NEURAL NETWORK MODELS AND SENSITIVITY ANALYSIS FOR THE PRODUCTION OF ISOPROPYL MYRISTATE IN SEMIBATCH REACTIVE DISTILLATION

by

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LIST OF ABBREVIATIONS

ANFIS	Adaptive neuro-fuzzy interface system
ANN	Artificial Neural Network
BA	Butyl acetate
BRD	Batch reactive distillation
BRMV	Batch reactive middle vessel
BRR	Batch reactive rectifier
BRS	Batch reactive stripper
CBD	Conventional batch distillation
CRBD	Conventional reactive batch distillation
D	Distillate rate
Da	Damkohler number
DAE	Differential algebraic equation
EA	Ethyl acetate
EG	Ethylene Glycol
EO	equation oriented
EPP	Entry point project
EQ	Equilibrium stage model
ETP	Economic Transformation Programme
FF	Feedforward
FFNN	Feedforward neural network
H_2O	Water
IBD	Inverted batch distillation
IP	Isopropanol

IPA	Isopropyl acetate
IPM	Isopropyl myristate
k-mc	K-mean clustering
LA	Lactic acid
LM	Levenberg-Marquardt
M	Methanol
MA	Methyl acetate
MESH	Material, equilibrium relationship, summation and heat balance
MIMO	Multiple inputs - multiple outputs
MISO	Multiple inputs - single output
MM	Methyl myristate
MSE	Mean square error
NARMAX	Non-linear auto-regressive moving average with exogenous input
NARX	Non-linear auto-regressive exogenous
NRTL	Nonrandom two liquid models
ODE	Ordinary differential equation
PAEE	Ethyl ester pentanoic acid
PLS	Partial least squares regression
p-nn	p-nearest clustering
Q-N	Quasi network
RBF	Radial basis function
RD	Reactive distillation
SBRD	Semibatch reactive distillation
SDRMV	Semicontinuous distillation with chemical reaction in middle vessel

VLE	Vapor-liquid equilibrium
VRRBD	Vapor compression reactive batch distillation

LIST OF SYMBOLS

		Unit
E_H	Forward activation energy	J/mol
E_R	Reverse activation energy	J/mol
F	Feed flow rate	kmol/h
K_H	Forward reaction rate constant	m^3/mol·h
K_R	Reverse reaction rate constant	m^3/mol·h
$n_{,IP}$	Amount of isopropanol in reboiler	kmol
$n_{,IPM}$	Amount of isopropyl myristate in reboiler	kmol
$n_{,M}$	Amount of methanol in reboiler	kmol
$n_{,MM}$	Amount of methyl myristate in reboiler	kmol
$n_{IP,o}$	Initial batch charge of isopropanol	kmol
$n_{M,o}$	Initial batch charge of methanol	kmol
$n_{MM,o}$	Initial batch charge of methyl myristate	kmol
Q_b	Reboiler duty	Gcal/h
R^2	R-squared value	-
RR	Reflux ratio	-
t_b	Main cut period	h
T_k	Temperature at stage k	°C
x	Actual state variable	-
x_μ	Mean of state variable	-
x_B	Bottom composition	kmol/kmol
x_D	Distillate composition	kmol/kmol
x_{IPM}	Isopropyl myristate composition	kmol/kmol

x_M	Methanol composition	kmol/kmol
x_σ	Standard deviation of state variable	-
y	Normalized state variable	-

Greek Letters

σ	Standard deviation	-
μ	Mean	-

MODEL RANGKAIAN NEURAL DAN ANALISIS KEPEKAAN UNTUK PENGHASILAN ISOPROPIL MIRISTAT DALAM PENYULINGAN REAKTOR SEPARA KELOMPOK

ABSTRAK

Isopropil miristat (IPM) adalah bahan kimia yang penting di dalam industri kosmetik dan farmaseutikal. IPM boleh dihasilkan sama ada melalui proses pengesteran atau proses transesterifikasi dengan menggunakan penyulingan reaktor separa kelompok (BRD). Walau bagaimanapun, proses transesterifikasi masih kurang diselidik secara meluas. Proses transesterifikasi di dalam BRD boleh diterjemahkan melalui persamaan matematik, walau bagaimanapun, persamaan ini akan menghasilkan banyak persamaan pembezaan dan kos yang tinggi serta memerlukan masa yang lama untuk diselesaikan. Oleh itu, model empirik seperti rangkaian neural tiruan (ANN) menawarkan penyelesaian yang lebih baik kerana kebolehannya menyelesaikan struktur yang sangat tidak lelurus dan kompleks.

Di dalam kerja ini, penghasilan IPM didalam BRD yang berskala industri melalui proses transesterifikasi telah disimulasi menggunakan Aspen Plus dan hasil simulasi menunjukkan keputusan yang setanding seperti yang dilaporkan dalam kajian lepas. Model yang telah disahkan ini kemudiannya digunakan untuk analisis kepekaan bagi menentukan hubungan antara pembolehubah masukan-keluaran. Ujian tidak berparameter digunakan dan pembolehubah masukan terpilih disusun mengikut kedudukan masing-masing berdasarkan kepada kepekaan purata keseluruhan. Berdasarkan keputusan, duti pengulang didih, bilangan mol awal isopropanol, metil miristat, nisbah refluk, kadar suapan masuk dan suhu dulang 32 dipilih sebagai

pembolehubah masukan dalam pembangunan model ANN bagi menganggar komposisi bawah dan komposisi sulingan.

Enam ANN model yang terdiri daripada dua model berbilang-masukan berbilang-keluaran (MIMO) iaitu (MIMO-1, MIMO-2) dan empat model berbilang-masukan satu keluaran (MISO) iaitu (MISO-1, MISO-2, MISO-3, MISO-4) telah dibangunkan. Reka bentuk rangkaian optimum yang diperolehi adalah untuk MIMO-2, MISO-2 dan MISO-4 adalah masing-masing [12-12-2], [11-12-1] dan [11-11-1]. Model MIMO-2 menunjukkan prestasi yang memuaskan apabila disahkan dengan data pengesahan dimana MSE adalah 0.0006 dan R^2 adalah masing-masing 1.0000 dan 0.9998 untuk komposisi bawah (x_B) dan komposisi sulingan (x_D). Kedua-dua model iaitu MISO-2 dan MISO-4 juga berjaya meramal dengan tepat apabila diuji dengan data ujian dengan nilai masing-masing MSE 0.0004 dan 0.0007 serta nilai R^2 bagi kedua-dua model adalah 0.9998. Model MIMO-2 juga diuji dengan data ujian beserta dengan gangguan . Keputusan menunjukkan model tersebut dapat meramal nilai sebenar dengan MSE 0.0124 manakala R^2 menunjukkan 0.9924 untuk x_B dan 0.9953 untuk x_D.

Dengan menggunakan model yang optimum, kajian keupayaan ekstrapolasi telah dilakukan untuk menilai keupayaan model meramal data yang di luar daripada julat data latihan. Keputusan menunjukkan model MIMO-2 dan MISO-2 mempunyai padanan yang baik apabila diuji dengan data ekstrapolasi 1, dengan ketepatan MSE yang dicapai adalah masing-masing 0.0078 dan 0.0063 untuk MIMO-2 dan MISO-2. Nilai R^2 yang diperolehi untuk MIMO-2 dan MISO-2 masing-masing adalah 0.9986 dan 0.9975. Walau bagaimanapun, data ekstrapolasi 2 menunjukkan padanan yang

lebih baik di mana semua model ANN yang di uji menunjukkan MSE kurang daripada 0.0005 dengan nilai R^2 bersamaan dengan 0.999.

NEURAL NETWORK MODEL AND SENSITIVITY ANALYSIS FOR THE PRODUCTION OF ISOPROPYL MYRISTATE IN SEMIBATCH REACTIVE DISTILLATION

ABSTRACT

Isopropyl myristate (IPM) is an important chemical in the cosmetic and pharmaceutical industries. The IPM can be produced either through esterification or the transesterification process in semibatch reactive distillation (BRD). However, the latter process is not widely explored. The transesterification process in BRD can be represented by a mathematical model, however, this model will end with a large number of differential equations and be very expensive to solve and will also be time consuming. Hence, the empirical model such as the artificial neural network (ANN) model provides better solution as it can deal with highly nonlinear and complex structures.

In this work, the production of industrial scaled IPM in BRD through the transesterification process is simulated using Aspen Plus and the simulation result achieved shows a comparable result as reported in the literature. The validated model is then used for sensitivity analysis to determine the relationship between the process input-output variables. The nonparametric test is used and the selected inputs are ranked according to their mean overall sensitivity. From the results, the reboiler duty, the initial mole of isopropanol, methyl mysistate, the reflux ratio, the feed flowrate and the temperature at stage 32 are considered as the input variables in the ANN model development to predict the bottom and distillate composition.

Six ANN models which consisted of two multiple inputs-multiple outputs (MIMO) models (MIMO-1, MIMO-2) and four multiple inputs-single output (MISO) models (MISO-1, MISO-2, MISO-3, MISO-4) were developed. The optimum network architecture obtained were [12-12-2], [11-12-1] and [11-11-1] for MIMO-2, MISO-2 and MISO-4, respectively. The MIMO-2 model performed satisfactorily with the validation data and provided MSE of 0.0006 and R^2 of 1.0000 and 0.9998 for the bottom composition (x_B) and the distillate composition (x_D), respectively. Both MISO-2 and MISO-4 models also managed to accurately predict the testing data with MSE value of 0.0004 and 0.0007, respectively with R^2 value for both models of 0.9998. The MIMO-2 model also tested with the noise in the output data. The result shows that the model can predict the true value with MSE achieved 0.0124 while R^2 shows 0.9924 for x_B and 0.9953 for x_D.

By using the optimum models, the extrapolation capability study was performed to evaluate the model ability to predict the out of training range data. The result showed MIMO-2 and MISO-2 have good generalization when tested with extrapolation data 1, with MSE accuracy achieved at 0.0078 and 0.0063 for MIMO-2 and MISO-2, respectively. The respective R^2 obtained for MIMO-2 and MISO-2 were 0.9986 and 0.9975, respectively. However, better generalization was obtained for extrapolation data 2 where all the ANN models showed MSE less than 0.0005 with R^2 equaled to 0.999.

CHAPTER 1

INTRODUCTION

1.1 Research background

Fatty esters are natural based chemicals used in different areas and applications, such as the food industry, the cosmetic industry, solvents, plastics, pharmaceuticals and other applications. Fatty ester is produced by the fatty acid and is one resource that is not greasy and provides an environmentally safer function. Thus, they are expected to be the main demand of countries that have a strict environmental policy. One of the fatty esters that are widely used in the industries is isopropyl myristate.

1.1.1 Isopropyl Myristate

Isopropyl myristate (IPM) is a synthetic oil widely used in the cosmetics and pharmaceutical industries as a lubricant and an emollient. IPM is favourable in the cosmetic and pharmaceutical industries due to its less greasy nature and easily absorbed by the skin. One application of IPM as a phamaceutical product is its use as a non-pesticide alternative for treating head lice infestations (Scott and Halprin, 2012). IPM is commonly manufactured by esterification and alternatively by the transesterification process. IPM is colourless and mild in odor. It is also commonly used as an additive in oral hygiene products such as mouthwash. Due to the demand of IPM as an ingredient in specialty products, the demand in the production of IPM has increased.

Its can be seen from the change of goverment direction to develop the down-stream sector of the palm oil industry. One of the aims is to expend the production of high value oleo derivatives under the Entry Point Project (EPP) 6 (Yakcop and Jala, 2011). The same scenario is observed in the global market, as reported by Global Industry Analysts, Inc. operating in California U.S.A. According to the report, the fatty esters market demand is expected to increase by the year 2015. The key factors driving market growth include a wide application offered by fatty esters in the industrial arena, eco-friendly characteristics, and increased demand from the developing Asia-Pacific market (Global Industy Analysts, 2012).

1.1.2 Neural network application in batch reactive distillation

Batch reactive distillation (BRD) is a dynamic process and operates in unsteady state condition. In this process, couple reaction and distillation process leads to the complex relationship which involve the thermodynamic equilibrium and chemical equilibrium at every stages. For modelling the nonlinear process, three different model structures can be used i.e. white box models, empirical models and hybrid models. The fundamental models is derived from the mass, the energy and the momentum balance, while empirical models used existing monitoring data in the plant without priori knowledge of process behaviour and hybrid models combine both fundamental and empirical models. Once a dynamic model has been developed, the model can be solved using numerical software such as FORTRAN®, gPROMS®, Matlab® and modular software such as Aspen plus®.

Developing a theoretical rigorous model may not be practical for the complex process as BRD and as an alternative approach is developing an empirical model.

Artificial neural network (ANN) model is one of the available empirical models. It is used to solve various mathematical problems in BRD such as in modelling (Reusch et al., 2001; Osorio et al., 2004), control system (Engell and Fernholz, 2003), soft sensor (Bahar and Özgen, 2010; Jithin Prakash et al., 2011), combination of soft sensor and control (Konakom et al., 2010a, 2011) and optimization (Mujtaba and Greaves, 2006) application due to its ability to predict the highly nonlinear functions effectively. The ANN is relatively less sensitive to the noise and unknown information and also can deal with higher level of uncertainty. Thus, self-learning ability of ANN eliminates the use of complex mathematical model (Malar and Thyagarajan, 2009).

1.2 Problem statement

The growing importance of specialty chemicals makes batch process more attractive. The batch process is utilized especially for the production of low volume, high value specialty chemicals, and high flexibility seasonal products. Typically, this process is used to produce chemicals, food, and in the cosmetic and pharmaceutical industries where flexibility is required. The process regularly consists of the batch reactor and followed by the distillation column for separation. Recently, more attention is given to process intensification which couples reaction and distillation in a single unit.

The batch reactive distillation (BRD) process is recommended especially for reversible esterification and the transesterification process to enhance yield and selectivity. The removal of one component continuously can avoid reaction equilibrium restrictions due to reaction rate enhancement. Modeling the BRD has

been a challenging task since it involves many components incorporated with large numbers of parameters. The purpose of mathematical modeling is to express the real process by representative mathematical equations.

Recently the BRD model has gained more attention in various aspects such as feasibility study, mathematical model, optimization and control. There is intensive literature on the white box model which includes complex mathematical models and simplified models on the esterification process such as ethyl acetate, butyl acetate, methyl acetate, hydrolysis of lactic acid and isopropyl acetate. However, there is limited literature that covers the industrial scaled batch esterification process.

The modeling of the transesterification process for long chain fatty esters in the reactive distillation (RD) is scarce. Only a few works on this subject has been reported in the literature. Li et al., (1998a), (1998b) and Arellano-Garcia et al., (2002), (2008) studied the transesterification of methyl myristate and isopropanol in the industrial scaled semibatch reactive distillation. Other researchers worked on other various types of fatty esters for the esterification process (Bock et al., 1997; Dimian et al., 2004; Jong, 2010).

Li et al., (1998a) developed a thorough mathematical model of IPM production in BRD. However, the model suffers from the large number of equations which increases the model complexity and is very expensive to solve. In addition, the model is based on the assumption, where the accuracy of the developed model will decrease over time if natural degradation of the plant is not taken into consideration (Smrekar et al., 2010). Hence, it is important to gather the industrial operating plant data in

order to capture the real plant situation such as plant uncertainty, changes of the process parameter and changes of the process specifications.

The empirical model is typically used to represent the real plant condition because this model only considers the input and output of the experiment or plant data even though the physical reactions are unknown. Moreover, this model is usually simpler than the mathematical model and can be solved in real time (Seborg et al., 2011). From the literature, only the neural network model has been used to develop an empirical model for BRD. However, it is meant for the production of methyl acetate, (Reusch et al., 2001; Engell and Fernholz, 2003), wine production (Osorio et al., 2004) and ethyl acetate production (Mujtaba and Greaves, 2006; Bahar and Özgen, 2010; Konakom et al., 2010b; Jithin Prakash et al., 2011; Konakom et al., 2011).

In all the ANN models for BRD that were developed, none of them have performed sensitivity analysis prior to their model development. It is important to implement the sensitivity analysis prior to model development for the selection of significant input-output variables. The model quality is strongly influenced by the quality of the data used (Osman and Ramasamy, 2010). The inputs of the model can come from the current time instant and also from previous time instant (historical data). The historical data will provide the short term memory to the network which will use this memory when forecasting the output (Samarasinghe, 2007). Thus, considering the past and present input in the model is useful in the prediction of the dynamic system. However, in previous related studies, only a few of them have considered historical data as input variables.

The min-max scaling is a typical method that is performed prior to the ANN model development, which is significantly effective to predict the model within the training range. However, other training methods such as z-score normalization have yet to be tested for both the interpolation and extrapolation study of BRD. At the same time, the selection of the model structure also plays an important role in the ANN model. Most of the work reported on the MISO model and none reported on the comparison between the MIMO and the MISO structure.

In this study, two neural network structures were developed: multiple inputs-multiple outputs (MIMO) and multiple inputs and single output (MISO) models to represent the nonlinear behavior of the industrial scaled semibatch reactive distillation process. The data for training, validation and testing data sets were simulated using a validated fundamental model. Prior to that, the significance of the inputs and the outputs was evaluated using nonparametric sensitivity test methods which can classify the high and less impact of the input variables. To ensure the input and output variables were at the same magnitude, they were scaled using the z-score normalization method. The ANN training was carried out using the Levenberg-Marquardt algorithm and their optimum selection was made based on the validation and testing performed. Finally, the extrapolation capability of the optimum ANN developed was tested.

1.3 Objectives of the research

The aim of this research is to develop the artificial neural network model for the production of Isopropyl myristate in an industrial scaled semibatch reactive distillation. The measurable objectives are:

(i) To simulate an IPM production of the industrial scaled BRD process using Aspen Plus (Batchfrac).

(ii) To determine any relationship among the key variables in the process using non-parameteric test sensitivity analysis.

(iii) To develop neural network models for the industrial scaled semi batch reactive distillation column.

(iv) To evaluate the extrapolation capability of the neural network models developed.

1.4 Organization of Thesis

Chapter 1 provides a brief introduction of Isopropyl Myristate and its market demand. Subsequently, the problem statement is highlighted and the objectives are outlined. Finally, the organization of the thesis is given at the end of the chapter.

Chapter 2 consists of the literature review related to this study. First, the modeling of batch reactive distillation related issues is reviewed. Three types of models are explained and their respective literature is reviewed. Then, a general review of the transesterifications process and isopropyl myristate is explained. Finally, the neural network model development for the production of isopropyl

myristate in the industrial scaled semibatch reactive distillation is discussed. In addition, the application of sensitivity analysis to determine the significant input and output variables in the related literature is also reviewed.

Chapter 3 outlines the methodology adopted in this work. It covers all the procedures involved from the simulation stage up to the neural network model development. This step includes the simulation procedure, sensitivity analysis, data generation, nonlinear neural network process identification and extrapolation capability test.

Chapter 4 presents the results and discussion obtained in this work. It covers the results of the model verification with Aspen Plus and the sensitivity analysis study. Based on the results, the degree of the nonlinearity of the process is determined and presented. The results from the neural network model such as the performance evaluation of the neural network models based on the number of hidden neurons, the effect of the structures and the historical input data of the NN model developed are also discussed. The validation results of the NN model on the industrial data is also evaluated. Finally, the extrapolation capability of the model is demonstrated.

Chapter 5 provides the conclusion that summarizes the overall study including the main findings of this research. Recommendations and suggestions for future work are also briefly discussed in this chapter.

CHAPTER 2

LITERATURE REVIEW

This chapter begins with the description on the various types of batch reactive distillation (BRD). After that, three types of models are explained and the related literature is reviewed. The subsequent section explains the transesterification process in general and the long chain of isopropyl myristate production in industrial scaled semibatch reactive distillation. Finally the related literature on sensitivity analysis and the application of the artificial neural network (ANN) in BRD is reviewed.

2.1 Batch reactive distillation

In the chemical industry, the chemical reaction and the purification of the desired products by distillation are usually carried out sequentially. The integration of the reaction with a separation operation results in reactive distillation (RD) and it offers advantages over conventional applications in the chemical industry. Reactive distillation can reduce the number of equipments used in the plant, which leads to a reduction of capital investment. At the same time, it allows the direct utilization of the thermal heat of the reaction for separation, thus lowering the operating cost. This process also permits the continuous removal of light key components from the reaction zone. The continuous removal results in the suppression of equilibrium limitation on conversion. It also causes the avoidance of azeotrope, hence shifting the reaction to increase the yield and selectivity of the product (Doherty and Buzad, 1992; Venimadhavan et al., 1999; Malone and Doherty, 2000; Sun et al., 2009). The reactive distillation can be utilized either as a continuous or a batch mode of operation.

Batch processes are typically used when the production volume is low, when isolation is required for reasons of sterility or safety, and when frequent changes in the market demand are necessary especially for the production of specialty chemicals and pharmaceutical products (Bonvin et al., 2001). The integration of the separation process (distillation column) and the batch process with chemical reaction is known as batch reactive distillation (BRD). BRD can be classified into four types of configuration i.e batch reactive rectifier (BRR), batch reactive stripper (BRS), batch reactive with middle vessel (BRMV) and semibatch reactive distillation (SBRD).

2.1.1 Configuration of batch reactive distillation

The BRR consists of the reboiler at the bottom of the distillation column, a distillation column and a condenser. The chemical reaction of this process occurs in the reboiler where the initial batch amount of the component is charged into it. The distillate consists mainly of the lower boiling point product than the reactant and other products. At the end of the batch process, the excess reactant and the other products remain in the reboiler (Arellano-Garcia et al., 2008).

On the other hand, the reactive section of the BRS is located at the condenser. The initial amount of the batch component is charged into the condenser whereas the products are withdrawn at the bottom of the rectifying section (Qi and Malone, 2010). The products are obtained in the order of decreasing boiling point from the bottom of the column and a light-boiling fraction can be obtained at the condenser (Demicoli, 2005).The composition in the condenser relies on the removal of the bottom product and the chemical reaction (Chin and Lee, 2008).

The BRMV consists of the condenser at the top, the stripping section, the middle vessel, the rectifying section and the reboiler at the bottom. The reaction takes place in the middle vessel and loads with a mixture of the initial batch feed. The product is continuously removed from the stripper and the rectifier thus pushing the reaction to shift to the product side. The light and heavy-boiling products are simultaneously obtained from the column's top and bottom (Demicoli, 2005). The temperatures in the middle vessel can be kept low throughout the process thus it can reduce the thermal exposure of the component in the charge. Therefore, BRMV shows better performance than BRR and BRS (Arellano-Garcia et al., 2008).

The batch process is often used for low capacity products and it is not suitable for intermediate product capacity and higher production rate. Moreover, the continuous process is the most efficient for a high production rate but it loses its economic benefit when the production rate is decreased. Thus, the SBRD is introduced to offer a cost effective process for intermediate production rate (Adams and Seider, 2006). The continuous feed flow is fed into the column after a few hours of operation. Figure 2.1(a-d) shows the configuration of BRR, BRS, BRMV and SBRD, respectively.

Several literature discusses the feasibility of the BRD configurations that is explained earlier (Guo et al., 2003; Chin et al., 2006; Steger et al., 2006; Chin and Lee, 2008; Stéger et al., 2009).

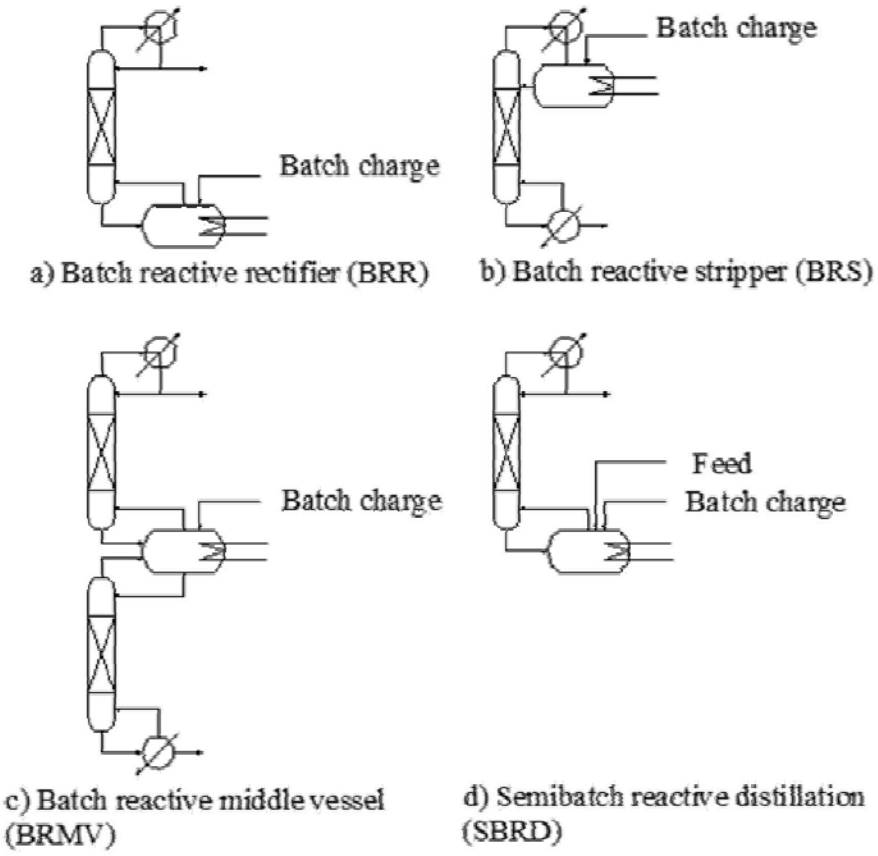

Figure 2.1 The configurations of batch reactive distillation (a) BRR (b) BRS (c) BRMV) (d) SBRD (Cui et al., 2009).

2.2 Modelling and simulation in batch reactive distillation

The dynamic model plays an important role in the chemical process for a few reasons: it can be used to improve the understanding of the process in which the process behavior can be investigated without plant interruption. The model can also be employed for operator training to run complex units and can also be utilized for process improvement such as the development of control strategy and process optimization.

Once a dynamic model has been developed, it can be used to study the behavior of the process for different operating conditions including various changes

in the input variables. To solve this dynamic model, various numerical integration techniques such as the Euler and Runge-Kutta method, the Newton-Raphson, the gear method and the Implicit Euler method can be applied. For solving a dynamic model that contains a large number of equations, standard software that is available such as MALTAB®, POLYMATH®and Mathematica® can be used. This software allows integrating DAE and ODE equations to determine the response while the inputs are changing (Seborg et al., 2011). Simulators such as Batchfrac®, CHEMCAD®, Batch Plus®, and BatchCAD® are also available for modeling batch processes (Bonvin et al., 2001).

Modeling BRD poses a great challenge because of its complex dynamics due to the integration of reaction and separation. The model deals with complex interactions between vapor-liquid equilibrium (VLE), chemicals kinetics, intrinsic process condition, and so on. Thus, it is important to develop a reliable model in order to understand the behavior of the process. There are three types of models that can be adopted to model the system i.e. white box (fundamental) model, black box (empirical) model and grey box (hybrid) model.

The white box model is derived from physical laws, conservation relations, and established physical-chemical relations. The black box model can be viewed as a highly parameterized structure such that in principle any input-output mapping. Meanwhile, the grey box model takes advantage of the fundamental and empirical model where all available fundamental knowledge is used to build a white box modeling part while the missing information is estimated using the black box model (Romijn et al., 2008).

2.2.1 White box model

The white box model is built from the prior knowledge of the process. It is derived from conservation laws such as the conservation of mass and energy. This model shows a very high accuracy which provides physical insight into the process behavior and is valid over wide ranges of conditions. The following literature discusses the fundamental approach for the BRD model development.

Due to the lack of information and knowledge on the production of ethyl ester pentanoic acid (PAEE) in BRD, Bollyn and Wright (1998) developed a rigorous model which helped them to understand the fundamentals of the process. All the required data was gathered for simulation by using the BatchCAD simulator. This package uses rate-control chemical reactions and a rigorous dynamic mass transfer based distillation model. The model developed was fitted well with the plant data and can be utilized to determine the optimum conditions of the process.

Li et al. (1998a) developed the detailed dynamic model of industrial scale semibatch reactive distillation for the production of Isopropyl Myristate (IPM). The aim of their work was to determine the optimal process of the BRD operation. The model was developed using detailed material balance, equilibrium relationship, summation and energy balance (MESH) equations. The Newton-Raphson method was applied to solve the algebraic equations that were performed in the FORTRAN® program. The detailed dynamic model was validated with the experiment conducted in the industrial site and showed satisfactory agreement between the model and the experimental result.

The model developed by Li et al. (1998a) was used by Arelano-Garcia et al. (2002) to study the properties of the new operational mode. Typically in batch distillation, the distillate is accumulated in two accumulators to collect the desired purity (main-cut) and not desired purity (off-cut). In this new operational mode, the off-cut was recycled in the form of a continuous feed flow into the column and the model is used for the optimization study.

The detailed rigorous dynamic rate-based approach was used by Schneider et al. (2001) to develop the detailed model including mass transfer and chemical reaction. This model leads to complex and highly nonlinear DAE equations which were solved using the Newton method. To prove the reliability of the developed model, it was validated by the pilot plant data. The result showed that the rigorous model was able to predict the dynamic process behavior. The sensitivity analysis to determine the effect of the liquid holdup in the column periphery was also considered in the study.

The aim of the work by Elgue et al. (2002) was to perform an optimization strategy for the production of methyl acetate (MA). They simulated the detailed model developed by Elgue et al. (2001) and verified with the pilot plant data obtained from Bonnaillie et al. (2001). The model was simulated by using DISCo, a general DAE solver based on the Gear method. The result obtained by the model showed a good agreement between the pilot plant data and the model developed.

Brüggemann et al. (2004) developed a robust dynamic simulation method for the heterogeneous BRD and the DAE model was solved using gPROMS®. The case study of butyl acetate (BA) was used to validate the robustness of the dynamic simulation strategy. The reasonable computational times of up to 10 hours per simulation were obtained using this simulation strategy.

Kumar et al. (2006) explored a novel esterification strategy to perform esterification, distillation and hydrolysis in a single unit. The ODE model was developed and its reliability was compared with the result obtained from the experimental work. All the equations were solved using ODE15s solver in Matlab. The model was also used to obtain the optimum conditions of the process.

Adams II and Seider (2006) worked on semicontinuous distillation with a chemical reaction in the middle vessel (SDRMV) using the forced cyclic method for the production of 2,4-dimethyl-2,3-dioxolane. The model was simulated using Aspen Plus and the economic analysis was performed and a comparison was made between the continuous and the batch processes operation.

The model developed by Li et al. (1998a) was further improved by Arellano-Garcia et al. (2008). In their work, they modeled and simulated the new operation mode of the start-up operation (middle vessel BRD) with the cold and empty batch columns as the initial state. A detailed rigorous model was developed including the start-up phase. The total equation system and reaction kinetics were combined to describe the reaction both in the middle vessel and the respective column section which was then solved using gPROMS.

The model developed by Jana and Adari (2009) and Kathel and Jana (2010) was embedded in the control scheme. Jana and Adari (2009) developed the dynamic model for the production of ethyl acetate (EA) while Kathel and Jana (2010) developed the model for the production of butyl acetate. The model that was developed was used to investigate the closed loop process dynamic with the application of control algorithm.

Edreder et al. (2008) performed a study to determine the optimal operation of BRD for the production of ethyl acetate. The dynamic model was developed by including mass, energy equations, column holdup, phase equilibria and chemical reaction. The model was simulated using gPROMS modeling software and the simulated model was used to determine the feasible range of the feed composition for the optimization study. The aim of the optimization study was to determine the maximum conversion of the process. The model developed by Edreder et al. (2008) was again used by Edreder et al. (2010) for a similar process and the dynamic optimization problem was formulated that incoporated the developed model.

The model for the production of industrial grade ethyl acetate 90 mole% in a conventional BRD was developed by Konakom et al. (2010b) and (2011). The mathemetical model developed was based on the material and energy balance which were used for the model based optimization. The DAE equations were solved using Matlab.

Edreder et al. (2011) developed two models, the conventional (CBD) and the inverted column (IBD) model, to optimize the operation of the hydrolysis of lactic

acid. The model was derived from the MESH equations and was embedded in the process optimization which was solved using gPROMS software.

Qi and Malone (2011) evaluated the vapor-liquid and the liquid-liquid phase equilibrium for the production of isopropyl acetate (IPA). They used semibatch reactive distillation to overcome the loss of isopropanol (IP) in the aquous phase. The simulation was carried out using the Aspen BatchSep simulator and the performance was compared with conventional BRD. The semibatch reactive distillation gave better results because the IPA was in the form of binary mixture with water (H_2O) instead of a ternary mixture of IP-IPA-H_2O .

Khazraee et al. (2010) developed the dynamic model of BRD for ethyl acetate production. The model was developed using MESH equations and the simulation was performed by solving DAE simultaneously with the numerical integration method. The simulation result based on the model developed was verified with the experimental result from the pilot plant.

Johri et al. (2011) simulated the BRD model for the production of ethyl acetate based on the fundamental model development. The developed model was used to evaluate the performance of energy integration in the presented BRD. Two types of columns were investigated and compared; conventional BRD (CRBD) and vapor compression BRD (VRRBD). The model developed was used to simulate both processes for comparison. The result showed that, the proposed energy VRRBD scheme had the ability to provide more than 65% of energy savings.

Jithin Prakash et al. (2011) considered the production of ethyl acetate to evaluate the closed-loop process dynamics. The process model was developed using the fundamental model which considered MESH equations. Later, the model developed was used to be incorporated with the control scheme.

Mujtaba et al. (Mujtaba et al., 2012) developed the dynamic model for the esterification of lactic acid with methanol. The model was developed using the material and the energy balance with the reaction taking place in the reboiler. The model developed was also used to simulate the dynamic process by optimizing the reflux ratio for energy saving via minimization of the production time. The model equations were solved using gPROMS.

The models developed from fundamental knowledge is a good source of process information however, they are always complex and time consuming to solve. To overcome the drawbacks of the rigorous model, some researchers proposed to develop a simplified model as proposed by Venimadhavan et al. (1999); Balasubramhanya and Doyle III (2000); Gadewar et al. (2000); Huerta-Garrido et al. (2004) and Qi and Malone (2010). This method is computationally inexpensive and provides quick estimates for the target over the various operating conditions Gadewar et al. (2000).

2.2.2 Black box model

The development of a rigorous theoretical model may not be practical for some complex models which require a large number of equations with a significant number of process variables and unknown parameters such as chemical and physical

properties. Thus, the empirical model which makes use of the experimental or industrial data can be an alternative. The empirical model is simpler than the theoretical model and offers advantages for real time applications since the computational time required for the model solution is shorter than the fundamental model (Seborg et al., 2011).

The empirical model, also known as the black box model, is based entirely on the available data with the absence of priori physical knowledge. It is not derived from assumptions and physical principles based on the relationship between the variables. The validity of the model depends on regression correlation and error between the predicted model and the actual data. In the common batch processing, modeling is often done empirically using the input-output static model on the basis of the experimental design. The operation parameter is decided at the beginning of the process while the quality is measured at the end of the process (Bonvin et al., 2001). There are a number of empirical models available such as ANN, Wiener model, ANFIS, Hammerstein model, NARMAX model, NARX and PLS model.

Engell and Fernholz (2003) developed the ANN model for the production of methyl acetate in semibatch reactive distillation. The developed MISO model consisted of past and present process inputs and past process outputs. The identification the ANN model was implemented in the nonlinear control system to predict the future mole fraction of methyl acetate and water over the fixed time horizon.

Mujtaba and Greaves (2006) replaced the rigorous dynamic model with the neural network model for the production of ethyl acetate. The objective of their work was to develop a tool that can forecast batch time, productivity, profitability, and energy cost when changing the product specification. The NN model was developed and simulated by using the NN tool in MATLAB. The optimal product yield, optimal heat load, optimal maximum conversion and optimal reflux ratio profiles were successfully predicted using this model.

Khazraee et al. (2010) proposed the application of the adaptive neuro-fuzzy interface system (ANFIS) as the model estimator. The artificial neural network and fuzzy logic were combined to establish a fuzzy neural network for the production of ethyl acetate. The ANFIS model that was developed was utilized to estimate distillate composition at the top tray. The results were compared with the data generated by the dynamic model, which was priori validated with the pilot plant data.

Konakom et al. (2010a, 2011) presented the modeling of the neural network model of the ethyl acetate process that was implemented as model base in the control system. Two models were developed in their work; the model for the estimator and the model for controller. The simulated data from the dynamic model was used for the training procedure for the MISO and the MIMO models for the estimator and process model, respectively. The inputs to the estimator consisted of present and past data which were used to predict current output, which was later used as a part of the input parameter to the process model. The process model was embedded into the control scheme to predict the future distillate composition and temperature.

2.2.3 Grey box model

The hybrid model or grey box model is the combination of the white box and black box models. Since the white box model always deals with its complexity in the online application, the black box model shows its advantage when implemented in the online application. Knowledge of the process can be used to develop the white box model while the hard part to be formulated is modeled using the black box model.

Reusch et al. (2001) considered the heterogeneously catalyzed production of the methyl acetate process in a semi batch reactive distillation column in their study. The dynamic model of the theoretical stage was developed, which consisted of the mass balance and the energy balance for each stage. Besides that, the VLE relationship also had to be derived and the equations consumed a large part of all the MESH equations. Thus, the VLE relationship was modeled using the black box model and simulated by gPROMS. The result obtained from the hybrid model was compared with the dynamic model on its capability of predicting VLE.

The BRD model for wine production was developed by Osorio et al. (2004). The DAE model developed was transformed into a set of ordinary differential equations (ODE) by pre-solving the nonlinear algebraic equations for VLE and the partial condenser using the Gauss-Newton routine (FSOLVE) from MATLAB. These two equations were later replaced by the polynomial and NN model to reduce the complexity of the dynamic model. This hybrid model, which combined the model equations and the empirical model, was compared with the dynamic model that was developed before. The dynamic model combined with the NN model accurately

predicted the DAE model when compared to the hybrid model with the polynomial approach.

Tables 2.1 to 2.3 show the summary on the available literature for the white box, the black box and the grey box models, respectively. From these tables, it can be concluded that, there was lack of works in BRD modeling for the transesterification process and only a few of them using industrial scale data for the model development. Moreover, most of the model that has been developed in BRD was white box model and only a few of them considered empirical and hybrid models. The observation from tables also shows that the developed models were solved by using equation oriented simulators. Consequently, the development of empirical model for BRD has getting attention in recent works and most of the model chosen is NN. However the process considered were not a transesterification process for the production of IPM. Moreover, the table also shows that none of the reviewed works were considered the sensitivity analysis before the NN development. Thus in this work, the NN for transesterification process in industrial scale BRD will be developed.

Table 2.1 Summary of modeling and simulation using fundamental model in BRD.

No.	Author	Product	Type of model	Simulator/ Software	Industrial/ laboratory	Sensitivity study
1.	Bollyn and Wright, (1998)	PAEE	Rigorous dynamic mass transfer	BatchCAD	P & I	No
2.	Li et al., (1998a)	IPM (T)	Dynamic model	Fortran	I	No
3.	Li et al., (1998b)	IPM (T)	Dynamic model	Fortran	I	No
4.	Venimadhavan et al., (1999)	BA (E)	Simplified model	Na	Sim	No
5.	Balasubramhanya and Doyle III, (2000)	EA (E)	Low order nonlinear model	Matlab	Sim	No
6.	Gadewar et al., (2000)	Alkylation of Butane	Simplified model	Na	Sim	Yes
7.	Schneider et al., (2001)	MA (E)	Rigorous dynamic rate-based	Numerical solver	P	Yes
8.	Elgue et al., (2002)	MA (E)	Dynamic model	DISCo	P	No
9.	Arellano-Garcia et al., (2002)	IPM (T)	Dynamic model	Fortran	I	No
10.	Brüggemann et al., (2004)	BA (E)	Dynamic model	gPROMS	Sim	No
11.	Huerta-Garrido et al., (2004)	isomerization	Simplified model	Batchfrac	Sim	No
12.	Kumar et al., (2006)	LA (E)	Dynamic model	ODE15s, Matlab	L	Yes