

# Volatile Products Formed in the Thermal Decomposition of a Tobacco Substrate

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**ABSTRACT:** The identification and quantification of volatile species formed in the thermal degradation of tobacco substrates was investigated by TG-FTIR analysis. A specific experimental methodology was developed to obtain quantitative data on key components of interest present in evolved gases during TG-FTIR runs in air and nitrogen at low heating rates. Multivariate deconvolution techniques were used to identify the contributions of the key components of interest to the overall FTIR spectra. Validation runs were carried out to test the limits of the TG-FTIR technique. Significant data were obtained for the quantitative characterization and the emission profiles of some key components of evolved gases, such as acetaldehyde, carbon dioxide, carbon monoxide, nicotine, and water. A different experimental strategy based on the use of a fixed bed reactor was applied to the characterization of glycerol evolved from the tobacco substrate, thus obtaining a complete figure of the main components of the evolved gases formed during the slow thermal decomposition of tobacco substrates in nitrogen and air.

## 1. INTRODUCTION

The identification and quantitative characterization of evolved gases formed in the thermal degradation of biomass substrates is a critical issue in the development, scale-up, and optimization of thermal-based biomass valorization processes. A huge number of applications are reported for biomass slow pyrolysis, ranging from the energy sector to food preparation.<sup>1,2</sup> The investigation of slow pyrolysis and thermal decomposition of tobacco substrates is of importance in the tobacco industry. The process of cigarette smoking is complex, involving pyrolysis, as well as oxidation and secondary reactions. The characterization of volatile species evolution during tobacco pyrolysis is thus crucial for improved product design.<sup>3</sup>

Several experimental techniques are proposed for the quantitative analysis of volatiles evolved during the slow pyrolysis of biomass: e.g., gas chromatography (GC),<sup>4</sup> gas chromatography coupled with mass spectrometry (GC/MS),<sup>4–6</sup> high-performance liquid chromatography (HPLC), and HPLC/MS.<sup>6</sup> In recent years, thermogravimetry (TG) coupled to Fourier Transform Infrared (FTIR) spectrometry was proposed as an effective screening tool for the quantification of products formed in the thermal degradation of organic substrates.<sup>3,7–12</sup> Barontini et al. applied the TG-FTIR technique to the characterization of gaseous products generated in the thermal decomposition of brominated flame retardants and flame retarded materials.<sup>13–17</sup>

A specific calibration technique allowing a straightforward quantitative analysis of evolved gases was proposed by Marsanich et al.<sup>18</sup>

The methodology was successfully applied to the quantification of specific compounds evolved during TG runs, such as hydrogen bromide, ammonia, and several other species.<sup>14,16,17</sup> However, the applications to date were limited to a direct analysis of FTIR spectra, without the integration with a deconvolution procedure. Thus, the application of the methodology was limited to rather “simple” evolved gas mixtures, where the absorbance of the single species considered could be clearly identified and interference from other species on specific wavelength regions selected for the analysis could be reasonably neglected.<sup>13–19</sup>

The present study focused on the quantitative analysis of evolved gases from a tobacco substrate. Thermogravimetry coupled to FTIR analysis of evolved gas was applied to the quantitative determination of compounds formed in the slow pyrolysis and thermal decomposition of tobacco samples. Eight representative key components of interest were considered: acetaldehyde, carbon dioxide, carbon monoxide, glycerol, isoprene, nicotine, phenol, and water. These compounds were selected since they are representative of the more significant categories of compounds emitted in the pyrolysis or slow combustion of tobacco.<sup>3,8</sup> In particular, carbon dioxide, carbon

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monoxide, and water are very important products formed in combustion processes. Acetaldehyde and phenol are representative of aldehydes and phenols, respectively, while isoprene represents a typical aliphatic compound. Nicotine is of key interest in tobacco pyrolysis and combustion. Since the tobacco substrate contained glycerol as an aerosol-former, this compound was expected as well to be a main component of evolved gases during the pyrolysis or combustion of the tobacco sample.

The methodology developed by Marsanich et al.<sup>18</sup> was coupled to a specific multivariate deconvolution technique to obtain the emission profiles and to identify the quantities of evolved gases formed in the TG-FTIR runs. Multivariate chemometric deconvolution techniques based on iterative target transformation factor analysis (ITTFA) were successfully applied to the identification of single compounds in complex FTIR spectra collected during TG-FTIR experiments.<sup>3,8,9,20</sup> However, the potential of such techniques concerning the quantitative characterization of a complex mixture of volatile products still needs to be explored in detail. Thus, specific validation runs were carried out to assess the quality of the quantitative TG-FTIR data obtained.

Both pyrolysis (pure nitrogen) and slow combustion conditions were explored, in order to obtain a complete picture of the main compounds evolved in the thermal degradation of a tobacco substrate. Apparent kinetic data were obtained to assess and compare the evolution of the different key components. An alternative methodology was developed and applied to the determination of glycerol, since preliminary tests indicated that the TG-FTIR technique was not able to provide reliable results for this substance.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** The experimental runs aimed at the characterization of products in evolved gases were carried out on a tobacco substrate supplied by Philip Morris Products, S.A. The substrate was manufactured as described in a specific patent.<sup>21</sup> The sheet of homogenized tobacco material contained glycerol as an aerosol-former. The tobacco samples were supplied both in rods and as shredded tobacco material. Prior to the experiments, samples were stored 48 h at room conditions at a temperature between 25.0 and 26.2 °C, and humidity was maintained between 61 and 71%.

Both liquid and gaseous substances were used for calibration runs. The following standard gaseous mixtures supplied by SOL (Milan, Italy) were used for gas-pulse calibration runs: carbon monoxide/nitrogen, 0.200% CO mol/mol; carbon dioxide/nitrogen, 0.246% and 0.999% CO<sub>2</sub> mol/mol.

The following compounds supplied by Sigma-Aldrich (Milan, Italy) were used for vaporization-based calibration runs: acetaldehyde (>99.9% purity), isoprene (99.9% purity), nicotine (99.4% purity), and phenol (99.7% purity). Demineralized water was used in calibration runs. Carbon tetrachloride (99.9% purity) supplied by Baker (Milan, Italy) was used for the preparation of acetaldehyde, isoprene, nicotine, and phenol solutions.

The following compounds were used for validation runs: furfural (99.3% purity), furfuryl alcohol (98.7% purity), hydroxyacetone (95.4% purity), limonene (97.8% purity), supplied by Sigma-Aldrich (Milan, Italy), acetone (99.9% purity), and methanol (99.9% purity), supplied by Carlo Erba (Milan, Italy).

Glycerol (99.9% purity), butane-1,2,4-triol solution in pyridine (1000 mg/L), N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA), acetone, n-heptane, and pyridine were supplied by Sigma-Aldrich (Milan, Italy).

**2.2. Experimental Devices.** Simultaneous thermogravimetric (TG) and differential scanning calorimetry (DSC) data were obtained using a Netzsch STA 409/C thermoanalyzer. Constant heating rates of 5, 10, and 20 °C/min were typically used in experimental runs. Typical sample weights of 1–30 mg were employed. The atmosphere surrounding the samples was controlled using a continuous purge gas flow (60 mL/min) of pure nitrogen or air.

Differential Scanning Calorimetry (DSC) runs were carried out with a TA Instrument DSC Q2000. Constant heating rates of 5, 10, and 20 °C/min were used in experimental runs. Typical sample weights of 0.5–3 mg were employed. The atmosphere surrounding the samples was controlled using a continuous purge gas flow (50 mL/min) of pure nitrogen or air.

FTIR measurements were carried out using a Bruker Equinox 55 spectrometer equipped with DTGS and MCT detectors.

TG-FTIR simultaneous measurements for the online analysis of volatile compounds formed during TG runs were carried out coupling the FTIR spectrometer to the Netzsch thermoanalyzer using a 2 mm internal diameter Teflon tube. The 800 mm long transfer line and the head of the TG balance were heated at a constant temperature of 230 °C to limit the condensation of volatile decomposition products.

FTIR measurements were carried out with the MCT detector in a specifically developed low volume gas cell (8.7 mL) with a 123 mm path length, heated at a constant temperature of 250 °C. The gas flow from the TG outlet to the IR gas cell was of 60 mL/min and a residence time of 30 s in the transfer line could be evaluated for the evolved gases. This value was assumed as the time delay correction to be used for the comparison of TG and IR results. During TG-FTIR runs, spectra were collected at 4 cm<sup>-1</sup> resolution, coadding 16 scans per spectrum. This resulted in a temporal resolution of 9.7 s, more than sufficient to follow the gas evolution rates characteristic of TG runs at the heating rates used in the present work.<sup>13–17</sup>

Besides the conventional setup of the TG-FTIR coupling system, a modified configuration was used for calibration experiments of gaseous compounds (CO and CO<sub>2</sub>): the gas flow was sent from the gas supply to the transfer line head through a gas injection system consisting of a rotary sample valve allowing a carrier gas to purge a known-volume loop, previously filled with a calibration gas of known composition.<sup>18</sup> Thus, the system allows a known quantity of gas to be carried to the measurement cell by the carrier gas flow. Volumes of available loops were 3, 12, 50, and 200 mL.

A laboratory-scale fixed bed reactor (FBR) was used to carry out tobacco thermal decomposition runs in inert or oxidizing atmosphere. Constant heating rates of 5, 10, and 20 °C/min were used in experimental runs. The experiments were aimed at the recovery and characterization of the condensable fraction of evolved volatile products, specifically of glycerol. The scheme of the experimental apparatus is reported elsewhere.<sup>13,14</sup>

An Agilent 7890A gas chromatograph (GC) equipped with an autoinjector, a cool-on-column inlet, a DB-5 ht (5% phenyl, 95% methyl polysiloxane) capillary column (15 m length, 0.32 mm internal diameter, 0.1 µm film thickness), and a flame ionization detector (FID) was used for the quantitative determination of glycerol. A Fisons MD 800 mass spectrometer (MS) interfaced to a Fisons GC-8060 gas chromatograph was used for GC/MS analysis.

**2.3. Experimental Procedures for Runs on Tobacco Samples.** For TG-FTIR runs on tobacco samples, typical

Table 1. Composition of Mixtures Used in TG-FTIR Validation Experiments

component		Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7	Mix 8	Mix 9	Mix 10
acetaldehyde	(mg)	0.89	0	0	0.64	0	0	0	0	0	2.35
acetone	(mg)	0	0	0	0	0.59	0	0		0	1.51
carbon tetrachloride	(mg)	0	0	0	2.65	2.27	0	0	8.52	0	0
furfural	(mg)	2.17	0	2.28	0	0	1.43	2.14	0	0	0
furfuryl alcohol	(mg)	0	2.15	0	0	0	1.73	1.60	0	0	0
hydroxyacetone	(mg)	0	0	0	0	0.82	1.19	1.42	0	3.32	0
isoprene	(mg)	0	0	0	0.55	0.39	0	0	0	0	0
limonene	(mg)	0	1.26	0	0	0.68	0	0	1.26	0	0
methanol	(mg)	0	0	0	0.69	0	0	0		0	1.39
nicotine	(mg)	2.49	2.14	2.38	0	0	1.14	0	0	2.58	0
phenol	(mg)	0	1.96	1.78	0	0	0	1.35	0.98	1.32	0
water	(mg)	2.49	0	0	0	0	0	0	0	0	1.93

Table 2. Results of the Analysis of FTIR Calibrations Data<sup>a</sup>

component	$K$ (s mg <sup>-1</sup> )	$r$	$n_{\min}$ (mg)	$n_{\max}$ (mg)	$ES_a$ (mg)	$E_a$ (mg)	$E_{\max}$ (mg)
acetaldehyde	28.8	0.9776	0.309	1.60	0.102	0.089	0.155
carbon dioxide (high concentration range)	59.0	0.9983	0.014	3.657	0.065	0.052	0.138
carbon dioxide (low concentration range)	95.3	0.9998	0.014	0.225	0.0015	0.0012	0.0029
carbon monoxide	138.4	0.9999	0.007	0.466	0.0017	0.0014	0.0025
isoprene	51.6	0.9908	0.091	0.489	0.019	0.013	0.038
nicotine	30.7	0.9972	0.092	6.19	0.153	0.124	0.301
phenol	107.6	0.9995	0.087	3.11	0.030	0.021	0.069
water	46.5	0.9979	1.13	6.27	0.115	0.097	0.203

<sup>a</sup> $K$ : calibration constant;  $r$ : Pearson coefficient;  $n_{\min}$ : minimum quantity;  $n_{\max}$ : maximum quantity;  $ES_a$ : average square error;  $E_a$ : average error;  $E_{\max}$ : maximum absolute error.

sample weights of 15 mg and alumina crucibles (internal diameter, 5.5 mm; internal height, 4 mm) were used. TG-FTIR runs were carried out both on the shredded sample and on samples obtained from the tobacco rods. Tobacco rods were unrolled, and samples with diameter equal to crucible internal diameter were obtained through a hollow punch, each element weighing approximately 3.5 mg. During TG-FTIR runs the atmosphere surrounding the samples was controlled using a continuous purge gas flow (60 mL/min). Experimental runs were carried out using pure nitrogen or air (21% oxygen by mol). Constant heating rates of 5, 10, and 20 °C/min from 30 to 550 °C were used in experimental runs.

For DSC runs on tobacco samples, typical sample weights of 0.5–3 mg and aluminum crucibles (internal diameter, 5.0 mm; internal height, 2.3 mm) were employed. DSC runs were carried out on samples obtained from the tobacco rods. Tobacco rods were unrolled, and samples with diameter equal to crucible internal diameter were obtained, each element weighing approximately 2.8 mg. During DSC runs the atmosphere surrounding the samples was controlled using a continuous purge gas flow (50 mL/min). Experimental runs were carried out using pure nitrogen or air (21% oxygen by mol). Constant heating rates of 5, 10, and 20 °C/min from 30 to 550 °C were used in experimental runs.

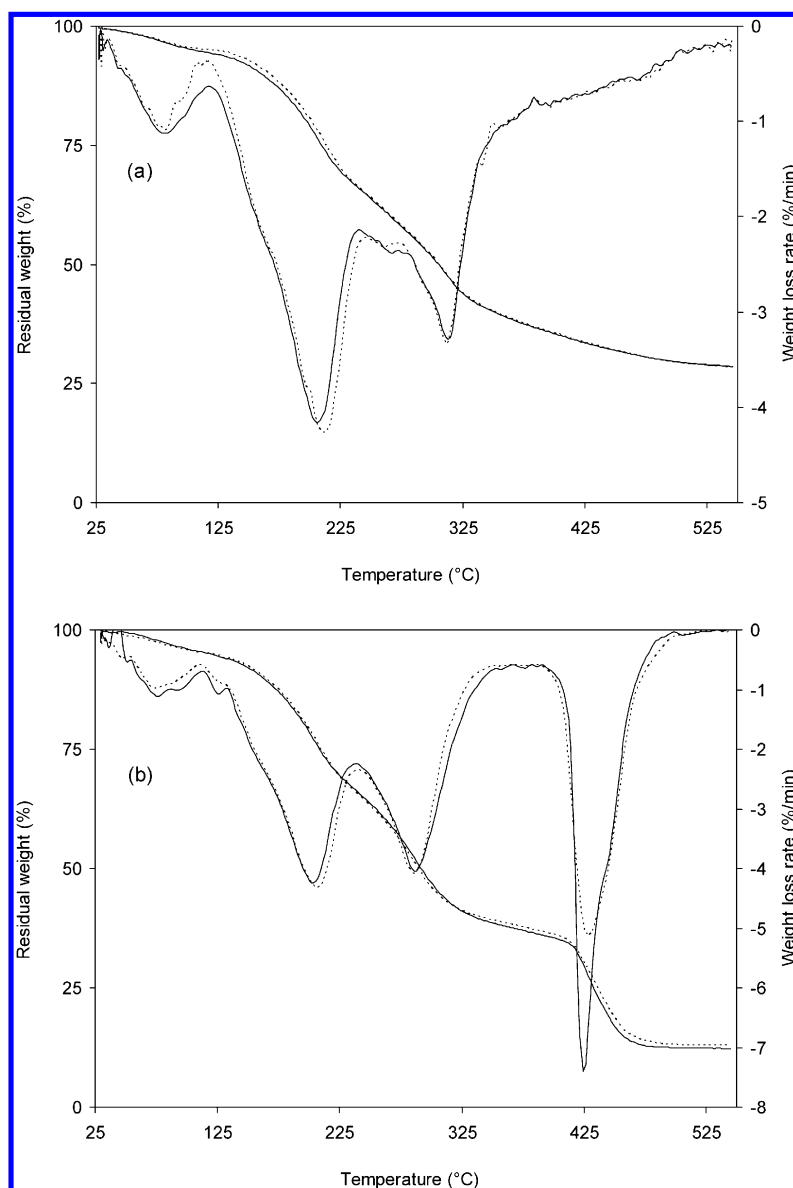
For FBR runs on tobacco samples, typical sample weights of 0.7–0.9 g of tobacco rods were used. During FBR runs the atmosphere surrounding the sample was controlled using a continuous purge gas flow (50L/h) of pure nitrogen or air. Constant heating rates of 5, 10, and 20 °C/min were used in experimental runs. Runs were carried out quenching the sample at the desired final temperature. Volatile products evolved during tobacco degradation were transferred by the purge gas flow in a train of cold traps, maintained at –20 °C by a sodium

chloride brine/ice bath, to allow the recovery of condensable products. Condensable products were recovered at the end of the run using acetone, n-heptane, and pyridine as solvents. The quantitative determination of glycerol in the collected solutions was performed according to the ASTM D6584 standard test method<sup>22</sup> (derivatization with N-methyl-N-(trimethylsilyl)-trifluoroacetamide followed by GC-FID analysis using butane-1,2,4-triol as internal standard).

**2.4. Experimental Procedures for the Calibration of the TG-FTIR System.** Two different procedures were applied in calibration runs: a gas-pulse method and a vaporization-based method.<sup>18</sup>

In the gas-pulse calibration method, a known quantity of the gaseous compound of interest was sent to the IR measurement cell using the gas injection device and the system configuration described in Section 2.2. As discussed above, loops of different volume were used for the experimental runs. A 100% nitrogen carrier gas flow rate of 60 mL/min (25 °C) was used. Calibration runs were carried out on carbon monoxide and carbon dioxide.

In the vaporization-based calibration method, TG-FTIR measurements were performed vaporizing liquid solutions of the compound of interest in the TG analyzer. At the beginning of each calibration run, a quantity of solution in the range of 1–20  $\mu$ L was inserted in a crucible using a chromatographic syringe. A pierced lid was typically positioned on the crucible, to limit evaporation caused by gas-phase diffusion at the beginning of the TG run. The initial weight of the sample and the composition of the solution allowed the calculation of the quantity of the compound of interest vaporized in the TG run. The use of solutions having different concentrations and of samples of different weight allowed the vaporization of different quantities of the compound of interest, which were carried to the FTIR



**Figure 1.** TG and dTG results obtained for the tobacco substrate (continuous lines: shredded sample; dotted lines: rod sample) using a 10 °C/min constant heating rate and a 60 mL/min purge gas. a) Pure nitrogen. b) Air.

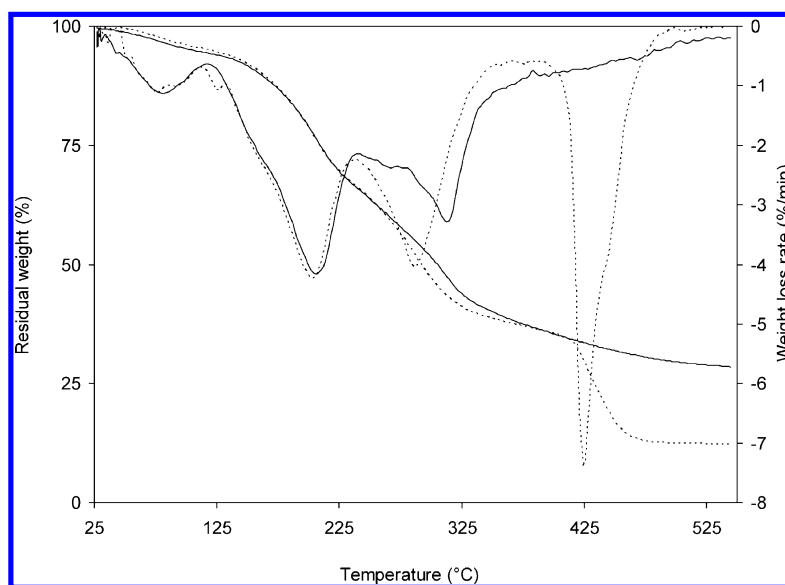
measurement cell by the carrier gas flow. The carrier gas was 100% nitrogen, and a gas flow rate of 60 mL/min was used. Experimental runs were performed on acetaldehyde, isoprene, nicotine, phenol, and water. Pure water was vaporized in water calibration runs. Vaporization of the pure compounds as well as vaporization of carbon tetrachloride solutions were used in acetaldehyde, isoprene, nicotine, and phenol calibration runs. The following temperature programs were used in experimental runs: i) water calibration runs: constant heating rate of 10 °C/min from 30 to 110 °C, then 15 min isothermal at 110 °C; ii) acetaldehyde and isoprene calibration runs: constant heating rate of 5 °C/min from 30 to 200 °C, then 10 min isothermal at 200 °C; iii) nicotine calibration runs: constant heating rate of 10 °C/min from 30 to 400 °C, then 20 min isothermal at 400 °C; and iv) phenol calibration runs: constant heating rate of 10 °C/min from 30 to 400 °C.

## 2.5. Experimental Procedures for Quantitative Evolved Gas Data Validation Experiments.

Validation

runs were performed on ten different mixtures. Table 1 reports the composition of the ten validation mixtures used. Validation mixtures were prepared mixing at least two different liquid components. Stock mixtures were prepared from pure materials by accurately weighing at least 0.1 g of each compound.

TG-FTIR validation experiments were performed vaporizing a known quantity of each mixture in the TG analyzer. At the beginning of each validation run, a quantity of mixture in the range of 2 to 10  $\mu$ L was introduced in an aluminum crucible using a chromatographic syringe. A pierced lid was typically positioned on the crucible, to limit evaporation caused by gas-phase diffusion at the beginning of the TG run. The initial weight of the sample and the composition of the stock mixture allowed the calculation of the quantities of the different components vaporized in the TG run, that were carried to the FTIR measurement cell by the carrier gas flow. The carrier gas was 100% nitrogen, and a gas flow rate of 60 mL/min was used.



**Figure 2.** Comparison of TG and dTG results obtained for the shredded tobacco sample in inert and oxidizing atmosphere using a 10 °C/min constant heating rate (continuous lines: nitrogen atmosphere; dotted lines: air).

**Table 3. Results of TG Runs Carried out on the Tobacco Substrate<sup>a</sup>**

sample form	heating rate (°C/min)	atmosphere	Region I (30–120 °C)			Region II (120–250 °C)		Region III (250–370 °C)		Region IV (370–550 °C)	
			WL (%)	WL (%)	$T_{\max}$ (°C)	WL (%)	$T_{\max}$ (°C)	WL (%)	$T_{\max}$ (°C)	WL (%)	$W_{550}$ (%)
shredded	5	N <sub>2</sub>	6.5	29.8	191	24.5	304	8.9	29.8		
rod	5	N <sub>2</sub>	7.3	30.8	194	24.1	300	8.8	28.5		
shredded	10	N <sub>2</sub>	4.7	30.2	207	26.0	314	9.7	29.2		
rod	10	N <sub>2</sub>	5.3	31.0	208	25.4	311	9.2	28.9		
rod, double weight	10	N <sub>2</sub>	5.7	30.9	224	24.7	307	9.2	29.4		
rod, half weight	10	N <sub>2</sub>	6.7	29.2	192	23.6	309	8.2	32.2		
shredded	20	N <sub>2</sub>	6.0	27.7	220	26.0	317	9.9	30.3		
rod	20	N <sub>2</sub>	8.4	28.2	222	24.7	314	9.5	29.1		
shredded	5	air	7.5	30.2	189	25.4	278	22.8	14.0		
rod	5	air	7.7	30.6	189	24.0	276	23.3	13.6		
shredded	10	air	5.6	31.1	204	26.2	287	25.4	11.5		
rod	10	air	4.8	32.0	205	25.4	284	24.7	12.9		
shredded	20	air	6.0	27.9	220	25.7	297	25.4	14.9		
rod	20	air	6.8	29.0	222	23.7	289	25.8	14.5		

<sup>a</sup>WL: weight loss;  $W_{550}$ : residual weight at 550 °C;  $T_{\max}$ : maximum devolatilization rate temperature.

The following temperature programs were used in experimental runs: i) constant heating rate of 10 °C/min from 30 to 110 °C, then 15 min isothermal at 110 °C (Mix 4 in Table 1); ii) constant heating rate of 5 °C/min from 30 to 200 °C, then 10 min isothermal at 200 °C (Mix 10 in Table 1); and iii) constant heating rate of 10 °C/min from 30 to 400 °C, then 20 min isothermal at 400 °C (Mixes 1, 2, 3, 5, 6, 7, 8, and 9 in Table 1).

### 3. METHODOLOGY FOR QUANTITATIVE EVOLVED GAS ANALYSIS

**3.1. Deconvolution of FTIR Data.** The analytical approach used in the present study involved multivariate data deconvolution. The approach is based on the statistical techniques of Principal Component Analysis (PCA) (also called Factor Analysis (FA)). A variation of FA in the form of Parallel Factor Analysis (PARAFAC)<sup>23–27</sup> in combination with a curve resolution (deconvolution) technique called Iterative Target

Transformation Factor Analysis (ITTFA) was used.<sup>25,26,28,29</sup> The combined techniques may be summarized as follows:

1. The multivariate spectral data of the target components with known quantities were analyzed in parallel with the unknown mixture data collected as a function of time under the same experimental conditions.

2. FA and ITTFA were used to identify the presence of a target component by submitting a test vector of a known spectrum and using the optimum number of factors suggested by FA in the data to model it.

3. The abstract output of the FA spanning the time direction of the data for both known (calibration) and the unknown samples were transformed by the ITTFA process with a least-squares process to yield real physically meaning responses curves.

ITTFA has the ability to determine the presence of a known target (spectrum) in the presences of other unknown entities and therefore enables deconvolution of the target in very complex mixture data similar to the ones analyzed in this study.

**3.2. Quantification of the Key Components in Evolved Gases.** As described in Section 2, pulse calibration techniques were used for the quantitative analysis of TG-FTIR data.<sup>18</sup> In calibration runs known quantities of the key components of interest were sent to the FTIR gas cell. The gas flow rate and the FTIR acquisition parameters were kept constant and equal to those used in calibration runs and in runs carried out on validation mixtures.

The deconvolution process yielded response curves for each component in both calibration and sample runs. The integration with respect to time of the response curve yields a quantity,  $D$ , that is related to the quantity of the species,  $n$ , that flows through the FTIR measurement cell during the  $(t_1, t_2)$  time interval<sup>18</sup>

$$D = \int_{t_1}^{t_2} \text{Response} \cdot dt = K \cdot n \quad (1)$$

where  $K$  is a calibration constant.

The time integrals of the response profiles and the known quantities of substance in calibration runs were used to generate calibration curves, which were then applied to assess the quantities of the key components in evolved gas during TG-FTIR runs carried out on tobacco samples and on validation mixtures (eq 1).

The values of the calibration constants,  $K$ , calculated by linear regression for each of the key components of interest are reported in Table 2. Table 2 includes the values obtained for the Pearson correlation coefficient, the average square error, the average error, and the maximum absolute error of calibration data.

The results obtained for carbon dioxide were influenced by the concentration range of the calibration standards. Two standard gaseous mixtures with quite different concentrations of  $\text{CO}_2$  were used in calibration runs (0.246% and 0.999% mol  $\text{CO}_2$  in  $\text{N}_2$ ). This resulted in data well correlated for the two concentration regions, while the overall calibration curve showed a poor fit. The carbon dioxide concentration during TG-FTIR runs on tobacco samples was in the low concentration region for runs in nitrogen atmosphere and in the high concentration region for runs in air. Thus, the “low” and the “high” range calibration constants in Table 2 were used respectively for the runs in nitrogen and in air.

**3.3. Apparent Kinetic Model for the Emission of Evolved Gases.** The emission profiles of the gaseous compounds with respect to time obtained by the FTIR data were analyzed in order to propose an apparent kinetic model relevant to the pyrolysis and slow combustion processes. The apparent kinetic model was developed with the only aim of comparing the emission profiles and obtaining further insights on the formation of gaseous decomposition products by an assessment of the apparent kinetic parameters. Thus, the analysis was performed only on the temperature range between 100 and 400 °C.

The definition of apparent kinetic equations is suitable for the analysis of well-defined emission phenomena, dominated by thermally activated processes. Therefore, low rate emissions, which are spread on a very broad range of temperatures, cannot be effectively modeled. Hence, the kinetic analysis was limited to the main peaks of evolved gas emission in the range of temperatures previously identified. The peaks analyzed were delimited by the identification of a reference baseline. The quantity emitted in each peak considered for the kinetic analysis was calculated by numerical integration.

A multiple-step lumped reaction model was applied to fit experimental data. The kinetic model was based on an apparent conversion parameter ( $\xi_j$ ). The basic link between the experimental data and the apparent conversion parameters is the following

$$D_t = \sum_{j=1}^{n\_step} \left( \alpha_j \cdot \frac{d\xi_j}{dt} \right) \quad (2)$$

where  $\alpha_j$  is the total mass emitted by step  $j$  and  $D_t$  is the emission rate at the time  $t$  (mass emitted per unit of time) as recorded in the test. The conversion parameter for the generic step  $j$  can be obtained rearranging eq 2

$$\xi_j = \frac{1}{\alpha_j} \cdot \int_0^t \left( D_t - \sum_{k=1}^{j-1} \left( \alpha_k \cdot \frac{d\xi_k}{dt} \right) \right) \cdot dt \quad (3)$$

where the subscript  $k$  refers to the emission steps occurred before the  $j$ th step under assessment.

An Arrhenius rate equation was used to model the kinetics of the emission in each step

$$\frac{d\xi_j}{dt} = k_j \cdot (1 - \xi_j)^{n_j} = A_j e^{-E_j/RT} (1 - \xi_j)^{n_j} \quad (4)$$

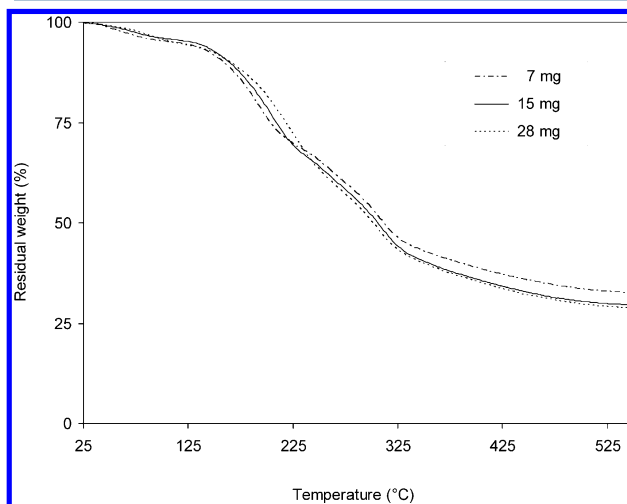
where  $A_j$  is the apparent pre-exponential factor for step  $j$ ,  $E_j$  is the activation energy for step  $j$ ,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $n_j$  is the apparent reaction order.

A best fit approach was applied to calculate the parameters of the kinetic equation. This was based on a linear regression of the Arrhenius plot.

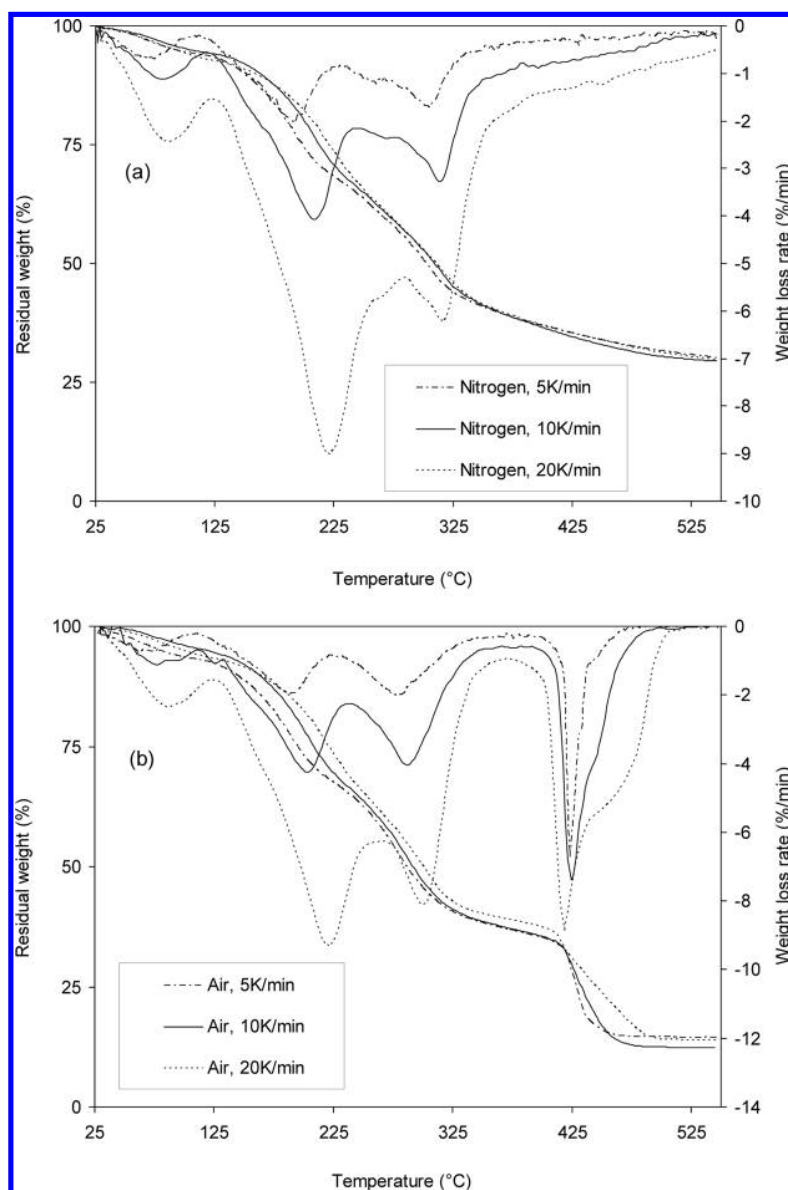
Discrete values were chosen for the reaction order ( $n_j$ ). In particular, the following set of values was tested for each emission step, selecting the one that yielded the most linear correlation on the Arrhenius plot for the range of data of interest: [0; 0.5; 1; 1.5; 2].

## 4. RESULTS AND DISCUSSION

**4.1. Thermal Decomposition of the Tobacco Substrate.** TG-FTIR runs were carried out both on the shredded tobacco sample and on samples obtained from the tobacco



**Figure 3.** TG results obtained for the tobacco rod sample with different initial sample weights (nitrogen atmosphere, 10 °C/min heating rate).



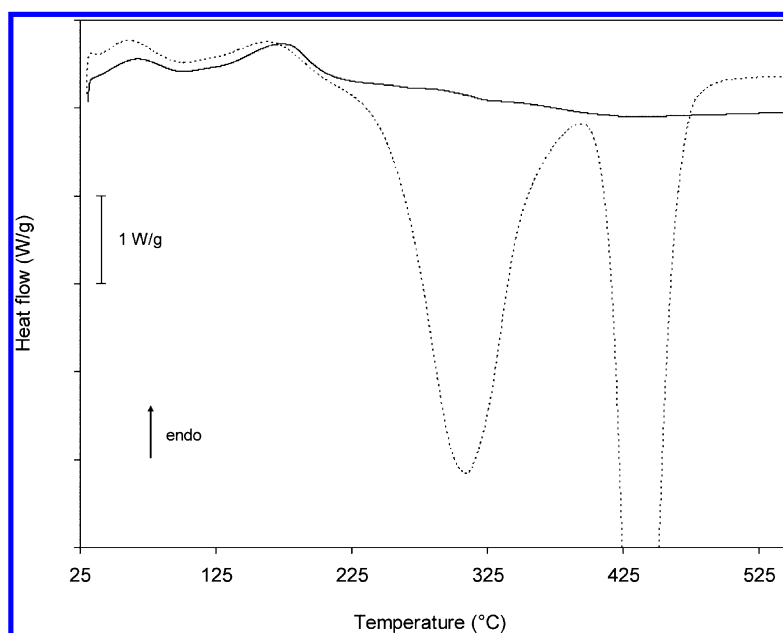
**Figure 4.** TG and dTG results obtained for the shredded tobacco sample at different heating rates. a) Nitrogen atmosphere. b) Air.

rods, in order to investigate the possible influence of sample grinding on the thermal decomposition process of the tobacco substrate. Figure 1 reports the residual weight and the weight loss rate as a function of temperature obtained in TG runs carried out in inert and oxidizing atmospheres at a 10 °C/min constant heating rate on a shredded tobacco sample and on a sample obtained from a tobacco rod. Unless otherwise stated, the TG and dTG data reported in the present study were calculated as the mean of at least three experimental runs.

The analysis of the differential thermogravimetric (dTG) curves allows observing the presence of 4 regions of weight loss, both in inert and oxidative conditions. The first region (Region I: 30–120 °C) is related to the release of moisture. The second and the third regions (Region II: 120–250 °C; Region III: 250–370 °C) are related to a two-stage thermal decomposition and evaporation phenomena. The fourth region (Region IV: 370–550 °C) is related to a further thermal decomposition (runs in nitrogen) or to a combustion (runs in air) of the residue obtained from the primary decomposition process.

A direct comparison of the weight loss behavior in inert and oxidizing atmosphere for the shredded sample is shown in Figure 2. A slightly lower temperature was observed in air for the maximum in the weight loss rate in Region III with respect to results obtained in nitrogen. In order to better understand the thermal decomposition behavior, TG runs in nitrogen atmosphere were carried out heating the sample to 200 or 300 °C (10 °C/min heating rate) and keeping it in isothermal conditions at the final temperature for one hour. The TG and dTG results obtained suggest that no further decomposition occurs during the isothermal period of the run at the temperatures considered. Thus, the decomposition phenomena up to 300 °C are completed during the heating of the sample at the low heating rates used in the present study (5–20 °C/min).

Table 3 reports the average values obtained for the weight losses related to the weight loss regions identified, in all the experimental conditions explored in the present study. The temperatures values corresponding to the maximum devolatilization rate are also included in Table 3. The data reported in



**Figure 5.** DSC results obtained for the tobacco substrate in inert and oxidizing atmosphere at 10 °C/min heating rate (continuous line: nitrogen atmosphere; dotted line: air).

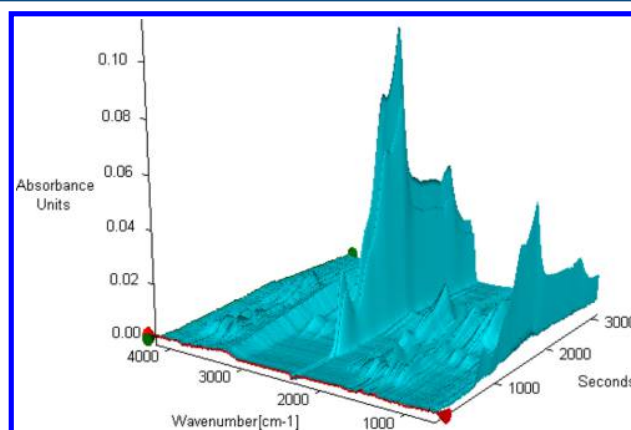
the table were calculated as the mean of at least three experimental runs. The standard deviation values of weight loss and temperature data were typically less than 1% and 2 °C, respectively.

The results shown in Figure 1 and Table 3, which include data obtained at the different heating rates used in the present study, reveal that sample grinding has a negligible influence on the results of TG runs.

In order to check the influence of sample mass on the thermal degradation behavior, TG-FTIR runs in nitrogen atmosphere were carried out on samples with different initial weight. Figure 3 reports the results obtained for samples having a weight respectively half and double with respect to that used in standard runs (15 mg). As shown in Figure 3 and Table 3, in the range analyzed, sample weight has a limited influence on the results of TG runs. However, an increase in sample weight resulted in a limited shift toward higher temperatures of the devolatilization in Region II.

Figure 4 shows the results obtained for the shredded sample at three different constant heating rates (5, 10, and 20 °C/min), using pure nitrogen or air as a purge gas. As expected, increasing the heating rates resulted in slightly increased devolatilization temperatures.

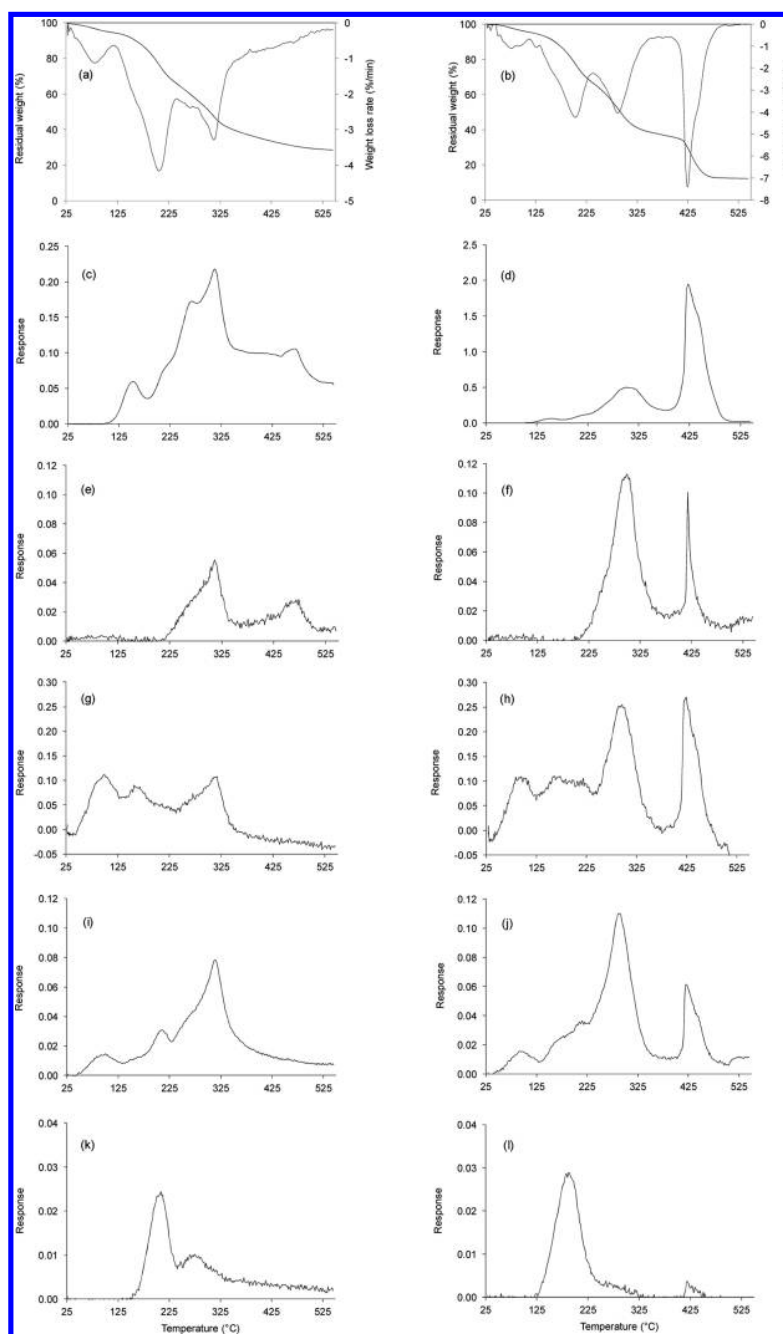
Although the present study did not focus specifically on the investigation of the thermal effects of the decomposition process of the tobacco substrate, DSC runs were performed to obtain a better insight into the substrate degradation behavior. Figure 5 reports the DSC curves obtained at a 10 °C/min constant heating rate using pure nitrogen or air as purge gas. A first endothermic peak is evident at temperatures lower than 100 °C, which may well be related to moisture evaporation. In nitrogen atmosphere, a second endothermic peak is observed in the 100–250 °C temperature range, while no clear thermal effect may be detected at temperatures higher than 250 °C. Using air as purge gas, no difference is observed with respect to runs carried out in nitrogen up to 230 °C. At higher temperatures, two exothermic peaks are observed. These results



**Figure 6.** Stack plot of FTIR spectra of evolved gases in the TG run showed in Figure 1 (shredded tobacco sample, nitrogen atmosphere, 10 °C/min heating rate).

agree with the behavior observed in TG runs: the presence of oxygen has a negligible influence on the first stage of tobacco thermal decomposition (Region II), but it clearly affects the second stage (Region III). A strong exothermic effect is finally associated with the combustion of the residue (Region, IV, 400–500 °C). Qualitatively similar results were obtained using heating rates of 5 and 20 °C/min. Average values of 128 ( $\pm 6$ ) J/g and 141 ( $\pm 10$ ) J/g were obtained for the thermal effect corresponding to the endothermic peak in Region II respectively for nitrogen and air purge gas flows.

**4.2. Emission Profiles of Key Components in Evolved Gases.** Figure 6 shows an example of the cascades of FTIR spectra obtained for the evolved gases in TG-FTIR runs carried out on the tobacco substrate. The deconvolution procedure described in Section 3 was applied to these data, yielding response profiles as a function of time for the key components of interest. Figure 7 reports the emission profiles of acetaldehyde, carbon dioxide, carbon monoxide, nicotine, and water



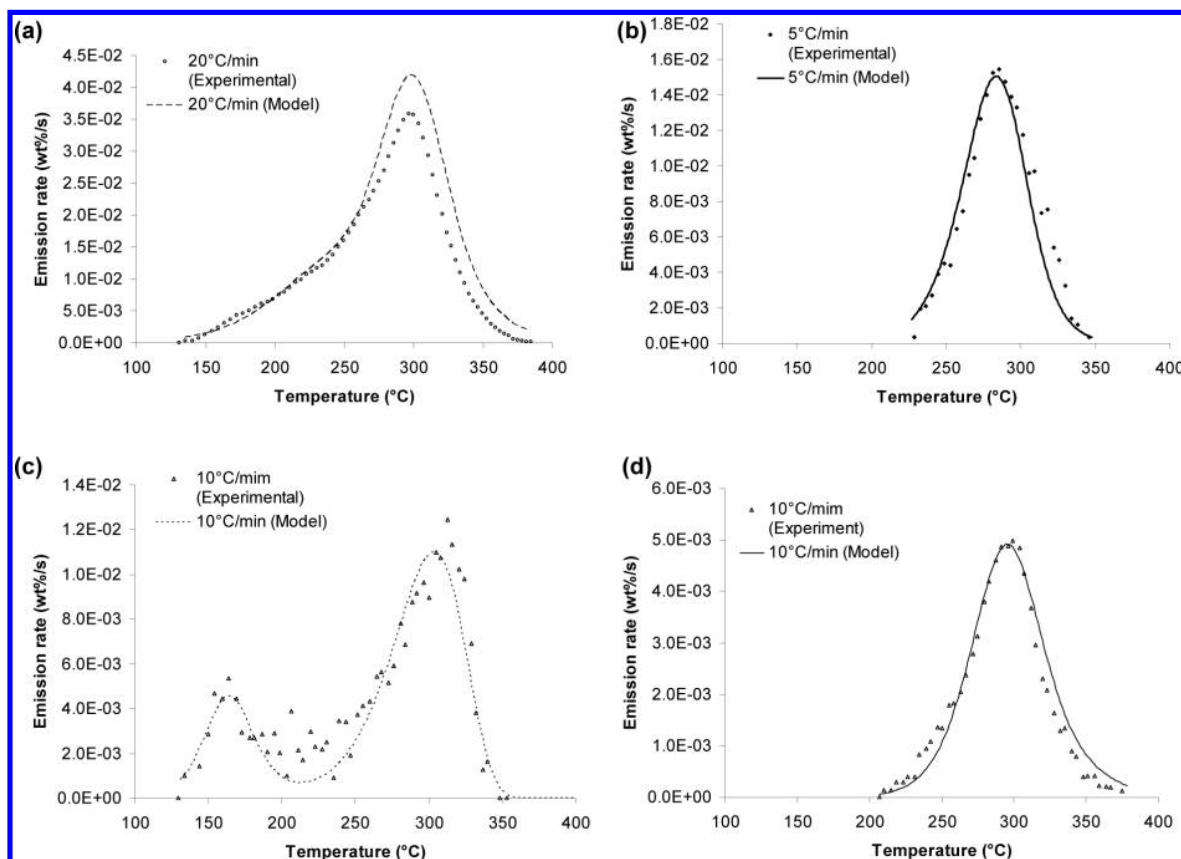
**Figure 7.** Results of evolved gas analysis for TG-FTIR runs performed on shredded tobacco sample at 10 °C/min heating rate. (a) TG and dTG of sample in pure nitrogen; (b) TG and dTG of sample in air. Emission profiles of carbon dioxide in nitrogen (c) and in air (d), carbon monoxide in nitrogen (e) and in air (f), water in nitrogen (g) and in air (h), acetaldehyde in nitrogen (i) and in air (j), nicotine in nitrogen (k) and in air (l).

as a function of sample temperature in the TG furnace, obtained from the deconvolution process applied to the results of runs carried out on shredded tobacco samples at 10 °C/min constant heating rate in nitrogen and air atmosphere. Qualitatively similar results were obtained in all other runs and are not reported for the sake of brevity.

For isoprene and phenol reliable data could not be obtained: a poor correlation between reference and predicted spectra was obtained in the deconvolution process. The concentrations of isoprene and phenol in the evolved gases, if present, were too low to be detected confidently under the current experimental conditions. Thus, neither quantification nor kinetic analysis

could be carried out for these components. The detection limit of the method could be roughly estimated based on the lowest quantity for which it was possible to obtain reliable results in calibration runs. These quantities correspond to 0.091 mg and 0.087 mg for isoprene and phenol, respectively (data in Table 2). If a typical tobacco sample weight of 15 mg is considered, a detection limit of about 0.006 mg/mg of tobacco could be calculated for both isoprene and phenol.

The profiles of evolved gases, as those reported in Figure 7, show a good correspondence to the weight loss behavior, confirming the phenomena that are actually taking place in the different temperature ranges and reaction environments



**Figure 8.** Results obtained in the fitting of the apparent kinetic model to experimental data for emission rates of different compounds: a) acetaldehyde, purge gas: air; b) water, purge gas: air; c) water, purge gas: nitrogen; d) carbon monoxide, purge gas: air.

(release of moisture, two-stage thermal decomposition, residue degradation or combustion). Quite complex evolution patterns were obtained for the components of interest, confirming the general trends observed by Bassilakis et al.<sup>8</sup> in previous TG-FTIR pyrolysis studies on tobacco samples.

The first region of weight loss (Region I: 30–120 °C) is likely related to the evaporation of water adsorbed in the sample (Figure 7(g,h)).

As evident from Figure 7, in Region II (120–250 °C) the emission of acetaldehyde, carbon dioxide, nicotine, and water was detected, both in inert and oxidizing environments. The emission peaks for acetaldehyde and nicotine show a good correspondence to the dTG peak (Figure 7(a,b)).

Figure 7 also shows that Region III (250–370 °C) is associated with the release of acetaldehyde, carbon dioxide, carbon monoxide, nicotine, and water. In the case of acetaldehyde, carbon dioxide, carbon monoxide, and water the peak in the evolution profile matches with the peak in the dTG curve, both in nitrogen and air atmosphere.

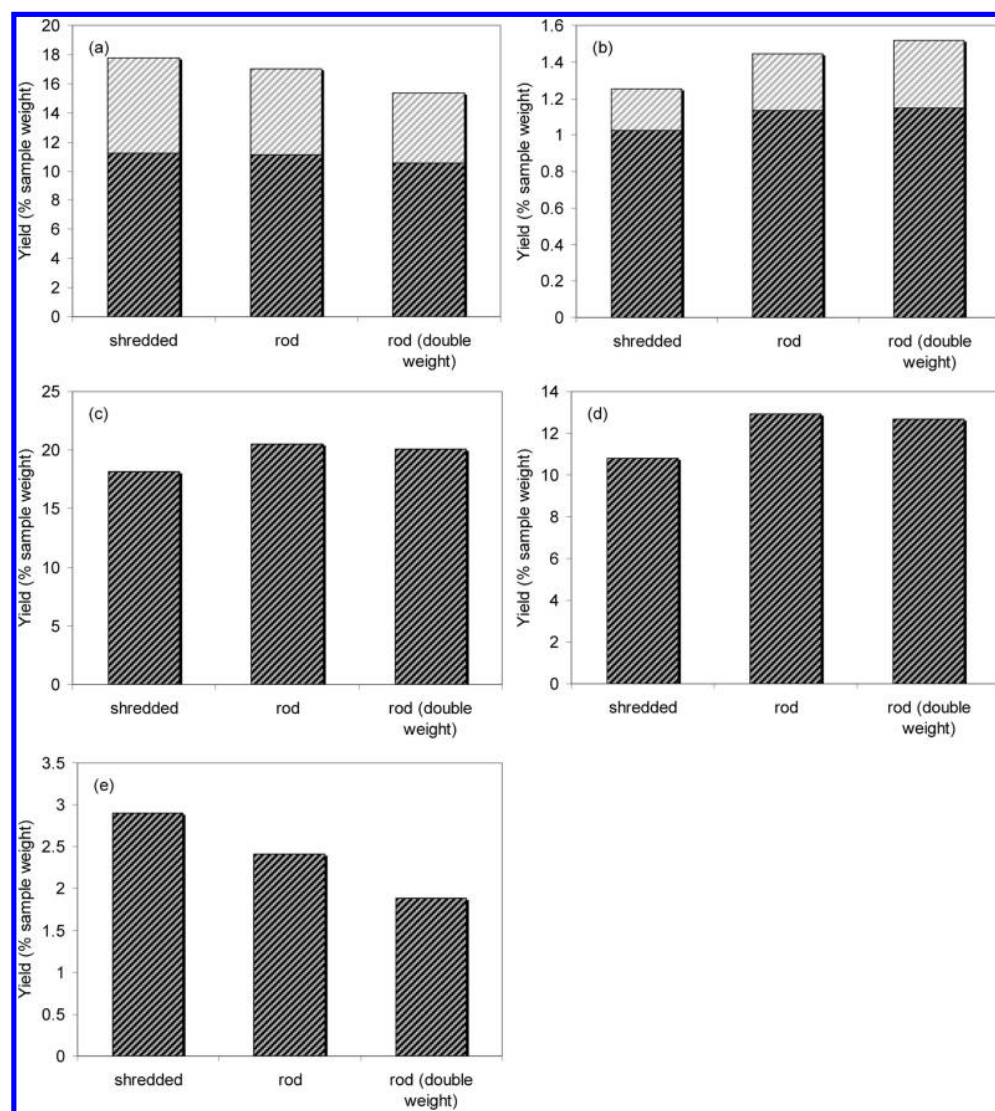
Qualitatively similar product evolution patterns were observed at the different heating rates used in the present work (5, 10, and 20 °C/min). Thus, the evolution of products such as acetaldehyde and nicotine could be detected in the thermal decomposition of the tobacco substrate, with nicotine evolving mainly in the low temperature range (Region II), while acetaldehyde evolves in the higher temperature range (Region III).

During the degradation of the residue (Region IV) in inert environment, the release of carbon dioxide and carbon monoxide was identified, as evident from Figure 7. The oxidation of

**Table 4.** Apparent Kinetic Parameters for the Emission of the Key Components of Interest from the Tobacco Substrate

key component	E (kJ/mol)	A (1/s)	n (-)	$\alpha$ (mg/mg)
<i>Purge Gas: Nitrogen</i>				
acetaldehyde (peak 1)	66.5	$1.10 \times 10^{05}$	1	0.0158
acetaldehyde (peak 2)	108.1	$4.99 \times 10^{07}$	2	0.0701
carbon dioxide (peak 1)	141.0	$4.77 \times 10^{15}$	2	0.0047
carbon dioxide (peak 2)	116.4	$1.61 \times 10^{09}$	1	0.0200
carbon dioxide (peak 3)	141.4	$2.65 \times 10^{10}$	1	0.0298
carbon monoxide	95.8	$2.19 \times 10^{06}$	1	0.0077
nicotine	95.6	$8.84 \times 10^{08}$	1.5	0.0212
water (peak 1)	124.7	$1.07 \times 10^{13}$	2	0.0106
water (Peak 2)	108.3	$3.98 \times 10^{07}$	1	0.0418
<i>Purge Gas: Air</i>				
acetaldehyde (peak 1)	58.2	$1.13 \times 10^{04}$	1	0.0202
acetaldehyde (peak 2)	137.2	$5.56 \times 10^{10}$	2	0.0813
carbon dioxide (peak 1)	141.2	$4.77 \times 10^{15}$	2	0.0078
carbon dioxide (peak 2)	99.8	$8.89 \times 10^{06}$	2	0.2316
carbon monoxide	145.5	$1.96 \times 10^{11}$	2	0.0202
nicotine	91.5	$2.19 \times 10^{08}$	1.5	0.0177
water	141.3	$7.96 \times 10^{10}$	1.5	0.1025

the residue in air atmosphere leads to the emission of carbon dioxide, carbon monoxide, and water, as shown in Figure 7. The acetaldehyde and nicotine peaks detected in correspondence of the oxidation of the residue (Region IV – purge gas: air), and the acetaldehyde peak in Region I, are probably spurious and affected by spectral interferences, thus these peaks were neglected in the evaluation of the quantities of evolved



**Figure 9.** Results of quantitative analysis of evolved gases in TG-FTIR runs carried out on the tobacco substrate at 10 °C/min heating rate in nitrogen atmosphere. Black and gray columns represent the quantities of product evolved in the tobacco main decomposition steps (30–370 °C), and during residue degradation (370–550 °C), respectively. (a) Carbon dioxide. (b) Carbon monoxide. (c) Water. (d) Acetaldehyde. (e) Nicotine.

products. The presence of spurious peaks for acetaldehyde is further discussed in the following.

The emission profiles of the evolved products were analyzed in order to obtain apparent kinetic parameters relevant to the pyrolysis and slow combustion processes. The analysis was performed on the temperature range between 100 and 400 °C, corresponding to Regions II and III, applying the procedure described in Section 3.3. A multiple-step lumped reaction model was applied to fit experimental data, and an Arrhenius rate equation was used to model the emission process in each step. Sample results are reported in Figure 8. In the case of nicotine, it was not possible to obtain consistent emission rate curves for the all the different experimental runs, probably due to diffusive limitations or to partial condensation/evaporation phenomena.

The best-fit values of the kinetic parameters obtained for the formation and release of the compounds of interest in nitrogen and air are reported in Table 4. The data in Table 4 show that some emission steps have similar activation energies independently on the purge gas used (first peak of carbon dioxide,

both peaks of acetaldehyde, nicotine), suggesting an emission phenomenon that is independent of the gas surrounding the sample.

#### 4.3. Quantities of Key Components in Evolved Gases.

The use of the methodology discussed in Section 3 allowed for the quantitative assessment of evolved products. The integration of the emission profiles with respect to time (eq 1) and the use of the calibration constants reported in Table 2 yielded the detected quantity of each of the evolved compounds of interest. The integrals were calculated both on the temperature interval corresponding to the main decomposition step of the tobacco substrate (30–370 °C), thus excluding the degradation or combustion of the residue (Region IV), and on the entire temperature range up to the maximum temperature used in experimental runs (550 °C). These values obviously differ only for carbon dioxide, carbon monoxide, and water (for the latter, only in an oxidizing environment), since no other compounds evolved in Region IV.

Figure 9 reports the results of the quantitative analysis of evolved gases in TG-FTIR runs carried out on the tobacco

Table 5. Results of Quantitative Analysis of Evolved Gases in Experimental Runs Carried out on the Tobacco Substrate<sup>a</sup>

key component	heating rate (°C/min)	N <sub>2</sub> – 30–370 °C quantity (% sample wt)	N <sub>2</sub> – 30–550 °C quantity (% sample wt)	air – 30–370 °C quantity (% sample wt)	air – 30–550 °C quantity (% sample wt)
acetaldehyde	5	9.13 (±0.94)	9.13 (±0.94)	10.27 (±0.79)	10.27 (±0.79)
	10	12.02 (±1.30)	12.02 (±1.30)	13.82 (±1.53)	13.82 (±1.53)
	20	10.65 (±0.72)	10.65 (±0.72)	12.79 (±0.21)	12.79 (±0.21)
average, all runs	---	11.08 (±1.60)	11.08 (±1.60)	12.29 (±1.81)	12.29 (±1.81)
carbon dioxide	5	8.66 (±1.37)	15.52 (±4.23)	43.24 (±2.49)	102.77 (±5.88)
	10	11.05 (±0.31)	16.98 (±1.06)	35.91 (±1.33)	94.81 (±3.75)
	20	9.48 (±0.24)	15.56 (±1.58)	23.92 (±0.24)	73.70 (±0.81)
average, all runs	---	10.17 (±1.21)	16.34 (±1.92)	34.35 (±8.82)	90.43 (±13.80)
carbon monoxide	5	1.04 (±0.11)	1.77 (±0.07)	2.80 (±0.04)	3.41 (±0.11)
	10	1.09 (±0.08)	1.38 (±0.24)	2.09 (±0.10)	2.60 (±0.23)
	20	0.97 (±0.06)	1.44 (±0.23)	1.68 (±0.01)	2.22 (±0.03)
average, all runs	---	1.05 (±0.09)	1.48 (±0.25)	2.19 (±0.51)	2.75 (±0.56)
nicotine	5	2.59 (±0.19)	2.59 (±0.19)	1.15 (±0.20)	1.15 (±0.20)
	10	2.50 (±0.59)	2.50 (±0.59)	1.81 (±0.85)	1.81 (±0.85)
	20	1.99 (±0.53)	1.99 (±0.53)	2.28 (±0.83)	2.28 (±0.83)
average, all runs	---	2.41 (±0.52)	2.41 (±0.52)	1.75 (±0.74)	1.75 (±0.74)
water	5	10.58 (±0.33)	10.58 (±0.33)	19.74 (±4.71)	26.62 (±5.10)
	10	19.49 (±1.53)	19.49 (±1.53)	29.28 (±3.58)	39.18 (±3.24)
	20	15.87 (±0.13)	15.87 (±0.13)	25.21 (±0.54)	34.38 (±1.00)
average, all runs	---	16.71 (±3.95)	16.71 (±3.95)	24.75 (±5.04)	33.39 (±6.30)
glycerol	5	ND <sup>b</sup>	8.06	ND <sup>b</sup>	6.07
	10	ND <sup>b</sup>	7.68	ND <sup>b</sup>	8.19
	20	ND <sup>b</sup>	8.09	ND <sup>b</sup>	7.36
average, all runs	---	---	7.94 (±0.23)	---	7.21 (±1.07)

<sup>a</sup>Standard deviation is indicated in parentheses. All data except for glycerol are obtained from TG-FTIR runs; data for glycerol are obtained from FBR runs. <sup>b</sup>ND, not determined.

substrate at a 10 °C/min heating rate in nitrogen atmosphere. The quantities of product evolved in the tobacco main decomposition step and during residue degradation are shown in the figure. The results obtained are directly compared in Figure 9 for each of the five components of interest. The values in the figure are yield values expressed as the ratio of the weight of the product over the initial weight of the sample multiplied by 100. No important differences in the yields of evolved gas products were observed among the results obtained in runs carried out using shredded or rod samples and samples with different initial weight. This seems to indicate a limited influence of sample grinding and of sample mass on the quantities of evolved products, thus confirming TG data.

The results of the quantitative analysis of evolved gases for the five compounds of interest in all the experimental conditions explored in the present work are summarized in Table 5. Yield values expressed as the ratio of the weight of the product over the initial weight of the sample multiplied by 100 are shown in the table. The table reports the average values obtained using both shredded and rod samples, for the different heating rates and different purge gases used. The overall average results obtained for runs in nitrogen and for runs in air are also reported.

With respect to carbon dioxide, nicotine, and water, the quantitative results obtained are comparable to those obtained by previous TG-FTIR investigations on tobacco pyrolysis,<sup>3,8</sup> although significantly higher quantities of acetaldehyde were estimated in the present study with respect to those reported in the literature.<sup>3,8</sup>

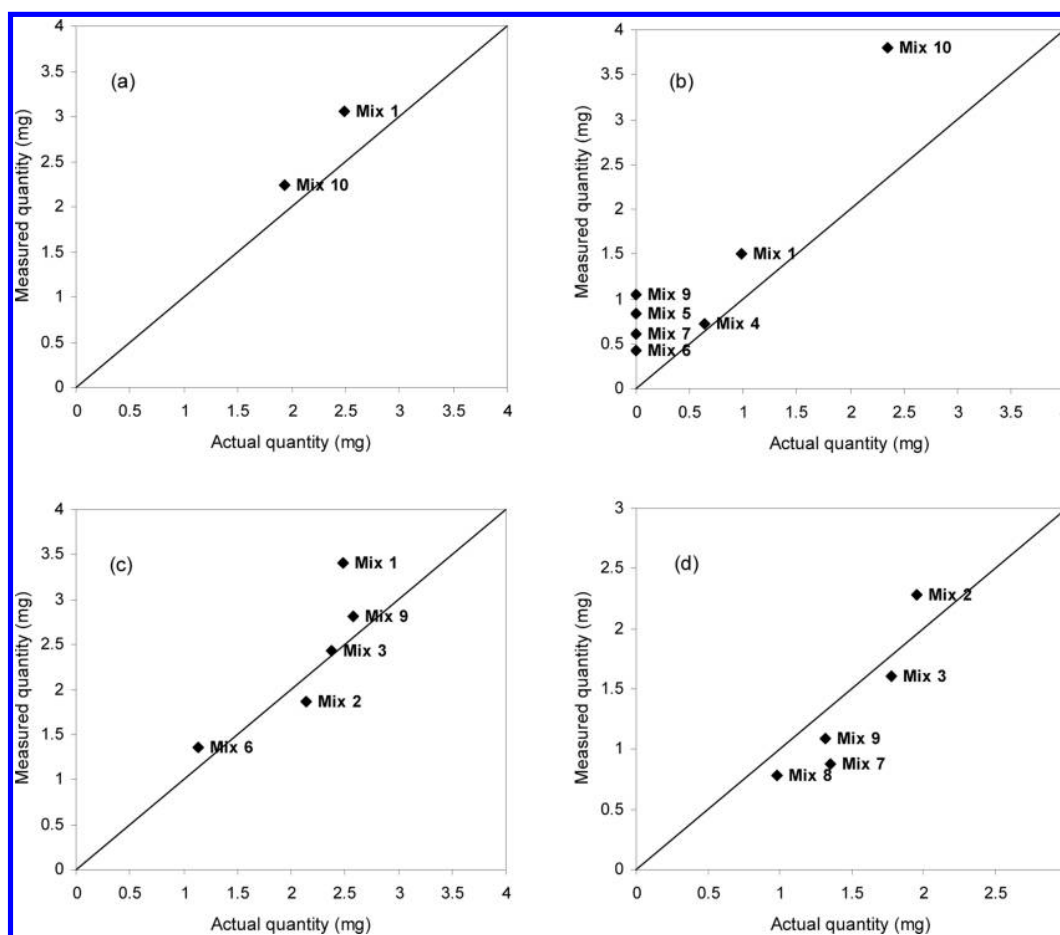
The results obtained thus suggest that the methodology used for the quantitative analysis of evolved gas may overestimate acetaldehyde, due to the possible occurrence of spectral

interferences in the deconvolution of FTIR data. A specific validation activity was carried out to verify the performance and the reliability of the deconvolution procedure applied for the characterization of complex mixtures of volatile products, such as those evolved in the pyrolysis of the tobacco samples.

Specific validation TG-FTIR runs based on the vaporization of mixtures having known composition were performed. A set of ten validation runs was carried out, vaporizing in the TG furnace mixtures where known amounts of the key components of interest and of possible interfering species were present. The composition of the test mixtures used in experimental runs is reported in Table 1. Each mixture contains at least one key component and one interfering compound. Typical products formed in the pyrolysis of biomass substrates<sup>5,8,30,31</sup> were selected as interfering species.

The results of the quantitative analysis of evolved gases in TG-FTIR validation runs are shown in Figure 10. The figure reports parity plots comparing the actual quantity of the key component in the test mixture to that calculated from the application of the methodology applied for quantitative TG-FTIR data analysis. In the parity plots, only the mixtures where the presence of the key component was detected were reported.

The results of the validation trial indicate the method provides acceptable results in the case of nicotine and water, with errors in general lower than 20%. When applied to acetaldehyde, the method seems to systematically overestimate the evolved quantities (roughly around +50%). Furthermore, for four over seven mixtures where acetaldehyde was not present, a false emission peak was detected. Finally, the validation results evidence that the method seems to slightly underestimate phenol (average around –20%).



**Figure 10.** Comparison of measured vs actual content of validation mixtures for the different key components. (a) Water. (b) Acetaldehyde. (c) Nicotine. (d) Phenol.

Thus, it may be concluded that deconvolution of TG-FTIR data, at least with the conventional experimental setup used in the present study, should be applied with caution to the quantitative assessment of evolved gas products when complex gaseous mixtures with potentially interfering compounds are formed. The detection limits of the experimental technique, and the actual potentialities of the deconvolution method, may represent critical issues for the application of the TG-FTIR technique to quantitative evolved gas analysis.

**4.4. Glycerol Emission in Evolved Gases.** As discussed above, the tobacco substrate contained glycerol as an aerosol-former, thus glycerol was expected to be a main component of evolved gases during the pyrolysis or combustion of the tobacco sample. However, preliminary experimental tests evidenced that it was not possible to obtain the straightforward characterization of evolved glycerol by the TG-FTIR device and technique adopted. Actually it was not possible to obtain reliable calibration data for glycerol in the experimental system used. Evidence of condensation phenomena and partial decomposition were obtained in the calibration runs, which showed the presence of carbon dioxide, carbon monoxide, and water in the gas cell of the FTIR analyzer during the vaporization of glycerol.

Thus, a specific experimental technique was applied to obtain data on glycerol emission, completing the assessment of the main components evolved during the thermal decomposition of the sample tobacco substrate used for experimental runs.

A fixed bed reactor was used to carry out tobacco thermal decomposition runs in inert or oxidizing atmosphere. Runs were carried out in pure nitrogen and in air up to a final temperature of 550 °C using different heating rates (5, 10, and 20 °C/min). The results of the quantitative analysis of evolved glycerol are reported in Table 5. The use of different final temperatures in experimental runs allowed assessing that the emission takes place mostly between 150 and 250 °C, thus in the low temperature range Region II previously identified. Results were sensitive to parameters such as sample mass, sample grinding, and evaporating surface, suggesting an important role of transport phenomena in glycerol emission.

## 5. CONCLUSIONS

The thermal degradation process of a tobacco substrate was investigated by TG-FTIR analysis. Multivariate deconvolution techniques were used to identify the contributions of the key components of interest to the overall FTIR spectra. A range of experimental conditions (different heating rates and purge gas) compatible with the limits of the TG analyzer were explored. Emission profiles and quantitative data on key compounds evolved in the different experimental conditions were obtained. The assessment of the results by specific validation runs evidenced the limits of the TG-FTIR technique in the quantitative characterization of complex mixtures, even using an advanced deconvolution technique. Nevertheless, significant data were obtained for the quantitative characterization and the

emission profiles of some key components of evolved gases, such as acetaldehyde, carbon dioxide, carbon monoxide, nicotine, and water. A different experimental strategy based on the use of a fixed bed reactor was developed for the characterization of evolved glycerol from the tobacco substrate, thus obtaining a complete figure of the main components present in evolved gases formed during the slow thermal decomposition of tobacco substrates in nitrogen and air.

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### Notes

The authors declare no competing financial interest.

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