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Characterization of emissions during the heating of tyre contaminated scrap

A. Arion [a], F. Baronnet [b,*], S. Lartiges [a], J.P. Birat [a]

[a] *IRSID (Centre Procédés, USINOR), Voie Romaine, BP 30320, F-57283 Maizières-lès-Metz, France*
[b] *Département de Chimie Physique des Réactions, UMR no 7630 CNRS-INPL, 1 rue Grandville, BP 451, F-54001 Nancy Cedex, France*

Abstract

In order to characterize the compounds (type and quantities) emitted during melting of organic contaminated scrap and to investigate the mechanism of their formation, an experimental set-up has been designed and built to study precisely the influence of temperature and gas atmosphere in the conditions of an electric arc furnace. These experiments lead to the determination of mass balances (C, H, O, S) and to the quantification of unburnt compounds (tars, carbon monoxide, volatile organic compounds (VOCs), benzene, toluene, ethylbenzene and xylenes (BTEX), polyaromatic compounds (PAHs)). Degradation conditions (gas atmosphere and temperature) corresponding to different areas in the electric furnace have also been investigated. Such experiments lead to a better understanding of degradation mechanisms; this interpretation is not possible from investigations performed in an industrial furnace since there are many uncontrolled parameters (large dispersion of the results).

Keywords: Oxidation; Pyrolysis; Recycling

1. Introduction

Scrap contains mainly iron, but also non-ferrous metals and small amounts of organic comaterials (less than 1%w/w). Their preparation is a very important step because it aims to separate the non-ferrous elements from the ferrous ones and to cut to the required size for the loading into the furnace. For example, shredders dismantle old household objects (washing machines, etc) and cars then a fan sucks fluff (foams in a car, etc) and a magnetic drum separates the cleaned scrap from the remaining non-ferrous components (plastics and other metals).

When melting organic contaminated scrap, i.e., when this scrap preparation has not been properly carried out, the thermal degradation of organic materials associated with steel leads to the emission of various organic and inorganic compounds. As steel is more and more largely produced in electric arc furnaces using scrap as a raw material and as regulations on stack emissions are being drastically enforced, monitoring and reduction of the effluents emanating from the furnace are essential.

The aim of this study is to characterize precisely these compounds (type and quantities) and to investigate the mechanisms of their formation and destruction in order to define how to obtain non-pollutant smokestack fumes.

It is rather difficult to give a comprehensive bibliographic review since it is a rather applied subject and our investigation is specifically focused on the electric arc furnace.

However papers from Conesa et al. (1996, 1997) concern the validation of a kinetic model for the thermal decomposition of tyre wastes and the nature of products emitted under pyrolytic conditions. Papers such as that of Rausa and Pollesel (1997) are focused on the effect of temperature on the pyrolysis of automotive shredder

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[*] Corresponding author.

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residues. More general papers deal with the thermal recovery from the effluents of tyre pyrolysis: Williams et al., 1995; Avenell et al., 1996; Napoli et al., 1997.

In this paper, we have tried to perform a systematic investigation by selecting experimental conditions which are found in the different zones of an electric arc oven (Fig. 1). The conditions can be considered as limiting cases and there are of course a large number of zones in which the experimental conditions are intermediary.

In an electric furnace, which is a batch reactor, a large range of atmospheres and temperatures varying according to time and space is observed (Arion, 1998) which can be classified as follows:

- near the injection nozzles and the furnace openings, at the beginning of the melting process, the gas phase can be represented by air and the temperatures range from 300°C to 600°C;
- between the electrodes and the furnace walls, the gas phase can be represented either by air or by N_2/CO_2 (60/40 v/v) and the temperatures range from 900°C to 1100°C;
- near the steel bath, i.e., at the end of the melting process, the temperature is about 1500°C and the atmosphere is either air or a mixture of CO_2/CO.

It is not possible to carry out a detailed investigation in a large scale electric arc furnace (even in a pilot plant) because this work aims at studying the influence of temperature and composition of the furnace atmosphere and also to determine the mechanism of formation of volatile organic compounds (VOCs), especially benzene, toluene, ethylbenzene and xylenes (BTEX) and polyaromatic compounds (PAHs) which are in very small amounts. Such an investigation requires well-defined conditions, which cannot be obtained in an electric arc furnace. For this reason, a laboratory equipment has been designed in order to perform small-scale experiments under well-controlled temperatures and gas atmospheres, with a good reproducibility and interpretability.

2. Materials and methods

Old cars are an important source of scrap iron. In France, two million cars have to be disposed of by shredding them every year; this generates 1.2 million tons of scrap metal. Three representative types of organic compounds contained in this scrap have been selected: used engine oil for the hydrocarbons, PVC putty for the plastomers, and a new car tyre for the elastomers. Pyrolysis of used engine oil has been carried out; two kinds of atmosphere (air and a mixture N_2/CO_2) and temperatures ranging from 300°C to 1500°C were tested and described in detail elsewhere (Arion et al., 1998). Only emissions emanating from the tyre degradation will be presented in detail here.

The tyre rubber was cored through the tyre tread; the sample therefore contains vulcanized elastomers (47%w/w), black carbon (25%w/w), steel cord (16%w/w) and other materials (textile, anti-oxidizing agent, etc). Table 1 shows the elementary analysis of the tyre rubber studied.

Fig. 2 shows the experimental set-up used. The small piece of tyre rubber on its steel sample holder is placed in a Lenton LTF 75/14/450 furnace at the temperature and under the atmosphere (air or N_2/CO_2) studied. The gaseous effluents originating from the oil degradation are cooled at the furnace exit: heavy products such as tars and aerosols are then condensed and filtered through Raschig rings and a quartz filter. The eight

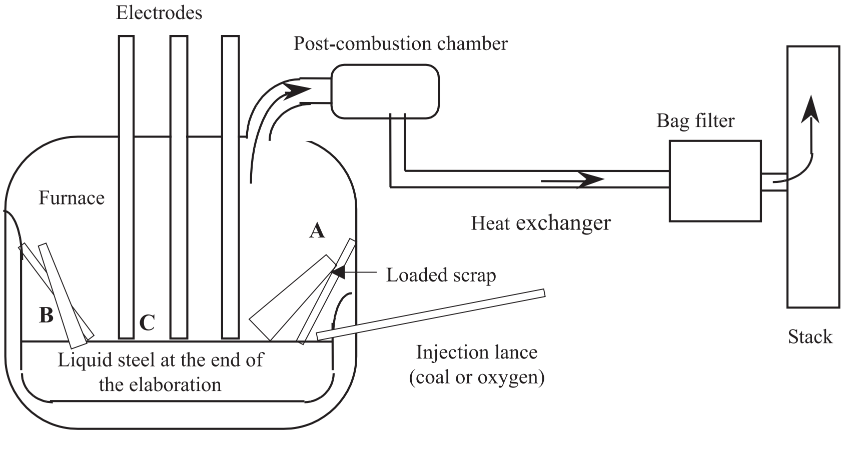

Fig. 1. Electric arc furnace and the different areas inside the furnace (batch): A – just after the loading of scrap (temperature: 300–600°C under air); B – at an intermediary step of steel melting (temperature: 500–900°C under air or N_2/CO_2 coming from the oxidation of injected coal or scrap iron); C – at the end of the process when most scrap has been melted (temperature 1100–1500°C under N_2/CO_2).

Table 1
Elementary analysis of the tyre rubber studied

Element	C	H	O	S	N	Cl	Fe	Ashes
(%w/w)	73.8	5.3	0.11	1.71	0.44	0.04	16.2	1.6

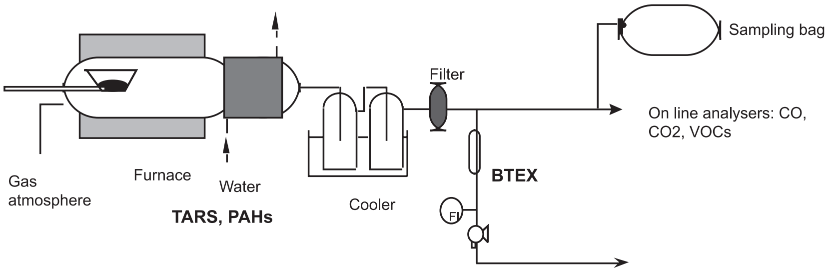

Fig. 2. Experimental set-up.

PAH emitted in fumes and subject to government regulations in France are analyzed by high-pressure liquid chromatography (HPLC) coupled with a fluorescence detector. Elementary analyses are made for tars and aerosols. The fumes are simultaneously sampled in different ways:

- with on-line specific analyzers for CO/CO_2 (Siemens Ultramat 22), O_2 (Siemens Oxymat) and total VOC (Siemens Fidamat 5E-E);
- with a sampling bag in Tedlar and off-line analysis by gas chromatography (GC) coupled with a flame ionization detector (FID) for light hydrocarbons or a GC/TCD (catharometer) for hydrogen and other inorganic gases;
- by trapping BTEX with activated charcoal and subsequent analysis by GC/FID.

In order to characterize the emissions of organic compounds during the recycling of organic contaminated scrap, four conditions corresponding to both representative areas in an electric furnace and to different kinds of degradation were chosen (Fig. 1):

- at 500°C under air (low temperature oxidation);
- at 900°C under air (combustion);
- at 900°C under N_2/CO_2 (pyrolysis);
- at 1100°C under N_2/CO_2 (pyrolysis with part of CO conversion).

3. Results

Main products of the thermal degradation were ash residues remaining on the sample holder, tars trapped in the cooler (high ratio of C/H), carbon oxides, water, VOCs (mainly alkanes and alkenes C_1–C_4, benzene and toluene, Figs. 3 and 4) and sulphur dioxide (Table 2). Satisfactory mass balances were obtained (Figs. 5–8) and Conesa et al. (1996) and Erdogan et al. (1991) observed the same distribution of the products.

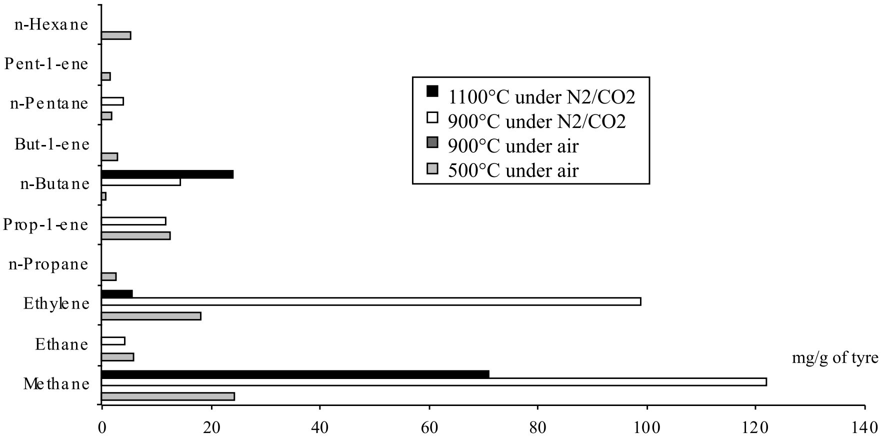

Fig. 3. Low molecular weight VOCs emitted during the degradation of tyre rubber.

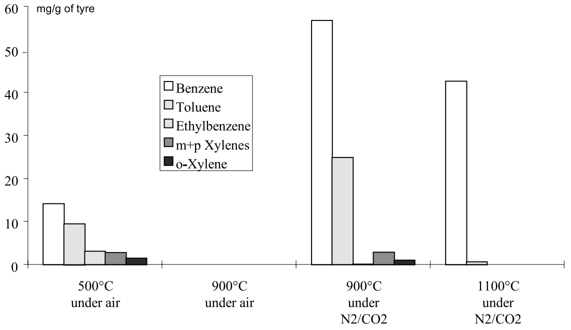

Fig. 4. Benzene and its derivatives emitted during the degradation of tyre rubber.

The effect of temperature and gas atmosphere on oxygen consumption is shown in Table 3. The amount of oxygen required for the tyre degradation is more important under air than under N_2/CO_2, because compounds resulting from primary cracking ignite in air above 400°C, whereas in the mixture N_2/CO_2 the dominant reaction is pyrolysis. The sample holder is oxidized above about 750°C (under air, $Fe + 1/2\ O_2 \rightarrow FeO$ and under N_2/CO_2, $Fe + CO_2 \rightarrow FeO + CO$).

The formation of small quantities (or traces) of other monoaromatic compounds and polyaromatic hydrocarbons (PAHs) was observed. Benzene and toluene were the main monoaromatic compounds emitted with increased emission of benzene with temperature and higher pyrolytic conditions (Fig. 3), whereas fluoranthene was the major PAH emitted (Fig. 9).

Under air at low temperature (500°C), one noticed the pyrolysis of the elastomers and a partial oxidation of the emitted hydrocarbons leading to large emissions of unburnt compounds such as initial carbon black of the tyre, emitted VOCs and CO but few PAHs. Under air at 900°C, no aromatics (PAHs and BTEX) were formed because the oxidation conditions were satisfactory and the other products (CO, VOCs) were formed only in trace amounts. Water and carbon dioxide were the major products and made up most of the mass balance.

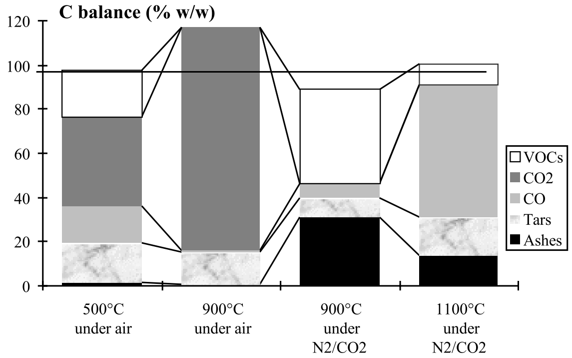

Fig. 5. Carbon balances obtained during the thermal degradation of tyre rubber.

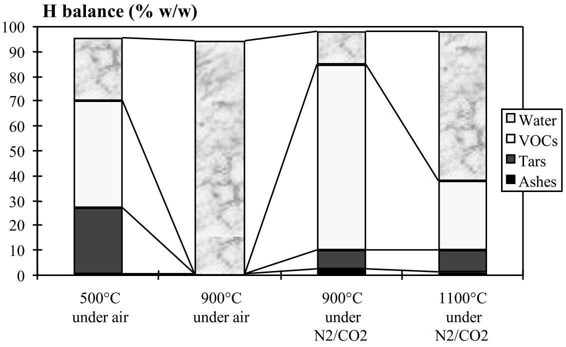

Fig. 6. Hydrogen balances obtained during the thermal degradation of tyre rubber.

Under N_2/CO_2, pyrolysis was the dominant reaction leading to large amounts of VOCs, especially aromatic compounds. At high temperature, the carbon dioxide present in the oven atmosphere reacts with the iron scrap and with the pyrolytic carbon from the tyre; this reaction leads to the formation of large amounts of carbon monoxide.

Sulphur was mainly emitted through gaseous sulphur dioxide but is also present in condensed matter in ash residues and tars.

Table 2
Major products emitted during the thermal degradation of tyre rubber (in mg/g of tyre)

Conditions	500°C under air	900°C under air	900°C under N_2/CO_2	1100°C under N_2/CO_2
Non-ferrous ashes	30.2 ± 6.2	13.5 ± 0.7	291 ± 3	204 ± 19
Tars	260 ± 17	119 ± 25	211 ± 45	283 ± 39
CO	283 ± 79	20.1 ± 3.3	136 ± 20	1691 ± 32
CO_2	1101 ± 152	2740 ± 767	Consumption	Consumption
Total VOCs	178 ± 24	0.26 ± 0.15	369 ± 28	133 ± 8
SO_2	21.6 ± 5.4	26.5 ± 6.3	14.0 ± 0.4	11.1 ± 0.2
H_2O	119 ± 32	448 ± 90	53 ± 7	254 ± 31

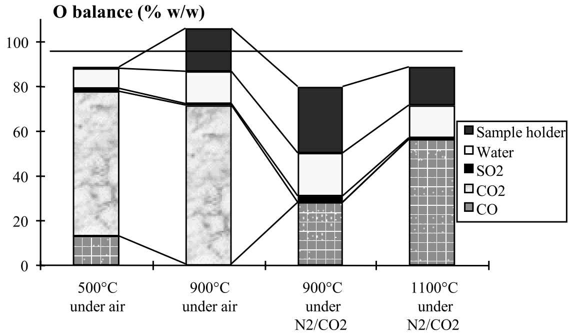

Fig. 7. Oxygen balances obtained during the thermal degradation of tyre rubber.

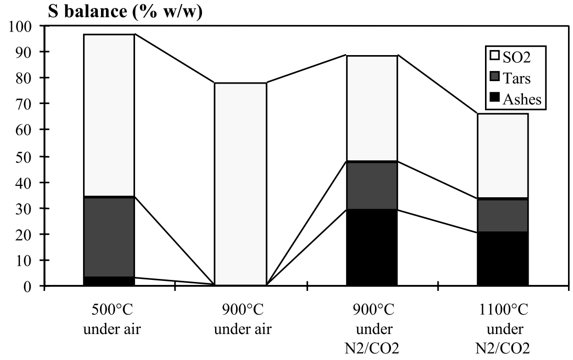

Fig. 8. Sulphur balances obtained during the thermal degradation of tyre rubber.

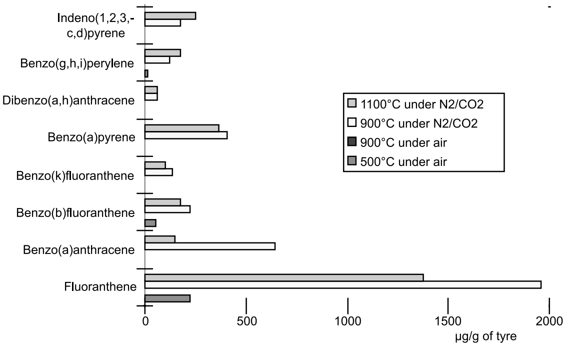

Fig. 9. PAHs emitted during the degradation of tyre rubber.

4. Discussion

The composition of the rubber of a car tyre is quite complex: natural rubber (polyisoprene), synthetic rubber (especially butadiene styrene copolymer), black carbon and various additives especially those containing sulphur for the vulcanization process.

As a consequence, it is practically impossible to write a reaction scheme; we can only discuss our results in a qualitative way, taking into account the basic knowledge of the thermal reactions of hydrocarbons.

It is also worth noting that in the thermal reactions of a single reactant (for instance an alkane) there are common steps for the pyrolysis and oxidation reactions. The situation should be the same for thermal reactions of complex mixtures.

The degradation of the tyre components is due both to pyrolysis and oxidation reactions; their relative importance depends on the temperature and on the concentration of oxygen.

Under pyrolytic conditions (Chauvel et al., 1980), hydrocarbons are thermodynamically unstable above 500°C. Generally their stability decreases when the molecular weight increases. Methane is also the most stable compound below 1000°C. A double bond is more stable than a single one. Because of the resonance energy, aromatic compounds are very stable at high temperature. Compared to other hydrocarbons excepting aromatic compounds, alkynes are stable between 1000°C and 1200°C. Fig. 10 shows the influence of temperature on the different steps of hydrocarbon pyrolysis.

Therefore under oxidizing conditions as seen before, both pyrolysis and oxidation take place, leading to the emission of numerous molecules more or less oxidized: final products like carbon dioxide and water, inert gases but also unburnt compounds such as H_2, CO, tars, VOCs, PAHs, etc.

Concerning the thermal degradation of the tyre rubber, taking into account the chemical composition (various types of rubbers, additives, etc), the temperature and the oxygen concentration linked to the residence time, the decomposition paths can be summarized as follows:

- volatilization of low molecular compounds (plastifiers, etc) (Kim et al., 1995);
- breaking down of the S–S bonds (reaction 1, Fig. 11), so that vulcanized rubbers behave like elastomers (Janowska and Slusarki, 1995);

Table 3
Oxygen mass balance related to the thermal degradation of tyre rubber and to the oxidation of the iron sample holder (in mg/g of tyre)

Conditions	500°C under air	900°C under air	900°C under N_2/CO_2	1100°C under N_2/CO_2
Fe sample holder	9.24 ± 1.37	368 ± 55	81 ± 45	289 ± 35
Tyre rubber	889 ± 6	1559 ± 421	80 ± 70	1425 ± 275
Total	898 ± 4	1927 ± 366	181 ± 25	1714 ± 240

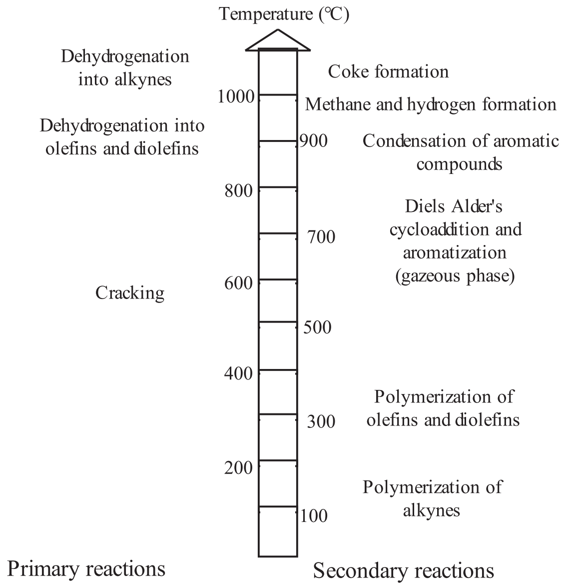

Fig. 10. Influence of temperature on the different steps of pyrolysis (Chauvel et al., 1980).

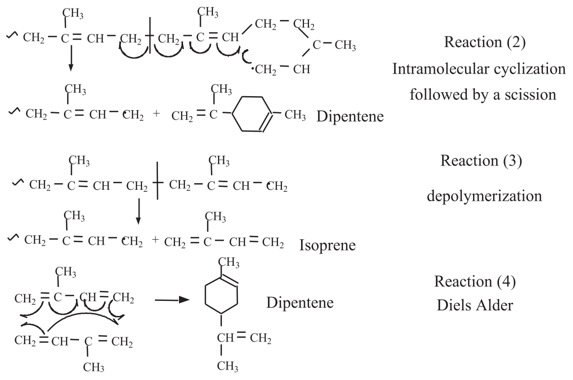

Fig. 11. Some possible decomposition paths of vulcanized elastomers.

- decomposition of the elastomers (primary cracking by unzip depolymerization and also intramolecular cyclization followed by scission) leading to oligomers but also compounds from reactions of these primary products like alkenes, benzene, etc and hydrocarbons up to $C_{16}H_{26}$ (Chien and Kiang, 1979; Groves and Lehrle, 1991).

Most of these compounds are aromatic or lead very easily to aromatics (by Diels–Alder reactions for example), which explain why during our experiments large amounts of benzene and its derivatives were produced in pyrolytic conditions, even at relatively low temperature.

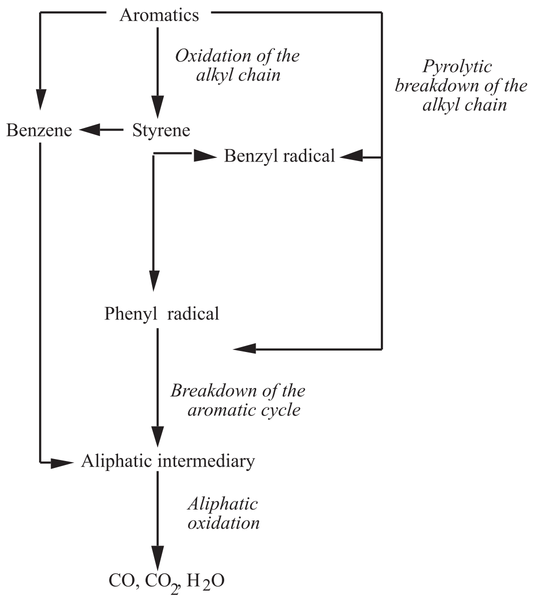

Fig. 12. Degradation of aromatics in an oxidizing medium.

Due to their carcinogenic properties, aromatic molecules need to be closely monitored; three different factors have an impact on their formation (Brezinsky et al., 1986):

- aromatic radicals present in the oven atmosphere;
- degradation occurring at high temperature;
- pyrolytic conditions.

Aromatic compounds with a side chain behave like aliphatic compounds, i.e., only the side chain is decomposed producing benzene and toluene, and then phenyl and benzyl radicals. PAHs are formed by condensation of aromatic radicals under pyrolytic conditions. Aromatic compounds (with or without side chain) can be formed by a Diels–Alder reaction from diolefins and olefins. The aromatic compounds are stable at high temperature under pyrolytic conditions (ratio between oxygen and hydrocarbon greater than 2), whereas under oxidizing conditions PAHs are not produced because the monoaromatic molecules (their precursors) are quickly oxidized (Fig. 12) into aliphatic hydrocarbons and then into water and carbon dioxide (Venkat et al., 1982; Brezinsky et al., 1986).

5. Conclusion

The laboratory equipment used allows a reproducible and detailed study of organic compounds emitted during pyrolysis of tyre rubber, temperature and atmosphere being two well-controlled parameters. Such experiments lead to a better understanding of degradation mechanisms, which is not possible in an industrial furnace, as there are too many varying factors (large dispersion of results).

The previous discussion on the possible reaction steps and our experimental results, especially these shown in Figs. 4 and 9 show that an efficient oxidation (close to the combustion conditions) is necessary to avoid the emission of aromatic species.

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