Supplementary Information (SI) for Polymer Chemistry.

Supplementary Materials
Wet oxidation of polyethylene under elevated oxygen pressure: revisiting product selectivity

Vadim V. Zefirov*[1], Polina S. Kazaryan[1], Svetlana V. Stakhanova[2], Elizaveta V. Shmakova[2], Alexander V. Dudkin[2], Ivan A. Godovikov[1], Elena P. Kharitonova[3], Marat O. Gallyamov[1,3], Alexei R. Khokhlov[1,3]

[1] A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova St. 28, 119991 Moscow, Russia

[2] Department of Analytical Chemistry, Dmitry Mendeleev University of Chemical Technology of Russia, Miusskaya Sq. 9, 125047 Moscow, Russia.

[3] Faculty of Physics, M.V. Lomonosov Moscow State University, Leninskie Gory 1-2, 119991 Moscow, Russia

S1. The contribution of the gaseous wet oxidation products to the pressure in the autoclave during the process

To determine the possible excess pressure produced by gas products of polyethylene degradation, the following calculations were carried out. Using gravimetry, we determined that increasing the pressure in the autoclave used with pure oxygen to 20 bar increases the mass of the autoclave by ≈390 mg. Using this data, we can calculate the number of moles of oxygen molecules, which is ≈0.0122 mol. Then, using the ideal gas equation, we can calculate the volume occupied by the gas, which is ≈14 ml. The corresponding pressure is 28.9 bar (without the contribution from water vapor pressure). To calculate the pressure of gases formed during decomposition, we will take into account the data from the analysis of the gas phase (77% O_2, 20.5% CO_2, 0.5% CO, 2% N_2). Taking into account all the gases formed, as well as the fact that after decomposition the mass of the gas phase is 340 mg, allows us to estimate the new number of moles of gas ≈0.0099 mol. Again using the ideal gas approximation, we obtain a new value for the pressure in the system due to gases at 150 ºC ≈23.4 bar. The water formed during the process does not contribute to the pressure change, since the saturated vapor pressure is independent of the volume of water. Thus, we add the saturated vapor pressure of water (4.7 bar) and get the final estimate ≈29 bar in the system at 150 ºC.

S2. GC-MS and capillary electrophoresis study of the wet oxidation liquid products

The practical application of the GC-MS method to aqueous solutions of carboxylic acids is complicated by the fact that due to the highly reactive hydroxyl groups, the substances being studied adsorb in the injector and chromatographic column. This results in the transformation of the substances, their loss and distortion of the results of quantitative determination. To avoid this, the analyzed components were first derivatized to convert polar hydroxyl groups into non-polar ones without disrupting the main structure of the substance, and then transferred to the organic phase by extraction. For the derivatization, an aliquot of the aqueous phase (0.050 ml) was mixed with 0.050 ml of concentrated hydrochloric acid and 0.5 ml of tributyl borate in a tightly sealed vessel. The reaction was conducted at 95℃. After cooling, the excess acid was neutralized by adding 5 ml of a saturated sodium bicarbonate solution. The resulting butyl esters of the carboxylic acids were then extracted with hexane in the presence of acetonitrile, using an aqueous-to-organic phase ratio of 5:1. Chromatography was carried out under the following conditions: a 12–25 m long quartz capillary column coated with a methylsiloxane phase was used. The injector temperature was 250 ºC, the detector temperature was 290 ºC, and the column temperature was varied from 40 to 280 ºC at a rate of 10 deg/min. Helium was used as the carrier gas. The mass spectra were interpreted using NIST databases.

Capillary electrophoresis was used to quantify the content of carboxylic acids. A capillary electrophoresis system CAPEL-105 M (Lumex, Russia) equipped with a spectrophotometric detector and a quartz capillary tube (internal diameter 75 µm, effective length 50 cm, total length 60 cm) and Elforun® software (Lumex, Russia) was used. The assay was carried out under the following conditions: the capillary temperature was thermostatically maintained at 25 °C; the voltage applied to the capillary tube was −20 kV; the hydrodynamic injection of the sample was performed at 30 mbar for 12 s. The background electrolyte consisted of 10 mM benzoic acid supplemented with 0.5 mM cetyltrimethylammonium hydroxide with pH adjusted to 8.6 using diethanolamine. Indirect UV detection was used at a wavelength of 254 nm. Between measurement series, the capillary was rinsed for 5 min with water, then with 1 M solution of HCl for 5 min, then with water for 5 min, then with 1 M solution of NaOH for 5 min, and then with water for 5 min again. Probes of the liquid fractions obtained in the TOD process were centrifuged at 12,000 rpm for 5 min and diluted 100-fold with Milli-Q purified water before analysis. An external calibration method was used to obtain quantitative results.

S3. Iodometric titration for the determination of hydroperoxides in liquid products

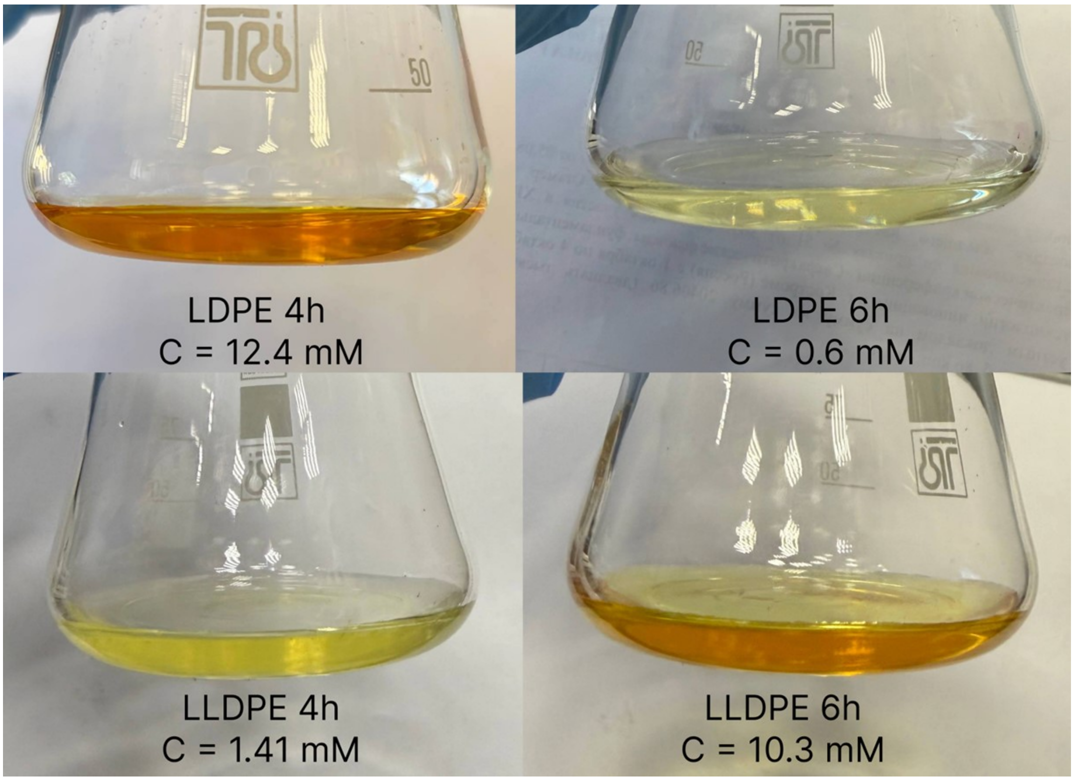


Figure S1. Photographs of mixtures of liquid products of wet oxidation with 2M H_2SO_4 (2.5 mL) and 10 wt.% KI (5 mL) after exposition in dark for 3 minutes.

S4. X-ray diffraction study of initial LLDPE and LDPE

Figure S1 shows X-ray diffraction data for LLDPE and LDPE samples. Based on the obtained data, the crystalline fractions of the polymers were calculated using the diffractometer software, which were 48% for LLDPE and 46% for LDPE.

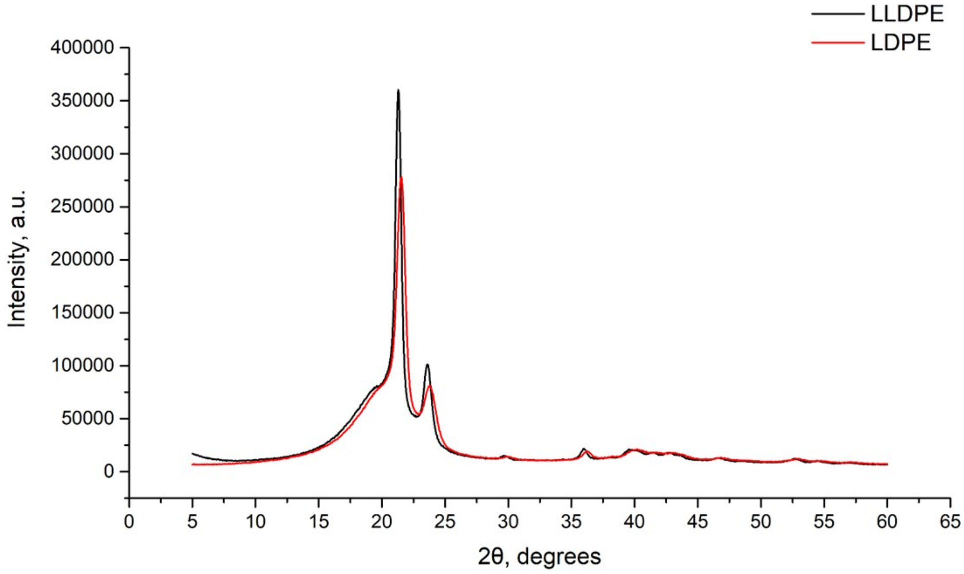


Figure S2. XRD pattern of LLDPE and LDPE used in this work.

Figure S3 shows the kinetic curves of acid formation, collected on one graph for better visualization of the concentration ratio.

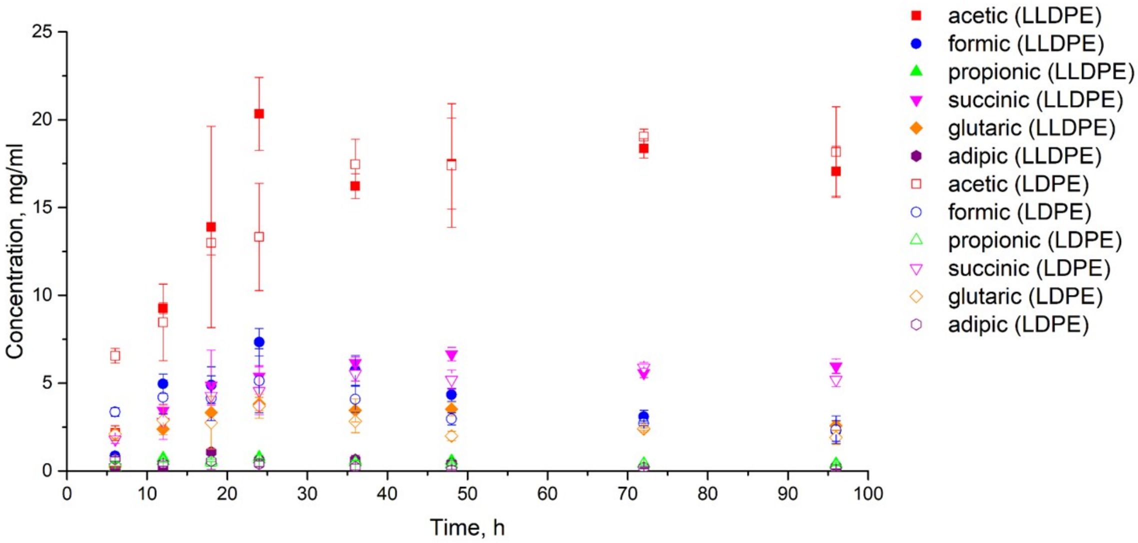


Figure S3. Kinetic curves of accumulation of soluble carboxylic acids during wet thermooxidation of LDPE and LLDPE.

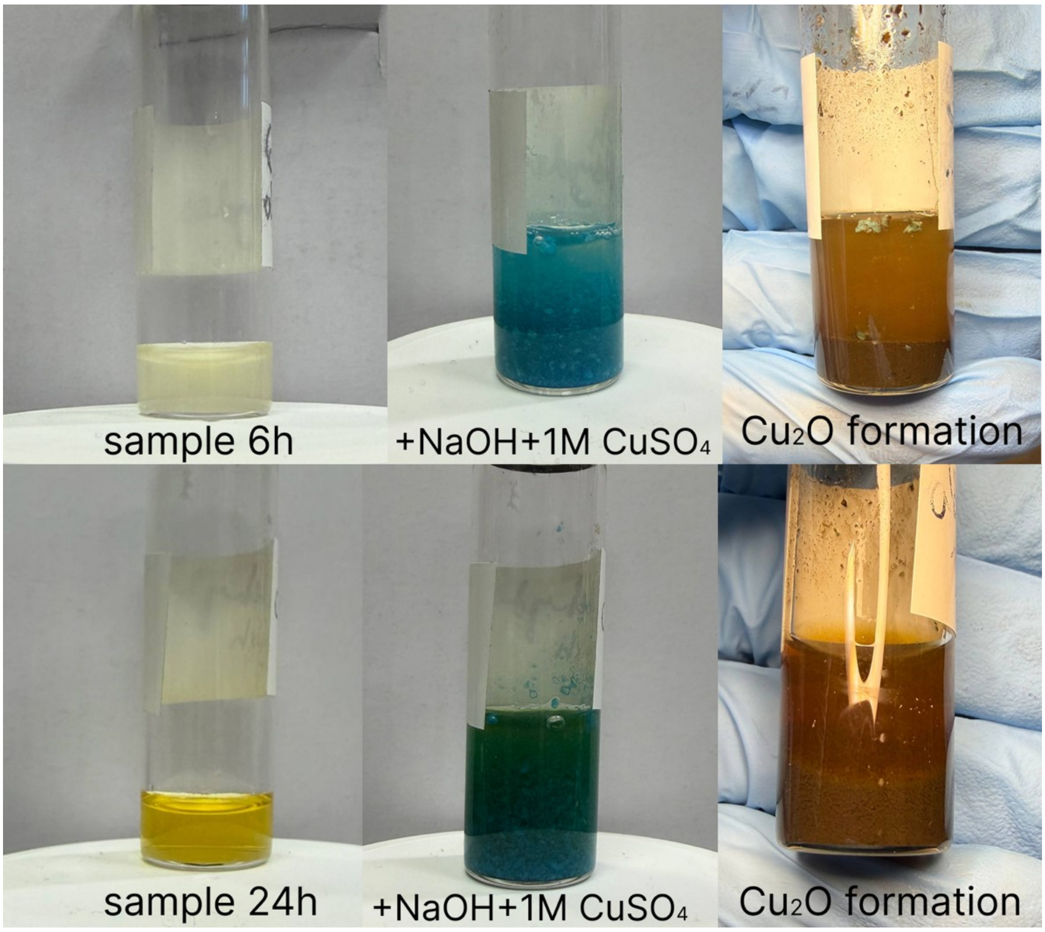
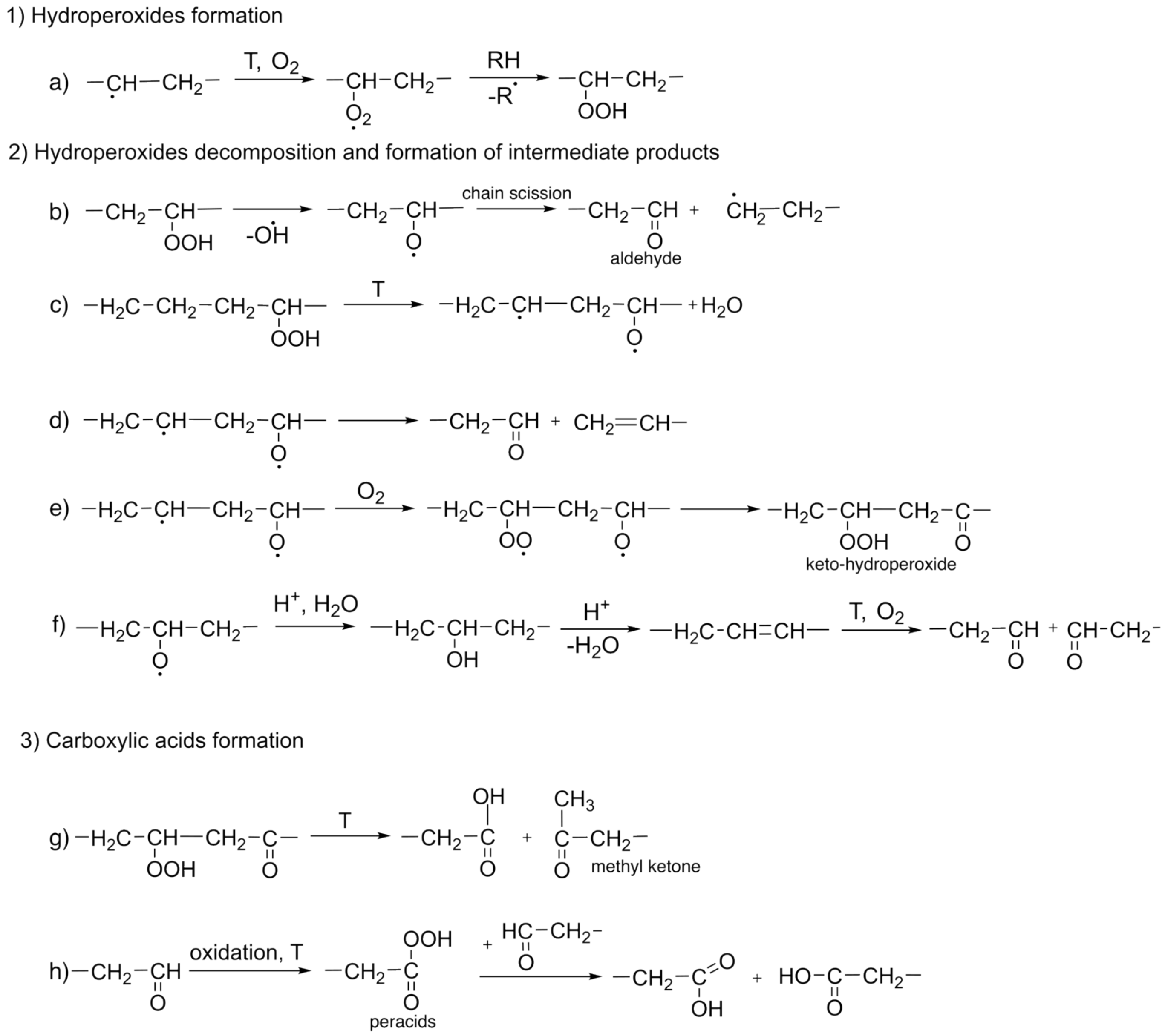


Figure S4. The stages of qualitative reaction on aldehydes presence in liquid products obtained after 6 and 24 hours of PE wet oxidation. A brick-red color due to Cu_2O formation is observed, which indicates the unambiguous presence of aldehyde groups in the reaction mixture compounds.

S4. Possible radical and ionic mechanisms of carboxylic acids formation during wet oxidation of PE



Scheme S1. (1) Formation of hydroperoxides during PE oxidation. (2) The possible routes for hydroperoxide decomposition and formation of carbonyl groups containing products. (3) Some of the potential pathways for carboxylic acid formation during PE wet oxidation. The presence of hydroperoxides and aldehydes (as well as aldehyde-like formic acid) in liquid products was confirmed by iodometric titration and qualitative reactions with $Cu(OH)_2$ in alkaline solution correspondingly. The aforementioned reactions are not exhaustive and represent only some of the processes that occur during PE oxidation.

The reactions (1) on Scheme S1 correspond to the hydroperoxides formation, reactions (2) correspond to the possible routes of hydroperoxides decomposition and intermediates products formation, and reactions (3) correspond to the possible pathways for carboxylic acids formation from these intermediates. The mentioned reactions are not exhaustive and represent only some of the processes that occur during PE oxidation. Oxygen uptake leads to the formation of peroxy radicals on the polymer backbone, which then abstract hydrogen atoms from adjacent chains, resulting in the formation of hydroperoxides (Scheme 1a). In our experiments the presence of hydroperoxides in the products was confirmed and estimated by iodometric titration.

Most of the products in the PE oxidation process are formed as a result of the hydroperoxide decomposition processes [1]. The β-chain scission of alkoxy radicals formed during the hydroperoxide decomposition leads to the formation of carbonyl groups (aldehydes, ketones) and chain-end radicals, or by formation of aldehydes and vinyl groups [2] (Scheme 1b-d). Since both the formation and further oxidation of these products occur extremely rapidly [1], Iring et al consider them to be an active intermediate in the process, leading to further degenerated branching and formation of carboxyl groups. During oxidation, the polyethylene melt in a water/oxygen mixture at 150ºC decomposes into shorter oxidized oligomers. With the accumulation of polar carbonyl groups and a decrease in molecular weight, these fragments lose their hydrophobicity and dissolve into the aqueous phase [3]. The alkyl radicals formed during oxidation may quickly transform into the peroxy radical (Scheme 1e); further reaction of the alkoxy-peroxy biradical can quickly lead to the formation of α,γ-keto-hydroperoxides [4]. The presence of the aldehydes and aldehyde-like formic acid was confirmed by standard qualitative reaction of the liquid decomposition products with $Cu(OH)_2$ in alkaline solution (Figure S1). A brick-red color due to Cu_2O formation was observed, which indicates the unambiguous presence of aldehyde groups in the reaction mixture compounds.

Carboxylic acids can form via a variety of competing or sequential pathways involving radical, ionic, and molecular mechanisms [2]. Acids formed in the reaction mixture can catalyze subsequent ionic reactions, accompanied by proton migration, molecular isomerization, and cycles of hydration and dehydration and leading to the formation of unsaturated intermediate products (Scheme 1f) [5,6]. Alongside carboxylic acid, subcritical water itself can act as an acid catalyst [7,8] and carbonic acid generated from dissolved CO_2 [9] may also enhance dehydration.

Scheme 1 (3), illustrates several potential pathways for carboxylic acid formation. It can be attributed to decomposition of keto-hydroperoxides, and radical induced/molecular mechanisms of carbonyl compounds oxidation [2]. For example, the thermal decomposition of α,γ-keto-hydroperoxides —formed during autoxidation— produces a methyl ketone and a carboxylic acid and proceeds at a high rate (Scheme 1g). In the later stages of degradation, as ketone and acid groups accumulate and catalyze further breakdown, the decomposition of α,β-keto-hydroperoxides becomes significant, yielding both an aldehyde and a carboxylic acid. Aldehydes may also be oxidized to peracids, which can subsequently convert into carboxylic acids either through reaction with double bonds or by thermolysis. During the Baeyer-Villiger reaction both the aldehyde and the peracid can be transformed into carboxylic acid (Scheme 1h) [2]. This reaction is an ionic reaction catalyzed by acids. One of the most effective routes to acid formation at 150–160 °C is the reaction of aldehydes with primary or secondary hydroperoxides. For primary ROOH, the reaction yields a new aldehyde; for secondary ROOH, it yields a ketone. In addition to aldehydes, hydroperoxides can also react with ketones—abundantly formed during PE oxidation—to produce unstable hemiketals. During thermolysis, these intermediates generate carboxylic acids and alkoxyl radicals.

Figure S5 shows photographs of dried under vacuum at 40°C LLDPE samples subjected to degradation for 4, 6, and 12 hours. The 4-hour sample clearly shows orange-colored areas, which apparently underwent more severe oxidation. The oxidized polyethylene itself becomes softer and more brittle after 4 hours of degradation.

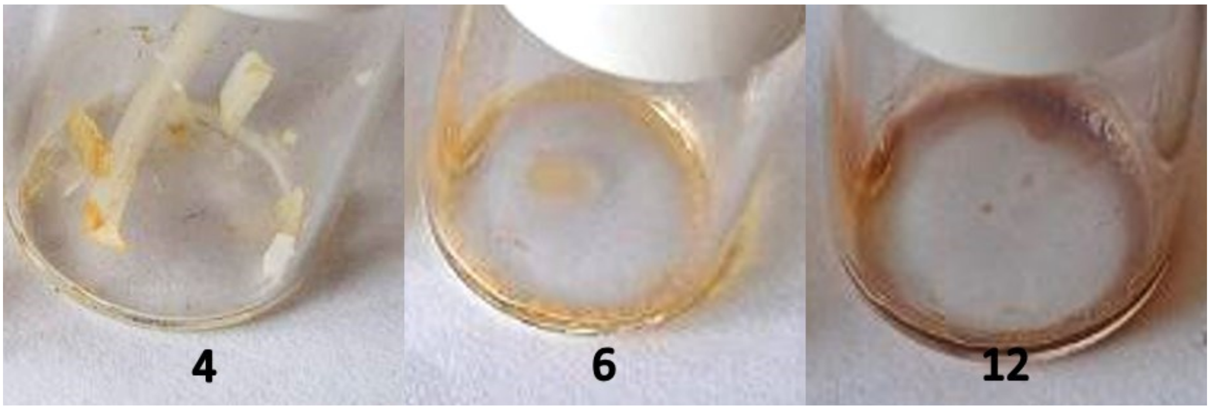


Figure S5. Photographs of dried LLDPE samples subjected to degradation for 4, 6, and 12 hours.

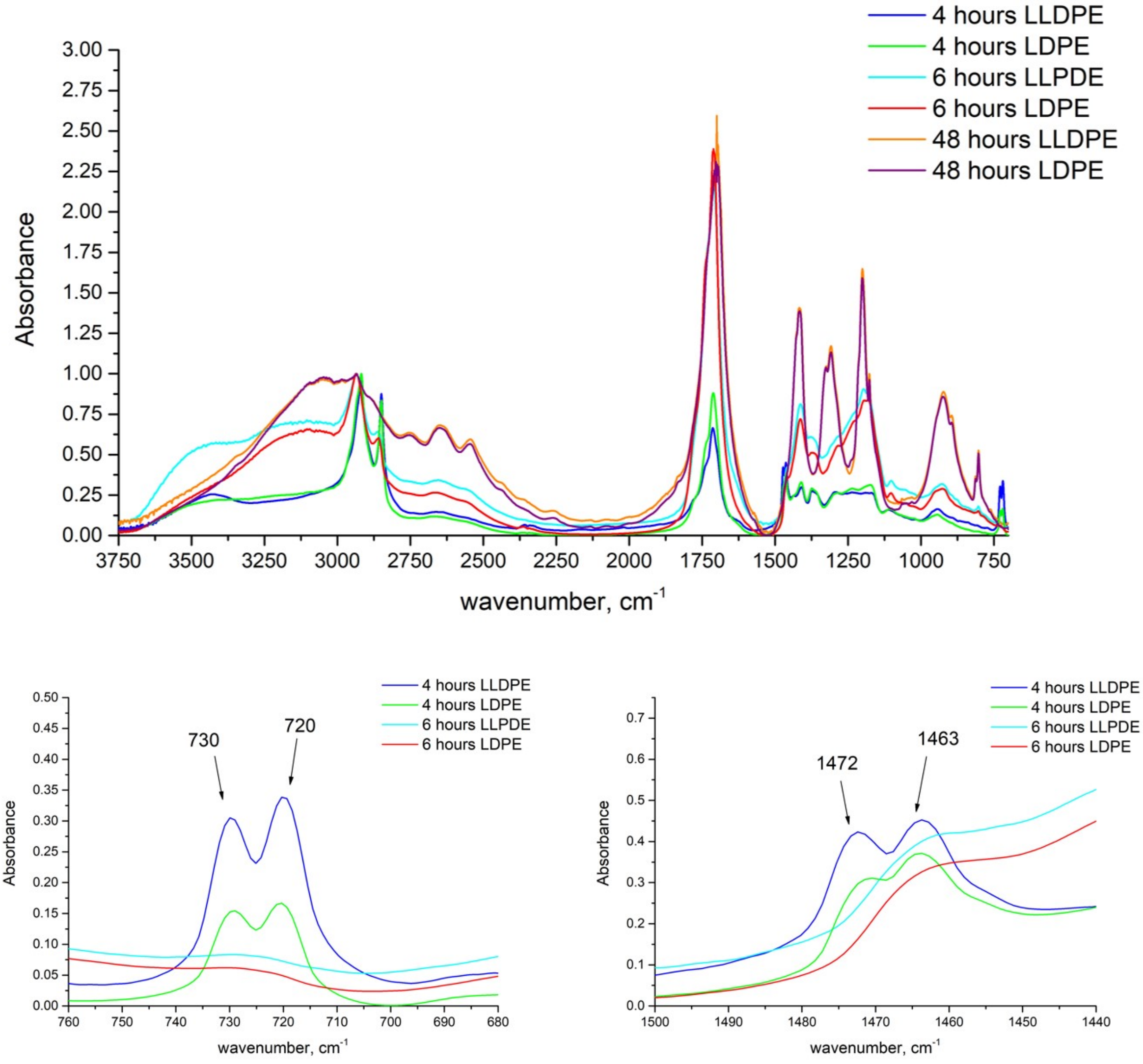


Figure S6. Typical FTIR spectra of vacuum dried samples obtained by wet oxidation of LLDPE and LDPE at different destruction times (in hours). The bottom row shows enlarged parts of the spectrum, which contain doublet bands associated with the ordered structure of the polymer.

Figure S7 shows typical gas chromatograms obtained for wet oxidation samples of LLDPE with exposure times of 12, 24, and 96 hours. It is important to note that the data for the 12- and 24-hour samples were obtained significantly later than for the 96-hour sample, so the instrument calibration shifted slightly toward longer exit times. It is clearly evident that the peak corresponding to carbon dioxide increases with increasing exposure time, while the other peaks remain unchanged.

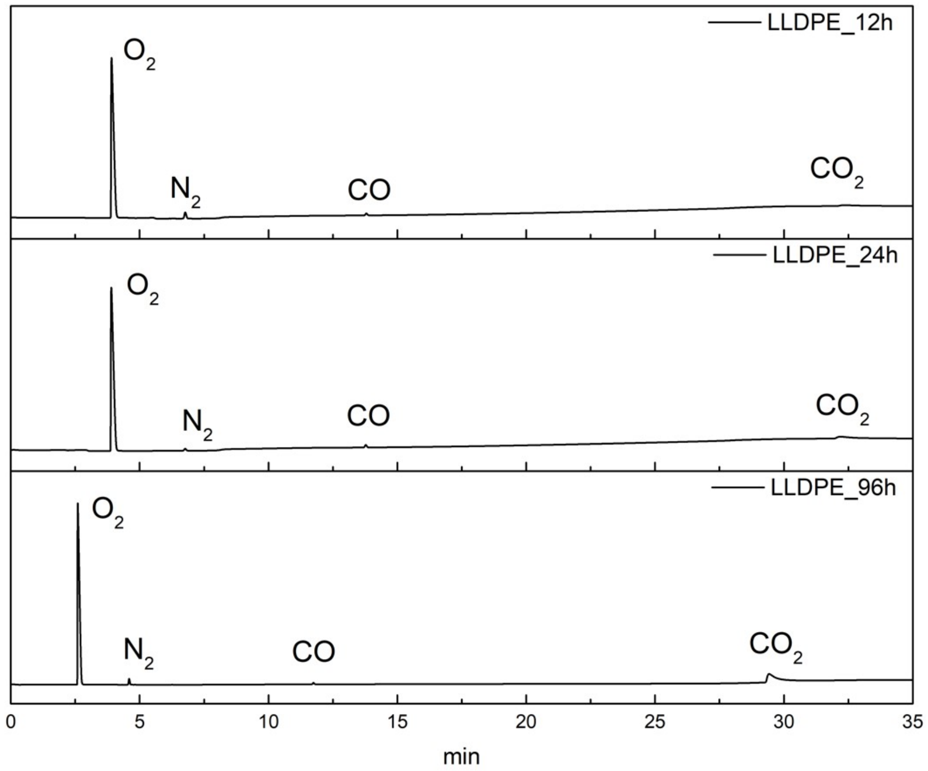


Figure S7. Typical gas phase chromatograms of decomposition products.

Table S1. Elemental composition and mass of dried oligomeric residues obtained by wet oxidation of LLDPE for a given time.

Processing time, hours	Oligomer residues mass, mg	C content, wt.%	H content, wt.%	O content, wt.%	N content, wt.%
12	29±3	52.2	6.9	40.7	0.1
24	19±3	44.8	6.1	49.0	0.1
96	8±2	42.8	5.4	51.5	0.3

Table S2 presents detailed carbon balance data compiled based on the results obtained in this work. Importantly, we compared the resulting total carbon in the products with the initial carbon in the polymer to determine whether all products were accounted for. As a result, we showed that for 96 hours, the difference between experiment and theory was only 0.4% carbon, meaning that all experimentally described products indeed contained all of the initial carbon. In the case of 12 and 24 hours, a significant portion of the initial carbon (25.7% and 19.4%, respectively) was not captured in the products. As noted earlier, we analyzed only the most stable acids present in all samples. Obviously, in experiments with shorter oxidation times, there is a high probability of unaccounted unstable acids appearing. We believe that the observed discrepancy in carbon amounts arises precisely from these unaccounted unstable acidic products. Therefore, for the sake of calculation accuracy, we designated these products as "other acids" and included them in the overall carbon balance.

Table S2. Elemental composition and mass of dried oligomeric residues obtained by wet oxidation of LLDPE for a given time.

Processing time, hours	acetic acid	formic acid	propionic acid	succinic acid	glutaric acid	adipic acid	other acids	CO_2	CO	oligomeric fraction
12	10.3	3.6	1.1	3.9	4.1	1.1	25.7	3.5	2.5	43.6
24	22.6	5.3	1.1	6.1	4.8	0.9	19.4	11.3	1.0	27.4
96	19.0	1.6	0.6	6.7	3.2	0.3	0.4	52.9	2.0	13.0

References

1. Iring M., Tudos F. Thermal oxidation of polyethylene and polypropylene: Effects of chemical structure and reaction conditions on the oxidation process // Prog. Polym. Sci. 1990. Vol. 15, № 2. P. 217–262.
2. Gugumus F. Physico-chemical aspects of polyethylene processing in an open mixer. Part 25: Mechanisms of aldehyde and carboxylic acid formation // Polym. Degrad. Stab. 2006. Vol. 91, № 12. P. 3416–3428.
3. Davydovich O. et al. Mild aqueous metal catalyzed oxidative conversion of low-density polyethylene to low molecular weight aliphatic carboxylic acids // Green Chem. Royal Society of Chemistry, 2024. Vol. 26, № 20. P. 10390–10396.
4. Gugumus F. Thermolysis of polyethylene hydroperoxides in the melt 5. Mechanisms and formal kinetics of product formation // Polym. Degrad. Stab. 2002. Vol. 76, № 3. P. 381–391.
5. Galkin A.A., Lunin V. V. Subcritical and supercritical water: a universal medium for chemical reactions // Russ. Chem. Rev. 2005. Vol. 74, № 1. P. 21–35.
6. Avola S. et al. Organic chemistry under hydrothermal conditions // Pure Appl. Chem.

2012. Vol. 85, № 1. P. 89–103.

7. Jin F. et al. Conversion Mechanism of Cellulosic Biomass to Lactic Acid in Subcritical Water and Acid–base Catalytic Effect of Subcritical Water // Chem. Lett. 2004. Vol. 33, № 2. P. 126–127.
8. Mangi M.A. et al. Preparation of acetic acid from crop residues via hydrolysis coupled with oxidation in subcritical water // Ind. Crops Prod. 2025. Vol. 232. P. 121208.
9. Pigaleva M.A. et al. A biphase H 2 O/CO 2 system as a versatile reaction medium for organic synthesis // RSC Adv. 2015. Vol. 5, № 125. P. 103573–103608.