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Department of Chemistry, Materials and Chemical Engineering "Giulio Natta"

M.Sc. Program in Chemical Engineering

DYNAMIC SIMULATION AND PLANTWIDE CONTROL OF AN ABE/W SEPARATION PLANT

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Abstract

This M.Sc. thesis work deals with the dynamic simulation and plantwide control of an acetone-butanol-ethanol (ABE) process downstream separation plant.

It is the product of the work carried out in collaboration with the SUPER (SUstainable Process Engineering Research) group of the Department of Chemistry, Materials and Chemical Engineering "Giulio Natta" of Politecnico di Milano with the aim of validating the previous M.Sc. thesis work by A. Boffa "La fermentazione acetone-butanolo-etanolo. Analisi e ottimizzazione dello schema di purificazione." also developed in collaboration with the aforementioned research team.

The thesis enters the activities of the Green Chemistry National Cluster and specifically it relates to the Task 5.3 of the LIDIA (LIgnocellulosic DIcarbossilic Acids) Project.

The ABE fermentation was the most spread industrial scale fermentation process during the first half of the 20th century but it has been progressively abandoned because of the low competitiveness of alcoholic fermentation processes with respect to the rising oil and petrochemical industry. During last 15 years anyway there has been an increasing interest for the production of chemicals and fuels from renewable resources because of growing concerns about global warming and climatic change, increasing crude oil price and existing legislations restricting the use of nonrenewable energy sources. Furthermore, the generation of biofuels contributes to the reduction of CO_2 emissions .

This thesis work can be divided into three parts.

The first one concerns the degrees of freedom analysis of the plant subsections in order to know the number of specifications needed and of variables to be controlled.

The second section is about the plantwide control layouts; several configurations have been tested and the most stable and effective one has been chosen and shown.

Finally, the third and most relevant part is relative to the dynamic simulation of plant subsections. Startup and shutdown procedures have been defined and steady state results have been reported. Then, the study of control loops responses to the most likely perturbations have been performed in order to test the selected control layout stability and evaluate how these disturbances influence the system separation performances.

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La presente tesi si occupa della simulazione dinamica e del layout di controllo di un impianto di separazione a valle del processo di fermentazione acetone-butanolo-etanolo (ABE).

Essa è il frutto del lavoro svolto in collaborazione con il gruppo SUPER (SUstainable Process Engineering Research) del Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta" del Politecnico di Milano ed ha lo scopo di convalidare il precedente lavoro di tesi "La fermentazione acetone-butanolo-etanolo. Analisi e ottimizzazione dello schema di purificazione." svolta da A. Boffa sempre in collaborazione con il gruppo di ricerca sopra menzionato.

La presente tesi rientra nelle attività del Green Chemistry National Cluster e nello specifico è relativa al Task 5.3 del progetto LIDIA (LIgnocellulosic DIcarbossilic Acids).

Il processo di fermentazione ABE è stato il processo di fermentazione più diffuso in scala industriale durante la prima metà del 20mo secolo ma è stato progressivamente abbandonato a causa della scarsa competitività dei processi di fermentazione alcolica rispetto alle emergenti industrie petrolifera e petrolchimica. Durante gli ultimi 15 anni tuttavia è rinato l'interesse per la produzione di chemicals e combustibili da risorse rinnovabili dovuto alle crescenti preoccupazioni circa il riscaldamento globale e il cambiamento climatico, al prezzo sempre in aumento del greggio ed alle leggi restrittive circa l'uso di fonti energetiche non rinnovabili. Inoltre, la produzione di biocarburanti contribuisce alla riduzione delle emissioni di CO_2.

Il presente lavoro consiste di tre parti.

La prima si occupa dell'analisi dei gradi di libertà delle sottosezioni dell'impianto al fine di identificare il numero di specifiche necessarie e di variabili da controllare.

La seconda parte riguarda la configurazione del sistema di controllo dell'impianto; diverse soluzioni sono state testate e la più stabile ed efficace è stata scelta e mostrata.

Infine, la terza e più sostanziale parte si riferisce alla simulazione dinamica delle varie sottosezioni dell'impianto. Sono state definite le procedure di startup e shutdown e riportati i risultati dello stazionario.

È stato quindi condotto lo studio della risposta dei loop di controllo ai disturbi più plausibili con il fine di testare la stabilità della configurazione scelta e di valutare in che modo tali perturbazioni incidono sulle prestazioni del sistema di separazione.

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1 State of the art

The Acetone, Butanol and Ethanol (ABE) fermentation process was the most spread industrial scale fermentation process during the first half of the 20th century. It was discovered first in 1916 by Chaim Azriel Weizmann, a belarusian biochemist, that isolated a bacterial strain (Clostridium acetobutylicum) able to produce alcohols metabolizing cereals and potatoes. He observed that acetone, butanol and a little ethanol were produced, therefore the ABE fermentation using Clostridium acetobutylicum process was scaled up in order to obtain acetone useful to produce Cordite, required by the british war industry during World War I.

With the increasing role of oil and petrochemical industry, alcoholic fermentation processes have been progressively abandoned because of their low competitiveness with respect to refineries. Only a few plants worked beyond the 60's, i.e. in South Africa until 1980, in Russia until 1990 and in China until 2004 [1].

In the late 80's anyway a renewed interest in biochemistry and fermentation can be noticed. Thanks to these studies the fermentation mechanism primarily implicated in the solventogenesis process in batch fermentations of Clostridium acetobutylicum could be examined and understood in considerable detail [2].

Once understood the biochemical mechanism lying behind this process, the reactor design optimization was the new challenge: Groot et al. in 1989 [3] compared performances of the batch and the continuous fermenters integrated with product recovery by gas stripping. These studies assessed the higher productivity of the latter configuration and focused the attention of researchers on products separation.

The problem of ABE fermentation was still its low productivity and cost efficiency compared to the petrochemical processes used to produce the same compounds (butanol, ethanol and acetone).

Therefore two ways to solve this problem were detected:

- Find a bacterial strain whose affection by product inhibition is sensibly lower;

- Perform an effective separation downstream the fermenter.

Even process integration is possible, i.e. the removal of products from the fermentation broth in order to increase the productivity and lower the product inhibition effect.

Membrane solvent extraction and pervaporation looked immediately like the most promising separation techniques [4].

Thus, sensitivity analysis of performances with respect to the membrane type and operating conditions were performed in several studies [5], beside their economical evaluation [6].

Also mutant bacterial strains (hyper amylothic) have been improved and economical feasibility of the plant have been studied but its scale up was still far from market targets and investor interest [7].

During last fifteen years anyway there has been an increasing interest for the production of chemicals and fuels from renewable resources. Reasons for this trend include growing concerns about global warming and climatic change, increasing crude oil price and existing legislations restricting the use of nonrenewable energy sources (sustainable development goals). Further, the generation of biofuels may improve the local employment opportunities and contributes to the reduction of CO_2 emissions [8].

Anyway the issues to cope with are not different than the past, a better understanding of physiological principles of solvents production and metabolic engineering have been achieved but lack of studies about butanol tolerance is still present [9].

The most interesting improvements in ABE fermentation design can be found in several studies concerning downstream processing of the fermentation broth.

The passage from a single step or single unit operation analysis to hybrid multi-stage integrated processes analysis occurred and the most various separation methods have been taken into account (cfr. Table 1 and Table 2 [10]).

However nowadays the only technology completely developed at commercial scale is distillation, that unfortunately involves high operational costs (cfr. Table 3 [11]).

Extraction looks attractive but, even if different solvents have already been screened [12], its development is still at lab scale level.

Anyway the coupling of biological and engineering researches let the authors hope for an oncoming scale up of ABE fermentation plants [13].

The last old technology ABE fermentation plant was dismissed in China in 2004 [1]; anyway China is still the most promising country for this kind of process. In 2009 Ni and Sun [14] already noticed that the technological advantages of the ABE fermentation process in the very last years combined with the actual energy situation would have brought new opportunities and

Strategy	ABE Productivity (g/L/h)	Yield (g/g)	Titer (g/L)	Ferment. mode[c]	Comment	Reference
Pervaporation	0.18	0.31–0.35	155.0	F	Silicalite/silicone	Qureshi et al. 2001
	0.14	0.34	42.0	F	Polypropylene	Qureshi et al. 1992
	1.72	0.28	13.1	C	Polypropylene	Gapes et al. 1996
	0.98	0.43	165.1	F	Silicone	Qureshi and Blaschek 2000
	0.30	0.35	57–195	C	Polydimethylsiloxane	Van Hecke et al., 2012
Liquid–liquid extraction	0.14	0.35	23.8	F	Oleyl alcohol	Qureshi et al. 1992
	–	0.40	29.8	B	Crude palm oil	Ishizak et al. 1999
	–	0.38	27.9	B	Oleyl alcohol	
	–	–	29.9	B	Biodiesel	Li et al. 2010a
	2.5	0.35	25.3	C	Oleyl alcohol/decanol	Bankar et al. 2012
	10.9	0.38	20.3	C	Oleyl alcohol/decanol	Bankar et al. 2013
Gas stripping	0.26	0.38	69.1	F	Condenser, 0–3 °C	Qureshi et al. 1992
	0.41	0.32	108.5	F	Condenser, 1 °C	Lu et al. 2012
	1.16	0.47	232.8	F	Condenser, ~2 °C	Ezeji et al. 2004
	0.59	0.36	81.3	F	Condenser, ~2 °C	Ezeji et al. 2007
	0.53	0.36	172.1	F	Condenser, ~2 °C	Xue et al. 2012
Vacuum	0.34	0.26	45.9	B	Condenser, 4 °C	Mariano et al. 2011
Perstraction	0.21	0.44	136.6	B	Oleyl alcohol/silicalite	Qureshi and Maddox 2005
	0.24	0.37	57.8	F	Oleyl alcohol/silicone	Qureshi et al. 1992
Adsorption	0.92	0.32	23.2	B	Polyvinylpyridine	Yang and Tsao 1995
	1.33	0.32	59.8	F	Polyvinylpyridine	
	0.92[a]	0.32[a]	29.8[a]	B	Polyvinylpyridine	Yang et al. 1994
	0.30[b]	0.20[b]	31.6[b]	F	Activated carbon	Our study

[a] 180.0 g of PVP is added
[b] The data are butanol titer, productivity, and yield
[c] Batch, fed-batch, and continuous fermentation were abbreviated as B, F, and C, respectively

Table 1: Integrated inhibitory product recovery strategies for enhanced ABE fermentation

Strategy	Advantages	Disadvantages	Selectivity	Energy requirements (MJ/kg)
Pervaporation	High selectivity	Fouling problem, membrane material cost	2–209	2–145
Liquid–liquid extraction	High selectivity	Emulsion, extractant cost, toxic to culture, extractant recovery and loss	1.2–4100	7.7 or 26[a]
Gas stripping	No fouling, easy to operate, no harm to the culture	Low selectivity, low efficiency	4–22	14–31
Vacuum fermentation	No fouling, easy to operate, no harm to the culture	Low selectivity, low efficiency	15.5–33.8	–
Perstraction	High selectivity, low toxicity to the culture	Fouling problem, emulsion, and material cost	1.2–4100	7.7
Adsorption	Easy to operate, low energy requirement	High material cost, low selectivity, adsorbent regeneration	130–630	1.3–33

Data for selectivity and energy requirements are from: Roffler et al. 1987b, Groot et al. 1992, Oudshoorn et al. 2009b, and Mariano et al. 2011
[a] The energy requirement of 26 MJ/kg is for ABE solvent

Table 2: Comparison of various integrated processes for butanol recovery

Technology	Efficiency	State of development	Scale	Capital cost	Operating cost	Technology status
Distillation	High	Complete	Commercial	Med	High	Commercial
Gas Stripping	Medium	Research	Lab	High	High	Research
Solvent Extraction	High	Research	Lab	Med	Med	Research
Pervaporation	High	Development	Pilot	High	High	Research
Adsorption	High	Research	Commercial	High	Low	Research

Table 3: Comparison and state of development of various integrated processes for ABE products recovery

challenges for the re-emerging ABE fermentation industry.

With the progresses in strain improvement, process techniques, and potential for utilization of low price lignocellulosic biomass, it was expected the traditional ABE fermentation industry in China to be economically viable in a few years.

Two years later, indeed, Green confirmed that ABE fermentation process has recently been re-established in China. Newly installed production capacity can be optimized and expanded with further improvements to the microbe and refinements to the fermentation process. Over time, it should be possible to convert plants to use cheaper cellulosic feedstocks [15].

Researches about ABE fermentation process are still ongoing nowadays. The most useful publications for this M.Sc. thesis work were made by Liu et al. in 2004 [16] and Kraemer et al. in 2011 [17] that demonstrated, by a process flowsheet economical optimization, that the most cost-effective plant configuration for ABE products separation from the fermentation broth consists in a hybrid extraction-distillation process made up of:

1. Liquid-liquid extraction unit;

2. Solvent distillation unit;

3. Further products distillations.

Moreover they identified a certain amount of compounds giving good performances as solvent.

Finally, the present M.Sc. thesis is the natural continuation of the design M.Sc. Thesis "La fermentazione Acetone-Butanolo-Etanolo. Analisi e

ottimizzazione dello schema di purificazione." by A. Boffa, A.Y. 2014-2015 [18], that consists in a design thesis with the aim of analyzing and optimizing, from an economical point of view, the separation section of an ABE fermentation process plant.

The present work, in the end, has the aim of testing the plant performances by mean of a dynamic simulation according with the design obtained by the cost optimization, in order to complete its economical and technical feasibility assessment.

No dynamic simulation studies have been performed and reported yet in the actual scientific bibliography, therefore this thesis work represents an innovative and original step forward for the production of these products through the described process, fulfilling the required characteristics for a M. Sc. thesis project.

2 Why

"Motivation" literally means "what moves actions" therefore, before doing "anything", we do "because of something". That's why this thesis work starts with the explanation of the reasons why it is worth doing what I am going to do, before explaining the topic itself.

Thus, every part of the title will be analyzed in the following sections and the reasons why it is worth performing all of them will be explained in detail.

2.1 Why simulation

Whenever we have to design a plant, or whatever, we have to deal with several degrees of freedom. Some of them are usually saturated by constraints, others are saturated by specifications. Certain constraints (physical laws, legal laws, safety standards, quality standards etc.) reduce the set of all imaginable scenarios to the set of possible scenarios. Furthermore other constraints (time, process, operative conditions, raw material resources etc.) reduce the set of possible scenarios to the one of plausible scenarios. Finally, the remaing degrees of freedom (if present) have to be defined by solving an economical optimization problem giving the optimal scenario for our project.

However, in chemical plants design, relationships between variables are not as easy as would be required in order to solve the optimization problem pen-on-paper. On the other hand, much more simple short-cut equations are not as reliable and accurate as required for the project. Thus, usually, a trial and error solution is needed.

Of course, in order to test our estimations, it's not possible to build and tear down as many plants as our attempts are.

Moreover, even when experimental approach is theoretically possible, it could be not feasible due to:

- Inaccessible inputs and outputs;

- Experiments may be too dangerous and risky;

- Cost of experimentation may be too high;

- Time constants of the system may not be compatible with human dimensions;

- Experimental behaviour might be obscured by disturbances. [19]

On the contrary we can perform as many simulations, reflecting the system behaviour, as we need. Beside the huge number of attempts required by trial and error solving methods, there are several additional reasons why simulation is so important in process design:

- Predict the course and results of certain actions;

- Understand why observed events occur;

- Identify problem areas before implementation;

- Explore the effects of modifications;

- Confirm that all variables are known;

- Evaluate ideas and identify inefficiencies;

- Communicate the integrity and feasibility of your plans. [20]

Therefore we can definetely state that simulating (that intrinsically means "modelling") allows us to create a lot of parallel worlds where everything may happen before happening in the one that counts more: the real world. This way we gain a predictive power over the plant (or the system in general) perfomances as they would really be once started up and we may change as many variables as the degrees of freedom are without even moving from our chair.

2.2   Why dynamic

When we talk about process simulation we may refer to two different kind of it:

- Steady-state simulation;

- Dynamic simulation.

Steady state was introduced to simulate stationary processes, i.e. non time-depend processes, in an equilibrium state. It is a powerful tool to evaluate the system performances and the final value of each parameter.

Anyway what happens in between the "run" button pushing and the steady state achievement is completely neglected. Everything looks perfect and self controlling but real world is rather different.

Disturbances and deviation from the stationary conditions are always present and we need to know the system responses (e.g. holdups, thermal changes etc.) to every of them both for safety and performance reasons.

Dynamic simulation express the time-dependence of variables (i.e. accumulation terms) via derivative terms. It allows time-dependent description, prediction and control of real processes in real time.

Dynamic simulation can be used in both an online and offline fashion. The former case being model predictive control, where the real-time simulation results are used to predict the changes that would occur for a control input change, and the control parameters are optimised based on the results. The latter can be used in the design, troubleshooting and optimisation of process plant as well as the conduction of case studies to assess the impacts of process modifications [21].

Moreover, dynamic modelling and simulation of the system allows us to estimate the characteristic times of the transients. During start-up and shutdown procedures (either planned or not) it is often required by the system to go off and then to come back to the standard operating conditions. A lot of time for these procedures means long time of non-productive activity, meaning in return big money losses.

Dynamic simulation allows us to optimize start-up and shut-down procedures, minimizing the non-productive times, i.e. minimizing the money losses.

Finally, dynamic simulation can be also used for operators training.

2.3   Why control

It is common belief that performances and safety are about power and strength at the expenses of money. This is not strictly true. We may think a plant to be performant and productive if it is big, to be safe if equipments are thick and strong or if we have a lot of safeguards and alarms, but these beliefs about dimensions may be double edged weapons.

The only certainty we have is that a plant is performant if it is efficient, where "efficient" means that it does its job the way it has to.

A system, a process plant in particular, does its job if its variables follow the desired trajectory during the process (servo problem) and/or counteracts the effects of external disturbances (regulator problem).

Moreover, it is not of minor importance the economically efficiency that

is definetely not in contradiction with performances if a good design is performed.

All these concepts may be resumed in one word: control.

Given the above considerations, there are three general classes of needs that a control system is called on to satisfy:

1. Suppressing the influence of external disturbances;

2. Ensuring the stability of a chemical process;

3. Optimizing the performance of a chemical process. [22]

In our case study we'll see that all of them will be required. The third point in particular can be referred to the start up procedure, as already highlighted.

Finally, it is worth remarking that the best control system is the simplest that does the job.

2.4   Why ABEW separation plant

With the considerable growth of transportation sector and demand for transport fuels rising globally, beside the fossil fuel price increase, the IEA (International Energy Association) assesses biofuels as one of the key technologies to reduce both CO_2 emissions and the dependency on fossil transport fuels. Their report shows how global biofuel consumption can increase in a sustainable way from 55 million tonnes of oil equivalent (MTOE) today to 750 MTOE in 2050; i.e a growth form 2% today to 27% in 2050 of the global share of biofuel in total transport fuel.

With substantial investments in place, most biofuel technologies could get close to cost-competitiveness with fossil fuels, or even be produced at lower costs in the longer term. In total, the report assesses the expenditure on biofuels required to meet the roadmap targets between USD 11 trillion to USD 13 trillion over the next 40 years, depending on the actual production costs [23].

For this reason, ABE (acetone, butanol and ethanol) fermentation has seen renewed attention for the production of butanol, which has wide applications in the energy and chemical industries. Although China is leading the re-commercialization of ABE fermentation with over 210,000 MT of butanol capacity, plans for different stages of preparation and scale-up in Brazil, the US, the UK and France are also underway [24].

Biobutanol, produced in appreciable amount by the ABE process, is the product of major concern, since it is a possible substitute of bioethanol or even better. Indeed, it is already employed both as fuel additive and as pure fuel instead of standard gasoline because, differently from ethanol, it can be directly and efficiently used in gasoline engines. Moreover it has the great advantage that can be shipped and distributed through existing pipelines and filling stations.

Finally n-butanol is widely used as a direct solvent for paints, coatings, varnishes, resins, dyes, camphor, vegetable oils, fats, waxes, shellac, rubbers, and alkaloids.

The butyl acrylate application of n-butanol has a wide scope for its expansion, which in turn would help in increasing the consumption for n-butanol globally. Butyl acrylate was the biggest n-butanol application in 2014 and is projected to be worth USD 3.9 billion by 2020 [25].

However, the major limit for an industrial-scale production of bio-butanol is the high separation cost, due to the presence of other fermentation products and to its low final concentration in the ABE fermentation broth.

Indeed, microorganisms used in ABE fermentation suffer from product inhibition giving a low ABE final concentration in a batch process [9].

Therefore both process and cost efficient separation methods for separation of the ABE mixture form the broth (mainly water) and subsequent separation of the ABE mixture products themselves are required in order to scale it up at an industrial scale.

2.5 Additional remarks

The present M.Sc. thesis is about simulation and plantwide control of an ABE separation plant given a certain number of specifications. As remarked above it is the natural continuation of the design M.Sc. Thesis "La fermentazione Acetone-Butanolo-Etanolo. Analisi e ottimizzazione dello schema di purificazione." by A. Boffa, A.Y. 2014-2015 [18].

Therefore every design parameter is based on the results of the aforementioned work while simulation related choices and control system design configurations are the real subject of study of the present M.Sc. thesis work.

3 Degrees of freedom

"Degrees of freedom" is the expression used to name the amount of variables that can independently change in a system. In general, the way we evaluate them has been explained yet, anyway it is important to remark that, since the d.o.f.s of a system are the amount of variables of a system that can change independently, they are also the maximum amount of variables that can be controlled by our control system. We can't definetely manipulate more variables than the ones that are free to change.

After this needful remark we could go deeper in the analysis of the d.o.f.s of our system but, before doing that, we have to know what system we are talking about.

3.1 ABE separation plant configuration

Our ABE/W mixture separation plant can be divided mainly in three big sections according to their respective purposes and listed according to their subsequentiality in the separation process:

- Dewatering section;

- ABE fermentation products purification section;

- Azeotropic distillation of water-butanol system.

Every of these sections will be briefly explained below and then the corresponding d.o.f.s will be calculated for each of them in paragraph 3.2.

3.1.1 Dewatering section

The aim of the dewatering section is to remove water from the fermentation broth. For the previously mentioned reasons, we know that the fraction of water present in the broth is very high, thus in order to obtain a significant ABE productivity it is necessary to perform a good separation.

The dewatering section is made up of two equipments and one heat exchanger (Figure 1).

The first equipment is a liquid-liquid extraction column and performs the separation; the second equipment is a distillation column whose aim is the recovery of the solvent as well as the concentration of the ABE mixture to send to the purification section. Since at these point of the separation we
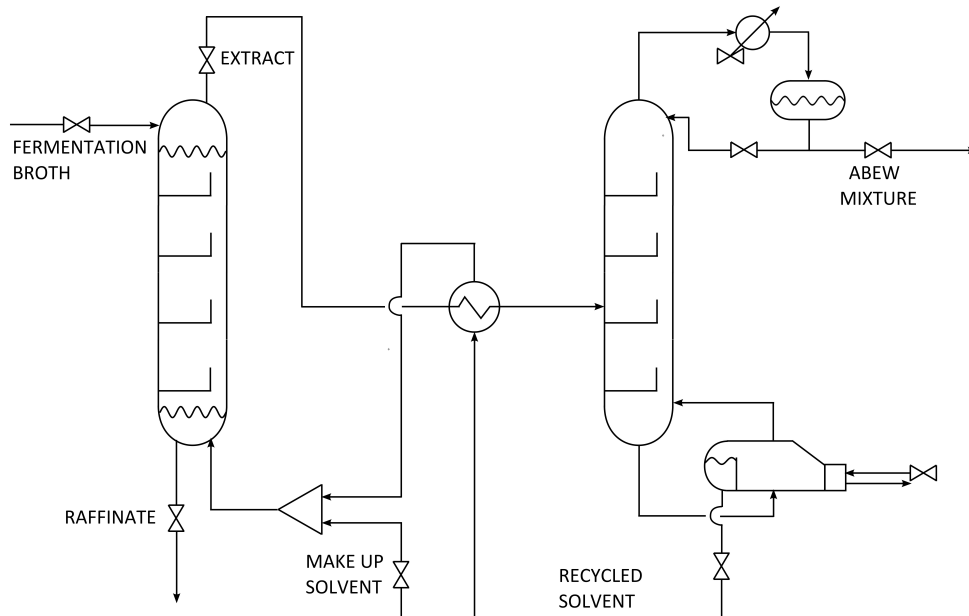
Figure 1: Dewatering section PFD

just want to distinguish what is ABE from what is water, we may state that in the extraction column a pseudo-ternary mixture is present, while in the distillation column a pseudo-binary mixture is processed.

The heat recovery is performed in order to efficiently use the high thermal content of the solvent exiting from the bottom of the column. The pre-heating of the feed improves the distillation efficiency; moreover, cooling down the solvent favours the demixing in the extraction unit operation.

3.1.2   ABE products purification section

The aim of this purification section is the recovery of acetone and butanol with the desired degree of purity (98 and 99 % wt. respectively) from the ABE mixture, because they're the most valuable products. Taking into account also the azeotropic species we should have six product streams exiting this section, i.e. five distillation columns would be required. Anyway we're just interested in the aforementioned two species therefore we may achieve our goal with three consecutive distillation columns and four product streams:
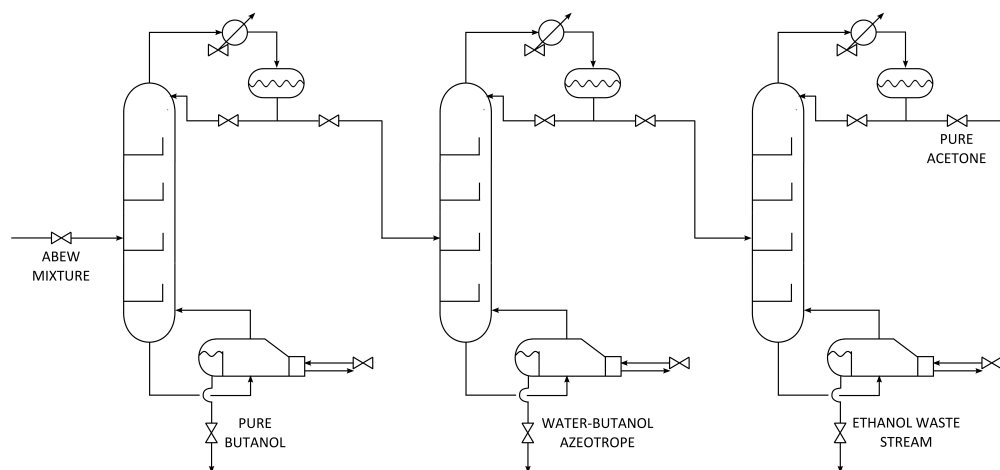
- Pure butanol;

Figure 2: Products purification section PFD

- Water-butanol azeotrope;

- Pure acetone;

- Water, the entire amount of ethanol and traces of acetone and butanol.

The last stream is considered as a waste product stream, while the azeotrope will be further separated in order to perform an additional butanol recovery.

In order to obtain the desired separation, different consecutive distillation columns configurations are possible. After an accurate optimization study [9] the indirect configuration (from the heaviest to the lightest fraction) turned out to be the most convenient (Figure 2).

3.1.3 Azeotropic distillation section of water-butanol mixture

The azeotropic distillation has the aim to perform an additional butanol recovery separating the azeotropic water-butanol mixture obtained from the second column of the purification section.

The amount of butanol that would be loss if this stream was wasted is rather high, moreover butanol is the most valuable product of the ABE mixture therefore it is worth paying for this additional separation. The azeotropic distillation section of the plant is relatively cheap, it is made up of two distillation column and a drum where a cooling utility allows the demixing of the
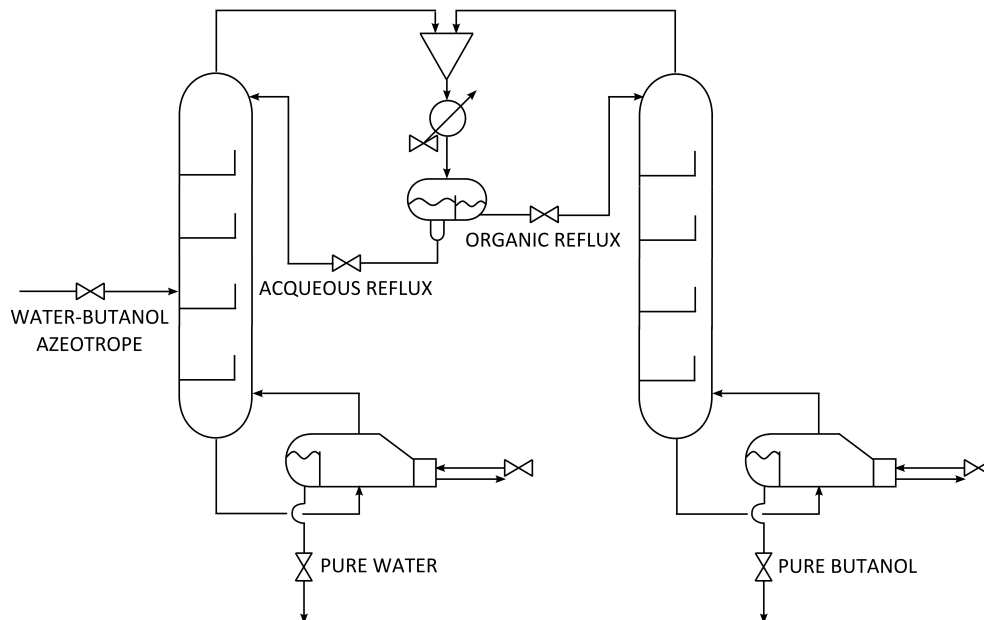
Figure 3: Azeotropic distillation section PFD

acqueous and organic phases. The two columns are used to further concentrate the butanol and water product streams until the desired specification.

3.2 Degrees of freedom evaluation

In view of the above premises it is possible to proceed to the d.o.f.s evaluation.

The d.o.f.s analysis can be performed on every system, however small. It means that it is possible to divide a big system (e.g. the entire ABEW separation plant) into smaller sub-systems (e.g. each section or each equipment), to calculate the d.o.f.s of each of them. After that, it is possible to evaluate the d.o.f.s of the entire system by combining the results achieved this way with proper considerations.

The decision of the control volumes then it's somehow free; for the sake of simplicity the ABE/W separation plant system will be divided first into each one of the aforementioned sections and then the d.o.f.s of each equipment of the section will be analyzed standalone.

Finally the d.o.f.s of all the equipments will be combined in order to obtain the d.o.f.s of each separation section and to proceed to the control

system configuration.

The d.o.f.s analysis procedure can be summarized in the following steps:

1. Evaluation of all the system variables considered in the assumed model (i.e. not necessarily all the system variables really existing);

2. List of all the constraints (i.e. equations) of the assumed model (i.e. not necessarily all the physically possible equations);

3. Evaluation of the known (or imposed) variables;

4. Calculation of the d.o.f.s of the system according to the relationship:

$$D.O.F.s = unknowns - equations - known/given\ variables$$

3.2.1   Dewatering section

The analysis of the dewatering section will proceed visually from the left to the right of the pfd. It means that the first equipment to be analyzed is the extraction column, then the heat exchanger will be studied and in the end the distillation column d.o.f.s will be evaluated.

Extraction column   The extraction column involves two phases, respectively aqueous and organic, and the ABE mixture components are distributed in them according to the equilibrium conditions. Given the temperature (and pressure), the composition of each component of the ABE mixture in each phase can be univocally determined by the equilibrium relationship. Pressure drops and thermal effects (even if poor) will be considered as well. (Figure 4)

System variables:

- Aqueous phase composition: $4 \cdot (N+1)$, $\widetilde{x}_{0,i...n}$;

- Organic phase composition: $4 \cdot (N+1)$, $\widetilde{y}_{1,i...n+1}$;

- Aqueous phase flowrates: $N+1$, $F_{0,i...n-1}, R$;

- Organic phase flowrates: $N+1$, $E, S_{2,i...n+1}$;

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(a) Top tray

(b) Intermediate tray

(c) Bottom tray
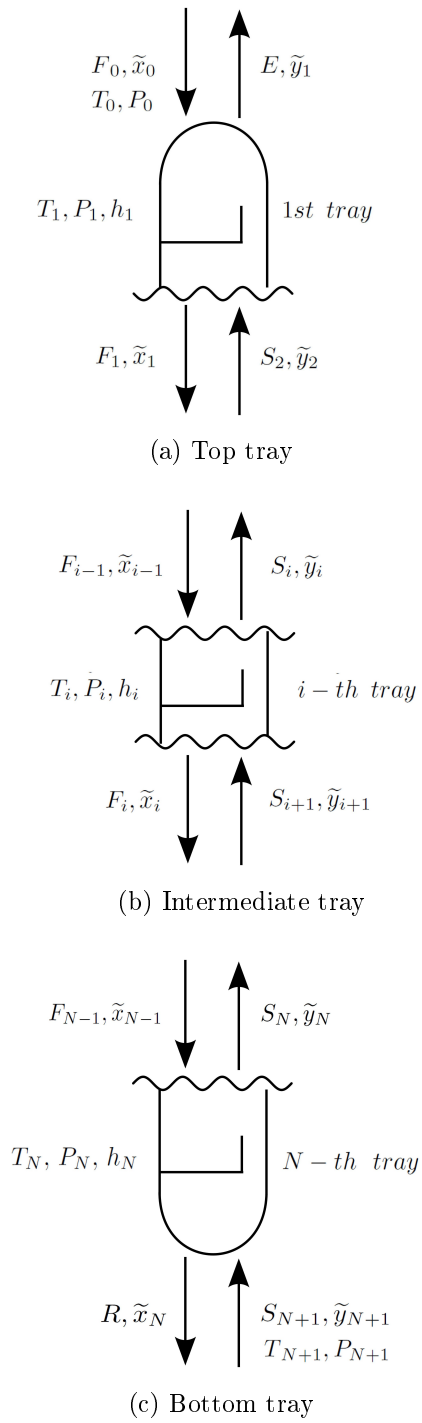
Figure 4: Extraction column trays scheme

- Trays and feeds temperatures: $N + 2$, $T_{0,i...n+1}$;

- Trays and feeds pressures: $N + 2$, $P_{0,i...n+1}$;

- Phase (aqueous or organic) holdup: N, $h_{1,i...n}$.

Overall unknowns: $13 \cdot N + 14$.

Model equations:

- Equilibrium equations: $5N$;

- Mass balances: $5N$;

- Energy balances: N;

- Momentum balances: N;

- Hydraulic relationships: N;

Overall equations: $13 \cdot N$.

$$D.O.F.s = 13 \cdot N + 14 - 13 \cdot N = 14$$

This result represents the overall number of d.o.f.s of the system. From a process control point of view, it coincides with the maximum number of controllable variables in our system in order to have a correctly specified system (i.e. nor redundant neither underspecified).

Anyway there are some data we already know about this system, therefore the real number of d.o.f.s is lower.

Known variables:

- Feed flowrate: 1, F;

- Feed composition: 4, $\widetilde{x}_0$;

- Feed temperature and pressure: 2, T_0, P_0;

- Solvent composition: 4 (considered known because it will be an unknown of the distillation column d.o.f.s analysis), $\widetilde{y}_{N+1}$;

- Solvent temperature and pressure: 2 (considered known because they will be unknowns of the distillation column d.o.f.s analysis), T_{N+1}, P_{N+1}.

Since we know 13 variables out of 14 d.o.f.s, there is only 1 d.o.f. remaining that will be defined by one specification to impose.
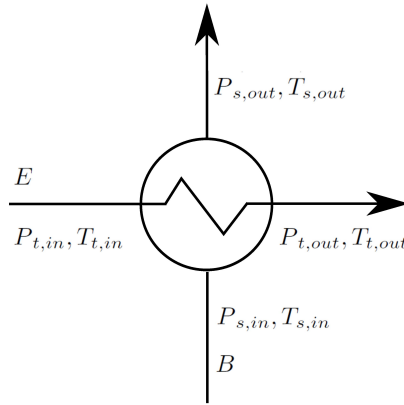
Figure 5: Heat exchanger scheme

Heat exchanger In the heat exchanger mass and composition are conserved since nor reaction neither mass transfer occur. Therefore only momentum and thermal balance will be considered. (Figure 5)

System variables:

- Shell side inlet pressure and temperature: 2, $P_{s,in}, T_{s,in}$;

- Tube side inlet pressure and temperature: 2, $P_{t,in}, T_{t,in}$;

- Shell side outlet pressure and temperature: 2, $P_{s,out}, T_{s,out}$;

- Tube side outlet pressure and temperature: 2, $P_{t,out}, T_{t,out}$.

Overall unknowns: 8.

Model equations:

- Energy balances: 1;

- Momentum balances: 2;

Overall equations: 3.

Known variables:

- Inlet pressures: 2, $P_{s,in}, P_{t,in}$;

- Inlet temperatures: 2, $T_{s,in}, T_{t,in}$.

The inlet variables are considered as known variables because they are already evaluated as unknowns in the d.o.f.s analysis of the other equipments of this section.

Then we have:

$$D.O.F.s = 8 - 3 - 4 = 1$$

Only one specification is required to fulfill the d.o.f.s requirement of the heat exchanger equipment.

Distillation column   The distillation column of this plant is a "standard" distillation column, it means it fulfills the following conditions:

- Only one feed at an intermediate tray;

- Full condenser;

- Partial reboiler;

- No intermediate product withdrawal;

- No intermediate heat flows.

The first part of the d.o.f.s analysis is then suitable for every standard distillation column, i.e. also for the columns of the products purification section.

After that, the analysis will take into account the number of components present in the column, i.e. 5 components. The molar fractions needed in order to define univocally the composition of each stream is $NC - 1$ (in this case 4) because we can use the summation equation to obtain the fifth one.

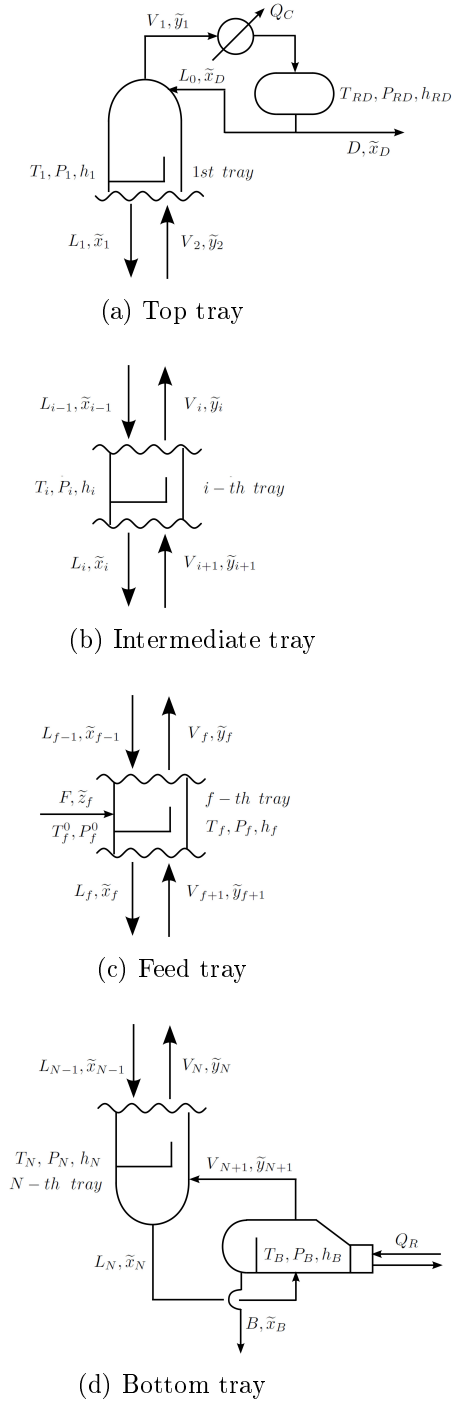Pressure and temperature profiles will be considered.

(a) Top tray

(b) Intermediate tray

(c) Feed tray

(d) Bottom tray

Figure 6: Distillation column trays scheme

System variables:

- Liquid phase composition: $(NC - 1) \cdot (N + 3)$, $\widetilde{x}_{i...n,D,B}, \widetilde{z}_f$;

- Vapour phase composition: $(NC - 1) \cdot (N + 1)$, $\widetilde{y}_{i...n,n+1}$;

- Liquid phase flowrates: $N + 4$, $L_{0,i...n}, F, D, B$;

- Vapour phase flowrates: $N + 1$, $V_{i...n,n+1}$;

- Trays, condenser, reboiler and feed temperatures: $N + 3$, $T_{f,i...n,B,RD}$;

- Trays, condenser, reboiler and feed pressures: $N + 3$, $P_{f,i...n,B,RD}$;

- Liquid holdup: $N + 2$, $h_{i...n,B,RD}$;

- Heat duties: 2, Q_C, Q_R.

Overall unknowns: $2 \cdot NC \cdot N + 4 \cdot NC + 3 \cdot N + 11$.

Model equations:

- Equilibrium equations: $NC \cdot (N + 1)$, i, B;

- Mass balances: $NC \cdot (N + 2)$, i, B, RD;

- Energy balances: $N + 2$, i, B, RD;

- Momentum balances: $N + 2$, i, B, RD;

- Hydraulic relationships: $N + 2$, i, B, RD.

Overall equations: $2 \cdot NC \cdot N + 3 \cdot NC + 3 \cdot N + 6$.

$D.O.F.s = 2 \cdot NC \cdot N + 3 \cdot N + 4 \cdot NC + 11 - (2 \cdot NC \cdot N + 3 \cdot NC + 3 \cdot N + 6) = NC + 5$

Since in our case $NC = 5$, $D.O.F.s = 10$.

Known variables:

- Feed flowrate: 1, F;

- Feed composition: 4 $(i.e.\ NC - 1)$, $\widetilde{z}_f$;

- Feed temperature and pressure: 2, $T^0{}_f, P_f^0$.

Since we know 7 variables out of 10 d.o.f.s, in order to univocally determine our distillation column variables we need to fix 3 specs.

It is worth noticing that the number of d.o.f.s doesn't depend on the number of trays. Moreover, if the feed characteristics are given as known datum, the number of d.o.f.s of the column does not even depend on the number of components:

$$D.O.F.s = NC + 5 - 1 - (NC - 1) - 2 = 3$$

Therefore, whatever the column, if it is standard and if we know the feed composition, flowrate, pressure and temperature, the number of d.o.f.s is 3 in any case or, if we know the composition at least, it doesn't depend on the number of components.

3.2.2 ABE products purification section

The calculations concerning the purification section are much easier since it is made up of three standard distillation columns in series and we can proceed by analogy with the previously achieved results.

Column 1 $D.o.f.s = NC + 5$

Known variables:

- Feed flowrate: 1, F;

- Feed composition: $NC - 1$, $\widetilde{z}_f$;

- Feed temperature and pressure: 2, $T^0{}_f, P_f^0$.

The number of remaining d.o.f.s is 3.

Column 2 & column 3 Since the feed of each column is the product of the previous one, the know variables are always the same, i.e. feed flowrate, composition, temperature and pressure.

Thus, also the second and the third column have 3 remaining d.o.f.s each.

3.2.3   Azeotropic distillation of water-butanol mixture

Finally we have to deal with the d.o.f.s analysis of the azeotropic distillation section. It is made up of two binary distillation columns with only one common reflux drum with boot where demixing occurs.

Even in this case pressure and temperature gradients will be considered. N_1 and N_2 are the number of trays of the first and second column respectively.

System variables:

- Liquid phase composition: $N_1 + N_2 + 5$, $\widetilde{x}^1_{i...n_1}, \widetilde{x}^2_{i...n_2}, \widetilde{z}_f, \widetilde{x}^1_B, \widetilde{x}^2_B, \widetilde{x}^{a,o}_{RD}$;

- Vapour phase composition: $N_1 + N_2 + 3$, $\widetilde{y}^1_{i...n_1,n_1+1}, \widetilde{y}^2_{i...n_2,n_2+1}, \widetilde{y}_{mix}$;

- Liquid phase flowrates: $N_1 + N_2 + 5$, $L^1_{i...n_1}, L^2_{i...n_2}, F, B_1, B_2, L^{a,o}_0$;

- Vapour phase flowrates: $N_1 + N_2 + 3$, $V^1_{i...n_1,n_1+1}, V^2_{i...n_2,n_2+1}, V_{mix}$;

- Trays, condenser, reboilers, reflux and feed temperatures: $N_1 + N_2 + 5$, $T^1_{i...n_1}, T^2_{i...n_2}, T_f, T^1_B, T^2_B, T_{RD}, T_{mix}$;

- Trays, condenser, reboiler and feed pressures: $N_1 + N_2 + 4$, $P^1_{i...n_1}, P^2_{i...n_2}, P_f, P^1_B, P^2_{B_2}, P_{RD}$;

- Liquid holdup: $N_1 + N_2 + 4$, $h^1_{i...n_1}, h^2_{i...n_2}, h^1_B, h^2_B, h^{a,o}_{RD}$;

- Heat duties: 3, Q_C, Q^1_R, Q^2_R.

Overall unknowns: $7 \cdot N_1 + 7 \cdot N_2 + 32$.

Model equations:

- Equilibrium equations: $2 \cdot (N_1 + N_2 + 3)$, i_1, i_2, B_1, B_2, RD;

- Mass balances: $2 \cdot (N_1 + N_2 + 4)$, $i_1, i_2, B_1, B_2, RD, mix$;

- Energy balances: $N_1 + N_2 + 3$, i_1, i_2, B_1, B_2, C;

(a) Top trays

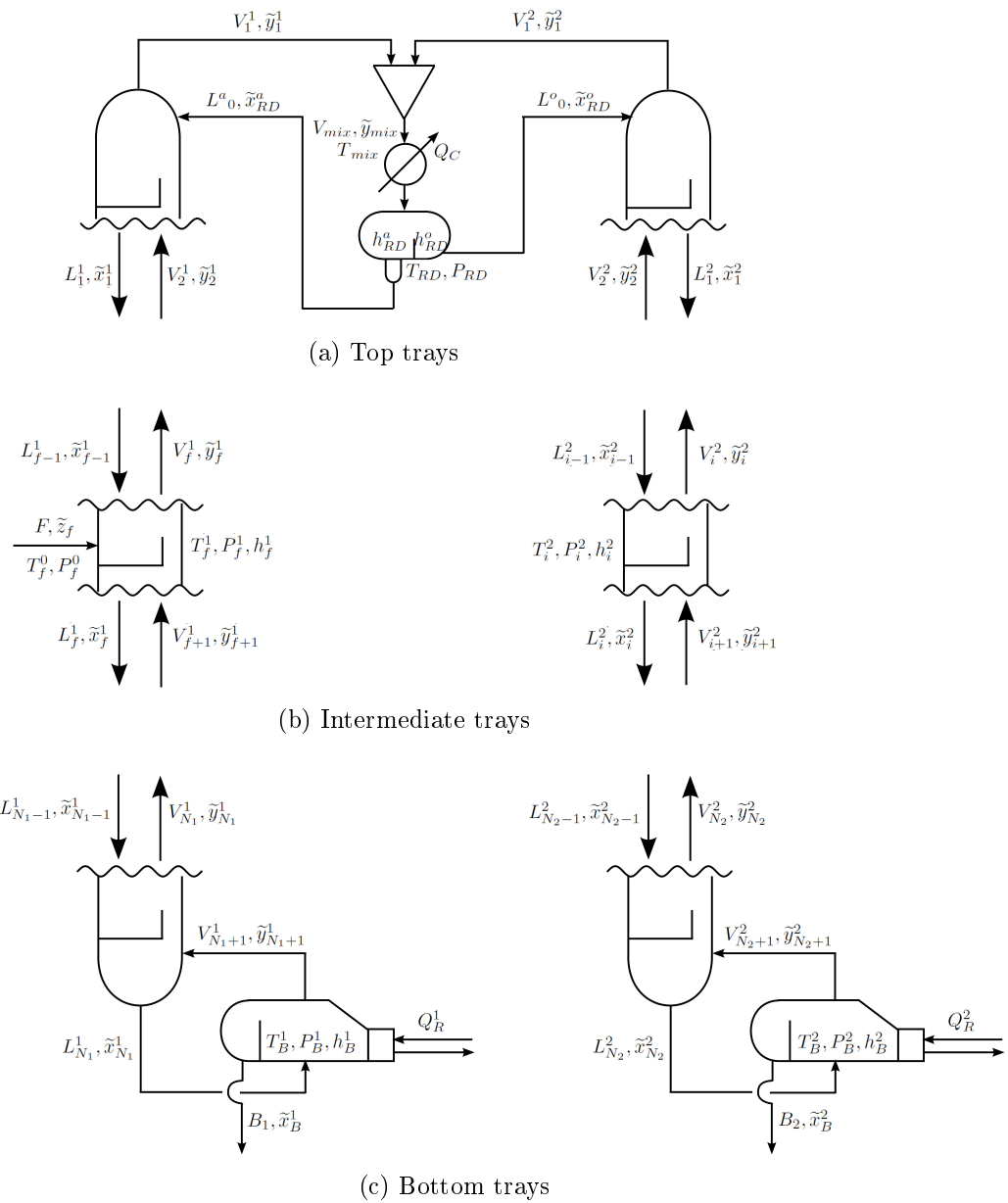(b) Intermediate trays

(c) Bottom trays

Figure 7: Azeotropic distillation columns trays scheme

- Momentum balances: $N_1 + N_2 + 3$, i_1, i_2, B_1, B_2, RD;

- Hydraulic relationships: $N_1 + N_2 + 4$, $i_1, i_2, B_1, B_2, RD^{a,o}$.

Overall equations: $7 \cdot N_1 + 7 \cdot N_2 + 24$.

$$D.O.F.s = 7 \cdot N_1 + 7 \cdot N_2 + 32 - (7 \cdot N_1 + 7 \cdot N_2 + 24) = 8$$

Known variables:

- Feed flowrate: 1, F;

- Feed composition: 1 $(i.e.\, NC - 1)$, $\widetilde{z}_f$;

- Feed temperature and pressure: 2, $T^0{}_f, P^0_f$.

Therefore we have:

$$D.O.F.s = 8 - 4 = 4$$

Four specs are required to fulfill the d.o.f.s requirement of the azeotropic distillation section.

3.3 Specifications

For each section the remaining d.o.f.s evaluated so far have to be fulfilled by the same number of specifications. In this case study the same specifications of [9] will be used in order to be coherent with our purpose. For each section of the plant they will be briefly exposed.

3.3.1 Dewatering section

The dewatering section, summing up the extraction column, the heat exchanger and the distillation column, requires an overall number of 5 specs. They can be either design or products specifications.

1. ABE productivity: 1550 kg/h;

2. Saturated liquid as feed of the distillation column;

3. Top pressure of the distillation column: 1 atm;

4. Butanol recovery ratio: 99.9 %;

5. Solvent recovery ratio: 99.9 %.

A remark is needed about the second spec, i.e. the thermodynamic conditions of the liquid stream exiting the heat exchanger, since it is a design spec. This means that it is used during the design phase to determine the heat transfer area that, obviously, is not a variable that can be modified continously during the plant lifetime.

Thus this spec won't be controlled by the control loops of the dynamic simulation and the design result will be used to fulfill this d.o.f.

3.3.2 Purification section

The purification section is made up of three standard distillation columns with 3 d.o.f.s each. They will be satisfied by the following design and products specs:

Column 1

1. Top pressure: 1 atm;

2. Reflux ratio: 0.05;

3. Butanol concentration: 99 % wt..

Column 2:

1. Top pressure: 1 atm;

2. Ethanol recovery ratio: 0.95 wt. ;

3. Water recovery ratio: 0.9855 wt..

Column 3:

1. Top pressure: 1 atm;

2. Acetone recovery ratio: 0.95 wt.;

3. Ethanol recovery ratio: 0.95 wt..

3.3.3 Azeotropic distillation of water-butanol mixture

The azeotropic distillation section is made up of two columns with a common demixing reflux drum and it needs 4 specifications to set:

1. First column top pressure: 1 atm;

2. Second column top pressure: 1 atm;

3. Butanol concentration: 99% wt.;

4. Water concentration: 99% wt..

4   Process and plantwide control philosophy

Process control is an inherent feature of dynamics. In steady state simulation we just input a value for each parameter we need to set and it remains unchanged after simulation but real world is rather different.

In reality we have both process materials and duties storages at a given pressure and temperature and we need pressure differences to let them flow.

In plants, pressures between equipments are regulated by valves that communicate through pipes. Every time temperatures, compositions or whatever change, pressure changes as a consequence and flowrates change in turn.

Then, in order to manage flowrates, i.e. temperature, pressure etc. as a direct consequence, we need to manage pressure nodes, i.e. valves, during the whole lifetime of our system (start up and shut down included), until the desired process variables are achieved. This job is performed by controllers. They calculate the offset between the process variable and the desired setpoint and acts accordingly.

In view of the above, the ending point of each control action is a valve and the managed variable, whatever the controlled one is, is the opening of the valve, that is a flowrate as a direct consequence.

Even when the steady state conditions are achieved, control systems has still to be working both because external disturbances, differently from the "virtual world", are always present and then need to be suppressed, and because the desired setpoint may be a dynamic variable itself according to economical or process optimization needs.

Since we have already determined the system degrees of freedom and the specification required, now we have to set the control loops for each equipment. Every equipment present in the plant is not a standalone unit but it is part of the entire plant section, therefore we can control some variables even manipulating flowrates that looks far from it, that's why we talk about "plantwide control".

Several control layouts proposed in the most influential literature [26, 27] have been analyzed and simulated (when simulation has been performed) in order to test their stability and their performances in our specific case. Pros of each solution have been combined to match the system needs and to best control the separation units.

In the following paragraphs the selected control strategy for each section of the plant will be explained and both controlled and manipulated variables will be shown.
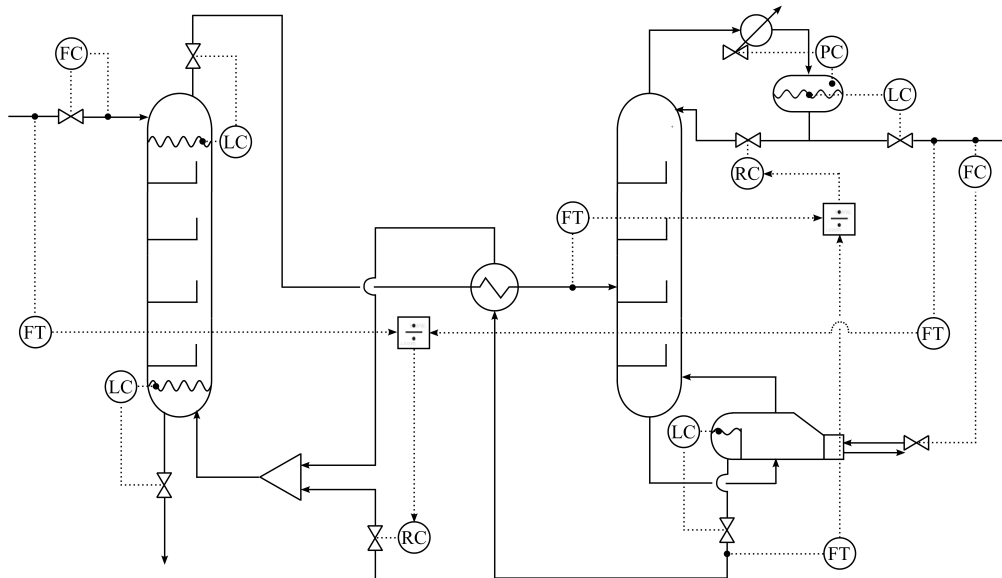
Figure 8: Dewatering section control scheme

4.1 Dewatering section

In the light of the calculations performed in chapter 3, the remaining degrees of freedom of this section of the plant are 4 and they are saturated by the aforementioned specifications, i.e. ABE productivity, butanol and solvent recovery, top pressure of the distillation column. Naturally all the specs will be set as controlled variables, moreover there are some additional variables to be controlled; they are respectively the feed flowrate and the liquid levels in the reboiler, in the reflux drum and in the last stage of the extraction column.

The resulting control loops needed are then listed below and shown in Figure 8:

- Flowrate controller (FC) (x2);

- Level controller (LC) (x4);

- Pressure controller (PC) (x1);
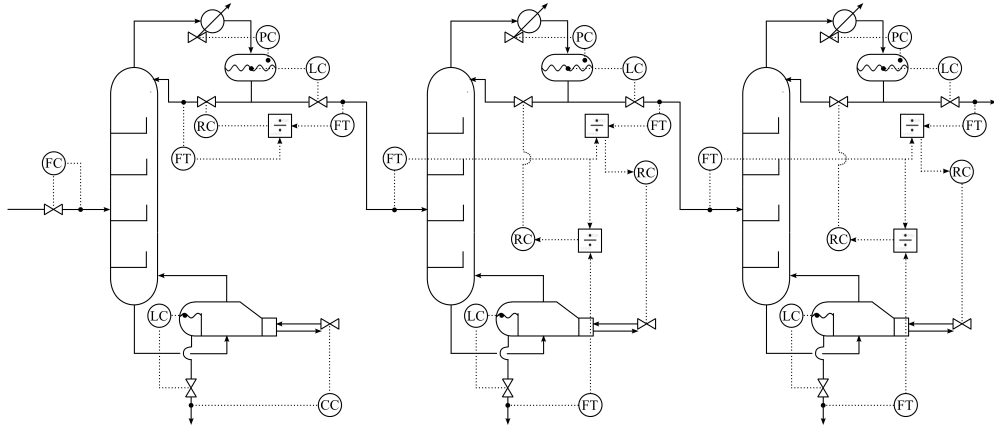
- Recovery ratio controller (RC) (x2).

Figure 9: Products purification section control scheme

4.2 Products purification section

In the purification section there are 3 d.o.f.s per column to set, the corresponding specifications are reflux ratio and butanol concentration for column 1, recovery ratio for water and ethanol for column 2, recovery ratio of ethanol and acetone for column 3 and finally the top pressure for all of them. All the specs will be controlled, moreover we need to control the feed flowrate for the first column and the liquid level in the reflux drum and in the reboiler for every column.

The resulting control loops needed are then listed below and shown in Figure 9:

- Flowrate controller (FC) (x1);

- Level controller (LC) (2x3);

- Pressure controller (PC) (x3);

- Reflux ratio controller (RC) (x1);

- Composition controller (CC) (x1);
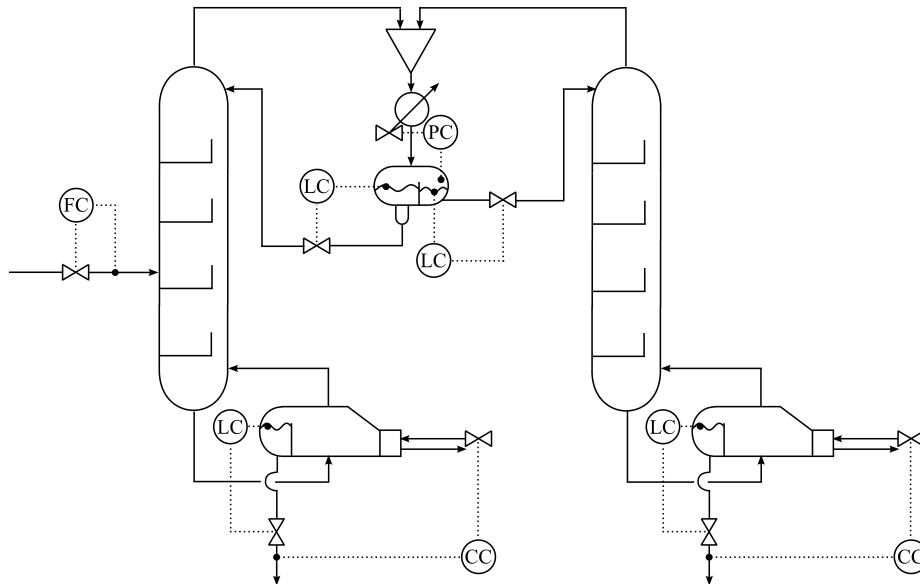
- Recovery ratio controller (RC) (2x2).

Figure 10: Azeotropic distillation section control scheme

4.3   Azeotropic distillation of water-butanol mixture

In the azeotropic distillation section there are 4 remaining d.o.f.s. For each of them we set a specification, i.e. the top pressure for each column and both water and buthanol concentrations. In addition to these specs, that will be controlled for sure, we need to control also the feed flowrate, the liquid levels in the reboilers and the liquid levels both for the acqueous and organic phases in the reflux drum. Moreover it is worth highlighting that, since the reflux drum is the same, we will need just one pressure controller in order to control both columns' top pressures.

The resulting control loops needed are then listed below and shown in Figure 10:

- Flowrate controller (FC) (x1);

- Level controller (LC) (2x2);

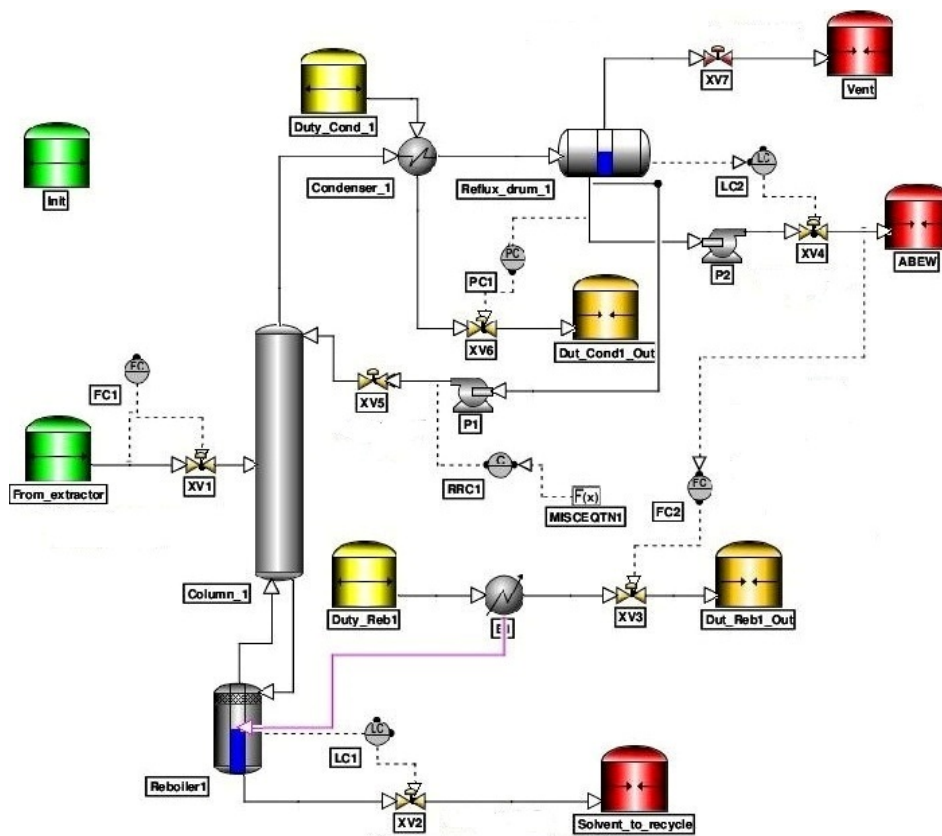- Pressure controller (PC) (x1);

- Composition controller (CC) (x2).

Figure 11: Solvent recovery column Dynsim simulation PFD

5 Simulation

5.0.1 Introduction

Part of the dewatering section (Figure 11) and the whole products purification section (Figure 12) of the ABEW separation plant have been simulated. The azeotropical distillation section has several criticalities concerning thermodynamics and, even if the study about its degrees of freedom and process control configuration are part of this thesis work, its simulation will be the subject of study of further works.

Moreover, DYNSIM is not able to simulate separation equipments without any vapour holdup (e.g. liquid-liquid extraction), therefore the solvent recovery column is the only equipment of the dewatering section that has been simulated.
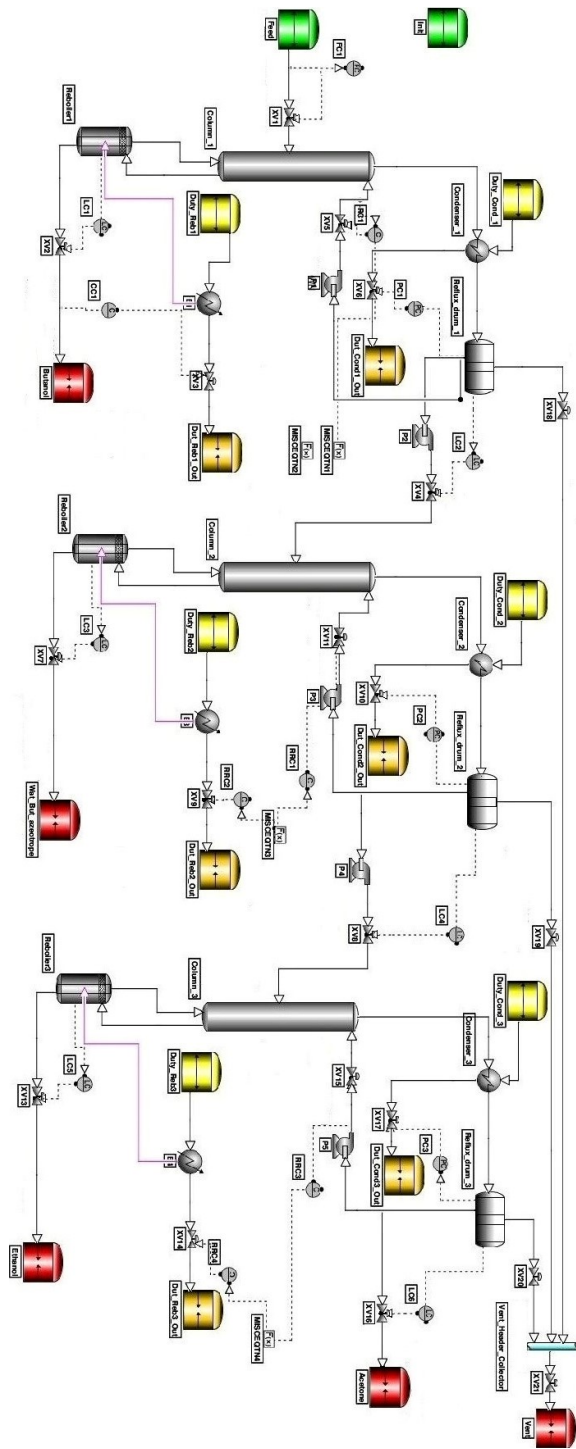
Figure 12: Products purification section Dynsim simulation PFD

Anyway, before going any further it's worth clarifying in brief what actually means that the simulation has been "accomplished".

The simulation, in order to be considered successfull, has to satisfy all the real plant needs. In particular two different areas of needs to be satisfied can be distinguished: stability and performances.

In particular we can go deeper in the analysis of them both, highlighting which conditions have to be fulfilled in order to say that our simulation has been correctely performed.

As far as stability is concerned, the main conditions to be satisfied are:

- Coherent pressure nodes and profiles along the whole plant;

- Continous operations;

- Keep away the plant from hazardous conditions;

- Achievement of a steady state.

On the other hand, to ensure the good performance of a chemical plants means:

- Achieve the desired specifications;

- Suppress quickly enough any disturbances.

All design data (e.g. sizing of the equipments, thermodynamics, duties etc. etc.) have been taken from the steady state simulations [18]; afterwards some of them, mostly duties and thermodynamic settings, have been modified in order to enhance the performances and ensure a better stability.

The control philosophy has been kept the same suggested previously in chapter 4.

A first, coarse, tuning of the controllers has been performed as shown in paragraph 5.1.

Each column of the products purification section has been simulated standalone first and, once optimized, they have been connected together.

5.0.2   Plots remarks

At the end of each chapter the resulting plots will be analyzed; before going any further it is worth remarking how they have been obtained and how related issues have been managed.

Every graph has been plotted by exporting the variables from DYNSIM to Microsoft Office Excel as CSV from the tool "trends".

Simple variables, i.e. flowrates, compositions, are calculated by the simulator by default; on the other hand more complex variables, i.e. recovery ratio, reflux ratio, have to be computed through the tool named "Miscellaneous Equation". The formulas of the recovery/reflux ratios have been manually input in this tool and they calculate the value of the function for every simulation step. This procedure leads to two unavoidable main issues:

- Delayed calculation: since the tool calculates the ratio between the actual recovered species and the actual feed flow of the species, the time needed by the feed to pass through the column delays the calculation, that is I'm calculating the actual recovered species coming from the feed flow of some minutes ago. Then what we can see in the plots it's not the real time recovery ratio but a delayed recovery ratio until the steady state is reached;

- Near zero denominator: every time we calculate a ratio, there is an existence condition of the result, i.e. non zero denominator. We can avoid this problem by adding to the denominator a very small number that does not affect the reliability of the calculation. Anyway, when the variables in the denominator are zero, even if we don't have an error in calculation, we have a very small denominator value that leads to very high values of the function that obviously have no physical meaning (even lower relevance if we take into account the fact that it is a delayed calculation).

What we are trying to say is that, if the feed from a column to the next one is zero, the value of recovery ratios can runaway higher than ten thousands, taking into account that we are recovering what was previously (not actually) fed to the column.

Therefore some points of our plots are not reliable at all; for this reason the outliers of each trend have been identified and corrected manually, in order to have meaningful resulting graphs.

Moreover, this delay effect explains the reasons of sharp oscillating trends of columns 2 and 3 controlled variables reported in the next chapters.

5.1 Tuning of the controllers

The expression "controller tuning" refers to selection of the controller parameters which produce the desired output. Moreover, it allows for process optimization and minimizes the error between the controlled variable and its set point. If a mathematical model of the system is available, the parameters of the controller can be explicitly determined, otherwise the parameters have to be determined experimentally.

There are several and widely known types of controller tuning methods, they include trial and error method as well as process reaction curve methods [28, 29]. The most used are:

- Ziegler-Nichols method;

- Cohen and Coon method;

- Tyreus-Luyben method;

- Damped oscillation method;

- Chien, Hrones and Reswich (CHR) method;

- Minimum error criteria (IAE, ISE, ITAE) method.

In the light of the above, in order to perform some of them, we would need to know the mathematical model of our simulation, on the other hand, to use the remaining ones, we should analyze the system response to a step variation of our controlled variables.

However, even if we actually know the model equations of our system or better, precisely because we know our model equations, we are aware that they are very complex and correlated each other, thus it would require lots of efforts to tune the controllers this way even for a single variable modification.

In turn every variable of the system is strictly correlated to the other ones as well, therefore a single variation of pressure, temperature, or whatever may trigger an unpredictable chain effect on the other variables making all our accurate work really inaccurate.

Since the tuning of the controllers "one by one" has been definetely considered ineffective, or at least inconvenient, the only way to perform a rigorous tuning of all the controllers of our system is to tune the whole system at the same time, anyway it is a really complex practice, it requires time, experience, and a powerful optimization algorithm to develop.

Therefore, in order to have a well working control system in a time and efforts saving way the controllers have been tuned "by feel" following reasonable and wise practices [30] and analyzing in deep the system responses to any parameter variation.

In brief, the practices taken into accounts to tune the controllers are:

1. "Don't tune the controller" : it may look strange but it turned out to be the most effective practice during the controllers tuning of our ABE/W separation plant. Very often the problem of control loops is an equipment-related issue, therefore changing tuning parameters is really ineffective. The modification of the dimensions of the valves, the sizes of the vessels or choosing more suitable thermal duties, often turned out to be the solution to the control loop instability: e.g. in case of too long residence times, the dimensions of vessels have been reduced and viceversa; in case of too sluggish response, the size of the valves has been increased and viceversa, etc. etc.
Obviously this practice shows convenient during the plant design phase, while it results really unpracticable to tune the controller of already existing plants.

2. "Define process needs": each controller has its needs according to the process involved, some responses have to be fast, others have to be slow, both for performances and safety reasons.

3. "Choose the right tuning": Derivative terms have been used only if strictly necessary, that is when a fast-responding control has been critical and when PI alone was not good enough.

4. "Monitor the results": every time a process equipment was modified the stability and performance of the controllers has been checked and eventually the loop was tuned again.

5.2   Startup procedures

As for real plants, even simulated plants need a startup procedure, or better dynamic simulation can be a powerful tool to define thoroughly the startup procedure for chemical plants to be built or revamped.

Once the process equipments have been set up and they're ready to start working, they are empty, that means they're filled by air only. Then the feed

stream enters the first equipment and so on. Anyway at the beginning no products exit from the equipment and, after that, the outcoming products streams are out of spec for a certain time.

Moreover, the startup procedure is crucial not only for performance needs, i.e. to minimize the amount of out of specs product and the time of non-operative conditions, but even for stability and safety reasons. We have to decide when to start providing heat as well as the right time to open the relief valves and let the air flow out, everything in stable pressure and temperature conditions.

For this purpose, for every simulated section of the plant a scenario with all the procedures steps has been written down and then insert into the simulator in order to make every step automatically achieved.

Each equipment of each section has been simulated and started up on its own first in order to check the stability and have a general idea of the steps to follow, then the equipments have been combined to obtain the whole section and a section startup procedure, based on the equipments' one, has been outlined.

5.2.1 Solvent recovery column

Thanks to the Dyinsim function "Scenario" the startup procedure can be easily integrated to the simulation.

For the solvent recovery column the startup procedure is defined as below:

e.g. # Action description (introduced as comment by "//" in the code)
    ACTION COMMAND;

1. Run the simulation:
   RUN;

2. Switch off specs controllers:
   SET FC2.MA=0.000;
   SET RRC1.MA=0.000;

3. Open vent valve:
   SET XV7.OP=1.000;

4. Switch on the reboiler duty:
   WAIT UNTIL Reboiler1.L>0.1;
   SET FC2.MA=1.000;

5. Switch on the reflux:
   WAIT UNTIL Reflux_drum_1.L>0.1;
   SET RRC1.MA=1.000;

6. Close vent valve when vent is completed:
   WAIT UNTIL S15.Z[N2]<0.001;
   SET XV7.OP=0.000;

Some remarks about the startup procedure and the simulation configuration of the solvent recovery column are worthy of being done.

First of all we can notice the absence of the blowdown line because it is part of the extractor equipment since the bottom product of the column is the recovered solvent to be recycled.

The specs controllers are almost immediately set on auto, this is because the feed flowrate and the thermal capacity of the liquid in the reboiler are high enough to require a long time to be heated up, thus there are no problems of too elevated temperature in the reboiler when it is consistently empty.

Finally there's the need to highlight that the vent gas, after the very first part of the startup, contains a considerable amount of hydrocarbon species beside nitrogen, therefore they have to be abated before being vented in the atmosphere to avoid the discharge of toxic and explosive mixtures.

5.2.2 Products purification section

For the products purification section the startup procedure is defined as below:

1. Run the simulation:
   RUN;

2. Open the header vent valve:
   SET XV21.OP=1.000;

3. Open columns 2 & 3 top valves:
   SET XV12.OP=1.000;
   SET XV22.OP=1.000;

4. Switch off columns 2 and 3 specs controllers:
   SET RRC1.MA=0;
   SET RRC2.MA=0;

```
        SET RRC3.MA=0;
        SET RRC4.MA=0;
```

5. // COLUMN 1 STARTUP

6. Open column 1 vent valve:
   ```
   SET XV18.OP=0.100;
   ```

7. Slightly open the reboiler duty:
   ```
   SET CC1.MA=0;
   SET CC1.OUT=0.080;
   ```

8. Set on AUTO the reboiler spec controller:
   ```
   WAIT UNTIL Reboiler1.L>0.55;
   SET CC1.MA=1;
   ```

9. Close the vent valve:
   ```
   WAIT UNTIL S56.Z[N2]<0.001;
   SET XV18.OP=0.000;
   ```

10. // COLUMN 2 STARTUP

11. LOAD IC 1; // or WAIT UNTIL Column 1 steady state

12. Open column 2 vent valve:
    ```
    SET XV19.OP=0.010;
    ```

13. Set on AUTO the bottom product spec controller:
    ```
    WAIT UNTIL Reflux_drum_2.L>0.2;
    SET RRC1.MA=1;
    ```

14. Set on AUTO the distillate spec controller:
    ```
    WAIT UNTIL Reboiler2.L>0.4;
    SET RRC2.MA=1;
    ```

15. Close the vent valve:
    ```
    WAIT UNTIL S60.Z[N2]<0.001;
    SET XV19.OP=0.000;
    ```

16. // COLUMN 3 STARTUP

17. LOAD IC 2; // or WAIT UNTIL Column 2 steady state

18. Open column 3 vent valve:
    SET XV20.OP=0.010;

19. Slightly open reboiler duty and reflux valve:
    SET RRC3.OUT=0.010;
    SET RRC4.OUT=0.007;

20. Close the vent valve:
    WAIT UNTIL S62.Z[N2]<0.001;
    SET XV20.OP=0.000;

21. Set on AUTO the distillate spec controller:
    WAIT UNTIL Reboiler.3.L>0.5;
    SET RRC3.MA=1;

22. Set on AUTO the bottom product spec controller:
    WAIT UNTIL Reflux_drum_3>0.25;
    SET RRC4.MA=1.

In the light of the above, it's worth remarking the reasons why some steps have been performed.

First of all we can notice that the vent valves are not completely open when the air relief is performed. This is because the vent valves should be much bigger than the dimension required for venting function only since they could be also used for emergency reliefs.

Moreover, the vent streams, after a while, are not made by nitrogen only but they contain a considerable hydrocarbon fraction, so they must be treated to abate it before venting to the atmosphere in order to aviod toxic or explosive mixtures discharge.

In columns' startup, boiler duty valves are often slightly opened manually. This procedure ensures a minimum vapour stream inside the column since the very beginning, as feeds are all in liquid phase, and speeds up the startup since the condenser starts filling up earlier; on the other hand, leaving the controllers on auto mode would increase too fast the temperature in the reboilers even if the liquid level is not high enough, putting the system under hazardous conditions.

Finally it is evident that we have a lot of products out of specs leaving the columns until steady state is achieved. Obviously these products can't be sent to the pure products storage, thus they should be withdrawn through

a blowdown line or better they can be recycled to the feed storage tank to avoid products waste, that is the usual procedure.

5.3   Steady state results

The trends of the controlled variables of each equipment have been reported from the start to the steady state conditions.
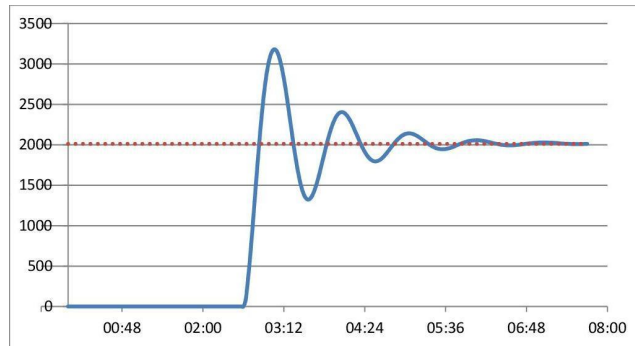
5.3.1   Solvent recovery column

The solvent recovery column has three degrees of freedom, therefore three out of four specifications related to the dewatering section have been controlled to fulfill the d.o.f.s requirement:

- ABE mixture flowrate: 2011.121 kg/hr;

- Solvent recovery ratio: 0.999;

- Top pressure: 1 atm.

The trends of these three controlled variables during the startup procedure are shown in Figure 13.

Moreover, the flow summary of the solvent recovery column section is reported in Table 4; the flow summary is relative to the very first moment steady state is achieved, this means that it could slightly change, keeping unchanged the specifications, during the running of the simulation (i.e. of the plant).

At first sight the solvent recovery column flow summary itself has poor meaning. On the other hand the comparison between Table 4 and Table 5, reporting the flow summary of the solvent recovery column simulated using PRO/II in the design thesis [18], is much more interesting.

(a) ABE mixture flowrate [kg/hr]
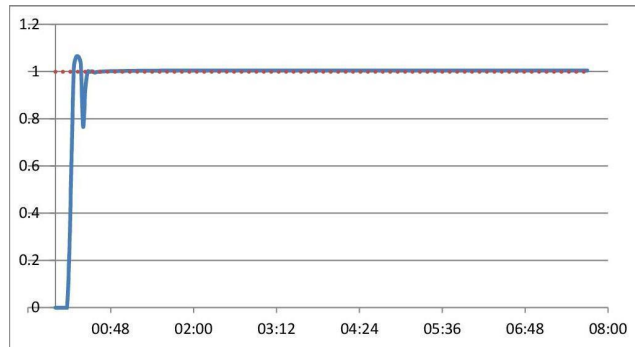
(b) Solvent recovery ratio
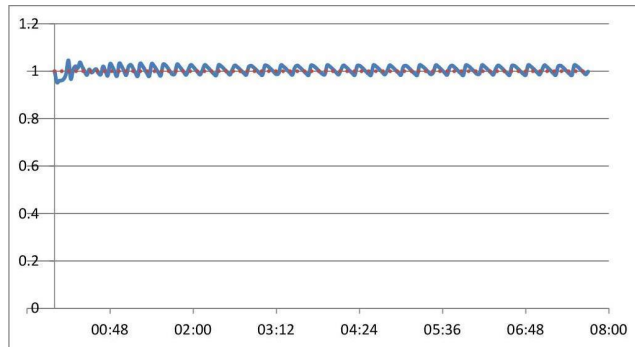
(c) Top pressure [atm]

Figure 13: Solvent recovery column: startup controlled variables trends

The solvent recovery column section shows a very standard trend about all the variables; pressure is stable from the very beginning of the simulation as well as the solvent that is completely recovered after less than one hour. The ABE mixture flowrate has an oscillating path perfectly compatible with standard setpoint achievements trends.

	Feed	ABE	Solvent
Flowrate [kg/hr]	16397	2011	14386
Temperature [°C]	129.4	89	262
Composition [mol basis]			
Water	0.1557	0.5368	0.0
Acetone	0.0186	0.0615	0.0
Butanol	0.1176	0.3913	0.0
Ethanol	0.003	0.0104	0.0
2-Ethylhexanol	0.7051	0.0	1.0
Nitrogen	0.0	0.0	0.0

Table 4: Solvent recovery column flow summary

	Feed	ABE	Solvent
Flowrate [kg/hr]	16397	2011	14595
Temperature [°C]	129.4	84.49	87.2
Composition [mol basis]			
Water	0.1557	0.5268	0
Acetone	0.0186	0.063	0
Butanol	0.1176	0.3977	0.0001
Ethanol	0.003	0.0101	0
2-Ethylhexanol	0.7051	0.0024	0.9999
Nitrogen	0	0	0

Table 5: PRO/II simulation : solvent recovery column flow summary

	Feed	ABE	Solvent
Flowrate [kg/hr]	1	1	0.986
Temperature [°C]	1	1.053	3.004
Composition [mol basis]			
Water	1	1.019	1
Acetone	1	0.976	1
Butanol	1	0.984	1
Ethanol	1	1.030	1
2-Ethylhexanol	1	0	1
Nitrogen	1	1	1

Table 6: Solvent recovery colum : DYNSIM vs PRO/II flow summaries ratio

In order to let the comparison be more immediate it is possible to create a new Table 6 computing the ratio between the values of the two previous tables (using 1 when both the values are 0).

As we can clearly notice, the values of flowrates, compositions and physical properties, with the exception of the solvent temperature, are practically the same. Part of this equality is due to the fact that the same thermodynamic package, i.e. UNIQUAC, has been used. This result shows the full success and coherence of the two simulations and can be considered a powerful validation of the design project.

5.3.2 Products purification section

The products purification section has nine degrees of freedom, therefore three variables for each column have been controlled to fulfill the d.o.f.s requirement:

Column 1

1. Reflux ratio: 0.05;

2. Butanol concentration: 99 % wt. (i.e. 0.96 mol);

3. Top pressure: 1 atm.

Column 2:

1. Ethanol recovery ratio: 0.95 wt. ;

2. Water recovery ratio: 0.9855 wt.;

3. Top pressure: 1 atm.

Column 3:

1. Acetone recovery ratio: 0.95 wt.;

2. Ethanol recovery ratio: 0.95 wt.;

3. Top pressure: 1 atm.

The trends of these controlled variables during the startup procedure are shown in Figures 14, 15, 16 and 17.

For this section the flow summary has been reported in Table 7 and it is relative to the very first moment steady state is achieved; this means that it could slightly change, keeping unchanged the specifications, during the running of the simulation (i.e. of the plant).

Even in this case the comparison with the PRO/II simulation can be useful. For the sake of simplicity the flow summary relative to the main interest products streams only has been reported in Table 8 and the ratio between DYNSIM and PRO/II results in Table 9 (using 1 when both the values are 0).
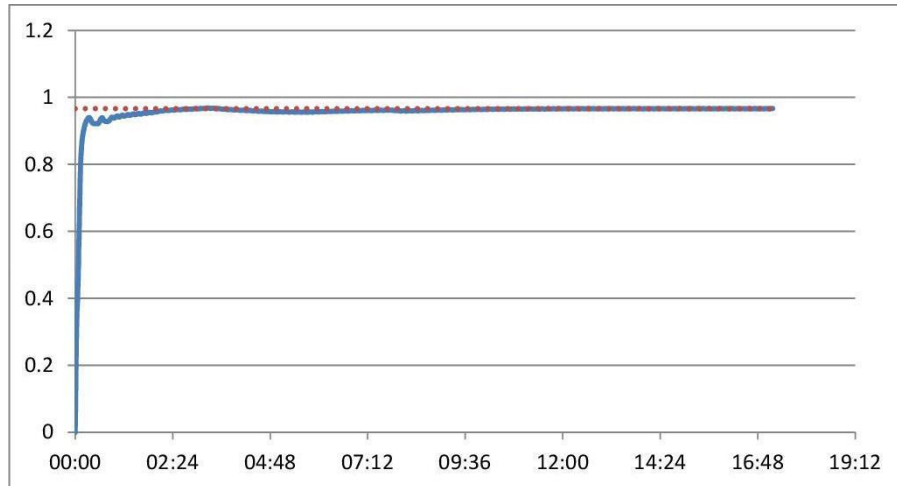
(a) Butanol molar fraction
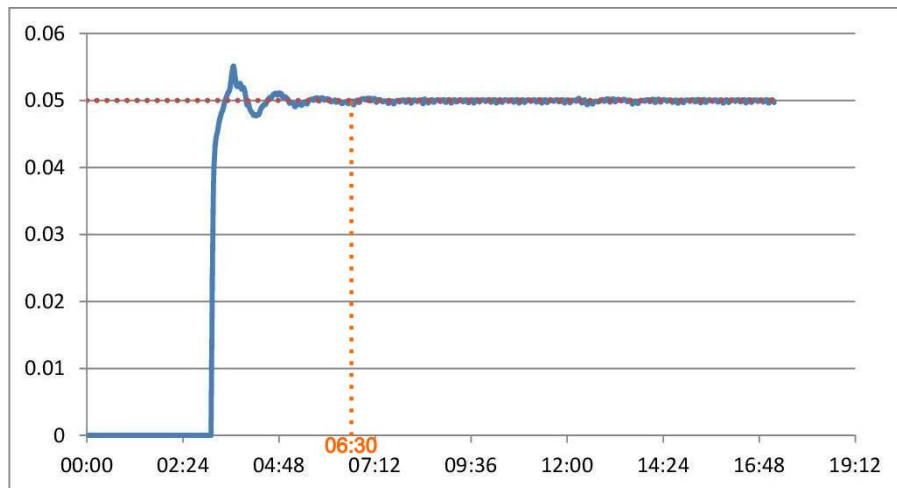
(b) Reflux ratio

Figure 14: Column 1: startup controlled variables trends

Even the first column's variables show no anomalies in their trends; the steady state is reached relatively quickly and the out of spec time of the butanol stream is very short, so there is almost no waste of butanol product. The reflux begins when the setpoint in the reflux drum is reached and the distillate stream starts feeding the second column. The controlled variables steady state is stably achieved after 6:30 hrs ca..
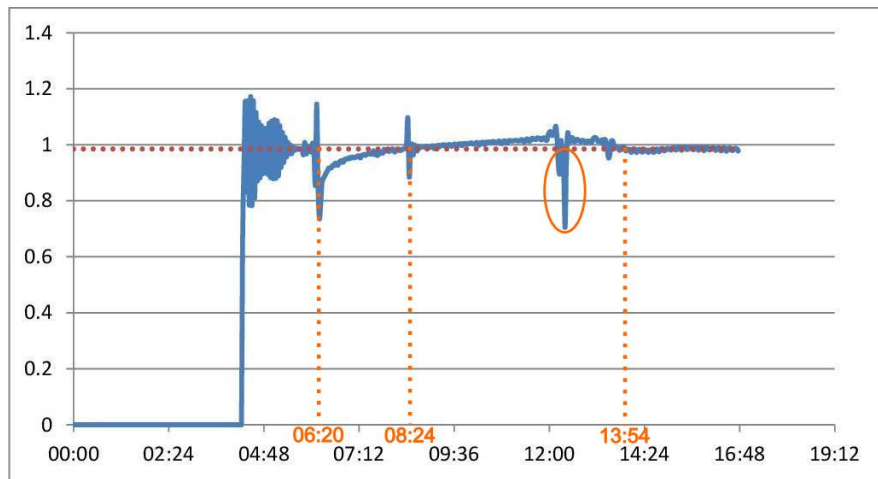
(a) Water recovery ratio
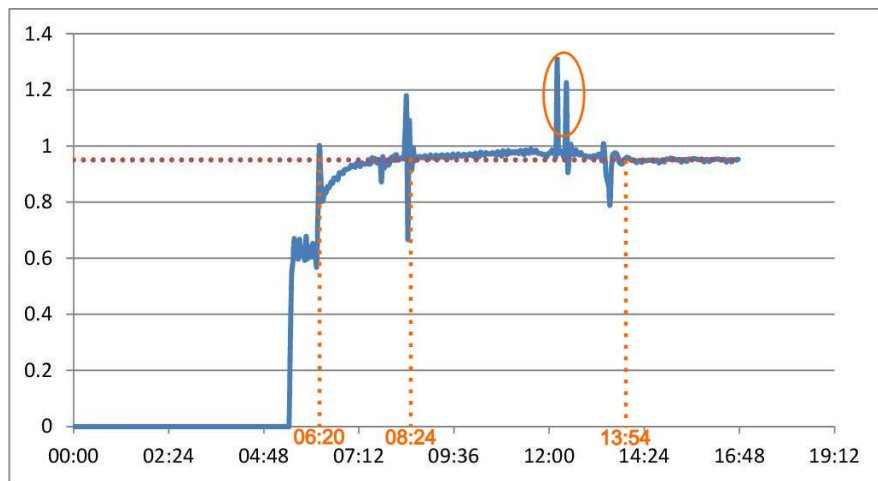
(b) Ethanol recovery ratio

Figure 15: Column 2: startup controlled variables trends

Column 2 controlled variables are led to the setpoint asynchronously, i.e only when the water recovery ratio controller achieves the setpoint the ethanol one is turned on. The initial oscillations in Figure 15a are related to the setpoint attainment of reflux drum 1 level. The very first oscillations in Figure 15b are related to the first spec controller setpoint achievement as well. The first controller is turned on at about 6:20 hrs ca., i.e. column 1 steady state, while the second one at 8:24 hrs ca., when the first one is approaching the setpoint. This switches can be identified in the most relevant oscillations of the two plots. The steady state conditions are definetely attained after 13:54 hrs ca..

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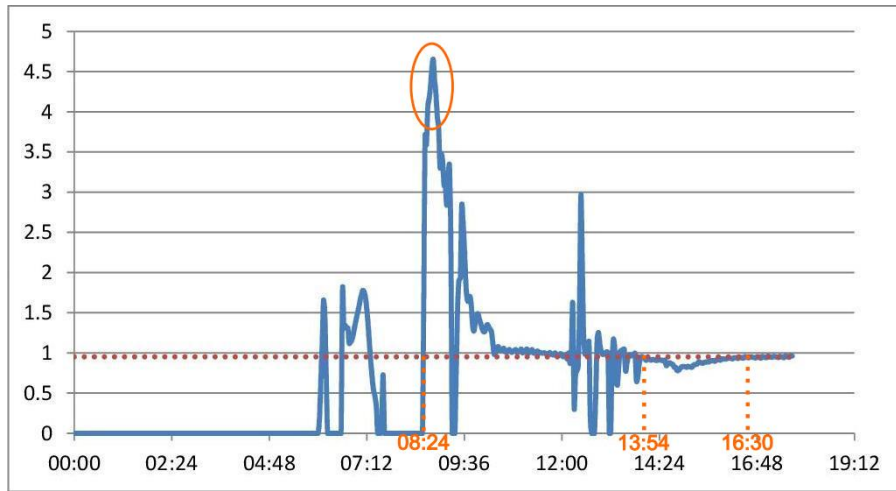
(a) Ethanol recovery ratio
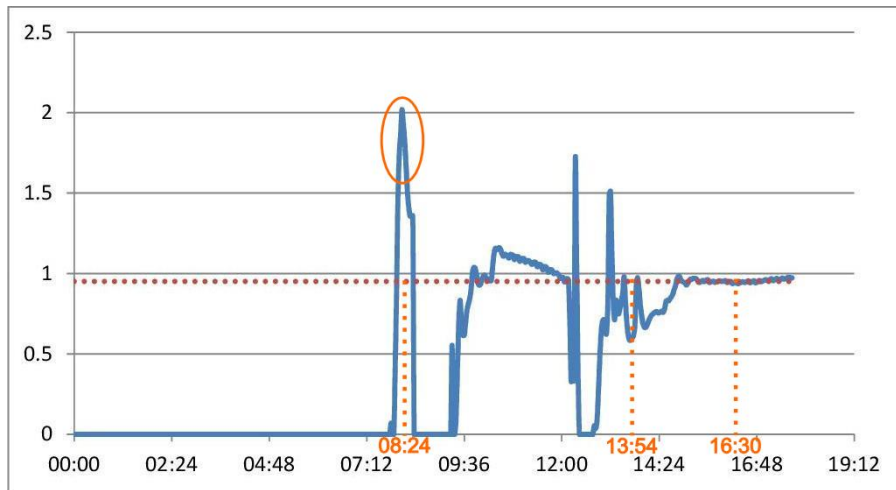
(b) Acetone recovery ratio

Figure 16: Column 3: startup controlled variables trends

The same observation of column 2 applies. Even if column 2 is definetely on steady state after 13:54 hrs ca., the spec controllers are switched on before this time in order to speed up the startup procedure. All the perturbations before this time have to be attributed to column 2 distillate oscillations, after that time the controlled variables trends can be related to column 3 controllers performances only. The turning on of the acetone spec controller can be clearly observed at 9:18 hrs ca.. Steady state conditions can be considered definetely achieved after 16:30 hrs ca..
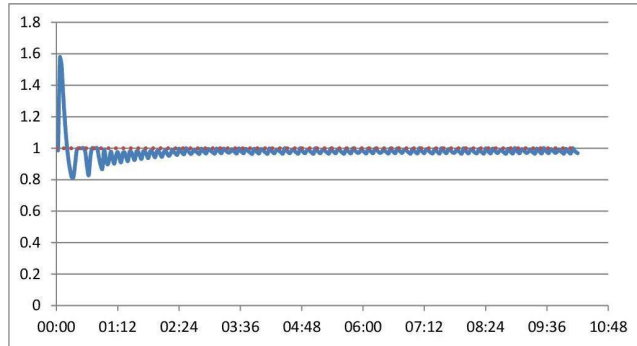
(a) Column 1
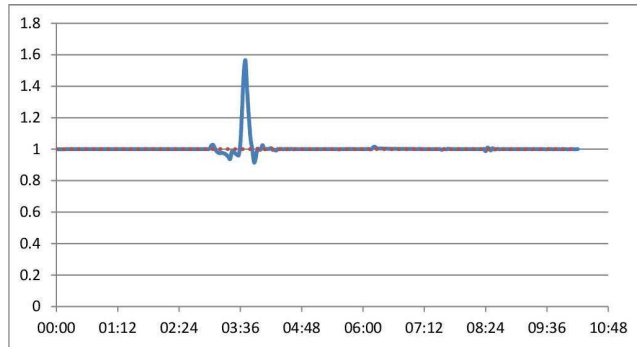
(b) Column 2
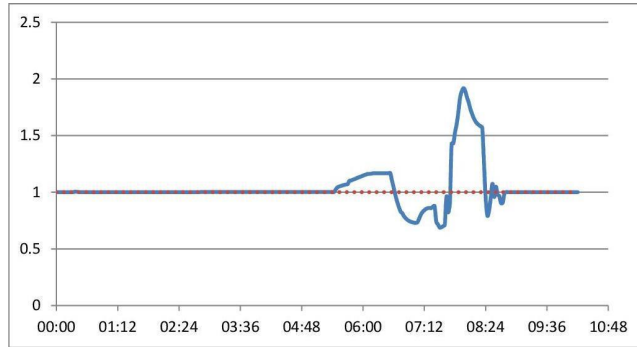
(c) Column 3

Figure 17: Startup top pressures trends [atm]

During the startup, pressures are quite stable, a max. of 1.9 atm and a min. of 0.7 are achieved both in column 3, that is the more sensitive. The higher peaks are related to reboiler duties openings, the lower peaks to reflux counteractions. Instabilities are quite short excepted the third column. Anyway, once the setpoints are achieved, they are mantained with no problem.

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	Feed	But	Top 1	Azeot.	Top 2	Ace	Eth
Flowrate [kg/hr]	2011	1060	986.63	806.39	177.808	96.17	82.27
Temperature [°C]	84.5	129.8	81.447	94.79	68.64	55.32	110.9
Composition [mol basis]							
Water	0.5246	0.0196	0.7371	0.7735	0.5146	0.0101	0.7744
Acetone	0.0627	0.0064	0.0870	0.0410	0.3669	0.9899	0.0482
Butanol	0.3960	0.9600	0.1574	0.1643	0.1149	0.0000	0.1718
Ethanol	0.0167	0.0140	0.0185	0.0212	0.0036	0.0000	0.0056
Nitrogen	0	0	0	0	0	0	0

Table 7: Products purification section flow summary

	Feed	Butanol	Acetone
Flowrate [kg/hr]	2011	1060	96.17
Temperature [°C]	84.5	129.8	55.32
Composition [mol basis]			
Water	0.5246	0.0196	0.01009
Acetone	0.0627	0.0064	0.98987
Butanol	0.396	0.96	0
Ethanol	0.0167	0.014	0.00004
2-Ethylhexanol	0	0	0
Nitrogen	0	0	0

Table 8: PRO/II simulation : products purification section flow summary

	Feed	Butanol	Acetone
Flowrate [kg/hr]	1	1.757	0.584
Temperature [°C]	1	1.07	0.902
Composition [mol basis]			
Water	1	0.49	1.2
Acetone	1	1	1.02
Butanol	1	0.9999	1
Ethanol	1	1	0.001
2-Ethylhexanol	1	1	1
Nitrogen	1	1	1

Table 9: Products purification section : DYNSIM vs PRO/II flow summaries ratio

In general the results are comparable with the exception of some compounds. Part of these discrepancies are due to some modifications in the thermodynamic settings needed to make the system stable, part to the relatively short time of steady state conditions after whom the flow summary of the dynamic simulation has been evaluated and the main part is due to the fact that these compounds are present in traces, therefore a small absolute change can cause a considerable relative variation. Anyway even this results can be considered a good validation of the design project.

5.4 Shut down procedures

The shut down procedure is relative much easier than the startup one.

The out-of-spec products can't be sent to the pure products storage, therefore, when the products go out of spec, the blowdown line has to be opened with an unavoidable waste of products that could eventually be sent back to the fermentation broth storage in order to be saved for later.

5.4.1 Solvent recovery column

For the dewatering section the shutdown procedure is defined as below:

1. Load steady state conditions:
   LOAD IC 1;

2. Run the simulation:
   RUN;

3. Feed interruption:
   SET FC1.MA=0.000;
   SET XV1.OP=0.000;

4. Switch off of reboiler duty:
   SET FC2.MA=0.000;
   SET XV3.OP=0.000;

5. Reflux interruption:
   SET RRC1.MA=0.000;
   SET XV5.OP=0.000.

Even in this case the trend of the controlled variables have been reported in Figure 18.

A little remark is needed about the shutdown procedure.

The ending of outcoming streams from the column has been considered as the ending of the shutdown. Anyway, at this point, the column is still filled by hydrocarbon's vapours. This means that air has to be fed to the column in order to restore the very initial condition and to empty the equipment from the aforementioned vapours.

These outcoming vapours, as well as the ones of the startup procedure, must be treated to abate the hydrocarbon components before being vented to the atmosphere in order to aviod toxic or explosive mixtures discharge.
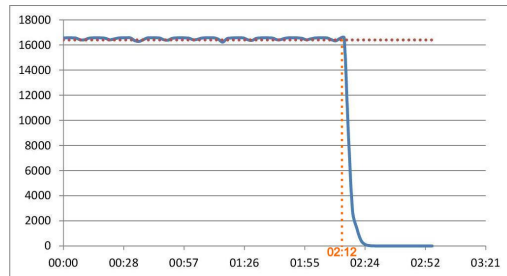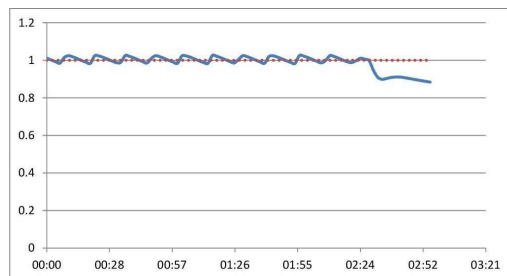
(a) Feed flowrate [kg/hr]
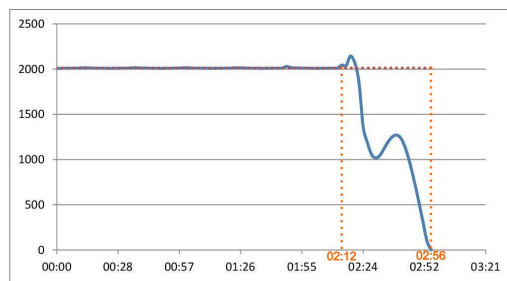
(b) ABE mixture flowrate [kg/hr]
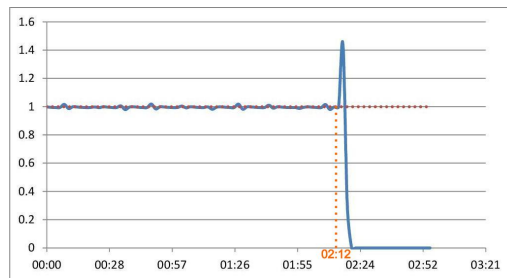
(c) Solvent recovery ratio

(d) Top pressure [atm]

Figure 18: Solvent recovery column: shutdown controlled variables trends

The solvent recovery column shutdown is very smooth. All the variables decrease coherently and in 1 hr ca. there are no more outcoming streams.

5.4.2   Products purification section

For the products purification section the shutdown procedure is defined as below:

1. Load steady state conditions:
   LOAD IC 3;

2. Run the simulation:
   RUN;

3. Stop feed flow:
   SET FC1.MANSET=0;

4. Switch off column 1 reboiler duty:
   SET CC1.MA=0.000;
   SET XV3.OP=0.000;

5. Switch off column 2 duty and reflux:
   WAIT UNTIL S11.W<500;
   SET RRC1.MA=0.000;
   SET XV11.OP=0.000;
   SET RRC2.MA=0.000;
   SET XV8.OP=0.000;

6. Switch off column 3 duty and reflux:
   WAIT UNTIL S11.W<180;
   SET RRC3.MA=0.000;
   SET XV15.OP=0.000;
   SET RRC4.MA=0.000;
   SET XV14.OP=0.000.

The trends of the controlled variables during the shutdown of the products purification section have been reported in Figures 19, 20, 21 and 22.

The same remark of solvent recovery column applies. Air should be fed after the outcoming streams stop and the hydrocarbon fraction in vapours has to be abated before discharging them in the atmposphere.
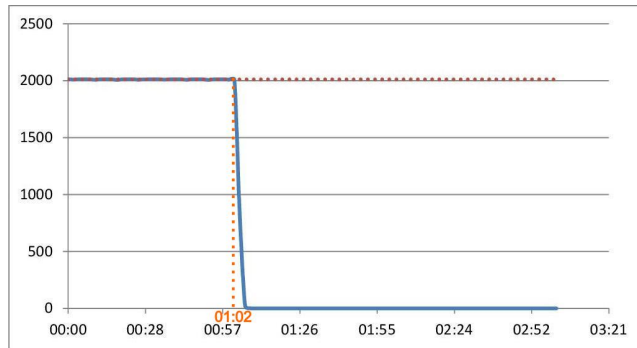
(a) Feed flowrate [kg/hr]
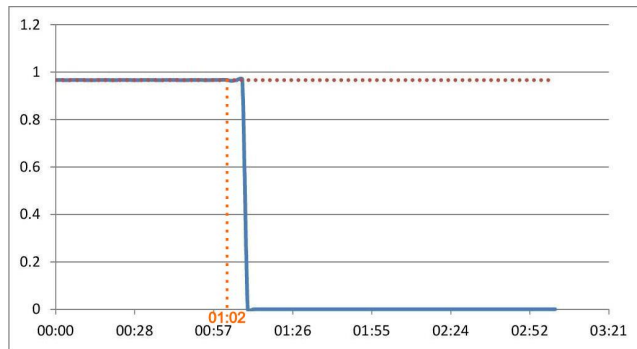

(b) Butanol molar fraction
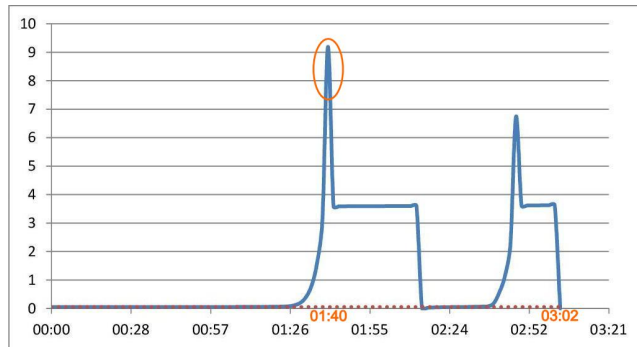
(c) Reflux ratio

Figure 19: Column 1: shutdown controlled variables trends

Feed flowrate is suddenly interrupted and the bottom stream stops after some minutes as well. The peaks of the reflux ratio are due to a computational factor related to the stop of the distillate stream that leads to a near zero denominator in the equation, anyway they have poor physical meaning. In 2 hrs ca. the shutdown of column 1 is completed.
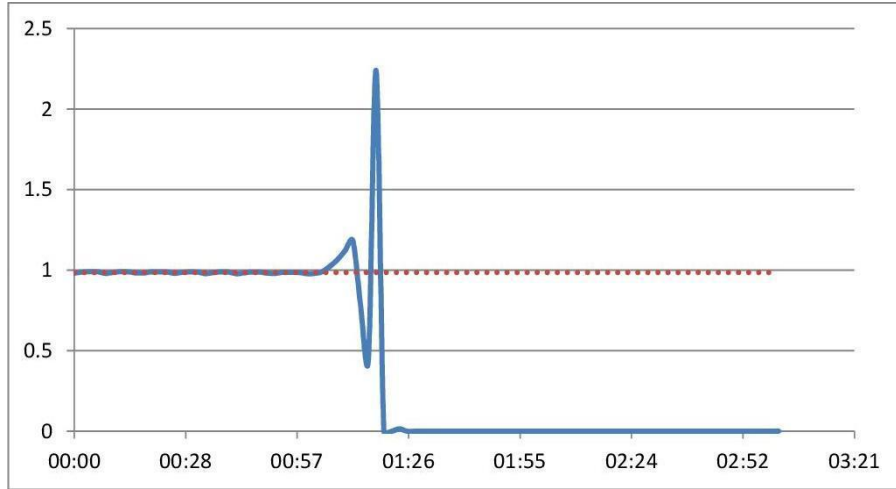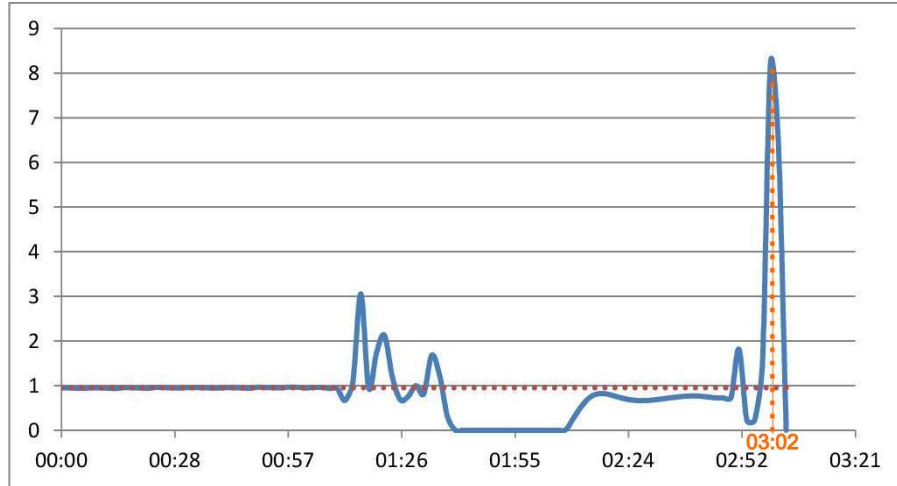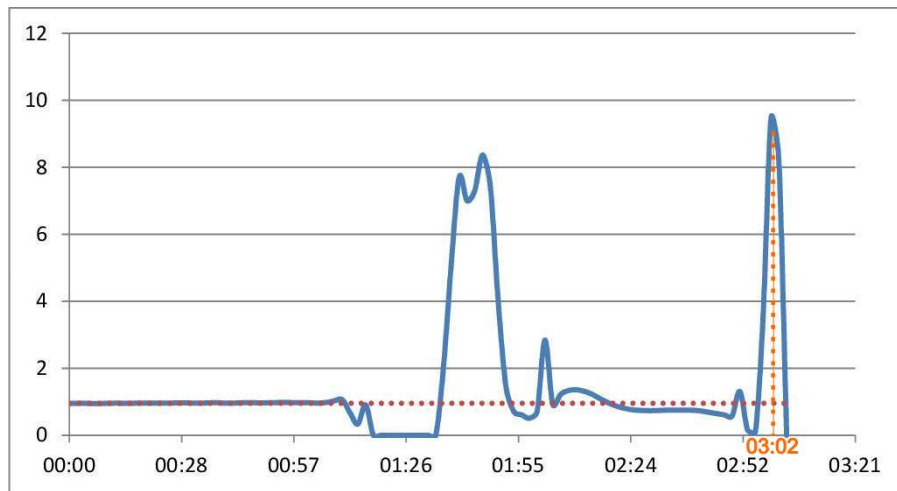
(a) Water recovery ratio
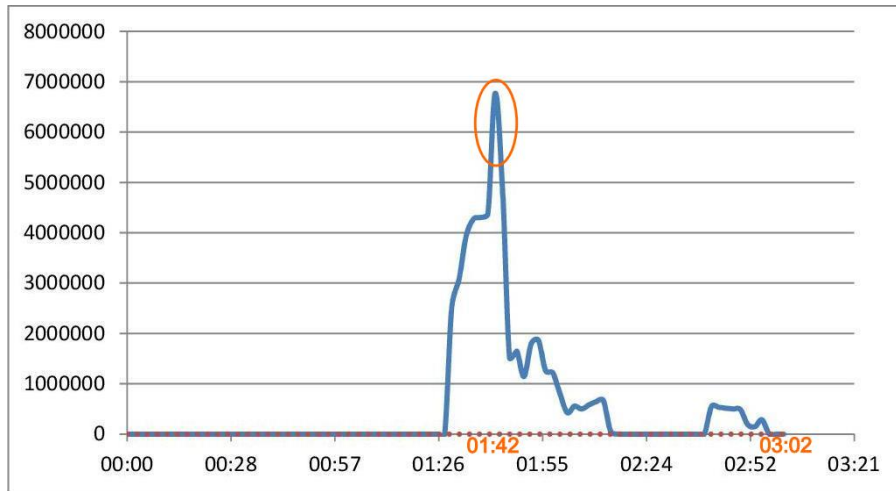
(b) Ethanol recovery ratio

Figure 20: Column 2: shutdown controlled variables trends

The peaks of recovery ratios are related to the interruption of the feed, i.e. column 1 distillate stream, after 1:40 hrs ca. leading to a near zero denominator while reboiler and reflux are still emptying. After 3 hrs ca. the shutdown of column 2 is completed.

(a) Ethanol recovery ratio

(b) Acetone recovery ratio

Figure 21: Column 3: shutdown controlled variables trends

The same observation of previous figure applies. The peaks of recovery ratios are related to the interruption of the feed, i.e. column 2 distillate stream, after 2:58 hrs ca. leading to a near zero denominator in the recovery ratios equations while reboiler and reflux are still emptying. After 3:10 hrs ca. the shutdown of column 3 is completed.

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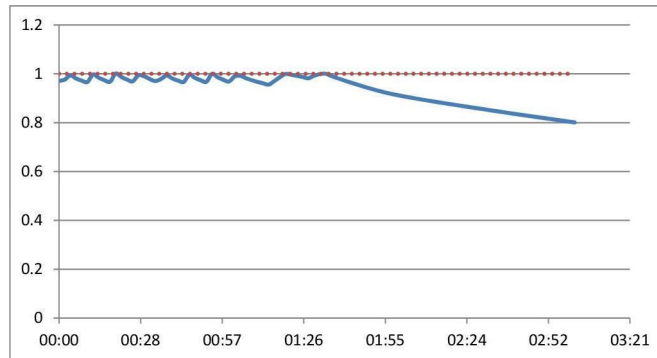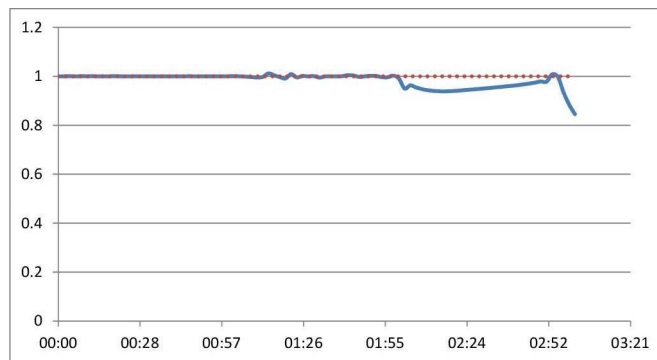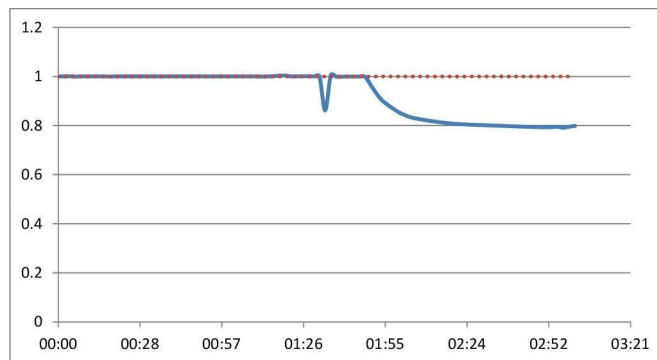
(a) Column 1

(b) Column 2

(c) Column 3

Figure 22: Shutdown top pressures trends [atm]

Pressure trends are the most immediate to have an overview of the shutdown process. As duties are switched off and columns are going to empty, pressures start decreasing slowly until the very final moments when they go to steady state condition.

	Trays (feed)	Height/ length [m]	Diameter [m]	Orientation	Level SP [m]	Duty T [°C]
Solvent recovery						
Column 1	17+1 (9)	0.6096 (per tray)	0.5	/	/	/
Reflux drum	/	4	2	Horizontal	1	20
Reboiler	/	3	2	Vertical	1.5	275
Products separation						
Column 1	25+1 (20)	0.6096 (per tray)	0.4	/	/	/
Reflux drum	/	4	1.5	Horizontal	0.75	20
Reboiler	/	3	1.5	Vertical	1.5	160
Column 2	28+1 (9)	0.6096 (per tray)	0.5	/	/	/
Reflux drum	/	2	1	Horizontal	0.5	20
Reboiler	/	2	1	Vertical	1	150
Column 3	37+1 (31)	0.6096 (per tray)	0.381	/	/	/
Reflux drum	/	0.5	0.5	Horizontal	0.25	20
Reboiler	/	1	0.5	Vertical	0.5	125

Table 10: Equipments sizing and configuration

5.5   Equipments sizing and configuration

In order to have a reproducible simulation and for the sake of completeness, all the main equipments data about sizing and configuration are provided for each section in Table 10.

Some of them are the same as the ones provided in the design thesis by A. Boffa [18], others are different according to the adjustments performed during the dynamic simulation in order to obtain a more stable system.

The tray added to each column refers to the reboiler; moreover, each column is lifted off the ground by 4.6 m.

6 Stability tests

One of the three main purposes of a control loop is to effectively respond to perturbations.

As discussed in previous paragraphs, disturbances are always present in real life and a simulation, in order to be considered reliable, has to perform as if real.

The sensitivity study is crucial and it's the very last stage of the design validation and feasibility assessment of a plant.

The products purification section is the object of study for what concerns the suppression of perturbations. Two variables have been chosen to be varied with a step disturbance according to what may actually happen during the operating conditions of the plant:

- Feed flowrate: fermentation processes are usually batch processes, anyway a continous operation has been assumed in this project, therefore the incoming fermentation broth flowrate has a very oscillating nature according to the fermentation behaviour. Thus substantial ABE flowrate variations are possible for the separation units and this could affect considerably the performances of the plant. Then it is very important to verify that, after an accommodation transient, the plant keeps on performing good separation even when the changes in feed flowrate are very high.

- Water molar fraction: the interest about changes in molar fraction is both based on the very high dependency of the success of the separation on the composition of the species and on the considerable probability of a low performant dewatering section. This means that the response to water molar fraction perturbation gives us both an idea on how specs fulfillment depends on composition and a very practical information about the plant response in case of dewatering section malfunctioning.

All the details of these tests, the resulting flow summaries and trends of the controlled variables are reported in the following corresponding paragraphs.

6.1 Feed flowrate perturbation

The feed flowrate of the products purification section has been varied during the simulation by changing the FC1 setpoint after steady state conditions
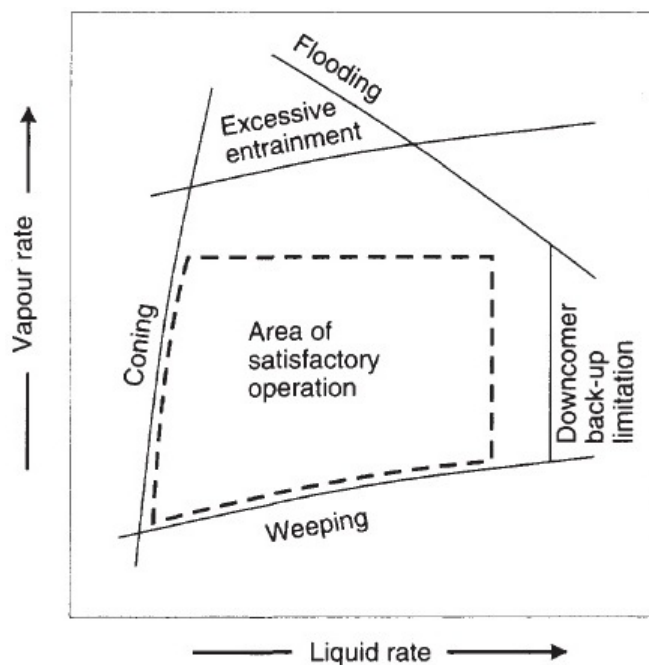
Figure 23: Sieve tray performance diagram

have been loaded. Since the controller acts immediately we can consider it as a step variation (Figure 24a and 27a).

As discussed in the introduction, the feed flowrate has been both increased and decreased in order to test both high and low flow conditions.

This plant subsection was designed for a flowrate of 2011 kg/hr of ABE, this obviously means that it can't be suitable for "any" flowrate value; anyway the effectiveness of the dewatering section and the amount of broth coming from the fermentor can vary considerably during time.

Therefore the modifications of +50% and -20% have been chosen to test the stability of the plant responses.

The fact that the two percentages are different is related to the managing of low flow by sieved trays distillation columns that would require instead more specific tray types or packed fillings in order to avoid weeping and other similar undesired phenomena as shown by the diagram in Figure 23 [31].

Every figure and flow summary will be analyzed in detail in each corresponding paragraph.

It is expected to have poor changes in composition and modification in

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	Feed	But	Top 1	Azeot.	Top 2	Ace	Eth
Flowrate [kg/hr]	3016.7	1486.7	1513	1241.7	275.1	155.41	119.69
Temperature [°C]	84.5	135.326	80.93	99.65	69.17	56.18	99.96
Composition [mol basis]							
Water	0.5246	0.0178	0.7369	0.7741	0.5189	0.0599	0.7723
Acetone	0.0627	0.0067	0.0865	0.0401	0.3615	0.9400	0.0453
Butanol	0.396	0.9614	0.1588	0.1660	0.1165	0.0000	0.1774
Ethanol	0.0167	0.0141	0.0178	0.0198	0.0031	0.0001	0.0050
Nitrogen	0	0	0	0	0	0	0

Table 11: Feed flowrate perturbation +50% : flow summary

flowrates proportional more or less to the perturbation percentage.

6.1.1 High flow

The products purification section responses for an increment of feed flowrate from 2011,121 kg/hr to 3016,68 kg/hr (+50%) have been reported in Figures 24, 25 and 26.

Pressure profiles have not been reported because no changes in columns pressures occur.

Moreover, the resulting flow summary after steady state has been achieved again is shown in Table 11.
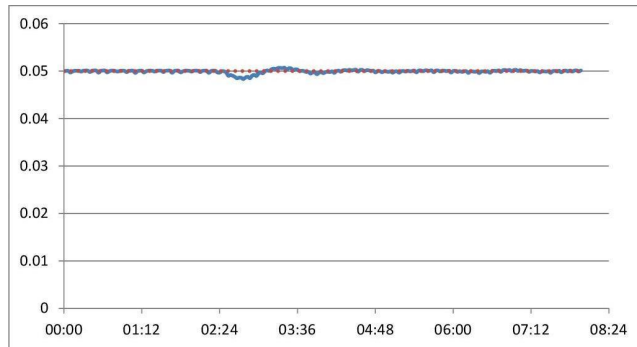
In order to compare "perturbated" steady state conditions to standard ones, it could be useful to report in Table 12 the ratio between Table 11 and Table 7 (using 1 when both the values are 0).
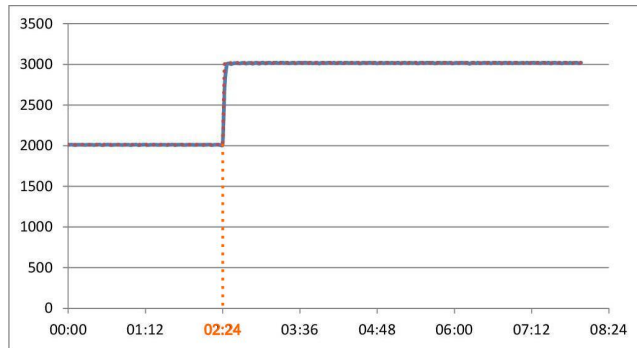
(a) Feed flowrate [kg/hr]
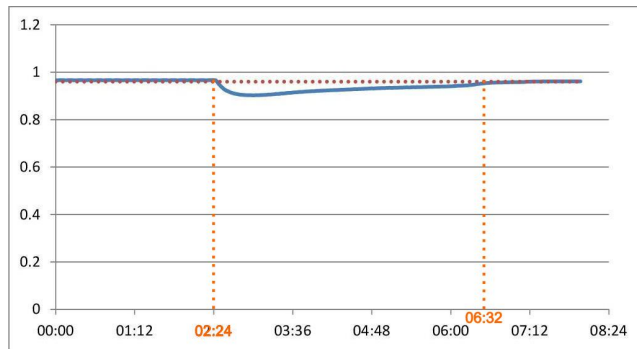

(b) Butanol molar fraction

(c) Reflux ratio

Figure 24: Column 1: High flow +50% controlled variables trends

The effects of flowrate perturbation on column 1 are mainly visible in butanol composition trend, while the reflux ratio is affected at the very first moments only. Butanol composition requires a considerable amount of time to go back to the setpoint, anyway the offset is restrained and it's not worth being considered a problem for the system stability.
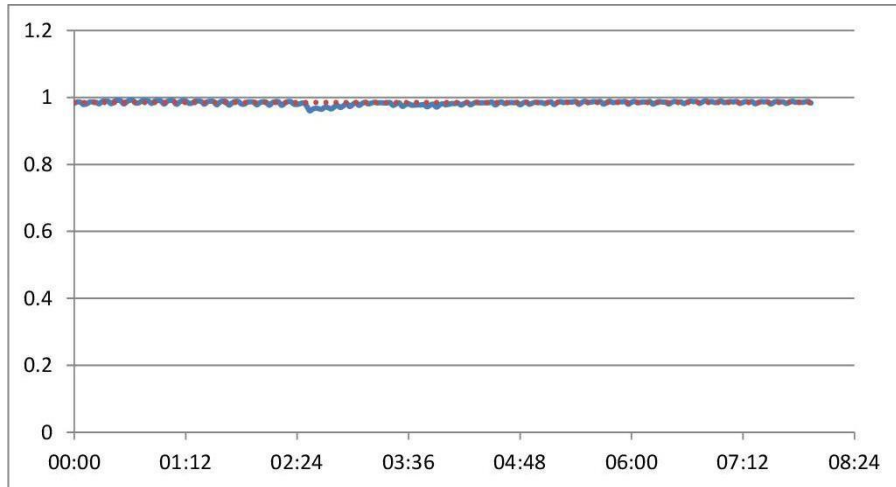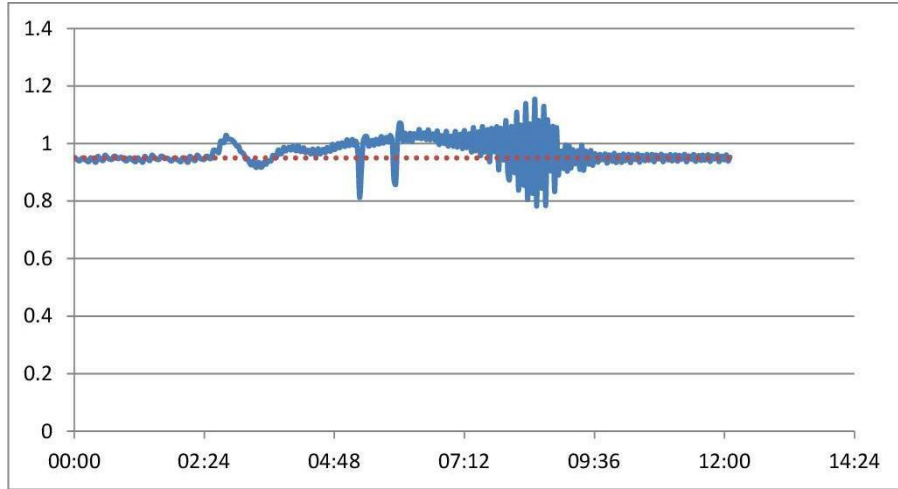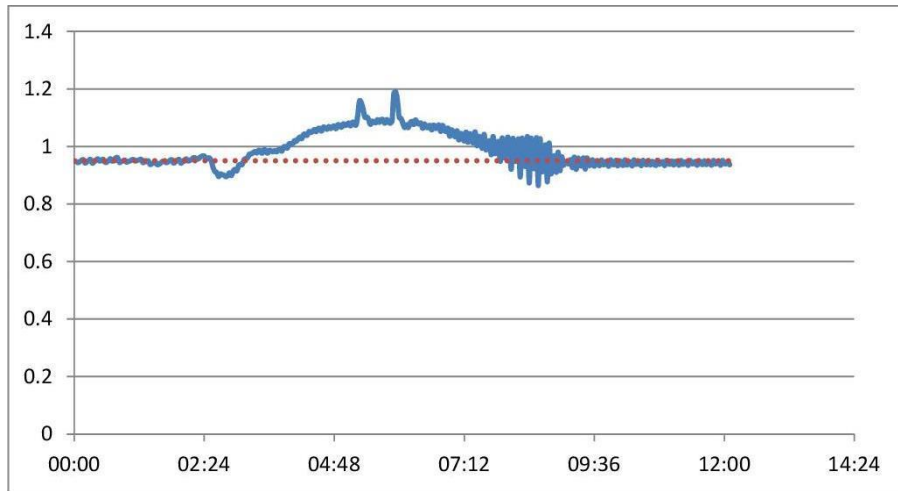
(a) Water recovery ratio
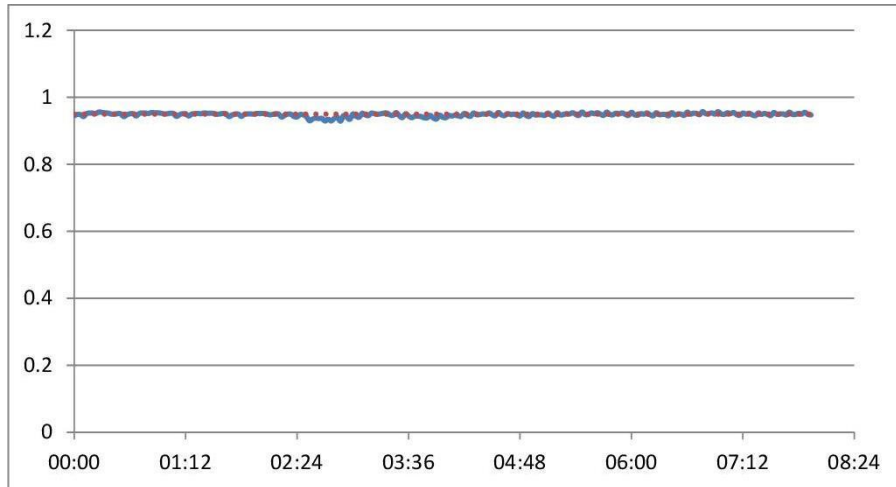
(b) Ethanol recovery ratio

Figure 25: Column 2: High flow +50% controlled variables trends

Column 2 is for sure the less affected by the feed perturbation. Beside very little offsets after the feed flow step change, almost no modifications occur.

(a) Ethanol recovery ratio

(b) Acetone recovery ratio

Figure 26: Column 3: High flow +50% controlled variables trends

Column 3, that is the most sensitive, is the most disturbed by the perturbation. Anyway the trends of the controlled variables are just a little bit over the required specifications and the final oscillations are mainly due to the attainment of the level setpoints and not to the duties adjustment.

	Feed	But	Top 1	Azeot.	Top 2	Ace	Eth
Flowrate [kg/hr]	1.50	1.40	1.53	1.54	1.547	1.616	1.455
Temperature [°C]	1	1.043	0.994	1.051	1.008	1.016	0.901
Composition [mol basis]							
Water	1	0.91	0.999	1.001	1.008	5.94	0.997
Acetone	1	1.042	0.994	0.978	0.985	0.950	0.940
Butanol	1	1.002	1.009	1.010	1.013	1	1.033
Ethanol	1	1.004	0.958	0.934	0.864	0.590	0.888
Nitrogen	1	1	1	1	1	1	1

Table 12: Feed flowrate perturbation +50% : flow summaries ratio

It is clear that compositions are perfectly compatible with the exception of some compounds of the acetone stream that are present in traces and for which a small absolute change reflects as a considerable relative variation. The flowrates are more or less set to the 150 % of standard conditions as expected; some differences could be also justified by the fact that the flow summary has been taken out only few hours after the steady state conditions has been achieved again.

	Feed	But	Top 1	Azeot.	Top 2	Ace	Eth
Flowrate [kg/hr]	1608.9	857.51	813.2	653.94	144.2	74.45	69.45
Temperature [°C]	84.5	125.15	81.46	93.99	68.84	55.44	111.21
Composition [mol basis]							
Water	0.5246	0.0168	0.7416	0.7769	0.5143	0.0091	0.7584
Acetone	0.0627	0.0055	0.0851	0.0403	0.3672	0.9909	0.0683
Butanol	0.396	0.9626	0.1558	0.1625	0.1152	0	0.1683
Ethanol	0.0167	0.0151	0.0175	0.0203	0.0033	0	0.0050
Nitrogen	0	0	0	0	0	0	0

Table 13: Feed flowrate perturbation -20% : flow summary

6.1.2 Low flow

The products purification section responses for a decreasing of feed flowrate from 2011,121 kg/hr to 1608,9 kg/hr (-20%) have been reported in Figures 27, 28 and 29.
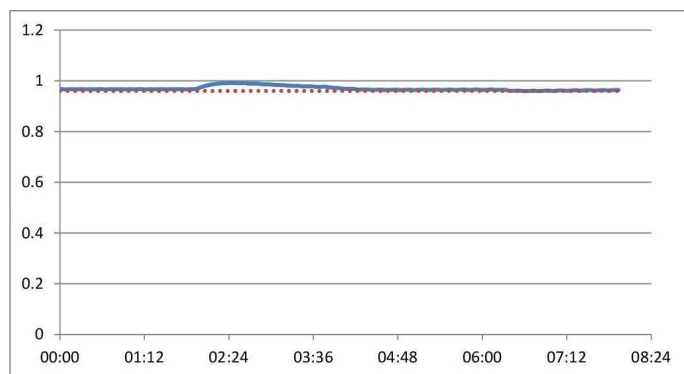
Pressure profiles have not been reported because no changes in columns pressures occur.

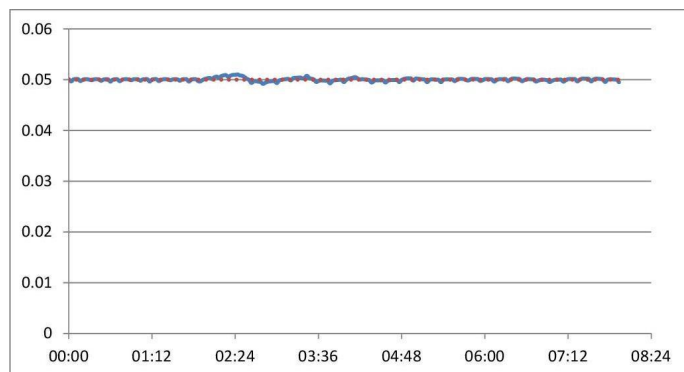Moreover, the resulting flow summary after steady state has been achieved again is shown in Table 13.

As well as the high flow case, Table 14 reports the ratio between Table 13 and Table 7 (using 1 when both the values are 0).
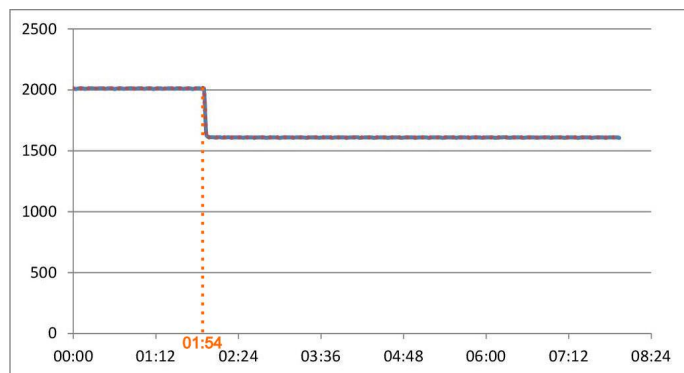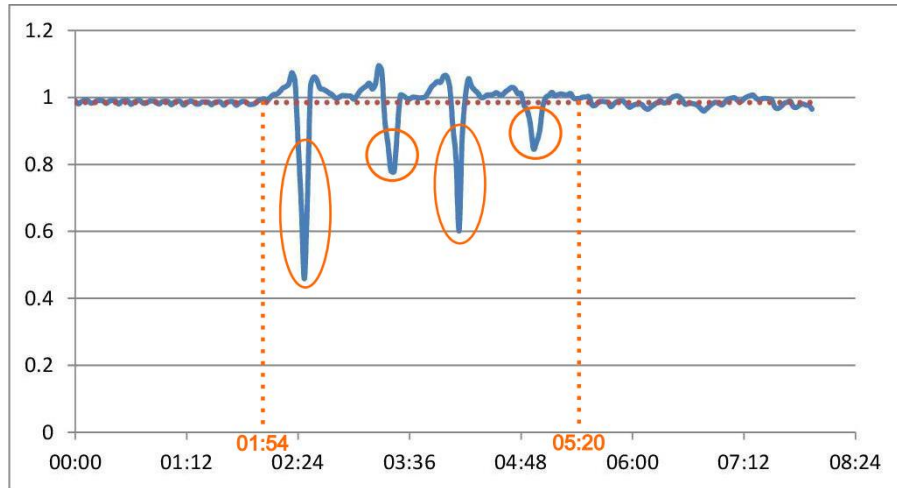
(a) Feed flowrate [kg/hr]
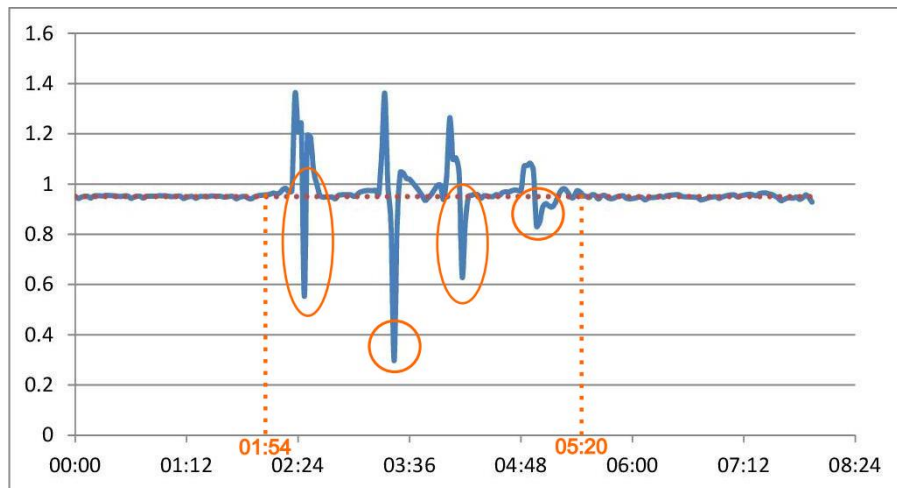

(b) Butanol molar fraction

(c) Reflux ratio

Figure 27: Column 1: Low flow -20% controlled variables trends

Even in case of low flow, column 1 variables are only slightly affected, butanol composition increases for a while and reflux ratio looks almost constant with the exception of the first 10 minutes after the disturbance occurs.
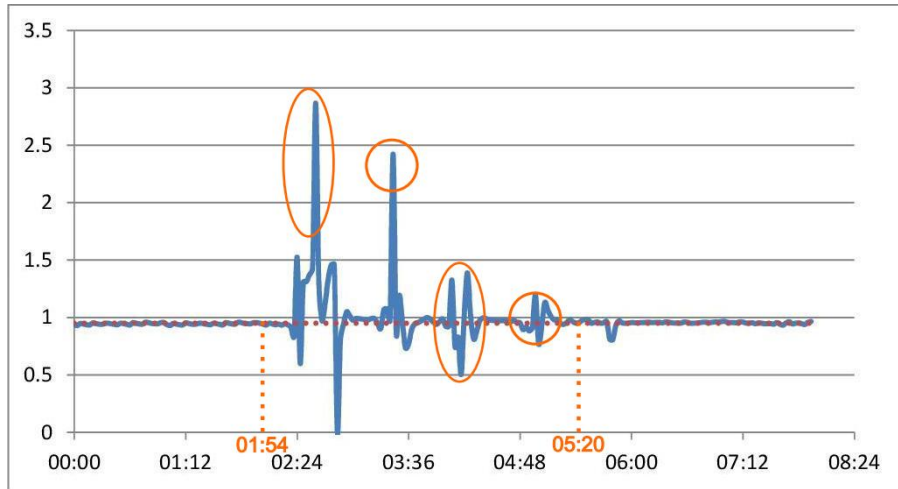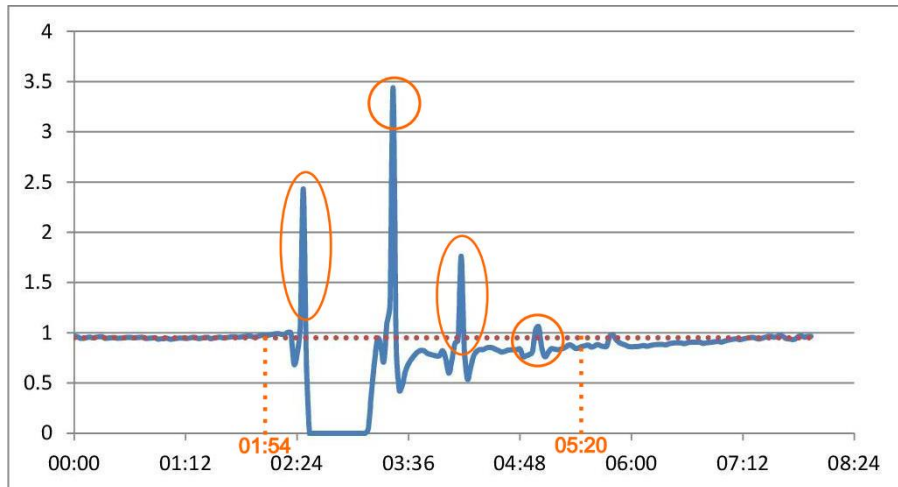
(a) Water recovery ratio

(b) Ethanol recovery ratio

Figure 28: Column 2: Low flow -20% controlled variables trends

Column 2 controlled variables result strongly affected by the adjustments
of column 1 distillate flowrate. As well as column 1 reflux ratio, after 10
minutes they start oscillating. This behaviour is demonstrated by their spec-
ular trends while, in case of control loop instability, their trends would have
been opposite. The steady state is achieved again 3:30 hrs ca. after the
perturbation.

(a) Ethanol recovery ratio

(b) Acetone recovery ratio

Figure 29: Column 3: Low flow -20% controlled variables trends

Same observations of column 2 applies. It's evident that after column 2 is stable, column 3 rapidly achieves the steady state in a little bit more than 1 hr.

	Feed	But	Top 1	Azeot.	Top 2	Ace	Eth
Flowrate [kg/hr]	0.800	0.809	0.824	0.811	0.811	0.775	0.844
Temperature [°C]	1	0.964	1.000	0.992	1.003	1.002	1.003
Composition [mol basis]							
Water	1	0.859	1.006	1.004	0.999	0.904	0.979
Acetone	1	0.848	0.978	0.983	1.001	1.001	1.417
Butanol	1	1.003	0.990	0.989	1.002	1	0.979
Ethanol	1	1.080	0.943	0.958	0.911	1	0.906
Nitrogen	1	1	1	1	1	1	1

Table 14: Feed flowrate perturbation -20% : flow summaries ratio

In this case data are even more compatible, flowrates are almost the 80% of the standard ones as expected and compositions poorly modified.

6.2 Feed composition perturbation

The feed composition of the products purification section has been varied during the simulation by changing the "From_extractor" source composition after steady state conditions have been loaded.

Since the change acts immediately we can consider it as a step variation (Figure 30a and 33a).

The water molar fraction in the feed has been both increased and decreased in order to test both higher and lower dewatering section performances conditions. Moreover, the change in feed composition can be caused, as highlighted in paragraph 5.2, by the recycle of the out of spec products during the initial transient of the startup procedure.

Therefore the values of 0.4 and 0.6 have been chosen to test the stability of the plant responses.

For the estimation of the other species' molar fraction in the feed two different procedures have been followed:

- for low effective dewatering section, i.e. $z_{H_2O} = 0.6$, a simulation with PRO/II has been performed considering a worse butanol recovery ratio (i.e. 0.69) corresponding to the desired water molar fraction;

	Feed	But	Top 1	Azeot.	Top 2	Ace	Eth
Flowrate [kg/hr]	2011	702	1309	1074	235	150	85
Temperature [°C]	84.5	132.6	81.02	98.41	69.035	60.2	107.4
Composition [mol basis]							
Water	0.6	0.0234	0.7336	0.7702	0.5144	0.3094	0.753
Acetone	0.072	0.0063	0.0879	0.0409	0.3692	0.6513	0.043
Butanol	0.316	0.9596	0.1659	0.1745	0.1144	0.0393	0.200
Ethanol	0.012	0.0107	0.0126	0.0144	0.0020	0.0000	0.004
Nitrogen	0	0	0	0	0	0	0

Table 15: Water composition 0.6 : flow summary

- for a lower water molar fraction in the feed, i.e. $z_{H_2O} = 0.4$, the molar ratios between the other compounds have been kept constant since the dewatering section simulation is not able to perform such a good separation.

Every figure and flow summary will be analyzed in detail in each corresponding paragraph. Compositions are crucial for the success and the conditions of the separation, therefore it is difficult to estimate the behaviour before the simulation, anyway it is expected to have higher productivity of butanol for lower water molar fraction, i.e. a more performant dewatering section, and viceversa.
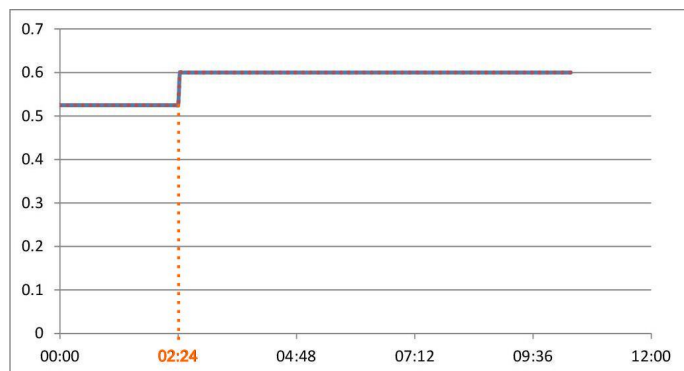
6.2.1 Higher water molar fraction

The products purification section responses for an increment of water molar fraction from 0.5246 to 0.6 have been reported in Figures 30, 31 and 32.
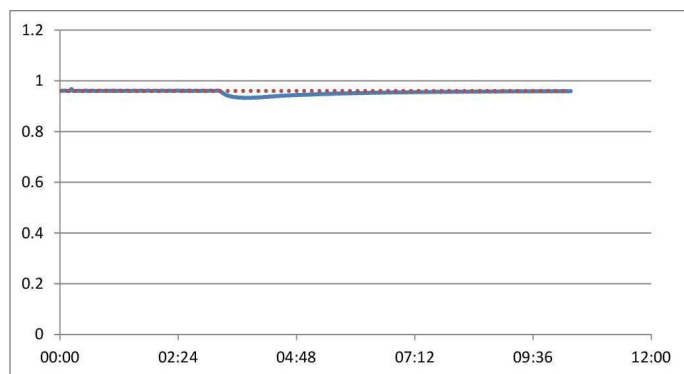
Pressure profiles have not been reported because no changes in columns pressures occur.

Moreover, the resulting flow summary after steady state has been achieved again is shown in Table 15.
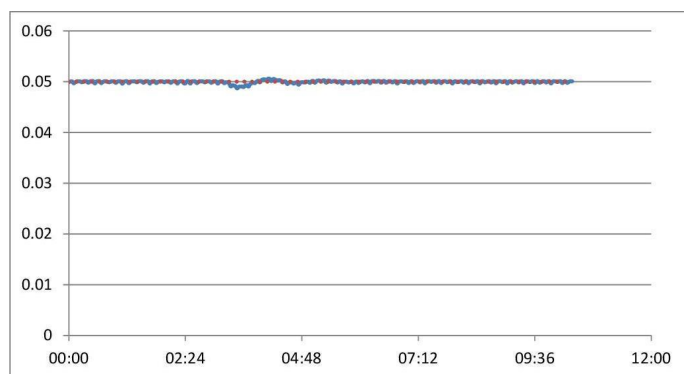
The ratio between Table 15 and Table 7 (using 1 when both the values are 0) has been reported in Table 16.
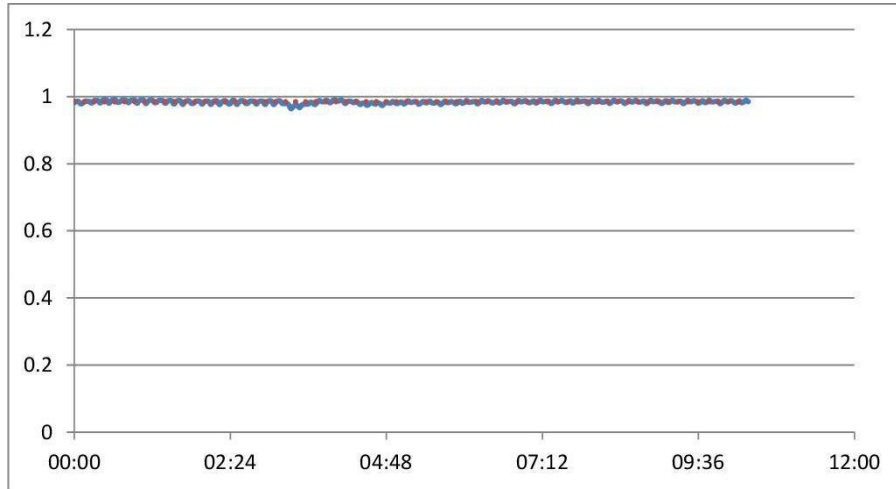
(a) Water molar fraction

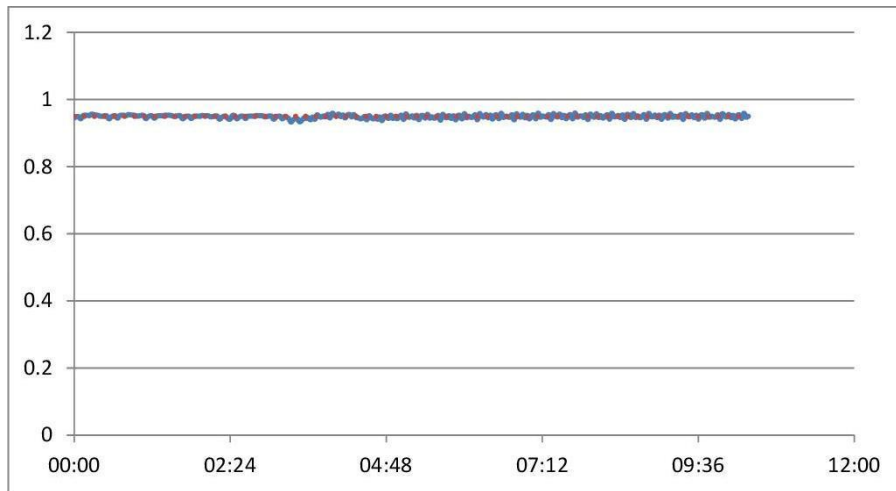(b) Butanol molar fraction

(c) Reflux ratio

Figure 30: Column 1: Water composition 0.6 controlled variables trends

Column 1 shows, as usual, very stable to the disturbance. A short deviation of controlled variables after 1 hr ca. can be detected but everything is very smooth and steady state conditions are achieved again quite fast.
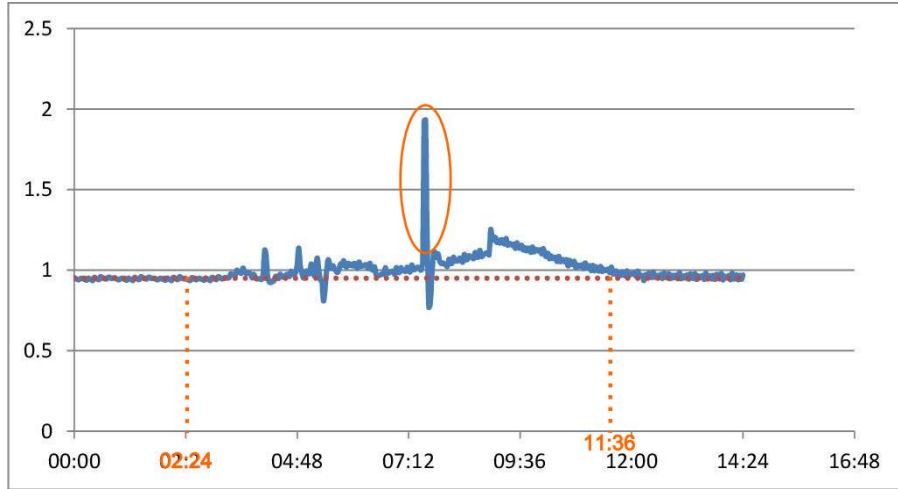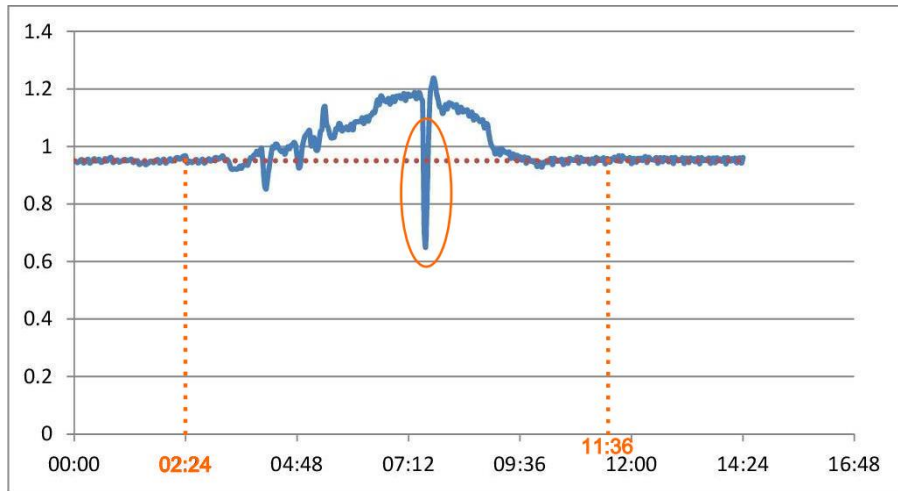
(a) Water recovery ratio

(b) Ethanol recovery ratio

Figure 31: Column 2: Water composition 0.6 controlled variables trends

Column 2 response is practically absent, or at least much more moderate than in flowrate perturbations cases. This demonstrates that the control loop is stable and oscillations of paragraph 6.1 were related to the first column distillate flowrate ones.

(a) Ethanol recovery ratio

(b) Acetone recovery ratio

Figure 32: Column 3: Water composition 0.6 controlled variables trends

Even controlled variables of column 3, that is always the most sensitive, have a much more moderate response. With the exception of one peak at 7:34 hrs, they're always near or over the setpoint and, after 8:30 hrs ca. from the perturbation, steady state conditions have been attained again.

	Feed	But	Top 1	Azeot.	Top 2	Ace	Eth
Flowrate [kg/hr]	1	0.662	1.327	1.332	1.322	1.560	1.033
Temperature [°C]	1	1.021	0.995	1.038	1.006	1.088	0.968
Composition [mol basis]							
Water	1.144	1.197	0.995	0.996	1.000	30.66	0.972
Acetone	1.148	0.985	1.010	0.999	1.006	0.658	0.886
Butanol	0.798	1.000	1.054	1.062	0.995	1	1.166
Ethanol	0.718	0.759	0.680	0.678	0.567	0.513	0.762
Nitrogen	1	1	1	1	1	1	1

Table 16: Water composition 0.6 : flow summaries ratio

Comparisons between compositions have poor sense because, changing the feed composition, all the equilibria are perturbated. Anyway it is possible to identify a general, as obvious, increase of water molar fraction in almost every stream. The butanol stream flowrate decrease with a sensiblly lowering production of the most desired compound, thus a low performance of the dewatering section causes a non negligible loss of productivity, i.e. of money return.

|	Feed	But	Top 1	Azeot.	Top 2	Ace	Eth
Flowrate [kg/hr]	2011	1245.5	765.35	650.03	134.19	86.429	47.84
Temperature [°C]	84.5	123.77	80.29	93.495	61.42	55.694	110.4
Composition [mol basis]							
Water	0.4	0.0149	0.6934	0.7582	0.3465	0.0098	0.715
Acetone	0.079	0.0077	0.1253	0.0378	0.5976	0.9902	0.156
Butanol	0.5	0.9593	0.1582	0.1782	0.0525	0	0.124
Ethanol	0.021	0.0181	0.0231	0.0258	0.0034	0	0.006
Nitrogen	0	0	0	0	0	0	0

Table 17: Water composition 0.4 : flow summary

6.2.2 Lower water molar fraction

The products purification section responses for a decrease of water molar fraction from 0.5246 to 0.4 have been reported in Figures 33, 34 and 35.
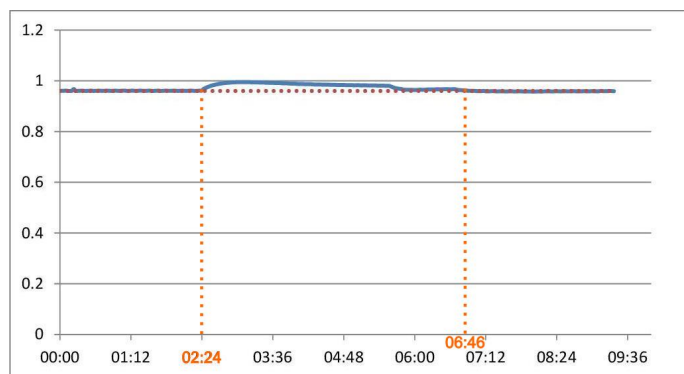
Pressure profiles have not been reported because no changes in columns pressures occur.

Moreover, the resulting flow summary after steady state has been achieved again is shown in Table 17.

The ratio between Table 17 and Table 7 (using 1 when both the values are 0) has been reported in Table 18.
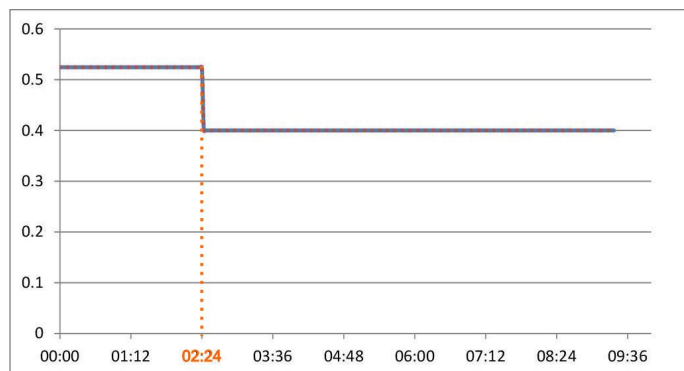
(a) Water molar fraction

(b) Butanol molar fraction
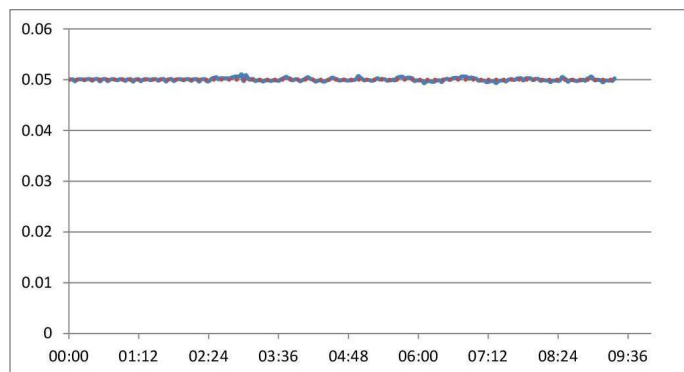
(c) Reflux ratio

Figure 33: Column 1: Water composition 0.4 controlled variables trends

With decreasing water fraction, butanol composition in the reboiler increases for a while, then it goes back to the spec value. Reflux ratio is just slightly affected, anyway column 1 variables look the most stable even in this case.

(a) Water recovery ratio
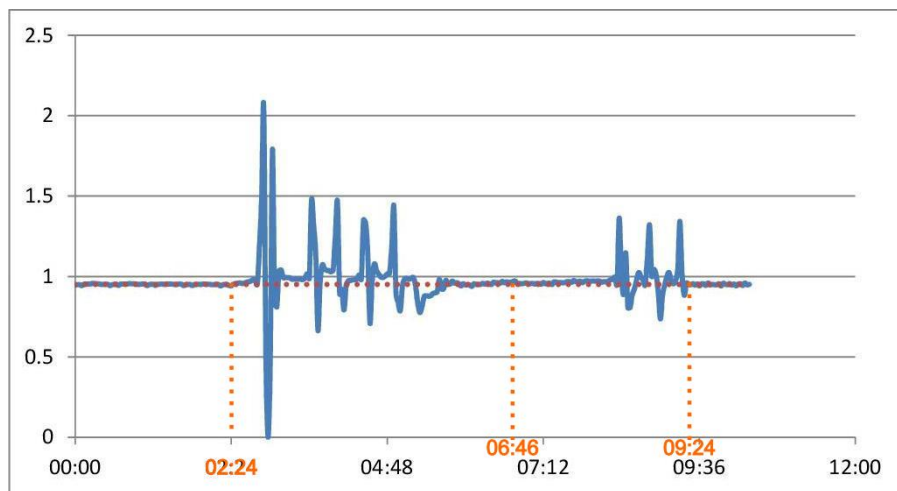
(b) Ethanol recovery ratio

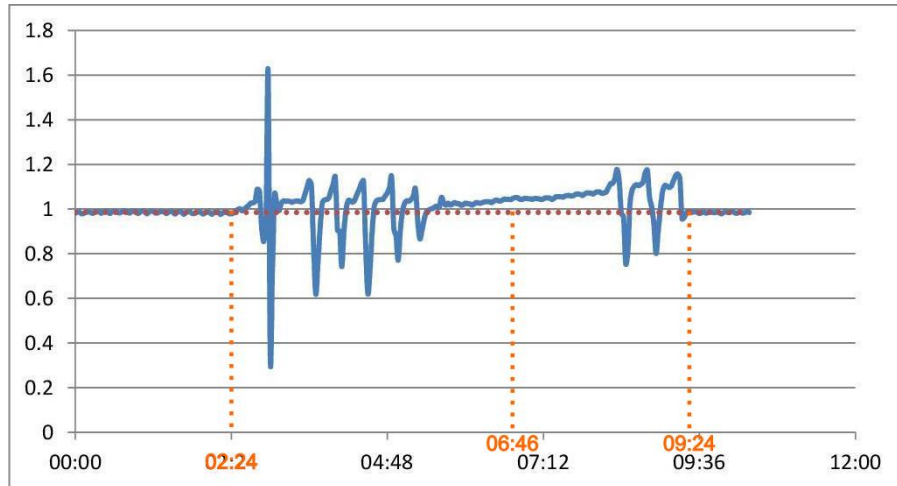Figure 34: Column 2: Water composition 0.4 controlled variables trends

Column 2 is strongly affected by the low composition perturbation because a lower water molar fraction makes the water recovery more difficult and the ethanol recovery ratio becomes unstable as direct consequence. It takes some hours to achieve again steady state conditions that, anyway, are stably attained by the control loop.
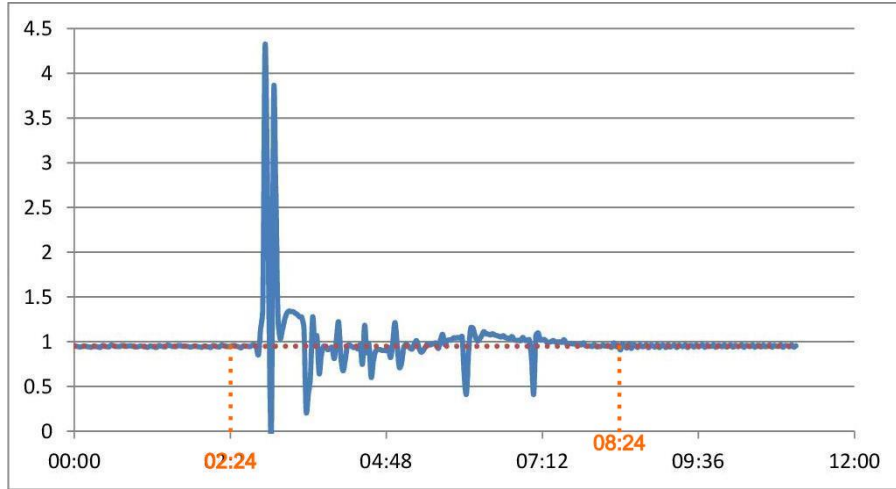
(a) Ethanol recovery ratio
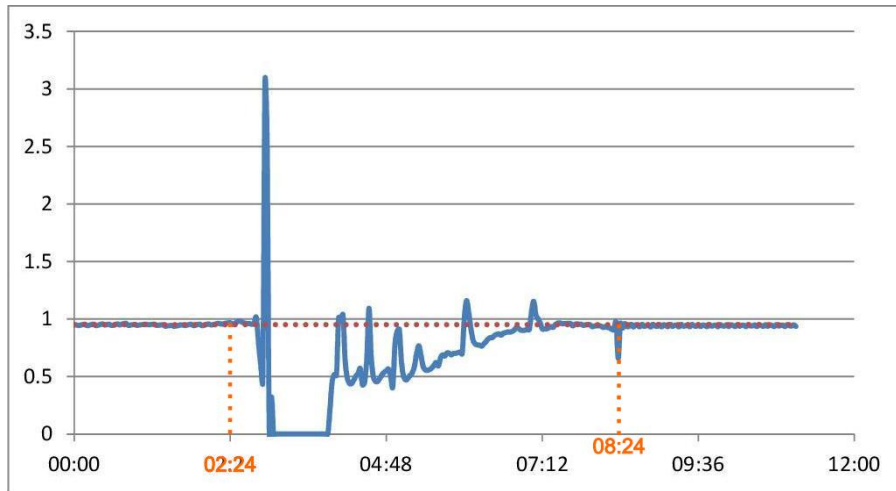
(b) Acetone recovery ratio

Figure 35: Column 3: Water composition 0.4 controlled variables trends

Column 3 controlled variables act as a reflection of the instability of column 2, while the control loop itself is stable. This is proved by the fact that column 3 achieves stability even before the preceding column and the variables keep on being stable until the whole system is at steady state again.

	Feed	But	Top 1	Azeot.	Top 2	Ace	Eth
Flowrate [kg/hr]	1	1.175	0.776	0.8061	0.755	0.899	0.582
Temperature [°C]	1	0.954	0.986	0.986	0.895	1.001	0.996
Composition [mol basis]							
Water	0.763	0.763	0.941	0.980	0.673	0.971	0.923
Acetone	1.256	1.192	1.440	0.923	1.629	1.000	3.231
Butanol	1.263	0.999	1.005	1.085	0.457	1	0.721
Ethanol	1.257	1.291	1.246	1.217	0.951	1	1.067
Nitrogen	1	1	1	1	1	1	1

Table 18: Water composition 0.4 : flow summaries ratio

On the contrary of Table 16, Table 18 shows how a lower water molar fraction in the feed, i.e. a better separation by the dewatering section, causes an increase in the productivity of butanol. In general there is a decrease in the fraction of water, that is a not interesting product, in all the streams with a increase of other species, mostly acetone.

7 Conclusions

In the light of the previous chapters, there's no doubt that all the purposes of this M. Sc. thesis and of this project in general have been accomplished.

The analysis of the system degrees of freedom has been carried out successfully as well as the control loops configuration design.

The most substantial part of this study is for sure the dynamic simulation of plant subsections; simulation results have been reported time after time in chapters 5 and 6 and they have been qualitative and quantitative analyzed.

From a qualitative point of view it is possible to clearly state that the simulation is stable and accomplished in all its aspects: pressure nodes and profiles along the whole plant are coherent; continous operations is ensured; hazardous conditions are never reached in any equipment of the plant and the control system is reliable and performant.

From a quantitative point of view compositions and flowrates have been evaluated and commented. In solvent recovery column section, they were perfectely coherent with steady state simulations with PRO/II; in purification section only few differences can be detected, mainly related to products present in traces due to the modification in thermodynamic package and to the fact that flow summaries have been reported after a relative short time of steady state conditions.

Startup and shutdown procedures result effective and stable; steady state and shutdown of the plant are attained in a relative short time.

The responses to perturbation are controlled pretty good and, wherever recovery ratios show oscillating trends, this is due to the flowrates adjustments not to drastic compositions variations, i.e. products purity losses. Feed flowrate modifications of the products purification section show proportional flowrates variations with no considerable changes in compositions, as expected. Feed water composition modifications show coherent flowrate changes of water rich or poor streams as well.

Therefore the design thesis [18] and the whole project results are validated by this dynamic simulation. A further dynamic optimization considering out of spec products during startup procedures and in case of perturbations as cost items could be the next step before taking into account the concrete chance to start developing biorefineries configurations based on this project for the production of the involved chemicals.

With this M. Sc. thesis the feasibility assessment of the proposed design configuration can be considered definetely accomplished.

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