ABSTRACT

ELLINGTON, GRANT HUAL. Investigation into the Correlation Among Nitrogen Oxides and TSNAs in Flue-Cured Tobacco. (Under the direction of Dr. Mike Boyette.)

Research established the most significant mechanism associated with Tobacco Specific Nitrosamine (TSNA) formation in flue-cured tobacco was a result of the exposure to nitrogen oxides (NO_x) that reacted with the naturally occurring alkaloids in the green leaf. Curing with a direct-fired heating system was determined to be a significant source of TSNA formation in flue-cured tobacco and as a result the tobacco industry mandated a conversion to indirect-fired heating. This work began with random monitoring of direct- and indirect-fired bulk curing barns to better understand the NO_x concentrations that the green leaf is exposed to during the curing process. The predominate NO_x species measured for a direct-fired system was nitrogen dioxide (NO_2), but for an indirect-fired system was nitric oxide (NO). The combustion modifications associated with a heat exchanger resulted in changing the primary NO_x nitrosation agent from predominately NO_2 to NO.

Controlled exposure tests were conducted during the 2004 and 2005 seasons to evaluate differences in the cured leaf TSNA response as a result of exposure to NO or NO_2 during curing. Two electric heated curing barns were utilized to perform the exposure study. The treated barn was dosed with a NO_x species and the control was untreated. A total of six cures were conducted during the 2005 season of which three were dosed with NO and three with NO_2. Cured leaf samples from both barns were analyzed for TSNAs. Over the two year study, a total of 6 cures were treated with NO_2 and 5 cures were treated with NO. The TSNA levels in the cured leaf, averaged across both seasons, was approximately 1.891 ppm an

0.505 ppm for the cures treated with NO_2 and NO respectively. Based on the 2005 TSNA data, the treatment differences were significant at the 5 percent level. The adsorption or diffusion of NO_2 in the green leaf and the consequent reaction with the alkaloids resulted in higher TSNA levels in the cured leaf as compared to NO.

Investigation into the Correlation Among Nitrogen Oxides and TSNAs in Flue-Cured Tobacco

by
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DEDICATION

The value of an education was always emphasized by my parents and this work is dedicated to them.

BIOGRAPHY

Grant Ellington was born on June 16, 1970 and grew up in the small Harnett County town of Angier, N.C. He graduated from Harnett Central High School in 1988 and from an early age planned to attend North Carolina State University in Raleigh, N.C. He graduated with a B.S. degree in Biological and Agricultural Engineering in 1992. As an undergraduate student he worked as part-time help for Dr. C.W. Suggs during the summers with the Tobacco Mechanization program in the BAE Department, which initiated and ultimately was responsible for his career choice.

He began working full time as a research engineer for the BAE Department in 1993 and also completed an M.S. degree in Biological and Agricultural Engineering in 1999 from North Carolina State University. During this time period he worked as an engineer for Drs. Charles W. Suggs, Bill H. Johnson, and Michael D. Boyette on numerous tobacco mechanization projects. Shortly after obtaining his M.S. degree, he decided to pursue a Ph.D. degree in Biological and Agricultural Engineering under the direction of Dr. Michael D. Boyette. Grant also married his wonderful wife Dawn in 1998 and they had their first son Garrett in 2002. Beginning in 2002 he also began work has an Extension Associate in the BAE Department at North Carolina State University. Grant and Dawn’s second son Dylan was born in 2008.

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Chapter 1 Introduction

Flue-cured tobacco remains one of the major agricultural commodities produced in the southeastern U.S. and continues to rank in the top five in cash farm receipts for North Carolina (National Agricultural Statistics, 2006). Although the Federal tobacco program has changed significantly in recent years, the 2007 U.S. flue-cured production was estimated at 225,000 acres resulting in approximately 455 million pounds of cured leaf (Flue-Cured Tobacco Information, 2008). Approximately 330 million pounds or 72 percent was produced in North Carolina during the 2007 season. At an average yield of 2050 pounds per acre and average cured leaf price of $1.50 per pound this corresponds to a value of approximately 690 million dollars (Flue-Cured Tobacco Information, 2008). Maintaining the highest quality tobacco remains very important for growers to receive the best prices and is essential for the U.S. tobacco industry to remain competitive in the expanding global flue-cured market.

1.1 Curing

Flue-cured tobacco is cured in bulk barns that utilize forced air ventilation and temperature control to maintain the desired conditions inside the barns. The green leaf is placed in box containers or spiked racks that are then positioned in the barn (Figure 1.1). Bulk barns that utilize box containers are the most common due to the increased green leaf capacity and ease of integration into a mechanized loading and handling system. The quantity of green leaf loaded per box, and consequently the barn, will vary due to differences in the number of boxes per barn (8 to 10 typical), fan capacity, stalk position harvested, and quality

Figure 1.1 Conventional bulk curing barns (left side) and a loaded box container (right side).

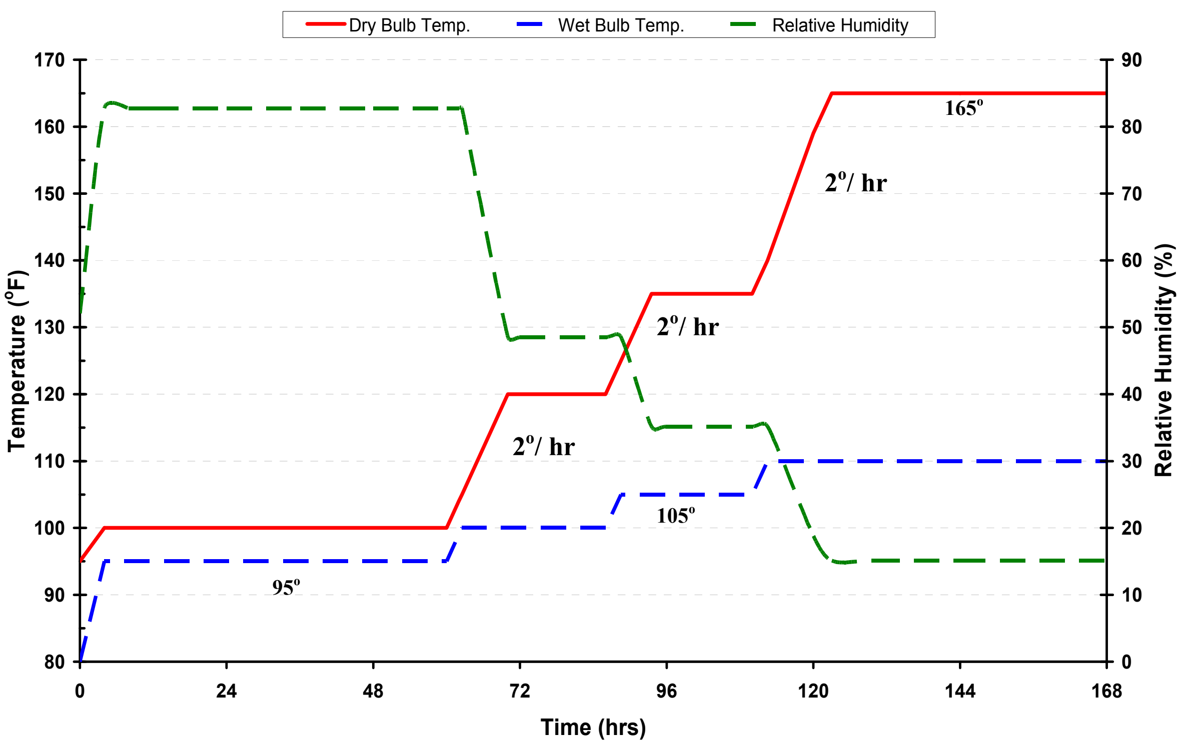

Figure 1.2 Typical curing schedule for normal ripe tobacco.

of the tobacco among others. A typical bulk barn loading rate ranges from 16,000 to 24,000 pounds of green tobacco of which approximately 85% is water.

The curing process is an essential part of flue-cured tobacco production. The use of heat to yellow the tobacco and then dry the leaf on the Slade farm located in Caswell county N.C. in 1839 is often credited with the start of "flue-cured" tobacco (Collins and Hawks, 1993). A more scientific approach by Johnson et al., (1960) generated a bulk curing schedule that has developed over the years since. The curing process requires a seven to eight day schedule that involves three sequential steps or phases of *yellowing, leaf (lamina) drying*, and *stem drying*. A typical curing schedule is shown in Figure 1.2 in terms of the dry- and wet-bulb temperatures and the corresponding relative humidity. The temperature and relative humidity will vary with time and are typically controlled manually by the grower. However, as fuel prices have increased significantly in recent years more growers are implementing automatic control technology, particularly ventilation controls, to assist with minimizing energy consumption during the curing process. Although the curing schedule shown is a general guide for normal ripe tobacco, growers will deviate from this based on many factors such as agronomic practices, weather, leaf maturity and ripeness, and leaf stalk position. The ability to make adjustments in the curing schedule based on their curing experience and maintain the desired cured leaf qualities is the art form of curing.

The cured leaf quality is greatly dependent upon the temperature and relative humidity control, especially during the yellowing phase, to allow completion of biological and physiological processes in the leaf (Watkins and Boyette, 1992). During yellowing, the leaf metabolic activity is maintained to enhance chlorophyll oxidation, starch to sugar conversion and proteolysis (Tso, 1990). For these and other biochemical conversions to occur completely, the proper humidity is very important. Although the starch conversion and chlorophyll breakdown occur simultaneously, the processes are independent of each other (Collins and Hawks, 1992). Therefore, the yellowing stage is a general visual indicator of sugar formation, but the degree of yellowing at a given time can vary with varieties. Any temperature or humidity conditions that accelerate drying before yellowing is complete may damage the leaf quality. As the temperature is increased to around 120^{o}F (49^{o}C) the leaf cells die as a result of thermal effects or desiccation and the color and chemical composition of the leaf are set. The dry-bulb temperature is advanced at a maximum rate of 2^{o}F per hour during any phase of the schedule. If the temperature is increased too rapidly during the transition between yellowing and leaf drying, the leaf temperature may become high enough with sufficient moisture in the leaf to result in "scalding" or oxidized browning, which is highly undesirable. Although some moisture has been removed during the yellowing process, the majority of drying occurs during leaf and stem drying as the difference between the dry-bulb and wet-bulb temperatures is increased to increase the drying potential of the air. The stem is more difficult to dry and as a result the dry-bulb temperature is increased to approximately 165^{o}F (74^{o}C). Stem drying temperatures that exceed this tend to scorch the leaf resulting in a reddish color, which is an undesirable quality.

At the end of the curing process the leaf moisture content is essentially zero and moisture must be added, which is commonly referred to as ordering, for efficient handling and market preparation. The maximum cured leaf moisture content accepted by the tobacco industry is 18% wet-basis (w.b.) and as a result moisture contents typically range from 12 to

18% w.b. Ideally, growers reintroduce moisture by forcing humid outside air through the dried tobacco. However, this process efficiency is very dependant on the ambient air conditions and may result in non-uniform moisture contents and extended ordering times. To minimize these problems, many growers use a portable spray system, consisting of 4 to 6 nozzles that connect to the existing water supply. Some growers add a fractional horsepower pump to increase the system operating pressure and improve atomization of the water, which increases the ordering process efficiency. The cured leaf is packaged in a 42-inch by 42-inch by 40-inch bale that weighs approximately 750 lb (340 kg), with a +/- 100 lb (45 kg) tolerance allowed.

1.2 Direct-fired Heating and TSNAs

Until recently, a direct-fired heating system supplied the heat to evaporate the moisture and dry the leaf. The most common direct-fired system consisted of an open flame ring-type burner (400,000 to 600,000 Btu/hr typical) that was mounted directly beneath a tube-axial fan operated by a 7.5 or 10 hp electric motor. Other configurations consisted of a similar capacity forced-air burner mounted above a centrifugal fan. Regardless of the system type, the direct-fired heating systems allowed all the combustion products to mix with the air supplied by the fan and consequently the green leaf was exposed to the product gases.

Nitrogen oxides (NO_x) are combustion products released into the atmosphere from localized high temperature combustion sources such as industrial, commercial, and domestic heating facilities and internal combustion engines. The NO_x gases are a result of multiple chemical kinetic mechanisms that are affected by the combustion process operating parameters. Nitrogen oxides directly affect human health and cause environmental problems such as acid rain, photochemical smog, and corrosion of metals (Derwent, 1999). A broad range of epidemiological studies have shown that lower exposure levels, as occur on many days in urban areas, can have effects on public health, especially in causing respiratory diseases (Ackermann, 1999).

Because Tobacco Specific Nitrosamines (TSNAs) are known carcinogens, they have recently come under intense study throughout the tobacco industry. In addition, research in recent years has recognized that one of the most significant factors contributing to TSNAs found in flue-cured tobacco is the reaction of NO_x combustion products with compounds in the green leaf. The nitrosation of the naturally occurring tobacco alkaloids is commonly accepted as the mechanism for TSNA formation in flue-cured tobacco (Peele, et al, 1999). The nitrosating agents are either microbial or NO_x gas exposure to the green leaf during the curing process. Although microbial activity may result in elevated TSNA levels in the cured leaf, research has established that NO_x exposure is the most important contribution in flue-cured tobacco (Peele, et al, 1999). Other tobacco varieties, such as burley for example, use ambient air to dry the leaf and are more susceptible to the microbial mechanism. The increased microbial activity is a result of the prolonged drying time at ambient conditions. Since TSNA levels are not present or are below detectable limits in the green leaf, TSNA formation and accumulation are generally considered to occur during the curing process.

In their seminal research, Peele, et al, demonstrated the significance of direct-fired curing as a source of TSNA formation in flue-cured tobacco. In an initial experiment, tobacco was cured in two small-scale reduced capacity curing barns. One barn was direct-fired with liquid propane gas (LPG) and the second barn (control) utilized electric resistance heat. At the end of the cure, leaf samples were collected and analyzed for TSNA levels. The electric heated barn resulted in TSNA levels below detectable limits, less than 0.1 parts per million (ppm), compared to an average level of approximately 2 ppm from the direct-fired barn. Additional leaf samples were analyzed from a number of existing direct-fired conventional barns and compared to barns that had been retrofitted with a heat exchanger (indirect-fired). The TSNA levels were significantly reduced in the indirect-fired barns as compared to the direct-fired barns.

During the 2000 growing season additional cured leaf samples were taken and analyzed from approximately 375 conventional barns, consisting of direct-fired and indirect-fired heating systems. Direct comparison of the TSNA levels from indirect- to direct-fired systems resulted in approximately a 93 percent reduction (Boyette and Hamm, 2001).

1.3 Indirect-Fired Heating and TSNAs

As a result of responsible product stewardship, the industry converted approximately 35,000 curing barns from direct-fired to indirect-fired heating systems over an approximate two year span (2000 and 2001). Indirect-fired systems use an air-to-air heat exchanger and vent the combustion products externally to the barn. This process eliminates the combustion products from mixing with the curing air and consequent exposure to the uncured leaf. The most common hydrocarbon fuel used is LPG, but a limited number of growers use natural gas or No. 2 diesel fuel. Also, there are a few systems that use a water-to-air heat exchanger and a centrally located boiler to heat the water that is circulated through each barn connected to the system. Prior to 1970, the majority of the U.S. tobacco was cured in smaller capacity barns that used wooden sticks to loosely hang the green leaf. Most of the stick barns utilized a heat exchanged flue system with natural ventilation and were fired using wood, coal, or fuel oil. However, with the introduction of bulk curing and the energy crisis during the 1970's, the increased capacity bulk barns utilized direct-fired heating to improve the system energy efficiency.

The major competitors of U.S. flue-cured tobacco have cured for many years with indirect-fired heating systems, which are typically smaller in capacity and utilize wood. As a result, it is critical that TSNA levels in U.S. flue-cured tobacco are kept to a minimum to maintain the desired cured leaf quality and global marketability. Additionally, if any FDA (Food and Drug Administration) regulations are developed and applied to any tobacco products, TSNA levels are anticipated to be monitored and an allowable threshold established.

1.4 Objective

Research concerning the production of TSNAs in tobacco established that they are developed primarily as a result of two distinct mechanisms. The most significant mechanism associated with TSNA formation in flue-cured tobacco is a result of the combustion gases reacting with the alkaloids in the uncured leaf. A direct-fired heating system was used in the past and allowed the combustion products to mix with the air that is circulated through the barn. With the application of indirect-fired heating the combustion gases are vented from the barn and this resulted in a significant reduction in TSNA formation in flue-cured tobacco.

Based on the preliminary findings when measuring the NO_x concentrations in direct-fired and indirect-fired bulk barns, the primary focus of this work was to perform a series of exposure tests to determine if there is a difference in the TSNA levels in the cured leaf as a result of exposure to nitrogen oxide (NO) or nitrogen dioxide (NO_2) during the curing process. The targeted exposure concentrations are levels that might be encountered in a bulk curing barn as a result of a leaking heating system. Additionally, there has been a very limited amount of work investigating TSNA levels and the NO_x mechanism in flue-cured tobacco. This work will also provide additional information related to actual NO_x concentrations measured in bulk curing barns to benefit growers and the tobacco industry in the future.

Chapter 2 Literature Review

2.1 Tobacco Specific Nitrosamines (TSNAs)

Nitrosamines are organic compounds found in many natural products that include soil, water, and food. They are referred to as free radicals and some are known to be carcinogens. Nitrosamines that are found only in tobacco products, and possibly in some other nicotine containing compounds, are called tobacco specific nitrosamines. They are widely considered to be among the most important carcinogens in smokeless tobacco products and cigarette smoke (Stepanov et. al, 2006). The tobacco industry has been examining tobacco products for nitrosamines for many years and TSNAs are sometimes found in cured tobacco, but not in the uncured leaf (Maw et. al, 2003). Since TSNA levels are not present or are below detectable limits in the green leaf, TSNA formation and accumulation are generally considered to occur during the curing process. The nitrosation of the naturally occurring tobacco alkaloids is commonly accepted as the mechanism of TSNA formation in flue-cured tobacco. Among the many alkaloid materials found in commercial tobaccos, nicotine is considered to be the principle (Tso, 1990). Next to nicotine, nornicotine and anabasine are among the most commonly found alkaloids in tobacco. Tobacco types, cultural practices, degree of ripening, and fertilizer treatment are some of the key factors that determine the alkaloid levels. The alkaloid level increases as the plant matures, especially during the period after topping, and as a result the levels are highest in the leaves from the upper part of the plant (Tso, 1990).

The nitrosation agents focused on are the microbial reduction of nitrate to nitrite and exposure to the combustion products that react with the alkaloids in the leaf. While microbial activity is considered the prevalent mechanism in air-cured tobacco varieties, the use of direct-fired burners in flue-cured exposes the green leaf to the combustion products during curing. Air-cured varieties, such as burley, use ambient air to dry the leaf and are more susceptible to microbial activity. An environment is created and maintained for an extended period of time, 3 or more weeks typical, which promotes and prolongs the microbial activity. However, the flue-cured schedule during yellowing maintains the dry-bulb temperature at approximately 100 to 105^{o}F (38 to 41^{o}C) for a limited time (48 to 72 hours typical). The temperature is then increased to rapidly dry the leaf and as a result the environment for microbial activity is suppressed or eliminated. In air-cured burley tobacco, the effects of fertilization rates, harvest dates, and other factors that influence TSNA formation have been reported (Anderson et al., 1987). Others have conducted research on the effect of fertilization rates and curing conditions on the level of TSNAs in air-cured tobacco (Long et al., 1999). However, a limited amount of work has been reported on TSNA formation in flue-cured tobacco.

The most frequent TSNAs found in tobacco are NNN (N-nitrosonornicotine), NAB (N-nitrosoanabasine), NAT (N-nitrosoanatabine), and NNK (4-(N-methyl-N-nitrosamino)-1-(3-pyridyl)-1-butanone) (Peele et al., 1999). The highest concentration of the four in flue-cured is typically NNK and is considered to be derived from nicotine (Peele et al., 1999). The NNN is derived from both nicotine and nornicotine. Both NNK and NNN are consistently carcinogenic in laboratory animals and have recently been evaluated by the International

Agency for Research on Cancer as carcinogenic to humans (Stepanov et. al, 2006). NAB is a weak carcinogen and NAT apparently lacks activity (Hecht, 1998). The NNN, NAB, and NAT may be formed in a single-step simple nitrosation. Microbial reduction of nitrate to nitrite, which also reacts with the leaf alkaloids, is an additional mechanism for TSNA formation during curing. Typically, TSNA levels resulting from exposure to the combustion products are significantly higher than levels due to microbial activity in flue-cured (Peele, et. al, 1999). However, microbial activity may contribute to TSNA levels in flue-cured if problems such as barn rot or soft rot are present during the early stages of the curing process. Soft rot is a soil-borne bacterium that enters the leaf or stem through broken places (Watkins and Boyette, 1992). These problems in particular might accelerate and prolong the microbial activity in the leaf. Higher levels of nitrogen fertilization can result in higher levels of alkaloids. In a study by Chamberlain et al., (1986) involving flue-cured tobacco and different nitrogen fertilization treatments, it was found that the higher levels of fertilization resulted in higher levels of alkaloids and NNN. Based on a converter plant study, nornicotine was a more efficient precursor of NNN than nicotine (Tso, 1990). Converter plants have significantly higher levels of nornicotine and therefore have a direct and simple pathway to TSNA formation even in the absence of any external nitrosating agents. The combination of a nitrosating agent and leaves from a converter plant might result in increasing the TSNA formation in the cured leaf. However, the nitrosating agents are independent of the tobacco variety and converter plants are rare in flue-cured varieties.

2.1.1 TSNAs in Flue-Cured

Peele et al. (1999) demonstrated the significance of direct-fired curing as a source of

Table 2.1 Effect of burner configuration on TSNA levels in the cured leaf.

Barn Type	Burner Configuration	TSNA (ppm)	Estimated NO_x from Combustion (lb)
8-Rack	Electric	BDL	0
8-Rack	Direct-fired	2	0.39
Conventional	Direct-fired	13	2.53

TSNA formation in flue-cured tobacco. In an initial experiment, two small 8-rack capacity curing barns and a direct-fired conventional barn were loaded with green tobacco and the resulting TSNAs compared. Both of the 8-rack barns were loaded with approximately 990 pounds (450 kg) of green tobacco. One barn (control) utilized electrical resistance heating rated at approximately 68,000 Btu/hr (20 kW) while the other was equipped with a direct-fired LPG burner rated at approximately 75,000 Btu/hr (22 kW). Leaf samples were collected at the end of each cure and analyzed for TSNAs. The experiment results are summarized in Table 2.1. The electric heated barn resulted in TSNA levels below detection limits (BDL), less than 0.1 parts per million (ppm), compared to levels of approximately 2 ppm from the similar capacity direct-fired barn. The conventional direct-fired barn also resulted in elevated TSNA levels. The burner capacity on a conventional direct-fired barn can range from approximately 400,000 to 600,000 Btu/hr (117 to 175 kW), but the actual firing rate was not reported for the full-size barn tested. The quantity of NO_x (lb) reported by the investigators was estimated based on the recorded LPG fuel consumption and the U.S. Environmental Protection Agency (EPA) emission factor for NO_x (14 lb NO_x/1000 gal LPG) (EPA, 1993). It

Table 2.2 Effect of exogenous NO on TSNA levels.

Barn Type and Burner Configuration	NO Treatment (lb)	TSNA (ppm)
Electric (control)	0	1
Electric	4	174
LPG Direct-fired (control)	0	5
LPG Direct-Fired	4	107

should be noted that emission factors from the EPA are rated from "A to E" to provide the user with an indication of the information reliability with "A" being excellent and "E" being poor. The NO_x emissions reported in Table 2.1 utilized EPA data giving the rating of "E". The tobacco used for all the studies was mid- to upper-stalk tobacco, variety K-326, and the resulting TSNA analyses are the sum of NNN, NNK, NAB, and NAT.

Following these findings, additional experiments were conducted to investigate the effect of introducing NO_x into the curing barns. Tobacco was loaded into four different 8-rack capacity curing barns. Two of the barns were electric heated and the other two were direct-fired with an LPG burner. Into one electric and one direct-fired barn, approximately 4 lb (1.8 kg) of nitric oxide (NO) gas was introduced during the last 24 hours of the yellowing period. The tobacco in all the barns was yellowed for 48 hours and followed the same curing schedule. The remaining electric and direct-fired barns were not exposed to any additional NO gas and were considered controls. Cured leaf samples from each barn were then analyzed for TSNA levels. The data is summarized in Table 2.2 and shows that the TSNA levels from the direct-fired control barn were higher than the electric heated control barn. Also, the introduction of the NO gas increased the TSNA levels found in the cured leaf, regardless of the barn heating system. It should be noted that the NO_x gas used was NO and it is assumed the entire quantity was introduced instantaneously or over a very short time interval. Although the response indicates the significance of NO gas exposure, this input rate and quantity is not practically obtainable during the actual curing process. Based on the EPA emission factor, 4 lb of NO_x would require approximately 286 gallons of LPG. From actual on-farm fuel consumption studies, that quantity of LPG is more typical of the fuel consumption for the entire curing process.

Given the responses observed, an additional experiment was conducted with tobacco loaded into two electric heated barns. A varying quantity of NO gas was introduced during the last 24 hours of the yellowing phase to observe a dose-related response. Into one barn, 1 lb (0.45 kg) of NO gas was introduced and the other barn received 4 lb (1.8 kg) of NO gas. The barn with the higher dose resulted in cured leaf TSNA levels approximately an order of magnitude higher. Data collected from these studies by Peele et al., (1999) supported the contention that direct-fired curing provides the nitrosating agent, which can contribute significantly to TSNA formation during curing. Direct-fired curing was shown to be the primary mechanism for TSNA formation in flue-cured tobacco. Furthermore, work by Peele et al., has shown that no significant TSNA formation or accumulation occurred during proper storage of flue-cured tobacco.

Maw et al., (2003) investigated the feasibility of utilizing a heat-pump-dehumidifier in comparison with a conventional direct-fired barn to provide the heat energy required

Table 2.3 Mean TSNA (ppm) levels comparing tobacco cured in a conventional barn with a barn utilizing a heat-pump-dehumidifier, 1999-2001.

Stalk Position	Heat-Pump Barn TSNA	Conventional Barn TSNA
1	BDL	0.839
2	BDL	0.751
3	BDL	0.850
4	BDL	1.105
5	BDL	0.865

BDL = less than 0.1 ppm

during curing. Although this study was primarily focused on reducing the curing energy cost, cured leaf samples were also collected for TSNA analysis from both barn types for direct comparisons over a three year study. The TSNA levels shown in Table 2.3 are averaged for a given stalk position over three curing seasons. There was a significant reduction in TSNAs in the tobacco cured in the heat-pump barn as compared to the conventional direct-fired barn. This also supports the findings that in the absence of any nitrosating agents, assuming limited or no microbial activity, TSNAs can be minimized in the cured leaf.

The accumulation of TSNA is known to be formed by living microbes and be time dependent also (Maw, et al., 2003). During the heat-pump study the tobacco was also sampled at various stages in the curing process to demonstrate the TSNA levels varied with respect to time. The average TSNA levels were approximately 0.0299 ppm for the heat-pump and 0.0239 ppm for the conventional cured barn from leaf sampled immediately after yellowing, which are considerably lower than the final levels obtained (Table 2.3). Peele et al., also sampled tobacco prior to any NO_x treatment and subsequently on a 12 hour schedule

Table 2.4 TSNA sampling summary from conventional curing barns (1998 & 1999).

Year	Barn Type	Fuel	Burner Configuration	Number of Samples	TSNA (ppm)
1998	Stick	Wood	Flue Pipes	6	0.3
	Bulk	Diesel	Heat Exchanger	27	1.0
	Bulk	LPG	Heat Exchanger	23	BDL
	Stick	LPG	Direct-fired	1	5.9
	Bulk	LPG	Direct-fired	43	11.0
1999	Bulk	LPG and N.G.[1]	Heat Exchanger	-	1.3
	Bulk	LPG and N.G.	Direct-fired	-	7.1

[1] N.G. = Natural Gas

Table 2.5 Summary statistics of the 2000 TSNA flue-cured states sample study.

Heating System	Average TSNA (ppm)	Max. (ppm)	Min. (ppm)	Std Dev (ppm)
Direct-fired[1]	4.35	42.5	0.12	4.45
Indirect-fired[2]	0.30	3.09	BDL	0.44

[1]n = 102 samples
[2]n = 273 samples

for 48 hours after exposure to 4 lb (1.8 kg) of NO. The results showed the TSNA levels increased rapidly during the first 24 hours after exposure and continued to increase, but at a slower rate, over the duration of the cure. These observations suggest that any NO_x absorbed or adsorbed by the leaf can continue to react with the alkaloids to form TSNA.

The limited amount of research conducted has focused on the leaf exposure to nitrogen oxide (NO_x) compounds as a result of direct-fired curing. Although microbial activity may result in elevated TSNA levels in flue-cured tobacco, research has established that the leaf exposure to NO_x gases during curing is the most important mechanism.

2.2 On-Farm TSNA Sampling

Peele et al., (1999) sampled a number of conventional bulk barns from numerous locations to compare direct-fired barns to barns retrofitted with heat exchangers. This work was conducted during the 1998 and 1999 curing seasons. Table 2.4 summarizes the cured leaf TSNA levels for the various barns sampled during both seasons. A number of different barn types were sampled to represent varying agronomic, harvesting, and curing practices. Comparisons made with direct-fired and indirect-fired curing barns during the 1999 season showed approximately an 80 percent reduction in TSNAs for indirect-fired barns. All the barns sampled during the 1999 season used either LPG or natural gas fuel. Data from both years demonstrated that the TSNA levels were significantly reduced in the barns that were retrofitted with heat exchangers, which eliminates the leaf exposure to the combustion products during curing.

During the 2000 growing season leaf samples were taken and analyzed from approximately 375 conventional barns, consisting of direct-fired and indirect-fired heating systems (Boyette and Hamm, 2000). Curing barns were sampled from the five flue-cured producing states and therefore represented many of the varying harvesting and curing practices. Direct comparison of the average TSNA levels from indirect- and direct-fired systems showed an approximately 93 percent reduction for the indirect-fired barns. Table 2.5 summarizes the results from this multi-state sampling study. The TSNA values reported were the sum of NNN, NNK, NAB, and NAT. It should be noted that some of the indirect-fired systems sampled resulted in high TSNA values. If the heating system was leaking or curing problems occurred, then the mechanisms for TSNA formation were present.

Based on the data presented by Peele et al., (1999) to the tobacco industry, growers began retrofitting curing barns prior to the 2000 growing season. Beginning in 2001 and thereafter, growers were required by the industry to convert their curing barns to indirect-fired heating. A typical indirect-fired heating system consists of a forced-air burner and heat exchanger that results in venting all the combustion products external to the barn and consequently eliminates any exposure to the green leaf. Although most indirect-fired heating systems use an air to air heat exchanger, a very limited number of growers utilize hot water with a water to air heat exchanger installed in each barn. The commercial hot water systems are non-pressurized and use a conventional fuel (LPG or No. 2 diesel) to heat the water, but the burner is external to the barns. The heating capacity of the commercial hot water systems used is only adequate to operate a limited number of barns (3 to 6) per unit. However, one major benefit of a hot water system is any leaks that develop in the barn heat exchanger will not affect or promote TSNA formation in the leaf as a result of leaking water only.

2.3 Nitrogen Oxides Exposure Study

Oh and Boyette (2004) investigated the absorption of NO_x gas in flue-cured tobacco in a series of exposure studies. Sample leaves (flue-cured variety K-326) were harvested from three stalk positions (lower, middle, and upper third) from the Central Crops Research Station. The leaves were stored for one day at a constant temperature and relative humidity of 55^{o}F (13^{o}C) and 89% respectively. Prior to each test the leaves were cut into four smaller pieces and approximately 1.0 lb (0.45 kg) was placed inside a small container fabricated from expanded metal that was used to maintain a consistent packing density. The green tobacco

Table 2.6 Summary of the green leaf NO_x exposure tests (Oh and Boyette, 2004).

Test Number	Chamber	Temperature (^oF)	Packing Density (lb/ft^3)	Stalk Position	NO_x (ppm)
1	empty	82	-	-	4.46
2	empty	104	-	-	4.46
3	empty	126	-	-	4.46
4	empty	82	-	-	5.35
5	filled	82	4.61	upper	4.46
6	filled	82	4.61	upper	5.35
7	filled	82	4.61	middle	4.46
8	filled	82	4.61	lower	4.46
9	filled	82	6.43	upper	4.46
10	filled	82	2.77	upper	4.46
11	filled	104	4.61	upper	4.46
12	filled	126	4.61	upper	4.46

was then placed inside a temperature controlled chamber. For the tests, the temperature was maintained at three different levels. Each green tobacco sample was exposed to NO_x gas for approximately 40 minutes. Two different binary gas mixtures with the balance nitrogen were used for the test. One tank mixture contained approximately 4.07 ppm of NO and 0.39 ppm of nitrogen dioxide (NO_2) with the balance nitrogen (NO_x concentration of 4.46 ppm). The second tank was a mixture of approximately 5.17 ppm of NO and 0.18 ppm of NO_2 in nitrogen (NO_x concentration of 5.35 ppm). The NO_x gas was metered into the temperature controlled chamber and the outlet gas flow rate was measured at approximately 0.106 ft^3/min (3,000 ml/min). The actual NO_x concentrations were measured continuously with a chemiluminscence NO-NO_2-NO_x analyzer. After exposure the leaf samples were removed and a TSNA analysis was performed by a commercial testing laboratory. The test conditions are summarized in Table 2.6.

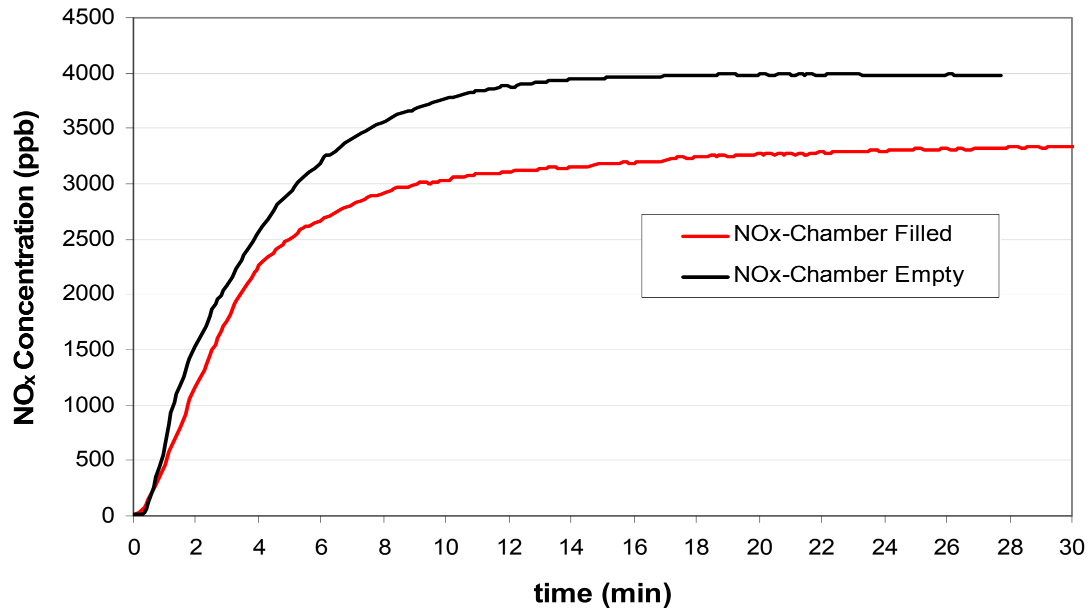

Figure 2.1 Temporal changes in the NO_x levels at 104°F with an empty and filled chamber (NO_x = 4.46 ppm).

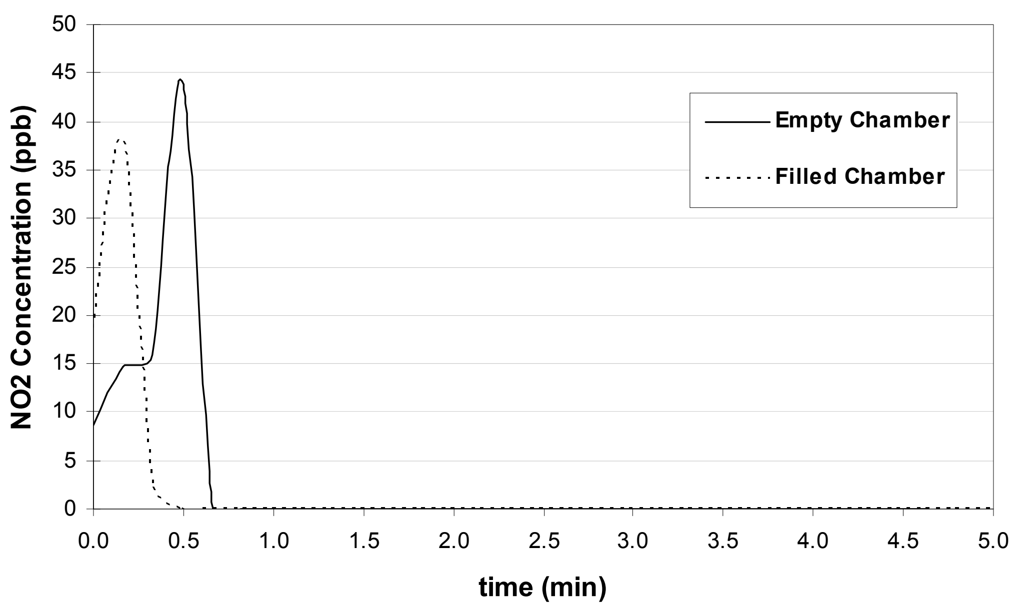

Figure 2.2 Temporal changes in the NO_2 levels at 104°F with the chamber filled and empty.

Table 2.7 TSNA results from the green tobacco leaves exposed to NO gas for 40 minutes.

TSNAs	82°F (28°C)	104°F (40°C)	125°F (52°C)
NNN (ppm)	BDL	BDL	BDL
NAT (ppm)	BDL	BDL	BDL
NAB (ppm)	BDL	BDL	0.769
NNK (ppm)	BDL	BDL	0.859
Total (ppm)	BDL	BDL	1.63

Figure 2.1 shows the NO_x concentration profiles versus time during exposure for the empty and filled chamber. The chamber temperature was approximately 104°F (40°C) for both cases. The difference in the steady state concentrations is due to the NO_x gas absorption in the green tobacco. The NO_2 gas concentration disappeared rapidly for both cases as a result of the very low initial concentrations (0.39 ppm) which can be seen in Figure 2.2. The NO_2 component was consumed by reactions with the ambient air (oxygen and water vapor) or absorption in the green leaf (Oh and Boyette, 2004). As a result, the NO gas species is the only NO_x component measured in Figure 2.1. The green leaf absorption of the NO gas is also simultaneously occurring with several chemical reactions with the ambient air (Oh and Boyette, 2004).

There was also a difference in the equilibrium concentrations from different stalk positions when exposed to 4.46 ppm of NO_x at 82°F (28°C) and a packing density of 4.61 lb/ft^3 (0.074 g/cm^3). The lower stalk tobacco had the lowest equilibrium concentration for these test conditions, which suggests that the lower stalk tobacco absorbs more NO_x gas per unit weight. Tests were also performed using the same exposure concentration (4.46 ppm NO_x) and temperature conditions (82°F), but the packing density was varied. The highest green leaf packing density of approximately 6.43 lb/ft^3 (0.103 g/cm^3) resulted in the lowest equilibrium concentration under the conditions of 82°F (28°C) and a NO_x gas concentration of 4.46 ppm. Additional tests were performed to evaluate the temperature effect using upper-stalk tobacco exposed to a NO_x concentration of 4.46 ppm and loaded at a packing density of approximately 4.61 lb/ft^3. The absorption at 104°F (40°C) and 126°F (52°C) were similar, but higher than the quantity absorbed at 82°F (28°C). Table 2.7 summarizes the TSNA analysis from the upper-stalk green tobacco exposed to NO_x gas (4.46 ppm) for approximately 40 minutes at a packing density of approximately 4.61 lb/ft^3. The TSNA levels were below the detection limit except for the NAB and NNK of the test treated at the highest temperature (126°F). This result agrees with the fact that the green leaf has minimal TSNAs and any found in the cured leaf are formed as a result of the NO_x gas exposure.

Chapter 3 Nitrogen Oxides

The seven nitrogen oxides that are known to occur are NO, NO_2, NO_3, N_2O, N_2O_3, N_2O_4, and N_2O_5 (Air Pollution Control, 2002). Of these seven, nitric oxide (NO) and nitrogen dioxide (NO_2) are the two most important air pollutants because they are emitted in large quantities. As a result, when dealing with air pollution work these two species are commonly referred to collectively as NO_x. These nitrogen compounds that are generated during the combustion process have been the subject of study for many years. The majority of this work has been motivated by the impact these emitted compounds have on the environment and human health. They play an important role in acid rain, the formation of harmful ozone and photochemical smog in the lower atmosphere and the depletion of the beneficial ozone in the upper atmosphere (Waibel, 1997).

Nitrogen oxide emissions from combustion sources are due to the oxidation of atmospheric nitrogen or the oxidation of nitrogen containing compounds chemically bound in the fuel (Air Pollution Control, 2002). For most stationary combustion systems approximately 95 percent of the NO_x formed leaves the flame zone as NO, but at ambient temperatures in the atmosphere chemical equilibrium favors the conversion of NO to NO_2 (Waibel, 1997). Control of nitrogen oxides is a field of very active research, but the detailed mechanisms of NO_x formation are not precisely known (Air Pollution Control, 2002).

The NO_x formation mechanisms during the combustion process can occur through three chemical kinetic processes with each having unique characteristics. Each pathway contributes to the total NO_x formation, but the amount varies with location in the combustion zone and is influenced by the flame fuel-air mixture. The mechanisms are Thermal (Zel'dovich) NO_x, Prompt NO_x, and Fuel NO_x. The relative importance of these three sources to the total NO_x emissions from a particular combustion device will depend on the operating parameters and fuel composition (Fossil Fuel Combustion, 1991). Because NO is typically the predominant species produced from combustion devices, the three mechanisms discussed are based on NO formation.

3.1 Thermal (Zel'dovich) NO

In the combustion of fuels that do not contain nitrogen compounds, the thermal mechanism is the principle source of nitric oxide emissions. Thermal NO is initiated with the high temperature dissociation of atmospheric nitrogen molecules. Nitrogen has a triple atomic bond and is very stable, but at very high flame temperatures the nitrogen molecules will dissociate into individual N atoms. The oxygen molecules are also decomposed into individual O atoms and react with the nitrogen. In the absence of nitrogen compounds found directly in the fuel, the thermal mechanism is a significant source of NO emissions. The three principal reactions governing the formation of thermal NO from molecular nitrogen are,

$$O + N_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} NO + N \tag{3.1}$$

$$N + O_2 \underset{k_4}{\overset{k_3}{\rightleftarrows}} NO + O \tag{3.2}$$

$$N + OH \underset{k_6}{\overset{k_5}{\rightleftarrows}} NO + H \tag{3.3}$$

These chemical reactions are often referred to as the extended Zel'dovich mechanism. The forward and reverse rate coefficients ($k_1 - k_6$) for all three reactions have been measured over a wide temperature range and increase exponentially with temperature (Fossil Fuel Combustion, 1991). The rate coefficients are evaluated from the expression,

$$k_i = A_i T^{B_i} e^{(-C_i/T)}, \quad i = 1...6 \tag{3.4}$$

where A_i and C_i are constants and the exponent B_i is zero or unity. These reactions have high activation energies and therefore are kinetically controlled. The formation of thermal NO is extremely temperature sensitive and becomes rapid only at high temperatures (3000 to 3600^{o}F), which are required to break the nitrogen bonds (Air Pollution Control, 2002). When there is sufficient oxygen, as in a fuel-lean flame, the rate of consumption of the free N atoms becomes equal to the rate of its formation and a steady state can be established (Fossil Fuel Combustion, 1991). The rate of production of the N atoms by reaction (3.1) is equal to the rate of removal by reactions (3.2) and (3.3). This assumption is valid for most cases, except in extremely fuel-rich combustion conditions. Utilizing the reactions (3.1) – (3.3), the NO and N atom formation rate can be expressed by,

$$\frac{d(NO)}{dt} = k_1(O)(N_2) - k_2(NO)(N) + k_3(N)(O_2) - k_4(NO)(O) + k_5(N)(OH) - k_6(NO)(H) \tag{3.5}$$

$$\frac{d(N)}{dt} = k_1(O)(N_2) - k_2(NO)(N) - k_3(N)(O_2) + k_4(NO)(O) - k_5(N)(OH) + k_6(NO)(H) \tag{3.6}$$

In order to determine the NO formation rate, values of the local temperature and local species concentrations of H, O_2, O, N_2, and OH are required. The thermal mechanism involves the O atoms and OH radicals, which also play an important role in the fuel oxidation process. Since the kinetics of the thermal NO formation are considered to be several orders of magnitude slower than the fuel oxidation reactions, following the suggestion by Zel'dovich, the thermal NO formation mechanism can be decoupled from the fuel oxidation process (Miller and Bowman, 1989). The result is most of the thermal NO is formed after the fuel combustion reactions are complete. Using this approximation and the steady-state N atom assumption, the formation rate can be calculated assuming equilibrium values of temperature and species concentrations. The O atom and OH concentrations can be determined from the partial equilibrium consideration of the following reactions,

$$1/2O_2 \rightarrow O \tag{3.7}$$

$$1/2O_2 + 1/2H_2 \rightarrow OH \tag{3.8}$$

From these reactions, the expressions for the O and OH concentrations are,

$$(O) = K_{p1}(O_2)^{1/2}(R_u T_e)^{-1/2} \tag{3.9}$$

$$(OH) = K_{p3}(O_2)^{1/2}(H_2)^{1/2} \tag{3.10}$$

where K_{p1} and K_{p3} are equilibrium constants for the reactions, which are a function of temperature, R_u is the universal gas constant, and T_e is the equilibrium flame temperature. From these equilibrium reactions, the concentrations of the radical species (O and OH) can be expressed in terms of the stable species O_2 and H_2. Utilizing the steady state assumption for the N atom concentration, the NO formation rate due to the thermal mechanism can be expressed as,

$$\frac{d(NO)}{dt} = 2[k_1(O)(N_2) - k_2(NO)(N)] \tag{3.11}$$

Substituting the expression for the O atom concentration (3.9), the formation rate can be expressed as,

$$\frac{d(NO)}{dt} = 2[k_1(K_{p1})(O_2)^{1/2}(R_uT_e)^{-1/2}(N_2) - k_2(NO)(N)] \tag{3.12}$$

From equation (3.12), it is evident that the NO formation rate is exponentially dependent on the flame temperature (k_i), the square root of the O_2 concentration, and proportional to the N_2 concentration. Additionally, the residence time or amount of time the fuel-air mixture is exposed to the maximum flame temperature will affect the NO formation rate. Equation (3.11) can be integrated to obtain an expression for the NO concentration as a function of time,

$$(NO) = \frac{k_1(O)(N_2)}{k_2(N)}(1 - e^{-2k_2(N)t}) \tag{3.13}$$

From (3.11) it can also be seen that the maximum initial NO formation rate, when the NO concentrations are small ($NO << NO_{eq}$), is twice the reaction (3.1).

3.1.1 Fuel-Air Mixtures

The *equivalence ratio* (ϕ) is used to describe fuel-air mixtures and is defined as the ratio of the actual fuel-air ratio (F/A) to the theoretical or stoichiometric fuel-air ratio $(F/A)_{st}$ for a combustion process, which is expressed as,

$$\phi = \frac{(F/A)}{(F/A)_{st}} \tag{3.14}$$

In practice, the amount of air actually supplied may be greater or less than the stoichiometric amount, depending on the application. Another ratio that is commonly used to describe fuel-air mixtures is the percent *excess air*, which is the actual air mass minus the stoichiometric air mass divided by the stoichiometric air mass. The percent excess air can be expressed in terms of the equivalence ratio by,

$$\%Excess\,Air = \left(\frac{1-\phi}{\phi}\right) \times 100 \tag{3.15}$$

It is common to plot combustion properties, such as flame temperature and species concentrations, verses the equivalence ratio because many of these properties will have a maximum or minimum at an equivalence ratio of approximately unity (Fossil Fuel Combustion, 1991). The reactants form a fuel-lean mixture when the equivalence ratio is less than unity ($\phi < 1$) and fuel-rich mixture when greater than unity ($\phi > 1$). At stoichiometric conditions the equivalence ratio is equal to unity. The stoichiometric quantity of air supplies sufficient oxygen for complete oxidation of the hydrogen and carbon elements in the fuel and the resulting combustion products are only stable species of carbon dioxide (CO_2), N_2, and H_2O. At stoichiometric conditions, the fuel and oxygen are fully consumed. Stoichiometric combustion is very seldom obtainable because of difficulty in achieving adequate mixing of the fuel and air. As a result, most combustion equipment is operated with excess air ($\phi < 1$) but at the lowest amount practically obtainable to maximize efficiency.

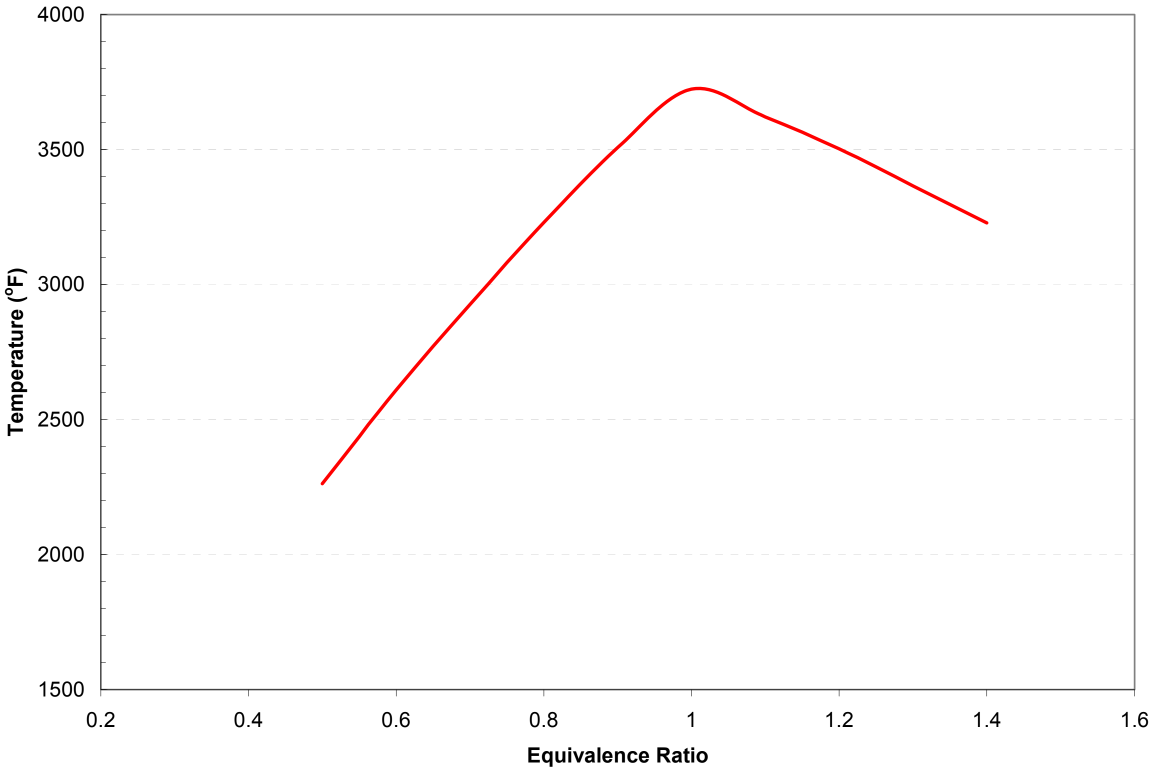

Figure 3.1 Estimated adiabatic flame temperature versus equivalence ratio for burning LPG in air.

3.1.2 Flame Temperature and Thermal NO

The adiabatic flame temperature is the theoretical temperature attained when a fuel-air mixture is burned to completion and all of the sensible and chemical energy of the reactants is transferred to the combustion products (Waibel, 1997). The estimated adiabatic flame temperature as a function of the equivalence ratio is shown in Figure 3.1 for burning LPG with air. The peak flame temperature occurs at an equivalence ratio of approximately unity and decreases significantly as the fuel-air mixture becomes increasingly lean or rich. An online chemical equilibrium software tool (Colorado State University) was used to determine the combustion equilibrium temperature and product concentrations at different equivalence ratios. The initial reactant temperature and pressure are at ambient conditions of 77^oF (25^oC) and 1 atmosphere respectively. Figure 3.1 is a typical response for burning hydrocarbon fuels in air and illustrates the effect excess air has on the flame temperature. Although the flame temperature calculated is considered the maximum, the actual flame temperature obtained in practice is less as a result of heat transferred away from the flame zone.

The factors that affect the thermal NO mechanism are the N_2 and O_2 concentrations (flame stoichiometry), flame temperature, and time of exposure at peak temperature (residence time). Longer residence times increase the amount of thermal NO due to increased exposure at high temperatures. Most practical combustion equipment requires excess air ($\phi < 1$) to provide additional oxygen beyond the stoichiometric requirement to minimize the emission of carbon monoxide (CO) and other unburned hydrocarbons. The excess air results in an increase in the oxygen concentration in the flame zone, which enhances fuel oxidation, but also increases NO formation. However, excess air also reduces the flame temperature and if the excess air is steadily increased, the flame temperature decreases until the reduction in NO due to the temperature decrease overcomes the increase in NO due to the oxygen concentration increase and the thermal NO peaks (Waibel, 1997).

The residence time is defined as the time it takes for a gas element to travel from the burner nozzle or port to the flame tip (Principles of Combustion, 1986). For laminar diffusion flames the residence time can be estimated based on the flame height and the average gas velocity inside the nozzle. The average gas velocity can be estimated assuming a typical

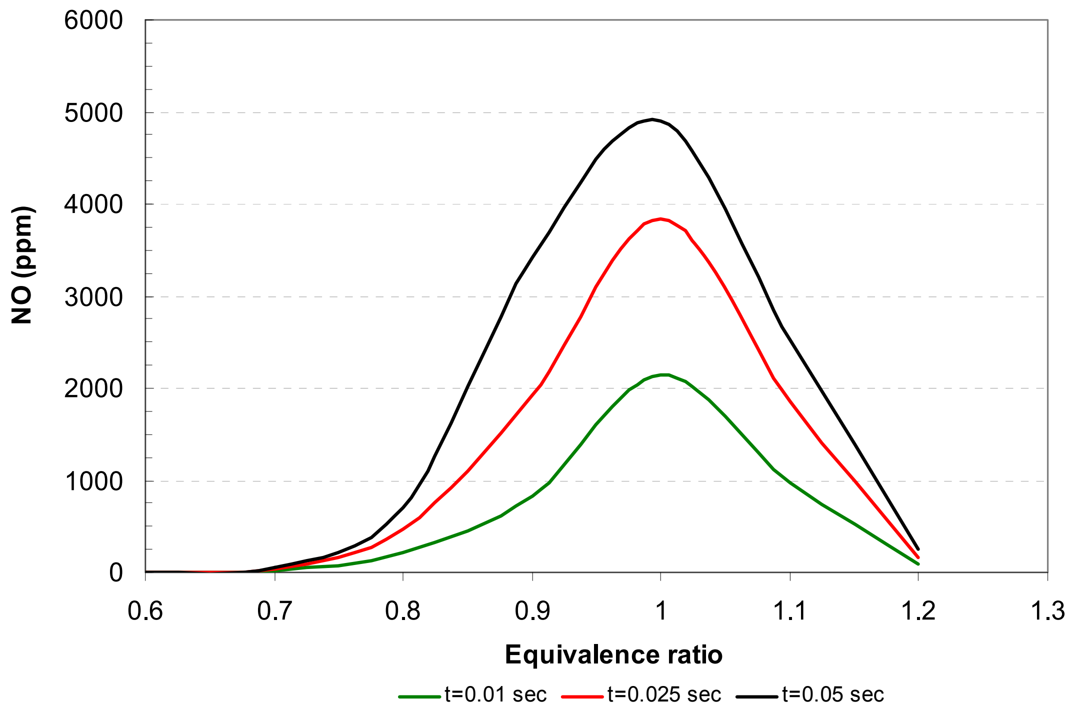

Figure 3.2 Nitric oxide concentrations versus equivalence ratio burning LPG in air.

burner firing rate and the actual burner geometry (nozzle diameter). Also, the maximum flame length will be less than the combustion chamber dimensions. Using actual nozzle specifications (0.356-inch diameter) from a burner manufacturer, a firing rate of 400,000 Btu/hr, and an assumed flame height of 30-inches, the estimated residence time is 0.04 seconds. This simple example is used to illustrate the time scale associated with residence times. Although this is based on a laminar diffusion jet, the actual flow regime is turbulent.

Utilizing the expression in (3.13) along with the equilibrium concentrations and flame temperatures calculated using the chemical equilibrium software, the NO concentration is plotted versus the equivalence ratio for three different assumed residence times in Figure 3.2.

It should be noted that the temperatures used are the adiabatic flame temperatures and the actual obtained will be less. Although actual temperatures and the consequent NO concentrations in practice may be less, the relationship between the NO concentration, time, and equivalence ratio can be seen. The concentration peaks at an equivalence ratio of approximately unity for all three residence times, which corresponds with the maximum flame temperature and illustrates the importance of temperature on thermal NO emissions. Increasing the equivalence ratio from approximately 0.6 to 0.8 increases the NO concentration by an order of magnitude or more. Also, the NO concentration increases significantly as the residence time is increased for a given equivalence ratio. At equivalence ratios less than unity, more air and therefore more oxygen are available, but the flame temperature is reduced significantly and the NO concentration decreases also. However, as the fuel-air mixture becomes very fuel-lean the flame might become unstable and blow out. The fuel-lean flammability limit for hydrocarbons is at an equivalence ratio of approximately 0.5 or 100% excess air (Roberts, 2003). When the equivalence ratio exceeds unity, the amount of fuel is in excess of the amount of oxygen available resulting in a fuel-rich mixture, which also results in reducing the flame temperature and NO formation. Unfortunately, for most practical combustion devices that are operated at a high flame temperature to maximize thermal efficiency also tend to increase the NO formation as a result of the thermal mechanism.

The process furnace temperature will also affect the thermal NO emissions by the rate of heat transfer from the flame. The lower the furnace temperature, the higher the heat transfer rate from the flame and the lower the actual peak flame temperature within the flame zone (Waibel, 1997). As a result, the thermal NO formation will decrease also. Conversely higher furnace temperatures result in higher flame temperatures and increased NO emissions associated with the thermal mechanism.

3.2 Prompt NO

Nitric oxide formation during the combustion of hydrocarbon fuels can exceed those accounted for by the thermal mechanism (Zel'dovich) and was first identified by C. P. Fenimore. Work by Fenimore showed that in the flame zone a mechanism other than the Zel'dovich reaction path contributes to NO formation and is referred to as prompt NO (Miller and Bowman, 1989). This pathway of formation is only found in hydrocarbon flames. Formation occurs in the early part of the flame where the fuel and air first begin to react and is formed at a faster rate than the thermal mechanism. In this region the fuel molecules are decomposing into C-atoms and CH radicals that react with the N_2 in the air and subsequently with O_2 to form NO. In this part of the flame very little thermal NO should be formed, and by definition, prompt NO is formed from molecular nitrogen that is in excess of the NO predicted by the thermal mechanism (Waibel, 1997). Prompt NO is most prevalent in fuel-rich flames and involves a complex series of reactions and many possible intermediate species. Typically, prompt NO is only a small portion of the total NO from conventional burners. However, as NO control techniques that are utilized to decrease the thermal mechanism improve, the prompt NO that is produced accounts for a larger percentage of the total NO (Waibel, 1997). Although this mechanism is not fully understood, there are three reaction paths postulated for forming prompt NO and the relative importance of these depends on the conditions during the combustion process.

3.2.1 Fenimore Prompt Mechanism

One source of prompt NO in hydrocarbon flames is based on a reaction sequence that is initiated by the reaction of hydrocarbon radicals (C, CH, CH_2) with molecular nitrogen during the decomposition of the fuel in the initial reaction zone. The hydrocarbon radicals react with molecular nitrogen to form amines or cyano compounds. Consequently these resulting compounds react with other free radicals to form NO, following the Zel'dovich pathway. This is often referred to as the Fenimore prompt mechanism. A number of species resulting from the fuel fragmentation that have been suggested as a source of prompt NO include C, CH, CH_2, and CN radicals. The Fenimore prompt kinetics considers the following initiating reactions,

$$CH + N_2 \leftrightarrow HCN + N \tag{3.16}$$

$$CH_2 + N_2 \leftrightarrow HCN + NH \tag{3.17}$$

$$CN + H_2 \leftrightarrow HCN + H \tag{3.18}$$

$$C + N_2 \leftrightarrow CN + N \tag{3.19}$$

These cyano and amine species products tend to form NO when combined with other free radicals. Many of the subsequent steps involve O, OH, or H radical species that lead directly to the steps involved in the thermal mechanism. The quantity of HCN formed increases with the concentration of the hydrocarbon radicals, which increases with the equivalence ratio. As the equivalence ratio is continually increased, the Fenimore prompt NO formation increases initially and then decreases due to a deficiency in oxygen (Fossil Fuel Combustion, 1991).

3.2.2 Super-equilibrium Values

An additional source or subclass of the prompt mechanism is due to the super-equilibrium concentrations of O atoms and OH radicals in the flame zone, which might accelerate the Zel'dovich mechanism. In lean and slightly rich flames the partial equilibrium assumption of reactions (3.7) and (3.8) may not be the case. Near the flame zone the ratio of the maximum concentration to the equilibrium concentration of both species may be different by an order of magnitude or more resulting in higher NO_x formation rates. In fuel rich flames, the rapid NO_x formation rates near the flame cannot be explained by the super-equilibrium concentrations of O atoms and OH radicals (Fossil Fuel Combustion, 1991).

3.2.3 Nitrous Oxide Mechanism

A third subclass of prompt NO involves the reaction of the intermediate species nitrous oxide (N_2O) and the O-atom. Nitrous oxide is produced in the flame by the following reaction,

$$O + N_2 + M \leftrightarrow N_2O + M \tag{3.20}$$

where M is any arbitrary available third body species, which facilitates the reaction. The additional subsequent steps in this pathway to NO_x formation are,

$$H + N_2O \leftrightarrow NO + NH \tag{3.21}$$

$$O + N_2O \leftrightarrow 2NO \tag{3.22}$$

At low temperatures the N_2O formation reaction can exceed the reaction steps involved in the thermal mechanism. This mechanism provides an alternative path for NO formation under conditions that diminish formation from the thermal mechanism. For fuel-lean flames at low temperatures and high pressures, the nitrous oxide reaction sequence becomes an important source of NO emissions (Fossil Fuel Combustion, 1991).

3.3 Fuel NO

Fuel-bound nitrogen is an important NO forming mechanism in liquid fuels and coal fired combustion systems because of the high nitrogen content of the fuels. Some fuels may contain 0.5 to 2.0 percent organic nitrogen by weight and those fuels produce significantly

higher NO_x emissions as compared to fuels that do not (Miller and Bowman, 1989). The source of nitrogen in the fuel is single bonded to the fuel oil molecule and less stable as compared to the triple bonded nitrogen in the atmosphere. The fuel NO emissions do not increase linearly with the fuel nitrogen content because the fraction of bound nitrogen converted to NO is a function of the nitrogen concentration in the fuel (Waibel, 1997). The nitrogen compounds will most likely undergo some thermal decomposition prior to entering the combustion zone. Experimental results have determined that the flame temperature, stoichimoetry, and the initial concentrations of the nitrogen compound affect the extent of the fuel nitrogen to NO conversion (Fossil Fuel Combustion, 1991). The conversion is almost completely independent of the identity of the parent fuel nitrogen compound. As the fuel burns, all of the bound nitrogen dissociates to form unstable nitrogen radicals such as HCN, N, CN, and NH. These nitrogen radicals will either be oxidized to form NO or bond with another N-atom to form N_2. As less oxygen is available ($\phi > 1$) to react with the nitrogen radicals, the more the reaction will favor the formation of N_2. Additionally, the higher fuel nitrogen content favors the reaction to molecular nitrogen even in lean flames.

Although the pathway leading to fuel NO formation is not completely understood, hydrogen cyanide (HCN) and ammonia (NH_3) oxidation are considered the two major intermediates (Miller and Bowman, 1989). After the initial reactions, the formation of NO from HCN proceeds in a very similar method as discussed in the Fenimore prompt mechanism. Although there are a number of reaction mechanisms by which HCN is converted to NO, the O + HCN sequence is considered to be the dominant, under a variety of combustion conditions, with some contribution from the OH + HCN reaction sequence only under fuel-rich conditions (Miller and Bowman, 1989).

The important feature of the ammonia oxidation is the conversion of ammonia to NH_2 and its oxidation to NO. For most conditions the conversion to NH_2 is by,

$$NH_3 + OH \leftrightarrow NH_2 + H_2O \tag{3.23}$$

In lean flame conditions the reaction with O atoms and in rich flame conditions the reaction with H-atoms can also make significant contributions to NH_2 formation. The NH_2 or NH radicals are subject to subsequent reactions resulting in oxidation leading to NO or reacting with NO to form N_2. The radical species primarily responsible for determining the NO/N_2 product distribution depends on the equivalence ratio. For equivalence ratios much less than unity, the critical radical species is NH_2, but as the equivalence ratio increases the greater number of H atoms results in a shift in the critical species from NH_2 to NH to N (Miller and Bowman, 1989). The NH_2 product is oxidized through a reaction sequence to form NO. The formation of N_2 from the reaction of NO with NH_2 occurs either directly or through an intermediate species NNH. The NH can be oxidized to NO directly through,

$$NH + O_2 \leftrightarrow NO + OH \tag{3.24}$$

$$NH + O \leftrightarrow NO + H \tag{3.25}$$

The reaction of NH radicals with NO produces N_2O, which can be converted to N_2 by the reaction with H-atoms. The production and destruction of NO by N-atoms occurs through the extended Zel'dovich mechanism. As the equivalence ratio is increased, less oxygen is available and the reactions will favor the formation of molecular nitrogen. For this reason the NO levels are lower in fuel-rich conditions. The fraction of fuel nitrogen converted to NO can be an order of magnitude less as compared to fuel-lean or near stoichiometric conditions (Combustion, 1987). However, even in fuel-rich systems the resulting NO concentration is still significantly greater than the equilibrium value at the flame temperature. Although the fuel NO discussion is focused on liquid or solid fuels, gaseous fuels containing HCN or NH_3 will also produce elevated NO emissions.

3.4 NO_2 Formation

Although it has been generally accepted that NO_2 accounts for approximately five percent of the total NO_x emissions from combustion processes, significant concentrations of NO_2 have been measured in the exhaust of practical combustion systems, gas turbines, diesel and spark ignition engines, and in laboratory combustion systems (Hori, 1986). As noted in the prompt and fuel mechanisms, the NO formed during combustion can react subsequently with hydrocarbon fragments to form cyano species or with amine species to form N_2. In addition to these reactions, NO can also react with various oxygen-containing species to form NO_2. Chemical equilibrium considerations indicate that for typical flame temperatures (T > 2200^{o}F), the NO_2/NO ratios are negligible (Fossil Fuel Combustion, 1989). However, Coutant et al., (1982) observed NO_2/NO ratios of one and higher in the emissions of range-top burners. Cernansky and Sawyer (1975) measured NO and NO_2 concentrations using turbulent diffusion flames of a round jet of propane issuing into a slightly swirled coaxial flow of air. They concluded that the most likely source of NO_2 in the combustion region is the oxidation of NO to NO_2 by HO_2 and O-atom radicals in fuel lean regions where temperatures have been rapidly reduced. Very rapid mixing and cooling occurs allowing the formation of NO_2. Hori (1988) also investigated NO_2 formation by measuring both NO and NO_2 in a double concentric jet, consisting of a central hot combustion gas jet from a propane and air burner and an annular cold air jet confined in a cylindrical duct. The double concentric jets simulated the mixing and cooling process of hot combustion gas with cold air in combustion systems. The mechanism of NO_2 formation was believed to be the NO to NO_2 conversion by the HO_2 radical during the rapid cooling process in the mixing region between the hot combustion gas and cold air.

Miller and Bowman (1989) suggested that the NO_2 destruction and formation in flames can occur by the following reactions sequence,

$$NO + HO_2 \leftrightarrow NO_2 + OH \tag{3.26}$$

$$NO_2 + H \leftrightarrow NO + OH \quad (3.27)$$

$$NO_2 + O \leftrightarrow NO + O_2 \quad (3.28)$$

In the low temperature regions of flames, significant HO_2 radical concentrations exist that can react with the NO formed in the high temperature regions and transported by diffusion to the low temperature region. Both of the NO_2 removal reactions are rapid and in the presence of high radical concentrations, NO_2 will be converted rapidly back to NO. At flame temperatures NO_2 can only exist as a transient species and if it is to occur in the combustion products, then there must be quenching of the NO_2 formed in the flame (Miller and Bowman, 1989). As reported by other investigators, this quenching might occur in turbulent flames by rapid mixing of hot and cold fluid elements that serves to quench the NO_2 removing reactions by reduction in the radical concentrations. In enclosed combustion devices, such as gas-fired boilers, excess air (ϕ <1) is provided for complete combustion and is mixed rapidly with the fuel in a highly turbulent zone in the combustion chamber. Any NO_2 produced in the flame is subject to a combination of conditions, high temperature and excess oxygen, necessary for its reduction to NO (Coutant et. al, 1982).

3.5 NO_x Control Strategies

Although the focus of this work is not to implement or evaluate NO_x control strategies, a brief overview is included for stationary sources. The two broad categories of NO_x control are combustion modifications and flue gas treatment. Combustion modifications are used to limit the formation of NO_x during actual combustion and flue gas treatment techniques are utilized to remove the NO_x after formation. Typical reduction capabilities range from 30 to 60% for combustion modifications and 30 to 90% for flue gas treatment technologies (Yeh et. al, 2005).

Thermal NO_x is strongly influenced by flame temperatures and therefore the key to controlling or minimizing thermal NO_x is to reduce peak temperatures. Conventional methods to control the thermal mechanism generally involve modification of the combustion process to reduce the temperature and or the availability of oxygen. Both of these approaches are directed toward reduction of the formation rate rather than enhancing the NO removal rate, which is very slow at typical exhaust air temperatures (Fossil Fuel Combustion, 1991). Thermal NO_x control techniques include flue gas recirculation (FGR), air or fuel combustion staging, and excess air control (LEA).

3.5.1 Flue Gas Recirculation (FGR)

Flue gas recirculation can be utilized alone or in combination with staged combustion to reduce thermal NO_x emissions. This process involves the addition of inert combustion products into the air or fuel prior to combustion. In a FGR system, a percentage of the flue gas is recirculated from the exhaust stack and mixed with the combustion air via air foils or other mixing devices prior to the burner. A typical FGR system requires installation of a separate hot gas fan to extract the desired quantity of flue gas from the exhaust stack and the necessary duct work connecting the flue gas and combustion air. The recycled flue gas species act as inerts during the combustion process. The NO_x emissions are reduced by two mechanisms. The recirculated gas acts as a diluent that decreases the maximum flame temperature, which suppresses the thermal NO_x mechanism. To a lesser extent, FGR also reduces the NO_x formation by decreasing the local oxygen concentrations in the flame zone. The amount of recirculated flue gas is a key parameter that influences NO_x emission rates for these systems. In a typical FGR application, approximately 10 to 25% of the flue gas is recirculated back to the combustion zone and may result in lowering NO_x emissions up to 80% (ETEC Inc., 2008). As the FGR rate is increased above 30%, the effectiveness decreases and also generates undesired operational problems such as flame instability (Waibel, 1997).

3.5.2 Low-excess-air Firing (LEA)

Low-excess-air (LEA) firing provides only limited benefit, but is compatible with, and can be used together with most of the other control techniques. In recent years, the development of advanced instrumentation has allowed continuous automatic furnace monitoring and improved control of excess air. New low-NO_x burners represent the most common equipment design change for reducing NO_x formation. Basically, low-NO_x burners inhibit NO_x formation by controlling the mixing of the fuel and air by automating LEA and staged combustion. Tests indicate that low-NO_x burners reduce emissions by 40 to 60% compared with older, conventional burners (Air Pollution Control, 2002). For new systems, the most cost effective approach is to install low-NO_x burners to minimize initial formation while adding postcombustion technology if additional emission reductions are needed (Kitto, 1996).

3.5.3 Staged Combustion

Nitrogen oxides emissions can be reduced by introducing either the combustion air or the fuel into the flame in stages. With air staging a portion of the combustion air, typically 50 to 75%, is supplied to a primary combustion zone with all the fuel resulting in a fuel-rich ($\phi >$

1) zone (Waibel, 1997). The remainder of the combustion air is injected downstream, forming a secondary fuel-lean ($\phi < 1$) zone flame zone where combustion is completed. The NO_x formation is decreased in the first zone as a result of the fuel-rich combustion conditions and is decreased in the secondary zone as a result of fuel-lean conditions that reduce the flame temperatures. The excess air provided in the secondary zone also helps minimize the CO and hydrocarbon species produced from the fuel-rich zone. Air staging reduces both the thermal and fuel NO_x and is the most effective in controlling the conversion of fuel bound nitrogen to NO_x (Waibel, 1997). Fuel staging is the reverse of air staging and results in a fuel-lean primary zone and a fuel-rich secondary zone.

If the lean and rich combustion zones are organized properly, an additional NO_x control technique is referred to as reburning. This process relies on combustion products from the lean first zone to pass through the rich secondary zone prior to a final burnout zone. The NO_x generated in the first zone is able to react with the N-atoms in the rich zone to form N_2 or to react with the hydrocarbon radicals and recycle back to HCN. The nitrogen molecules that were in the form of NO have an increased chance to form N_2 rather than remain as NO (Waibel, 1997).

3.5.4 Postcombustion (Flue Gas Treatment Techniques)

Selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) technologies are the major systems applied for postcombustion control of NO_x. In both of these technologies, NO_x is reduced to N_2 and H_2O through a series of reactions with a reagent injected into the flue gas (Kitto, 1996). These processes cost more to implement than the combustion modifications.

In a SCR system, ammonia (NH_3) or urea is injected into the combustion flue gases, in a specific temperature zone, and reacts with NO_x as the gas passes over a catalyst. The most common catalyst used are base metals, that typically contain titanium and vanadium oxides and with small amounts of molybdenum, tungsten, and other active chemical agents (Kitto, 1996). The optimal operating temperature is dependent on the specific catalyst and is usually in the range of 600 to 800^{o}F (Air Pollution Control, 2002). Typically, SCR systems are designed to reduce emissions by 45 to 90% depending on the regulatory air quality requirements and inlet NO_x concentrations (Kitto, 1996). SCR systems are a high efficiency technology but may represent a higher cost alternative for controlling emissions as compared to the combustion modifications.

SNCR involves the injection of NH_3 or urea into the furnace at relatively high temperatures to react with the NO_x. This technology is very dependent on temperature and sufficient residence time at the appropriate reaction temperature. The desired reaction occurs in the temperature range of 1600 to 2000^{o}F (Kitto, 1996). If the temperature is above this range, the reagent may be oxidized resulting in the formation of additional NO_x. At temperatures below this range, the reaction is slowed and may result in excessive emissions of the unreacted agent.

3.6 Bulk Curing Barn Heating Systems and NO_x Emissions

The NO_x formation mechanisms were discussed to provide an overview of the chemical kinetic processes for each and how the formation rates are affected by the combustion system operating parameters. The hydrocarbon fuels used to provide the thermal energy required during curing are LPG, natural gas, and No. 2 diesel fuel, and as a result all three of the formation mechanisms are relevant. From the TSNA study (Boyette and Hamm, 2001) performed that sampled approximately 375 curing barns, approximately 82 percent used LPG. That percentage may even be higher now since some of the growers utilizing No. 2 diesel have converted to LPG due to the significant difference in fuel prices.

In order to minimize fuel consumption and increase the heating system thermal efficiency, all the heat exchanger burners, regardless of the fuel type, should be annually inspected and the excess air adjusted. From a practical standpoint, the burners are typically adjusted to operate with an equivalence ratio less than unity. The burners are very seldom inspected again in a given season, unless problems occur, and as a result excess air is provided to minimize CO and unburned hydrocarbon emissions. The general practice is to supply 5 to 50% excess air ($0.67 < \phi < 0.95$), but the exact amount will depend on the fuel burned, combustion equipment, and other factors (ASHRAE Fundamentals, 1997). Based on a number of barns (n=18) randomly sampled for exhaust stack data using an IMR Model 1400 Gas Analyzer (IMR Environmental Equipment International, St. Petersburg, FL) the average equivalence ratio was approximately 0.80 (25% excess air) with a standard deviation of 0.11. The barns sampled included LPG and No. 2 diesel fuel.

The burners that are using LPG or natural gas are expected to have contributions from both the thermal and prompt mechanisms. Although the fuel-air mixture is fuel lean, the actual flame temperatures should be sufficient to promote the thermal mechanism. However, actual flame temperatures have not been measured. The heat exchanger efficiency, which is affected by many variables, can also play an important role in the actual flame temperature and consequently the thermal NO formation mechanism. Additionally, two of the prompt subclasses may also contribute to NO_x formation in the retrofit heating systems. The excess oxygen from the fuel lean flame conditions may result in an abundance of O and OH radicals, which enhance the thermal mechanism. The hydrocarbon radical species concentrations may also be elevated enough to promote the Fenimore prompt mechanism. However, the Fenimore component of prompt NO_x is expected to dominate if flame conditions become fuel-rich. The total NO_x formation would be contributions from both prompt and thermal mechanisms for the gaseous fuels.

For the units burning No. 2 diesel, the fuel can contain a small percentage of fuel-nitrogen and under fuel-lean conditions the reaction favors the formation of NO_x versus molecular nitrogen. Considering this the total NO_x levels may involve contributions from all three mechanisms when burning fuels containing fuel bound nitrogen species. For the same flame conditions, the total NO_x concentrations may be higher from the liquid fuels as compared to the gas fuels used.

The postcombustion control strategies are probably not cost-effective solutions for minimizing NO_x concentrations in the heating systems used for curing tobacco. The system heating capacities are relatively small compared to industrial units and also only operate for approximately 10 to 12 weeks in a given year. However, the combustion modifications, particularly new low-NO_x burners, may need to be investigated. As the existing burners need to be replaced, these new technology burners and integration of advanced controls could possibly be implemented. If these units can reduce NO_x emissions by 40 to 60% as tests indicate (Air Pollution Control, 2002) this might be a cost-effective solution to assist with minimizing the concentrations exposed to the green leaf as a result of a leaking heating system without a loss in thermal efficiency.

Chapter 4 Direct-fired and Indirect-fired NO_x Measurements

Prior to the 2001 growing season, the flue-cured tobacco industry required all growers to retrofit their existing curing barns with heat exchangers to eliminate the green leaf exposure to the combustion products. With the implementation of indirect-fired heating, the industry was also interested in developing diagnostic equipment to assist with determining if a heat exchanger has developed any leaks and therefore defeating their primary purpose.

A very limited amount of information was available related to the NO_x levels that might be encountered inside a conventional curing barn. The only source available prior to this work is summarized in Table 4.1 (Izac, 1999 unpublished data). The NO_x (NO and NO_2) concentrations were monitored in direct-fired and indirect-fired empty barns at several temperatures with a chemiluminscence NO_x analyzer. The barns were operated for approximately 1 to 1.5 hours and the temperature was increased in successive steps of approximately 15^{o}F (8.3^{o}C) from 100^{o}F (38^{o}C) to 160^{o}F (71^{o}C). As expected the NO_x levels increased as the temperature increased, which is a result of the burner firing for a longer period of time. The NO_x concentrations listed are the maximum levels measured in each barn. Additionally, the average NO/NO_2 ratio for the direct-fired barns measured indicated an almost equal distribution of the two gas species for three of the barns checked and predominately NO_2 for one barn. The NO_x concentration measured in the indirect-fired barn was significantly less than any of the direct-fired barns.

This information provided some indication of the NO_x concentrations that any prototype diagnostic equipment must be able to detect. Existing NO_x analyzers capable of

Table 4.1 Summary of NO_x measurements from empty curing barns (Izac, 1999).

Burner Configuration and Barn Capacity	Maximum NO_x (ppb)	Average NO/NO_2
Direct-fired – 126 Rack	3,400	0.03
Direct-fired – 96 Rack	3,500	1.3
Direct-fired – 32 Rack	1,000	1.1
Direct-fired – 32 Rack	1,100	1.1
Indirect-fired – 32 Rack	75	0.8
Indirect-fired[1] – 32 Rack	25	0.2

[1] *Ambient levels*

detecting low concentrations (ppb levels) are expensive, complicated to operate, and not designed for mobile field measurements. As a result, an inexpensive prototype device to accurately measure NO_x levels in retrofitted curing barns was developed and tested during the 2000 and 2001 growing seasons.

Shown in Figure 4.1 is the prototype opto-electronic meter that utilized colorimetry to determine the NO_x concentration in air. The meter consisted of an aluminum housing assembly, vacuum pump for air sampling, and electronics for signal conditioning and automation. A solution of o-tolidine and ethanol (20 grams per liter) was applied to a 1.5-inch (3.8 cm) diameter Whatman filter paper that was used as the chemical substrate to absorb the NO_x gas (Oh, 2005). The meter housing contained three light emitting diodes (LED), which were operated at a wavelength of approximately 450 nanometers, and a photo transducer to measure the light intensity. The LEDs and photo transducer are centered on opposing sides and aligned with each other (Figure 4.1). The chemical sensor paper was

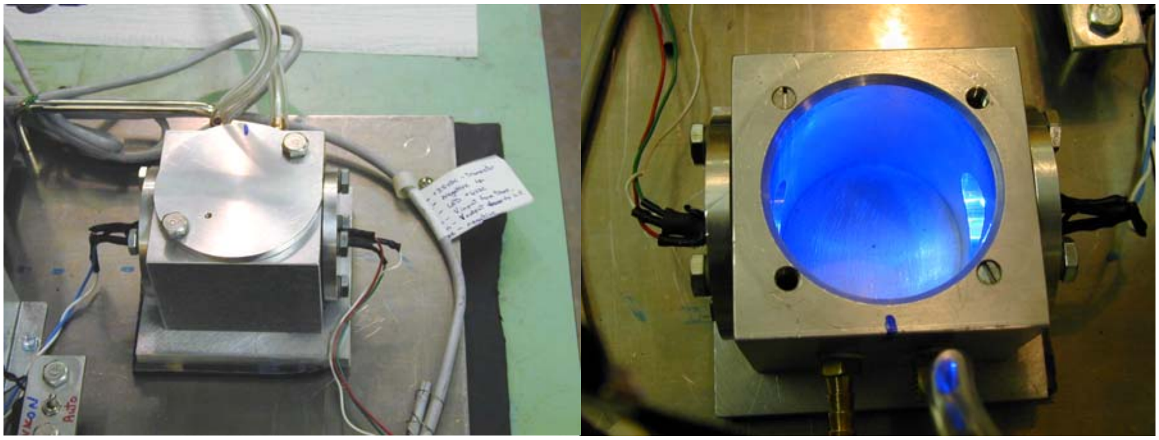

Figure 4.1 Prototype NO_x meter.

positioned on the bottom side of the removable meter top and held in place with a spring-loaded clip. The LEDs, photo transducer, and sensor paper are aligned when the top is secured. The sensor paper is oriented perpendicular to the LED's and photo transducer, but parallel to the incoming air sample. The air sample flow rate was approximately 0.035 ft^3/min (1000 ml/min). The NO_x gas in the air sample reacts with the filter paper chemical substrate and promotes a color change. As a result, the quantity of light that passes through the sensor paper is decreased and the change in light intensity is linearly proportional to the NO_x concentration and time of exposure. At the time of developing the prototype meter, the chemical sensor utilized was calibrated based on NO_2 gas only. As will be discussed next, NO_2 was the predominant gas species measured when monitoring randomly selected direct-fired barns.

4.1 On-Farm Nitrogen Oxide Measurements

During the 2000 and 2001 growing season on-farm measurements were performed with the prototype NO_x meter and with a Model 42 chemiluminescence NO-NO_2-NO_x analyzer (Thermo Environmental Instruments, Inc., Franklin, MA). These field measurements were necessary to assist with evaluating the prototype meter, but also provided NO_x concentration data from conventional barns. The Model 42 analyzer is capable of continuously monitoring NO_x concentrations from sub parts per billion (ppb) up to 20 parts per million (ppm) with a precision of +/- 0.5 ppb. The analyzer generates a 0 to 10 volt output signal for the NO, NO_2 and NO_x concentrations for continuous data collection. The detection full-scale range for each channel (NO, NO_2 and NO_x) is menu selectable and for the field measurements was set at 10 ppm. The analyzer output signals were connected to a Dell INSPIRON 2650 laptop computer using a portable DAQCard-1200 data acquisition device (National Instruments, Houston TX). The PC card device was interfaced through the computer PCMCIA cardbus. A program was developed using *LabVIEW* (National Instruments) graphical programmable software package to record the data. The model 42 averaging time interval is also software selectable from 10 to 300 seconds in multiples of 10 and was set at the minimum of 10 seconds. The lower the averaging time, the faster the analyzer display and output signals will respond to concentration changes.

The Model 42 was used as a reference to make direct comparisons with the prototype meter. Very high relative humidity levels (> 85% initially) can occur inside a curing barn, depending on the phase of the curing process. Based on recommendations by TEI, an ice bath was used to assist with removing moisture from the air sample prior to entering the

Figure 4.2 TEI Model 42 NO_x analyzer and prototype opto-electronic meter portable field setup.

instrument. The portable field setup is shown in Figure 4.2. The instrument was field calibrated prior to measurements at each location. This involved introducing zero grade air (National Specialty Gases, Durham, N.C.) into the analyzer for at least five minutes of stable readings. Once the zero background corrections are established, the process is repeated with a span gas. The span gas concentration was a binary mixture of 5.17 ppm NO (5.35 ppm NO_x) with the balance nitrogen (National Specialty Gases, Durham, N.C.).

Some of the curing barns randomly checked were loaded with green tobacco and at different stages in the curing process. The measurement procedure was the same for both the Model 42 analyzer and prototype meter. The NO_x measurements were performed

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Figure 4.3 Air sampling lines positioned inside a direct-fired curing barn.

simultaneously with both units for approximately 10 minutes. If the barns contained green tobacco, these measurements were only "snapshots" or the instantaneous NO_x concentration at that point in time during the curing process. The sample lines were positioned above the tobacco at the top of a curing container (box or rack) in the return or upper air plenum inside the barn (Figure 4.3). Random tests included direct-fired and indirect-fired curing barns. Prior to any measurements, the ambient NO_x concentrations were recorded, which typically ranged from 10 to 50 ppb.

Tables 4.2 through 4.4 summarize the NO and NO_2 concentrations, averaged over approximately 10 minutes, measured in both direct- and indirect-fired barns with the Model 42 analyzer. The direct-fired measurements included barns with green tobacco, stored cured tobacco (carry-over) from the previous growing season and barns that contained no tobacco. If the barns were empty, the burner thermostat was typically elevated 30 to 40^{o}F above the ambient temperature to ensure the burner cycled on during testing. However, if the barn contained green tobacco then the temperature was not adjusted. All of the indirect-fired barns

Table 4.2 Average NO_x concentrations measured in direct-fired barns during the 2000 and 2001 growing seasons.

Sample	NO	NO_2	NO_X	NO/NO_2	Temperature (^oF)	Comments
1	130	602	732	0.22	140	
2	52	225	286	0.23	100	***(Yellowing)***
3	105	178	283	0.59	120	***Carryover***
4	216	379	595	0.57	130	***Carryover***
5	355	474	829	0.75	140	***Carryover***
6a	190	237	431	0.80	140	***Above tobacco***
6b	222	356	580	0.62	140	***Below tobacco***
7a	147	172	319	0.86	160	***Above tobacco***
7b	124	353	477	0.35	160	***Below tobacco***
8	28	692	720	0.04	140	**Empty**
9	52	516	547	0.10	140	**Empty**
10	47	822	869	0.06	160	**Empty**
11	53	661	714	0.08	160	**Empty**
12	55	965	1019	0.06	140	**Empty**
13	49	738	788	0.07	140	**Empty**
14	63	1163	1226	0.05	160	**Empty**
15	58	951	1010	0.06	160	**Empty**
16	171	1300	1475	0.13	140	**Empty**
			Avg.	0.31		
			Std Dev	0.28		

sampled contained no tobacco and the same measurement procedure was followed.

4.1.1 Direct-fired Barns

Table 4.2 summarizes the average NO, NO_2, and NO_x (NO + NO_2) concentrations and the resulting NO/NO_2 ratio for the direct-fired barns tested. Each sample number represents a different barn. Samples 1 through 7 are for barns with green leaf at different stages in the curing process or cured tobacco and samples 8 through 16 are from empty barns. In all the direct-fired barns measured the NO_2 concentration was greater than the NO, resulting in a NO/NO_2 ratio less than unity. Additionally, in the empty direct-fired barns checked the NO_2 concentration was significantly higher than the NO. The resulting NO/NO_2

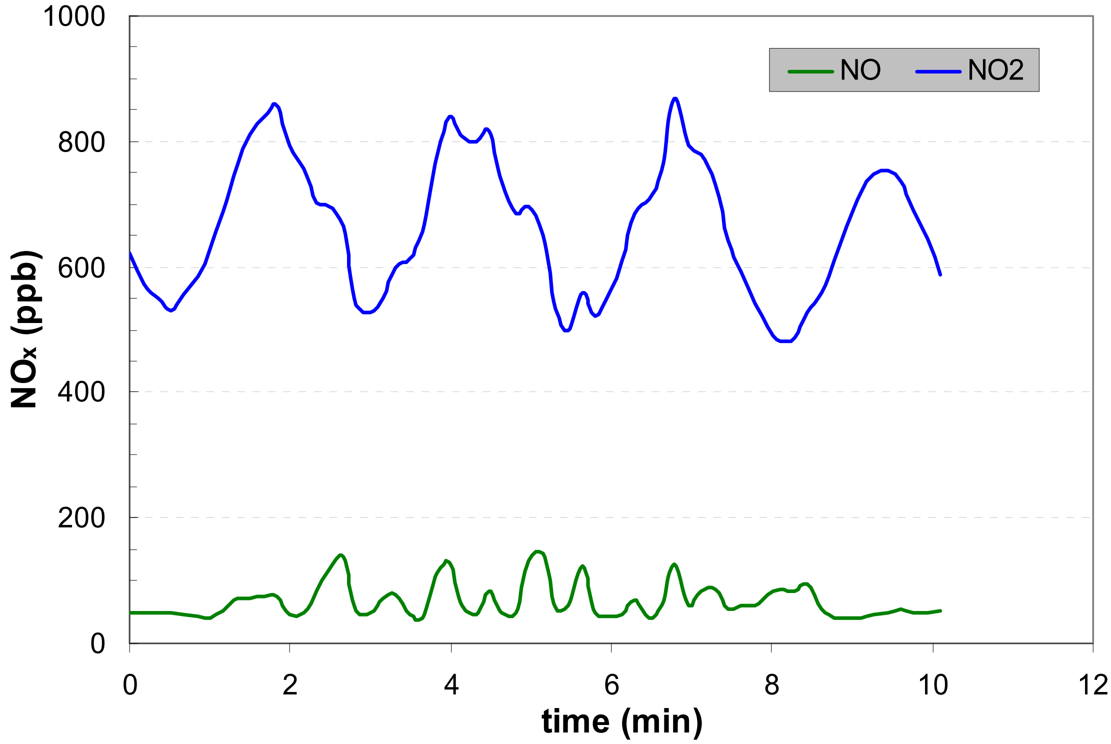


Figure 4.4 Measured NO_x response in an empty direct-fired barn.

ratio was also approximately an order of magnitude less for these samples. Typically, in the barns with green or cured tobacco the measurement was performed in the air plenum above the tobacco (Figure 4.2). However, for two different barn measurements the air was sampled from the supply plenum below the tobacco, designated 6b and 7b. The NO and NO_2 concentrations were greater below the tobacco, which is prior to the air passing through the tobacco. However, a comparison with the measurements above the tobacco, samples 6a and 7a, the NO concentration change was considerably less than the NO_2 concentration change. This is also evident in the resulting NO/NO_2 ratio based on the measurements above the tobacco for these two barns. Although only two observations, it appeared the NO_2 gas absorption or reaction with the green tobacco was greater than the NO gas. Figure 4.4

graphically illustrates both species concentration profiles verses time for an empty direct-fired barn measured (sample 11). The NO_2 concentration profile is significantly higher than the NO concentration and fluctuates as the burner cycles on and off during this time interval.

4.1.2 Indirect-fired Barns

Table 4.3 summarizes the time averaged NO_x concentrations measured in curing barns retrofitted with an indirect-fired system. The NO_x concentrations inside the barn remained at ambient levels, which were observed in samples 1 through 9. However, in samples 10 through 21 the concentrations were elevated significantly above ambient and as a result it was suspected that the retrofit system developed a leak. The leak may be the result of a cracked heat exchanger or exhaust duct connection located inside the barn that was not properly sealed. Also, NO was the predominant NO_x species measured. The resulting NO/NO_2 ratio was significantly greater than unity for all samples except one (sample 20).

For many of the barns sampled, the measurements were “snapshots” of the NO_x concentration profiles that might be encountered during curing. The concentration profiles are anticipated to vary with time during the curing process. Initially, during yellowing the dry-bulb temperature is only a few degrees above ambient and the burner may operate intermittently for short periods of time. However, as the schedule advances from yellowing to leaf drying, the temperature and ventilation are increased. As a result, the burner on time will increase and consequently the NO_x concentrations inside the barn should increase.

Based on these measurements, it is not anticipated that the NO_x concentrations during an actual curing process will approach the levels assumed in the exposure studies by Peele et al. It appeared the major NO_x gas species for a leaking indirect-fired system was NO.

Table 4.3 Average NO_x concentrations measured in indirect-fired curing barns during 2000-2001 growing seasons.

Sample	Burner System	NO (ppb)	NO_2 (ppb)	NO_X (ppb)	NO/NO_2
1	Indirect-fired	15	5	20	–
2	Indirect-fired	0	8	8	–
3	Indirect-fired	16	5	21	–
4	Indirect-fired	3	10	13	–
5	Indirect-fired	11	17	28	–
6	Indirect-fired	21	28	49	–
7	Indirect-fired	9	14	23	–
8	Indirect-fired	19	12	31	–
9	Indirect-fired	28	17	50	–
10	Indirect-fired w/leak	197	15	212	13.13
11	Indirect-fired w/leak	146	13	159	11.23
12	Indirect-fired w/leak	529	15	544	35.27
13	Indirect-fired w/leak	220	26	246	8.46
14	Indirect-fired w/leak	270	31	301	8.71
15	Indirect-fired w/leak	151	24	175	6.29
16	Indirect-fired w/leak	600	60	660	10.00
17	Indirect-fired w/leak	420	33	453	12.73
18	Indirect-fired w/leak	413	95	508	4.35
19	Indirect-fired w/leak	400	18	418	22.22
20	Indirect-fired w/leak	65	175	240	0.37
21	Indirect-fired w/leak	195	25	220	7.80
				Avg.	11.71
				Std Dev	9.1

However, in a barn that utilized a direct-fired system NO_2 was the major species and was always greater than the NO concentration. Although the direct-fired barns with green or cured tobacco did result in NO/NO_2 ratios less than unity, a higher concentration of NO waspresent as compared to an empty direct-fired barn. The maximum NO_x concentration measured for any barn tested, regardless of heating system configuration, was approximately 1.5 ppm, although the majority of the measurements were less than 1 ppm. The amount of time the burner operates will affect the peak NO_x concentrations inside the barn, but other factors such as burner firing rate and excess air (flame stoichiometry), fuel type, (liquid versus gas), and ventilation management will also contribute.

4.1.3 Continuous NO_x Measurements

Izac (1999) continuously monitored the NO_x concentration inside a few conventional barns at the Southern Piedmont Agricultural Research and Extension Center (AREC) in Blackstone, VA. Two conventional direct-fired barns and a 32-rack capacity retrofitted barn were monitored during the entire curing process. The concentrations for each barn were recorded (averaged over a minute) throughout the curing process with a chemiluminescence NO-NO_2-NO_x analyzer. The concentrations listed in table 4.4 are the approximated 24 hour average concentrations obtained from the concentration profiles versus time. The concentrations increased with time as expected due to the increase in temperature and increased time the burner operated. The NO_2 concentration can be obtained by subtracting the NO from the NO_x concentration. The maximum average NO_x concentration for the direct-fired barns was approximately 2000 ppb as compared to 50 ppb for the barn retrofitted with a heat exchanger. The peak concentration measured for any cure was approximately 2500 ppb.

The percentage of time the burner operates and consequent fuel consumption during the curing process will vary due to numerous factors such as the barn structural air leaks, insulation, ventilation management, burner firing rate (Btu/hr), heat exchanger efficiency, fan capacity, and ambient temperatures to name a few. Actual on-farm fuel consumption data and the dry-bulb temperature profile for a cure are shown in Figure 4.5. The LPG consumption (cubic feet of vapor) was monitored with an AL-425 (American Meter Company, Horsham, PA) diaphragm meter. The meter reading was recorded daily and

Table 4.4 Average 24 hour NO_x concentrations for continuously monitored barns.

	Powell - 126 rack (Direct-fired)		Powell - 96 rack (Direct-fired)		BulkTobac - 32 rack (Direct-fired)		BulkTobac - 32 rack (Indirect-fired)	
Time (hrs)	NO (ppb)	NO_x (ppb)	NO (ppb)	NO_x (ppb)	NO (ppb)	NO_x (ppb)	NO (ppb)	NO_x (ppb)
24	100	600	200	400	400	500	-	50
48	100	1000	200	400	400	500	-	50
72	100	1000	600	1300	750	1000	-	50
96	200	2000	500	1000	1250	2000	-	50
120	200	2000	500	900	1250	1500	-	50
144	200	1750	200	400	1250	1700	-	50

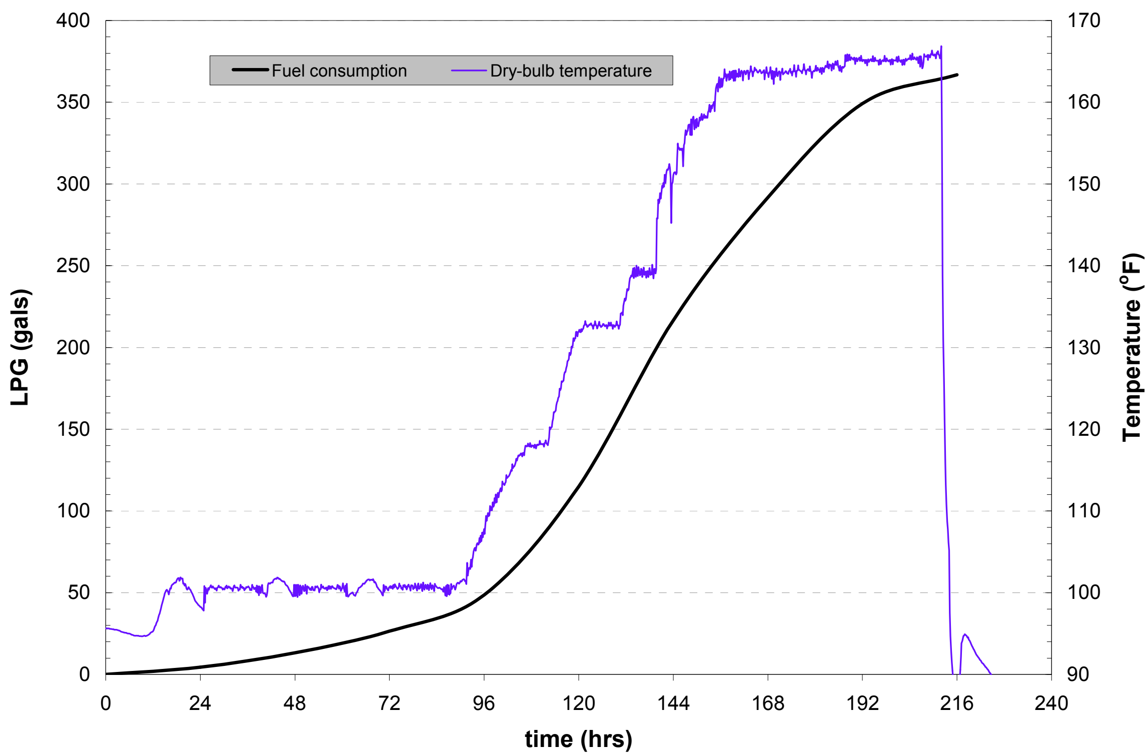


Figure 4.5 Fuel consumption and temperature profile during curing for lower stalk tobacco.

converted to gallons of LPG. The figure is included to demonstrate the change in fuel consumption, and consequent burner firing, as a function of time. The fuel consumption (gals/hr) was at a minimum during yellowing, but as the temperature and ventilation are increased the fuel consumption increases also. However, as the temperature is increased to approximately 165^{o}F, the fresh air ventilation is decreased significantly and the fuel consumption decreases during this transition. The burner firing rate for this barn was approximately 350,000 Btu/hr (103 kW) which corresponds to a maximum fuel consumption rate of approximately 3.8 gallons per hour. Even during leaf drying when the energy requirement is at a maximum the burner continues to cycle, which suggests the firing rate probably could be reduced, but growers prefer to have a small quantity of excess capacity. Fuel consumption can vary from grower to grower and even among barns for a given location based on the many factors mentioned earlier.

4.2 Carbon Dioxide and Nitrogen Oxide Measurements

At the end of the 2002 season, many of the tobacco companies reported elevated levels of TSNAs in the cured leaf samples randomly tested. Elevated is a relative term that will vary with each purchasing company, but any increase in TSNA levels can potentially reduce the cured leaf value. Although the biological mechanism can contribute to TSNA formation, it was suspected that some of the heat exchangers may have developed leaks and are therefore defeating their primary function of venting the combustion products externally to the barn. Unfortunately, some of the heat exchangers were not well designed from a thermal efficiency standpoint. Also, the burner firing rates (Btu/hr) may not have been properly adjusted, 300,000 to 400,000 Btu/hr typical (88 to 117 kW), if at all. Excessive burner firing rates can result in thousands of expansion and contraction cycles of the heat exchanger in a single season. An excessive firing rate and a poorly designed heat exchanger could potentially result in thermal stresses exceeding the material limits in a short period of time. Also, exhaust stack connections located inside the upper or lower air plenums may not have been properly sealed. A simple and inexpensive method was urgently needed by the industry to assist growers with determining if the retrofit system had developed a leak. Also, due to the installation constraints, many of the retrofits are not easily accessible to visually check the heat exchanger for structural failures.

Instead of measuring the NO_x concentrations directly, a simpler approach was to use carbon dioxide (CO_2) measurements as an indirect indicator for the presence of NO_x. During the combustion process, many gas species are formed, but CO_2, N_2, and water vapor account for over 90 percent of the total flue-gas volume produced. When LPG is burned at stoichiometric conditions, the corresponding CO_2 concentration in the product gas volume is approximately 13.7 percent. In actual practice excess air is supplied resulting in a fuel-lean mixture ($\phi < 1$) to ensure complete combustion and the CO_2 concentration will be less than the stoichiometric value. However, the CO_2 concentration is typically several orders of magnitude more than the NO_x concentration. The commercially available equipment to to measure CO_2 is simpler to operate, significantly less expensive, and easier to transport in the field compared to existing NO_x monitoring equipment. Based on this, the objective was to utilize an existing CO_2 meter to test retrofitted barns for elevated levels of CO_2. If a leak has developed in the heating system, then elevated levels of CO_2 and other combustion products,

Figure 4.6 Carbon dioxide transmitter with remote sensing probe.

specifically NO_x, are present also. The CO_2 meter utilized was a GMT220 (Vaisala, Inc., Woburn, MA) transmitter with remote sensing probe (Figure 4.6). The instrument measurement range selected was 0 to 5000 ppm and included a 0 to 10 Volt full scale, analog output signal for data acquisition. Initially, on-farm measurements were performed on retrofitted curing barns to determine the concept feasibility. Simultaneous NO_x and CO_2 concentrations were monitored and recorded for randomly checked barns. The NO_x concentrations were monitored with the TEI (Model 42) chemiluminescence NO-NO2-NO_x analyzer. Both meter analog output signals were recorded with a laptop computer (Dell INSPIRON 2650) utilizing the DAQCard-1200 (National Instruments, Houston, TX) PC card and *LabVIEW* software.

Typically, the meter remote sensing probe was positioned inside the barn through the front exhaust vent. The first step establishes an ambient CO_2 level inside the barn with the intake vents closed and the fan operating only. The ambient levels ranged from 300 to 500 ppm. After establishing an ambient reading, the thermostat was increased to ensure the burner operated continuously for approximately 10 minutes. Elevated CO_2 levels measured as the burner is operating indicates that the heat exchanger or some component of the heating system is allowing combustion gases to mix with the air inside the barn. Barns loaded with green tobacco at early stages in the curing process can not be checked accurately due to the CO_2 formed as a result of the leaf respiration process. The CO_2 levels are elevated significantly inside the barn while the leaf is still alive and determining the contribution from a leaking heat system would be difficult to evaluate. Carbon dioxide levels that remained at or near the ambient levels (300 to 500 ppm) while the burner was operating indicated the heating system integrity was intact.

The response from an indirect-fired barn without a heating system leak resulted in negligible concentration changes for both NO_x and CO_2 gases. It should be noted that for many of the samples only the NO_x channel of the Model 42 analyzer was recorded. In contrast, a leaking heating system resulted in the concentration responses shown in Figure 4.7. Initially the concentrations (NO_x and CO_2) are at ambient levels until the burner is operated and as a result both species concentrations increase until the burner cycles off. For this barn sampled, all of the Model 42 analyzer outputs were recorded and the predominant NO_x component was NO.

This procedure was developed to assist growers with identifying which barn may

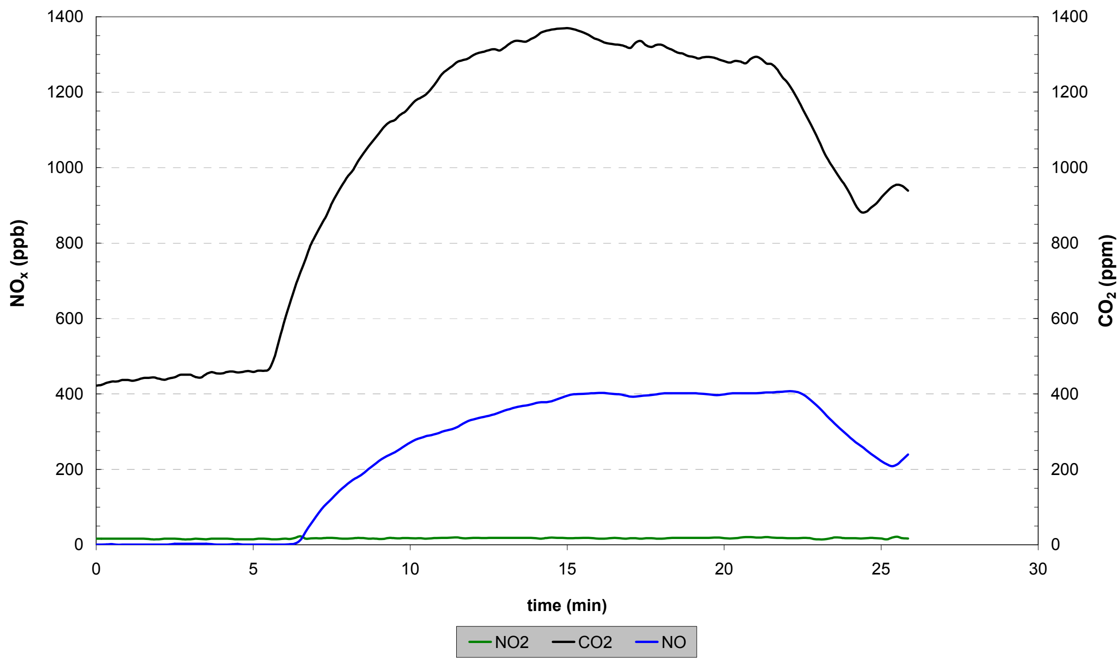


Figure 4.7 Carbon dioxide and NO_x concentration profile from barn with a leaking heating system.

have a leaking heating system and was not used to determine the leak location. A barn can be checked with this procedure in a limited amount of time, typically 15 minutes or less. Any cracked heat exchanger or leaking exhaust system is not going to improve and therefore increases the chance that elevated TSNA's could be found in the cured leaf. Figure 4.8 is a summary of both gas species maximum concentrations for a number of empty curing barns. Each data point represents a different barn checked. As the CO_2 level increases, the NO_x level increased linearly. The NO_x species distribution was not recorded for these measurements except for one or two barns. Although any leak will result in some level of

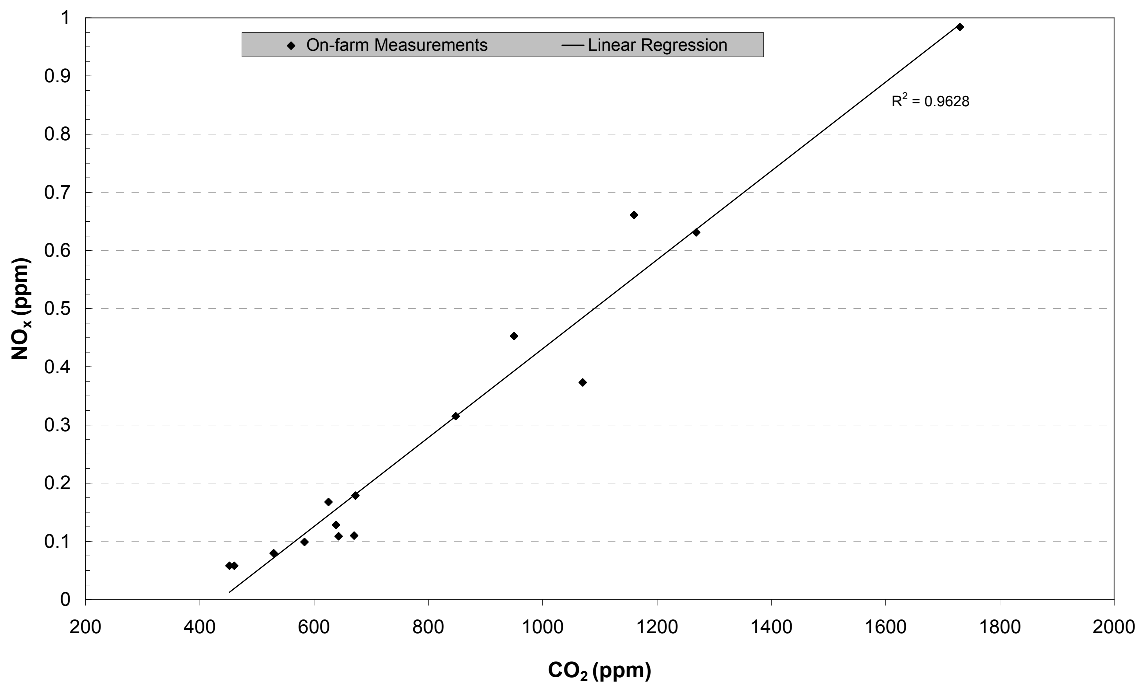


Figure 4.8 Summary of the maximum CO_2 and NO_x concentrations measured in indirect-fired barns.

NO_x exposure, the location of the leak relative to the fan can affect the concentrations encountered. Some heat exchangers and associated exhaust connections are installed above the fan, which is typically the low-pressure side. Depending on the leak location, this configuration can result in exacerbating any heating system leak. However, majority of the units are mounted below the fan, which is the high-pressure side, and the fan may actually blow air into the unit and suppress the leak. The result is the CO_2 procedure may not detect a potential leak if this is the case.

4.3 Summary of the On-Farm NO_x Measurements

Preliminary work was conducted to assist with evaluating the prototype NO_2 colorimetric meter and determining the feasibility of utilizing CO_2 measurements as an indicator of a leaking retrofit system. These field measurements provided a significant amount of information about the NO_x concentrations encountered in a curing barn. The maximum NO_x concentration recorded was approximately 1.5 ppm for all the barns checked and the majority of the measurements were less than 1 ppm. If the barns were loaded with tobacco, these measurements were only “snapshots” or the instantaneous levels at a particular point in the curing schedule.

The most prominent observation was that the distribution of the NO_x species varied between the direct- and indirect-fired heating systems. In the direct-fired barns, the NO_2 concentrations were higher than the NO concentrations, especially in an empty barn, resulting in an average NO/NO_2 ratio of approximately 0.31. However, the NO concentration increased in the barns with tobacco (green or cured) and the average NO/NO_2 ratio increased to approximately 0.55. Most of the ring-type direct-fired burners were mounted below the tube-axial fans that are capable of air deliveries in the 12,000 to 18,000 cubic feet per minute (cfm) range, depending on the static pressure the fan operates against. The rapid oxidation of NO to NO_2 (eqn. 3.26) could be occurring as a result of the high volume of air provided by the fan and the consequent rapid cooling process between the hot combustion gases and air resulting in significant HO_2 radical concentrations. The rapid mixing of hot and cold fluid elements also tend to quench the NO_2 removal reactions (eqns. 3.27 – 3.28) as a result of significant reductions in the H-atom and O-atom radical species concentrations. Additionally, the ring-type burner geometry will result in shorter flames and therefore decreased residence times, which will reduce the NO formation rate.

In comparison, the indirect-fired systems that were leaking combustion products resulted in considerably higher concentrations of NO as compared to NO_2 and the average NO/NO_2 ratio was approximately 11.71. This was the case for 10 out of the 11 barns randomly measured. As reported by Waibel (1997), for most stationary combustion systems approximately 95 percent of the NO_x formed leaves the flame zone as NO. Although most of the indirect-fired barns checked utilized LPG, samples 10 through 12 did use No. 2 diesel. The large variability in the field measurements are partly due to the many factors that can affect the NO_x formation rates. Majority of the burner details and operating parameters were not obtained for any of the field measurements and are not easily controlled. The burner fuel-air mixture (flame stiochiometry) and corresponding flame temperature are expected to vary. Additionally, the heat exchanger design and burner firing rates and consequent furnace temperatures will influence the actual flame temperature. The burner geometry and associated residence times in the high temperature combustion zone will also vary. All of these factors, especially flame temperature, can contribute significantly to the NO formation rates and the NO concentrations measured as a result of a leaking system. The indirect-fired barn measured that resulted in a NO/NO_2 ratio less than unity is not completely understood. However, leaks can occur at various locations on the heat exchanger and the NO_x species concentrations may also vary spatially.

This information does suggest that any prototype device developed to monitor the NO_x levels in a retrofitted barn needs to be capable of detecting NO gas. Additionally,

Table 4.5 Summary statistics for the randomly sampled curing barns.

	Indirect-Fired w/Leak (Empty)			*Direct-Fired (Loaded)*			*Direct-Fired (Empty)*		
	NO (ppm)	**NO_2 (ppm)**	**NO/NO_2**	**NO (ppm)**	**NO_2 (ppm)**	**NO/NO_2**	**NO (ppm)**	**NO_2 (ppm)**	**NO/NO_2**
Mean	301	44.2	11.7	171	331	0.55	61.6	867.6	0.07
Min.	65.0	13.0	0.4	52	172	0.22	28.2	516.1	0.04
Max.	600	175	35.27	355	602	0.86	171	1300	0.13
Std Dev	168	47.4	9.1	88	144	0.2	42.6	251.7	0.03

depending on the heating system type the NO_x species distribution can vary significantly. However, for the current indirect-fired systems NO gas appears to be the predominate NO_x species. Although the direct-fired systems are no longer in use, it is of interest to determine if there is a difference in the cured leaf TSNA response as a result of similar exposure levels to NO_2 or NO. If there are significant differences in the TSNA response in the cured leaf between the two NO_x species, then this information could assist the tobacco industry with developing strategies to minimize levels in the cured leaf. Table 4.5 summarizes the descriptive statistics for the direct-fired barns (loaded and empty) and the indirect-fired barns suspected of a leaking heating system.

Chapter 5 - NO and NO_2 Absorption

5.1 Materials and Methods

Flue-cured tobacco was exposed to both NO and NO_2 gas to observe differences in the green leaf absorption. A small insulated curing chamber (24-inch by 24-inch by 72-inch) was loaded with a single rack that contained approximately 4 lbs (1.8 kg) of upper-stalk (flue-cured variety K326) tobacco harvested from the Central Crops Research Station, Clayton, NC. Samples of green tobacco were exposed to both gas species individually and simultaneously. The gases used were a primary standard grade binary mixture (National Specialty Gases, Durham, N.C.). The NO concentration was 5.21 ppm (+/- 0.10 ppm) and the NO_2 concentration was 5.40 ppm (+/- 0.10 ppm) with the balance nitrogen for both tanks. The empty and loaded curing chamber is shown in Fig. 5.1.

The initial procedure was to determine the flow rates to obtain a steady state concentration inside the curing chamber of less than 1 ppm for both gas species. This level was based on the concentrations encountered during the field measurements. However, at the given tank concentrations, the gases had to be diluted to achieve this level. Therefore, the existing tank mixtures were blended with a tank of zero grade air (National Specialty Gases, Durham, N.C.) to eliminate the need to purchase lower tank concentrations and without extending the time required to obtain a steady state concentration inside the chamber. The NO and NO_2 volumetric flow rates were approximately 0.07 ft^3/min (2 L/min) and mixed with 0.28 ft^3/min (8 L/min) of zero grade air prior to entering the chamber. A 45^o laterals fitting was used to blend the gases (NO_x species and zero air) prior to entering the chamber.

Figure 5.1 Empty and loaded test chamber utilized for the exposure tests.

The actual gas flow rate was measured with a model FL-202 (OMEGA Engineering, Inc., Stamford, CT) hand held rotameter. A small capacity (70 cfm) AC powered axial fan (Dayton Electric Mfg., Chicago, IL) was positioned inside the curing chamber (Fig. 5.1) to assist with mixing the air and minimize spatial concentrations in the chamber. The exposure gas was introduced at the bottom of the chamber and the model 42 analyzer sampling line was inserted at the top of the chamber above the rack of tobacco. The analyzer and data acquisition arrangement is shown in Fig. 5.2. The data acquisition system was similar to the field measurements performed with the model 42 analyzer. The only difference was a 16-bit DAQCard-6036E (National Instruments, Houston, TX) data acquisition device was used to

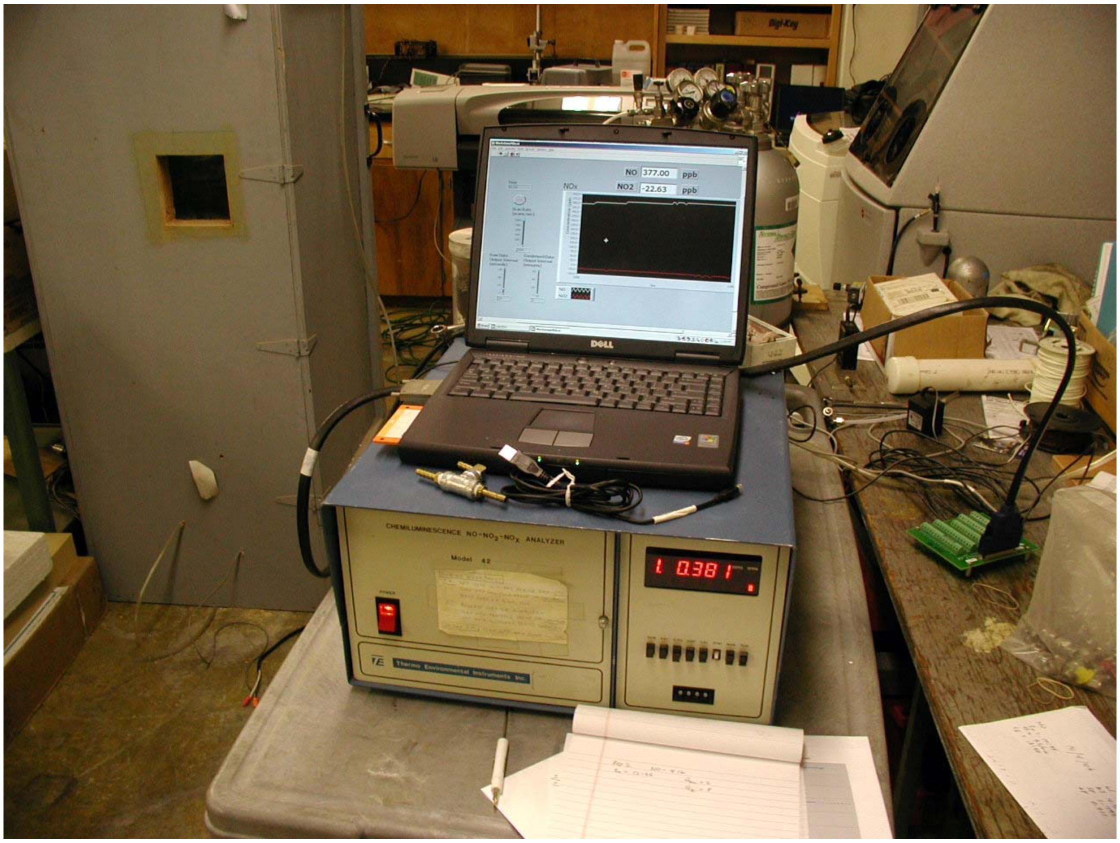


Figure 5.2. Model 42 NO_x analyzer and data acquisition system.

interface the laptop and analyzer outputs. The concentrations were recorded using *LabVIEW*. The analyzer averaging time and the data logging interval were set at 10 seconds. The temperature inside the curing chamber during all the exposure tests was approximately 68^oF (20^oC). The green tobacco sample exposed was replaced with a new sample after each test.

5.2 Results and Discussion

The concentration profiles for the exposure tests are shown in Figs. 5.3 through 5.6. Figure 5.3 shows the temporal changes in the NO concentration profile for the empty and

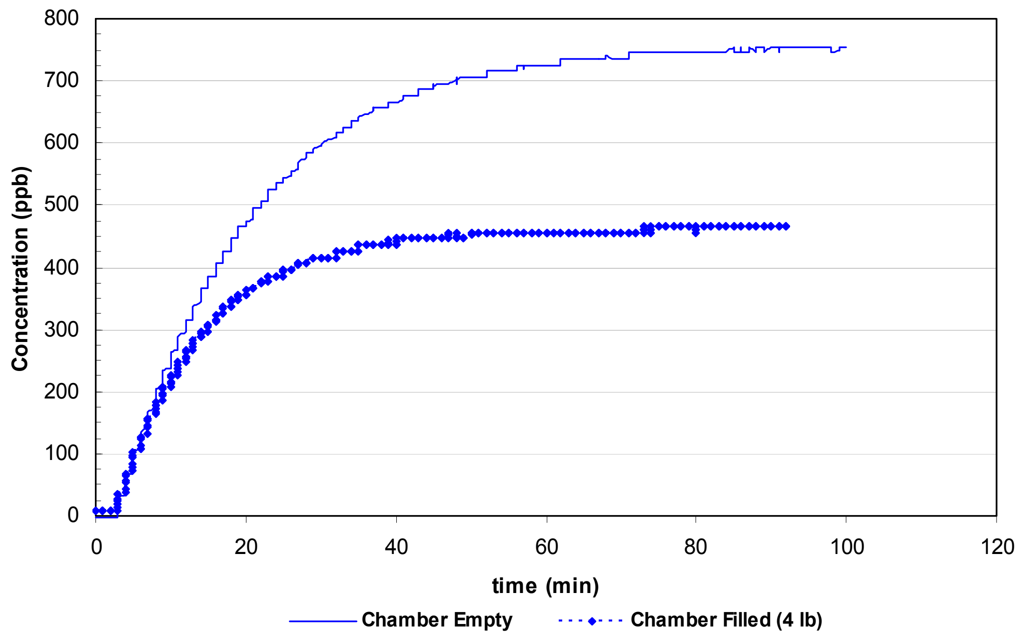


Figure 5.3 NO concentration profiles for the empty and filled chamber at 68°F and input concentration of 5.21 ppm.

loaded chamber conditions. Nitric oxide (5.21 ppm balance nitrogen) was blended with the zero grade air and introduced into the chamber for approximately 1.5 hours. The empty and filled chamber equilibrium concentrations were approximately 750 and 450 ppb respectively. The difference was approximately 37% and is assumed to be as a result of the gas absorption in the green tobacco. In comparison, Fig. 5.4 shows the NO_2 concentration profiles for the loaded chamber conditions. The NO_2 (5.40 ppm balance nitrogen) was blended with the zero grade air and introduced for approximately 1.25 hours. The empty chamber NO_2 equilibrium concentration was approximately 525 ppb, which was approximately 70% of the NO concentration obtained in the empty chamber. Although the chamber was empty, there are

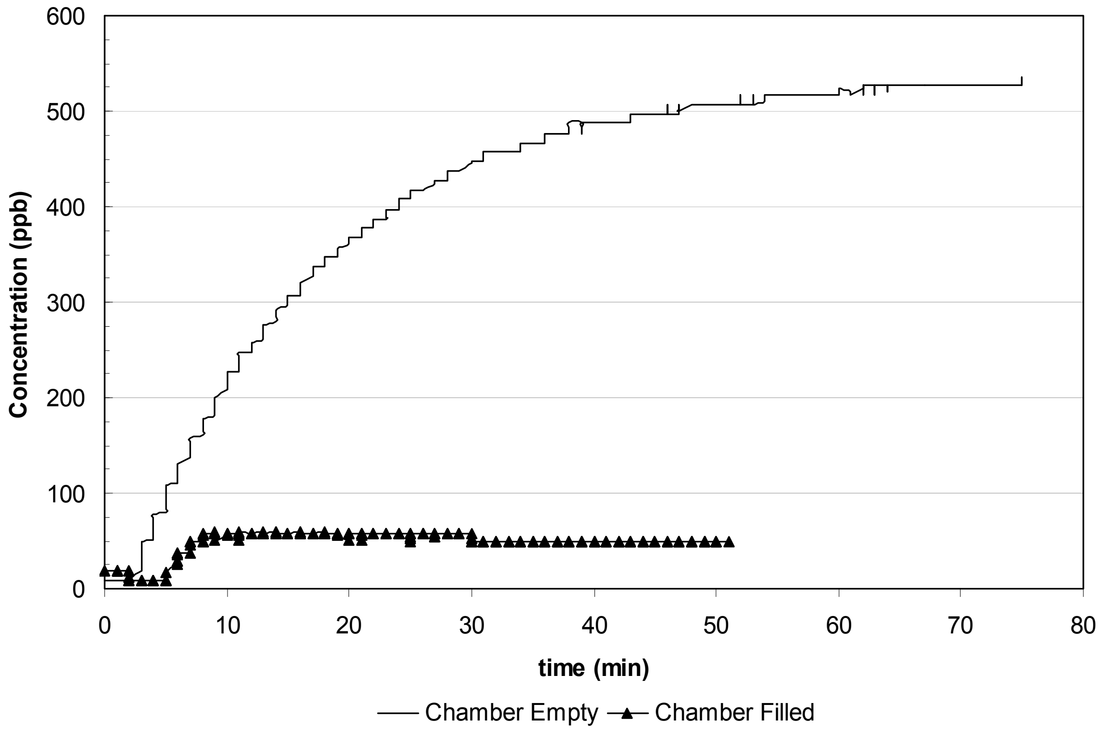


Figure 5.4 NO_2 concentration profiles for the empty and filled chamber at 68°F and input concentration of 5.40 ppm.

several chemical reactions that can occur with the oxygen and water vapor in the ambient air as reported by Oh (2004).

$$NO + NO_2 + H_2O \leftrightarrow 2HNO_2 \tag{5.1}$$

$$3NO_2 + H_2O \leftrightarrow 2HNO_3 + NO \tag{5.2}$$

The difference in the chamber concentration when loaded with tobacco and exposed to NO_2 was approximately 90% less than the empty chamber concentration. Additionally, the NO_2 reached a steady state concentration in approximately 10 minutes as compared to approximately 40 minutes for the NO loaded chamber test. It appeared that the NO_2 and NO absorption in the green leaf are significantly different under these test conditions.

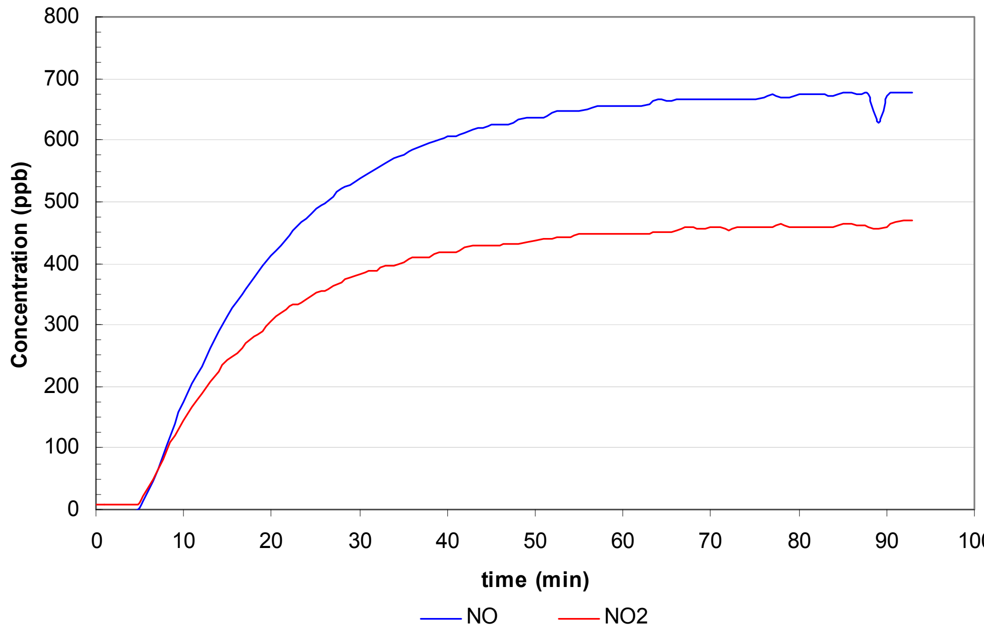


Figure 5.5 NO and NO_2 concentration profiles in the empty test chamber at 68°F and both species introduced simultaneously.

Additionally, any NO_2 gas that is not absorbed by the green leaf may be consumed rapidly as a result of reactions with the ambient air H2O vapor, especially at lower concentrations. The humidity level did increase to approximately 90% when the closed chamber was loaded with green tobacco. The NO_2 loaded chamber test was also discontinued after approximately 50 minutes due to the limited amount of time required to obtain a steady state value.

Both gas species were also introduced simultaneously at the same flow rates as the individual tests. This was done to observe any differences that might occur due to the interaction with both gases. Also, it is possible that a leaking heating system may produce both gas species. A tee fitting was added to the exposure gas input line to accommodate mixing both gas species and the zero grade air prior to entering the chamber. Figure 5.5 shows the concentration profiles for the empty chamber. After 1 hour, the concentrations are

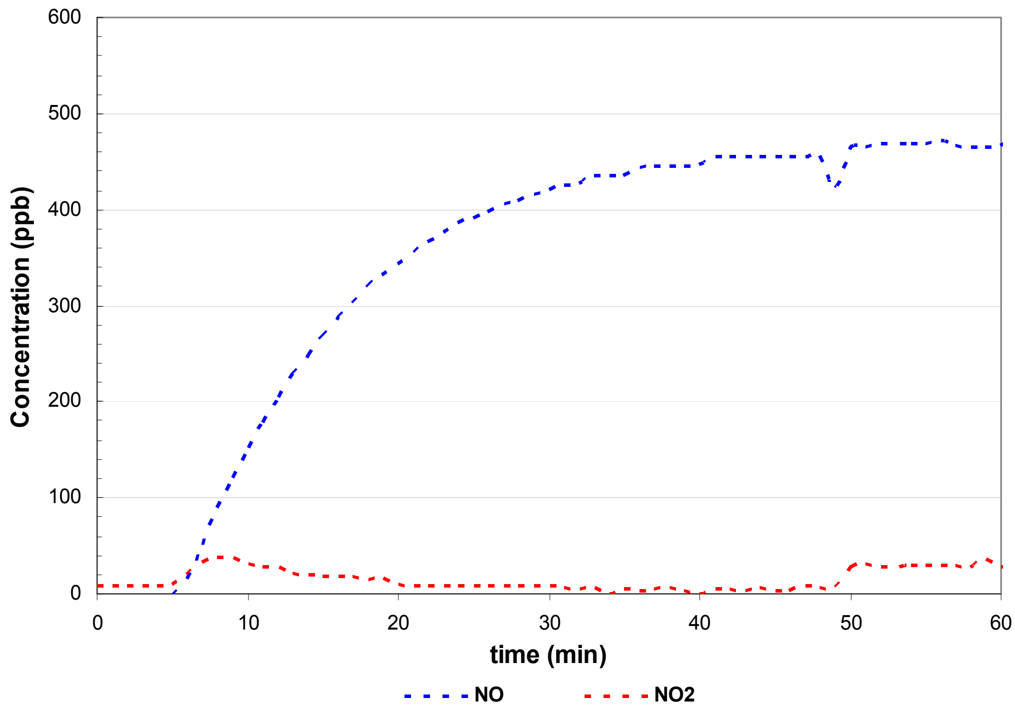


Figure 5.6 NO and NO_2 concentration profiles with the chamber filled at 68°F and both species introduced simultaneously.

approximately 650 ppb and 450 ppb in the empty chamber for NO and NO_2 respectively. These concentrations are approximately 10% lower than the concentrations obtained when the gas species were introduced separately in the empty chamber after 1 hour. Figure 5.6 shows the concentration profiles for both gases introduced simultaneously with green tobacco in the chamber. The responses were similar to the results obtained when introduced separately, but the NO_2 gas steady state concentration was less. As was the case when a single species was introduced, the NO_2 concentration measured above the tobacco in the loaded chamber was approximately an order of magnitude less than the empty chamber.

Chapter 6 NO and NO_2 Exposure Studies During Curing

6.1 Introduction

The focus of this work was to investigate the cured leaf TSNA response as a result of exposure to NO or NO_2 gas during curing. The exposure tests were based on the monitoring data from the direct- and indirect-fired curing barns. Although the direct-fired furnaces are no longer in use, the predominate NO_x gas species measured was NO_2. However, NO was the major species measured as a result of a leaking indirect-fired system. Exposure tests were conducted during the 2004 and 2005 growing seasons at the Southern Piedmont Agricultural Research and Extension Center (AREC) located in Blackstone, VA.

A parallel study was to assist with evaluating a continuous NO_x monitoring technology. Philip Morris, USA was also interested in testing commercially available NO_2 passive diffusion tubes (Gradko International LTD, England) that are used to quantitatively determine the NO_2 concentration in air. The potential benefits of this concept are the tubes are inexpensive, simple to analyze, and could possibly be used throughout the curing season to monitor the heating system integrity. The tubes are placed inside the barn and the reagent substrate that is located in the tube cap is exposed to the air in the monitoring environment. The NO_2 concentrations are then determined colorimetrically as nitrite using a continuous flow analyzer. Additional tubes are also used to monitor the ambient air NO_2 concentrations. Direct comparisons are performed between the exposure concentrations determined analytically between the tubes positioned inside the barn and the ambient. A very limited discussion will be included concerning the diffusion tube results.

Figure 6.1 Curing chambers utilized for the NO_x exposure studies performed at the AREC research station, Blackstone, VA.

6.2 Materials and Methods (2004)

The experiments were initiated during the 2004 growing season at the AREC station in Blackstone, VA. The curing experiments utilized two 8-rack capacity barns that were capable of holding approximately 800 pounds (363 kg) of green tobacco (Fig. 6.1). Both barns utilized electric resistance heat rated at approximately 17,000 Btu/hr (5 kW). Airflow was provided by a centrifugal fan (Dayton Electrical Mfg., Chicago, IL) powered by a ½-hp electric motor operated at 1750 rpm. Barn number 1 was the treated barn that was dosed with NO or NO_2 during the curing process and barn number 2 was the untreated control.

Since the barns did not use a hydrocarbon fueled heating system, the NO_x gas was introduced exogenously to simulate a leaking indirect-fired furnace. The NO_x gas was a certified grade binary mixture (National Specialty Gases, Durham, NC) of NO or NO_2 with the balance nitrogen. The tank concentrations were approximately 2000 ppm for each species with the balance nitrogen. A Zelio Logic 2 (Telemecanique, Palatine, IL) programmable relay was used to energize an 8262G (ASCO Valves, Florham Park, NJ) series 2-way direct-acting solenoid valve. An m-series metering valve (Swagelok, Solon, OH) was used to adjust the gas flow rate and obtain the desired exposure concentration. An inline model FVL-1606 (Omega Engineering, Stamford, CT) volumetric flow meter was used to record the gas flow rate in cubic feet per minute (cfm). The flow meter measurement range was 0 to 0.177 cfm (5 l/min). The NO_x supply tank delivery pressure was set at approximately 25 psi (172 kPa) for each cure. The gas was introduced into the supply air plenum just below the fan outlet and mixed with the air that was then forced upward through the tobacco. An inline check valve (WATTS, North Andover, MA) was installed in the gas delivery line prior to entering the barn.

To simulate a leaking heating system the relay was programmed to energize the normally closed solenoid valve based on a predetermined duty cycle. The duty cycle is a fixed repetitive pattern over a given period of time that is expressed as the ratio of time the solenoid valve is open to the cycle period. The solenoid valve on/off times could be adjusted with the relay. Preliminary data from the conventional barn NO_x measurements were utilized to assist with simulating a leaking heating system. The procedure was to determine a target NO or NO_2 concentration based on the conventional barn NO_x measurement range and adjust the metering valve to obtain the desired level. The NO_x concentrations inside the curing chamber were continuously monitored with a Model 42C (Thermo Electron Corporation, Waltham, MA) NO-NO_2-NO_x analyzer. The analyzer and laptop were interfaced for continuous data acquisition using the DAQCard-6036E input/output PC card. The analyzer outputs were recorded at 30-second intervals using a *LabVIEW* program.

6.2.1 Initial Exposure Tests

During the 2004 season, the first three cures were trial and error efforts adjusting the system components and working through problems with the delivery system. At the initial NO or NO_2 binary tank mixture concentrations (100 ppm balance Nitrogen) the flow rates required to obtain concentrations similar to those encountered in conventional barns resulted in depleting the gas supply within 12 to 36 hours of exposure. Some initial problems were also encountered with the data acquisition system components. The barns were loaded the same day with approximately 400 lbs (182 kg) of green tobacco (flue-cured variety GL350) from the same field and stalk position. An employee of the research station managed the daily curing operations for both barns, utilizing the same schedule.

Table 6.1 summarizes the exposure test conditions during the 2004 season. The duty cycle was held constant during cures 4, 5, and 8, but during cures 6 and 7 the duty cycle was increased to 50% at 48 hours into the curing process. This was performed to increase the NO_x input and simulate the increased time the burner operates as a result of increasing the temperature and ventilation during leaf drying. Initially, the dry-bulb temperature set point can range from 95 to 105^{o}F and the burner will operate for only a short period of time. As a result, the NO_x gas introduction was delayed 24 hours after loading the barns for each test.

Table 6.1 Summary of exposure tests during the 2004 season.

Cure	Gas IN (min)	Gas OFF (min)	Duty Cycle (%)	NO_x Species	Flow (L/min)	Estimated exposure time (hrs)
1	1	5	17	NO_2	5	-
2	5	55	8.3	NO_2	13 - 15	< 36
3	3	17	15	NO_2	-	< 12
4	2	8	20	NO	1	120
5	2	8	20	NO_2	3	> 72
6	2	8	20	NO	0.5	48
	5	5	50		0.5	24+
7	2	8	20	NO_2	4	48
	5	5	50		2	48
8	2	8	20	NO_2	[1] Q_o = 2	48+

[1] **Flow was adjusted throughout cure 8 to maintain a constant exposure concentration**

Figure 6.2 Model 42C NO_x analyzer and data acquisition setup during the 2004 exposure tests.

Figure 6.3 Front view of the treated barn (1) with the green leaf loaded and the NO_2 diffusion tubes positioned above and below the tobacco (close-up of tubes included).

Figure 6.2 shows the model 42C NO_x analyzer and the data acquisition system. Also, an ice bath was used again to condense water vapor from the air sampled. Random cured leaf samples were obtained from all four racks after each cure and submitted for TSNA analysis. The green leaf and the NO_2 diffusion tubes positioned above and below the racks is shown in Fig. 6.3. The NO_x analyzer sampling line was positioned below the tobacco to measure the concentration in the air sampled prior to passing through the tobacco.

6.3 Results and Discussion (2004)

Tables 6.2 and 6.3 summarize the TSNA results for cures 4 through 8. The results include the NAB, NNN, NAT, NNK, and the total TSNA for each sample. Random samples were removed from each of the four racks and are labeled rep1 through rep4. Cures 1 through

Table 6.2 Treated barn TSNA summary statistics for the 2004 exposure tests.

		TSNA (ppb) - Treated Barn					
Treatment	**Cure**	**Rep_1**	**Rep_2**	**Rep_3**	**Rep_4**	***Mean***	***Std Dev***
NO	4	177	346	272	280	*269*	*69.6*
NO	6	690	588	356	275	*477*	*194*
	Mean	433.5	467	314	277.5	373	*91.5*
NO_2	5	700	837	719	919	*794*	*103*
NO_2	7	3177	3684	2653	2732	*3062*	*475*
NO_2	8	829	1046	667	1173	*929*	*225*
	Mean	1939	2261	1686	1826	1595	*245*
	Overall					1106	

Table 6.3 Control barn TSNA summary statistics for the 2004 exposure tests.

		TSNA (ppb) - Control Barn					
Treatment	**Cure**	**Rep_1**	**Rep_2**	**Rep_3**	**Rep_4**	***Mean***	***Std Dev***
NO	4	249	196	147	234	*207*	*45.5*
NO	6	187	346	282	117	*233*	*101*
	Mean	218	271	215	176	220	*39.2*
NO_2	5	112	145	139	108	*126*	*18.7*
NO_2	7	167	139	231	139	*169*	*43.4*
NO_2	8	454	428	670	315	*467*	*148*
	Mean	140	142	185	124	254	*26.3*
	Overall					240	

3 are not included due to the problems associated with delivering the desired exposure concentration. The maximum exposure time was less than 36 hours for the first three cures and the TSNA levels were not included. Also, the NO_x species introduced for these three tests was NO_2. Averaged across five cures (4 – 8), the control barn TSNA level was approximately 0.240 ppm compared to approximately 1.106 ppm for the treated barn. The

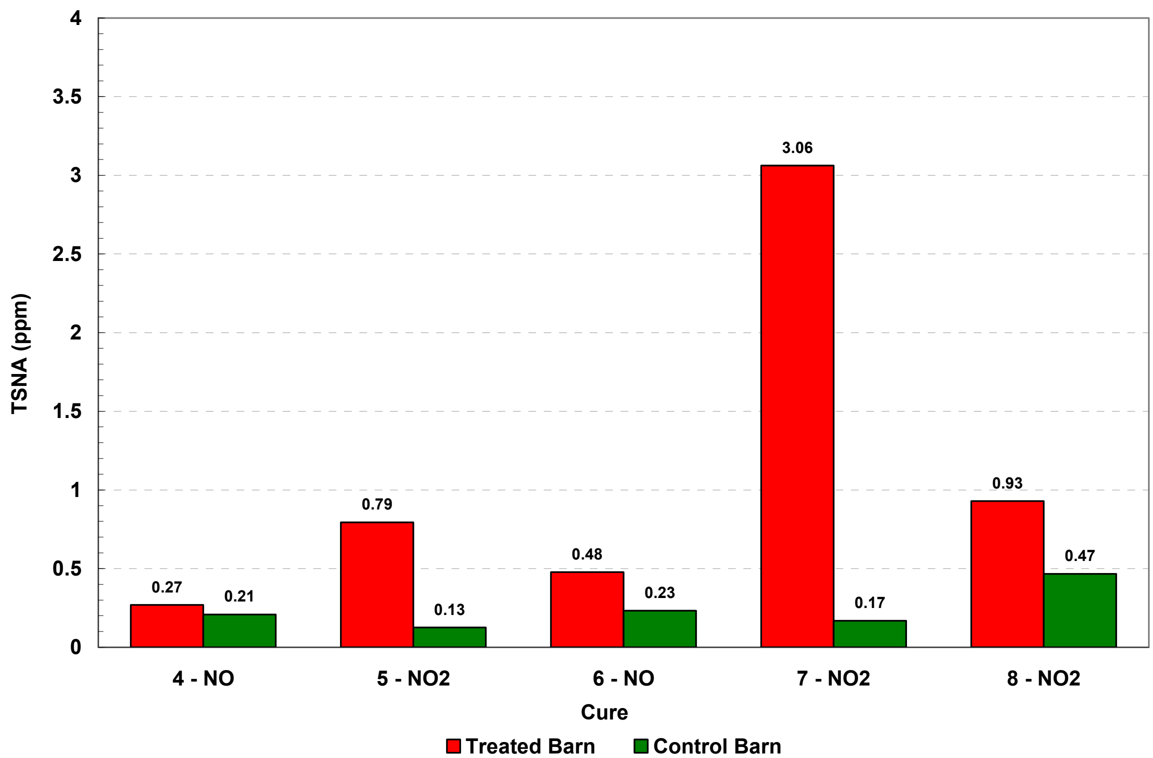


Figure 6.4 Average TSNA levels for the treated and control barns (2004).

NNN, NAT, and NNK average levels from the treated barn were approximately 27%, 33%, and 37% respectively of the total TSNA. The NAB levels were less than approximately 3% of the total. The NNN, NNK, and NAT contribute significantly to the total level. Although the TSNA levels were less in the untreated control barn, the distribution among the NNN, NNK, and NAT was very similar.

The average TSNA levels for the treated and control barn (cures 4 through 8) are shown in Figure 6.4. The duty cycles for cures 4 and 5 were the same, but the NO_2 supply tank was depleted early in cure 5 and as a result the exposure time was greater for cure 4. Cures 6 and 7 utilized the same duty cycles for direct comparison also. Although cure 4 was

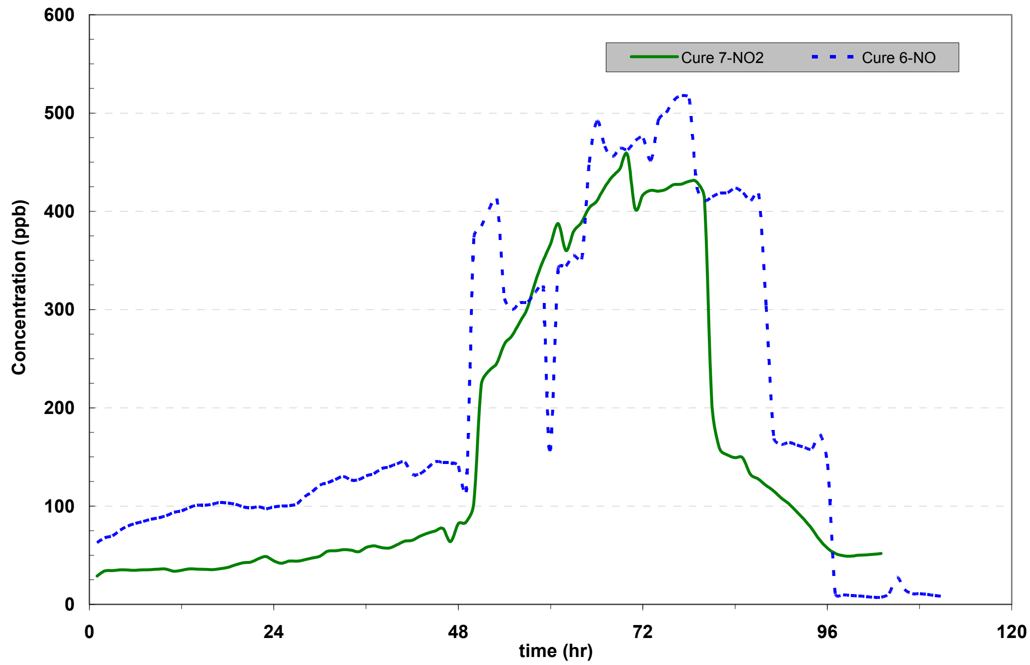


Figure 6.5 NO_x concentration profiles averaged hourly for cures 6 and 7 (Duty cycle 20% for 48 hrs, then increased to 50%).

exposed to gas injections longer than cure 5, the average TSNA level was approximately 2.9 times greater in the treated barn exposed to NO_2 gas as compared to NO gas. Similar results were observed comparing cures 6 and 7, but the average TSNA level was approximately 6.4 times greater as a result of exposing the tobacco to NO_2 versus NO. Figure 6.5 shows the temporal change in the NO and NO_2 concentration profiles averaged over hourly intervals for cures 6 and 7. The duty cycle was also increased during these two cures from 20% during the first 48 hours of exposure to 50% the remainder of the cure and as a result, the concentrations increased rapidly (Fig. 6.5). The hourly average concentrations for cure 6 (NO exposure) during the initial duty cycle was approximately twice that for cure 7 (NO_2 exposure). Both cures 5 and 7 were exposed to NO_2, but the TSNA levels were greater in cure 7. The exposure time was less and the duty cycle remained constant for cure 5 and as a result the concentration profile was less. During the last exposure test, NO_2 was injected at a constant duty cycle (20%) for the duration of the cure. Additionally, the flow rate was adjusted manually to maintain a constant exposure profile until the supply tank was depleted. During a gas injection time interval, the peak NO_2 concentration was maintained at approximately 100 ppb or less. The exposure concentration profile could be viewed using the *LabVIEW* program which included a waveform chart that displays the real-time data acquired.

Based on these initial observations of four cures, the TSNA response was greater as a result of exposure to NO_2 versus NO for similar concentration profiles. The average TSNA levels for the NO exposure cures (4 and 6) was approximately 0.373 ppm and for the NO_2 exposure cures (5 and 7) was approximately 1.93 ppm. Green tobacco exposed to similar concentrations of NO and NO_2 resulted in higher TSNA levels in the cured leaf if the nitrosating species was NO_2. As a result of these initial findings, the exposure study was repeated in 2005 for additional replication.

6.4 Materials and Methods (2005)

6.4.1 Conventional Barn Monitoring

During the 2005 curing season, two conventional curing barns were monitored continuously for two cures. The indirect-fired barns monitored were a 32-rack (Bulktobac) and 126-rack (Powell) capacity barns located on the AREC research station in Blackstone, VA. The main objective was to monitor the indirect-fired barns to assist with determining the exposure concentrations that are reasonable to duplicate in the exposure tests. The

Figure 6.6 Conventional barn NOx monitoring setup.

concentrations were continuously monitored with the model 42C chemiluminescenc NO_x analyzer. The analyzer generates a voltage output signal for NO, NO_2, and the total NO_x. The analyzer concentration range selected was 0 to 10 ppm and the corresponding analog output signal for each channel was 0 to 10 volts. The outputs were connected to a HOBO (Onset Computer Corporation, Pocasset, MA) U12 series 4-channel external data logger. The sampling interval for the data logger was set at 30 seconds for all three output channels. The barn dry-bulb temperature data was recorded with an HOBO U12 thermocouple logger that utilized an external type-T thermocouple. The temperature sampling interval was also set at 30 seconds. An ice bath was used to assist with removing moisture from the air sample prior

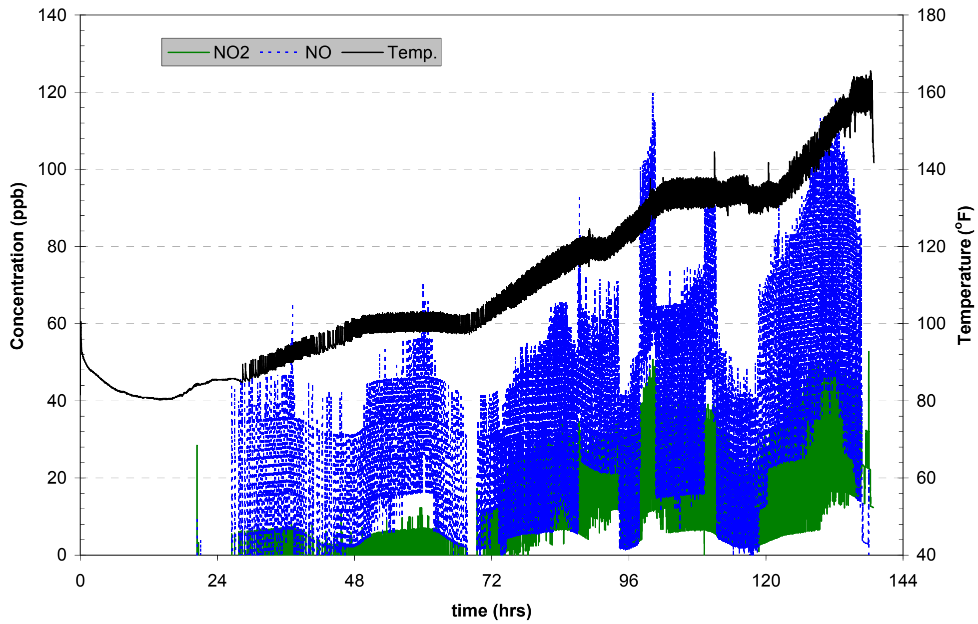


Figure 6.7 NO_x concentration and temperature profiles from the 32-rack Bulktobac barn.

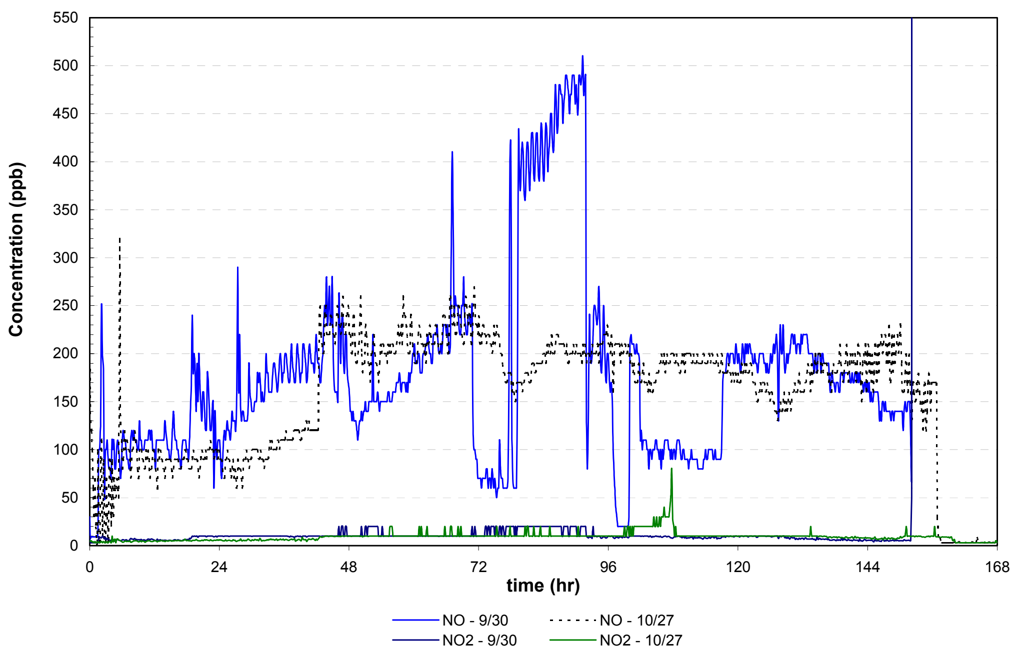
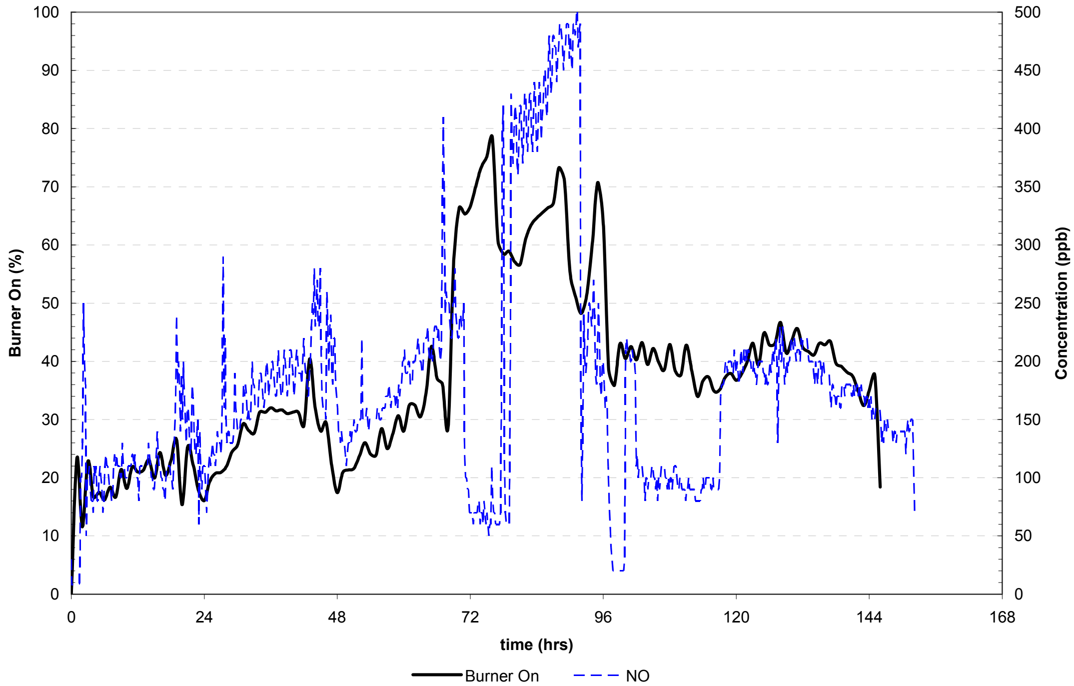


Figure 6.8 Hourly averaged NO and NO_2 concentration profiles monitored from the 126-rack Powell barn for two cures during the 2005 season.

to entering the instrument. The monitoring equipment and data acquisition arrangement can be seen in Figure 6.6. The analyzer air sampling line was placed inside the barn through the front exhaust vent and positioned below the tobacco. The first conventional barn monitored was the 32-rack Bulktobac barn. This barn was monitored prior to any of the exposure tests during 2005. Figure 6.7 shows the temporal changes in the NO_x concentration and temperature. The NO and NO_2 concentrations fluctuate as the burner cycles, but the peak concentration was approximately 120 ppm and the predominate species was NO. The peak NO_2 concentration was approximately 50 ppb. As the temperature is increased the concentration peaks trend upward also. This is a result of the increased frequency the burner is firing to maintain the desired temperature. However, based on the peak concentrations it would appear the leak is small for this heating system.

The second indirect-fired conventional barn monitored on the research station was the 126-rack capacity Powell barn. This barn was monitored twice during the season, concurrently as the exposure studies were performed. Utilizing the model 42 and 42C NO_x analyzers provided the capability to monitor the NO_x treated barn and a conventional barn simultaneously. Figure 6.8 shows the hourly averaged temporal changes in the NO and NO_2 concentrations for both cures monitored. The major species was NO and significantly overshadowed the NO_2 concentrations, which remained constant or at ambient levels throughout both cures. The concentration spikes that occurred periodically during the curing process (Fig. 6.8) are a result of problems with the data acquisition system. The system would record an extremely high voltage measurement that was not physically explainable. The reason this occurred is not known, but did happen multiple times throughout the



6.9 Hourly NO concentration profile and percent time the burner is on (Powell barn, 9/30).

exposure study during both seasons. It should be noted that initially for both cures the fan only was operated for approximately 24 hours before the burner was operated. The data acquisition system start was delayed 24 hours also after the barn was loaded and an additional day should be added to Fig. 6.8 to obtain the total cure length.

Although the concentrations shown in Fig. 6.8 are for the same barn, there is a noticeable difference in the averages, especially during the 72 to 96 hour interval. Many factors, such as ventilation management, ambient temperatures, and quality of tobacco can affect the amount of time the burner operates for the same barn. Figure 6.9 combines the temporal change in the hourly averaged NO concentration profile and the burner percent on time per hour for the first cure monitored (9/30) using the Powell barn. The burner run time was measured with a HOBO (Onset Computer Corporation, Pocasset, MA) U9 state logger, which monitors an electric motor on/off status and the amount of time of each cycle. The state logger was mounted directly to the motor housing. Twenty-four hours is added to Fig. 6.9 to determine the total cure length as a result of the time the fan was operated only.

During the first 2 to 3 days the burner percent on time fluctuates up to a maximum of approximately 40%. As the temperature is increased from yellowing to leaf drying, the percent of time the burner operates each hour increases. The NO concentration profile also closely followed the increase or decrease in burner operating time. For this barn, the maximum amount of time the burner operated in a given hour was approximately 80 percent. As the curing process transitions from leaf drying to stem drying, the burner percent on time begins to decrease as does the NO concentration. Additionally, the increased ventilation can reduce the NO concentration inside the barn due to the diluting effect of the volume of ambient air introduced. This might be illustrated in Fig. 6.9 at approximately 72 hours where the burner percent on time increases, but the NO response decreases and lags behind. Although the temperature profile was not recorded, the considerable increase in the burner on time is an indication that the temperature was increased and the ventilation is typically at a maximum during this stage in the curing process to maximize water removal. Based on the NO response, it was determined this heating system has a leak.

An interesting note is the 126-rack Powell barn monitored during curing was the same barn that was monitored during curing by others (Izac, 1999). Most of the data reported by Izac was performed at the AREC research station. The results from the initial measurements when a direct-fired system was used indicated the major NO_x species for this

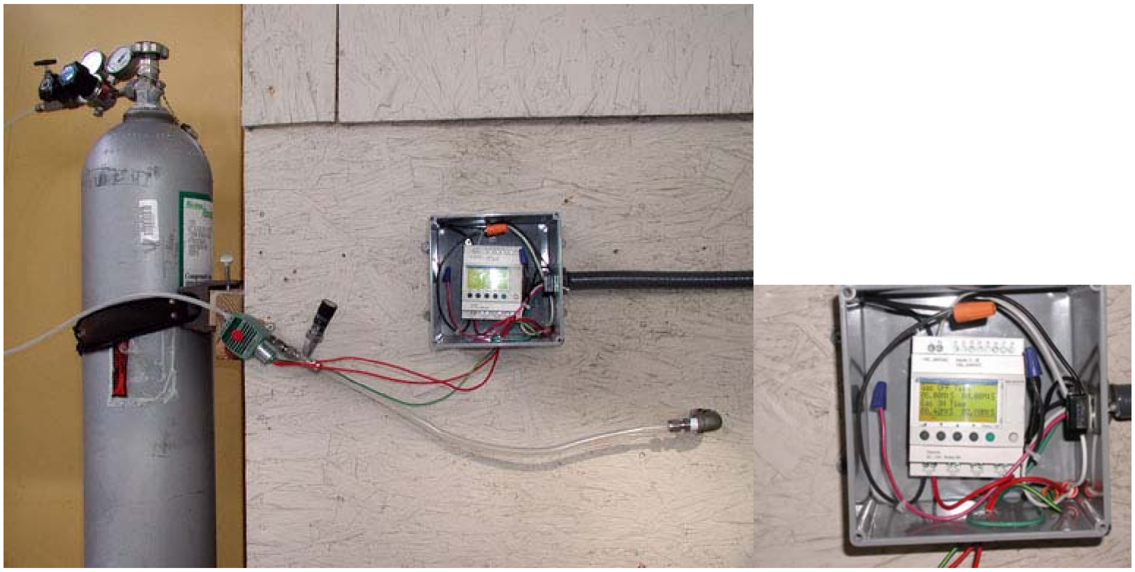


Figure 6.10 The NO_x gas delivery system and programmable relay used during the 2004 and 2005 curing tests.

barn was NO_2 (Tables 4.1 and 4.4). However, the major species measured for the same barn with a leaking indirect-fired system was NO.

6.4.2 Exposure Barn Monitoring and NO_x Gas Delivery System

The exposure tests during the 2005 season were performed at the AREC research station utilizing the same two barns from 2004. The barn fan and heating system remain unchanged. Barn 1 was the treated barn and barn 2 the untreated control. The exposure gas delivery system was identical to that used in 2004 and is shown in Fig. 6.10. The programmable relay was used to energize the solenoid valve and introduce a NO_x gas species into the curing barn. The gas was introduced into the supply air plenum just below the fan.

The NO or NO_2 concentrations were continuously monitored with the model 42 NO_x analyzer utilizing the same data acquisition arrangement (Fig. 6.2) as 2004. The *LabVIEW*

Table 6.4 Summary of the exposure tests conducted in 2005.

Cure	Gas IN (min)	Gas OFF (min)	Duty Cycle (%)	NO_x Species	Flow (L/min)	Exposure Time (hrs)
1	2	8	20	NO_2	<0.5	48
	2	3	40		-	48+
2	1	9	10	NO	0.2-0.3	48
	2	3	40		-	48+
3	1	9	10	NO	0.34	48
	2	3	40		-	48+
4	2	8	20	NO_2	0.57	48
	2	3	40		1	48+
5	2	8	20	NO_2	0.8	48
	2	3	40		1.65	48+
6	1	9	10	NO	0.25	48
	1	4	20		0.5	48+

program recorded the data at 30-second intervals. In order to minimize the file size, the program was modified to include an additional 10-minute averaged NO_x concentration output file. A similar concentration profile for each cure was targeted, but the gas species introduced alternated to obtain the same number of replications for each species. The flue-cured variety harvested was GL-350 and both chambers were loaded the same day with 4-racks of green tobacco with a total weight of approximately 400 lb (182 kg). Additionally, the tobacco was from the same stalk position each cure. Random cured leaf samples were obtained from each rack and submitted for TSNA analysis. Due to the limited quantity of flue-cured tobacco on the station available for curing studies (general crop), only the bottom tier of each barn was filled. This also would increase the total number of cures and consequent exposure tests.

Table 6.4 summarizes the exposure test conditions during the 2005 season. Although the initial duty cycle targeted was 20%, it was decreased to 10% for the cures injecting NO. Even with similar tank concentrations, the time and volumetric flow rate were decreased when injecting NO to obtain comparable concentrations when injecting NO_2. Approximately 48 hours after the gas injections were initiated, the duty cycle was increased for all of the cures to simulate an increase in the time the burner operates as the temperature and ventilation are increased during curing. Both the NO and NO_2 supply tank concentrations were approximately 2000 ppm with the balance nitrogen. As was the case in 2004, the gas input was initiated 24 hours after the barns were loaded.

6.5 Results and Discussion (2005)

6.5.1 Treated Barn NO_x Concentration Profiles

Figures 6.11 through 6.15 show the temporal changes in the NO or NO_2 concentrations for each cure. The concentrations are the average over a 10 minute interval. Based on the duty cycles, gas injections occur 6 times per hour for the first 48 hours and then they are increased to 12 times per hour the remainder of the curing process. Due to the file size, the raw data concentration profiles for each cure (2004 and 2005) are included in Appendix A. Based on the conventional barn monitored prior to the exposure tests and field measurements from previous seasons, the peak concentrations targeted were limited to a maximum of 1 ppm. During the first exposure interval (48 hrs), the flow rates and valve “on” time were adjusted by trial and error to obtain concentrations in the range of only a few hundred ppb, but during the second exposure interval the concentrations were anticipated to increase as a result of the increased duty cycle.

The temporal changes in the NO and NO_2 concentrations for cures 1 and 2 are shown collectively in Fig. 6.11. During cure 2, the data acquisition system malfunctioned numerous

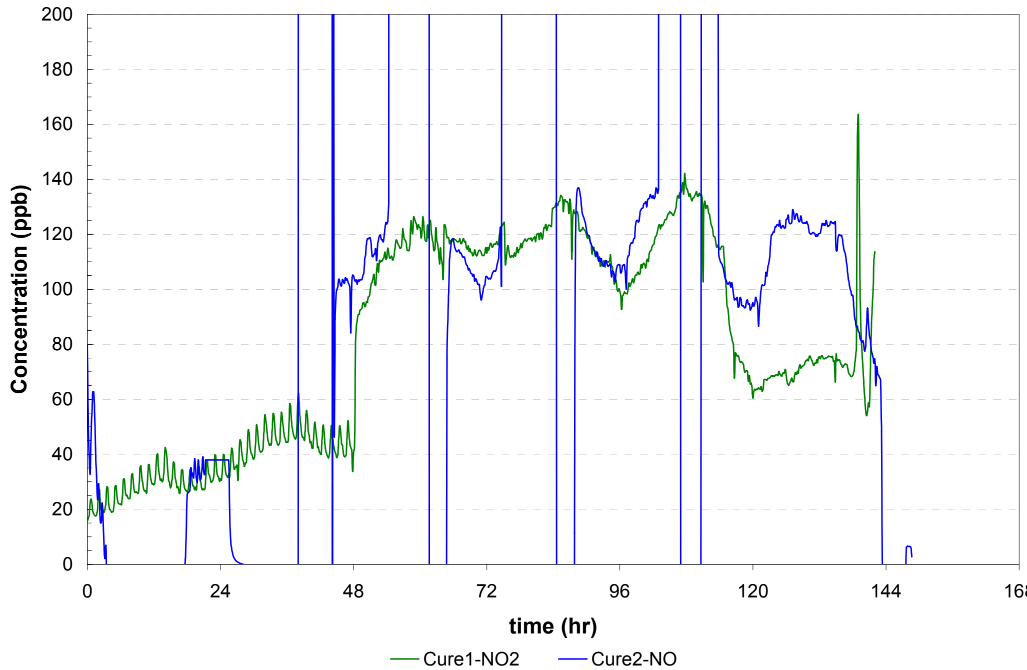


Figure 6.11 Temporal changes in the NO_2 and NO concentration profiles for cures 1 and 2 (10-minute averaged concentrations).

times throughout the entire cure, resulting in unreasonable concentration spikes (vertical lines that appear in Fig. 6.11). During the time intervals when the system recorded the concentrations, the profiles appeared similar for both cures. Figure 6.12 shows the temporal change in the NO_2 and NO concentration profiles for cure 1 only. Although the species injected was NO_2, the supply tank contained a small component of NO. As a result, a larger than anticipated NO concentration occurred simultaneously when injecting NO_2. In comparison, when NO was introduced the average NO_2 concentration was significantly less. This response is illustrated in Figure 6.13 for cure 3 when NO was injected.

Figure 6.14 shows the temporal changes in the concentration profiles for cure 3 and 4. The average concentrations for these two cures were similar to cures 1 and 2 during the

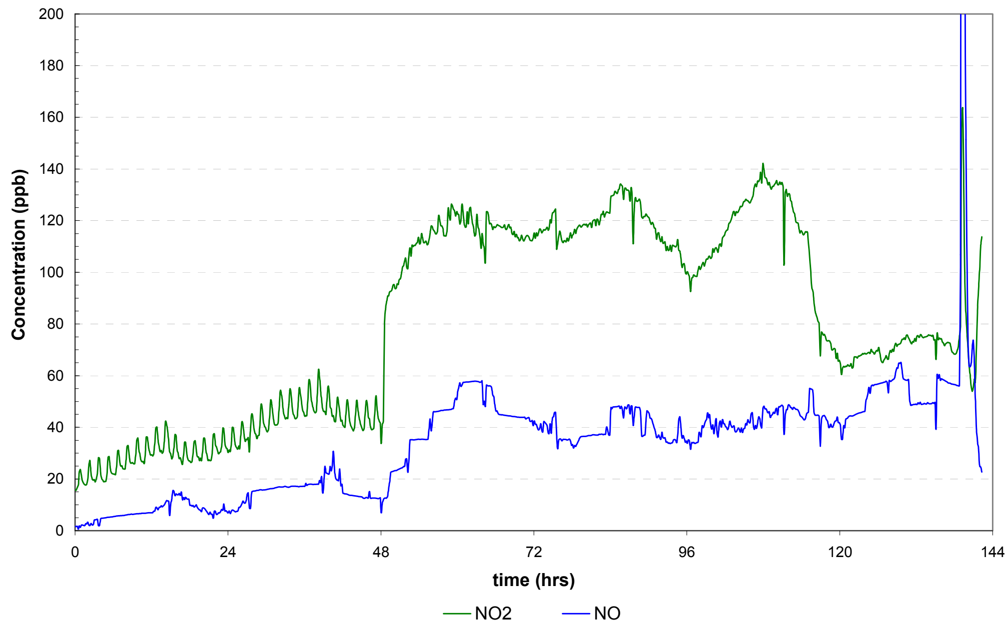


Figure 6.12 Temporal changes in the NO_x concentration profiles for cure 1 (10-minute averages).

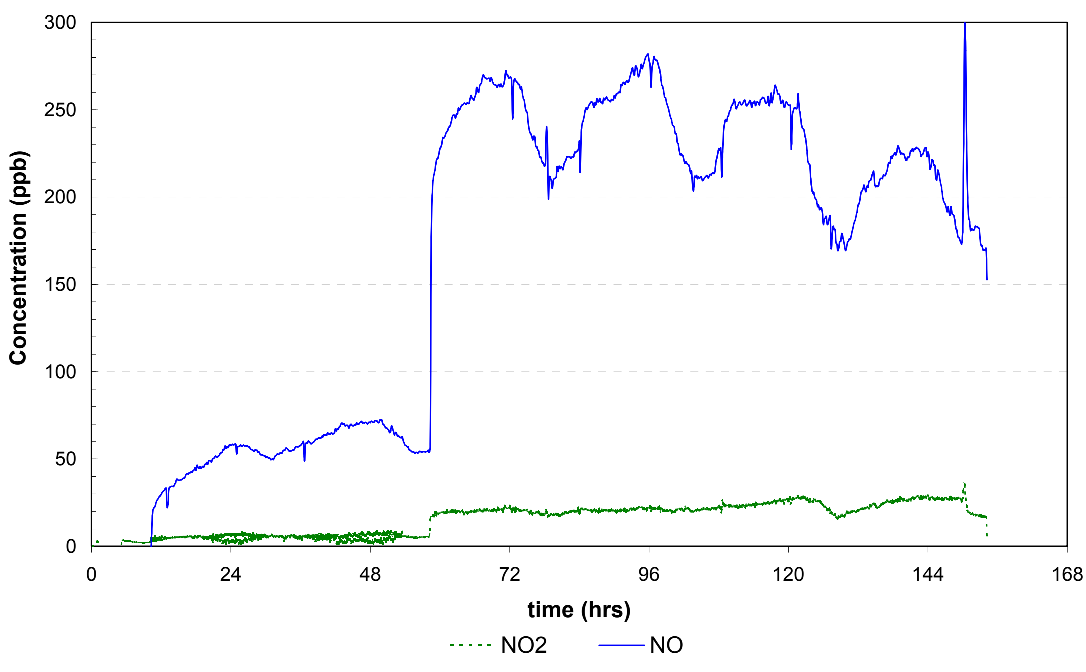


Figure 6.13 Temporal changes in the NO_x concentration profiles for cure 3 (10-minute averages).

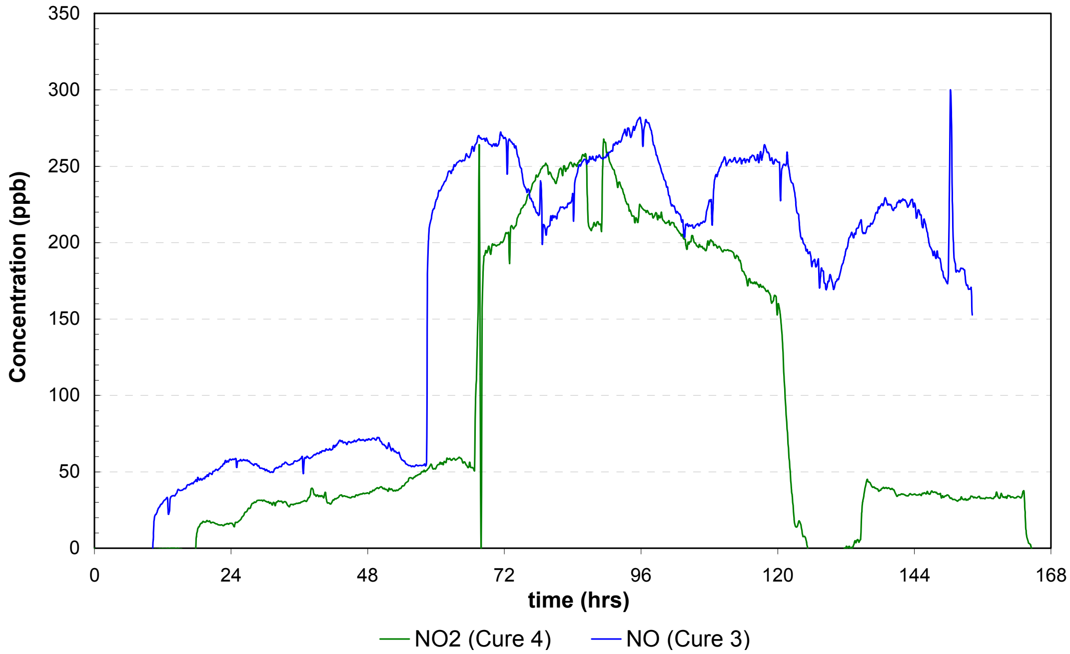


Figure 6.14 Temporal changes in the NO_x concentration profiles for cures 3 and 4 (10-minute averages).

first injection interval. During the second exposure interval, the average concentrations were approximately twice the average levels for the first two cures. The NO_2 supply tank during cure 4 was depleted prior to the end of the cure, which is evident in Fig. 6.14 as the concentration decreased very rapidly. Additionally, as the tank volume decreased, the pressure decreases also and as a result the gas input flow rate into the barn can fluctuate, especially when the tank pressure becomes less than the pressure set on the second stage regulator.

The temporal changes in the concentration profiles for cures 5 and 6 are shown in Figure 6.15. Although the concentration profiles for the first 48 hours were similar to the

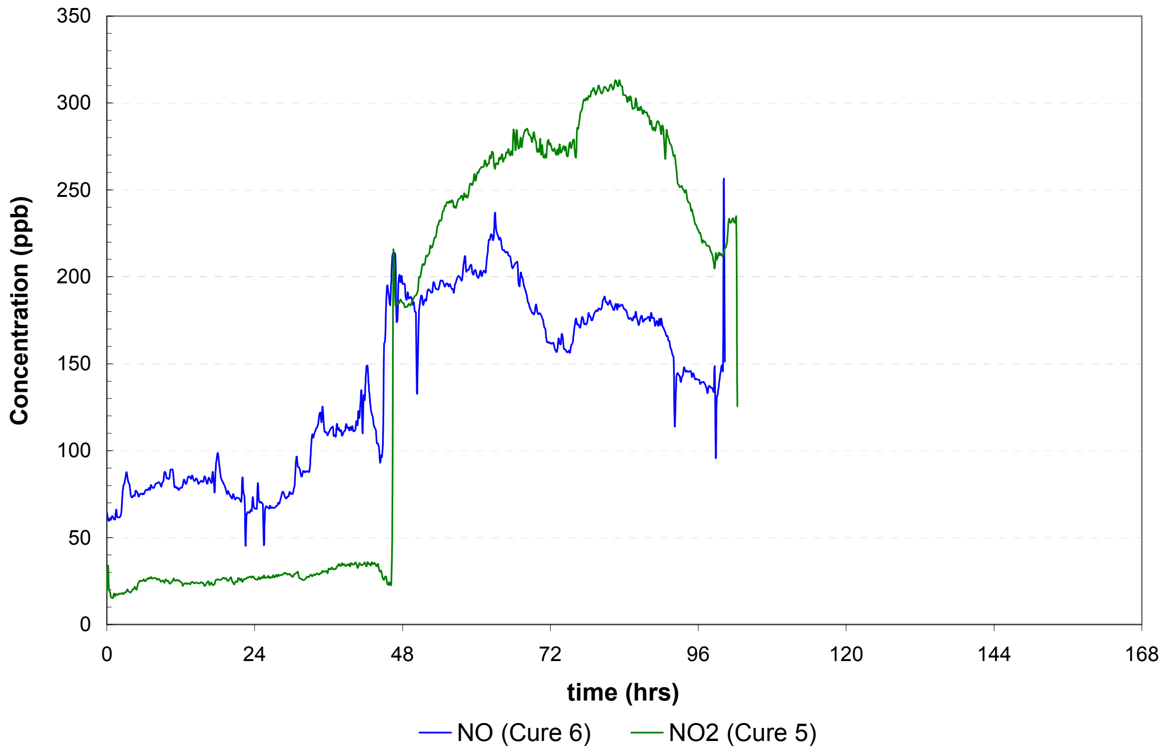


Figure 6.15 Temporal changes in the NO and NO_2 concentration profiles for cures 5 and 6 (10-minute averages).

previous cures, the flow rates were increased for both gas species when the duty cycle was increased (Table 6.4). As a result, the NO_2 concentration increased as compared to the earlier cures. The major difference between cures 5 and 6 was the NO_2 concentration profile during the second exposure interval for cure 5 was greater than the concentrations for cures 1 and 4, which were also exposed to NO_2, during the same time interval. The data acquisition system malfunctioned during the last two cures at approximately the same point in time and as a result the last 48 hours were not recorded. The 10 minute averaged concentration profiles were similar for most of the cures, but cure 5 resulted in the highest NO_2 concentration profile during the 48 to 96 hour gas injection interval.

Table 6.5 Treated barn TSNA summary statistics for the 2005 exposure tests.

Treatment	Cure	TSNA (ppb) - Treated Barn Rep$_1$	Rep$_2$	Rep$_3$	Rep$_4$	*Mean*	*Std Dev*
NO	3	600	1294	391	365	663	434
NO	6	946	526	636	690	700	178
NO	2	524	344	606	190	416	186
	Mean	690	721	544	415	593	
NO2	1	1841	2119	2378	1594	1983	340
NO2	4	1310	1150	1410	2220	1523	477
NO2	5	3403	2462	2323	4023	3053	805
	Mean	2185	1910	2037	2612	2186	
	Overall					1389	

Table 6.6 Control barn TSNA summary statistics for the 2005 exposure tests.

Treatment	Cure	TSNA (ppb) - Control Barn Rep$_1$	Rep$_2$	Rep$_3$	Rep$_4$	*Mean*	*Std Dev*
-	3	415	458	223	298	349	108
-	6	398	472	187	178	309	149
-	2	245	402	141	203	248	111
	Mean	353	444	184	226	302	
-	1	159	199	380	308	262	101
-	4	170	100	130	100	125	33
-	5	357	120	528	274	320	170
	Mean	229	140	346	227	235	
	Overall					269	

6.5.2 TSNA Results

The TSNA summary statistics for all six cures are summarized in Tables 6.5 and 6.6. The TSNA levels are the sum of NNN, NNK, NAT, and NAB. Averaged across all cures the

TSNA levels were approximately 1.389 ppm and 0.269 ppm for the treated and control barns respectively. The average TSNA levels were approximately 5.2 times greater in the cures exposed to NO or NO_2. The NNN, NNK, and NAT distribution averaged across all samples were approximately 24%, 35%, and 38% respectively. Detailed tables of the TSNA levels for both years are included in Appendix B. A similar distribution was observed in the 2004 tests, which suggests that all three components contribute significantly to the total TSNA levels. On average, the NNK and NAT contributions were almost equal for both seasons and were greater than the NNN contribution. As was the case in 2004, the average NAB contribution was less than 5% of the total TSNA levels.

The average TSNA levels for both the treated and control barns are shown in Figure 6.16. Average TSNA levels from the treated barns were significantly ($P<0.05$) different than the control barns (Table 6.7 and 6.8). Additionally, the TSNA levels were approximately 4.77, 2.30, and 4.36 times greater for the cures exposed to NO_2 as compared to NO. Comparing the average TSNA levels (2005) exposed to NO_2 and NO, the differences were significant at the 5 percent level (LSD = 920 ppb). The average TSNA levels for the three cures exposed to NO_2 and NO were approximately 2.18 ppm and 0.59 ppm respectively. Although the cures exposed to NO were significantly less than those exposed to NO_2, the values were always greater than the control barn. As a result of depleting the NO_2 supply prior to the end of the curing process, the exposure length of cure 4 was approximately 24 hours less than any cure. Cure 5 was exposed to the highest NO_2 concentrations and the resulting TSNA level was also the maximum for any cure.

The control barn average TSNA levels were approximately 0.240 and 0.269 for the

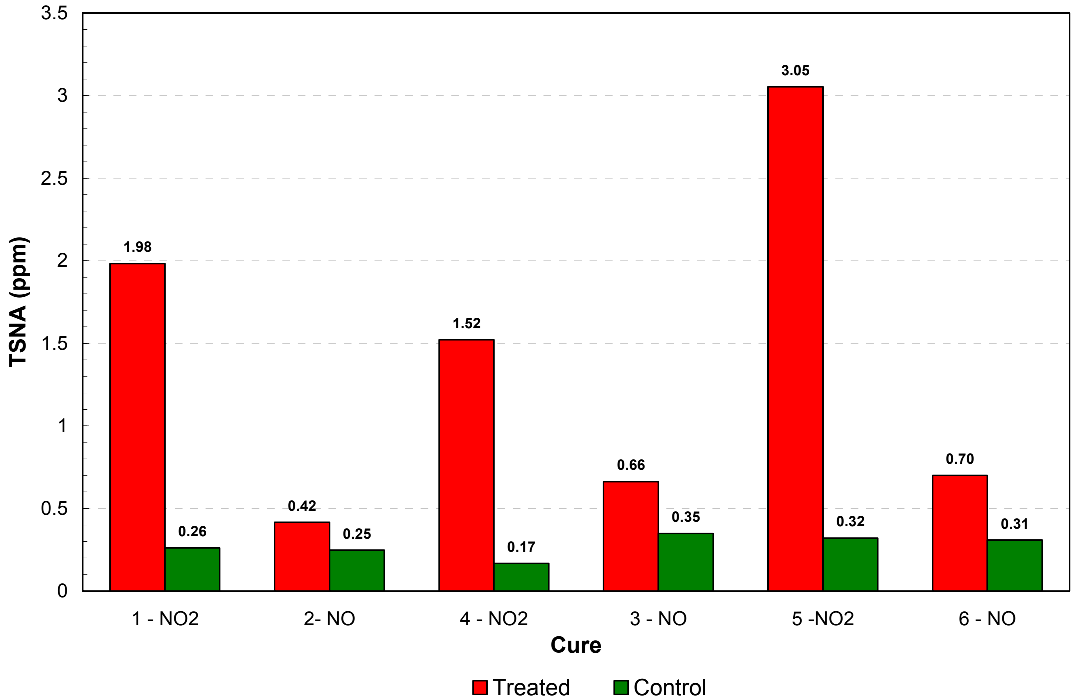


Figure 6.16 Average TSNA levels for the treated and control barns during the 2005 exposure test.

Table 6.7 ANOVA of main effects for the 2005 TSNA data (6 cures).

Source of Variation	DF	SS	MS_q	F	P-value
Treatments	1	3808067	3808067	11.899*	0.02607
Error	4	1280145	320036		
Total	5	5088211			

*** Significant at the 5% level**

Table 6.8 ANOVA of main effects for the 2004 and 2005 TSNA data (10 cures).

Source of Variation	DF	SS	MS_q	F	P-value
Treatments	1	5609523	5609523	9.810*	0.00576
Error	18	10292671	571815		
Total	19	15902194			

*** Significant at the 5% level**

2004 and 2005 seasons respectively. Even with no external nitrosation agent, measurable TSNA levels occurred. Nitrosation may be occurring from exposure to the limited NO_x in the ambient air. An additional contribution may be associated with any microbial activity present during the early stages of the curing process while the leaf is still alive. However, as the curing process advances with time the microbial activity is eliminated.

6.5.2.1 Conventional Barn TSNA Levels

The 126-rack Powell barn was monitored concurrently during the exposure study tests. The concentration profiles for two cures monitored are shown in Fig. 6.8. An indirect-fired heating system is used and the predominate NO_x species was NO. Random cured leaf samples were also submitted for TSNA analysis. The average TSNA levels for the Powell barn were approximately 0.34 ppm and 1.02 ppm for cures 1 (9/30) and 2 (10/27) respectively. The first conventional barn sampled corresponded with the exposure study cure 4, which was dosed with NO_2. Comparing the concentration profiles for the conventional barn (Fig. 6.8) and exposure barn (Fig. 6.14 - cure 3) monitored simultaneously, the conventional barn was exposed to higher concentrations and for a longer period of time. However, the treated barn resulted in TSNA levels approximately 4.5 times greater. Cure 6 was dosed with NO and the resulting average TSNA level was approximately 0.70 ppm. The average TSNA level was approximately 1.02 ppm from the conventional barn second cure, which was also exposed to NO as a result of a leaking heating system. Comparing the average exposure concentration profiles for these two cures (Fig. 6.8 and Fig. 6.15 – cure 6), the conventional barn was exposed to higher concentrations for a longer duration also.

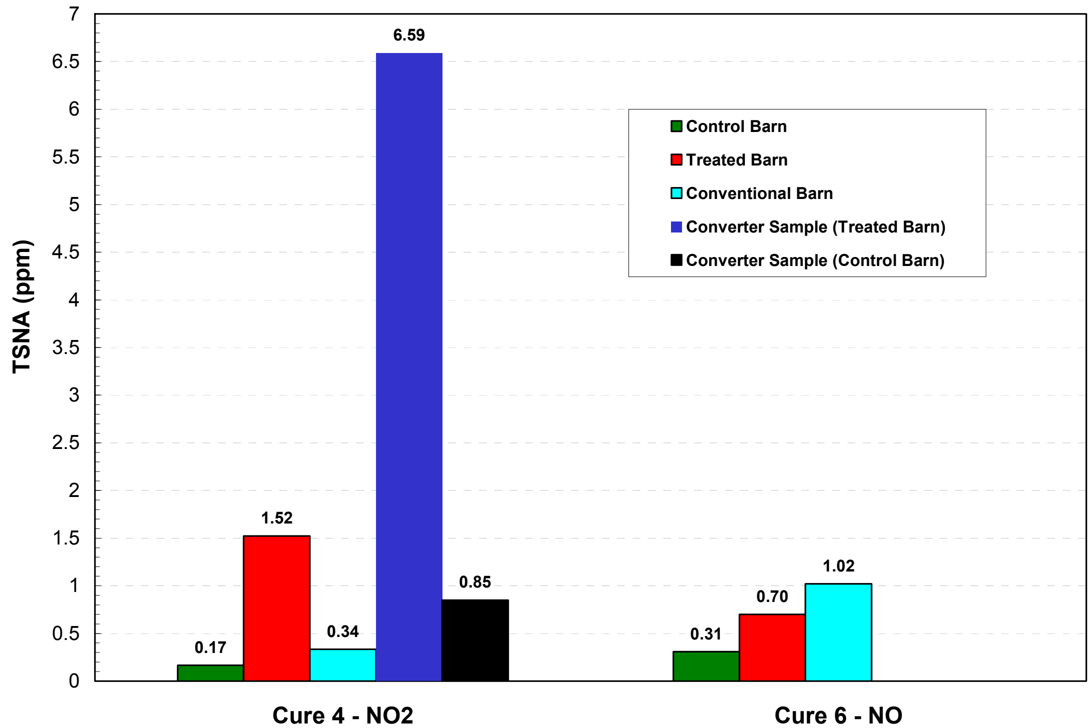


Figure 6.17 TSNA results for the conventional barn, treated barn (cures 4 and 6), and converter leaf samples.

6.5.2.2 Converter Leaf TSNA Levels

During the exposure study fourth cure, leaves from converter plants were observed and removed from both the treated and control barns. Converter plant leaves are indicated by bright red spots on the cured leaf. The total number of leaves collected was approximately a dozen from which a random sample was submitted for TSNA analysis for both barns. The TSNA levels were approximately 6.59 ppm and 0.85 ppm for the converter samples obtained from the treated and control barns respectively. The NNN component of the total TSNA for both barns was approximately 83%. Converter plants have significantly higher levels of nornicotine, which is a more efficient precursor of NNN than nicotine (Tso, 1999).

Therefore, the converter plant has a simple and direct pathway to TSNA formation even in the absence of any external nitrosating agents. This is evident in the TSNA level from the control barn, which is approximately 5 times greater than the average level in the control barn sample (0.17 ppm) for cure 4. Figure 6.17 summarizes the TSNA results from the conventional barn and converter plant sample.

6.5.3 Diffusion Tubes

The diffusion tube study was expanded in 2005 to include NO_x and NO_2 tubes. Both tube types were positioned inside the conventional barn on the research station in addition to the treated and control barns. If the cure treatment was NO_2, an elevated concentration was measured using the NO_2 tubes, especially when compared to the ambient tubes. The NO_x tubes in the same treated barns would indicate an elevated level compared to the ambient tubes, but the concentration difference between the NO_x tubes and ambient tubes was not as great as the difference between the NO_2 exposed tubes and the ambient tubes. However, when the curing treatment was NO, both tube types showed only small concentration differences, if any, between the exposed and ambient tubes. Similar results were obtained when monitoring the conventional barn with a known leak also. The conclusion was if a leaking heating system is producing predominately NO, the diffusion tubes (NO_2 or NO_x) may not be able to reliably discriminate between an indirect-fired heating system that has a leak from one that does not during curing. The NO_2 tubes might be feasible if a leaking indirect-fired system produced elevated levels of both NO_x species.

Chapter 7 Summary

Research established the most significant mechanism associated with TSNA formation in flue-cured tobacco was a result of the green leaf exposure to NO_x gas during curing and the subsequent reactions with the naturally occurring alkaloids in the leaf. As a result, the tobacco industry mandated converting the direct-fired heating systems to indirect-fired heating. This study began with monitoring both direct- and indirect-fired bulk curing barns to measure the NO_x concentrations the green leaf is exposed to during the curing process. The predominate NO_x species measured for a direct-fired system was NO_2, but for an indirect-fired system was NO. Although the random field measurements were only snapshots, most of the concentrations observed were below 1 ppm. However, the conventional barns located on the research station that were continuously monitored during multiple cures also resulted in maximum NO_x concentrations less than 1 ppm (Appendix A). This research is one of the first to experimentally evaluate the TSNA response in the cured leaf as a result of exposure to both NO_x gas species at concentrations based on levels measured in conventional barns during the curing process.

Exposure tests were conducted during the 2004 and 2005 seasons to evaluate any differences in the cured leaf TSNA response due to exposure to NO or NO_2 during curing. Two electric heated curing barns were utilized to perform the exposure study. The treated barn was dosed with a NO_x species and the control was untreated. The control barn NO_x levels were not monitored and assumed to be negligible throughout the curing process. During the two year study, a total of 6 cures were treated with NO_2 and 5 cures with NO.

Random cured leaf samples were obtained from both barns and analyzed for TSNAs.

The concentrations simulated in the treated barn were based on actual NO_x measurements. The elevated concentrations in an indirect-fired barn are a result of a leaking heating system. Many factors can affect the NO_x formation rate and the amount of time the burner is operating. Some of these factors are interrelated such as the burner firing rate and heat exchanger efficiency. The NO formation rate is exponentially dependent on the flame temperature. As a result, the exposure concentration profiles to which the green tobacco might be subjected are numerous. However, the concentrations duplicated during the exposure tests are examples of realistic levels encountered as a result of a leaking indirect-fired system. The following conclusions are based on this research.

- Averaged across both seasons, the TSNA response in the cured leaf was approximately 3.74 times greater in the cures treated with NO_2 as compared to the cures treated with NO. The treatment differences were significant at the 5 percent level. The adsorption or diffusion of NO_2 in the green leaf and the consequent reaction with the tobacco alkaloids is a more efficient process as compared to NO at the concentrations in the exposure tests.
- The combustion modifications associated with the heat exchangers that replaced the direct-fired heating units resulted in changing the primary NO_x species produced from predominately NO_2 to NO. Therefore, if a leak develops in the indirect-fired heating system, the green leaf will be exposed to mainly NO, which is not as efficient of a

nitrosating agent as NO_2. However, any leak has the potential to elevate TSNA levels in the cured leaf if the exposure concentration is high enough regardless of the NO_x species.

- Any diagnostic equipment developed to monitor the indirect-fired heating systems for leaks must be capable of detecting NO_x levels in the ppb range. Additionally, the detection device must be capable of measuring both NO and NO_2.

Although retrofitting significantly reduced TSNAs in the cured leaf, very limited detailed information was known about the NO_x nitrosating agents. In order to minimize TSNAs in flue-cured tobacco, a better understanding of the NO_x nitrosating mechanisms and their formation will assist the tobacco industry with developing future strategies. As a result of the increased global marketability of U.S. tobacco, maintaining the highest cured leaf quality is critical. Currently, TSNA levels are self-regulated and therefore an acceptable level will vary with each company, but future FDA regulation, which many expect to occur, may require the industry to maintain TSNA levels below an established threshold. As a result of retrofitting curing barns with indirect-fired furnaces, the most significant mechanism associated with TSNA formation in flue-cured was eliminated. Additionally, if a leak does occur the predominate NO_x species present is the least efficient nitrosation agent associated with the NO_x mechanism.

7.1 Future Work

As it becomes necessary to replace the heat exchangers, some of the NO_x control strategies should be investigated. In particular, the low-NO_x burner technology is a proven and mature technology utilized to reduce NO_x emissions in stationary combustion systems. Future research may involve measuring and comparing the NO_x emissions from the low-NO_x burners and existing burners under the same operating parameters. As a result of the significantly rising energy costs, adjustable firing rate burners have become more appealing to minimize energy consumption. These systems might also have potential benefits associated with decreased NO_x emissions as a result of reduced burner firing rates and consequent flame temperatures, which can have a significant effect on the thermal NO_x formation rates. Additional research could investigate any time dependency on the NO_x exposure and resulting TSNA formation during the curing process.

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APPENDICES

Appendix A Treated barn exposure concentration profiles for both seasons

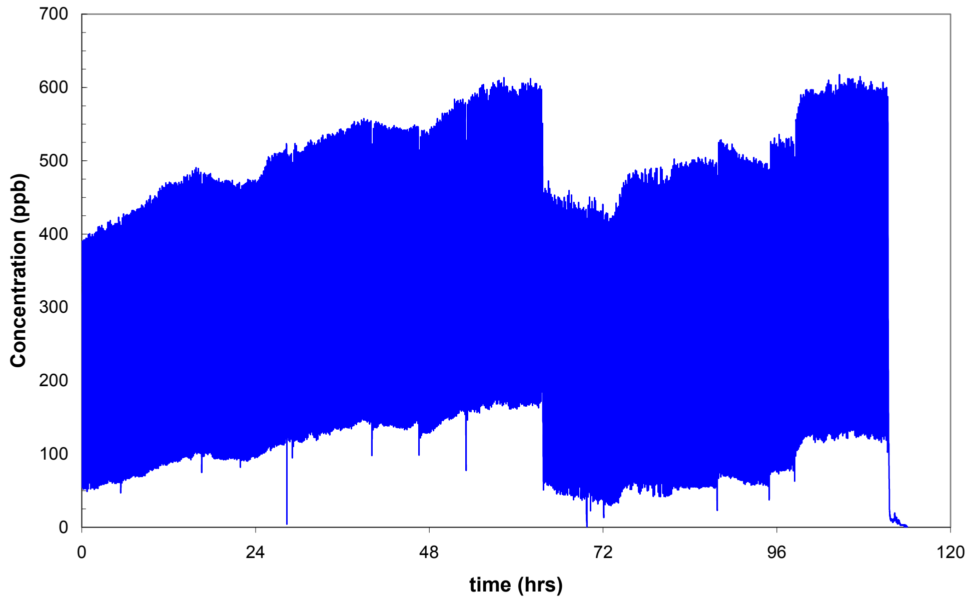

Figure A.1 NO concentration profile for cure 4, 2004.

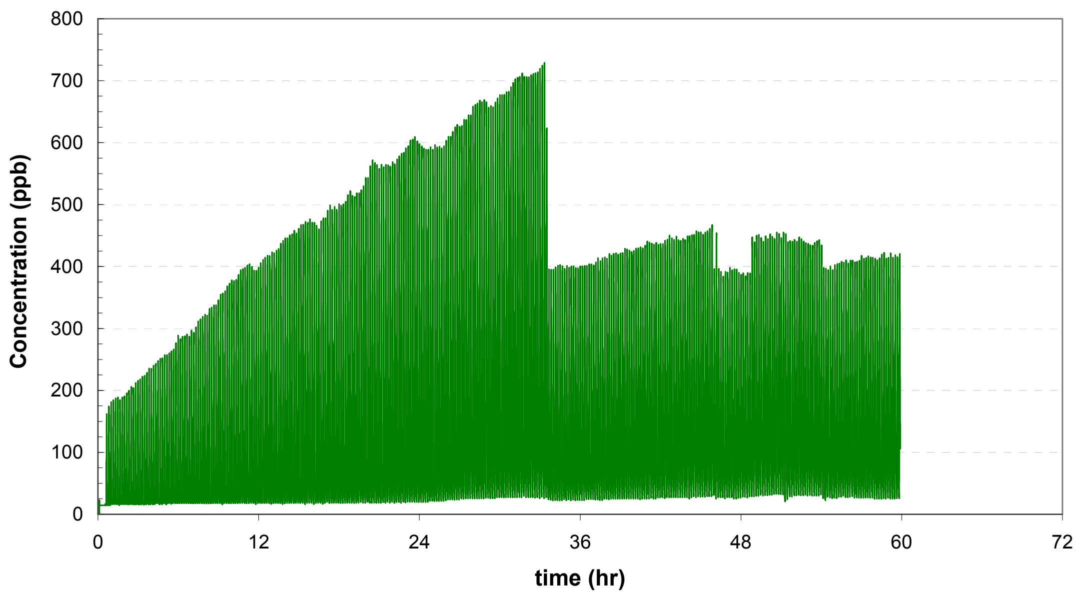

Figure A.2 NO_2 concentration profile for cure 5, 2004.

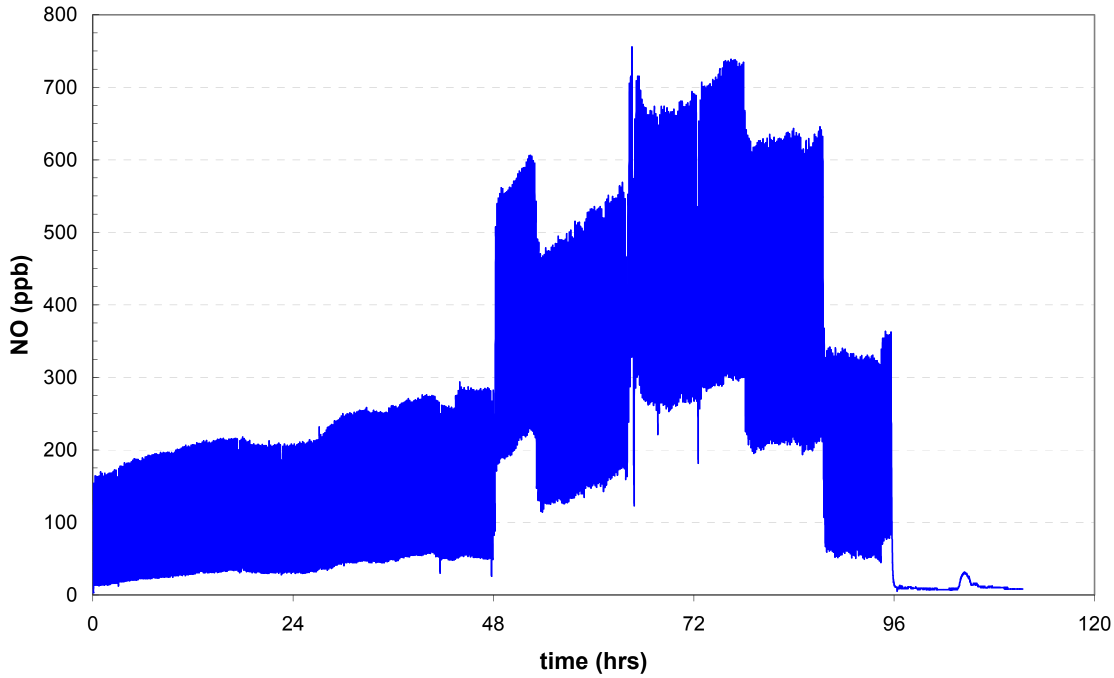

Figure A.3 NO concentration profile for cure 6, 2004.

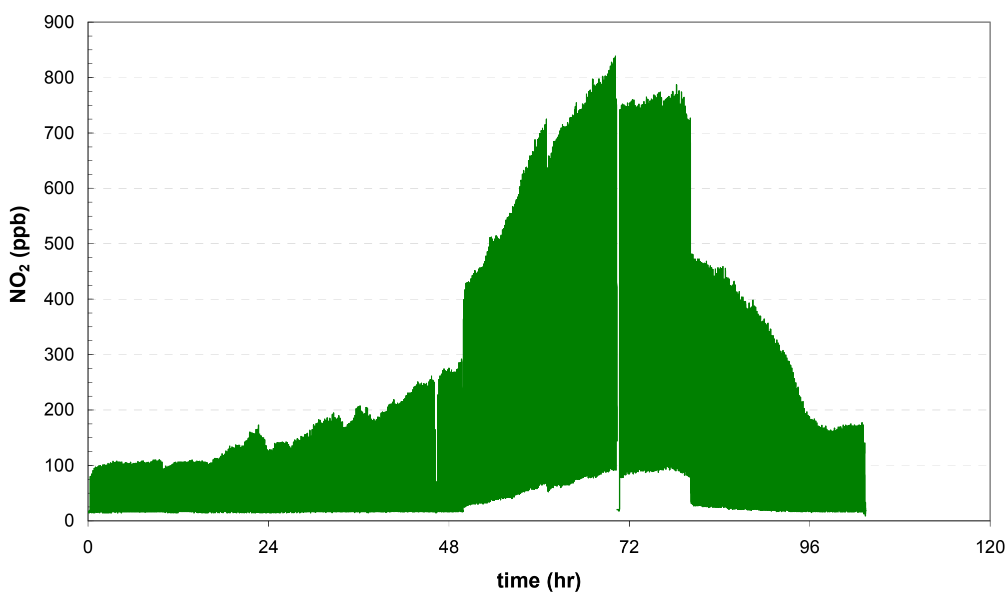

Figure A.4 NO_2 concentration profile for cure 7, 2004.

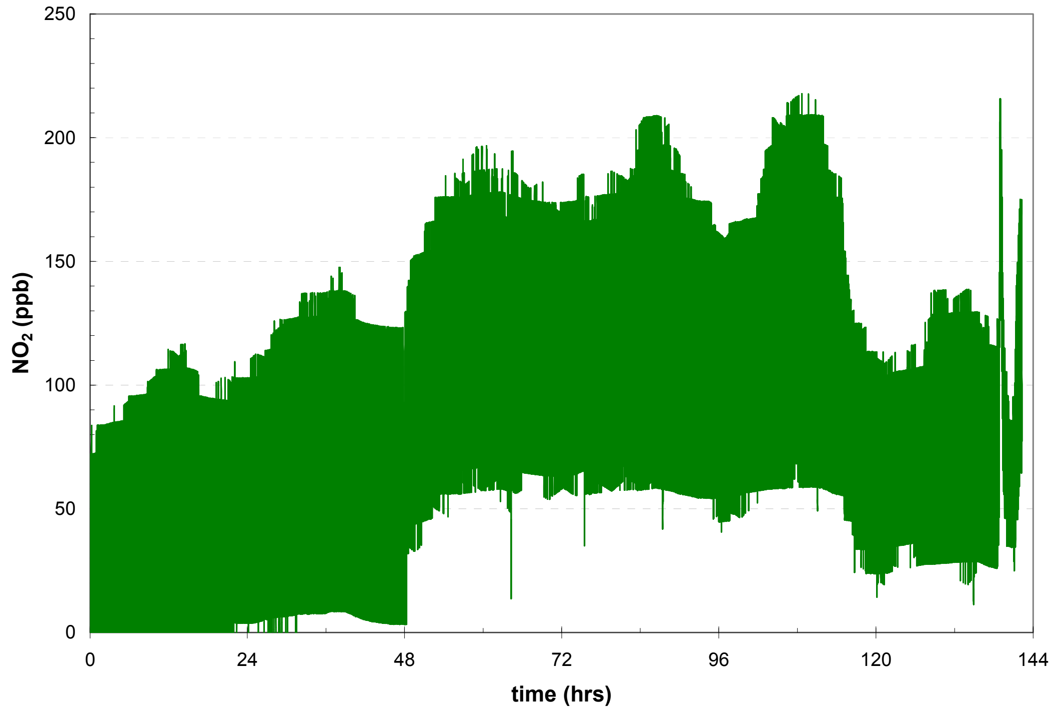

Figure A.5 NO_2 concentration profile for cure 1, 2005.

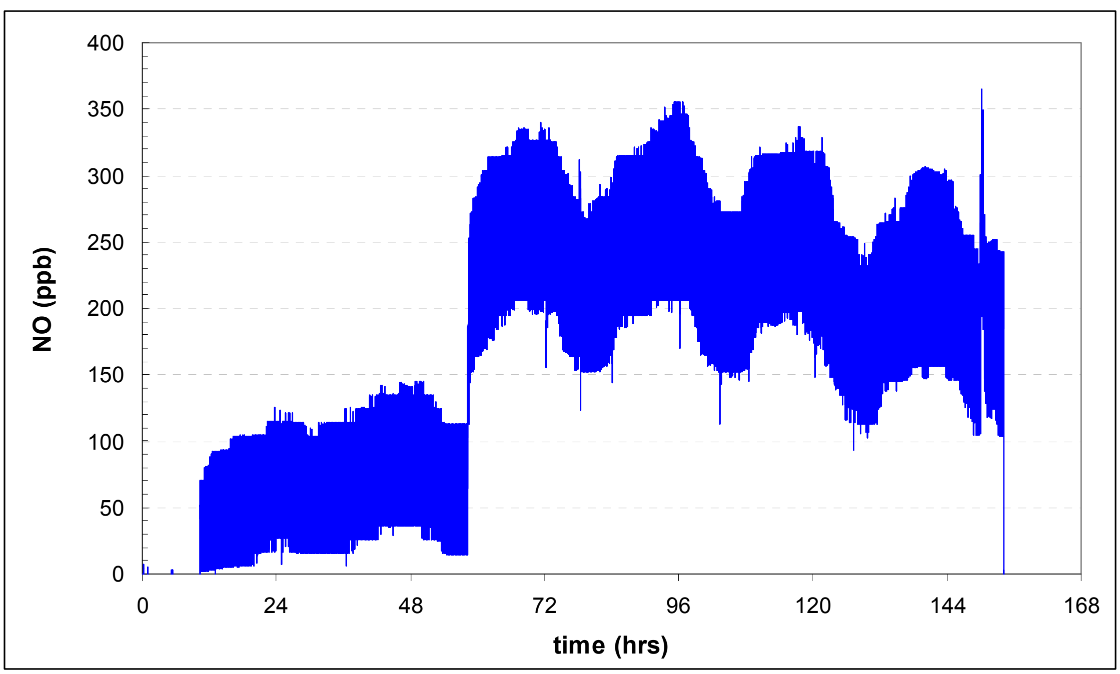

Figure A.6 NO_2 concentration profile for cure 3, 2005.

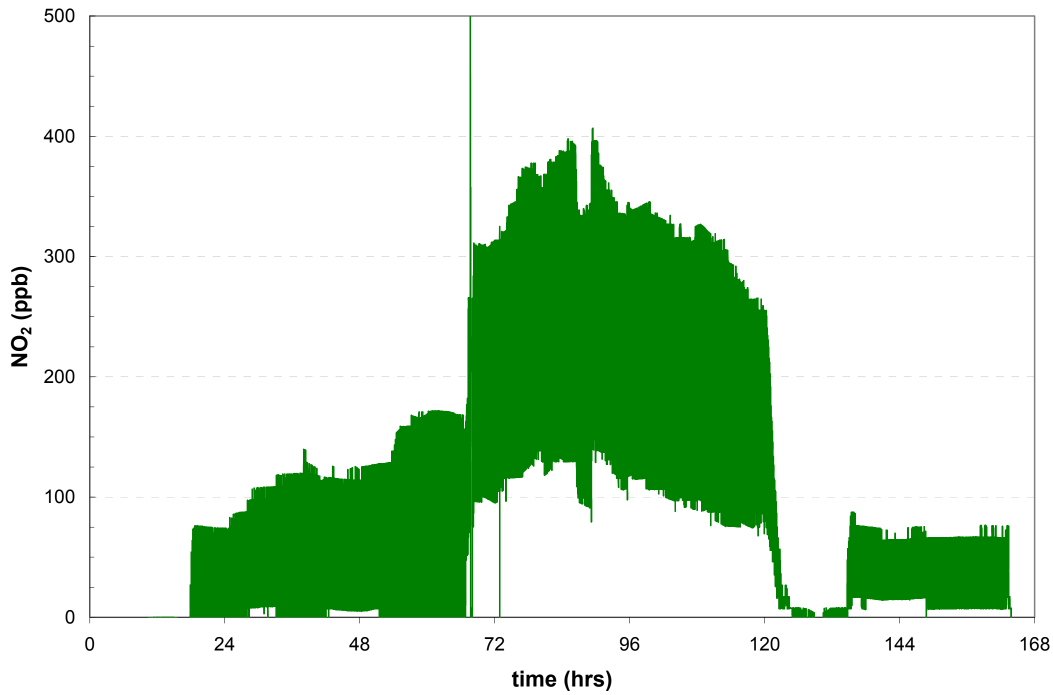

Figure A.7 NO_2 concentration profile for cure 4, 2005.

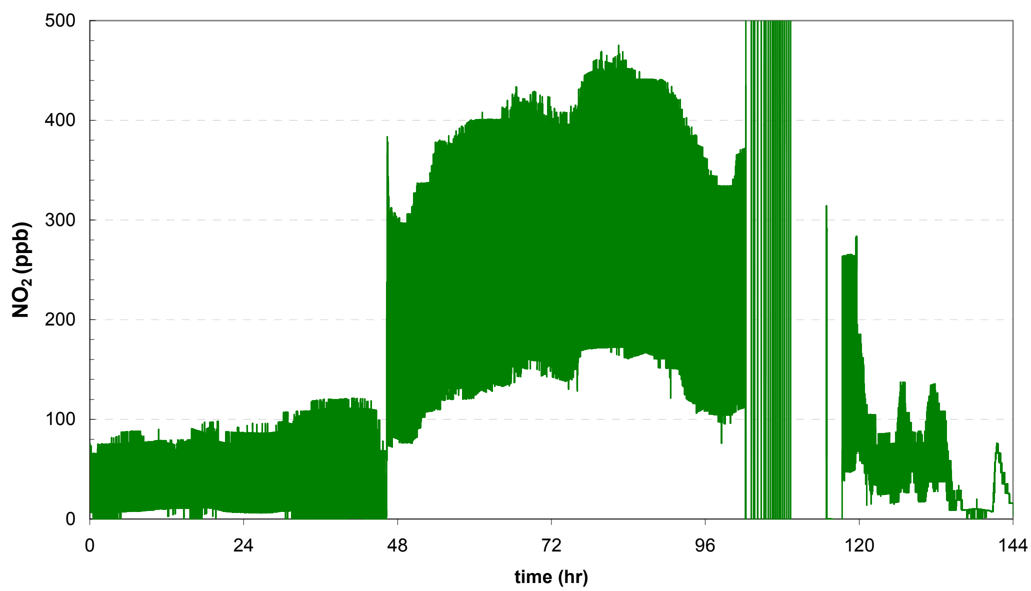

Figure A.8 NO_2 concentration profile for cure 5, 2005. Data acquisition system error during monitoring for approximately 20 hours.

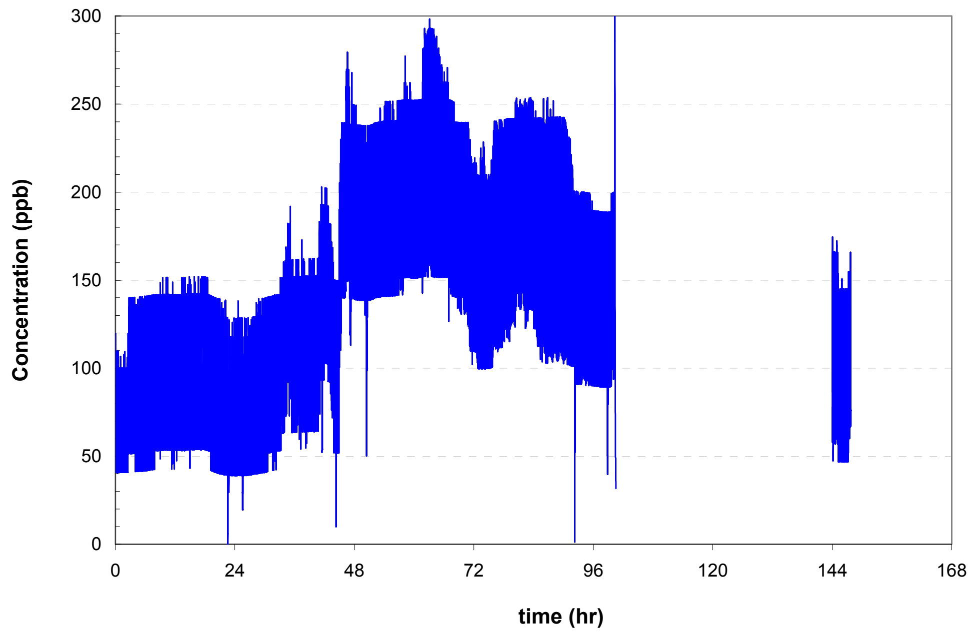

Figure A.9 NO concentration profile for cure 6, 2005. Data acquisition system error occurred during monitoring for approximately 48 hours.

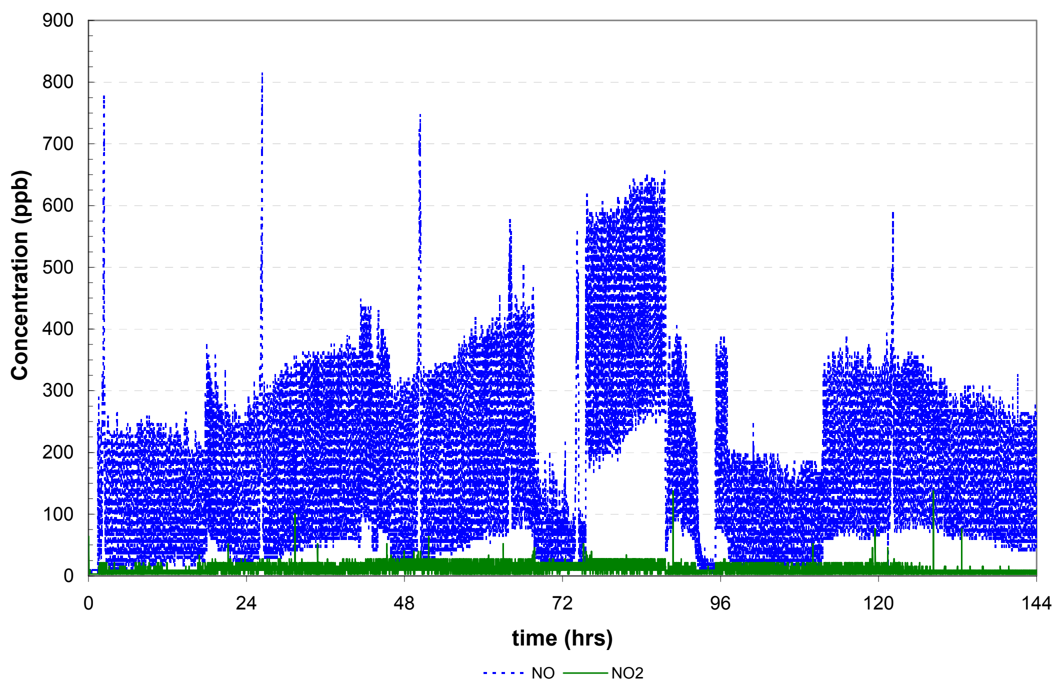

Figure A.10 Temporal changes in the NO_x concentrations from an indirect-fired conventional barn (Powell 126-rack) monitored on the AREC research station (mid-stalk tobacco).

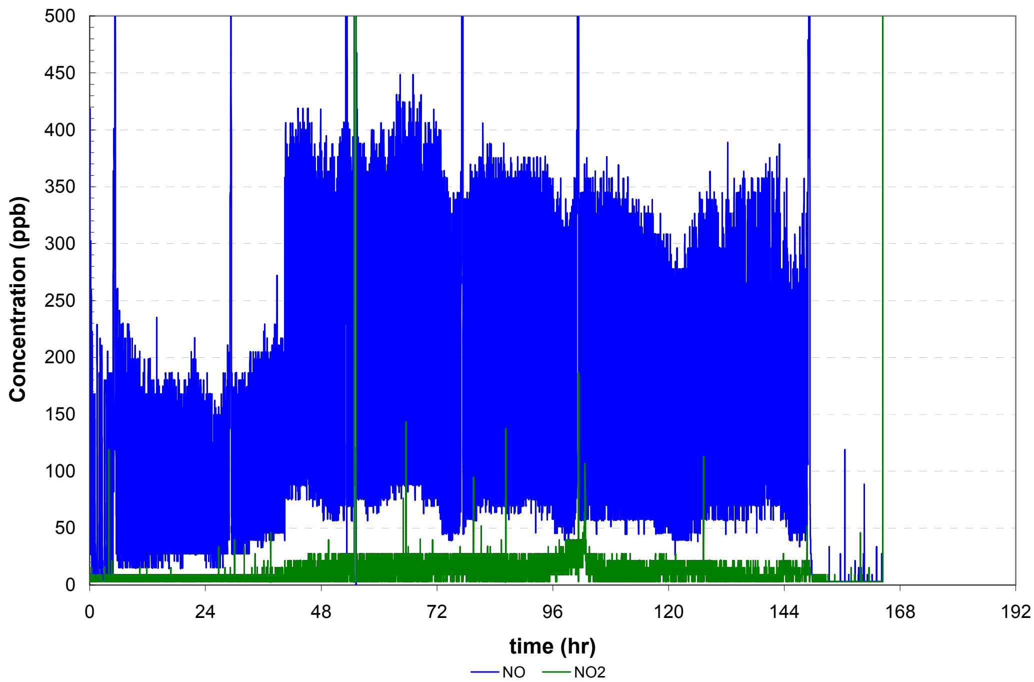

Figure A.11 Temporal changes in the NO_x concentrations from an indirect-fired conventional barn (Powell 126-rack) monitored on the AREC research station (upper-stalk tobacco).

Appendix B TSNA summary data for the 2004 and 2005 exposure tests

Table B.1 TSNA data for the 2004 season exposure tests

		Barn 1 (Treated)						Barn 2 (Control)					
	TSNAs	**1A**	**1B**	**1C**	**1D**	***Mean***	***Std Dev***	**2A**	**2B**	**2C**	**2D**	***Mean***	***Std Dev***
Cure 4 NO	NAB (ppb)	11	19	14	14	*15*	*3.3*	18	17	18	24	*19*	*3.2*
	NAT (ppb)	60	123	98	98	*95*	*26.0*	102	74	47	84	*77*	*23.0*
	NNK (ppb)	71	108	104	108	*98*	*17.9*	56	63	48	69	*59*	*9.1*
	NNN (ppb)	35	96	56	60	*62*	*25.3*	73	42	34	57	*52*	*17.2*
	Total	177	346	272	280	*269*	*69.6*	249	196	147	234	*207*	*45.5*
Cure 5 NO_2	NAB (ppb)	20	16	21	28	*21*	*5.0*	15	16	16	15	*16*	*0.6*
	NAT (ppb)	220	130	246	247	*211*	*55.3*	40	49	47	36	*43*	*6.1*
	NNK (ppb)	247	164	271	227	*227*	*45.8*	36	46	45	36	*41*	*5.5*
	NNN (ppb)	213	527	181	417	*335*	*165.5*	21	34	31	21	*27*	*6.8*
	Total	700	837	719	919	*794*	*103.2*	112	145	139	108	*126*	*18.7*
Cure 6 NO	NAB (ppb)	19	16	8	6	*12*	*6.2*	N/A	11	9	N/A	*10*	*1.4*
	NAT (ppb)	269	216	119	89	*173*	*83.7*	68	135	120	43	*92*	*43.2*
	NNK (ppb)	239	237	178	132	*197*	*51.5*	81	112	98	52	*86*	*25.8*
	NNN (ppb)	163	119	51	48	*95*	*55.8*	38	88	55	22	*51*	*28.3*
	Total	690	588	356	275	*477*	*194.2*	187	346	282	117	*233*	*101.2*
Cure 7 NO_2	NAB (ppb)	66	79	41	47	*58*	*17.5*	6	7	8	N/A	*7*	*1.0*
	NAT (ppb)	1035	1440	723	911	*1027*	*303.6*	58	67	112	51	*72*	*27.5*
	NNK (ppb)	1389	1440	1296	1113	*1310*	*143.9*	57	51	60	54	*56*	*3.9*
	NNN (ppb)	687	725	593	661	*667*	*55.6*	46	14	51	34	*36*	*16.5*
	Total	3177	3684	2653	2732	*3062*	*474.8*	167	139	231	139	*169*	*43.4*
Cure 8 NO_2	NAB (ppb)	21	27	15	29	*23*	*6.3*	12	17	17	9	*14*	*3.9*
	NAT (ppb)	324	352	228	404	*327*	*73.9*	156	166	218	130	*168*	*36.9*
	NNK (ppb)	228	222	236	235	*230*	*6.6*	100	93	82	73	*87*	*11.9*
	NNN (ppb)	256	445	188	505	*349*	*150.7*	186	152	353	103	*199*	*108.5*
	Total	829	1046	667	1173	*929*	*225.0*	454	428	670	315	*467*	*148.3*

Table B.2 TSNA data for the 2005 season exposure tests

		Barn 1 (Gas Exposure)						Barn 2 (Control)					
	TSNAs	**1A**	**1B**	**1C**	**1D**	***Mean***	***Std Dev***	**2A**	**2B**	**2C**	**2D**	***Mean***	***Std Dev***
Cure 1	NAB (ppb)	30	42	48	27	*37*	*9.9*	N/A	N/A	11	9	*10*	*1.4*
NO_2	NAT (ppb)	666	864	864	607	*750*	*133.5*	71	89	200	150	*128*	*59.0*
	NNK (ppb)	680	821	896	616	*753*	*128.0*	47	59	69	61	*59*	*9.1*
	NNN (ppb)	465	392	570	344	*443*	*98.3*	41	51	100	88	*70*	*28.4*
	Total	1841	2119	2378	1594	*1983*	*339.6*	159	199	380	308	*262*	*101.0*
Cure 2	NAB (ppb)	12	7	14	N/A	*11*	*3.6*	7	11	N/A	6	*8*	*2.6*
NO	NAT (ppb)	258	146	284	79	*192*	*96.1*	123	223	70	104	*130*	*65.8*
	NNK (ppb)	114	83	118	58	*93*	*28.2*	48	46	35	37	*42*	*6.5*
	NNN (ppb)	140	108	190	53	*123*	*57.5*	67	122	36	56	*70*	*36.8*
	Total	524	344	606	190	*416*	*186.2*	245	402	141	203	*248*	*111.4*
Cure 3	NAB (ppb)	21	36	11	11	*20*	*11.8*	19	16	12	13	*14*	*2.1*
NO	NAT (ppb)	310	514	157	133	*279*	*175.5*	237	245	102	151	*166*	*72.7*
	NNK (ppb)	144	182	124	136	*147*	*25.1*	50	55	48	38	*47*	*8.5*
	NNN (ppb)	125	562	99	85	*218*	*230.1*	109	142	61	96	*100*	*40.6*
	Total	600	1294	391	365	*663*	*433.9*	415	458	223	298	*326*	*120.0*
Cure 4	NAB (ppb)	130	BDL	150	210	*163*	*41.6*	BDL	BDL	BDL	BDL	N/A	N/A
NO_2	NAT (ppb)	470	470	530	780	*563*	*147.7*	170	BDL	130	BDL	*150*	*28*
	NNK (ppb)	440	430	420	710	*500*	*140.2*	BDL	BDL	BDL	BDL	N/A	N/A
	NNN (ppb)	270	250	310	520	*338*	*124.2*	BDL	BDL	BDL	BDL	N/A	N/A
	Total	1310	1150	1410	2220	*1523*	*477.2*	170	N/A	130	N/A	*150*	*28*
Cure 5	NAB (ppb)	71	42	43	72	*57*	*16.8*	14	6	21	10	*13*	*6.4*
NO_2	NAT (ppb)	1188	762	736	1254	*985*	*274.0*	187	55	274	139	*164*	*91.5*
	NNK (ppb)	1219	1132	1100	1656	*1277*	*257.8*	77	39	108	54	*70*	*30.0*
	NNN (ppb)	925	526	444	1041	*734*	*293.3*	79	20	125	71	*74*	*43.0*
	Total	3403	2462	2323	4023	*3053*	*805.3*	357	120	528	274	*320*	*170.0*
Cure 6	NAB (ppb)	41	19	25	30	*29*	*9.3*	17	18	10	9	*14*	*4.7*
NO	NAT (ppb)	464	284	315	375	*360*	*79.2*	210	240	92	92	*159*	*77.8*
	NNK (ppb)	186	96	128	133	*136*	*37.3*	94	73	53	45	*66*	*21.9*
	NNN (ppb)	255	127	168	152	*176*	*55.6*	77	141	32	32	*71*	*51.6*
	Total	946	526	636	690	*700*	*177.9*	398	472	187	178	*309*	*148.9*

BDL = 0.1 ppm (100 ppb)