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THE EFFECTS OF EXTERNAL FLUE-GAS RECIRCULATION  
ON EMISSIONS FROM LIQUID AND SOLID FUEL COMBUSTION

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THE EFFECTS OF EXTERNAL FLUE-GAS RECIRCULATION  
ON EMISSIONS FROM LIQUID AND SOLID FUEL COMBUSTION

by

T. D. Brown\* and G. K. Lee\*

ABSTRACT

The use of flue-gas recirculation as a control measure for nitric oxide emissions has been investigated in a pilot-scale research boiler with particular attention being paid to the side effects on other emissions e.g. sulphur trioxide and combustibile particulate matter. The research boiler has a full-load steaming rate of 750 kg/hr at  $10^6$  N/m<sup>2</sup> and is fired with twin opposed burners inclined downward over a refractory hearth.

In the case of liquid fuel, experiments were carried out at full- and part-load with variable conditions of excess-air level, recirculation ratio and fuel-nitrogen content. At the full-load condition reductions in NO emissions of approximately one-third were achieved by reducing the excess-air level from 15% to 5%; this was accompanied by a small increase in the soot (unburned carbon) loading of the combustion products and a slight

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change in the measured sulphur trioxide concentration. Recirculation of flue gas resulted in 15% and 30% reductions of NO emissions from the high- and low-nitrogen fuel oils respectively; the absolute magnitude of the reduction was the same for both fuels.

It had been anticipated from theory that reductions in flame temperatures due to recirculation would reduce sulphur trioxide concentrations but a slight increase was actually measured.

The reduced flame temperatures and residence times in the research boiler (due to recirculation) militated against complete burn-out of the soot and carbonaceous residues which formed early in the flame. An approximate doubling of the solids concentration in the flue gases was observed as the recirculation ratio approached 0.4.

In experiments using a Saskatchewan lignite, (11% ash; 1.1% N<sub>2</sub>; as fired) it was demonstrated that external recirculation of flue gas was moderately effective in controlling nitric oxide emissions (reduction  $\approx$  10%). However, major increases in the unburnt carbon carry-over were observed. These increases were probably exaggerated (relative to industrial practice) by the short residence time in the research boiler. The extent of sulphur dioxide neutralization by the alkaline constituents of the ash remained essentially unchanged as the recirculation ratio increased.

It was established that external flue-gas recirculation has limitations as a technique for the control of nitric oxide emissions from both liquid and solid fuels.

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## INTRODUCTION

Nitric oxide (NO), the dominant oxide of nitrogen emitted by combustion processes, is a primary reactant in the formation of photochemical smogs. Consequently, NO emission standards have been enacted around the world, especially stringent in areas such as the south west coast of the United States where conditions are conducive to diurnal smog episodes. In Canada, studies are in progress to identify regions where the potential for photochemical smogs may exist and federal standards for NO emissions are in various stages of promulgation.

The advent of progressively more stringent NO emission standards has led to the development of a number of control techniques which have been applied to modern fuel-fired boilers with varying degrees of success. However, the available literature contains few references on the relative contributions of fuel-nitrogen and atmospheric-nitrogen to NO formation.

This paper describes the effects of excess combustion air, external flue-gas recirculation and combustion intensity on NO formation in a pilot-scale research boiler. It also evaluates the combined role of these parameters on the conversion of fuel nitrogen to nitric oxide and on other pollutant emissions when four different fuels were burnt.

## NITRIC OXIDE FORMATION IN FLAMES

Nitric oxide formed in flames can originate from either atmospheric-nitrogen or fuel-nitrogen. Although the formation of NO from atmospheric-nitrogen has been examined in detail and considerable kinetic data are available, the oxidation of nitrogenous compounds in the fuel has not received the same attention and relatively little is known about the reaction process which they undergo in flames.

As a precursor to the experimental investigation described in this paper, a simple model of nitric oxide formation in a plug-flow reactor was formulated<sup>(1)</sup>. The model, based on the Zeldovitch rate expression for atmospheric nitrogen reaction, incorporates additional low activation energy terms to accommodate fuel-nitrogen reactions that could produce both molecular nitrogen and nitric oxide. The model shows 1) that reductions in peak flame temperatures to below 1900°K, by use of external flue-gas recirculation, will eliminate air-source nitric oxide and 2) that no reduction in fuel-source nitric oxide can be expected unless flame temperatures are reduced to impractical levels. The model study also suggests that nitric oxide production from atmospheric nitrogen will be a maximum at an excess-air level of 6%.

The results from the model study show the importance of both temperature and oxygen partial pressure (excess-air level) in nitric oxide formation in flames. These two variables are also known to affect the formation of sulphur trioxide and combustion efficiency in flames. Low excess-air combustion reduces sulphur trioxide formation but unless it is achieved in well-designed combustion systems it can lead to high soot emissions from oil flames and to excessive carry-over of unburnt carbon from pulverized-coal flames.

#### THE EXPERIMENTAL BOILER

Combustion experiments were carried out in the pilot-scale research boiler using No. 2 fuel oil, crude oil, No. 6 fuel oil and Saskatchewan lignite. The boiler, illustrated in Figure 1, has a full-load steaming rate of 750 kg/hr (1600 lbs/hr) at a pressure of  $10^6$  N/m<sup>2</sup> (150 psig). The firing system consists of two opposed burners inclined downward over a refractory-lined chamber. The



furnace is of membrane-wall construction and will accept a maximum heat release rate of about  $0.9 \times 10^6 \text{W/m}^3$  ( $\approx 85,000 \text{ Btu/ft}^3\text{hr}$ ).

When the system is fired with a fuel oil, mechanical atomizing nozzles are used; swirled primary air is supplied via an annulus which is concentric with the fuel supply and swirled secondary air is supplied via a second annulus. Both the primary and secondary air can be preheated up to  $200^\circ\text{C}$ .

During pulverized coal combustion experiments a burner of the type illustrated schematically in Figure 2 is used.

Combustion gases leave the furnace at temperatures between  $750^\circ\text{C}$  and  $900^\circ\text{C}$ , pass through a transition section, 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 temperatures between  $250^\circ\text{C}$  and  $400^\circ\text{C}$ . For external flue-gas recirculation, a high-pressure blower, connected to the breeching, supplies controlled quantities of flue gas at  $200^\circ\text{C}$  to the secondary-air annuli 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 flames.

The research boiler is manually controlled except for some electrical interlocks to ensure a safe start-up and shutdown procedure.

The usual operating procedure was to bring the boiler to an equilibrium thermal condition for each excess-air level and recirculation ratio. When thermal equilibrium was established, the following parameters of performance were measured continuously:

- 1) CO<sub>2</sub>, CO and O<sub>2</sub> by non-dispersive infra-red and paramagnetic analysis;
- 2) NO, NO<sub>2</sub>, SO<sub>2</sub> by automated wet chemistry using modified Saltzman and West-Gaeke methods; an alternative chemiluminescent analytical system was used for NO and NO<sub>2</sub>.
- 3) SO<sub>3</sub> by a modified Shell-Thornton method (This measurement was made only during trials with No. 6 fuel oil).
- 4) Particulate matter in the flue gas by means of either an Anderson or CCRL sampling system.

The locations at which these samples were taken are shown in Figure 1.

Combustion tests were conducted at both full-load and part-load, with excess-air level and recirculation ratio being superimposed variables.

The definition of recirculation ratio adopted in these experiments was that due to Hedley<sup>(2)</sup>.

$$\text{Recirculation Ratio, } R = \frac{M_r}{M_r + M_a + M_f}$$

Where  $M_a$ ,  $M_f$  and  $M_r$  are the mass flows of air, fuel and recirculated flue gases respectively.

## EXPERIMENTAL RESULTS

### No. 2 Fuel Oil Combustion

Nitric oxide levels measured during the full- and part-load with No. 2 fuel oil are shown in Figures 3 and 4 for various levels of excess-air and recirculation ratio respectively.

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

$$\text{NO (g/kg fuel)} = 0.70 + 0.10 \{O_2\}$$

$$\text{NO (g/kg fuel)} = 0.37 + 0.13 \{O_2\}$$

### Crude Oil Combustion

The nitric oxide concentrations, illustrated in Figure 5, were higher than those measured with No. 2 oil at comparable excess-air levels and combustion intensities reflecting the higher fuel nitrogen content. Reducing the combustion intensity from  $0.9 \times 10^6 \text{ W/m}^3$  to  $0.66 \times 10^6 \text{ W/m}^3$  reduced the nitric oxide emissions by 50%; reductions in the excess-air level at both combustion intensities produced small (14%) reductions in the nitric oxide emissions.

External flue-gas recirculation ( $R = 0.2$ ) reduced NO emissions by as much as 50% at the higher combustion intensity but was less effective at the lower combustion intensity. At the higher combustion intensity, regression analysis of the results from individual excess-air levels generated lines which all had closely similar slopes, correlation coefficients above 0.90 and different Y-intercepts. The Y-intercept corresponds to the NO emission without recirculation and this was used to normalize the data obtained at each excess-air level.

These normalized results, shown in Figure 6, can be represented by the linear equation

$$\frac{\text{NO}^+}{\text{NO}^{++}} = 1.00 - 3.3 \{R\}$$

where  $\text{NO}^+$  is the NO emission in g/kg fuel at a recirculation ratio R.

$\text{NO}^{++}$  is the NO emission in g/kg fuel at a recirculation ratio  $R = 0$ .

At the lower combustion intensity, regression analysis of the results from individual excess-air levels generated lines which had different slopes and Y-intercepts. The normalization procedure described above could not, therefore, be applied to this data. The individual results are presented in Table 1.

TABLE 1

The Reduction of NO Emissions by External Flue-Gas Recirculation from Crude Oil Combustion at Heat Release Rate of  $0.66 \times 10^6 \text{W/m}^3$

Nominal Excess-Air Level %	Reduction in Nitric Oxide Emission
15	$\frac{\text{NO}^+}{\text{NO}^{++}} = 1 - 1.45\{R\}$
10	$\frac{\text{NO}^+}{\text{NO}^{++}} = 1 - 0.5 \{R\}$
3	$\frac{\text{NO}^+}{\text{NO}^{++}} = 1 - 0.8 \{R\}$
<p>NO<sup>+</sup> is the emission in g/kg fuel at recirculation ratio R</p> <p>NO<sup>++</sup> is the emission in g/kg fuel at recirculation ratio R = 0</p>	

Previous work<sup>(3)</sup> had indicated that the use of externally recirculated flue-gases might reduce the amount of unburnt solids and smoke associated with the combustion of crude oil. This was not confirmed by experiment. Levels of gas-borne particulate material were low, varying from 0.005 to 0.035% of the fuel input; no systematic effect due to external flue-gas recirculation was discernible.

At the high combustion intensity, a significant (0.2%) concentration of carbon monoxide was generated. This was eliminated by the introduction of externally recirculated flue-gas; the increase in burner momentum due to the increased mass flow produced an improvement in fuel-air mixing within the flame.

#### No. 6 Fuel Oil Combustion

Two No. 6 fuel oils with different fuel-nitrogen contents were selected for use in these experiments so that the effect of flue-gas recirculation on the conversion of fuel-nitrogen to NO might be established. The analyses of the fuels are given in Appendix A.

Experiments were carried out at full- and part-load. Under these conditions the firing rates of 12 and 8.75 Igph corresponded to volumetric heat release rates of  $0.83 \times 10^6$  W/m<sup>3</sup> and  $0.66 \times 10^6$  W/m<sup>3</sup>. The results obtained at the two firing rates were significantly different in character and are presented separately.

#### Results at the Higher-Firing Rate

Nitric oxide levels measured in the system are shown in Figures 7 and 8 where it can be seen that the level of nitric oxide was higher than that measured with crude oil. Reductions due to reduced excess-air level were 33% for both the high- and the low-nitrogen fuels.

External flue-gas recirculation, (R = 0.3) reduced NO emissions by 15% for the high-nitrogen fuel and by 40% for the low-nitrogen fuel. The absolute magnitudes of the reductions were similar (1.5 - 2.0 gm/1000 gm fuel) and the slopes of the regression lines shown in Figure 9 were closely similar for both fuels at the 15% excess-air (3% O<sub>2</sub>) level.

The regression lines can be represented by the following equations:

0.48% N<sub>2</sub> in Fuel

$$15\% \text{ excess-air; } \frac{\text{NO}^+}{\text{NO}^{++}} = 1 - 0.95 R$$

0.28% N<sub>2</sub> in Fuel

$$15\% \text{ excess-air } \frac{\text{NO}^+}{\text{NO}^{++}} = 1 - 0.97 R$$

$$10\% \text{ excess-air; } \frac{\text{NO}^+}{\text{NO}^{++}} = 1 - 1.12 R$$

$$5\% \text{ excess-air } \frac{\text{NO}^+}{\text{NO}^{++}} = 1 - 1.62 R$$

It was postulated, incorrectly, that the reductions in flame temperature (and consequently oxygen atom concentration) due to external flue-gas recirculation would lead to a reduction in the SO<sub>3</sub> concentration in the flue-gas. The measured SO<sub>3</sub> concentrations at sample location 2 are given in Figure 9. It appears that a slight increase in SO<sub>3</sub> concentration occurred. The distribution of SO<sub>3</sub> within the research boiler, Table 2, shows a maximum concentration in the furnace.

TABLE 2

Sulphur Trioxide Concentrations in the Research Boiler from No. 6 Fuel Oil Combustion at Heat Release Rate of  $0.83 \times 10^6$  W/m<sup>3</sup>, 3% Oxygen in Flue-Gas

Sampling Location (see Fig 1)	SO <sub>3</sub> , ppm	% Conversion $\frac{SO_3}{SO_2 + SO_3} \times 100$
A	18	1.4
1	7	0.5
2	3	0.2

The effect of external flue-gas recirculation on the solids loading of the flue-gas is shown in Figure 10. An approximate doubling of the solids concentration was recorded as the recirculation ratio approached 0.4.

#### Results at the Lower-Firing Rate

Nitric oxide levels measured in the system are shown in Figures 11 and 12; the concentrations are generally one-half of those recorded at the higher firing rate. With the high-nitrogen fuel a reduction in the excess-air level from 15% to 5% reduced the nitric oxide emission by 15%. This reduction was one half of the reduction observed at the high-firing rate.

The introduction of recirculated flue-gas did not lead to an immediate reduction in NO emission; significant reductions with the high-nitrogen fuel were achieved only at recirculation ratios above 0.3. At recirculation ratios below 0.3 increases in the nitric oxide emission were observed.

## Saskatchewan Lignite Combustion

The effects of external flue-gas recirculation on emissions from the research boiler during operation with pulverized lignite are shown in Figures 13 and 14. The fuel analyses and size distribution are given in Appendix A.

These experiments were carried out using the pulverized-coal burners illustrated in Figure 2. The recirculated flue-gas was introduced into the secondary-air annulus surrounding the fuel supply.

Reductions in excess-air level from 15% to 5% resulted in a reduction in the nitric oxide emission of 50%. Figure 15 shows that this did not result in a major increase in the unburnt carbon content of the fly-ash.

The introduction of externally recirculated flue-gas ( $R = 0.3$ ) produced reductions in nitric oxide emissions of between 30% and 50% depending on the excess-air level.

Figure 16 shows that the unburnt carbon content of the fly-ash and the thermal penalty associated with this carbon were only slightly affected by low excess-air combustion. On the other hand, externally recirculated flue-gas was found to have a marked effect on unburnt carbon as can be seen in Figure 16. It appears that these effects become more serious, and can introduce progressively more severe thermal penalties, as the overall excess-air level is reduced.

An important emission control process which occurs naturally in coals having alkaline ash constituents is the neutralization of  $SO_2$  by alkali metal ions in the ash. This can significantly reduce the  $SO_2$  concentrations in the flue-gas. Table 3 shows that neither excess-air level nor external flue-gas recirculation had a major effect on the extent of sulphur neutralization.



TABLE 3

The Effect of Recirculation Ratio  
on Sulphur Neutralization

Nominal Excess Air Level %	Recirculation Rate	% SO <sub>2</sub> Neutralization <sup>1/</sup>
25	0.00	54
	0.20	47
	0.23	49
	0.26	54
15	0.00	
	0.23	48
	0.27	51
	0.28	50
	0.29	67
5	0.00	43
	0.26	43
	0.27	58
	0.30	46

$$\frac{1}{\%} \text{ SO}_2 \text{ Neutralization} = \frac{\text{SO}_2 \text{ theoretical} - \text{SO}_2 \text{ measured}}{\text{SO}_2 \text{ theoretical}} \times 100$$

THE ROLE OF EXTERNALLY RECIRCULATED FLUE-GAS IN COMBUSTION

The principal effect of recirculated flue-gas is to reduce flame temperature; a secondary effect is to increase the burner momentum and, consequently, to modify the mixing history of the fuel and air.

The magnitude of the activation energy for the formation of NO from atmospheric nitrogen (thermal NO) implies that it is extremely sensitive to temperature and calculations using the Zeldovich rate expression show that the rate of reaction is extremely low at

temperatures below 1800°K. On the other hand, the postulated activation energies for the reactions of fuel nitrogen which produce NO are low (<30,000 kcal/mole) and the rate of reaction remains rapid at temperatures as low as 1200°K. These considerations mean that flue-gas recirculation will affect the total nitric oxide produced in the flame in different ways, i.e. from different nitrogen sources (fuel and air).

Reductions in flame temperature will reduce thermal NO and could conceivably eliminate this emission completely in a flame where no temperatures exceed 1800°K. Modifications to the mixing history within the flame can lead to either increases or reductions in the NO emissions originating from the fuel-nitrogen (fuel NO). Increases in burner momentum generally produce improvements in mixing, thus giving more intense flames and, where momentum increases are due to externally recirculated flue-gases, a consequent increase in the conversion of fuel-nitrogen to nitric oxide is probable.

#### NITRIC OXIDE FROM NO. 6 FUEL OIL COMBUSTION

In experiments with both No. 6 fuel oils at the higher combustion intensity, the introduction of external flue-gas recirculation produced a continuous reduction in NO emissions at all excess-air levels. The absolute magnitudes of these reductions were similar from both fuels suggesting that both the yield of thermal NO and the effect of recirculation on the yield were similar for both fuels. In addition, the composition and viscosity of the fuel and the close control of combustion conditions such as fuel flow rate, atomization temperature, fuel viscosity, excess-air level, air temperature, primary- to secondary-air ratio, recirculation mass flow, and recirculation gas temperature all combine to allow the assumption that the difference in NO formation ( $\Delta NO$ ) in comparable experiments was solely due to the difference in the nitrogen content of the two fuels.

The complete conversion of the fuel nitrogen from the high- and low-nitrogen fuels (Fuel A and Fuel B) leads to NO emissions of  $NO_A$  and  $NO_B$  respectively. The fractional conversion of fuel-nitrogen in the high-nitrogen fuel is given by:

$$\text{Fractional Conversion, } F_A = \frac{\Delta NO}{NO_A - NO_B}$$

If all the nitrogen in the high-nitrogen fuel behaves in the same manner, then the total NO emission is given by

$$NO_A, \text{ measured} = F_A NO_A + \{\text{thermal } NO\}_A$$

and the contribution of atmospheric nitrogen  $\{\text{thermal } NO\}_A$  to the total emission can be conveniently calculated.

Excess-Air Level and Fuel-Nitrogen Conversion

Fuel-nitrogen conversion levels, calculated as described above, are shown in Table 4.

TABLE 4

The Effect of Excess-Air Level  
on Fuel-Nitrogen Conversion

Nominal Excess-Air Level %	% Conversion of Fuel-Nitrogen to NO Fuel-Nitrogen = 0.48%	
	High Combustion Intensity	Low Combustion Intensity
15	30	37
10	20	-
5	29	-

The indication of a minimum at 10% excess-air is at variance with previously published data and also with other results from the authors' laboratory where consistent increases in the fractional conversion with increasing excess-air have been recorded.

Recirculation Ratio and Fuel-Nitrogen Conversion

The calculated results, showing the effect of recirculation on the conversion of fuel-nitrogen, are presented in Table 5.

TABLE 5

The Effect of Recirculation Ratio  
on Fuel-Nitrogen Conversion

Nominal Excess-Air Level %	Recirculation Ratio	% Conversion of Fuel-Nitrogen to NO Fuel-Nitrogen = 0.48%	
		High Combustion Intensity	Low Combustion Intensity
15	0.0	30	37
	0.1	31	52
	0.2	31	55
	0.3	32	46
	0.4	32	60

At the higher combustion intensity, recirculation had no effect on the conversion of fuel-nitrogen to nitric oxide; the extent of conversion is within the range reported by other workers and confirms previous assumptions that external flue-gas recirculation only affects NO formation from atmospheric nitrogen.

At the lower combustion intensity, a significant increase in the extent of conversion occurred and it is concluded that the increase in burner momentum, due to the recirculated flue-gases, modified fuel-air mixing in such a way as to minimize the size and distribution of oxygen deficient regions in the flame. Despite this increase in fuel-nitrogen conversion, there were only small increases in the total NO emission.

Excess-Air Level and Thermal NO

Table 6 shows the effect of excess-air level on thermal NO and illustrates clearly the small contribution made by atmospheric nitrogen at the lower combustion intensity.

TABLE 6

The Effect of Excess-Air on Thermal NO

Nominal Excess-Air Level %	Thermal NO As a Percent of Total Fuel-Nitrogen=0.48%	
	Higher Combustion Intensity	Lower Combustion Intensity
15	56	6.5
10	68	-
5	49	-

The existence of a maximum emission of thermal NO at 10% excess-air is in agreement with experimental results from a natural-gas-fired system<sup>(4)</sup> where the source of nitric oxide was atmospheric nitrogen.

Recirculation Ratio and Thermal NO

The effect of external flue-gas recirculation on thermal NO is shown in Table 7. Clearly, reductions in thermal NO were only significant at the higher combustion intensity and any reductions achieved at the lower combustion intensity did not contribute significantly to nitric oxide emission control.

TABLE 7

The Effect of Recirculation Ratio on Thermal NO

Nominal Excess-Air Level %	Recirculation Ratio	Thermal NO Emission; g/1000 g. Fuel Fuel-Nitrogen = 0.48%	
		Higher Combustion Intensity	Lower Combustion Intensity
15	0.0	4.0	0.25
	0.1	3.5	0.25
	0.2	3.0	0.2
	0.3	2.5	0.0
	0.4	2.0	

PARTICULATE EMISSIONS FROM NO. 6 FUEL OIL COMBUSTION

The increases in unburnt carbon carry-over from residual fuel oil combustion, that were measured when external flue-gas recirculation was introduced, can be directly attributed to the reductions in flame temperature and residence time. The magnitudes of these increases observed in the research boiler were probably enhanced above those which will occur in industrial systems where total residence times in the combustion chamber will be greater than the 0.3 seconds typical of this experimental system.

SULPHUR TRIOXIDE EMISSIONS FROM NO. 6 FUEL OIL COMBUSTION

The apparent increase in sulphur trioxide emissions that were observed in these experiments can be explained in terms of the formation mechanism postulated by Hedley(5). Hedley suggested that "super-equilibrium" concentrations of SO<sub>3</sub> could occur in a region of high atomic-oxygen concentration; that is, within the flame

envelope. These concentrations would subsequently decay to sub-equilibrium levels and subsequent SO<sub>3</sub> formation could proceed via a molecular oxidation of SO<sub>2</sub>.

The introduction of external flue-gas recirculation will reduce residence times in the combustion chamber and will, therefore, lead to a "freezing" of the decay of super-equilibrium SO<sub>3</sub> concentrations. Measurements at a given location in the boiler system would consequently show an increase in SO<sub>3</sub> concentration.

#### NITRIC OXIDE EMISSIONS FROM SASKATCHEWAN LIGNITE COMBUSTION

It appears from the experimental data that low excess-air combustion is a more practical control technique than flue-gas recirculation. It offers prospects of NO control without the thermal penalty associated with recirculation. The magnitude of the reductions achieved by external flue-gas recirculation at excess-air levels of 10% and 25% suggest that a significant proportion (>50%) of the nitric oxide produced during combustion of this fuel came from atmospheric nitrogen.

#### UNBURNT CARBON FROM SASKATCHEWAN LIGNITE COMBUSTION

The thermal penalty associated with unburnt carbon carry-over in the fly ash is dependent on both the excess-air level and the recirculation ratio. If external flue-gas recirculation is to be used as a nitric oxide control measure it may be necessary to increase excess-air levels to maintain combustion efficiency. A boiler efficiency penalty will be incurred and an optimization of the conflicting parameters must be undertaken.

## CONCLUSIONS

External flue-gas recirculation was found to be effective, with reservations, in controlling nitric oxide emissions when burning distillate, crude, and residual fuel oils and typical Saskatchewan lignite.

With residual fuel oil, slight penalties of increases in sulphur trioxide and unburnt carbon carry-over were observed with increasing recirculation ratio. On the other hand, with Saskatchewan lignite, the pronounced increase in unburnt carbon carry-over could constitute a significant thermal penalty.

It would, therefore, be unwise to proceed with nitric oxide control by external flue-gas recirculation without regard to other, perhaps more important, emissions.

## REFERENCES

- (1) T. D. Brown and F. D. Friedrich, "The Formation of Nitric Oxide in Distillate Oil Flames - Prediction and Measurement". Paper No. 25a. 25th Canadian Chemical Engineering Conference. Nov 2-5, 1975.
- (2) A. B. Hedley and E. W. Jackson, "Recirculation and Its Effect On Combustion Systems". J. Inst. Fuel 1965. 38 . 39.
- (3) R. Kamo, P. W. Cooper, B. N. Glicksberg and F. A. Fitzgerald, "Non Luminous Combustion of Distillate Fuel Oil Achieved by Recirculation". API Research Conference on Distillate Fuel Combustion 1964.
- (4) C. Halstead, C. Watson and J. Munro. "Nitrogen Oxides Control In Gas-Fired Systems Using Flue-Gas Recirculation and Water Injection". Paper to the IGT/AGA Conference On Natural Gas Research and Technology. Atlanta, Georgia. June 1972 .



- (5) A. B. Hedley. "A Kinetic Study of Sulphur Trioxide Formation In a Pilot Scale Furnace". Paper No. 11, Proceedings of the Marchwood Conference on the Mechanism of Corrosion by Fuel Impurities. Pub. Butterworths. 1963.

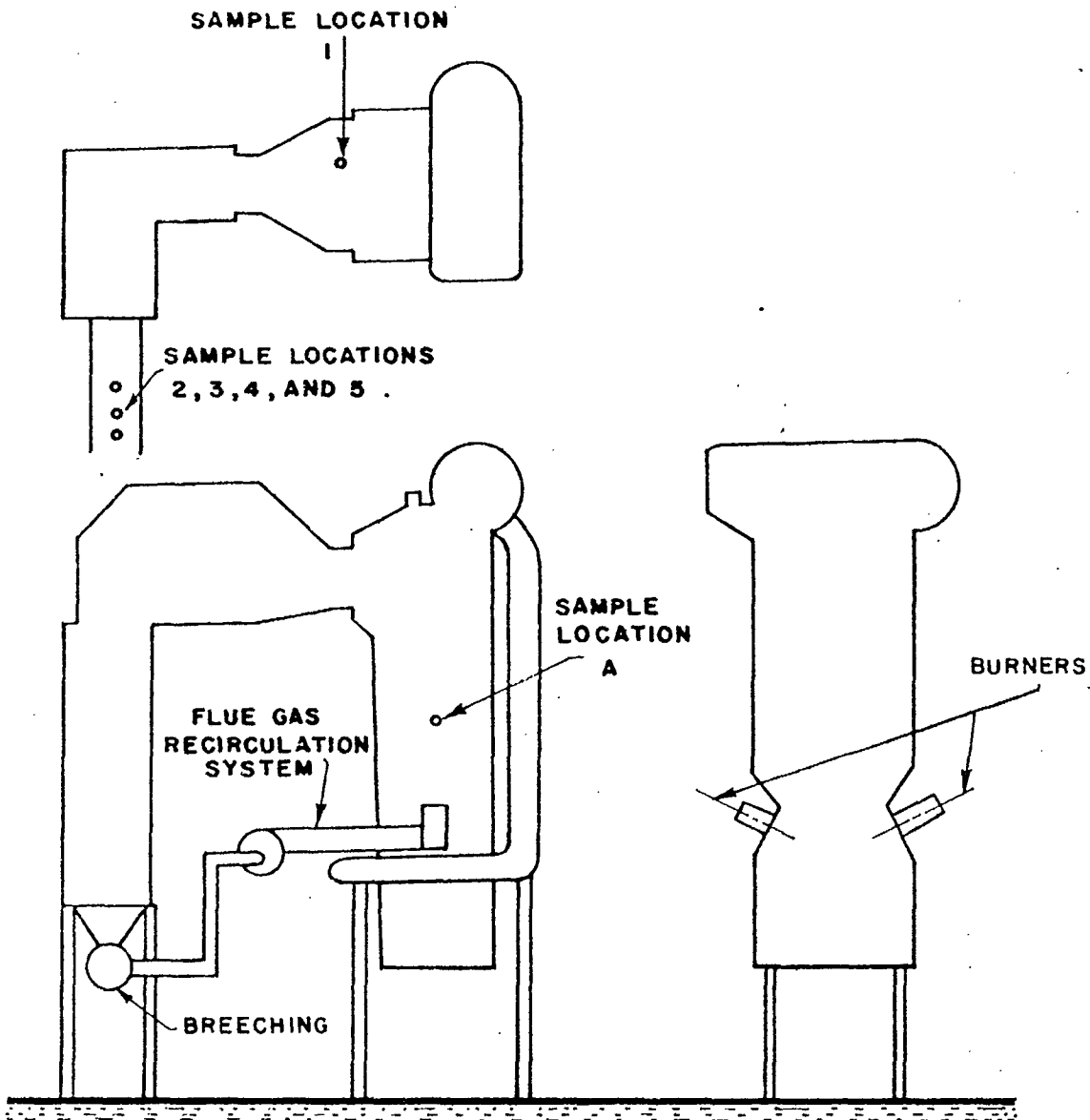


Figure 1. Schematic of the Pilot-Scale Research Boiler

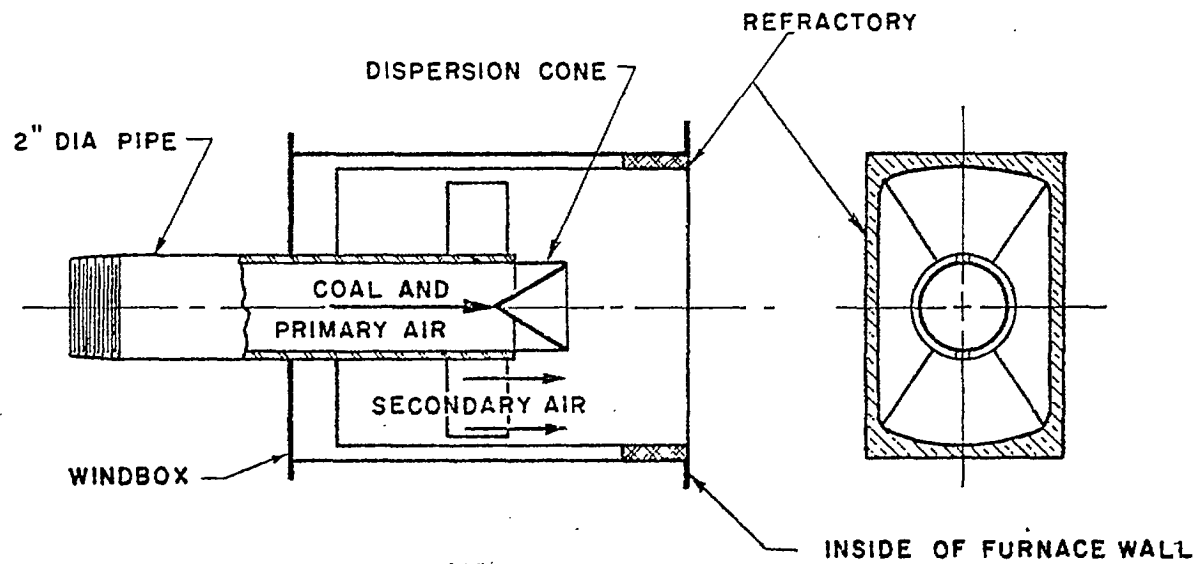


Figure 2. Schematic of the Pulverized-Coal Burner.

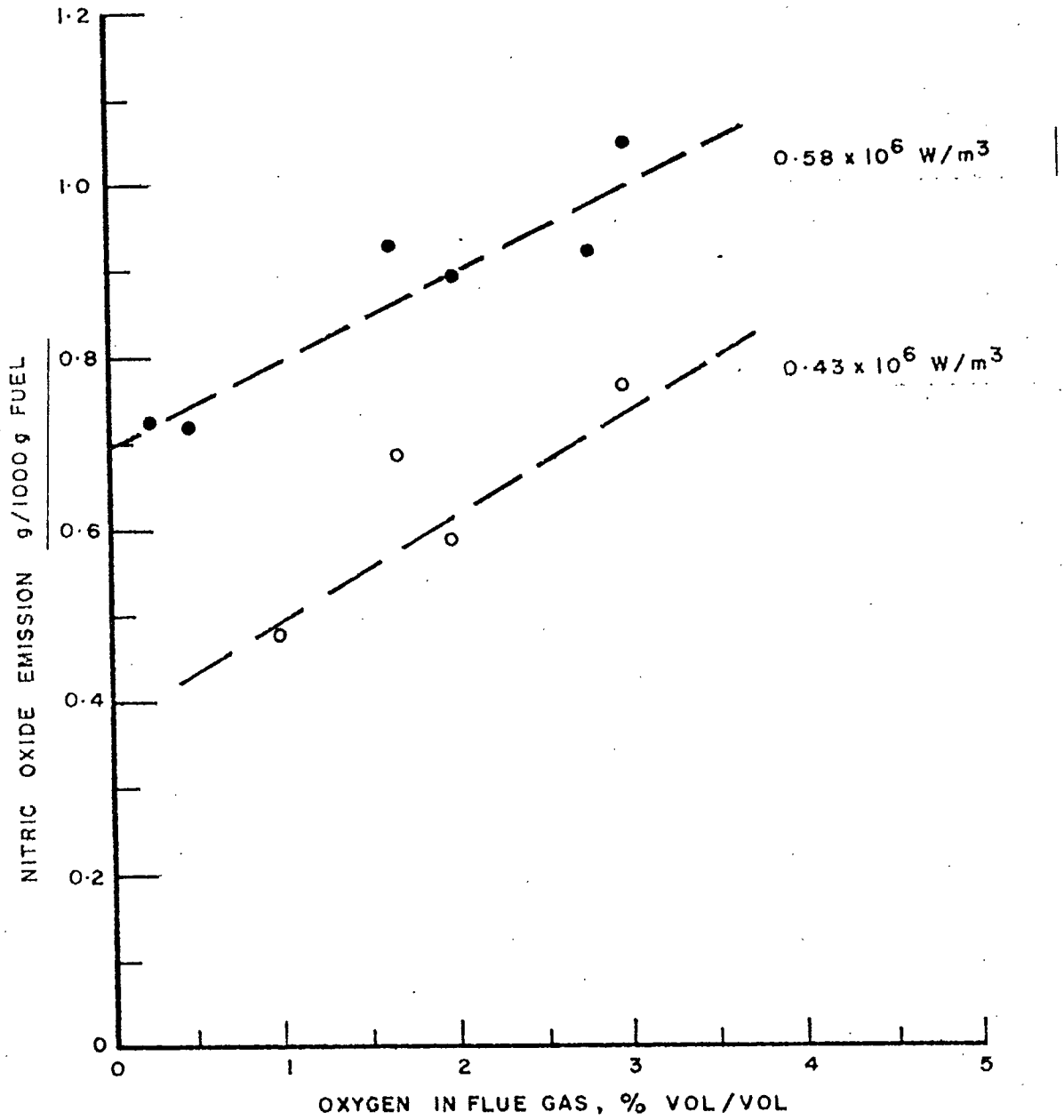


Figure 3. The Effect of Excess-Air Level and Combustion Intensity on Nitric Oxide Emissions from No. 2 Fuel Oil Combustion

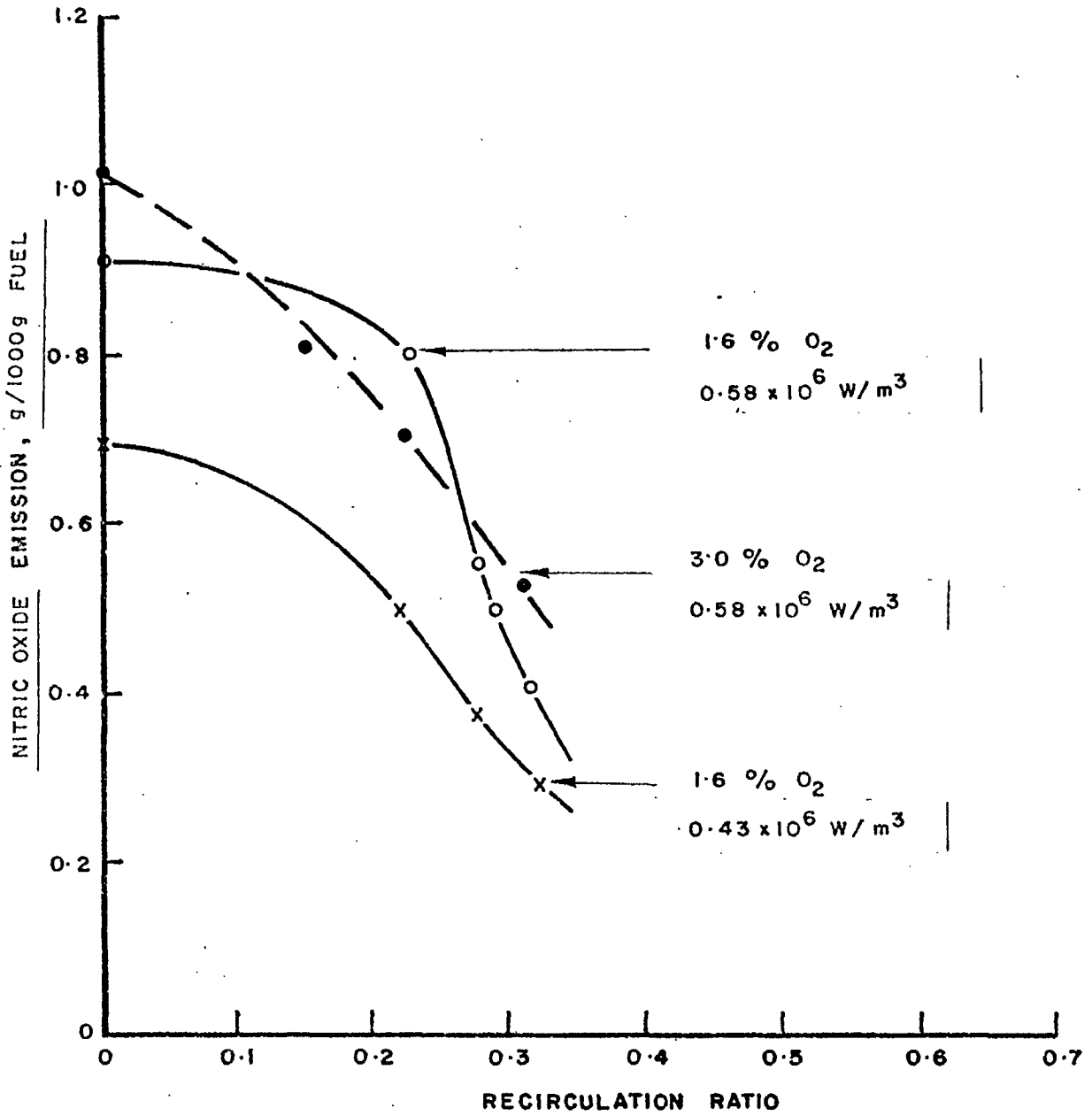


Figure 4. The Effect of Recirculation Ratio on Nitric Oxide Emissions from No. 2 Fuel Oil Combustion

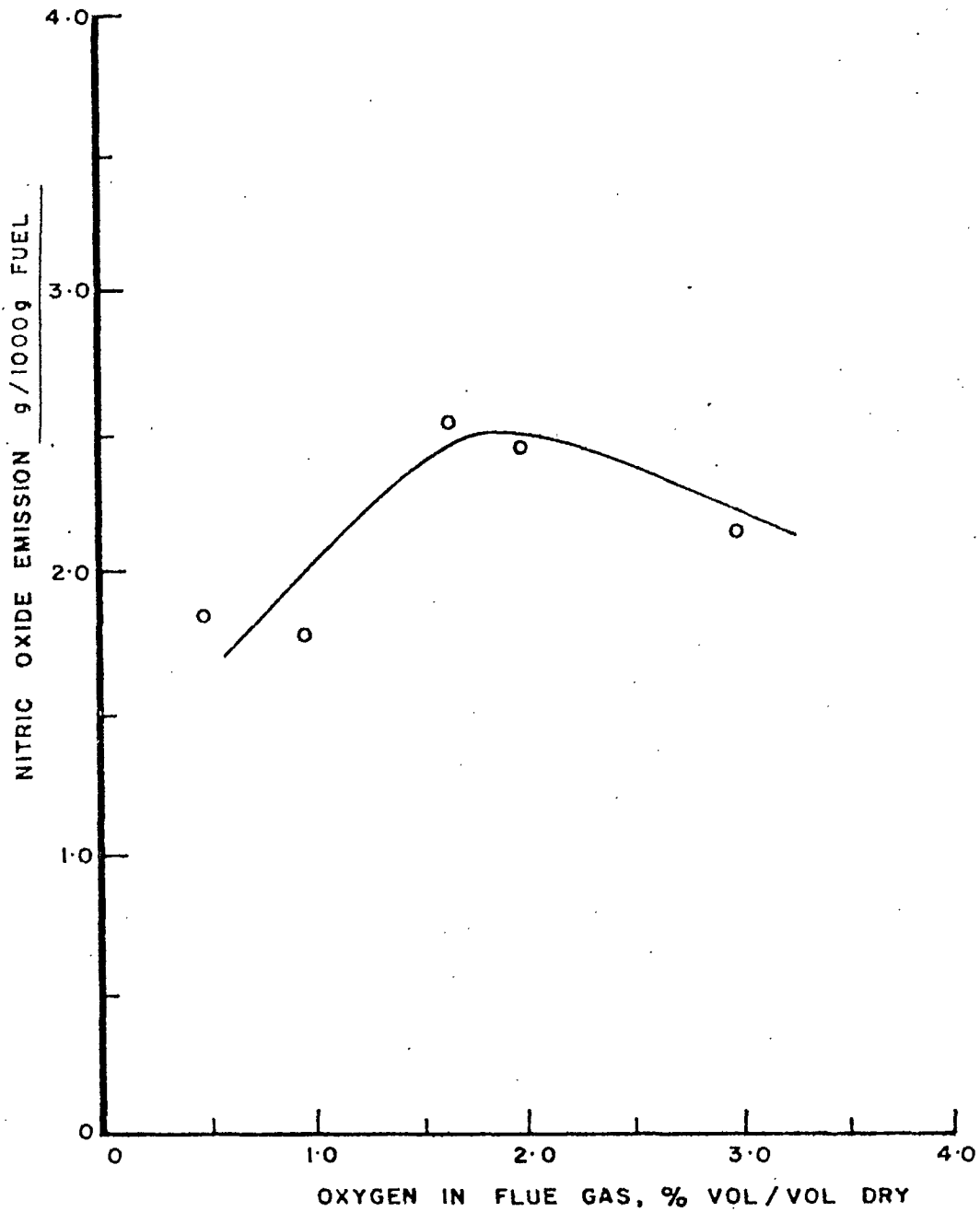


Figure 5. The Effect of Excess-Air Level on Nitric Oxide Emissions from Crude Oil Combustion

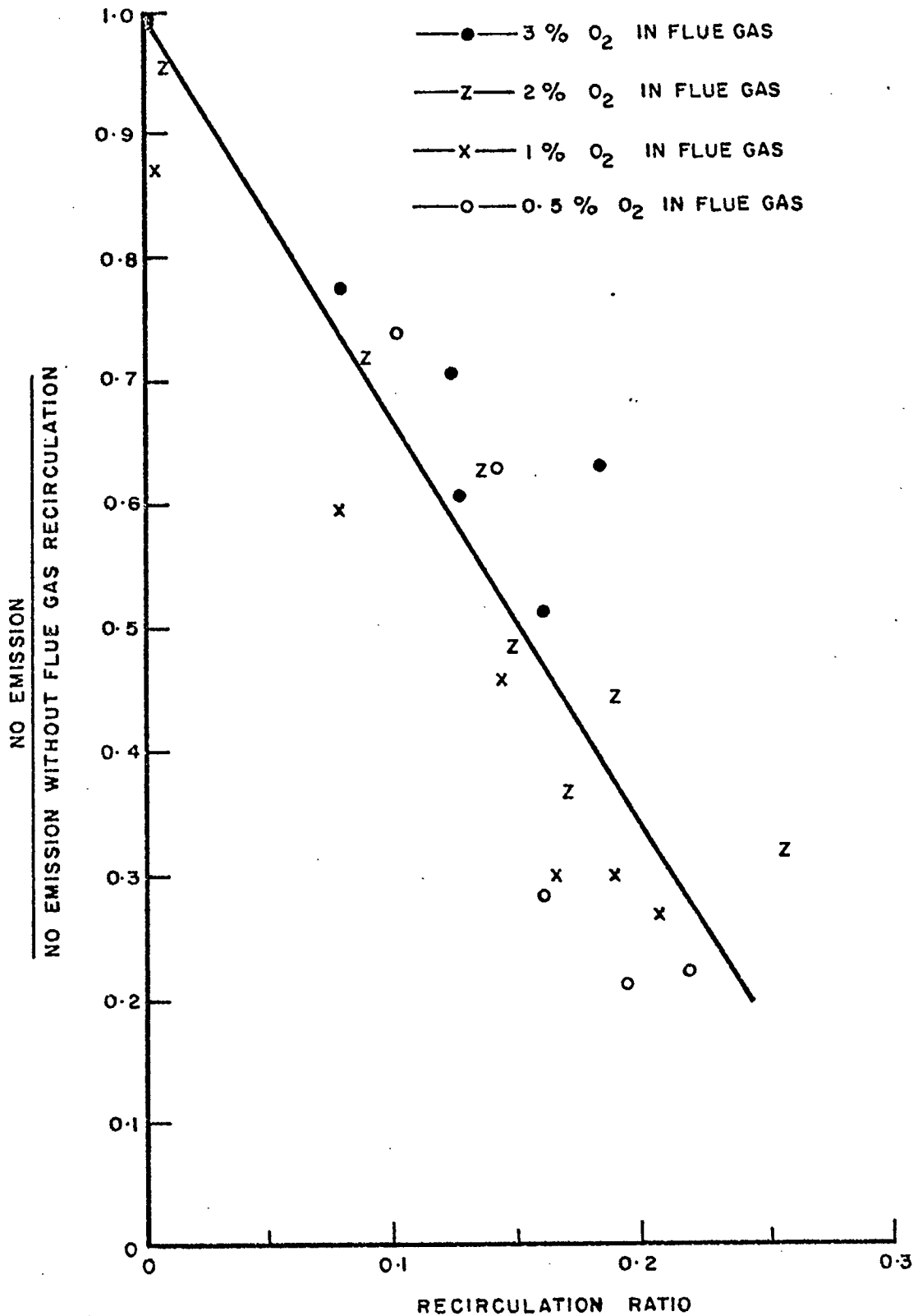


Figure 6. The Effect of Recirculation Ratio on Nitric Oxide Emissions from Crude Oil Combustion at Heat Release Rate of  $0.83 \times 10^6 \text{ W/m}^3$

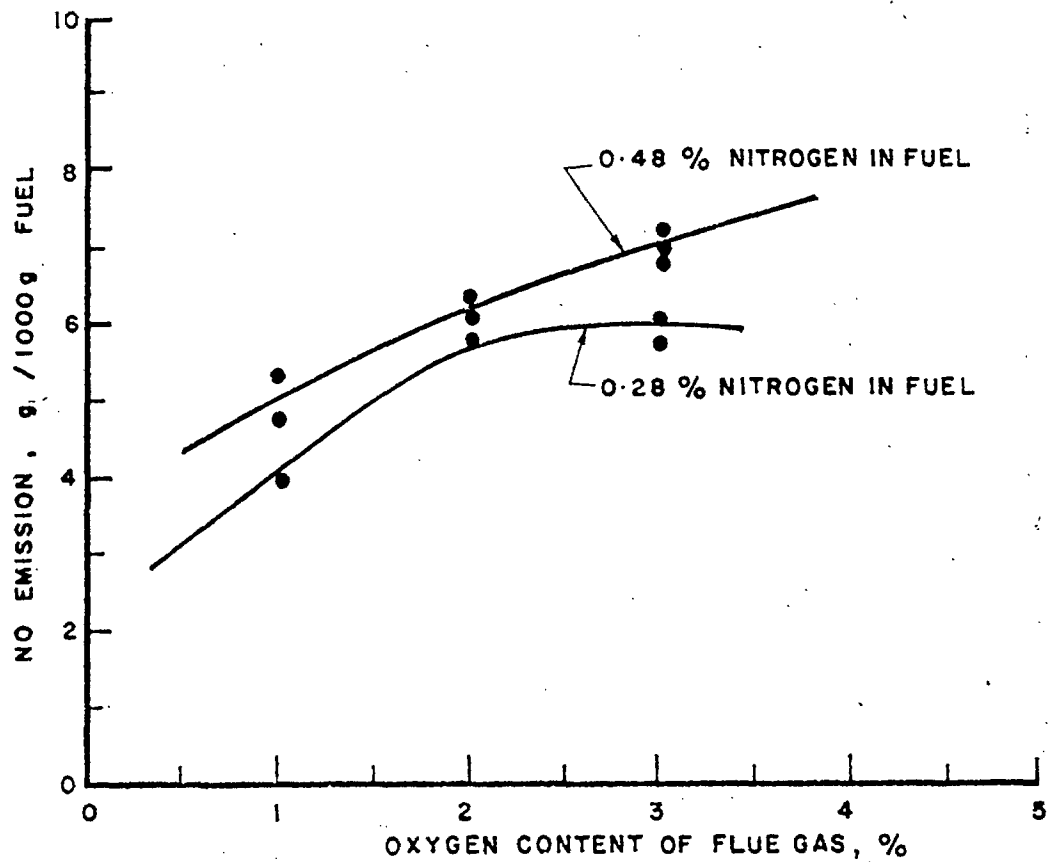


Figure 7. The Effect of Excess-Air Level on Nitric Oxide Emissions from No. 6 Fuel Oil Combustion at Heat Release Rate of  $2.83 \times 10^6 \text{ W/m}^3$



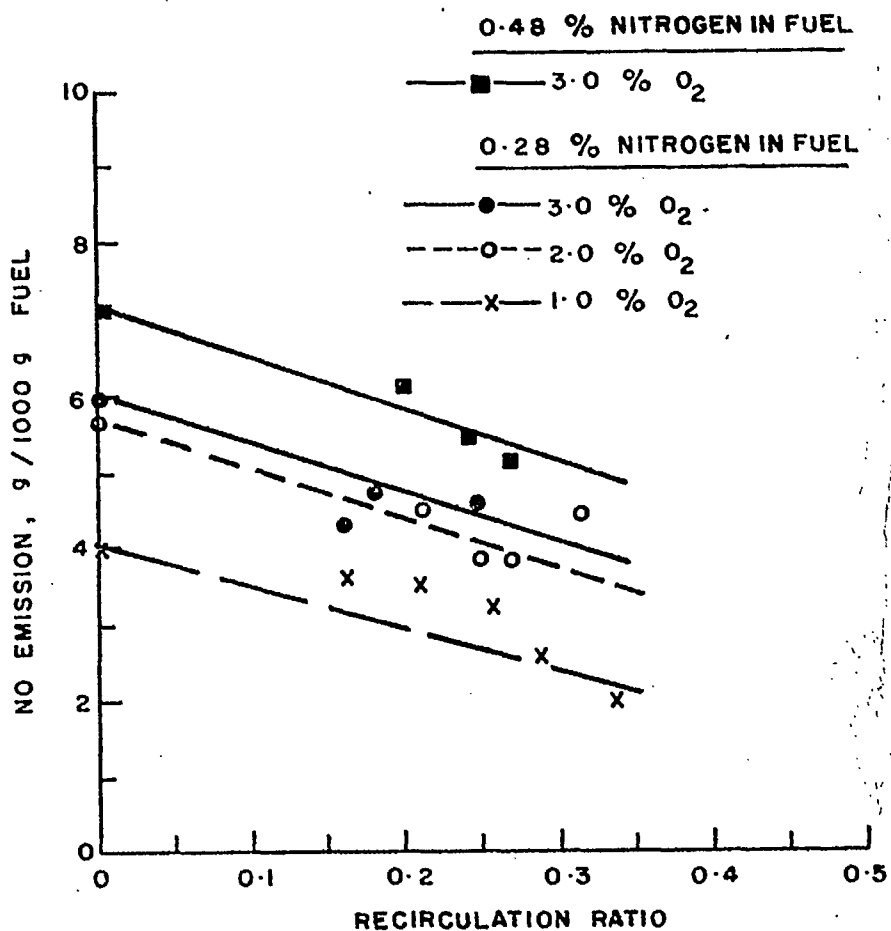


Figure 8. The Effect of Recirculation Ratio on Nitric Oxide Emissions from No. 6 Fuel Oil Combustion at Heat Release Rate of  $0.83 \times 10^6 \text{W/m}^3$

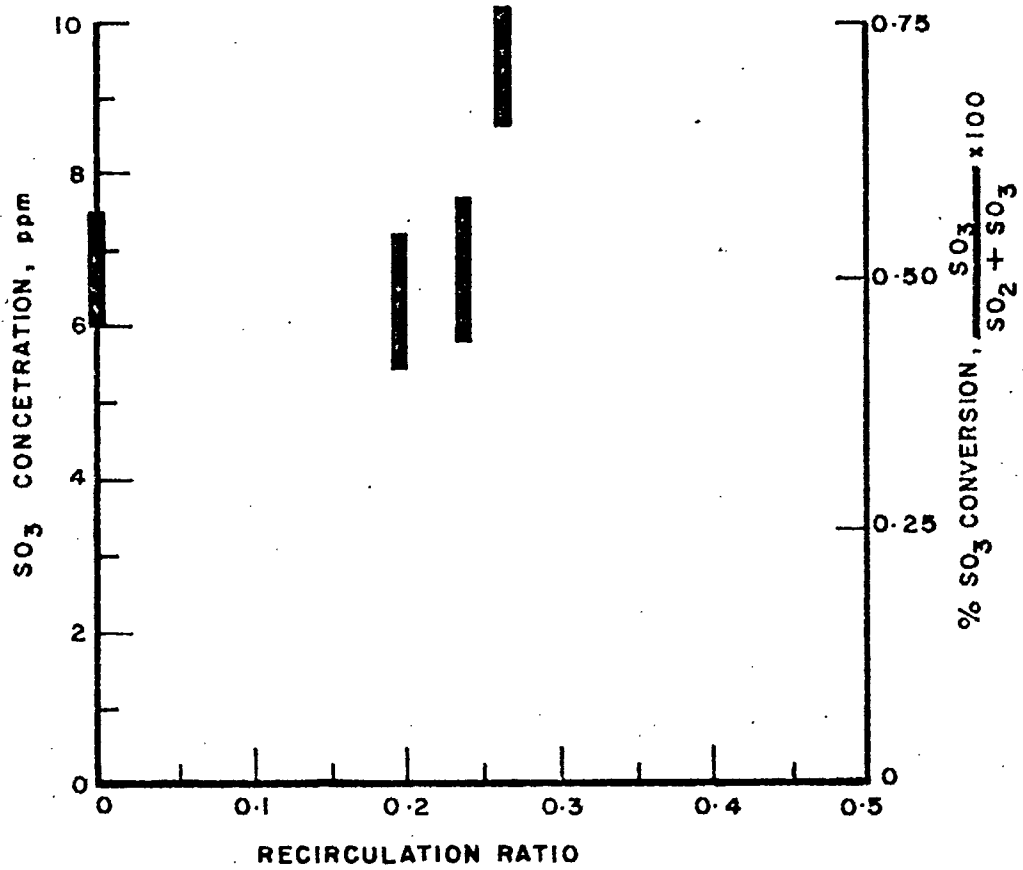


Figure 9. The Effect of Recirculation Ratio on Sulphur Trioxide Formation from No. 6 Fuel Oil Combustion at Heat Release Rate of  $0.83 \times 10^6 \text{W/m}^3$

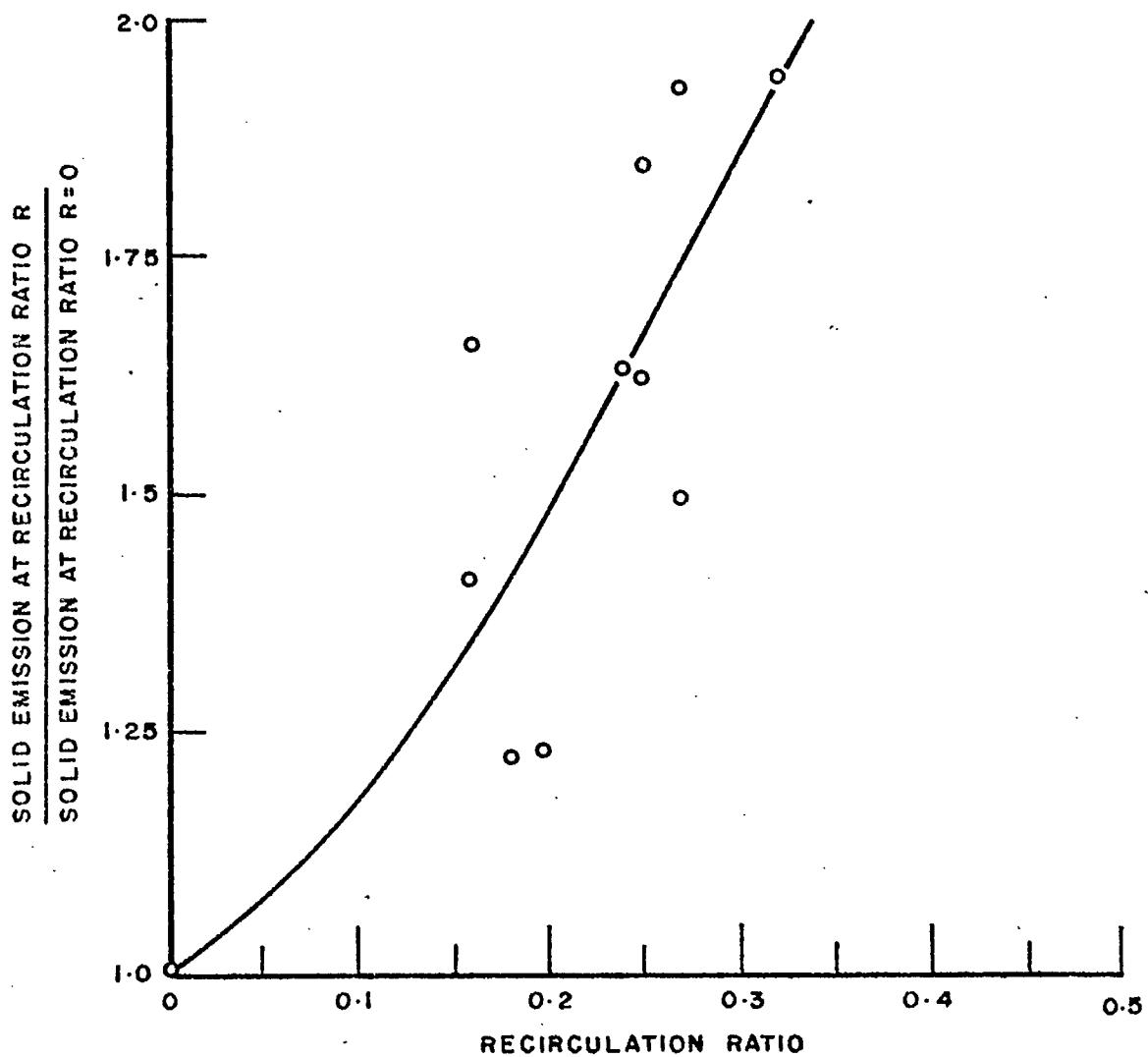


Figure 10. The Effect of Recirculation Ratio on Solids Loading in the Flue Gas of No. 6 Fuel Oil Combustion at Heat Release Rate of  $0.83 \times 10^6 \text{W/m}^3$

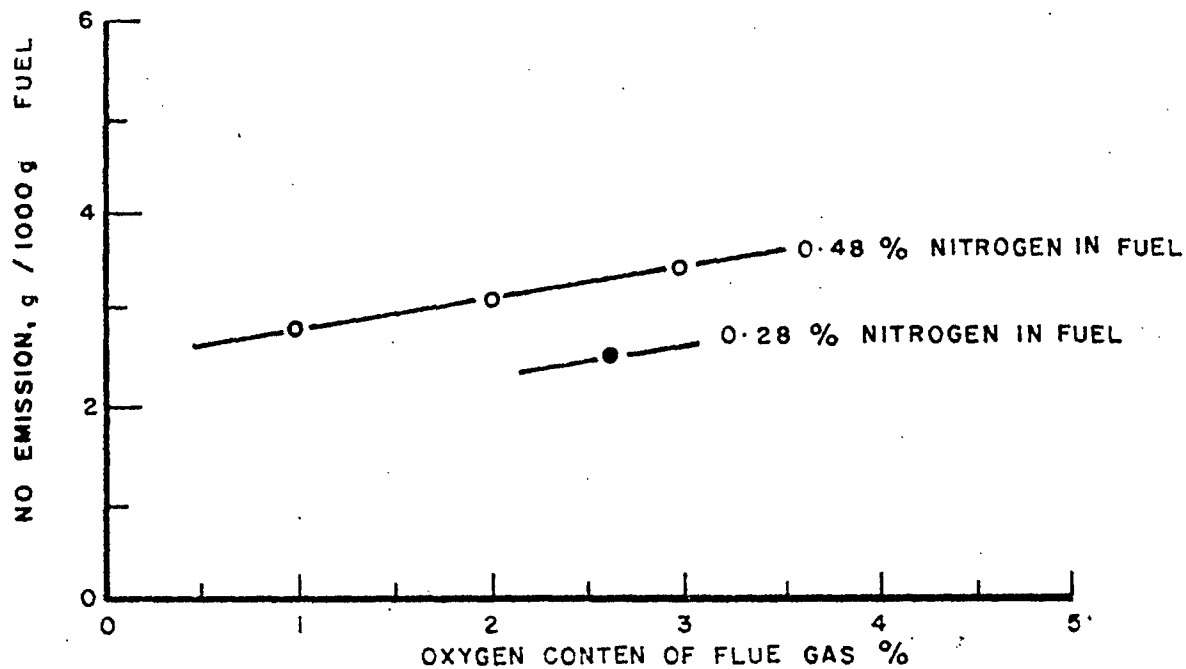


Figure 11. The Effect of Excess-Air Level on Nitric Oxide Emissions from No. 6 Fuel Oil Combustion at Heat Release Rate of  $0.66 \times 10^6 \text{ W/m}^3$

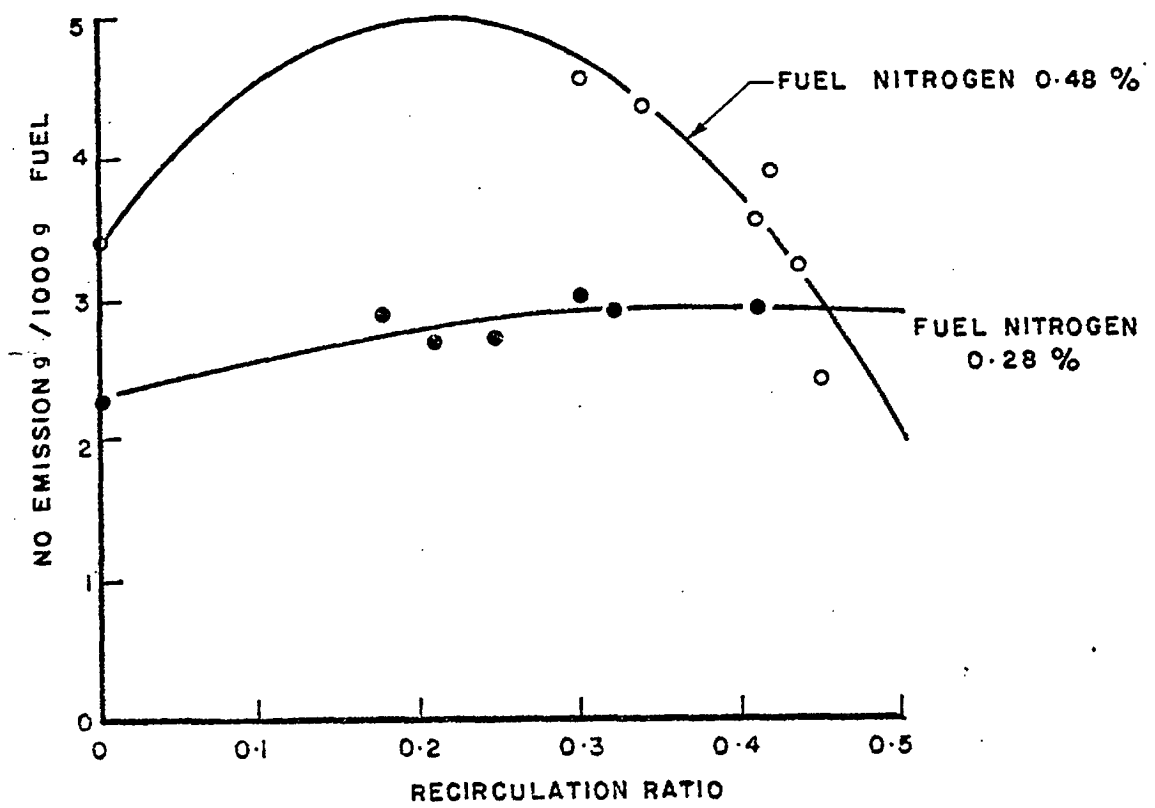


Figure 12. The Effect of Recirculation Ratio on Nitric Oxide Emissions from No. 6 Fuel Oil Combustion at Heat Release Rate of  $0.66 \times 10^6 \text{ W/m}^3$

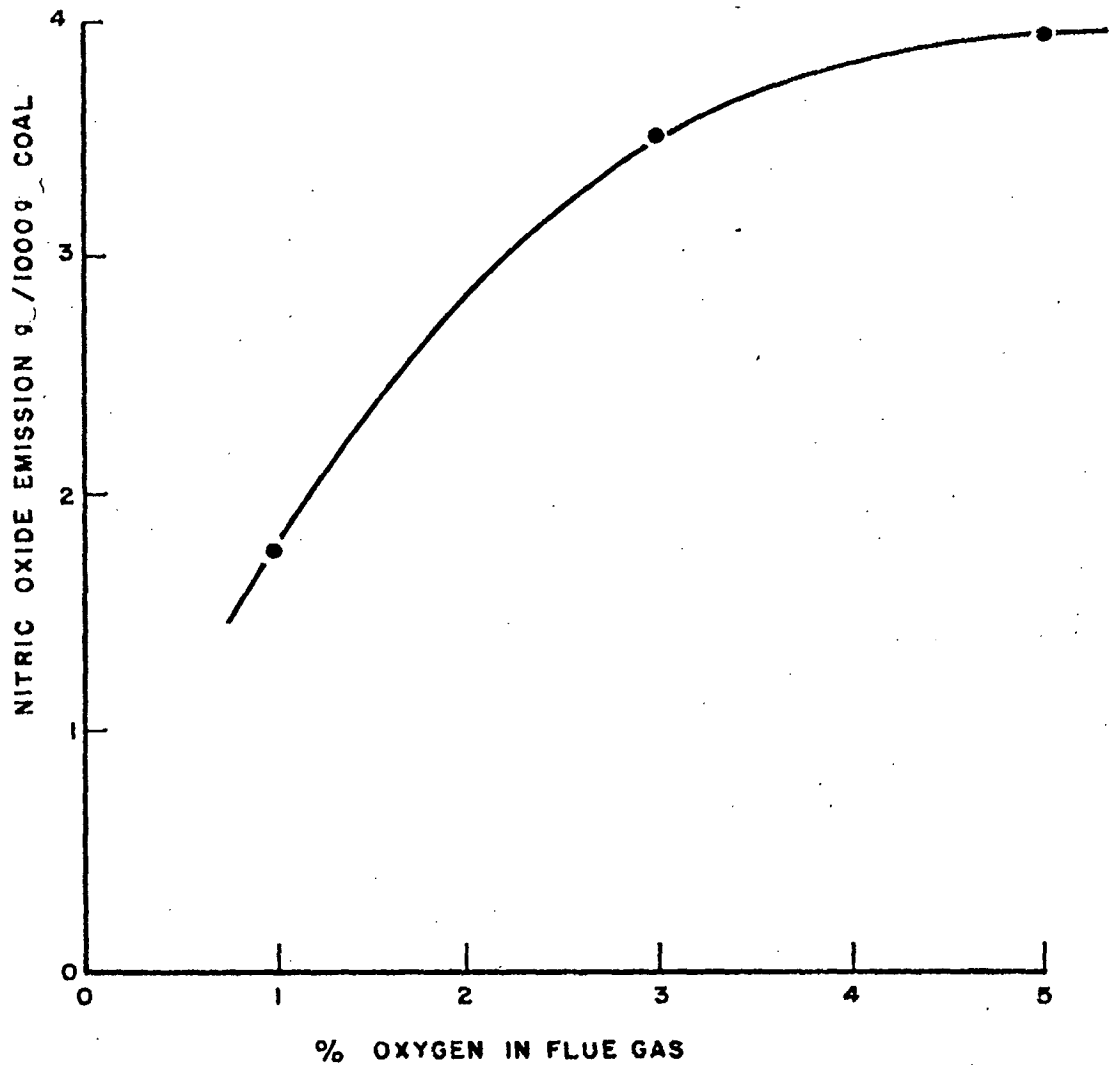


Figure 13. The Effect of Excess-Air Level on Nitric Oxide Emissions from Saskatchewan Lignite Combustion

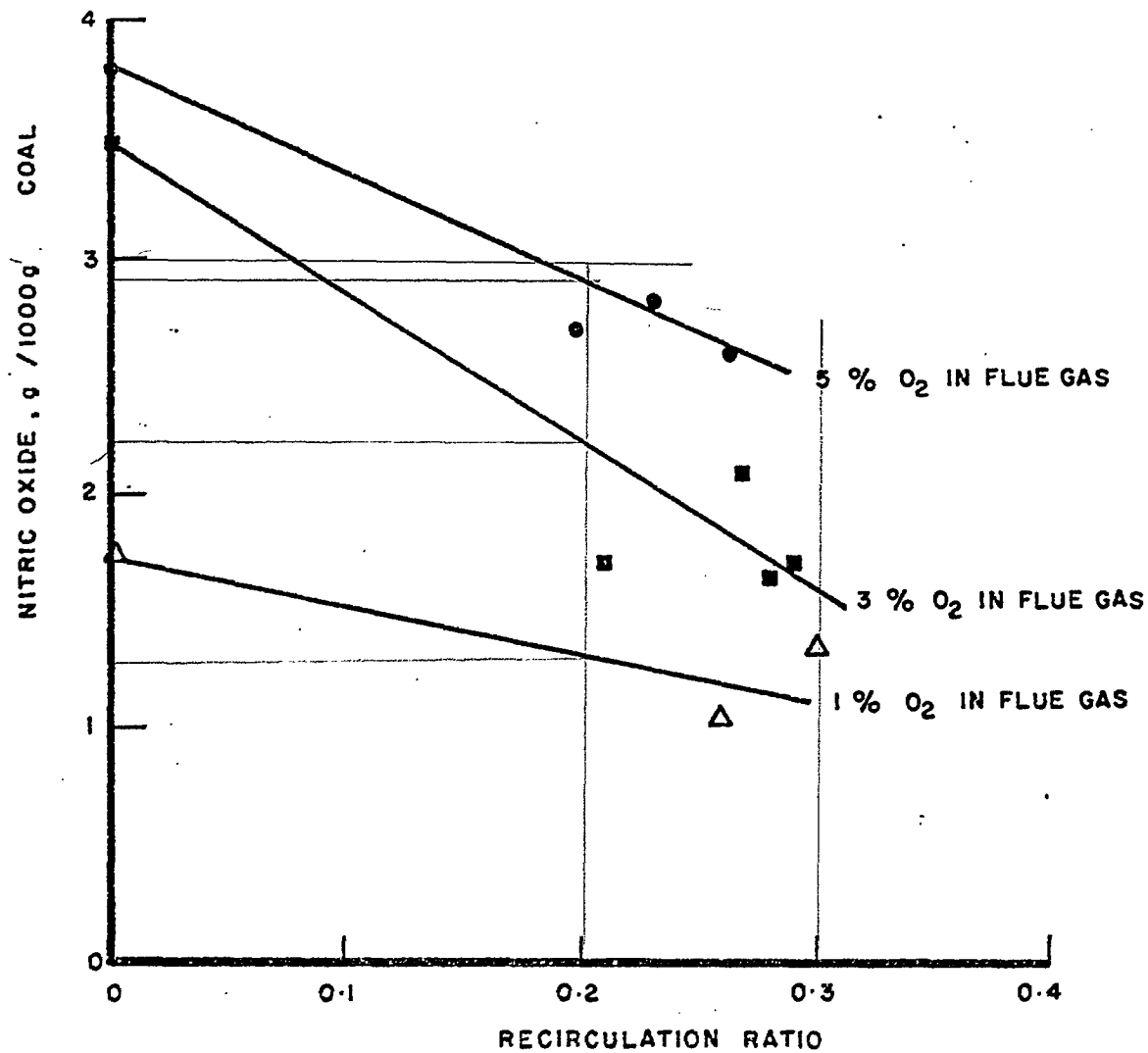


Figure 14. The Effect of Recirculation Ratio on Nitric Oxide Emissions from Saskatchewan Lignite Combustion

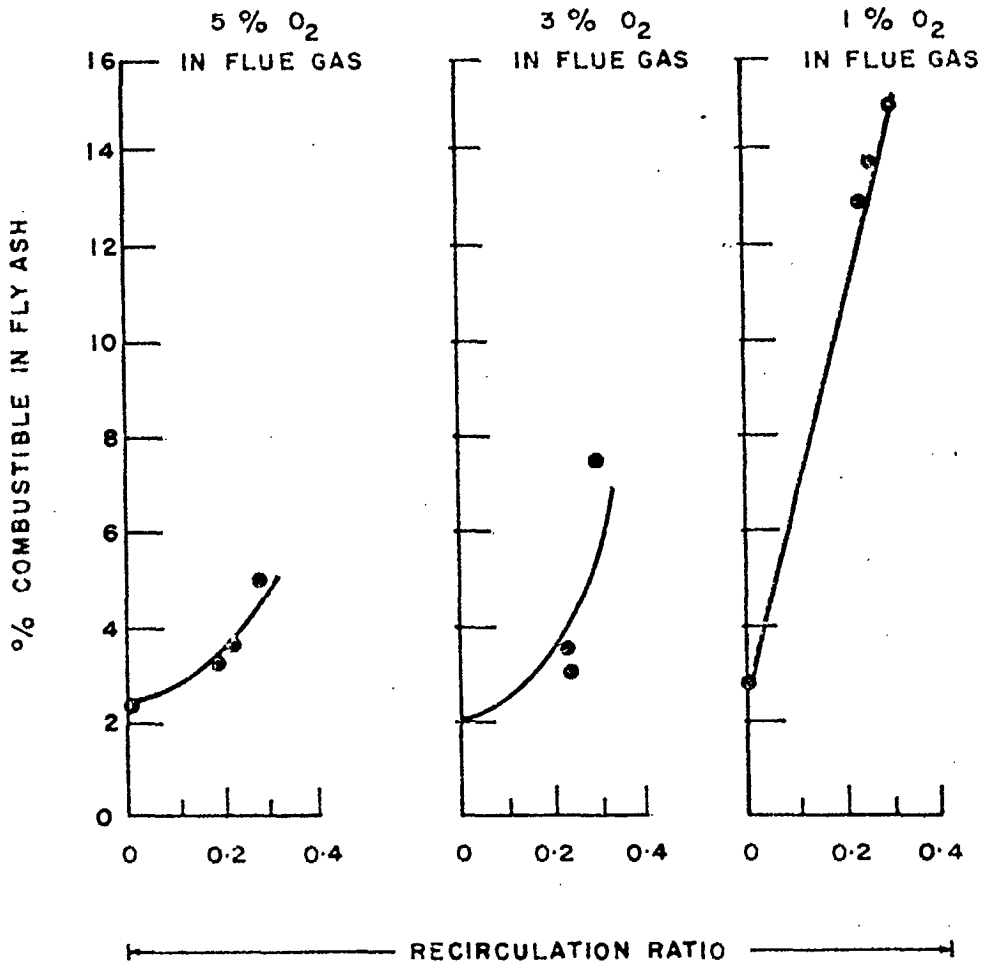


Figure 15. The Effect of Recirculation Ratio and Excess-Air Level on the Fly Ash from Saskatchewan Lignite Combustion



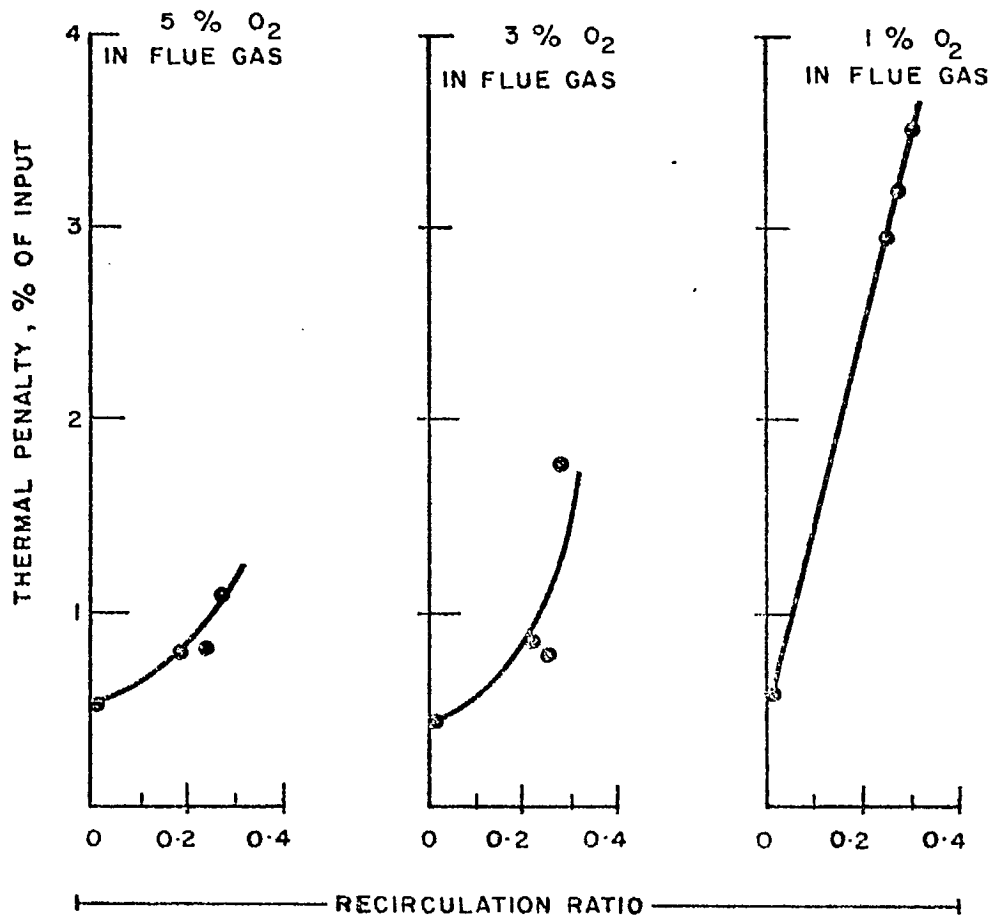


Figure 16. The Effect of Recirculation Ratio on the Thermal Penalty Due to Unburnt Carbon in the Fly Ash from Saskatchewan Lignite Combustion

APPENDIX A

ANALYSES OF THE EXPERIMENTAL FUELS

TABLE A1

Liquid Fuels

	No. 2 Fuel Oil	Crude Oil	No. 6 Fuel Oil	
			A	B
Specific Gravity 60°/60°F	0.888	0.840	0.968	0.983
Viscosity, cSt 100°F	3.5	3.83	206.4 (@ 122°F)	278.2
Carbon %	85.25	86.1	85.8	86.37
Hydrogen %	12.26	13.4	11.48	10.44
Sulphur %	0.26	0.51	2.44	2.49
Nitrogen %	0.0115	0.14	0.28	0.48
Gross Calorific Value				
Btu/lb	19,590	19,003	18,403	18,140
kJ/kg	45,220	43,865	42,480	42,230

APPENDIX A

ANALYSES OF THE EXPERIMENTAL FUELS

TABLE A2

Saskatchewan Lignite

Proximate Analysis of Pulverized Lignite

Moisture	5.36 %
Ash	14.89 %
Volatile Matter	36.08 %
Fixed Carbon	43.67 %

Ultimate Analysis of Pulverized Lignite

Carbon	56.90 %
Hydrogen	3.68 %
Sulphur	0.62 %
Nitrogen	0.98 %
Ash	14.89 %
Oxygen (by difference)	17.57 %
Moisture	5.36 %

Gross Calorific Value: 9,290 Btu/lb; 21,445 kJ/kg

Size Distribution of Pulverized Lignite

Screen Size	% in Fraction
+ 140	17.3
140 - 200	14.1
200 - 325	17.1
325 - 0	51.5