# Thermo-Oxidative Degradation of Low-Density Polyethylene Close to Industrial Processing Conditions

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# **Synopsis**

Thermo-oxidative degradation of low density polyetylene (LDPE) at a low degree of volatilization (about 4%) at 264–289°C was studied. Gas chromatography-mass spectrometric analysis was used to separate and identify the products of LDPE decomposition. Altogether 44 compounds representing hydrocarbons, alcohols, aldehydes, ketones, acids, cyclic ethers, cyclic esters, and hydroxycarboxylic acids were identified. Sixteen oxygen-containing products were quantified. Among the components identified, the fatty acids and aldehydes predominated. The most abundant product was formic acid. The mechanism of formation of the degradation products is discussed.

# **INTRODUCTION**

Considerable research has been devoted to the thermo-oxidation of polyethvlene (PE). Prediction of useful service life of PE compositions and knowledge of the mechanism of elementary steps of oxidation of PE at relatively low temperatures are very important topics in these studies. In addition, the generation of gaseous combustion products in fires, especially poisonous gases, has been recognized as a serious problem. The majority of investigations concerning the volatiles formed during thermo-oxidative degradation of PE have been performed at temperatures of 150–200°C<sup>1-4</sup> or under pyrolysis conditions at temperatures above 350°C,<sup>5–7</sup> i.e., exceeding the industrial conditions. The temperature range of 284-355°C have also been studied.<sup>8,9</sup> However, no information concerning volatiles formed during degradation of PE has been published. Most of those processing methods for PE are performed at temperatures between 200°C and 320°C. The increasing demands of safe production conditions with respect to the health of workers employed in the plastic industry necessitate knowing the nature of volatiles which could be evolved during conventional processing. This includes the temperature range mentioned above, short time spans, and a low degree of volatilization. The most dangerous toxic gases formed during thermo-oxidation of PE are oxygen-containing low molecular weight products such as aldehydes, ketones, and acids. There is information in the literature stating that certain toxic compounds such as formaldehyde, formic acid, acrolein, and acrylic acid among others are formed during the thermo-oxidation of PE.1,2,5,6 Therefore, the objective of this study is to identify and quantify the dangerous toxic products evolved during normal processing conditions.

It should be mentioned that the knowledge of the composition and the relative

amounts of the volatiles evolved at thermo-oxidation of PE could also yield more information about the mechanism of the elementary steps.

To identify and quantify the volatiles formed during thermo-oxidation of PE gas chromatography-mass spectrometric analysis (GC/MS) was used.

# **EXPERIMENTAL**

# Materials

The low density polyethylene (LDPE) used, Unifos DFDS 6600, was supplied by Unifos Kemi AB, Stenungsund, Sweden. It was a high-pressure product produced in a tubular reactor and free from additives. It has following charateristics: density,  $0.922 \text{ g/cm}^3$ ; melt index, 0.31 g/10 min;  $\overline{M}_W = 97 \times 10^3 \text{ (GPC)}^8$ ; and  $\overline{M}_N = 31 \times 10^3 \text{ (GPC)}^8$ 

#### Apparatus

A LKB 9000 GC/MS apparatus with a laboratory-made gas chromatograph equipped with an Altema MID (multiple-ion detector) was used. The operating conditions were as follows: ion source temperature 230°C; accelerating voltage 3500 V; trap current 40  $\mu$ A. The transfer line and the two-state jet-separator were kept at 220°C. The selected ion monitoring (SIM) chromatograms were recorded on a three-channel strip chart recorder (Linear 595 instrument). The total ion current (TIC) chromatograms were recorded at ionization energy of 20 eV, and SIM chromatograms were recorded at ionization energy of 70 eV. Mass spectra were obtained with an ionization energy of 70 eV. Normalized mass spectra were received by an interfaced laboratory-programmed M-8 Intertechnique computer and displayed on a TV screen. Scan limits in the range 20–250 m/e were used.

## **Oxidation Procedure**

The generation of the volatile products were carried out with a thermal degradation system, which consists of three parts: a thermal degradation tube, a movable furnace, and an enrichment section (Fig. 1). The polymer sample<sup>11</sup> is located in the tube of Pyrex glass (4), which is loosely connected to a T-piece junction (3). The flow rate of helium is set to 40 mL/min. Simultaneously the pump (9), which is regulated to give a flow rate of 20 mL/min is started. The additional flow by-passes the opening of the glass tube and thus precludes diffusion of laboratory air into the glass tube. The thermal degradation is started when the furnace (5) is moved into the position shown in Figure 1(a). The volatiles evolved are enriched on the glass beads in the glass trap (8), which is cooled by liquid nitrogen. The trap (about 230  $\mu$ L) and the glass beads (40/60 mesh) are silanized. The trap is attached to a six-port valve (7). The injection of the volatiles into the gas chromatograph is performed as follows. The furnace is withdrawn, the liquid nitrogen taken away, and the valve switched to the position shown in Figure 1(b). At the same time the glass trap is heated to 200°C within 3 s, and the enriched compounds are injected into the column. The constructed apparatus, which consists of highly inert materials (glass, Teflon, tantal) is simple



Fig. 1. Thermal degradation sampling system 1 = three-port valve; 2 = flow controller (0–100 mL/min), Porter DFC 1400; 3 = T-piece junction made of glass; 4 = thermal degradation tube made of Pyrex glass; 5 = thermostated, movable aluminumblock furnace (0–600°C); 6 = transfer section kept at 125°C; 7 = six-port valve (Carle 2821) kept at 150°C; 8 = glass trap; 9 = pump; 10 = thermostated electric heating spiral; 11 = sample; 12 = capillary

and versatile, and enables one to obtain reproducible results. The flow through the degradation tube can be varied between 0 and 100 mL/min. This can be effected in two ways: (a) by sealing the tube with a teflon tube and a spring to the T-piece junction and regulated by the flow controller; (b) by connecting the degradation tube loosely to the T-piece junction and varying the flow rate through the pump with the variable restriction between valve and pump. When using the pumping arrangement, air could be used as atmosphere even if the glass trap is cooled with liquid nitrogen so that no freeze-out of oxygen occurs. This is due to the slightly reduced pressure in the glass trap. The reduced pressure is achieved by inserting a restriction (glass wool) in the glass capilillary between the degradation tube and the valve. The temperature of the transfer section could be easily changed and thus serve as a trap of high boiling compounds, which otherwise could cause severe background problems in the course of GC/MS experiments.

Polymer samples  $(2.8 \pm 0.2 \text{ mg})$  were heated to a final temperature of 264°C, 274°C, 280°C, and 289°C during 4 min in dry air atmosphere; air flow was kept 20 mL/min; kinetics of the heating of the samples in the pyrolyzer are shown in Figure 2. The samples were stamped out to have approximately the same surface area. Before and after the degradation experiments the samples were weighted on a Cahn thermobalance GR-HV. The observed weight loss of the samples during degradation is ca. 4% at 280°C.

## **Gas Chromatographic Separation**

Separation of the thermo-oxidation degradation products of PE was performed on silanized glass columns (2.0 m  $\times$  1.8 mm i.d.) packed with 6% OS-138 coated on Tenax GC 80/100 mesh or Carbopack C 80/100 mesh coated with 0.2% SP-1000. Used also were a Teflon column (1.0 m  $\times$  1.8 mm i.e.) packed with 8% Fluorad FC-431,<sup>11</sup> a fluorocarbon surfactant, and 0.6% H<sub>3</sub>PO<sub>4</sub> coated on Tenax GC 60/80 mesh and a Porapak T 80/100 mesh column (1.0 m  $\times$  1.8 mm i.d.).



Fig. 2. Kinetics of the heating of the samples in the thermal degradation tube.

Separation on the Carbopack C and OS-138 columns were performed using the following temperature program: at 30°C for 4 min, then programmed to 150°C at 7°C/min, and from 150°C to 210°C at 8°C/min. Carrier gas flow rate was 20 mL/min.

Separation on the Fluorade FC-431 column was performed using the following temperature program: at 30°C for 2 min, then programmed to 140°C at 6°C/min. The flow rate of helium was 20 mL/min.

Separation on Porapak T column was performed at isothermal conditions at 130°C, and at the same flow rate of helium as indicated above.

# Quantitative Measurements of the Volatile Organic Products Formed during Thermo-oxidation of PE

## a. Aldehydes (Propanal, Butanal, Acrolein, and Pentanal)

The chromatographic separation was performed on the OS-138 column. For butanal and pentanal the following ions were monitored: m/e 29, m/e 30, and m/e 31. For acrolein, propanal and acetone ions with m/e 56, m/e 57, and m/e58 were used. Standard solutions of the individual products at four concentrations were run. The calculations of the compounds evolved during thermooxidation of LDPE were made graphically by means of the calibration curves. The quantitative determination of acrolein, propanal, and acetone on the column used seemed to be quite difficult because all three components appeared almost as one peak on the chromatogram. In recording the chromatogram on the three-channel recorder at the above-mentioned values of m/e for these samples, three peaks with retention times 670 s (m/e 56), 677 s (m/e 57) and 678 s (m/e58) were obtained. The first peak belongs undoubtedly to acrolein, because the theoretical ratio of the abundances of ions m/e 56/m/e 57 is about 5.2 for acrolein,<sup>10</sup> as it was found, while it is only 0.06 for propanal and 0.1 for acetone. The amount of acetone was calculated as described below in the point c. To determine the amount of propanal the ion m/e 58 was used. By taking into consideration the quantity of acrolein and acetone found and by building the calibration curves for all three substances, it was possible to find the peak area of ion m/e58, which is due to propanal, and thereby calculate the amount of propanal.

#### b. Acids and Acetaldehyde

The chromatographic separation was performed on the Fluorad FC-431 column. The ions m/e 45 and m/e 46 were used for detection of acids, and the ion m/e 43 was used for detection of acetaldehyde. The calculations were made by means of calibration curves as in the case of aldehydes.

## c. Ketones and Butyrolactone

The chromatographic separation was performed on the Carbopack C column. The ions m/e 42 and m/e 43 were used for detection of the compounds. The calculations were performed as described above.

#### d. Formaldehyde

The chromatographic separation was performed on Porapak T column. The ion m/e 30 was used for detection of formaldehyde. The calculations were made as described above.

## RESULTS

To ensure as complete a separation of the compounds evolved during thermo-oxidation of LDPE as possible, four different columns were used. The 6% OS- 138 column has a good ability to separate the majority of the products formed. Carbopack C column gives the best results for separation of the ketones, while Fluorade FC-431 column is most advantageous for separation of acids. The results of identification of the individual compounds are summarized in Table I. Gas chromatograms of the products of thermo-oxidation of LDPE on three columns are illustrated in Figures 3, 4, and 5.

Altogether 44 products representing hydrocarbons, alcohols, aldehydes, ketones, acids, cyclic ethers, and cyclic esters were found. Among these products 10 compounds not described earlier were detected. To our knowledge, no mention has been made in the literature about formation from thermo-oxidative degradation of PE of the following volatile products: cyclopropane, furane, tetrahydrofurane (THF), isobutanal, methyl vinyl ketone, isovaleric acid, hydroxyvaleric acid, crotonic acid, caproic acid, and two lactones: valerolactone and butyrolactone. Most of these products are formed in low amounts, except of butyrolactone. The oxygen-containing compounds constitute an absolute majority, and the hydrocarbons, a minority of products detected during thermo-oxidation of LDPE. The results of the quantitative measurements o' some volatile oxygen-containing products are given in Table II. The mosu abundant products formed are  $C_1$  and  $C_2$  acids and aldehydes.

#### DISCUSSION

Since our results are obtained at temperatures intermediate to those published in the literature, we consider it pertinent to discuss briefly the literature, for comparison with the results, concerning the volatile products reported here.

The thermo-oxidative degradation of LDPE and high density polyethylene (HDPE) samples (0.2 g) at 150°C in oxygen was studied by Matveeva et al.<sup>1</sup>

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No.CompoundOS-138Carbopack CFluorade FC-431Identification GC1.Carbon dioxide21ab2.Water55ab3.Ethene3ab4.Propene72a5.Propane7ac6.Cyclopropane <sup>d</sup> 8cc7.Butane116aa9.Pentene14aa10.Pentane1415a11.Hexane18aa12.Hexane18aa13.Heptene22aa14.Heptane26ab15.Octane26ac16.Octane26ab17.Methanol9cc18.Ethanol13ab19.Furan <sup>d</sup> 9cc20.Tetrohydrofuran <sup>d</sup> 18cc27.Popanal154ab28.Butanal1912ab29.Methyl ethyl139ab20.Tetrohydrofuran <sup>d</sup> 139ab28.Butanal1912ab29.Methyl ethyl139ab20.Methyl ethyl139ab <t< th=""><th></th><th></th><th colspan="6">Peak No. on Column Fluorade Identification</th></t<>			Peak No. on Column Fluorade Identification					
No.         Compound         OS-138         Carbopack C         FC-431 $\overline{GC}$ $\overline{MS}$ 1.         Carbon dioxide         2         1         a         b           2.         Water         5         a         b           3.         Ethene         3         a         b           4.         Propene         7         2         a         c           6.         Cyclopropaned         8         a         -         c           6.         Cyclopropaned         8         a         -         c           7.         Butene         11         6         a         -         c           7.         Butene         11         8         a         -         -         c           9.         Pentane         14         15         a         -			Fluorade		Fluorade	Identification		
1.Carbon dioxide21ab2.Water55ab3.Ethene3ab4.Propene72a5.Propane72a6.Cycloropaned8c7.Butene116a8.Butane118a9.Pentene1415a10.Pentane1415a11.Hexane18aa12.Hexane18aa13.Heptene22aa14.Heptane26ab15.Octane26ab16.Octane26ab17.Methanol13ab18.Ethanol13ab29.Tetrohydrofurand18c21.Formaldehyde61623.Propanal154a24.Actolein154a25.Butanal1912a29.Methyl ethyl ethyl139a20.Methyl ethyl ethyl139a29.Captone2713c20.Methyl ethyl ethyl14ab30.Acetone171615a31.2Pentanone29cc <td< th=""><th>No.</th><th>Compound</th><th>OS-138</th><th>Carbopack C</th><th>FC-431</th><th>GC</th><th>MS</th></td<>	No.	Compound	OS-138	Carbopack C	FC-431	GC	MS	
2. Water       5       5       a       b         3. Ethene       3       a       b         4. Propene       7       2       a         5. Propane       7       2       a       c         6. Cyclopropane <sup>d</sup> 8       c       c       c         7. Butene       11       6       a       c       c         8. Butane       11       8       a       c       c         10. Pentane       14       15       a       c       c         11. Hexene       18       a       c       c       c         13. Heptene       22       a       a       b       c         14. Heptane       26       a       b       c       c         15. Octane       26       a       b       b       c       c         16. Octane       26       a       b       b       c <td>1.</td> <td>Carbon dioxide</td> <td>2</td> <td></td> <td>1</td> <td>а</td> <td>b</td>	1.	Carbon dioxide	2		1	а	b	
3.       Ethene       3       a       b         4.       Propene       7       2       a         5.       Propane       7       2       a         6.       Cyclopropane <sup>d</sup> 8       c       c         7.       Butane       11       6       a       c         8.       Butane       11       8       a       c         9.       Pentene       14       15       a       1         10.       Pentane       14       15       a       1         11.       Hexene       18       a       1       1         11.       Hexene       18       a       1       1         12.       Hexene       22       a       a       b         13.       Heptane       22       a       b       b         14.       Heptane       26       a       b       c       c         15.       Octene       26       a       b       c       c       c         15.       Furan <sup>d</sup> 9       a       b       c       c       c       c         21.       Formaldehyde	2.	Water	5		5	а	b	
4.       Propene       7       2       a         5.       Propane       7       a       c         6.       Cyclopropane <sup>d</sup> 8       c       a         7.       Butene       11       6       a       c         8.       Butane       11       8       a       c         9.       Pentene       14       15       a       1         10.       Pentane       14       15       a       1         11.       Hexane       18       a       1       1         12.       Hexane       18       a       1 <td< td=""><td>3.</td><td>Ethene</td><td>3</td><td></td><td></td><td>а</td><td>b</td></td<>	3.	Ethene	3			а	b	
5.       Propane       7       a         6.       Cyclopropaned       8       c         7.       Butane       11       6       a         8.       Butane       11       8       a       a         9.       Pentene       14       15       a       a       a         10.       Pentane       14       15       a       a       a       a         11.       Hexene       18       a       a       a       a       a       a         13.       Heptane       22       a       a       b       b       b       b       b       b       b       b       b       b       b       b       b       c	4.	Propene	7		2	а		
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7.       Butene       11       6       a         8.       Butane       11       8       a         9.       Pentene       14       15       a         10.       Pentane       14       15       a         11.       Hexene       18       a       a         12.       Hexane       18       a       a         13.       Heptene       22       a       a         14.       Heptane       22       a       a         16.       Octane       26       a       b         17.       Methanol       9       a       b         18.       Ethanol       13       a       b         19.       Furan <sup>d</sup> 9       c       c         20.       Tetrohydrofuran <sup>d</sup> 18       c       c         21.       Formaldehyde       6       1       6       a       b         22.       Actaldehyde       10       2       3       a       b         23.       Propanal       15       4       a       b       b         24.       Actolein       16       7       a	6.	Cyclopropaned	8				с	
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16.Octane26a17.Methanol9a18.Ethanol13a19.Furand9c20.Tetrohydrofurand18c21.Formaldehyde616a22.Acetaldehyde1023a23.Propanal154a24.Acrolein15ab25.Butanal1912a26.Isobutanald1912a27.Pentanal23ab28.Acetone167a29.Methyl vinyld14abketone139ab30.Methyl ethyl139abketone2713cc33.2-Heptanone2713c33.2-Heptanone2713c33.2-Heptanone2713c34.Formic acid171615a35.Acetic acid171615a36.Propionic acid2017a37.Acrylic acid2419a38.Butyric acid25ab39.Isovaleric acid <sup>4</sup> 28c40.Hydroxyvaleric <sup>d</sup> 36c41.Croproic acid25ab42.Caproic acid <sup>4</sup> 22 <td>15.</td> <td>Octene</td> <td>26</td> <td></td> <td></td> <td>а</td> <td></td>	15.	Octene	26			а		
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18. Ethanol       13       a       b         19. Furan <sup>d</sup> 9       c         20. Tetrohydrofuran <sup>d</sup> 18       c         21. Formaldehyde       6       1       6       a       b         22. Acetaldehyde       10       2       3       a       b         23. Propanal       15       4       a       b         24. Acrolein       15       4       a       b         25. Butanal       19       12       a       b         26. Isobutanal <sup>d</sup> 19       8       c       c         27. Pentanal       23       a       b       b         28. Acetone       16       7       a       b         29. Methyl vinyl <sup>d</sup> 13       9       a       b         xetone       13       9       a       b         31. 2-Pentanone       19       10       c       c         32. 2-Heptanone       27       13       c       c         33. 2-Heptanone       29       c       c       c         34. Formic acid       12       14       a       b         35. Acetic acid       17       a	17.	Methanol	9			a	b	
19.Furand9c20.Tetrohydrofurand18c21.Formaldehyde616a22.Acetaldehyde1023a23.Propanal154ab24.Acrolein15ab25.Butanal1912ab26.Isobutanald1912ab27.Pentanal23cc27.Pentanal23ab28.Acetone167ab29.Methyl vinyld139abketone2713cc31.2-Pentanone1910c32.2-Heptanone29cd34.Formic acid171615a35.Acetic acid171615a36.Propionic acid2017ab37.Acrylic acid24cc38.Butyric acid25ab39.Isovaleric acid25ab39.Isovaleric acid25ab39.Isovaleric acid25ab39.Isovaleric acid25ab39.Isovaleric acid25ab39.Isovaleric acid26cc39.Isovaleric acid25ab<	18.	Ethanol	13			а	b	
20.Tetrohydrofurand18c21.Formaldehyde616ab22.Acetaldehyde1023ab23.Propanal154ab24.Acrolein154ab25.Butanal1912ab26.Isobutanald1912ab26.Isobutanald1912ab27.Pentanal23ab28.Acetone167ab29.Methyl vinyld14abketone2713cc31.2-Pentanone1910c32.2-Hexanone2713c33.2-Heptanone29cc34.Formic acid171615a35.Acetic acid171615a36.Propionic acid2017ab37.Acrylic acid24cc38.Butyric acid2419ab39.Isovaleric acid25ab41.Crotonic acid25ab42.Caproic acid25ab43.Butyrolactoned22ab44.Varnel act and26ab	19.	Furan <sup>d</sup>		9			с	
21.Formaldehyde616ab22.Acetaldehyde1023ab23.Propanal154ab24.Acrolein15ab25.Butanal1912ab26.Isobutanald1912ab27.Pentanal23ab28.Acetone167ab29.Methyl vinyld14abketone139ab30.Methyl ethyl139abketone2713cc31.2-Pentanone1910c32.2-Hexanone2713c33.2-Heptanone29cc34.Formic acid1214ab35.Acetic acid171615ab36.Propionic acid2018ab38.Butyric acid2419ab39.Isovaleric acid25acc41.Crotonic acid25abc42.Caproic acid <sup>d</sup> 22ab443.Butyrolactone <sup>d</sup> 22ab	20.	Tetrohydrofuran <sup>d</sup>		18			с	
22. Acetaldehyde1023ab23. Propanal154ab23. Propanal154ab24. Acrolein15ab25. Butanal1912ab26. Isobutanald1912ab27. Pentanal23ab28. Acetone167ab29. Methyl vinyld14abketone30. Methyl ethyl139abketone31. 2-Pentanone1910c32. 2-Hexanone2713c33. 2-Heptanone29-c34. Formic acid1214ab35. Acetic acid171615ab36. Propionic acid2017ab38. Butyric acid2419ab39. Isovaleric acidd28-c41. Crotonic acid25ab42. Caproic acidd24ca43. Butyrolactoned22ab44. Sutheraded26-a	21.	Formaldehyde	6	1	6	a	b	
23. Propanal154ab24. Acrolein15ab25. Butanal1912ab26. Isobutanald1912ab27. Pentanal23ab28. Acetone167ab29. Methyl vinyld14abketone139ab20. Methyl ethyl139abketone2713cc30. Methyl ethyl1910cc31. 2-Pentanone2713cc33. 2-Heptanone29ccd34. Formic acid1214ab35. Acetic acid171615ab36. Propionic acid2018ab37. Acrylic acid2018ab38. Butyric acid2419ab39. Isovaleric acidd28cc41. Crotonic acid25ab42. Caproic acid24cc43. Butyrolactoned22ab44. Vibrarket are d26ab	22.	Acetaldehyde	10	2	3	а	ь	
24. Acrolein15ab25. Butanal1912ab26. Isobutanald198c27. Pentanal23ab28. Acetone167ab29. Methyl vinyld14ab29. Methyl ethyl139abketonec30. Methyl ethyl139abketonec31. 2-Pentanone1910c33. 2-Heptanone2713c34. Formic acid1214ab35. Acetic acid171615ab36. Propionic acid2017ab37. Acrylic acid2419ab38. Butyric acid25ab41. Crotonic acid25ab42. Caproic acidd25ab43. Butyrolactoned22ab	23.	Propanal	15	4		a	ь	
25. Butanal1912ab26. Isobutanald198c27. Pentanal23ab28. Acetone167ab29. Methyl vinyld14abketone139ab30. Methyl ethyl139abketone139ab31. 2-Pentanone1910c32. 2-Hexanone2713c33. 2-Heptanone29cc34. Formic acid1214ab35. Acetic acid171615ab36. Propionic acid2017ab37. Acrylic acid2419ab38. Butyric acid2419ab39. Isovaleric acidd25ab41. Crotonic acid25ab42. Caproic acidd25ab43. Butyrolactoned22ab	24.	Acrolein	15			a	ь	
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28. Acetone167ab29. Methyl vinyld14abketone139ab30. Methyl ethyl139absketone139ab31. 2-Pentanone1910c32. 2-Hexanone2713c33. 2-Heptanone29c34. Formic acid1214ab35. Acetic acid171615a36. Propionic acid2017ab37. Acrylic acid2018ab38. Butyric acid2419ab39. Isovaleric acidd28cc40. Hydroxyvalericd36ccacid25ab41. Crotonic acid25ab42. Caproic acidd25ab43. Butyrolactoned22ab	27.	Pentanal	23			а	b	
29. Methyl vinyld14abketone139ab30. Methyl ethyl139abketone139ab31. 2-Pentanone1910c32. 2-Hexanone2713c33. 2-Heptanone29c34. Formic acid1214a55. Acetic acid171615a36. Propionic acid2017ab37. Acrylic acid2018ab38. Butyric acid2419ab39. Isovaleric acidd28cc40. Hydroxyvalericd36ccacid25ab41. Crotonic acid25ab42. Caproic acidd22ab43. Butyrolactoned22ab	28.	Acetone	16	7		а	ь	
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ketone       19       10       c         31. 2-Pentanone       27       13       c         32. 2-Hexanone       27       13       c         33. 2-Heptanone       29       c       c         34. Formic acid       12       14       a       b         35. Acetic acid       17       16       15       a       b         36. Propionic acid       20       17       a       b       b         37. Acrylic acid       20       18       a       b         38. Butyric acid       24       19       a       b         39. Isovaleric acid <sup>d</sup> 28       c       c         40. Hydroxyvaleric <sup>d</sup> 36       c       c         acid       25       a       b         41. Crotonic acid       25       a       b         42. Caproic acid <sup>d</sup> 24       c       c         43. Butyrolactone <sup>d</sup> 22       a       b	30.	Methyl ethyl		13	9	а	b	
31.2-Pentanone1910c32.2-Hexanone2713c33.2-Heptanone29c34.Formic acid1214ab35.Acetic acid171615ab36.Propionic acid2017ab37.Acrylic acid2018ab38.Butyric acid2419ab39.Isovaleric acid <sup>d</sup> 28cc40.Hydroxyvaleric <sup>d</sup> 36ccacid25ab41.Crotonic acid25ab42.Caproic acid <sup>d</sup> 22ab43.Butyrolactone <sup>d</sup> 22ab		ketone						
32.2-Hexanone2713c33.2-Heptanone29c34.Formic acid1214ab35.Acetic acid171615ab36.Propionic acid2017ab37.Acrylic acid2018ab38.Butyric acid2419ab39.Isovaleric acid <sup>d</sup> 28cc40.Hydroxyvaleric <sup>d</sup> 36ccacid25ab41.Crotonic acid25ab42.Caproic acid <sup>d</sup> 22ab43.Butyrolactone <sup>d</sup> 22ab	31.	2-Pentanone		19	10		с	
33.2-Heptanone29c34.Formic acid1214ab35.Acetic acid171615ab36.Propionic acid2017ab37.Acrylic acid2018ab38.Butyric acid2419ab39.Isovaleric acidd28cc40.Hydroxyvalericd36ccacid25abc41.Crotonic acid25ab42.Caproic acidd22ab43.Butyrolactoned22ab	32.	2-Hexanone		27	13		с	
34. Formic acid1214ab35. Acetic acid171615ab36. Propionic acid2017ab37. Acrylic acid2018ab38. Butyric acid2419ab39. Isovaleric acidd28cc40. Hydroxyvalericd36caacid25ab41. Crotonic acid25ab42. Caproic acidd22ab43. Butyrolactoned22ab	33.	2-Heptanone	29				с	
35.Acetic acid171615ab36.Propionic acid2017ab37.Acrylic acid2018ab38.Butyric acid2419ab39.Isovaleric acid <sup>d</sup> 28cc40.Hydroxyvaleric <sup>d</sup> 36ccacid25ab41.Crotonic acid25ab42.Caproic acid <sup>d</sup> 24c43.Butyrolactone <sup>d</sup> 22ab44.Valenchet ared26ab	34.	Formic acid	12		14	a	b	
36. Propionic acid2017ab37. Acrylic acid2018ab38. Butyric acid2419ab39. Isovaleric acidd28c40. Hydroxyvalericd36cacid25ab41. Crotonic acid25ab42. Caproic acidd24c43. Butyrolactoned22ab44. Velarene at angle26c	35.	Acetic acid	17	16	15	a	b	
37. Acrylic acid2018ab38. Butyric acid2419ab39. Isovaleric acidd28c40. Hydroxyvalericd36cacid25ab41. Crotonic acid25ab42. Caproic acidd24c43. Butyrolactoned22ab44. Velarene targed22ab	36.	Propionic acid	20		17	a	b	
38. Butyric acid     24     19     a     b       39. Isovaleric acid <sup>d</sup> 28     c       40. Hydroxyvaleric <sup>d</sup> 36     c       acid     36     c       41. Crotonic acid     25     a       42. Caproic acid <sup>d</sup> 24     c       43. Butyrolactone <sup>d</sup> 22     a       44. Valaralactore <sup>d</sup> 22     a	37.	Acrylic acid	20		18	а	b	
39. Isovaleric acid <sup>d</sup> 28     c       40. Hydroxyvaleric <sup>d</sup> 36     c       acid     25     a     b       41. Crotonic acid     25     a     b       42. Caproic acid <sup>d</sup> 24     c       43. Butyrolactone <sup>d</sup> 22     a     b	38.	Butyric acid	24		19	a	b	
40. Hydroxyvaleric <sup>d</sup> 36     c       acid     41. Crotonic acid     25     a     b       42. Caproic acid <sup>d</sup> 24     c       43. Butyrolactone <sup>d</sup> 22     a     b	39.	Isovaleric acid <sup>d</sup>	28				с	
41. Crotonic acid25ab42. Caproic acid <sup>d</sup> 24c43. Butyrolactone <sup>d</sup> 22ab44. Velorablestand20ab	40.	Hydroxyvaleric <sup>d</sup>		36			с	
41. Ortoinin actual     20     a     b       42. Caproic acid <sup>d</sup> 24     c       43. Butyrolactone <sup>d</sup> 22     a     b       44. Valencelectone <sup>d</sup> 20     a     b	11	Crotonic seid	95			а	Ь	
43. Butyrolactoned   22   a   b     44. Valuenclactoned   22   a   b	41.	Caproic acidd	20		24	u	c v	
A Valenciastand 22 -	43	Butyrolactoned		22	41 <b>X</b>	а	ĥ	
44 Valerolacione Zh C	44	Valerolactoned		26		u	г С	

TABLE I Products of Polyethylene Thermo-oxidation

<sup>a</sup> According to retention time.

<sup>b</sup> According to retention time.
<sup>b</sup> According to mass spectra of individual compounds.
<sup>c</sup> According to mass spectra compared with Ref. 10.
<sup>d</sup> Compounds which are identified probably for the first time.



Fig. 3. Gas chromatography analysis of products of thermo-oxidation of LDPE on OS-138 column.

They found water to be the most abundant product of oxidation. Among the organic components, acids were found to be the most predominant, followed by formaldehyde and acetaldehyde. The aldehydes constitute about 30% of the total amount of acids. Acids were formed to a greater extent in the case of HDPE than for LDPE.

Bevilacqua et al.<sup>2</sup> were first to observe the formation of formic and acetic acids at thermo-oxidation of PE at 150°C. They came to the conclusion that the yield of acids depends on temperature and the crystallinity of the samples.

The thermo-oxidation of PE at  $150^{\circ}$ C and  $160^{\circ}$ C in oxygen atmosphere was studied by Barabás et al.<sup>3</sup> By means of GC 15 oxidation products were identified.



Fig. 4. Gas chromatography analysis of products of thermo-oxidation of LDPE on Carbopack C column.



Fig. 5. Gas chromatography analysis of products of thermo-oxidation of LDPE on Fluorade FC-431 column.

Among the organic compounds found the predominant component was acetaldehyde, the amount of which was much higher than of any other product during the investigated time of degradation. A considerable amount of ethylene, propanal, butanal and low-molecular-weight alcohols were also detected.

The products formed during the thermo-oxidation of PE (72 h, 20 g of polymer) in the temperature range 75–200°C at oxygen concentration levels of 0–100% were studied with GC by Spore and Bethea.<sup>4</sup> At 200°C and 33% of oxygen, 10 oxygen-containing compounds were found. The prinicpal constituents were acetaldehyde (160 ppm), ethanol (260 ppm), and 2-pentanone (110 ppm).

The evolution of fatty acids, acrolein, and formaldehyde during smouldering combustion of PE was studied by Morikawa.<sup>5</sup> He has found that the maximum yield of these volatiles was obtained at 300–400°C. At 350°C during 30 min of heating the yield of formaldehyde was about 78,000 ppm, acetic acid, 9500 ppm, formic acid, 8700 ppm, propionic acid, 2300 ppm, and acrolein, 16,500 ppm.

Michal and co-workers<sup>6</sup> studied the products formed during thermo-oxidation of PE at 350°C in air. The main components found were  $C_3-C_{15}$  aldehydes, representing 48.8% of the chromatographic area; oxygen-containing products in next abundance were ketones (2.8%). Epoxy compounds and ethanol were also identified. The remains were hydrocarbons, predominatingly olefines.

Thermo-oxidation of PE at 700–1000°C apart from carbon oxides and water leads to the formation of short chain linear hydrocarbons  $C_{1-}C_{16}$ . No organic oxygen-containing products were found in that research.<sup>7</sup>

In the present work, at temperatures 264–289°C, intermediate to those above, significant differences in thermo-oxidative degradation of PE were noticed. Ten additional volatile compounds were detected (see Table I). These products have not been previously mentioned in the literature. The quantitative measurements

	Temperature, °C						
Compound	264	274	280	289			
Aldehydes:							
Formaldehyde	900	1320	1780	2380			
Acetaldehyde	1370	1770	1950	2400			
Propanal	270		370	440			
Acrolein	230		280	370			
Butanal			700				
Pentanal			540				
Ketones:							
Acetone			250				
Methyl ethyl ketone			320				
Methyl vinyl ketone			30				
2-Pentanone			290				
Acids:							
Formic	2440	2980	3450	4120			
Acetic	870	1200	1400	1760			
Propionic		660	700	780			
Acrylic		120	180	340			
Butyric	85	205	230	300			
Lactones:							
Butyrolactone			290				

 TABLE II

 Polyethylene Degradation Product Concentrations,\* µg/g Polymer (ppm)

<sup>a</sup> Mean values for at least three experiments; the relative deviation is about  $\pm 15\%$ .

of the major products formed during oxidation at 264–289°C (Table II) give evidence that the main components among the degradation products are formic acid followed by formaldehyde, acetaldehyde, and acetic acid. The remainder of the products quantified are formed in amounts 5–20 times less than formic acid, except for the minor product methyl vinyl ketone.

According to Barabás et al.<sup>3</sup> and Spore and Bethea<sup>4</sup> acetaldehyde was found to be the principal product of thermo-oxidation of PE at 150°C and 160°C. Barabás et al.<sup>3</sup> have also shown that the kinetic curve of acetaldehyde evolution is very similar to that of oxygen absorbtion by PE. Acetaldehyde, according to that work,<sup>3</sup> was present in an amount exceeding that of any other component by nearly one order of magnitude. Morikawa,<sup>5</sup> who worked at essentially higher temperature (300–400°C), has found that the main oxidation product was also an aldehyde, although formaldehyde. In our study we have found formic acid to be the main oxidation product. It is formed in amounts almost twice as much as acetaldehyde.

The discrepancies in the results obtained by different authors might likely arise from different experimental conditions (temperature and atmosphere) and from varying gas chromatographic conditions, e.g., using columns that are not proper, for separation of acids.

The effect of oxygen content and the effect of the temperature on the formation of different volatile products during thermo-oxidation of PE is illustrated by the following examples. Spore and Bethea<sup>4</sup> have shown that the increase in oxygen content from 33 vol % to 100 vol % at 200°C results in a fourfold increase of the yield of formaldehyde and a sevenfold increase of the yield of acetaldehyde.

The effect of the temperature of LDPE oxidation during 4 min on the yield of the four most abundant products detected in our study is shown in Figure 6. As can be seen, formaldehyde formation is more sensitive to the rise of the oxidation temperature than acetaldehyde and the acids in our experimental conditions.

# **Degradation Reaction Mechanisms**

The mechanism of thermal oxidation of hydrocarbons in the absence of additives could be described by well-known sequences of reactions presented in the following:

Scheme I

$$RH + O_2 \rightarrow \text{production of radicals}$$
(1)  
(R, HO<sub>2</sub>, OH, OR)

$$\mathbf{R} \cdot + \mathbf{O}_2 \to \mathbf{R}\mathbf{O}_2 \cdot \tag{2}$$

- $RO_2 + RH \rightarrow ROOH + R.$  (3)
- $HO_{2} + RH \rightarrow H_{2}O_{2} + R.$ (4)

$$RO \cdot + RH \to ROH + R \cdot \tag{5}$$

$$ROOH \rightarrow RO \cdot + \cdot OH \tag{6}$$

$$H_2O_2 \rightarrow 2 \cdot OH \tag{7}$$



Fig. 6. The effect of temperature on the yields of some aldehydes and acids formed during oxidation of LDPE.

$$2 \operatorname{R} \rightarrow \operatorname{products}$$
 (8)

$$RO_2 + R \rightarrow products$$
 (9)

$$2 \operatorname{RO}_{2} \rightarrow \operatorname{products} + \operatorname{O}_2 \tag{10}$$

$$RO + R' \rightarrow products + R' - H$$
 (11)

where  $\cdot \mathbf{R}' =$  any radical formed.

The first step of thermal oxidation is the formation of free radicals, the socalled primary initiation reaction, which can generally be represented by reaction (1). The reactions (2)-(5) represent propagation steps. Reaction (2) is very rapid, having an activation energy (E) of about zero value.<sup>12</sup> Reaction (3) is less rapid; the formation of hydroperoxide can proceed both by inter- and intramolecular hydrogen abstraction. When secondary and tertiary peroxides are involved, E is about 10.5 kcal/mol<sup>12</sup> for intermolecular reaction. The intramolecular hydrogen abstraction implies a ring transition state, the value of E varies in this case between 11 and 37 kcal/mol,<sup>12</sup> depending on the number of carbon atoms in the ring transition state. Reaction (5) for secondary and tertiary alkoxy radicals has an E value of about 3-11 kcal/mol.<sup>12</sup> Reactions (6) and (7) account for an initiation step. Reaction (6) for secondary and tertiary alkoxy radicals has an E value of about 44 kcal/mol.<sup>13</sup> The reactions (8)–(11) are termination steps, and are generally very fast. The value of E for these reactions is about  $3 \text{ kcal/mol.}^{14}$  However, in the presence of oxygen (<100 torr) steps (8) and (9) may be neglected.<sup>14</sup> Reaction (11) is a termination step, involving alkoxy radicals considerd to be of importance in the thermo-oxidative degradation of PE under the conditions described.<sup>9</sup> At high oxidation temperatures of hydrocarbons, formation and decomposition of peroxides and hydroperoxides can be expected to proceed very rapidly, thus resulting in formation of alkoxy radicals. The oxidized hydrocarbon fragments, as well as the various functional groups within the polymer, are formed in reactions of alkoxy radicals, resulting from the decomposition of hydroperoxides.<sup>15</sup>

Before discussing the results, it should be stated that the formation of oxidized volatiles in the thermal degradation sampling system probably proceeds in two different conditions. Partially on and under the surface of the melted polymer, with restricted access of oxygen, and partially in the gas phase, rich with oxygen, by oxidation of fragments of decomposed polymer, volatile at the experimental conditions. This situation, which is quite usual during industrial processing, complicates the interpretation of the experimental results.

The destruction of the polymer, which occurs in the melt, is accompanied by chain scissions. This contributes to the formation of volatile, partially oxidized fragments of hydrocarbon. The volatiles are oxidized further in the gas phase rich with oxygen. The gas phase oxidation contributes probably in a high degree to the formation of short chain oxidized molecules. It should also be kept in mind that the volatiles escaping the polymer melt, which is kept at a rather high temperature (264–289°C), are cooled in a 200-mm-long transfer section, kept at 125°C, before reaching the glass trap. Thus the oxidation in the gas phase is performed in conditions of a certain temperature gradient.

The most probable paths of formation of different classes of organic products during thermal oxidation of LDPE in the temperature range of 284–355°C were discussed thoroughly by Holmström and Sörvik.<sup>9</sup> The reactions were considered

to account for the formation of aldehydes, ketones, alcohols, THF derivatives, and vinyl and vinylene groups within the polymer melt. However, these reactions are not completely adequate to explain some results found in our study, e.g., the high yield of  $C_1$  and  $C_2$  aldehydes and acids. Among the organic products found, the most abundant is formic acid, which is followed in abundance by formaldehyde, acetaldehyde, and acetic acid, respectively.

High concentrations of alkoxy radicals in the gas phase during thermo-oxidation of PE at 350°C have been reported.<sup>16</sup> An alkoxy radical may react as follows:

$$\mathbf{R} - \mathbf{C}\mathbf{H}_2 - \mathbf{O} \longrightarrow \mathbf{R} - \dot{\mathbf{C}}\mathbf{H}_2 + \mathbf{O} = \mathbf{C}\mathbf{H}_2 \tag{12}$$

$$\begin{array}{cccc} R - CH - CH_2 - O \rightarrow R - CH - CH_3 + O = CH_2 \\ | \\ CH_3 \end{array}$$
(13)

$$\begin{array}{ccc} R & - & CH & - & O & - & CH_3 & - & CHO & + & \cdot R \\ & & & & & \\ & & & & & \\ & & & & CH_3 \end{array}$$
(14)

Reaction (12) and reaction (13)<sup>14</sup> contribute to formation of formaldehyde, while reaction (14)<sup>14</sup> favors formation of acetaldehyde. Due to their labile hydrogen, the aldehydes formed are considered to undergo a rapid hydrogen abstraction and subsequent loss of carbon monoxide at temperatures about 264–289°C, reactions (15) and (16):

$$R-CHO \xrightarrow[-R'-H]{+R'} R-\dot{C} = 0$$
(15)

where R' is any radical present

$$R-\dot{C} = 0 \rightarrow R \cdot + CO \tag{16}$$

Thus it can be presumed that formaldehyde and acetaldehyde found are formed in the gas phase oxidation of volatile hydrocarbon fragments, rather than in the polymer melt. An alternative path for  $C_1$ - $C_2$  aldehyde formation in the gas phase oxidation may well involve methyl (methoxy) and ethyl (ethoxy) radicals. These radicals might come from gas-phase oxidation of escaped hydrocarbons or longer chain oxygen-compounds. Spore and Bethea<sup>4</sup> have shown that the rise of oxidation temperature and oxygen content during PE oxidation has a profound effect on the yield of methane. Methyl radicals, which are the precursors of methane, should in an oxygen-rich atmosphere form methyl peroxides and eventually methoxy radicals. The latter may serve as a source for formation of formaldehyde and formic acid.<sup>17</sup>

The rather high amounts of methyl end groups essential to account for formation of short chain aldehydes, acids, and ketones could have been generated within the polymer melt in oxygen starved conditions. The methyl groups could have been formed in the course of intermolecular [reaction (17)] and intramolecular (back-biting) reactions<sup>18–22</sup> (18) and (19) of hydrogen abstraction by a primary radical. The value of E for hydrogen abstraction by a primary radical is about 10 kcal/mol<sup>23</sup> both for inter- and intramolecular reactions:

`CH<sub>2</sub>

$$\begin{array}{c} R \\ | \\ R - \dot{C}H_2 + R - CH - CH_2 - R \rightarrow R - CH_3 + R - \dot{C} - CH_2 - R \\ | \\ H \end{array}$$

$$\begin{array}{c} R \\ | \\ H \end{array}$$

$$\begin{array}{c} R \\ (17) \\ (17$$

$$R - CH_{2} - CH \xrightarrow{CH_{2} - CH_{2}} CH_{2} \rightarrow R - CH_{2} - \dot{C}H \xrightarrow{CH_{2} - CH_{2}} CH_{3}$$
(18)  
$$R - CH_{2} - CH \xrightarrow{H} \dot{C}H_{2} \rightarrow R - \dot{C}H \xrightarrow{CH_{3}} CH_{3}$$
(19)  
$$CH \xrightarrow{CH} CH \xrightarrow{CH} CH_{3} \xrightarrow{CH_{3}} (19)$$

The aldehydes present in the gas phase can easily lose a hydrogen atom in reactions of chain transfer (15), thus forming acyl radicals. Depending on oxygen pressure, the acyl radicals either decarbonylate [reaction (16)] or form acylperoxy radicals [reaction (20)], which attack hydrocarbon fragments with the formation of peracids [reaction (21)]:

$$R - \dot{C} = 0 + O_2 \longrightarrow R - C - 0 - 0$$
(20)

`CH,

Peracids can further participate in reactions as follows:

$$R-CO_{3}H \xrightarrow{-\cdot OH} R-O_{2^{*}} \rightarrow R_{*} + CO_{2}$$
(22)

$$R \longrightarrow CO_{3}H + R' \longrightarrow C \longrightarrow R \longrightarrow COOH + R' \longrightarrow COOR''$$

$$Acid (R'' = H), ester (R'' = R)$$

$$(23)$$

$$R - CO_{3}H + R' - CH = CH - R'' \longrightarrow R - COOH + R' - CH - CH - R''$$
(24)

The peracids formed in the polymer melt would most probably decompose, according to reaction (22). The peracids formed in the gas phase can oxidize ketones to esters, leaving acids, or can oxidize aldehydes to acids. Vinylene compounds in the gas phase can be converted to epoxides, leaving acids. No epoxides or acyclic esters were detected by the GC/MS analysis. However, rather high amounts of acids were found. It can be presumed that the  $C_1$  and  $C_2$  aldehydes detected represent only a part of these products formed, which escaped further transformations. The other part of the aldehydes formed in the gas phase have presumably been involved in reactions (15) and (20) giving peracids, and thus enabling formation of acids. Formation of acids and 2-ketones can also proceed according to a reaction analogous to that described by Sharp et al.<sup>24</sup> for oxidation of diisopropyl ketone.

$$R_{2} - CH - C - CH - R \rightarrow R_{2} - CH - C - C - R \rightarrow$$

$$R_{2} - CH - C - CH - R \rightarrow R_{2} - CH - C - C - R \rightarrow$$

$$R_{2} - CH - C - C - R \rightarrow$$

$$R_{2} - CH - R - C \rightarrow$$

$$R_{2} - CH - C \rightarrow$$

$$R_{2} - CH - C \rightarrow$$

$$R_{2} - C - R \rightarrow$$

$$R_{$$

The 2-ketones are the only type of ketones found in this study. The reaction (25) represents one of the possible paths for the formation of these.

Whatever the actual pathways of formation of formic and acetic acids are, this study confirms the result obtained by Matveeva et al.<sup>1</sup> at 150°C and 170°C that  $C_1$  and  $C_2$  acids are the main organic products formed during thermo-oxidation of PE even at considerably higher temperatures (264–289°C).

Two cyclic ethers furan and THF have been found in only very low amounts in this study. One of the most probable pathways for the formation of THF derivatives implies hydrogen abstraction<sup>12</sup> according to reaction (26) with a subsequent cyclization,<sup>12</sup> reaction (27):



Reactions (26) and (27) were considered by Holmström and Sörvik<sup>9</sup> to be responsible for the formation of ether bonds in LDPE, which was oxidized at 284-355°C in an oxygen-deficient system (oxygen content below 1.2%). If the reaction (26) proceeds in the polymer melt, THF is formed only when R = R' =R'' = H. If THF formation takes place in the gas phase, the radical formed in reaction (26) would most probably react with oxygen.

Valerolactone, butyrolactone, and hydroxyvaleric acid are products of PE thermal oxidation observed probably for the first time. Among these butyrolactone is the main compound formed in amounts close to the most ketones. The probable path of formation of butyrolactone is a conformationally favorable cyclization of peroxybutyric acid, with subsequent elimination of water.

# CONCLUSION

The composition of volatile products formed during thermo-oxidation of LDPE in the temperature range of 264–289°C in air at low values of weight loss was studied.

Altogether 44 compounds representing hydrocarbons, alcohols, aldehydes, ketones, acids, cyclic ethers, cyclic esters, and hydroxycarboxylic acids were identified.

Sixteen oxygen-containing products were quantified. The fatty acids are the principal organic products of thermo-oxidation of LDPE, followed by aldehydes and ketones. The most abundant product formed is formic acid.

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