

Data Processing of Ethylbenzene Oxidation Process using the Artificial Neural Networks

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Abstract

A target intelligent system for analysing data of liquid-phase oxidation process in an industrial method of obtaining valuable oxygen-containing compounds has been developed. A multilayer artificial neural network is the main part of this system for digital data processing. These neural network Clear simulations on the effect of the catalytic system and catalytic additives used in the process of ethylbenzene oxidation on the concentrations and selectivity for hydroperoxide of ethylbenzene, acetophenone, methyl phenyl carbinole, were obtained and analyzed for different catalysts by the means of an artificial. The neural network, after training, accurately reproduces the studied data from a sample of experiments and predicts the result of the study in extended time ranges and concentrations of catalytic impurities. The formed predictions and estimations allow experimenters to select the most promising direction when they wanna determine the concentration of active catalytic substances.

Keywords ¹

Ethylbenzene Oxidation, Neural Networks, Catalyst, Acetophenone

1. Introduction

Artificial neural networks are widely applied in various technological and scientific fields particularly in the chemistry. Approximately 80% of chemical and petrochemical productions in the world are associated with catalytic processes. This also applies to the processes of liquid-phase oxidation of hydrocarbons.

In the modern industry the homogeneous catalytic liquid-phase oxidation of ethylbenzene (EB) to acetophenone (AP) and hydroperoxide of ethylbenzene (HPEB), which are used as starting materials for styrene and a large number of other products of organic synthesis, is widely used.

The chemical processes of liquid-phase oxidation of hydrocarbons by molecular oxygen have a relatively low selectivity for the target products and a low conversion. With a further increase in the conversion of hydrocarbons, there is a sharp decrease in selectivity due to the accumulation of by-products, primarily acids, and esters, in the oxidate. A low conversion rate leads to appearing additional significant energy costs for the recycling of unreacted hydrocarbons. All of the mentioned above demonstrates the urgency of creating new efficient catalytic systems that can be used to improve the selectivity and increase the conversion of the original hydrocarbon.

The important ways to improve the existing homogeneous catalysts is the use of modifiers of different nature, which improves the technical and economic performance of liquid-phase oxidation

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processes. At the same time the existing experimental knowledge database is not enough to determine the mechanism of action of these additives and predict their impact on oxidation reactions.

Therefore, the technical task of creating new highly selective catalytic systems based on salts of metals of variable valence (MVV), modified with various compounds for the oxidation of ethylbenzene and other aromatic compounds remains relevant.

The scientific novelty of the study is to significantly increase the efficiency of determining the effect of additives on the ratio of oxidation products of ethylbenzene in the presence of a binary catalytic system: industrial catalyst cobalt naphthenate - salts of metals of variable valence.

2. Related Works

Artificial neural networks are also used in the following technological and scientific fields. Among the technological and applied fields: energy generation and distribution [1], engineering [2, 3], agriculture [4], environmental protection [5, 6]. In the oil industry [7] and financial markets [8, 9], models for forecasting are often developed and implemented on the basis of neural networks. This approach facilitates the control of production as a whole. Artificial intelligence (AI) is used to improve the management of technical systems, which involves improving parameters such as quality, safety, efficiency and logistics in production [10]. AI is also used in many natural areas, particularly biology [11, 12], physics [13], chemistry: catalyst [14, 15], oxidation [16, 17, 18], molecular dynamics simulations [19].

3. Proposed mechanism

Wide use of the binary catalytic oxidation systems of ethylbenzene is an effective way to increase the speed and selectivity of the process. Previous studies show that use of different organic additives can have significant impact on the processes of oxidation of aromatic and "aromatic-like" (e.g. cyclohexane) compounds. In other scientific works various organic salts of different metals of variable valence [20, 21] as components of the catalyst system were used and various compounds were used as catalytic additives to the main catalyst (salts of MVV).

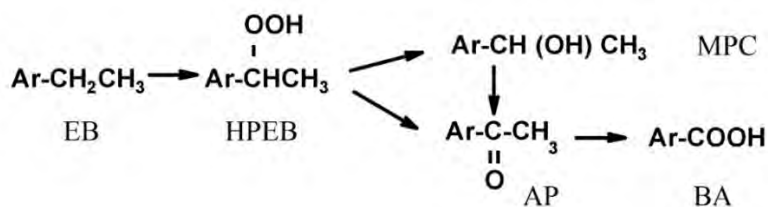


Figure 1: Chemical scheme of liquid-phase oxidation of ethylbenzene: EB – ethylbenzene, HPEB - hydroperoxide of ethylbenzene, MPC - methyl phenyl carbinole, AP – acetophenone, BA - benzoic acid

The use of binary catalytic oxidation systems of ethylbenzene is an effective way to increase the speed and selectivity of the process. Previous studies show that use of different organic additives can have significant impact on the processes of oxidation of aromatic and "aromatic-like" (e.g. cyclohexane) compounds. In works as components of the catalyst system were used various organic salts of different metals of variable valence [20-22] and various compounds used as catalytic additives to the main catalyst (salts of MVV) [20].

Studies of the effect of the use of individual surfactants on the oxidation process of ethylbenzene have shown that they to a greater or lesser extent affect the oxidation process. Thus, the next step in the research should be to study the effects of binary catalyst systems.

Figure 1 shows the chemical scheme of liquid-phase oxidation of ethylbenzene. In the presence of salts of MVV direct oxidation of ethylbenzene to secondary products (acetophenone (AP) and methyl phenyl carbinole (MPC)) is possible.

The concentration of benzoic acid (BA) formed as a result of oxidation of EB in these conditions is insignificant, and is omitted in the work.

Table 1

Oxidation of ethylbenzene in the presence of binary catalyst systems (MVV-SA). P = 0.4-0.45 MPa, T = 403 K. MVV salt - cobalt naphthenate

Catalyst	time, min	C _(HPEB) mol/l	C _(AP) mol/l	C _(MPC) mol/l	Conversion of EB. %
NC	10	0,006	0,011	0,003	0,24
	60	0,028	0,03	0,011	0,85
	120	0,048	0,067	0,016	1,62
	180	0,068	0,089	0,018	2,15
	210	0,068	0,113	0,021	2,48
	10	0,006	0,011	0,003	0,24
NC+PEG	10	0,012	0,012	0,001	0,3
	60	0,055	0,036	0,0013	1,13
	120	0,098	0,051	0,003	1,87
	180	0,124	0,08	0,005	2,58
	210	0,165	0,104	0,013	3,46
	240	0,157	0,227	0,051	5,35
NC+Ch	10	0,012	0,013	0,004	0,35
	60	0,042	0,032	0,005	0,98
	120	0,064	0,159	0,006	2,80
	180	0,069	0,207	0,006	3,46
	210	0,09	0,219	0,006	3,86
	240	0,087	0,259	0,006	4,31
NC+CEE	10	traces	0,013	0,004	0,19
	60	traces	0,022	0,006	0,33
	120	traces	0,033	0,008	0,49
	180	traces	0,039	0,009	0,59
	210	traces	0,04	0,010	0,60
	240	traces	0,047	0,012	0,72

Regularities of liquid-phase oxidation of ethylbenzene in the presence of catalytic systems [MVV salt - surfactant (SA)] were studied at a temperature of 403K and a pressure of 0.4 – 0.45 MPa. The concentration of MVV salt was $1.0 \cdot 10^{-3}$ mol/l. The mass ratio of salt MVV/SA was 1/1. An industrial catalyst, cobalt naphthenate (NC), was used as an MVV salt.

The results obtained by oxidation of ethylbenzene in the presence of catalytic systems [NC-SA] were compared with those achieved by oxidation of ethylbenzene in the presence of individual NC under the same conditions.

The content of HPEB was determined titrimetrically, the content of AP and MPC - by gas-liquid chromatography.

The data obtained during the experiments are presented in table 1. As surfactants, the following compounds were taken:

- Polyethylene glycol (PEG)
- Chromoxane (Ch)
- Cyanethyl ether (CEE)

4. Neural network model

The input layer of the neural network consists of 8 input neurons. The values of the input signals are normalized to 1. The neural network has three hidden layers, consisting of 20 neurons. The output

layer has 4 neurons. The structure of the neuron network is presented in Figure 2. This artificial network makes it possible to sharpen the required number of neurons in the layers.

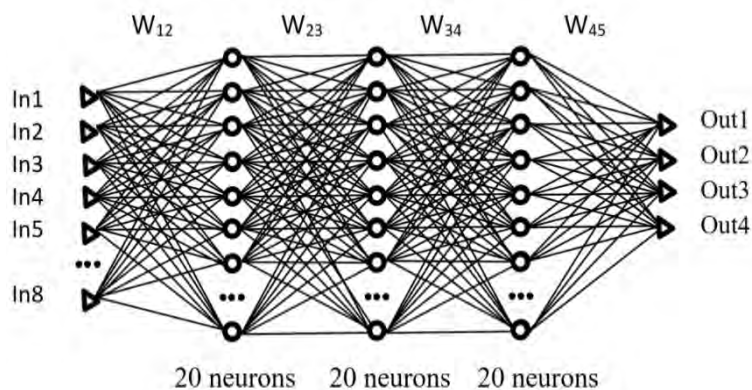


Figure 2: Multilayer artificial feedforward neural network

The basis of neural network training is training, which is based on the repetition of training samples that have the expected values of the output data of the neural network for the corresponding values of the input data.

The mechanism of training is to regulate the weight/priority of neurons. To assess the performance of neural networks, it is important to pay attention to criteria such as learning outcomes and effectiveness.

The work uses a five-layer fully connected neural network of direct propagation, which was studied on the basis of experimental data obtained during the oxidation of cyclohexane. The input parameters used by the neural network are taken 8. The values of the input parameters are normalized to 1. The output layer of the neural network has 4 neurons that characterize the concentrations of substances formed by oxidation. This network has three hidden layers of 20 neurons each

The neural network is trained on the basis of 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.

5. Results and discussion

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

Input parameters:

1. The initial concentration of ethylbenzene hydroperoxide
2. The initial concentration of acetophenone
3. The initial concentration of MPC
4. The initial concentration of ethylbenzene
5. Normalized concentration of additive (polyethylene glycol)
6. Normalized concentration of additive (chromoxane)
7. Normalized concentration of additive (cyanethyl ether)
8. Normalized reaction time,

During the reaction, the four aim substances (HPEB, AP, MPC and BA) can be formed from EB not directly but as a result of the formation of intermediates (for example, MPC). Therefore, the initial concentration of selected substances for neural network training is necessary.

Binary cobalt naphthenate catalyst is used as the main catalyst. The ratio of catalyst components: [cobalt naphthenate] / [additive] = 1/1. Reaction time (sampling of experimental data did not exceed 250 minutes, so the rationing was currently underway).

Output parameters:

1. The final concentration of HPEB
2. The final concentration of AP
3. The final concentration of MPC

4. The final concentration of EB.

Intermediate data were also used to create the training sample. For example, the input data is the result of the experiment for 120 minutes, and as initial values the result of the experiment at a later time.

After training, the network provides the rate of reactions, which is presented in Figure 1.

In Figures 3-6 shows the dependences of the concentration of substances formed during the oxidation reaction of EB. Only NC was used as a catalyst. Dependencies are clearly not linear.

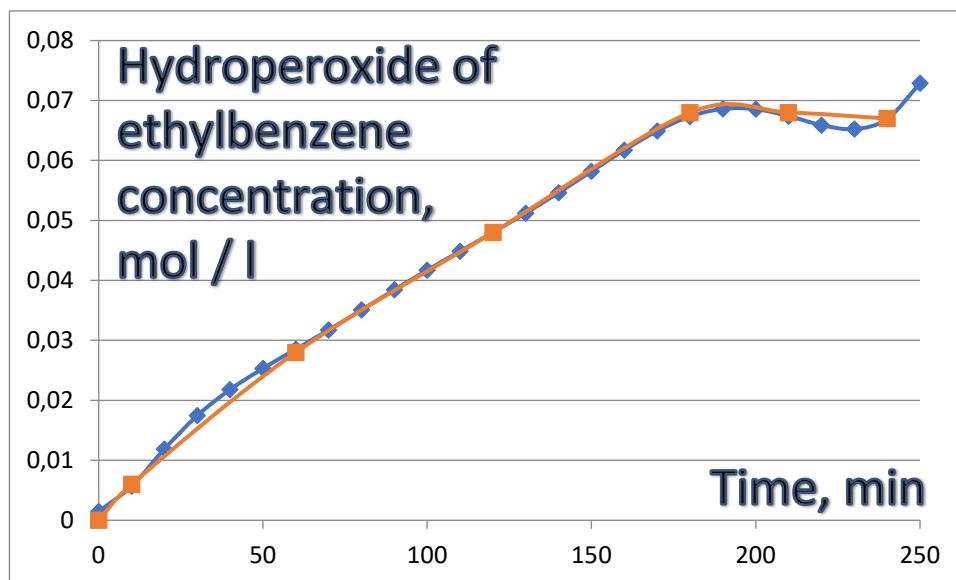


Figure 3: Dependence of hydroperoxide of ethylbenzene concentration from reaction time

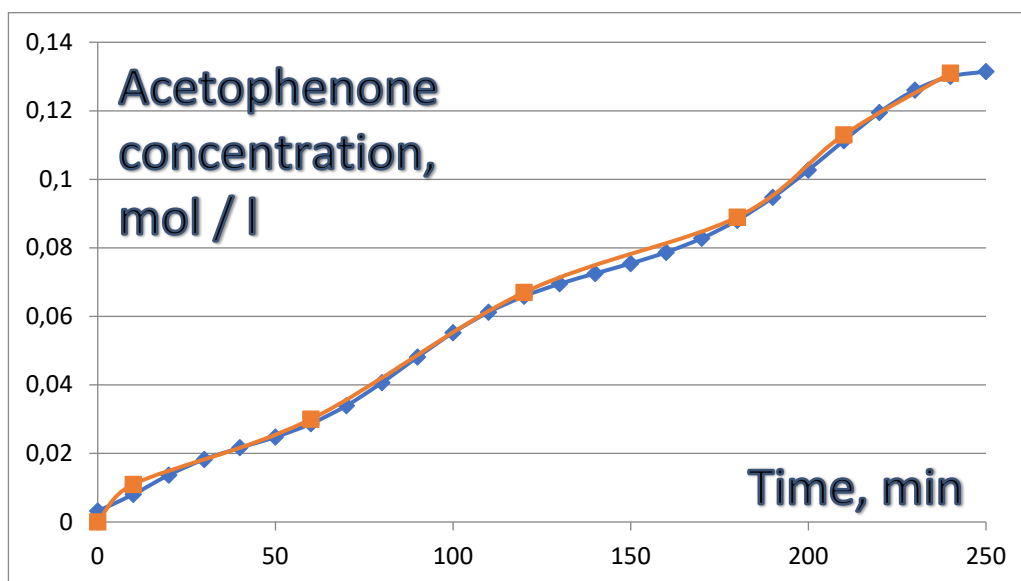


Figure 4: Dependence of acetophenone concentration from reaction time

On Figures 3-6 red points mark experimental data, blue points are predicted by the neural network, after training.

As can be seen from Figures 3-6. After training, the neural network reproduces the results of the experiment and provides intermediate results.

As can be seen from Figures 3-5. The effect of NC is associated primarily with the formation of an active catalytic complex [NC - substrate]. The presence of such complex directs the oxidation process of ethylbenzene along a less energy-efficient reaction route - oxidation into HPEB. The nature of the kinetic curve of HPEB accumulation in the reaction medium can be explained by the fact that after about 160-180 min the experiment reaches the maximum possible, for these conditions, HPEB

concentration and then along with the process of direct oxidation of ethylbenzene to AP starts oxidation of HPEB to AP. This assumption is also confirmed by a sharp increase in the rate of accumulation of AP after 160-180 min of the experiment.

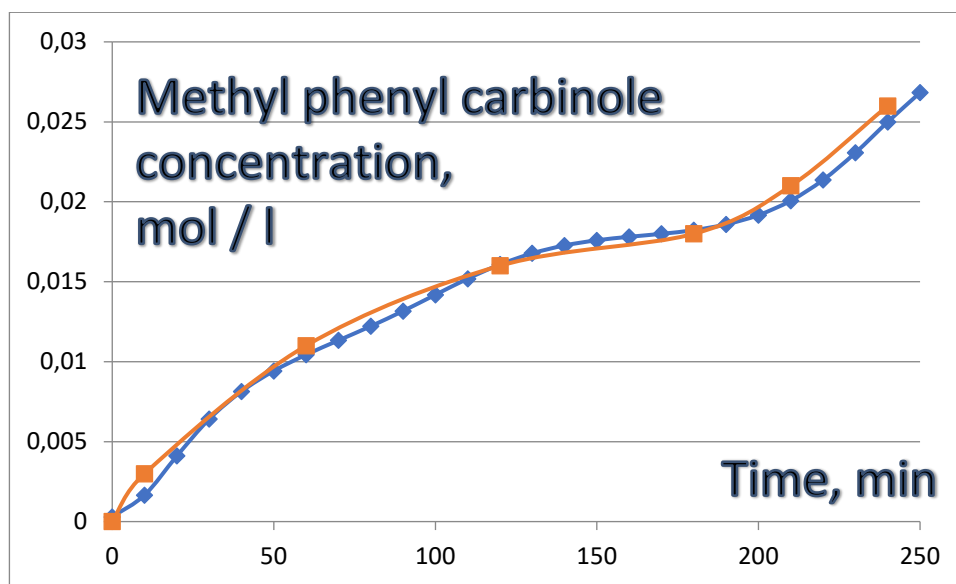


Figure 5: Dependence of methyl phenyl carbinole concentration from reaction time

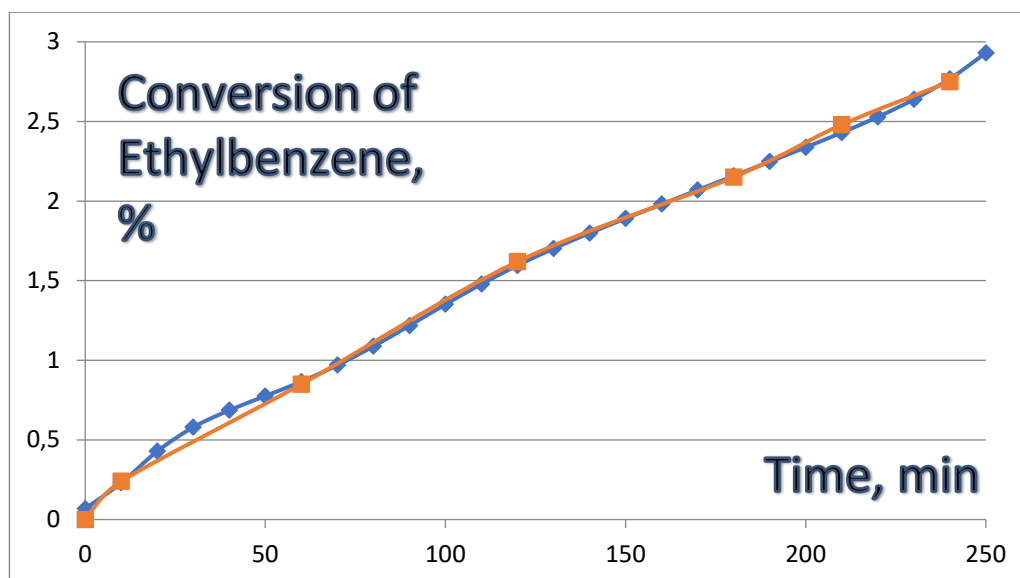


Figure 6: Dependence of ethylbenzene conversion from reaction time

On Figures 7-10 are presented the dependences of the concentration of substances formed during oxidation reaction of EB. As a catalyst we used NC + PEG system. are presented the dependences of the concentration of substances formed during oxidation reaction of EB. As a catalyst we used NC + PEG system.

On Figures 7-10 red points mark experimental data, blue points are predicted by the neural network, after training.

The data presented in Figures 6-9 show that the use of a binary catalytic system NC - PEG leads to an increase in the amount of formed HPEB in the reaction medium.

Based on the obtained data, it was suggested that the use of PEG as a catalytic additive leads to the formation of a new active catalytic complex [NC - PEG - substrate], the presence of which in the reaction medium facilitates the oxidation reaction.

As in the case of the use of individual NC as a catalyst, the maximum possible concentration of HPEB, for these conditions, in the reaction medium is observed, followed by a sharp increase in the rate of accumulation of secondary oxidation products (AP and MPC). However, it should be noted that this concentration is higher (compared to the use of individual NC) and is achieved later (200-210 minutes of the experiment).

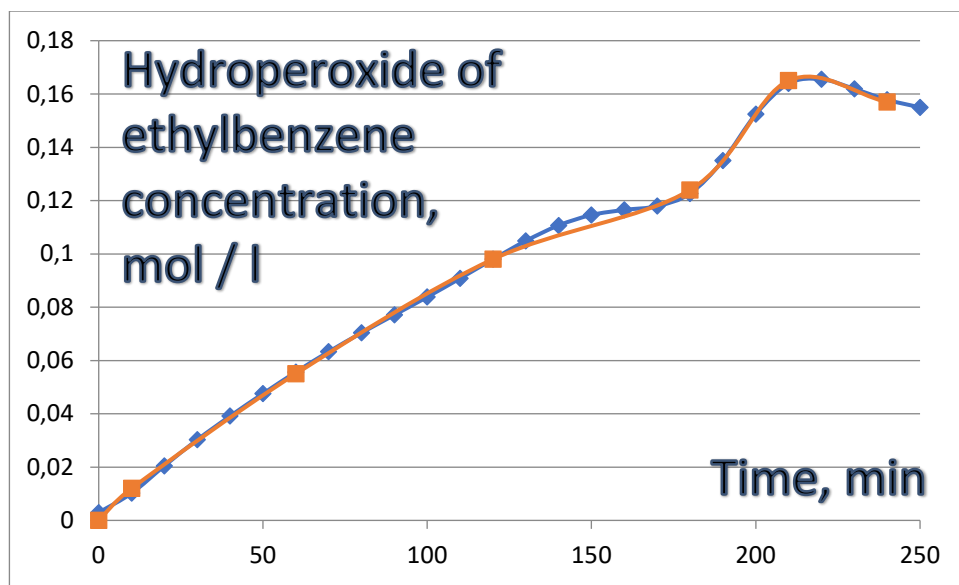


Figure 7: Dependence of hydroperoxide of ethylbenzene concentration from reaction time

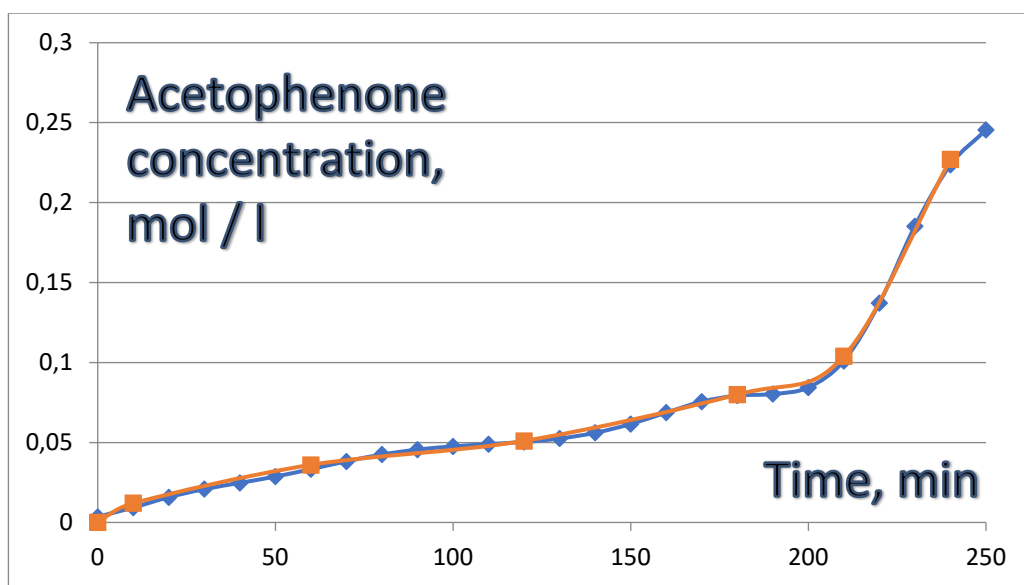


Figure 8: Dependence of acetophenone concentration from reaction time

On Figures 11-14 are presented the dependences of the concentration of substances formed during oxidation reaction of EB. As a catalyst we used a system NC + Ch.

Figure 12 shows that the experimental points are poorly correlated with the data issued by the neural network. This effect may be explained due to the fact that the amount of MPC formed as a result of the reaction is very little, and it has little to non-effect on the rest of the reaction. As a result, when searching for the local minimum of error, the neural network did not establish clear effects of the formation of this substance as a result of the reaction.

On Figures 11-14 red points mark experimental data, blue points are predicted by the neural network, after training.

The data presented in Figures 11 - 14 show that the effect of the catalytic system, with the presence chromoxane as a catalytic additive, is associated with the existence of two influencing factors. The first is the formation of a catalytically active complex [NC - Ch - substrate], the presence of which in the reaction medium leads to an increase in the amount of formed HPEB (compared with the use of individual NC as a catalyst), and the second is related to the mechanism of chromoxane influence.

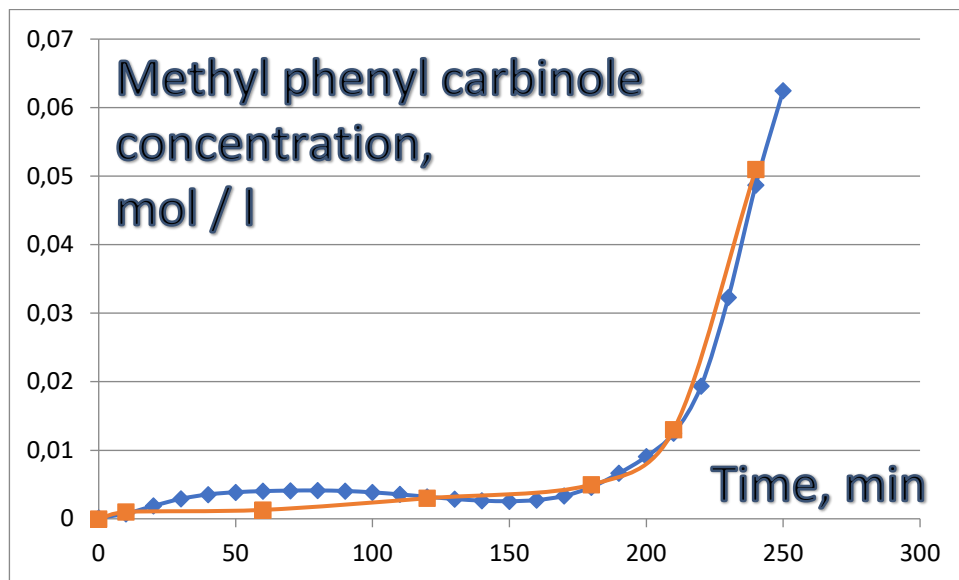


Figure 9: Dependence of methyl phenyl carbinole concentration from reaction time

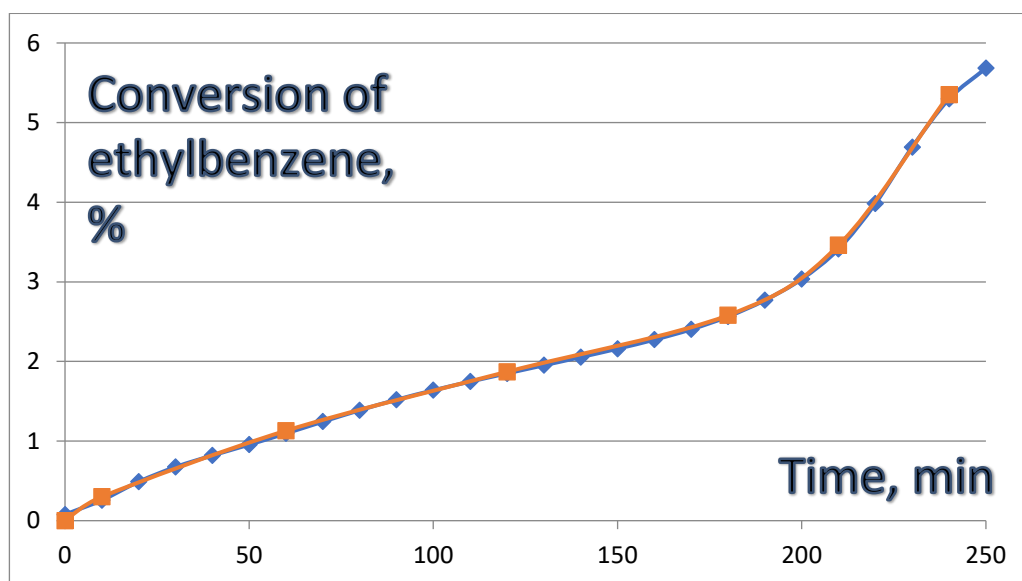


Figure 10: Dependence of ethylbenzene conversion from reaction time

This effect of the use of Ch leads to an increase in the total amount of AP formed during the experiment. On Figures 15 -17 are presented the dependences of the concentration of substances formed during the oxidation reaction of EB. As a catalyst we used NC + CEE system.

During the EB oxidation reaction very small values of the substance HPEB are recorded in the samples (within the error) Table 1., so some minimum value of this substance was chosen for training. In practice, this means that HPEB with such catalysts is almost immediately converted into AP or MPC.

This leads to the fact that the neural network does not notice a significant impact of various factors on the concentration of the formed HPEB. This input parameter is redundant, and it would be more

appropriate to train the neural network without this parameter. The fact that the neural network tries to compare the amount of HPEB with the formation of other substances leads to distortion of the expected results of the neural network. This is clearly seen in Fig. 15-17.

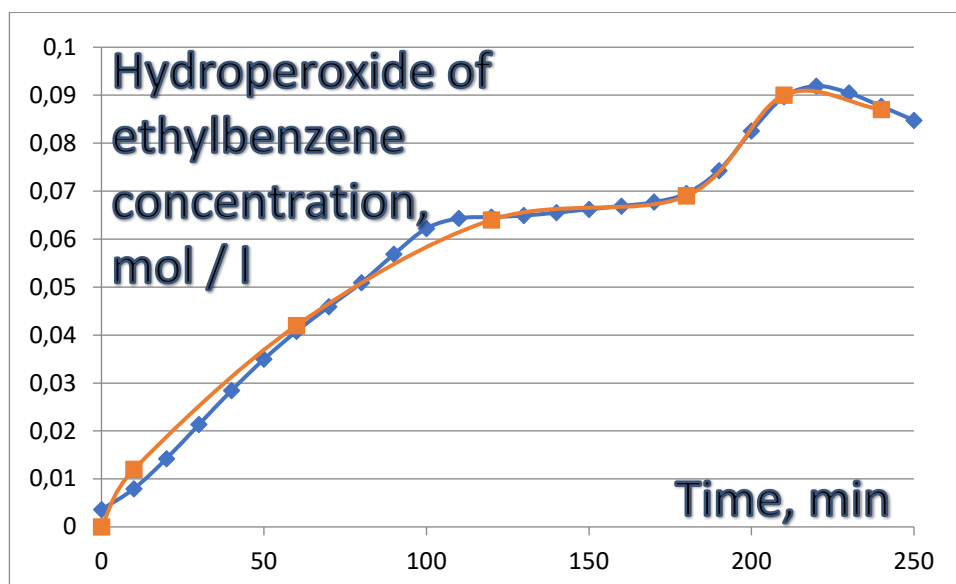


Figure 11: Dependence of hydroperoxide of ethylbenzene concentration from reaction time

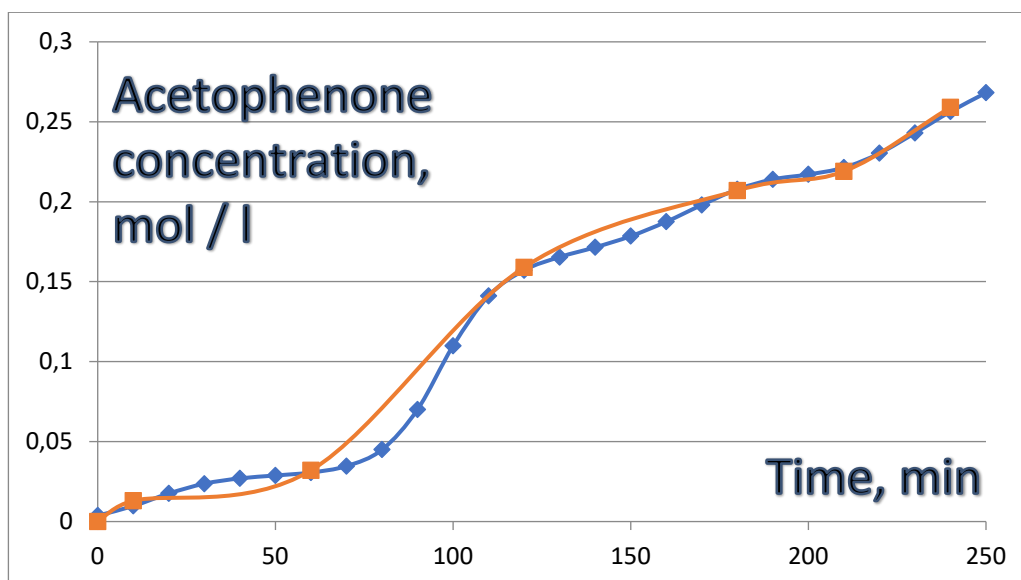


Figure 12: Dependence of acetophenone concentration from reaction time

On Figures 15-18 red points means experimental data, blue points means predicted by the neural network, after training process.

During the experiment process, there was an almost complete absence of HPEB in reaction products, along with a significant reduction the amount of formed AP and MPC (compared with the use of individual NC as a catalyst for oxidation).

This behavior of CEE can be explained by the fact that CEE in its structure contains a triple bond and by its nature is an inhibitor of accession reactions. Due to the formation of the [NC - CEE] complex, this complex deactivates of the main catalyst, leading to a decrease in all kinetic process parameters. When experimenter trained the neural network trained in a limited set of experimental data he can expand the range of data that he can deal with.

However, it should be noted that the data provided by the neural network do not give 100% accuracy.

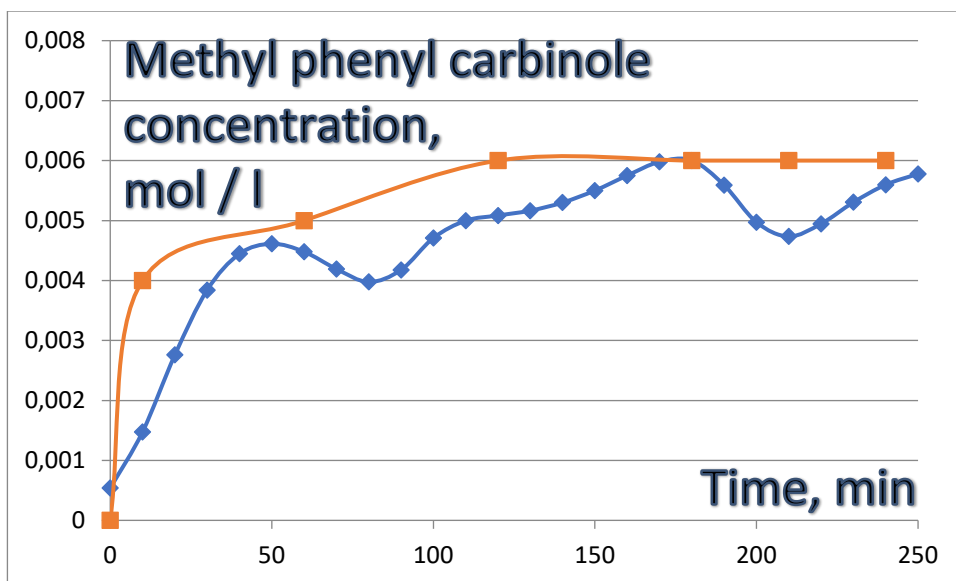


Figure 13: Dependence of methyl phenyl carbinole concentration from reaction time

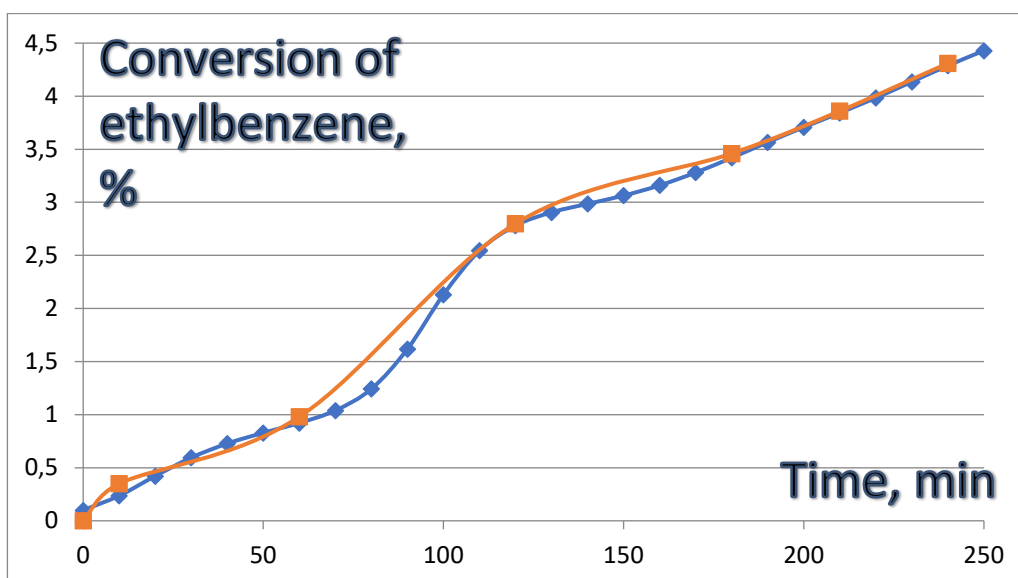


Figure 14: Dependence of ethylbenzene conversion from reaction time

6. Conclusions

Studies results are demonstrates a significant effect of surfactant additives on the oxidation of ethylbenzene. The quantitative and qualitative effect parameters depends on the additives properties and varies widely from accelerating the oxidation process to almost complete deactivation of the catalyst. The use of artificial neural network allows identify significant factors influencing additives, also allows exclude insignificant ones, which creates new opportunities and prospects for planning future research and more qualified use of early obtained results in existing technological processes.

Forecast data formed by neural networks allow us to identify and clarify ways to increase the catalysis process efficiency, which makes it possible to carry out the ethylbenzene oxidation at higher rates of conversion of raw materials, or to increase the yield of the desired substance as a result of chemical reaction. The approach proposed in article can provides additional data for rapid preliminary analysis of the identification of components of the catalysis process and also can reduces the cost factors for raw materials and energy. It is shown that in data forecasting very important to take into

account only important features of the value of the exact dependence of the predicted variable and then the time and resources needed for preparation of time-consuming experiments is reduces.

The use of neural networks should be used to expand the range of values of the required values with a limited set of experimental data. All subsequent experiments can increase the range of data used for training a neural network, which, in turn, will improve the picture of the oxidation of ethylbenzene.

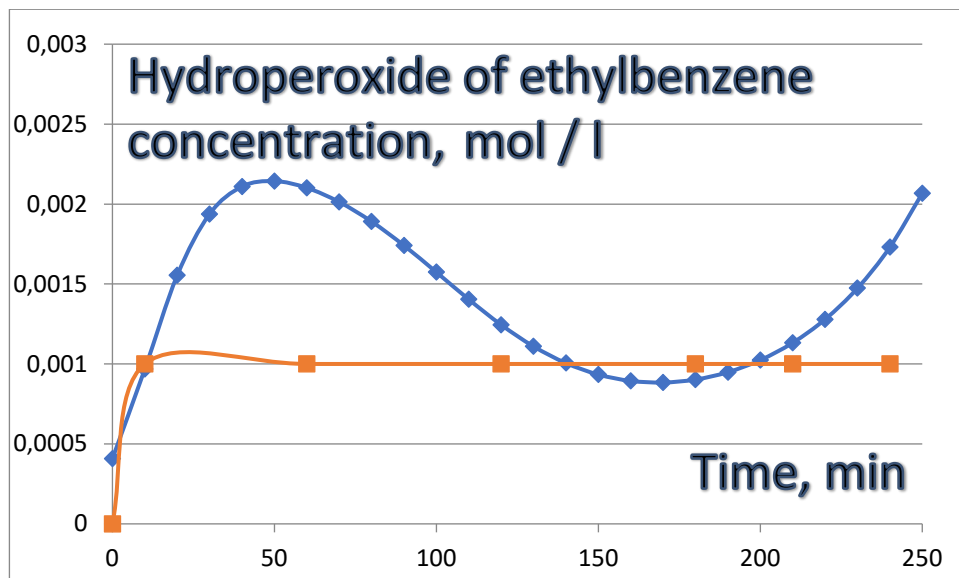


Figure 15: Dependence of hydroperoxide of ethylbenzene concentration from reaction time

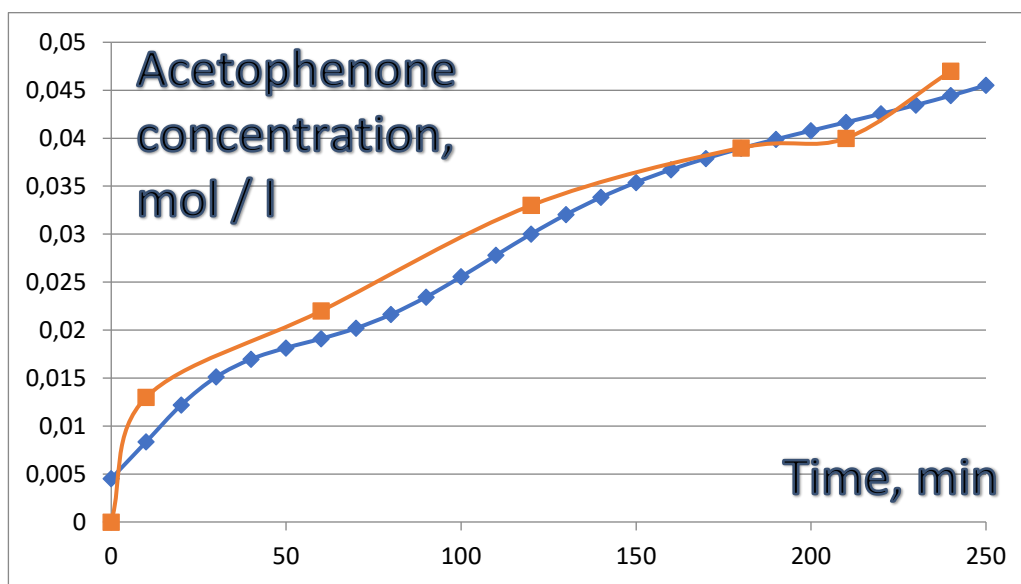


Figure 16: Dependence of acetophenone concentration from reaction time

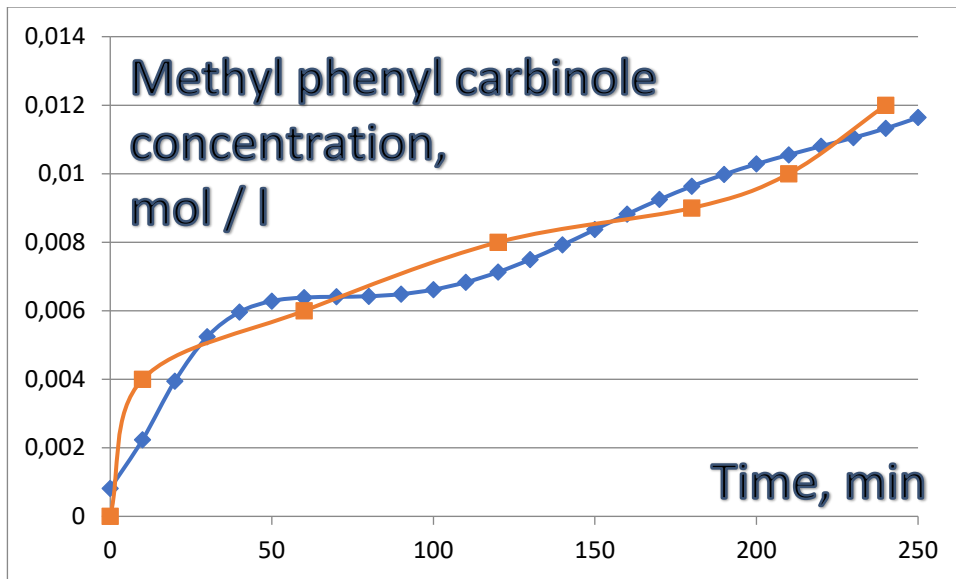


Figure 17: Dependence of methyl phenyl carbinole concentration from reaction time

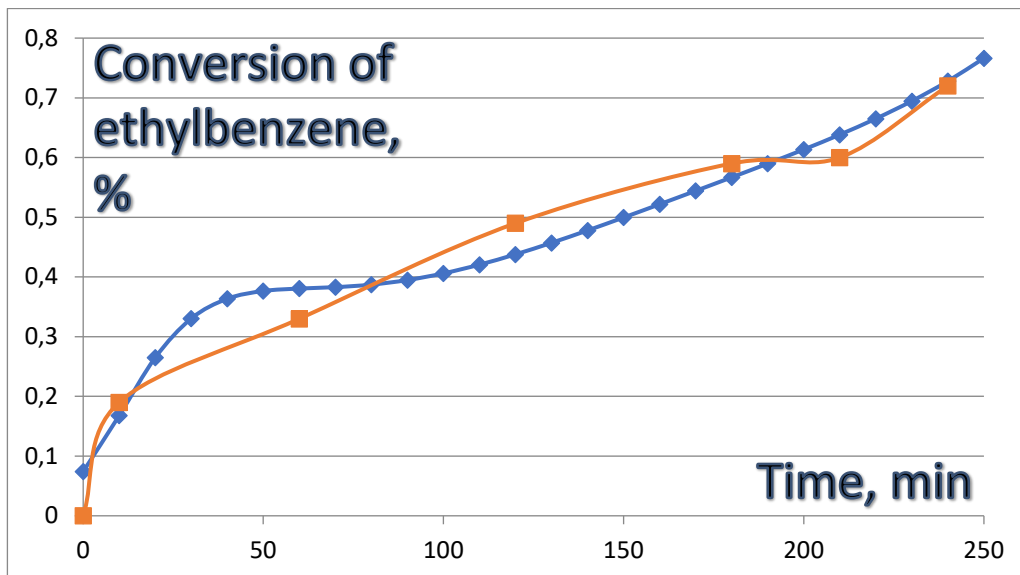


Figure 18: Dependence of ethylbenzene conversion from reaction time

7. References

- [1] Z. Liu, H. Li, X. Tang, X. Zhang, F. Lin, and K. Cheng, "Extreme learning machine: a new alternative for measuring heat collection rate and heat loss coefficient of water-in-glass evacuated tube solar water heaters," SpringerPlus, vol. 5, no. 1, p. 626, Dec. 2016, doi: 10.1186/s40064-016-2242-1.
- [2] Alsulaili Abdelrahman, and Refaie Abdelrahman "Artificial neural network modeling approach for the prediction of five-day biological oxygen demand and wastewater treatment plant performance" Water Supply, Vol 21, Issue 5, Pages 1861-1877. DOI 10.2166/ws.2020.199
- [3] Chaikovskiy T, Sus' B, Bauzha O and Zagorodnyuk S "Multicomponent analyzer of volatile compounds characterization based on artificial neural networks," CMIS-2020 2608 pp 819-831. URL: <http://ceur-ws.org/Vol-2608/paper61.pdf>
- [4] S. Haider et al., "LSTM Neural Network Based Forecasting Model for Wheat Production in Pakistan," Agronomy, vol. 9, no. 2, p. 72, Feb. 2019, doi: 10.3390/agronomy9020072.

- [5] Havránková E., Peña-Méndez E., Csöllei J., and Havel, J. Prediction of biological activity of compounds containing a 1,3,5-triazinyl sulfonamide scaffold by artificial neural networks using simple molecular descriptors. *Bioorganic Chemistry*, Vol. 107, February 2021, Article number 104565, doi: 10.1016/j.bioorg.2020.104565
- [6] Gopi Kiran M., Das Rajab, Behera Shishir Kumar, Pakshirajan Kannana and Das Gopal Modelling a rotating biological contactor treating heavy metal contaminated wastewater using artificial neural network. *Water Supply*, Vol. 21, Issue 5, Pages 1895-1912 August 2021, doi: 10.2166/ws.2020.304.
- [7] Ahmed, Ali, Elkhatny, and Abdulraheem, "New Artificial Neural Networks Model for Predicting Rate of Penetration in Deep Shale Formation," *Sustainability*, vol. 11, no. 22, p. 6527, Nov. 2019, doi: 10.3390/su11226527.
- [8] M. Tkáč and R. Verner, "Artificial neural networks in business: Two decades of research," *Applied Soft Computing*, vol. 38, pp. 788–804, Jan. 2016, doi: 10.1016/j.asoc.2015.09.040.
- [9] X. Zhong and D. Enke, "Predicting the daily return direction of the stock market using hybrid machine learning algorithms," *Financ Innov*, vol. 5, no. 1, p. 24, Dec. 2019, doi: 10.1186/s40854-019-0138-0.
- [10] A. Rácz-Szabó, T. Ruppert, L. Bántay, A. Löcklin, L. Jakab, and J. Abonyi, "Real-Time Locating System in Production Management," *Sensors*, vol. 20, no. 23, p. 6766, Nov. 2020, doi: 10.3390/s20236766.
- [11] F. Chen, H. Li, Z. Xu, S. Hou, and D. Yang, "User-friendly optimization approach of fed-batch fermentation conditions for the production of iturin A using artificial neural networks and support vector machine," *Electronic Journal of Biotechnology*, vol. 18, no. 4, pp. 273–280, Jul. 2015, doi: 10.1016/j.ejbt.2015.05.001.
- [12] M. Haesemeyer, A. F. Schier, and F. Engert, "Convergent Temperature Representations in Artificial and Biological Neural Networks," *Neuron*, vol. 103, no. 6, pp. 1123-1134.e6, Sep. 2019, doi: 10.1016/j.neuron.2019.07.003.
- [13] Y.-F. Shen, R. Pokharel, T. J. Nizolek, A. Kumar, and T. Lookman, "Convolutional neural network-based method for real-time orientation indexing of measured electron backscatter diffraction patterns," *Acta Materialia*, vol. 170, pp. 118–131, May 2019, doi: 10.1016/j.actamat.2019.03.026.
- [14] 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.
- [15] Q. Zhao, Y. Xu, J. Greeley, and B. Savoie, "Deep Reaction Network Exploration at a Heterogeneous Catalytic Interface," *Chemistry*, preprint, Nov. 2021. doi: 10.26434/chemrxiv-2021-8d0gn.
- [16] T. Chaikivskyy, B. B. Sus, O. S. Bauzha, S. P. 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.
- [17] J.R. Boes, J.R. Kitchin, "Neural network predictions of oxygen interactions on a dynamic Pd surface," in Jan. 2017 *Molecular Simulation* 43(5-6):1-9 doi:10.1080/08927022.2016.1274984.
- [18] T. Chaikivskyy, V. Maliarenko, B. Sus, O. Bauzha, S. Zagorodnyuk and V. Reutskyy, "Development of Artificial Neural Networks for Cyclohexane Oxidation Data Analysis," 2021 IEEE 16th International Conference on Computer Sciences and Information Technologies (CSIT), 2021, pp. 25-28, doi: 10.1109/CSIT52700.2021.9648746.
- [19] Suresh Kondati Natarajan, Jörg Behler, "Neural network molecular dynamics simulations of solid-liquid interfaces: Water at low-index copper surfaces," in Oct. 2016 *Physical Chemistry Chemical Physics* 18(41), doi:10.1039/c6cp05711j.
- [20] V. Bernales, M. A. Ortuño, D. G. Truhlar, C. J. Cramer, and L. Gagliardi, "Computational Design of Functionalized Metal–Organic Framework Nodes for Catalysis," *ACS Cent. Sci.*, vol. 4, no. 1, pp. 5–19, Jan. 2018, doi: 10.1021/acscentsci.7b00500.
- [21] N. Yan and Y. Wang, "Catalyst: Is the Amino Acid a New Frontier for Biorefineries?," *Chem*, vol. 5, no. 4, pp. 739–741, Apr. 2019, doi: 10.1016/j.chempr.2019.03.016.
- [22] K. Yan, M. L. Huddleston, B. A. Gerdes, and Y. Sun, "Electrosynthesis of amino acids from biomass-derived α -hydroxyl acids," *Green Chem.*, vol. 24, no. 13, pp. 5320–5325, 2022, doi: 10.1039/D2GC01779B.