Modeling of Epoxidation Process by the Means of Artificial Neural Network

Taras Chaikivskyi[1], Bohdan Sus[2], Sergiy Zagorodnyuk[2] and Oleksandr Bauzha[2]

[1] *Lviv Polytechnic National University, Bandera Str, 12, Lviv, 79013, Ukraine*
[2] *Taras Shevchenko National University of Kyiv, Kyiv 01033, Ukraine*

Abstract

An artificial neural network based on experimental data from the process of epoxidation of soybean oil with epoxidizing system: hydrogen peroxide / acetic anhydride / catalyst was created. This allows you to select the optimal parameters, control the epoxidation process at the stage of synthesis and improve the technology of epoxidized products. A method for calculating the results of epoxidation of mixtures of unsaturated compounds has been developed. It allows to control the epoxidation process at the stage of synthesis and to improve the technology of obtaining epoxidized products. The obtained optimal conditions of the epoxidation process are adequate for other vegetable oils.

Keywords

Artificial neural networks, Model, Soybean Oil, Catalyst, Epoxidation

1. Introduction

The current state of computer technology and the level of information technology involves solving a range of practical issues, including the procedure of deep machine learning [1]. Computational problems are successfully solved by the means of artificial neural networks belonging to different areas. In particular, by applying a multilayer differential neural network to the analysis of electroencephalograms of a person expressing a phrase, it was possible to build a human speech synthesizer [2] which can predict and define those words and fixed phrases, which a person has previously expressed, but during the operation of the synthesis can be not remembered. In medicine, artificial neural networks are used to analyze X-rays, which can determine the service life and degree of wear of artificial implants and prostheses installed in the patient's body [3]. In chemistry, artificial neural networks are implemented to predict the result of a chemical reaction under different sets of experiment conditions and the concentration of different catalysts [4, 5]. Artificial neural networks in robotics are used to calculate the trajectories of automated mechanisms and manipulators [6] as well as for the rational consumption of energy and resources. In natural sciences, which include mathematics, physics, oscillations, and waves, the mathematical physics of artificial neural networks find the solution of classical fundamental equations [7], which describe real multidimensional systems for which such numerical solutions were not available [8].

In physics, artificial neural networks are used for mathematical description of the phenomenon of energy conversion in the form of electromagnetic radiation, taking into account the processes of absorption, secondary radiation, and scattering [9], processing information from sensors for substance identification [10]. Artificial neural networks are especially widely used in physical problems of electromagnetic wave propagation [11] and ultrasound [12] in bulk solid media, ie in optics, astrophysics, atmospheric science and remote sensory technologies.

COLINS-2022: 6th International Conference on Computational Linguistics and Intelligent Systems, May 12–13, 2022, Gliwice, Poland
EMAIL: taras.v.chaikivskyi@lpnu.ua (T. Chaikivskyi); bnsuse@gmail.com (B. Sus); szagorodniuk@gmail.com (S. Zagorodnyuk); asb@univ.kiev.ua (O. Bauzha)
ORCID: 0000-0002-1166-8749 (T. Chaikivskyi); 0000-0002-2566-5530 (B. Sus); 0000-0003-3415-7746 (S. Zagorodnyuk); 0000-0002-4920-0631 (O. Bauzha)

The main principle of green chemistry is the use of renewable, environmentally friendly raw materials, which will further biodegrade and reduce the toxicity during the production of polymers. [13]

Soybean oil polymerization is important to produce polymers for printing inks. Epoxidized oils are widely used, especially to improve the performance of rubbers, as components for the production of light-sensitive films, packaging materials for baby food, and in the production of medical materials [14]. Studies on the synthesis of solid polymeric materials based on soybean oil with mechanical properties. Such polymers can be used as structural materials. Epoxides are cyclic esters, metabolites that are often formed by cytochromes that act on aromatic or double bonds. A specific site on a molecule that experiences epoxidation is its site (SOE). Artificial intelligence technologies can significantly improve the identification of SOE molecules and select the optimal pairs of parameters to control the epoxidation process at the stage of product synthesis. Artificial neural networks, which are technical software implementations of the biological neural structure of the human brain, allow such training. Networks are also called connection systems because the principal part of artificial neural networks is a structure of connections that allow one neuron to form a route of signal propagation to other neurons and, conversely, to receive from them the same signals.

The increase in the use of epoxidized oils is directly related to the growth of production of polyvinyl chloride PVC and polymers based on it, as epoxidized oils are one of the best stabilizers-plasticizers of such polymers. Epoxidized oils have several advantages over other types of stabilizers, so the introduction of epoxidized stabilizers into the polymer significantly increases its thermal stability. It also prevents the decomposition of the polymer under the action of ionizing radiation. Epoxidized oils can perform the functions of hardener (in compositions with different oligomers) and stabilizer (in compositions with PVC). The use of epoxidized oils in the paint industry is constantly increasing - they are part of paint products based on epoxy, essential cellulose oligomers and PVC, as well as plasticizers of organically dispersed coatings [15, 16].

Organic peracids are used for liquid-phase epoxidation of unsaturated organic substances [17, 18].

2. Experimental

Research [19] [suggested use of epoxidizing system hydrogen peroxide (H_2O_2)/ formic acid / catalyst. In this system, the epoxidizing agent is also an organic peracid, which is formed in situ by the interaction of hydrogen peroxide with organic acid in the presence of a catalyst (Figure 1). Organic acid circulates in the system [20] replaced formic acid with acetic acid, which is more affordable and cheaper.

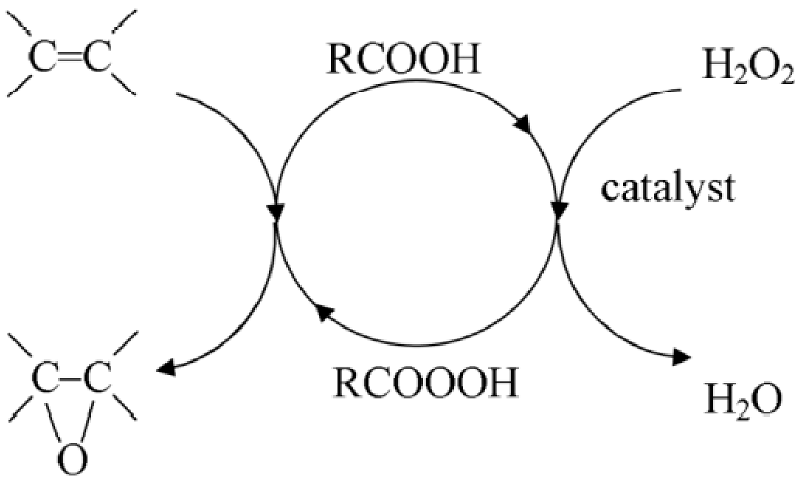

Figure 1: Chemical scheme of liquid-phase epoxidation of vegetable oil by epoxidizing system: hydrogen peroxide / organic acid / catalyst

We have suggested using its anhydride instead of organic acid, which will reduce the amount of water in the reaction mixture and accelerate the reaction of the formation of peracetic acid.

Therefore, this work aims to improve the technology of epoxidized oils; specify optimal conditions for economically feasible production of epoxidized oils, the quality of which meets the standards (Table 1); making changes in the technology of production of this product.

Table 1
Quality indicators of epoxidized oils

Physico-chemical indicator	Standard for brands (technical conditions *)		
	ST	SU	S
Epoxy number,% (oxirane oxygen content), not less than	6.5	6.4	6.0
Iodine number, g I_2/100g, not more than	1.5	2.0	8.0

* As stabilizers and plasticizers for PVC-based polymers

The practical value of the research is the use of a neural network process model that allows quality control of epoxidized oil during the synthesis stage. epoxidation process on: initial concentration of acetic anhydride, hydrogen peroxide, catalyst (ion exchange resin KU-2x8); process conditions for the optimal concentration calculation of epoxy mixture reagents, process duration, and temperature.

It has been experimentally established that the dependence of the epoxy number of epoxidized soybean oil at different concentrations of acetic anhydride, hydrogen peroxide, the amount of catalyst, and the duration of the process is complex. As the temperature and catalyst concentration increase, the reaction rate increases, but at extremely high temperatures (> 348 K) and catalyst concentration (>15g per 100 cm^3) the achieved epoxy number may decrease due to secondary epoxy opening reactions.

Therefore, to find the optimal conditions for the process, it is reasonable to develop a mathematical model and calculate the optimal conditions for the process using special methods.

To create a model, the following factors and limitations are accepted:

- x_1 - concentration of acetic anhydride, wt.% $2<x_1<9$
- x_2 - concentration of hydrogen peroxide 46%, wt.% $25<x_2<40$
- x_3 - concentration of catalyst, wt.%, $x_3<15$
- x_4 - temperature, K, $333 <x_4<353$
- x_5 - process duration, min, $x_5<360$

3. Methods

A sample of data was created to study the neural network from experimental results. Neural network inputs characterize the experimental conditions. Outputs characterize the results (concentrations of the obtained substances).

Input parameters:

1. Acetic anhydride (AA) concentration (normalized)
2. Hydrogen peroxide (H_2O_2) concentration (normalized)
3. Catalyst (KU-2×8) concentration (normalized)
4. Normalized temperature
5. Normalized reaction time
6. Initial value of Epoxy number (normalized)
7. Initial value of Iodine number (normalized)

It is assumed that the initial values of the Epoxy number and Iodine number affect the process of the experiment. Reaction time (sampling of experimental data did not exceed 400 minutes with the rationing. The temperature range of reactions was 423-443 K.

Initial parameters:

1. Final value of Epoxy number (normalized)
2. Final value of Iodine number (normalized)

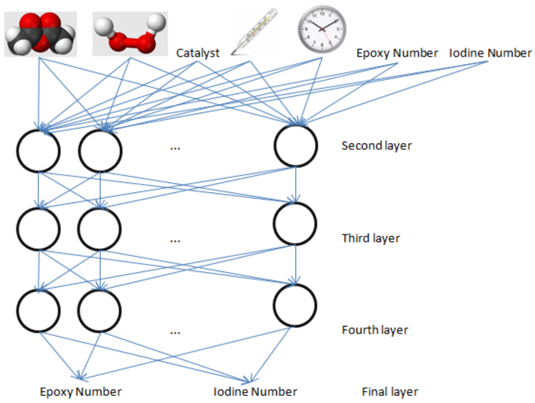

Figure 2: Type of neural network.

Figure 2 shows a five-layer neural network, which was studied based on experimental data obtained during the epoxidation of soybean oil used by the neural network are taken 7. The values of the input parameters are normalized to 1. The output layer of the neural network has 2 neurons. This network has three hidden layers of 20 neurons each.

The neural network is trained based on the training mechanism. To determine the minimum of the error function, it is necessary to perform an algorithm for the inverse propagation of errors using the stochastic gradient descent model.

In principle, the model is over fitted. It was possible to limit the number of hidden layers with fewer neurons. The learning process of the network is fast and the training ends in about 800 epochs, because a limited sample of experimental data was used..

4. Results and discussion

As can be seen from Figure 3, which was obtained after training the neural network, increasing the concentration of hydrogen peroxide in the mixture leads to a rapid increase in Epoxy number during the first 100 minutes of reaction. At low concentrations of hydrogen peroxide in the mixture, in the first 60 minutes the Epoxy number increases rapidly to values of 3-4, and further growth is slow. The data obtained during the experiment is limited by the number and range of argument values. However, as a result of learning, the neural network increases the range of arguments and interpolates the resulting values into a more detailed graph. New data will be added to the database on which the neural network is trained, and will make it possible to clarify this relationship.

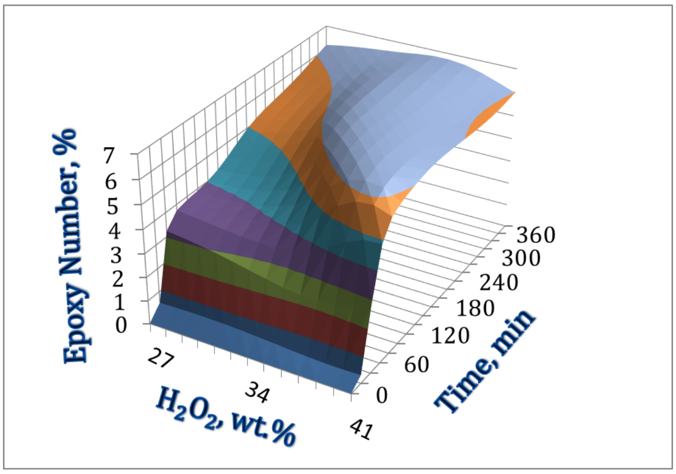

Figure 3: Dependence of Epoxy number on hydrogen peroxide and time of soybean oil epoxidation reaction. The calculations were performed by the interaction of a solution of soybean oil in toluene with the epoxidizing system: H_2O_2 / AA / catalyst. Concentration AA = 5.72 wt.%, catalyst concentration 5 wt.%, reaction temperature T = 343 K.

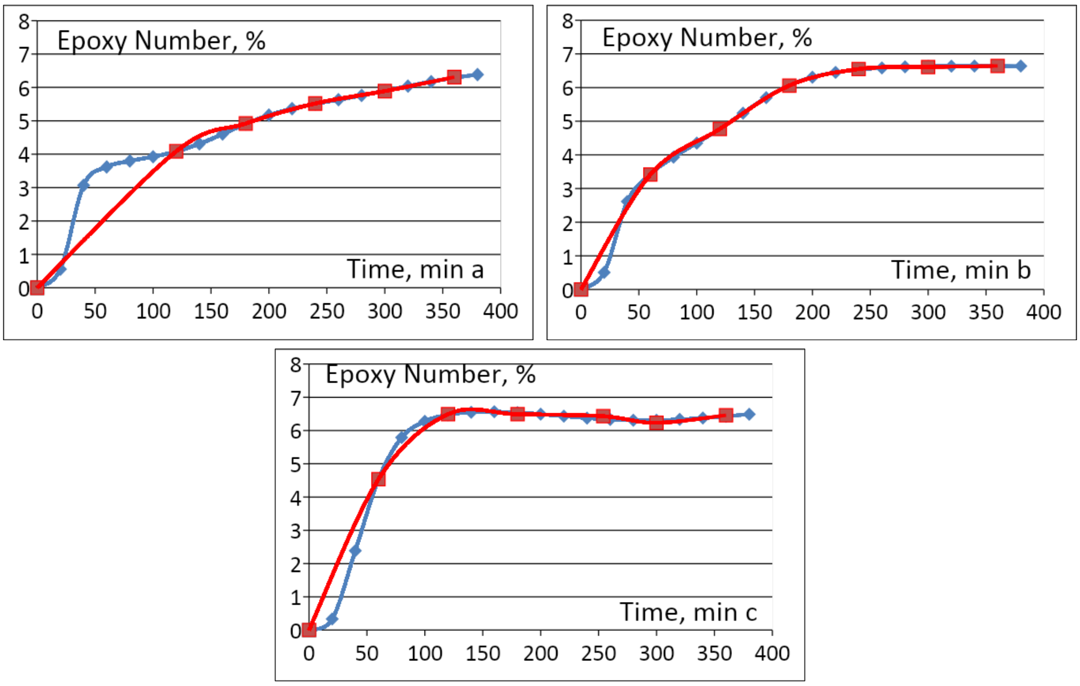

Figure 4: Comparison of the dependences Epoxy number on the concentration of hydrogen peroxide and the time of the epoxidation reaction of soybean oil. Experimental data -red lines and predicted by the neural network -blue lines. The calculations were performed by the interaction of a solution of soybean oil in toluene with the epoxidizing system: H_2O_2/ AA / catalyst. Concentration AA = 5.72 wt.%, Catalyst concentration 5 wt.%, reaction temperature T = 343 K. a - concentrations of H_2O_2 in a mixture of 29 wt.%, b - 33.1 wt.%, c - 38.59 wt.%.

Figure 4 shows a comparison of experimental data and data (large range) obtained after training the neural network. As a result of training, the neural network processes the entered data quite accurately to predict the result of the experiment beyond the experimental data.

The convexity of the dependence, which can be seen from Figure 4 a, at low reaction times, is because the network was studied on the intermediate results of the experiment. That is, the total input data were considered.

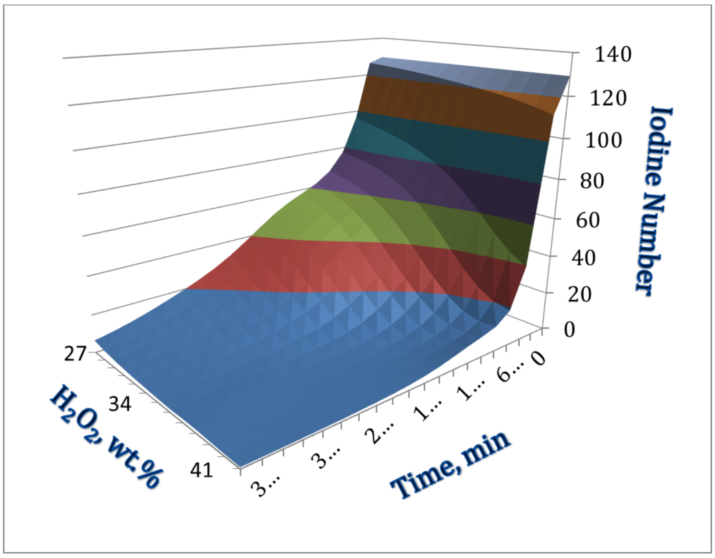

Figure 5: Dependence of Iodine number on hydrogen peroxide and time of soybean oil epoxidation reaction. The calculations were performed by the interaction of a solution of soybean oil in toluene with the epoxidizing system H_2O_2/ AA / catalyst Concentration AA = 5.72 wt.%, Catalyst concentration 5 wt.%, reaction temperature T = 343 K.

As can be seen from Figure 5, which was obtained after training in the neural network, the increase of the concentration of hydrogen peroxide in the mixture leads to a sharp decrease in ionic number. At low concentrations of hydrogen peroxide in the mixture, the Iodide number has a much slower dependence of the decrease.

As with the Figure 3, the data obtained during the experiment are limited by the number and range of argument values. However, as a result of learning, the neural network increases the range of arguments and interpolates the resulting values into a more detailed graph.

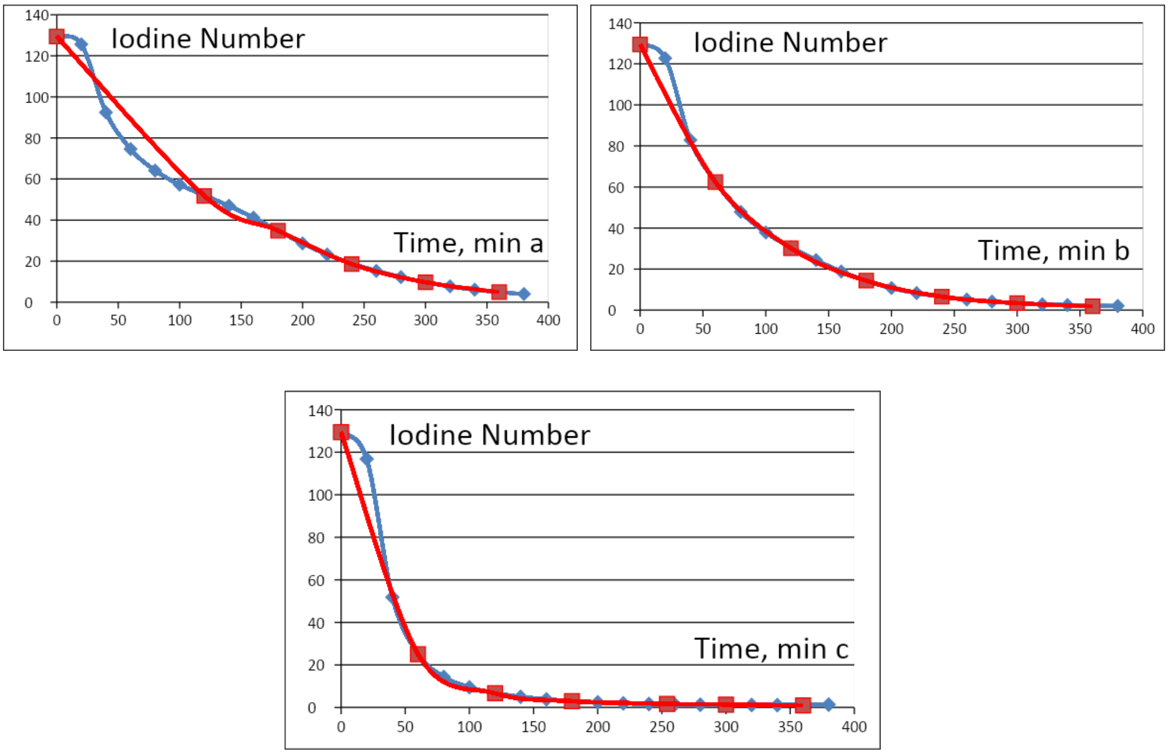

Figure 6: Comparison of the dependences of the iodine number on the concentration of hydrogen peroxide and the time of the epoxidation reaction of soybean oil. Calculations were performed by the interaction of a solution of soybean oil in toluene with epoxidizing system H_2O_2/AA/catalyst Concentration AA = 5.72 wt.%, Catalyst concentration 5 wt.%, Reaction temperature T = 343 K. a - concentrations H_2O_2 in the reaction mixture of 29 wt.%, b - 33.1 wt.%, c - 38.59 wt.%

Figure 6 shows a comparison of experimental data and data (in a larger range) obtained after training the neural network. As a result of training, the neural network accurately reproduces experimental data and predicts the outcome of the experiment beyond this data.

As shown in Figure 6, the convex dependence, a, at low reaction times, is provided by the neural network. As can be seen from the figure, the first experimental point was taken after 120 minutes, and the real dependence Iodine number on time is unknown. Based on the whole array of experimental data, the neural network assumes that the iodine number must vary according to this dependence.

As can be seen from Figure 7, which was obtained after neural network training, increasing the concentration of acetic anhydride in the mixture leads to a rapid increase in the dependence of the Epoxy number in the first 60 minutes of the reaction. At low concentrations of acetic anhydride mixture a cascading increase in epoxy numbers is observed.

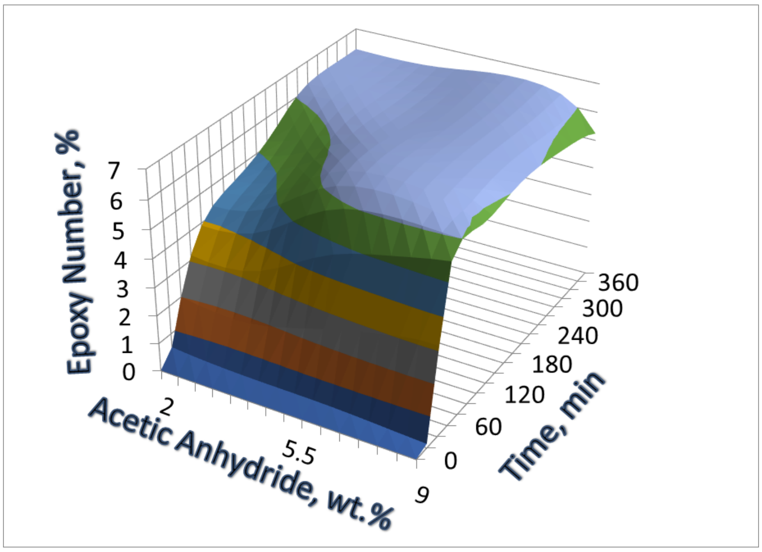

Figure 7: Dependence of Epoxy number on acetic anhydride concentration and time of soybean oil epoxidation reaction. Calculations were performed by the interaction of a solution of soybean oil in toluene with epoxidizing system H_2O_2/AA/catalyst. Concentration H_2O_2 = 38.59 wt.%, Catalyst concentration 5 wt.%, Reaction temperature T = 343 K.

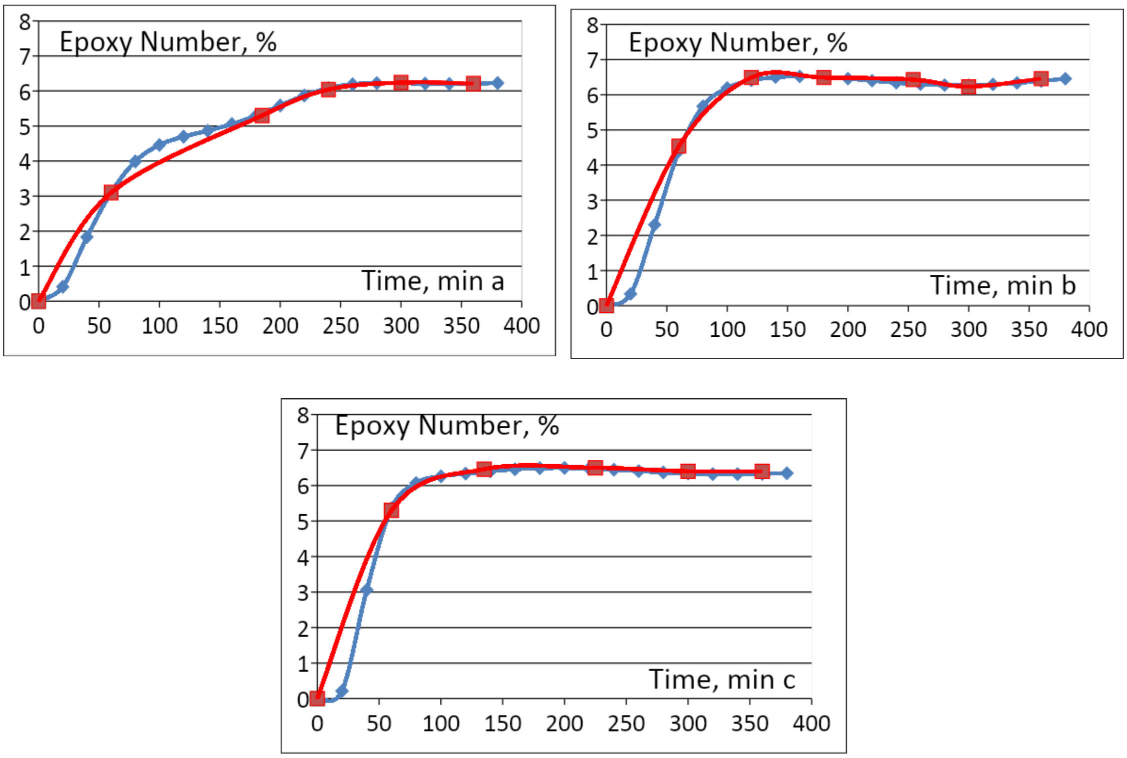

Figure 8: Comparison of the dependences Epoxy number on the concentration of acetic anhydride and the time of the epoxidation reaction of soybean oil. The calculations were performed by the interaction of a solution of soybean oil in toluene with the epoxidizing system H_2O_2/AA/catalyst. Concentration H_2O_2 = 38.59 wt.%, Catalyst concentration 5 wt.%, Reaction temperature T = 343 K. **a** - concentrations of AA in the mixture of 2.86 wt.%, **b** - 5.72 wt.%, **c** - 7.79 wt.%.

As can be seen from Figure 8, the neural network repeats the experimental points well and expands the range of points that predict the result of the reaction.

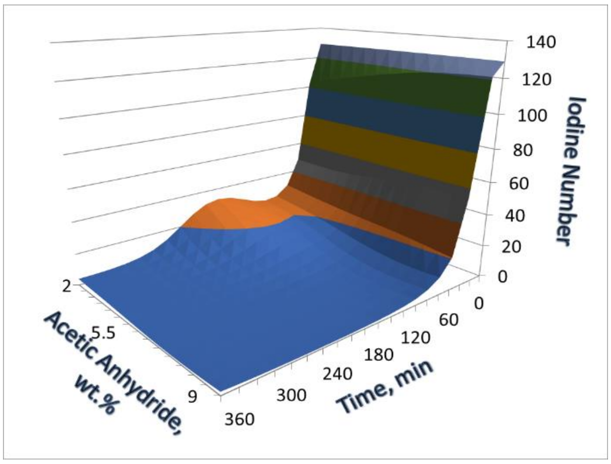

Figure 9: Dependence of Iodine number on acetic anhydride concentration and time of soybean oil epoxidation reaction. Calculations were performed by the interaction of a solution of soybean oil in toluene with the epoxidizing system H_2O_2/ AA / catalyst Concentration H_2O_2 = 38.59 wt.%, Catalyst concentration 5 wt.%, Reaction temperature T = 343 K.

As can be seen from Figure 9, which was obtained after training in the neural network, the increase in the concentration of hydrogen peroxide in the mixture leads to a sharp decline in iodine value. At low concentrations of hydrogen peroxide in the mixture, the ionic number does not change monotonically, the dependence has a maximum.

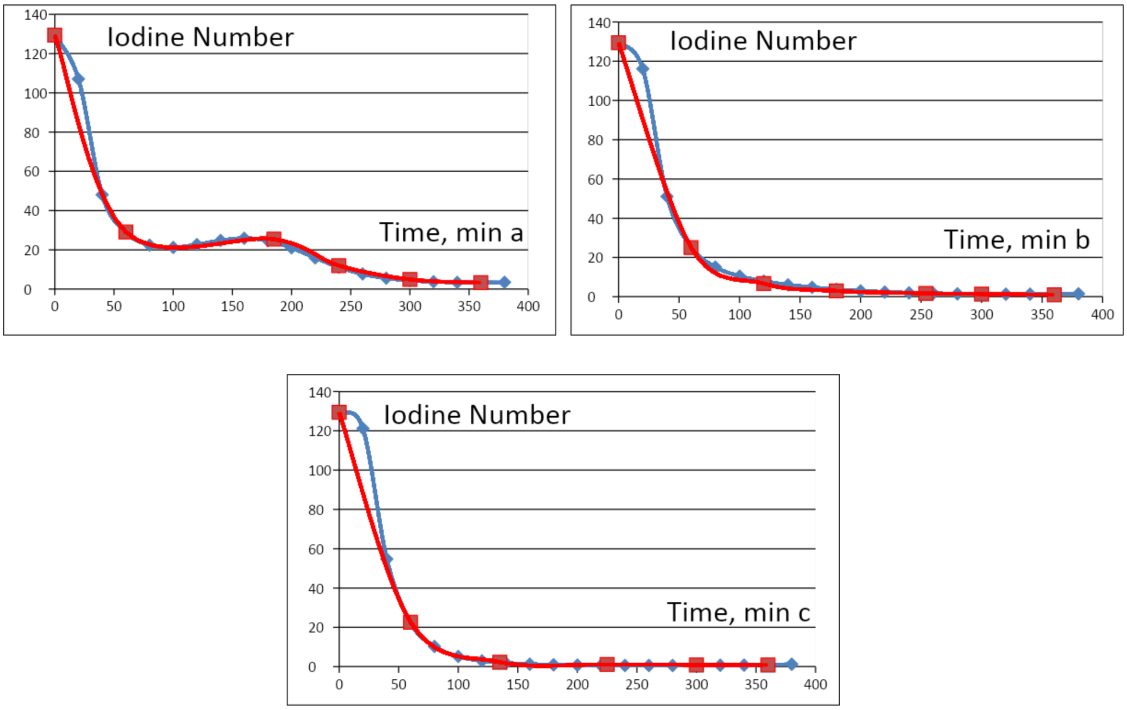

Figure 10: Comparison of the dependences of the iodine number on the concentration of hydrogen peroxide and the time of the epoxidation reaction of soybean oil. Calculations were performed by the interaction of a solution of soybean oil in toluene with the epoxidizing system H_2O_2/AA/catalyst. Concentration H_2O_2 = 38.59 wt.%, Catalyst concentration 5 wt.%, Reaction temperature T = 343 K. **a** - concentrations of AA in the mixture of 2.86 wt.%, **b** - 5.72 wt.%, **c** - 7.79 wt.%.

As can be seen from the data presented in Figure 10, the neural network repeats the experimental points and expands the range of points that assume the consumption of unsaturated bonds (reduction of iodine value).

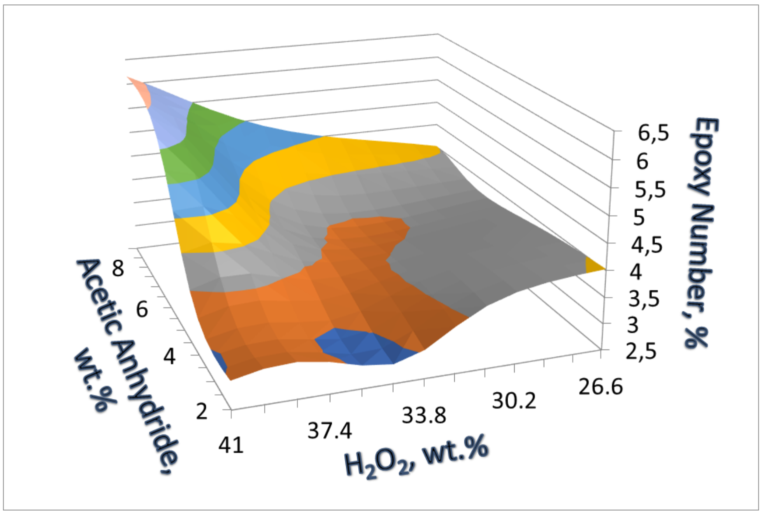

Figure 11: Dependence of Epoxy number on acetic anhydride concentration and hydrogen peroxide during soybean oil epoxidation reaction. Calculations were performed by reacting a solution of soybean oil in toluene with epoxidizing system H_2O_2/ AA / catalyst. Catalyst concentration 5 wt.% Mixture, reaction temperature T = 343 K. Reaction time 60 min.

The neural network, after training, operates with initial functions from many variables (in our case from 7), and gives the opportunity to see the projections of the calculated (learned) functions on the selected axes of parameters that interest us. For example, in Figure 11 shows the dependence of the Epoxy number after the epoxidation reaction of soybean oil on the concentration of acetic anhydride and hydrogen peroxide. The reaction time and catalyst concentration are taken as constants.

As can be seen from the figure, the simultaneous increase in the concentration of acetic anhydride and the concentration of hydrogen peroxide leads to an increase in the reaction rate. However, the local minimum of the Epoxy number is not at the point of minimum concentrations of acetic anhydride and hydrogen peroxide.

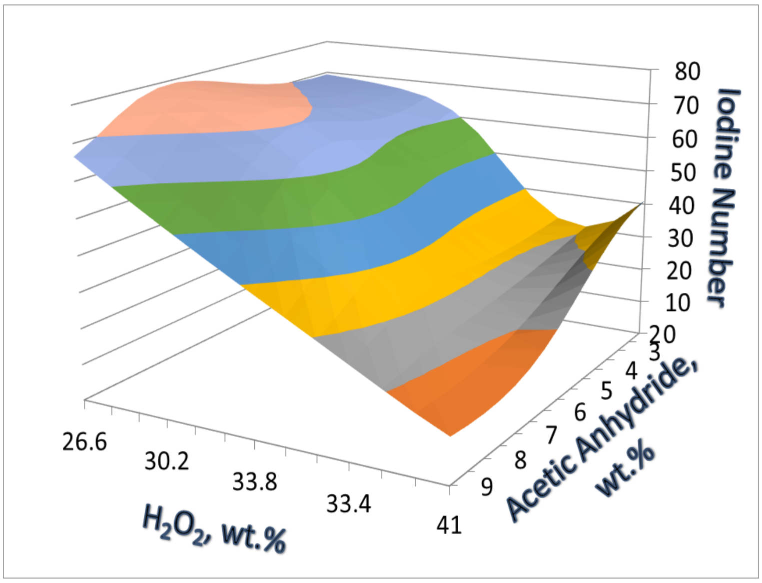

Figure 12: Dependence of Iodine number on acetic anhydride concentration and hydrogen peroxide during soybean oil epoxidation reaction. Calculations were performed by reacting a solution of soybean oil in toluene with epoxidizing system H_2O_2/ AA / catalyst. Catalyst concentration 5 wt.% Mixture, reaction temperature T = 343 K. Reaction time 60 minutes.

In Figure 12 we have similar dependences as in Figure 11, for the Iodine number. As can be seen from the figure, the maximum concentration (in the selected range) of the concentration of acetic anhydride and hydrogen peroxide leads to the formation of the minimum value of the iodine value. However, the slowest reaction does not occur at minimum concentrations of acetic anhydride and hydrogen peroxide.

5. Conclusions

In this paper, we presented a method for finding parameters of the epoxidation process of soybean oil (in this case, the dependences on the concentration of acetic anhydride and hydrogen peroxide, the amount of catalyst, and reaction time). The use of the neural network demonstrated the possibility of quantitative prediction of the epoxidation result (Epoxy and Iodine numbers) with a small sample of experimental data. The proposed approach makes it possible to obtain additional information about the course of the epoxidation reaction of soybean oil.

The optimal conditions for the process of epoxidation of oil by epoxidizing system acetic anhydride: hydrogen peroxide: catalyst KU-2x8, duration, temperature.

Although experimental studies were performed on soybean oil, the dependences obtained as a result of the work were used for other vegetable oils (castor, rapeseed, flaxseed, sunflower). Experiments conducted in these optimal conditions showed good results, especially for linseed (EN = 8.49%) and sunflower oils (EN = 6.39%), which confirms the adequacy of the results of the neural network.

6. Acknowledgments

This work has been supported by the Ministry of Education and Science of Ukraine: Grant of the Ministry of Education and Science of Ukraine for perspective development of a scientific direction "Mathematical sciences and natural sciences" at Taras Shevchenko National University of Kyiv.

PhD Orest Pyrig for significant contribution to chemical research, OJSC "Gallak" (Borislav) for the provided scientific laboratory, equipment and reagents.

7. References

[1] E, W., Yu, B. The “Deep Ritz Method: A Deep Learning-Based Numerical Algorithm for Solving Variational Problems”. Commun. Math. Stat. 6, (2018), pp,1-12. doi: 10.1007/s40304-018-0127-z.

[2] D. Llorente, M. Ballesteros, D. Cruz-Ortiz, I. Salgado & I. Chairez “Brain Computer Interface for Speech Synthesis Based on Multilayer Differential Neural Networks”, Cybernetics and Systems, 53:1, (2022) pp.126-140, doi: 10.1080/01969722.2021.2008685.

[3] G. Urban, S. Porhemmat, M, Stark B. Feeley, K. Okada, P. Baldi, “Classifying shoulder implants in X-ray images using deep learning”, Computational and Structural Biotechnology Journal, vol. 18, 2020, pp. 967-972, ISSN 2001-0370, doi: 10.1016/j.csbj.2020.04.005.

[4] T. Chaikivskyi, BB Sus, OS Bauzha, SP Zagorodnyuk, and V. Reutskyy, “Development of Neural Network for Cyclohexane Oxidation Data Processing,” in 2021 IEEE 3rd Ukraine Conference on Electrical and Computer Engineering (UKRCON), Lviv, Ukraine, Aug. 2021, pp. 10–14. doi: 10.1109 / UKRCON53503.2021.9575213.

[5] H. Li, Z. Zhang, and Z. Liu, “Application of Artificial Neural Networks for Catalysis: A Review,” Catalysts, vol. 7, no. 10, p. 306, Oct. 2017, doi: 10.3390/catal7100306.

[6] Sweafford Jr, Jerry, and Farbod Fahimi. "A neuralnetwork model-based control method for a class of discrete-time nonlinear systems." Mechatronic Systems and Control, Vol. 49, No. 2, 2021 doi: 10.2316/J.2021.201-0134.

[7] Lye, Kjetil O., Siddhartha Mishra, and Deep Ray. "Deep learning observables in computational fluid dynamics." Journal of Computational Physics 410 (2020): 109339. doi: 10.1016/j.jcp.2020.109339.

[8] Han, Jiequn, Arnulf Jentzen, and E. Weinan. "Solving high-dimensional partial differential equations using deep learning." Proceedings of the National Academy of Sciences 115.34 (2018): 8505-8510. doi: 10.1073/pnas.1718942115.

[9] Siddhartha Mishra, Roberto Molinaro. "Physics informed neural networks for simulating radiative transfer." Journal of Quantitative Spectroscopy and Radiative Transfer 270 (2021): 107705.ISSN 0022-4073, doi: 10.1016/j.jqsrt.2021.107705.

[10] T. Chaikivskyi, B. Sus, O. Bauzha, and S. Zagorodnyuk, "Multicomponent analyzer of volatile compounds characterization based on artificial neural networks," in CEUR Workshop Proceedings, 2020, vol. 2608, pp. 819–831. [Online]. http://ceur-ws.org/Vol-2608/paper61.pdf

[11] T Kusumoto, K Mori. "Prediction of ultrashort pulse laser ablation processing using machine learning." Laser Applications in Microelectronic and Optoelectronic Manufacturing (LAMOM) XXVI. Vol. 11673. International Society for Optics and Photonics, 2021. doi: 10.1117/12.2577447

[12] K Shukla, PC Di Leoni, J Blackshire et al. "Physics-informed neural network for ultrasound nondestructive quantification of surface breaking cracks." Journal of Nondestructive Evaluation 39.3 (2020): pp.1-20. doi:10.1007/s10921-020-00705-1.

[13] Hughes TB, Miller GP, Swamidass SJ. "Modeling Epoxidation of Drug-like Molecules with a Deep Machine Learning Network." ACS Cent Sci. 2015; 1 (4): pp.168-180. doi: 10.1021 / acscentsci.5b00131.

[14] Montero de Espinosa, L. Plant oils: The perfect renewable resource for polymer science?! / L. Montero de Espinosa, MAR Meier // European Polymer Journal. - 2011. - Vol. 47, Issue 5. - pp. 837–852. doi: 10.1016 / j.eurpolymj.2010.11.020.

[15] Stemmelen, M. A fully biobased epoxy resin from vegetable oils: From the synthesis the precursors by thiol-ene reaction to the study of the final material / M. Stemmelen, F. Pessel, V. Lapinte, S. Caillol, J.-P. Habas, J.-J. Robin // Journal of Polymer Science Part A: Polymer Chemistry. - 2011. - Vol. 49, Issue 11. - pp. 2434–2444. doi: 10.1002 / half.24674.

[16] Tsujimoto, T. Green Nanocomposites from Renewable Plant Oils and Polyhedral Oligomeric Silsesquioxanes / T. Tsujimoto, H. Uyama, S. Kobayashi, H. Oikawa, M. Yamahiro // Metals. - 2015. - Vol. 5, Issue 3. - pp. 1136–1147. doi: 10.3390 / met5031136.

[17] Pikh, Z., Nebesnyi, R., Ivasiv, V., Pich, A., Vynnytska, S. "Oxidation of unsaturated aldehydes by organic peracids". Chemistry and Chemical Technologythis link is disabled, 2016, 10(4), pp. 401–411. doi: 10.23939/chcht10.04.401.

[18] Parker, R.-E.; Isaacs, N. "Mechanisms of epoxide reactions". Chem. Rev. 1959, 59, 737−799.

[19] Patent UA83020 Process for the preparation of epoxidated vegetable oil // Hrynchuk Y.M., Starchevskyi V.L., Nykypanchuk M.V. 27.08.2013. https://uapatents.com/4-83020-sposib-oderzhannya-epoksidovano-roslinno-oli.html

[20] Nykulyshyn, I., Pikh, Z., Shevchuk, L., & Melnyk, S. "Examining the epoxidation process of soybean oil by peracetic acid". Eastern-European Journal of Enterprise Technologies, (2017), vol. 3/6 (87), pp.21–28. doi: 10.15587/1729-4061.2017.99787.