Chapter

A Review on AI Control of Reactive Distillation for Various Applications

Vandana Sakhre

Abstract

In this chapter, previous studies on reactive distillation process control including control using conventional as well as soft sensor control, membrane assisted reactive distillation design and simulation, estimation and control are discussed. The review of literature in different dimensions is carried out to explore the opportunities in the field of research work. The chapter is focused on dynamics and control of Reactive distillation, its control using Conventional Techniques, Model Predictive Control MPC), Reactive Distillation using Soft Sensors/Soft Controllers, Membrane assisted reactive distillation, Biodiesel in Reactive Divided Wall Column: Design and Control and Membrane reactive divided wall column. These control techniques are proposed and analyzed by many researchers. These techniques have potential use in process industries to have better soft sensor control of nonlinear processes.

Keywords: control, divided wall column, model predictive control, reactive distillation

1. Introduction

Reactive distillation is a part of process intensification technique which aims at carrying out reaction to form products which are then separated in the same column based on difference in boiling points. Dynamic study of any chemical process is the most crucial part which should be performed at early design stage as the dynamic nature leads to nonlinearity. This nonlinearity introduces sluggish behavior in the system which will lead to distract the process output out of the range. The dynamic behavior or nonlinearity was usually studied by rigorous modeling or using simulation software to predict the nature of system. For this advanced control systems are designed and implemented to get effective control strategies. Neural network based soft controller are suitable for reactive distillation system as these are suitable to overcome with multiplicity issues. The dynamic performance of reactive divided wall distillation column with nonlinear control structures is proven to be cost effective. The use of reactive distillation with membrane separation techniques are emerged as effective separation techniques which give corresponding recoveries as well.

2. Reactive distillation dynamics and control

Non linearity of reactive distillation was first reported by Ciric and Gu et al. [1] using simulation of reactive distillation processes involving simultaneous solution of material and energy balances and stoichiometric relationship which corresponds to the solution of a considerable large set of non-linear modeling equations of reactive distillation column. They have used a mixed integer nonlinear programming (MINLP) approach was used to synthesize an optimum reactive distillation column. The MINLP minimizes the total annual cost subject to a MESH model. The solution of this MINLP yields the optimal number of trays, the tray holdups, the feed tray locations, and their feed distribution. Amte et al. [2] presented a MINLP optimization technique that would assist to identify a suitable configuration for selectivity maximization at conceptual design level. Results obtained through MINLP gives a good agreement with those obtained by performing independent simulation using ASPEN PLUS. In this work, authors have considered feed and catalyst tray location, reflux as the variables for the maximization of selectivity. Thus, MINLP optimization process proves conceptual design for the selectivity engineering with reactive distillation. Doherty et al. [3] have given pioneering contributions to the analysis and design of the reactive distillation and developed thermodynamically based approach for analyzing equilibrium limited, thermally neutral reactive distillation systems. This work employed a novel composition coordinate system to transform the problem into a form completely analogous to nonreactive distillation.

Subawalla and Fair et al. [4] worked on dynamic study of TAME synthesis in reactive distillation column by considering different design parameters such as number of trays, feed flow rate etc., resulting into nonlinear interaction of these input parameters. He has also provided some intuitive guidelines about coupling of these design parameters order. Schenk et al. [5] have presented equilibrium and non-equilibrium models for predicting the steady state and dynamic behavior of RDC based on a rate-based model in which mass transfer rates between liquid and vapor phase are considered explicitly, based on the Maxwell-Stefan equations. A switching policy makes it possible to switch from one model to the other, based on the knowledge gained, by following the Gibbs free energy as a function of time. Cardoso et al. [6] have proposed a new simulation/optimization model for the Mixed Integer Nonlinear Programming (MINLP) formulation of reactive distillation columns as used by Ciric and Gu [1], where the simulation algorithm is based on conventional distillation and optimization is performed by stochastic algorithm. Estimate of the initial composition profile in the column was obtained by relaxation method and material balance equations are solved by Newton–Raphson method, to compute the composition profile. Vora and Daoutidis et al. [7] represented work on dynamics of reactive distillation by proposing a different feed configuration for two feed and two product system. They have also presented control of an ethyl acetate reactive distillation system to achieve higher conversion than the previously proposed configuration which involves single feed reactive distillation column. Taylor and Krishna et al. [8] have presented work on modeling of homogeneous and heterogeneous reactive distillation processes by considering equilibrium stage models, non-equilibrium stage modeling, the conventional NEQ model, NEQ modeling, hydrodynamics, and mass transfer. Dynamic simulation for NEQ model without back mixing was also presented by Kataria et al. [9] in which model equation for reactive distillation without back mixing was developed for open loop system. For the NEQ model with partial mixing, bifurcation behavior with stability analysis and simulation were carried out which confirmed the existence of oscillation in the NEQ model as well. Once the nonlinear nature of reactive distillation is confirmed, various control strategies were reported by the authors to make the system linear. Linearization was carried out to make system to oscillate around the set points of desired parameters which makes the system easy to operate without much affecting the performance over the time. Mehran et al. [10] have employed Takagi-Sugeno fuzzy model to express the local dynamics of each fuzzy implication by a linear system model to plot the resultant error of surface with time and reported that although system's non linearity can be linearize to some extent but still many control problems involve uncertainties in the model. In view of this, Gruner et al. [11] have taken an industrial case of reactive distillation and proposed a nonlinear control scheme for the system operated by Bayer AG.

Interaction of various parameters in a reactive distillation leads to higher order nonlinearity and dynamics like interaction between number of trays, reflux ratio, reboiler duty, etc. This interaction will lead to multiple steady states and multiplicity in the system. The type of multiplicity will limit the values which should be broken by application of suitable controllers. Heath et al. [12] studied the interactions of design variables and applied control schemes for an ethyl glycol reactive distillation system and assumed that the process variables are fixed i.e. no revamping is done. Author has taken process economics as a major issue which ultimately depends on the number of variables interacting in a system and its control was achieved as per the desired objective. For the same assumptions, Schenk et al., [13] and Georgiadis et al. [14] have worked on interaction of design variables in a reactive distillation column and proposed advanced optimization technique for the control of a reactive distillation system to smoothen the operability and increase the system efficiency.

Figure 1 shows general control scheme of reactive distillation column. The common controls used are Flow Control (FC), Level Control and Composition Control (CC). Level control is given in condenser and reboiler while composition control is provided to condenser, reboiler and one of the feed flow rates to get tighter composition analysis. Flow control is provided to feed flow rate at the top of the reactive section.

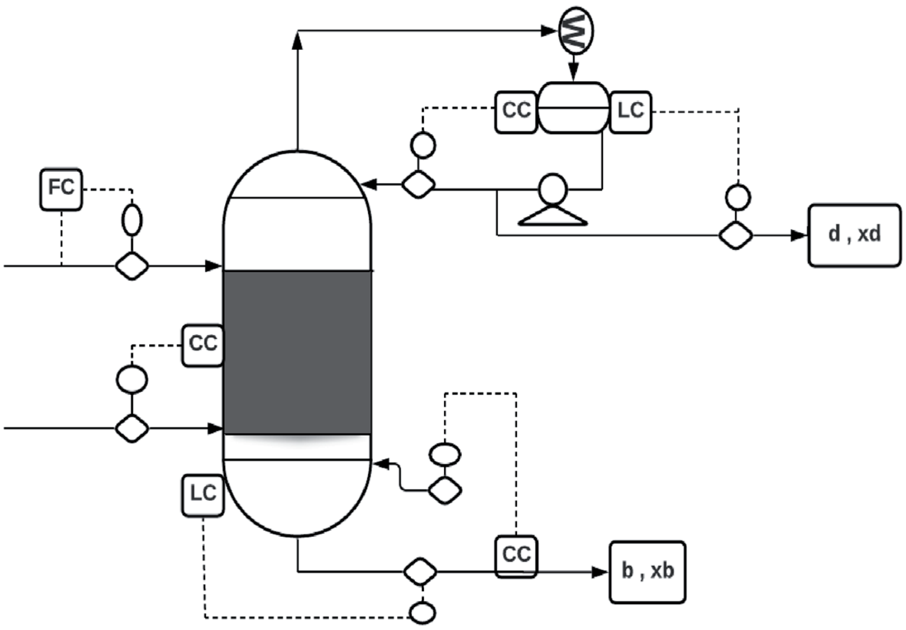

Figure 1.
Reactive distillation control.

2.1 Control using conventional techniques

Simplified models clarify process dynamics but cannot represent the process under wide range of operating condition. Thus, various mathematically driven controllers like proportional, integral, derivative or a combination of theseareusedas hardware sensor-controller system which are mathematically functioned or scripted. Furthermore, the RD process contains a large degree of uncertainties, which cannot be well described using single mathematical expression. Therefore, techniques without using exact process models are more attractive for RD control. Monroy-Loperena et al. [15] studied the control problem of reactive distillation system for ethyl glycol by proposing a robust PI control configuration. They have also revealed the existence of input multiplicity in the system and proposed a first order output feedback control system to regulate the product composition. The control design involves interpretation of error signal whose dynamic is again constructed based on available data. Sneesby et al. [16] moved in process control by highlighting an integrated control scheme by taking ETBE as the case column. He proposed to change control objective to reflect changing economic variables like starting from optimum purity, minimum number of trays, optimum reflux ratio, etc. In view of this author has also presented a rigorous MESH based modeling to represent the main chemical reaction. Al-Arfaj & Luyben et al. [17] applied different conventional PI, PID and other conventional controller scheme for reactive distillation as well as for simple reactor. They compared the control of both these systems to produce methyl acetate. Various control strategy was proposed in this paper, the first one was for a composition and temperature control while second scheme was based on tow temperature controllers. A comparison between these schemes shows that different scheme corresponds to over design or under design system hence proper balancing of degree of freedom of a system is equally important.

Various tuning methods are proposed in the literature to calculate the ultimate period or ultimate gain. Chandra et al. [18] have calculated ultimate gain and ultimate period using Ziegler Nicolas tuning rule for an ARX model structure. The objective was to control the desired product purity in distillate stream. In this work, an ARX model structure relates the plant output with present and past plant input output to formulate a predictive control. Recursive least square estimator was used which provides updated parameters to ARX model. Goyal et al. [19] have presented support vector regression to tune a PID controller. Model gain scheduling was included in one of the control strategies for reactive distillation. Temperature control was given priority because to balance the stoichiometry, temperature of feed trays can be used to adjust the fresh feed streams. For this the gain of controller was define as the change in temperature with respect to the feed flow rate. Nizami et al. [20] have constructed one or two loop composition PID controller, however, the conventional controllers applied for the control of reactive distillation was not capable of actually control the simultaneous interacting parameters because of occurrence of reaction and separation in single column. Lei et al. [21] have described the design and optimization of reactive distillation column for the synthesis of Tert-Amyl Ethyl Ether (TAEE), the temperature–composition cascade strategy was proposed to control the Reactive Distillation (RD) process for the synthesis of TAEE. In those optimized conditions, the proposed control strategy was introduced to manage the RD process by changing the sensitive variables. Dimian et al. [22] have carried out thermodynamic analysis in residue curve map and simulation of reactive distillation column. Process dynamic and control was considered in detail to design the column. The feasibility of fatty acid esterification with individual alcohol was studied by means of residue curve maps. By sensitivity analysis it was found that the reflux of heavy alcohol is the key manipulating variable for controlling the water content in the reactive liquid phase.

The controllability of the system could be studied using tools from control theory. Feedback control of inventory is measured, and a feedback control loop is implemented with the fresh feed as manipulating variable. Konakom et al. [23] have proposed to control distillate rate subject to a given product purity constraints. A conventional batch reactive distillation model described by a system of differential algebraic equations is formulated and solved using an optimal control algorithm. In open loop simulation of production of industrial grade ethyl acetate of 90% purity, dynamic optimization programming was implemented which increases the purity as per the product specification.

2.2 Model predictive control and other control techniques

Due to the complexity of the process dynamics involved in reactive distillation, conventional control technologies, e.g. PI, PID control, cannot provide satisfactory control performance, while the application of modern control technology requires good process models. A reasonable process model as described by Sneesby et al. [24] contain hundreds of equations for the RD process which is to be controlled. Pattern-based predictive control (PPC) is such a method that does not rely on exact process models while providing improved control performance for complex processes over conventional, e.g. PI, control algorithms. Some progress has been made in this direction, like for time delay compensation, Zhao et al. [25] worked for dynamic models that reject disturbances. Since various chemical processes possess time delays and uncertainties, for example, the flowing fluid in a pipe was taken as time delay variable. To represent such system the proposed model works on first order lag dynamics to compensate for uncertainties. Bode plots were also constructed to show that pattern based fuzzy predictive allows a trade-off between robustness and the performance. Seem et al. [26] have proposed a novel predictive scheme by considering a proportional integral controller in which the gain and integral time is calculated automatically and hence they have given such system a name of self-regulating system. However, this scheme was based on the pattern reorganization methodology, but author has asserted that this scheme requires less memory and is more efficient as compared to the conventional techniques. Jang et al. [27] worked on fuzzy predictive control which does not depends on exact process model but considers a pattern predictive control that provides improved performance in both set point tracking and disturbance rejection, shown for the RD process. Local optimum was identified to minimize prediction error and global optimum was then identified through various subsystems. The nonlinear transformation, feature pattern extraction, and PP design was discussed in detail by Tian et al. [28] who have designed a pseudo input–output linear process gain, which needs only a rough and easily obtained knowledge of the steady state characteristics of the process. Author has worked on one-point control strategy i.e. control of bottom purity by considering reflux ratio and reboiler duty as the variables. They also used state estimation approaches for measurement of sample at multiple rates.

Bansal et al. [29] have developed an algorithm for solving Mixed Integer Dynamic Optimization (MIDO) problems. This algorithm is different from other conventional algorithm as they do not depend on the use of a particular primal dynamic optimization method. However, overthe last decades, many versions of Extended Kalman filter (EKF) has coined that deals with the measurements at multiple rates. Patwardhan et al. [30] have worked on output feedback system for the case of plant mismatch. The EKF for nonlinear systems has been explored by Beccera et al. [31]. The concept involves the use of a time varying linearization of differential algebraic equation in which estimation was performed using a simplified EKF that was integrated with the differential algebraic equation model which accommodate measurements obtained only from the differential states. This technique has serious limitations. This limitation has been overcome by Mandela et al. [32]. They presented formulations for EKF and Unscented Kalman Filter, in which measurements of differential as well as algebraic states were recorded. To achieve more rigorous control of reactive distillation nonlinear system over a wide operating range, various successive linearization based nonlinear predictive control scheme was developed by Huang et al. [33]. They proposed error feedback scheme that introduces integral action in the controller for controlling a multi rate sampled data system. Author has not implemented the conventional linear feedback but adopted a novel variable feedback concept that effectively reduces the noise making the system quite robust for the designer. Akesson et al. [34] have developed a scheme in which control objective was to keep the output close to a specified reference trajectory in such a way that large control signal variations are avoided and possible hard constraints on the state and inputs was satisfied. Main control objective of this work was to minimize the cost. Procedure was adopted by the authors in which controller was trained directly to minimize the cost for a data set, without having to compute the optimal MPC control signals by off-line optimizations.

MPC are classified to various type such as dynamic matrix control (DMC), quadratic dynamic matrix control (QDMC), robust multivariable predictive control technology (RMPCT), generalized predictive control (GPC), and other advanced control techniques and was reviewed in brief by Sharma et al. [35]. They also presented work on comparison of conventional strategies with MPC and neural network predictive control by considering a TAME reactive distillation column for different load changes and proved that NNPC and MPC provide much accurate result as compared to conventional PIDs. **Figure 2** shows the general MPC structure.

2.3 Control of reactive distillation using soft sensors/soft controllers

Design of a soft sensor for a reactive distillation column includes three steps: first, selection of secondary measurement of the process, second, moving data collection and processing this data, and the last, modeling of process based on selected

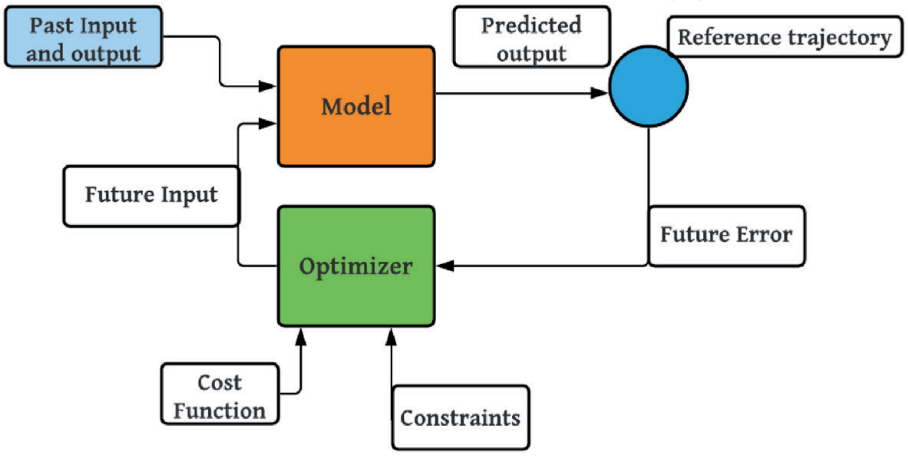

Figure 2.
General MPC structure.

secondary measurements and processing of data. Generally, the differential algebraic equations (DAE), describes the dynamics of a reactive distillation column. Soft computing techniques are methods in which real practical situation could be dealt in the same way as human deals them i.e. based on intelligence, common sense, reasoning, analogies, etc. Fuzzy logic is the oldest control schemes used not only in process industries but in vast area of other engineering applications also. In view of this, Babusk et al. [36] have first coined up the detailed concept of fuzzy logic in both static and dynamic system and proved fuzzy system as an interactive method, facilitating the active participation of the user in a computer-assisted modeling session. The fuzzy model proposed by Takagi and Sugeno described by fuzzy 'IF-THEN' rules represents local input–output relations of a nonlinear system. Rico et al. [37] applied the fuzzy control technique to control the process output from distillation column inthe desired range for different input disturbances. As an initiation to fuzzy logic, industries as well researchers move toward the field of soft sensing and control using soft computing techniques. These techniques were initially based on local optimization such as given by Pekkanen et al. [38] for a stage by stage specification of reactive distillation. They initiated the control procedure from each column ends i.e., from top as well the bottom while making the design specifications at each stage.

Soft controllers are also known by an alternative name known as intelligent control technique or inferential control as these controllers can estimate and control the process based on past experiences. Use of soft computing approaches take its first start up with the launch of natural evolution based algorithms like genetic algorithm, ant bee search algorithm etc. and merged toward more rigorous approach by combining one algorithm with other such as artificial neural networks or ANN's and fuzzy logic as a black box technique to model systems and gained substantial interest in different areas of engineering. These are also known as hybrid techniques which consist of a frame- work of dynamic mass and energy balances, supplemented with fuzzy models. The hybrid models have shown that the use of fuzzy logic in hybrid modeling introduces flexibility, which enables the description of complex behavior with a pre defined, interpretable overall model structure. Araromi et al. [39] designed a continuous RD using hybrid Fuzzy Hammerstein (FH) model consisting nonlinear fuzzy model and linear state space model was then developed. The developed model was compared with linear autoregressive input exogenous (ARX) and nonlinear autoregressive input exogenous (NARX). Sumana et al. [40] investigated the use of gramian covariance matrices for sensor configuration in continuous multi component reactive distillation by applying extended Kalman Filter to obtain the instantaneous composition information from temperature sensors data of reactive distillation column. The sensors configurations were further evaluated by IAE criteria incorporating the measurements suggested by the state estimator. **Figure 3** shows general soft sensor control.

Soft computing or inferential computing is the most advanced stage of control schemes. At present, neural network is one of the most demanded intelligent controllers which works on the imitation of working of neurons in human brain. Wang et al. [41] have taken a case-based modeling program with an industrial example of distillation column. The basic features of this case base modeling described in brief were discreteness, nonlinearity, contradiction and complexity. Theyreported that neural network is promising in process control and fuzzy distributed neural network can be used to design a soft sensor for a high purity distillation column. Multi-layer neural network was utilized when creating a system inverse neural model. In view of this, Zilkova et al. [42] have developed three-layer feed forward neural network with one hidden layer elected to approximate nonlinear function. The first subsystem served for desired current component reconstruction and second system

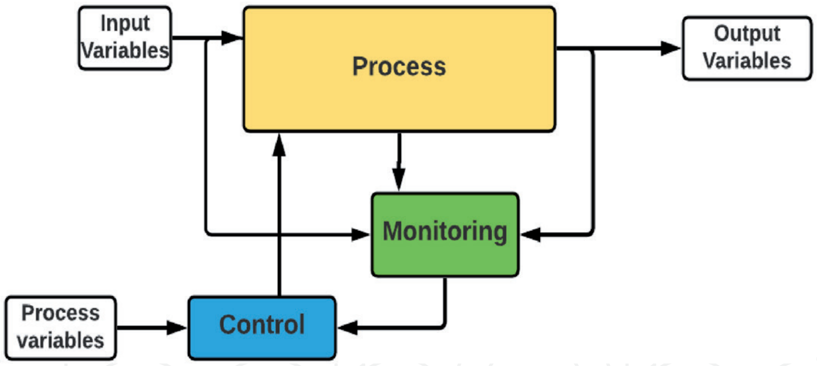

Figure 3.
General structure of soft sensor control.

serves for corresponding voltage components reconstruction for PWM converter. This was carried out using Simulink model. Simulation result verified the effectiveness of proposed controller. Akesson et al. [34] have taken control objective to keep the output close to a specified reference trajectory in such a way that large control signal variations were avoided and possible hard constraints on the state and inputs were satisfied. Main control objective of this work was to minimize the cost. For a data set, without having to compute the optimal MPC control signals by off-line optimizations. Raghavan et al. [43] have developed a Recurrent Neural Network (RNN) based inferential state estimation scheme for an ideal reactive distillation column. The performance of the estimator for both open loop and close loop was compared with that of kalman filter in terms of qualitative and quantitative indices and concluded that RNN has better level of inferential control over the conventional suggested methods. Prakash et al. [44] proposed an artificial neural network based nonlinear control algorithm for simulated batch reactive distillation column by considering a homogenously catalyzed esterification reaction which was controlled using ANN based state predictor. The open loop dynamic was presented in detail for this system and the proposed law was tested against gain scheduling controller to compare the performance. Bahar et al. [45] presented an Elman neural network to control the product composition from distillation column using temperature measurements inferentially. The main limitation of the neural network controller was that substantial offline computations may be needed in order to train it properly, and for some choices of cost functions it may not even be feasible to achieve satisfactory accuracies.

Other soft sensing techniques like genetic algorithm, particle swarm optimization, ant colony optimization etc. are although very old but are still being employed for inferential control which is based on natural evolution theory. Nithya et al. [46] have used real world experimentation in which pneumatic control valve is used to control the flow of water in and out of the tank. Using the black box modeling, the transfer function has been derived which was used to design a PI controller to find the values of gain and transfer function. Fuzzy logic controller has been designed for spherical tank considering nonlinear system. For tuning of the PI and Fuzzy Logic controller, genetic algorithm was used and the responses for servo and load disturbance were observed. Idris et al. [47] have considered the case of methyl acetate production in a continuous reactive distillation column in which tracking index term has been coined which was define as squared sum of differences between the predicted outputs and set points change over the prediction horizon. The control algorithms were applied in gPROMS against various tuning parameters and concluded that optimizing controller can be easily applied to a simulated complex model of reactive distillation to enable real time dynamic optimization.

Sujatha et al. [48] have considered a MIMO system defining integration of manipulated variable and control variable. Various novel techniques such as relative gain array, Niederlinski index, singular value decomposition, Morari Resiliency Index, dynamic relative gain array, hankel interaction index array, participation matrix and H_2-norm were studied for the interactions and subsequently for input output pairing.

Differential evolution is one of the latest coined soft controlling techniques which aims at approaching toward global minimum. Subudhi et al. [49] have developed a differential approach based on a jumping rate fittest approach in which individual were selected from the union of current population and opposite population. The aim was to approach toward global minimum and then LM was used to move forward achieving fast convergence. LM is a gradient based algorithm to increase convergence speed. Opposition based learning improves the chance of starting with better initial population by checking the opposite solutions. Lu et al. [50] have developed a differential algorithm based stochastic search technique which is a powerful and global optimizer. The author has proposed a Modified Differential Evolution Fuzzy Neural Network (MDEFNN) which consists of a FNN identifier, a MDE estimator, a computation controller, and a hitting controller. Lawrynczuk et al. [51] have reported model predictive control strategy for a high purity, high pressure ethylene ethane distillation column. In this study, multi-layer perceptron neural network was applied with one hidden layer and a linear output. In the MPC-NPL algorithm, the nonlinear neural model was linearizing using eight repetitive steps such as estimation, approximation, control increment, and iteration. Kandanapitiya [52] has recently reported Modeling of Reactive Distillation for Acetic Acid Esterification. The mathematical model considered material balance equations, equilibrium relationships, summation equations and energy balance equations. The model was simulated for acetic acid and ethanol esterification reaction. Wierschem [53] has worked on design of Continuous Enzymatic Reactive Distillation with Immobilized Enzyme Beads. Based on kinetic and thermodynamic data, a detailed rate-based model of the ERD is developed. Simulation results and experimental data of the ERD setup are in good agreement. Zhang [54] has designed centralized and decentralized stochastic adaptive fuzzy output feedback control by using dynamic surface control method. Fuzzy systems are used to approximate unknown nonlinear continuous function. For the online process, the young's inequality norm of fuzzy basis vector is adjusted. Peng [55] has shown that two riccati equations were employed with relaxing the agent dynamics for uncertain nonlinear systems. The author has developed a cooperative output feedback adaptive control (COFAC). The NN identification of the individual uncertain dynamics is decoupled from the network topology, which is useful for practical implementations since the uncertain nonlinear dynamics can be suppressed by local NN. Cui [56] deals with the problem of adaptive decentralized NN control by combining Lyapunov-Razamikhin functional approach, minimum learning parameter algorithm and back stepping design technique. Here only adaptive parameter needs to be estimated for each subsystem which shows that all signal in close loop system are uniformly ultimately bounded in probability.

2.4 Membrane assisted reactive distillation

Membrane not only plays the role of a separator, but also used in the reaction itself. Membrane assisted reactive distillation has emerged as a novel technique of hybrid process intensification to achieve higher efficiency and yield in the production of bulk chemicals. In several cases, non-ideal aqueous-organic mixtures are formed which tend to form azeotropes. They can be overcome using membrane separations like pervaporation and vapor permeation since they are very selective and not limited by vapor-liquid equilibrium Rautenbach [57]. The choice of membrane type to be used in membrane reactor depends on parameters such as the productivity, separation selectivity, membrane life time, mechanical and chemical integrity at the operating conditions and, particularly, the cost. Consequently, a hybrid process consisting of membrane-assisted reactive distillation contributes to sustainable process improvement due to arising synergy effects and allows for reduction of investment and operational costs. A review of hybrid processes combining pervaporation with one or more other separation technologies was given by Lipnitzki et al. [58]. The analysis of hybrid separation processes combining membrane separation with conventional distillation was described in Kreis and Gorak [59]. They have presented various configurations corresponding to this hybridization which offers significant advantages like reduced energy requirement, lower production cost, etc.

Membrane hybrid processes can achieve separations which are impractical to achieve with either conventional process. An example for the investigation of a reactive hybrid process concept is the transesterification of methyl acetate and butanol to butyl acetate and methanol by the combination of reactive distillation and pervaporation, as studied by Steinigeweg and Gmehling [60]. They carried out experiment using various catalytic packing is like Katapak S, Katapak SP and Sulzer. However, experiment was not presented for the hybrid technique but only simulation results have been reported. The industrially operated hybrid process for the continuous production of fatty acid esters by reactive distillation and pervaporation was presented by Scala et al. [61]. Ozdemir et al. [62] presented an overview of the commercial polymers used as membranes as well as of other polymers having high potentially for application as a membrane material. However, many industrial processes involve operations at high temperatures. Luo et al. [63] showed that integration of a membrane unit for a side stream withdrawal from the section of reactive distillation where the azeoptrope is liable to form which further improves the product yield.

Polymeric membranes are not generally useful in hybrid reactor and therefore inorganic membranes are preferred. Gorak et al. [64] have shown higher efficiency and capacity of membrane assisted reactive distillation with special focus on Pervaporation unit. Author has deeply identified the current challenges and future predicted trends for implementation of this hybrid technique in the field of chemical and biochemical industry. Holtbruegge et al. [65] represented synthesis of dimethyl carbonate using this hybrid technique to overcome the limitation of chemical equilibrium and azeotrope formation. Replacing membrane at various location in reactive distillation yield different efficiency, which is rigorously studied by Bida et al. [66]. They proved that placing pervaporation membrane at the bottom shows remarkably improved performance with effective economy and energy efficiency. Thus, we can say that combination of pervaporation and reactive distillation exploits the advantages of minimization of cost by reducing energy expenditures and making higher degree of separation.

2.5 Biodiesel in reactive divided wall column: design and control

Due to gradual depletion of world petroleum reserves and impact of environment pollution there is a need for alternative fuels for use in diesel engine. Biodiesel has emerged as a promising alternative because it is renewable and environment friendly and leads to reduction of exhaust emission. Masjuki et al. [67] first researched on the various aspects of use of biodiesel as future fuel by considering the rising cost and increased pollution from conventional carbon containing fuels. They proposed that biodiesel can be manufactured from easy to available raw material like animal oil or used vegetable oil which is generally discarded as a waste. This mishandling also serves as a matter for pollution in water or soil. Thus, biodiesel also minimizes the waste in one way or other. We [68] worked on the effect of molecular weight of fatty acid on the octane rating of biodiesel. There are many processes to convert vegetable oil into biodiesel, but transesterification reaction was found to be most viable process of oil modification. Biodiesel can be produced from animal as well vegetable oil, which is reported by Cr et al. [69]. Today economic factors along with environmental concerns are playing a key role in increase in thermal efficiency. Studies show that biodiesel is much better fuel than fossil fuel-based diesel in term of engine performance, emission reduction, lubricity, and environmental benefits. The production of biodiesel by transesterification in existing conventional processes requires excess alcohol. This excess alcohol must be recovered and purified for reusing by rectification and distillation, which involves additional capital and operating cost. Kiss et al. [70] first reported reactive divided wall distillation column consisting of one condenser, one reboiler, reactive zone a pre fractionators and main column in a single shell leads to process integration and intensification, leading to cost saving and increased purity of final product and side streams product. Later on, several research works have been carried out in the field of reactive divided wall distillation column for biodiesel production. Kiss et al. [71] described the increase in purity and energy reduction of 30% in a divided wall column in which at the bottom of diving wall section, the vapor flow was split proportionally to the cross sectional area of each side. They focused on enhanced methanol recovery from the DWC unit. Delgado et al. [72] recommended the use of petluyk distillation column when the molar fraction of middle component is low. **Figure 4** shows divided wall distillation column.

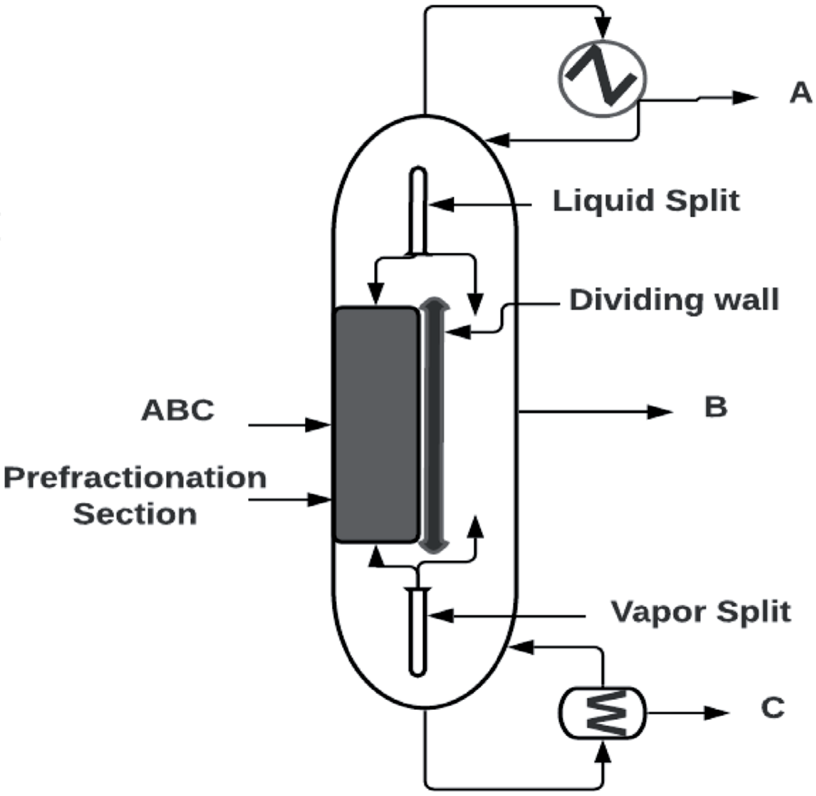

Figure 4.
Divided wall distillation column.

Since reactive divided wall distillation column is a case of process intensification, there is a complex interaction between vapor liquid equilibrium, vapor liquid mass transfer, intra catalyst diffusion and chemical kinetics. Such interactions and strong nonlinearity lead to multi steady states and complex dynamics. Bravo et al. [73] verified this nonlinearity of divided wall in laboratories as well as small pilot plants. The work has been carried out to study the various control system for reactive divided wall distillation column which can lead to process optimization. R-DWC was designed for a quaternary reactive system – two reactants (one in excess) and two products – more difficulties concerning the process control may be expected due to consideration of the high degree of integration of the process. Study was carried to tackle the optimal design, dynamics, and control of such an integrated unit and proposes an efficient control structure for a biodiesel process based on reactive DWC technology. Chongkhong et al. [74] proposed the novel distillation technologies for enhanced bioethanol dehydration, by extending the use of dividing-wall columns (DWC) to energy efficient Extractive Distillation (ED) and Azeotropic Distillation (AD). This technology is beneficial because the industrial production of anhydrous bioethanol requires energy demanding distillation steps to overcome the azeotropic behavior of the ethanol-water mixtures. A recently proposed process by Gomez- Castro et al. [75] depicts control of divided wall technology involving the use of short chain alcohols at supercritical condition that avoids the use of catalyst and this condition was applied to a reactive petlyuk column that results in thermal coupling and more of vapor liquid interactions. Aspen Plus and Aspen Dynamics were used as computer aided process engineering (CAPE) tools to perform the rigorous steady-state and dynamic simulations, as well as the optimization of the new R-DWC based biodiesel process. These control structure described the excellent performance of RDWC for biodiesel production.

2.6 Membrane assisted reactive divided wall column

The production of biodiesel by transesterification in existing conventional processes requires excess alcohol. This excess alcohol must be recovered and purified for reusing by rectification and distillation, which involves additional capital and operating costs. For production of biodiesel various techniques have been proposed such as Reactive Divided Wall. However, a major question remains that which material should be used to make that wall in middle of the column. For this Atadashi et al. [76] have reported membrane biodiesel production technique to provide high quality biodiesel fuel. In this technique the membrane system exploits the characteristic of high selectivity, high surface area and their potential for controlling mixing between two phases. The author has taken canola oil as the base oil for biodiesel synthesis and has studied the effect of membrane pore size and catalyst on the performance of membranes. The results show that membrane reactor restrict the passage of unreacted oils to the biodiesel product mixture and the use of alkaline catalyst result into soap formation while acid catalyst avoids the same.

There are various types of membrane separation processes available like ultrafiltration, microfiltration, pervaporation, etc. Vapor permeation along with RD is a novel technique in which the volatile components are separated by nonporous membrane. One possible process alternative using vapor permeation was suggested by Buchaly et al. [77] for n-propyl propionate synthesis, in which Amberlyst 46 was used to compete the side product formation. The author has used online data reconciliation by satisfying mass, component, and reaction rates as boundary conditions. In another work by Buchaly et al. [78] on same case, a comparison of most common modeling depths such as Maxwell Stefan's equation, equilibrium model with and without considering reaction kinetics was presented. Thermal coupling

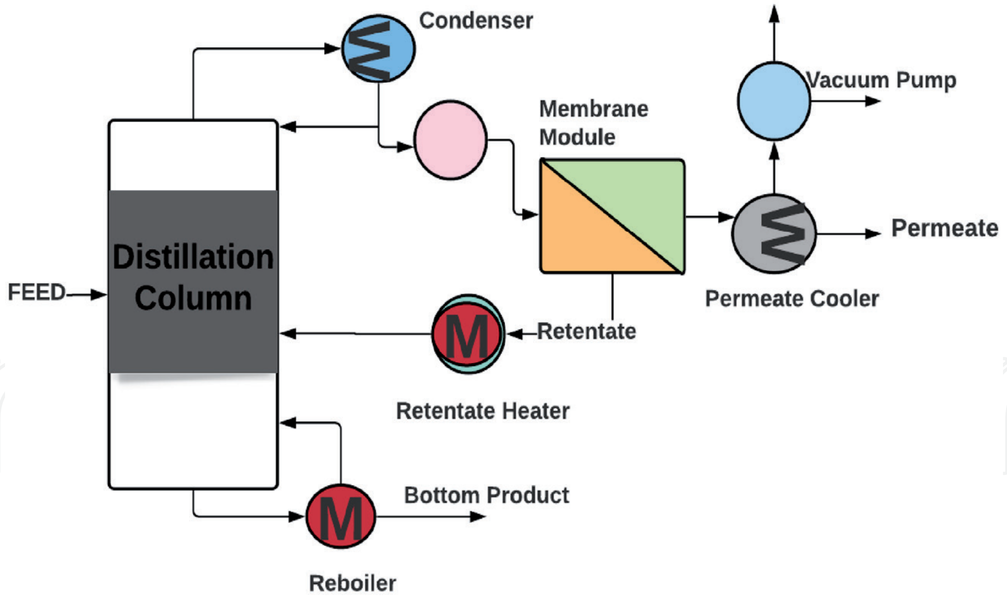

Figure 5.
Membrane reactive distillation column.

between two columns in a sequence has proven to be very successful in providing energy savings with respect to conventional trades. The control of thermally coupled membrane RDWC was presented by Wang et al. [79]. It was reported that controlled stage temperature shows no multiplicity and proper temperature control can maintain reactant inventory. These thermally coupled systems show higher thermodynamic efficiency. Some improvement for dividing wall distillation column likes catalytic packing and non-welded walls have also been proposed by Aspiron et al. [80]. A rigorous study of ASTM standards for biodiesel was carried out by researchers and reported that Membrane biodiesel separation processes provides high-quality biodiesel fuel. He et al. [81] and Saleh et al. [82] have shown that a refining step is necessary to be accompanied with transesterification of biodiesel. Also, the membrane separation processes for biodiesel were carried out under moderate temperature and pressure conditions and their scale-up process found less cumbersome. Sarmento et al. [83] critically examined the production and refining of biodiesel using membrane technology.

Some application and future aspects of dividing wall column with bioethanol production was investigated by Delgado [84]. He has also reviewed practical application of dividing wall column by performing simulation studies. The major emphasis was given on environmental impact of fuel burning and prices of oil and biofuels and the results obtained were compared and summarized by taking the difference between them. The schematic diagram of membrane reactive distillation is presented in **Figure 5**.

3. Conclusion

Reactive distillation as highly nonlinear and practically difficult to control process is challenging study. The current chapter is focused on giving deep review of work carried out by many researchers in the field of reactive distillation design, control and advances in conventional processes. The control of such highly interactive and nonlinear process is possible with several models predictive control techniques including neural network control, fuzzy models, hybrid control structures, adaptive model predictive control and optimization, reactive divided wall concept and membrane divided wall techniques. The focus is given to have wide range application and use of reactive distillation column, its control using advanced techniques and advanced synthesis methods. Many processes and reactions including catalytic reactions are equilibrium limited and reactive distillation is best techniques to get higher conversion. Many advanced techniques of controlling such highly nonlinear processes are proven to be cost effective. The increased use of membrane and synthesis in membrane assisted reactive distillation is also proven to get higher product purity and higher solvent recovery rate.

Acknowledgements

The author is gratefully acknowledge the assistance provided by AICTE, New Delhi and administrative support provided by Madhav Institute of Science & Technology, Gwalior, India and Manipal Academy of Higher Education, Dubai campuses to carry out extensive research work.

Author details

Vandana Sakhre
Manipal Academy of Higher Education, Dubai, UAE

*Address all correspondence to: vandana.sakhre@manipaldubai.com

References

[1] Amy R. Ciric, Deyao Gu, Synthesis of non-equilibrium reactive distillation processes by MINLP optimization, AIChE Journal, Process system engineering, Vol. 40, 1994, pp. 1479-1487.

[2] Vinay Amte, H. Nistala, S. M. Mahajani, R. K. Malik, Optimization based conceptual design of reactive distillation for selectivity engineering, European Symposium on Computer Aided Process Engineering, Vol. 20, 2010, pp. 1-10.

[3] M. Miniotti, M.F. Doherty, Design for simultaneous reaction and liquid-liquid extraction, Ind. Eng. Chem. Res., Vol. 37, 1998, pp. 4748-4755.

[4] Hoshang Subawalla, James R. Fair, Design Guidelines for Solid-Catalyzed Reactive Distillation Systems Ind. Eng. Chem. Res., Vol. 38, 1999, pp. 3696-3709.

[5] M.A. Schenk, Design of operable reactive distillation columns, PhD Thesis. University of London, 1999.

[6] M. F. Cardoso, R. L. Salcedo, Optimization of reactive distillation processes with simulated annealing, Chemical Engineering Science, Vol. 55, 2000, pp. 5059-5078.

[7] N. Vora, & P. Daoutidis, Dynamics and control of an ethyl acetate reactive distillation column, Industrial and Engineering Chemistry Research, Vol. 40, 2001, pp. 833-845.

[8] R. Taylor and R. Krishna, Reactive Distillation: Status and Future Directions, Modeling of Homogeneous and Heterogeneous Reactive Distillation Processes, Vol. 55, 2000, pp. 5183-5229.

[9] Amit M. Katariya, R. S. Kamath, K.M. Moudgalaya, S. M. Mahajani, Non equilibrium stage modeling and nonlinear dynamic effects in the synthesis of TAME by reactive distillation, Computers and Chemical Engineering, Vol. 32, 2008, pp. 2243-2255.

[10] Kamyar Mehran, Takagi-Sugeno Fuzzy Modeling for Process Control, Industrial Automation, Robotics and Artificial Intelligence (EEE8005), Thesis, 2000.

[11] S. Gruner, K.D. Mohl, A. Kienle, E.D. Gilles, G. Fernholz and M. Friedrich, Non-linear control of a reactive distillation column, Control Engineering Practice, Vol. 11, 2003, pp. 915-925.

[12] J.A. Heath, I. Kookos and J.D. Perkins, Process control structure selection based on Economics, American Institute of Chemical Engineers, Vol. 46, 2000, pp. 1998-2016.

[13] M. Schenk, R. Gani, D. Bogle and E. N. Pistikopoulos, A Hybrid Modelling Approach for Separation Systems Involving Distillation, Chemical Engineering Research and Design, Vol. 77, 1999, pp. 519-534.

[14] M.C. Georgiadis, M. Schenk, E.N. Pistikopoulosand, R. Gani, The interactions of design, control and operability in reactive distillation systems, Computers and Chemical Engineering, Vol. 26, 2002, pp. 735-746.

[15] Monroy-Lopera, E. Perez-Cisneros and J. Alvarez-Ramirez, A robust PI control configuration for a high purity ethylene glycol reactive distillation column, Chemical Engineering Science, Vol. 55, 2000, pp. 4925-4937.

[16] M.G. Sneesby, M.O. Tade, T.N. Smith, A multi-objective control scheme for an ETBE reactive distillation column", Chemical Engineering

Research and Design, Vol. 78, 2000, pp. 283-292.

[17] Al-Arfaj and W.L. Luyben, Comparative control study of ideal and methyl acetate reactive distillation. Chemical Engineering Science, Vol. 57, 2002, pp. 5039-5050.

[18] PVS Ravi Chandra, Ch. Venkateshwarlu, Multistep model predictive control of ethyl acetate reactive distillation column, Indian journal of Chemical Technology, Vol. 14, 2007, pp. 333-340.

[19] Sonal Goyal, *A. rani*, V. Singh, SVR tuned PID controller design for reactive distillation process, International Journal of Applied Engineering Research,Vol.7, 2012, pp. 1-6.

[20] Muhammad Shoaib Nizami, Development of a Fuzzy Logic Controller for a Distillation Column Using Rockwell Software, Thesis, 2007.

[21] Zhao Lei , Chunhai Yi , Bolun Yang, Design, optimization, and control of reactive distillation column for the synthesis of tert-amyl ethyl ether, Chemical Engineering Research and Design, Vol. 91, 2013, pp. 819-830.

[22] A.C. Dimian, C.S. Bildea, F. Omata, A.A. Kiss, Innovative Process for fatty acid esters by dual reactive distillation, Computers and Chemical Engineering, Vol.33, 2009, pp. 743-750.

[23] Kwantlp Konakom, A. Saengcham, P. Kittisupakorn, High purity ethyl acetate production with a batch reactive distillation column using dynamic optimization strategy, Proceedings of the World Congress on Engineering and Computer Science , Vol. 2, 2010 , pp. 978-988.

[24] M.G. Sneesby, O.M. Tade and T.N. Smith, Two-point control of a reactive distillation column for composition and conversion, Journal of Process Control, Vol. 9, 1997, pp. 19-31.

[25] F. Zhao, J. Ou, and W. Du, Pattern based fuzzy predictive control for a chemical process with dead time, Eng. Appl. of Artificial Intelligence, Vol. 13, 2000, pp. 37-45.

[26] J.E. Seem, A new pattern recognition adaptive controller with application to HVAC systems, Automatica, Vol. 34, 1998, pp. 969-982.

[27] M.J. Jang and C.L. Chen, Fuzzy successive modelling and control for time-delay system, Int. J. System Science, Vol. 27, 1996, pp. 1483-1490.

[28] Y.C. Tian, Inference of conversion and purity for ETBE reactive distillation, Brazilian J. of Chem. Eng., Vol. 17, 2000, pp. 617-625.

[29] Vikrant Bansal, V. Sakizlis, R. Ross, J. D. Perkins, New algorithm for mixed integer dynamic optimization, Computers and Chemical Engineering, Vol. 21, 2003, pp. 647-668.

[30] S. C. Patwardhan, S. Narasimhan, J. Prakash, R.B. Gopaluni, S. L. Shah, Nonlinear Bayesian State Estimation, Review and Recent Trends, Control Engineering Practice, Vol. 20, 2012, pp. 933—953.

[31] V.M. Becerra, P.D. Roberts, G.W Grifiths, Applying the extended Kalman filter to systems described by nonlinear differential-algebraic equations, Control Engineering Practice, Vol. 9, 2001, pp. 267-281.

[32] R. K. Mandela, R. Rengaswamy and S. Narasimhan, Recursive state estimation techniques for nonlinear differential algebraic systems, Chemical Engineering Science, Vol. 65, 2010, pp. 4548-4556.

[33] B. Huang, and R. Kadali, Dynamic Modeling, Predictive Control and

Performance Monitoring. Springer publication, 2009, pp.1-10.

[34] Brent M Akesson, H.T. Toivonen, A neural network model predictive controller, Journal of Process Control, 2006, Vol. 16, pp. 937-946.

[35] N. Sharma, Control of Reactive Distillation- A review, International Journal of Chemical Reactor Engineering, 2010, pp. 4-10.

[36] Robert Babusk, Fuzzy Systems, Modeling and Identification, IEEE Transactions on systems, man, and cybernetics, Vol.15, 1985, pp. 116-132.

[37] Fatima Barcelo Rico, Jose M. Gozalvez-Zefrilla, Jose Luis Diez, and Asuncion Santafe-Moros, Modeling and Control of a Continuous Distillation Tower through Fuzzy Techniques, Chemical Engineering Research and Design, 2011, Vol. 89, pp.107-115.

[38] M. Pekkanen, A local optimization method for the design of reactive distillation, Computers & Chemical Engineering, Vol. 19, 1995, pp. 235-240.

[39] D.O. Araromi, J. O. Emuoyibofarhe, J. A. Sonibare , Fuzzy Hybrid Modeling of a Reactive Distillation Column for Ethyl Acetate Process, International Journal of Engineering and Technology, Vol.2, 2012, pp. 888-899.

[40] C. Sumana, Ch. Venkateshwarlu, Optimal selection of sensors for state estimation in a reactive distillation process, Journal of Process Control, 2009, Vol. 19, pp. 1024-1035.

[41] Xudong Wang, Rongfu Luo, Huihe Shao, Designing a Soft Sensor for a Distillation Column with Fuzzy Distributed Radial Basis Function Neural Network, Decision and Control, Vol. 2, 1996, pp. 1714-1719.

[42] Jaroslava Zilkova, Nonlinear System Control Using Neural Networks, Acta Polytechnica, Vol. 3, 2006, pp. 85-90.

[43] S.R. Vijaya Raghavan, T.R. Radhakrishnan, K.Srinivasan, Soft Sensor Based Composition Estimation and Controller Design for an Ideal Reactive Distillation Column, ISA transactions, 2011, Vol. 50, pp. 61-70.

[44] K.J. Jithin Prakash, Neuro estimator based GMC Control of Batch Reactive Distillation, ISA Transaction, Vol. 50, 2011, pp. 537-539.

[45] Almila Bahar, and Canan Ozgen, State Estimation and Inferential Control for a Reactive Batch Distillation Column, Engineering Applications of Artificial Intelligence, Vol. 23, 2010, pp. 260-270.

[46] S. Nithya, N.S ivakumaran, T. Balasubramanian, Controllers implementation based on soft-computing for non-linear process, Proceedings of the World Congress on Engineering and Computer Science, Vol. 2, 2010, pp. 978-988.

[47] Elrashid Idris, S. Engell, Real Time Optimization Nonlinear Control Applied to a Continuous Reactive Distillation Process, International Federation of Automatic Control, Vol. 18, 2011, pp. 4892-4897.

[48] V. Sujatha, R. C. Panda, Control configuration selection for multi input multi output processes, Journal of Process Control, Vol.23, 2013, pp. 1567-1574.

[49] Bidyadhar Subudhi, Nonlinear system identification using memetic differential evolution trained neural networks, Neurocomputing, Vol. 74, 2011, pp. 1696-1709.

[50] Hung-Ching Lu, Ming-Hung Chang, Cheng-Hung Tsai, Parameter estimation of fuzzy neural network controller based on a modified differential evolution Neurocomputing, Vol. 89, 2012, pp.178-192.

[51] Maciej Lawrynczuk, Explicit nonlinear predictive control algorithms with neural approximation, Neurocomputing, 2014, Vol. 129, pp. 570-584.

[52] K. K. C. W. Kandanapitiya, Modeling of Reactive Distillation for Acetic Acid Esterification, Journal of the Institution of Engineers, Vol. 48, 2015, pp. 17-23.

[53] Matthias Wierschem, Continuous Enzymatic Reactive Distillation with Immobilized Enzyme Beads, AICHe, Annual meeting, 2015.

[54] Tianping Zhang, Xiaonan Xia, Decentralized adaptive fuzzy output feedback control of stochastic nonlinear large scale systems with dynamic un certainties, Information Sciences, Vol. 315, 2015, pp: 17-18.

[55] Zhouhua Peng, Dan Wang, Hongwei Zhang, Yejin Lin, Cooperative output feedback adaptive control of uncertain nonlinear multi-agent systems with a dynamic leader" Neurocomputing, Vol. 149, 2015, pp. 132-141.

[56] Guozeng Cui, Zhen Wang, Guangming Zhuang, Yuming, Chu, Adaptive Centralized NN control of large scale stochastic nonlinear time delay systems with unknown dead zone inputs, Neurocomputing, Vol. 158, 2015, pp. 194-203.

[57] Rautenbach, Separation potential of pervaporation, Journal of Membrane Science, Vol. 25, 1997, pp. 25-31.

[58] F. Lipnitzki, R. W. Field and P. K. Ten, Pervaporation-based hybrid process: a review of process design, applications and economics, Journal of Membrane Science, 1999, Vol. 153, pp. 183-210.

[59] P. Kries, A. Gorak, Process analysis of hybrid separation processes combination of distillation and Pervaporation, Chem. Eng. Res. Des. 2006, Vol. 84, pp. 595-600.

[60] Sven Steinigeweg, Jurgen Gmehling, Transesterification processes by combination of reactive distillation and pervaporation, Chemical Engineering and Processing, 2004, Vol. 43, pp. 447-456.

[61] Von Scala, J. Fassler, E. Gerla, 2005, Maus, Kontinuierliche Herstellung von kosmetischen Fetts aureestern mittels Reaktivrektifikation and Pervaporation, Chem. Ing. Tech., Vol. 77, pp. 1809-1813.

[62] S.S. Ozdemir, Catalytic Polymeric Membrane: Preparation & Application, Appl. Catal A. Gen, Vol. 307, 2006, pp. 167-183.

[63] G.S. Luo, M. Niang, P. Schaetzel, Separation of ethyl tert-butyl ether-ethanol by combined pervaporation and distillation, Chemical Engineering Journal, Vol. 68, 1997, pp. 139-143.

[64] A. Gorak, Reactive and membrane assisted distillation: recent developments and perspective, Chemical Engineering Research, and design, 2013, Vol. 91, pp. 1978-1991.

[65] J. Holtbruegge, M. Wierschem, Hybrid configuration of reactive distillation and vapor permeation for the production of dimethyl carbonate and propylene glycol, A Thesis, 2013.

[66] L.V. Bida, Gongping Liu, Xueliang Dong, Wang Wei, and Wanqin Jin, Novel Reactive Distillation–Pervaporation Coupled Process for Ethyl Acetate Production with Water Removal from Reboiler and Acetic Acid Recycle, *Ind. Eng. Chem. Res.*, 2012, Vol. 51, pp. 8079-8086.

[67] H. Masjuki, Biofuels as diesel fuel alternative: An overview, Journal of

energy heat mass transfer, 1993, Vol. 15, pp. 293-304.

[68] Kloptenstem We, Effect of molecular weight of fatty acid esters on cetane numbers as diesel fuels, J Amer oil chemical society, 1988, Vol 65, pp. 1029-1031.

[69] Engler Cr, Le Pori We, Animal fats as alternative diesel fuels from renewable resources, Proc Altern Energy conference Amer Society, 1992, pp. 89-96.

[70] Anton A. Kiss, J. J. Pragt, C. J. G. van Strien, Reactive dividing-wall columns: towards enhanced process integration, Distillation Absorption, 2010, pp. 253-258.

[71] Anton A. Kiss, 2012, Enhanced bioethanol dehydration by extractive and azeotropic distillation in dividing wall columns, Separation and Purification technology, Vol. 86, pp. 146-153.

[72] Raul Delgado, S. Hernandez, F. Omar, B. Munoz, J. Gabriel, S. Hernandez, A.J.C. Montoya, From simulation studies to experimental tests in a reactive dividing wall distillation column, Chemical Engineering Research and Design, 2012, Vol. 90, pp. 855-862.

[73] J.L. Bravo, A. Pyhalathi and H. Jaervelin, Investigation in a catalytic distillation pilot plant: vapor/ liquid equilibrium, kinetics and mass transfer issues, Ind. Eng. Chem. Res., 1993, vol. 32, pp. 2220-2225.

[74] S. Chongkhong, Biodiesel production by esterification of fatty acid distillate, Biomass and Bioenergy, 2007, Vol. 31, pp. 563-568.

[75] Fernando Israel Gomez-castro, V. R. Ramirez, J.G.S. Hernandez, S. Hernandez, Feasibility study of a thermally coupled reactive distillation process for biodiesel production, Chemical Engineering and processing, Vol. 49, 2010, pp. 262-269.

[76] I. M. Atadashi, M.K. Aroua, A.R. Abdul, N.M.N Sulaiman, Membrane biodiesel production and refining technology: A critical review, Renewable and Sustainable Reviews, 2011, pp. 1-12.

[77] Carsten Buchaly, Peter Kreis, Andrej Gorak, Experimental Investigation of reactive Distillation in Combination with Membrane Separation, Chair of Fluid Separation processes, Vol. 152, 2006, pp. 373-383.

[78] Carsten Buchaly, Peter Kreis, Andrej Gorak, Hybrid separation Processes-Combination of Reactive Distillation with Membrane Separation, European Congress of Chemical Engineering, Vol. 6, 2007, pp. 1-17.

[79] San Jang Wang, David S.H. Wong, Shuh-Woei Yu, Design and control of transesterification reactive distillation with thermal coupling, Computers and Chemical Engineering, Vol.32, 2008, pp. 3030-3037.

[80] Asprion N, Kaibel G. Dividing wall columns: Fundamentals and recent advances, Chem Eng Process, 2010, Vol. 49, pp. 139-146.

[81] H.Y. He, X. Guo, Comparison of membrane extraction with traditional extraction method for biodiesel production, Journal of American Oil Chemist Society, Vol. 83 2006, pp. 457-460.

[82] Saleh, Effect of soap, methanol and water on glycerol particle size in biodiesel purification, Energy Fuels, Vol. 24, 2010, pp. 6179-6186.

[83] L. A. Sarmento, C.B. Spiricigo, Performance of reverse osmosis membrane in separation of CO_2 and

essential oil, Journal of membrane Science, 2004, Vol. 237, pp. 71-76.

[84] Raul Delgado-Delgado, Some operational aspects and applications of dividing wall columns: energy requirements and carbon dioxide emissions, Clean Technologies and Environmental Policy, 2015, Vol. 17, pp. 657-665.