# Correlation of Fuel Nitrogen Conversion to NOx During the Combustion of Shale Oil Blends in a Utility Boiler

by

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In an oil fired utility boiler, nitric oxides are formed by two basic mechanisms; the thermal fixation of atmospheric nitrogen at elevated temperature within the flame zone, and the conversion of organically bound nitrogen in the fuel to NOx during the combustion process. NOx formation by thermal fixation, normally referred to as thermal NOx is essentially dependent upon flame temperature and concentration of oxygen and atmospheric nitrogen within the flame zone. The conversion of organically bound nitrogen to NOx, is directly related however, to the nitrogen content of the fuel.

Research on the reduction of nitrogen oxides produced from the reaction of atmospheric oxygen and nitrogen has been in progress for many years. More recently, attention has been given to the formation of nitrogen oxides from nitrogen compounds contained within the fuel. This source of nitrogen oxides becomes increasingly important as high nitrogen content fuels derived from shale and coal grow in use.

Recently, combustion tests have been conducted by Southern California Edison Company to evaluate NOx emission characteristics of shale oil (0.7% sulfur and 2% nitrogen) when burned in a utility boiler. The tests were conducted in a 45 MW Combustion Engineering boiler equipped with six

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face mounted oil burners each rated at 85 million Btu/hr. To comply with Air Quality Management District fuel sulfur content requirements shale oil was blended with low sulfur oil so that the average sulfur content of the fuel blend did not exceed 0.5%. Nitrogen content of the low sulfur fuel ranged between 0.2-0.25%. The NOx emission was evaluated when burning shale oil blends using both conventional and off-stoichiometric modes of combustion. The emission levels were determined for a developmental low NOx burner (LNB) and a conventional mechanical atomizing Peabody type burner.

As one might expect, NOx emission level increased as the quantity of shale derived oil in the blend was increased. The incremental increase in NOx emission level was proportional to the shale oil blending ratio which suggested that the increase in emissions was mainly caused by the high nitrogen concentration within the fuel. It was superising to note, however, that the conversion efficiency of fuel nitrogen into NOx decreased, as shown in figure 1, as the fraction of shale oil (and fuel bound nitrogen) increased. It was also found that changing burner stoichiometry from fuel lean to rich achieved a substantial reduction in fuel nitrogen conversion rate, particularly in the case of the Peabody burner.

While a number of explanations can be offered to such result, it is felt that the reduction in nitrogen conversion efficiency illustrated in figure 1 appears to be the result of two competing processes. (a) The formation of NOx which increases as the nitrogen

containing shale oil content increases, and (b) the reduction of NOx by its reaction with high boiling hydrocarbons introduced with the shale oil and which is later released in the combustion process. The proposed model syggests that NOx is reduced after it is formed - a technique quite different from the classical approaches of slowing down NOx production by reducing the reaction temperature. The model assumes that the first process is a first order reaction with respect to fuel bound nitrogen and hence to the concentration of shale oil. The reduction process, however, is a second order reaction depending upon both NOx and the shale oil concentration, where the later term determines the residual hydrocarbon released late in the process. On this basis, the relative rate of NOx production would be given by:

$$\frac{1}{NOx}\frac{d(NOx)}{dt} = k1\ (\text{shale oil}) - k2\ (NOx)\ (\text{shale oil})$$

or

$$\frac{d(NOx)}{NOx(\text{shale oil})} = [k1 - k2\ (NOx)]\ dt$$

A plot of $\frac{(NOx)}{(NOx)(\text{shale oil})}$ vs. (NOx) should be linear for equal residence times t. Such a plot is illustrated in figure 2 where a good correlation results.

The mechanism suggested here can lead to a general technique for reducing NOx formation by proper fuel blending. Burner design parameters could be also selected to enhance this delayed fuel vaporization while maintaining good burner flame stability. The

delayed vaporization of fuel, achieved through the use of high boiling temperature hydrocarbons or through optimization of burner design will then reduce NOx generated during the early phase of the combustion process. The concept is quite consistent with the general concept of staged combustion except that staging is accomplished by the natural separation processes occuring during fuel evaporation.

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