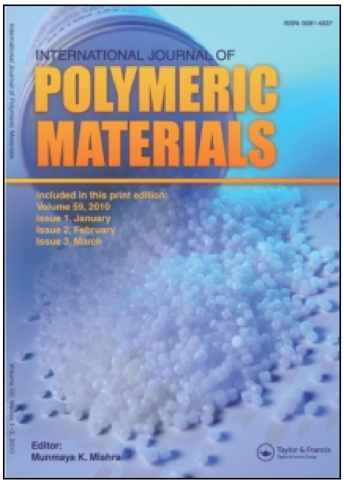

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Chemicals and Energy from Medical Polymer Wastes
I. Pyrolysis of Disposable Syringes

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The pyrolysis of the disposable syringes has been studied and reaction products have been characterized by gas-chromatography, density, refractive indices, aniline point analysis and spectroscopic methods. It has been concluded that pyrolysis offers a solution for treatment of this kind of medical polymer wastes and fuels and/or chemicals can be obtained.

Keywords: Medical waste; syringes pyrolysis; polyethylene; polypropylene; PE/PP blends

1. INTRODUCTION

Medical wastes are materials generated as a result of patient diagnosis, treatment or immunization. They can be classified as: infectious (waste contaminated with communicable disease agents such as HIV and the hepatitis B viruses), pathological and hazardous wastes. Hazardous waste (so called red bag wastes) is a solid waste or combination of solid

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wastes which because of its quantity, concentration or physical, chemical or infectious characteristics may cause or significantly contribute to an increase in mortality or an increase in serious irreversible or incapacitating reversible illness, or pose substantial hazard to human health, if it is improperly treated, stored, transported or disposal otherwise managed [1,2].

The amount of waste generated by hospitals and other health care facilities has increased with wide acceptance of single use items. Approximately 466,000 tons of biohazardous wastes are generated in the US each year by 377,000 health facilities [3].

Some local municipalities and states prohibit the disposal of infectious and hazardous waste in landfills without prior treatment.

The methods of disinfection currently used are [1,4,5]: chemical disinfection, steam sterilization or autoclaving (this is the preferred method especially in Europe), thermal (dry heat) inactivation, gaseous exposure, incineration, recycling, etc. A number of new methods to dispose of medical wastes have been develop by Bio' oxidation Inc., Synthetica Technologies Inc., Nutek Corp., such as pyrolysis -- oxidation, plasma pyrolysis, microwaving and electron-beam irradiation [6,7], that use very high temperatures. The quantity of stack emissions (particulates, nitrogen oxides, trace metals, etc.) is significantly lower and dioxins and benzofurans are near zero if the newly developed methods were applied in place of incinerators.

Hospitals traditionally have incinerated their medical wastes, but tightening air quality regulations are focusing the closure of many onsite incinerators. Off-site disposal, not only is more costly but also raises concerns about liability should problems occur after the waste leaves the hospital [8].

Incineration sterilizes and detoxifies because the combustion process destroys pathogens and reduces the volume of waste, heat can be also recovered from the process. As other methods of decontamination-destruction, it reduces the volume of the hazardous wastes by more than 90% and its weight by 80%.

Studies have shown that HCl and heavy metals are emitted from medical waste incinerators causing air pollution. Evidence of toxic pollutants from the medical waste incinerator are attributed to polyvinyl chloride and some metallic constituents of the wastes [9]. There is concern about the danger of dibenzodioxins, polychlorinated biphenyls and dibenzofurans [10], resulting from the burning of plastic medical supplies. To address these problems, new technologies have been proposed (several have been already mentioned) including recycling, autoclaving, microwaving and chemical disinfection.

The main components of the medical wastes are [3]: paper, plastics, cotton, metals, etc. The plastics commonly found in medical wastes (33 wt %) are polyethyleneterephthalate, polyolefins (high density polyethylene, low density polyethylene, polypropylene), polyurethanes, polystyrene, polyvinylchloride (60 % from total plastics in medical wastes), etc. These plastics have a high potential as hydrocarbons sources for chemical industry. Medical waste appear from the disposable products such as: syringes, gloves, tubes, bags, bowls, prostheses, medicine containers, diapers etc. During their use, these products undergo only an insignificant aging process but their degree of contamination is very high. Contamination results either from various medicines as antibiotics, vitamins, etc., and especially from blood, viruses, serum, etc. The later kind of contamination make almost impossible their recycling by reprocessing due to the health risk of processors.

Pyrolysis is a practical way to recover the material content of plastic waste. Under appropriate conditions, the pyrolysis could be successful on the market through recovered products (gas and oil) and satisfactory ecological factors. Pyrolysis simultaneously generates oils and gases which are suitable for chemical utilization or generation of energy. The advantages of pyrolysis over combustion is a reduction in the volume of produced gases by a factor of 5 to 20 which leads to considerable savings in the gas conditioning equipment. Furthermore, the pollutants are concentrated in a coke-like residue matrix. It is possible to obtain hydrocarbon compounds as gas or oil. The gaseous and oil pyrolyzates may be suitable for common petrochemical separation processes [11]. In comparison with landfilling or incineration, pyrolysis of plastic waste is not economical for small quantities. This will change if the price of crude oil excalates and other methods of waste disposal increase their costs. Larger quantities requiring larger plants are an economically attractive.

This paper reports about the pyrolysis of the disposable syringes that enables us to obtain valuable chemicals.

2. EXPERIMENTAL

2.1. Materials

The disposable syringes subjected to the pyrolysis were manufactured by many companies (such as POLFA, DISCARDIT, DUTCHMED, RECAP, ERG, FEFARMA, TERUMO, etc.). On the basis of IR-spectra (Fig. 1), melting interval and gravimetric determinations, the composition of these syringes has been established. IR identification was made comparing IR spectra with those from the literature [12] (Fig. 1a).

Polypropylene (PP) was the main constituent of several syringes, but the most of them have the body from PP and the piston from high density polyethylene (HDPE). In the last case, the two polymers were in approximately equal quantities. Several syringes are provided with a rubber sealant.

In the IR-spectra of both constituents of the syringes appear some supplementary small bands assigned to the oxygen containing groups such as C—O—C (1800 cm^{-1}) and =C=O (1720 cm^{-1}) (Fig. 1b). According to the product specifications given by the manufacturing companies these bands correspond to the ethylene oxide used for sterilization and products resulted during this operation.

The elementary analysis data (Tab. I) indicated also the presence of 8.5–15 wt % oxygen in the sample composition and additionally

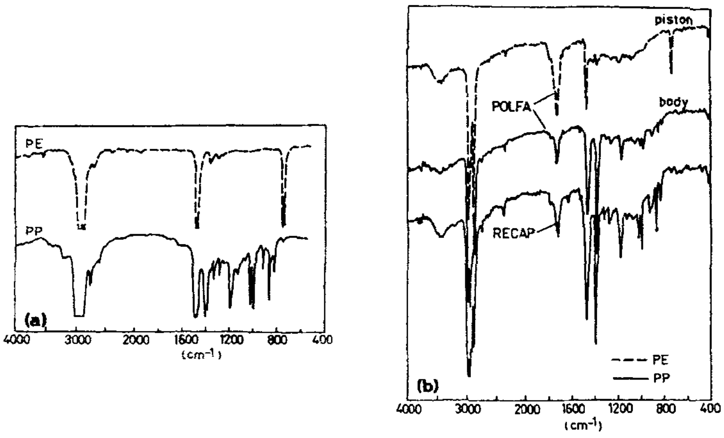


FIGURE 1 IR Spectra of PP, PE (a) and material of RECAP and POLFA syringes (b).

TABLE I Elementary analysis results for the disposable syringes subjected to the pyrolysis

Syringe Type	*C(wt%)*	*H(wt%)*	*N(wt%)*	*Cl(wt%)*	*O(wt%)*
POLFA	78.38	11.62	0.25	1.165	8.585
BD DISCARDIT	74.22	9.11	0.36	1.56	14.75
TERUMO	76.85	11.4	0.355	1.465	9.93

1–1.5 wt % chlorine and 0.25–0.35 wt % nitrogen. The last two elements probably belong to some impurities.

The average composition of the syringes was: 49 wt % PP, 47.98 wt % PE and 2.77 % rubber with above mentioned impurities.

In this study the disposable syringes containing approximately equal quantities of PE and PP have been employed.

2.2. Pyrolysis Experiments

The technological flow of the thermal treatment including pyrolysis of medical waste is presented in Figure 2.

Before pyrolysis, the syringes were sterilized by a chloramine chemical treatment and by boiling in water for 3–4 hours. The pyrolysis of

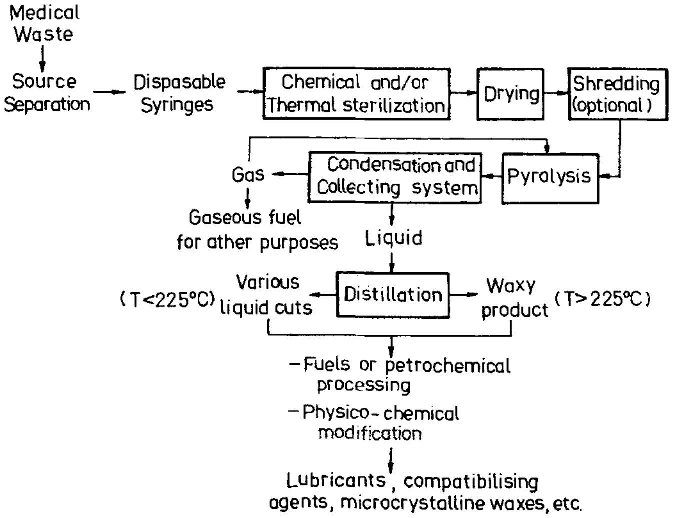


FIGURE 2 Technological flow of the pyrolysis process.

plastics is complicated by the fact that plastics show poor thermal conductivity while the degradation of macromolecules require considerable amounts of energy. In the polyolefin decomposition, due to the relatively rapid melting, the heat transfer is adequate in a bench reactor provided with stirrer and temperature control. The whole installation was under a small depression (vacuum) for extraction of the gaseous pyrolyzates at the pyrolysis temperature.

The pyrolysis experiments were conducted at 450 and 550°C. Sometimes in order to improve the heat transfer, the waste must be shredded. The pyrolysis products were condensed, collected and distilled. Finally, some applications were proposed and demonstrated elsewhere [13].

The evolution of the gaseous product during reaction is presented in the Figure 3. The gas volume increased and the reaction time decreased with pyrolysis temperature (T_p). The pyrolysis was complete in about 85 minutes at $T_p = 450°C$ and in 40 min at $T_p = 550°C$.

In both cases the condensed product is a light yellow wax-like material. The yield was 78–84 wt % in respect to the starting material. The gaseous product plus losses were about 15 wt % at 450°C and 20–22 wt % at 550°C. The pyrolysis conditions (temperature and duration) could be considered sufficient for sterilization.

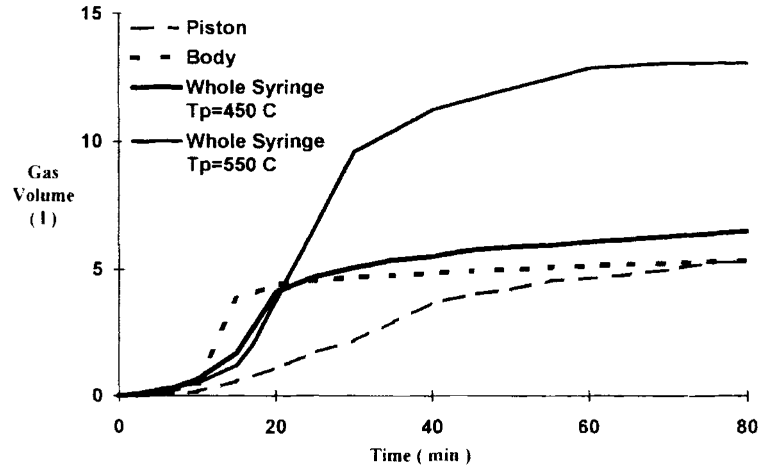


FIGURE 3 Gas volume versus pyrolysis time of the disposable syringes.

By optimizing the operating conditions for high waxy or oil yields, economic advantage favors raw material production over fuel substitutes [13].

2.3. Characterization of the Pyrolysis Products

Global characterization of the pyrolysis products was performed according to the STAS-methods and other methods previously described [14]. Besides STAS-methods as behavior at fractional distillation, refractive indices and aniline point determinations, have been also used chromatographic and spectroscopic analysis, elemental analysis and ebuliometry for number average molecular weight determinations.

The gaseous products were analyzed by a Carlo Erba-gas chromatograph equipped with two stainless steel columns, using argon or hydrogen as carriers. The first column of 4 m length, ϕ 5 mm i.d. and packed with Chromosorb 102, 80/100 mesh, was used for carbon dioxide and hydrocarbons' analysis and the second of 1m length ϕ 5 mm i.d. and packed with molecular sieves 5 Å was used for hydrogen and CO analysis.

The liquid products were analyzed by means of a high performance gas chromatography-mass spectrometry in the following conditions: HP 5890 Series II Chromatograph, HP 5971 Mass spectrometer, column HP1 (25 m × 0.32 mm × 0.52 μm) packed with Ultra 1 crosslinked methyl silicone gum, injector temperature 250°C, detector temperature 280°C, heating rate 1°C/min or 10°C/min, carrier gas was helium, flow rate 0.8 ml/min, monitoring ion m/e from 14 (30) to 500, injection 0.1 μl in hexane. Three minutes after injection, the solvent was completely eliminated. Identification of the components was made with a computerized WILLEY library of 135 000 mass-spectra.

The information about molecular structure and composition of reaction products are obtained by spectroscopic methods, especially from ^{1}H-NMR spectra, recorded at 90 MHz with $CDCl_3$ and CCl_4 as solvents. The IR spectra were recorded from a thin layer of liquid and the waxy product was deposed on KBr tablets.

2.4. Thermogravimetry

Thermogravimetry was employed to clarify some pyrolysis aspects. The thermogravimetric (TG) and differential thermogravimetric (DTG) curves were recorded on a Paulik-Paulik-Erdey-type Derivatograph, MOM Budapest, under the following operational conditions: heating rate (β) $12\,\mathrm{K\,min^{-1}}$, temperature range 20–600°C, sample weight 50 mg, using powdered samples in platinum crucibles, $30\,\mathrm{cm^3\,min^{-1}}$ air flow. Three or four repeated readings (temperature and weight loss) were performed on the same TG curve, each of them having at least 15 points.

Kinetic analysis of the TG data was carried out, using a single curve methods of Coats Redfern [15], Reich – Levi [16] and Swaminathan [17]. This means that both integral (Coats – Redfern, Reich – Levi) and differential (Swaminathan) methods of the kinetic parameter evaluation were used. A PASCAL program has been used that coupled all evaluation methods. The subscripts in the corresponding tables indicate the evaluation method.

3. RESULTS AND DISCUSSION

3.1. Pyrolysis Study

All results of the disposable syringes (PE/PP, 1/1 mixture) pyrolysis or decomposition are comparatively discussed with those obtained from experiments performed with separate components PE and PP (body and piston respectively) and pure polyolefins.

Figures 3 and 4 present the variation of gas volume and respectively gas density versus pyrolysis time. It can be remarked that the both values are higher for the mixture in respect with those of separate components.

The average composition of the gaseous products resulted from the pyrolysis of the disposable syringes at the two T_ps was given in the Table II.

It can be remarked that the higher is T_p, the higher is the amount of light components, the ethene and propene monomers content also increased. Carbon dioxide may appears from the oxygen containing groups existing in pyrolysing material and from the surrounding reaction medium.

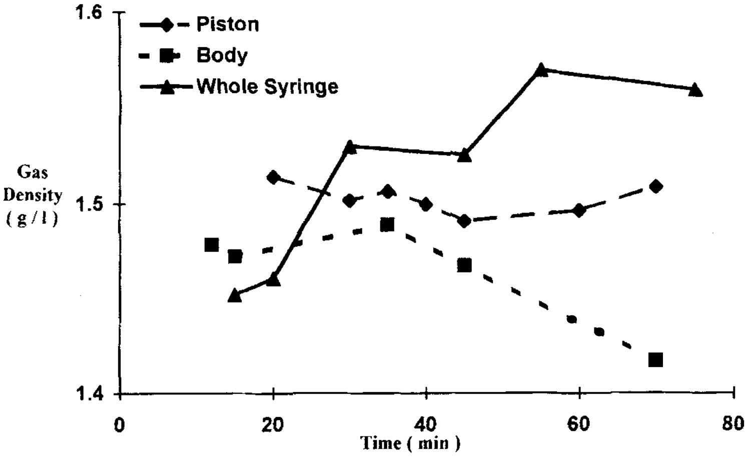


FIGURE 4 Density of the gaseous pyrolysis product versus pyrolysis time.

TABLE II Average composition of the gaseous product resulted from the pyrolysis of the disposable syringes

Component	*Composition (Vol %)*	
	$T_p = 450°C$	*$T_p = 550°C$*
Hydrogen	0.155	0.625
Carbon Dioxide	0.750	0.250
Methane	4.400	7.250
Acetylene	8.125	2.500
Ethene	4.750	8.250
Ethane	5.750	16.75
Propene	10.825	20.00
Propane	10.875	18.87
C-4 Fraction	54.37	25.50

Due to the high content of hydrocarbons, the gaseous product could be used as fuel in the process for self-running the pyrolysis plant or for other purposes. The gaseous product is highly energetic fuel with a calorific value of about 80–90 MJ/m^{3}N that decreases with the pyrolysis temperature as indicated by the data given in the Table III. Both heating values are superior to those of all known synthetic gaseous fuels [18].

TABLE III Upper (Hs) and lower (Hi) heating values of the gaseous pyrolysis products

Gaseous product obtained at	*Hs(MJ/m^3N)*	*Hi(MJ/m^3N)*
$T_p = 450°C$	105.15	97.48
$T_p = 550°C$	92.26	85.62

There were no significant differences between general characteristics of the waxy products obtained at $T_p = 450°C$ and 550°C and those obatined from piston, body and the whole syringes.

The distillation curves overlap (Fig. 5) while the densities (Fig. 6), refractive indices (Fig. 7), aniline points (Fig. 8) and average molecular weight (Fig. 9) increase with average boiling point of the cuts. The values corresponding to the mixture lie close to those of separate components. Such a behavior has been found for the pyrolysis products resulting from other polymer wastes [19]. Correlation indices and characterization factors indicated the prevalent paraffinic character of both products but some aromatics appear in the product (and its cuts) at $T_p = 550°C$. The increase of aromatic content with pyrolysis temperature is in accordance with literature data [11].

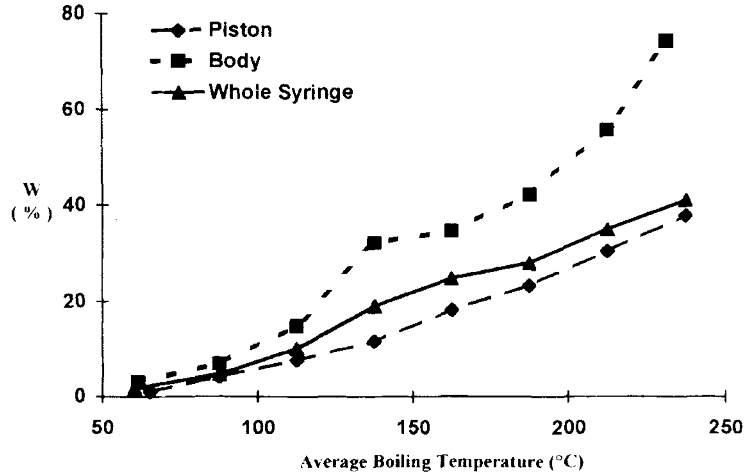


FIGURE 5 Distillation curves for condensable pyrolysis products resulting from the disposable syringes.

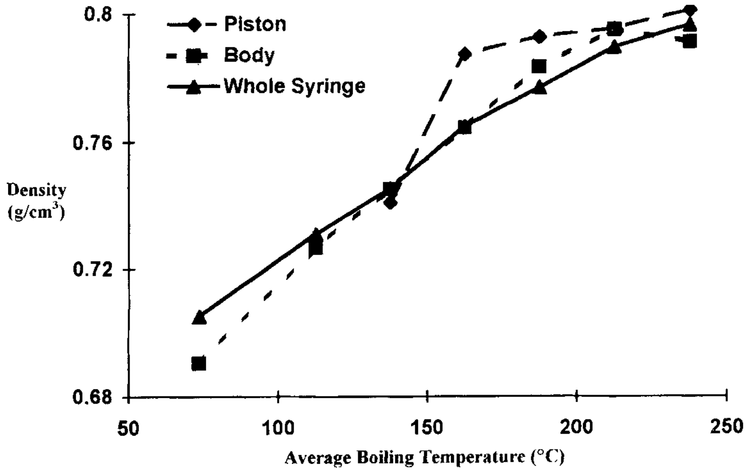


FIGURE 6 Density of the cuts versus average boiling point.

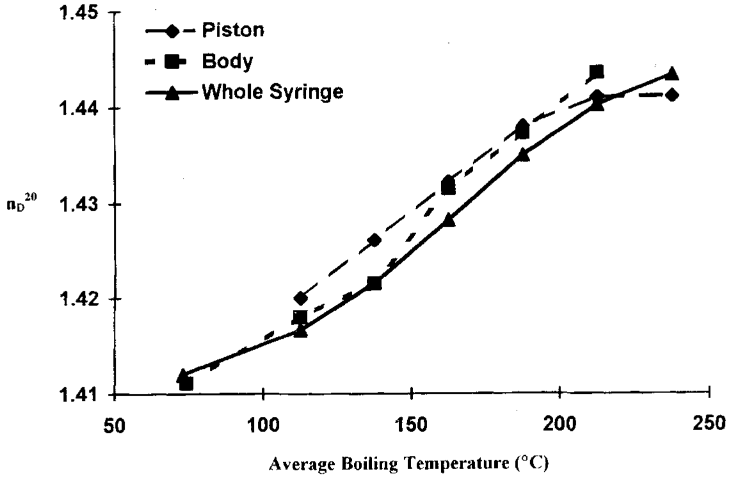


FIGURE 7 Refractive indices of the cuts versus average boiling point.

The IR (Figs. 10a and b) and ^{1}H-NMR (Figs. 11a and b) spectra of the waxy products confirm the conclusion drawn from the general characterization of condensable products and additionally other structural and compositional information can be obtained.

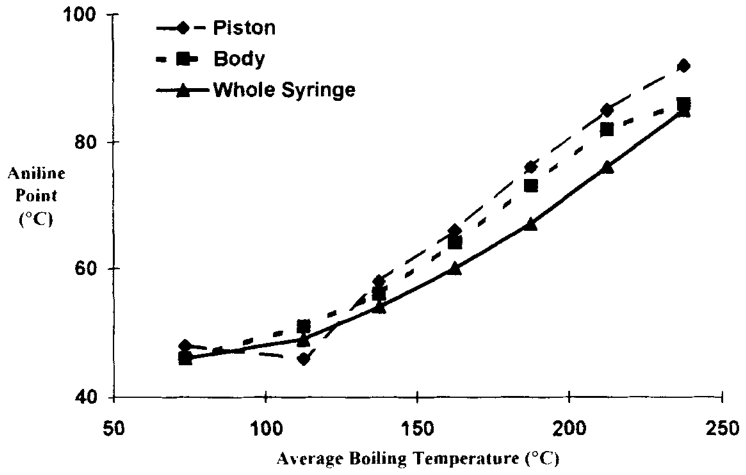


FIGURE 8 Aniline points of the cuts versus average boiling point.

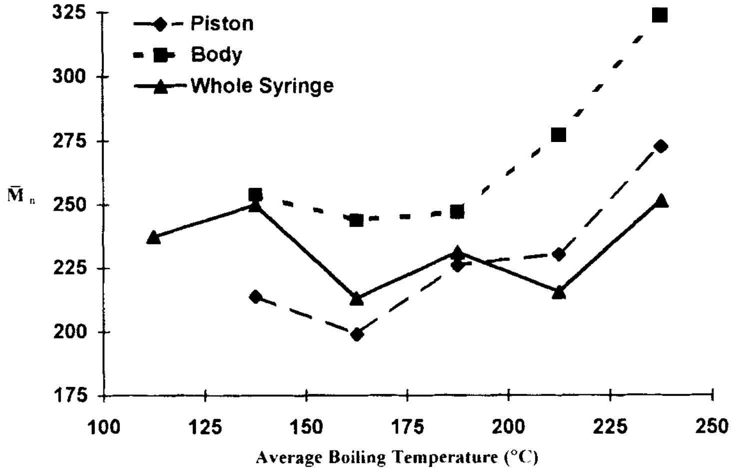


FIGURE 9 Average number molecular weight of the cuts versus average boiling point.

In the IR spectra of the low-boiling points cuts, the 3500 and 1680–1850 cm^{-1} bands are present, but these bands are missed in the cuts with average boiling point above 200°C. The IR spectra of the waxy products, the 100–125 and 125–150 and $T_b > 220$°C cuts contain all bands corresponding to the polyethylene and polypropylene

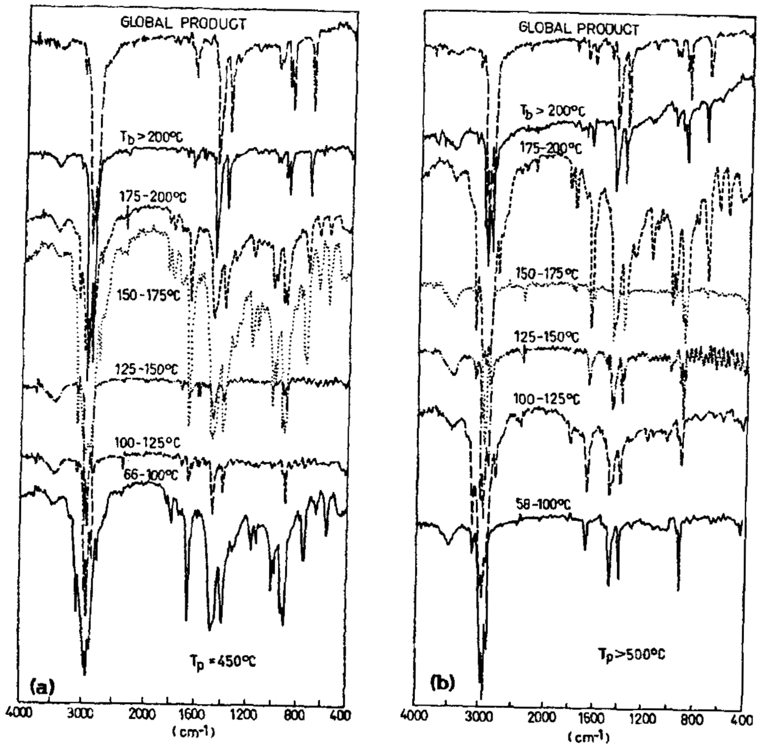


FIGURE 10 IR spectra of the global condensable pyrolysis product and its cuts obtained at $T_p = 450°C$ (a) and at $T_p = 550°C$ (b).

fragments and very weak bands corresponding to $=C=O$ and $-C-O-C-$ groups, while strong and very strong bands in 1720 and 500–800 cm^{-1} region were present in the spectra of the 50–100, 150–175 and 175–200°C cuts for both pyrolysis temperatures. These cuts had a high contamination degree. This fact was also evidenced in ^{1}H-NMR spectra but it is as expected, less evident. On the basis of NMR spectra it is possible to assign the 600–800 cm^{-1} bands to the aromatic hydrocarbons, which appear only in the cuts with low boiling temperature, namely < 100 and 100–125°C cuts, evidenced by the signal from 7–8 ppm region (Fig. 11) and Table IV.

A difference appears also in the 4–6 ppm region corresponding to the unsaturated protons, the ratio between vinyl and vinylidene groups being changed with pyrolysis temperature.

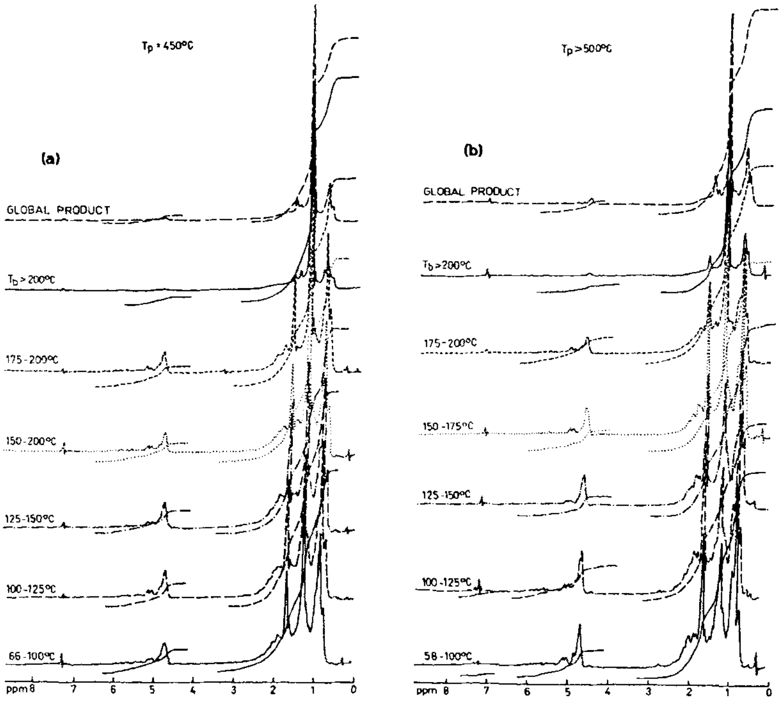


FIGURE 11 H-NMR spectra of the global condensable pyrolysis product and its cuts obtained at $T_p = 450°C$ (a) and at $T_p = 550°C$ (b).

It can be concluded that the differences appear only in the composition and the structure of the cuts with low boiling points. The distillation residue (with a boiling point higher than 225°C) has the same composition for both pyrolysis temperatures. It contains a small number of double bonds. This waxy material had the simplest IR and NMR-spectra, it was obtained in a prevalent amount (70 wt %) and had a molecular weight of ~ 1000. As we have shown in a previous paper, after a further chemical modification a high value product was obtained [13].

Elemental composition of the pyrolysis products and cuts is given in the Table V.

The oxygen content decreases with the increase of the boiling point of the cut. So, it could explain the presence of several alcohols and carbonyl compounds in the composition of the low boiling point cuts (Tabs. VI and VII).

TABLE IV ^{1}H-NMR data for the pyrolysis products and corresponding cuts resulting from the pyrolysis of the disposable syringes

Product or cut	*Aromaticity Index (%)*	*Unsaturation Index (%)*	*Saturation Index (%)*
	$T_p = 450°C$		
75–100	–	10.45	89.54
100–125	–	9.44	90.55
125–150	–	10.22	89.57
150–175	–	8.67	91.32
175–200	–	9.00	90.00
Distillation residue	–	3.93	96.06
Unfractionated Product	–	4.61	95.18
	$T_p = 550°C$		
< 100	0.871	11.32	87.79
100–125	2.78	15.08	82.13
125–150	–	9.34	90.65
150–175	–	9.61	90.38
175–200	–	8.78	91.21
Distillation Residue	–	3.20	96.79
Unfractionated Product	–	5.60	94.35

TABLE V Elemental composition of the waxy pyrolysis products and their cuts

Product or Cut	*C (%)*	*H (%)*	*N (%)*	*Cl (%)*	*O (%)*
100–125	65.91	14.34	–	–	19.75
150–175	73.68	12.35	traces	–	13.96
175–200	82.68	13.80	1.24	–	2.28
Distillation Residue	81.17	14.70	0.42	–	3.71
Unfractioned Product	85.15	13.70	traces	–	1.15

The chromatograms of the cuts (Fig. 12) resulted from the pyrolysis products of the body, piston and the whole syringes reveal also differences only in the composition of cut with low boiling point (Fig. 12a – see labelled peaks from the 0–12 retention time region).

The cuts with high boiling point (Fig. 12b) have many similarities. The pyrolysis products of the whole syringes has the composition as the average of that of the cuts from the body and piston of syringes.

The main components of the 100–125 and 150–175°C cuts (area % > 0.5) are listed in the Tables VI and VII. They are mainly homologous series of saturated and unsaturated hydrocarbons, in

TABLE VI Components of the 100–125°C cut resulted from pyrolysis of Piston, Body and the Whole Syringe

Piston (PE)	*Body (PP)*	*Whole Syringe (PE/PP, 1/1)*
1-methyl-2-ethyl-cyclopropane	1-methyl-2-(3-methylpentyl)-cyclopropane	**1,1-dimethyl-2-(2-methylpropyl)-cyclopropane**
1-methyl-2-pentyl-cyclopropane	1,2,3,4-tetramethyl-cyclobutene	1-ethyl-2-heptyl-cyclopropane
1-heptyl-2-methyl-cyclopropane	2-butenal	2-butenal
2-methyl-2-butene	1,2-dimethyl-3-methylene-cyclopentane	1,2-dimethyl-3-methylen-cyclopentane
2,3-dimethyl-1,3-butadiene	1,2,3-trimethyl-cyclopentane	1,2,3-trimethyl-cyclopentane
1-methyl-2-propyl-cyclopentane	1,1,3,4-tetramethyl-cyclopentane	1,1,3,4-tetramethyl-cyclopentane
2-methyl-propyl-cyclopentane	2-methylpropyl-cyclopentane	(2-methyl-1-propenyl)-cyclopentane
1-methyl-2-(2-propenyl)-cyclopentane	1-ethyl-2-methyl-cyclopentane	1-pentene
1-methyl-3-(2-methylpropyl)-cyclopentane	1-ethyl-3-methyl-cyclopentane	3-methyl-2-pentene
1-hexyl-3-methyl-cyclopentane	3-methyl-2-pentene	2-propyl-1-pentene
4-pentenal	2-propyl-1-pentene	**2,3,3-trimethyl-1,4-pentadiene**
1,2,3-trimethyl-cyclohexane	2,3-dimethyl-1,3-pentadiene	1,2,3- and 1,3,5-trimethyl-cyclohexane
ethyl-cyclohexane	1,2,3- and 1,3,5-trimethyl-cyclohexane	**1,1,4,4-tetramethyl-cyclohexane**
2-propenyl-cyclohexane	1,1′-(1,2-dimethyl-1,2-ethyl)-cyclohexane	1-hexene
ethylidene-cyclohexane	2,5- and 3,3-dimethyl-1-hexene	cyclohexene
1- and 3-methyl-cyclohexene	3,5,5-trimethyl-cyclohexene	2,4-hexadiene
1-ethyl-cyclohexene	2,3,4,5-tetramethyl-3-hexene	2,5-dimethyl-1,3-hexadiene
2-methyl-2,3-hexadiene	1-ethyl-2-hexene	2,3,5-trimethyl-1,3-hexadiene
2,3-dimethyl-1,4-hexadiene	1,4- and 2,4-hexadiene	3-hexyne
heptane	3-methyl-2,4-hexadiene	heptane
methyl-cycloheptane	2,5-dimethyl-2,4-hexadiene	3-methylene-heptane
3-methyl-1,4-heptadiene	2,3,5-trimethyl-1,3-hexadiene	5-methyl-1-heptene
Octane	3-hexyne	2-heptenal
1-,2-,3- and 4- Octene	3,3-diethyl-4,5-dimethyl-4-hexen-2-one	1,2-dimethyl-cycloheptene
2-butyl-1-octanol	4-methyl-cyclohexanone	2,3-dimethyl-1,3-heptadiene
nonane	4-methyl-heptane	3,5-dimethyl-1,6-heptadiene

1-nonene
3-transnonene
1-nonyne
1-nonanol
1,9-nonanediol
decane
bicyclo [7.1.0] decane
1-,2- and 5-decene
cyclodecene
3-decen-1-ol
2-ethyl-1-decanol
cyclodecanol
undecane
1-undecene
dodecane
cyclododecane
1- and 2-dodecene
tridecane
1-tridecene
tetradecane
1-,3-,5-,6- and 7- tetradecene
1-tetradecanol
1-hexadecene
pentacosane
hexacosane
heptacosane
octacosane
nonacosane
1,3-dimethyl-benzene
xylene

5-methyl-1-heptene
2,4-heptadiene
2,3-dimethyl-1,3-heptadiene
2,4-dimethyl-2,4-heptadiene
1,4-dimethyl-cyclooctane
2,5-dimethyl-1,6-octadiene
4,8-dimethyl-1,7-nonadiene
isononenal
2- and 4-methyl-decane
2,6,7-trimethyl-decane
7- and 8-methyl-2-decene
7-methyl-4-decene

2,4-dimethyl-2,4-heptadiene
octane
4-methyl-octane
cyclooctane
3,3-dimethyl-1-octene
N-octane-3-ene
7-methyl-3,4-octadiene
nonane
2-methyl-3-methylene-nonane
4,8-dimethyl-1,7-nonadiene
4-methyl-decane
2,6,7-trimethyl-decane
4- and 7-methyl-2-decene
cyclodecene
1-decanol
undecane
1-undecene
4-methyl-2-undecene
4,5-dimethyl-2-undecene
1-and 2-dodecene
6- and 7-tetradecene
1-pentadecene
methylbenzene
decahydronaphthalene

TABLE VII Components of the 150–175°C cut resulted from pyrolysis of Piston, Body and the Whole syringe

Piston (PE)	*Body (PP)*	*Whole Syringe (PE/PP, 1/1)*
1,2-dibutylcyclopropane	1-hexyl-2-propyl-cyclopropane	**1,2,3-trimethyl-cyclopropane**
1-pentyl-2-propyl-cyclopropane	2,3-dicyclohexyl-butane	**1-methyl-2-octyl-cyclopropane**
1-heptyl-2-methyl-cyclopropane	2,3,3-trimethyl-pentane	**1-heptyl-2-methyl-cyclopropane**
4-methyl-2-pentene	1,2,3-trimethyl-cyclopentane	**1-butyl-2-ethyl-cyclobutane**
2,4-dimethyl-heptane	1,1,3,4-tetramethyl-cyclopentane	3-methyl-2-pentene
octane	propyl-cyclopentane	**propyl-cyclopentane**
2-octene	1-butyl-2-ethyl-cyclopentane	2-methylpropyl-cyclopentane
n-octan-3-ene	1,2-dibutyl-cyclopentane	1,2-dibutyl-cyclopentane
5-methyl-3-octyne	1-pentyl-2-propyl-cyclopentane	**2,3,4-trimethyl-hexane**
nonane	3-methyl-2-pentene	1,3,5-trimethyl-cyclohexane
decane	2,3-dimethyl-1-pentene	**1,2-diethy-1-methyl-cyclohexane**
bicyclodecane	2-propyl-1-pentene	3,3-dimethyl-1-hexene
1- and 4-decene	1,1,2-, 1,1,3-, 1,2,3-, 1,2,4-	cyclohexene
cyclodecene	and 1,3,5-trimethyl- cyclohexane	2,4-hexadiene
undecane	1,2,4,5-, 1,1,4,4- and 1,1,3,5-	2-methyl-1,5-hexadiene
1-,4- and 5-undecene	tetramethyl-cyclohexane	2,5-dimethyl-1,5-hexadiene
1-undecyne	1-methyl-1,2-diethyl-cyclohexane	3-hexyne
dodecane	ethyl-cyclohexane	1-heptyne
cyclododecane	4-ethyl-3,4-dimethyl-cyclohexane	3,3,6-trimethyl-1,4-heptadiene
cyclododecene	3-ethyl-5-methyl-1-propyl-cyclohexane	2-octene
1,11-dodecadiene	1-ethyl-2-propyl-cyclohexane	2,5-dimethyl-1,6-octadiene
tridecane	2,4-diethyl-1-methyl-cyclohexane	nonane
1- and 6-tridecene	1,2-diethyl-3-methyl-cyclohexane	1-nonene
1,12-tridecadiene	3,3-dimethyl-1-hexene	4,8-dimethyl-1,7-nonadiene
tetradecane	2,5,5- and 3,5,5-trimethyl-1-hexene	decane

1- and 7-tetradecene
pentadecane
1-pentadecene
hexadecane
1-hexadecene
5-hexadecyne
heptadecane
1-heptadecene
3-eicosene
hexatriacontane

3,5-dimethyl-2-hexene
3-ethyl-3-hexene
1,5-hexadiene
2,5-dimethyl-1, 5-hexadiene
5-methyl-1-heptene
2-methyl-3-heptene
2,2- and 2,3-dimethyl-3-heptene
3,5-dimethyl-1,6-heptadiene
cyclooctane
1-methyl-3-propyl-cyclooctane
butyl-cyclooctane
2,5-dimethyl-1,6-octadiene
2-methyl-3-methylene-nonane
4,8-dimethyl-1,7-nonadiene
2- and 4-methyl-decane
2,4-dimethyl-1-decene
4- and 7-methyl-2-decene
3-decene
5-methyl-4-decene
2,9-dimethyl-3,7-decadiene
7-methyl-1-undecane
4-methyl-2-undecene
4-undecene
6-dodecene
1,1-bis-(dodecyloxy)-hexadecane
9-octadecene
11-tricosene

1-decene
2,4-dimethyl-1-decene
7- and 8-methyl-2-decene
undecane
4-methyl-undecane
2-methyl-2-undecene
4-undecene
dodecane
cyclododecane
5-dodecene
tetradecane
1- and 7-tetradecene
1-pentadecene
1-hexadecene

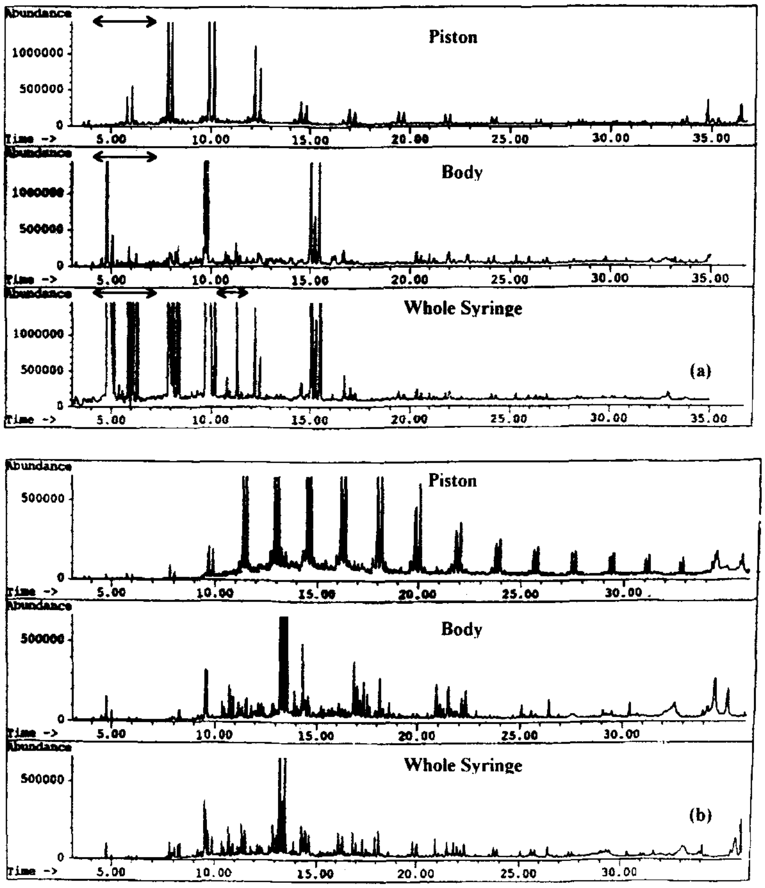


FIGURE 12 Chromatograms of the 150–175°C cut (a) and 200–225°C (b).

accordance with literature data [20]. Of course, the linear hydrocarbons are main components resulted from PE and the branched hydrocarbons from PP decomposition.

Among the components found in low quantities (area % < 0.5) could be enumerated: *hydrocarbons*: cyclopropane; methyl-cyclopropane; methyl-butene; methyl-cyclopentane; methyl-pentene; cyclopentene; cyclohexane; methyl-cyclohexane; methyl-hexene; dimethyl-hexene; methyl-heptane; heptene; cycloheptene; methyl-octene; methyl-nonene; cyclododecane; eicosane; decahydronaphtalene; *alcohols*: 2,7-dimethyl-1-octanol; methyl-decanol; decanediol; undecanol; dodecanol; tridecanol; pentadecanol;

hexadecanol; octadecanol; tetracosanol; hexacosanol; *aldehydes and ketones*: cyclopropyl-ethanone; 3-penten-2-one; 4-methylene-2-hexanal; 2,4-hexadienal; octanal; isooctanal; 4-cyclooctene-1-one; octadecanal; methyl-benzaldehyhe; *esters*: 2-ethylhexyl ester acetic acid; isononyl ester acetic acid; 3-octanyl acetate; octyl ester 10 undecenoic acid; *others*: furane; carboxylic acids.

Several additional peaks are presented in the chromatogram of the cut of the pyrolysis product resulting from the whole syringe (PE/PP mixture), in respect with separate components (piston – PE, body – PP). The corresponding compounds are listed in the Tables VI and VII and in the 100–125°C cut they are: 1,1,2,3-tetramethyl-cyclopropane; 2-ethyl-1,1-dimethyl-cyclopentane; 2,3,3-trimethyl-1,4-pentadiene; 2,5-dimethyl-1,3-hexadiene; 2,4-dimethyl-heptane; 3,3-dimethyl-1-octene; while in 150–175°C cut exist: 1,2,3-trimethyl-cyclopropane; 1,3-dimethyl-3-methylene-cyclopropane; 1,1-dimethyl-2-allyl-cyclopropane; pentyl-cyclopropane; 1-butyl-1-methyl-2-propyl-cyclopropane; 1-methyl-2-octyl-cyclopropane; 1-butyl-2-ethyl-cyclobutane; 2-methylpropyl-cyclopentane; 2,3,4-trimethyl-hexane; 3,7-dimethyl-3-vinyl-5-octene.

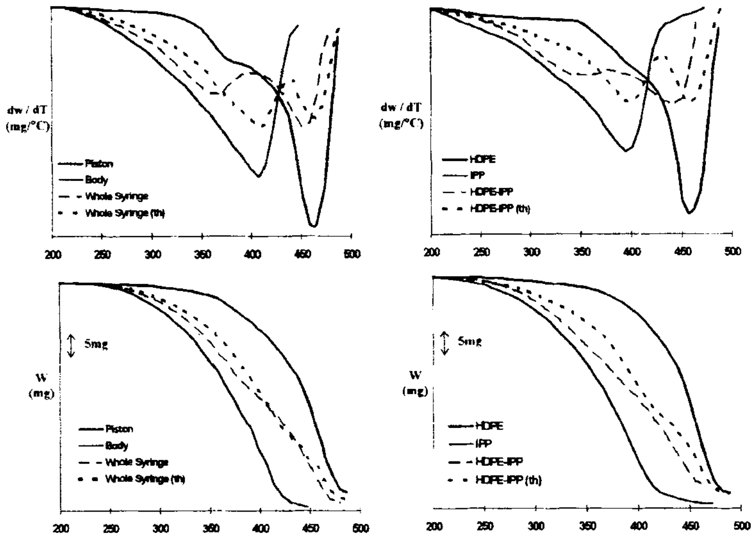
They are high branched and cyclic hydrocarbons indicating a possible interaction of radicals from both polyolefins during pyrolysis at high temperature. Supplementary proofs for this interaction were provided by thermogravimetric study.

3.2. Thermogravimetric Study

The TG and DTG curves of polyolefin components of syringes with the above mentioned composition as well as for pure polyolefins together with their mixture are presented in Figure 13.

It can be observed that the both polyolefin constituents of syringes decompose in a single step, the polypropylene decomposition peak being placed at lower temperature range than that corresponding to the PE decompostion. In the DTG curve of PE, an inflexion is present at about 375°C that appears much clearer in the DTG curve of PE from syringes. This indicates that this PE has many more weak bonds than the pure PE.

The mixture of the two polyolefins shows two decomposition steps with the temperatures of the maximum decomposition rate at 375°C and 463°C respectively. The two peaks from DTG curves are less



(a) (b)

FIGURE 13 Derivatograms (TG and DTG curves) of PE, PP and their mixtures from syringes (a) and pure polyolefins (b); th-additive curve for an 1/1 mixture.

delimeated than those corresponding to the additive curves (th) constructed as an average value of TG and DTG curves of components at each temperature (at least 30 points were read out in such an evaluation). It should also be noted that the decomposition of the mixtures of syringes and of pure polyolefins occurs in a narrower decomposition temperature range than predicted by the additive (th) calculated DTG curve of the mixture (Tab. VIII). In other words the decomposition of the mixture is completed sooner than expected. This behavior could be due to a reciprocal influence of the two polyolefins during decomposition, noted in pyrolysis experiments and mentioned also by other authors [21].

The overall kinetic parameters are given in the Table IX.

Mentioned has to be made on a particular behavior of the polyolefins from syringes in respect with the corresponding pure ones. The first ones show higher weight losses at 500°C (Tab. VIII) and higher decomposition rates at temperatures around 300–360°C in respect with the pure polyolefins and mixture of these. At higher temperatures, the differences in the decomposition rates are insignificant.

TABLE VIII Characteristic temperatures and weight losses for thermoxidative decomposition of PE, PP and their mixtures

Sample	$T_i(°C)$	$T_m(°C)$	$T_f(°C)$	$(dw/dT)_{300°C}$	$(dw/dT)_{360°C}$	$w\%_{360°C}$	$w\%_{final}$
HDPE	347	457	490	0.0714	0.2125	1.2	89
HDPE_{syr}	350	463	493	0.1333	0.5222	1.8	87
IPP	194	396	472	0.3750	0.6438	44.0	98
IPP_{syr}	212	409	447	0.3040	0.8214	40.4	98.3
HDPE/IPP	214	$T_1 = 355$ $T_2 = 442$	464	0.4167	0.4063	33.9	90
HDPE/IPP (th)	194	$T_1 = 401$ $T_2 = 459$	490	0.2000	0.3875	23.4	93.4
HDPE/IPP_{syr}	212	$T_1 = 363$ $T_2 = 452$	480	0.2500	0.4833	31.2	96.5
HDPE/IPP_{syr} (th)	212	$T_1 = 412$ $T_2 = 464$	491	0.1747	0.5125	24.6	95.2

T_i, T_m, T_f – onset temperature, temperature corresponding to the maximum rate of weight loss and final temperature, Δw – weight losses at various temperatures, dw/dT – the rate of weight loss, in mg/°C.

TABLE IX Overall Kinetic Parameters for Thermoxidative Decomposition of PE, PP and their Mixtures

Sample		E_{CR} *(KJ/mol)*	lnA_{CR}	n_{CR}	E_{SM} *(KJ/mol)*	lnA_{SM}	n_{SM}	E_{LR} *(KJ/mol)*	T_{max} *(°C) DTG*	T_{iso} *(°C)*
HDPE		139.35	22.10	0.7	154.14	24.14	0.4	156.94	457	455.58
HDPE$_{syr}$		107.94	16.53	0.5	96.85	14.67	0.6	135.43	463	461.23
IPP		64.88	10.62	0.9	60.57	9.74	0.9	81.81	396	392.90
IPP$_{syr}$		74.59	12.45	0.9	71.40	11.48	0.7	90.33	409	388.15
HDPE/IPP	step 1	90.73	16.98	1.2	65.88	11.44	0.6	105.242	355	326.70
	step 2	162.01	26.96	0.9	155.88	25.12	0.3	201.41	442	434.49
HDPE/IPP (th)	step 1	56.94	8.62	0.4	59.05	8.47	1.5	79.43	401	398.87
	step 2	371.73	61.24	1.3	413.80	68.26	1.4	420	496	458.81
HDPE/IPP$_{syr}$	step 1	81.69	14.41	1.0	69.34	11.70	0.7	100.18	363	356.56
	step 2	597.42	101.35	2.5	651.36	107.48	1.6	445.48	452	443.38
HDPE/IPP$_{syr}$ (th)	step 1	72.68	11.81	0.9	67.24	10.16	0.2	90.72	412	398.32
	step 2	649.92	107.01	1.9	627.74	98.97	6.5	800	464	459.31

E – overall activation energy evaluated by various methods denoted by subscript; *A* – pre-exponential factor, *n* – reaction order; T_m – temperature corresponding to the maximum rate of weight loss; T_{iso} – isokinetic temperature.

Generally, the syringes and their PE component show lower values for all kinetic parameters (Tab. IX) than those corresponding to pure PE or mixture based of pure polyolefins. The reaction orders are close to unity or less than unity, this suggest that some diffusion processes accompany decomposition reaction, such as the removal of heavy pyrolysis (decomposition) products from decomposing melts.

As already shown [22], a relation between ln$A$ and E characterizes the polyolefin decomposition in various conditions. For this reason, the comparison of their behavior must be based using the rate constants evaluated at many different temperatures.

The dependence of activation energy evaluated by Reich-Levi method on conversion degree is presented in Figure 14. Constant values for the activation energy were obtained for $\alpha > 0.2$. These values are listed in Table IX. The concordance of the overall values of kinetic parameters obtained by both the differential and integral methods allows us to discuss the decomposition behavior of these polyolefins.

For $\alpha < 0.2$ it appears an important decrease of activation energy with conversion degree. The conclusion that could be drawn is that in the initial moments, the reaction occurs autocatalytically. This is possible due to the weak bonds present especially in polyolefins from syringes (in this case the decrease is more rapid) or oxygen attack. It is well known that the presence of oxygen traces in polymer decomposition has a catalyst or initiator role in thermal or thermoxidative decomposition of polyolefins. The dependence of activation energy on conversion degree is logarithmic, namely: $E = p - q \ln\alpha$ where q takes the values: 37.49 for HDPE and piston and 12.64 for IPP, HDPE/IPP, body and whole syringe. P takes various values for each decomposition run and evaluation correlation coefficient had an average value of 0.97105.

Flynn [23] showed that E and ln$A$ value could be affected by significant errors due to the dependence on temperature of the kinetics of reactions. These errors are diminished in isothermal or isoconversional condition. The compensation effect is minimized by evaluation of the rate constants. The rate constant have been evaluated for the conversion degree interval $0 < \alpha < 0.2$ where a pronounced E-α dependence was observed. We considered the temperature corresponding to each α and an average temperature in the same α interval. The results are given in the Figures 15a and b for HDPE and respectively IPP.

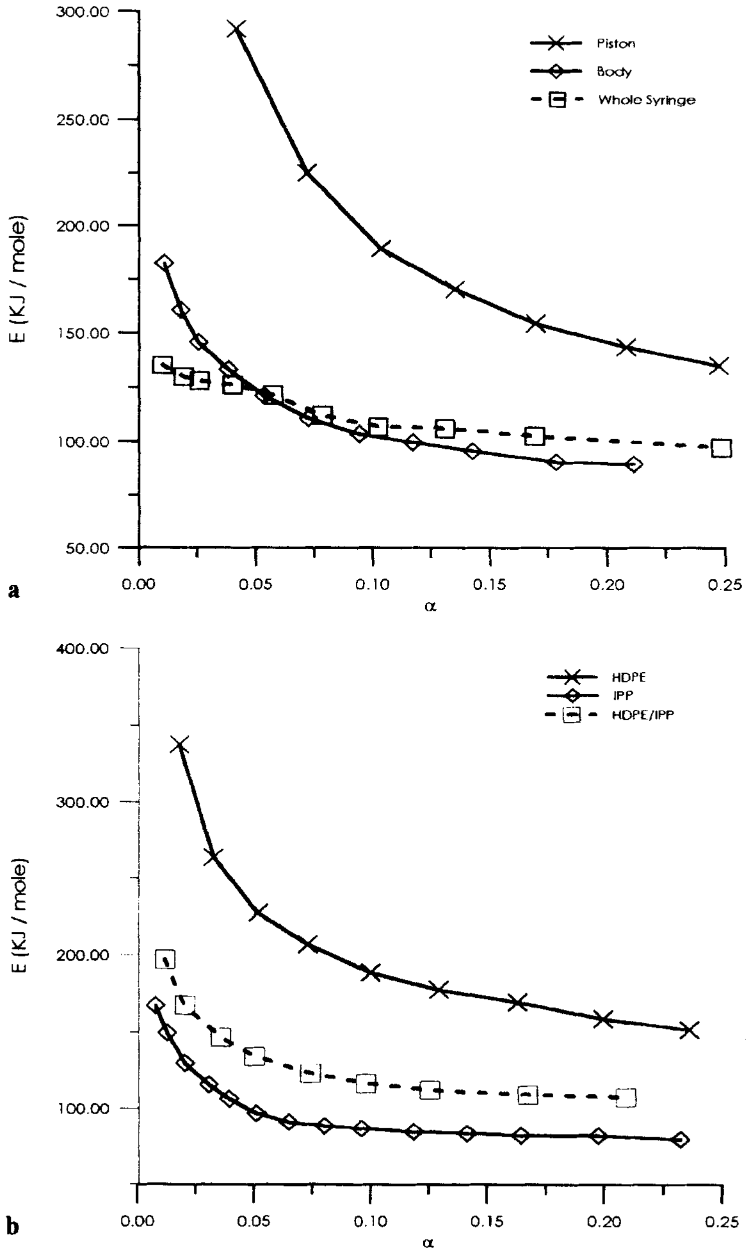


FIGURE 14 E_{RL} versus conversion degree for syringes and separate polyolefins (a) and pure polyolefins and their mixture (b).

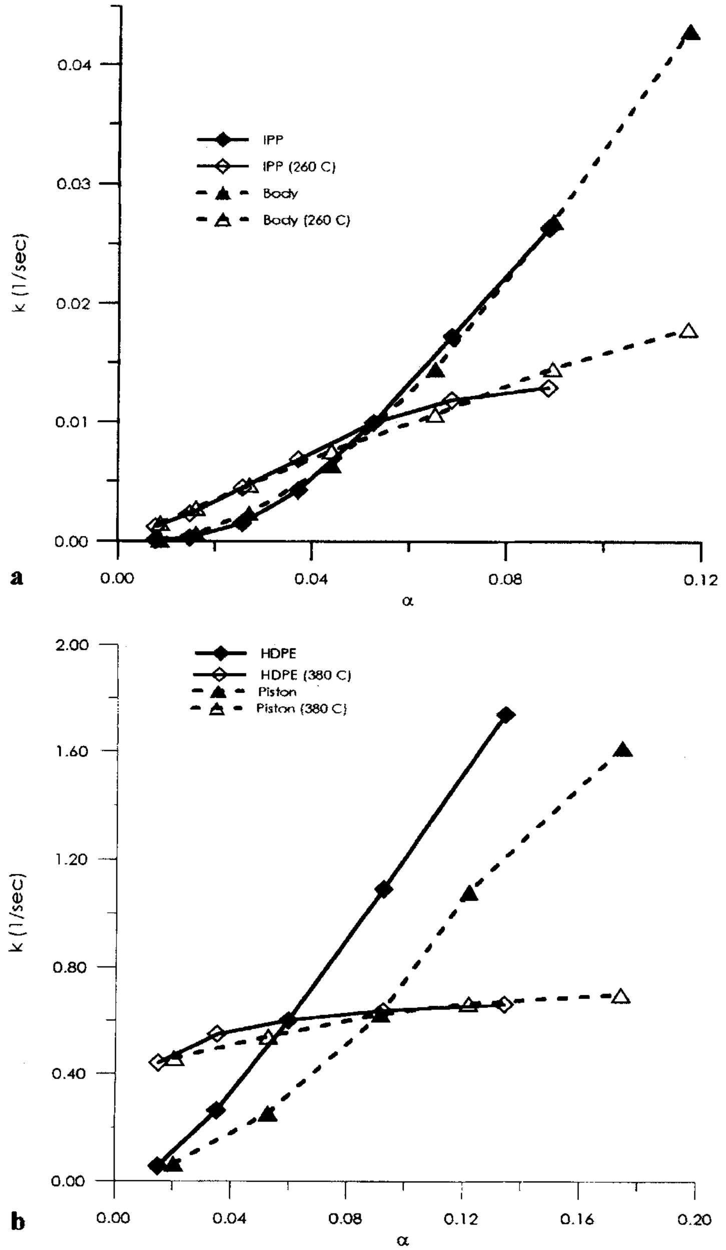


FIGURE 15 Rate constant versus conversion degree for IPP and syringe body (a) and HDPE and syringe piston (b).

It is very easy to note that the temperature dependence is the most important for the rate constant of decomposition of both polyolefins. The approximately constant values were obtained considering an average temperature for PE while for PP an increase of k values with conversion degree is evident even for a constant temperature. Therefore the autocatalytic thermoxidative decomposition of this polymer (PP), component of syringes could change the pyrolysis pathway.

The syringes (or mixture) behavior is close to that of PP. The PP is much more unstable in thermoxidative conditions, so the PP radicals attack could destabilize the pyrolyzing material. This explains the shorter pyrolysis and decomposition time and also the presence of new compounds in the composition of the low-boiling point cuts.

CONCLUSION

Pyrolysis of the disposable syringes at low temperatures leads to the 15–20 wt % of gaseous product and 78–84 wt % of light yellow wax. Both pyrolysis products have a high heating value and can be used as a high grade fuel. From the waxy product, after purification by distillation and further chemical modification a high value product has been also obtained. The IPP influence on the pyrolysis of polymer waste has been evidenced.

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