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Prediction of Polyvinyl Alcohol (PVOH) Properties Synthesized at Various Conditions by Artificial Neural Networks Technique

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ABSTRACT

In this research samples of PVOH were synthesized at various reaction conditions (temperature, time and amount of catalyst). First at 25 °C and 45 °C and constant catalyst weight samples of PVOH were prepared with different degrees of hydrolysis at various times. For investigation of the effects of temperature, at times 20 and 40 min and constant weight of catalyst PVOH was prepared at various temperatures. Increasing the time and temperature of the hydrolysis reaction caused degree of hydrolysis to increase and reduced the molecular weight of the samples. Considering the variation of reaction condition, the effects of each parameter on molecular weight, degree of hydrolysis and conversion were investigated individually and also collectively. Also, by an artificial neural network method, using experimental results (temperature, time and catalyst amount as input and conversion, degree of hydrolysis and molecular weight as output) a network by Levenberg-Marquardt (LM) back propagation with tan-sigmoid transfer function was established. Finally, the established model presented a good prediction capability and enabled us to predict the output in terms of arbitrary inputs. PVOH is an important polymer and predicting its properties during production significantly improves the quality of the products. Neural network technique is used to model the chemical processes to predict the behavior of the process. In this research we investigated the effects of various processing parameters on the properties of PVOH.

1. Introduction

PVOH was prepared for the first time by Herrmann et al. in 1924 [1]. After that, unexpectedly, Sakurada used PVOH to produce acetalized water resistant fibers in 1942 [2]. Before World War 2 PVOH industry advanced in Japan by introducing

vinylon fibers which had not been produced commercially before World War 2. PVOH was used as raw material for the production of fibers by Nichibo and Kuraray companies commercially [3]. Nowadays PVOH is used in industries such as textile, adhesive, paper, colloid protection for emulsion

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polymerization and preparation of polyvinyl butyral. Properties such as compatibility with environment, solubility in water, high tensile resistance, chemical resistance in alkaline environment, low gas diffusion and good optical properties are the reasons this polymer is used in textile, paper making packaging and medical industries [4-6]. Biological degradation is an attractive property of PVOH. Since vinyl alcohol monomer is not stable, polyvinyl acetate is used as the main source for the production of PVOH and other sources are only used for research purposes [7]. Commercial PVOH is available in different grades, and their ultimate properties depend on degree of hydrolysis and molecular weight. These grades have various viscosity and acetyl groups which are used in different areas [8]. Degree of hydrolysis affects properties such as surface tension, compatibility, reaction rheology and solubility in water. Partially hydrolyzed PVOH has low melting and degradation temperature, the higher degree of hydrolysis reduces the solubility and increases resistance to the water [9]. For each application a specific degree of hydrolysis and molecular weight is required. For example, in emulsion polymerization of polyvinyl acetate partially hydrolyzed PVOH is used. Polymerization condition of vinyl acetate affects polyvinyl acetate and hence PVOH properties directly. For example, low molecular weight PVOH can be prepared by polymerization of acetaldehyde in the presence of sodium amalgam as initiator at 20-80 °C. Linear PVOH with high crystallinity can be prepared using polyvinyl acetate which has been prepared at low temperature with low transfer reaction constant solvent. Reaction condition is effective on molecular weight and degree of

hydrolysis of PVOH. According to degree of hydrolysis and molecular weight (low, intermediate and high), PVOH can be classified in various grades as Table 1 and 2 [10-12].

Table 1

Different grades of PVOH according to degree of hydrolysis [8].

Grade	Degree of hydrolysis (%)
Super	99.3 %
Fully	97-99 %
Intermediate	95-97 %
Partially	87-89 %

Table 2

Viscosity versus degree of polymerization [3].

Viscosity	Degree of polymerization
Low (5cp)	500
Intermediate (40-50 cp)	1700
High (higher than 60 cp)	2000

This classification for molecular weight and degree of hydrolysis has also been done by PVOH producers. The classifications of PVOH by Sekisui Chemical Co. are presented in Table 3 and 4 [13].

Table 3

Different grades of PVOH by degree of hydrolysis, classified by Sekisui Co. [13].

Grade	Degree of hydrolysis (%)
Super	99.3 %
Fully	98.0-98.8 %
Intermediate	90.0-97.0 %
Partially	87.0-89.0 %

Many scientific papers present that polyvinyl acetate with specific molecular weight and degree of branching can be prepared by variation of polymerization reaction condition. In this research PVOH was prepared from polyvinyl acetate at

various reaction conditions (temperature, time, amount of catalyst assumed x, y and z as input variables respectively) in methanol as solvent. The results (conversion, degree of hydrolysis and molecular weight assumed u, v

and w as output variables respectively) were determined and finally using a neural network method a model to predict the properties of the polymer was obtained [14-15].

Table 4

Classification of molecular weight by Sekisui Co. [13].

Viscosity(cp)	Viscosity type	Degree of polymerization	Molecular weight range(g/mol)
3-4	Ultra low	150-300	13000-23000
5-6	Low	350-650	31000-50000
22-30	Medium	1000-1500	85000-124000
45-72	High	1600-2200	146000-186000

4 % aqueous solution viscosity

Neural networks which are a metaheuristic method inspired by nature with the purpose of gaining knowledge about behavioral patterns of data, are a massively parallel distributed processing system made up of highly interconnected neural computing elements that have the ability to learn and thereby acquire knowledge and make it available for use [16], have attracted increasing attention in recent years, particularly for process modeling [17].

An ANN consists of an interconnected group of processing elements called neurons or nodes that are sorted into three different layers: input, hidden and output layers [18]. The first layer is called the input layer, while the second and the third layers are called the hidden layer and output layer, respectively [19]. Different types of neural networks exist, depending upon type of training. The training is basically the optimization of weights to reduce the output error of a number of input-output sets [20]. More detailed description of NN is beyond the scope of this study and is documented in literature as well.

2. Experimental

2.1. Materials and methods

Polyvinyl acetate from Aldrich as raw material, methanol from Iran Petrochemical Co., sodium hydroxide from Merck as solvent and catalyst respectively were used in the experiments. To stop the reaction and neutralize the solution, acetic acid from Merck was used after the reaction at desired time and temperature had taken place. For mixing a mechanical mixer with 500rpm was used for all experiments.

To investigate the input data in hydrolysis of polyvinyl acetate and their effects on the properties of PVOH, a sample of polyvinyl acetate with average molecular weight of 5.0×10^5 g/mol was used. In the experiments polyvinyl acetate was dissolved in methanol and sodium hydroxide solution was added as catalyst to conduct the hydrolysis reactions. PVOH precipitates as white powder. After neutralization at 30 °C and 20 min, the samples were dried in an oven and were made ready for further testing. The amount of sodium hydroxide in tables and figures is presented as weight ratio to used polyvinyl acetate.

To obtain the various properties of PVOH the following tests were carried out:

Degree of hydrolysis (DH)

Determination of hydrolysis degree of PVA samples was also made using JIS K6726 standard method. According to this method, dried sample (~1 g) was dissolved in a solution (40 mL) of 1:3V/V MeOH/distilled water. After addition of 50 mL aqueous solution of 0.1 N KOH, it was refluxed for 2 h under continuous stirring (500 rpm) to hydrolyze residual acetate groups on the polymer chains. The moles of potassium hydroxide consumed are equivalent to the number of hydrolysable acetate groups and are determined by back titration with an aqueous strong solution of 0.1 N HCl. The degree of hydrolysis is calculated from this number and the initial sample weight [21]:

$$\text{DH of PVOH} = 100 - \frac{[(a-b) \times 0.43]}{m \times p} \quad (1)$$

Where m, b, a, and p are the initial sample weight, the volume of HCl consumed for blank, the volume of HCl consumed for sample, and the sample pure component (solid content), respectively.

Molecular weight

The molecular weight is determined using measurement of intrinsic viscosity. The Mark-Houwink formula for different DH is shown in Table 5. First, $\eta_{sp} \times C^{-1}$ is plotted against C and then it is extrapolated to zero concentration. Then using Mark-Houwink equation the weight average molecular weight is determined [8, 22].

Table 5
Mark-Houwink equation for various DH [8].

Percentage of hydrolyse (%)	Mark-Houwink equation
86.8	$(8 \times 10^{-4})M_w^{.58}$
93.5	$(7.4 \times 10^{-4})M_w^{.60}$
96.4	$(6.9 \times 10^{-4})M_w^{.61}$
100	$(5.95 \times 10^{-4})M_w^{.63}$

3. Results and discussion

By various characterization techniques such as FTIR, DSC, EDX and DMTA and comparison with commercial samples it was ensured that the synthesized samples at different temperatures, time and catalyst amount are PVOH. After preparation of the samples DH, conversion and molecular weight were determined.

3.1. Samples prepared at 25 °C and 45 °C, 4 % catalyst and various time

In the first series of experiments temperature and catalyst amount (two input variables from three independent effective variables) were kept constant. Conversion, DH and average weight molecular weight were determined. These experiments were conducted at two temperatures (25 °C and 45 °C).

As it is observed in Table 6 conversion and produced PVOH at 45 °C is high in comparison with 25 °C for all time intervals, which presents higher reaction efficiency at high temperature. The difference of conversion for 25 °C and 45 °C is sensible and at longer reaction time it approaches 3 % to 4 %. Another point is that the conversion for both temperatures approaches 90 % of the final conversion during 40 min. This shows that the reaction has proceeded to an acceptable conversion after 40 min and it is not feasible to increase the reaction time. The results of DH for both temperatures are presented in Fig. 1 for various times.

DH for 5 min at 25 °C is around 86 % and at 45 °C is around 89 % which can be attributed to the high reaction rate in pure methanol as solvent in conjunction with proper amount of sodium hydroxide as catalyst. Various methods such as addition of other solvent to the methanol and using other catalysts to reduce the reaction rate have been considered in the literature.

Table 6

Results of the experiments at various times.

Run No.	Temperature(x) (°C)	Time (y) (min)	Catalyst (z) (%)	Conv. (u) (%)	DH (v) (%)	M _w (w) (g/mol)
1	45	5	4	21.4	89.7	48168
2	45	10	4	27.8	91.8	40934
3	45	20	4	45.3	93.1	39061
4	45	30	4	45.7	94.5	40306
5	45	40	4	46.6	95.6	34011
6	45	60	4	48.2	96.1	34151
7	45	90	4	48.3	96.5	33734
8	45	120	4	49.2	97.4	31275
9	45	240	4	49.8	97.6	29545
10	25	5	4	12.6	85.9	102601
11	25	10	4	23.6	87.4	96910
12	25	20	4	34.6	91.9	78712
13	25	30	4	39.5	92.2	76676
14	25	40	4	40.6	93.2	74662
15	25	60	4	42.7	95.3	75267
16	25	90	4	42.8	95.7	73757
17	25	120	4	42.9	95.8	71886
18	25	240	4	45.6	96.2	71514

In Fig. 1 the end point of curve of DH has not reached to 97 % (complete hydrolysis) at 25 °C, therefore this temperature is not suitable for preparation of high DH of PVOH. Fully hydrolyzed PVOH can be prepared at 45 °C after 120 min. It seems that with increasing the temperature the required time to prepare fully hydrolyzed PVOH will be reduced and

reach the feasible time of complete hydrolysis. Finally, it can be seen in Fig. 1 that after 60 min variation in DH is about 1 % to 1.5 %. This presents the reduction of hydrolysis reaction rate in times longer than 60 min. These temperatures are suitable for preparation of PVOH with intermediate DH.

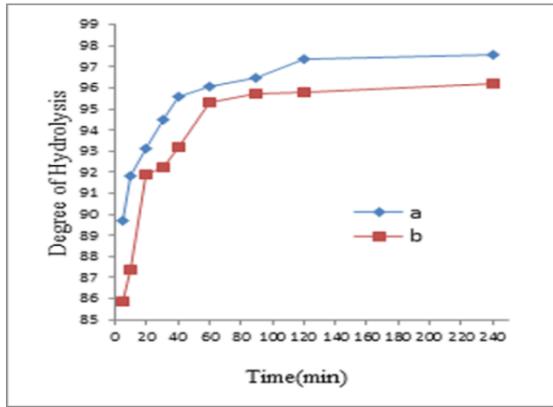


Figure 1. DH versus time, (a): 45 °C, (b): 25 °C.

The results of molecular weight determination at 25 °C and 45 °C are presented in Fig. 2.

The difference between the original polyvinyl acetate (500000 gr/mol) and PVOH molecular weight increases with progress in the reaction. These reduced molecular weights are 30000 and 70000 for 45 °C and 25 °C respectively. This difference between molecular weights can be attributed to high possibility of separation of hydrolysable branches of polyvinyl acetate (Fig. 3) from backbone and also breaking the main chains at high temperature [23, 24].

In Fig. 2 considering the nature of the hydrolysis reaction, similar to the results for

DH, after 40 min the weight average molecular weight does not change more than 5000. Therefore the molecular weight at 40 min can be used to estimate the molecular weight at longer time. Considering the molecular weight at 45 °C (30000), this temperature can be used to prepare low molecular weight PVOH (31000-50000). Intermediate molecular weight PVOH (85000-124000) can be prepared at 25 °C. Considering the trend of the curves in Fig. 2 the temperature lower than 25 °C will produce intermediate molecular weight PVOH.

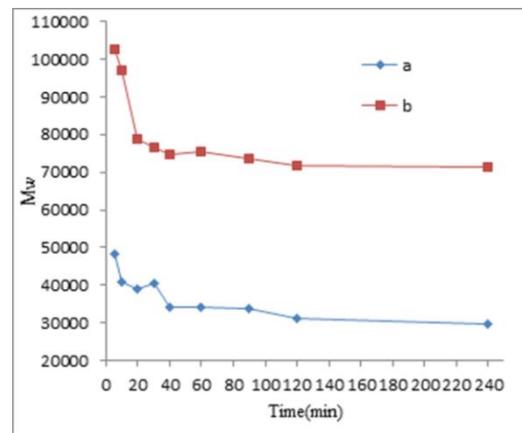


Figure 2. Molecular weight at various times, (a): 45 °C, (b): 25 °C.

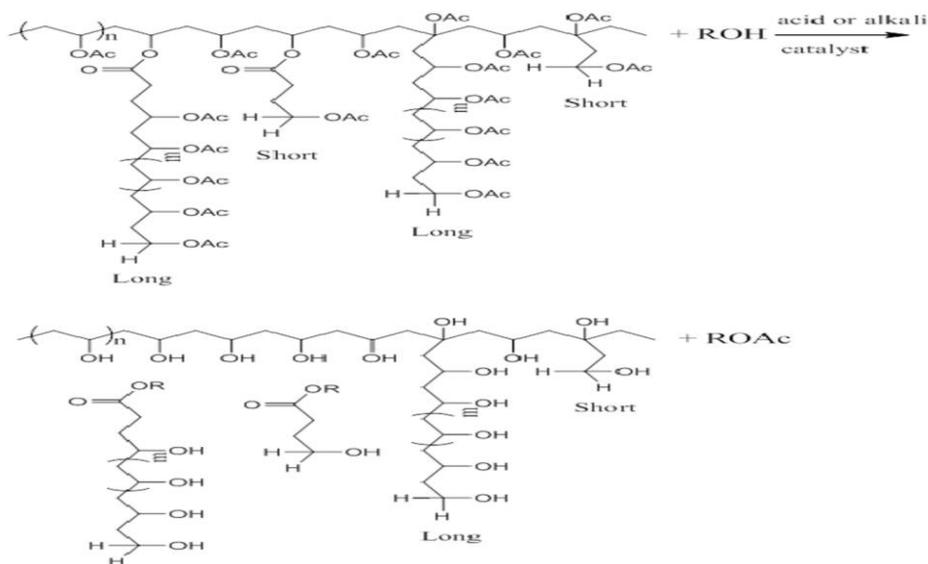


Figure 3. Separable and inseparable of branches in the structure of polyvinyl acetate.

3.2. Samples prepared at 20 min and 40 min, 4 % catalyst and various temperatures

In second series of experiments at 4 % catalyst and 20 min and 40 min, the effect of temperature on variable parameters

(conversion, DH, and molecular weight) was investigated. The results are shown in Table 7 (to complete the experiments at 60 °C, experiments were done at 60 min and 120 min).

Table 7

Results for 20 min and 40 min for various times.

Run No.	Temperature(x) (°C)	Time (y) (min)	Catalyst (z) (%)	Conv.(u) (%)	DH (v) (%)	M _w (w) (g/mol)
19	20	40	4	41.3	92.4	77285
20	30	40	4	43.2	93.9	65293
21	40	40	4	45.2	94.3	59330
22	50	40	4	45.8	95.7	27982
23	60	40	4	46.2	97.8	24834
24	60	120	4	47.9	98.2	21004
25	70	40	4	50.5	98.7	12433
26	20	20	4	31.1	90.7	90287
27	30	20	4	37.2	91.8	68942
28	40	20	4	39.1	92.9	66246
29	50	20	4	45.6	94.5	34533
30	60	20	4	46.1	97.1	30206
31	60	60	4	46.5	98.2	25701
32	70	20	4	48.8	98.5	16296

DH at 20 min and 40 min and various temperatures is shown in Fig. 4.

As it is observed in Fig. 4 Fully hydrolyzed PVOH (97 % - 99 %) can be prepared at temperatures above 60 °C and both 20 min and 40 min. Considering the trend of the curves in Fig. 4 it can be predicted that with increasing the time above 40 min and

temperature above 70 °C Super hydrolyzed (+99.3 %) PVOH can be prepared.

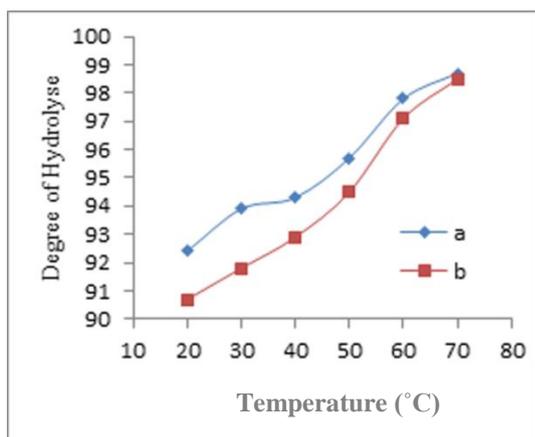


Figure 4. DH versus temperature, (a): 40 min, (b): 20 min.

Depending on the application, the suitable temperature to prepare PVOH with intermediate DH (90 % -97 %) can be derived from Fig. 4. The results of molecular weight for second series of experiments are shown in Fig. 5.

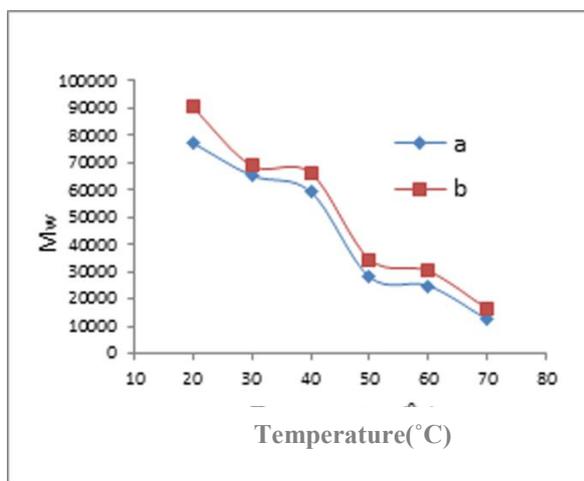


Figure 5. Molecular weight versus temperature, (a): 40 min, (b): 20 min.

The reduction in molecular weight at 40 min and 20 min increases with increasing temperature. At 70 °C maximum reduction in molecular weight appears and the molecular weights are 1600 and 1500 at 20 min and 40 min respectively. The intensity of molecular weight reduction after 40 °C is high. Considering the curves in Fig. 5 and

considering the fact that the hydrolysis reaction has enough and acceptable progress after 40 min, for each temperature a molecular weight can be defined and derived. This helps us to adjust the temperature to prepare a PVOH with certain molecular weight. For example, 60 °C to 70 °C is suitable to prepare ultra-low molecular weight and 40 °C to 50 °C is suitable for low molecular weight. To prepare intermediate and high molecular weight PVOH the temperature below 20 °C is suitable. Another method to prepare intermediate and high molecular weight PVOH is using high molecular weight polyvinyl acetate and less catalyst.

3.3. Samples prepared at 45 °C and 40 min, and various amounts of catalyst

The last series of experiments were carried out at 45 °C and 40 min at various amounts of catalyst. Conversion, DH and molecular weight were determined and are shown in Table 8. According to the observations during the experiments, very fine particles form when the amount of catalyst is below 2 %. Separation of these particles is very difficult. If the mixing is not properly performed or the solvent is not enough in the presence of more than 4 % catalyst, agglomerates of PVOH form which makes mixing very difficult and prevents the reaction progress. Therefore the catalyst amount between 2-4 % is suitable for PVOH synthesis. In this range increasing the amount of catalyst from 2 % to 4 % increases the molecular weight up to 20000. According to the data of Table 8 each 0.5 % increases in catalyst increases the DH around 1 % approximately. It can be concluded that variations in catalyst amount increase the DH 2 to 3 % ultimately, thus temperature and time are effective factors on DH.

Table 8

Results for various catalyst amounts.

Run No.	Temperature(x)(°C)	Time (y) (min)	Catalyst (z) (%)	Conv. (u) (%)	DH (v) (%)	M _w (w) (g/mol)
33	45	40	1	15.2	80.5	92403
34	45	40	1.5	21.5	83.3	74566
35	45	40	2	35.2	92.6	56434
36	45	40	2.5	38.9	93.1	45441
37	45	40	3	42.4	94.7	41250
38	45	40	3.5	43.1	95.3	36122
39	45	40	4.5	49.8	95.6	30206
40	45	40	5	50.7	95.8	29413

3.4 Modeling using neural network technique

In the cases where a deterministic model cannot adequately describe a system, then the use of a neural network, which is actually a 'black box', can give better results [17]. In this paper after normalizing experimental data, (x, y, z) are used as inputs and (u, v, w) are used as output layer.

Temperature, time and weight of catalyst as input data and conversion, molecular weight and DH as output were considered. Geometry and various configurations of inputs were tested with Matlab and Neural Power. Several ANN structures with different hidden layer and one output layer of linear neurons were tested to identify the most appropriate number of hidden nodes and other properties of network.

Finally the error of regression and MSE were determined. Table 9 and Fig. 6 present

the results. Graphical representation of the above two networks and relative importance of each parameter can be seen in Fig. 6. As it can be seen in Table 9 the Levenberg-Marquardt Algorithm with a sigmoid function and network configuration with 2 hidden layers with 5 and 6 neurons respectively is the best possible configuration. Based on the above configuration network gives the least regression error and MSE. Of course, between various neural networks, the one that has the lowest hidden layers is valuable. With investigation of Levenberg-Marquardt method, single hidden layer and 9 neurons (least neuron between investigated neurons) were selected. This configuration has relatively the best regression error \otimes and MSE. To prevent the table being too long the configurations 3-2-3 to 3-8-3 were not given in the table and the best result with least neurons (9) was given in the Table.

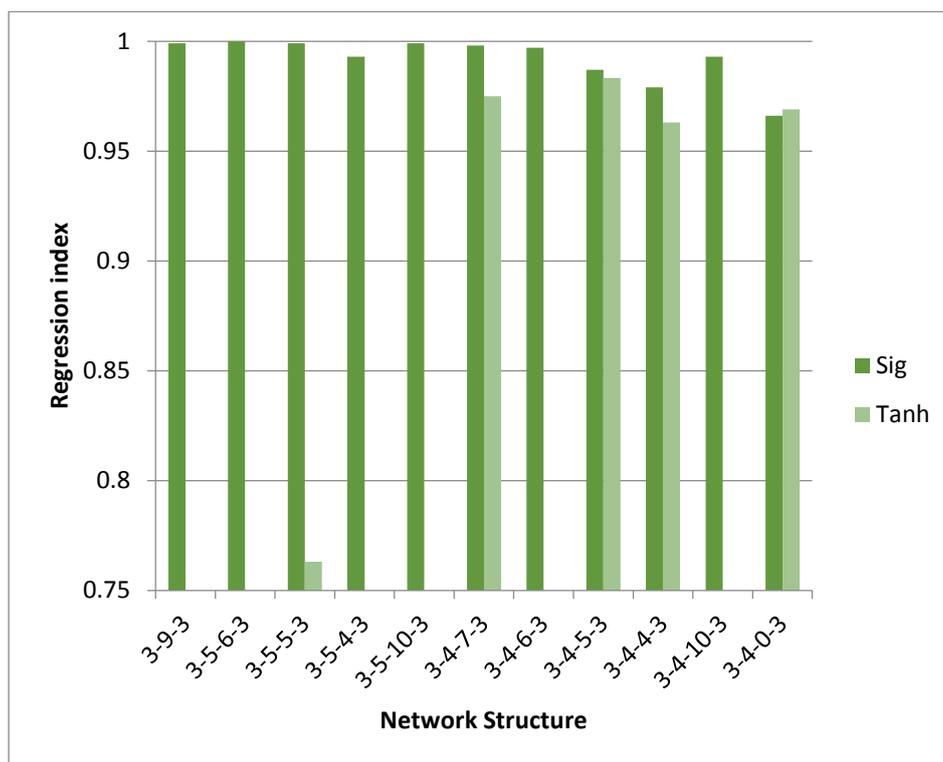


Figure 6. Regression index of models with different ANN properties.

Table 9

The results of regression and MSE for various geometries, algorithms and transfer functions.

Geometry	Algorithm	Transfer function	Regression(R)	(MSE)
3-4-0-3	QP	Tanh	0.969	1990
3-4-4-3	QP	Tanh	0.963	1359
3-4-5-3	QP	Tanh	0.985	680
3-4-7-3	QP	Tanh	0.975	904
3-5-5-3	QP	Tanh	0.763	2977
3-4-0-3	QP	Sig	0.966	1469
3-4-5-3	QP	Sig	0.984	530
3-4-7-3	QP	Sig	0.997	75
3-4-10-3	QP	Sig	0.999	4
3-5-10-3	QP	Sig	0.999	7

Prediction of Polyvinyl Alcohol (PVOH) Properties Synthesized at Various Conditions by Artificial Neural Networks Technique

3-4-5-3	IBP	Tanh	0.989	378
3-4-10-3	IBP	Sig	0.987	782
3-4-5-3	BBP	Tanh	0.984	433
3-4-5-3	BBP	Sig	0.988	507
3-4-4-3	LM	Sig	0.979	56.54
3-4-5-3	LM	Tanh	0.975	842
3-4-5-3	LM	Sig	0.989	4.71
3-4-6-3	LM	Sig	0.997	176.93
3-4-7-3	LM	Sig	0.999	5.91
3-5-4-3	LM	Sig	0.993	42.72
3-5-5-3	LM	Sig	0.999	3.55
3-5-6-3	LM	Sig	1	0.61
3-9-3	LM	Sig	0.999	0.98

A feed forward network with one hidden layer contains 9 neurons that use Levenberg-Marquardt (LM) back propagation with tan-sigmoid transfer function (tansig) is applied for the cases shown in Fig. 7.

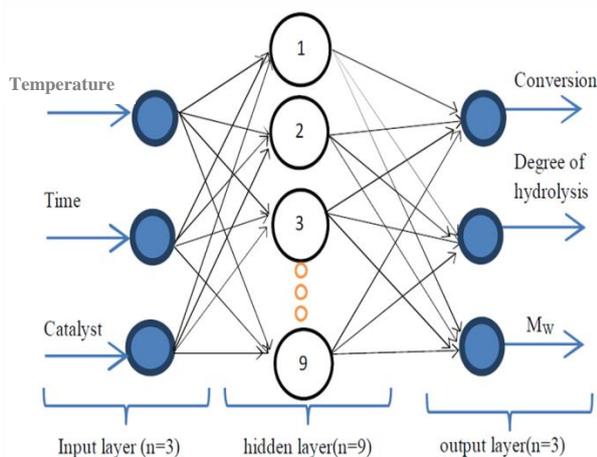


Figure 7. Multilayer perception with one hidden layer.

The tan-sigmoid transfer function is expressed as Eq. 2 and for normalizing the

data in the 0.1–0.9 range the formula 3 is used [17]. Normalization of variable values was carried out in order to avoid using data spanning over different orders of magnitude:

$$F(x) = \frac{2}{1 + e^{-2x}} - 1 \quad (2)$$

$$0.8 \left(\frac{X_{\max} - X_i}{X_{\max} - X_{\min}} \right) + 0.1 \quad (3)$$

Where X_i is the input or output variable X , and X_{\min} and X_{\max} are the minimum and maximum value of variable X .

At the start of training run, the biases and weights were initialized at random values in the range between +1 and -1. The most common problem with ANN-based models is the lack of generalization capability which means that they would memorize only the

training set if not properly trained. So one common problem encountered during ANN training is over fitting or overtraining. In such a case, the predictive ability of the trained network on new or unseen data is lost. To avoid over fitting, early stopping was employed during the ANN training, splitting the entire data set into training, validation, and test sets [18]. The training was done with MATLAB software. So 40 experimental records are separated as (70 %-15 %-15 %) to devote to them. External validation of the models was done by means of three statistical quantities including squared correlation coefficient (R^2), root mean square error (RMSE) and average relative deviation (ARD) was calculated by applying the following formula [25]:

$$RMSE = \sqrt{\frac{\sum_1^n (Y_{\text{observed}} - Y_{\text{predicted}})^2}{n}} \quad (4)$$

$$ARD = \frac{\sum_1^n |Y_{\text{observed}} - Y_{\text{predicted}}|}{n} \quad (5)$$

$$R^2 = 1 - \frac{\sum_1^n (Y_{\text{observed}} - Y_{\text{predicted}})^2}{\sum_1^n (Y_{\text{observed}} - \bar{Y})^2} \quad (6)$$

The results are (RMSE= 0.98, ARD=0.96, R=0.999) and good fitness of prediction is shown in Fig.8.

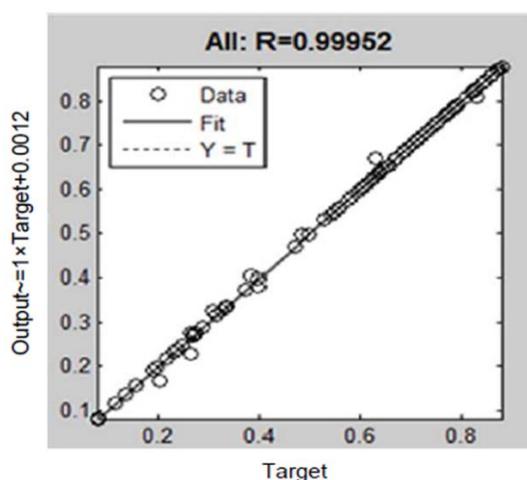


Figure 8. Output and target data.

The results show a correct estimation of the parameters and the created model is successful. Finally by giving specified output to the network (conversion=40, DH=95 %, Mw=80000), optimum inputs (time, temperature and catalyst amount) can be designed for the experiments. Neural network technique does not give a relationship between outputs and inputs to present as a graph. The quality of the model is characterized using parameters such as: mean square error (RMSE), average relative deviation (ARD) and average absolute deviation (AAD), which have been determined in the paper.

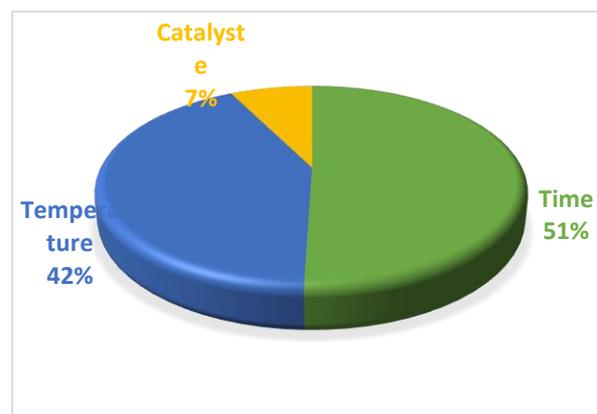


Figure 9. Weight of parameters on outputs.

4. Conclusions

According to the results of this research with adjusting temperature, time and catalyst amount in the process of PVOH production various DH and molecular weight can be achieved. Also, to prepare any grade of PVOH an optimum temperature, time and catalyst amount can be defined. Neural network can predict the outputs (DH, MW, and conversion) for arbitrary input data (Catalyst percentage, Temperature, Time) very well and can present importance and effectiveness of individual input data on output variables quantitatively.

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