

# THE INFLUENCE OF FUEL COMPOSITION AND FLAME TEMPERATURE ON THE FORMATION OF THERMAL AND FUEL NO<sub>x</sub> IN RESIDUAL OIL FLAMES

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A 900 kw model package boiler and a 20 kw laboratory tunnel furnace were used to study fuel and thermal NO<sub>x</sub> formation during heavy oil combustion. Package boiler results indicated that atomizer design, spray/flow field interactions, and fuel composition were significant, dependent parameters. These effects were then investigated in detail in the laboratory furnace. One distillate and nine heavy oils were studied. Fuel NO<sub>x</sub>, isolated with an argon/oxygen/carbon dioxide oxidant, was found to be a major source of NO<sub>x</sub> emissions. Fuel NO<sub>x</sub> formation increased approximately linearly with increasing nitrogen content from 0.05 to 0.79 wt. percent nitrogen. Fuel nitrogen oxidation was insensitive to temperature changes (over the theoretical temperature range of 2100 to 2500°K) except for one oil which exhibited a sudden increase at the highest temperature. Fuel NO<sub>x</sub> was insensitive to drop size, but thermal NO<sub>x</sub> increased with decreased mean droplet size.

Percentage conversion of bound nitrogen decreased with increasing nitrogen content except for one oil containing substantial refractory nitrogen. Doping studies indicated that fuel sulfur can enhance fuel NO<sub>x</sub> formation and that nitrogen and hydrocarbon volatility are not first order parameters with a rapid mix burner under fuel-lean conditions.

## Introduction

Although the increased utilization of coal is seen as the major method of overcoming the energy crisis, the realities of retrofit capability necessitate the use of liquid fuels for many industrial applications. These fuels may be petroleum or coal-derived. In either instance there will be the potential for adverse environmental impact due to the emission of combustion-generated pollutants. Refinery operations will be geared to the production of gasoline, thus industrial users will be required to burn heavier residual fuels or coal-derived liquids of low hydrogen-to-carbon ratios with an increased smoke producing potential.<sup>1</sup> The two pollutants of major concern are nitrogen oxides (NO<sub>x</sub>) and fine particulate matter. This paper concentrates upon the production of NO<sub>x</sub> from residual liquid fuels, although an integral part of the same program is concerned with

how these same properties influence particulate production.

Nitrogen oxide emissions from stationary combustors can be reduced by combustion modification techniques which involve staging the heat release process. However, the application of these techniques to residual fuel oil-fired combustors has been only partially successful because of a trade-off in pollutants—the decrease in NO<sub>x</sub> emissions is quite often accompanied by an increase in particulate emissions. The optimization of combustion modification techniques to control NO<sub>x</sub> emissions from fuel oil-fired combustors has proved difficult because of the limited knowledge of the controlling phenomena. The complex interaction between the spray and the flow field and the effects of fuel composition on the formation of both NO<sub>x</sub> and particulate matter is ill-understood. Field testing results<sup>2,3</sup> have shown that staged combustion tech-

niques are far more effective for NO<sub>x</sub> control than flue gas recirculation, thereby suggesting the importance of fuel nitrogen oxidation. Laboratory studies on distillate oil doped with various nitrogen compounds have demonstrated the potential importance of fuel NO<sub>x</sub> and suggested that: (1) The percentage of conversion decreases significantly with increasing nitrogen content;<sup>4</sup> (2) the conversion to NO<sub>x</sub> is the same for all nitrogen compounds, irrespective of molecular type;<sup>5</sup> and (3) fuel/air ratio nonuniformities significantly affect the conversion.<sup>6</sup> Pilot-scale studies with actual residual fuel oils have proven definitively that fuel nitrogen oxidation is significant at high temperatures<sup>7</sup> and suggested its importance in practical systems.<sup>5</sup> Turner and Siegmund<sup>5</sup> also inferred that the percent conversion of fuel nitrogen to NO<sub>x</sub> was an unexplained function of fuel composition and that it decreased with increasing fuel nitrogen concentration. More recently, pilot-scale studies<sup>8</sup> have demonstrated the importance of the mixing between the liquid spray, the internal recirculation zone, and the combustion air.

The results presented in this paper are part of a study to investigate the influence of spray properties, fuel composition and heat release zone temperature on the formation of both thermal and fuel NO<sub>x</sub> in self-sustaining residual fuel oil flames. The technical approach taken was experimental, involving parallel programs in two combustors of different scales. A 900 kW ( $3 \times 10^9$  Btu/hr) combustor which simulates the firetube of a package boiler was used to define the overall effects of fuel composition, nozzle design and combustion air swirl on the formation of NO<sub>x</sub>, CO and particulate matter under conditions typical of real systems. A specially-designed 20 kW (70,000 Btu/hr) tunnel furnace was used to assess the influence of fuel chemistry and flame temperature on these same pollutants under conditions which were less difficult to interpret because the spray-flow field interaction was minimized. The overall objectives of the work are to provide general insight which will allow the design of practical, low pollutant combustion systems; to isolate those factors which are determined by fuel properties; and to help identify specific phenomena requiring further investigation through basic studies.

## Experimental Systems

### Package Boiler Simulator

The design and construction of the package boiler simulator have been described in detail elsewhere.<sup>9</sup> The axisymmetric steel combustion chamber is 0.5 m in diameter, 4.5 m in length and is divided into calorimetric sections cooled by heat transfer fluid.

The burner used in these investigations was a simple double-concentric arrangement capable of accepting a wide range of commercial oil nozzles. The unheated combustion air was supplied through an annular duct (inner diameter 5 cm, outer diameter 13 cm) which contained interchangeable fixed-vane swirl generators. The burner exit was a refractory cone of length 20 cm and 45 degree half-angle.

### Tunnel Furnace

The down-fired tunnel furnace is illustrated in Fig. 1 and was designed to allow utilization of commercially available spray nozzles and yet be capable of testing with artificial atmospheres. The vertical combustion chamber was 2.1 m long and 20 cm in diameter inside. The overall outer diameter was approximately 81 cm, and the walls consisted of insulating and high temperature castable refractories. The full load firing rate was 0.53 cc/sec fuel oil, which corresponds to a nominal heat release of approximately 20 kW. The furnace was operated under positive pressure at all times.

Under normal operating conditions combustion air was supplied from a 690 kPa air compressor. In certain tests the "air" was enriched or replaced with varying amounts of carbon dioxide, argon and oxygen, all of which were supplied from high-pressure cylinders. The atomization "air" was metered with a 600 mm rotameter and was not preheated. The main combustion "air" was metered with a 600 mm rotameter and preheated with an electric circulation heater.

The test fuels were electrically preheated in a small supply tank and drawn through a 60 micron filter into a variable speed Zenith metering pump. The pump outlet pressure was maintained constant during calibration and operation by means of a micro-needle valve. The oil flow rate was varied by direct mechanical adjustment of the pump speed.

Fuel and air entered the combustion chamber through the burner illustrated in Fig. 1. Several design iterations were necessary in order to provide a stable flame while preventing coke build-up at the nozzle. The combustion air was introduced axially (without any swirl) and a long refractory burner exit was used ( $l/d = 5.0$ ). The axial velocity of the combustion air could be varied by the use of interchangeable sleeves which were inserted into the burner throat. The removable fuel injection system consisted of a 19 mm diameter stainless steel tube which contained the atomizing air supply tube, the fuel oil supply tube, a cartridge heater for final oil temperature control, and a chromel/alumel thermocouple positioned at the injector tip, prior to the nozzle for accurate oil temperature measurement. A commercial ultrasonic oil atomizer (capacity 0.55 cc/sec) was used in this investigation because it provided adequate atomization of the heavy oils at

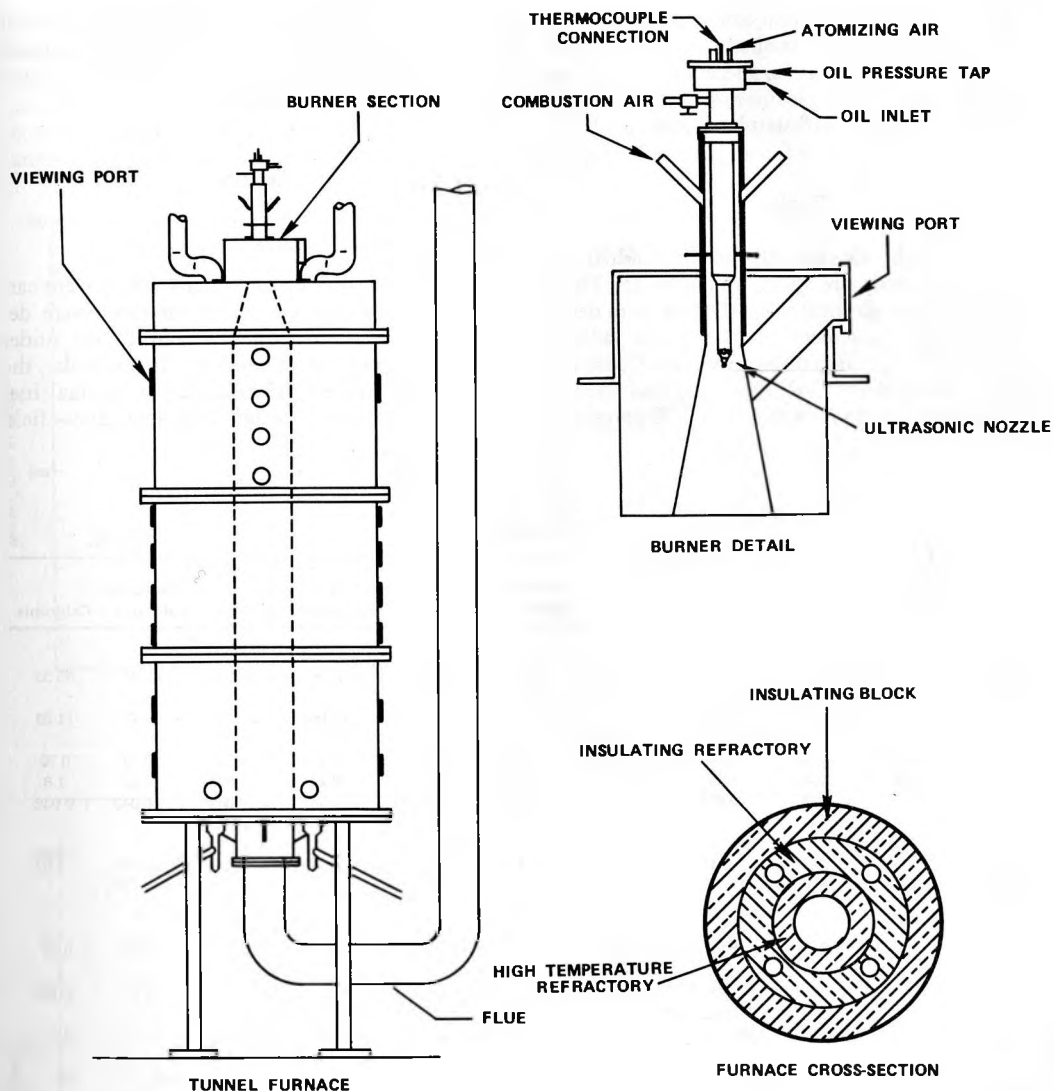


FIG. 1. Schematic of tunnel furnace.

relatively low flow rates. The tip of the fuel nozzle was positioned at the beginning of the burner divergent section (as shown in Fig. 1), and in general, the visible flame front was displaced approximately one nozzle diameter from the nozzle tip.

#### Analytical System

The same sampling and analysis system was used for both the package boiler simulator and the tunnel furnace. It allowed for continuous monitoring of NO, NO<sub>x</sub>, CO, CO<sub>2</sub>, O<sub>2</sub> and SO<sub>2</sub> using the instruments listed in Table I. Flue gas was withdrawn from the appropriate stack through a water-cooled,

TABLE I  
Analytical instrumentation

NO	Thermo Electron Model 10A Chemiluminescence Analyzer
NO <sub>x</sub>	TECO Model 10A with Stainless Steel Converter
O <sub>2</sub>	Servomex Paramagnetic
CO, CO <sub>2</sub>	Anarad Model AR-600 NDIR
SO <sub>2</sub>	Thermo Electron Model 40 Pulsed Fluorescence Analyzer

stainless steel probe. Sample conditioning prior to the instrumentation consisted of an ice bath water condenser, glass-wool filters, and a stainless/teflon sampling pump. All sample lines were 6.3 mm (1/4") teflon and all fittings 316 stainless steel.

0.79 percent, while sulfur ranged from 0.22 percent to 2.44 percent. Samples of the Venezuelan oil before and after desulfurization were included to define the effect of fuel processing.

## Fuels

Analyses of the distillate oil and the residual oils used in this study are given in Table II. These composition and physical property data were determined by an independent laboratory and indicate that the heavy oils ranged from the East Coast No. 5 (API = 24.9) to the Gulf Coast residual (API = 13.2). Nitrogen content varied from 0.16 percent to

## Results

### Package Boiler Simulator

The experimental investigations which were carried out in the package boiler simulator were designed to define overall emission trends under conditions typical of real systems. In particular, the experiments defined the influence of residual fuel properties, atomizer design and spray-flow field

TABLE II  
Fuel oil compositions

	Californian distillate	East Coast	Middle East	Indonesian/ Malaysian	Venezuelan desulfurized	Gulf Coast	Venezuelan	Alaskan	Wilmington California	California
Ultimate Analysis:										
Carbon, %		86.54	86.78	86.53	85.92	84.62	85.24	86.04	85.41	85.33
Hydrogen, %		12.31	11.95	11.93	12.05	10.77	10.96	11.18	11.44	11.23
Nitrogen, %	0.053	0.16	0.18	0.24	0.24	0.36	0.40	0.51	0.77	0.79
Sulfur, %	0.27	0.36	0.67	0.22	0.93	2.44	2.22	1.63	1.63	1.6
Ash, %		0.023	0.012	0.036	0.033	0.037	0.081	0.034	0.043	0.032
Oxygen, % (by difference)		0.61	0.41	1.04	0.83	1.78	1.10	0.61	0.71	1.02
Conradson Carbon Residue, %		2.1	6.0	3.98	5.1	14.8	6.8	12.9	8.72	9.22
Asphaltene, %		0.34	3.24	0.74	2.59	7.02	8.40	5.6	5.18	5.18
Flash Point, °F		205	350	210	176	155	210	215	—	150
Pour Point, °F		50	48	61	48	40	58	38	38	30
API Gravity at 60°F	32.6	24.9	19.8	21.8	23.3	13.2	14.1	15.6	15.4	15.1
Viscosity, SSU, at 140°F	30.8	131.2	490.0	199.0	113.2	835.4	742.0	1,071	854	748
at 210°F	29.5	45.0	131.8	65.0	50.5	181.0	196.7	194	128.6	132
Heat of Combustion:										
Gross Btu/lb	19,330	19,260	19,070	18,400	18,240	18,400	18,600	18,470		18,460
Net Btu/lb		18,140	17,960	17,960	17,300	17,260	17,400	17,580	17,430	17,440
Calcium, ppm		7.1	1.2	14	8.7	4.4	9.1	6.9	21	14
Iron, ppm		16	2.8	16	6.5	19	11	24	73	53
Manganese, ppm		0.09	0.02	0.13	0.09	0.13	0.09	0.06	0.8	0.1
Magne- sium, ppm		3.7	0.08	3.6	3.6	0.4	3.8	1.4	5.1	3.8
Nickel, ppm		6.7	13	17	19	29	52	50	65	82
Sodium, ppm		37	0.98	57	15	3.6	32	37	21	2.6
Vanadium, ppm		14	25	2.3	101	45	226	67	44	53

interactions. Figures 2 and 3 present examples of some of the data generated. In Fig. 2 the  $\text{NO}_x$  emitted at a constant firing rate of 900 kW is shown plotted as a function of overall excess oxygen for four commercial atomizer types. Two different swirl vane angles were used to vary the size and strength of

the swirl-induced toroidal recirculation zone. As the  $\text{NO}_x$  emitted is dependent upon the fuel/air mixing process, it can be seen that both atomizer design and the interaction of the spray and the flow field are dependent parameters. In general, increasing the degree of swirl causes a reduction in total emissions.

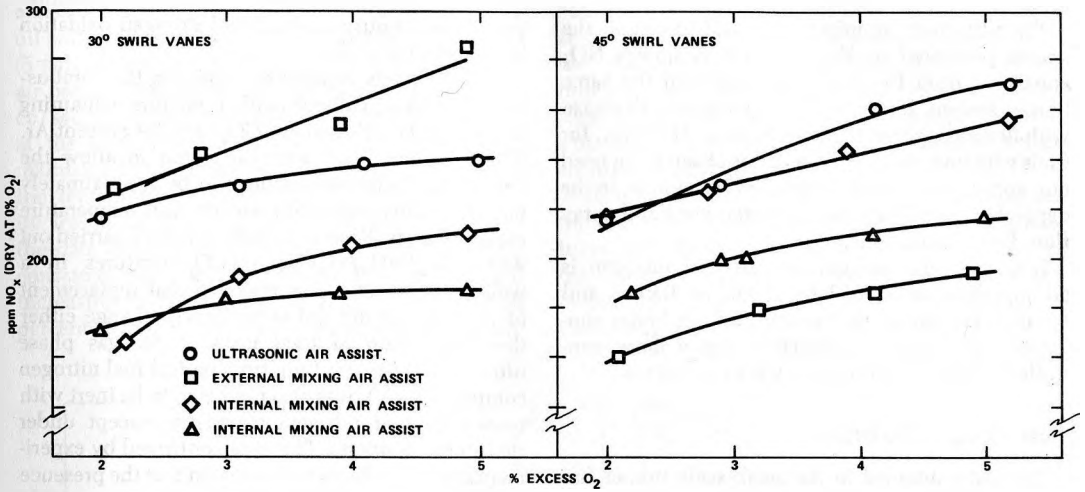


FIG. 2. Effect of fuel injector design (package boiler simulator, Indonesian oil).

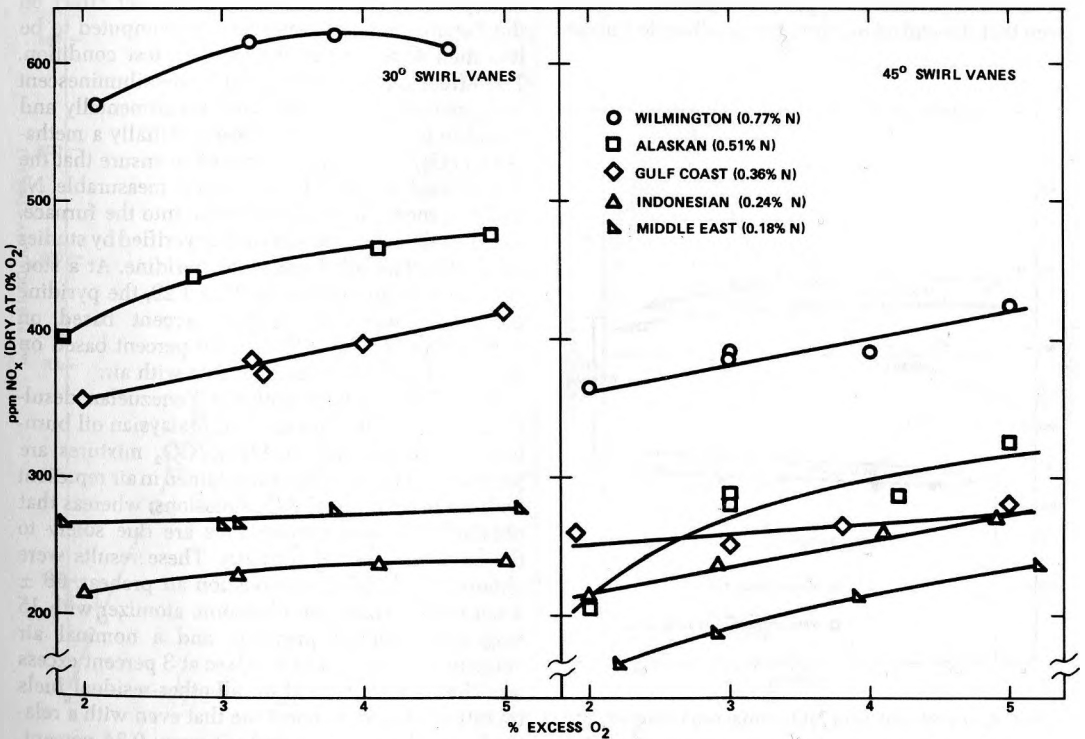


FIG. 3. Influence of fuel composition (package boiler simulator, ultrasonic nozzle).

However, the amount of that reduction is dependent upon the type of atomizer. The internal mix air-assist atomizer shows a complete reversal in emission rank. When the swirl vanes are changed the external mix air-assist atomizer gives increased emissions as the swirl is increased. Emissions from the ultrasonic atomizer appear to be relatively insensitive to swirl level.

The ultrasonic atomizer was used to obtain the results presented in Fig. 3 which compares NO<sub>x</sub> emissions from five fuels burning with the same burner system. In general, NO<sub>x</sub> emissions decrease with decreasing fuel nitrogen content. However, for fuels with low nitrogen content this observation need not apply, and the emission levels appear to be dependent upon both fuel nitrogen level and spray flow field interactions.

It is generally recognized that fuel nitrogen is an important source of NO<sub>x</sub> in fuel oil flames, and the obvious interactions in the package boiler simulator experiments necessitated that a more controlled series of experiments were carried out.

#### Fuel Nitrogen Oxidation

The data obtained in the small-scale tunnel furnace for two residual fuel oils are presented in Fig. 4. Shown in the same figure for comparison purposes are data reported by Turner et al.<sup>5</sup> which was obtained in a full-scale package boiler. It can be seen that the emissions from the small-scale furnace

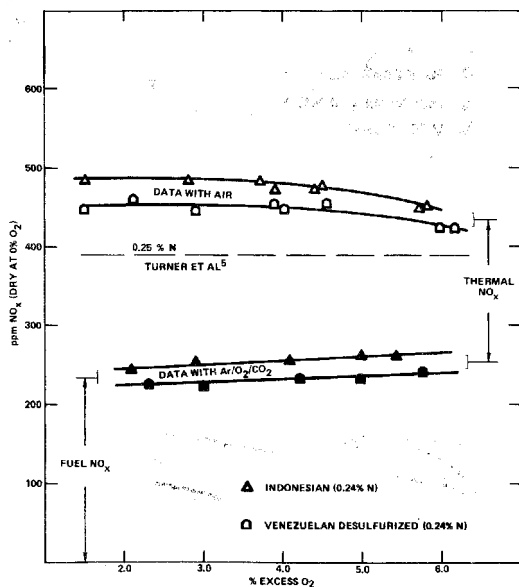


FIG. 4. Total and fuel NO<sub>x</sub> emissions (tunnel furnace, ultrasonic nozzle, 15 psi atomizing air, 405°F air preheat, 66 ssu fuel viscosity).

are of the same magnitude and have the same stoichiometry dependence as an actual commercial firetube boiler. This agreement is somewhat fortuitous as the results presented in Figs. 2 and 3 illustrate that burner parameters have a strong influence upon NO<sub>x</sub> formation. However, it can be concluded that the contribution of fuel NO<sub>x</sub> to the total emission for the tunnel furnace is approximately representative of the contribution of fuel nitrogen oxidation in full-scale systems.

Fuel NO<sub>x</sub> was isolated by replacing the combustion air with a synthetic oxidant mixture containing 21 percent O<sub>2</sub>, 20 percent CO<sub>2</sub>, and 59 percent Ar. The CO<sub>2</sub> was used with the argon to allow the theoretical flame temperatures to be approximately matched. This was confirmed by wall temperature measurements. Kinetic modeling studies carried out with CH<sub>4</sub>/NH<sub>3</sub>/O<sub>2</sub>/N<sub>2</sub>/Ar/CO<sub>2</sub> mixtures in a well-stirred reactor demonstrated that replacement of N<sub>2</sub> with Ar did not significantly change either the distribution of total mass or the gas phase nitrogen species resulting from typical fuel nitrogen compounds. CO<sub>2</sub> was also predicted to be inert with respect to fuel nitrogen chemistry, except under fuel-rich conditions. This was confirmed by experimental tests<sup>10</sup> which demonstrated that the presence of CO<sub>2</sub> in the oxidizer did not have an appreciable chemical effect on NO<sub>x</sub> formation. Argon and carbon dioxide have a more negative relative magnetic susceptibility than nitrogen, but the net effect on the Paramagnetic O<sub>2</sub> analyzer was computed to be less than 4 percent at the primary test condition. The effect of the argon on the chemiluminescent NO<sub>x</sub> analyzer was investigated experimentally and found to be less than 10 percent. Initially a methanol-Ar/O<sub>2</sub>/CO<sub>2</sub> flame was tested to ensure that the compressed gases did not contain measurable N<sub>2</sub> and that room air was not leaking into the furnace. The overall technique was further verified by studies using distillate oil doped with pyridine. At a stoichiometric ratio (SR, air/fuel) of 1.29, the pyridine conversion was 78.5 ± 0.5 percent based on Ar/O<sub>2</sub>/CO<sub>2</sub> data and 81.5 ± 2.6 percent based on the doped and pure distillate data with air.

Data obtained with both the Venezuelan desulfurized oil and the Indonesian/Malaysian oil burning in total air and in Ar/O<sub>2</sub>/CO<sub>2</sub> mixtures are presented in Fig. 4. The data obtained in air represent both fuel and thermal NO<sub>x</sub> emissions, whereas that obtained in argon atmospheres are due solely to the oxidation of fuel nitrogen. These results were obtained with 405°K combustion air preheat, 66 ± 4 ssu fuel viscosity, an ultrasonic atomizer with 15 psig atomizing air pressure, and a nominal air velocity in the throat of 9 m/sec at 3 percent excess air. The data are typical for all other residual fuels investigated, and demonstrate that even with a relatively small amount of fuel nitrogen, 0.24 percent, fuel NO<sub>x</sub> formation is significant. Both the Indone-

sian and the desulfurized Venezuelan oil have the same nominal nitrogen content. However, fuel  $\text{NO}_x$  emissions are higher with the Indonesian fuel.

### Fuel Chemistry

Figure 5 is a composite plot of the fuel nitrogen emissions and relative conversion for the distillate oil and residual oils at a stoichiometric ratio of 1.29 (5 percent excess  $\text{O}_2$ ). In each case the combustion air preheat was  $405 \pm 5^\circ\text{K}$ , the firing rate was 0.55 cc/sec, and the atomization pressure was 15 psig at the ultrasonic nozzle. The fuel viscosity was maintained at  $66 \pm 8$  ssu (by using the appropriate fuel temperature) except for the distillate oil (viscosity less than 40 ssu at room temperature). All of the data were obtained in  $\text{Ar}/\text{O}_2/\text{CO}_2$ . Fuel  $\text{NO}_x$  emissions increased approximately linearly with increasing fuel nitrogen from the distillate oil (0.05 percent N) to the California residual oil (0.79 percent N)

N). These data are representative of a high mixing intensity burner and have a slope of  $95 \text{ ppm NO}_x/0.1$  percent N.

In general, the percentage conversion of fuel nitrogen to  $\text{NO}_x$  decreased rapidly up to about 0.25 percent N. Beyond this point only a small decrease was observed. This is in marked contrast to previous coal work<sup>11</sup> where fractional fuel nitrogen conversion is much lower than that shown in Fig. 5. Also, the fraction percentage conversion is almost independent of nitrogen content. (Note expanded scale.) The Gulf Coast oil (0.36 percent N) shows a markedly higher conversion than would be expected from its nitrogen content.

To investigate the chemical differences between the oils, each was vacuum distilled into five fractions, and the total mass and nitrogen content of the fractions was determined by an independent laboratory. These data are shown in Fig. 6; the lower curve is the percent of the total mass evolved as

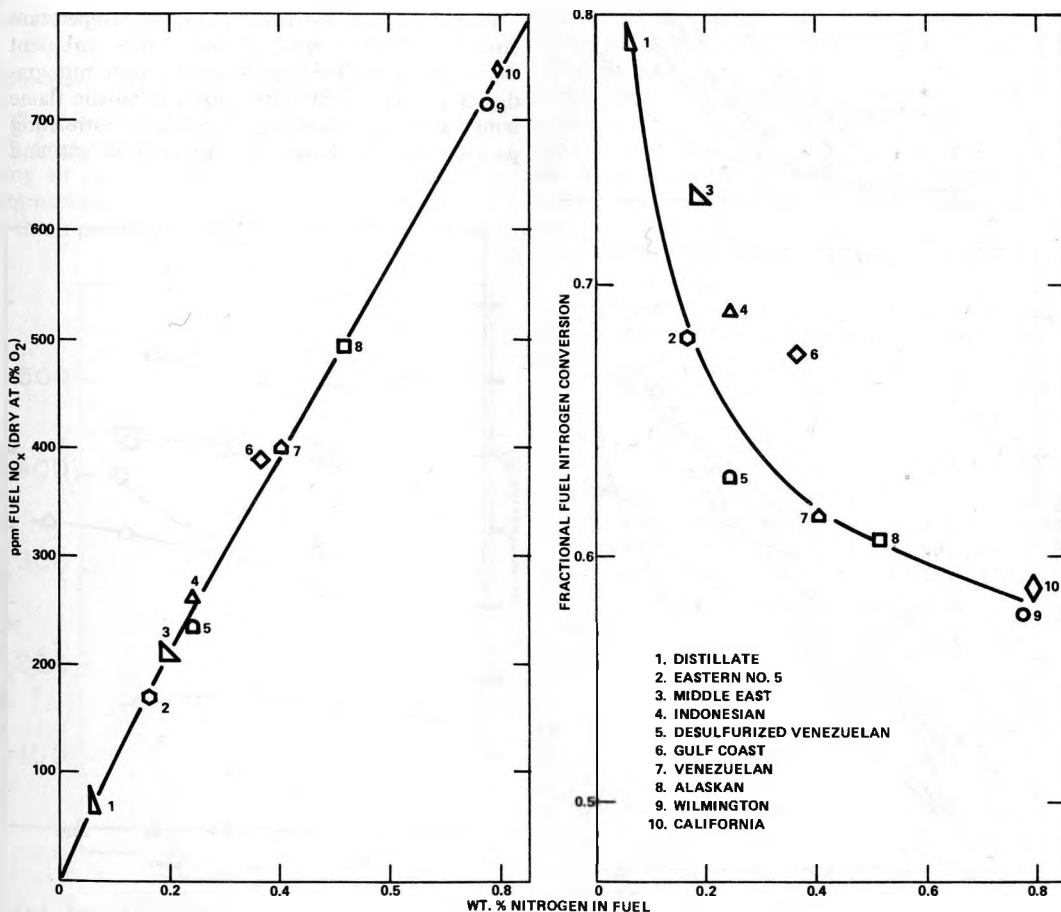


FIG. 5. Importance of fuel nitrogen content (all data taken in  $\text{Ar}/\text{O}_2/\text{CO}_2$ , tunnel furnace, ultrasonic nozzle, 5% excess  $\text{O}_2$ ).

a function of temperature. The Middle-East, Gulf Coast, and the Wilmington oils contain a large fraction of heavy hydrocarbon ends; only 55 percent of the mass distills below 1000°F. The Gulf Coast

oil also has a Conradson carbon residue (Table II) of 14.8 percent which is larger than that of any other oil tested. Desulfurization removed a small amount of the light ends from the Venezuelan oil, but the curve shape remained unchanged. The upper curve shows the percent of the fuel nitrogen evolved as a function of temperature and, in general, the percent nitrogen evolution is less than the hydrocarbon percentage.

The Gulf Coast oil gave an unusually high fuel nitrogen conversion (67 percent) for its nitrogen content, yet only 8 percent of the nitrogen is evolved below 1000°F. These data suggest that fuel NO<sub>x</sub> formation is increased by the presence of very heavy stable nitrogen species. The results of the vacuum distillations for the Indonesian/Malaysian and the desulfurized Venezuelan oil give no indication of the reasons for the different conversions measured with each oil.

*Overall Temperature Dependence*

Figure 7 shows the results of flame temperature studies with five residual oils. These turbulent diffusion flames had large internal temperature gradients and turbulent fluctuations. Adiabatic flame temperature was, therefore, chosen as the correlating parameter, even though the actual bulk gas and

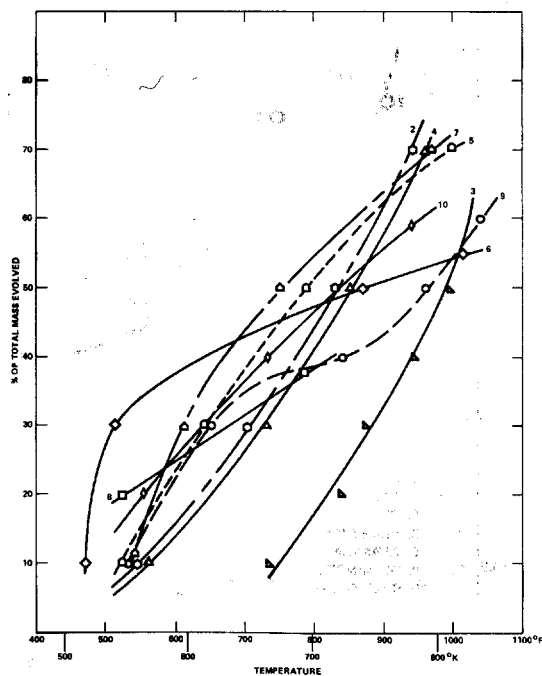
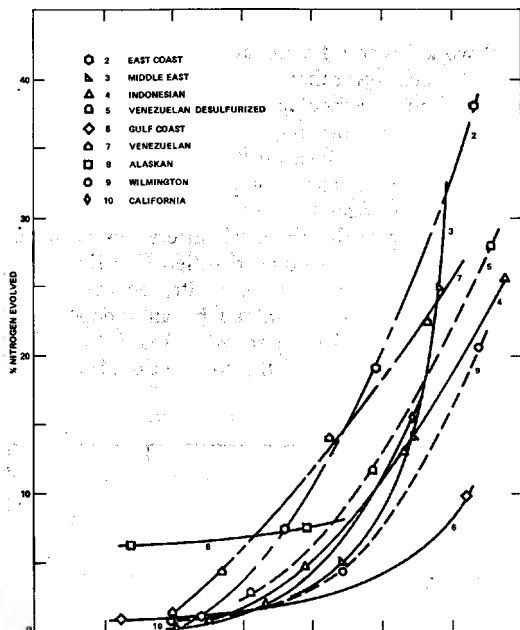


FIG. 6. Nitrogen and total mass evolution characteristics.

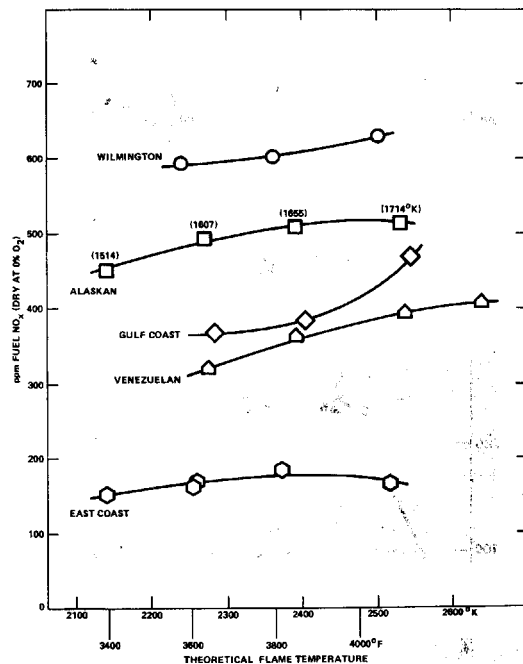


FIG. 7. Temperature dependence of fuel NO<sub>x</sub> (tunnel furnace, Ar/O<sub>2</sub> and Ar/O<sub>2</sub>/CO<sub>2</sub>, ultrasonic nozzle, 3% excess O<sub>2</sub>).



droplet temperatures were significantly lower. The adiabatic flame temperatures were calculated using an adiabatic chemical equilibrium model based on a free-energy minimization algorithm. In the experimental testing, the theoretical temperature was varied from 2100°K to 2600°K by variations of the  $\text{CO}_2$  concentration in the oxidizer ( $\text{Ar}/\text{O}_2/\text{CO}_2$ ) and by slight oxygen enrichment of the oxidizer. A suction pyrometer was used to measure the approximate bulk gas temperature 10 cm from the divergent exit. These data, taken with the Alaskan oil and shown in parenthesis in Fig. 7, revealed that a 400°K change in theoretical temperature corresponded to a 200°K change in bulk gas temperature.

All of the data shown in Fig. 7 were taken in argon at 3 percent excess  $\text{O}_2$ , 405°K oxidant preheat, 15 psi atomizing pressure and 66 ssu fuel viscosity. In general, fuel  $\text{NO}_x$  formation was found to increase only slightly with increasing flame temperature. However, the Gulf Coast oil showed a distinct increase at high flame temperature, behavior analogous to that observed previously with pulverized coal flames.<sup>11</sup>

#### Drop Size

The influence of droplet size on thermal and fuel  $\text{NO}_x$  formation was determined by varying the atomizing air pressure. Recent work conducted at the International Flame Research Foundation as part of this research project<sup>12</sup> has shown that for the

ultrasonic atomizer used in this study, the Rosin-Rammler mean diameter (based on laser-diffraction measurements) decreases with increasing atomization pressure. Above a pressure of approximately 12 psia, the droplet size distribution also becomes extremely narrow. These size data were used in conjunction with  $\text{NO}_x$  emissions data as a function of atomizing pressure to develop Fig. 8. Fuel  $\text{NO}_x$  formation was found to be relatively insensitive to mean drop size, but thermal  $\text{NO}_x$  production increased with small drops. The latter effect is attributable to more intense early combustion and higher local temperature.

#### Discussion

The available field and laboratory data indicate that  $\text{NO}_x$  formation in a commercial boiler is a complex function of the combustion fluid dynamics and the fuel chemistry. This study addressed the latter, and the results lend strong support to the hypothesis that fuel nitrogen is the major source of  $\text{NO}_x$  emissions in commercial oil-fired boilers.

The primary fuel composition parameter was shown to be nitrogen content; fuel  $\text{NO}_x$  formation increased almost linearly with fuel nitrogen level. Smaller, secondary composition effects were observed and attributed to differences in hydrocarbon evolution rate, distribution of nitrogen species, influence of fuel sulfur, etc. These effects were investigated in three sets of special doping studies. First, the distillate oil was doped with pyridine ( $\text{C}_5\text{H}_5\text{N}$ ) and thiophene ( $\text{C}_4\text{H}_4\text{S}$ ) to produce a fuel with primarily volatile nitrogen and hydrocarbon components and with nitrogen and sulfur contents equal to the California residual oil (0.79% N, 1.6% S). The fuel nitrogen conversion to  $\text{NO}_x$  with the light blend was significantly below the pure distillate, but was essentially identical to that with the California residual (Fig. 9), indicating that total bound nitrogen content is far more important than hydrocarbon volatility. These data also support utilization of doped distillate oils to simulate heavy residual oils in fundamental experimentation.

Second, synthetic heavy oils with significant amounts of volatile nitrogen were studied. Pyridine and thiophene were added to the Venezuelan desulfurized oil (0.24% N, 0.93% S) to produce blends matched to the: (1) Venezuelan oil before desulfurization (0.40% N, 2.2% S); (2) Alaskan oil (0.51% N, 1.6% S); and (3) California oil (0.79% N, 1.6% S). The synthetic blends and the pure oils gave equivalent conversions in each case as shown in Fig. 9. Thus nitrogen species that are volatile relative to the major fuel components (e.g., pyridine, B.P. 115.5°C) do not result in higher fuel nitrogen conversions. These results suggest that either the bulk of the fuel vaporizes and mixes prior to combustion

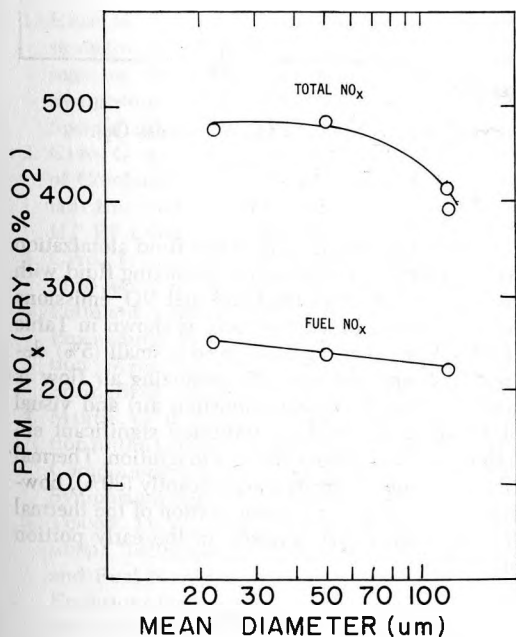


FIG. 8. Influence of drop size (tunnel furnace, ultrasonic nozzle, Indonesian oil).

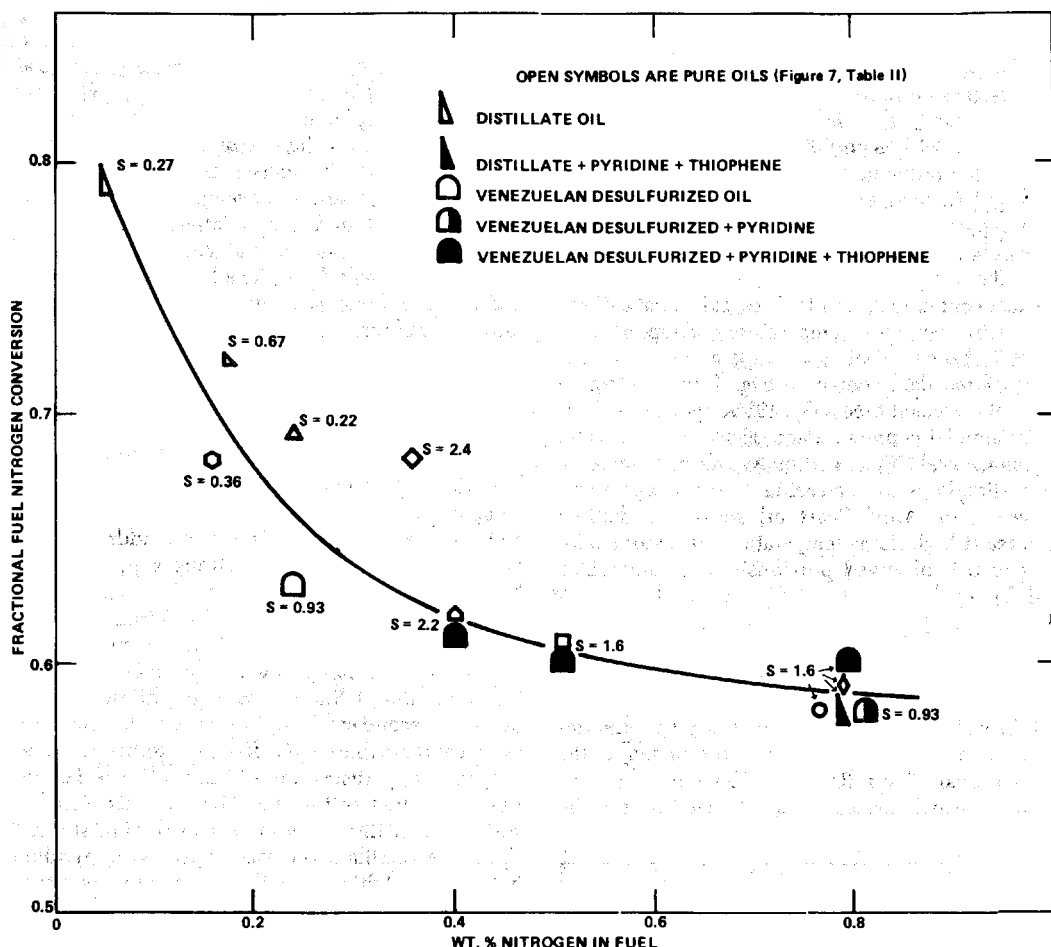


FIG. 9. Synthetic oil results (tunnel furnace, ultrasonic nozzle, Ar/O<sub>2</sub>/CO<sub>2</sub>, 5% excess O<sub>2</sub>).

(hence volatile and medium nitrogen species are equivalent) or there exists a local equilibrium insensitive to the original speciation. The data on the Gulf Coast oil (0.36% N, 2.4% S) suggest that the presence of extremely refractory nitrogen compounds (Fig. 6) results in increased conversion; however, it was not possible to check this hypothesis because such species are not available in pure form.

Third, the effect of fuel sulfur in actual heavy oils was studied by tests with the Venezuelan desulfurized oil doped to 0.79% N (via pyridine addition) with and without additional sulfur added as thiophene. The data (Fig. 9) indicate that fuel sulfur slightly enhances fuel nitrogen oxidation as reported by Wendt et al.<sup>13</sup> However, it was not possible to attribute the fuel composition effects shown in Fig. 5 solely to sulfur chemistry.

Finally, the details of the twin fluid atomization were studied by replacing the atomizing fluid with an inert (argon). Both total and fuel NO<sub>x</sub> emissions were determined for three fuels as shown in Table III. Fuel NO<sub>x</sub> emissions showed a small (5%) decrease as expected since the atomizing air flow is small (7% of the total combustion air) and visual observation of the flame indicated significant entrainment of secondary air prior to ignition. Thermal NO<sub>x</sub> emissions decreased significantly (30%), however, suggesting that a major portion of the thermal NO<sub>x</sub> is formed very quickly, in the early portion of the flame.

#### Acknowledgment

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TABLE III  
Influence of atomizing fluid  
(Tunnel furnace, ultrasonic nozzle, 3% excess O<sub>2</sub>)

Fuel	Atomizing fluid	Total NO <sub>x</sub> (air)	Fuel NO <sub>x</sub> (Ar/O <sub>2</sub> /CO <sub>2</sub> )	Thermal NO <sub>x</sub> (by difference)
Wilmington (0.77% N)	21% O <sub>2</sub> †	980	688	292
	argon	860	653	207
Venezuelan (0.40% N)	21% O <sub>2</sub>	650	402	248
	argon	540	378	162
Alaskan (0.51% N)	21% O <sub>2</sub>	705	ND*	—
	argon	580	ND	—

\*Not Determined.

†For total NO<sub>x</sub> the atomizing fluid was air; for fuel NO<sub>x</sub> the atomizing fluid was 21% O<sub>2</sub>/20% CO<sub>2</sub>/59% Ar.

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