Mathematical modeling of ethylene polymerization over advanced multisite catalysts: an artificial intelligence approach

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Received: 15 September 2019 / Accepted: 22 January 2020 / Published online: 6 February 2020
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Abstract

Recent developments in multisite catalysts based on metallocenes and post-metallocenes attracted the attention of researchers and industrial petrochemical companies due to the production of high-performance polymeric materials which generally are not achievable based on Ziegler–Natta catalysts. In this study, with the aim of predicting the average molecular weight of produced polyethylene and activity of ethylene polymerization using multisite catalysts, robust precise models based on artificial neural networks are developed. The average error for the prediction of the average molecular weight and activity are 3.76% and 5.89%, respectively. The Leverage method was used to check the reliability of the proposed model and the quality of experimental data which have been used for model development. The results showed that just a few data points are outside of the applicability domain of the developed models, confirming that both developed models and their predictions are statistically correct. Comparison of the artificial neural network models with other artificial intelligence approaches including support vector machine and group method of data handling type neural networks illustrates the better performance and robustness of the proposed models. The results of this study promise that neural networks can be used as reliable models with reasonable accuracy to estimate the performance of ethylene polymerization over this type of new metallocene/post-metallocene multisite catalysts.

Keywords Neural networks · Ethylene polymerization · Multisite catalyst · Mathematical modeling · Metallocene

1 Introduction

Polyolefin materials like polyethylene and polypropylene have significant properties like excellent mechanical/thermal properties, fine melt strength and high processability, recycling ability, light weight, high flexibility and good chemical resistance. Such properties result in considering these polymers as affordable raw materials for diverse applications from high-pressure pipes, fuel tanks, advanced heat floor pipes to shopping bags, toys, bottles and car bumpers [1, 2].

The invention of Ziegler–Natta catalysts in 1953 was led to the production of polyethylene and isotactic

polypropylene under mild reaction conditions. This success was a revolution in the polyolefin industry which led to Nobel prize for Ziegler and Natta in 1963 [3]. However, due to “uncontrolled” multisite nature of Ziegler–Natta catalysts, precise control over the microstructure of polymers produced by this types of catalyst is not possible. Unlike Ziegler–Natta catalysts, the single site metallocene catalysts, basically consisting of a sandwiched transition metal center between two cyclopentadienyl ligands, benefited by well-known active site structure. Taking this advantage, the precise control over the key architectural characteristics of the polymer such as weight average molecular weight (MW), distribution of molecular weight (MWD)

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and short chain branching distribution (SCBD) becomes possible [4–6]. Due to the well-known structure of this single site pre-catalysts, the systematic study of initiation, propagation and termination steps is provided. However, this type of catalysts produces polymers exhibiting narrow molecular weight distribution suffering from poor processability [7]. Furthermore, in order to implement this type of catalyst in industrial applications, it is necessary to immobilize metallocene and post-metallocene catalysts on a suitable support [7, 8]. Over the recent years, the multisite catalyst technology has been proposed by researchers to immobilize homogeneous active sites on different supports comprising MgCl_2 , silica, and graphene [7–10]. In this technology generally two or three different types of metallocenes and post-metallocene catalysts are immobilized on one or more preferred kinds of supports [8, 10–14]. As a consequence, polymers produced using multi component catalysts exhibit multi modal molecular weight distribution [7]. A series of multisite catalysts were developed by Mülhaupt and Co-workers in which bimodal or trimodal polyethylene possessing precisely controlled microstructures are obtained [8, 10–18]. One of their outstanding results, was the successful development of a polyethylene additive, that caused significant improvement in HDPE mechanical properties. The polymer stiffness, toughness and tensile strength were increased simultaneously, in terms of tensile strength (+ 392%), impact resistance (+ 197%) and Young's modulus (+ 365%) [8]. A comprehensive review of the literature on multisite catalysts has been conducted by Stürzel et al. [7].

Although a series of outstanding and useful experimental studies have been conducted in the area of multisite catalyst based ethylene polymerization, modeling the behavior of this type of catalysts has also a great importance from the both industrial and academic point of views, specially scale up issues. In addition, doing many experimental studies to check the different performance of the catalyst in diverse process conditions is many expensive, tedious and extremely time and energy-consuming. In this regard, a predictive approach like artificial intelligence (AI) can be helpful. Over recent years, AI approaches like artificial neural networks (ANN), group method of data handling type neural network systems (GMDH-NN) and least square support vector machines (LSSVM) have widely been used by researchers to model various chemical engineering systems [19–25]. Each one of this approaches benefited by its own advantages. For instance, based on GMDH-NN approach it is possible to obtain an explicit analytical relationship between input and output of the problem [21]. Also, the SVM approach has a different benefit compared to other AI approaches in which due to implementing of quadratic programming as a convex function only one global solution for the studied

system is found [26, 27]. On the other hand, neural networks have the benefit of fantastic flexibility to model highly non-linear systems. In this regards, in systems with much complexity, it is preferred to implement neural network models.

The aim of the current study is implementing ANN systems to model the average molecular weight of polyethylene obtained by advanced multisite catalyst besides the catalytic system activity. To the best knowledge of authors, to date, no mathematical models based on AI methods have been developed for this purpose. To develop the model, the concentration of pre-catalysts and polymerization time are considered as the input parameters and average molecular weight and activity are considered as the model outputs. The models performance is validated by various statistical functions. Also, the Leverage approach is used to evaluate the reliability of the ANN models and the experimental data. Ultimately, the artificial neural network model performance is compared with other AI approaches comprising SVM and GMDH to determine the superior model for this purpose.

2 Theoretical background

2.1 Multisite catalysts and multimodal PE

Generally, polyethylene with low molecular weight has high crystallization rate, low viscosity and high stiffness. While ultrahigh molecular weight polyethylene (UHMWPE) is benefitted by high toughness, much lower crystallization rate and higher melt viscosity. The high viscosity of this macromolecules originates from their highly entangled chains compared to medium molecular weight high-density polyethylene (HDPE). Figure 1 illustrates bimodal molecular weight distribution (MWD) for polyethylene in which UHMWPE with short chain branches plays the role of tie molecule and links polyethylene crystal lamellae. In this regard, the existence of UHMWPE in polyethylene structure causes the significant promotion of fatigue resistance, environmental stress crack resistance (ESCR), abrasion resistance and impact strength.

This type of MWD is necessary to produce sustainable lightweight materials possessing high resistance like high performance pipes (damage resistance) and under pressure tanks [7]. Development of cascade reactor technology to obtain in reactor blend of HDPE and UHMWPE compounds resulted in commercial manufacturing of PE pipes with enhanced performance. However, the state-of-the-art of production bimodal PE for pipe applications, has shown that maximum incorporation of UHMWPE in the product which is applicable based on cascade reactor technology is less than 3 wt% [7, 28–34]. While in the case

Fig. 1 Bimodal MWD of polyethylene and its schematic structure [7]

Fig. 2 Achievement of Multimodal MWD for polyethylene based on cascade reactor technology (above left) and multisite catalyst technology in single reactor (above right) [7]

of advanced multisite catalyst technology, the immobilization of various single site catalysts (metallocene/post-metallocene pre-catalysts) on a suitable support, results in the incorporation of almost 12 wt% of UHMWPE in HDPE. In this regard based on multisite catalysts, development of PE commodities with higher performances (improved mechanical properties) will be provided.

As can be observed in Fig. 2, according to the cascade reactor technology (in reactor blending of UHMWPE and HDPE) and using Ziegler–Natta catalysts, multimodal MWD can be achieved. Generally, in this technology the desired MWD is obtained by altering the process conditions, hydrogen and comonomer concentrations in three reactors. However, another technology which is based on multisite catalysts is performed in just one reactor and has more benefits compared to cascade reactor technology. In this type of catalyst, each single site catalyst polymerized ethylene to polyethylene with a certain range of molecular weight. Thus, one site can produce UHMWPE and another can be used for the production of HDPE and in this regard the required MWD is achieved in a single reactor. According to the report of the Univation Technologies company,

a value more than \$35 million will be the investment savings for a single UNIPOL™ PE Process reactor with 300 kta production in comparison with cascade reactor technology. Also, about 35% savings in operating costs is another advantage of this technology compared to cascaded reactor technology. Consequently, not only it is possible to produce polyethylene with promoted properties but also lower production costs are estimated using the multisite catalyst technology in a single reactor.

2.2 Artificial neural networks

As a general schematic of ANNs, they are a replication of brain process to analyze a phenomenon. ANNs consist of interconnected group of neurons in multiple layers making the backbone of ANNs. The information of the studied problem is introduced to the network by the first layer which is called “input layer” [35]. In addition, hidden layers which enrich the network for learning the system, have the duty of connecting the input and output layers. From the theoretical point of view, only one hidden layer with

appropriate neurons has the ability to learn any behavior of a system [36]. The relation between neuron output and the network is provided by a mathematic function called the transfer function. The most conventional transfer function for prediction of phenomena are the linear, sigmoid and Tansig transfer functions which are easy to differentiate to use in a learning scheme such as back propagation (BP) [37–39]. This transfer functions have following relations:

$$\text{Linear transfer function, } g(x) = x \quad (1)$$

$$\text{Sigmoid transfer function, } g(x) = \frac{1}{1 + e^{-x}} \quad (2)$$

$$\text{Tansig transfer function, } g(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}} \quad (3)$$

For a network with Tansig transfer function for one hidden layer the model output takes the following form:

$$y = \text{Linear}(W_2 \times (W_1 \times g(x)_{\text{Tansig}} + B_1) + B_2) \quad (4)$$

where W and B represents weights and biases respectively.

Generally, the Levenberg–Marquardt (LM) algorithm [40, 41] is implemented to optimize weights and biases of the network. In most cases ANN-LM models does not involve local minimums and even with an inappropriate initial guess the global minimum is obtained [42]. In this regard we used this algorithm for optimization of the ANN model. Since the concept of neural networks has been described well in literature, the authors ignored detailed description of this approach. The interested readers is referred to read refs. [43, 44] for more information.

2.3 Group method of data handling type neural networks

Following the Darwinism's theory, Ivakhneko proposed the group method of data handling (GMDH) technic [45, 46]. In sharp contrast to ANNs in which a group of weights and biases are generated as the output of the model, in the GMDH type neural networks (GMDH-NN) a group of simple polynomials are generated as the final structure of the model. In the GMDH-NN approach the grand correlation polynomial used to model a system takes the following form:

$$y = a + \sum_{i=1}^M \sum_{j=1}^M \dots \sum_{k=1}^M b_{ij\dots k} x_i^n x_j^n \dots x_k^n \quad (5)$$

where a and b are model constants and M stands for the number of independent variables. Detailed information of step by step modeling procedure of GMDH-NN can be find elsewhere [21, 23, 47].

2.4 Least square support vector machine (LSSVM)

The SVM is generally implemented for applications including pattern recognition, regression analysis and classification. LSSVM is an improved version of SVM which has been proposed to reduce the complexity of SVM approach [48, 49] with following cost function (CF):

$$CF = \frac{1}{2} w^T w + \frac{1}{2} \gamma \sum_{k=1}^N e_k^2 \quad (6)$$

where γ is an adjustable parameter preventing overfitting problem, w^T is the transposed output layer and e_k stands for variable error of train data. The following equality constraint is subjected to the cost function:

$$y_k = w^T \varphi(x_k) + b + e_k \quad (7)$$

where b is the bias vector and $\varphi(x_k)$ is the kernel function. The radial basis function (RBF) was used in the present study as the kernel function of LSSVM model due to its excellent performance for nonlinear systems. The RBF has following form:

$$\varphi(x, x_k) = \exp\left(\frac{-\|x_k - x\|^2}{\sigma^2}\right) \quad (8)$$

where σ^2 is the tuning parameter of kernel function. In this regard, there are two tuning parameter for LSSVM comprising σ^2 and γ which should be determined. In the present study we used coupled simulated annealing (CSA) approach [50] to achieve this purpose. The implemented algorithm to optimize the LSSVM-CSA model is shown in Fig. 3. More detailed information related to the SVM and LSSVM can be found in the previous studies [20, 48, 51–55].

3 Model development and evaluation

In this study, the experimental data which have been reported by Stürzel et al. [13] were used for model development. The authors developed three-site catalyst, immobilized on functionalized graphene in which CrBIP (see Fig. 4 for full name of pre-catalysts) pre-catalyst produces polyethylene wax with high crystallization rate, CrQCp forms UHMWPE, and FeBIP or ZrCp are as the active site responsible for HDPE production with variable intermediate molar mass. The mentioned active sites are shown in Fig. 4. Also, experimental data which have been implemented for the model training are tabulated in Table 1.

Since the aim is to model average molecular weight and activity, these parameters are supposed to be a function of

Fig. 3 Implemented algorithm to develop LSSVM-CSA model **Fig. 4** Types of the single-site pre-catalysts used in multisite catalyst by Stürzel et al. [13] to produce trimodal polyethylene

the concentration of pre-catalyst and time of polymerization (t_p) as below:

$$M_w = f(\text{CrBIP}, \text{FeBIP}, \text{ZrCp}, \text{CrQCp}, t_p) \quad (9)$$

$$\text{Activity} = f(\text{CrBIP}, \text{FeBIP}, \text{ZrCp}, \text{CrQCp}, t_p) \quad (10)$$

In this regard, two neural networks were developed separately to predict M_w and activity. Figure 5 illustrates a schematic of the proposed ANNs along with inputs and output to the model for the prediction of M_w . The same schematic can be drawn for the second neural network which predicts activity.

In order to develop the ANNs, the experimental data were randomly divided into three groups. The main part

Table 1 Experimental data used in this study to develop the models

Entry	CrBIP ($\mu\text{mol L}^{-1}$)	FeBIP ($\mu\text{mol L}^{-1}$)	ZrCP ($\mu\text{mol L}^{-1}$)	CrQCP ($\mu\text{mol L}^{-1}$)	t_p (min)	Activity ($\text{g mmol}^{-1} \text{h}^{-1}$)	Mw (Kg mol^{-1})
1	0	2	0	0	120	26,200	270
2	6.3	2	0	0.8	120	9300	230
3	6.3	1.3	0	0.8	120	15,300	650
4	6.3	0.7	0	0.8	120	16,900	400
5	6.3	1	0	0.8	120	14,900	470
6	6.3	1	0	1.6	120	16,200	570
7	6.3	1	0	3.2	120	14,400	1125
8	12.6	2.6	0	3.2	240	3100	660
9	7.9	1.7	0	1.9	180	5000	780
10	6.3	1.3	0	1.6	110	6800	570
11	0	0	24.7	0	30	4400	1600
12	9.2	0	2.3	4.7	30	12,800	1750
13	9.2	0	4.9	4.7	30	12,400	1240
14	9.2	0	9.9	4.7	30	12,000	830
15	9.2	0	9.9	2.3	30	4400	640
16	9.2	0	9.9	1.6	30	7800	610
17	18.5	0	2.3	4.7	30	10,100	710
18	18.5	0	4.9	4.7	30	11,000	680
19	18.5	0	9.9	4.7	30	13,300	450
20	18.5	0	9.9	2.3	30	7300	600
21	18.5	0	9.9	1.6	30	9200	400

Fig. 5 A schematic of the proposed neural network system to predict Mw

which forms 60% of the database was used for training of the model and the remained data was equally distributed to validate and test of the model. It must be emphasized that this is a practical approach to employ about 60–70% of the database to train the model and assigning

rest of data for training and testing [47, 56, 57]. Also, to avoid complexity in ANN models, one hidden layer was considered and the number of neurons was changed to find optimum structures. The optimized ANN structures to predict Mw and activity are shown in Tables 2 and 3 respectively.

3.1 Performance evaluation

To check the performance of an artificial intelligence model like ANN, it is necessary to implement different statistical functions including average relative deviation percentage (ARD%), regression coefficient (R^2), Root of mean square error (RMSE), average absolute relative deviation percentage (AARD%) and standard deviation (SD) which their mathematical functions are described below:

1. **ARD%** this function is used with the aim of investigating relative deviation between model results and their correspondence experimental data:

$$ARD(\%) = \frac{100}{N} \sum_{i=1}^N \frac{p^{calc} - p^{exp t}}{p^{exp t}} \quad (11)$$

Table 2 Architecture of the optimized ANN for prediction of Mw

Network type	Training algorithm	Input layer	Hidden layer		Output layer	
		No. of neurons	No. of neurons	Activation function	No. of neurons	Activation function
FFBP-ANN (<i>newff</i> MATLAB function)	<i>trainlm</i> MATLAB function	5	8	<i>tansig</i> MATLAB function	1	Linear (<i>purelin</i> MATLAB function)

Table 3 Architecture of the optimized ANN for prediction of activity

Network type	Training algorithm	Input layer	Hidden layer		Output layer	
		No. of neurons	No. of neurons	Activation function	No. of neurons	Activation function
FFBP-ANN (<i>newff</i> MATLAB function)	<i>trainlm</i> MATLAB function	5	8	<i>tansig</i> MATLAB function	1	Linear (<i>purelin</i> MATLAB function)

where N denotes the number of data points and P is the studied parameter like molecular weight or activity. In addition, the superscripts “calc” and “expt” stand for the data calculated by the models and experimental data, respectively. It should be noted that a positive $ARD(\%)$ value reflects the model overestimation, while a negative value reflects the underestimation of the model.

2. $AARD(\%)$:

$$AARD(\%) = \frac{100}{N} \sum_{i=1}^N \left| \frac{p^{calc} - p^{expt}}{p^{expt}} \right| \quad (12)$$

As a consequence, smaller $AARD(\%)$ is more desirable.

3. $RMSE$ This function reflects data dispersion around zero error line:

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (p^{calc} - p^{expt})^2} \quad (13)$$

4. SD Since this function also illustrates a criterion of data dispersion, error scattering reduces when SD is smaller.

$$SD = \sqrt{\frac{1}{N-1} \sum_{i=1}^N \left(\frac{p^{calc} - p^{expt}}{p^{expt}} \right)^2} \quad (14)$$

5. R^2 The mathematical form of this function is as below:

$$R^2 = 1 - \left[\frac{\sum_{i=1}^N (p^{calc} - p^{expt})^2}{\sum_{i=1}^N (p^{expt} - \bar{p})^2} \right] \quad (15)$$

where $\bar{p}$ stands for the average of experimental data. Values of R^2 close to 1 demonstrates good performance for a model.

3.2 Investigating applicability domain of the proposed models

In addition to error functions which were considered in the previous section, determining of applicability domain has also a great importance to evaluate the model performance. The Leverage approach as a popular method has been used in a number of researches for the purpose of outlier detection and to identify applicability domain of the models [20, 27, 42, 58–60].

Hat matrix and standardized residuals are the main concepts of Leverage approach [61] which are defined in Eqs. (16) and (17) respectively:

$$H = X(X^t X)^{-1} X^t \quad (16)$$

$$R_i = \frac{e_i}{\sqrt{MSE(1 - H_{ii})}} \quad (17)$$

In Eq. (16), X represents a $(i \times j)$ dimension matrix in which i and j are the number of data points and input variables respectively, and t is the transpose multiplier. It must be stressed that Hat values are in fact the diagonal elements of the H matrix (Leverages).

In Eq. (17) e_i refers to the deviation of model calculated data and its corresponding i th experimental data, MSE stands for the mean square of error for the proposed model and H_{ii} is the Hat index for the data point i (Leverage). To visualize and identify the suspected data or outliers, the Williams plot was used. In such figure commonly standardized residuals are plotted versus Hat values. Also a parameter called warning Leverage (H^*) is defined in Leverage method as below:

Fig. 6 Comparison between predicted data by the proposed models and experimental data for: **a** Mw and **b** Activity

$$H^* = \frac{3(p+1)}{n} \quad (18)$$

where p and n demonstrate the number of input parameters and data points, respectively.

Considering Leverage approach to judge statistically validation of a developed model, majority of hat index of data points should be in the range of $0 \leq H \leq H^*$ and $-3 \leq R \leq 3$ [53, 62]. Those group of data which are in the range of $H \geq H^*$ and $-3 \leq R \leq 3$ are considered as “Good High Leverage” which albeit are determined to be out of the applicability domain of the model but their standardized residuals are yet acceptable. On the other hand “suspected data” are data points with $R \leq -3$ or $R \geq 3$ which have large uncertainty compared to other data and locate in the outlier domain of the model.

Table 4 Statistical parameters of the proposed ANN models for estimation of Mw and activity

Statistical parameters	Value for Mw prediction	Value for activity prediction
<i>Training set</i>		
AARD%	4.48	6.58
ARD%	−2.5	6.31
RMSE	0.015	0.011
SD	3.91E−05	1.25E−06
R ²	0.99	1
Number of data points	15	15
<i>Validation set</i>		
AARD%	3.66	3.06
ARD%	3.66	2.97
RMSE	74.31	380.32
SD	0.073	0.063
R ²	0.60	0.99
Number of data points	3	3
<i>Test set</i>		
AARD%	0.25	5.23
ARD%	−0.25	−4.98
RMSE	0.069	0.35
SD	0.0001	3.98E−05
R ²	0.99	1
Number of data points	3	3
<i>Total set</i>		
AARD%	3.76	5.89
ARD%	−1.33	4.22
RMSE	0.026	0.009
SD	6E−05	1.08E−06
R ²	0.99	0.99
Number of data points	21	21

4 Results and discussion

As mentioned in previous sections, two ANN models were developed to predict Mw of the produced polymer and activity of the catalyst. A comparison between model results for both studied parameters (including average molecular weight and activity) and their correspondence experimental data is shown in Fig. 6. As seen, must data points are close to the diagonal line for both models illustrating reasonable conformity between calculated data by the proposed ANN models and experimental data. One of the main problems in ANN models is the “overfitting” issue in which the model has a good performance for train data while its performance for test data leads to wrong results. Table 4 illustrates the values of statistical parameters related to both models for train, test, validation and total data set. According to this results, the performance of both of the models for train, test, and validation is

Fig. 7 Effect of CrBIP/CrQCP molar ratio on Mw and activity ($t_p = 120$ min, ZrCP=0, FeBIP=0)

acceptable which clearly demonstrates that the models are not involved with overfitting issue.

In a valuable series of experimental studies by Mülhaupt et al. [8–10, 12, 13, 15–18, 34, 63], various multisite catalysts based on pre-catalysts in Fig. 4 have been developed which interesting results have been obtained in their experiments and observations. As one of their important and practical results, a combination of CrBIP and CrQCP on a single support can lead to a bimodal polyethylene which can be used as an additive to significantly promote HDPE mechanical properties. In this type of catalyst, CrQCP is used to produce long-chain polyethylene (i.e. UHMWPE) which is a reinforcement component for HDPE. However, the addition of UHMWPE to HDPE is a challenge due to the severe entanglement of UHMWPE and consequently high melt viscosity. This makes mixing of UHMWPE with HDPE to be impossible at high UHMWPE portions. So the CrBIP pre-catalyst is used in the multisite catalyst to produce low molecular weight polyethylene (LMWPE) to create nano-phase separation between UHMWPE chains and consequently fantastic improvement of processability is provided.

Figure 7 illustrates the effect of CrBIP/CrQCP molar ratio on Mw of polyethylene and also the catalytic system activity. For both curves, increasing the ratio of CrBIP/CrQCP leads to the decrement of the target properties. This means for a constant CrQCP concentration, as the concentration of CrBIP active site on support surface increases, not only polymers with shorter chains are produced but also the activity of catalyst will be suppressed. The CrQCP pre-catalyst is a half-sandwich (Fig. 4) chromium-based catalyst with chelating N-donor cyclopentadienyl ligand

which makes it a superior catalyst to produce ultrahigh molecular weight polyethylene [64]. Generally, the average molecular weight of the resulting PE based of this pre-catalyst lies in the range $2 \times 10^5 - 10^6$ g/mol for homogeneous polymerization, whereas higher molecular weight ranges are achieved when the pre-catalyst is immobilized on a solid support or when a modifier is used [65]. On the other hand, based on the reported data by Stürzel et al. [13] polymers produced on CrBIP pre-catalyst have low molecular weight. Thus, the predicted trend in Fig. 7 for Mw seems to be rational.

Also, since generally CrQCP has a more activity for ethylene polymerization than CrBIP [13], it is expected that increasing the molar ratio of CrBIP/CrQCP should be probably accompanied with a decrease in total activity of multisite catalyst. Such trend is observed in Fig. 7 for the model results.

The Williams plot was implemented to evaluate the reliability of the proposed ANN models, which the results can be seen in Fig. 8. As can be seen for the developed models most of the data points are in the range $-3 \leq R \leq 3$, confirming their reliability and validity from statistical point of view. It must be emphasized that due to the fact that four data points in Fig. 8.A are suspected data, the method recommends that more cautions should be considered when using this model. Also, it is worth noting that no data points have $H \geq H^*$ and thus there is no out of Leverage data.

It is worthful to note that when experimental data base for model development is small (e.g. costly and scarce experimental data for studied catalysts in this study) model validation tools become more important. In this regard,

Fig. 8 Williams plot for the proposed ANN models to identify applicability domain: **a** related to model for Mw, **b** related to model for activity

Fig. 9 Comparison of the ANN models with other AI approaches

the results of statistical functions to evaluate model accuracy and performance as well as Leverage approach to investigate applicability domain of the proposed models and outlier detection, confirmed the validity of the model. Other examples can be also found in literature which have used small data set for model development. For instance, Yildiz and Uzun [66] have developed a neural network to predict gas storage capacity of metal organic frameworks based on 13 experimental data. Although some statistical functions have been used for model validation, other statistical approaches to check applicability domain of the model have not been used in their study. Furthermore, AANs have been implemented by Anantawaraskul et al. [67] to determine the operating conditions needed to produce polyethylene with a specified microstructure based on 43 experimental data points. However, in their study neither statistical functions nor applicability domain approaches have been considered. But their cross-plot

Table 5 The optimized structures of GMDH-PNN models for MW and activity prediction

MW model
Layer 1
$N_1 = 101.345 + 8.62195x_1^2 - 0.0229752x_1^4 - 41.0123x_3$ $+ 0.00657143x_3^4 + 158.461x_4 - 2.2649e - 07x_5^4$
Layer 2
$N_2 = 322.848 - 8.01564x_2^4 - 0.00362347x_3^4 + 116.428x_4^2$ $- 24.8356x_4^3 + 7.19994e - 08x_5^4 + 4.70659e - 10N_1^4$
Output layer
$Mw = 391.251 - 12.4021x_2^4 + 4.34212e - 05x_5^3 + 0.00046328N_2^2$
Activity model
Layer 1
$N_1 = 22619.5 - 187.341x_2^4 - 0.0492045x_3^4 - 7786.08x_4^2$ $+ 1430.97x_4^4 - 233.98x_4^5 - 0.000174926x_5^3$
Layer 2
$N_2 = 481.653 + 2986.75x_2^2 - 3017.44x_3^3 + 840.304x_4^4$ $+ 42.2304x_4 - 7.632e - 09x_5^5 + 0.925525N_1$
Output layer
Activity = $6069.88 - 1393.18x_2^2 + 38.1018x_5 - 1.15532N_1$ $+ 7.1251e - 08N_2^3 - 7.25401e - 12N_2^4 + 2.02977e - 16N_2^5$
$x_1 = \text{CrBIP}(\mu\text{mol}), x_2 = \text{FeBIP}(\mu\text{mol}), x_3 = \text{ZrCP}(\mu\text{mol}), x_4 = \text{CrQCP}(\mu\text{mol}),$ $x_5 = \text{time (min)}$

between experimental data and model results exhibits reasonable performance of the developed model.

Finally, to compare ANN-LM with other AI approaches, LSSVM-CSA and GMDH-NN models were considered and their AARD(%) to predict MW and activity are shown in Fig. 9. As seen, for both properties the ANN-LM accuracy is more than others, illustrating the more flexibility of the ANN-LN model for the mentioned problem. Furthermore, the optimized structures of GMDH-NN models for MW and activity prediction are tabulated in Table 5. Although the AARD(%) of GMDH-NN models are more than ANN-LM and LSSVM-CSA, the main distinguished characteristic of GMDH-NN is obtaining explicit analytic relations as the final mathematical structure of the model which makes the model simpler and more applicable than other AI approaches. However, it must be noted that this superiority is acceptable when the accuracy is also in a reasonable range.

5 Conclusion

Many valuable experimental studies have been conducted in literature related to multisite catalysts based on metallocene and post-metallocene pre-catalysts. However, the present study deals with a new challenge

for advanced multisite catalysts to mathematically model and predict the Mw of the resulted polyethylene and also activity of ethylene polymerization catalysts. Two separate ANN models were developed according to the limited suitable experimental data. According to the results of the models, the AARD % for prediction of average molecular weight and activity were 3.76% and 5.89%, respectively. Although statistical functions as well as Leverage approach showed that proposed models in present study were reliable, but in order to develop a comprehensive model, experimental measurements of effect of temperature, pressure, pre-catalyst concentration, hydrogen response, co-catalyst concentration, co-monomer concentration and polymerization time on resulted polymer properties should be conducted. In addition, comparison of ANN-LM with other AI approaches illustrates the better accuracy and robustness of the ANN-LM model. However due to its intrinsic simplicity, the GMDH-NN models have also their own benefits. Altogether, the present study showed that the artificial intelligence approaches are promising tools to develop mathematical models to predict the performance and behavior of multisite catalysts for academic purposes, pilot plants, software and even industrial goals, though the results of such models are more reliable when experimental database is more complete.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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