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System Identification of Nylon-6 Caprolactam Polymerization Process

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ABSTRACT

The first Engineering Plastics are Polyamides or nylons and still represent the biggest and most significant class of these types of material. Nylon-6 and nylon-6, 6 are the first two commercial polyamides and are still the most important polyamides with respect to their production volumes. Modeling Nylon 6 polymerization process from first principle constitutes serious computational challenges due to the non-linear nature of the process. This work therefore developed simplified model for the process using time series modeling techniques. The steady state simulation was done using ASPEN polymer plus to measure the effect of the input variable on the outputs. The input variable was the temperature of water feed and the output variable were Caprolactam conversion, mass fraction of nylon produced in the product stream and mass flow rate of nylon 6. The steady state flow sheet was then exported to ASPEN dynamics to generate dynamic data needed for the process identification generated. The data generated from ASPEN dynamics were exported into the MATLAB environment in order to identify the process model. The two time series modeling techniques used are Nonlinear Auto Regressive with exogenous input (NARX) model and Hammerstein and Weiner model. The models developed using NARX model of the structure (10, 7, 1) for conversion gave a best fit of 71.78% while the one for mass flow rate of Nylon produced using structure (2,2,1) gave a best fit of 88.36% and that of produced Nylon 6 mass fraction using the structure (5,5,1) gave a best fit of 75.33%. The models developed using Hammerstein and Weiner for the Nylon mass fraction in the product stream using input nonlinear estimator of four (4) and output non linear estimator of two (2) gave a best fit of 77.98%, while the one of conversion of caprolactam using input nonlinear estimator of three (3) and output non linear estimator of three (3) gave a best fit of 88.67% and the produced Nylon 6 mass flow rate using input nonlinear estimator of four (4) and output non linear estimator of two (2) gave a best fit of 87.21%.

The residual analysis results show that the model is a good model because the residual autocorrelation function falls within the confidence interval of 99%. The results prove that the nonlinear ARX model and Hammerstein-Weiner model are able to capture the nonlinear dynamics behavior of the process. Nonlinear ARX model is performs better than Hammerstein-Weiner for Nylon 6 mass flow rate while Hammerstein -Weiner model performs better Nonlinear ARX for Caprolactam conversion and Nylon 6 mass fraction.

Keywords: NARX, System identification, nonlinear dynamics, ASPEN Tech, MATLAB, Hammerstein and Weiner

1. INTRODUCTION

The most essential polyamides with respect to their production volumes are nylon-6 and nylon-6,6. These polyamides account for more than 95% of the total amount of nylon used in the world, and nylon-6 is responsible for 59% of this quantity[1].

One of the commercial routes of producing nylon 6 is the hydrolytic polymerization of Caprolactam. The process involves the polymerization of caprolactam in the presence of water and it can be carried out batch wise or continuously [2]. Continuous process is usually carried out by using conventional column reactor called VK (Vereinfacht Kontinuierliches). VK column reactor is essentially a vertical tube operating at atmospheric pressure [12]. Due to its configuration, modeling this reactor from first principle might lead to highly complex model that cannot be useful for online application such real-time optimization and control.

Black box modeling, which is a data based approach, can provide alternative route to obtain moderately simplified model that can be employed for control design and implementation. Linear or nonlinear black –box techniques are commonly used control strategies for modeling the relationship between process input and output variables. The complexity and the uncertainty associated with the physical system are avoided through this means [8].

Black-box models, which are widely used in industries, are formulated using experimental data sets or field operation data sets with no requirement for a priori knowledge (such as fluid dynamics, thermal dynamics or chemical reactions, conservation law, kinetics data). Black-box models can be static and dynamic, linear and nonlinear regression models. Among the black box models are the families of basic ARX (Autoregressive model with exogenous input) or NARX (non-linear ARX) model structures [3]. A variant of this is combination of linear and nonlinear models arranged in series to improve predictive

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performance. Hammerstein-Weiner model belongs to this category. Black box modeling approaches have been employed to solve many chemical processes.

Recent work involving black box modeling are shown below [10] used least square criterion and neural network to identify ARX and NARX models respectively for prediction of dynamic process behavior of a reactor exchanger unit. [15] Worked on adaptive filter based on NARX model for recorded audio noise removal. The fitting and residual test shows that NARX model was good in estimating and filtering out noise well.

[5] also worked on the modeling of multivariable chemical processes using NARX structure with neural network as nonlinear regressor. [6] developed an input constrained non linear model predictive controller in a latent space through the use of partial least squares (PLS) based Hammerstein-Weiner models. [9] Used an iterative method for Weiner-Hammerstein systems parameter identification. [14] Worked on identification and control of Weiner type non linear processes. The effectiveness and simplicity of the proposed identification and control method was shown by the simulation examples. An identification and control method was proposed. [13] Developed and illustrate a new maximum likelihood based method for identification of Hammerstein model structures.

Dynamic data for polymerization are not easily obtained because of the sophisticated nature of the plant used for the process. However, simulated data from commercial software can be used as alternative. Many simulation works are found in literature on polymerization processes. [7] Simulated a reactor system for the production of alpha olefins (C_4 - C_{16}) by an ethylene oligomerization reaction using ASPEN. The kinetic data needed by ASPEN was obtained from literatures and experimentation. The product composition obtained through experimentation was compared with the simulation result. It was found out that the simulation result correlated with the experimental work. [11] modeled a semi batch reactor system used for production of olefins using, ASPEN. In this process they used a nickel based catalyst. Their model was developed to explain the differences between the data generated in the lab and the one collected in the plant. This model was then latter used to predict the behavior of some reaction in a series of flow reactors and its importance in future product development. [16] in his PhD thesis worked on research and development of simulation and optimization technology for commercial nylon 6 process. ASPEN polymer plus was used for the simulation.

2. PROCESS DESCRIPTION

The polymerization process for Nylon 6 can be batch or continuous, however the state of the art process for its manufacture is continuous polymerization. For a continuous process, Nylon 6 is usually produced in a

Vereinfacht Kontinuierliches VK column reactor which is a vertical tube operating at atmospheric pressure. Caprolactam, water and stabilizer are fed to the top of the VK column continuously. The diagram of the VK column is shown in Figure 1. The mechanics controlling water initiated polymerization is governed by five steps. These include: formation of caproic acid through ring opening of caprolactam; amide linkage formation from polycondensation reaction; polyaddition reaction of caprolactam with the amine end group of a polymer chain; formation of linear dimer through ring opening of cyclic dimer; and polyaddition reaction of a cyclic dimer to the amine end group of a polymer. The overall reaction is illustrated in Figure 2. The ring opening reaction initiates polymerization in zone 1 and there is evaporation of excess water in this zone. Polymerization proceeds under near adiabatic condition in zone 2. Water is not evaporated in this zone.

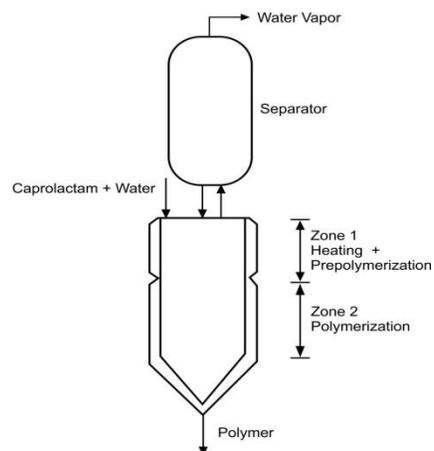


Fig 1: Vereinfacht Kontinuierliches (VK) Column

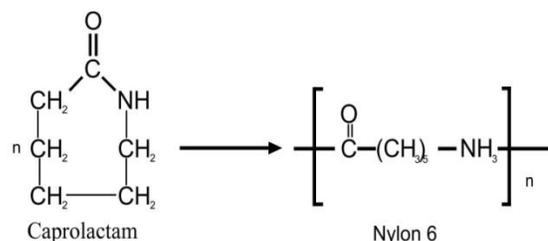


Fig 2: Overall reaction of caprolactams polymerization to Nylon 6

2.1 Steady and Dynamic State Simulation

The steady state model of process was simulated using ASPEN plus environment as shown in Figure 2. In the simulation the top portion of the VK column was modeled as two continuous stirred tank reactors CSTR1 and CSTR2. The bottom portion of the zone 2 was modeled as a plug

flow reactor. A flash tank was inserted after each stirred tank in zone 1 to account for the Vapour Liquid Equilibria calculations. The plug flow reactor was considered to be liquid filled. Figure 3 shows the process flow diagram. The condition of the process feed is shown in Table 1 while the operating condition is shown in Table 2.

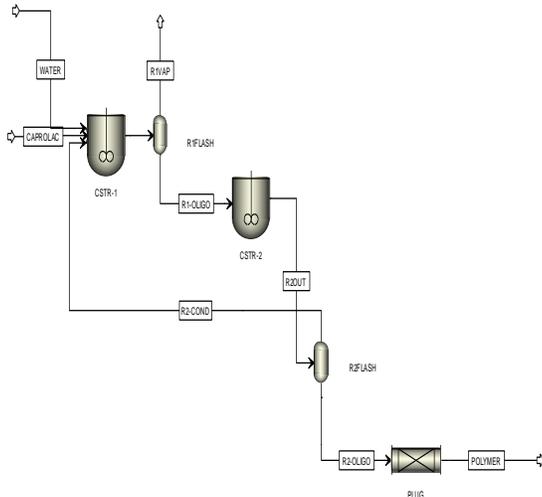


Fig 3: ASPEN Simulation of the process

Table 1: Conditions of process feed

Condition	Caprolactan	Water
Temperature (°C)	260	260
Pressure (atm)	1	1
Flowrate (kg/hr)	39.6	0.4
Seed	12345	

Source: [12]

The simulation was then exported to the dynamic environment of ASPEN. The pseudo random binary system (PBRs) was added to manipulate the water feed temperature (input variable) in order to monitor the effect on conversion of caprolactam, mass fraction of nylon 6 formed, mass flow rate of nylon 6 (output variables). The PBRs configuration is as shown in the Table 3

Table 3: PBRs Configuration

Property	Value	Units
Amplitude type	Variable	
Datum	250	°C
Amplitude	100	°C
Period	30	Min
Seed	12345	

3. MODEL STRUCTURE

3.1 Non linear ARX Model

An extension of the Linear ARX Structure is the Nonlinear ARX Model. A nonlinear ARX model can be understood as an extension of a linear model. The structure of a non linear ARX is shown in Figure 4

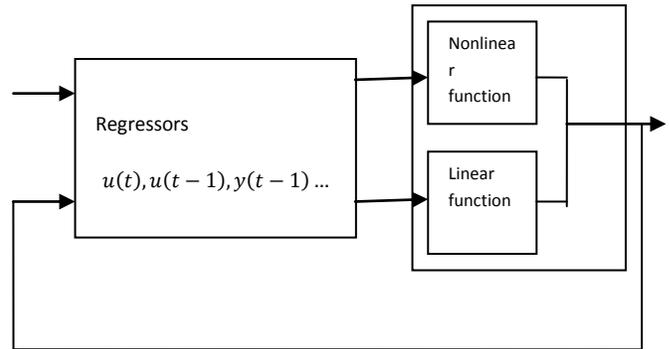


Fig 4: Structure of non linear ARX system

A linear SISO ARX model has this structure [17]

$$y(t) + a_1y(t-1) + a_2y(t-2) + \dots + a_nay(t-na) = b_1u(t) + b_2u(t-1) + \dots + b_nbu(t-na-nb+1) + e(t) \quad (1)$$

Where: y and u are output and input data,
 t is the discrete time instant
 na is the number of autoregressors
 nb is the number of exogenous regressors
 nk are the delay from input to output in terms of number of samples
 $e(t)$ is the modeling error

Non linear ARX model use non linear mapping f between the input and output data, rather than a weighted sum that represents linear mapping

$$y(t) = f[y(t-1) + y(t-2) + \dots + y(t-na), u(t) + u(t-1) + \dots + u(t-na-nb+1)] + e(t) \quad (2)$$

Where f is a nonlinear function. Inputs to f are model regressors.

The non linear function use in this work is wavenet. A non linear function $y=F(x)$ is usually defined by wavenet. x is an m dimensional row vector and y is scalar. Wavenet network function is represented by the following expansion. [17]

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$$\begin{aligned}
 F(x) = & (x - r)PL + a_{s-1} f \left(b_{s-1} \left((x - r)Q - c_{s-1} \right) \right) + \\
 & a_{s-n_s} f \left(b_{s-n_s} \left((x - r)Q - c_{s-n_s} \right) \right) + \\
 & a_{w-1} g \left(b_{w-1} \left((x - r)Q - c_{w-1} \right) \right) + \\
 & a_{w-n_w} f \left(b_{w-n_w} \left((x - r)Q - c_{w-n_w} \right) \right) + \\
 & d \tag{3}
 \end{aligned}$$

Where f is a scaling factor; g is the wavelet function; P and Q are m by p and m by q projection matrices respectively.

Principal component analysis of estimation data are used in determining P and Q which are the projection matrices. $P < m$ if the estimation data are linearly dependent but mostly $p = m$. The number of columns of Q , q , corresponds to the number of x used in the scaling and wavelet function. q is equal to the size of the nonlinear regressors property of the nonlinear system when it is used in a non linear ARX model.

r represents the mean value of the regressor vector computed from estimation data and is a m by m' vector; d, a_s, b_s, a_w, b_w are scalars. Parameters with the w subscript are wavelet parameters while parameters with the s subscript are scaling parameters; L is a P -by-1 vector; c_s and c_w are 1-by- q vectors. The wavelet function g and the scaling function are both radial function.

$$g(x) = (N_r - xx^r)e^{-0.5xx^r} \tag{4}$$

$$f(x) = e^{-0.5xx^r} \tag{5}$$

3.2 Hammerstein and Wiener

The Hammerstein-Wiener system has a cascade connection of a static nonlinearity block N1, a linear dynamic system LS after it which is then followed by a static nonlinearity block N2 [9]. The noiseless case is shown in Figure 5.

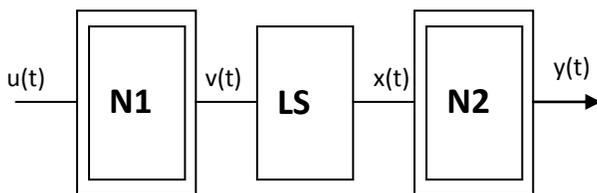


Fig 5: Structure of Hammerstein-Wiener systems

The first nonlinear static block is characterized by the mapping $f(\cdot)$:

$$v(t) = f[u(t)] \tag{6}$$

Where $u(t)$ and $v(t)$ are the inputs and outputs, respectively. The difference equation model of the linear dynamic block is:

$$x(t) = B(q^{-1})v(t) + [1 - A(q^{-1})]x(t) \tag{7}$$

Where $v(t)$ and $x(t)$ are the inputs and outputs, respectively, $A(q^{-1})$ and $B(q^{-1})$ are scalar polynomials in the unit delay operator q^{-1}

$$A(q^{-1}) = 1 + a_1q^{-1} + \dots + a_mq^{-m} \tag{8}$$

$$B(q^{-1}) = b_0 + b_1q^{-1} + \dots + bnq^{-n} \tag{9}$$

The second nonlinear static block is characterized by the mapping $g(\cdot)$:

$$y(t) = g[x(t)] \tag{10}$$

The second nonlinear block can be decomposed and written as follows:

$$y(t) = g_1x(t) + g'[x(t)] \tag{11}$$

where the internal variable $x(t)$ is separated.

The linear dynamic block equation can be written as

$$x(t) = b_0v(t) + [B(q - 1) - b_0]v(t) + [1 - A(q - 1)]x(t) \tag{12}$$

Where the internal variable $v(t)$ is separated.

The resulting output equation of the Hammerstein-Wiener model will be where the internal variable $v(t)$ is separated.

The resulting output equation of the Hammerstein-Wiener model will be

$$y(t) = g_1\{b_0f[u(t)] + [B(q^{-1}) - b_0]v(t) + [1 - A(q^{-1})]x(t)\} + g'[x(t)] \tag{13}$$

The model blocks features are directly projected into the model description through $f(\cdot)$ for N1, $A(q^{-1})$ and $B(q^{-1})$ for LS, and through $g'(\cdot)$ for N2. The model output equation can be significantly simplified through proper parameterizations of the two nonlinear blocks which might possibly lead to the linearity in all the model parameters [9].

4. RESULTS AND DISCUSSION

4.1 Model Output Results

Figure 6, Figure 8 and Figure 10 shows the model output for conversion, produced nylon 6 mass flow rate, and

produced nylon 6 mass fraction respectively using Non linear Autoregressive and Exogenous input (NARX) model. Comparison of the measured output with the simulated output as shown in Figure 6, Figure 8 and Figure 10 gave a fit of 71.78 for conversion (Using Autoregressors (na) of ten(10), Exogenous regressors (nb) of seven(7), Delay from input to output(nk) of one(1) and non linearity estimator: wavenet=72 units), 88.36% for produced nylon 6 mass flow rate(Using Autoregressors (na) of two(2), Exogenous regressors (nb) of two(2), Delay from input to output(nk) of one(1) and non linearity estimator: wavenet=6 units) and 75.33% produced nylon 6 mass fraction(Using Autoregressors (na) of five(5), Exogenous regressors (nb) of five (5), Delay from input to output(nk) of one(1) and non linearity estimator: wavenet=84 units).

Figure 7 shows the model output for conversion using Hammerstein-Weiner model. The fit of the measured output with the simulated output gave a fit of 88.67% using input nonlinear estimator piecewise linear with three units (3), output nonlinear estimator piecewise linear with three units (3) and a linear transfer function corresponding to the orders nb=2, nf=3 and nk=1. For mass flow rate of nylon-6 produced, Hammerstein and Weiner model using input nonlinear estimator piecewise linear of four units (4) and output nonlinear estimator piecewise linear of three units (3) and a linear transfer function corresponding to the orders nb=2, nf=3 and nk=1 gave a fit of 87.21%. This is shown in Figure 9.

Figure 11 shows the model output for conversion using Hammerstein-Weiner model. The fit of the measured output with the simulated output gave a fit of 77.98% using input nonlinear estimator piecewise linear with four units (4), output nonlinear estimator piecewise linear with two units (2) and a linear transfer function corresponding to the orders nb=2, nf=3 and nk=1. nb and nf are the orders of the error output model while nk is the delay.

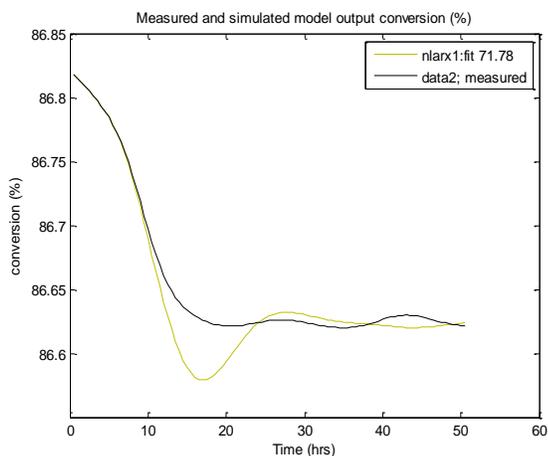


Fig 6: Model and simulated Output (conversion) Correlation (using nonlinear ARX)

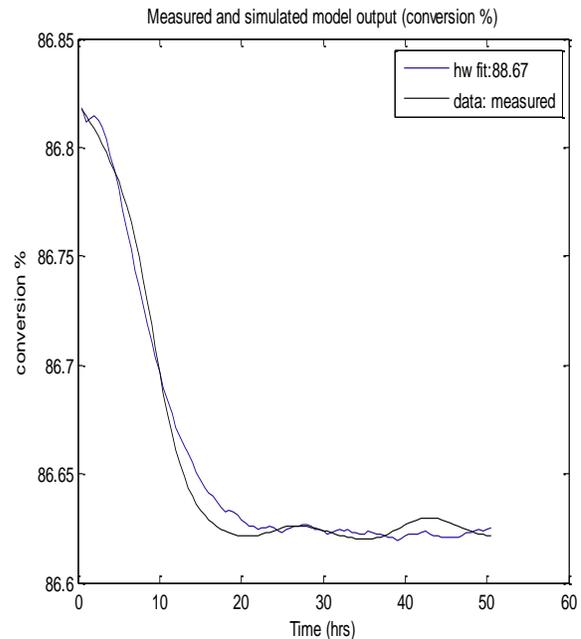


Fig 7: Model and Simulate conversion correlation (Using Hammerstein-Weiner)

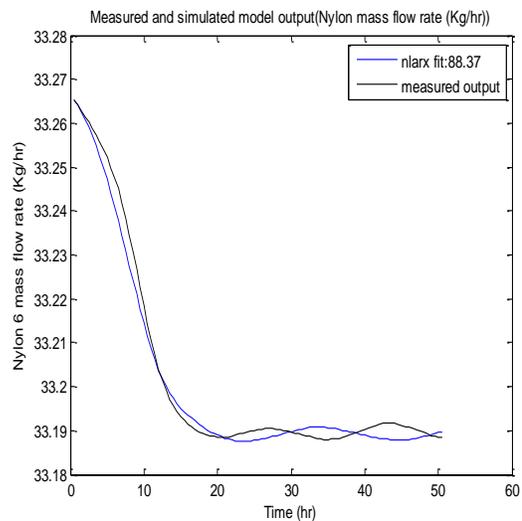


Fig 8: Plots of Measured and Simulated Outputs (Nylon mass flow (Kg/hr)) (Using non linear ARX model)

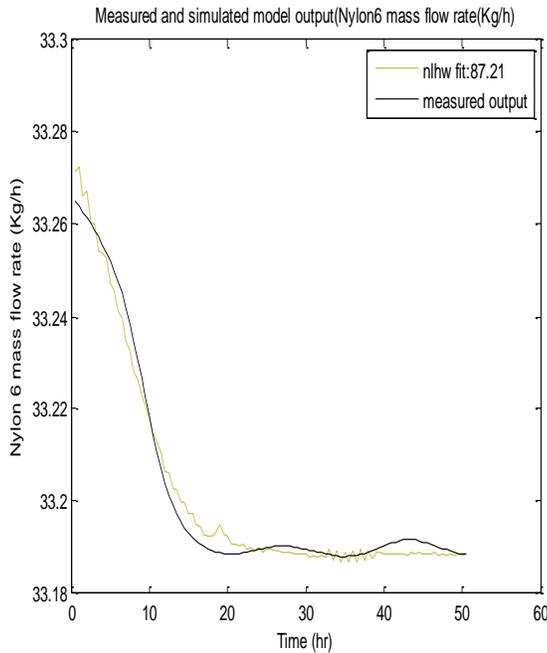


Fig 9: Plots of Measured and Simulated Outputs (Nylon mass flow (Kg/hr)) (using Hammerstein-Weiner model)

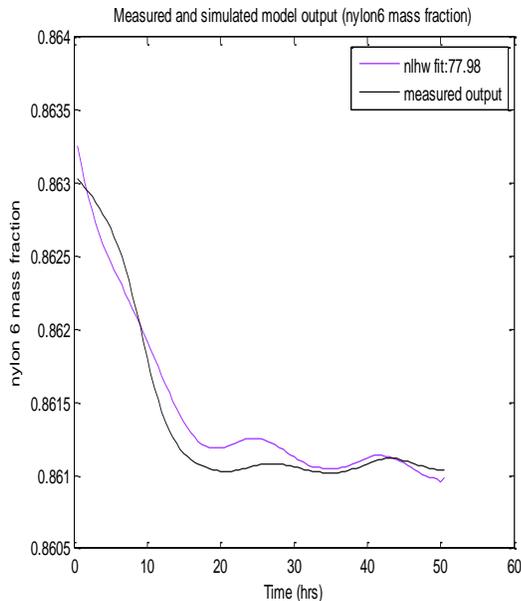


Fig 10: Model and Simulated Output (Mass fraction of Nylon) Correlation (using Hammerstein-Weiner model)

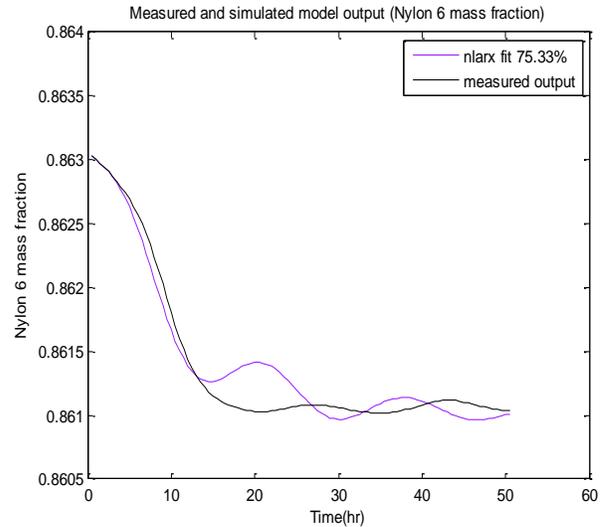


Fig 11: Model and Simulated Output (Mass fraction of Nylon) Correlation (using non linear ARX model)

It can be seen from the result above that Non linear ARX model performs better than Hammerstein Weiner model for Nylon 6 flow rate therefore Non linear ARX model is a suitable model for Nylon 6 mass flow rate while Hammerstein - Weiner model out performs Non linear ARX for caprolactam conversion and produced nylon 6 mass fraction therefore Hammerstein -Weiner model is suitable for caprolactam conversion (%) and Nylon 6 mass fraction.

4.2 Results of Residual Analysis

Figures 12 - 17 show the autocorrelation function for the residuals as well as the cross correlation functions between input and residuals. Figure 12 and 13 shows autocorrelation of residuals for output conversion (%) and cross correlation for input temperature of water feed and output caprolactam conversion (%) residual, Figure 14 and 15 shows autocorrelation of residuals for output (nylon mass fraction) and cross correlation for input temperature of water feed and output (nylon mass fraction) residual while Figure 16 and 17 shows autocorrelation of residuals for output (nylon mass flow rate) and cross correlation for input temperature of water feed and output (nylon mass flow rate) residual.

For the result of the residual analysis shown in Figure 12 to figure 17 have the confidential interval for this work is set as 99%. The confidential interval for these functions is shown as dashed lines.

The top axis of Figure 12 to Figure 17 shows the whiteness test while the bottom axis shows the independent test. The time difference (in samples) between the signals at which the correlation is estimated is the number of lags. This constitutes the horizontal scale. The whiteness test for Hammerstein- Weiner and nonlinear ARX show that the

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residuals are uncorrelated because they fall within the confidential interval. Also there is no correlation between the residual and the inputs when the independence test was performed because they also fall within the confidential interval. These tests prove that Hammerstein-Weiner and Nonlinear ARX are good models for this work.

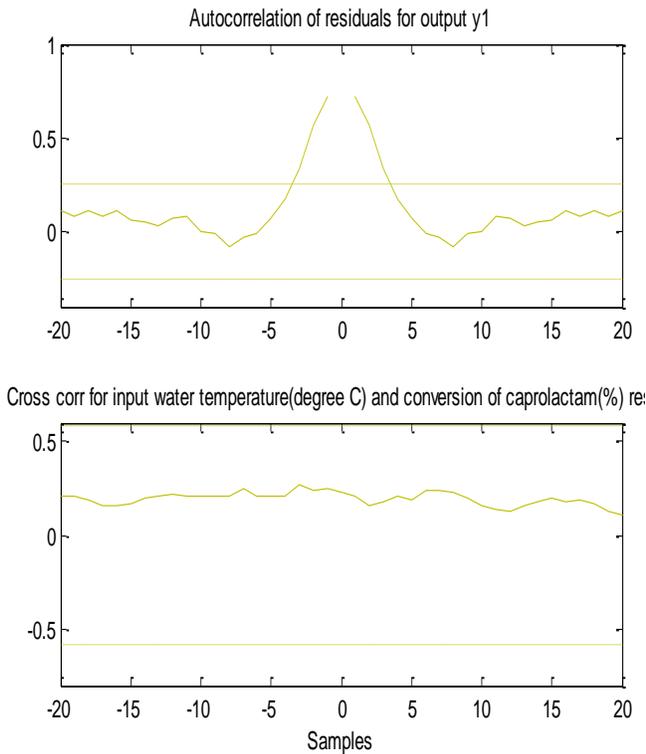


Fig 12: Autocorrelation of residuals for Output Conversion of caprolactam and cross Correlation for input water feed temperature and Output percentage conversion of caprolactam residual (using Non linear ARX model)

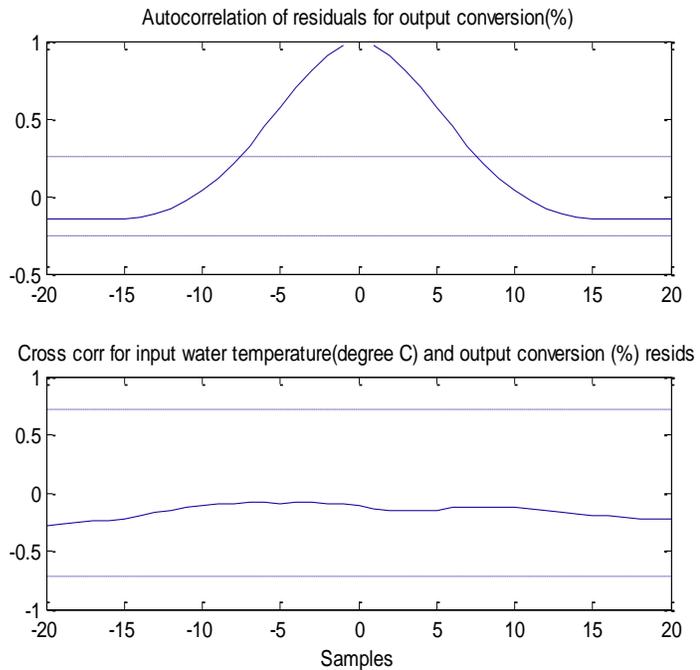


Fig 13: Autocorrelation of residuals for Conversion of caprolactam and cross Correlation for water feed temperature and percentage conversion of caprolactam residual (using Hammerstein-Weiner model)

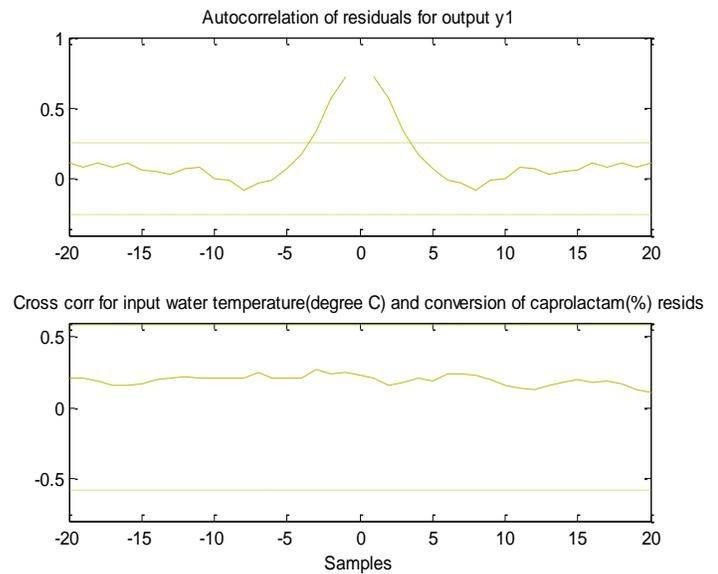


Fig 14: Autocorrelation of residuals for Output mass fraction of Nylon and cross Correlation for input water feed temperature and Output mass fraction of Nylon-6 residual (Using Hammerstein-Weiner model)

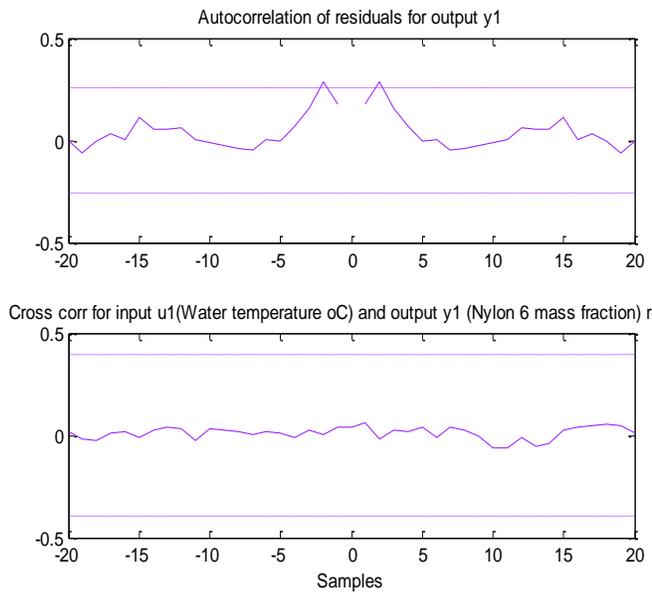


Fig 15: Autocorrelation of residuals for mass fraction of Nylon and cross Correlation for input water feed temperature and mass fraction of Nylon-6 residual (Using non Linear ARX model)

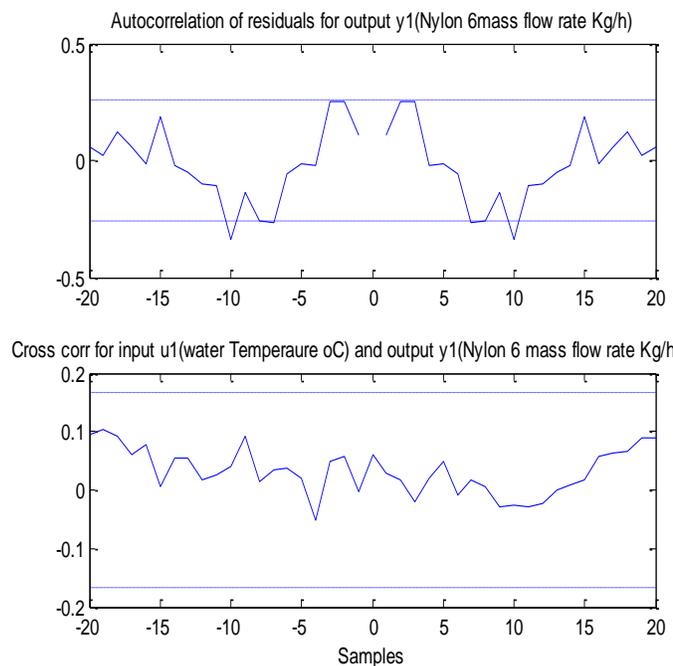


Fig 16: Autocorrelation of Residuals for Nylon mass flow rate And Cross Correlation For Input Water Feed Temperature And Output Nylon Mass Flow Rate Residual (Using non linear ARX).

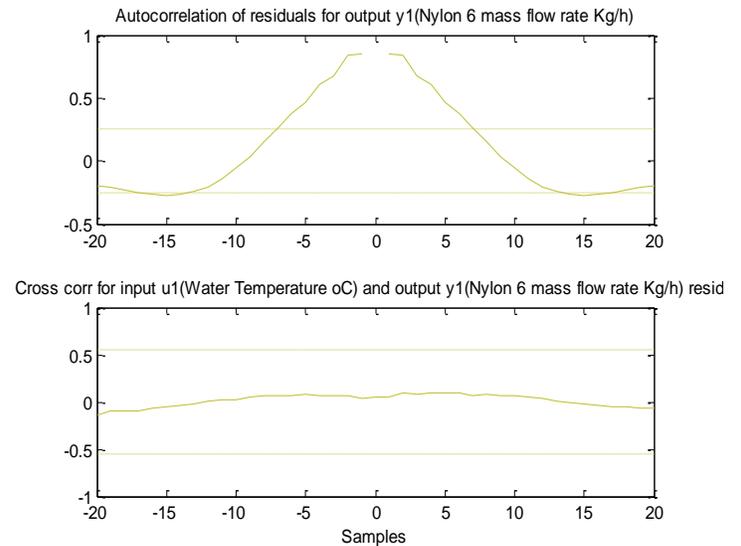


Fig 17: Autocorrelation of Residuals for Nylon mass flow rate And Cross Correlation for Input Water Feed Temperature and Nylon Mass Flow Rate Residual (Using Hammerstein and weiner model)

5. CONCLUSION

It can be concluded from the obtained Residual Analysis results that both Hammerstein- Weiner and Non Linear Autoregressive with exogenous input are good models for this process. The model output results show that Hammerstein –Weiner model is able to capture the relationship between feed water temperature s and caprolactam conversion. It is also able to capture the relationship between feed water temperature and produced Nylon 6 mass fraction while Non linear Autoregressive with exogenous input model is able to capture the relationship between feed water temperature and mass flow rate of nylon 6 produced.

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