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Faculty of Applied Chemistry and Materials Science
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**Ph.D. Thesis – Summary**

# Design and Control of Energy-Efficient Processes for Bioethanol and Biobutanol Dehydration

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**Keywords:** Bioethanol, Biobutanol, process design, process control, optimization, heat integration, economic evaluation, dividing wall-column, vapor recompression

# INTRODUCTION

World energy consumption keeps increasing and renewable energy becomes more attractive due to global warming caused by high $CO_2$ emissions from fossil fuels. Biomass is one of the renewable energy sources that can generate biofuels through the fermentation process. Bioethanol and biobutanol are considered good valuable competitors for biofuels. Bioethanol is already used in mixture with gasoline in car engines, but biobutanol features a higher energy content (36 MJ/kg) which makes it able to be used as independent biofuel without the modification of the present engines [1]. In order to benefit from these biofuels, the costs with upstream and downstream processing of biomass must be profitable. Chemical engineering is the one that deals with obtaining a higher concentration of biofuel by fermentation as well as the efficiency of the separation processes. The main separation techniques reported for ethanol and butanol separation are distillation, adsorption, gas stripping, liquid-liquid extraction, reverse osmosis, perstraction, pervaporation, and hybrid separations [1]. Among them, distillation is the separation technique largely used at an industrial scale, with a high potential of process intensification and heat integration. One of the well-known advanced distillation techniques is the dividing-wall column which can integrate multiple distillation columns into a single one to reduce the investment and operation costs [2]. For example, such a distillation column was designed by Kiss and Ignat for bioethanol dehydration [3]. Up to 40% energy savings were achieved by heat integration and adding vapour recompression technology (heat pump) [4]. The separation of the diluted ABE mixture should be approached in this way to design an energy-efficient process. The liquid-liquid extraction can also be considered to reduce the energy needs for water removal. Moreover, the applicability of each separation design should be proven by a dynamic and process control study.

## **CHAPTER 1 –** *From Substrate to bioethanol*

In bioethanol production, the upstream process plays an important role in the efficiency of the downstream process. The higher the concentration of ethanol after fermentation the lower is the cost of downstream processing. Bioethanol can be obtained from different types of feedstocks (agricultural products, lignocellulosic biomass, agricultural wastes or algae) which are subject to pretreatment (physical, chemical or biological), hydrolysis and fermentation.

The first generation of feedstocks (FGF) for bioethanol production comes from agricultural products (corn, wheat, barley, and sugarcane). The disadvantages of using these raw materials are the production costs, the type of plant, and the climate necessary to grow it. The second generation feedstocks (SGF) and third generation feedstocks (TGF), which not compete with food crops, are lignocellulosic biomasses from agricultural wastes, and respectively algae/seaweeds, with low lignin content [5]. However, just FGF and SGF have industrial potential.

The most expensive upstream processes at industrial scale are pretreatment and hydrolysis. Anyway, the pretreatment process of the biomass must be done to obtain high yield of ethanol in hydrolysis and fermentation process [6]. The pretreatment process is divided in several classes: physical, chemical, physical-chemical and biological [7].

The purpose of ***physical pretreatment*** is to reduce the size of the plant and to increase the surface area to make sugars more accessible to enzymes [8]. Physical pretreatment can be done using the following technics: milling and grinding, auto-hydrolysis (uncatalyzed steam explosion) and liquid hot water pressure [9]. ***Chemical pretreatment*** is basically used to degrade lignin and hemicellulose from biomass by acid hydrolysis, alkaline hydrolysis or oxidation [10]. The ***physical-chemical pretreatment*** can greatly influence the yield of lignocellulosic raw material. The hemicellulose is the most thermal sensitive component (150 °C), therefore a good pH, humidity and temperature are required [11]. ***Biological pretreatment*** is a time-consuming process (4 – 8 weeks) and delivers a high yield of the product without toxic compounds or inhibitors. Although the process is cheap and does not require much energy, it cannot be applied on an industrial scale [12]. There are three types of the biological pretreatment: microbial, enzyme and soft-rot fungi.

The process of ***hydrolysis*** aims to depolymerize cellulose and hemicellulose into glucose respectively pentose and hexose, by using water with enzymes or acids. A good quality of hydrolyzate can generate a higher yield of ethanol during the fermentation step, at low costs.

For example, the second generation feedstocks contain glucose, galactose, mannose, xylose, and arabinose delivering high ethanol yield in fermentation step, being also more complex than the starch of the first generation feedstocks, which contain just glucose [13; 14]. Acid hydrolysis involves treating the substrate with sulfuric acid and hydrochloric acid at a certain temperature and period of time to allow the conversion of hemicellulose and cellulose into sugars. Enzymatic hydrolysis is driven by expensive enzymes as cellulase and hemicellulase to break the bonds of cellulose and hemicellulose. Cellulase can be produced by different type of bacteries, as Clostridium, Cellulomonas, Thermomonospora, Bacillus, Bacteriodes, Ruminococcus, Erwinia, Acetovibrio, and Streptomyces [15].

The ***fermentation*** process is the most important step for the conversion of glucose and xylose into ethanol. In order to achieve this transformation, the substrate must be mixed with water and micro-organisms and left for submerged or solid-state fermentation in batch, fed-batch or continuous systems [16]. The yeasts, bacteria, and fungi are known as fermentation microorganisms able to ferment sugars and convert pyruvate into ethanol. The conversion efficiency may also depend on the bioreactor chosen. The bioreactor is chosen according to the following variables: mode of operation (batch, fed-batch or continuous), feedstock composition, productivity, operating conditions (temperature, pressure, degree of agitation, etc.), size and shape of the reactor, desired product, process economy, and safety [17; 18]. The operation mode is chosen based on the genetic stability of the microorganisms, type of substrate, productivity, flexibility, control, risk of bacterial contamination and the economy of the process.

The bioethanol produced in the fermentation process can reach a concentration at which the microorganisms can be inhibited, thus stopping the ethanol production. Therefore, the fermentation process is combined with a ***recovery technique*** to continually separate the ethanol from fermentation broth. Ethanol can be recovered from fermentation by separation techniques like distillation, pervaporation, adsorption, gas stripping, vacuum fermentation or solvent extraction [19]. Distillation is a separation technique based on the volatility of the components, used for many years for ethanol recovery. The adsorption technique uses a porous adsorbent capable of adsorbing and desorbing ethanol during the fermentation process, the broth being constantly recycled. Gas stripping technique uses anaerobic gas, such as carbon dioxide and nitrogen to recover ethanol from fermentation broth. Pervaporation is the separation technique usually applied for the separation of azeotropic mixtures, organic mixtures or solutions.

In this chapter some experimental results from the literature regarding the concentration and yield of bioethanol obtained from lignocellulosic biomass were collected and presented.

## **CHAPTER 2 –** *Conventional Bioethanol Dehydration Process*

Dehydration of the bioethanol by distillation is an energy-consuming process due to the low concentration of ethanol (10-12%wt.) obtained from fermentation and the ethanol-water azeotrope. The typical process for ethanol dehydration involves a pre-concentration step, where a near-azeotropic ethanol-water mixture is obtained, followed by breaking the ethanol-water azeotrope by means of extractive distillation using ethylene glycol as a mass-separating agent (figure 2.1). Kiss and Ignat [20] discuss the optimal design of a bioethanol dehydration plant, showing that the optimal concentration of pre-concentrated ethanol is 91% wt.. Dynamics and control is as important as economic optimization. Kiss, Ignat and Bildea [21] developed a flow-driven Aspen Dynamics simulation of the ethanol dehydration plant, which was used to prove the controllability of the optimal design. Although flow-driven simulation can be used for a quick assessment of the plant controllability, pressure-driven simulation is needed when a more realistic dynamic model is required. However, pressure-driven dynamic simulation is more challenging as it involves more detailed modelling of the pressure changes across the plant by means of the pumps, compressors, valves, and other hydraulic elements. Therefore, the goal of this chapter is to develop a pressure-driven dynamic simulation of the bioethanol dehydration plant and to use this model for a controllability study.

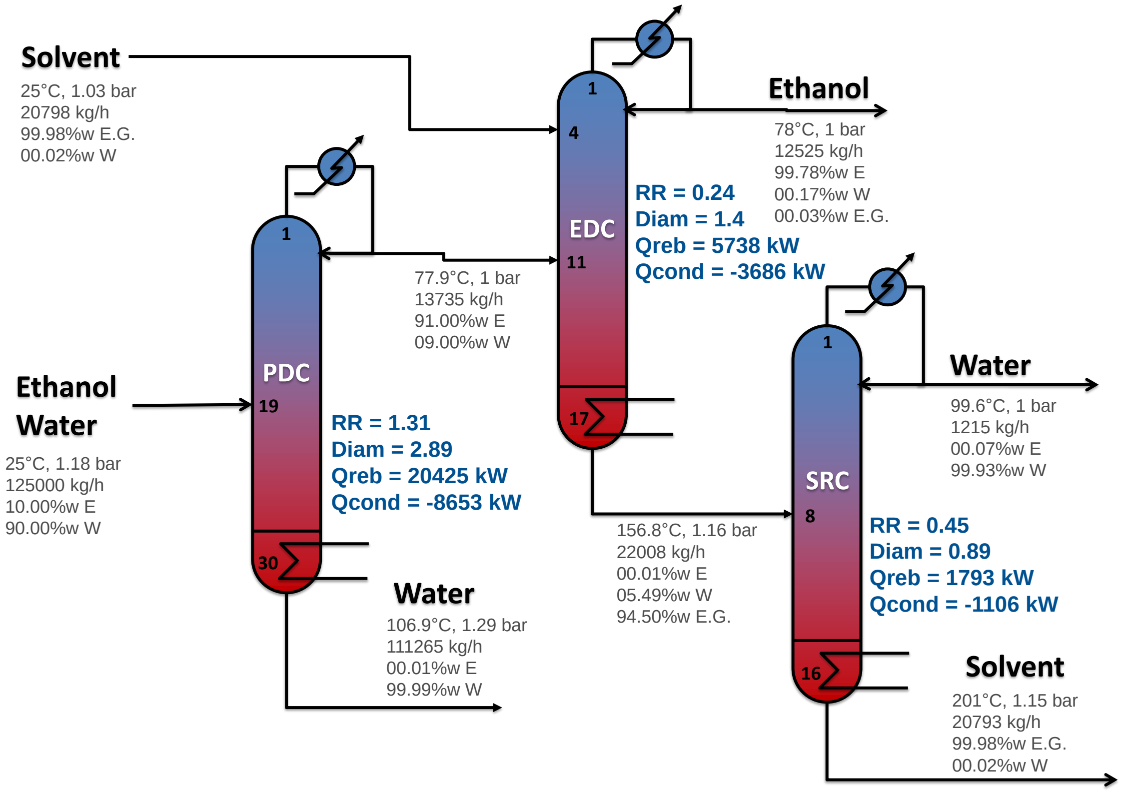

*Figure 2.1. Stream report and unit sizing for bioethanol dehydration plant*

A steady-state simulation was developed in Aspen Plus [21; 22], based on the design parameters provided by reference [20]. The NRTL model [23] was used to represent the non-ideality of the liquid phase, all the binary interaction parameters being available in the Aspen Plus database.

A pressure-driven dynamic simulation was developed using Aspen Dynamics. All vessels were sized based on 10 minutes residence time. The column diameter was obtained using the “tray sizing” facility offered by Aspen Plus.

The complete flowsheet, including the control loops is presented in Figure 2.1. The control of each distillation column is standard: the pressure is controlled by condenser duty; the sump and reflux drum levels are controlled by valve opening on the bottoms and distillate lines, respectively; one temperature in the stripping section is controlled by the reboiler duty. In the PDC, the reflux rate is kept constant. In the EDC and SRC, the mass reflux is used to control one temperature in the rectifying section. The trays used for temperature control were chosen as the most “sensitive” trays of the columns temperature profile [24]. The mass fraction of water in the ethanol product is measured by a concentration analyzer and kept at its setpoint by changing the EDC solvent / feed ratio. The level in the solvent buffer tank is controlled by the solvent makeup.

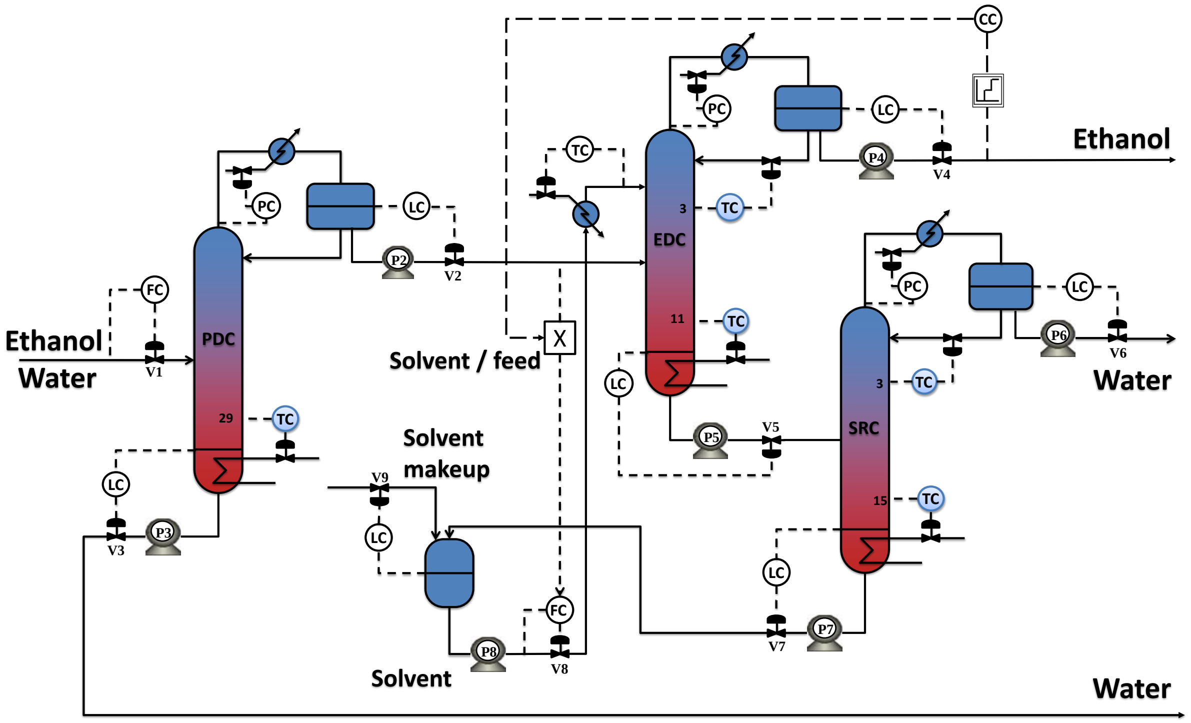

*Figure 2.2. Bioethanol purification plant dynamic control structure*

All the controllers are PI type. Controller tuning was achieved by the following procedure. For each control loop, appropriate ranges of the process variable PV and controller output OP where chosen around the nominal values, based on the accepted variation of PV from its setpoint and the maximum change of the manipulated variable OP. Then the controller gain was set to 1 %/%. The reset time was set equal to an estimated value of the process time constant. The tuning of ethanol concentration controller was achieved by finding the stability limit using the ATV procedure [25] and using the Tyreus-Luyben settings [25].

The performance of the control system with respect to feed rate disturbances is presented in Figure 2.3 (left). The simulation starts from steady state. The feed flow rate is increased from 125,000 kg/h to 150,000 kg/h in two steps at time *t* = 6 h and *t* = 14.5 h. Then, the flow rate is decreased to 100,000 kg/h in several steps (at time *t* = 24, 34 , 43 and 49 h) and then (at time *t* = 54 h) brought back to the initial value. The product flow rates (water and ethanol) change accordingly to the feed rate. Moreover, the flow rate of solvent to the EDC column is adjusted to match the flow rate of ethanol-water mixture fed to the EDC column. Despite the large disturbances, the product purities remain high, close to the nominal values.

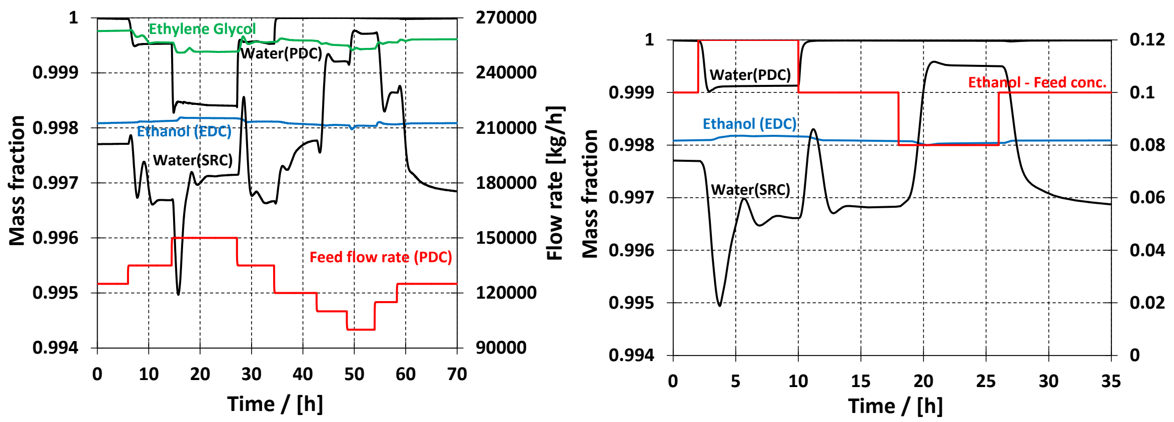

*Figure 2.3. Dynamic simulation results – change of the feed flow rate (left); change of the feed composition (right)*

The performance of the control system with respect to feed composition disturbances is presented in Figure 2.3 (right). As the ethanol concentration is changed from 10% wt. to 12% wt. or 8% wt., the purity of the ethanol product exceeds 99.8% wt. specification. The purity of water product also remains high.

The optimally-designed plant investigated in this work shows excellent controllability properties: the product purities are kept on-spec despite large disturbance in feed flow rate and composition.

# **CHAPTER 3 –** *Heat Pump Assisted Extractive Dividing-Wall Column for Bioethanol Dehydration*

Bioethanol is a renewable fuel produced in largest amounts, by various routes: corn-to-ethanol, sugarcane-to-ethanol, basic and integrated lignocellulosic biomass-to-ethanol. In all cases, the raw materials are pre-treated and then fermented to yield diluted bioethanol of 5-12% concentration [26; 27; 28]. This needs to be further concentrated to 99-99.8 %wt (depending on the standard), in an energy intensive process that involves distillation combined usually with extractive distillation [20]. The concentration of diluted streams from fermentation is not an issue related only to ethanol, but a more generic problem encountered in biorefineries [5]. Various energy improvements of the distillation process have been proposed for the ethanol separation and purification, such as the use of internally heat-integrated distillation columns (HIDiC) that are based on the vapour recompression principles [29; 30]. However, the HIDiC technology is hindered by large equipment costs (leading to long payback times) and it is also limited to producing only hydrated ethanol.

In a follow-up study, Kiss and Ignat (2012) proposed a novel extractive DWC configuration that integrates the three distillation columns of a classic process – pre-concentration distillation column (PDC), extractive distillation column (EDC), and solvent recovery column (SRC) – into a single unit [3]. On top of this integrated extractive DWC system, Luo et al. (2015) added also a vapour recompression (VRC) heat pump to further increase the energy savings up to 40% (see Figure 3.1) [4]. This elegant solution was also featured at the joint PSE-2015 & ESCAPE-25 conference (www.pse2015escape25.dk) among the best contributions in the process design section. But the authors were also challenged to prove the controllability of such a highly-integrated system.

The smart combination of heat pumps (e.g. vapour recompression) with extractive dividing-wall column (E-DWC) technology offers significant advantages in terms of low total annual costs and major energy savings of about 40%. But the controllability of the process is just as important as the cost savings, considering that the plant must be available and fully operable in order to deliver the expected design savings. The problem is that a more integrated system has less flexibility and fewer degrees of freedom hence being more difficult to control. To solve this problem, we investigate the dynamics of the process and propose a rather simple but effective process control structure that is able to reject common disturbances, within short settling times and with low overshooting.

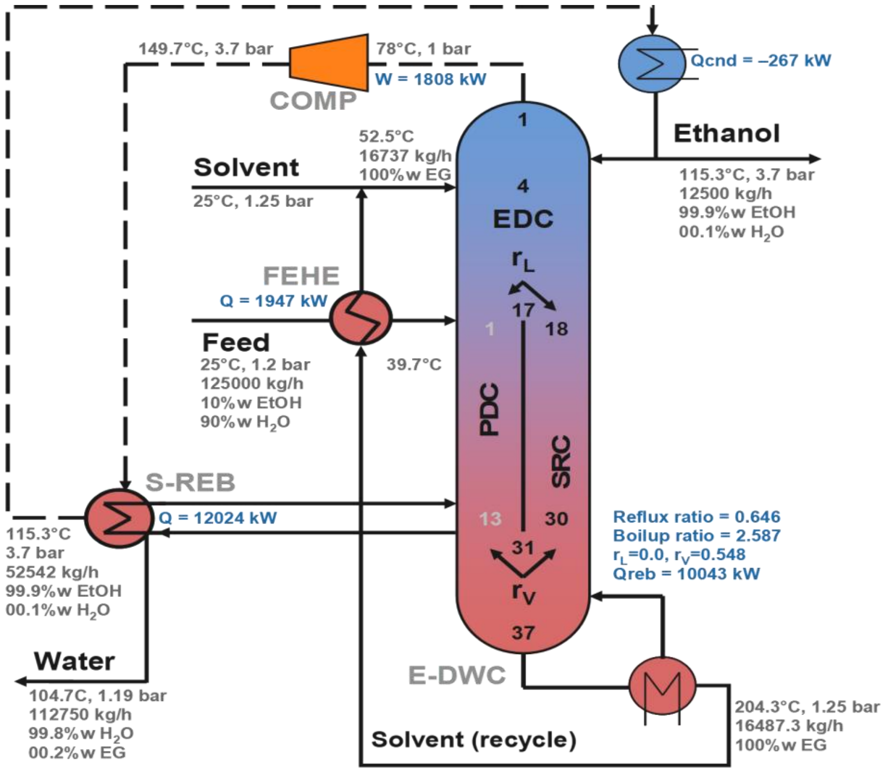

*Figure 3.1. Flowsheet of the VRC assisted extractive-DWC for bioethanol dehydration*

In this chapter, an efficient control structure is developed by addressing these tasks of plantwide control. To achieve this goal, dynamic simulations (carried out in Aspen Dynamics) were used to understand the dynamics of the process and to prove the effectiveness of the proposed control structures. The starting point is the VRC assisted E-DWC design proposed by Luo et al. (2015), which achieves 40% energy savings compared to the conventional separation sequence [4]. Note that further energy integration could be attempted by using the product streams for feed pre-heating. However, as there is no liquid flow from the main column to the pre-fractionator, the feed stream acts as reflux. Therefore, feeding below the boiling point improves separation efficiency. Figure 3.1 presents for details of the VRC assisted E-DWC, including the mass and energy balance.

The original Aspen Plus steady state simulation was exported to Aspen Dynamics. The simulation consists of two separate RADFRAC models which correspond to the PDC and EDC-SRC sides of the dividing-wall column and are inter-connected by vapour and liquid streams. The dynamic simulation model is presented in Figure 3.2, which includes the setpoint of the main controllers. The safety of a process is typically achieved by a combination of inherent safe design, safety relief valves and instrument protective functions. The process control system supports safety by controlling the liquid levels and gas pressures, thus ensuring that all the material is contained within the process boundaries.

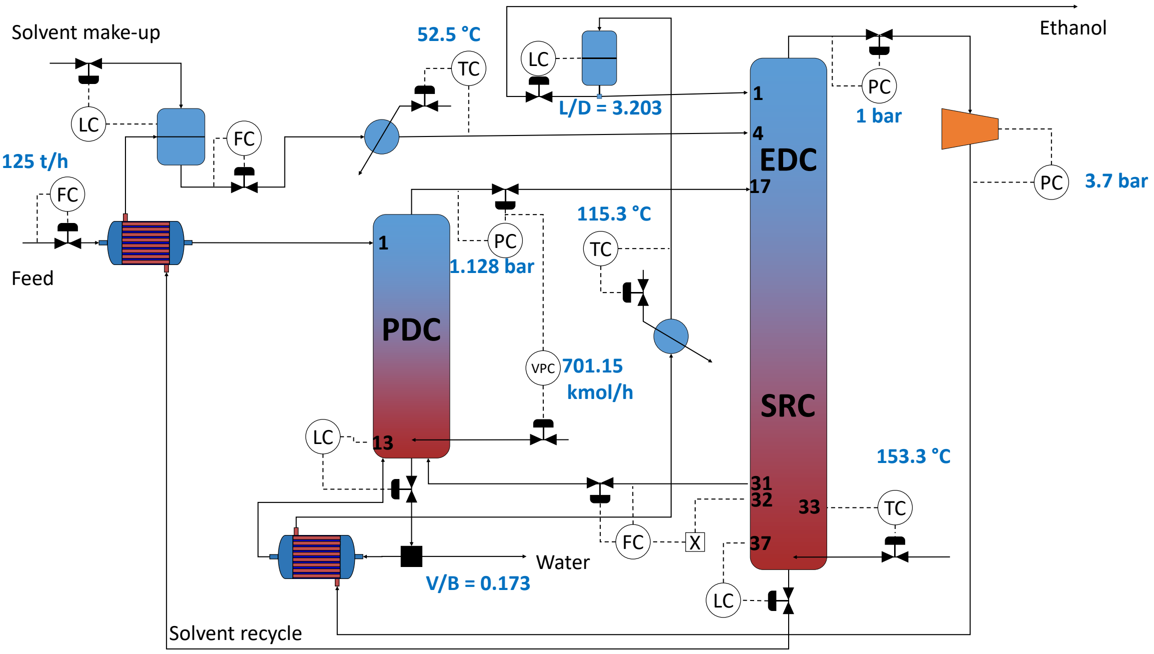

*Figure 3.2. Dynamic simulation model of the VRC assisted extractive-DWC for bioethanol dehydration including the control loops necessary for stabilizing the process*

After implementing the basic inventory control, the simulation can be run. Starting from the steady state, as long as the system is not disturbed, the process variables (flow rates, temperatures, pressures) stay at their nominal values. However, the simulation breaks for any small disturbances. Thus, quality control loops were added, as follows: a temperature controller was added on the condensate stream; a temperature controller for stage 33 (the most sensitive tray) was added by manipulating the EDC-SRC reboiler duty.

After these changes, the simulation is successful as long as it starts from the steady state and no disturbance is introduced. However, the simulation still breaks for any small increase of the feed rate, which shows that the operating point is unstable. What happens is the following. Increasing the flow rate of PDC feed (cold liquid) leads to a lower vapour flow rate along PDC. As a result, the pressure drops and less vapour is fed to the EDC-SRC section (the PDC pressure controller closes the vapour distillate valve). The pressure on the EDC-SRC section drops and the EDC-SRC pressure controller decreases the EDC-SRC vapour distillate rate. Then, less heat is transferred in the (heat-integrated) side reboiler, followed by further decrease of the vapour flow rate along the PDC. Simultaneously, more EG is found in the bottom section of the EDC-SRC which leads to further temperature increase (despite the lower pressure). The SRC-EDC temperature controller reacts and decreases the reboiler duty, leading to an additional reduction of the vapour flow along the EDC-SRC section (and therefore to further decrease of the SRC-EDC vapours distillate flow). Clearly, an appropriate control structure is required.

The key to stabilizing the system is adding a small duty to the last stage of the PDC column. This duty can then be used as new manipulated variable in a control loop which ensures that the vapour flow rate from the PDC to the SRC-EDC side is constant when the system is affected by disturbances.

When the valve-position controller VPC (Figure 3.3) is added, feed flow rate and composition disturbances can be introduced without affecting the stability of the process. However, the control structure shown in Figure 3.3 is not able to maintain the quality of the products, namely the purity of the water and ethanol streams. Moreover, measuring the flow rate of the vapour going from the PDC to the SRC-EDC side is difficult in practice. Dynamic simulations also reveal that the solvent feed and PDC bottoms heat exchangers require heating or cooling, depending on the disturbance.

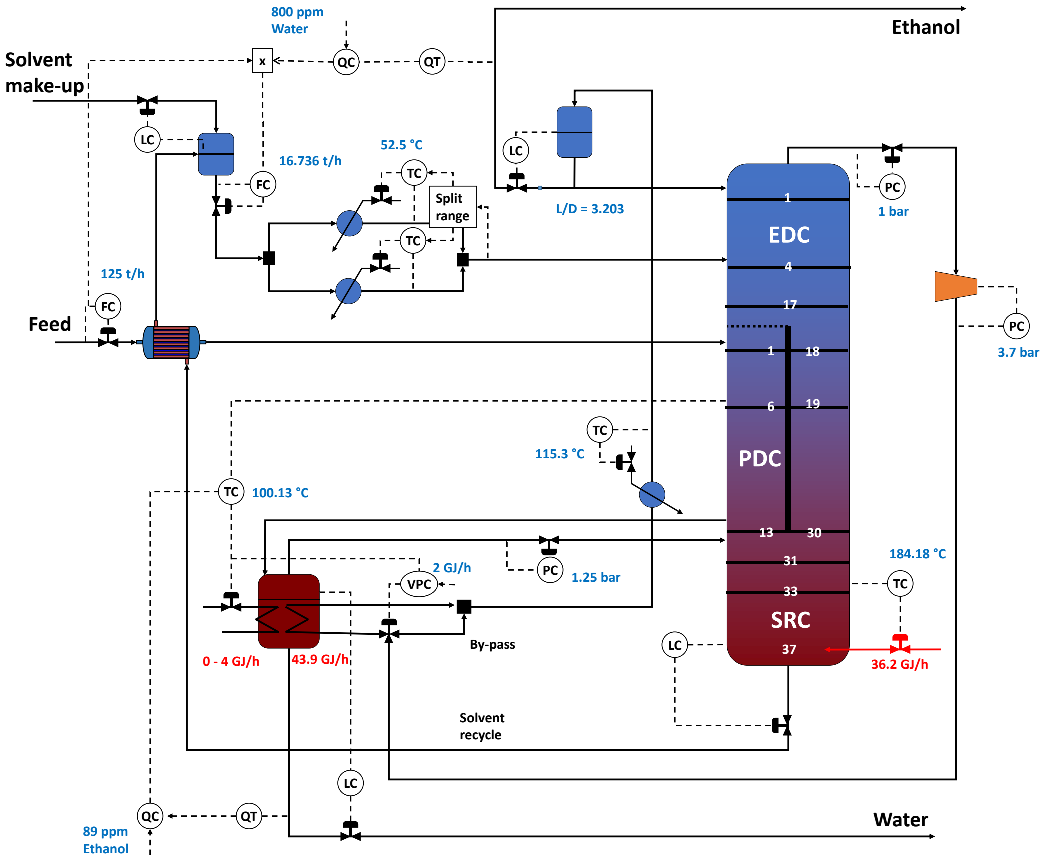

*Figure 3.3. Control structure of the VRC assisted E-DWC for bioethanol dehydration*

Figure 3.3 shows the control structure for the VRC assisted E-DWC. For convenience, the setpoint of several controllers are included. The production rate is set by changing the setpoint of the flow controller manipulating the feed stream flow rate. A ratio controller ensures that the amount of solvent used (make-up and recycle stream) is proportional to the feed flowrate. This ratio is set by a quality controller which achieves constant mass fraction of water impurity in the ethanol product. The temperature of the solvent added to the E-DWC unit is controlled by a split range setup, in which one of the heat exchangers cools-down or heats-up the solvent stream, as required.

The compressor is operated at constant outlet pressure – the pressure at which the valve on the outlet line opens – and variable flow rate, which is achieved by means of an internal recycle or other means. The duty of the PDC (external) reboiler is provided by a fraction of the compressed vapours (about 94% at design conditions) and by hot utility. The external duty provided by the hot utility is used to control the temperature on the PDC side of the dividing-wall column. When the tuning of this loop is sufficiently aggressive (large gain, small integral time), the system is stabilized.

The 'valve-position control' (VPC) loop ensures both rapid response to disturbances and energy efficiency. Thus, when higher duty is required by the PDC temperature controller, the flow rate of hot utility is increased. This has a fast effect on the controlled variable. Afterwards, the VPC controller gradually increases the flow rate of compressed vapours passing through the reboiler, until the utility flow rate returns to its design / set point value.

The set point of the PDC temperature controller is given, in cascade fashion, by a quality controller keeping constant the mass fraction of ethanol impurity in the water product stream. Note that the dynamics of the concentration transmitters (measurements) on the ethanol and water streams was modelled including 1 minute sampling interval and 1 minute dead-time.

Starting from the steady state, the feed rate is ramped up by 10% (from t = 2 h to t = 4 h), brought back to the initial value (at t = 12 h), decreased by 10% (at t = 22 h), and returned again to the initial value (at t = 32 h). Both the ethanol and water flow rates change accordingly to their feed rate and reach their new steady state values in a rather short time with almost no overshooting (Figure 3.4, left). It is remarkable that the composition of the ethanol and water stream products remains practically unchanged (Figure 3.4, right).

Figure 3.5 shows the key internal variables, for the same scenario. The various internal flow rates follow the change of the feed rate (plot a). The ethanol purity is maintained by changing the solvent/feed ratio (plot b). When the feed rate increases (from t = 2 h to t = 12 h), higher side-reboiler duty is required. This is achieved by increasing the external duty (plot c) and by reducing the by-pass around the side-reboiler (plot d). Note that when lower duty is required (from t = 22 h to t = 32 h), this is achieved by increasing the by-pass. while the external duty remains at the minimum value of 2 GJ/h.

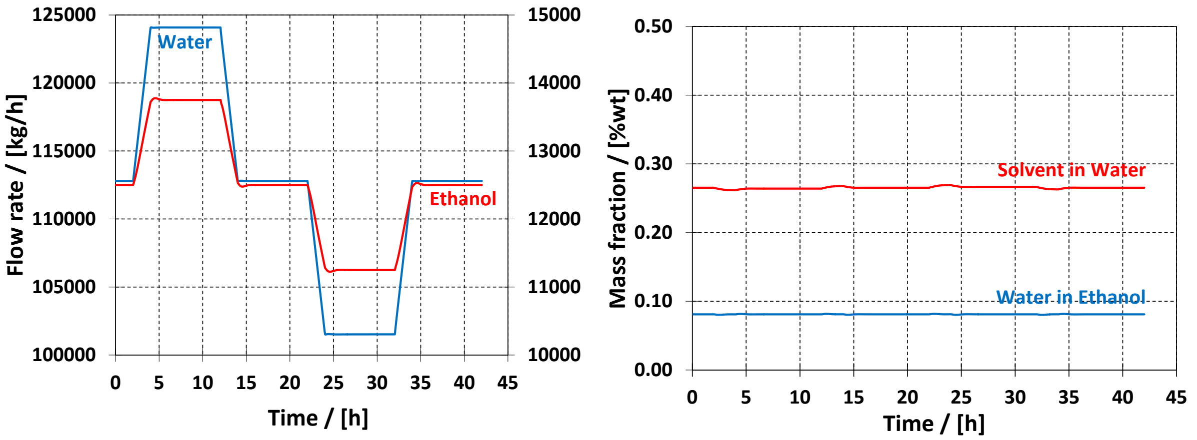

*Figure 3.4. Dynamic response of products flow rate and purity, for ±10% disturbance of feed flow rate*

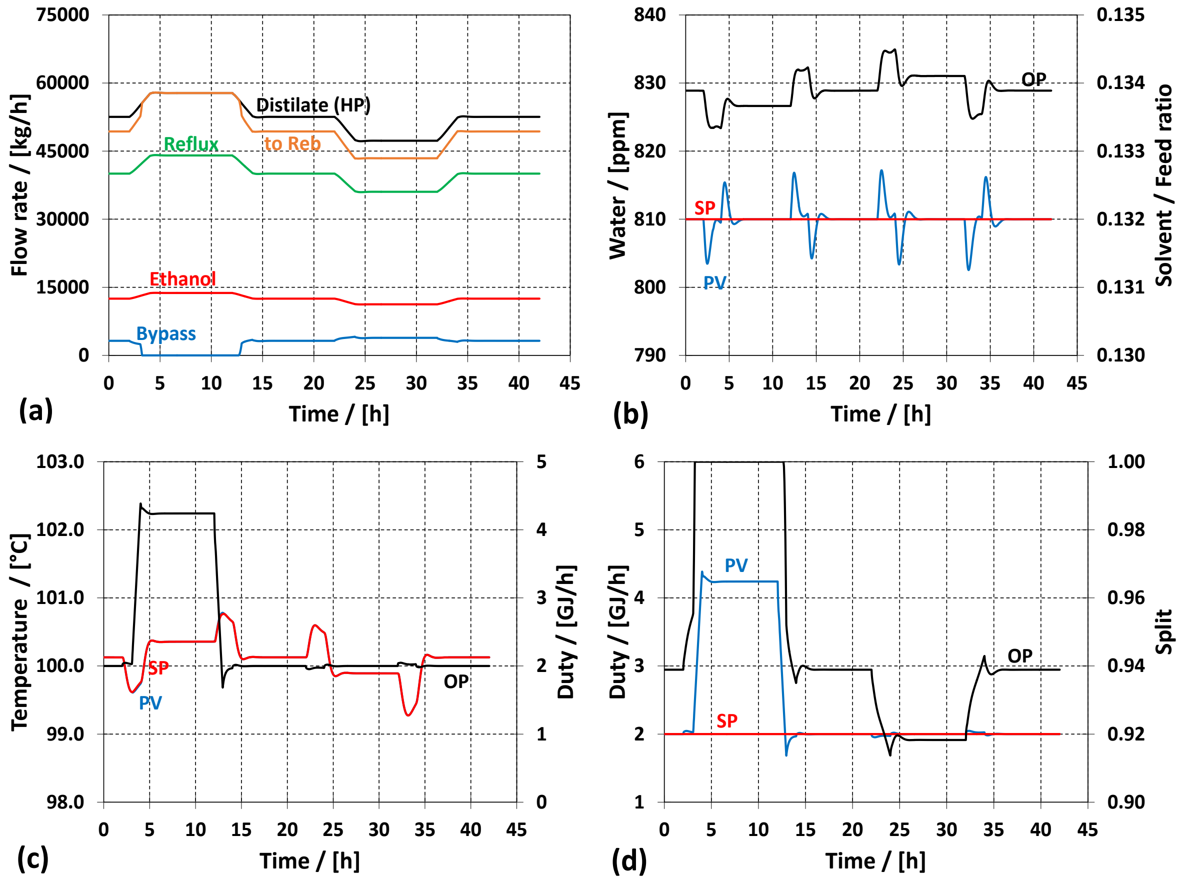

*Figure 3.5. Key internal variables for ±10% flow disturbance. a) Flow rates; b) Ethanol product composition controller; c) Prefractionator temperature controller; d) Side-reboiler external duty controller (VPC)*

An effective control structure that achieves the control objective is the main result of this study, which is the first to prove the controllability of vapour recompression assisted extractive DWC. The system is robust to ramp feed rate and feed composition disturbances and to ramp changes of ethanol purity setpoint. As step changes are not tolerated, this study provides a clear warning to process and control engineers that such changes should be implemented in a slow fashion.

# CHAPTER 4 – *From Substrate to Biobutanol in the ABE Process*

Butanol successfully compete with fossil fuels as gasoline, diesel, and also with the bioethanol. Among the alcoholic fuels that have properties similar to gasoline, butanol has several advantages over ethanol: the energy density of butanol is much higher (29.2 MJ/L) allowing higher mileage; the air-fuel ratio is higher (AFR=11.2) so it can be run at richer mixtures and produce more power; the octane rating of butanol is lower (RON=96) but similar to that of gasoline; and butanol has a lower vapour pressure and thus it is safer to handle. Just as bioethanol, butanol can be mixed with fossil fuels for reducing the $CO_2$ emissions, but butanol can be blended in any concentration and used in existing car engines without any modification. Moreover, compared to bioethanol, butanol has 25% more energy content, is less volatile and less corrosive, being a good transportation fuel.

Butanol fuel can be produced from crude oils or green sources, but it is obtained preferably from different lignocellulosic substrates as corn stover, wheat straw, corn fibre, barley straw, switch grass and wood residue. Biobutanol is produced in acetone-butanol-ethanol (ABE) fermentation process with low concentration <3% [1]. However, strain improvement by genetic engineering or mutation could overcome the problems of low concentration. For example, microorganisms as Clostridium Beijerinckii and Clostridium Acetobutylicum produce butanol with high yield in fermentation broth and avoid the butanol inhibition.

Three generations of biofuels (including butanol) are known to be delivered by fermentation processes. The 1st generation is obtained from sugars, vegetable oil, starch, grains, seeds and so on. This generation represents an inconvenience for food production, increasing the cost of crops and food. The 2nd generation of biofuels is obtained from lignocellulosic biomass and agricultural waste, which does not affect the food production and are preferable for biobutanol production. The 3rd generation of biofuels is obtained from substrates such as algae and seaweeds.

***Chemical pre-treatment*** uses concentrated acids (H2SO4, HCl), diluted acids (H2SO4), ammonia-recycled percolation (ARP), alkali solutions (NaOH, Ca(OH)2), organic solvents (ethylene glycol) and ionic liquids. ***Biological pre-treatment*** makes use of bacteria and fungi that produce enzymes as xylanases and cellulases, which are used for high yield conversion of sugars into butanol. ***Physical pre-treatments*** can be used, such as ammonia fibre explosion (AFEX), CO2 explosion, liquid hot water and steam explosion.

The ABE fermentation involves two phases: 1) acidogenesis where acetic acids and butyric acids are formed, and 2) solventogenesis where the acids are converted to solvents (acetone, butanol and ethanol). The simplest (conventional) reactors for producing butanol are batch and fed batch type. These reactors have disadvantages of butanol inhibition, prolonged lag phase and preparation time. The maximum yield of ABE-solvents and butanol productivity is achieved when the optimal butyrate concentration is controlled at 4 g/L by adjusting the pH. Neglecting the pH of the medium, butanol production can stop because butyric acid inhibits cellular growth, which declines with the increase of butyrate concentration [11].

ABE fermentation in continuous and semi-continuous bioreactors solves the problems of preparation time and lag phase, increasing the product yield and productivity by cell recycle or cell immobilizations. Moreover, the material and reactants can be fed continuously into a small reactor with higher mixing rates and flexible operating time.

Due to shear forces from continuous liquid flow in the bioreactor, the catalytic activity and stability of the cell are damaged. As a result, for long operation time, the reactor loses its productivity because of mass transfer restriction and build-up of dead biomass, leading to reactor or membrane deterioration due to blockage and channelling effects. To solve this issue, cell immobilization in bioreactor helps the production of butanol to run continuously. Further, fibrous matrices improve the utility of immobilized cells. The biomass concentration can successfully increase, and butanol toxicity decrease when combining continuous fermentation (including a cell retention system) with product recovery in a flash tank.

Several techniques can be used to increase the ABE concentration from fermentation (recovery): *Gas stripping* is an economic technique for in situ recovery of ABE solvent where fermentation gases (CO2, H2 and N2) are bubbled through the fermentation broth that the gases to capture ABE. Using the Clostridium Beijerinckii BA 101 strain in continuous fermentation coupled with gas stripping the ABE concentration reaches 460 g/L [26]. *Liquid-liquid extraction* is a recovery technique which uses a water-insoluble organic extractant mixed with fermentation broth. The extractant and fermentation broth are immiscible and can easily be separated without removing substrates, water or nutrients [28]. *Perstraction* technique uses a membrane between fermentation broth and extractant, providing a surface area for butanol exchange. *Pervaporation* is a technique for selectively removing the organic components from fermentation broth as vapours through a membrane, followed by recovery by condensation. *Adsorption* is a separation technique which uses hydrophobic adsorbents (often silica). *Reverse osmosis* is a recovery technique based on water removal by semipermeable membranes.

# **CHAPTER 5 –** *Butanol Separation in the ABE Fermentation Process by Conventional and Dividing-Wall Columns*

The ABE production via fermentation is facing great challenges due to the very low concentration (< 3 %wt. butanol) and yield owing to the severe butanol toxicity to microorganisms. One way to solve the problems is the modification of microorganisms for ABE fermentation by genetic engineering (to keep them alive and active under higher butanol concentrations), leading to increase of productivity, yield and concentration and thus reducing the production costs [31]. But this is an unrealized long term goal, and even if the modification of microorganisms becomes a reality, product separation and purification will still remain a critical challenge [32]. The other approach is the development of more efficient downstream processes for butanol recovery.

Several review papers describe the main separation techniques used, such as: distillation, adsorption, gas stripping, vacuum flash, liquid-liquid extraction (LLX), reverse osmosis (RO), perstraction, pervaporation, and hybrid separations [33]. While many of these technologies are still in the research and development phase, distillation remains an industrially-proven technology with significant potential to improve its energy efficiency by process intensification [34].

However, the use of distillation for butanol recovery is considered too demanding in terms of energy requirements, using up to 220% of the energy content of butanol. But this value could be drastically reduced (to about 20% or even less) when the distillation process is combined with in-situ product recovery (ISPR) techniques [35].

Figure 5.1 illustrates some of the options described in literature [36]. The problem is that all these designs have some major drawbacks that hinder their implementation in practice. For example, in designs A, B and C, the ethanol column must achieve extremely high recovery of this component. Otherwise, because the butanol / water separation delivers the products as bottom streams of distillation columns, ethanol (the lightest component) will accumulate in the recycle streams. This has clearly a negative impact not only on the investment and operating costs, but also on the process controllability. Also, design D incurs additional costs due to use of a large amount of solvent for water recovery. To solve these downstream separation problems, we propose a novel distillation sequence able to reduce the costs of the downstream distillation of butanol. The improvements include:

- the column separating ethanol is part of the recycle loop of butanol-water separation, in order to prevent ethanol accumulation;
- the first unit of the sequence is a decanter, without pre-concentration steps, improving energy efficiency and preventing phase separation in the first distillation columns;
- two distillation columns are replaced by a more efficient dividing-wall column;
- heat-integration is used to minimize the energy requirements [37].

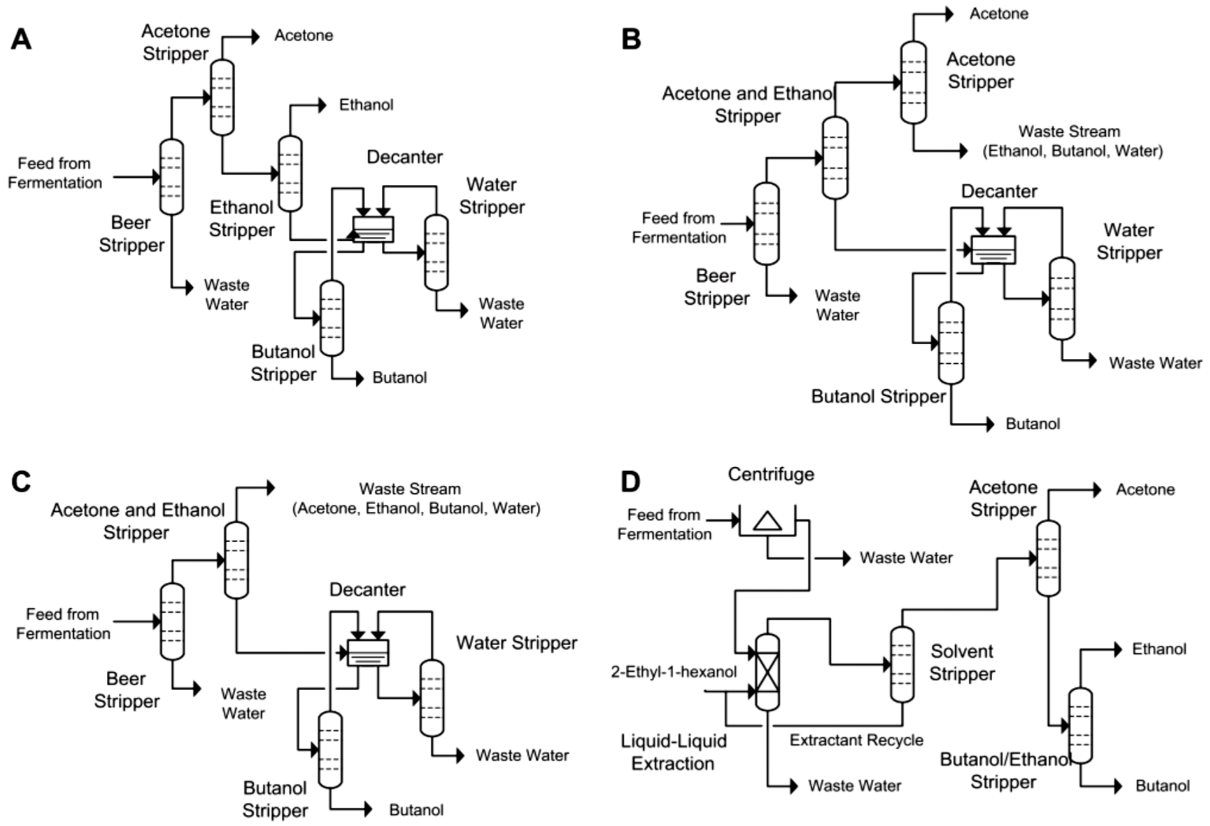

*Figure 5.1. Flow diagrams for downstream processing of biobutanol in the ABE process [36]*

In addition, rigorous dynamic simulations (flow-driven and pressure-driven) are also used to prove the good controllability of the proposed integrated process.

The process was simulated in Aspen Plus using the NRTL property model that is most suitable for these components and process conditions and in line with the recommendations for such systems [38]. Moreover, experimental composition of the binary system n-butanol / water obtained in the temperature range 323-393 K and pressures between 13.4 and 267 kPa [39] was used to check that the butanol / water LLE is correctly predicted by the NRTL model with default Aspen Plus binary interaction parameters (Figure 5.2, left). Occurrence of a heterogeneous azeotrope (Figure 5.2, right) is a feature of the butanol-water mixture which is neatly exploited to cross the distillation boundary and therefore to produce high purity products.

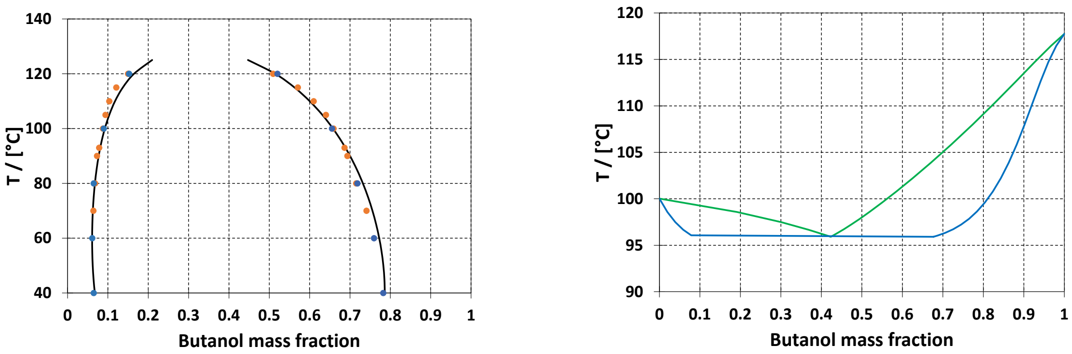

*Figure 5.2. Phase equilibrium of mixture butanol-water. Left: Comparison between LLE predicted by NRTL model (line) and experimental data (dots; Lee et al., 2004); Right: T-xy diagram, showing the occurrence of a heterogeneous azeotrope (1 bar).*

Figure 5.3 presents the mass balance of two alternatives for separating a n-butanol – water mixture with a composition close to that found in the ABE process. A simplified mass balance reveals that the amount of top distillate products with azeotropic composition obtained with pre-concentration (Figure 5.3, case A: 0.6485 kg distillate per kg feed) is much higher than the amount distilled when the separation sequence starts with the liquid-liquid split (Figure 5.3, case B: 0.2717 kg distillate per kg feed).

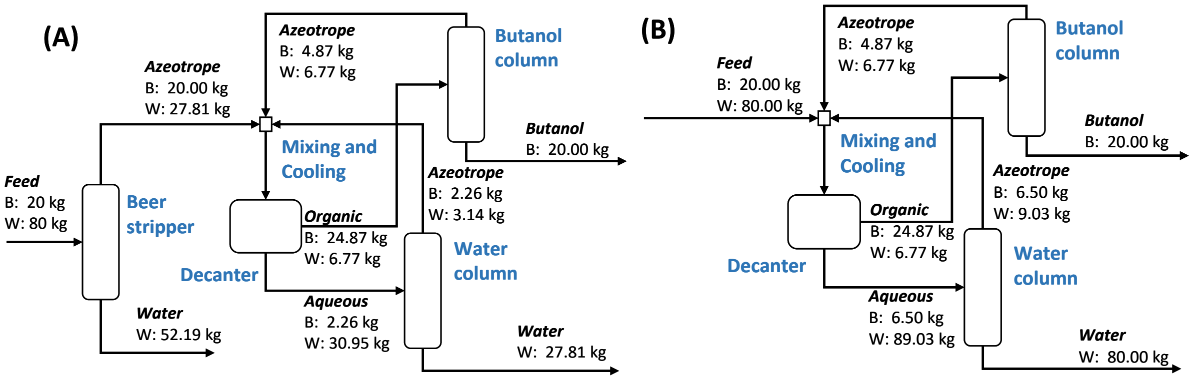

*Figure 5.3. Simplified alternatives for separation of a Butanol (20 %wt) – Water (80 %wt) mixture, with feed pre-concentration (Case A: 0.6485 kg total distillate / kg feed) and without feed pre-concentration (Case B: 0.2717 kg total distillate / kg feed)*

The results are provided for a plant capacity of 40 ktpy butanol, processing an effluent stream from an ABE fermentation process coupled with gas stripping and delivering products with purities of 99.4 %wt butanol, 99.4 %wt acetone and 91.4 %wt ethanol, thus meeting the standard ASTM D7862-13 specification of >96% purity for use as blendstock. Figure 5.4 presents the flowsheet of the new down-stream processing sequence for the ABE process, including the proposed control structure along with the mass balance and the key design parameters. The first unit of the sequence is a decanter. This minimizes the energy requirements as previously discussed and also prevents potential phase separations in the subsequent distillation columns.

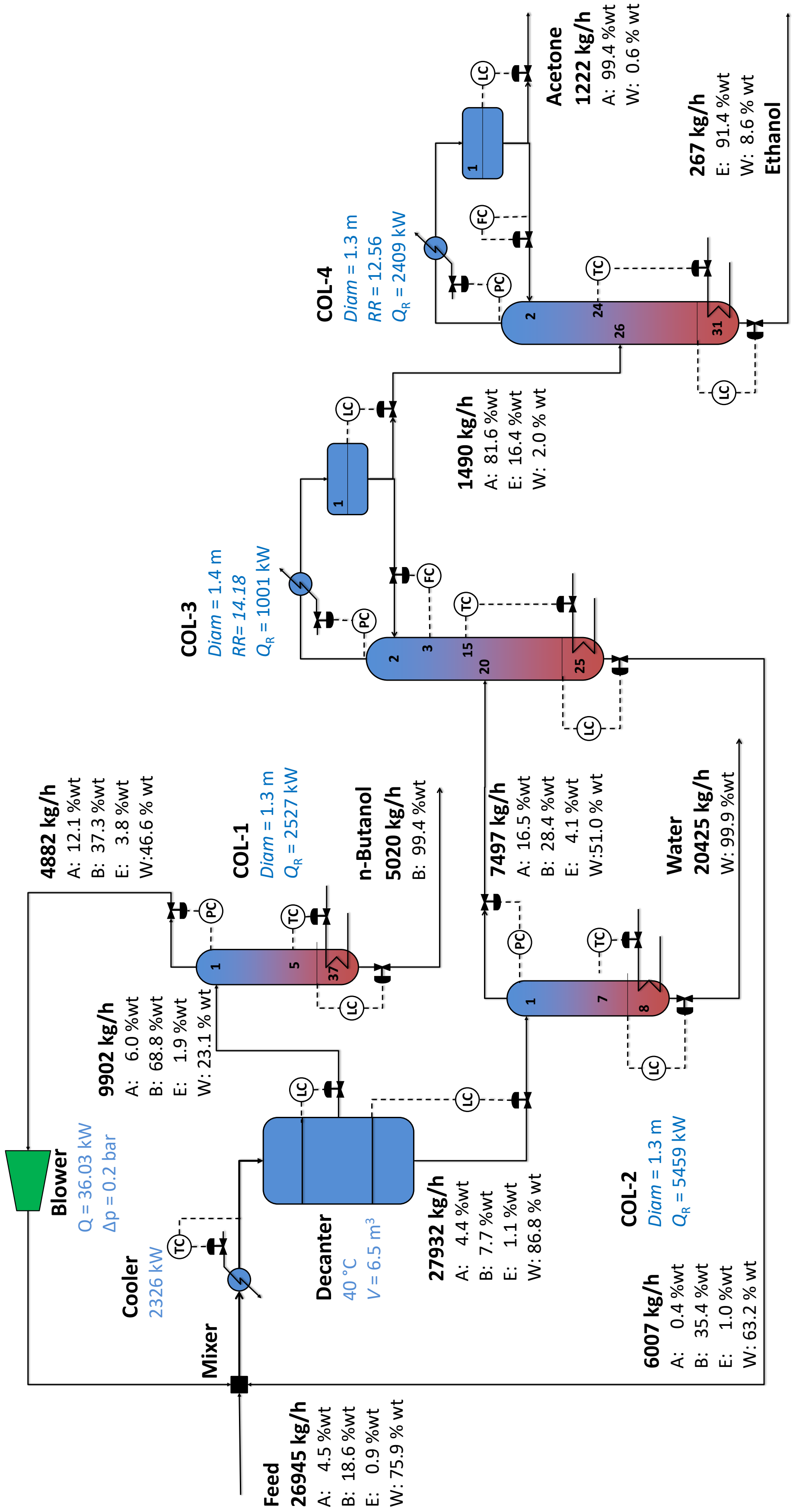

*Figure 5.4. Process flowsheet of the new down-stream separation sequence*

The organic phase (rich in butanol) goes to the first stripping column (COL-1) that separates butanol as bottom product and a water rich, top vapour stream which is recycled to the decanter by means of a blower. The aqueous phase from the decanter is fed to the stripping column (COL-2) that separates water as bottom product (main water outlet). The top stream of the stripping column (COL-2) is fed to the distillation column (COL-3) that separates an acetone-ethanol rich fraction (the amount of water roughly correspond to the ethanol/ water azeotrope) as top distillate stream and a butanol-water bottom stream that is recycled to the decanter. The acetone-ethanol stream from this column (COL-3) is sent to distillation column (COL-4) that separates ethanol and water as bottom product and acetone as top distillate. The column separating ethanol (COL-3), which is part of the recycle loop of the butanol-water separation, prevents ethanol accumulation although a high value for the ethanol recovery in the distillate is not required.

Considering the indirect sequence of columns (COL-2 and COL-3) that operate at similar conditions, it is certainly worth considering the option of using a dividing-wall column (DWC) to replace these two-distillation column [40; 33]. The first step in designing a DWC is to check in a shortcut model how the separation influences the duty requirement and the column configuration. A DWC is thermodynamically equivalent to a Petlyuk distillation setup consisting of a prefractionator and a main column [33]. The prefractionator (PF) and the main column are designed starting with a shortcut model to find the design parameters of the column (trays number, reflux ratio, duty requirements, liquid and vapour split ratios) and after that using a rigorous RADFRAC model in Aspen Plus. The following parameters are used for the minimization of the heat duty and total annual cost: number of stages in prefractionator and in the main column, feed stage location, position of the prefractionator in the main column, liquid and vapour split ratios. For convenience, Figure 5.5 presents the updated flowsheet of the new downstream processing sequence using a DWC that replaces two distillation columns (COL-2 and COL-3) of the base case, including the control structure, heat integration, mass balance and the design parameters.

The equipment cost, utilities cost (proportional to the energy requirements per each unit) and the total annual costs are: for the base case (TAC=$4214.5\cdot10^3$ US$/year), and for the heat integrated process with DWC (TAC=$3390.5\cdot10^3$ US$/year). In terms of specific energy requirements, this is 2.28 kWh/kg butanol for the base case, while for the heat integrated DWC process it amounts 1.71 kWh/kg butanol (about 25% reduction).

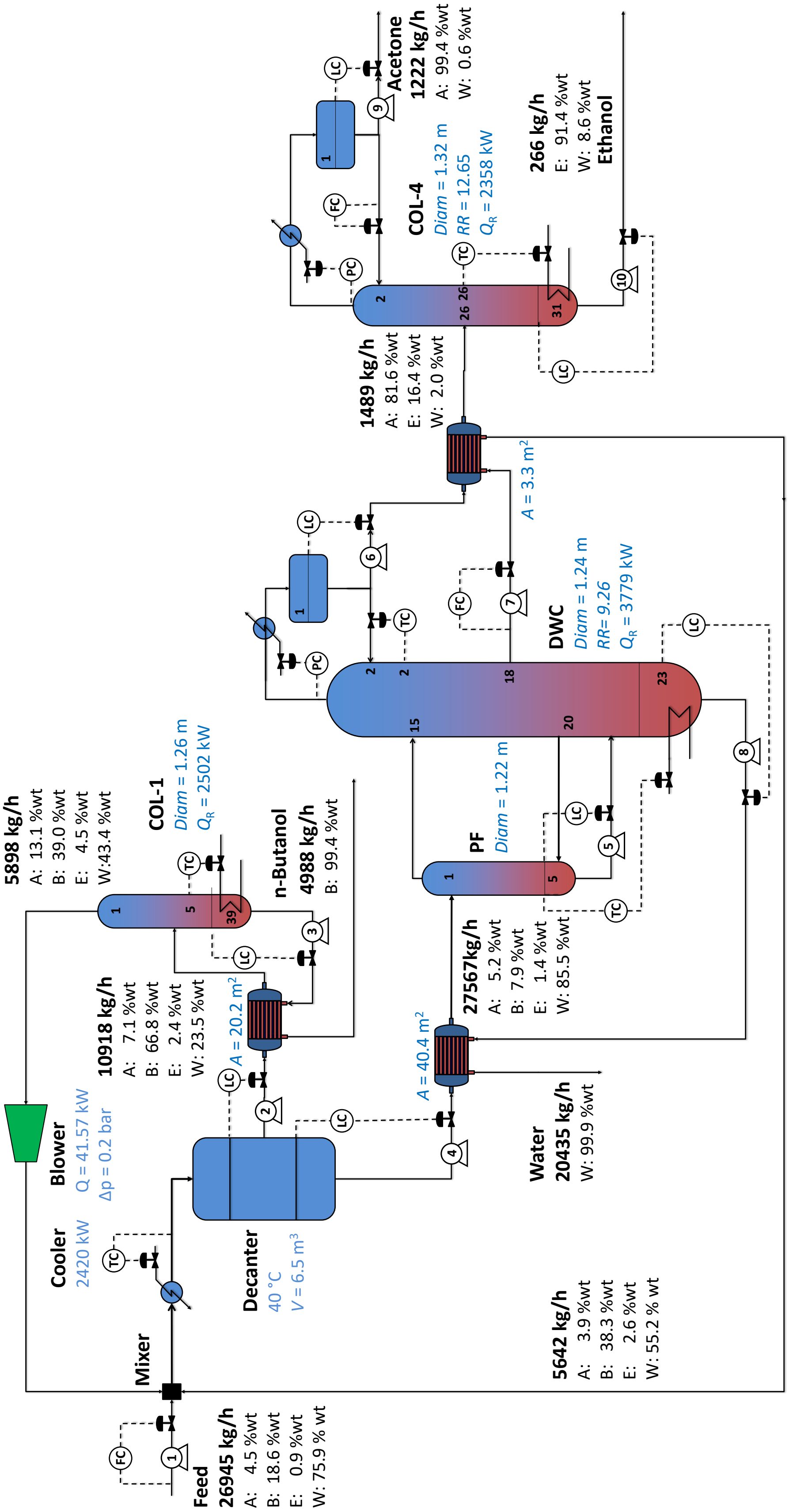

*Figure 5.5. Flowsheet of the process intensification alternative (using DWC) for the ABE downstream processing (40 ktpy butanol)*

Note that using heat pumps (such as vapour compression or vapour recompression) could further improve the efficiency of the distillation processes and reduce the primary energy use, but at the expense of higher CAPEX [4; 41]. Also, novel dual extraction processes could get to rather low energy requirements, but at the cost of using additionally non-biocompatible solvents [42].

Figure 5.6 and Figure 5.7 present results of pressure driven simulation, for changes in the feed flow rate (at time t = 2 h, the feed flow rate is increased by 10%, then at time t = 12 h, returns to its initial value, and at time t = 22 h the feed is reduced by 10%) and composition (from the initial value 18.5 %wt., the butanol mass fraction is increased, at time t = 2 h, to 20.4 %wt, while the mass fraction of the other components is decreased, proportionally to their concentration. At time t = 22 h, butanol mass fraction is decreased to 16.6 %wt).

The pressure-driven simulation give a more realistic view of process dynamics and allows a more rigorous controllability analysis. In particular, the change of the liquid flows down the prefractionator and the DWC affect the height of liquid on each tray and therefore the resistance to the vapour flow. While the flow-driven simulation assumes that the vapour split between the prefractionator and the main column is fixed, the pressure-driven simulation correctly calculates the flows based on pressure difference and trays hydraulic resistance.

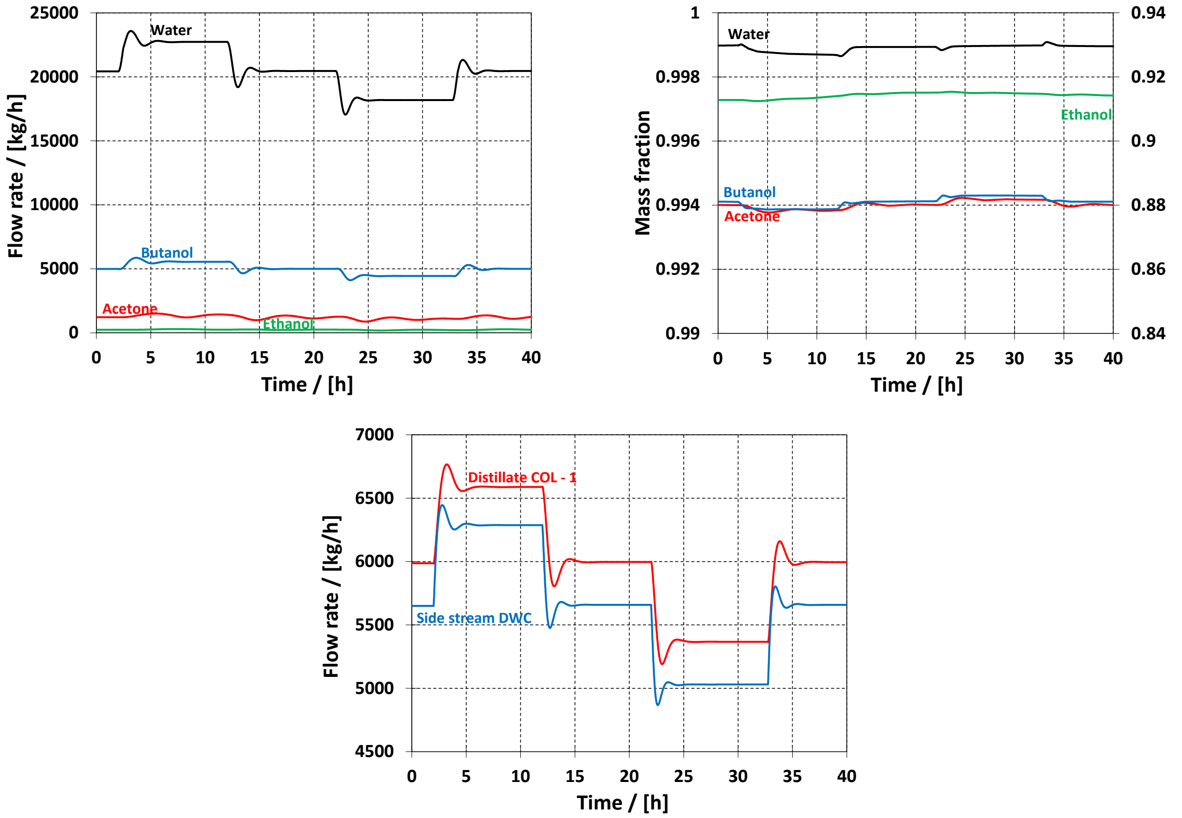

*Figure 5.6. Dynamic simulations results (pressure driven) – feed flow rate disturbance*

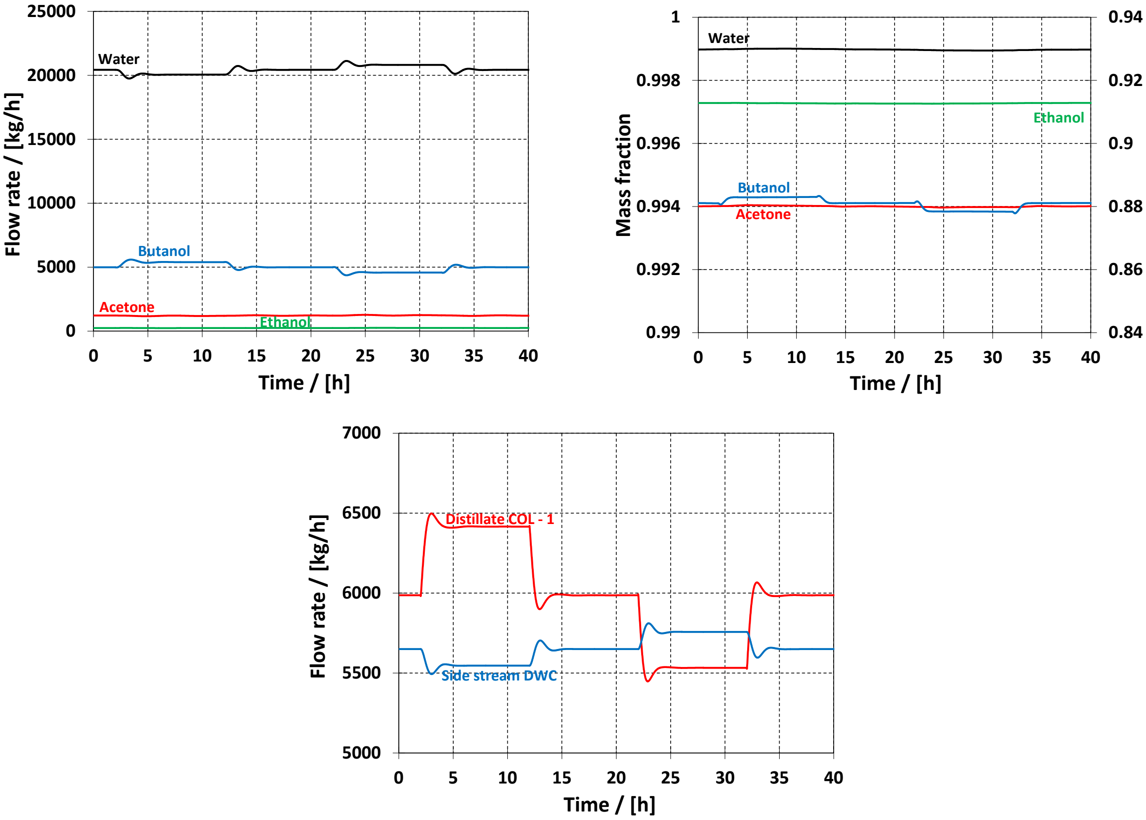

*Figure 5.7. Dynamic simulations results (pressure driven) - butanol concentration disturbance*

The new downstream processing distillation sequence proposed in this work allows the efficient separation of butanol using fewer equipment units and less energy as compared to previously reported studies [43; 36].

The main improvements include using a decanter as the first unit of the separation sequence avoiding the use of a pre-concentration step and preventing phase separation in the stripping and distillation columns, placing the column separating ethanol in the recycle loop of the butanol-water separation to prevent ethanol accumulation, using dividing-wall column as process intensification method of improvement, as well as employing heat integration. For a commercial plant capacity of 40 ktpy butanol, the total equipment cost (including decanter, blower, all distillation columns and heat exchangers) is $4232 \cdot 10^3$ US$, while the total energy costs are $2128 \cdot 10^3$ US$/year.

Remarkably, the specific energy requirements for the separation and purification of butanol is very low (1.24 kWh/kg butanol), especially considering that butanol fuel has an energy density of about 10 kWh/kg (36 MJ/kg). As this novel enhanced process uses only proven technology, it can be readily employed at large scale to improve the economics of the downstream processing in the ABE fermentation process.

# **CHAPTER 6 –** *Biobutanol Separation by Heat Pump Assisted Azeotropic Dividing-Wall column*

In the acetone-butanol-ethanol (ABE) fermentation process, biobutanol is obtained in diluted form, typically less than 3 %wt. concentration (owing to the severe butanol toxicity to micro-organisms). The key challenges in biobutanol production emphasize the idea of improving the efficiency of the ABE process by altering the upstream (e.g. pretreatment and fermentation) and the downstream steps (product recovery and purification) by various methods [44]. The ABE concentration can be increased by in-situ product recovery (ISPR) methods such as gas stripping technology to: 4.5 %wt. acetone, 18.6 %wt. butanol and 0.9 %wt. ethanol [45]. Process alternatives based on advanced distillation technologies have been also reported [46]. More insights into the appropriate selection and design of fluid separation processes (applicable also to biofuels) have been reported in a recent review paper [47].

This work proposes a new biobutanol downstream process based on combining azeotropic distillation in a dividing wall column (DWC) with vapour recompression technology [38, 41]. Remarkably, the azeotropic DWC integrates three distillation columns into one unit with enhanced thermodynamic efficiency, and further reduces the primary energy used for separation by employing heat pumping and energy integration.

The plant capacity considered here is 40 ktpy butanol. To account for a realistic composition of the ABE mixture such as reported in literature [45], impurities are also taken into account hence the mixture which must be efficiently separated contains: 4.5 %wt. acetone, 18.6 %wt. butanol and 0.9 %wt. ethanol, 0.1 %wt. CO2, 0.08 %wt. butyric acid and 0.04 %wt. acetic acid. The required product purities are butanol 99.4 %wt. and water 99.8 %wt.

The feed stream and all the products are at 25 °C. Regarding the design and operational constraints, when dividing wall technology is employed each side of the dividing wall must have the same number of trays and the temperature difference between the two sides should not exceed 20 °C. Moreover, the use of vapour recompression is limited by the maximum temperature of the compressed vapour, which is 150 °C.

The process is simulated in Aspen Plus, using non-random two-liquid (NRTL) as property model. Table 6.1 lists the boiling points of the components, while Figure 6.1 illustrates the T-xy diagram of the binary mixture butanol-water. Notably, both hetero- and homogeneous azeotropes are formed in this aqueous system, and this further complicates the separation.

*Table 6.1. Boiling points of the pure chemicals and azeotropes involved in the butanol recovery*

| **Component** | **Boiling point °C** (at 1.013 bar) |
|---|---|
| Acetone | 56.14 |
| Homogeneous azeotrope:<br>Ethanol (95.63% wt) / Water | 78.15 |
| Ethanol | 78.31 |
| Heterogeneous azeotrope:<br>n-Butanol (42% wt) / Water | 95.91 |
| Water | 100 |
| n-Butanol | 117.75 |
| Acetic acid | 118.01 |
| n-Butyric acid | 163.28 |

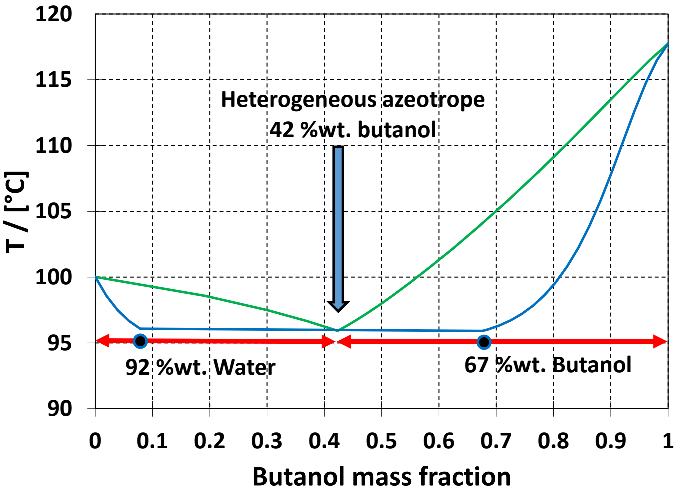

*Figure 6.1. T-xy diagram for the binary mixture butanol-water*

Figure 6.2 presents the conceptual design of the process. First, a distillation sequence is suggested (Figure 6.2, top) based on several heuristics, as follows [37]:

- Remove first the most plentiful component: the prefractionator column COL-1 removes a large amount of water as bottom product. This reduces both the investment and operation costs of the sub-sequent units. The distillate contains acetone, ethanol and water-butanol mixture with close to azeotropic composition. COL-1 can work as a stripper (feed on one of the top trays), as its main function is to remove the light components such that high purity water is obtained in the bottom stream, without having a tight specification on the distillate.
- Lights out first: from the distillate of COL-1, the lightest components (acetone and the ethanol-water azeotrope) are removed as distillate of column COL-2. A rectifying section is necessary to ensure high purity of the distillate, while the specifications of the bottom stream are not stringent (see below).

- Perform the most difficult separation last: removal of acetone, ethanol and a part of water in COL-2 is compatible with this heuristic, as the bottom product of COL-2 is a water-butanol azeotropic mixture, the most difficult to be separated into high purity products.
- Use liquid-liquid split to cross the distillation boundary induced by a heterogeneous azeotrope: The butanol-water azeotrope is cooled and separated in an organic and an aqueous phase. The aqueous phase can be split into water (heavy product) and butanol-water azeotrope (light product). As column COL-1 already performs this function, the aqueous phase is sent there. This also ensures that any acetone and ethanol which are left in the COL-2 bottoms are recycled to a location which still allows their separation to a product stream (preventing therefore accumulation). The composition of the organic phase allows separation into butanol (heavy product) and butanol-water azeotrope (light product). This is achieved in column COL-3, which can also work as a stripper (feed on the top stage, no tight specification on the top product). The butanol-water azeotrope is sent to the decanter.

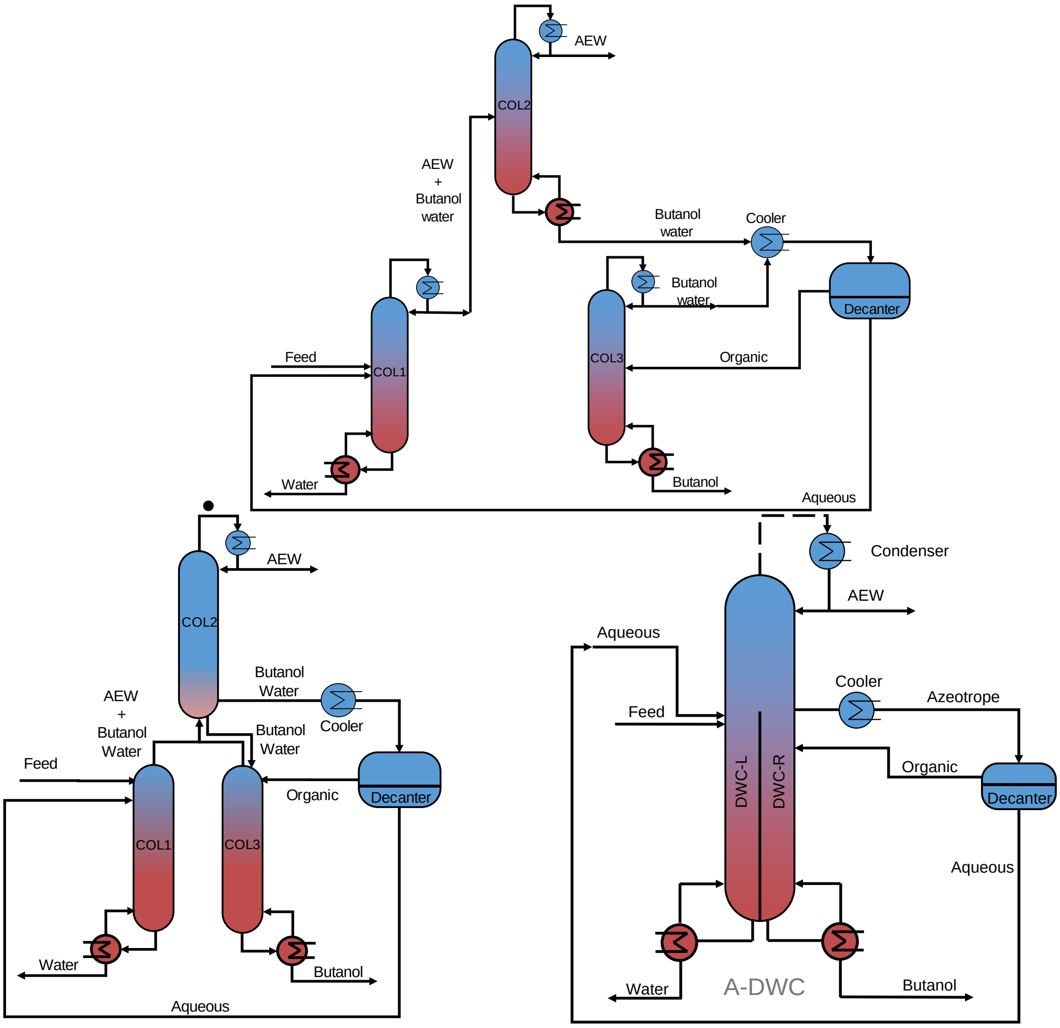

*Figure 6.2. Conceptual design of butanol separation: (top) sequence based on conventional distillation; (left) thermally coupled column (right) DWC equivalent configuration*

Next, one can consider energy coupling by combining the condensers of COL-1 and COL3 with the reboiler of COL-2. This leads to the flowsheet shown in Figure 6.2 (left). Note that the reboilers of COL-1 and COL-3 provide the vapours required for column COL-2. Finally, it can be observed that the boiling points of the COL-1 and COL-3 distillate streams are almost the same, corresponding basically to the boiling point of the butanol-water azeotrope. Moreover, because the bottom streams also have similar boiling points (water: 100 °C, butanol: 117.7 °C), the temperature profiles along COL-1 and COL-3 are expected to be similar. Therefore, columns COL-1 and COL-3 can be integrated into one section provided with a dividing wall. Thus, all three distillation columns can be combined into a single unit, as shown in Figure 6.2 (right).

The optimization of the process is performed by minimizing the total annual cost. For the optimization of TAC, the following decision variables and restrictions are considered:

- Number of stages in the distillation column (both sides). The same number of stages on each side of the dividing wall was considered in the optimization, as this is the normal constructive solution for large diameter trayed columns. However, the number of stages could be different on the two sides, particularly when (structured) packing is used.
- The design specifications for purity of product stream (e.g. butanol product 99.4 %wt., water by-product 99.8 %wt.).
- Max. 0.1 kg/h butanol in water-product (water quality) by changing the vapour flow rate
- Butanol purity min. 99.4 %wt. (butanol quality) by manipulating distillate flow rate.
- Max. 30 kg/h water in distillate (AEW quality), obtained by manipulating the reflux ratio.
- CO2 recovery in distillate is obtained manipulating the side flowrate.

The feed mixture, organic phase and aqueous phase are preheated at 97 °C. This reduces the energy requirement in reboilers, then by heat integration the hot streams will provide the necessary heating for cold feed streams.

Pinch analysis provides understanding of the energy targets and subsequent design of the optimal heat exchange network (HEN). The procedure was applied according to the literature [48]. A minimum temperature difference of 10 K was used. No additional correction factor was used, as only 1-pass shell & tube heat exchangers were considered – but other correction factors may be needed for other types of heat exchangers. The coefficient of performance (COP) is used for evaluating the feasibility of using a heat pump, while also accounting the additional costs and the payback time.

Figure 6.3 shows the mass and energy balance around the azeotropic dividing wall column, together with the main design parameters. The column has a total of 45 stages, 13 stages for the fractionation section and 32 stages for stripping sections. Butanol and water are the bottom products, while acetone and ethanol with some water (AEW) are obtained as distillate. The ABE feed and the aqueous phase recycled from the decanter are fed on 1st stage of the stripping section (14th stage of A-DWC), which separates water as bottom product. The liquid flowing down the column is routed to the right stripping section. From the 13th stage, a mixture close to the azeotropic composition is withdrawn as side stream, cooled, and sent to liquid-liquid separation. The organic phase is recycled on 2nd stage of the right stripping section (15th stage of A-DWC), from which butanol is obtained as bottom product. The aqueous phase is recycled to the left stripping section.

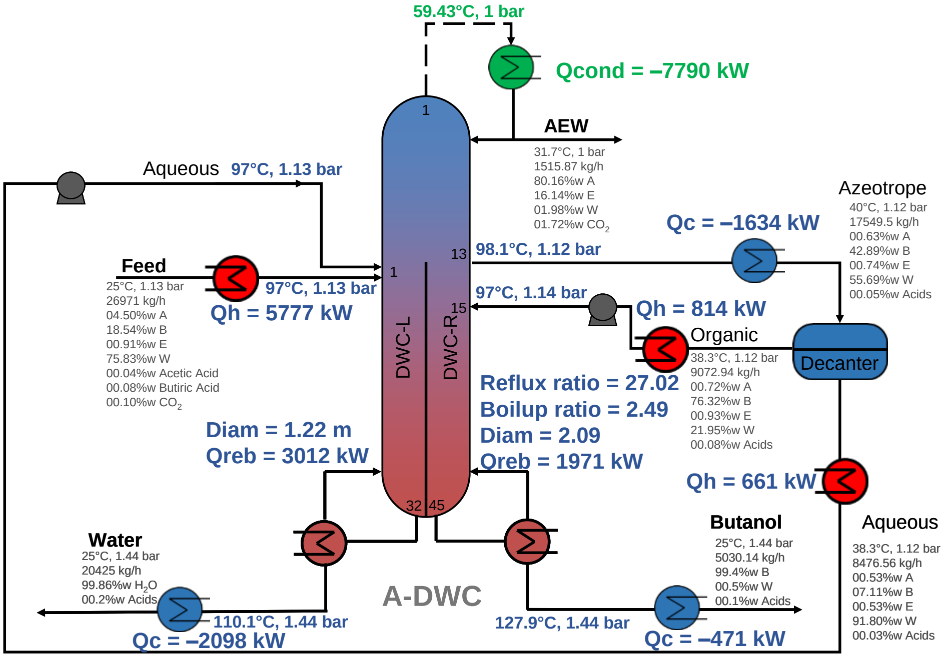

*Figure 6.3. Azeotropic dividing-wall column (without heat integration)*

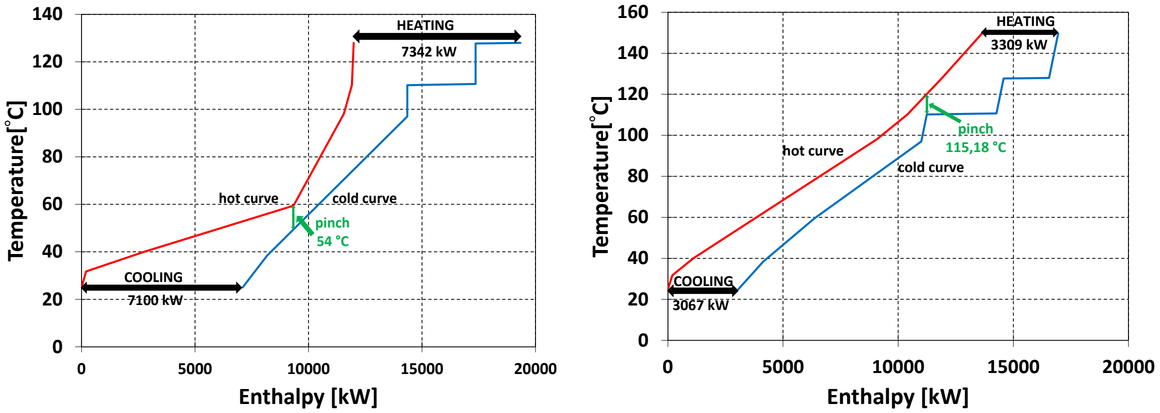

*Figure 6.4. Composite curve - heat integration (left) and heat pump assisted (right)*

Figure 6.3 (left) shows the composite curves that reveal the energy targets. Heat integration may lead to important reduction of heating and cooling requirements. However, the energy savings are rather small compared to previously reported separation sequences [46]. In particular, the vapour stream from the top of the A-DWC cannot be used for heat integration due to its low temperature. However, by recompression to 5.8 bar (which requires 1646 kW), it can be heated to 150 °C, which is useful for heat integration. More precisely, partial condensing the vapour stream, at about 116 °C, provides the heat (3012 KW) necessary to drive one reboiler of the A-DWC unit. Further condensation and sub-cooling to 54.5 °C makes available 5777 kW, which are used to preheat the feed stream. Figure 6.4 (right) shows that (for a Q/W ratio of 7.43) the vapour recompression heat pump helps to reduce the heating and cooling requirements by about 50% (equivalent to 2.7 MJ/kg butanol). This figure is impressive suggesting that applying heat pumping will be beneficial in this case. The hot utility requirements can be reduced from 7342 to 3309 kW, while the cold utility needs can be reduced from 7100 to 3067 kW (the rest being ensured by inter process streams transfer).

Figure 6.5 shows the grid diagram used for the development of the heat exchanger network (HEN), based on Pinch analysis. The proposed HEN reduces the energy requirement for separation close to the calculated values in the composite curve and grand composite curve.

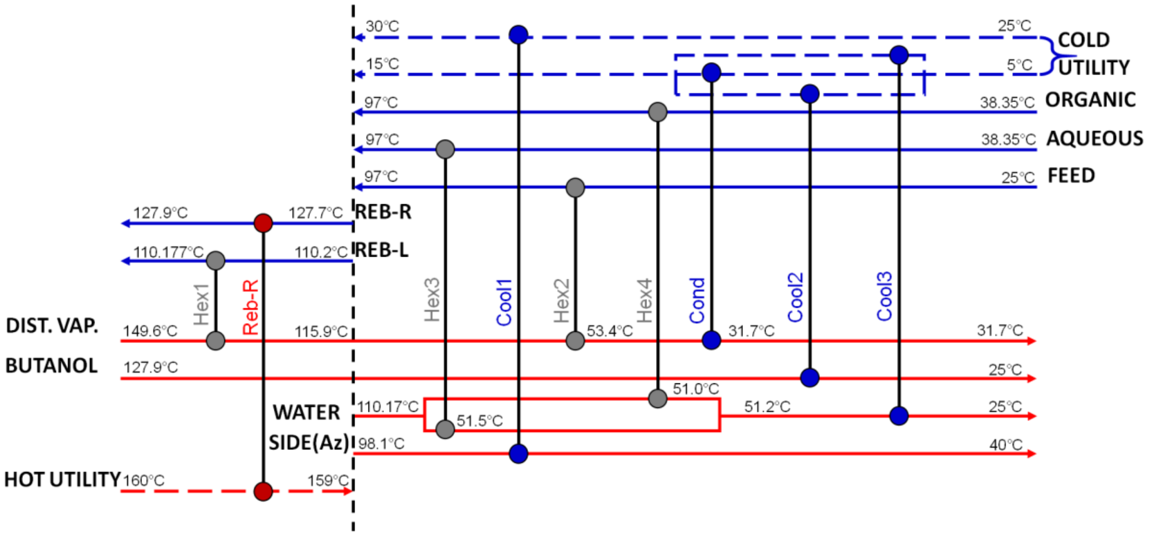

*Figure 6.5. Grid diagram showing the process streams and the heat exchangers network*

Figure 6.6 presents the process flowsheet including vapour recompression and energy integration. Compared to Figure 6.3, a key difference is that the top vapour stream is compressed from 1 to 5.8 bar (in order to increase its temperature from about 60 °C to 150 °C), thus upgrading its thermal energy to provide heat to the (left) side reboiler (HEX1), then to preheat the diluted ABE feed (HEX2) and is eventually getting condensed.

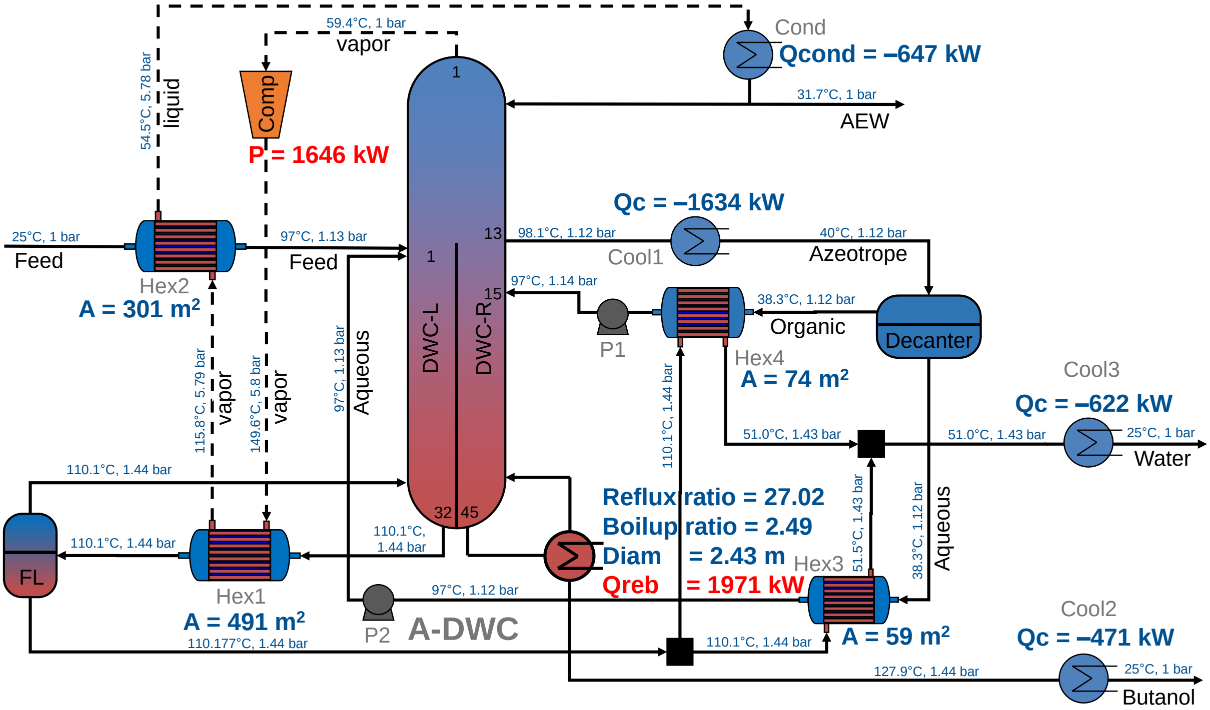

*Figure 6.6. Process flowsheet of the new downstream separation process based on heat pump assisted A-DWC (heat integrated)*

The energy required for heating without any heat integration and no heat pump assistance is 8.78 MJ/kg butanol. But the heat pump assisted A-DWC design requires only 2.7 MJ/kg butanol (amounting 58% less than the conventional separation sequence). The investment cost of the process (with a 40 ktpy capacity) is $5250 \cdot 10^3$ US\$, and the total operating cost is $1434 \cdot 10^3$ US\$/year. Nonetheless, using a heat pump increases the capital cost due to the expensive compressor (1581.5 k\$). Yet, considering the energy savings (1.69 MJ/kg butanol) evaluated at 1893 k\$/year, the payback time of the heat pump is only 10 months.

The biobutanol recovery from the ABE mixture obtained by fermentation can be efficiently achieved in only a few separation units: three classic distillation columns are combined in one azeotropic dividing-wall column (A-DWC) that is effectively coupled with a compressor for vapour recompression, and a decanter that is used for the liquid-liquid split of the heterogeneous azeotrope butanol-water. The novel downstream process proposed was successfully designed, optimized, and heat integrated using process intensification principles and process simulators.

It should be noted that in spite of the high degree of integration, a vapour recompression assisted dividing-wall column is still well controllable although some minor design modifications may be required for an easy start-up procedure – as demonstrated in the recent literature [49; 50; 51].

## **CHAPTER 7 –** *Dynamics and Control of a Heat Pump Assisted Azeotropic Dividing-Wall Column for Biobutanol Purification*

While upstream processing remains a long-term challenge, the development of more efficient downstream processes for butanol recovery is actually a realizable option [33; 46; 52]. In fact, achieving cost effective separations and process integration was shown to be an essential requirement for sustainable biorefineries [35]. A recent review paper provides more insights into the selection and design of fluid separation processes that are applicable also to biofuels [47]. Among the methods used for recovery of biofuels, advanced distillation techniques (e.g. heat pump assisted distillation and/or dividing-wall column) proved capable of obtaining significant energy savings [4; 41].

This work focuses on the dynamics and control of a heat pump assisted azeotropic dividing-wall column, with the aim of proving that such a highly integrated system is controllable and thus the energy savings are also achievable in practice [52]. Adding a heat pump into this process integration brings additional control challenges on top of those encountered in the classic control of DWC [41; 53]. The challenge regarding the configuration of the DWC is somewhat similar to the tert-butanol / water separation in a vapour recompression assisted DWC using cyclohexane as entrainer in heterogeneous azeotropic distillation [18], or the bioethanol dehydration in a heat pump assisted extractive DWC [49].

However, instead of exploiting the heterogeneity of the cyclohexane / water / tert-butanol azeotrope [50] or the change of ethanol / water relative volatility induced by ethylene glycol [49], the design analysed here exploits the heterogeneity of the n-butanol – water azeotrope, without adding a mass separation agent. Moreover, crossing the distillation boundary by the liquid-liquid split takes place in a side-decanter.

An efficient control structure is developed in this work by addressing the main task of plantwide control, namely the strategy of solving the dynamic problems of a process under the production (rate and quality) and safety constrains, while minimizing the costs. Achieving this goal requires dynamic simulations (carried out in Aspen Plus Dynamics) to understand the dynamics of the process and to prove the effectiveness of the proposed control structures. The starting point is the heat integrated VRC assisted A-DWC design proposed by Patrascu et al. (2018), which achieves 59.75% energy savings compared to the conventional separation sequence. Figure 7.1 shows the azeotropic dividing-wall (which combines three distillation columns in one single unit column) with the mass balance and some additional technical details.

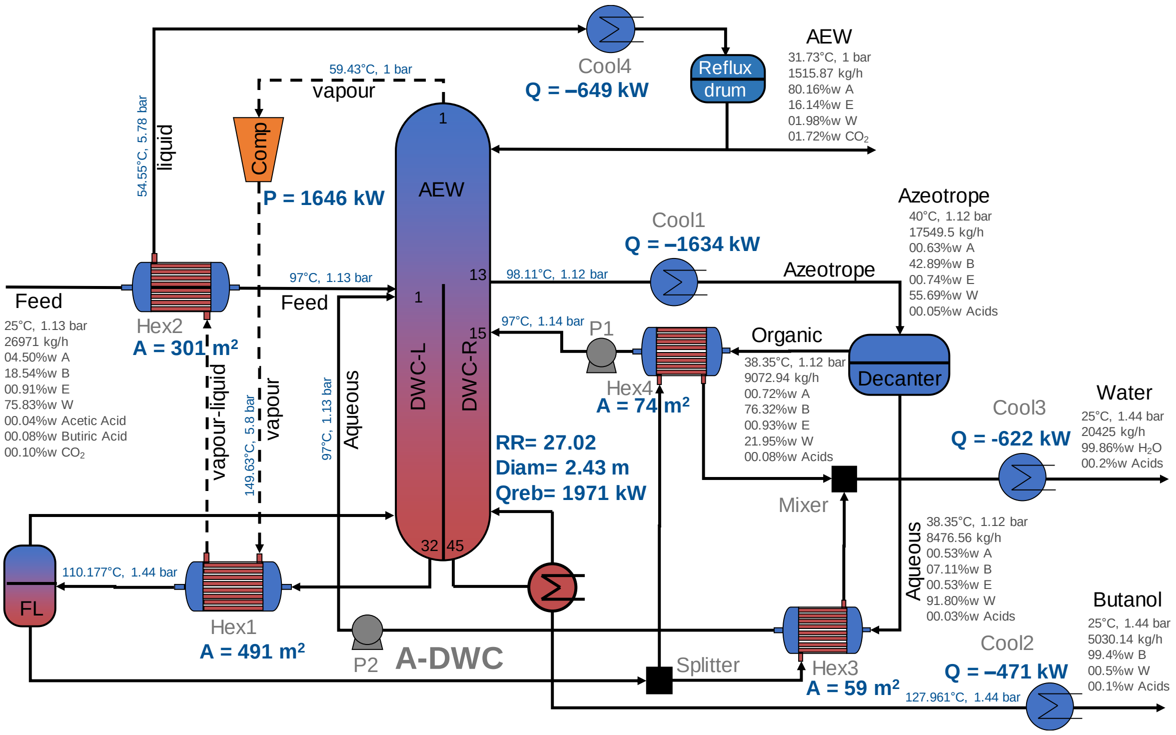

*Figure 7.1. Process flowsheet and mass balance of heat pump assisted A-DWC (heat integrated process) for butanol purification.*

The new design has two stripping section and one fractionation section. The cold fresh feed is preheated and partially vaporized from 25 °C to 97 °C, near the boiling point of the heterogeneous azeotrope butanol-water. The feed-side stripping section (DWC-L) removes the acetone, ethanol and butanol (with some water involved in the ethanol-water and butanol-water azeotropes) and delivers high purity water as bottom product. Therefore, the most-plentiful component is obtained here. The rectifying section (AEW) provides the light components (acetone and ethanol, with some water involved in the ethanol-water azeotrope) as distillate. The liquid flowing down from the fractionation section is routed to the second stripping section (DWC-R, opposite to feed). A large fraction of the liquid (with near azeotropic composition) is cooled to 40 °C and sent to decanting. The organic phase, which is returned to the column, is on the butanol-side of the azeotrope. Therefore, high-purity butanol can be obtained as bottoms product of the DWC-R section. The aqueous phase obtained from the decanter is mixed with the feed and sent to the water-removal section. In order to achieve energy savings, the top vapour stream is compressed from 1 bar to 5.8 bar. This way, the temperature increases from 60 °C to 150 °C, which is high enough to drive the reboiler of the water-removal stripping section and to preheat the fresh feed. Moreover, the hot water product is used to preheat the organic and aqueous phases obtained from decanting, before being returned to the column. In this way, 69% energy savings (57% due to use of heat pump, 12 % due to process-process heat exchange) is achieved compared to a simple A-DWC column.

The pressure-driven simulation is built in Aspen Plus, then exported to Aspen Dynamics. Two RADFRAC units are used to model the water removal section (DWC-L) and the combined rectifying (AEW) and butanol purification sections (DWC-R). The reboiler on the water-removal side is represented as a counter-current heat exchanger followed by a flash.

Several pumps and valves are provided on following streams: bottom stream of the water-removal stripping section, side stream, water and butanol product streams, distillate, reflux, organic and aqueous phase stream. No valves are necessary on the streams (internal flows) connecting the water-removal to the fractionation section, the vapour-liquid separator (FLASH) to the water-removal section, and the top main column to compressor.

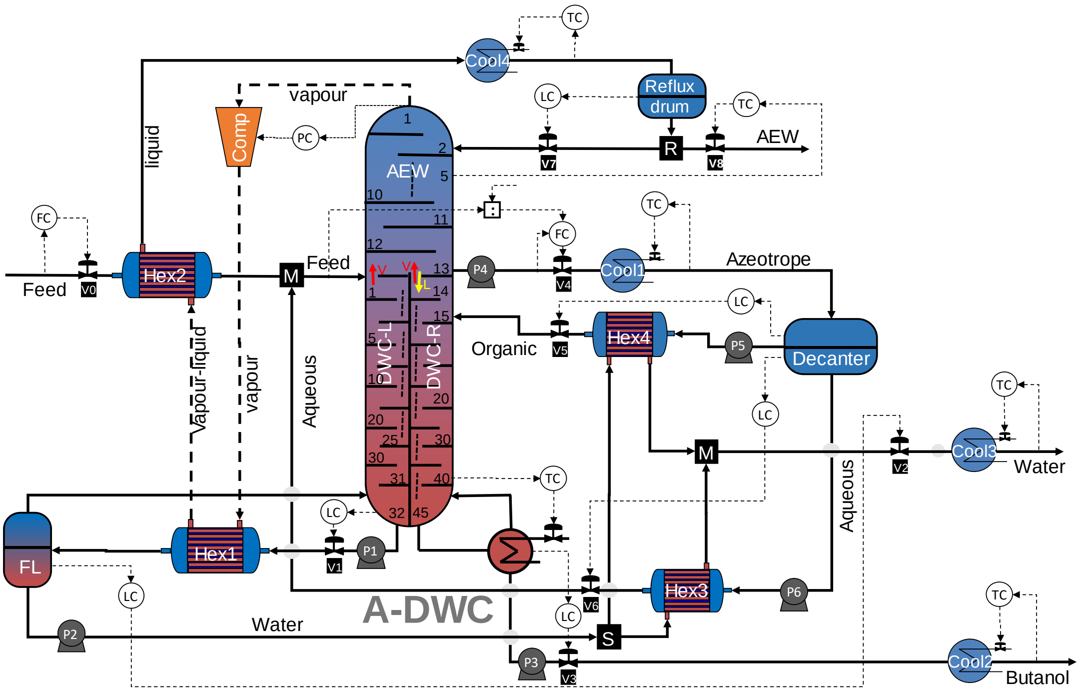

*Figure 7.2. Control structure of the highly integrated - heat pump assisted A-DWC for butanol purification – basic controllers*

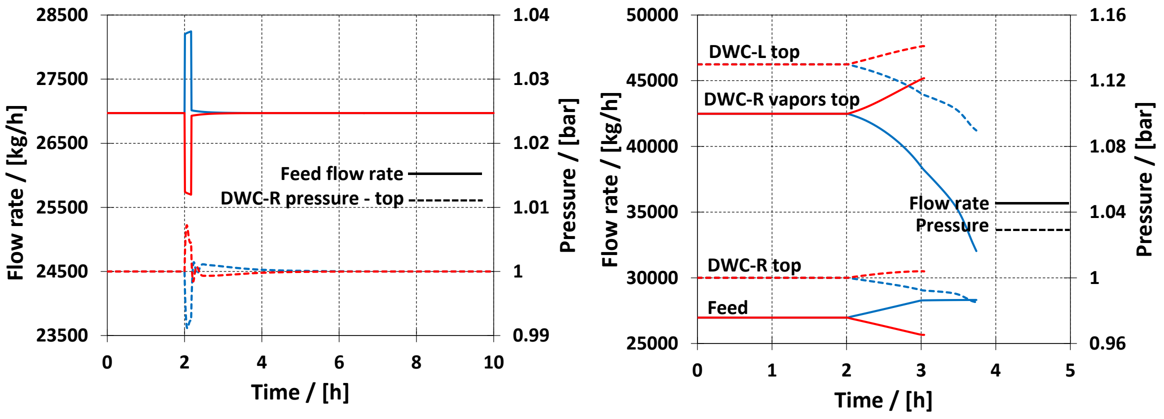

*Figure 7.3. Stability test of the basic control structure, for non-persistent disturbance (left) / persistent disturbance (right) - 5% disturbance in feed flow rate*

A basic control structure (Figure 7.2) can stabilize the process against small and non-persistent disturbances. For example, when the feed flow rate changed by ±5% for 10 minutes, the process returns to the initial operating point when the disturbance is removed (Figure 7.3 – left). However, when the feed flow rate is ramped by 5% over one hour, the stream entering the column cools down, the pressure and the temperature in column drop, less vapours are sent to rectifying section and to compressor (Figure 7.3 – right). This leads to further temperature decrease in the column. In the meantime, the temperature controller of stage 40 temperature of the butanol-purification tries to compensate the disturbance by increasing the reboiler duty. This affects the temperature of stage 5, so the top temperature controller closes the distillate stream valve. Further, the pressure controller reduces the brake power, trying to increase the column pressure. As a result, the vapours flow is too small to drive the water removal section. Therefore, some new manipulated variable is needed to provide the additional heat required to reject this disturbance.

When the feed flow rate is decreased by 5% and the disturbance persists for a long time (Figure 7.3 – right), the feed enters the column at higher temperature. In this case more vapours are sent to the rectifying section and more vapours are compressed, leading to continually temperature increase in the water removal section. As a result, more water is vaporized and eventually reaches the butanol product. Such disturbance could be rejected by controlling the temperature of the stream entering the column, but no manipulated variable is available.

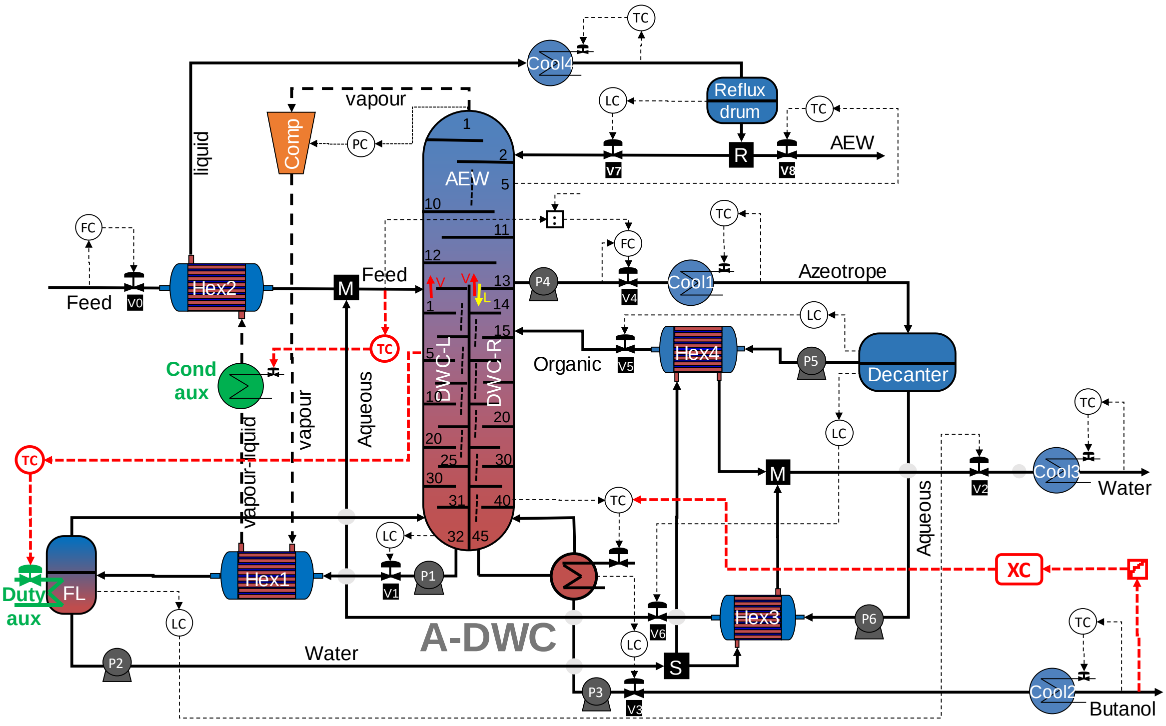

*Figure 7.4. Control structure of the heat-pump assisted A-DWC*

To overcome these control difficulties, two new variables to be manipulated were added (Figure 7.4). First one is a small additional duty (Duty-aux, 0.3 MW) on the vapour-liquid separator (the reboiler of the water-removal section), which represents 10% of the energy required. The second one is an additional cooler (Cond-aux, -0.68 MW) placed on the compressed vapour stream, between the reboiler and the feed preheating. These variables are used in new control loops as follows: temperature of the preheated feed, by manipulating the duty of the additional cooler; temperature on stage 5 in water-removal section (DWC-L), by manipulating the additional duty of vapour-liquid separator.

By introducing these controllers, the process can handle large feed flow rate disturbances for long time. As long as the right vapour flow is ensured by the new variables (additional duties), the pressure and temperature in top of the main column can be easily controlled by the compressor brake power and the distillate rate, respectively (Figure 7.5).

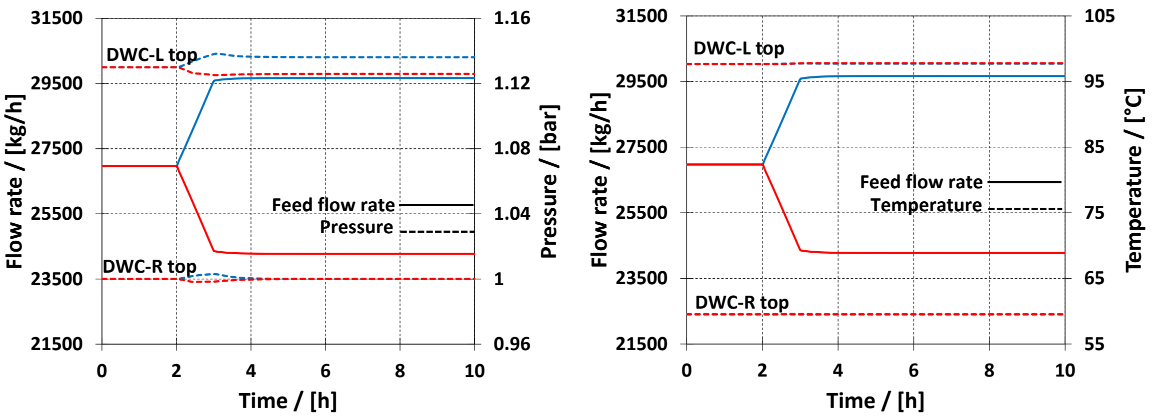

*Figure 7.5. Stability test of the control structure shown in Figure 7.4, for persistent disturbance - 10% change of the feed flow rate*

Note that choosing a stage from the upper part of the water-removal (DWC-L) section for temperature control is critical. For example, one could choose a stage in the lower part (for example, stage 25) with the idea that this would keep the purity of the water product closer to the required value, avoiding the use of a concentration control loop. However, dynamic simulations showed that disturbances in the fresh feed are seen by the control system too late, after they propagate from stage 1 to stage 25 of the DWC-L section. By now, the rectifying section is also seriously affected. Thus, increasing the duty of the auxiliary reboiler duty is not effective, and the compressor power must also be employed for temperature control purposes (override control should be included to avoid that the compressor-outlet temperature does not increase above a certain limit). Then, the only way to control the column pressure is by using the sub-cooled reflux.

If one wants to keep the purity of the butanol and water products exactly at their setpoints, concentration measurements are necessary. The slow dynamics of these measurement was taken into account by using the Aspen Plus Dynamics “sensor” model with 5 minutes sampling period and 5 minutes dead time. Just one concentration controller is provided. This adjusts the setpoint of the temperature controller of the butanol-purification section (stage 40). Figure 7.6 shows dynamic simulation result for the control structure employing the concentration controllers.

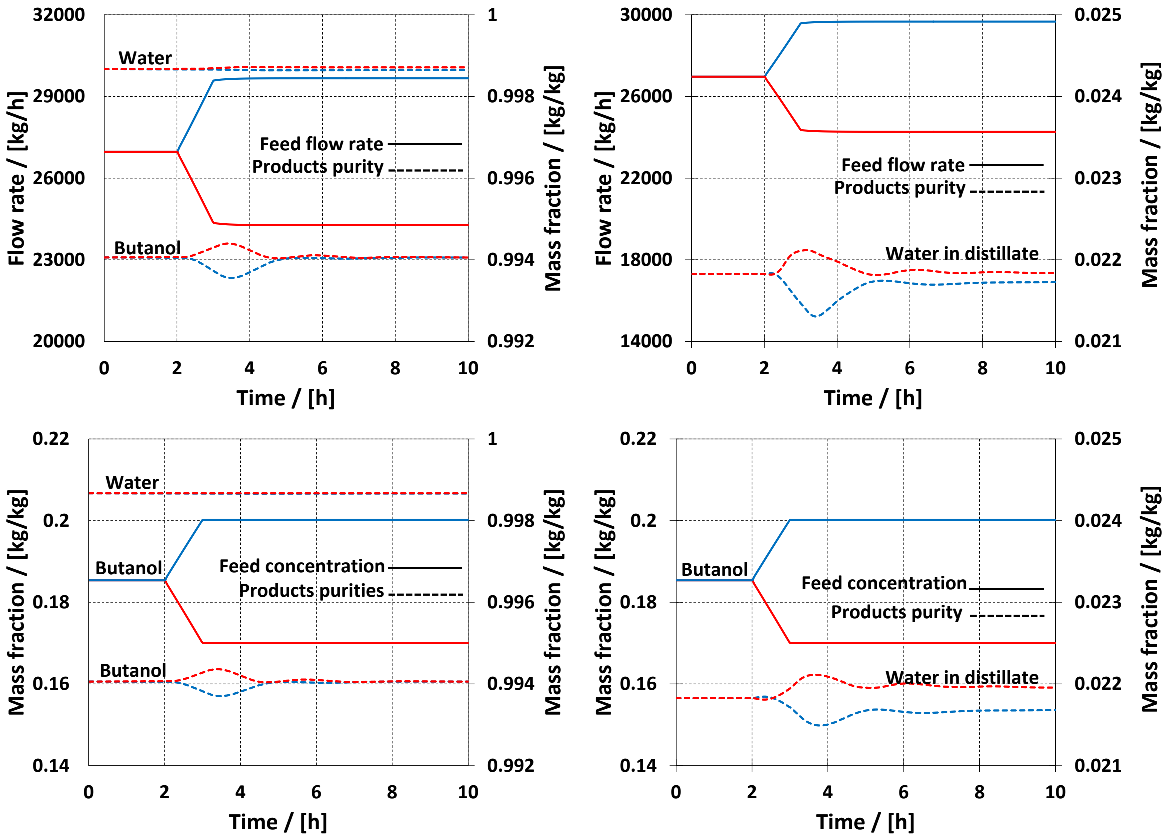

*Figure 7.6. Performance of the control structure shown in* ***Error! Reference source not found.****4. Top - 10% feed flow rate disturbances. Bottom - feed concentration disturbances.*

The downstream processing of biobutanol in the ABE process can be effectively performed in a heat pump assisted azeotropic dividing-wall column that is heat integrated and allows 59.75% energy savings as compared to a conventional separation sequence. Such integrated processes have more interactions between variables and fewer degrees of freedom as compared to conventional DWC systems, making it challenging to control and questioning the expected benefits.

The dynamics and control of this highly integrated process was successfully explored by using rigorous, pressure-driven dynamic simulations developed in Aspen Plus Dynamics.

## CHAPTER 8 – *Hybrid Separation Process for Butanol Purification*

Biobutanol is considered a bio-derived fuel with high energy content (32 MJ/kg butanol) that can be produced in the acetone-butanol-ethanol (ABE) fermentation process. Through the fermentation process, butanol cannot exceed 3% wt. in broth, because butanol inhibits the activity of microorganisms [44]. Anyway, the concentration of butanol can be increased to 18.6%wt. using gas stripping technique [54]. The separation of ABE mixture by distillation is an energy intensive method (14.7 to 79.05 MJ/kg butanol) [1]. This chapter presents two hybrid separation sequences which combine liquid-liquid extraction with conventional distillation columns. The liquid-liquid extraction is performed with two different solvents (mesitylene and 2-ethyl-1-hexanol). Both separation sequences are designed and optimized for a minimum of total annual cost (TAC). The most efficient hybrid sequence is further subject to process intensification through dividing-wall column technology and heat integration. Therefore, a new hybrid separation sequence is designed which features 34% energy savings and 25% TAC savings compared to the conventional hybrid separation sequence.

The ABE mixture obtained from the fermentation process contains a large amount of water. Separation of this water by distillation requires a large amount of energy. The liquid-liquid extraction technique can solve this problem and eliminate the most plentiful component (water) without energy costs. This technique requires a good solvent with low viscosity, different density than water, high selectivity for butanol, and which does not form azeotropes with the components from the mixture [43; 55].

There are several solvents used for ABE recovery e.g. oleyl alcohol, n-hexyl acetate, mesitylene and 2-ethyl-1-hexanol [43; 54; 55; 32; 36]. The most energy efficient hybrid processes are obtained using mesitylene (4.8 MJ/kg butanol) and 2-ethyl-1-hexanol (9.37 MJ/kg butanol) [43; 36]. These two studies neglect the impurities (acetic acid and butyric acid) present in the ABE mixture. According to azeotropic data predicted by Aspen Plus, mesitylene forms a high boiling point azeotrope with butyric acid. Moreover, this azeotrope can accumulate in the solvent recycle stream and must be removed, leading to a high economic penalty.

This work considers a feed stream mixture of 4.5%wt. acetone, 18.6%wt. butanol, 0.9 %wt. ethanol, 75.9 %wt. water and ppm butyric acid and acetic acid, which can be recovered from fermentation by gas stripping [54]. The constraints of downstream processing are a production rate of 40 kt/years butanol at 99.4 %wt. purity and water removal at 99.8 %wt..

The conceptual design is based on the following approach:

- remove the most plentiful component (water) by liquid-liquid extraction;
- recover the solvent with high purity;
- perform last the most difficult separation (butanol purification);
- purify the water product by removing the light components (acetone, ethanol)

***Design of the process using mesitylene as extraction solvent (Figure 8.1):*** The diluted ABE mixture and the solvent are fed on the top tray and on the bottom tray of the liquid-liquid extraction column, respectively. The raffinate containing water, acetone and ethanol is further sent for purification in the distillation column COL-3. The extract contains mainly solvent, butanol, acetone and ethanol. However, the liquid-liquid extraction selectivity in not 100%, and a small amount of water remains in the extract. The first distillation column (COL-1) serves for solvent recovery. Due to the presence of the butyric acid - mesitylene azeotrope, a side stream is necessary to avoid the accumulation of acids in the solvent recycle stream. The side stream of COL-1 is fed in the fourth column (COL-4) to avoid solvent loss.

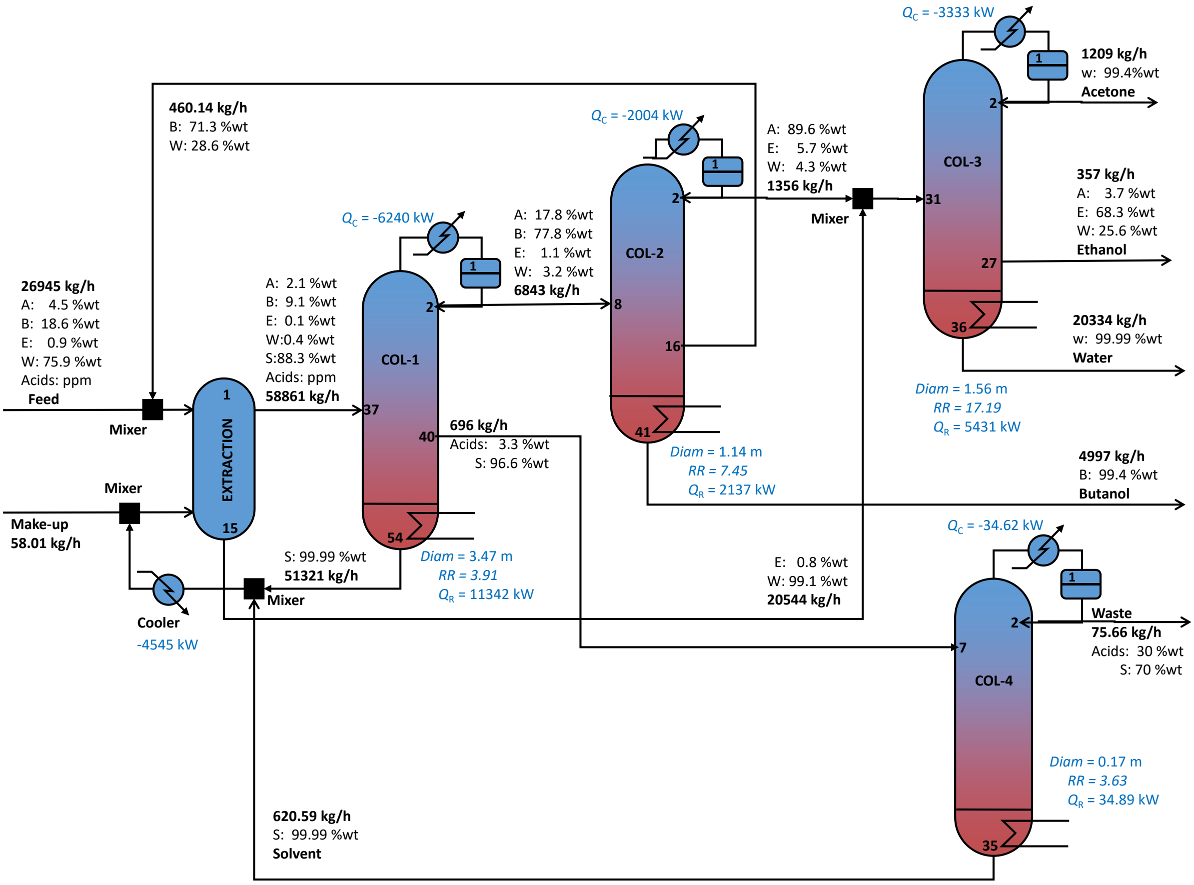

*Figure 8.1. Separation sequence with mesitylene as solvent*

***Design of the process using 2-ethyl-1-hexanol as extraction solvent (Figure 8.2):*** The ABE mixture is fed in the liquid-liquid extraction column on the top tray and 2-ethyl-1-hexanol is fed on the bottom tray. The raffinate (water with some ethanol and acetone) is sent to the column COL-3 for water purification. Because the liquid-liquid extraction process does not achieve 100% selectivity, a small amount of water is found in the extract. The extract is fed to COL-1. The solvent is recovered with high purity as bottom product and recycled. The distillate is fed to the column COL-2, which delivers high-purity butanol as bottom product, acetone and ethanol with small amounts of water as distillate, and a side stream containing butanol and water is sent to a decanter, from which the aqueous phase is recycled to the extraction column and the organic phase is fed to a lower tray of COL-2. Note that this process is more promising: it does not involve the formation of an azeotrope containing the solvent, thus fewer columns are required compared to the previous process.

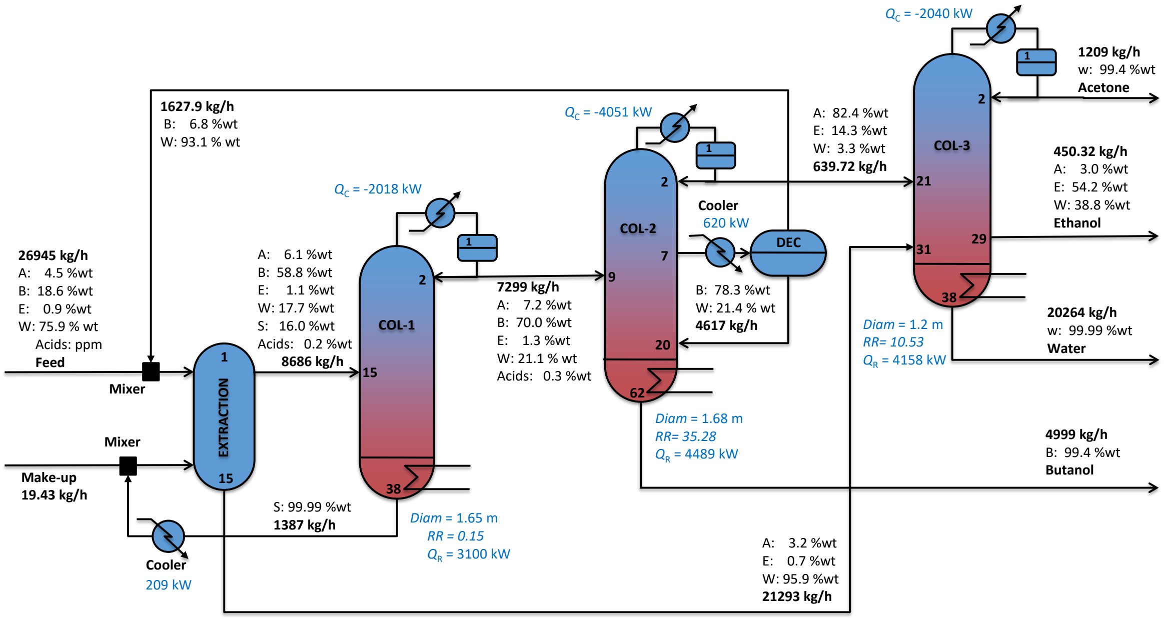

*Figure 8.2. Separation sequence with 2-ethyl-1-hexanol as solvent*

***Process design alternative (2-ethyl-1-hexanol as extraction solvent – Figure 8.3):*** The novel sequence uses 2-ethyl-1-hexanol for liquid-liquid extraction. This design uses a single dividing-wall (DWC) column to integrate the solvent recovery column (COL-1) and butanol purification column (COL-2). High-butanol purity (99.4 %wt.) is recovered in the side-stream. The dividing-wall column is simulated in Aspen Plus as a prefractionator (PF) and a main column (DWC). In this design, heat integration is applied for minimization of the energy requirement. Therefore, the extract is preheated to 60 °C before being fed to the prefractionator (PF), using the DWC side stream. The raffinate is also preheated from 25 °C to 95 °C using DC bottom stream, before being mixed with the DWC distillate and fed to the DC column.

This design is 25% more economical than the conventional design. The energy requirement for butanol purification is reduced by 34% compared to the conventional hybrid separation sequence.

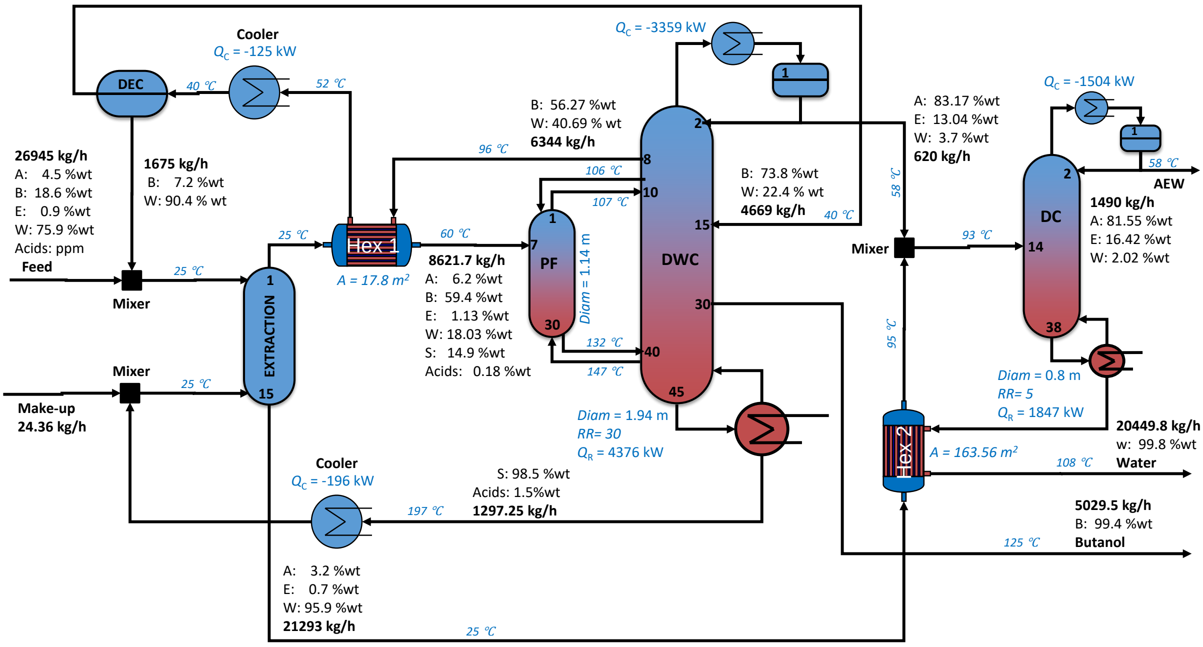

*Figure 8.3. Heat integrated DWC flowsheet (2-ethyl-1-hexanol)*

The design and optimization of each separation sequence is performed with Aspen Plus simulation software using NRTL property method to model the non-ideality of the liquid phase. In both conventional separation sequences, the distillation columns are optimized for a minimum of total annual cost (TAC). The optimization procedure for the distillation columns was done by following the next steps: specify the number of stages; set design specifications in order to keep the constraints of product purities; perform a sensitivity analysis to find the feed stage with the lowest energy requirement; calculate the total annual cost.

The conventional hybrid separation sequence which uses mesitylene as separation agent is an energy intensive process (11.05 MJ/kg butanol with a TAC of 6890.6·$10^3$ US$/year.) due to the high amount of solvent used and the mesitylene-butyric acid azeotrope. The solvent loss with this azeotrope is around 424·$10^3$ kg/year which means 1695·$10^3$ US$/year loss. However, the energy requirement when using 2-ethyl-1-hexanol as a solvent is much lower (6.76 MJ/kg butanol with a TAC of 4659.9·$10^3$ US$/year). An alternative heat integrated process has also been studied for the conventional separation sequence which uses 2-ethyl-1-hexanol. The new design uses a dividing-wall column to integrate two conventional columns in a single one. Thereby, the total annual cost is reduced to 3029.8·$10^3$ US$/year and the energy requirement is minimized by heat integration to 4.46 MJ/kg butanol.

# CONCLUSIONS

The production of biofuels from waste biomass feedstocks requires a lot of energy to obtain high purity products in downstream processes, due to the low concentration of alcohol in the fermented mixtures. However, the energy requirement and the total annual costs (TAC) can be reduced by process intensification, heat integration, or using a heat pump.

In this thesis the separation of Acetone-Butanol-Ethanol (ABE) mixture has been approached in three methods (Figure 9.1):

- Performing the decantation first (FD)
- Removing the most plentiful component first (water) and the decantation last (LD)
- Performing the liquid-liquid separation by using a solvent in the extraction column (LLE)

According to a preliminary mass balance, the energy requirement for the ABE separation is lower when the decantation takes place before distillation (FD-Conv vs LD-Conv). Using three conventional distillation columns (FD-Conv) and neglecting the acetone-ethanol purification, the energy requirement for heating is 1.8 kWh/kg butanol, with a total annual cost of $3231\cdot10^3$ US$. Further research led to a heat integrated separation sequence where the conventional columns have been combined step by step in a simple dividing-wall column (DWC), then into azeotropic DWC. The simple dividing-wall column (FD-HI-DWC) which combines two conventional distillation columns requires 1.24 kWh/kg butanol for heating and a TAC of $2421.4\cdot10^3$ US$. However, when the three conventional distillation columns were combined into one azeotropic DWC, the energy requirement and the TAC were the same.

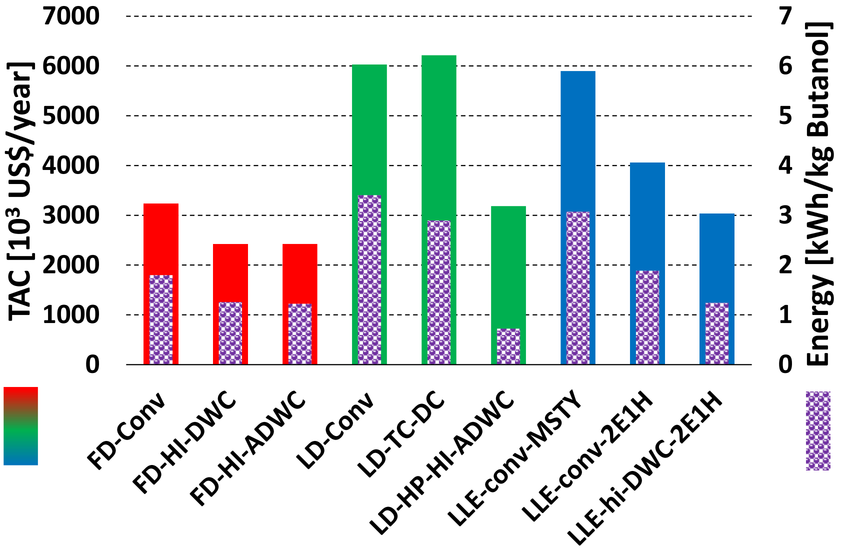

*Figure 9.1. Total annual cost and energy requirement for different ABE separation processes*

The removal of a large amount of water from the ABE mixture through a distillation column (LD-Conv) requires high energy (3.4 kWh/kg butanol) due to a large amount of mixture to be vaporized. The energy requirement drops to 2.9 kWh/kg butanol when the conventional distillation columns are thermally coupled (LD-TC-Conv), but the TAC is even higher. However, the large amount of vapors that reach the top of the column could be used for heat integration. The combination of the three distillation columns into a single azeotropic DWC, the use of Heat Pump, and heat integration led to an efficient separation sequence (LD-HP-HI-ADWC). Therefore the energy requirement is reduced to 0.75 kWh/kg butanol with a TAC of $3184 \cdot 10^3$ US$. Even if the TAC is higher than the previous best separation sequence, the payback time of the heat pump is only 10 months.

The liquid-liquid extraction approach for water removal was performed with two different solvents (mesitylene and 2ethyl-1-hexanol). The process that uses mesitylene as solvent (LLE-conv-MSTY) has the disadvantage of forming a high boiling point azeotrope with the butyric acid present as an impurity in the ABE mixture. This leads to high energy requirement (3.07 kWh/kg butanol), high TAC ($5898 \cdot 10^3$ US$), and loss of the solvent as a byproduct. However, using 2ethyl-1-hexanol as a solvent, the energy requirement, and TAC is by 30% lower (LLE-conv-2E1H). Moreover, combining two conventional distillation columns into a DWC and applying heat integration, the energy requirement was reduced to 1.24 kWh/kg butanol and the TAC was minimized to $3029 \cdot 10^3$ US$.

For the dynamics and control of the bioethanol or biobutanol processes, it was ensured a control structure to manage disturbances as ±10% of the production rate and ± 2% concentration of alcohol in the feed. The separation sequences that use conventional distillation columns can be easily controlled by using flow, pressure, level, temperature and ratio controllers. However, when the process is highly integrated, an azeotropic, or extractive dividing-wall column is implied and a heat pump is used, the process becomes unstable and hard to be controlled. The dynamic of this type of processes were studied in this thesis, and a control structure was developed for bioethanol and biobutanol plant. An additional heating duty was necessary for each plant, with a temperature control close to the feed tray section to obtain a quick reaction and ensure a vapour flow rate through the heat pump when disturbances were introduced in the system.

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