

Formation of Nitric Oxide during Tobacco Oxidation

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The sources of NO during biomass oxidation, and in particular tobacco oxidation, have been disputed. Literature results range from decomposition of nitrate to the oxidation of atmospheric nitrogen. To rectify these discrepancies, this study focuses on the sources of nitric oxide (NO) during the oxidation of tobacco samples. When Burley tobacco was heated in a partially oxidized atmosphere, NO was produced at two distinct temperature ranges, namely 275–375 °C (the low-temperature range) and 425–525 °C (the high-temperature range). The formation of NO at the low-temperature range with Burley tobacco was found to be unaffected by oxygen, while the formation of NO at the high-temperature range required an oxygen atmosphere. With Bright and Oriental tobacco, NO was produced only within the higher-temperature range. To understand the formation processes and the sources of NO formation within these two temperature ranges, several endogenous nitrogenous tobacco compounds were examined. These were mixed with non-nitrogenous biomass model materials, namely cellulose, pectin, xylan, or lignin, which also occur naturally in tobacco, and the mixtures were heated in a flow tube reactor under a partially oxidative atmosphere. A commercial gas analyzer was used to monitor the formation of NO during heating. Nitrate ion was determined to be the source of NO formation in the range of 275–375 °C. This ion was decomposed in a carbonaceous surrounding to produce NO. For NO formation at the higher temperature range, amino acids and proteins were shown to be the sources. The interaction between nitrogenous organic compounds (amino acids and proteins) and pectin first produced a nitrogen-containing char at a temperature below 350 °C. Oxidation of this char at the higher temperatures produced NO.

KEYWORDS: NO formation; pyrolysis; oxidation; nitrate; amino acids; proteins; pectin

INTRODUCTION

It is well known that the combustion of fossil carbonaceous materials, such as coal, and other biomass materials (e.g., wood), generates a substantial amount of nitrogen oxides (NO_x). The emission of nitrogen oxides from industrial and urban sources has drawn much attention by researchers and public health authorities, due to the serious environmental impact of nitrogen oxides. As a result, the effective and economical reduction of NO_x from the above sources has become a major focus of many academic and industrial research efforts. Studies on NO_x formation date back several decades, and more recent studies have focused on the NO_x-forming processes in the combustion of biomass and coal (1–5). These studies have also attempted elucidation of the mechanisms of NO_x formation. The fixed nitrogen in a carbonaceous surrounding (char) has been determined to be one of the sources of nitrogen oxides from coal pyrolysis or combustion (5). For biomass combustion, however, most studies have paid little or no attention to the sources for NO formation (6–8). Therefore, we have focused on the formation sources of NO during biomass oxidation.

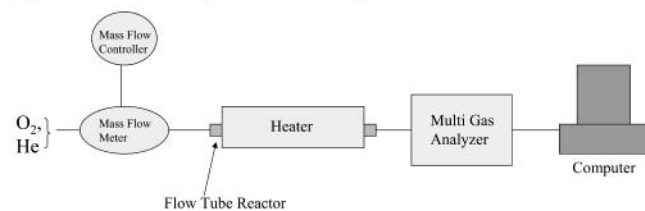
Emission of nitrogen oxides has also been observed in cigarette smoke (9, 10). Studies have shown nitric oxide (NO)

to be the major oxide of nitrogen in fresh cigarette smoke, although minor amounts of nitrogen dioxide (NO₂) (11–13) and nitrous oxide (N₂O) (14) have also been reported. The mainstream smoke (inhaled during puffing) of a cigarette can contain up to about 1000 ppm of nitric oxide per puff (13). In comparison, the sidestream smoke (smoke released to the environment during smoldering) contains an even larger amount of nitric oxide. The ratio of NO in the sidestream to that of mainstream smoke (SS/MS ratio) was determined to be between 3.5 and 12.8 depending on the cigarette type and smoking protocols used (13). This ratio is significantly higher than the ratio of the weight of tobacco consumed between puffs to the weight of tobacco consumed during puffs, which was reported to be in the range of 1.1 to 3.6 (15–17).

Previous studies on tobacco samples and cigarettes have suggested that nitrate and organic nitrogenous compounds were the major sources of NO in cigarette smoke (9–10, 15, 18–19). The amount of NO produced in the mainstream smoke correlated well to the level of nitrate in tobacco. Thus, nitrate was considered to be the major source of NO in the mainstream smoke (9–10, 15, 19). For sidestream smoke, NO was suggested to be produced from other sources besides nitrate (9, 15, 20). Norman et al. (19) reported that a significant amount of NO in both mainstream and sidestream smoke could not have arisen

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(a) Schematics of Experimental Setup



(b) Flow Tube Reactor

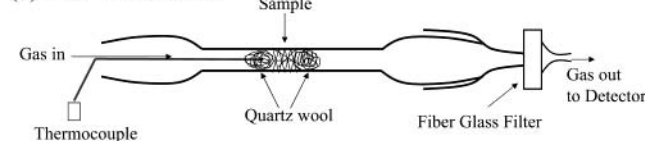


Figure 1. Schematic of the experimental setup and the flow tube reactor.

from nitrate decomposition, and consequently suggested that part of the residual NO arose from the oxidation of atmospheric nitrogen. Later, Umemura et al. (18) suggested that NO in sidestream smoke was formed both by thermal decomposition of nitrate and by the oxidation of organic nitrogenous compounds, such as amino acids.

In this study, the formation of NO during the oxidation of tobacco samples has been thoroughly investigated and the sources of NO formation have been identified. Some pathways for the formation of NO have been also suggested. In conducting this study, we employed a variety of tobacco samples and a series of biomass model systems. The samples were heated in a flow tube reactor under a partially oxidative atmosphere and the concentration of the resulting NO produced was monitored by an in-line IR spectrometer. It has been found that NO gas from different tobacco varieties generally evolves in two temperature ranges: a low-temperature range of 275–375 °C and a high-temperature range of 425–525 °C. The characteristics of the NO forming processes during the oxidation of tobacco and biomass model systems and the information on the distribution of nitrogenous compounds in tobacco have led us to identify the sources of NO in tobacco oxidation. The amount of NO produced at low temperatures correlates well with the amount of nitrate present in tobacco. By contrast, we believe that the nitrogen oxide produced at the high-temperature range originates from the oxidation of the fixed nitrogen in the tobacco char. This fixation of nitrogen arises from an interaction of nitrogenous organic compounds, such as amino acids and proteins in tobacco, with some non-nitrogenous constituents, such as pectin.

EXPERIMENTAL PROCEDURES

A. Equipment and Procedures. A schematic of the experimental setup is shown in **Figure 1**, displaying the components of the setup and the details of a flow tube reactor. Experiments were carried out in a quartz flow tube reactor (50-cm length \times 9.0-mm i.d.). A sample of ~100 mg was loosely packed in the middle of the reactor tube, sandwiched by two clean pieces of quartz wool, as shown in **Figure 1(b)**. The quartz flow tube was then placed inside a Thermocraft furnace, where its temperature was controlled during heating by a temperature controller. The sample temperature was separately monitored by an Omega K-type thermocouple inserted into the quartz wool to be as close to the sample as possible. In this way, possible interferences of the thermocouple with oxidative reactions can be avoided. The sample was heated from room temperature to a maximum of 700 °C at a heating rate of about 12 °C/min; the bed temperature remained uniform, and did not lag behind the furnace temperature. After each experiment, the reactor tube was unloaded, blown with air, washed with distilled water, and dried. During the experiment, the flow of inlet

gases into the reactor (He or mixed He/O₂) was controlled at about 1000 mL/min by a Teledyne model HFC-202 flow meter and a Hastings digital flow controller (model 400). Helium was provided from a gas line with 99.999% purity. For the experiments with oxygen, oxygen was added to helium from a separate line containing 21% oxygen in helium, where its flow was controlled by another Teledyne model HFC-202 flow meter. The actual concentration of oxygen was measured by the gas analyzer connected to the outlet of the reactor. An oxygen concentration of about 10% was used in the low temperature experiments. For the high temperature experiments (oxidation) we needed to have about 1% oxygen to fully oxidize the char produced from the thermal decomposition; therefore, we chose values between 2.5 and 4% to avoid any limitation by the oxygen availabilities for the oxidation. The concentration of NO in the effluent gases from the reactor was continuously monitored and analyzed using a commercial gas analyzer (NGA 2000, MLT4 multi-gas analyzer manufactured by Rosemount Analytical Inc.). According to the manufacturer, this analyzer has nondisperse near-infrared detectors for CO, CO₂, NO, and NO₂ measurement and a paramagnetic detector for O₂ measurement. The measured IR data were computer recorded.

B. Materials. Samples of Burley, Bright, and Oriental tobaccos were ground into powders with an average particle size of 100 μ m. Cellulose with > 99% purity (Avicel) was purchased from FMC Corporation, and xylan was purchased from Sigma. Pectin samples were obtained from ACROS and Sigma. ACROS pectin contains about 20% sucrose. The Sigma pectin is extracted from citrus fruits and was essentially sucrose free. Elemental analysis of the pectin from Sigma showed that it contained about 0.42 wt % of nitrogen, about 7% ash, and about 2% metal, mostly sodium. Lignin was purchased from Aldrich. Potassium nitrate was purchased from J. T. Baker. All of the alkaloids, such as nicotine, cotinine, and myosmine, were purchased from Sigma. Ammonium carbonate, all the amino acids (proline, asparagine, phenylalanine), and zein (a protein found in corn) were purchased from ACROS. All materials were used as received. Other proteins such as albumin and bovine gamma globulin (BGG) were obtained from PIERCE. These proteins were provided in 0.9% aqueous NaCl solution. A 5-mL sample of each protein solution (10 mg of protein) was mixed with 90 mg of cellulose, and the mixtures were air-dried. The pectin mixtures could not be prepared by this method, because they became gelatinous and could not be dehydrated. The mixtures of KNO₃ with tobacco samples and biomass model compounds (cellulose, pectin, and xylan) were prepared by physical mixing. To ensure the effectiveness of the physical mixing, cellulose was treated with an aqueous solution of KNO₃ and then air-dried. The results from both mixing methods were similar. Therefore, physical mixing was used for preparing the mixtures tested in this study. The percentages reported for the mixtures are all on a weight basis.

RESULTS AND DISCUSSION

The results and discussions are divided into three parts. Part one describes our observations on NO formation from tobacco oxidation and pyrolysis studies. Part two covers the experimental results and discussions for NO formation at the low-temperature range, while part three covers those for NO formation at the high-temperature range, using model compound samples. By comparing the results of model compound samples with those of tobacco, we can determine the sources of NO formation during tobacco oxidation.

I. Observations from Tobacco Studies. The data in **Figure 2** shows the formation of NO from Burley tobacco for pyrolysis (Curve (a)) and oxidation (Curve (b)) processes. As shown in **Figure 2(b)**, the oxidation of Burley tobacco in an oxidative atmosphere in a flow tube reactor produced nitric oxide in two distinct temperature ranges, namely 275–375 °C and 425–525 °C. The ratio of NO formed at the high-temperature range to that at the low-temperature range was about 10. The formation of NO at the lower temperature range was observed under both pyrolysis and oxidative conditions in Burley tobacco. For the

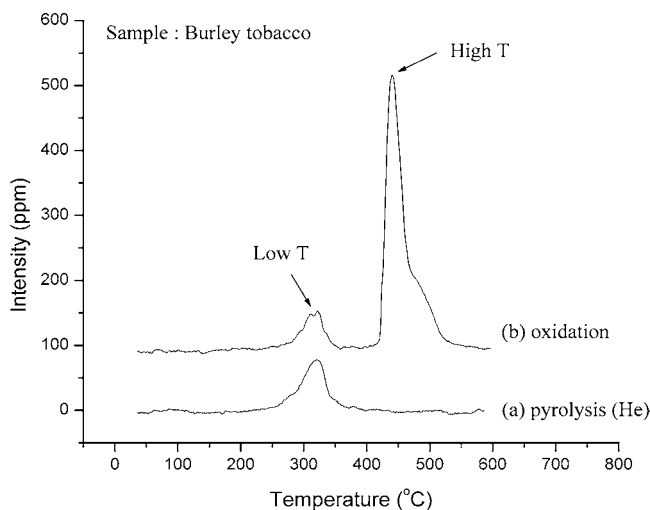


Figure 2. NO formation from (a) pyrolysis of Burley tobacco and (b) oxidation of Burley tobacco.

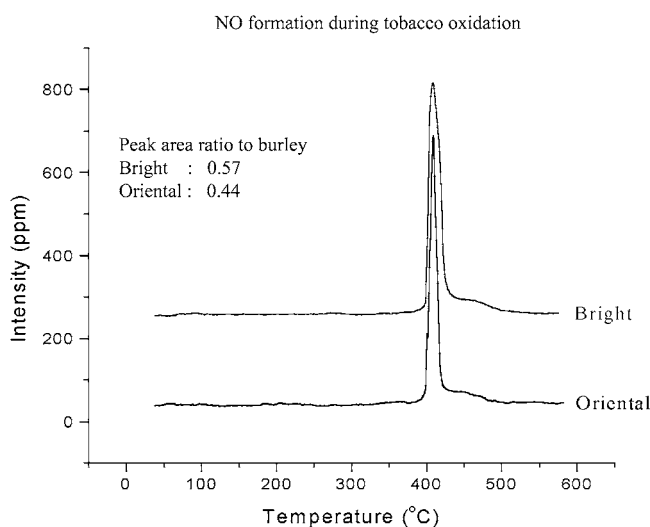


Figure 3. NO formation from two kinds of tobacco (Bright and Oriental) at the high-temperature range during oxidation.

high-temperature range, NO was only produced under oxidative conditions in Burley tobacco. In contrast, pyrolysis of other tobacco samples, namely Bright and Oriental tobaccos, produced no nitric oxide in either temperature range. However, as shown in **Figure 3**, the oxidation of these two tobacco samples did produce NO in the high-temperature range. When the peak area of the evolved NO for each tobacco was normalized to the same area for the Burley tobacco (**Figure 2(b)**), the ratios of 0.57 and 0.44 were obtained for Bright and Oriental, respectively. The peak area for Burley included both the low- and high-temperature NO. As shown in **Figure 4**, our experimental findings indicated that the yield of NO at the low temperature range is linearly proportional to the tobacco weight of Burley. The residual solid material (baseweb) sample was obtained after water-soluble components of Burley tobacco were removed by extraction with 60 °C water. This residual solid (baseweb), which presents about 50% of the starting tobacco, was further tested for its NO formation under both pyrolysis and oxidation conditions. **Figure 5** presents the results of the oxidation studies of Burley tobacco and its baseweb. The curve (a) in **Figure 5** represents NO intensity with temperature from the Burley tobacco, and the curve (b) is the NO intensity from the baseweb. The results indicated that the NO formation at low-temperature

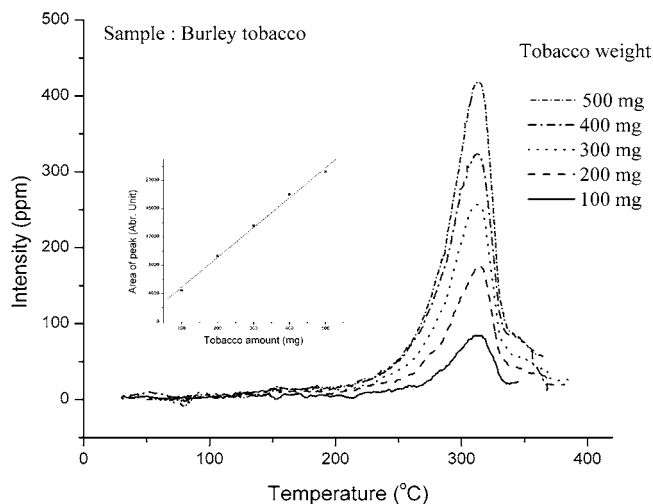


Figure 4. NO formation at the low-temperature range as a function of tobacco mass.

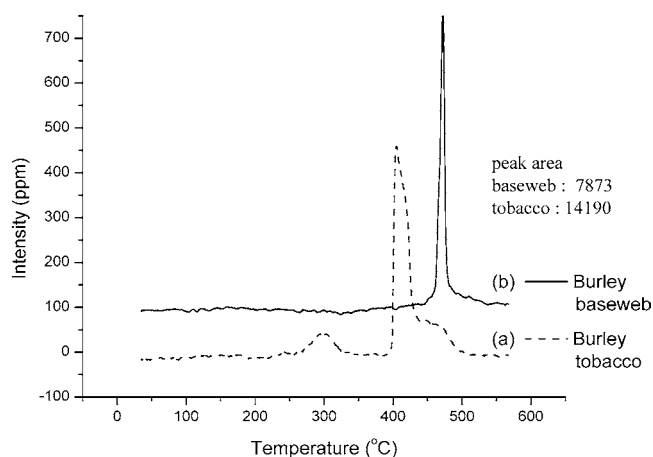


Figure 5. Comparison of NO formation between (a) Burley tobacco and (b) Burley baseweb.

had disappeared, and the intensity of NO at high temperature was lowered (45% reduction) for the baseweb. The formation temperature was also shifted to a higher temperature when compared to its parent tobacco.

II. NO Formation at the Low-Temperature Range. In tobacco, compounds such as cellulose, pectin, xylan (a major component of hemicellulose), and lignin are known to be major structural biopolymers and constitute a large percentage of the total mass. Consequently, each of these four compounds was used as a matrix sample for the model studies, combined with an NO source.

From the above observations, NO formation at the low-temperature range showed the following characteristics: no oxygen effect, high tobacco selectivity (i.e., from Burley tobacco only), and a linear dependency on the tobacco weight. These observations indicated that the source(s) of NO formation at the low-temperature range could be attributed to a compound that decomposes at low temperatures and should exist only in Burley tobacco. In addition, the source(s) should be hot-water-soluble compounds, because the Burley baseweb does not produce NO at the low-temperature range.

The distribution of the nitrogenous compounds in each of the tobacco samples was determined by Hempfling (23), and **Table 1** summarizes the amount of various classes of nitrogen in wt % of tobacco weight. The amounts can be classified as two types: water-soluble nitrogen and water-insoluble nitrogen.

Table 1. Nitrogenous Compounds Distribution in Tobaccos (Unit: wt %)

nitrogen compounds	tobacco		
	burley	bright	oriental
total nitrogen	4.97	2.82	2.38
(ratio to burley)	(1.00)	(0.57)	(0.48)
water insoluble nitrogen	1.84	1.23	1.10
water soluble nitrogen	nitrate nitrogen	0.46	0.01
	NH ₃ nitrogen	0.42	0.01
	others	2.25	1.57
		0.05	1.22

Water-soluble nitrogen consisted of nitrate nitrogen, ammonium salt nitrogen, and other soluble nitrogen sources such as alkaloids (including nicotine) and amino acids. The data in **Table 1** indicate that among water-soluble nitrogen, nitrate and ammonium nitrogen are much higher in Burley tobacco compared to Bright and Oriental, while the comparable amount of other soluble nitrogen is present in all three tobaccos. Therefore, one could predict that nitrate and/or ammonium nitrogen could be the sources of NO formation at the low-temperature range. To verify this point, we need to test salts of nitrates and ammonium in a tobacco sample. Potassium is the most abundant metal ion in the tobacco, and its nitrate, which is also water soluble, could be a more preferable model compound representing nitrates of tobacco. For the ammonium salts, there are many compounds such as ammonium citrate, acetate, phosphate, oxalate, and carbonate that could be equally right model compounds. However, potassium nitrate and ammonium carbonate were chosen to be tested as the candidates of NO source.

Pyrolysis of mixtures of ammonium carbonate with each of the biomass model compounds did not produce NO when heated to 500 °C. This indicated that ammonium salts might not be the source for NO formation at the low-temperature range. When mixtures of KNO₃ with each of the biomass model compounds (cellulose, pectin, xylan, and lignin) were heated under both pyrolysis (inert) and oxidative conditions with 10% oxygen, they produced NO at the low-temperature range (see **Figure 6(a)**). These results indicated that at this temperature range oxygen has no effect on the formation of NO (see **Figure 6(b)**), which suggests that only nitrate ions could be the source for NO formation at lower temperatures. Nitrate fits well with the above

prediction in that it is water-soluble and is present in high concentration in Burley tobacco.

It is well known that alkaline and alkaline-earth nitrates (e.g., NaNO₃, KNO₃, Mg(NO₃)₂, etc.) decompose thermally to NO at temperatures above 500 °C through very complicated redox reactions (21). In the absence of oxygen, KNO₃ decomposes to nitrogen oxides at temperature above 500 °C. As seen in **Figure 7(a)**, nitrogen dioxide is produced to a greater extent than nitric oxide. In an oxidative environment, the onset of NO₂ formation appears to occur at slightly higher temperature than 500 °C. Nevertheless, at least up to this temperature, the formation of nitrogen oxides are insignificant (**Figure 7(b)**), and the results are hardly different from the experiment with no oxygen. However, in an acidic and reducing medium, such as a carbonaceous matrix of biomass, the formation of NO from nitrate ions can be promoted (19). The experimental results of biomass mixtures support this fact well; the mixtures of KNO₃ and biomass model compounds produce NO at the temperature range between 325 and 350 °C, with no effect of oxygen. The results from model compound oxidation match well with those of tobacco oxidation. When KNO₃ was mixed with Bright tobacco, NO formation was observed at the low-temperature range (see **Figure 8**). In the experiment with KNO₃, the proportion of salt to tobacco was much higher (10 times) than what naturally occurs in tobacco. The only reason for this high value was to clearly observe the effects of nitrates. All of these observations support the contention that nitrate ion is the source for NO formation at the low-temperature range in tobacco oxidation.

III. NO Formation at the High-Temperature Range. At the high temperature range, NO is produced only in an oxidative environment for all of the tobaccos. This indicated that the nitrogen oxidation reaction resulted in NO formation at the high-temperature range. There are several nitrogen sources in tobacco besides nitrate. Nitrate ions cannot be the source for NO at high temperatures, because Bright and Oriental tobacco (low in nitrate) also produce NO, and any nitrate present would have been decomposed at 400 °C. Even the partial oxidation studies of the mixtures of ammonium carbonate with each of the biomass model compounds did not produce NO when those were heated to 700 °C. This indicated that ammonium ions are not a source for NO formation at the high-temperature range.

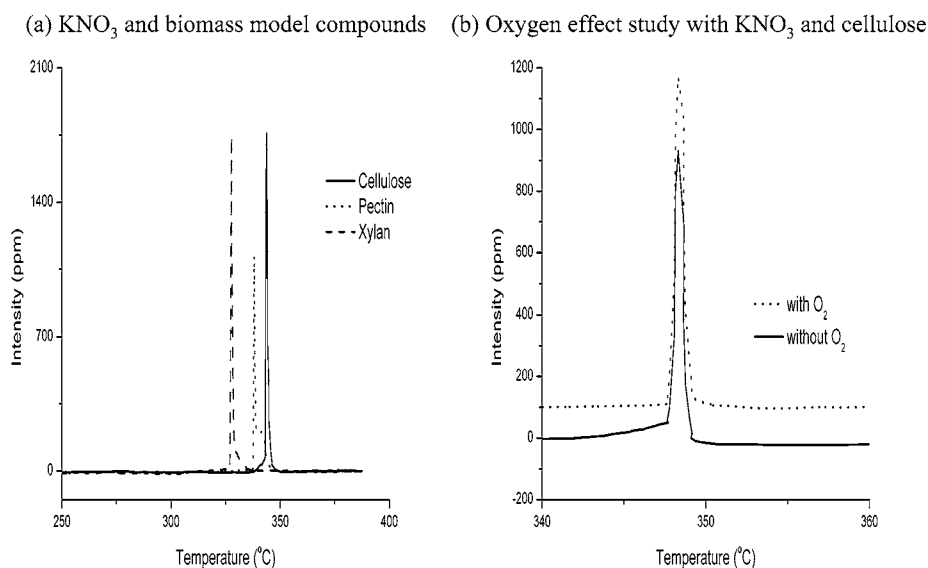


Figure 6. (a) NO formation at the low-temperature range from the mixtures of KNO₃ and biomass model compounds (cellulose, pectin, xylan, and lignin). (b) NO formation at the low-temperature range from the mixture of KNO₃ and cellulose with and without O₂.

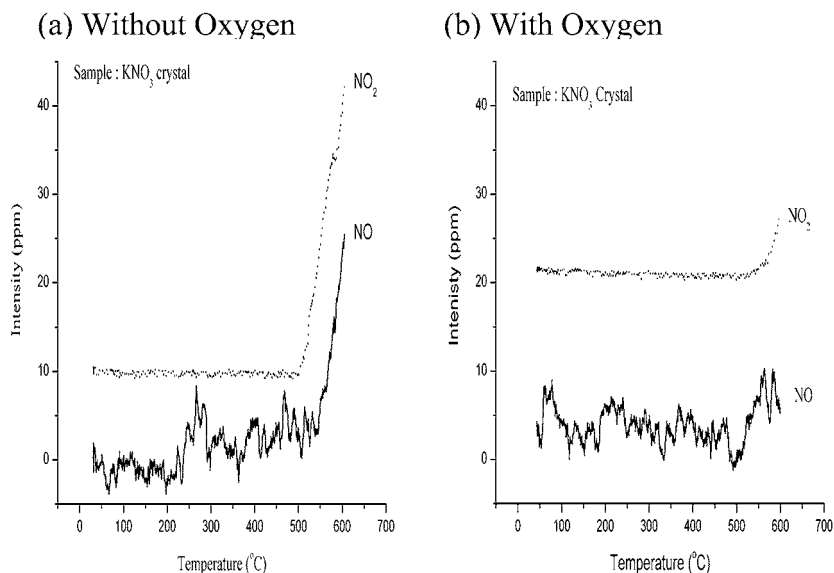


Figure 7. KNO_3 decomposition study in (a) an inert atmosphere and (b) the oxidative atmosphere.

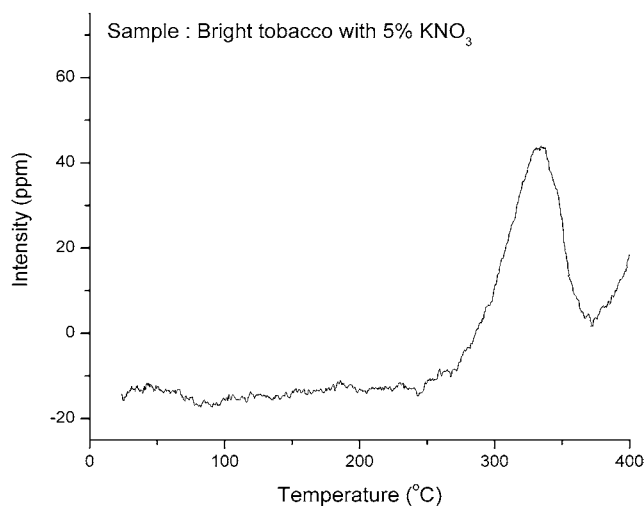


Figure 8. NO formation at the low-temperature range from the mixture of Bright tobacco and KNO_3 .

Other nitrogen sources in tobacco are nitrogenous organic compounds, such as amino acids, proteins, and alkaloids. The ratio of the NO peak areas in three types of tobacco (Burley/Bright/Oriental = 1.0:0.57:0.44) is very similar to that of the total nitrogen weight distributions (Burley/Bright/Oriental = 1.0:0.57:0.48) as shown in **Figure 3** and **Table 1**, respectively. Because it was observed that water-extracted tobacco (baseweb) produced less NO than its parent tobacco, the source compounds should be at least partially soluble in 60 °C water. These observations lead to the prediction that nitrogenous organic compounds could be responsible for NO formation at the high-temperature range. Because of this assumption, three amino acids (proline, asparagine, and phenylalanine), three proteins (albumin, BGG, and zein), and three alkaloids (nicotine, cotinine, and myosmine) were selected and tested for NO formation.

Most amino acids decompose from 300 to 350 °C, and those tested in this work did not individually produce NO during their oxidation. To examine NO formation at the high temperature range, oxidation studies were conducted using amino acids, proteins, and alkaloids chosen above and mixed with each of four biomass model compounds (cellulose, pectin, xylan, and lignin). **Figure 9** presents the results of the oxidation experi-

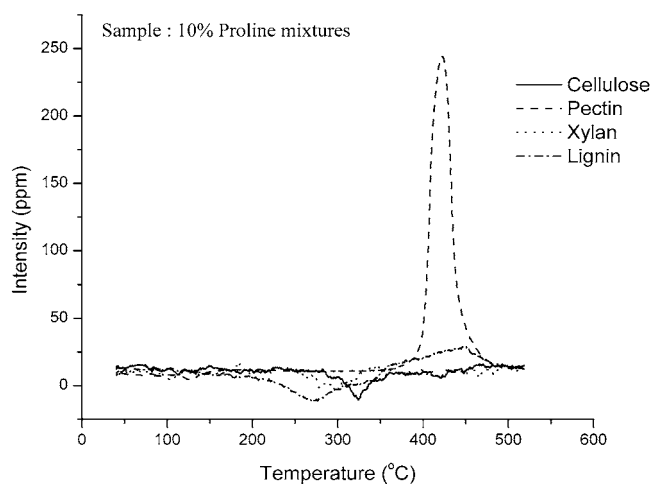


Figure 9. NO formation from the mixtures of proline with biomass model compounds (cellulose, pectin, xylan, and lignin) under oxidative condition.

Table 2. NO Formation Results from Tests with Various Model Mixtures at 425–525 °C with 3% O_2 in He

biomass N-compounds	cellulose	cellulose + sucrose ^a	cellulose + 2% KCl	pectin	xylan	lignin
proline	no	no	no	yes	no	no
asparagine	no	no	no	yes	no	no
phenylalanine	no	no	no	yes	no	no
zein	no	n/t	n/t	yes	no	no
albumin	no	n/t	n/t	n/t	n/t	n/t
BGG	no	n/t	n/t	n/t	n/t	n/t
nicotine	no	n/t	n/t	no	no	no
cotinine	no	n/t	n/t	no	no	no
myosmine	no	n/t	n/t	no	no	no
ammonium salt	no	n/t	n/t	no	no	no

^a n/t = not tested.

ments from the mixture of proline with several biomass model compounds, including pectin. The oxidation experiments with the biomass model compounds such as cellulose, xylan and lignin did not produce any measurable NO. These results clearly indicated that only the pectin mixture with proline produced NO at the high-temperature range. **Table 2** summarizes the results of the oxidation studies from various mixture combina-

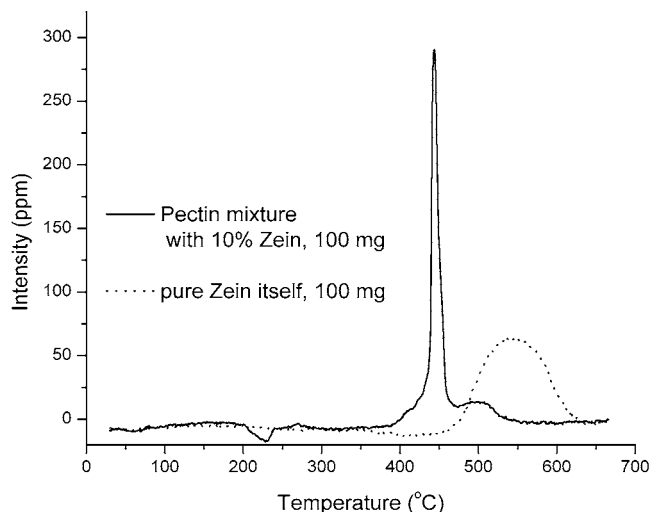


Figure 10. NO formation study from the mixtures of zein and pectin (solid line) and zein itself (dotted line) during the oxidation process.

tions. The data in **Table 2** shows that amino acids, when mixed with pectin, produce NO.

Zein is a protein obtained as solid form, and four mixtures of biomass model compounds with zein were readily prepared by physical mixing. Other proteins, such as albumin and BGG, were provided in solution, and only cellulose mixtures for these two proteins were prepared. The cellulose mixtures of these three proteins did not produce NO during the oxidation process. Similarly, as shown in **Table 2**, neither did the xylan mixture of zein produce NO. During oxidation, however, the pectin mixture of zein produced NO at the same temperature range as tobacco or other amino acids mixtures with pectin, as shown in **Figure 10** and **Table 2**. Even the pattern and the temperature of NO formation was the same as those of the other amino acids. Unlike amino acids, zein itself could produce NO during the oxidation (see **Figure 10**). However, the pattern and the temperature range of NO formation from zein itself were quite different from those of the pectin mixture. These observations indicate that proteins may also interact with pectin to produce NO during tobacco oxidation.

Alkaloids are another type of organic nitrogenous compound found in tobacco leaves. Nicotine, cotinine, and myosmine are some of the major tobacco alkaloids, and are also commercially available. These were selected and examined as mixtures with cellulose, pectin, xylan, and lignin. The mixtures of individual alkaloids with any of these biomass model compounds did not produce NO (see **Table 2**). The alkaloids evaporate at low temperatures before an interaction between the alkaloids and biomass compounds becomes possible. Thus, alkaloids may not be considered a possible source for NO formation.

Commercial pectin samples are not as pure as the cellulose used in this study. They usually contain some quantity of sugar and/or inorganic salts. The effect of sugar (typically sucrose) and inorganic salt on NO formation at the high temperature range was also examined. For the sugar test, cellulose with 10% sucrose was used, and for the inorganic salt, 2% of KCl was added. The rationale for choosing potassium chloride was a high level of potassium that naturally occurs in tobacco, which also promotes the formation of carbonaceous char at low temperature during the pyrolysis. The anions have a secondary role, and chlorine ion is found more readily than other anions in tobacco. The oxidation of cellulose-sugar and cellulose-KCl mixtures did not produce NO when mixed with 10% proline, asparagine, or phenylalanine. This indicated that the sugar or the inorganic

salt were not an important factor on NO formation at the high-temperature range (see **Table 2**).

Among the many organic nitrogenous compounds tested here, only the pectin mixtures with three amino acids and a protein (zein) produced NO during their oxidation at high temperature. These results suggest that pectin plays an important role in NO formation from amino acids and/or proteins. To better understand the role of pectin on the formation of NO, mixtures of pectin and 10% proline were heated to 350 °C in a partially oxidizing atmosphere. Most biomass materials decompose to produce char in the temperature range of 220 to 350 °C. In this temperature range, the char rarely oxidizes, and no measurable NO is produced from the char oxidation. When the char obtained from the above temperature range is further heated to higher temperatures in an oxidation condition, NO is produced. The observation on the pectin/proline char suggests that the nitrogen from the proline (amino acids) must have been incorporated into the char matrix during the thermolysis, which forms NO upon further heating and oxidation. Therefore, we propose that during the thermolysis process, amino acids and/or proteins interact and cross-link with pectin to form a nitrogen-rich char (char-N). Subsequently, char-N is oxidized in an oxygen-containing environment to form NO (22). The detailed mechanisms of nitrogen fixation on char are currently under investigation.

CONCLUSIONS

Low-temperature and high-temperature sources for NO formation from tobacco oxidation have been identified. The NO formation at the low temperature (275–375 °C) showed independence of oxygen presence, high tobacco selectivity (Burley tobacco only), and linear dependence on the amount of tobacco. The source for NO formation at the low temperature range was identified as nitrate ions in tobacco. Nitrate ions decompose to NO, probably due to the reducing nature of the carbonaceous char. The NO formation at high temperatures (>400 °C) showed a strong oxygen dependence and no tobacco selectivity. The sources for NO formation at the high-temperature range are the nitrogen-containing organic compounds, viz. amino acids and proteins. Before the NO formation at high temperatures, amino acids and proteins react with pectin at a temperature below 400 °C to produce a nitrogen char. Subsequent combustion of this char at higher temperatures produces NO.

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