

# Radiation-thermal approaches to the processing of complex polymer waste

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## 1. Introduction

Synthetic plastics were created to be durable materials, but the desire for durability now turns into huge problems in the management of plastic waste. In fact, humankind is able to reuse only a tenth of plastic waste. The rest is either incinerated or sent to landfills and to the environment. By 2050, this trend can burden the nature with 12,000 Mt of highly resistant plastic waste (Geyer et al., 2017). Reuse of landfill plastics is significantly complicated due to their inseparable compositions with lignocelluloses and other materials (Burillo et al., 2002; Geyer et al., 2017). Of course, over time, plastic undergoes decomposition by means of microorganisms and other natural factors (photochemical, thermochemical, electrochemical, catalytic, etc.). However, mankind so far knows little about the dynamics of natural degradation of plastics and the degree of danger of the resulting products. Accordingly, the challenge for science is to develop ways of rational handling of polymer waste, including accelerated methods for predicting the features of their degradation in spontaneous and regular landfills.

The International Atomic Energy Agency pays serious attention to this task. In particular, in December 2018, the consultative meeting “Polymer Processing: Potential Application of Radiation Technologies” was held ([www.naweb.iaea.org](http://www.naweb.iaea.org)). Radiation chemistry can modify plastics (via grafting, crosslinking, oxidation, decomposition, etc.) and, accordingly, can be used to enhance the handling of plastic waste (Burillo et al., 2002; Woods and Pikaev, 1994). New practical applications of radiation appear, such as sorting plastics (Albrecht et al., 2007), creating cement-plastic compositions (Schaefer et al., 2018), forming porous building materials (Jeong et al., 2016; Park et al., 2015), etc. In turn, high-temperature radiolysis is capable of depolymerizing and partially fragmenting macromolecules (Burillo et al., 2002; Ponomarev and Ershov, 2018; Woods and Pikaev, 1994). Accordingly, it can also be adapted for the recycling of polymeric wastes. This article, based on our previous and current research, summarizes several feasible ways to use thermal support radiolysis for recycling synthetic and natural polymers.

## 2. Experimental

Radiolysis of plastics in boiling solutions was carried out at 6 Gy/

pulse and 50 Hz pulse repetition rate using 3 MeV electrons generated by LINS-03-350 linac (from RadiaBeam Systems, USA). Electron-beam distillation of plastics was carried out at 6 Gy/pulse and 300 Hz pulse repetition rate using 8 MeV electrons generated by the UELB-10-10T linac (From TORII, Russia).

Low-density polyethylene (LDPE,  $\rho = 0.92$  g/ml) was purchased from KAZANORGSINTEZ (Russia). Polystyrene (PS), polycarbonate (PC), polypropylene (PP) and polyethylene terephthalate (PET) were taken from waste plastic packaging materials. A fraction with a particle size of 0.5–2 mm was used for experiments. Samples of hydrolytic coniferous lignin were purchased from the SEGEZHA Pulp and Paper Mill (Russia).

In this study, the DD mode was the usual dry distillation of the initial samples. Dry distillation of samples pre-irradiated at room temperature is designated as PRD mode (Post-Radiation Distillation). The combination of dry distillation with simultaneous electron beaming is designated as EBD mode (Electron-Beam Distillation). The EBDW mode was a version of the EBD mode when a mixture containing equal quotas of lignin and wax ( $C_{17}$ – $C_{120}$  paraffins synthesized via the Fischer–Tropsch process, from “Gazohim Techno”, Russia) was distilled. Studies of the above modes of dry distillation, as well as gas chromatography-mass spectrometric analysis of the products, corresponded to the procedures described previously (Gorbarev et al., 2019, 2018; Ponomarev and Ershov, 2014).

The vessel for plastic irradiation in boiling solutions is shown in Fig. 1. It includes two vertical cylindrical sections connected by inclined tubes. The evaporative section is equipped with a bottom electric heater and contains an upflow of boiling solution, while the return section contains a downflow. The upflow pulls the solution out of the return section into the evaporation section, creating a continuous circulation of the solution with a fairly even distribution of plastic particles. The slope of the connecting tubes limits the vapor bubbles within the evaporating section and prevents plastic particles from settling in the connecting tubes. The flotation rate of plastic particles was measured at room temperature in a measuring cylinder (30 cm height and 15 mm internal diameter) by upturning the occluded cylinder and measuring the range of time required for the ascent or sedimentation of the particles.

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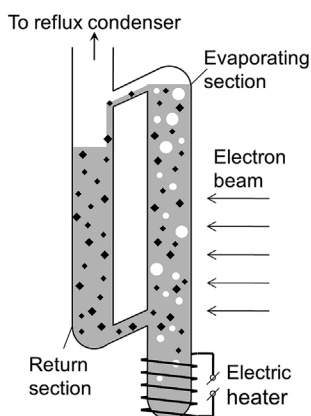


Fig. 1. Vessel for the irradiation of plastics in boiling solution.

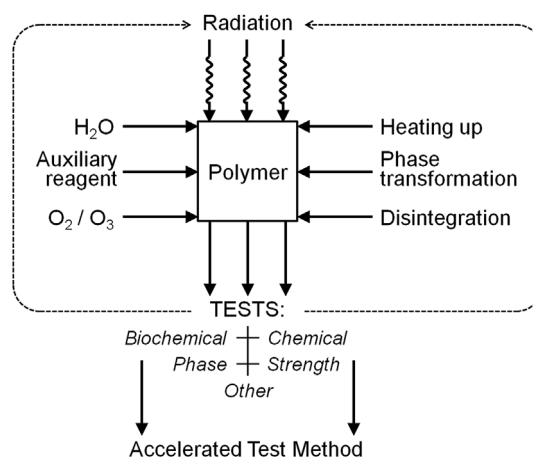


Fig. 3. Schematic representation of the development sequence of the accelerated testing method.

### 3. Results and discussion

#### 3.1. Path 1 - development of an accelerated test method for the degradability of plastics

The degradation of plastics in landfills depends on their interaction with air and the surrounding moist substrate supporting biochemical processes. The most common plastics are hydrophobic and difficult to oxidize. Hydrophobicity slows the penetration of chemically and biologically active medium into plastic and thereby prolongs the degradation of plastic waste. Radiation-chemical oxidation can reduce hydrophobicity (in particular, change the buoyancy, Fig. 2) and thereby contribute to biodegradation of plastics. The susceptibility of plastics to radiation-chemical oxidation gives rise to the idea of using radiolysis to develop a method for accelerated testing of plastics degradability.

Previously, radiation-chemical methods have already been used for accelerated tests on the durability of materials, for example, corrosion tests of stainless steels (Makarov et al., 1982) and tests of the durability of electrical paper insulation (Komarov et al., 2004). In both cases, the radiation serves to quickly create defects that under normal conditions are generated for many years. The same principle could serve as the basis for testing plastics. So far there is no such method, but its development seems very relevant and promising. The essence of the work ahead in this direction (Fig. 3) is to find the best method of radiation-supported oxidation of plastic particles both outside and inside, as well as the best method for monitoring their sensitivity to natural factors.

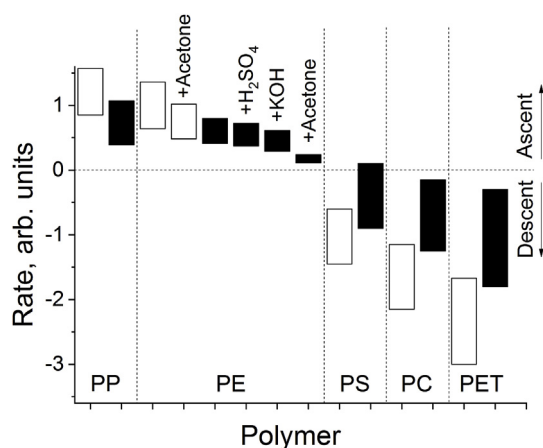


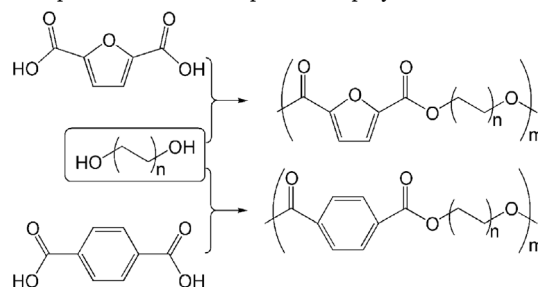
Fig. 2. The relative rate of ascent (↑) or descent (↓) of PE, PP, PS, PC and PET particles treated in boiling water and aqueous solutions (30 wt % for acetone; 0.5 wt % for  $H_2SO_4$  and KOH) without irradiation (white) or at 50 kGy (black). The absence of ascent or descent of plastic particles is indicated as zero (neutral buoyancy).

Most likely, there is a correlation between the resistance of plastic to natural oxidation and its resistance to radiation oxidation. This correlation should be found. In both cases, a measure of stability can be the consumption of energy and reagents for oxidation.

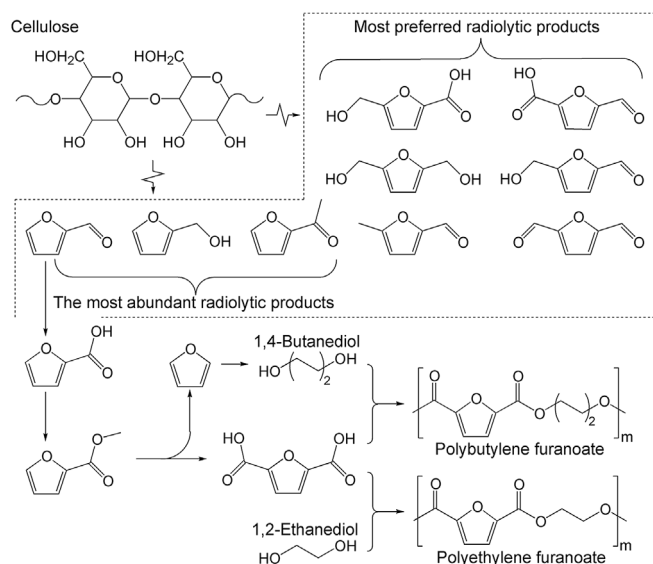
Both radiation-chemical and natural oxidation supply the plastic with the same oxygen-containing groups (hydroxyl, carbonyl, carboxyl, peroxide and alkoxy) and both are realized mainly in the surface layer due to the slow penetration of air and water into the plastic. However, radiation oxidation is much faster than natural oxidation. Model radiation-chemical oxidation can be further accelerated by heating, since an increase in temperature stimulates chemical reactions, diffusion of oxidizing agents, mobility of macroradicals, decay of intermediates, etc. However, the heating must be balanced, because the solubility of gases decreases with temperature. Along with atmospheric oxygen, ozone and water can also serve as a source of oxidative intermediates during radiolysis.

#### 3.2. Path 2 - the formation of feedstock for the synthesis of "green" plastics

Undoubtedly, the use of biodegradable plastics originating from renewable plant materials is consistent with the concept of sustainable development (Bozell and Petersen, 2010). In particular, 2,5-furadicarboxylic acid of plant origin could be used instead of petroleum-derived terephthalic acid in the process of polycondensation:



In this regard, there is a need for new ways to produce plant monomers. Furfural is the most accessible vegetable furan, which is obtained hydrolytically from less common polysaccharides, mainly from d-xylose and hemicellulose. However, traditional methods are unproductive in terms of cellulose-to-furfural conversion. As a result, the annual global production of furfural for various needs does not exceed 300,000 tons (Mamman et al., 2008). For its part, the thermoradiolysis of cellulose in EBD mode generates an unprecedentedly high yield of furans (about 50 wt %) due to the unique self-disassembly mechanism (Ponomarev and Ershov, 2014, 2018). The EBD mode produces several furans containing two oxygen-containing substituents,



**Fig. 4.** The most abundant and most preferable furan derivatives, obtained by electron-beam distillation of cellulose (within the dashed line), and the subsequent path of the catalytic conversion of furfural to 2,5-furandicarboxylic acid and polyolefin furanoates.

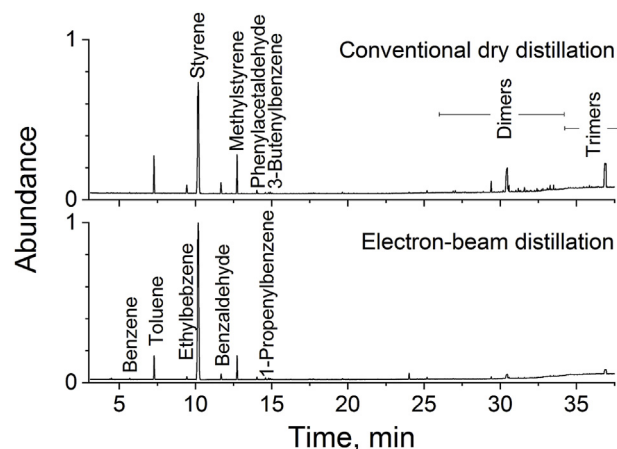
but the main products are furfural, 2-furanmethanol, and 2-acetylfuran (Fig. 4).

There are various catalytic methods for converting furfural to 2,5-furandicarboxylic acid and its derivatives (Pan et al., 2013; Shen et al., 2019, 2018; Zhang and Zhou, 2017), and it is possible to turn furfural into polybutylene furanoate without losing carbon (Fig. 4). The use of cellulose-to-furfural electron-beam conversion would avoid the shortage of raw materials for the production of 2,5-furandicarboxylic acid and, accordingly, for the production of furan-containing polymers. At the same time, the presence of disubstituted furans among radiolytic products indicates the possibility of modifying the EBD mode in order to increase the yield of such disubstituted monomers. The proposed mechanism of radiation-thermal degradation of cellulose (Ponomarev and Ershov, 2018) allows this.

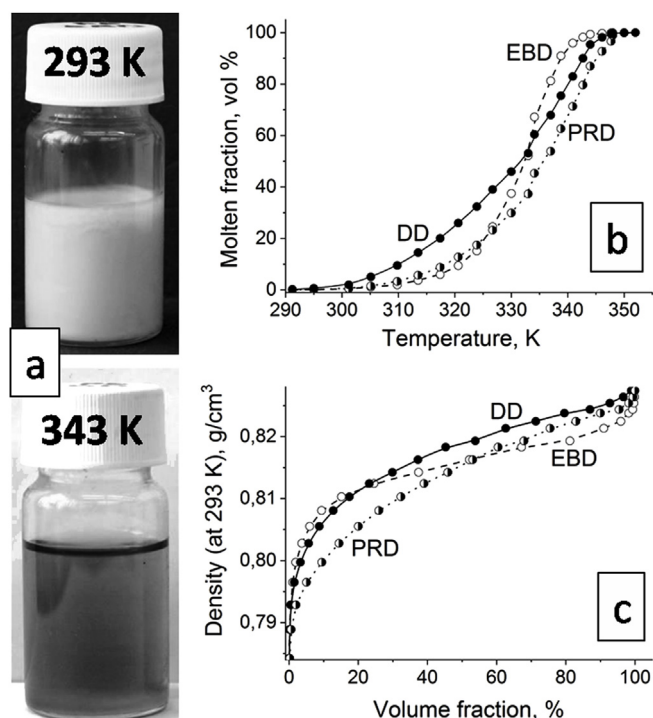
### 3.3. Path 3 - radiation-thermal depolymerization of plastics

Dry distillation of plastics, as a rule, occurs in accordance with the same principles as the dynamic cracking of high-molecular paraffins, natural bitumen and oil sludge (Bludenko et al., 2009; Metreveli and Ponomarev, 2016; Metreveli et al., 2018). Sometimes the main product of thermo-radiolysis and pyrolysis is the same. For example, the distillation of polystyrene in both the DD mode and the EBD mode gives mainly styrene (Fig. 5), that is, a depolymerization product. Side liquid products are toluene, ethylbenzene, methyl styrene and the like. Oxidized polystyrene forms also give rise to benzaldehyde and phenylacetaldehyde. At the same time, the liquid from the EBD mode contains much more styrene and less polycyclic compounds (dimers, trimers, etc.) compared to the DD mode (Fig. 5).

Distillation products of polyolefins in DD, PRD and EBD modes are also quite similar. For example, the product of polyethylene distillation is a low melting wax (Fig. 6a), or, if necessary, a mixture of gasoline and diesel fuel (Metreveli and Ponomarev, 2016). The DD mode converts LDPE to 65 wt% soft wax and 35 wt% gas, whereas the EBD mode produces mainly soft wax ( $\approx 90$  wt%), and at a lower temperature. The wax from the EBD and PRD modes starts to melt at a higher temperature than wax from the DD mode (Fig. 6c, b), and some solid particles remain in the melt up to 343 K. At the same time, the average density of wax from the EBD mode is somewhat lower (Fig. 6c). Such differences are due to the higher proportion of alkanes in the latter case.



**Fig. 5.** Chromatograms of a liquid product derived from polystyrene.



**Fig. 6.** Soft wax from LDPE, obtained via EBD mode (a), wax melting curves (b) and density of fractions separated during melting (c).

One of the options for thermal processing of plastic waste may consist in the production of synthesis gas, followed by the synthesis of diesel fuel using Fischer-Tropsch technology. However, this path also generates waste in the form of a mixture of heavy paraffins (wax), similar to low molecular weight polyethylene. Thermoradiolysis is suitable for the complete conversion of Fischer-Tropsch waxes to liquid fuels (Metreveli and Ponomarev, 2016) and, thus, to make a useful contribution to the management of plastic waste.

### 3.4. Path 4 - formation of back polymerization inhibitors

Liquid products of depolymerization of waste plastics are unstable, since they consist mainly of unsaturated compounds prone to back polymerization. Accordingly, effective and inexpensive back polymerization inhibitors are needed. Such inhibitors can be obtained from large-tonnage polyphenolic waste (Gorbarev et al., 2018). In particular, both pyrolysis and thermo-radiolysis of lignin produce tar containing

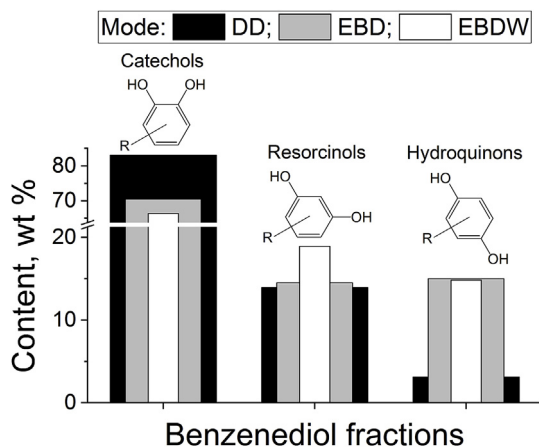


Fig. 7. Ratio of catechols, resorcinols and hydroquinones in the fraction of benzenediols of tar obtained in the DD, EBD and EBDW modes. R-CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, tert-C<sub>4</sub>H<sub>9</sub> or OCH<sub>3</sub>. Compiled from (Gorbarev et al., 2018).

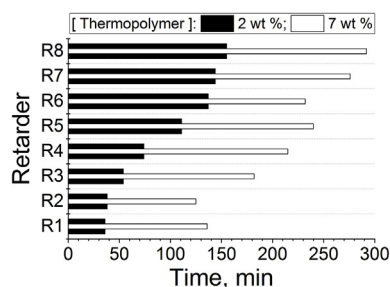


Fig. 8. The time of formation of 2 and 7 wt% polystyrene in styrene at 120 °C in the presence of 0.025 wt% of various inhibitors: R1 - tar from DD mode; R2 - methylbenzylphenols; R3 is 2,6-ditertbutyl-4-methylphenol; R4 - bis-(2-oxy-5-methyl-3-tertbutylphenyl)-methane; R5 - tar from EBD mode; R6 - di(methylbenzyl)phenols; R7 - tar from EBDW mode; R8 - 2,6-ditertbutyl-4-dimethylaminomethylphenol. Compiled from (Gorbarev et al., 2018).

benzenediols capable of well inhibiting polymerization (Fiege et al., 2000). The DD, EBD and EBDW modes generate different benzenediol levels in tar - 7.4, 31.3 and 40.7 wt %, respectively (Gorbarev et al., 2018). Moreover, the tar from the EBD and EBDW modes contains more hydroquinones and resorcinols (Fig. 7) with a higher degree of alkylation, as well as dihydroxy derivatives of diphenyl and acetophenone. As a result, the tar from the EBD and EBDW modes inhibits polymerization more efficiently. For example, a comparison of the induction periods of the thermopolymerization of styrene (Fig. 8) shows that phenolic tar from the DD mode is a very weak inhibitor, whereas tar from the EBD and EBDW modes is competitive compared to recognized commercial phenolic retarders of coke-chemical origin. Undoubtedly, refining in order to concentrate benzenediols would allow to further increase the inhibitory ability of tar, but would increase its cost. Therefore, it seems appropriate to consider the use of crude tar.

Thus, thermoradiolysis can both generate monomers from plastic waste and form back polymerization inhibitors from polyphenolic waste. Conversion of lignin to phenolic stabilizers could be a promising radiation-chemical direction, closely related to the treatment of lignocellulosic waste, as well as the recycling of waste plastics.

#### 4. Conclusion

Along with well-known methods of radiation modification of polymers at moderate temperatures, various radiation-thermal methods could significantly diversify the knowledge and possibilities in the field of recycling polymer waste. The development of a radiation-driven method for accelerated testing of the degradability of plastics could

give impetus to the progress in the synthesis of green plastics and the optimization of the management strategy for already accumulated plastic waste. Sharpening the techniques of thermo-radiolytic distillation of plant waste, as well as the deepening of knowledge on the mechanism of self-disassembly of macromolecules, could aim at a deficit-free raw material supply of the synthesis of biodegradable plastics, such as polyolefinfuranoates, polyurethanes and the like. Combining the thermal and radiolytic effects could generate an upgrade of the pyrolytic conversion paths of plastic waste with an increase in the yield of monomers and liquid fuel while reducing costs. In turn, the saving of the resulting secondary monomers could be ensured by means of phenolic stabilizers generated by the thermo-radiolysis of lignin-containing waste.

#### Acknowledgments

The work was performed under the theme AAAA-A16-116121410087-6 of the Russian Academy of Sciences using equipment provided by the Center for Collective Use of Physical Research Methods of the Frumkin Institute of Physical Chemistry and Electrochemistry.

#### References

- Albrecht, V., U., G., Husemann, K., Reinsch, E., Schünemann, R., Simon, F., 2007. Verfahren zur elektrostatischen Trennung von Kunststoffgemischen. Patent. DE102007055765.
- Bludenko, A.V., Ponomarev, A.V., Chulkov, V.N., Ershov, B.G., 2009. The synergistic effect upon the electron-beam distillation of wood-bitumen mixtures. High Energy Chem. 43, 516–517. <https://doi.org/10.1134/S0018143909060186>.
- Bozell, J.J., Petersen, G.R., 2010. Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy's "Top 10" revisited. Green Chem. 12, 539–554. <https://doi.org/10.1039/b922014c>.
- Burillo, G., Clough, R.L., Czvikovszky, T., Guven, O., Le Moel, A., Liu, W., Singh, A., Yang, J., Zaharescu, T., 2002. Polymer recycling: potential application of radiation technology. Radiat. Phys. Chem. 64, 41–51. [https://doi.org/10.1016/S0969-806X\(01\)00443-1](https://doi.org/10.1016/S0969-806X(01)00443-1).
- Fiege, H., Voges, H.-W., Hamamoto, T., Umemura, S., Iwata, T., Miki, H., Fujita, Y., Buysch, H.-J., Garbe, D., Paulus, W., 2000. Phenol derivatives. In: Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, pp. 521–582. [https://doi.org/10.1002/14356007.a19\\_313](https://doi.org/10.1002/14356007.a19_313).
- Geyer, R., Jambeck, J.R., Law, K.L., 2017. Production, use, and fate of all plastics ever made. Sci. Adv. 3, e1700782. <https://doi.org/10.1126/sciadv.1700782>.
- Gorbarev, I.N., Kasterin, A.I., Metreveli, P.K., Ponomarev, A.V., 2018. Thermopolymerization inhibitors generated via radiolysis of lignin. J. Wood Sci. 64, 675–682. <https://doi.org/10.1007/s10086-018-1746-4>.
- Gorbarev, I.N., Vlasov, S.I., Chulkov, V.N., Bludenko, A.V., Ponomarev, A.V., 2019. Degradation of plastics via electron-beam distillation. Radiat. Phys. Chem. 158, 64–67. <https://doi.org/10.1016/j.radphyschem.2019.01.016>.
- Jeong, J.-O., Park, J.-S., Lim, Y.-M., 2016. Development of styrene-grafted polyurethane by radiation-based techniques. Materials (Basel) 9, 441. <https://doi.org/10.3390/ma9060441>.
- Komarov, V.B., L'vov, M.Y., L'vov, Y.N., Ershov, B.G., Bondareva, V.N., Rubtsov, A.V., Seliverstov, A.F., 2004. Regeneration of cellulose insulation of windings of long-life power transformers. Power Technol. Eng. 38, 178–181. <https://doi.org/10.1023/B:HYCO.0000041823.11652.0e>.
- Makarov, I.E., Grigoriev, A.E., Pikaev, A.K., Nikishina, K.A., Kozhevnikov, O.A., Parshin, A.M., 1982. Test Method of Austenitic Stainless Steels and Alloys for Corrosion Resistance. Patent. SU 925181..
- Mamman, A.S., Lee, J.-M., Kim, Y.-C., Hwang, I.T., Park, N.-J., Hwang, Y.K., Chang, J.-S., Hwang, J.-S., 2008. Furfural: hemicellulose/xyloseederived biochemical. Biofuels, Bioprod. Biorefining 2, 438–454. <https://doi.org/10.1002/bbb.95>.
- Metreveli, A.K., Ponomarev, A.V., 2016. Radiation-initiated conversion of paraffins to engine fuel: direct and indirect initiation. Radiat. Phys. Chem. 124, 212–215. <https://doi.org/10.1016/j.radphyschem.2016.02.002>.
- Metreveli, P.K., Metreveli, A.K., Ponomarev, A.V., Pavlov, Y.S., 2018. Electron-beam processing of petroleum sludge. High Energy Chem. 52, 414–418. <https://doi.org/10.1134/S0018143918050119>.
- Pan, T., Deng, J., Xu, Q., Zuo, Y., Guo, Q.-X., Fu, Y., 2013. Catalytic conversion of furfural into a 2,5-furandicarboxylic acid-based polyester with total carbon utilization. ChemSusChem 6, 47–50. <https://doi.org/10.1002/cssc.201200652>.
- Park, J.-S., Lim, Y.-M., Nho, Y.-C., 2015. Radiation-Induced grafting with one-step process of waste polyurethane onto high-density polyethylene. Materials (Basel) 9, 13. <https://doi.org/10.3390/ma9010013>.
- Ponomarev, A., Ershov, B., 2014. Radiation-Induced high-temperature conversion of cellulose. Molecules 19, 16877–16908. <https://doi.org/10.3390/molecules191016877>.
- Ponomarev, A.V., Ershov, B.G., 2018. Radiation-induced degradation of cellulose: from partial depolymerization to complete self-disassembly. Radiat. Phys. Chem. 152, 63–68. <https://doi.org/10.1016/j.radphyschem.2018.07.004>.

- Schaefer, C.E., Kupwade-Patil, K., Ortega, M., Soriano, C., Büyükoztürk, O., White, A.E., Short, M.P., 2018. Irradiated recycled plastic as a concrete additive for improved chemo-mechanical properties and lower carbon footprint. *Waste Manag.* 71, 426–439. <https://doi.org/10.1016/j.wasman.2017.09.033>.
- Shen, G., Zhang, S., Lei, Y., Chen, Z., Yin, G., 2018. Synthesis of 2,5-furandicarboxylic acid by catalytic carbonylation of renewable furfural derived 5-bromofuroic acid. *Mol. Catal.* 455, 204–209. <https://doi.org/10.1016/j.mcat.2018.06.015>.
- Shen, G., Zhang, S., Lei, Y., Shi, J., Xia, Y., Mei, F., Chen, Z., Yin, G., 2019. Catalytic carbonylation of renewable furfural derived 5-bromofurfural to 5-formyl-2-furancarboxylic acid in oil/aqueous bi-phase system. *Mol. Catal.* 463, 94–98. <https://doi.org/10.1016/j.mcat.2018.11.021>.
- Woods, R., Pikaev, A., 1994. *Applied Radiation Chemistry. Radiation Processing*. Wiley, NY.
- Zhang, Z., Zhou, P., 2017. Catalytic aerobic oxidation of 5-hydroxymethylfurfural (HMF) into 2,5-furandicarboxylic acid and its derivatives. [https://doi.org/10.1007/978-981-10-4172-3\\_6](https://doi.org/10.1007/978-981-10-4172-3_6) 171-206.