Tutora

Małgorzata Dzięcioł, PhD
West Pomeranian University of Technology, Szczecin

Faculty of Chemical Technology and Engineering

Grau de Química

Treball Final de Grau

Volatile products of catalytic thermal decomposition of waste poly(ethylene terephthalate).
Productes volàtils de la descomposició tèrmica catalítica de residus de polietilè tereftalat.

Judith Solé Solé

June 2014

Universitat de Barcelona

Campus d'Excel·lència Internacional
B:KC Barcelona Knowledge Campus

If we knew what it was we were doing, it would not be called research, would it?

Albert Einstein

I would like to strongly thank Małgorzata Dzięcioł, the research project professor, for all her inconditional dedication, patience, and help she provided during the whole realization of this work.

To Javier Rodríguez, for all the suggestions, corrections and improvements towards this project.

To Victoria Sanz, for all the help and patience that made this Erasmus exchange possible.

Finally, thanks in general to all the West Pomeranian University staff that made my Erasmus stay unforgettable.

REPORT

CONTENTS

1. SUMMARY

Poly(ethylene terephthalate), commonly abbreviated as PET, is one of the most widely used thermoplastics in everyday life thanks to its excellent physical and chemical properties. Due to the slow biodegradability of PET wastes and the fact that its consumption is still increasing, there is a growing interest on recycling of post-consumer PET wastes to reduce its volume in land-fill sites. Among the recycling methods, chemical recycling is the most acceptable method in environmental terms as it leads to the formation of the materials from which the polymer is originally made or other raw materials. Moreover, the recycling of polymer waste by thermal processes (pyrolysis) can be an important source of hydrocarbons for the petrochemical industry, contributing to the environmental protection. However, this process requires high quantity of energy due to the poor thermal conductivity and endothermicity of plastics. To decrease thermal decomposition costs of polymeric material wastes, cheap catalysts have become of the most interest from a global recycling point of view.

In the present work, two kinds of fly ash (coal and biomass fly ash) were tested as catalysts to examine their influence on the volatile compounds emitted during thermal decomposition process of waste PET in selected conditions: 400ºC in N_2 atmosphere. Moreover, two methods of mixing sample with each fly ash were performed to compare their effects. The analysis was performed using gas chromatography method with different detectors and spectrophotometric method.

Keywords: Poly(ethylene terephthalate), PET, PET thermal decomposition, PET catalytic thermal decomposition, PET thermal degradation, PET cracking, PET pyrolysis, fly ash catalyst.

2. RESUM

El polietiletereftalat, sovint abreujat com PET, és un dels termoplàstics més utilitzats en la vida diària gràcies a les seves excel·lents propietats físiques i químiques. Degut a la lenta biodegradabilitat dels residus de PET i a que la seva consumició segueix augmentant, hi ha un interès creixent en el reciclatge d'aquest plàstic per tal de reduir el seu volum en els abocadors. Entre els mètodes de reciclatge, el reciclatge químic és el més acceptat des d'un punt de vista mediambiental ja que permet la formació dels materials dels quals el polímer és originalment produït o d'altres matèries primeres. A més, el reciclatge dels residus polimèrics mitjançant el procés de descomposició tèrmica (piròlisi) pot ser una important font de hidrocarburs per la indústria petroquímica, contribuint a la protecció del medi ambient. De totes maneres, aquest procés requereix grans quantitats d'energia a causa de la poca conductivitat tèrmica i endotermicitat. Per tal de reduir el cost de la descomposició tèrmica de residus de material polimèric, els catalitzadors econòmics han arribat a ser de gran interès per al reciclatge global.

En aquest projecte, dos tipus de cendra (de carbó i de biomassa) es van provar com a catalitzadors per tal d'examinar la seva influència en els compostos volàtils emesos durant la descomposició tèrmica de residus de PET en les condicions seleccionades: 400ºC i atmosfera de nitrogen. A més, es van dur a terme dos mètodes de barrejar la mostra amb cada una de les cendres per comparar els seus efectes. L'anàlisi es va dur a terme mitjançant cromatografia de gasos, emprant diferents detectors, i mitjançant el mètode espectrofotomètric.

Paraules clau: Polietiletereftalat, PET, descomposició tèrmica del PET, descomposició tèrmica catalítica del PET, degradació tèrmica del PET, craqueig del PET, piròlisi del PET, cendra com a catalitzador.

3. INTRODUCTION

3.1. POLY(ETHYLENE TEREPHTHALATE) - PET

Poly(ethylene terephthalate), commonly abbreviated as PET, is a polymer from the polyester family formed from the polycondesation of terephthalic acid with ethylene glycol [1]. It was first obtained in 1941 by the scientists J. R. Whinfield and J. T. Dickson, who patented it as a polymer to produce fibers due the need to find substitutes to the cotton imported from Egypt during the Second World War [2].

PET polymer consists of the repetition of molecular units, known as monomers, as shown in **Figure 1**. This semicrystalline polyester, which is a lightweight plastic that can be from semi-rigid to rigid, has several characteristics, such as high mechanical strength, negligible permeability to CO_2 and outstanding barrier properties, and good thermal and chemical resistance. It is colourless and transparent (although colour can be added too), nontoxic, harmless, inert, and it presents a lack of influence on flavour [3].

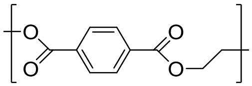

Figure 1. Poly(ethylene terephthalate) monomer.

Although PETs invention was meant to be used in the textile industry, all these characteristics have allowed the increase of the number of its applications. Nowadays, PET is being used in a wide range of areas such as packaging (from carbonated beverage bottles to many other containers) [6], engineering or electronics [4], causing an increase of its production year by year. On the other side, PET wastes grow as well from post-consumer PET products released from everyday life and becoming one of the substantial fractions in the solid waste stream [5]. PET products are inert and do not create a direct impact to the environment, but due its slow degradation in natural conditions (caused by its high resistance to the atmosphere, its poor biodegradability and photodegradability) more concern about the reduction of its volume has risen and studies about PET recycling and ways to reuse it are steadily increasing among the years [6].

3.2. PET RECYCLING

There are four main methods of PET recycling, and generally of plastics recycling [7-11]:

- Primary recycling or “in plant” recycling [7-11]. It involves the reprocessing of uncontaminated scrap plastics into products that have similar features from which they are generated, using conventional processing methods. Although it is the oldest way of plastic recycling as its simplicity and low cost, this process is only feasible with semi-clean industrial scrap plastics; therefore this process is not widely used.

- Secondary recycling or mechanical recycling [7-11]. It involves the reprocessing of the plastic via mechanical means (melting, shredding or granulating it). Stages of mechanical recycling include separation of plastics, removal of contaminants, crushing to reduce its size, extrusion by heat and reprocessing into new plastic The principal disadvantage of mechanical recycling is that it causes the degradation of the product properties each time that the plastic is recycled.

- Tertiary recycling or chemical recycling [7-11]. It involves the degradation of the polymer chain to obtain monomers (chemical depolymerisation), fuels or industrial chemicals. This kind of recycling requires not only a physical change but a chemical change, which can be achieved by using chemicals or under influence of heat. Chemical recycling processes are classified as hydrogenation, gasification, chemical depolymerisation (where the principals are glycolysis, methanolysis and hydrolysis), thermal treatments and catalytic cracking and reforming [11].

- Quaternary recycling [7-11]. It involves the recovery of energy content from plastics waste by its combustion: their chemical energy is transformed into heat or electricity by incinerating process. Although plastic wastes are valuable fuel due their heat capacity, especially high in the case of PET (h.c. of PET = 46 $MJ \cdot Kg^{-1}$ versus h.c. of heavy fuel oil = 41 $MJ \cdot Kg^{-1}$) [11], its incineration is ecologically unacceptable due to potential harmful substances produced during this process.

Among the recycling methods, chemical recycling contribution into global plastic waste management is very small due its limitation from the economical point of view [11]. However, it is the most acceptable method of recycling in environmental terms as it leads to the formation of the raw materials from which the polymer is originally made [10]. Moreover, the recycling of polymer waste by thermal processes (pyrolysis) can be an important source of hydrocarbons for the petrochemical industry and contributing to the environmental protection, as well [12].

3.3. PET THERMAL DECOMPOSITION PROCESS

During the thermal decomposition of PET, the molecular destruction of the polymer at high temperatures without oxygen, different parts of the polymeric chain start to react among them changing its properties. This widely discussed process occurs through consecutive random chain scissions and reactions: a proposed general mechanism [13,14] can be seen in **Figure 2**. The primary scission is believed to happen through a cyclic transition state: an ester linkage containing one β-hydrogen atom decomposes into a vinyl ester and a carboxyl end groups.

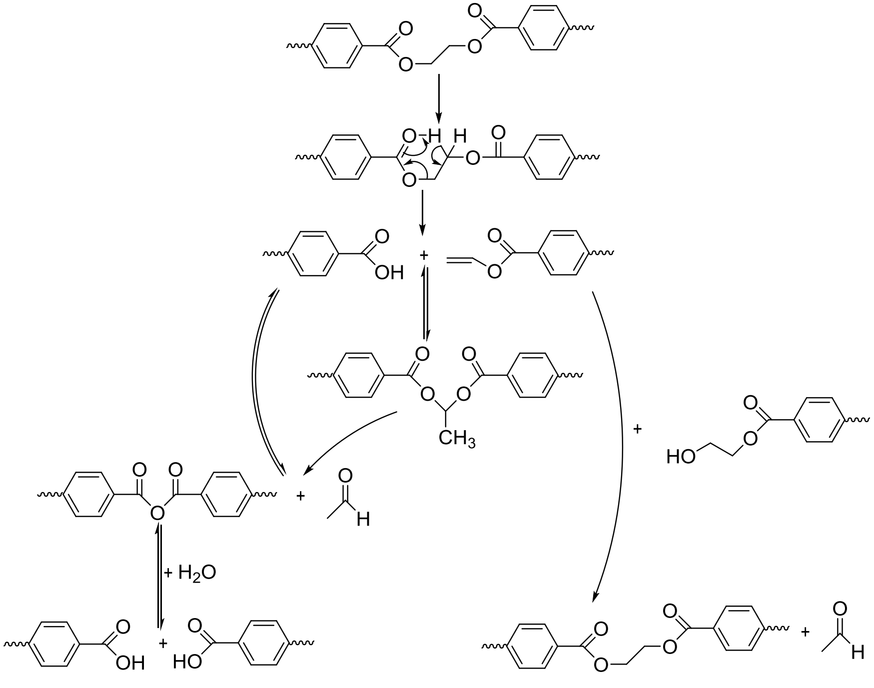

Figure 2. General thermal decomposition mechanism of PET.

It is not clear whether the thermal degradation of PET proceeds exclusively by heterolytic or homolytic processes, or whether the two processes are both present, perhaps varying in importance with test conditions (e.g., with temperature) [13].

The main primary and secondary compounds obtained through the thermal decomposition process of PET [15,16] can be seen in **Figure 3 and 4**. In general, there are three main thermal decomposition products: acetaldehyde, terephthalic acid and monovinyl terephthalate. Further decomposition of main products leads to the formation of other important secondary products as

CO, CO_2, benzoic acid and benzene. With long reaction times and high temperatures, chain scission will lead to the formation of smaller molecules while, conversely, branching and crosslinking reactions will occur, leading to the formation of highly aromatic residues.

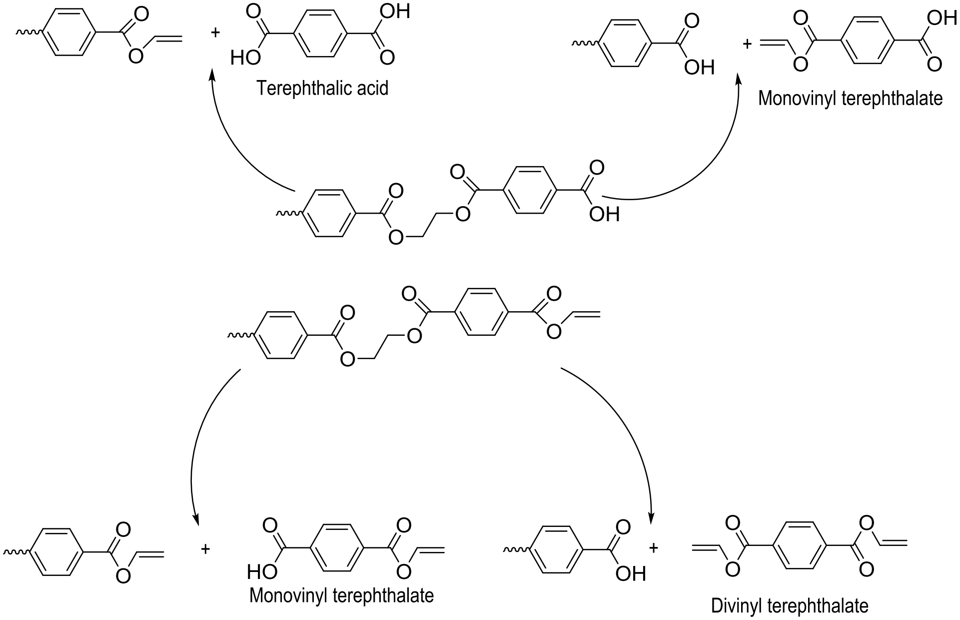

Figure 3. Terephthalic acid and its vinyl esters formation during PET thermal decomposition.

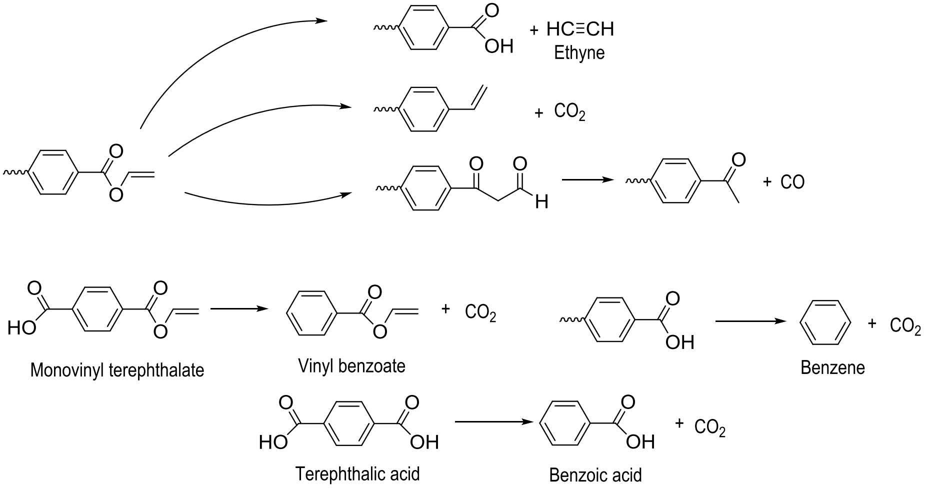

Figure 4. Secondary products obtained through PET thermal decomposition.

3.4. CATALYTIC THERMAL DECOMPOSITION OF PLASTICS

Thermal decomposition of waste plastics needs great quantity of energy due to their poor thermal conductivity [12] and endothermicity [17]. Applying an adequate catalyst in pyrolysis process at proper reaction conditions can provide some advantages over thermal degradation method, such as reducing the required high energy consumption, decreasing the time of the process, increasing the cracking ability of plastics, reducing the proportion of solid residue in final products, and narrow the product distribution [6].

For this reason, many new catalysts have been tested for the pyrolysis of plastics. Several kinds of metallic, non-metallic elements and other compounds have been developed as active phase of the synthesized catalysts along with different types of supporters [18] including alumina, silica, activated carbon, zeolites, carbides, olivine, etc. On the other side, homogeneous catalysts, acid mesoporous materials, non-acid mesoporous solids, FCC catalysts and metallic oxides have been studied as well as potential catalysts in catalytic pyrolysis of plastic wastes [19].

However, the use of expensive catalysts in the thermal decomposition process would not be viable for an industrial implementation due the high amounts of catalysts that would be required in a continuous operating plant [20]. Thus, the search of inexpensive and cheap catalysts for thermal decomposition of plastic wastes, and especially for PET, is of the most interest not only from the point of view of the economy of the process, but also from a global recycling point of view. Taking into consideration that pyrolysis of waste plastics would be only supported if the catalyst used had a practically zero costs, some industrial waste products or subproducts have been studied as potential catalysts in thermal decomposition process [19,21].

Among the waste materials considered to develop catalysts, fly ash generated during the coal combustion for energy production can be found. Fly ash particles are considered to be highly contaminating due to their enrichment in potentially toxic trace elements which condense from the flue gas [22]. Thus, the management of this fly ash has been a concern with various approaches for its beneficial use being investigated. A wide range of uses of fly ash have been reported [23], from the construction field (mixing it with concrete to improve its properties) to geotechnical applications. Moreover, fly ash treated to produce zeolites was confirmed as a catalyst in pyrolysis process of PE and PP plastic wastes [24]. However, there is no information about non treated fly ash applied in thermal decomposition of PET.

4. OBJECTIVES

The main objective of this work is to study the influence of selected catalysts on the composition of volatile compounds emitted during thermal decomposition of waste poly(ethylene terephthalate). In order to achieve this general purpose, the following issues will be addressed:

- To perform thermal decomposition process of waste PET in selected conditions: 400ºC in N_2 atmosphere.

- To identify and quantify volatile compounds emitted during thermal decomposition of PET.

- To examine the effect of different catalysts (coal fly ash and biomass fly ash), of which there are not previous studies, on the composition of the volatile compounds emitted during thermal decomposition.

- To compare two different methods of contacting PET with catalysts: physical mixing and impregnation method, to study their effect on the composition of the emitted volatile compounds in thermal decomposition process.

5. EXPERIMENTAL

5.1. MATERIALS, REAGENTS, INSTRUMENTS AND APPARATUS

5.1.1. Materials and reagents used in thermal decomposition process

- Waste PET from water bottles
- Biomass fly ash (Szczecin power plant)
- Coal fly ash Nº100170 (Stare Czarnowo power plant)

5.1.2. Reagents and standards

Reagents used to quantify formaldehyde were the following:

- Chromotropic acid sodium salt
- Concentrated sulphuric acid (p.a.)
- I_2 solution in KI
- Starch
- NaOH
- Formalin

Identification and quantification of other compounds were performed using these solvents and standards, all p.a, and provided by Aldrich and Fluka:

- Acetaldehyde
- Toluene
- Ethylbenzene
- Styrene
- Benzene
- Acetone
- Butyl acetate

5.1.3. Instrumentation

- Gas chromatograph *6890N* with mass selective detector *5973N, Agilent Technologies*
- Gas chromatograph *Chrom 5* with flame ionisation detector, *Laboratorni Pristroje Praha*
- Gas chromatograph *N-504* with thermal conductivity detector, *MERA-ELWRO*
- Spectrophotometer *Spekol 11*, *Carl Zeiss Jena*
- Compact Combustion Analyzer *Kane 400, Kane International*

5.1.4. Other instruments and apparatus

- Electric mill, *Profi Cook PC-KSW 1021*
- Sieves of different sizes

5.2. SAMPLE PREPARATION

Two bottles of Nałęczowianka mineral water were cut, frozen and grinded using the electric mill *Profi Cook PC-KSW 1021*. In order to cap off PET particles size, to minimize its effect [6], sieves were used to obtain a PET (0.3 - 1) mm fraction, which was used to perform thermal decomposition experiments.

Two different kinds of fly ash were provided by power station of Dolna Odra: coal fly ash and biomass fly ash. Both fly ashes, coal (CFA) and biomass (BFA), were characterized using sieves and measuring their pH value. Due to the different distribution in particle sizing obtained in the sieving, the whole fraction of coal fly ash < 0.3 mm (pH = 7.0) and the < 0.2 mm fraction of biomass fly ash (pH = 11.5) were used to perform thermal decomposition experiments.

In the first experiments PET, coal and biomass fly ashes were subjected to thermal decomposition separately to check their weight losses and study the emissions of volatile compounds; for that purpose these samples were weighed in ceramic boats.

Next, two different fly ashes were used applying two different preparation methods [5,6] to study its influence on PET decomposition process. The preparation methods of samples, detailed in **Table 1**, were the following: 1) Physical mixing: PET and fly ash were weighed and physically mixed in a ceramic boat; 2) Impregnation: PET and fly ash were weighed and mixed with 0.6 cm^3 of distilled water in a ceramic boat, left for 4 hours and then, dried 4 hours at 60 ºC.

All the ceramic boats were stabilized during at least 2 h in the desiccator before and after performing thermal degradation experiments in order to obtain a constant value of weight to study the percentage of weight loss of PET, which was object of other studies [25].

Sample	PET mass [g]	CFA mass [g]	BFA mass [g]	Preparation
PET	0.1000	---	---	---
CFA	---	0.1000	---	---
BFA	---	---	0.1000	---
PET + mCFA	0.1000	0.0100	---	Physical mixing
PET + iCFA	0.1000	0.0100	---	Impregnation
PET + mBFA	0.1000	---	0.0100	Physical mixing
PET + iBFA	0.1000	---	0.0100	Impregnation

Table 1. Samples for thermal decomposition experiments.

5.3. METHOD OF THERMAL DECOMPOSITION

In order to study the compounds emitted during PET decomposition, the thermal degradation system showed in **Figure 5** was used.

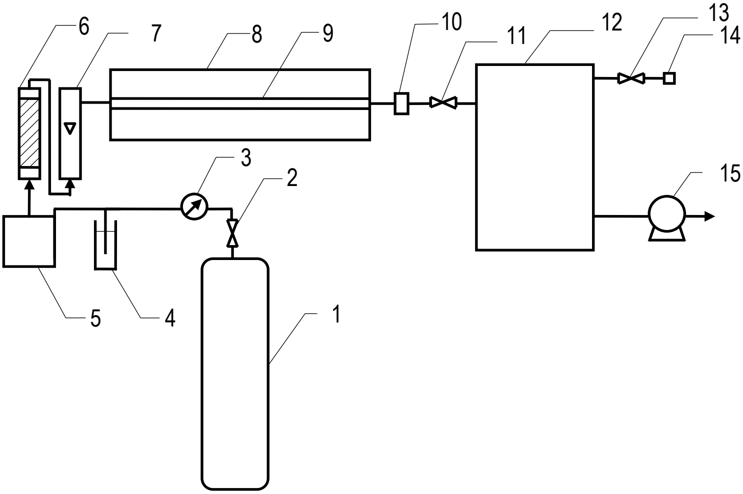

Figure 5. Scheme of apparatus used for the thermal degradation studies of materials in nitrogen atmosphere (*image from Dzięcioł et al, ref. 26*). (1) compressed nitrogen container; (2) pressure reducing valve; (3) manometer; (4) hydraulic regulator of pressure; (5) buffer container; (6) nitrogen cleaning system composed with molecular sieves 4A and silica gel ; (7) flowmeter; (8) flow tubular furnace; (9) ceramic tube; (10) glass fiber filter; (11) needle valve; (12) vacuum container with volume of 12,7 dm^3; (13) glass cock; (14) septum; (15) vacuum pump.

The system was stabilized during 2 h at 400ºC, temperature selected to perform thermal degradation experiments, and cleaned several times with the help of the pump to eliminate all volatile compounds. After cleaning the system, the purity of hermetic glass container was checked by injecting, into the *Chrom 5* and *N-504* chromatographs, 1 cm^3 and 2 cm^3 of the air container, respectively, in order to assure that all the volatile compounds were removed out of the system.

Once the system was cleaned, vacuum was generated in the hermetic glass container, and a dried glass fiber filter was placed in the system to keep non-volatile, solid degradation products that were subject of other studies [25].

Finally, a ceramic boat containing the sample was introduced into the furnace, and immediately nitrogen flow through the tube was started in order to reach atmospheric pressure exactly in 20 minutes. During experiment the volatile compounds were collected in the hermetic glass container. At the end of experiment, valves were closed and the hermetic glass container was left to stabilize during 30 minutes before analysis. Generally, each thermal degradation experiment was performed by these steps:

1) Stabilizing the system at 400ºC during 2 hours.

2) Cleaning the system under N_2 atmosphere several times.

3) Checking if the system was cleaned effectively.

4) Removing air from hermetic glass container under N_2 atmosphere, using vacuum pump.

5) Introducing the sample in ceramic boat into the ceramic tube of the system.

6) Setting a 0.025 $m^3 \cdot h^{-1}$ flow of N_2 during 20 minutes.

7) Closing the valves and letting the hermetic glass container stabilize during 30 minutes.

8) Performing analysis of volatile compounds from hermetic glass container (**5.4. section**).

5.4. ANALYSIS OF EMITTED VOLATILE COMPOUNDS

To identify and quantify the maximum number of compounds, different methods of analysis were performed depending on the nature of every substance. Knowing that in the same conditions substance retention time is characteristic, identification of most of compounds was carried out by two methods:

a) Using GC-MS and comparing the standard retention times with sample, and comparing each mass spectrum with the library data base.

b) Using GC-FID and GC-TCD by the comparison of the retention times of each peak from analysis sample with the retention time of proper standard.

Once compounds were identified properly, its quantification was performed mostly by external calibration method applying it in GC-FID (for high volatile, combustible compounds), GC-TCD (for carbon dioxide), and in colorimetric analysis (for formaldehyde). Combustion Analyzer was used, on the other side, to quantify carbon monoxide as it simplified that purpose.

For better comprehension, a schematic representation of the performed experimental procedure is shown in **Figure 6**.

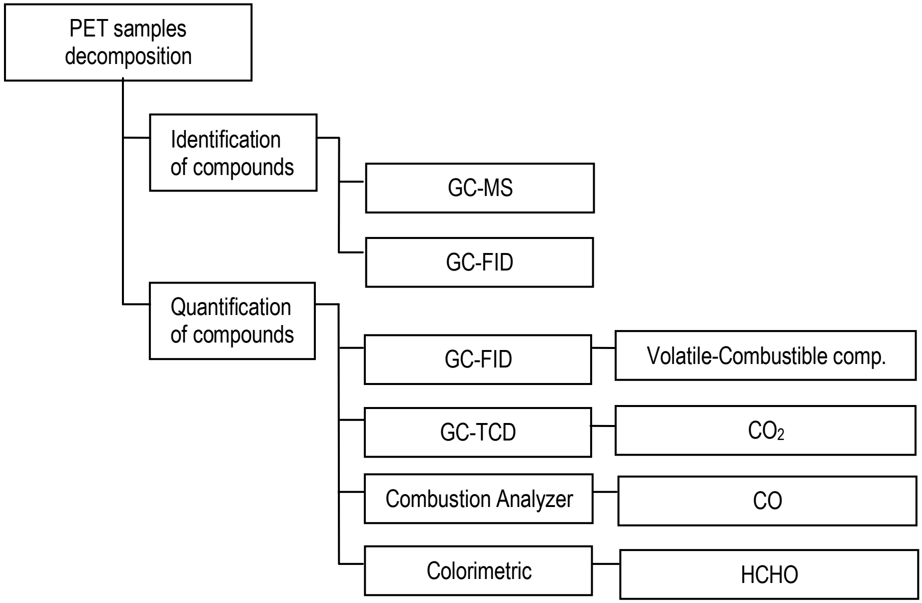

Figure 6. Schematic experimental procedure.

5.4.1. Gas chromatography with mass selective detector (GC-MS)

The identification of the emitted compounds was performed using an *Agilent 6890N* gas chromatograph with a *5973N* mass selective detector, equipped with a *7683* series injector. A *HP–5MSI* capillary column (5% phenylmethylpolysiloxane, 30 m x 0.25 mm I.D. and 0.25 µm film thickness) was used with the following temperature program:

50ºC (hold 5 min), 10ºC min^{-1} to 280ºC (hold 2 min)

Helium was used as a carrier gas at a constant flow rate of 1.2 cm^3 min^{-1}. The injection port temperature was 250ºC, 4 µL of sample was injected via split (1:10) injection. The mass selective detector conditions were as follows: electron impact ionization 70 eV, full scan mode (20-300 m/z), MSD transfer line temperature: 280ºC, MS quad: 150ºC; MS source: 230ºC.

In order to prepare samples for the GC-MS analysis the emitted volatile products were adsorbed on 0.15 g of active carbon 0,3-0,5 mm, 35-50 mesh (Merck), by aspirating them from hermetic glass container during 30 min with a flow rate of 35 dm^3·h^{-1}. Extraction of the analytes from active carbon was performed using 0.7 cm^3 of two solvents: butyl acetate (for the very volatile comp. such as acetaldehyde) and acetone (for the less-volatile aromatic hydrocarbons).

5.4.2. Gas chromatography with flame ionisation detector (GC-FID)

The chromatograph *Chrom 5* was equipped with two chromatographic columns with different polarity, that were used to identify and quantify the compounds which can be detected using FID detection system. The specific characteristics of each packed column were: Column A - *Chromosorb 102*, 80-100 mesh (1 m x 3 mm), and Column B - SE 30 (10%) + Carbowax 20M (0.3%) on a *Chromosorb W NAW*, 60–80 mesh (2 m x 3 mm).

Taking into account previous experiments [28], work conditions to perform analysis with each column were selected as shown in **Table 2**:

Parameters	Column A	Column B
Thermostat temperature [ºC]	100	50 and 120
Injector temperature [ºC]	120	140
Detector temperature [ºC]	150	150
N_2 flow ($cm^3 \cdot min^{-1}$)	40	
FID Air ($cm^3 \cdot min^{-1}$)	200	
FID H_2 ($cm^3 \cdot min^{-1}$)	25	
Sample volume (cm^3)	1	
Range	1	
Attenuation	8 and 64	8 and 256

Table 2. Conditions used during GC-FID analysis.

In order to perform identification of compounds by the comparison between retention times and perform quantification of each compound, three gas standards were prepared by injecting the liquid mixtures of standards via heated evaporator to an evacuated hermetic 1150 cm^3 glass container, cleaned several times using a vacuum pump. The prepared standards were:

- Standard of acetaldehyde: 0.5 cm^3 of acetaldehyde were mixed with 1 cm^3 of distilled water (injected volume: 3 µL).

- Standard of toluene, ethylbenzene and styrene: 2.2 cm^3 of acetone, 0.1 cm^3 of toluene, 0.1 cm^3 of ethyl benzene, and 0.1 cm^3 of styrene were mixed; (injected volume: 0.5 µL).

- Standard of benzene: 2.35 cm^3 of acetone and 0.15 cm^3 of benzene were mixed; (injected volume: 0.5 µL).

Quantitative determination of acetaldehyde, toluene, ethylbenzene, styrene and benzene was performed by injecting at least three times different volumes of each gas standard into the chromatograph-FID to build a calibration curve for each compound. The following equation was used to determine the concentration of each analyte in the hermetic glass container after thermal decomposition processes:

$$C = m \cdot 1000 \cdot / Vi \qquad (1)$$

where:

C - concentration of each compound ($mg \cdot m^{-3}$)

m - mass obtained from calibration curves of each analyte (µg)

Vi - volume of sample injected (1 cm^3)

5.4.4. Gas chromatography with thermal conductivity detector (GC-TCD)

Carbon dioxide, an incombustible compound which cannot be analyzed using FID system detection, was identified and quantified using a TCD detector. The chromatograph *N-504* was equipped with the following packed column: silica gel 50-100 mesh (1 m x 4 mm); this column worked at room temperature. Working conditions to perform analysis using this chromatograph are collected in **Table 3**:

Parameters	Column A
Temperature [ºC]	25
Electric signal [mA]	270
H_2 flow [$cm^3 \cdot min^{-1}$]	40
Sample volume [cm^3]	2
Attenuation	1

Table 3. Conditions used during GC-TCD analysis.

Identification of carbon dioxide was performed on the basis of its retention time value, using as standard CO_2 present in air. Quantitative determination of CO_2 was performed by building its calibration curve, injecting 1, 2, 3, 4, and 5 cm^3 of atmospheric air into the chromatograph-TCD, and taking into account that its concentration is 360 ppm of CO_2 [27] at 25ºC and 1 atm conditions. The following equation was used to convert ppm into $mg \cdot m^{-3}$:

$$C = (C_{ppm} \cdot M \cdot P) / (R \cdot T) \qquad (2)$$

where:

C - concentration of CO_2 ($mg \cdot m^{-3}$)

C_{ppm} - concentration of CO_2 in atmospheric air (360 ppm)

P - standard atmospheric pressure (1 atm)

R - gas constant ($0.08206\ atm \cdot L \cdot mol^{-1} \cdot K^{-1}$)

T - standard temperature (298.15 K)

M - molar mass of CO_2 ($44.01\ g \cdot mol^{-1}$)

obtaining finally this simplified equation:

$$C = C_{ppm} \cdot M / Vm \tag{3}$$

where:

Vm = molar volume at 298.15 K and 1 atm ($24.45\ dm^3 \cdot mol^{-1}$)

5.4.4. Analysis of carbon oxide by compact combustion analyser

A portable flue gas analyzer, the *Compact Combustion Analyzer Kane 400*, was used to measure the levels of carbon monoxide, simplifying its quantification without the need of calibration curves, giving the concentration value directly in ppm. Equation (3) was used to convert ppm into $mg \cdot m^{-3}$. In this case:

C - concentration of CO ($mg \cdot m^{-3}$)

C_{ppm} - concentration of CO from combustion analyser (ppm)

M - molar mass of CO ($28.01\ g \cdot mol^{-1}$)

5.4.4. Spectrophotometric determination of formaldehyde

In order to quantify formaldehyde, which cannot be analyzed by chromatographic methods without derivatization, colorimetric study was performed measuring with the spectrophotometer *Spekol 11* the absorbance of the formaldehyde - chromotropic acid complex at 570 nm. Quantifying formaldehyde spectrophotometrically, however, required the dissolution of formaldehyde in water, using an impinger, before colorimetric method could be applied. Sample was taken using an aspirator during 24 minutes with a flow rate of 10 $dm^3 \cdot h^{-1}$ (total volume of aspirated air: 4 dm^3). From that aqueous solution, equal to 5 cm^3, 1 cm^3 was placed into four beakers and then each sample was analyzed spectrophotometrically as explained below. On the other side, different solutions were required to prepare the standards for the calibration curve.

Basic standard solution of formaldehyde was prepared dissolving 1 cm^3 of formalin until 100 cm^3 of distilled water in a volumetric flask. In order to determine formaldehyde concentration in this solution, iodometric titration was performed 3 times by the following steps:

1) 5 cm^3 of the basic standard solution were placed into an Erlenmeyer flask, then 20 cm^3 of 0.1 n I_2 in KI solution and 3 drops of 30% NaOH solution were added (colour changed to a pale yellow);

2) after 10 minutes 5 cm^3 of HCl (1:5) were added;

3) after 10 minutes titration of the excess of iodine was performed, using 0.1 n sodium thiosulfate solution with starch as an indicator (added near of the end of titration).

Formaldehyde working standard solution I (0.1 mg·cm^{-3}) was prepared by adding 2.4 cm^3 of the basic standard solution (4.148 mg·cm^{-3}) into a volumetric flask of 100 cm^3. Formaldehyde working standard solution II (10 µg·cm^{-3}) was prepared by diluting 5 cm^3 of the working standard solution I (0.1 mg·cm^{-3}) with distilled water up to 50 cm^3.

Finally, calibration was performed by the addition of different amounts of formaldehyde solution II (10 µg·cm^{-3}) into eight beakers (0.0, 0.1, 0.2, 0.3, 0.5, 0.7, 0,8 and 1.0 cm^3) and filling up to 1 cm^3 with distilled water.

To perform quantification of formaldehyde, 0.2 cm^3 of chromotropic acid sodium salt solution 1% in distilled water was added to every beaker (with standard solutions and samples). After 3 minutes 5 cm^3 of concentrated H_2SO_4 was added and then after 20 minutes the absorbance of each solution was measured at 570 nm wavelength. On the basis of obtained values, calibration curve of formaldehyde was performed.

The following equation was used to determine the concentration of formaldehyde in the hermetic glass container after thermal decomposition processes:

$$C = (m \cdot Vw) / (Vs \cdot Vg) \qquad (4)$$

where:

C - concentration of formaldehyde (mg·m^{-3})

m - mass of formaldehyde from calibration curve (µg)

Vw - volume of water in the impinger (5 cm^3)

Vs - volume of sample (1 cm^3)

Vg - volume of gasses aspirated from the hermetic glass container (4 dm^3)

6. RESULTS AND DISCUSSION

6.1. IDENTIFICATION BY GAS CHROMATOGRAPHY WITH MASS SELECTIVE DETECTOR

Retention times and mass spectral data (characteristic ions and their relative intensities) for the compounds from the analyzed samples are collected in **Table 4**. The same compounds were observed in every experiment.

Compound	Solvent	Retention time	Characteristic ions [m/z] and relative intensity
Acetaldehyde	Butyl acetate	1.37	M^+=44(55), 43(32), 42(12), 29(100), 26(13)
Benzene	Acetone	2.01	M^+=78(100), 77(22), 52(12), 51(12), 50(10)
Toluene	Acetone	3.23	M^+=92(70), 91(100), 65(15), 63(13), 39 (18)
Ethylbenzene	Acetone	5.65	M^+=106(38), 91(100), 77(10), 65(11), 51(12)
Styrene	Acetone	6.57	M^+=104(100), 78(44), 77(22), 51(26), 50(17)

Table 4. GC-MS data of the volatile compounds emitted during thermal decomposition of PET at 400ºC.

In the **Appendices** (pages 42-44) are attached two examples of the chromatograms obtained by GC-MS analysis, and the comparison between mass spectra from the NIST 02 Library with the mass spectra of the main peaks in each chromatogram.

The first chromatogram, from the analysis of volatile products of non catalytic thermal decomposition of PET sample, using acetone as solvent, shows the biggest peak at the retention time of 2.01 min and a small peak at a retention time of 3.23 min. These compounds were identified as benzene and toluene, respectively; their mass spectra, which are below the chromatogram, shows that the compounds were identified with a high quality of comparison with the mass spectra from the NIST 02 Library: characteristic ions m/z values are almost the same in both cases. In the second chromatogram, from the analysis of volatile compounds emitted during catalytic decomposition of PET in the presence of biomass fly ash, using butyl acetate as solvent, the main peak had a retention time of 1.37 min. Its mass spectra, below the chromatogram, shows that the compound was identified as acetaldehyde.

Amounts of other compounds were so small that their peaks were not observable on the chromatograms, but characteristic ions were present in proper retention times.

6.2. IDENTIFICATION BY GAS CHROMATOGRAPHY WITH FID AND TCD DETECTORS

GC-FID and GC-TCD analysis showed that during thermal decomposition of studied catalysts (coal and biomass fly ash) emission of volatile compounds was not observed. Thus, both catalysts did not decompose at the selected temperature of 400ºC and therefore, volatile compounds analysed after each thermal decomposition experiment were emitted only from PET.

In the analysis by GC-FID and GC-TCD, compounds identification was performed successfully comparing retention times of the samples with each standard, on the basis that in the same conditions this value is the same. Retention times obtained in the analysis of the samples and the prepared standards, using GC-FID and GC-TCD, are collected in **Table 5**.

Compound	**Retention times of emitted volatile compounds**		
	GC-FID B 50ºC	**GC-FID B 120ºC**	**GC-FID A 100ºC**
Acetaldehyde	1’20’’	1’18’’	3’03’’
Benzene	6’13’’	2’01’’	---
Toluene	15’30’’	2’59’’	---
Ethylbenzene	---	4’40’’	---
Styrene	---	5’05’’	---
Compound	**GC-TCD A 25ºC**		
Carbon dioxide	1’35’’		

“---“ retention time >30 min

Table 5. Retention times of emitted volatile compounds analyzed by GC-FID and GC-TCD.

In **Table 5** can be observed that identified compounds were in agreement with the identification performed by GC-MS.

Examples of the chromatograms obtained from the analysis of samples, using GC-FID and GC-TCD, are attached in the **Appendices** (page 45). It can be observed an increasing tendency of compounds peak areas while using fly ash as catalyst in PET decomposition experiments, this information is discussed with more details in the next section (**6.3. Quantification of compounds**).

6.3. QUANTIFICATION OF COMPOUNDS

Quantification of compounds emitted from analyzed samples by GC-FID was performed taking into consideration the best obtained resolution in chromatograms at the different conditions, as it changes depending on the polarity of the column and the selected temperature. On the other side, some of the compounds detected by GC-FID were not identified.

Calibration curves equations used for quantification of analytes and analysis conditions (of column, temperature and range, in GC analysis), are collected in **Table 6**.

Compound	Method	Conditions	Att.	Equation $y = ax + b$ y = area [mm^2] x = mass [µg]	R^2
Acetaldehyde	GC-FID	Column-A 100 ºC	64	$y = 509.54x - 6.2184$	0.9993
Benzene	GC-FID	Column-B 50 ºC	8	$y = 21237x + 6.2117$	0.9963
Toluene	GC-FID	Column-B 120 ºC	8	$y = 16308x + 2.5211$	0.9999
Ethylbenzene	GC-FID	Column-B 120 ºC	8	$y = 13782x + 1.8415$	0.9666
Styrene	GC-FID	Column-B 120 ºC	8	$Y = 11564x + 4.9907$	0.9916
Carbon dioxide	GC-TCD	Column-A 25ºC	1	$y = 14.536x + 0.8402$	0.9956
Compound	**Method**	**Conditions**		**Equation $y = ax + b$ y = abs. [UA] x = mass [µg]**	**R^2**
Formaldehyde	Colorimetric	λ = 570 nm		$y = 0.00124x + 0.0183$	0.9979

Table 6. Calibration curves data used to quantify each compound.

With the calibration curves equations and using equations 1-4 detailed in the previous section, the concentration of each compound in the hermetic glass container was determined. The same compounds were observed in every experiment but in different amounts. Applying the following equation (5) masses of each compound from thermal decomposition experiments were obtained; these values are collected in **Table 7**.

$$m = C / Vc \qquad (5)$$

where:

m - mass of emitted compound (µg)

C - concentration of emitted compound (mg/m^3)

Vc - volume of hermetic glass container (12.7 dm^3)

Compound	Mass [µg]				
	PET	PET+mCFA	PET+iCFA	PET+mBFA	PET+iBFA
Carbon dioxide	3703.2	3990.8	5028.4	3586.7	9779.4
Carbon monoxide	1294.0	1453.9	1468.5	1468.5	1701.2
Acetaldehyde	4354.8	5077.6	4790.9	4324.0	5563.6
Formaldehyde	43.2	78.8	78.5	65.0	73.1
Benzene	39.7	41.4	42.4	47.1	49.0
Toluene	0.6	0.6	0.6	0.7	17.4
Ethylbenzene	0.5	0.5	0.5	0.5	0.5
Styrene	2.2	2.6	4.2	5.7	5.9

Table 7. Masses of volatile compounds emitted during non-catalytic and catalytic 0.1000 g PET decomposition at 400ºC.

In **Table 8** are collected the maximum values of %RSD obtained in the quantification of each compound. RSD values in GC-FID method were below 2% for all the compounds, except in the case of some minor compounds (toluene and styrene) where small variations caused higher deviations. Carbon dioxide, on the other side, was quantified successfully using GC-TCD method with a RSD below of 2%. Quantification of formaldehyde by colorimetric method had associated a RSD below 15%.

Compound	Method	RSD [%]
Acetaldehyde	GC-FID	<2
Benzene	GC-FID	<2
Toluene	GC-FID	<20
Ethylbenzene	GC-FID	<2
Styrene	GC-FID	<20
Carbon dioxide	GC-TCD	<2
Formaldehyde	Colorimetric	<15

Table 8. RSD values for each method applied in the quantification of emitted volatile compounds.

In the emitted volatile products carbon oxides, aliphatic aldehydes and aromatic hydrocarbons were observed. The main products were acetaldehyde, carbon dioxide and carbon monoxide; while toluene, ethylbenzene and styrene represented the minority of the emitted compounds.

Comparing bibliographic data, the emitted volatile compounds composition during thermal decomposition of waste PET was similar to the composition of the thermal decomposition of pure PET [26]: the main volatile products were acetaldehyde, carbon monoxide, carbon dioxide and benzene.

In the next pages graphical representations of the data from **Table 7** can be found to discuss the effect of the catalyst and the sample preparation method on the emitted volatile compounds amounts.

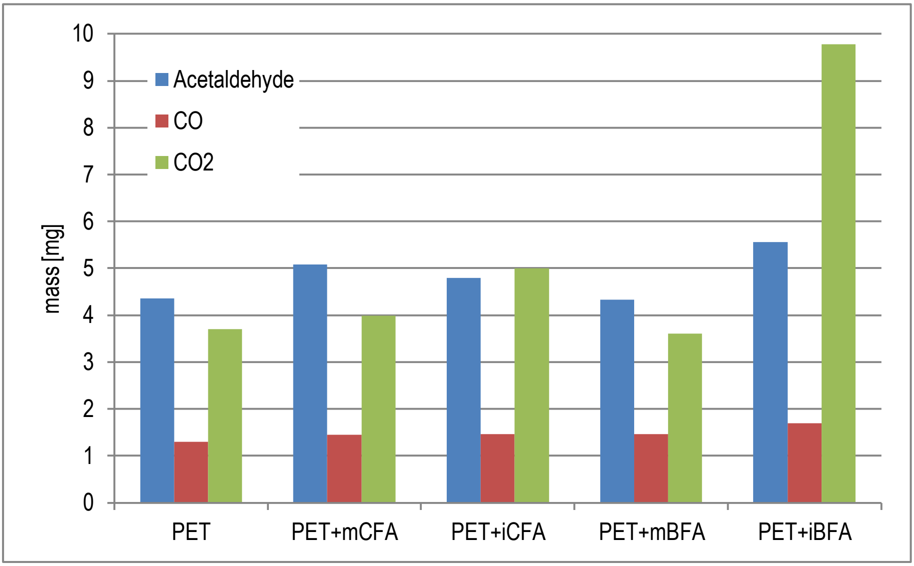

Figure 7. Masses of acetaldehyde, CO and CO_2 emitted from PET in different experiments.

Figure 7 shows a general increase of the amounts of the main volatile products (acetaldehyde, carbon monoxide and carbon dioxide) emitted during thermal decomposition of PET in the presence of fly ashes.

Using biomass fly ash provided higher values of carbon oxides amounts; on the one hand, higher concentrations of carbon oxides were observed for the both types of catalysts using impregnation method.

In the case of acetaldehyde, the biggest increase was observed using impregnated biomass fly ash; effect that was also observable, but in small magnitude, using impregnated coal fly ash. On the other side, the emission using impregnated coal fly ash was lower than using physical mixed coal fly ash.

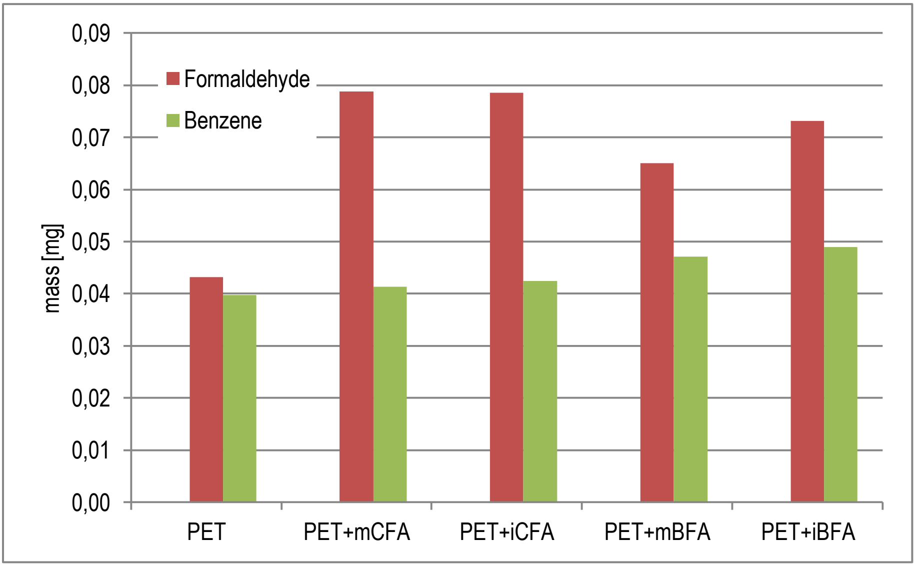

Figure 8. Masses of formaldehyde and benzene emitted from PET in different experiments.

On **Figure 8** it is shown quantification results of formaldehyde and benzene obtained from each sample decomposition. In this case, the same tendency was observed: higher amounts of compounds were produced while using both catalysts. However, this effect was more visible in the case of formaldehyde than in the case of benzene. Comparing results obtained for two types of fly ashes, using biomass fly ash provides slightly higher amounts of formaldehyde and benzene.

On the other side, impregnation method leads to obtain higher values of emitted masses of both compounds than physical mixing method.

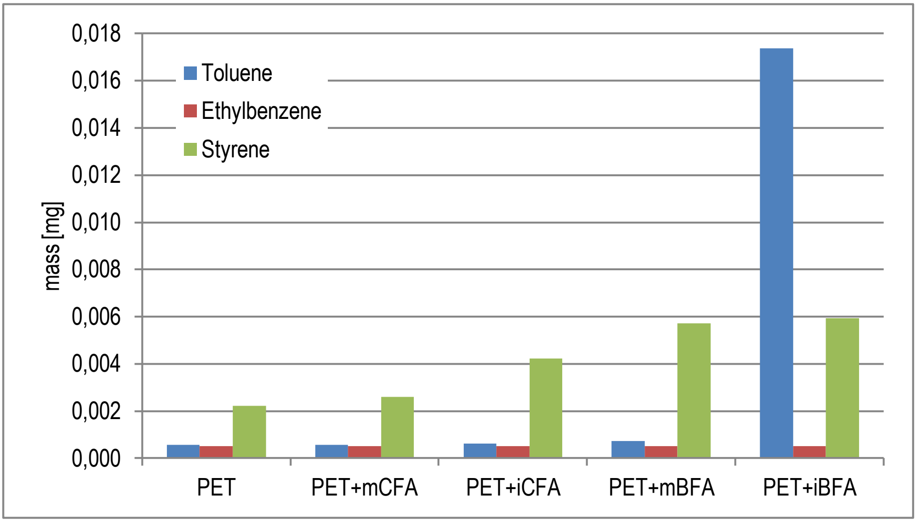

Figure 9. Masses of toluene, ethylbenzene and styrene emitted from PET in different experiments.

On **Figure** 9 it is shown that emitted masses of the minor compounds (toluene and styrene) produced during thermal decomposition experiments increased using the both types of fly ash. An exceptional increase of the emitted mass of toluene during thermal decomposition of PET using impregnated biomass fly ash as catalyst was observed. Although impregnated biomass fly ash provided also the highest value of emitted mass of styrene, that value was only a little higher than the obtained using physical mixing method.

Amounts of emitted ethylbenzene were very small in all experiments and for this compound it was not possible to observe any catalytic effect.

For the two compounds, toluene and styrene, impregnation method provided higher values of emitted masses than physical mixing method. On the other side, biomass fly ash showed higher catalytic properties than coal fly ash.

On **Table 9** the total masses of volatile compounds emitted from every thermal decomposition experiment are collected; these values were obtained summarizing the masses of all the volatile compounds for each experiment.

Sample	CFA	BFA	PET	PET+mCFA	PET+iCFA	PET+mBFA	PET+iBFA
Total mass of emitted volatile compounds [mg]	---	---	9.7	10.7	10.4	10.8	17.2

Table 9. Total masses of emitted volatile compounds during non-catalytic and catalytic thermal decomposition of 0.1000 g of PET at 400ºC.

Percentage of weight loss of PET samples and fly ashes was object of other studies [25]. However, they are collected in **Table 9** in order to compare them with the masses of the total emitted volatile compounds, collected in **Table 10**.

Sample	CFA	BFA	PET	PET+mCFA	PET+iCFA	PET+mBFA	PET+iBFA
Weight loss [%]	<0.2	<0.2	62.1	61.9	62.8	62.8	65.2

Table 10. Percentage of samples weight losses.

Graphical representations of **Table 9** and **Table 10** were made to compare more clearly the effect of the catalyst and the sample preparation method on the emitted volatile compounds, **Figure 10**, and in the percentatges of weight loss samples, **Figure 11**.

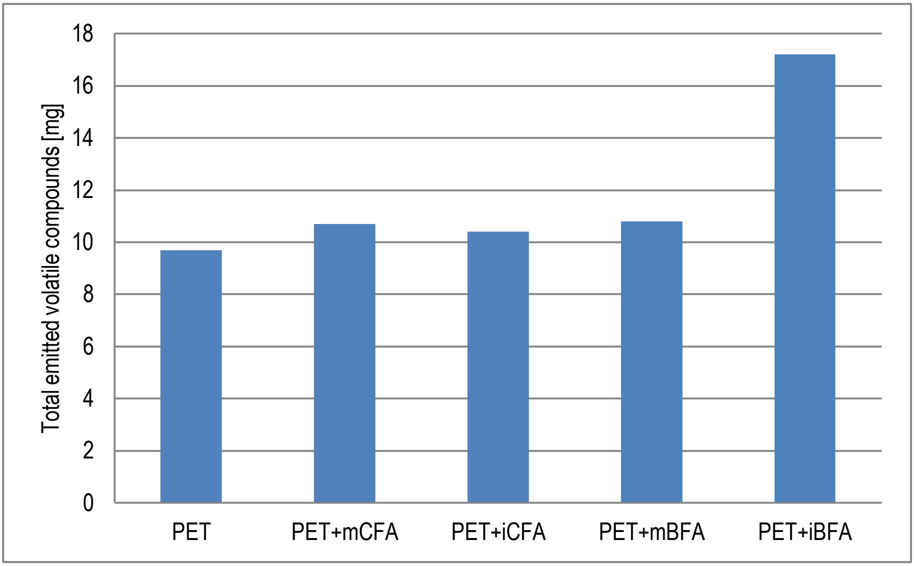

Figure 10. Total mass of emitted volatile compounds during each thermal degradation experiment.

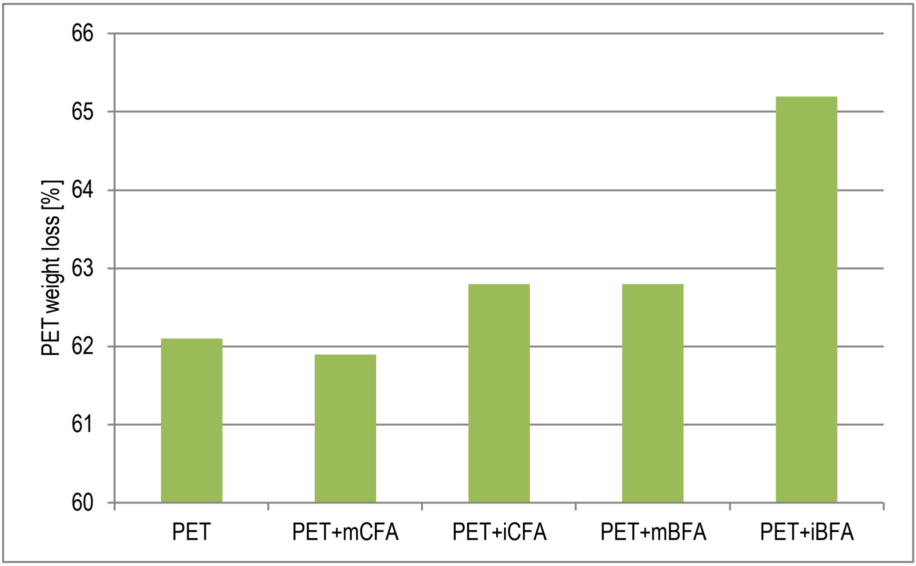

Figure 11. Percentage of PET weight loss in each experiment.

On **Figure 10** and **Figure 11** can be observed that generally, the two catalysts caused a small increasing of the total amounts of emitted volatile compounds and of the percentages of PET decomposition.

Biomass fly ash gave in the case of both methods, impregnation and physical mixing, higher results of volatiles emission and PET decomposition than using coal fly ash. The difference between the catalytic properties of coal and biomass fly ash can be caused by their pH values: biomass fly ash had a high pH value (11.5) caused by the high content of alkaline compounds, which can probably catalyze PET thermal decomposition.

On the other side, impregnation method provided the highest values of volatiles emission and PET decomposition, caused probably by a better surface contact between particles of waste PET and fly ash catalyst.

7. CONCLUSIONS

The aim of this project was to study the influence of selected catalysts (coal and biomass fly ash) on the composition of volatile compounds emitted during thermal decomposition of waste poly(ethylene terephthalate) at 400ºC in N_2 atmosphere. From this work we can conclude the following:

- Comparing non-catalytic and catalytic thermal decomposition of PET, the composition of the emitted volatile compounds was similar. The main volatile products were acetaldehyde, carbon dioxide and carbon monoxide. In smaller amounts formaldehyde, benzene and traces of other aromatic hydrocarbons were emitted.

- Both fly ashes caused a small increase of the amounts of emitted volatile compounds during thermal decomposition of waste PET, especially while using biomass fly ash. However, their catalytic effect was relatively small comparing the obtained results with the non catalytic process. The biggest catalytic effect was observed for carbon dioxide and toluene emission applying biomass fly ash impregnation method.

- The difference between the catalytic properties of coal and biomass fly ash can be caused by their composition. Biomass fly ash had a high pH value (11.5) due to high content of alkaline compounds.

- Impregnation method provided higher values of emitted volatile compounds during thermal decomposition of waste PET, probably due to a better surface contact between particles of waste PET and fly ash catalyst.

- A possible way to achieve higher thermal decomposition of PET could be: applying higher amounts of catalyst, increasing time of reaction, or performing experiments at higher temperature.

8. REFERENCES AND NOTES

1. Duvall, D.E. Environmental degradation of PET and its potential effect on long-therm mechanical properties of oriented PET products. *Polym. Plast. Technol. Eng*. **1995**, 34, 227.
2. Maldonado, M.A.; Medina, C.G. Diseño y construcción de una extrusora con capacidad de 1 kg/h, diseño del proceso y diseño del producto para el reciclaje mecánico del PET, Facultad de Ingeniería Mecánica, 2008.
3. Paszunn, D.; Spydhaj, T. Chemical recycling of poly(ethylene therephtalate). *Ind. Eng. Chem. Res*. **1997**, 36, 1373.
4. Herous, L.; Remadnia, M.; Kachi, M.; Nemamcha, M. Decay of Electrical Charges on Polyethylene Terephthalate Surface. *J. Eng. Sci. Technol. Review*. **2009**, 21, 87-90.
5. Chiu, S-J.; Cheng, W-H. Promotional effect of cooper(II) chloride on the thermal degradation of poly(ethylene therephthalate). *J.Anal. Appl. Pyrol*. **2000**, 56, 131-143.
6. Chiu, S-J.; Cheng, W-H. Thermal degradation and catalytic cracking of poly(ethylene therephthalate). *Polym. Degrad. Stab*. **1999**, 63, 407-412.
7. Patni, N.; Shah, P.; Agarwal, S.; Singhal, P. Alternate Strategies for Conversion of Waste Plastic to Fuels. *ISRN Renewable Energy*. [Online] 2013, 2013,7, http://dx.doi.org/10.1155/2013/902053 (accessed May 30, 2014).
8. Michell, P. *Tool and Manufacturing Engineers Handbook*, 1st ed.; Society of Manufacturing Engineers: New York, 1998; Vol. 8; p. 264-267.
9. Ceniceros, C.M. Reciclado de Polietilen Tereftalato (PE) Diversas Opciones, Universidad Juárez Autónoma de Tabasco, 2008.
10. Bartolome, L.; Imran, M.; Gyoo, B.; Al-Masry, W.; Hyun, D. Recent Developments in the Chemical Recycling of PET. *Material Recycling.* **2012**, 2012, 65-84.
11. Megiel, E. Chemical recycling of poly(ethylene terephthalate) (PET), Uniwersytet Warszawski Wydział Chemii, 2011.
12. Vasile, C.; Packdel, H.; Mihai, B.; Onu, P.; Darie, H.; Ciocâlteu, S. Thermal and catalytic decomposition of mixed plastics. *J. Anal. App. Pyrol.* **2011**, 57, 287-303.
13. Fairgrieve, S. *Degradation and Stabilisation of Aromatic Polyesters*, 1st ed.; Smithers Rapra Technology: Shrospire (UK), 2009.
14. Lechvik, S.; Weil, E. A review on thermal decomposition and combustion of thermoplastic polyesters. *Polym. Adv.Technol.* **2004**, *14*, 691-700.
15. Jabarin, S. *Polymeric Materials encyclopedia*, 1st ed.; CRC press: New York,1996; Vol. 8; p. 6114-6119.
16. Bednas, M.; Day, M.; HO, K.; Sander, R.; Wiles, D. Combustion and Pyrolysis of Poly(ethylene terephthalate). I. The Role of Flame Retardants on Products of Pyrolysis. *J. Appl. Polym. Sci.* **1981**, *26*, 277-289
17. Durmus, A.; Naci, S.; Selda, G.; Kasgoz, A. Thermal.catalytic degradation kinetics of polypropylene over BEA, ZSM-5 and MOR zeolites. *Appl. Catal. B-Environ*. **2005**, 61, 316-322.
18. Kaewpengkrow, P.; Atong, D.; Sricharoenchaikul, V. Pyrolysis and gasifications of landfilled plastic wastes with Ni-Mg-La/Al_2O_3 catalyst. *Environ. Technol*. **2012**, 33, 2489-2495.
19. López, A.; de Marco, I.; Caballero, B.; Laresgoiti, M.; Adrados, A.; Aranzabal,A. Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud. *Appl. Catal. B-Environ.* **2010**, 104, 211-219.

20. López, A.; de Marco, I.; Caballero, B.; Adrados, A.; Laresgoiti, M. Deactivation and regeneration of ZSM-5 zeolite in catalytic pyrolysis of plastic wastes. *Waste Manage*. **2011**, 31, 1852-1858.
21. Sushil, S.; Batra, V. Catalytic applications of red mud, an aluminium industry waste: A review. *Appl. Catal. B-Environ*. **2008**, 81, 64-77.
22. Ahmaruzzaman, M. A review on the utilitzation of fly ash. *Prog. Energ. Combust.* 2010, 36, 327-363.
23. Blissett, R.; Rowson, N. A review of the multi-component utilisation of coal fly ash. *Fuel*. **2012**, 97, 1-23.
24. Hyun, S; Jin, J.; Goo, S.; Chan, D. Pyrolysis of waste plastics using synthesized catalysts from fly ash, Korea Institute of Energy, 305-314.
25. Rodriguez, J. Effect of catalyst on solid thermal decomposition products of waste poly(ethylene terepthalate), Universitat de Barcelona, 2014.
26. Dzięcioł, M.; Trzeszczynski, J. Volatile products of poly(ethylene terephthalate) thermal degradation in nitrogen atmosphere. *J. Appl. Polym. Sci*. **1999**, 77, 1894-1901.
27. American Conference of Governmental Industrial Hygienists (ACGIH). Carbon dioxide. http://www.logico2.com/Documents/ACGIH%20recommendations%20for%20CO2.pdf (accessed May 30, 2014).

9. ACRONYMS

PET	Poly(ethylene terephthalate)
h.c.	Heat capacity
FCC	Fluid Catalytic Cracking
PE	Polyethylene
PP	Polypropylene
p.a.	Analytical purity
CFA	Coal fly ash
BFA	Biomass fly ash
PET+mCFA	Poly(ethylene terephthalate) and coal fly ash (physical mixing method)
PET+iCFA	Poly(ethylene terephthalate) and coal fly ash (impregnation method)
PET+mBFA	Poly(ethylene terephthalate) and biomass fly ash (physical mixing method)
PET+iBFA	Poly(ethylene terephthalate) and biomass fly ash (impregnation method)
GC-MS	Gas chromatography with flame mass selective detector
GC-FID	Gas chromatography with flame ionisation detector
GC-TCD	Gas chromatography with conductivity detector
I.D.	Internal diameter
m/z	ion mass / ion charge
MS and MSD	Mass selective detector
comp.	Compounds
FID	Flame ionisation detector
TCD	Conductivity detector
M^+	Molecular ion
RSD	Relative standard deviation

APPENDICES

APPENDIX 1: GC-MS DATA EXAMPLES

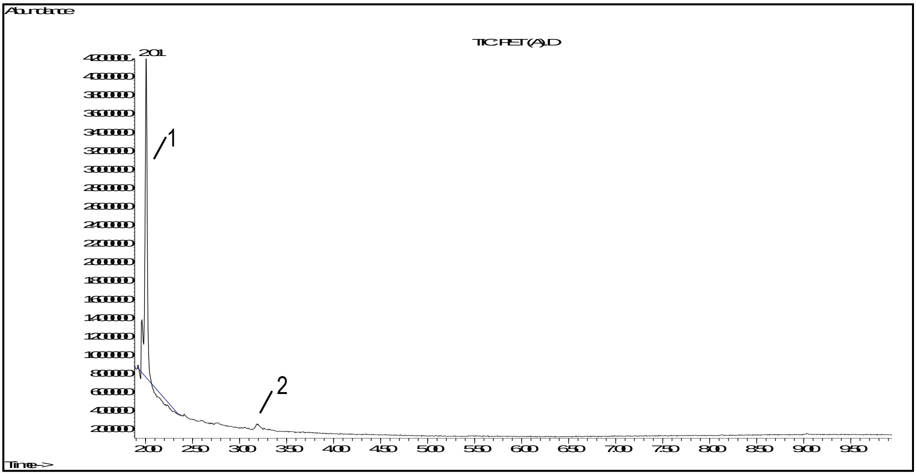

Figure 12. GC-MS chromatogram of emitted volatile compounds from PET sample using butyl acetate as solvent: 1- benzene, 2- toluene.

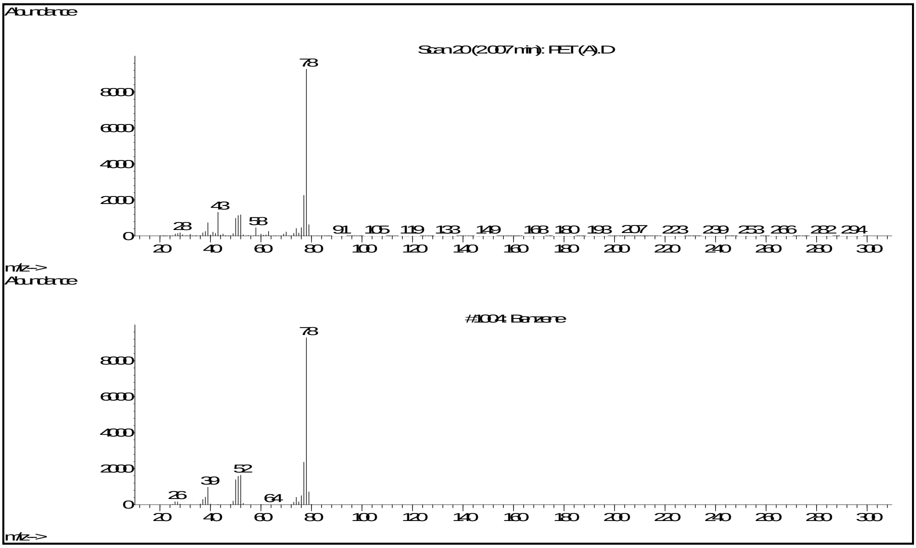

Figure 13. Mass spectrum of benzene emitted from PET sample compared with standard mass spectrum from NIST 02 Library.

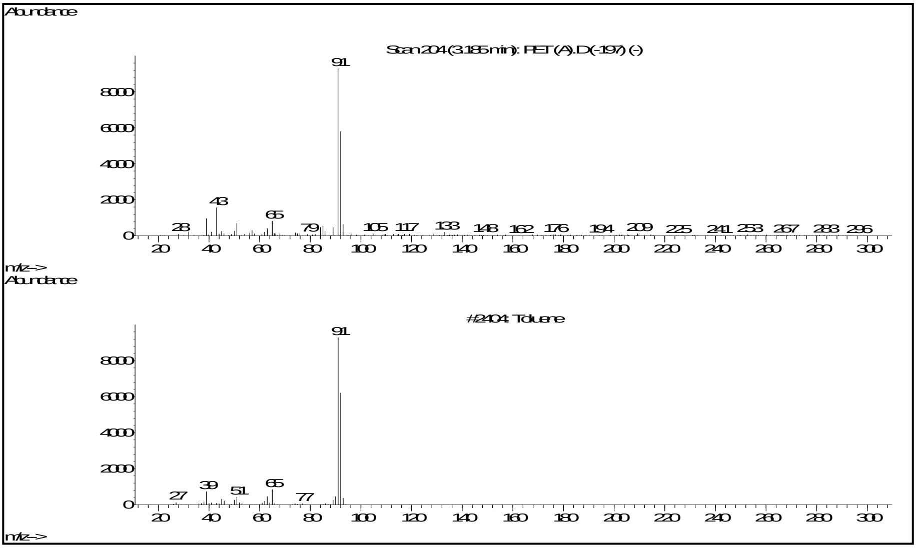

Figure 14. Mass spectrum of toluene emitted from PET sample compared with standard mass spectrum from NIST 02 Library.

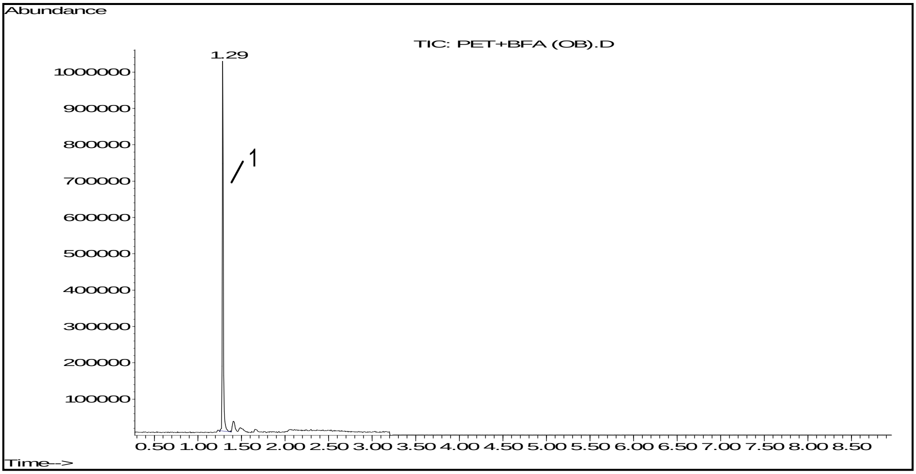

Figure 15. GC-MS chromatogram of emitted volatile compounds from PET+mBFA sample using acetone as solvent: 1- acetaldehyde.

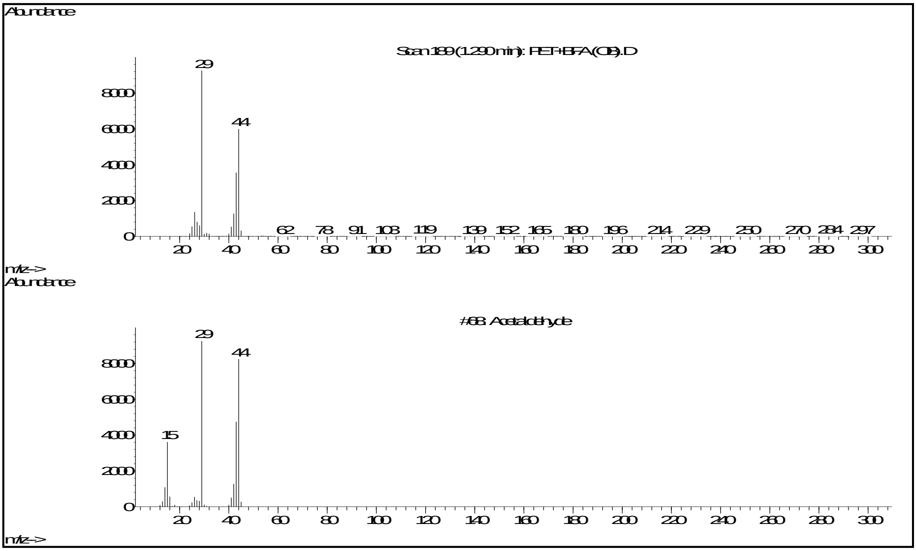

Figure 16. Mass spectrum of acetaldehyde emitted from PET+mBFA sample compared with standard mass spectrum from NIST 02 Library.

APPENDIX 2: GC-FID, GC-TCD DATA EXAMPLES

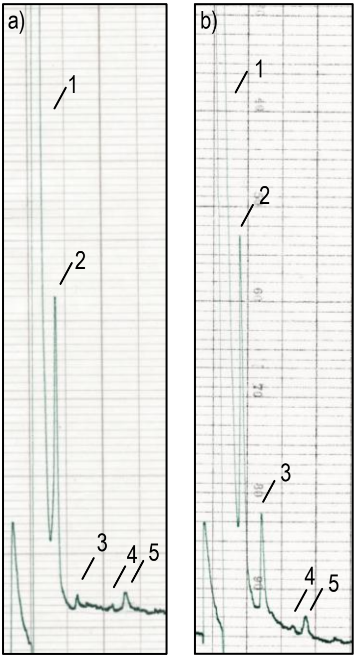

Figure 17. GC-FID chromatograms (column B, 120º, att. 8) of emitted volatile compounds from: a) PET, and b) PET+iBFA. Where: 1-acetaldehyde + unidentified comp, 2- benzene, 3- toluene, 4- ethylbenzene, 5- styrene.

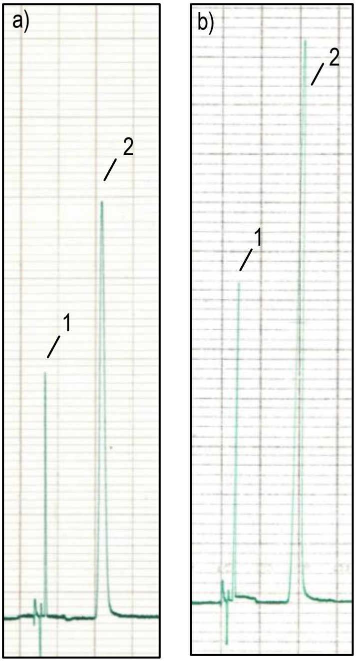

Figure 18. GC-FID chromatograms (column A, 100º, att. 64) of emitted volatile compounds from: a) PET, and b) PET+iBFA. Where: 1-unidentified comp, 2- acetaldehyde.

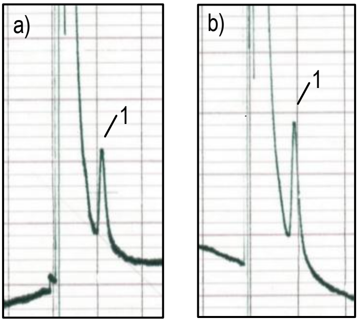

Figure 19. GC-TCD chromatograms (25º, att. 1) of emitted volatile compounds from: a) PET, and b) PET+iBFA. Where: 1-carbon dioxide.