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LOW NO_x COMBUSTION: THE EFFECT OF EXTERNAL FLUE GAS RECIRCULATION ON EMISSIONS FROM CRUDE OIL COMBUSTION

T. D. BROWN

Canadian Combustion Research Laboratory

FUELS RESEARCH CENTRE

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Low No_x Combustion: the Effect of External Flue Gas Recirculation on Emissions from Crude Oil Combustion (*)

T. D. Brown

Canadian Combustion Research Laboratory, Fuels Research Centre, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada

SUMMARY:

The initial results are presented from a continuing investigation of the production of nitric oxide (NO) during the combustion of two liquid fuels in a pilot-scale 16-gph (US) boiler.

Low-excess-air combustion is shown to be less effective than flue-gas recirculation in reducing the NO emission.

The emission of $(NO)^{\dagger}$ in g/kg fuel can be related to the recirculation ratio, R, and of the emission without recirculation $(NO)^{\dagger\dagger}$ by a general linear equation:

$$\frac{(NO)^{\dagger}}{(NO)^{\dagger\dagger}} = 1 - AR$$

At the two combustion intensities used in the experiments described in this paper, A is independent of the excess air level at the higher combustion intensity but is dependent on the excess air level at the lower combustion intensity.

RIASSUNTO:

Si presentano i risultati preliminari di uno studio sulla produzione dell'ossido di azoto (NO) durante la combustione di due combustibili liquidi in una caldaia pilota da 16 galloni/ora.

Si dimostra che la combustione con basso eccesso di aria è meno efficace del riciclo dei fumi nel ridurre l'emissione di NO.

L'emissione $(NO)^{\dagger}$ in g/kg di combustibile può essere collegata al rapporto di riciclo R e all'emissione senz ariciclo $(NO)^{\dagger\dagger}$ mediante un'equazione lineare generale:

$$\frac{(NO)^{\dagger}}{(NO)^{\dagger\dagger}} = 1 - AR$$

Alle due intensità di combustione adottate nelle esperienze qui descritte, A non dipende dall'eccesso d'aria all'intensità di combustione maggiore, mentre dipende da tale eccesso alla intensità di combustione minore.

(*) Paper presented at the « Italian Flame Day », Pisa, 20-21 March 1973.

(*) Fuels Research Centre Divisional Report FCR 73/5-CCRL.

Introduction

Nitric oxide is the most important oxide of nitrogen formed in modern high-temperature boilers and, after emission, it will react with atmosperic oxygen to produce toxic nitrogen oxides.

Atmospheric photochemical reactions between nitrogen oxides, oxygen, and hydrocarbons produce smog which reduces visibility and produces further reaction products including the lachrymatory peroxyacetyl nitrates. In high concentrations, the smog products damage vegetation and aggravate human respiratory difficulties. Nitrogen dioxide (NO_2) is more hazardous than carbon monoxide (CO) because it combines with haemoglobin and forms acids in the lungs.

The advent of control legislation limiting the emission of nitric oxide will undoubtedly pose new problems for combustion engineers because high-temperature operation for maximum boiler efficiency inevitabliy increases the formation of nitric oxide. The objectives of this research program are to define the relevant combustion performance parameters than can be controlled or manipulated in such a manner as to minimize the formation of nitric oxide in flames.

Nitric oxide formation

The formation of nitric oxide from atmospheric nitrogen in flames is thought to occur by a reaction sequence that can be represented as follows:

$$N_2 + O \rightarrow NO + N$$
$$O_2 + N \rightarrow NO + O$$

The kinetics of the reaction have been exhaustively examined by previous investigators and a rate expression of the form:

$$\frac{d(NO)}{dt} = A_1 \cdot e{-E_1/RT} \cdot [N_2]\,[O_2]^{1/2} — A_2 \cdot e{-E_2/RT}\ [NO]^2\ [O_2]^{-1/2}$$

is generally taken to represent the rate of formation of (NO, although argument persists as to the magnitude of the prex-exponential constants.

The magnitude of E_1 and E^2, 135,000 cal/mole and 90,000 cal/mole respectively, indicate that the rate of production of NO will primarily be a temperature dependent function with a secondary dependence on the oxygen partial pressure in the flame (excess air level). It is apparent that reductions in flame temperature and excess air level will both contribute to a reduction in the formation of nitric oxide in flames. The Canadian Combustion Research Laboratory has focused its attention on these two variables in a series of experiments designed to study their relative importance in the control of nitric oxide formation in flames from four fuels:

— No. 2 fuel oil
— crude oil
— No. 6 fuel oil
— pulverized coal.

This report presents the results obtained in the early stages of the program and is concerned only with data obtained from the combustion of the first two fuels listed.

The experimental boiler

The pilot-scale boiler shown in Fig. 1 has a full-load steaming rate of 1600 lb/hr at a pressure of 150 psig or less. The firing system consists of two pressure-atomized oil burners, opposed and inclined downwards over a refractory-lined chamber. The furnace is of membrane wall construction and will accept a maximum heat-release rate of about 0.7 kJ/m^3hr (80,000 Btu/ft^3hr). Primary air is supplied to the burners at a temperature of 200 °C (400 °F); secondary air is supplied via an annulus which is concentric with the primary air supply at any temperature up to 200 °C (400 °F).

Combustion gases leave the furnace at temperatures between 750 °C (1350 °F) and 900 °C (1650 °F), pass through a transition piece, then travel across the tubes of a high-temperature air heater. Finally, the combustion gases pass through the tubes of a three-pass conventional air heater and enter the laboratory exhaust system via a breeching at between 250 °C (500 °F) and 400 °C (750 °F). For external flue-gas recirculation, a high-pressure blower, connected to the breeching, supplies controlled quantities of flue gas to the secondary-air annulus of the burners; this provides variable blends of oxygen-lean flue gas and secondary combustion air for participation in the combustion process. There is also provision to recirculate the flue gases both above and below the flame.

The research boiler is manually controlled except for some electrical inter-locks to ensure that a correct start-up and shut-down procedure is observed.

Experimental procedures

Excess air level and recirculation ratio

Tests have been run at full load and part load; the variables super-imposed on these conditions being excess-air level and recirculation ratio. The definition of recirculation ratio adopted in these experiments is that due to

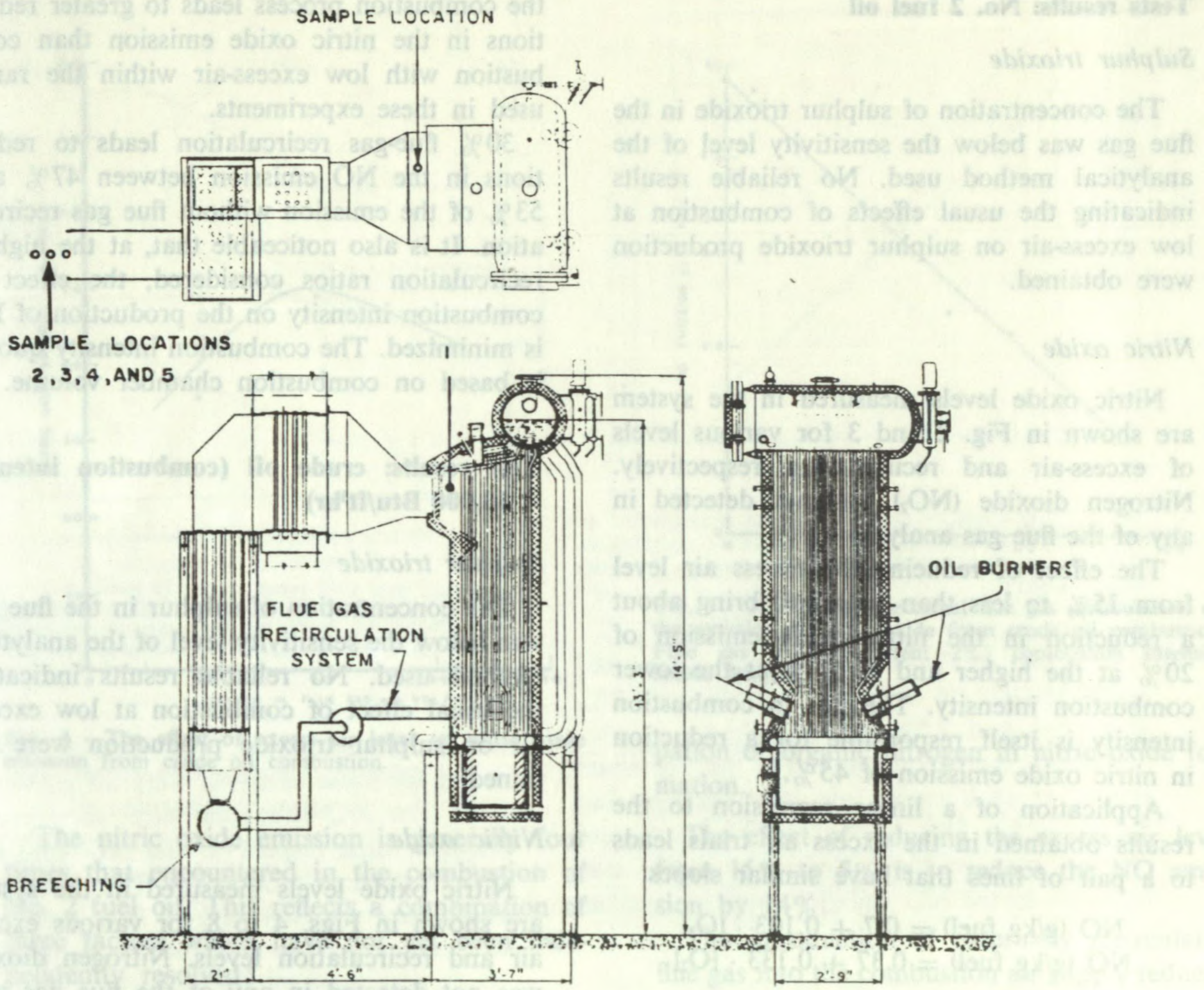

FIG. 1 - Schematic diagram of the experimental boiler.

HEDLEY (*):

$$R = \frac{M_x}{M_f + M_a + M_x}$$

where M_f, M_a, and M_x are the mass flow rates of fuel, air, and recirculated combustion products respectively.

Performance measurements

The usual operating procedure was to take the boiler to an equilibrium thermal condition at the excess air level and recirculation ratio required for the current experiment. The recirculation gas temperature was maintained at 200 °C.

The following parameters of performance were measured continuously during the combustion trial:

1) CO_2, CO, and O_2 by non-dispersive infrared and paramagnetic analysis;

2) NO, NO_2, SO_2 by automated wet chemistry using modified SALTZMAN and WEST-GAEKE methods;

3) SO_3 by modified SHELL-THORNTON System;

4) acid dewpoint and rate of acid build-up by means of a BCURA dewpoint meter; and

5) particulate matter in the flue gas by means of an isokinetic ANDERSON sampling system that took one sample per run.

The locations for which samples were taken for these determinations are shown in Fig. 1 with the corresponding numbers.

The low sulphur contents of both the No. 2 fuel oil and the crude oil meant that the measurements involving sulphur trioxide and acid dewpoint did not necessarily apply.

(*) A. B. HEDLEY, E. W. JACKSON- J. Inst. Fuel *38*, 39 (1965).

Tests results: No. 2 fuel oil

Sulphur trioxide

The concentration of sulphur trioxide in the flue gas was below the sensitivity level of the analytical method used. No reliable results indicating the usual effects of combustion at low excess-air on sulphur trioxide production were obtained.

Nitric oxide

Nitric oxide levels measured in the system are shown in Fig. 2 and 3 for various levels of excess-air and recirculation respectively. Nitrogen dioxide (NO_2) was not detected in any of the flue gas analyses.

The effect of reducing the excess air level from 15% to less than 5% is to bring about a reduction in the nitric oxide emission of 20% at the higher and of 35% at the lower combustion intensity. The fall in combustion intensity is itself responsible for a reduction in nitric oxide emission of 45%.

Application of a linear regression to the results obtained in the excess air trials leads to a pair of lines that have similar slopes.

$$NO \text{ (g/kg fuel)} = 0.7 + 0.103 \cdot [O_2]$$
$$NO \text{ (g/kg fuel)} = 0.37 + 0.133 \cdot [O_2]$$

The introduction of recirculated flue gas into the combustion process leads to greater reductions in the nitric oxide emission than combustion with low excess-air within the range used in these experiments.

30% flue-gas recirculation leads to reductions in the NO emission between 47% and 53% of the emission without flue gas recirculation. It is also noticeable that, at the highest recirculation ratios considered, the effect of combustion intensity on the production of NO is minimized. The combustion intensity quoted is based on combustion chamber volume.

Test results: crude oil (combustion intensity 80,000 Btu/ft³hr)

Sulphur trioxide

The concentration of sulphur in the flue gas was below the sensitivity level of the analytical method used. No reliable results indicating the usual effect of combustion at low excess-air on sulphur trioxide production were obtained.

Nitric oxide

Nitric oxide levels measured in the system are shown in Figs. 4 to 8 for various excess-air and recirculation levels. Nitrogen dioxide was not detected in any of the flue gas analyses.

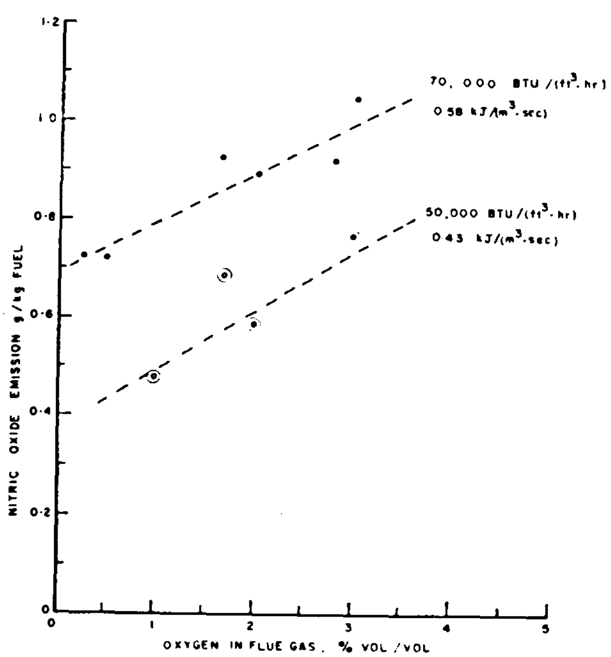

FIG. 2 - The effect of excess air level and combustion intensity on nitric oxide emission from No. 2 fuel oil combustion.

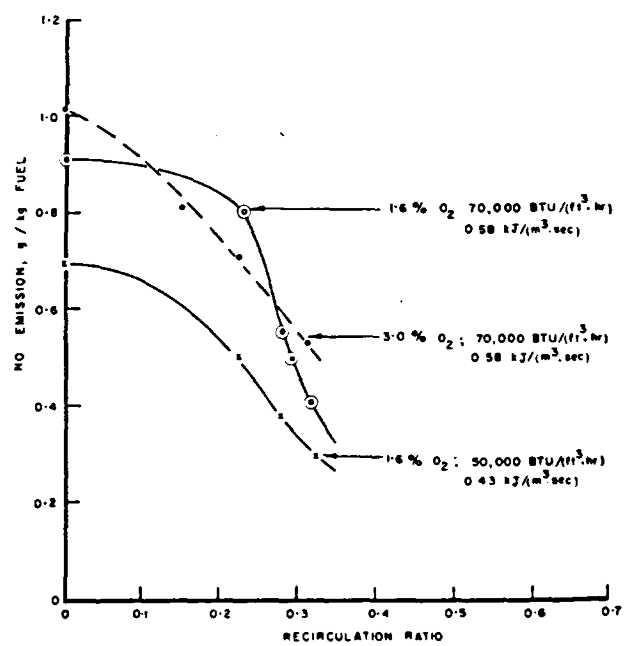

FIG. 3 - The effect of external flue gas recirculation on the emission of nitric oxide from No. 2 fuel oil combustion.

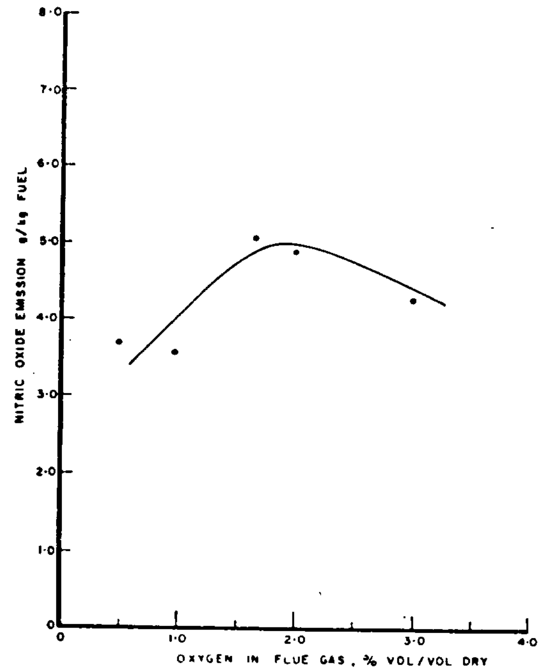

FIG. 4 - The effect of excess air level on nitric oxide emission from crude oil combustion.

The nitric oxide emission is generally four times that encountered in the combustion of No. 2 fuel oil. This reflects a combination of three factors which have not yet been independently resolved:

1) the higher combustion intensity;

2) the nature of the fuel and the effect of carbon: hydrogen ratio on flame temperatures; and

3) the nature of the fuel and the partici-

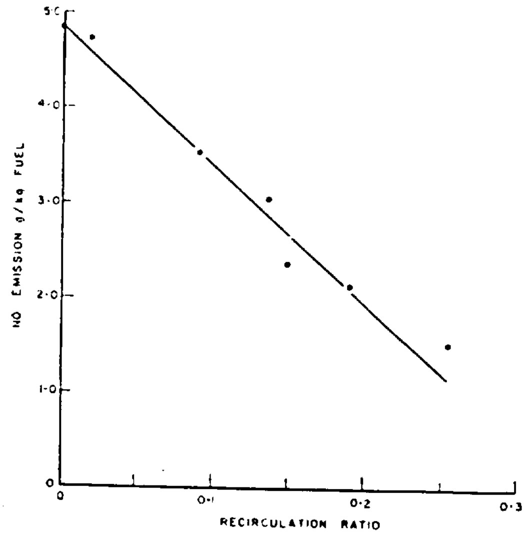

FIG. 6 - The effect of external flue gas recirculation on the emission of nitric oxide from crude oil combustion. Flue gas oxygen content 2%; combustion intensity 80,000 Btu/ft³hr.

pation of organic nitrogen in nitric oxide formation.

The effect of reducing the excess air level from 15% to 5% is to reduce the NO emission by 14%.

The introduction of externally recirculated flue gas into the combustion air supply reduced nitric oxide emission more than did low-excess air combustion within the range used in these experiments. A recirculation ratio of 0.2 gave a reduction of 50% in the NO emission with excess oxygen levels in the flue gas of 3%, 2%, 1% and 0.5% as shown in Figs.

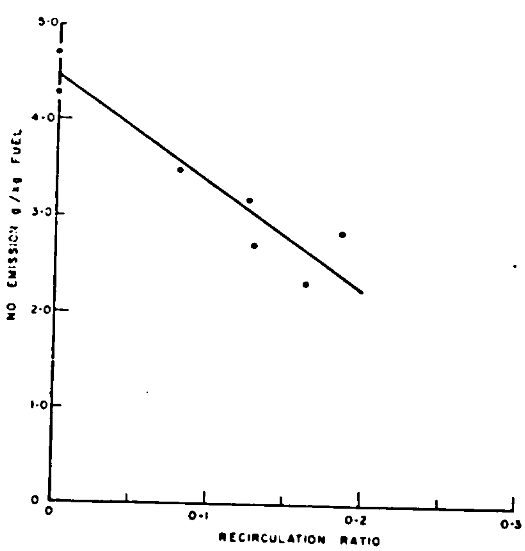

FIG. 5 - The effect of external flue gas recirculation on the emission of nitric oxide from crude oil combustion. Flue gas oxygen content 3%; combustion intensity 80.000 Btu/ft³hr.

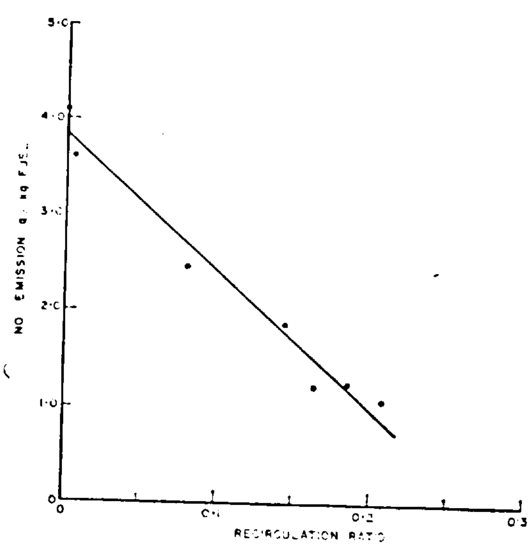

FIG. 7 - The effect of external flue gas recirculation on the emission of nitric oxide from crude oil combustion. - Flue gas oxygen content 1%; combustion intensiy 80,000

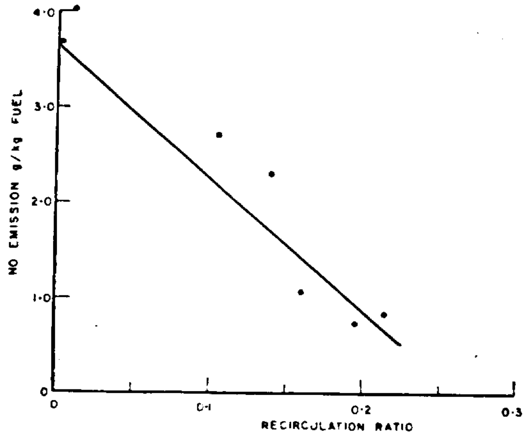

FIG. 8 - The effect of external flue gas recirculation on the emission of nitric oxide from crude oil combustion. Flue gas oxygen content 0.5%; combustion intensity 80,000 Btu/ft³hr.

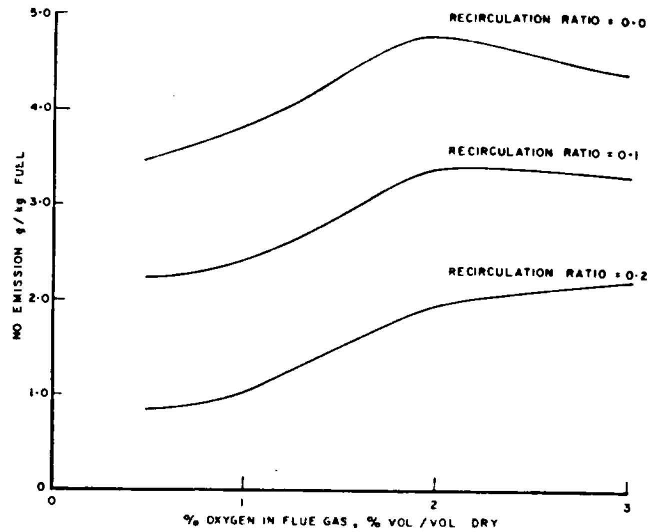

FIG. 10 - The effect of external flue gas recirculation and excess air level on the emission of nitric oxide from crude oil combustion. Combustion intensity 80,000 Btu/ft³hr.

5, 6, 7, and 8. These oxygen levels correspond approximately to excess air levels of 15%, 10%, 5% and 2.5% respectively.

A linear regression analysis of the individual results at each excess air level showed that the regression lines all had similar slopes and differed only in their Y-intercpet. (The corresponds to the NO emission without external flue-gas recirculation). The correlation co-efficients for these analyses were all greater than 0.90. The NO emissions were, therefore, normalized with respect to the NO emission at a recirculation ratio of 0. These normalized results are shown in Fig. 9. The linear equation, illustrated to describe the over-all effect of flue-gas recirculation, is:

$$\frac{(NO)_{\dagger}}{(NO)_{\dagger\dagger}} = 1.000 - 3.291\ [R]$$

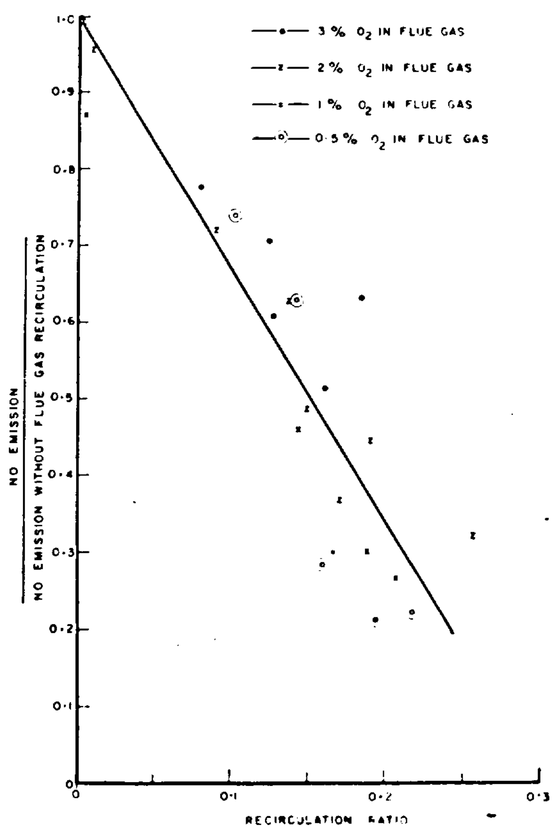

FIG. 9 - The effect of flue gas recirculation on the emission of nitric oxide from crude oil combustion. Combustion intensity 80,000 Btu/ft³hr.

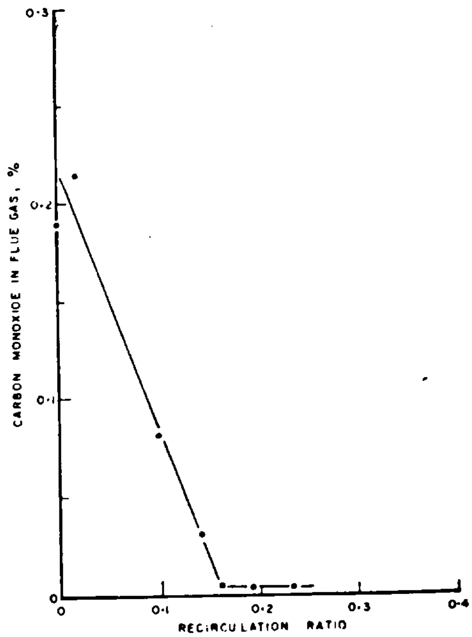

FIG. 11 - The effect of external flue gas recirculation on carbon monoxide production at a low excess air level during crude oil combustion. Flue gas oxygen content 0.5%; combustion intensity 80,000 Btu/ft³hr.

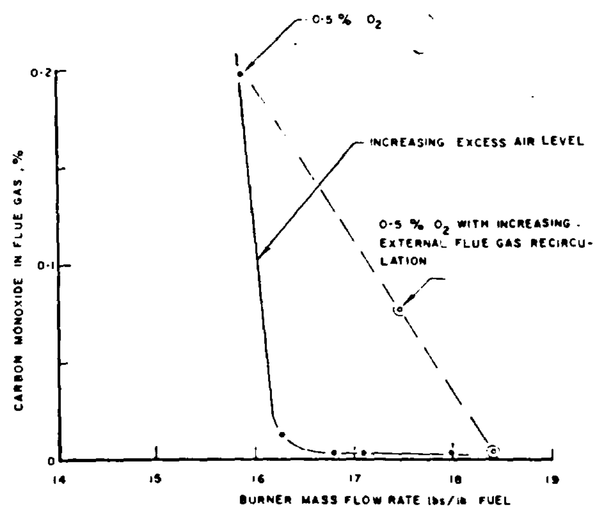

FIG. 12 - The effect of burner mass flow rate on carbon monoxide production during crude oil combustion. Combustion intensity 80,000 Btu/ft³hr.

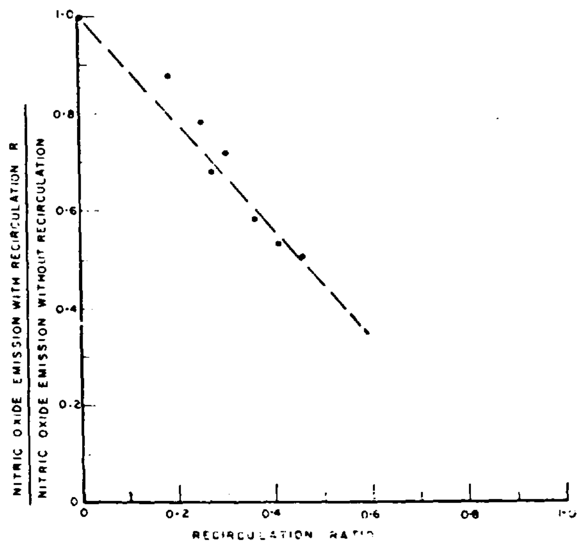

FIG. 14 - The effect of external flue gas recirculation on the nitric oxide emission from crude oil combustion. Flue gas oxygen 3%; combustion intensity 64,000 Btu/ft³h.

where

(NO)† is the NO emission in g/kg fuel at recirculation ratio R

(NO)†† is the NO emission in g/kg fuel at recirculation ratio $R = 0$.

A plot of the NO emission data from the regression lines of Figs. 5 to 8 against the nominal excess-air level leads to the family of curves shown in Fig. 10. This suggests the existence of a peak in the NO emission at 2% oxygen in the flue gases (10% excess-air) when combustion takes place without external recirculation of flue-gas. The external recirculation of flue-gas appears to decrease the magnitude of this peak and shift it to higher excess-air levels.

Carbon monoxide

The experimental system was generally capable of burning the fuel without generating significant quantities of carbon monoxide. However, there was one exception when measurable concentrations of carbon monoxide were produced at the lowest excess-air level investigated. In this case, the carbon monoxide was eliminated by the introduction of external flue-gas recirculation, see Fig. 11.

This was attributed to the increase in momentum when the mass flow through the secondary-air annulus was increased by the external flue-gas circulation. This increase in momentum represents an increase in the energy

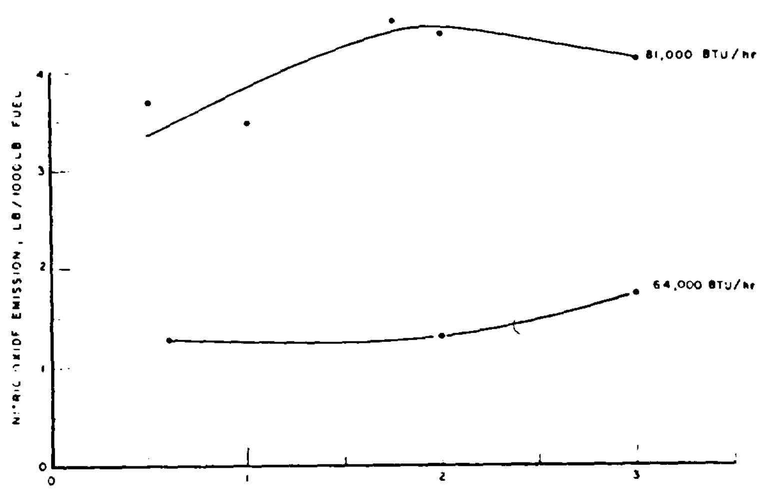

FIG. 13 - The effect of excess air level and combustion intensity on the nitric oxide emission from crude oil combustion.

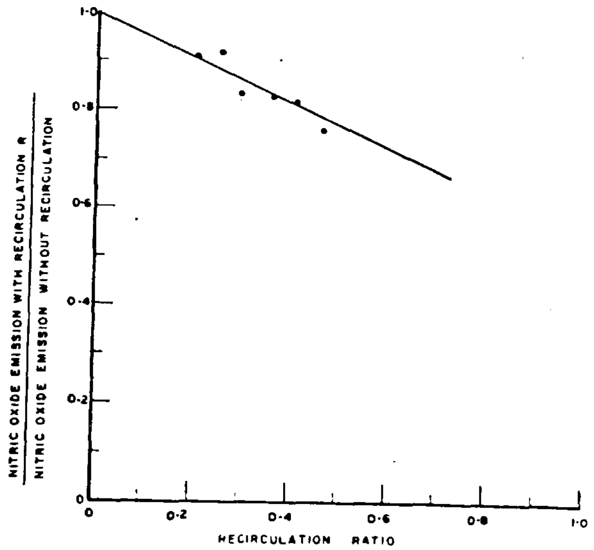

FIG. 15 - The effect of external flue gas recirculation on the nitric oxide emission from crude oil combustion. Flue gas oxygen content 2%; combustion intensity 64,000 Btu/ft³hr.

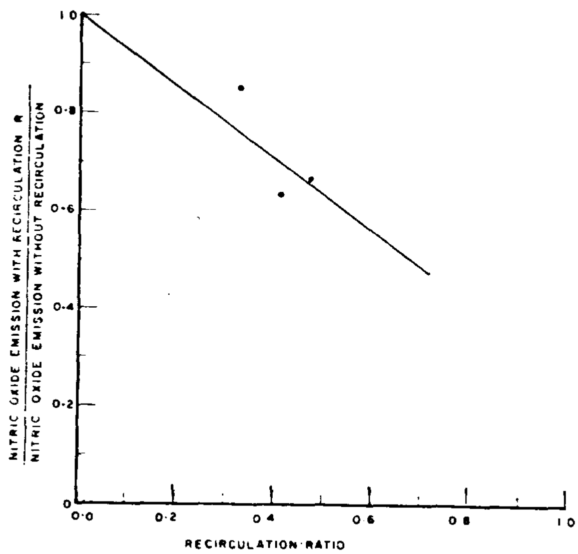

FIG. 16 - The effect of external flue gas recirculation on the nitric oxide emission from crude oil combustion. Flue gas oxygen content 0.6%; combustion intensity 64,000 Btu/ft³hr.

available for the mixing processes in the flame. An increase in momentum could also be obtained by increasing the excess air level. The mass flow rates at different excess-air levels and at different recirculation ratios are shown in Fig. 12, by which the importance of increased oxygen availability is clearly demonstrated. Increasing the mass flow rate by increasing the excess air level eliminated the carbon monoxide at a mass flow rate of 2260 lb/hr whereas increasing the mass flow rate by introducing recirculated flue-gas at a constant excess-air level did not eliminate the carbon monoxide until a mass flow rate of 2560 lb/hr was reached.

Solids loading of the gases

It was hoped that the use of externally recirculated flue-gases would reduce the amount of unburnt solids and smoke emission associated with the combustion of crude oil. This was not verified by experiment. Levels of gasborne particulate material were low, varying from 0.005% to 0.035% of hte input fuel; no systematic effect due to external flue gas recirculation was detected.

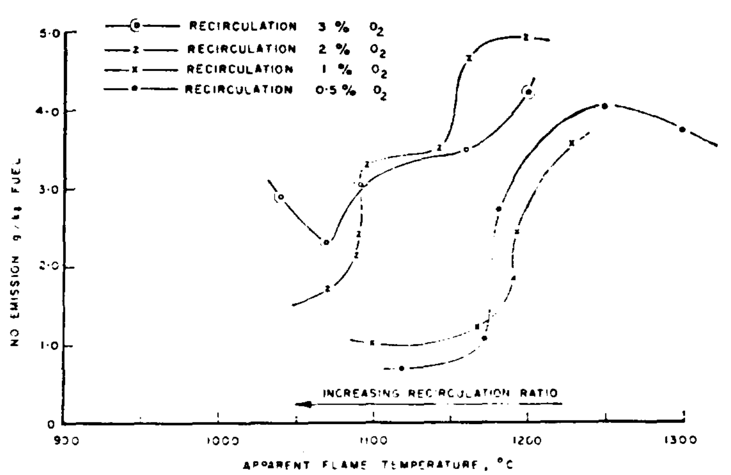

FIG. 17 - Nitric oxide emissioni in relation to an apparent flame temperature. Crude oil combustion 80,000 Btu/ft³hr.

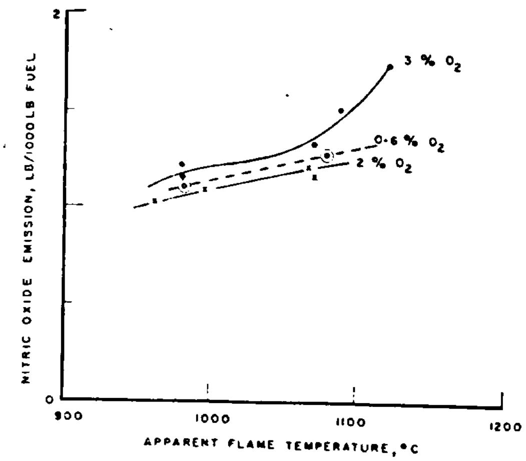

FIG. 18 - Nitric oxide emission in relation to an apparent flame temperature. Crude oil combustion 64,000 Btu/ft^{3}hr.

Test results: crude oil (combustion intensity 64,000 Btu/ft^{3}hr)

Nitric oxide

Nitric oxide levels measured in the system are shown in Figs. 13 to 16 for various excess-air and recirculation levels. Nitrogen dioxide was not detected in any of the flue gas analyses.

The nitric oxide emission was generally one third of that measured at the higher combustion intensity.

The effect of reducing the excess air level from 15% to 3% was to reduce the NO emission by 25%

The introduction of externally recirculated flue-gas into the combustion air supply reduced the nitric oxide emission more than did low excess-air combustion within the range used in these experiments.

Appraisal

The comparative reductions in NO emissions brought about by the flue-gas recirculation at different combustion intensities have been represented by the simple linear regression equations shown in the Table.

It can be seen that the slope of the regression lines at the lower combustion intensity is not the same at all excess-air levels and is consistently lower than that observed at the higher combustion intensity. Measurements of an apparent flame temperature (Figs. 17 and 18) made during the trials indicate that the temperature levels in the low-combustion-intensity system were already low; external flue-gas recirculation could not therefore be expected to reduce NO formation as dramatically as in the higher-combustion-intensity system where the general temperature level was higher.

The reduction of NO *emission by external flue gas recirculation*

Combustion intensity, Btu/ft^{3}hr	Excess air level, %	Reduction in NO emission
80,000	A11	$\frac{NO\dagger}{NO\dagger\dagger} = 1 - 3.3\ R$
64,000	15	$\frac{NO\dagger}{NO\dagger\dagger} = 1 - 1.45\ R$
	10	$\frac{NO\dagger}{NO\dagger\dagger} = 1 - 0.5\ R$
	3	$\frac{NO}{NO} = 1 - 0.79\ R$

NO† = emission in g/kg fuel at recirculation ratio R; NO†† = NO emission in g/kg fuel at recirculation ratio $R = 0$.

Conclusions

The control of nitric oxide emission from crude oil combustion using low-excess combustion air is less effective than is external flue-gas recirculation.

Reductions in nitric oxide emission due to external flue-gas recirculation are most marked at high combustion intensities; under these experimental conditions the reductions were greatest at the highest excess-air level.

Acknowledgements

All the members of the staff of the Canadian Combustion Research Laboratory have contributed to the research program of which this report forms part. The author wishes to acknowledge the valuable discussion and encouragement from all his colleagues. In particular, the experimental and analytical assistance given by Mr. R. G. FOUHSE, Mr. B. C. POST, and Mr. R. K. JEFFREY have contributed greatly to the results reported here