[1.] Kenechi NWOSU-OBIEOGU, [2.]Muofunnaya UMUNNA

RUBBER SEED OIL EPOXIDATION: EXPERIMENTAL STUDY AND SOFT COMPUTATIONAL PREDICTION

[1.]Chemical Engineering Department, Faculty of Engineering, Michael Okpara University of Agriculture, Umudike, Abia State, NIGERIA
[2.]Agric and Bioresources Engineering Department, Faculty of Engineering, Michael Okpara University of Agriculture, Umudike, Abia State, NIGERIA

Abstract: Artificial neural network compared with Adaptive neuro-fuzzy inference system (ANFIS) to predict the optimum conversion of unsaturated fatty acid present in rubber seed oil to epoxide using hydrogen peroxide and acetic acid in the presence of H_2S0_4 as the catalyst. The resultant epoxide product was confirmed with the help of Fourier transform infrared spectroscopy (FTIR) (at 1636.3 cm^{-1}). Physiochemical characterization of the rubber seed before and after epoxidation confirms that the oil is suitably epoxidized. Sensitivity analysis shows that catalyst concentration and stirring speed are the most important two-input combination of oxirane value. The oxirane prediction indices are ANN (R^2= 0.99, MSE=5.074E-12) and ANFIS (R^2= 0.69, MSE= 0.0019). ANN gave a better prediction than ANFIS, though both models had good predictions. Hence, this indicates that chemically modified RSO derivatives can be used as a potential epoxide base stock.
Keywords: ANFIS, Artificial neural network, rubber seed oil, epoxidation

1. INTRODUCTION

Issues related to health, non-biodegradability, environmental pollution, climate change, propelled ecological protection policies, exploration for cost-effectiveness, the quest for renewability, recyclability, ecological safety and sustainability have spurred researchers to search for natural materials that exploit the synthetic capabilities of nature to substitute most of our industrial feedstocks based on petrochemical or non-renewable origin due to their realizable potential [1-3].

Vegetable oils are natural, renewable, biodegradable and abundantly available materials. They are unreactive materials modified to explore the reactive sites and improve their physicochemical properties [4]. The unsaturated fatty acids present in vegetable oil are oleic, linoleic, and linolenic acid; these are the reactive sites for chemical modification in vegetable oils [3]. The epoxides formed are further modified to bio-based polymeric resins [5]. Several researchers have reported on the extraction and characterization of rubber seed oil [6-8], epoxidation of rubber seed oil [9, 10]; their findings implied that rubber seed oil is suitable for epoxidation.

The relationship between epoxidation process conditions such as time, stirring speed, catalyst concentration, temperature, and the oxirane value is complicated and vague most times. Hence the need to adopt soft computing techniques such as artificial neural network(ANN) and Adaptive neuro-fuzzy inference system (ANFIS) for simulation and prediction of the vegetable oil seed epoxidation, Artificial Neural Network (ANN), and Adaptive Neuro-fuzzy inference system (ANFIS) seems to be an excellent model to map the interaction of the process parameters on the oxirane value. ANNs and ANFIS have gained increasing applications where the dependency between dependent and independent variables is either unknown or very complex [11]. Neural network models provide accurate results for complicated system analysis than conventional mathematical models [12]. Moreover, a limited number of researchers have focused on modelling and optimization of vegetable oil seed epoxidation. However, several studies had been conducted on the extraction of oil from vegetable seeds [13-16].

Few studies have been carried out using ANN and ANFIS to predict material processing parameters. Khoshnervisan et al. [17] predicted wheat grain yield based on energy inputs using the ANFIS model compared with the ANN models result illustrated that the ANFIS model predicted the yield more precisely. Kaveh et al.[18] compared ANN and ANFIS model in predicting the drying characteristics of potato, garlic, and cantaloupe at convective hot air dryer, ANFIS had the highest ability to evaluate all output as compared to ANN method. Naresh et al. [19] compared ANN and ANFIS models for better prediction of wire electro-discharge machining responses like material removal rate and surface roughness of a Nitinol alloy; as per the statistical measures perspectives, the ANFIS model had better accuracy for anticipation of EDM attributes of a Nitinol alloy than ANN. Uzuner and Cekmecelloglu [20] applied ANN and ANFIS models to predict polygalacturonase production via fermentation. The results showed that both models performed similarly in terms of accuracy. Masoudi et al. [21] compared prediction temperature in machining using ANN and ANFIS models; according to the results, the ANFIS model had a better prediction than ANN.

Okwu and Adetunji [22] applied ANN and ANFIS models in distribution system with non-deterministic inputs, and ANFIS predicted the inputs better than ANN. ANN or ANFIS has not been reportedly used as a soft computing tool for predicting rubber seed oil epoxidation parameters; thus, this work bridges the gap by predicting rubber seed oil epoxidation parameters using Artificial Neural Network and Adaptive Neuro-fuzzy inference system.

2. MATERIALS AND METHODS

— Materials

Pure rubber seed oil, acetic acid (85%) obtained from Sigma Aldrich, Poole, England, hydrogen peroxide (30wt %) from MERCK. Sodium carbonate obtained from GFS Chemicals, Inc.USA.

— Epoxidation procedure

The epoxidation method reported by [23] was used with slight variation in the procedure. 30 g of rubber seed oil was placed in a three-necked bottom flask, 4 g of acetic acid was added to the flask after about 5 minutes, the mixture was stirred continuously for 30 minutes. Then 16.15 g of 30 wt% aqueous hydrogen peroxide was added dropwise to the reaction mixture, as oxygen donor, at a rate such that the hydrogen peroxide addition was completed within half an hour. The mole ratio of the components used is 1:1.5:0.5; H_2O_2: HCOOH. After the complete addition of hydrogen peroxide, the mixture was heated under reflux at the optimum temperature (65 ºC) with rapid stirring. The stirring was maintained throughout the experiment to achieve fine dispersion of oil and avoid high peroxide concentration zones that could lead to the explosive mixture. The collected samples of the Epoxidised Rubber seed oil (ERSO) were washed with sodium carbonate (Na_2CO_3), dissolved in distilled water to remove the free acids and other unreacted components. 10g of Na_2C0_3 was first dissolved in 100ml of distilled water. Then, another 100ml of distilled water was further added to the mixture. The total mixture was added to the sample and separated by a separating funnel. Subsequent extraction was used to recover the remaining samples after washing.

— Analytical techniques

Iodine value, acid value and saponification value were determined according to the methods of [24]. The Specific gravity was determined using a pycrometer gravimetric method as described by [25]. The percentage of the oxirane oxygen was determined by a direct method established by [26].

— FT-IR analysis

The pure and epoxidized rubber seed oil was characterized using Fourier Transform Infrared (FTIR) Spectroscopy Technique to determine surface functional groups present. The FTIR analyses were carried out on the samples using Shimadzu FT-IR-8400S Spectrophotometer with a resolution of 4 cm-1 in the range of 4000 - 500 cm-

— ANN model development

Artificial neural network (ANN) architecture was developed in MATLAB 8.4 (R2015b) software environment inspired by biological neurons to perform a brain-like task where model training, validation, and testing were carried out. A three-layer ANN with a tangent sigmoid transfer function (tansig) at the hidden layer, a linear transfer function (purelin) at the output layer. The input layer corresponds to the three experimental parameters, which are stirring speed (rpm), time (hours) and catalyst concentration (mol). The output layer is the oxirane value. All the data obtained from the epoxidation of rubber seed oil were randomly divided into three groups (training, validation, and testing) with a ratio of 70%, 15%, and 15%, respectively. In this study, ten neurons were used as default testing to determine the perfect algorithm for the prediction. 1–15 neurons in the hidden layer and one neuron in the output layer were applied, and data used were obtained from multiple factors at a time experiment.

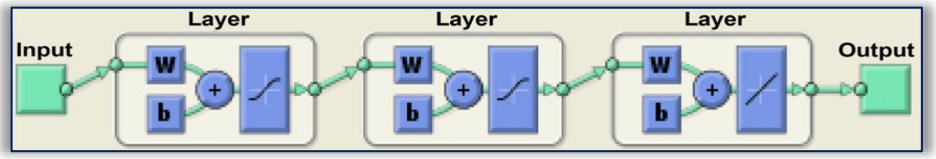

Figure 1: Proposed ANN structure

— ANFIS Modelling

The "exhsrchfunction" in MATLAB 8.4 (R2014b) software environment was implemented in an exhaustive search within the available inputs of the epoxidation process (catalyst concentration, time and stirring speed) to select the set of one and two variable input combinations that has the maximum influence on the oxirane value. Exhaustive search builds an ANFIS model for each combination of inputs, trains it for one thousand epoch, and reports the performance achieved.

The data samples obtained from the epoxidation of rubber seed oil using multiple factors at a time experiment were used. The three-input attribute is catalyst concentration, time and stirring speed. The predicted output variable is the oxirane value. The data set was then partitioned into a training set (odd-indexed samples) and checking set (even data samples). The ANFIS structure was trained using different membership functions, including gbell, gauss1, gauss2, dsig, tri, trap, pi, and psig.

— **Performance of developed ANN and ANFIS model**

To determine the efficiency and performance of the ANN and ANFIS models developed for oxirane value, various statistical parameters are adopted in analyzing the generalization error. Presently in this work, R^2, RMSE, and MSE were used. The value of MSE and RMSE close to zero and the R^2 value (correlation coefficient) close to one shows the degree of predictability and reliability of the model [27].

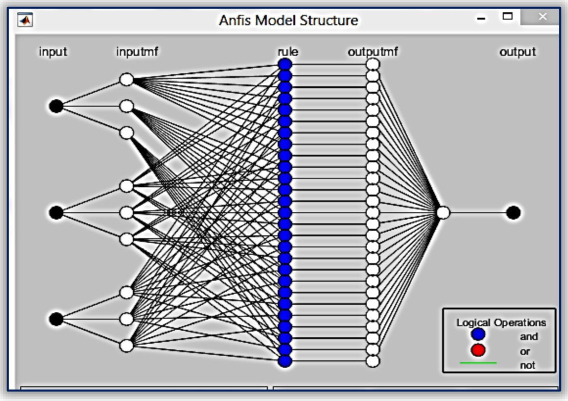

Figure 2: Proposed ANFIS structure

3. RESULTS AND DISCUSSION

— **ANN model simulation**

Eleven backpropagation (BP) algorithms were compared to select the best suited BP algorithm. A three-layer ANN with a tangent sigmoid transfer function (tansig) at the hidden layer and linear transfer function (purelin) at the output layer was used for all BP algorithms. Ten neurons were used in the hidden layer for all BP algorithms; the benchmark comparison displayed loss on the optimality of the estimates/results produced by some BP training algorithms.

Table 1: Comparison of 11 backpropagation with ten neurons in the hidden layers with oxirane value as output

Algorithm	MSE	R^2	IN
Levenberg-Marquardt	3.90895E-6	9.99999E-1	1000
Bayesian Regularization	4.27843E-6	9.99999E-1	1000
Scaled Conjugate Gradient	381.60666	9.99263E-1	38
Trainrp	713.1892	0.99893	35
Traincgf	319.3281	0.9994	41
Traincgp	527.3242	0.99914	24
Trainbfg	296.2963	0.99953	1000
Trainoss	2.1504E03	0.99585	19
Traingd	1.0778E06	0.85919	6
Traingdx	665.7337	0.9986	108
Traingdm	7.4340E05	0.67553	6

As shown in Table 1, the Levenberg-Marquardt was the best of all 11 BP, having the smallest MSE 3.90895E-6 for oxirane value. However, the *traingp* produced the most significant error of 1.0778E06. The loss on the optimality of the estimates/results produced by some BP training algorithms can be attributed to the experimental data's combinatorial nature and non-linear structure. Hence, the complexity analysis of the problem was validated by the various training algorithms used in the benchmark comparison.

— **Optimization of the ANN structure**

The optimal architecture of the ANN model and its parameter variation were determined based on the minimal value of the MSE of the training and prediction set from the Levenberg-Marquardt algorithm. In optimizing the network, the minimal MSE was obtained at the tenth neuron; hence the best validation performance and plot of fit are shown in fig 3 and 4.

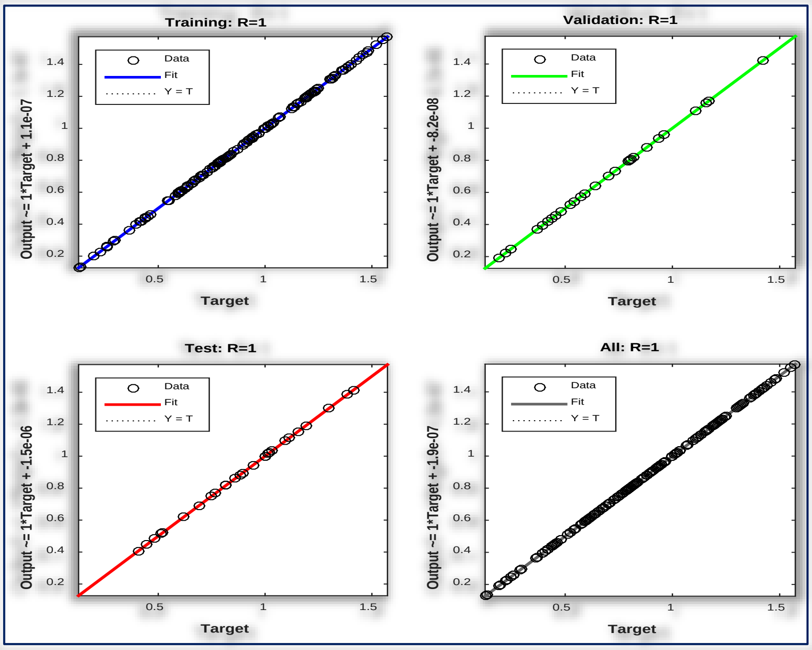

Figure 3. ANN regression graph for oxirane value prediction

There is a high correlation between the predicted values and the measured values. The correlation coefficient is one, and the validation performance of 5.074e-12 was obtained at epoch 210 for Levenberg-Marquardt algorithm, which implies that the model succeeded in predicting the oxirane value. This result is in agreement with [28]

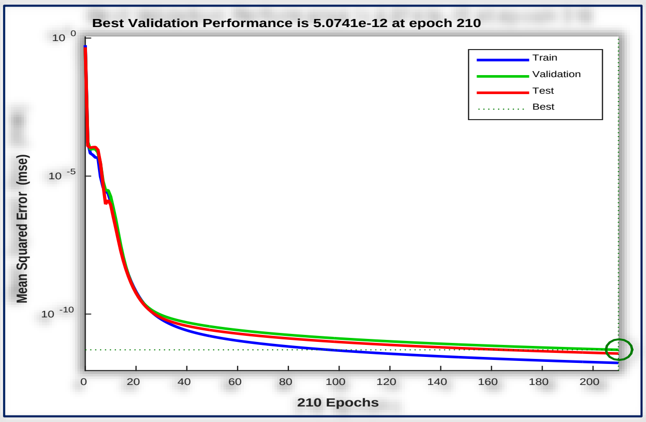

Figure 4. Training error (mean squared error, MSE) curve for oxirane value prediction (Levenberg-Marquardt algorithm).

— **Exhaustive search result for one input and two-input variable ANFIS model for oxirane value**

The ANFIS models using different input variable combinations were investigated with the exhaustive search method to determine the input variable that has the most significant effect on the epoxidation using RMSE as the performance indicator. Table 2 shows an exhaustive ANFIS model result with a single input variable. It was observed that catalyst concentration possessed the least RMSE; this indicated that catalyst concentration was the most relevant variable concerning oxirane value. Also, from table 3, that catalyst concentration and stirring speed were the best two input variables that mainly affected the oxirane value. There, the two inputs were considered for the FIS structure.

Table 2: Exhaustive search result of one-input variable ANFIS model for oxirane value

No of input	Input variable	RMSE training	RMSE Checking
1	Catalyst concentration	0.1946	0.1738
1	Time	0.2923	0.2778
1	Stirring speed	0.2227	0.2235

Table 3: Exhaustive search result of two-input variable ANFIS model for oxirane value

No of input	Input variable	RMSE training	RMSE Checking
2	Catalyst concentration, time	0.1884	0.1723
2	Catalyst concentration, stirring speed	0.0629	0.0590
2	Time, stirring speed	0.2158	0.2192

— **ANFIS simulation results**

To obtain the best prediction of rubber seed oil epoxidation, the developed ANFIS structure was simulated at various input membership functions (mf) such as gauss mf, gauss2 mf, gbell mf, tri mf, trap mf, psig mf and dsig mf. The correlation coefficient (R^2) and the root mean square error (RMSE) were used as statistical criteria to evaluate the degree of reliability of the network.

— **Prediction efficiency of ANFIS model for oxirane value**

Table 4 summarizes ANFIS model prediction efficiency for oxirane, MSE and R^2 are the statistical criteria to judge the model's performance. The effects of different input membership functions (mf) such as gbell, gauss, gauss2, trap, pi, dsig and psig on oxirane value were tested and verified with a single output MF type to determine the best input MF. Table 4 indicates that the dsig mf had the best prediction for R^2, although all R^2 values are within range, tri mf had the lowest MSE value; hence it is employed for the rest of the ANFIS prediction from the statistical performance point of view, the prediction of oxirane value for rubber seed oil is similar to existing investigation on ANFIS modelling [29-30]

Table 4: Prediction efficiency of ANFIS model for oxirane value using linear output membership function

Input membership function	MSE	R^2
Gauss	0.00554	0.63995
Gauss2	0.01048	0.60593
Gbell	0.00316	0.64755
Tri	0.0019	0.63235
Trap	0.0124	0.60325
Pi	0.012033	0.58657
Dsig	0.038413	0.69651
Psig	0.038405	0.69208

— **Prediction model comparison**

The evaluation of the predictive capabilities between ANN and ANFIS for oxirane value was assessed using statistical parameters such as RMSE (root mean square error) and R^2(correlation coefficient). The results obtained shows that ANN and ANFIS model have R^2 of 0.9999 and 0.69, respectively. Additionally, the MSE of ANN and ANFIS for oxirane value prediction gave 5.074e-12 and 0.0019. These statistical comparisons suggest that ANN performed better than the ANFIS model, although the R^2 and RMSE performance was satisfactory for both models.

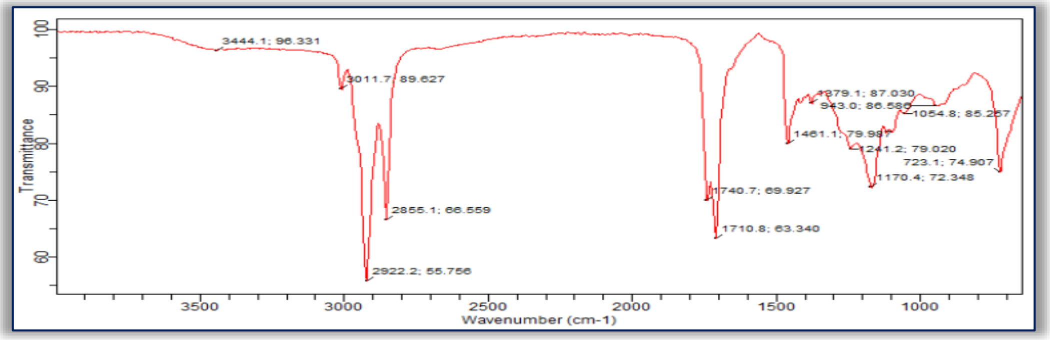

Figure 7: The Fourier transform infrared spectroscopy of the pure sample of RSO

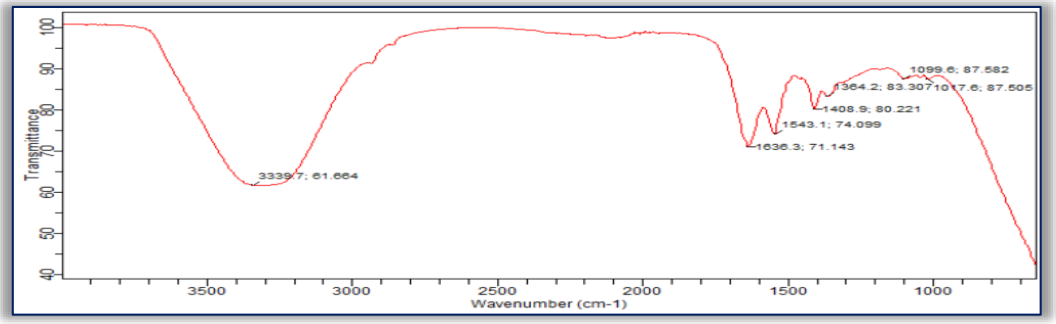

Figure 8: The Fourier transform infrared spectroscopy of the epoxidized sample of RSO

Figure 7 and 8 show the FTIR spectroscopy of the pure sample of RSO and Epoxidized RSO (ERSO). In the FT-IR spectra, it is noticed that the presence of carbon-carbon double bonds (C=C) in the untreated rubber seed oil was indicated by the appearance of a peak at 1710.8cm^{-1}. This disappears in the FTIR spectrum of ERSO, which implies the disappearance of the (C=C) bond. An absorption band of 1636.3 cm^{-1} in the ERSO spectrum showed cyclic ether group of the epoxy functionality; this peak was missing in the untreated oil. This is in agreement with [7,10].

Table 5: Physico-chemical characteristics of rubber seed oil

Properties	RSO	ERSO
Iodine value (gI_2/100g)	130.28	37.90
Specific gravity (30°C)	0.912	0.875
Acid value (MgKOH/g)	137.86	29.30
Oxirane value (%)		1.6
Saponification value (MgKOH/g)	187.23	204.63

Table 5, the iodine and acid value decreased when the oil was epoxidized, which confirms a successful transformation of the unsaturated triglycerides to oxirane rings and reduction in structural residues when epoxidized, the saponification value increased when epoxidized; this indicates more structural linkages to the oxirane rings during epoxidation, the specific gravity reduced due to the decrease in unsaturation of the pure rubber seed oil. These findings are in agreement with [9,10]

4. CONCLUSION

The parametric analysis using exhaustive search showed that catalyst concentration is the single influential input variable affecting oxirane value. Combining catalyst concentration and stirring speed is ranked as the most combined two variables that affect the oxirane value. The statistical comparison for ANN and ANFIS results suggests that both models can estimate rubber seed oil epoxy content. On the contrary, this study showed that ANN gave the best prediction of both models.

References

[1] Seniha, F.G., Y. A. Yusuf, and E. Tuncer 2006. Polymers from triglyceride oils. Progress in polymer science, 633- 639.
[2] Adhvaryu, A. and S. Z. Erhan 2002. Epoxidised soyabean oil as a potential source of high-temperature lubricants. Industrial Crops Prod. 2002. 15: 247-254.
[3] Adekunle K., D. Åkesson, and M. Skrifvars 2010. Synthesis of reactive soybean oils for use as a biobased thermoset resin in structural natural fibre composites. Journal of Applied Polymer Science, 115: 3137-3145.
[4] Saurabh, T., M. Patnaik, S. L. Bhagat and V. C. Renge 2012. Studies on the synthesis of biobased epoxide using cottonseed oil. Int. J. Adv. Eng. Res. Stud.1: 279-284.
[5] Dinda, S., A.V. Patwardhan, V. V. Goud and N. C.Pradhan 2008. Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalyzed by liquid inorganic acids. Bioresource. 99: 3737-3744.
[6] Onoji, S., S. Iyuke, I. A. Igbafe and OM Daramola 2017, *Hevea brasiliensis* (rubber seed) oil: modelling and optimization of extraction process parameters using response methodology and artificial neural network techniques, Biofuels 6: 1–15.

[7] Jisieike, C. F. and E. Betiku 2020. Rubber seed oil extraction; effects of solvent polarity, extraction time and solid-solvent ration on its yield and quality. Biocatalysis and Agricultural Biotechnology, Elsevier, 24.
[8] Mohammed F. V., I. O. Bakare and F. E. Okieimien, 2020. Characterization of Rubber seed oil modified for bio lubricant feedstock application. 149th Annual meeting and Exhibition supplemental proceedings, Springer: 2025-2035.
[9] Okieimen, F.E., O. I. Bakare and C. O. Okieimen, 2002. Studies on the epoxidation of rubber seed oil, Industrial Crops and Products, 15: 139-144.
[10] Obanla, O. R., J. D. Udonne, O. O. Ajani, M. E. Ojewumi, O. J. Omodara and B. A. Oni, 2019. Studies of the in-situ epoxidation of Rubber (Hevea Brasiliensis) seed oil by performic acid. J. Phys. Conf. Ser. *1378*: 1-8.
[11] Almeida, J. S. 2002. Predictive Non-linear Modelling of Complex Data by Artificial Neural Networks. Curr. Opin. Biotech. 4: 1372–76.
[12] Alam, M. A. and P. K. Naik, 2009. Impact of Soil Nutrients and Environmental Factors on Podophyllotoxin Content among Podophyllum Hexandrum Populations of North-Western Him Alayan region using Linear and Nonlinear Approaches. Commun. Soil Science Plant 4: 2485 –2504.
[13] Li H., Z. Zhang and Z. Liu, 2017. Application of artificial neural networks for catalysis: A review, Catalysts, 7: 1-19.
[14] Paul, K. A., B. U, Borugadda, S. M. Bhalerao and V. V. Goud, 2017. In situ epoxidation of waste soybean cooking oil for the synthesis of bio lubricant basestock: A process parameter optimization and comparison with RSM, ANN and GA, Can. J. Chem. Eng. 9999:1-17.
[15] Eletta, O. L. Adewoye, S. Mustapha, A. Adeniyi, O. Ogunleye and O. Aladerokun, 2019. Modelling and Optimization of Oil Extraction from Loofah (*luffa cylindrica*) seeds using a binary solvent mixture. JOTCSB. 2: 57-68.
[16] Yue, X., Y. Chen and G. Chang, 2008. Accurate modelling of biodiesel production from castor oil using ANFIS; Energy Sources, Part A: Recovery, Utilization and Environmental Effects. 1: 1-7.
[17] Khoshnevisan, B., S. Rafiee, M. Omid and H. Mousazadeh, 2014. Development of an intelligent system based on ANFIS for predicting wheat grain yield on the basis of energy inputs information processing in agriculture 1: 14-22.
[18] Kaveh, M., V. R. Sharabiani, R. A. Chayjan, E. Taghinezhad, I. Abbaspour-Gilandeh and I. Yousef, I. Golpour Iman, 2018. ANFIS and ANNs model for predicting moisture diffusivity and specific energy consumption potato, garlic and cantaloupe was drying under convective hot air dryer. Information processing in Agriculture, (5): 372-379.
[19] Naresh, C., P.S.C. Bose and C.S.P. Roro 2020. Artificial neural networks and adaptive neuro-fuzzy models for predicting EDM machining responses for Nitinol alloy: Comparative study. SN Applied Science, 2.
[20] Uzuner,S., and D. Cekemecehoglu 2016. Comparison of Artificial neural networks (ANN) and Adaptive Neuro-fuzzy inference system (ANFIS) models in simulating polygalacturonase production. Bioresources, 11:8676-8685.
[21] Maosudi, S., M. Sima and M. Tolouei-Rad, 2018. Comparative study of ANN and ANFIS models for predicting temperature in machining. 13: 211-225.
[22] Okwu, O. M., and O. Adetunji, 2018. Comparative study of artificial neural network (ANN) and adaptive neuro-fuzzy inference system (ANFIS) models in distribution system with non-deterministic inputs. International Journal of Engineering Business Management. 10:1-17.
[23] Goud, V. V., A. V. Patwardhan and N. C. Pradhan 2006. Studies on the epoxidation of mahua oil (*Madhumica indica*) by hydrogen peroxide. Bioresource Technol. 97: 1364-1371.
[24] AOAC. Official Methods of Analysis (19th Edition), Association of Official AnalyticalChemist, Washington, DC, USA 2012.
[25] Pearson, D. 1981. The Chemical Analysis of Foods. Churchill Living Stone, Edinburgh, London, 121 – 150.
[26] Swern, D., T. W. Findley, G. N. Billen, J.T. and J Scalan, 1947. Determination of Oxirane Oxygen, Anal Chem, 19, 414-415.
[27] Kalogirou, S. A. 2000. Application of artificial neural networks for energy systems. Applied Energy, 67: 17–35.
[28] Ude, C. N., O. D. Onukwuli, C. Nwobi –Okoye, O. E. Anisiji, C. U. Atuanya and M. C. Menkiti 2017. Performance evaluation of cottonseed oil methyl esters produced using CaO and prediction with an artificial neural network, Biofuels, 11: 77-84.
[29] Sonmez, Y. A. S. Kale, C.R. Ozdemir, E. A. and E. Kadak 2018. An adaptive neuro-fuzzy inference system (ANFIS) to predict Cadmium (Cd) concentrations in the Filyos River, Turkey. Turkish Journal of fisheries and Aquatic Sciences, 18 (2018) 1333-1343.
[30] Roy, K., A. Mukherjee, K. D. Jana 2019, Prediction of maximum oil yield from almond seed in chemical industry: A novel type-2 fuzzy logic approach, *SAJCE*, 29: 1-9.

ISSN 1584 – 2665 (printed version); ISSN 2601 – 2332 (online); ISSN-L 1584 – 2665