

Quantitative Analysis of Evolved Gas in the Thermal Decomposition of a Tobacco Substrate

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Thermogravimetry coupled to FTIR analysis of evolved gas was applied to the quantitative determination of key-components formed in the slow pyrolysis and thermal decomposition of tobacco samples. Eight key-components were selected for the study: carbon dioxide, carbon monoxide, water, acetaldehyde, glycerol, isoprene, nicotine, and phenol. Specific calibration techniques developed for FTIR evolved gas analysis were applied to carry out the quantitative analysis of evolved gases. Deconvolution techniques were applied to identify the contributions of the key-components of interest to the overall FTIR spectra. The results obtained allowed the characterization of evolution profiles of most of the key components of interest. Phenol and isoprene results were below the detection limits of the technique, while the calibration technique was not suitable for glycerol characterization due to condensation and decomposition phenomena during calibration runs. Quantitative data were obtained for carbon dioxide, carbon monoxide, water, acetaldehyde and nicotine evolution in pure nitrogen and dry air.

1. Introduction

Biomass slow pyrolysis has a wide number of applications, ranging from the energy sector to food preparation (Yaman, 2004; Balat et al., 2009). The identification and quantification of volatile species formed in the thermal degradation of biomass substrates is a key element for the development and optimization of several biomass applications. The quantitative assessment of components present in evolved gases during TG-FTIR experiments was applied with success to the quantitative determination of chemical species which have specific absorption intervals that may be easily identified in the FTIR spectra recorded during TG-FTIR experiments (Giuntoli et al., 2009; Granada et al., 2012). 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 (Basilakis et al., 2001; Baker et al., 2005). However, the potentiality of such techniques concerning the quantitative characterization of a complex mixture of volatile products still needs to be explored in detail.

Marsanich et al. (2002) proposed a shortcut method for the quantitative analysis of evolved gases during thermogravimetric (TG) runs coupled to Fourier Transform Infrared (FTIR) analysis of evolved gases. The methodology was successfully applied to the quantification of specific compounds evolved during TG runs (Barontini et al., 2004, Marsanich et al., 2003), as hydrogen bromide, ammonia, and several other species

(Barontini et al., 2005; Barontini et al., 2006). However, the applications to date were limited to a direct analysis of FTIR spectra, without any deconvolution procedure (Gomez et al., 2012). This limited the application of the methodology 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 (Marsanich et al., 2002, Barontini et al., 2001).

In the present study, thermogravimetry coupled to FTIR analysis of evolved gas was applied to the quantitative determination of key-components formed in the slow pyrolysis and thermal decomposition of tobacco samples. Eight key-components of interest were selected for the study: carbon dioxide, carbon monoxide, water, acetaldehyde, glycerol, isoprene, nicotine, and phenol. The methodology developed by Marsanich et al. (2002) 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. Both pyrolysis (pure nitrogen) and slow combustion conditions were explored.

2. Experimental Section

2.1 Materials

Experimental runs were carried out both on shredded tobacco substrate and tobacco rods manufactured at Philip Morris Products, S.A. as described in (Philip Morris Products S.A., 2012). The sheet of homogenised tobacco material for use in such rods contained glycerol as an aerosol-former.

Prior to the experiments, samples were stored 48 hours at room conditions at a temperature between 25.0°C and 26.2°C, and humidity between 61 and 71% of humidity.

Standard gaseous mixtures used in calibration runs (carbon monoxide/nitrogen, 2000 ppm CO; carbon dioxide/nitrogen, 2460 and 9990 ppm CO₂) were supplied by SOL (Milan, Italy). Acetaldehyde, glycerol, isoprene, nicotine, phenol used in calibration runs were supplied by Sigma-Aldrich (Milan, Italy). Carbon tetrachloride supplied by Baker was used for the preparation of acetaldehyde, isoprene, nicotine and phenol solutions.

2.2 Experimental devices

Simultaneous thermogravimetric (TG) and 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 1-30mg were employed.

The atmosphere surrounding the samples was controlled using a continuous purge gas flow (60Nml/min). FTIR measurements were carried out using a Bruker Equinox 55 spectrometer. TG-FTIR simultaneous measurements for the on-line analysis of volatile compounds formed during TG runs were carried out coupling the FTIR spectrometer to the Netzsch TG using a 2mm internal diameter teflon tube. The 800mm 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 (8.7ml) with a 123mm pathlength, heated at a constant temperature of 250°C. The gas flow from the TG outlet to the IR gas cell was of 60Nml/min and a residence time of 30s 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 4cm⁻¹ resolution, co-adding 16 scans per spectrum. This resulted in a temporal resolution of 9.7s, more than sufficient to follow the gas evolution rates characteristic of TG runs at the heating rates used in the present work.

2.3 Experimental procedures

In order to carry out quantitative assessment of evolved gaseous products, calibration runs were carried out using the methodologies described by Marsanich et al. (2002) for eight selected components of interest: carbon monoxide, carbon dioxide, water, acetaldehyde, glycerol, isoprene, nicotine, phenol. In particular, depending on the species of interest, either gas loops containing known volumes of gaseous standard mixtures or vaporization of known amounts of sample substances were used for calibration. Further details on the experimental set-up and the analysis of data to build calibration curves are reported elsewhere (Marsanich et al., 2002).

TG-FTIR runs were carried out using shredded tobacco samples and samples obtained from tobacco rods. Typical sample weights of about 15mg and alumina crucibles were employed. Experimental runs were carried out using a purge gas flow (60Nml/min) of pure nitrogen or air (21% oxygen by mol). Constant heating rates of 5, 10 and 20°C/min from 30°C to 550°C were used in experimental runs.

2.4 Deconvolution of FTIR data

In order to apply the methodology described by Marsanich et al. (2002) to the quantitative analysis of the eight components of interest in the evolved gas from tobacco pyrolysis or slow combustion, a deconvolution procedure of FTIR data was necessary. A multivariate data deconvolution procedure based on the statistical techniques of Principal Component Analysis (PCA) (also called Factor Analysis (FA)) was applied. A variation of FA in the form of Parallel Factor Analysis (PARAFAC) (Harshman, 1970; Kumar and Mishra, 2012; Malinowski, 2002; Real et al., 2012; Tauler et al., 1993) in combination with a curve resolution (deconvolution) technique called Iterative Target Transformation Factor Analysis (ITTFA) was used (Malinowski, 2002; Real et al., 2012; Tetteh, 1997; Tetteh et al., 2009). The contribution to absorption due to the compound of interest hereafter named "Response", was calculated by the deconvolution technique in both calibration and sample runs. The time integral of Response was then calculated as follows:

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

where (t_1 ; t_2) is the time interval of interest (e.g. the duration of the TG run). The quantity of compound in evolved gas, n , is calculated as follows:

$$n = D/K \quad (2)$$

3. Results and Discussion

Figure 1(a) shows the residual weight and the weight loss rate as a function of temperature obtained in TG runs carried out on shredded tobacco samples at three different constant heating rates (5, 10 and 20°C/min) using a pure nitrogen (60Nml/min) purge gas flow. No relevant differences were detected using samples obtained from tobacco rods or different sample weights and TG curves showed a high reproducibility. Unless otherwise stated, the data reported in the present study were calculated as the mean of at least three experimental runs.

The analysis of the dTG curve allows observing the presence of 4 regions of weight loss. 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. The fourth region (Region IV: 370-550°C) is related to the decomposition of the residue.

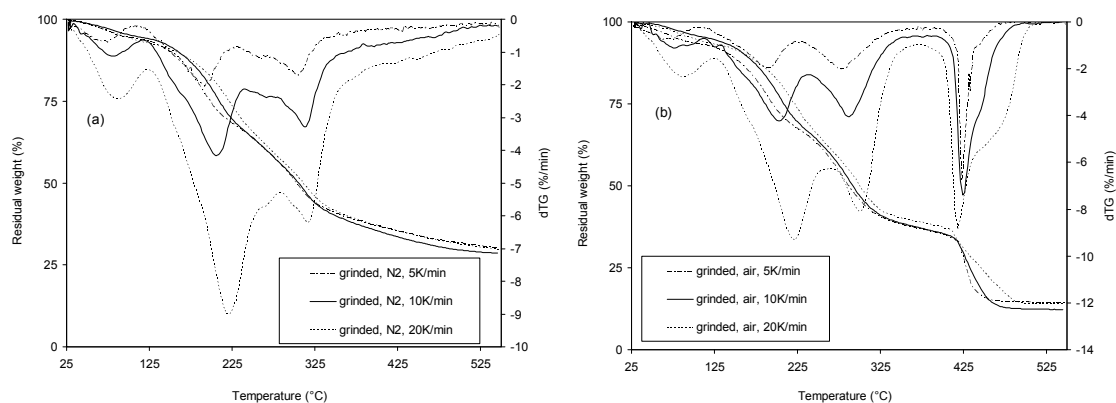


Figure 1: TG and dTG results obtained for the tobacco substrate at different heating rates. (a) Nitrogen. (b) Air.

Figure 1(b) shows the correspondent results obtained using air (60Nml/min) as the purge gas. Also in this case four regions of weight loss were observed: Region I (30-120°C), related to moisture release, Region II (120-250°C) and Region III (250-370°C), related to a two-stage thermal decomposition, and Region IV (370-550°C). The latter region is related to the combustion of residue. A lower temperature was observed for the maximum in the weight loss rate in Region III with respect to results obtained in nitrogen.

Figure 2 reports an example of the cascades of FTIR spectra obtained in TG-FTIR runs. The deconvolution procedure described in section 2 was applied to these cascades of spectra obtained from the FTIR analyzer during the TG runs. Qualitatively similar results were obtained in all other runs, and are not reported for the sake of brevity. The profiles of evolved gases, as obtained from the cascades shown in figure 2 and from the deconvolution procedure, show a good correspondence to the dTG peaks,

confirming the phenomena that are actually taking place in the different temperature ranges and reaction environments (release of humidity, two-stage thermal decomposition, combustion).

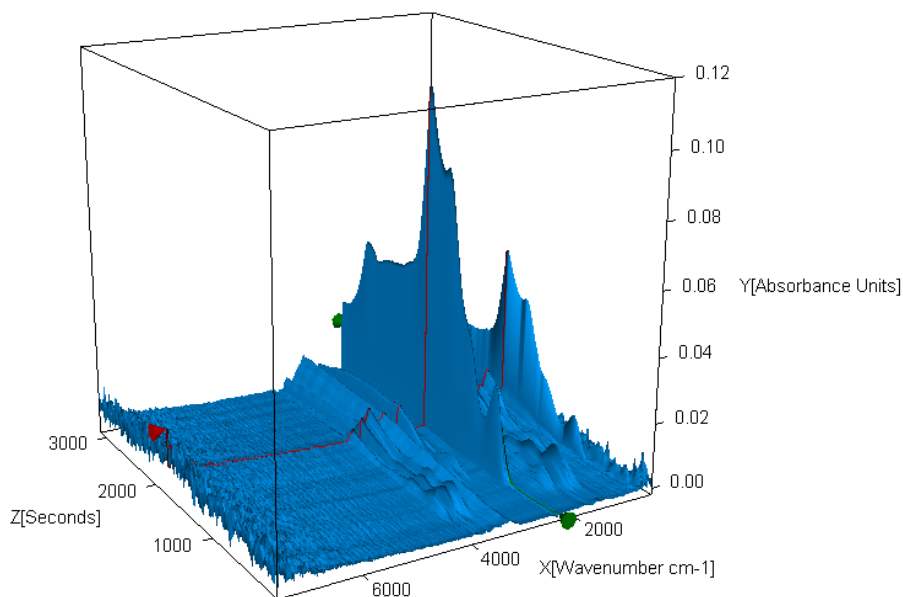


Figure 2: Cascade of FTIR spectra obtained from evolved gas analysis in the TG run showed in figure 1 (nitrogen atmosphere, 10°C/min heating rate).

The analysis of evolved gases was carried out for seven of the eight compounds of interest listed in section 2.3. Actually it was not possible to obtain reliable calibration data for glycerol in the experimental system used. Evidence of partial decomposition were obtained in the calibration runs, that showed the presence of carbon dioxide, carbon monoxide and water in the gas cell of the FTIR analyzer during the vaporization of glycerol. These results clearly suggested that different experimental strategies need to be adopted for the quantitative assessment of glycerol in evolved gas during thermal decomposition or slow combustion of tobacco substrates.

The analysis of the cascade of spectra allowed obtaining for each of the seven other compounds of interest emission profiles as a function of time. Figure 3 shows some examples of the profiles obtained.

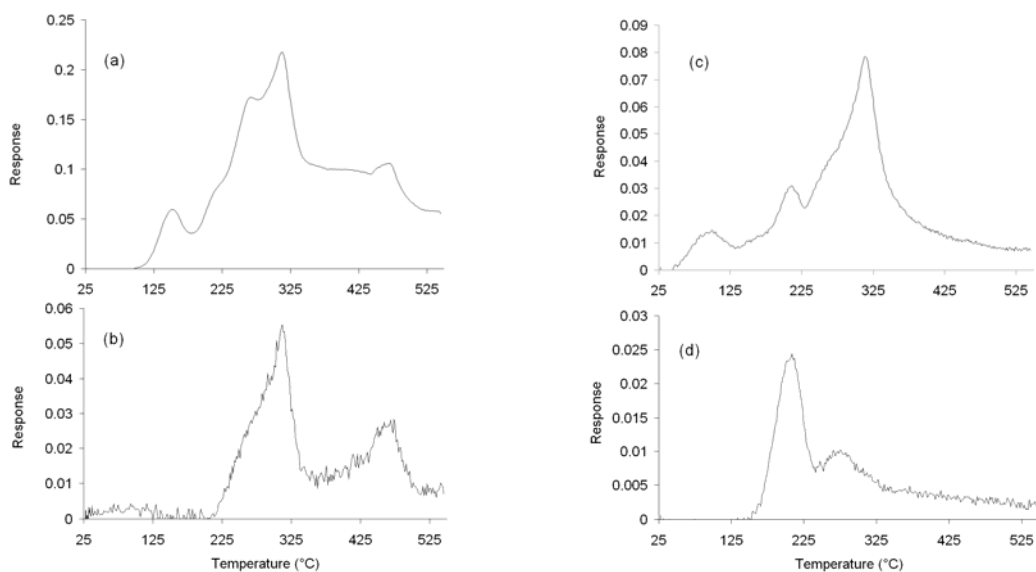


Figure 3: Emission profiles obtained for carbon dioxide (a), carbon monoxide (b), acetaldehyde (c) and nicotine (d) in a TG-FTIR run performed on the tobacco substrate in nitrogen at 10°C/min heating rate.

The integration of the emission profile on the basis of the calibration results should allow obtaining the quantity emitted of each of the compounds. Although calibration curves were obtained for phenol and isoprene, the signals calculated for these species during tobacco pyrolysis were very low and in the range of the background signals. A poor correlation between reference and predicted spectra was obtained for both phenol and isoprene. Thus, for both isoprene and phenol the peaks present in evolved gas profiles were too low to be detected, and quantification was not possible for these components.

The results of the quantitative analysis of evolved gases for the five other compounds of interest are reported in Table 1. The results were obtained from the application of the deconvolution process and the quantitative calibration data discussed in section 2. Acetaldehyde and nicotine emission is mainly related to the sample thermal decomposition (Region II and III). Carbon dioxide and carbon monoxide are released both during sample thermal decomposition (Region II and III) and during degradation or combustion of the residue (Region IV). Water is released in Region I, II and III, and during combustion of the residue (Region IV in air).

With respect to carbon dioxide, water and nicotine, the quantitative results obtained are comparable to those obtained by previous TG-FTIR investigations on tobacco pyrolysis (Bassilakis et al., 2001; Wójtowicz et al., 2003), although higher quantities of acetaldehyde were estimated in the present study with respect to those reported in the literature (Bassilakis et al., 2001; Wójtowicz et al., 2003).

Table 1: Results of quantitative analysis of evolved gases for TG-FTIR runs in nitrogen and air

Key-component	Heating rate (°C/min)	N ₂ - Average quantity (% initial sample weight)	N ₂ - Standard deviation	Air - Average quantity (% initial sample weight)	Air - Standard deviation
Carbon dioxide	5	15.52	4.23	102.77	5.88
	10	16.98	1.06	94.81	3.75
	20	15.56	1.58	73.70	0.81
Carbon monoxide	5	1.77	0.07	3.41	0.11
	10	1.38	0.24	2.60	0.23
	20	1.44	0.23	2.22	0.03
Water	5	10.58	0.33	26.62	5.10
	10	19.49	1.53	39.18	3.24
	20	15.87	0.13	34.38	1.00
Acetaldehyde	5	9.13	0.94	10.27	0.79
	10	12.02	1.30	13.82	1.53
	20	10.65	0.72	12.79	0.21
Nicotine	5	2.59	0.19	1.15	0.20
	10	2.50	0.59	1.81	0.85
	20	1.99	0.53	2.28	0.83

4. Conclusions

A straightforward methodology for the quantitative analysis of TG-FTIR data was applied to investigate evolved gases formed from the pyrolysis and slow combustion of a tobacco substrate, coupling a specific simplified calibration technique to a multivariate deconvolution method for the analysis of FTIR data. The TG-FTIR method proved to be a practical screening tool to obtain quantitative data on some species evolved in tobacco thermal decomposition. However, the method could not be applied to the quantitative analysis of glycerol, due to its decomposition during calibration runs. In the case of isoprene and phenol, deconvoluted signals were of the order of magnitude of the background. However, the methodology provided useful experimental data concerning the emission profiles and quantities of carbon monoxide, carbon dioxide, water, acetaldehyde and nicotine present in the decomposition or combustion products. The quantitative data obtained are an important starting point for the development of kinetic models for gas formation during the pyrolysis and slow combustion of tobacco substrates.

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