating at the minimum heat output.

The concentration of CO increased with time of operation without pronounced fluctuations throughout the tests. Fig 4 shows the plot of CO concentration versus time for the duration of operation. In tests with heaters A and B the rate of CO generation increased in the later stages of the experiments as shown by the increase in concentration. Heater B was exceptional in producing more CO at minimum output than at the maximum output.

Performance during prolonged tests with shut down devices made inoperative. a. Radiant heaters

In order to operate these heaters for a prolonged time in a sealed room, in which combustion products would accumulate, it was necessary to render the shut-down devices inoperative. This was done without affecting the operation of the heaters in other respects.

The tests were continued until the burner of the heaters became unstable. Fig 5 shows the increase in concentration of CO_2 , as a percentage by volume, with time of operation in the sealed room. All curves indicate that the rate of CO_2 generation did not vary very much throughout the tests.

Fig 6 shows the concentration of CO in the atmosphere in the same tests. The curves show that the heaters, with the possible exception of heater C at minimum output, showed a continuous increase in the rate of CO generation with time of burning.

Fig 7 shows plots of the CO/CO_2 ratios for the three heaters until flame instability occurred, when the tests were stopped. Heater B when operated at maximum heat output reached a maximum ratio of 0.05, but the other two heaters did not exceed the ratio of 0.025, at either maximum or minimum heat output.

Fig 8 shows the plot of the concentration of unburned fuel gas in the atmosphere in the same tests. With the exception of heater A operated at the maximum output, a sharp increase in output of fuel gas occurred towards the end of the test period.

These sudden increases coincided with the lift-off and instability of the flame from the ceramic burner.

Fig 9 shows the concentration of unburnt hydrocarbons within the sealed chamber plotted as a percentage of the gas supplied to the burner. The curves indicate that, when the shut-down device was rendered inoperative, after a period at a steady rate there is a very rapid drop in the efficiency of the burners.

b. Catalytic heaters

These tests were carried out in an identical manner as the tests with the radiant heaters, but with catalytic heaters there is no visual indication how the combustion is proceeding. Rapid analysis of the room atmosphere for unburnt flammable gases however gave warning of the development of possibly hazardous conditions. Figs 10 and 11 show the plot of CO_2 and CO concentration against time respectively. No heater gave rapid changes in the rates of generation of CO, but each appeared to give a gradual reduction of the rate of generation of CO_2 .

Fig 12 shows the plot of the percentage by volume of unburnt gas in the room against time and Fig 13 shows the same values expressed as a percentage of total gas released, indicating the efficiency of the appliance. The concentration of the unburnt gas reached the highest values with heaters D and E. The equivalent efficiencies with these two heaters (Fig 13) at the end of test were 76 and 64 per cent respectively. It was thought unsafe to extend the experiments to the stage when the catalytic heater shut-down devices operated. The operating temperature of the flame failure device was ascertained by heating and cooling the thermocouple junction in a sand bath until it opened and shut the valve. Table 3 lists the temperature required to open and close the flame failure devices of heaters D and F. The valve for heater F failed to close in 2 out of 3 tests.

T.	A	BI	E	3

Test	Heater D		Heater F	
No	Temperature to open	Temperature to close	Temperature to open	Temperature to close
1	190	72	247	239
2	157	80	257	*
3	140	78	348	*
4	114	75		
5	130	70		
6	125	86		*valve jammed

Temperature to operate the combustion failure devices, °C.

DISCUSSION

Appraisal of hazards presented by the vitiated atmospheres

Heaters burning gaseous fuel in poorly ventilated rooms can in principle create both explosion and toxic hazards, discussed below. However these can only occur under extreme conditions most unlikely to be met in practice. Many of the heaters used in the current investigation were provided with shut-down devices which, if operating correctly, would give protection against explosion and toxic hazards.

Life hazards can arise from the depletion of oxygen (0_2) or the presence of CO_2 or CO in sufficient amounts. These effects occurring simultaneously may present greater risks to life than the sum of the effects of individual agents. If the presence of these gases is accompanied by an increase in ambient temperature there may be further increase in the risks². Tables 4, 5 and 6 give the individual toxic effects of CO, CO₂ and the effect of oxygen depletion.

The life hazards created by space heating appliances are recognised. Many national standards specify a maximum CO/CO_2 ratio which must not be exceeded. In the UK a maximum ratio of 0.02 is allowed, but in the USA and Canada the maximum ratio permitted is 0.01. These limits apply to heaters functioning in air at normal temperatures, and are intended to restrict CO emission. The above criteria have been applied for a long time to liquid fuel (kerosene) appliances with which explosion hazards are most unlikely. However the more recently introduced catalytic appliances release some unburnt fuel gas and also may be subject to deterioration on ageing, thus increasing the explosion hazard.

There is little published information on the performance of space heating applicances in vitiated atmospheres, A D Kent² investigated the performance of various appliances used in USA and Canada, but portable domestic space heating applicances were not included in this investigation. More recently P A Breysse³ investigated the performance of four catalytic heaters under vitiated conditions and drew the broad conclusion that they could be potentially dangerous to humans exposed to the exhaust products for a prolonged period of time, because of the combined toxic effects of CO_2 , CO and low oxygen levels. However the report does not indicate a severe hazard.

Performance of CO₂ activated shut down devices

The function of the CO₂ activated control device, is to shut down the fuel supply before the atmosphere in which the heater is operating could introduce life hazards.

All the shut-down devices tested satisfied these conditions, and shut-down took place before a life hazard from the individual constitutents was reached. At the time of shut-down the following ranges were recorded: CO2 1-2 per cent, CO 20-80 ppm and 0, 19-20 per cent. Once the fuel supply was interrupted the heater could not be started until the concentration of CO, was reduced below 1-2 per cent. All devices were of simple construction, with little to go wrong, and all were 'fail-safe' in operation. In order to achieve this level of performance, the basic structure of the traditional flame failure device was retained, and only small modifications to the pilot jet were required. At present catalytic heaters are not fitted with CO2 activated shut down devices, but prototype devices have been produced abroad and some catalytic heaters in future are likely to be supplied with such devices built in. However the principle of operation of a CO, operated device requires a continual pilot flame. This feature will alter the operational characteristics of catalytic space heaters, which until now operated in a flameless manner after start up. It has been argued that the absence of flame improves the operational safety of such heaters when these are functioning in presence of easily ignitable solids such as clothing. It is however likely that because heaters must be fitted with guards preventing contact with fabrics such an advantage is of minor importance in domestic areas when compared with the importance of toxic hazards.

Explosion hazards produced by the heaters after prolonged working in vitiated atmospheres

Fig 14 shows the limits of flammability of butane in air with N₂ and CO₂ added from tests carried out in a tube 6 ft long and 2 in diameter⁴.

The lower flammable limit for butane in air is 1.9 per cent³. The dilution of air with CO_2 to 15.0 per cent (Vol) of oxygen (O_2) and with nitrogen (N_2) to 12.5 per cent (Vol) of O_2 will prevent the flame propagating and extinguish an existing flame⁴.

From this it follows that radiant (flame) heaters should cease to operate when atmospheres are brought to compositions similar to these. Tests described in this paper have shown that radiant heaters functioning in atmospheres having 11 or 12 per cent 0_2 content, had unstable flames which began to lift-off. It is probable that flames on a ceramic burner could continue to exist in a somewhat lower 0_2 concentration, than those shown in Fig 14, because of the considerable preheating of reactants before they entered the flame zone⁴. Thus radiant heaters might continue to function in atmospheres which were outside the ambient temperature flammable limits.

The measured concentrations of unburned hydrocarbons produced by radiant heaters in the sealed chamber, Fig.9, clearly indicate that the operational efficiency of radiant heaters did not change substantially until the concentration of CO₂ exceeded 3 per cent where efficiency started to decrease rapidly. At this stage however the flames lifted off and became unstable.

The catalytic heaters were allowed to function until the 0_2 concentration was reduced to 11 per cent. At these concentrations the catalytic beds were able to function, but at very low efficiencies, one heater oxidising only 69 per cent of supplied fuel. Nevertheless only a small quantity of CO was produced, the CO/CO_2 ratio remaining substantially unchanged. Thus catalytic beds may permit heaters to function in 0_2 concentrations below those at which radiant heaters go out. There is no information to indicate the temperature at which a catalytic reaction will cease to operate at a given 0_2 concentration. It is possible that it may continue to operate at temperatures below those at which a flame failure device would interrupt the fuel supply. In no test was the flammable gas concentration in the chambers more than half the lower explosion limit (L.E.L) (Fig.14).

The results of analysis of the unburnt gases showed that when the concentration of CO₂ in the surrounding atmosphere exceeded 3 per cent, a sudden change took place in the reactivity of the catalytic bed, see Figs 10 and 13. The efficiency of combustion then declined rapidly and the volume of unburnt flammable gas discharged increased.

Within the operational period when the CO_2 concentration was less than 3 per cent the rate at which unburnt gases escaped depended on the efficiency of the heater as determined in a normal atmosphere. Fig 12 shows clearly that with heater E within the period from start to the time when CO_2 concentration reached 3 per cent, very little unburned butane passed through the catalytic bed. At this time the butane concentration was 0.1 per cent, well below the LEL. Once the concentration of CO_2 exceeded 3 per cent, the rate of discharge of unburnt fuel increased, and at the end of the test there was 1.39 per cent of unburnt butane within the chamber. At this stage the composition of the atmosphere within the chamber was 12.5 per cent O_2 9.5 per cent CO_2 and 78.0 per cent N_2 , which is well outside the LEL. In fact there was not enough O_2 to allow flame combustion even if all the inert gas were N_2 .

Therefore this heater, while working in such a small volume as the leakproof chamber would have to function at a substantially lower efficiency, for an explosion atmosphere to be formed before oxygen depletion removed the risk of explosion.

The capability of a heater for creating an explosible atmosphere is a function of heater output and efficiency, and the volume of the sealed space within which the heater operates. Under practical conditions in a room of volume appropriate for the heater, the production of explosion atmospheres would be most unlikely unless there was an extreme loss of efficiency of combustion.

CONCLUSIONS AND RECOMMENDATIONS

- 1. The CO/CO_2 rate for radiant and catalytic heaters can and should be reduced to 0.01.
- 2. The safety performance of all heaters can be improved by fitting CO₂ triggered shut down devices.
- 3. Both radiant and catalytic heaters are unlikely to produce explosive atmospheres when functioning in poorly ventilated spaces, if their efficiencies in normal atmospheres are better than 95 per cent.
- 4. Tests for performance in vitiated atmospheres should be included in standards.
- 5. Catalytic heaters can create hazardous atmospheres by depletion of O_2 and by CO_2 formation. On the other hand radiant heaters can produce toxic concentrations of CO before oxygen depletion and toxic CO_2 concentration become hazardous. This can be avoided by a CO_2 shut-down device.
- 6. Catalytic heaters are unlikely to create explosive atmospheres when operated in a room of appropriate volumes unless they are very inefficient.

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UNBURNT HYDROCARBONS EXPRESSED AS

PERCENTAGE OF TOTAL RELEASED

Time min	HEATER		
	A	В	C
2	0,22	0.46	1.8
5	0.24	0.42	0.59.
10	0.21	0.27	0.37
20	0.22	0.33	0.32
30	0.25	0.29	0.35

TABLE 1 Radiant Heaters

TABLE 2 Catalytic Heaters

Time	HEATER		
шти	D	E	F
2	4.3	24.2	5.2
5	3•5	10.0	2.8
10	3.0	6.0	2.8
20	2.4	4.6	2.8
30	2.3	4•5	3.1

TABLE 4 Response of Humans to Various Concentrations of Carbon Monoxide

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Concentration, ppm	Symptoms
25	TLV for conditions of heavy labour, high temperatures,
	and decreased air pressure
50	TLV and MAK value
100	No poisoning symptons even for long periods of time,
	allowable for several hours
200	Headache after 2 to 3 hours, collapse after 4 to 5 hours
300	Headache after 1.5 hours, distinct poisoning after 2 to
	3 hours, collapse after 3 hours
400	Distinct poisoning, frontal headache, and nausea after
	1 to 2 hours, collapse after 2 hours, death after
	3 to 4 hours
500	Hallucinations felt after 30 to 120 minutes
800	Collapse after 1 hour, death after 2 hours
1000	Difficulty in ambulation, death after 2 hours
1500	Death after 1 hour
2000	Death after 45 minutes
3000	Death after 30 minutes
8000 or above	Immediate death by suffocation
12,800	Unconsciousness after 2 or 3 breaths, death in
	1 to 3 minutes

TABLE 6 Response of Humans to Various Concentrations of Oxygen^{1,2}

Concentration per cent	Symptoms
21	Normal concentration in air
17	Respiration volume increased, muscular co-ordination
	diminshed, more effort required for attention and
	clear thinking
12 to 15	Shortness of breath, headache, dizziness, quickened
	pulse, quick fatigue upon exertion, loss of muscular
	co-ordination for skilled movements
10 to 14	Faulty judgement
10 to 12	Nausea and vomiting, exertion impossible, paralysis
	of motion
6 to 8	Collapse and unconsciousness, but rapid treatment can
	prevent death
6 or below	Death in 6 to 8 minutes
2 to 3	Death in 45 seconds

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Concentration	Symptoms
250 to 350	Normal concentration in air
900 to 5000	No effect
5000	TLV and MAK value
18,000	Ventilation increased by 50 per cent
25,000	Ventilation increased by 100 per cent
30,000 . Weakly narcotic, decreasing acuity of hearing, i	
	in pulse and blood pressure
40,000	Ventilation increased by 300 per cent, headache, weakness
50,000	Symptons of poisoning after 30 minutes, headache,
	dizziness, sweating
80,000	Dizziness, stupor, unconsciousness
90,000	Distinct dyspnoea, loss of blood pressure, congestion,
	death within 4 hours
100,000	Headache and dizziness
120,000	Narcosis, immediate unconsciousness, death in minutes
200,000	Narcosis, immediate unconsciousness, death by suffocation

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Figure 2 Carbon monoxide:carbon dioxide ratio (under hood) - catalytic heaters at maximum output



Figure 3 Carbon dioxide in atmosphere in leakproof chamber - radiant heaters with CO₂ shut-down device operative - heaters operated at maximum and minimum output



Figure 4 Carbon monoxide in atmosphere in leakproof chamber – radiant heaters with CO₂ shut-down device operative – heaters operated at maximum and minimum output



Figure 5 Carbon dioxide in atmosphere in leak-proof chamber - radiant heaters with CO₂ shut-down device inoperative - heaters operated at maximum and minimum output



Figure 6 Carbon monoxide in atmosphere in leak-proof chamber - radiant heater with CO₂ shut-down device inoperative - heaters operated at maximum and minimum output



Figure 7 Carbon monoxide/carbon dioxide ratio in leak-proof chamber - radiant heaters with CO₂ shut-down device inoperative - heaters operated at maximum and minimum output



Figure 8 Unburnt hydrocarbons in atmosphere in leak-proof chamber – radiant heaters with CO₂ shut-down device inoperative – heaters operated at maximum and minimum output



Figure 9 Percentage of supplied hydrocarbons unburnt – tests in leak-proof chamber – radiant heaters with CO₂ shut-down device inoperative – heaters operated at maximum and minimum output







Figure 11 Carbon monoxide in atmosphere in leak-proof chamber – catalytic heaters – heaters operated at maximum and minimum output



Figure 12 Unburnt hydrocarbons in atmosphere in leak-proof chamber - catalytic heaters - heaters operated at maximum and minimum output



Figure 13 Percentage of supplied hydrocarbons unburnt - catalytic heaters in leak-proof chamber - heaters operated at maximum and minimum output



(From Coward and Jones, Bulletin 503, Bureau of Mines, Dept of Interior, USA 'Limits of flammability of gases and vapors')

Figure 14 Limits of flammability of butane in mixtures of air and nitrogen, and of air and carbon dioxide