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Self-Optimizing Control of a Gas Oil Hydrodesulfurization Plant

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ABSTRACT

This work aims to give an appropriate introduction to an innovative technique of plantwide control, based on economics, recently developed by Professor Sigurd Skogestad of NTNU University of Trondheim (NOR); and then its application to a well known post-treatment process: a hydrodesulfurization process plant. The procedure is note as “self-optimizing control” and it is based on the search of some variables which kept near to their optimal point can give acceptable results without too much loss. With this project the main steps of the procedure will be analyzed and then applied and finally a control structure will be developed, leaving to next work the possibility to increase and amply the choice of different controllers or different value of parameters. The unit plant has been modeled in AspenHYSYS®, starting from different examples found in literature; the same procedure has been followed for the kinetics adopted. This model has been the basis on which test the so-called “self-optimizing control”. The structure has been tested on two main disturbances: feed flow and its composition. This choice has been done in order to make it possible a right approaching to the technique, because even if it its simplicity is its main characteristic, it is worth to note that its application on a whole unit plant it is still at the beginning. This approach to plantwide control is innovative because it can give the right orderliness and a mental guideline to follow when whoever starts thinking about the control everything: from the single equipment till the complete plant.

Starting from the choice of the main variables to control the procedure ends with the selection of the appropriate control structure, whose nature remains free to be chosen among the different ones present in literature.

Reasonable results have been obtained from the point of view of sulfur removed, in line with what European Commission decided and at steady state conditions. However even if the dynamic simulation has been found to be correct, the dynamic behavior of the plant is difficult to control and some numerical problems gives the wrong way to the system.

ABSTRACT

Questo lavoro di tesi prevede l'utilizzo di una nuova procedura tecnica di controllo dell'impianto basata fondamentalmente sull'economia dello stesso. Questo approccio avveniristico sviluppato negli ultimi anni dal Professor Sigurd Skogestad dell'Università NTNU di Trondheim (Norvegia), il cosiddetto "self-optimizing control" prende il nome da alcune variabili peculiari sulla cui ricerca si basa essenzialmente la procedura stessa: "self-optimizing variables" il cui controllo se effettuato efficacemente e con logica permette di mantenere il sistema su valori vicini all'ottimo di normale funzionamento senza di conseguenza avere perdite dal punto di vista economico.

La struttura del progetto ha previsto differenti fasi: dal periodo presso l'Università di Trondheim fino al successivo completamento preso il Politecnico di Milano.

L'articolazione del lavoro di tesi invece segue una svolgersi più regolare, attraverso una breve introduzione all'argomento si passa alla storia del processo (tornato di recente in auge viste le sempre più restrittive norme in materia di inquinamento e di emissioni nocive da parte di autoveicoli/industrie stesse); quindi viene affrontata il processo di modellazione a partire da differenti esempi tratti dalla letteratura, dai quali si studia la collocazione dei differenti dispositivi in campo e i valori delle grandezze in gioco. Seguendo la presentazione di diversi lavori sull'argomento dell'idrodesolforazione delle cariche di gasolio e altre più pesanti si prendono in atto differenti articoli trattanti le cinetiche di questo processo. Vengono selezionate tre cinetiche per l'occasione e ne vengono vagliate le caratteristiche e soprattutto la riproducibilità di risultati coerenti con quanto richiesto da un siffatto impianto; verificate anche dal punto di vista della disponibilità di tali dati in quanto è stato possibile sperimentare direttamente l'impossibilità di fruire di alcune cinetiche in quanto coperte da brevetto e parte di un pacchetto commerciale di simulazione (nel caso specifico la cinetica proposta da Gilbert Froment e non più disponibile a detta dello stesso insigne Professore). Selezionata la cinetica si è passato alla modellazione reale dell'impianto, andando a simularlo attraverso AspenHYSYS®, noto pacchetto commerciale di simulazione della AspenTech®. Attraverso successive semplificazioni dell'impianto si è giunti ad una configurazione stabile in grado di predire i risultati ricavati dagli articoli precedenti. Il modello è stato testato e successivamente si passati alla vera e propria procedura per il controllo.

L'approccio proposto dal Professor Sigurd Skogestad è stata quindi spiegata passo a passo e illustrata attraverso l'esemplificazione dei passaggi e il confronto con altri significativi sistemi di controllo sulla base dei quali in parte è stato costruito quest'ultimo. I differenti

metodi matematici adottati sono stati integrati con materiale ad hoc e il tutto è stato quindi applicato al modello e nel dettaglio al processo: brevemente il modello è stato sottoposto a differenti cicli di ottimizzazione atti ad ottenere i valori ottimali del processo che saranno quindi i set-point da adottare nei controllori, sulla base dei “gradi di libertà” del sistema in esame stesso; terminata questa prima fase si è indagato a fondo sulle “self-optimizing varibles” da controllarsi insieme ai suddetti gradi di libertà per incrementare l’efficacia e la robustezza del controllo.

Terminata la scelta delle variabili supposte essere le migliori per il controllo dunque, il tutto è stato implementato in una struttura di controllo e questa è stata verificata per verificarne l’efficacia; i risultati della simulazione in dinamico sono quindi stati riportati per completezza di informazione.

È stato possibile verificare dunque la possibilità di applicazione di questa procedura su un impianto a livello industriale, pur rimanendo vero il fatto che notevoli semplificazioni sono state effettuate in modo tale da permetterne la realizzazione pratica. Questo risulta essere un notevole spunto in vista di miglioramenti e quindi l’introduzione di sistemi di controllo più articolati quali MPC o se la potenza di calcolo dovesse consentirlo, nel caso specifico la velocità di calcolo, l’implementazione di una RTO. La maggior parte dell’attenzione è stata volta n ella ricerca e nello studio del processo.

Chapter 1

Motivations, introduction and approach of the hydrodesulfurization process

“*One*”
U2

1.1 INTRODUCTION

The automotive industries has today the necessity to face and try to satisfy the environmental prescriptions in terms of human health and reducing air pollution.

Even if in the last decades there have been a wide development focused to new energy solutions (i.e. hydrogen cars, solar cells, PEM and electric cars more in general); we have not to forget that the greatest part of the automotive industry is covered by gasoline and diesel cars. For this reason we have not to surprise if the major Environmental Agencies in whatever country aim to reduce the pollutants coming from the exhaust gases of these two type of engines. In this sense we mean the engine that works following the Otto’s cycle, and that is fed by gasoline and the Diesel’s cycle which uses for its right working a mixture of higher weighted hydrocarbons (i.e. paraffin oils) compared with Otto’s fuel.

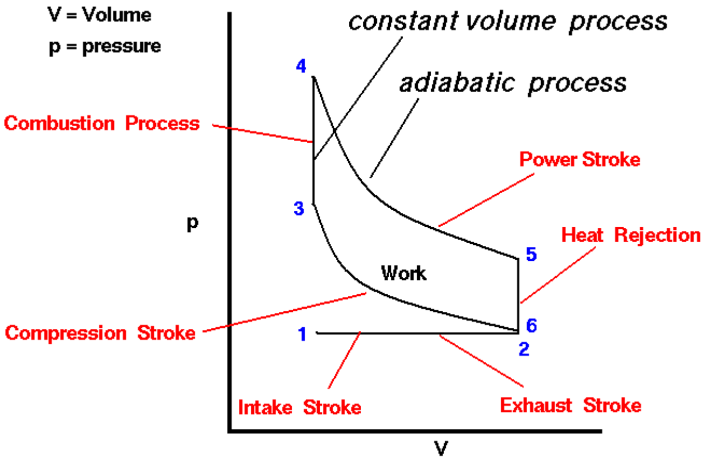

Figure 1: ideal Otto cycle, NASA, *Otto Cycle*,http://www.grc.nasa.gov/WWW/k-12/airplane/otto.html, accessed on March 2014

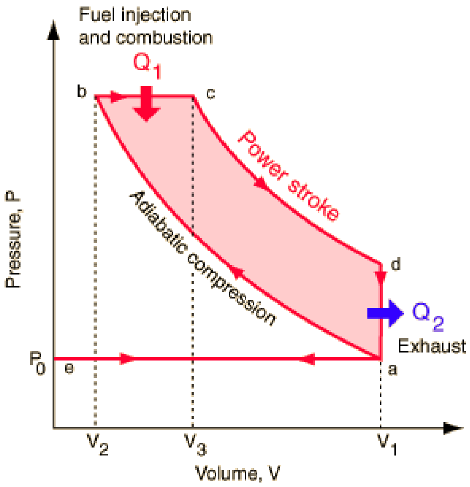

Figure 2: ideal Diesel, HYPERPHYSIC, *Diesel Cycle*, http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/imgheat/diescyc.gif, accessed on March 2014

In general for what concerns the distribution of this two main groups of cars we have to note that in the last years diesel engines have raised their spread[1], losing its natural tiling to the thinking of it as only truck engine; and this because of the improvements of the diesel engines performances (e.g. the introduction of the Common Rail®[2] technology and Multijet® system[3]) and reduced consumes. Anyway a trend line can be traced, highlighting that gasoline cars are the most used for civil and private transportation, while the diesel engines are used for power plants, energy supply and naval transportations.

Considering all these application we can note how really is spread this typology of engine.

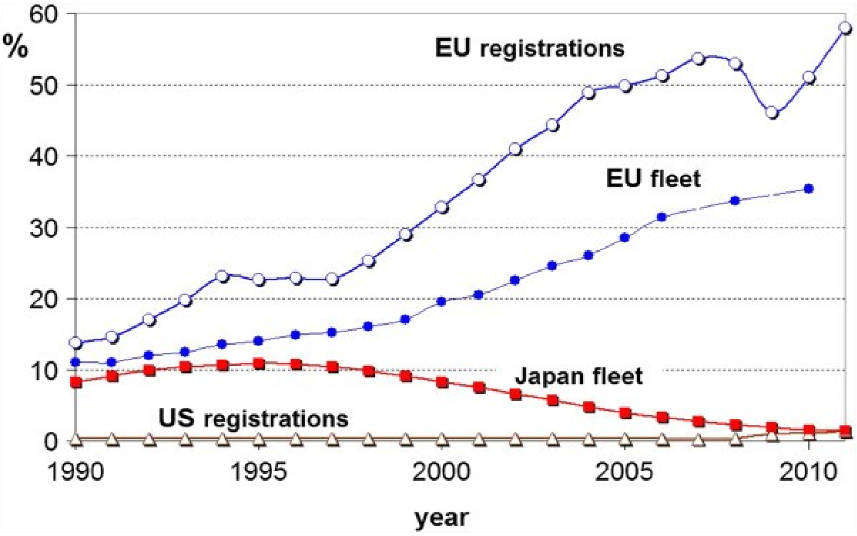

Figure 3: Diesel car penetration in major world markets, **MICHEL CAMES, ECKARD HELMERS**, ***Critical evaluation of the European diesel car boom - global comparison, environmental effects and various national strategies*, *Environmental Sciences Europe* 2013,** 25:**15**

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[1] MICHEL CAMES, ECKARD HELMERS, *Critical evaluation of the European diesel car boom - global comparison, environmental effects and various national strategies*, *Environmental Sciences Europe* 2013, **25:**15

[2] FIAT, *Common Rail*,http://www.fiat.it/fiatpedia/glossario/common-rail, accessed on March 2014

[3] *Ibidem*

Consequently it is obvious the reason that pull the most important environmental institutions to take care and control the emission of diesel engines.

How could it be possible to reduce the noxious pollutant from these engines? It depends. There are several ways to act in this sense; but first of all it is necessary to distinguish between two groups of treatment: pre-treatment and post-treatment. The difference lies where the process studied and applied, works. Basically all pre-treatment aims to reduce upstream the presence of pollutant, letting the post-treatment to keep on reducing them till the desired values; for what concerns instead the post-treatment they work properly downstream with the use of post-combustion system or particulate filter in order to mechanically reduce the non-desired combustion byproducts.

It is clear that the best result is achieved with both the system that act concurrently; but while post-treatment can be mounted directly on the device uses the diesel engine, a pre-treatment has is goal on the fuel fed and for this reason we have to operate on large scale and particularly on a unit of a plant.

Among the major cause of pollution and damage to human health there are the so-called combustion oxides, i.e. Co_x, NO_x and SO_x. Where the "x" means the generic number of oxidation where the oxide could be present.

These kind of oxides are noxious for their effects both on the environment and the human health. Especially the sulfur oxides are responsible of the so called "acid rains[4]" and some human pathologies on lung[5] and respiratory system.

This is a strong motivation to the will of reduce this kind of emissions. Diesel fuel specifications are being tightened throughout the world as part of efforts to improve air quality. At the same time, the demand for diesel is increasing necessitating use of lower quality feedstocks. All of this results in a great burden on refineries, which have to face this important task. New hydrotreating capacity and revamp of existing facilities are needed to meet the future diesel specifications and even if today's emphasis is on the reduction of sulfur content, it is not strange that in the next future the focus will be set to all the other toxic and noxious compounds presents in diesel exhaust gases.

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[4] $SO_2 + H_2O \rightarrow H_2SO_3$
$SO_3 + H_2O \rightarrow H_2SO_4$

[5] IARC, *IARC: DIESEL ENGINE EXHAUST CARCINOGENIC*, http://www.iarc.fr/en/media-centre/pr/2012/pdfs/pr213_E.pdf, accessed on March 2014

There are different normative dealing with the maximum sulfur content in the emissions of car vehicles; different from country to country with a common intent to unify them in the next future.

The Environmental Protection Agency (EPA) has proposed new guidelines to limit sulfur in diesel fuels from low sulfur diesel (LSD) of 500 [ppm wt/wt] to ultra low sulfur diesel (ULSD) of less than 15 [ppm wt/wt] in 2010[6]; in California, transit bus fleets must use a 15 [ppm wt/wt] sulfur diesel by October, 2002 and it is expected that this limit will be extended to more fleets shortly afterward. The same procedure has been proposed by European Commission[7], while the same path is going to be followed by other legislations, introducing, moreover, limitations on aromatic content in diesel fuels to less than 20 % in the near future.

In the EU, current diesel specifications (2000) limit sulfur is to a maximum of 350 [ppm wt/wt]. By the year 2005, the sulfur content *must* be reduced to 50 [ppm wt/wt], and diesel containing a maximum of 10 [ppm wt/wt] must also be available. By the first of January of 2009 all on-road diesel in EU would have a specification of maximum 10 [ppm wt/wt] sulfur. Another example in Europe in Germany 10 [ppm wt/wt] sulfur diesel will be mandatory from 2003.

In Japan, there are the more severe restrictions and the government is considering plans to reduce sulfur content to below 10 [ppm wt/wt] by 2008. Another interesting point is that the demand for diesel is growing in both Asia and Europe: we can see it clearly for what concerning the Asia Pacific demand which has remained still from 1996-1998, while it has raised to 4.6% in 1999. Such a request is forecast to be equivalent of a 5-8% per year.

In Europe has been quite constant and fixed at about 1.2% per annum[8].

In parallel we have a decreasing demand for some fractions not more necessary for the sustaining of the economy (i.e. home heating oil and fuel oil cutter stocks). That is index of an evolution in term of quality and increasing in specification for everyday's use.

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[6] Kim G. Knudsen and Barry H. Cooper, Ultra Deep Desulfurization of Diesel: How an understanding of the underlying kinetics can reduce investment costs, Practical Advances in Petroleum Processing, pp 297-316, Springer 2006

[7] http://ec.europa.eu/italia/attualita/archivio/trasporti_energia/11078bab270_it.htm

[8] *Ibidem* [6]

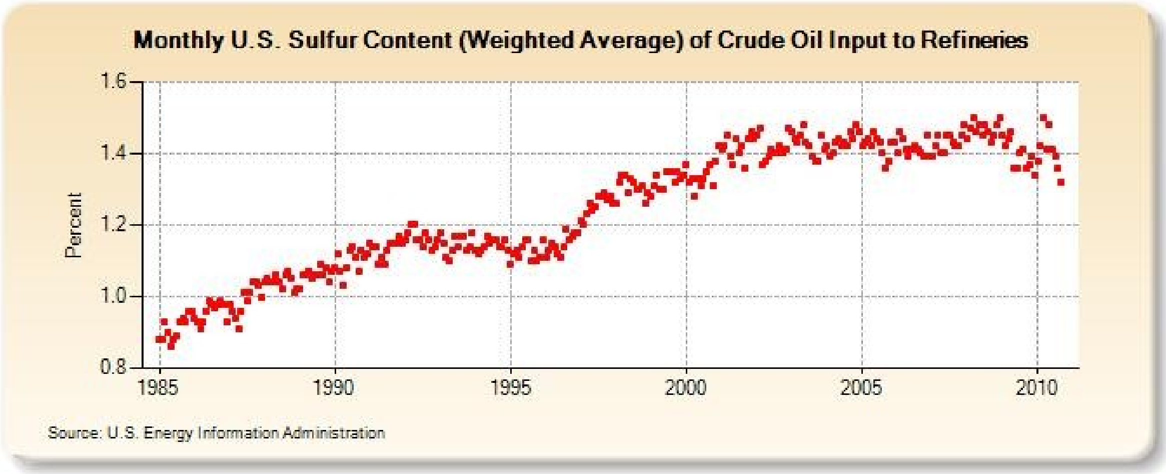

Figure 4: sulfur content of crude oil to refineries, EIA, http://www.eia.gov/, accessed on March 2014

We have to note that a reduction in aromatic content is useful first of all to decrease gas emission (hydrocarbons and particulate matter), to improve the cetane index (i.e. the equivalent of the octane number for gasoline) and decrease the density of the fuel. As explained before it is expected that ultra deep hydrodearomatization (HDA) and hydrodesulphurization (HDS) of gas oils may be considered necessary in order to satisfy the market and environmental requirements.

1.2 THE APPROACH

It is clear that to make possible this drastic reduction and then accomplish the new environmental requirements, it is necessary the removal of refractory sulfur aromatics compounds. It is note anyway that these hindered compounds are remaining in the diesel fuel after the sulfur reduction to 500 [ppm wt/wt] level by conventional HDS process because of the inhibiting effects of co-existing polyaromatics and nitrogen compounds in the feed, responsible for a H_2 consumption (even if it is necessary to specify that those compounds are more stable to bland operative conditions); moreover we have to consider that the kinetics of deep desulfurization is governed by the extent to which desulfurization (HDS) occurs by direct sulfur extraction, or by hydrogenation of the sulfur -containing molecule, and that the presence of H_2S is an inhibiting factor on the overall reaction of hydrodesulfurization.

However it is more difficult for the refineries to achieve less than the 15[ppm wt/wt] (ULSD) sulfur specification with the currently employed catalysts and use of typical operating conditions.

To increase this result, many aspects such as the catalysts, process variables, and the quality of feedstock could play a major role on the shift from normal desulfurization (LSD) to ultra deep desulfurization (ULSD) of diesel feeds.

It is also clear that the beginning sulfur content is function of the coming crude oil, as we can observe in Figure 5:

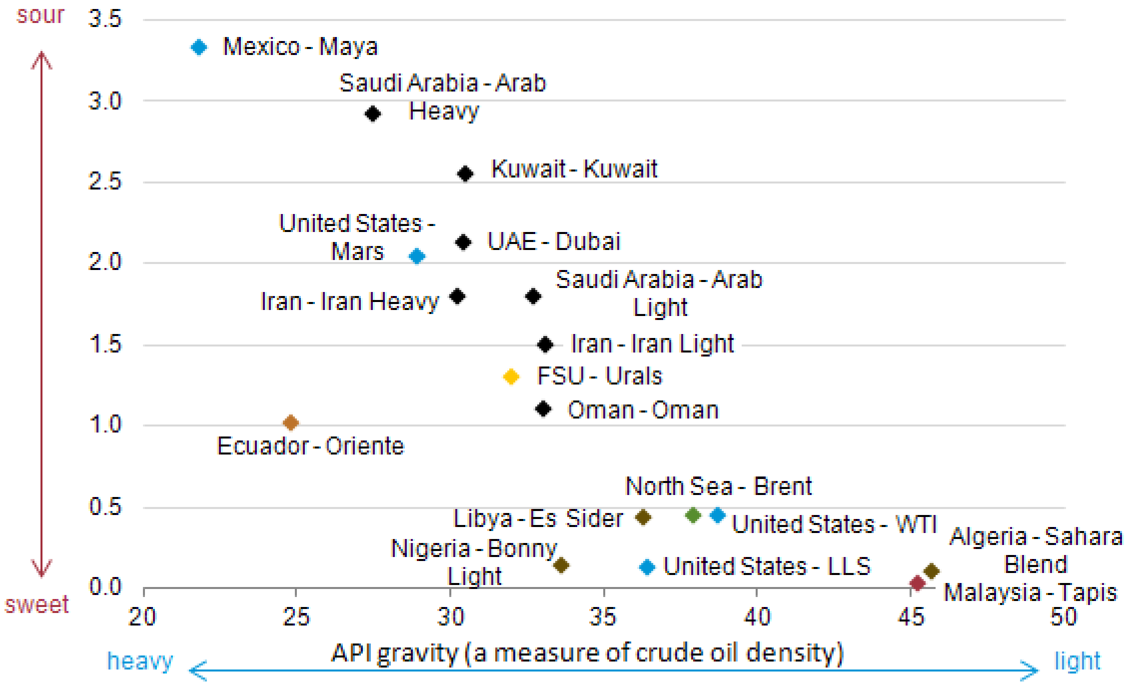

Figure 5: density and sulfur content of selection crude oils, EIA, http://www.eia.gov/, accessed on March 2014

The shift from LSD to ULSD with low aromatics content is a very convoluted technical issue; and it is clear that any improvements could be obtain working concurrently by taking into consideration both catalyst and process issues (HDS and HDA of diesel fuels requires either severe process conditions such as temperature, pressure and space velocity or the use of novel effective catalysts). It is well known that HDS reactions at high reaction temperature will result in higher rates, but the same increasing is responsible for the coke formation on the catalyst, which in turn tends to deactivate the catalyst rapidly leading in this way a lower reaction rate; moreover it is note that using low Liquid Hourly Space Velocity (LHSV, $[h^{-1}]$) will result in decreasing hydrotreating efficiency, because of the scarce turbulence that will develop (we have to remember that a typical HDS reactor consists in a trickle bed system where there is the concurrent presence of a liquid phase, i.e. the charge feed, a solid phase, that is the catalyst, and a gaseous one, obviously the hydrogen). Hence, deep understanding of chemistry involved in removing the sulfur and the influences of the important operating conditions are extremely necessary. And more necessary is an optimization of the above-mentioned variables. This is the real aim and goal of whatever approach we want to adopt.

In this perspective, this work aims to give its support giving a clear and schematic procedure about how to optimize, or better “self optimize” a hydrodesulfurization unit in order to see what are the most important variables to take into consideration to follow the specification imposed (accomplish them) and to make possible to provide a system able to give a product pre-treated with a sulfur content as low as it could be possible to post-treat till the desired specification.

This project is dealing with a common unit of hydrodesulfurization for which it is investigated the possibility to obtain a simple and robust control structure based basically on economics; that is done facing the problem on the basis of the so-called plantwide control, adopting a procedure that has been developed for the last 25 years by Professor Sigurd Skogestad of NTNU – Norwegian University of Science and Technology, with whom I’ve dealt with the problem.

It will follow the presentation of the project, specifying the procedure adopted and the plant scheme studied and used to simulate the behavior of the unit. A comparison with literature data has validate the correct simulation of this modeled system. Both kinetics and example feed have been searched and taken from literature; hence studied, they have been implemented in a simulated model built with AspenHYSYS® suite. In this way the process has been understood and verified at steady state conditions (necessary condition to implementation of the control procedure) and then controlled dynamically.

Here it will follow an explanation about the procedure and its precursors and then the real application of it to the above mentioned process, giving an example of application.

Chapter 2

The hydrodesulfurization process: history, scheme and equipment

"Show me the way"
Peter Frampton/The Cranberries

2.1 INTRODUCTION

Hydrotreating is a very general term which can be applied in all processes where there is a feedstock which is enhanced in some manner by passing it over a catalyst in the presence of hydrogen. Meant in this sense the terms hydrotreating, hydroprocessing, hydrocracking, and hydrodesulfurization are used rather loosely in the industry because, in the processes hydrodesulfurization and hydrocracking, cracking and desulfurization operations occur simultaneously and it is relative as to which predominates.

Generally in the process, there is essentially no reduction in molecular size of the feed. The objective has most often been to reduce the sulfur content of the feed (due to environmental restrictions or in order to grant better performance in some oil or lubricants); but it's also practiced

to reduce nitrogen content, saturate olefins, and to reduce aromatics, HDN and HDA respectively. In particular the process of hydrodesulfurization (HDS process) has received in the last year a greater consideration due to sulfur impact on environment (eliminate pollutants) especially for what concerns diesel fuel.

In this process sulfur is the easiest to remove, followed by nitrogen, and the aromatics. Saturation of olefins overlaps sulfur and nitrogen.

2.2 HISTORY

Among the petroleum refining processes, hydrotreating and hydrocracking are the oldest catalytic ones[9]. Hydrotreating has its origin in the hydrogenation work done by Sabatier and Senderens, who were the first of all that in 1897 published their discovery regarding

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[9] DONALD ACKELSON, *UOP UNICRACKING PROCESS FOR HYDROCRACKING*, in Robert A. Meyers (ed.), *Handbook of Petroleum Refining Processes*, 3rd ed. (2003)

unsaturated hydrocarbons; and in particular the possibility that they could be hydrogenated in the vapor phase over a nickel catalyst. After few years, in 1904, Ipatieff understood that that reaction was directly connected to hydrogen partial pressure and he noted that it could be extended in the range of feasible hydrogenation reactions by the introduction of elevated hydrogen pressures.

We have to consider that at the time, the progress of the automobile industry was expected to entail a considerable increase in the consumption of gasoline; and this was the context that led to the experimental work by Bergius[10], started in 1910 in Hanover, Germany who sought to produce gasoline by cracking heavy oils and oil residues as well as converting coal to liquid fuels. That was the first attempt to try to convert a solid fuel in a liquid one and it is clear the reason of that work: a liquid fuel could be easier moved, transported and then fed and used for Benz engine. He realized that to remedy the inferior quality of the unsaturated gasoline so produced (with this Coal To Liquid precursor process), the hydrogen removed mostly in the form of methane during the cracking operation has to be replaced by addition of new hydrogen. In this way, formation of coke was avoided and the gasoline produced was of a rather saturated character. Parallel with this saturation of olefin to paraffin Bergius also noted that the sulfur contained in the oils was eliminated for the most part as hydrogen sulfide, H_2S. Instead of nickel as catalyst, ferric oxide was used in the Bergius process to remove the sulfur. Actually, the ferric oxide and sulfides formed in the process acted as catalysts, though the activity was very poor (ferric oxide is always present in part in all processes as byproduct of corrosion of the equipment). The first plant for hydrogenation of brown coal was put on stream in Leuna Germany in 1927 where they were employed to convert lignite to gasoline and subsequently to treat petroleum residues to distillable fractions. And the past large scale industrial development of hydrogenation in Europe, particularly in Germany, was due entirely to military considerations: Germany used hydrogenation extensively during World War II to produce gasoline: 3.5 million tons were produced in 1944; we have to remember that any availability of gasoline coming from distillation of a crude or any petroleum feed was to consider impossible due to military accordance. So the only way to become self-sufficient from the point of view of

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[10] Friedrich Karl Rudolf Bergius (born October 11, 1884, Goldschmieden, near Breslau, Germany [now Wrocław, Poland]—died March 30, 1949, Buenos Aires, Argentina), German chemist and corecipient, with Carl Bosch of Germany, of the 1931 Nobel Prize for Chemistry; http://www.britannica.com/EBchecked/topic/61797/Friedrich-Bergius, accessed on February 2014

the fuel production was to exploit the natural sources of their land, that means to use coal from the inner region of Germany (e.g. Saar).

The first commercial hydrorefining installation in the United States was at Standard Oil Company of Louisiana in Baton Rouge in the 1930s. Following World War II, growth in the use of hydrocracking was slow. These plants were developed by Humble Oil and Refining Company and Shell Development Company, though there was considerably less dependence on hydrogenation as a source of gasoline. Moreover it has to be concerned that the availability of Middle Eastern crude oils reduced the incentive to convert coal to liquid fuels, and new catalytic cracking processes proved more economical for converting heavy crude fractions to gasoline. Even though hydrogenation has been of interest to the petroleum industry for many years, little commercial use of hydrogen-consuming processes has been made because of the lack of low-cost hydrogen. In a common plant for any hydrotreatment we have to note that the major voice to take into account for an economic evaluation of the plant costs is the price of hydrogen; and in that period there weren't sufficient alternative sources available to feed hydrogen at low price.

That changed in the early 1950s with the advent of catalytic reforming which made available by-product hydrogen. That brought up an extensive and increased interest in processes that will utilize this hydrogen to upgrade petroleum stocks. Indeed in the 1950s, hydrodesulfurization and mild hydrogenation processes experienced a tremendous growth: this was due to large availability of great quantities of by-product hydrogen were made from the catalytic reforming of low-octane naphthas to produce high-octane gasoline. The first modern hydrocracking operation was placed on-stream in 1959 by Standard Oil Company of California. The unit was small, it was producing only 1000 (BPSD)[11]. As hydrocracking units were installed to complement existing fluid catalytic cracking (FCC) units, in the refineries the hydrocracking process was quickly recognized to have the flexibility to produce varying ratios of gasoline and middle distillate. In this sense there has been rapid growth in U.S. hydrocracking capacity from about 3000 BPSD in 1961 to about 120,000 BPSD in 1966.

Between 1966 and 1983, U.S. capacity grew eightfold, to about 980,000 BPSD. Outside the United States, early applications involved production of liquefied petroleum gas (LPG) by hydrocracking naphtha feedstocks. The excellent quality of distillate fuels produced

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[11] barrels per stream day: a measurement used to denote rate of oil or oil-product flow while a fluid-processing unit is in continuous operation (abbreviated BSD). McGraw-Hill Dictionary of Scientific & Technical Terms, 6E, Copyright © 2003 by The McGraw-Hill Companies, Inc.

when hydrocracking gas oils and other heavy feedstocks led to the choice of the hydrocracking process as a major conversion step in locations where diesel and jet fuels were in demand. Interest in high-quality distillate fuels produced by hydrocracking has increased dramatically worldwide. As a result of the enormous growth of hydrotreating, as of the beginning of 2001, there were more than 1,600 hydrotreaters operating in the world with a total capacity in excess of 39,000,000 [B/day] (4,800,000 [Mtonn/day]). And as of 2002, more than 4 million BPSD of hydrocracking capacity is either operating or is in design and construction worldwide.

In general, *hydrotreating* refers to a relatively mild operation whose primary purpose is to saturate olefins and it will refer also to reduce the sulfur and/or nitrogen content (and not to change the boiling range) of the feed. *Hydrocracking* instead refers to processes whose primary purpose is to reduce the boiling range and in which most of the feed is converted to products with boiling ranges lower than that of the feed. It means that the operation is conducted in more severe operative conditions. Hydrotreating and hydrocracking set the two ends of the spectrum and those processes with a substantial amount of sulfur and/or nitrogen removal and a significant change in boiling range of the products versus the feed are called hydroprocessing in the wider sense of the term.

A mentioned before all these processes are processes whose aim is to catalytically stabilize petroleum products and/or remove objectionable elements from products or feedstocks by reacting them with hydrogen. When we speak about stabilization, we usually mean all reactions involved to convert unsaturated hydrocarbons such as olefins and gum-forming unstable diolefins to paraffins. The principal elements removed with this process (hydrotreating in general) include sulfur, nitrogen, oxygen, halides, and trace metals; and in this sense is common use to indicate the process as HDS (i.e. HydroDeSulfurization), HDN (that is HydroDeNitrification) and so on.

For what concerns hydrotreating, it is a versatile treatment that can be applied to a wide range of feedstocks, from naphtha to reduced crude. What change from feedstock to feedstock is the amount of required hydrogen, the composition of the catalyst involved in the reaction and the severity of the overall operating conditions. Moreover in the last decades, to meet environmental regulations[12], that are becoming more stringent every year,

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[12] http://ec.europa.eu/environment/air/quality/legislation/existing_leg.htm, seen on March 2013

it also may be necessary to hydrogenate aromatic rings to reduce aromatic content by converting aromatics to paraffins; in particular the major attention is focused on some delicate compounds note for their proved damage on human health: the so-called PAH, i.e. Polycyclic Aromatic Hydrocarbon[13, 14].

Although there are about 30 hydrotreating processes available for licensing[15], most of them have essentially the same process flow for a given application. There is a common way to operate and treat the feed fed to the plant so in general a common explanation can be done about it. We just remember that cause the extreme variation range of feedstock, it will be possible to find some differences between the operative conditions and the catalyst adopted during the treatment.

2.3 THE PROCESS

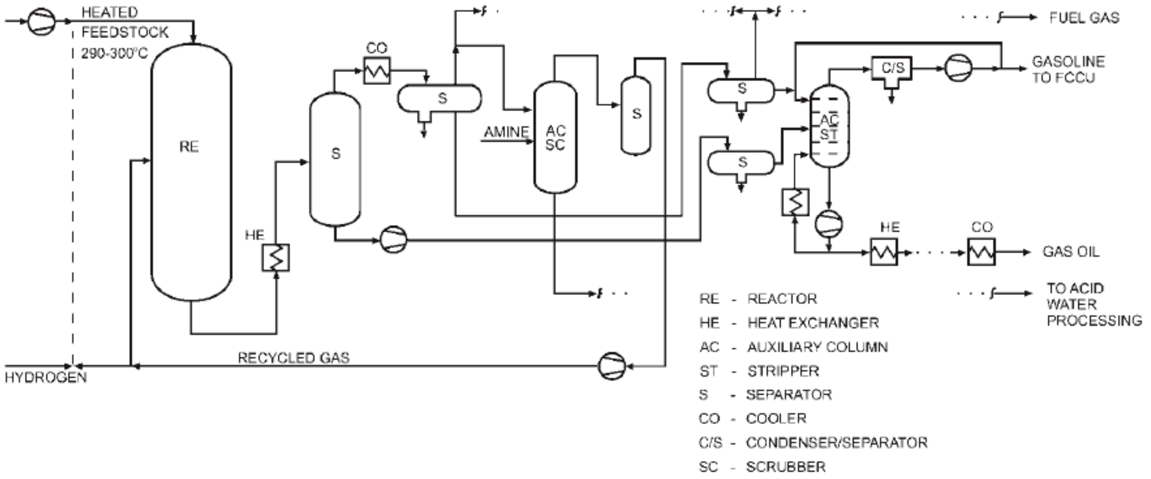

Figure 6: typical process plant scheme; OZREN OCIC, Oil Refineries in the 21st Century: Energy Efficient, Cost Effective, Environmentally Benign, Wiley 2005

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[13] UNITED STATES ENVIRONMENTAL PROTECTION AGENCY, OFFICE OF ENVIRONMENTAL INFORMATION, *Emergency Planning and Community Right-to-Know Act – Section 313: Guidance for Reporting Toxic Chemicals: Polycyclic Aromatic Compounds Category,* EPA 260-B-01-03, Washington, DC, August 2001

[14] http://nepis.epa.gov/Exe/ZyNET.exe/900B0H00.TXT?ZyActionD=ZyDocument&Client=EPA&Index=2000+Thru+2005&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A\zyfiles\Index%20Data\00thru05\Txt\00000011\900B0H00.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h|-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=p|f&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=1&SeekPage=x&ZyPURL, seen on March 2013

[15] JAMES H. GARY, GLENN E. HANDWERK, *Petroleum Refining Institut Français du Pétrole*, 4th ed., CRC Press, 2001

As noted previously hydrocracking is one of the most versatile of all petroleum refining processes and as we refer in general to hydrocracking we have to understand that in this sense any fraction from naphtha to non distillables can be processed to produce almost any desired product with a molecular weight lower than that of the chargestock. At the same time that hydrocracking takes place, sulfur, nitrogen, and oxygen are almost completely removed, and olefins are saturated so that products are a mixture of essentially pure paraffins, naphthenes, and aromatics. In this way the severity of operative conditions in this process make possible the parallel reaction of cracking of the charge, lumping the feed into different product with a obvious different market price; then it is possible to reduce impurities present in the chargestock in form of sulfur, nitrogen, oxygen and metal compounds. It is specified that they are impurities cause the toxicity of the above mentioned compound for human health and their impact on the environment. With reference to Table 1, it is possible to illustrate the wide range of applications of hydrocracking by listing typical chargestocks and the usual desired products.

As possible to see the first eight chargestocks are virgin fractions of petroleum crude and gas condensates; while the last four are fractions produced from catalytic cracking and thermal cracking.

Table 1: applications of Unicracking Process

Chargestock	Products
Naphtha	Propane and butane (LPG)
Kerosene	Naphtha
Straight-run diesel	Naphtha and/or jet fuel
Atmospheric gas oil	Naphtha, jet fuel and/or distillates
Natural gas condensates	Naphtha
Vacuum gas oil	Naphtha, jet fuel, distillates, lubricating oils
Deasphalted oils and demetallized oils	Naphtha, jet fuel, distillates, lubricating oils
Atmospheric crude column bottoms	Naphtha, distillates, vacuum gas oil and low-sulfur residual fuel
Catalytically cracked light cycle oil	Naphtha
Catalytically cracked heavy cycle oil	Naphtha and/or distillates
Coker distillate	Naphtha
Coker heavy gas oil	Naphtha and/or distillates

From: DONALD ACKELSON, *UOP UNICRACKING PROCESS FOR HYDROCRACKING*, in Robert A. Meyers (ed.), *Handbook of Petroleum Refining Processes*, 3rd ed. (2003)

All these streams are being hydrocracked commercially to produce one or more of the products listed; and the reason that drives this decisions is purely economic, due to the major added value that some products have respect with other ones especially for the feedstock. This flexibility gives the hydrocracking process a particularly important role as refineries attempt to meet the challenges of today's economic climate. The combined influences of low-quality feed sources, capital spending limitations, hydrogen limitations, environmental regulatory pressures, and intense competition have created a complex optimization problem for refiners.

Hydrotreaters, with this term we mean the reactor able to conduct all the above mentioned processes, are designed for and run at a variety of conditions depending on many factors such as type of feed, desired cycle length, expected quality of the products (we have in fact seen a brief explanation of the different charge fed to this process), but in general they will operate at the following range of conditions:

- LHSV: from 0.2 to 8.0
- H_2 circulation from 300 to 4,000 SCFB (i.e. 50 – 675 [Nm^3/m^3*])
- H_2 Partial Pressure: ranging from 200 to 2,000 [psia] or 14 – 138 [bar]
- SOR temperatures ranging between 550 and 700[°F], that is 290 – 370[°C], with the lower limits representing minimum operating conditions for naphtha hydrotreating (that has the minimum value of temperature) and the higher values showing operating conditions used for hydrotreating atmospheric residues, those are the feedstock which require the most severe condition of treatment.

Until about 1980, hydrotreating was a licensed technology being offered by a fairly large number of companies. In the past 25 years, hydrotreating catalysts have become commodities and the process has been offered without licensing fees.

Except for the cycle dealing with the purification of off-gases and the subsequently purification for the recycle of hydrogen to the reactor, we can simplify the process diagram as follows:

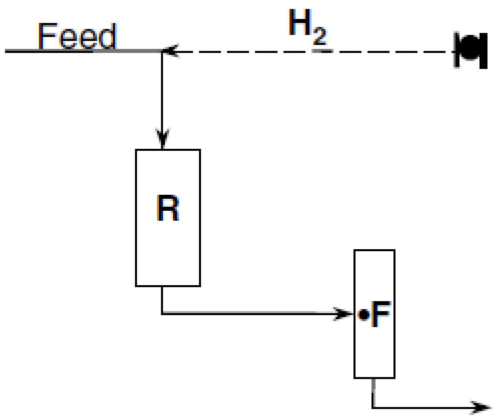

Figure 7: simplified process diagram; DAVID S. J. JONES, PETER R. PUJADÓ, *Handbook of Petroleum Processing Handbook of Petroleum Processing,* Edited by DAVID S. J. “STAN”, 2006

Where with letter “R” we mean the reactor section of the plant and “F” stands for the fractionation part of the same (i.e. product purification, or better all processes involved in the recovery of the non-reacted H_2 through first a flash tanks separator, then through an absorption column with its subsequently recovery loop).

We can better observe what mentioned before, taking into consideration these two zooming in of the previous plant scheme (Figure 1).

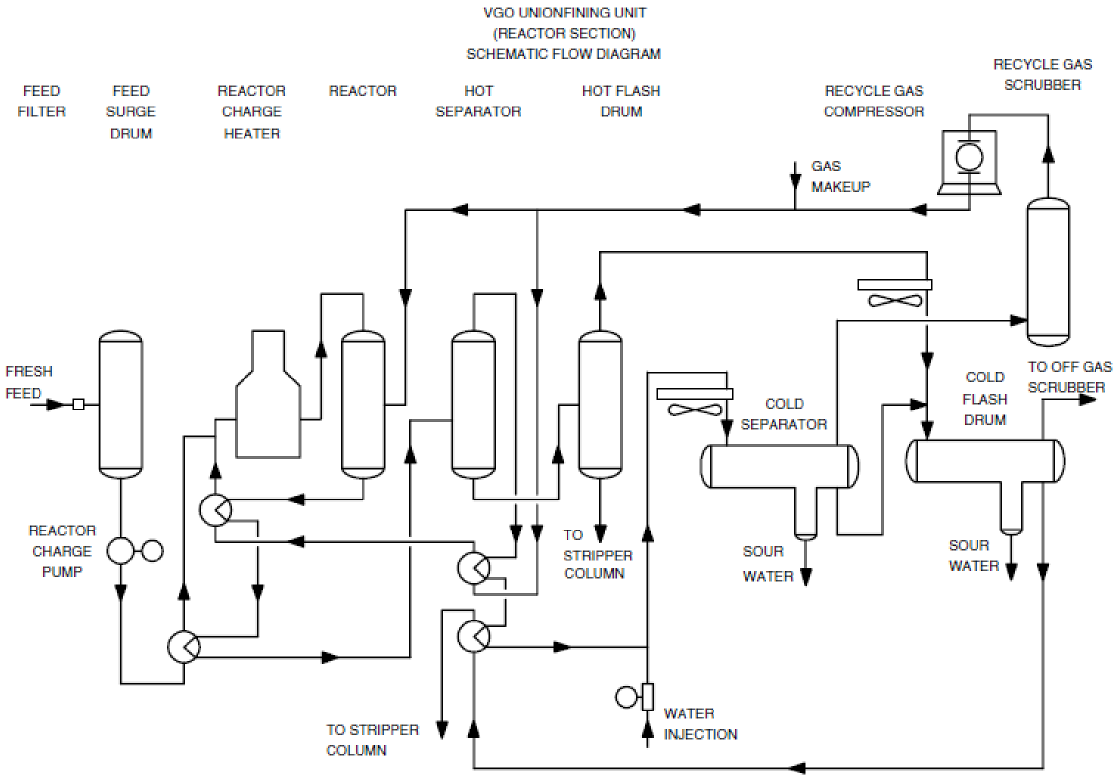

Figure 8: VGO Unionfinning Unit (Reactor Section), DAVID S. J. JONES, PETER R. PUJADÓ, *Handbook of Petroleum Processing*, Springer 2006

Which shows the "R"eactor part of the simplified diagram; and:

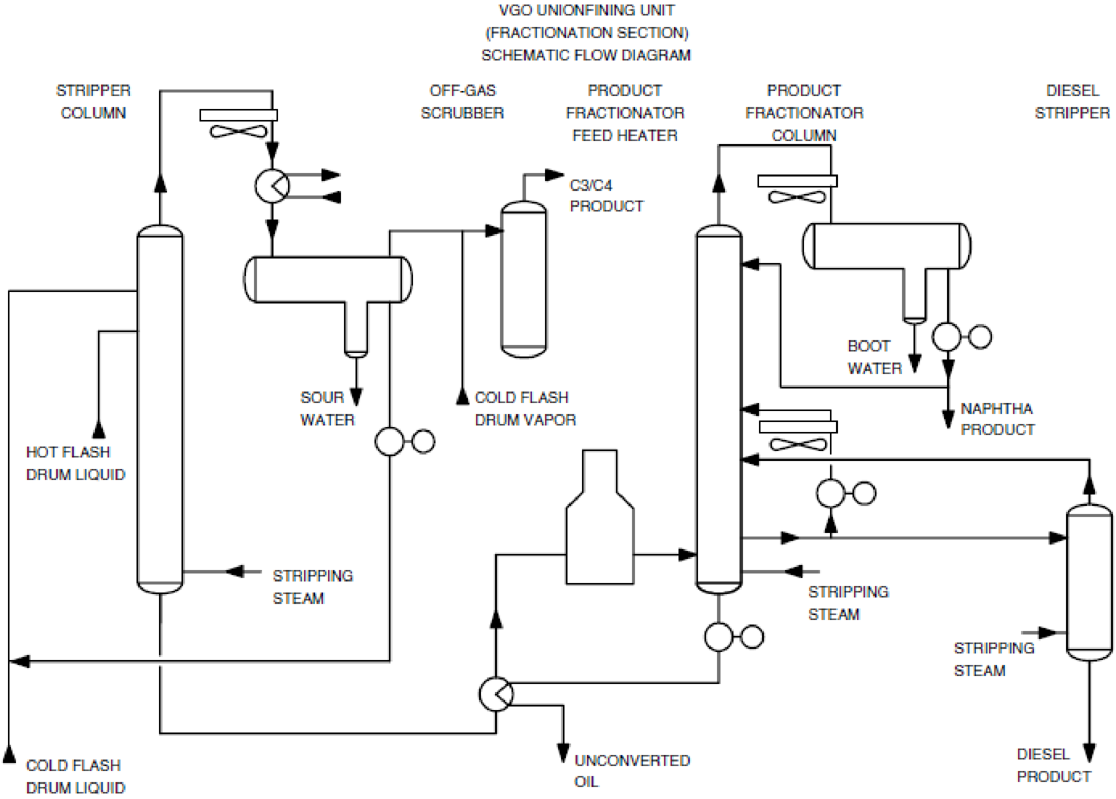

Figure 9: VGO Unionfinning Unit (Fractionation Section), DAVID S. J. JONES, PETER R. PUJADÓ, *Handbook of Petroleum Processing*, Springer 2006

which represents the section dealing with the post proceeding of the product to respect the specification and in order to be able to recover as much as possible the most expensive raw material of all the process: the hydrogen.

Starting from the beginning it will be given a brief explanation of all the process without focalized in particular on a specific kind of process, while considering the most general class of the "hydrotreating process". It obvious it has several different applications (e.g. desulfurization, i.e. our specific case, olefin saturation, denitrogenation, and so on) and is used for a variety of petroleum fractions from naphtha to atmospheric residue. But as hinted previously, practically all units have the same flow scheme: it consists of a higher pressure reactor section and a lower pressure fractionation section as we can observe schematically in Figure 3 – 4.

We start now analyzing the reactor section of the plant proceeding then to the fractionation part of the same.

2.3.1 REACTOR SECTION

This section is what concerns the major pieces of equipment; we have to consider in this part *feed/effluent exchangers*, *reactor charge heater*, *reactor(s)*, *reactor effluent condenser*, *products separator*, *recycle gas compressor* and *make-up gas compressors*.

In some cases it is possible to find several other pieces of equipment: *fresh feed filters*, *reactor effluent hot separator* and *recycle gas scrubber*. Each equipment is typical of a peculiar configuration and is the best solution for that process. If we want to find the above-mentioned equipment it is sufficient to look at Figure 3, i.e. the flow diagram of a reactor section including all the equipment.

Now, to better understand each part of the equipment will be analyzed and briefly explained.

2.3.1a Feed Filters

When we consider a unit that has to deal with a feed, the common way, that is preferred, is feeding the feed directly from an upstream unit to the other one without going through intermediate storage. Why? Because if we use storage facilities, feed filters are, or better should be used in order to make the filter to retain the particulate matter (mostly corrosion products) picked by the feed while in storage: that is a common problem linked directly with the nature itself of the tank/pipeline material.

The feed filters are either automatic backwash filters operating on a pressure drop setting or manual cartridge (disposable) filters. The difference is mainly due to durability of the former respecting with the latter. Moreover the choice of one instead of the other is connected with the process and with the degree of purity that has to be reached before the processing.

2.3.1b Feed/effluent exchangers

Because in a generic plant economics is really important, the major voice in the costs list is due to energy required to heat/cool; the most commonly used is heat recovery scheme, where the reactor effluent in a series of feed/effluent exchangers preheats the reactor charge before entering the reactor charge heater. In this way it is possible to recover as much heat as possible from the heat of reaction, and then avoid to spend money to heat or preheat the charge.

Depending on the configuration of the process scheme liquid feed may be preheated separately with reactor effluent exchange before combining with the recycle gas. Reactor charge heater is responsible to heat together gas and liquid feed to desired reactor inlet temperature. In case of very heavy feed, i.e. the atmospheric residue units, the liquid feed is preheated separately with reactor effluent exchange and only the recycle gas is heated in the heater upstream of the reactor. In this way is possible to decrease viscosity and increase the fluidity of the feed, making possible the subsequent contact between the liquid charge and the gaseous reactant.

2.3.1c The make-up hydrogen system

As specified before hydrogen is one of the most important cost's voice in the economical balance for a hydroprocessing plant. It is then obvious that the make-up hydrogen is really important too. This line is usually obtained from H_2 produced by units of naphtha reforming or manufacturing plants, exempli gratia steam reforming[16].

Considering that hydrogen is usually kept in storage at pressure of 1 to 6 [bar], it is necessary to compress this reactant till the desired operative pressure. In order to achieve this result reciprocating compressors are used; they are known also as piston compressors, i.e. they are a positive-displacement compressor that uses pistons driven by a crankshaft to deliver gases at high pressure. After this procedure make-up gas could be introduced into recycle gas system. This is what regards the make-up gas, but we have to understand that not all the hydrogen fed to the reactor reacts as wanted: is then necessary to recycle some of this.

After the separation of gas and liquid phases in the separator, the gas phase goes to the recycle gas compressor. It is usually sent to an amine scrubber to remove the H_2S produce after the hydrogenation process in the reactor. The recycle gas compressor is often a

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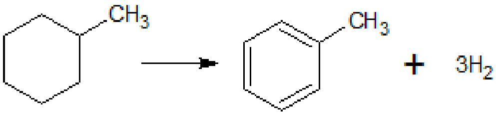
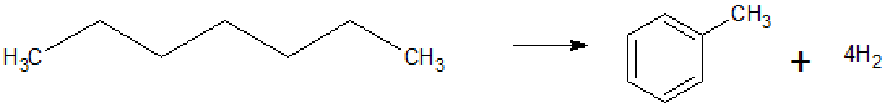
[16] Typical naphtha reforming reactions dealing with the production of H_2 are:

- The dehydrogenation of naphthenes to convert them into aromatics:



- The dehydrogenation and aromatization of paraffins to aromatics (commonly called dehydrocyclization):



While speaking of steam reforming we usually refer to this kind of reaction, characterized by this stoichiometry $C_nH_m + n\ H_2O \leftrightarrow (n + m/2)\ H_2 + n\ CO$

separate centrifugal machine; but it is not strange that it could also be a part of the make-up gas compressors, as additional cylinders. Considering the large volume of gas this kind of compressor is designed in order to pump this volume at a relatively low compression ratio. Any other solution would be unfeasible unless excessive costs. After the reactor, the product is composed by two phases: a liquid phase which contains the wanted product and partially dissolved some gases; and a gaseous one which is rich of H_2S because of the sulfur remove. If hydrogen sulfide remained in the recycle gas stream, it would reduce the hydrogen partial pressure leading then to catalyst's activity suppression. It clear and quite obvious that higher the sulfur content higher the effect on the catalyst, with a more pronounced effect and for the same feedstock, the heavier the cut, the higher the sulfur content is.

In a parallel sense, increasing the recycle gas hydrogen purity will decrease the catalyst deactivation rate. This essentially happens because the sulfur compounds responsible for the catalyst poisoning react with a greater probability and then they do not stay or deposit on the catalyst's surface. Hydrogen purity is then function of the feedstock and type of unit. Some measures those are able to increase the hydrogen content may include hydrogen enrichment and/or membrane separation, which contributes to greater level of purity.

2.3.1d The reactor

As possible to see in the previous diagrams, the feed and the recycle gas (with its make-up if needed) after being preheated till the desired temperature, they can be introduced at the top of the reactor. The system can be assumed as a trickle bed reactor[17] in which the downward movement of a liquid and gas happen over a packed bed of catalyst particles. As the reactants flow downward through the catalyst bed, various exothermic reactions occur and the temperature undergoes to an increase.

Different typologies of reactor design are available; the choice is usually on multiple catalyst beds, with the possibility to add reactor in order to meet the goal of the process considering heat of reaction, unit capacity and/or type of hydrotreating unit. In summa specific reactor designs will depend upon several variables. Nonetheless it is possible to specify some "thumb rules" those made possible the sizing of reactors, or better some guidelines. For example reactor diameter is typically set by the cross-sectional liquid flux: as the unit capacity increases, the reactor diameter increases to the point where two parallel

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[17] SATTERFIELD, C. N., *Trickle-bed reactors*, AIChE journal [0001-1541], year:1975 volume: 21, issue:2, pages: 209 -228

trains would be considered. At the same time reactor height is a function of the amount of catalyst and number of beds required to achieve the objective of the process.

Then for what concerns the expected heat of reaction, cold recycle gas is brought into the reactor at the interbed quench points in order to cool the reactants and in this way to make possible to control the reaction rate.

A good distribution of reactants at the reactor inlet and at the top of each subsequent catalyst bed is essential for optimum catalyst performance and to avoid the presence of hot spots guilty of a non uniform heat distribution with the associated possibility to damage the catalyst.

For every design there is a company that patent the internals. These internals are reactor inlet diffuser, top liquid distribution tray, quench section which includes quench inlet assembly, quench and reactants mixing device and redistribution tray, the reactor outlet device. But it is not a rule that all reactors have the internals described previously. They are a kind of precautions that make possible an improvement of the reactor performance according to the charge and the operative conditions.

After the treatment in the reactor the charge has to be cooled and most of the cooling is achieved in the feed/effluent exchangers; while final cooling of the reactor effluent is obtained in air fin coolers and/or water trim coolers. Water is injected into the stream before it enters the coolers in order to prevent the deposition of salts that can corrode and foul the coolers: it is a trick that improve and increase the reliability of the overall process.

As briefly hinted before the main impurities are represented by the sulfur and nitrogen contained in the feed and after the treatment they are converted to hydrogen sulfide and ammonia. Because of the presence of these two compound with opposite behavior if we consider their acidic or basic affinity (i.e. hydrogen sulfide is an acid, while ammonia is well known for its basic effects), they combine to form ammonium salts[18] that can solidify and precipitate as the reactor effluent is cooled. In parallel, ammonium chloride may be formed if there is any chloride in the system, due essentially to contamination of the feed or to some corrosion byproduct. Water introduced has the double purpose to prevent their precipitation keeping them in solution and transport them out of the reaction loop. There are different patented systems about the quality of the water injection, but in general use of boiler feed water is preferred.

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[18] $H_2S + NH_3 \rightleftharpoons (NH_4)^+ SH^-$

The exact method of separating vapor and liquid will vary depending on the optimum heat integration scheme. There can be used up to four separate vessels to disengage and individually remove vapor, water and liquid hydrocarbon. In order to recover as much as possible the heat in the plant, a hot separator is sometimes installed after the feed/effluent exchangers to collect the heavier hydrocarbon material from the reactor effluent and send it to fractionation via the hot flash drum.

The overhead vapor of this separator continues through an air cooler into a cold separator. This kind of two separator system is at the basis of what is called: heat integration scheme.

2.3.2 FRACTIONATION SECTION

This section provide the plant to be able to separate the reactor effluent into the desired products. This can be achieved with either a one or a two-column fractionation scheme, depending on the type of hydrotreating unit and what is the feed charge to the reactor with the sequent products.

Taking into consideration the two columns scheme, the flash drum liquids combine and go to a stripper column. Here, steam and/or a fired heater is used to strip naphtha (if desired) and lighter material overhead. This is an optimal way to recover lighter products. The stripper bottoms go to a fractionator where it is further separated into naphtha (if desired) and heavier products. The charge to the fractionator is typically preheated with a recovery of the heat of the bottoms and with a fired heater before entering the column. As device to strip lighter material up the column, steam is used; this is choice is usually made because of the availability of this source in whatever plant, for economic reason and then because it is easier to separate after having stripped the stream. Various product strippers could be used to pull side-cut products to the desired specifications.

2.4 THE CHEMISTRY OF REACTION

When we speak generally of hydrotreatment we mean all processes those use hydrogen as reactant to make possible some reactions; and depending on the impurities present in the feed to treat it could be possible that some reactions either occur in parallel or they could be happen because there are not the right conditions.

It will be shown now the main and more important reactions in a typical operation of hydrotreatment, dividing them into different categories based on the impurities have to be removed, remembering that the principal ones remain sulfur, nitrogen, oxygen and some metals[19]. The previous three elements are quite always present in any charge feed to treat, while there are some reactions which impact in the overall hydrogen consumption is function of origin and cut of the feedstock.

Table 2: different hydrotreating processes and their products

Compound	Process	Product
Sulfur	HDS – Hydrodesulfurization	H_2S
Nitrogen	HDN – Hydro-denitrogenation	NH_3
Oxygen	Oxygen removal	H_2O
Organo-metallic	Hydro-demetallation	$[M]^{2+}S^{2-}$ *
Olefins	Olefin saturation	// → / **
Aromatics	HAD – Hydro-dearomatization	aromatics → naphtenes
Halides	Halides removal	halides → hydrogen hylides ***

* where [M]2+ is whatever metal which present a number of oxidation equal to two

** organic compound with double bonds are converted to their paraffinic homologue

*** a halide is a binary compound, of which one part is a halogen atom and the other part is an element or radical that is less electronegative (or more electropositive) than the halogen, from WIKIPEDIA, THE FREE ENCYCLOPEDIA, *Halide*, seen on February 2014.

It is quite clear, for example, that a feedstock as naphtha which is extremely depending on the source of feed stock. For example, naphtha will contain extremely poor of organo-metallic compounds will present a lower contribute by this reaction while an atmospheric residue which is very rich in sulfur compounds will have a great consume of hydrogen due to hydrodesulfurization. E.g., most middle eastern crudes contain much more sulfur than some crudes from Indonesia or North Africa[20].

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[19] DAVID S. J. JONES, PETER R. PUJADÓ, *Handbook of Petroleum Processing,* Springer 2006

[20] *Ibidem*

Take into consideration that it is not a must that impurities have always to be present. Or better for what concerns halides, aromatics and olefins they are function of the maturation conditions of the crude; and in this case is important to consider the Francis' diagram:

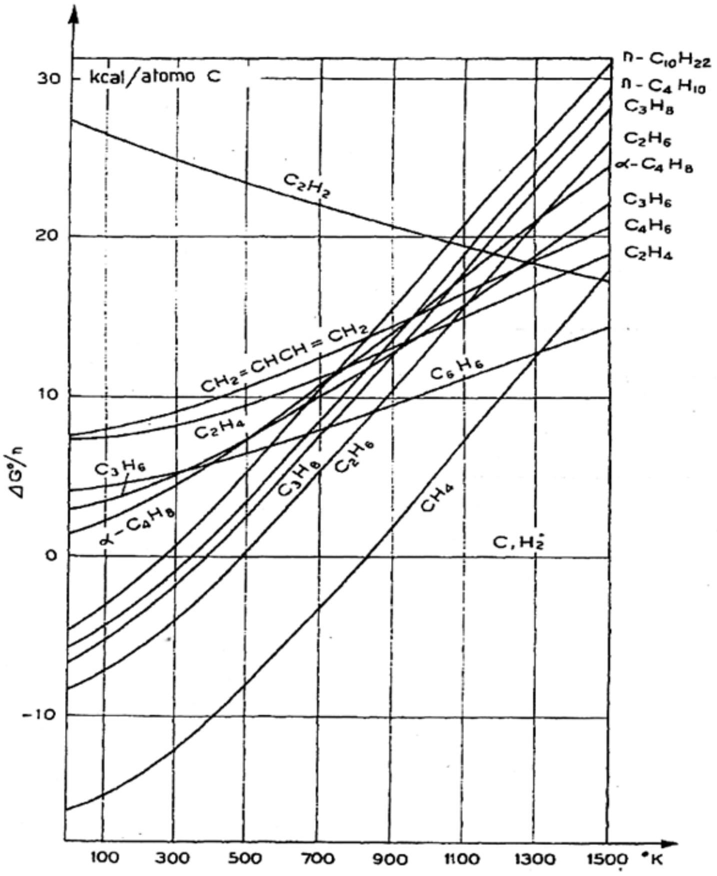

Figure 10: Francis' Diagram, Giulio Natta, Italo Pasquon, *Pricipi della Chimica Industriale*, Milano: Tamburini, 1966

Where we can find and see the real amount of a certain compound in a determinate feed, on the basis of its past conditions.

Considering the previous reactions, it is possible to ordinate them in increasing order of difficulty: first of all we find metals removal, then the saturation of olefin, followed by hydrodesulfurization, hydro-denitrogenation, oxygen removal and the last one, i.e. the halides removal.

Because we generally speak of *hydrotreatment* we have to remember that all reactions occur only in presence of hydrogen and all of them consume it. The contaminant removal in residue hydrotreating involves controlled breaking of the hydrocarbon molecule at the point where the sulfur, nitrogen or whatever impurity present is joined to carbon atoms. To have an idea of how much it influence the charge, consider that cracking occurs in residue normally less than 20% [vol/vol] of the fresh feed charge.

For what concerns the consume of hydrogen we can have this order of magnitude, that is representative of the real impact of the impurity on the feed:

- the desulfurization reaction consumes 100–150 [SCFB/wt% change] or 17–25 [Nm^3/m^3/wt% change]
- and the denitrogenation reaction consumes 200–350 [SCFB/wt% change] or 34–59 [Nm^3/m^3/wt% change].

Taking into consideration the heat of reactions, that it is released because hydrogenation reactions are always exothermic is partially compensate by the mass treated and it is about 0.02 [°F/SCFB H_2], 0.002 [°C/Nm^3/m^3H_2].

A brief summarizing of what it has been showed till this point is therefore presented: first of all considering the rates of reactions too, hydrodesulfurization and olefin saturation are the most rapid reactions; then while the former is very quite heat-releasing, the latter liberates the most heat per unit of hydrogen consumed. Denitrogenation and aromatic saturation are the most difficult reactions and obviously hydrogen consumption is related to heat of reaction are related.

Now it will be shown the main reactions take place in a hydrotreating reactor on the basis of the different impurity element present in order to have a clear visual of what is produced after the treating and as byproduct.

2.4.1 SULFUR

As mentioned before, the sulfur removal has as final product H_2S of the organic sulfur compounds present in the feedstock. This element is present in the petroleum fraction in the form of many hundreds of different organic sulfur compounds which, can be classified in six different categories[21] (considering the generic cut from naphtha to atmospheric residue):

1- mercaptans
2- sulfides
3- di-sulfides
4- thiophenes
5- benzo-thiophenes
6- di-benzo-thiophenes

Now it will be shown an example for each class of compound pointed before.

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[21] DAVID S. J. JONES, PETER R. PUJADÓ, *Handbook of Petroleum Processing,* Springer 2006

2.4.1a Mercaptans

Known also as *thiols*[22], they are a class of organic chemical compounds similar to alcohol and phenol, but they replace oxygen atom with a sulfur one. They are also remarkable for their characteristic scent, that make possible the traceability of natural gas too.

$R - SH + H_2 \rightarrow R - H + H_2S$

2.4.1b Sulfides

The term usually means all the three different classes containing the element sulfur[23]. Those three classes are inorganic, organic and phosphine sulfides. The first one is characterized by ionic bound where there is the negative charged sulfide ion S^{2-}; the second one are compounds with sulfur responsible of covalent bond; while the last one are chemical compounds derived by the combination with phosphine and sulfur: they have both ionic and covalent properties.

$R_1 - S - R_2 + 2H_2 \rightarrow R_1 - H + R_2 - H + H_2S$

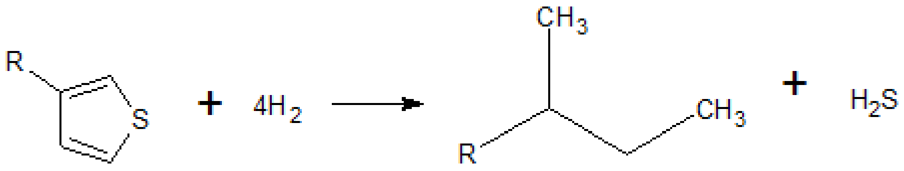
2.4.1c Di-Sulfides

As seen before in the previous paragraph sulfides are whatever organic compound containing sulfur; when there are more than one sulfur atom contained in the compound, then we refer to them as di-sulfides. For what concerns the reaction in which they are typically involved, it is not so far from the sulfide's reaction:

$R_1 - S - S - R_2 + 3H_2 \rightarrow R_1 - H + R_2 - H + 2H_2S$

2.4.1d Thiphenes

They are the simplest sulfur-containing aromatic compound[24]. They are very similar to benzene in its chemical and physical properties too. Thiophene is also present with benzene in coal tar.



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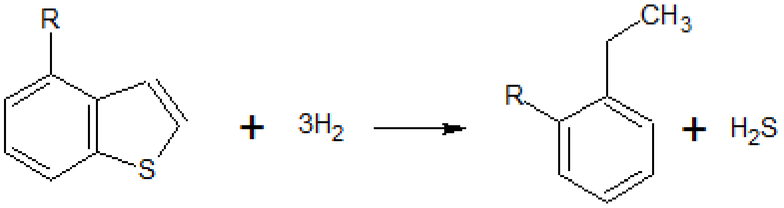
[22] ENCYCLOPÆDIA BRITANNICA ONLINE, *Thiol*, www.britannica.com/EBchecked/topic/592252/thiol, accessed on February 2014

[23] ENCYCLOPÆDIA BRITANNICA ONLINE, *Sulfide*, www.britannica.com/EBchecked/topic/572504/sulfide, accessed on February 2014

[24] ENCYCLOPÆDIA BRITANNICA ONLINE, *Thiophene*, www.britannica.com/EBchecked/topic/592288/thiophene, accessed on February 2014

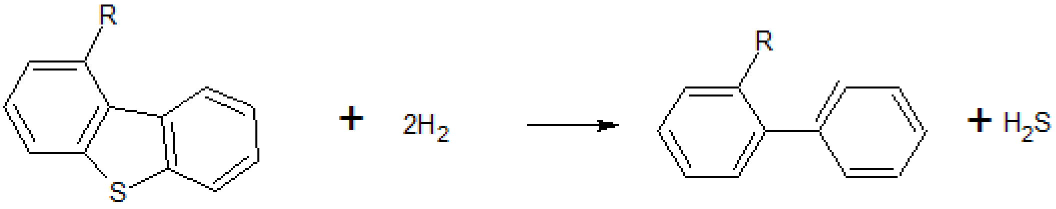
2.4.1e Benzothiophenes

This sulfur compound present an aromatic ring with another ring in which there has been a substitution with a sulfur atom[25]. For what concerns the properties of this substance, it is really affine to naphthalene, from which it presents the similar odor. It is volatile with steam and it is soluble in common organic solvents; lignite tar presents this compound as byproduct of distillation.



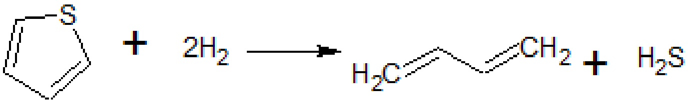
2.4.1f Di-Benzothiophenes

They are the benzothiophenes corresponding as disulfide were for sulfides. The properties of these compound resemble those of the above mentioned benzothiophene, even if it has a higher specific weight and more chemical stability.

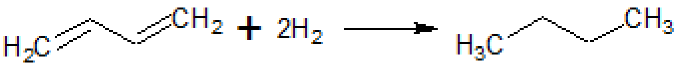


The mechanism of hydrodesulfurization of aromatic compounds has been widely investigated and finally the supposed path of reaction has been postulated and even if it is more complicated because of the different reactions that occur contemporarily; it could be possible to highlight a "norm" which proceed through these two steps:

1- the removal of sulfur atom from the ring



2- the saturation of the corresponding olefin



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[25] THE MERCK INDEX ONLINE, *benzothiophene*, www.rsc.org/Merck-Index/monograph/mono1500009455/thianaphthene?q=authorize, accessed on February 2014

As possible to understand the above mentioned classes of sulfur compound are not all easy to remove: the ease of removal is exactly the way they are presented, starting from mercaptans (the easiest one) to dibenzothiophenes (the most difficult to process). Moreover we must remember that the ease of removal is function of the kind of fraction we mean to treat: a heavier fraction is usually more difficult to process than a naphtha one. This is due to the content of aromatics in the two different cuts.

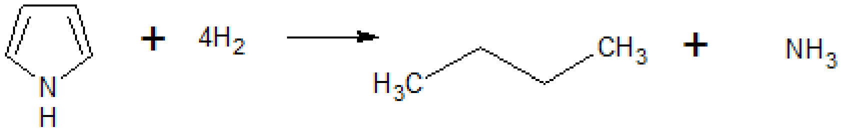
2.4.2 NITROGEN

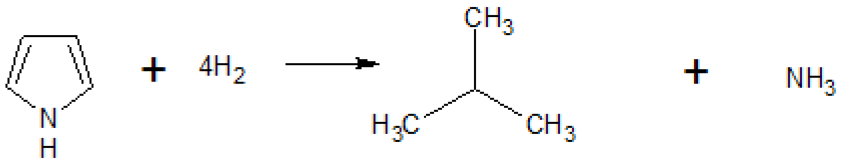
If sulfur was found in heavier petroleum fraction, nitrogen is present in the heaviest end of these ones, in aromatic compounds (five or six member rings). Higher the boiling point, higher the nitrogen content. If we consider the path of reaction the process occurs in the same previous passages of hydrodesulfurization, but starting from saturation and then proceeding through the nitrogen removal. The byproduct of this reaction is ammonia.

As example we can take into consideration the following compounds that are often found in heavy fraction:

2.4.2a Pyrrole[26]

With this term it usual to indicate an organic compound of heterocyclic series where the ring structure is composed by four carbon atoms and one of nitrogen. The simplest one is pyrrole itself. They are very common substances and we can find them in amino acids, alkaloids and other compounds produced by plants.





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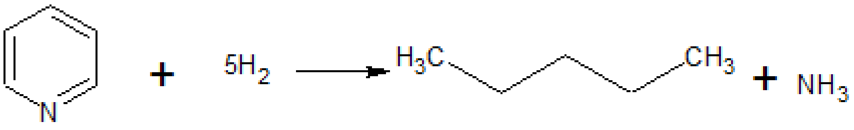
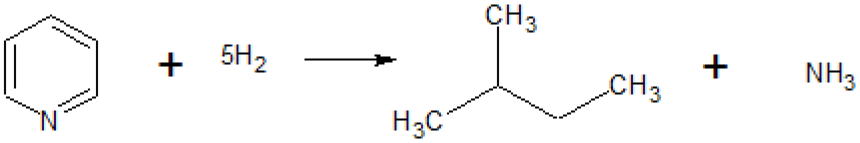
[26] Encyclopædia Britannica Online, *Pyrrole*, www.britannica.com/EBchecked/topic/485130/pyrrole, accessed on February 2014

2.4.2b Pyridine[27]

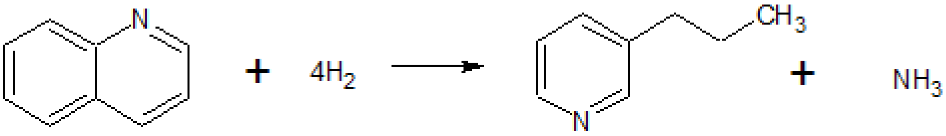
In this case this term is applied to any class of aromatic heterocyclic characterized by six member ring structure, whose five of them are carbon while the last is nitrogen. It is possible to find it in coal tar.





2.4.2c Quinoline[28]

In this case the term stands for any of a class of organic compounds f the aromatic heterocyclic series characterized by double-ring structure, where one is the benzene, while the other is a pyridine ring. It is important for the manufacturing of nicotine and it is produced by coal tar.



As anticipated briefly before, the mechanism of hydrogenation of chemical compound containing nitrogen is very difficult, it needs more hydrogen and it occurs with opposite passages with referring to hydrodesulfurization process: first of all we have aromatic hydrogenation, then hydrogenolysis and the last passage is the denitrogenation itself; exemplified:

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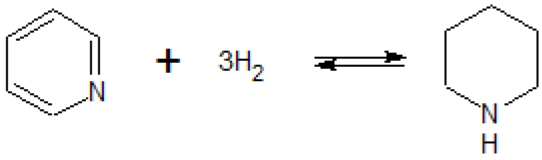
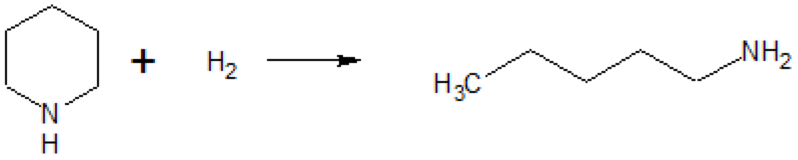
[27] Encyclopædia Britannica Online, *Pyridine*, www.britannica.com/EBchecked/topic/484880/pyridine, accessed on February 2014

[28] Encyclopædia Britannica Online, *Quinoline*, www.britannica.com/EBchecked/topic/487446/quinoline, accessed on February 2014

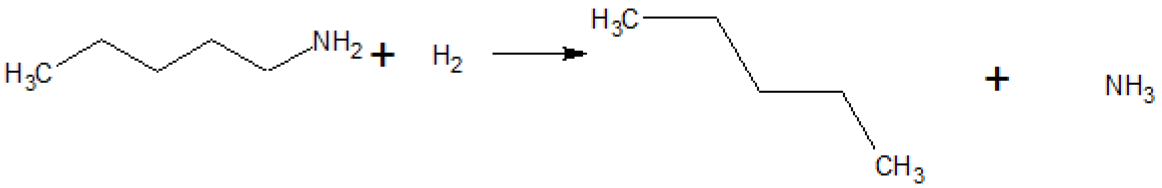
1- Hydrogenation



2- Hydrogenolysis



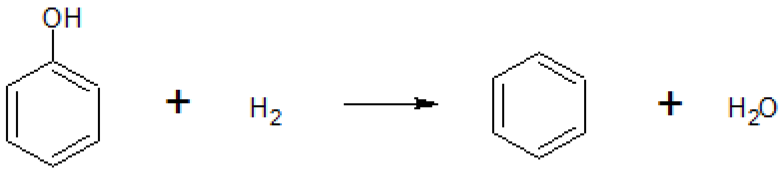
3- Denitrogenation



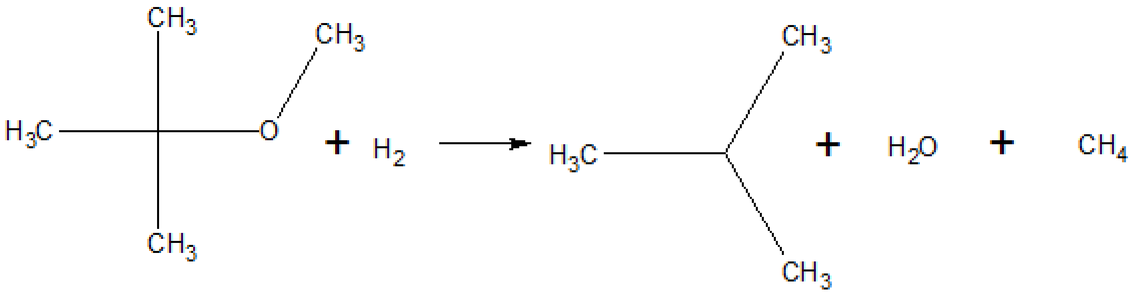
2.4.3 OXYGEN

Even if in minor measure, this class of impurities can affect some petroleum fractions. The byproduct in this case is pure water. Some examples are shown :

2.4.3a Phenols



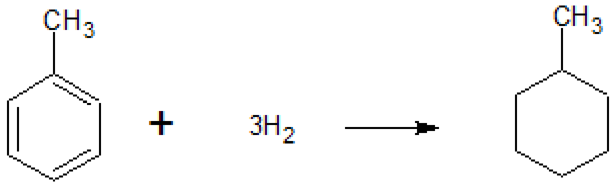
2.4.3b Oxygenates



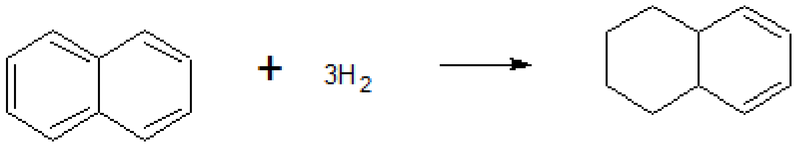
2.4.4 AROMATIC SATURATION

In order to complete the description of the different reactions involved during the hydrotreating it could be interesting to see also the hydrogenation of aromatic, because it occurs often during this refining process and because it is cause of improving qualities in petroleum fractions.

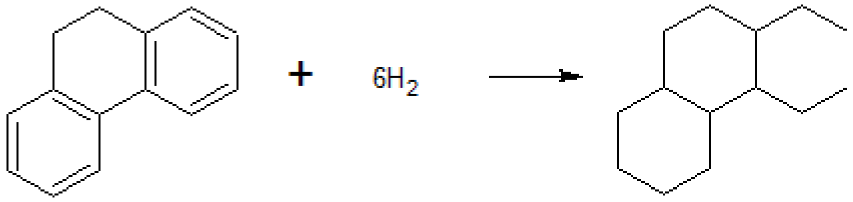
2.4.4a Toluene



2.4.4b Phenanthrene



2.4.4c Naphthalene



The other involved reactions undergo the same steps and they have as byproduct the corresponding hydrogenated compound with the impurity as second element. As clear example of the above mentioned reaction of halide, after the treatment we obtain the wanted product without halogen element and as byproduct hydrogen bounded covalently with the halogen element. Because they are not present in great amount in the reactions of hydrotreatment of petroleum feedstock, no more examples will be given.

In order to make it possible these reactions occur, or better, to make it possible they happen in acceptable time and with operative conditions able to guarantee the feasibility of the process; these reaction proceed with the help of a catalyst. It is now possible analyze the characteristics that have to be present in a good formulation of it and highlight how the performances are influenced by catalyst.

2.5 THE CATALYST

Catalyst, this is the chemical definition[29], is any substance that increases the rate of a reaction without itself being consumed. In nature this happens every day in all biological systems: enzymes indeed are naturally occurring catalysts responsible for many essential biochemical reactions.

As any catalyst found in chemical engineering those for hydrotreating processes are provided by a high surface area that is made by the active component (responsible for the correct path of reaction, with lower values of activation energy) and a promoter (specific for the reaction it has to aid), both dispersed on a support, that provides the mechanical and structural characteristic to the catalyst itself.

The most common catalyst support is usually the so-called γ -Al_2O_3, with some small parts of silica (SiO_2) or phosphorous added; the choice is on this material because of its high surface and an optimal pore structure.

As noted before hydrotreating catalysts contain metals dispersed on a support. That support is γ -alumina which is arrived at by synthesis. The raw materials can be used to produce the γ –alumina are essentially the sequent:

- Gibbsite (α-alumina trihydrate)
- Bayerite (β-alumina trihydrate)
- Boehmite (α-alumina monohydrate)

For what concerns the active component it depends by the type of the feedstock and normally it is molybdenum sulfide, MoS_2; but it is not strange to find some catalyst compositions with tungsten, generally for special applications such as lube oil processing.

Taking into consideration the molybdenum catalysts, the typical used promoters are both cobalt (CoMo) and nickel (NiMo). The main role of these compound added in different quantity and with a particular dispersion is to “promote” the effectiveness of the catalyst activity; while the acidity of the support can be increased to boost the catalyst activity for (hydro)cracking and isomerization reactions.

Typical composition is about 25% [wt/wt] promoter and 25% [wt/wt] active component.

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[29] ENCYCLOPÆDIA BRITANNICA ONLINE, *Catalyst*, www.britannica.com/EBchecked/topic/99128/catalyst, accessed on February 2014

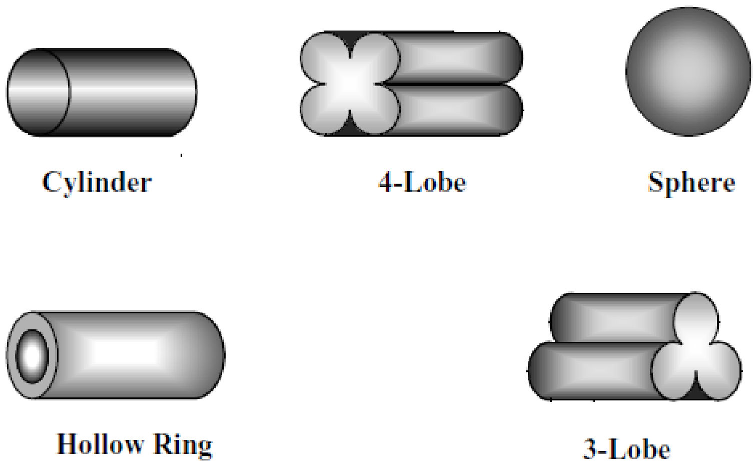

Figure 11: typical shape of hydroprocessing catalyst, David S. J. Jones, Peter R. Pujadó, *Handbook of Petroleum Processing,* Springer 2006

Then depending on manufacturer there are different sizes and shape as you can note in Figure 6.

Size and shape are not casual: the choice is made as in order to minimize pore diffusion effects in the catalyst particles (and for this reason the requirement is small size) and pressure drop across the reactor (requiring large particle sizes).

Although the physical characteristics vary from manufacturer to manufacturer and the intended use of the catalyst (it depends on charge quality, operative conditions and so on), a general guideline is this:

- High surface area = 150 [m^2/g] or higher
- Pore volume = 0.6–1.0 [ml/g]
- Average pore radius = 30–100 [Å]
- Compacted bulk density = 35–55 [lb/ft^3]
- Crushing strength = 4–20 [lbs/in^2]
- Average length (not for spheres) = 1/8–3/8 [in]

We will now analyze and highlight some peculiar characteristics of some kind of catalysts.

2.5.1 COBALT-MOLYBDENUM

CoMo catalysts have been designed primarily for desulfurization, and for this process they can achieve the best results, then denitrogenation and demetallation is also achieved. The particularity of this catalyst is the ability to treat feedstocks of widely varying properties. CoMo catalysts have the lowest hydrogenation activity, therefore they have the lowest hydrogen consumption for a given sulfur removal. And if you consider that they also have the lowest sensitivity of H_2 consumption to changes in operating pressure, the CoMo catalysts have the highest desulfurization performance at the lower operating pressures (pressures are at about 40 [barg]).

Considering on the other side the denitrogenation performance, this is not achieve with great results because they have a low hydrogen activity.

The best operative conditions are set at lower pressures and short hydrogen supply.

2.5.2 NICKEL-MOLYBDENUM

NiMo catalysts are the best choice for hydrogenation and denitrogenation even if they have been designed for desulfurization too. Due to its nature this catalyst can achieve also metal removal. In this sense NiMo catalysts have higher denitrogenation activities than CoMo ones and are therefore used heavy fractions where the denitrogenation is as important as hydrodesulfurization; this means for very heavy cuts and for the treatment of lube oil.

The performance of NiMo catalysts is very good at high pressures and differing from the CoMo catalyst, NiMo show a greater response in denitrogenation and desulfurization performance to changes in H_2 partial pressure than the previous one.

High-pressure operations (e.g. FCC and hydrocracking feed pretreatment), could use and prefer NiMo catalysts. Their use is also useful for reforming units pre-treating.

2.5.3 NICKEL-TUNGSTEN and NICKEL-COBALT-MOLYBDENUM

There are other different compositions and formulations for these catalyst; other two catalysts used in hydrotreating are NiW and NiCoMo. The former has applications in treating feeds where higher hydrogenation activity is required than is available from either NiMo or CoMo; while the latter attempt to combine the benefits of CoMo and NiMo, even if they are rarely used.

As general rule we have to remember that their desulfurization activity is poor at the pressure levels used in hydrotreating; while NiW in sulfided form exhibits hydrocracking activity surpassing that of both CoMo and NiMo.

Another improvements that can increase the hydrocracking activity can be done with promoters or zeolite.

NiW catalysts can be made selective for saturating one of the double bonds in diolefins in light feeds.

All the catalyst mentioned before based their manufacturing on one of these methods:

- Impregnation = where the support is first made and then treated by wet impregnation (a solution with a dispersed solution of the active metals); the shape can be either spherical or extruded
- Co-mulling = where we have the combination of both the metals and the dry alumina in a mix-muller, followed by the extrusion of the wanted catalyst
- Hot soaking = as you can observe in Figure , the preparation it is made mixing the "ingredients" at high temperature, in order to eliminate directly in the mixing passage the solvent used to solubilize the active metals.

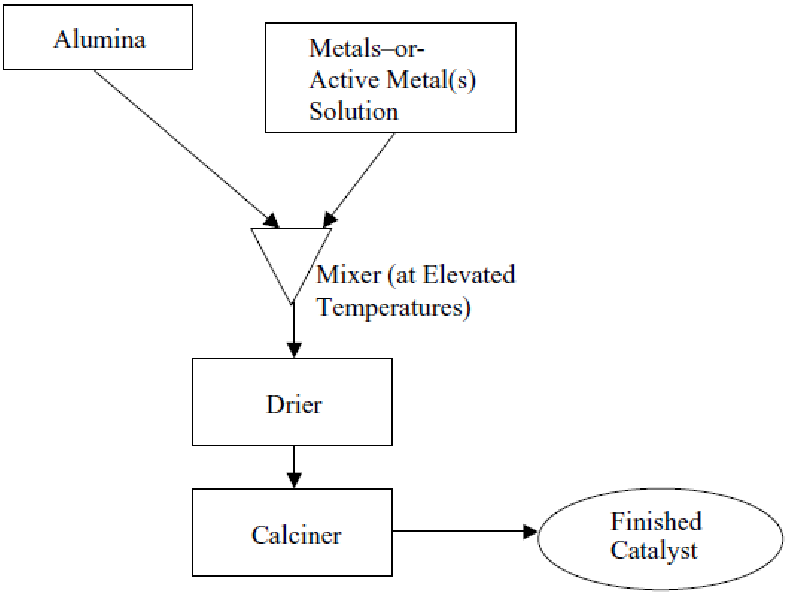

Figure 12: Hot Soaking, DAVID S. J. JONES, PETER R. PUJADÓ, *Handbook of Petroleum Processing,* Springer 2006

It is important to keep in mind the different variables those influence the final product; among those we can find:

- Mixing intensity → influences the pore size
- Peptization → responsible of mesh of active metal
- Calcination → time, temperature and concentration
- Additives to mixing
- Metals application
- Solution preparation → contacting, time, order and drying
- Handling and screening

2.6 REACTORS

After having mentioned and deepened the catalyst preparation is time to see and analyze the structure of what contains catalyst, the core of the hydroprocessing unit: the reactor. Basically hydrotreating reactors are downflow (they exploit gravity force to make possible the contacting of the fluid proceeding from the top of the reactor till the bottom), fixed-bed catalytic reactors; and for the nature of the reactant fed they generally operate in trickle flow regime (we have the solid phase of the catalyst, which have to treat a liquid charge with the hydrogen which cause its supercritical behavior remains in these conditions too, in gas phase).

Even if some catalysts can operate at middle pressures, because hydrotreating instead occurs at moderately high pressure and relatively high temperature, the choice for the thickness of the vessels' wall is o high depth.

The shape of these equipment is the cylinder, typical structure for almost all the reactors' vessels and as usual from the beginning of the "refining era".

The material instead has undergone a change from the older reactors (e.g. for hydrotreating of naphtha) made by lower alloys, to the last 10-years equipments whose raw materials are typically 11/4 Cr –1/2 Mo or 21/4 Cr – 1 Mo base metal with a lining of stabilized austenitic stainless steel for added corrosion protection (we have to remember that the byproduct of these treatment is almost always acid compound which could easily damage and disrupt the same vessel or corrode the reactor itself). With this choice, there is the possibility to give strength to the base and at the same time the excellent corrosion resistance.

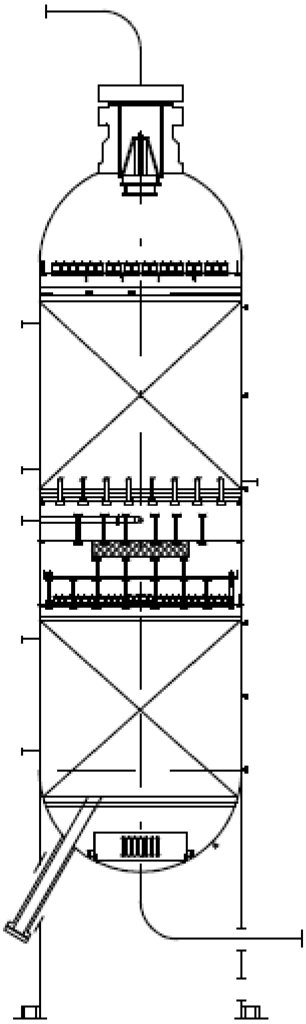

Figure 13: typical vessel shape, DAVID S. J. JONES, PETER R. PUJADÓ, *Handbook of Petroleum Processing,* Springer 2006

The choice is made considering different items; and even if concerning the use of austenitic stainless steels in hydrotreating units, the possibility of corrosion is lowered, it exists for corrosion cracking instead if the proper procedures are not followed.

This kind of corrosion can occur through chloride attack or polythionic acid attack. The former can be prevented by minimizing the amount of chloride in the process material, eliminating it immediately from the process lines. Then to improve the results, during startup and shutdown operations precautions should be taken to limit the chloride content in any flushing, purging, or neutralizing agents used in the system.

The latter occurs as the result of the action of water and oxygen on the iron sulfide scale that forms on all items made of austenitic stainless steel.

If one of these previous two processes happened, it causes intergranular corrosion and cracking.

The polythionic acid attack is possible to prevent maintaining the temperature above the dew point of water in those areas containing stainless steel: this avoid water to condensate on the surface of the reactor. For safety reasons and because there would not be the necessity the system is ideally without oxygen. However, when the system is depressurized and the equipment is opened to air, in order to permit the normal maintenance operations it becomes necessary to maintain a nitrogen purge to prevent air from entering (or whatever neutral purge in order to avoid contacting oxygen with the surface of vessels and also because depressurizing and lowering the temperature it could be possible to make water to condensate on the inner surface with the possibility of polythionic corrosion).

If this is not possible, a protective neutralizing environment should be established: a 5% soda solution is used to neutralize the austenitic stainless steel.

The bed of catalyst is function of the feed treated: most naphtha hydrotreaters only have one catalyst bed; but it is not unusual that many reactors processing cracked feedstocks will have several beds to facilitate temperature control by cooling with hydrogen quench between the catalyst beds.

The reactor vessel is designed to allow maximum utilization of catalyst; and this done by creating equal flow distribution (no preferential channel), providing maximum liquid/vapor mixing, and providing multiple beds with quench zones for efficient catalyst use.

The internals of the reactor usually have some devices useful to improve the reactor characteristics, even if it is not necessary they have to have. Some of them are:

- Inlet diffuser
- Top vapor/liquid distribution tray

- Quench section → only when there are multiple catalyst beds
- Catalyst support grid → only when there are multiple catalyst beds
- Outlet collector

Considering the size of the hydroprocessing reactors they vary widely on the basis of design conditions, the LSHV and the acceptable pressure drops (function of diameter). An important key factor to achieve the best performances is to control the temperature of the reactor; the maximum allowable ΔT is about 42[°C]. If that temperature is not expected to be exceeded, a reasonable solution could be reactor mono bed and temperature control will be exercised by changing the reactor inlet temperature.

On the other hand if the maximum reactor difference of temperature is expected to exceed the previous value, a multiple bed reactor should be installed, where the coolant is the hydrogen which quenches the charge inserting in the quench section of reactor (inter bed).

Considering the operative conditions of a classical hydroprocessing reactor, the hydrotreating catalyst gradually loses some of its activity. It is a direct consequences of fouling, sintering and coking. But in order to maintain the desired quality of the products at the design feed rate, the solution consists in increasing the bed temperature, about 1 [°C/month].

Once the bed temperature reaches a value close to the design maximum, there no other solution than replacing the catalyst (or regenerate it). The catalyst average lifetime is about several years. More often the replacement or regeneration of the catalyst is necessary because of the pressure drop due to fouling.

At the base of all these discussion there is kinetics; kinetics is the study of the rates of reaction; these rates of reaction determine the key properties of a catalyst. In fact as mentioned before the role of the catalyst is to reduce the activation energy, providing a reaction path different from the thermal activation one. In hydrotreating, the key properties are *initial activity*, *stability*, and *product quality*.

The temperature required to obtain the desired product at the start of the run measures the initial activity (it is different from the use of a catalyst and without it). Catalyst stability is a measure of change of reaction rate over time and the product quality is a measure of the ability of the process to yield products with the desired use specification.

Chapter 3

Process Design: layout and modification

“*Patterns*”

Simon and Garfunkel

3.1 INTRODUCTION

Having the theoretical basis to understand how the process works and his historical background, we can now introduce the process design path that has been adopted to simulate it.

In this chapter it will be shown criteria and some assumptions that have made possible the best design accordantly with the simulation program used and with the data available from literature.

3.2 LITERATURE BACKGROUND

As mentioned before for a good design we necessary have to had a solid basis on which have the possibility to build a realistic project.

The starting point is the literature research: from this it has been possible obtaining different designs which have been evaluated and tried in order to select the most appropriate model. In the same way a literature search was moved in order to find the best kinetics able to describe the HDS processes.

In both cases the more realistic compromise has been chosen among the possible ones: the choice has been made taking account for REALISM and ACCURACY of RESULTS, CONVERGING TIME and REPEATABILITY between the different optimization runs. With these evaluation criteria the project has been modeled.

3.3 PLANT SCHEME from LITERATURE

Hydrotreating processes has a specific goal: they aim at removing impurities, usually are represented by sulfur (not by a change a distinction among oils is made for their sulfur content) and nitrogen, from distillate fuels (naphtha, kerosene and gas oils). In order to do this they treat the feed with hydrogen in a very high condition of severity: elevated temperature and pressure in the presence of a catalyst.

Because in recent years hydrotreating has been extended to atmospheric residues in order to increase their commercial value (decreasing sulfur and metal content essentially), that is the upgrade of the feed; we obviously have that operating conditions of this kind of treatment are a function of FEED TYPE and of desired treated product DESULFURIZATION’s LEVELS.

Taking account for these points we will have a wide range of different configurations of an HDS plant.

From literature the usual feed types considered are NAPHTHA, KEROSENE, GAS OILS and ATMOSPHERIC RESIDUES or REDUCED CRUDES in crescent grade of severity of the treatment.

It will be now shortly present how scheme plants differ one from another based on the feed type fed to the system. Then the focus will be point on GAS OIL plant scheme introducing and explaining all changes made in order to set the best configuration possible and most realistic one.

3.3.1 NAPHTHA HDS UNIT

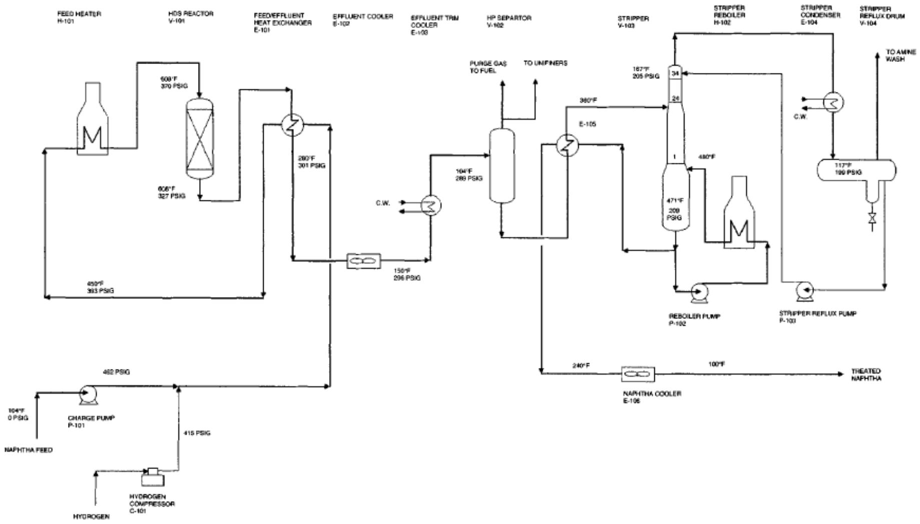

Figure 14: Surinder Parkash , Refining Processes Handbook, Gulf Professional Publishing, 2003

3.3.1a Process Description

Naphtha (or full range naphtha) is defined as the fraction of hydrocarbons in petroleum boiling between 303 [K] and 473 [K][30]. Its composition consists of a hydrocarbon mixture generally having between 5 and 12 carbon atom. It typically constitutes 15–30% of crude oil, by weight.

Hydrodesulphurization of naphtha is done to make the feed suitable for subsequent treatment, among those: catalytic reforming to improve octane or steam reforming in order to produce hydrogen. In the first case, this takes the name pretreatment.

The process consists of treating the feed with hydrogen in the presence of a catalyst under suitable operating conditions. Because its physical properties and being one of the lowest petroleum cuts it is possible operate in less drastic conditions.

In this sense, following the previous chart, the naphtha feed enters the unit through charge pump P-101. The petroleum feed is then mixed with hydrogen gas coming from a catalyzed reforming unit or hydrogen plant. The mix is heated in succession through heat exchange with reactor effluent (E-101) and fired heater (H-101). Now it's time for the mix to enter the HDS reactor V-101. The desulfurization reactions take place over a Co-Mo on γ-Al_2O_3 catalyst contained in the reactor. At the out of the reactor we have: the desulfurized naphtha, excess hydrogen, H_2S, and light end elements formed as a result of reaction of sulfur in the feed with hydrogen in the presence of the catalyst.

The reactor effluent is then cooled and partially condensed through the previous heat exchanger (E-101), an air cooler E-102, and a trim cooler E-103, before flowing into high-pressure (HP) separator V-102. Here we obtain the separation between the vapor and liquid phases. The vapor from this drum (essentially made by H_2S, light hydrocarbons and excess hydrogen) is purged and sent out of unit's battery limit. The liquid from V-102 is preheated through a heat exchanger with the stripper bottom in heat exchanger E-105 before charging to the stripper column V-103, where we have the separation between the dissolved H_2 and H_2S as overhead product. The gross overhead product from V-103 is then partially condensed (E-104). The uncondensed vapor, that is essentially made by H_2S, is sent to an amine unit. The liquid is responsible for the reflux of the column (P-103). The column is reboiled by a fired heater H-102. P-102 is the pump used for bottom recirculation. The

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[30] PRESTVIC, RUNE; KJELL MOLJORD, KNUT GRANDE, ANDERS HOLMEN ,*"Compositional analysis of naphtha and reformate"*, 2004.

bottom product coming from the stripper is cooled by heat exchange with incoming feed in E-105 and next in E-106 to 811 [K] before exiting the unit's battery limits.

Table 3: Operative Conditions Naphtha Unit, SURINDER PARKASH , *Refining Processes Handbook*, Gulf Professional Publishing, 2003

OPERATING PARAMETERS	UNITS
Reactor Inlet Temperature	
SOR	593 [K]
EOR	643 [K]
Total pressure at separator drum	2.1 [MPa]
H_2 partial pressure (reactor outlet)	1.1 [MPa]
Liquid Hourly Space Velocity	4.00 [h^{-1}]
H_2 consumption	45 [scf/bbl]

Note that a naptha hydrotreater (NHDT) or "*light naphtha isomerization plant*" is projected to operate at specified duty under a set and range of conditions. With the progress of time the catalyst gets deactivated and temperature is increased to compensate the deactivation. The period between SOR and EOR is called *cycle length*. The lowest temperature at which plant is commissioned to yield desired product quality is called SOR. When the catalyst has reached the limit before having to be regenerated, we say that it has achieved EOR.

3.3.2 KEROSENE HDS UNIT

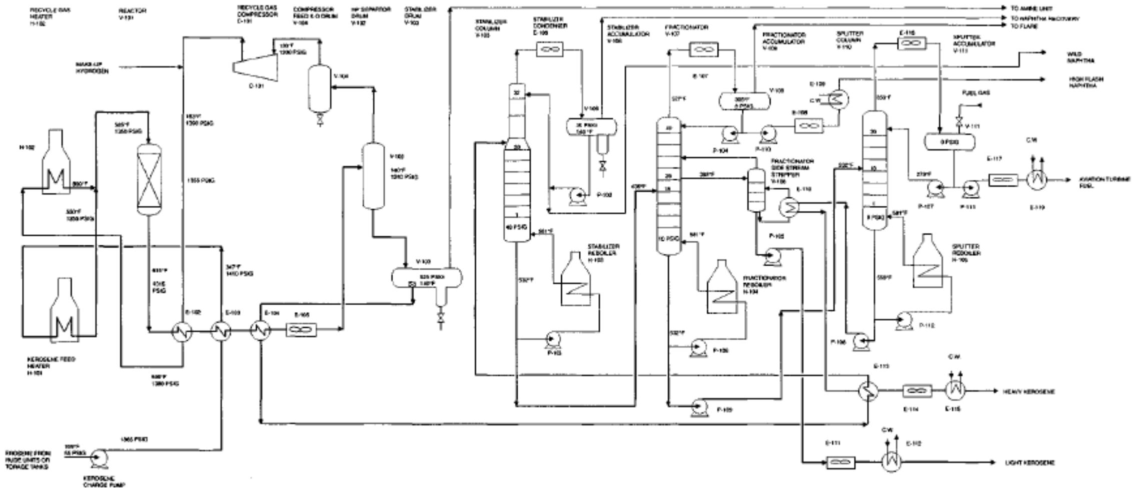

Figure 15: Surinder Parkash , Refining Processes Handbook, Gulf Professional Publishing, 2003

3.3.2a Process Description

As every HDS plant, the objective of kerosene hydrotreating is to upgrade raw kerosene to produce products by specification suitable for market as kerosene itself and jet fuel.

The will of removing sulfur and mercaptans from the raw kerosene cuts (crude distillation unit) lays in possible corrosion’s problems in aircraft engines and fuel handling and storage facilities. Beside sulfur’s problem we have to handle the content of nitrogen in the raw kerosene feed that can cause color stability problems.

For aviation turbine fuels (ATF), we have very specific rules; e.g.: the ASTM distillation, flash point, freeze point and smoke point (which is a function of the aromatic type hydrocarbons in the cut: higher aromatic content yields lower smoke point kerosene cuts; that is we can control aromatics content by severity of the treatment).

This purpose is reached by columns’ distillation in order to remove gases, light ends, and heavy kerosene fractions. The upgrading is achieved by treating the feed and the hydrogen in the presence of a catalyst, where sulfur and nitrogen compounds are converted into hydrogen sulfide and ammonia. For the same reasons explained before, the ATF product can have only straight run kerosene or hydrotreated blend components.

In order to understand how it’s possible to do this we can observe the previous diagram and analyze the process itself. Kerosene feed is pumped via charge pump (P-101) and preheated in a heat exchanger E-103 and then followed by final heating in fired heater H-101. This effluent next joins the recycle hydrogen coming from compressor C-101 and is heated again in the heat exchanger E-102, subsequently by a fired heater H-102. The heated kerosene feed and hydrogen mix flow through reactor V-101 (loaded with a Co-Mo or Mo-Ni catalyst), where the reactions of hydrodesulfurization and hydrodenitrification take place.

Because these reactions are exothermic, the effluents can be used in heat exchanger (E-102, E-103 and E-104). In E-105 (air cooler) we have a further cooling before the flash in HP separator (V-102), where the temperature is about 1000 [K]. Vapor phase (rich in hydrogen) is compressed and sent back to the reactor by the compressor (C-101). The hydrocarbon liquid from the same separator is flashed in drum V-104.

The flash gas is sent to the amine unit for H_2S in order to remove it, while the liquid from the flash drum is sent to a stabilizer column V-105. The overhead vapor of the column is partially condensed in air cooler (E-106) and flows into accumulator V-106. Here the liquid is partially returned as reflux to the column, while the remaining part is kept as it is (wild naphtha). The bottom of the column is sent to fractionator column V-107, where we cut a high flash naphtha as overhead product. The other cuts are withdrawn as sidestream (e.g. light kerosene base stock). We have a further passage in side stripper V-108 in order to adjust the flash point of the kerosene. The stabilizer column has its reboiler (a fired heater H-103). The aviation turbine kerosene is withdrawn as an overhead product from the splitter column V-110. It's heated by H-106 (fired heater) and the bottom product is cooled in an air cooler E-114 and then in a water trim cooler (E-115). The product can be used as it is or mixed in order to obtain different blends or cutter for various oil grades.

Table 4: Operative Conditions Kerosene Unit, SURINDER PARKASH , *Refining Processes Handbook*, Gulf Professional Publishing, 2003

OPERATING PARAMETERS	UNITS
Reactor Inlet Temperature (W.A.B.T.)	
SOR	593 [K]
EOR	643 [K]
Total reactor pressure	9.3 [MPa]
H_2 partial pressure	7.6 [MPa]
Reactor ΔT	20 [K]
Reactor ΔP	0.2 [MPa]
H_2 consumption	555 [scf/bbl]
Recycle Ratio	3072 [scf/bbl]
% Desulfurization	99.6
% Denitrification	98.0

3.3.3 GAS OIL HDS UNIT

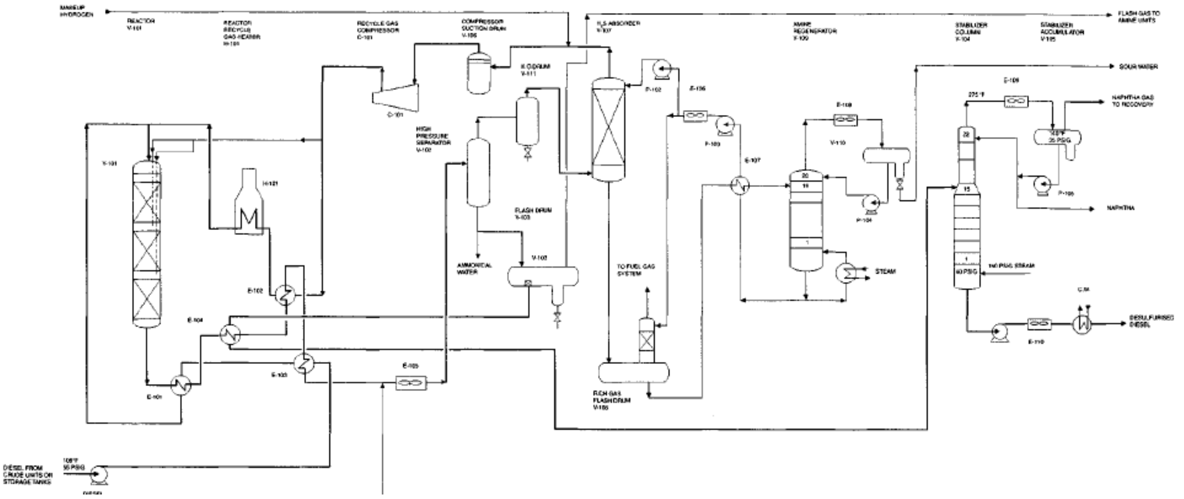

Figure 16: Surinder Parkash , Refining Processes Handbook, Gulf Professional Publishing, 2003

3.3.3a Process Description

Gas oil hydrodesulfurization is designed to reduce the sulfur and other impurities (e.g. nitrogen, heavy metal and other different compounds) present in the raw gas oil cuts.

The feed to the unit could be very different: from a straight run diesel cut coming from the crude distillation unit to a secondary units such as FCCU (Fluid Catalytic Cracking Unit) or delayed coker. These last kind of feed may contain significant amount of olefinic hydrocarbons, which has to be converted to saturates in the diesel hydrotreating unit (stability problems during the storage).

As for the previous charts the primary improvement in product quality is with respect to sulfur and conradson carbon (raw diesel cut from Middle Eastern crudes may contain as much as 1-2% sulfur). Until a few years ago 1.0% sulfur was acceptable, but in the last years for the extraordinary rapid increase of diesel vehicles, the pollution level has risen exponentially; so sulfur specifications in most developed countries have fallen to 0.005 wt% or lower.

In the diagram we will analyze how to proceed a gas oil feed and to treat it in order to join the specifications.

The diesel feed is pumped by pump P-101 to heat exchangers E-103 and E-101, then it joins the hot recycle hydrogen stream before entering reactor V-101 (it's loaded with the catalyst, Co-Mo or Ni-Mo on alumina type). Note that the recycle gas, from compressor C-101 is heated in heat exchanger E-102 and then in a fired heater H-101; subsequently it's mixed with the hydrocarbon feed before going to HDS reactor V-101. In the reactor we have the common hydrodesulfurization and hydrodenitrification reactions.

Cause the exothermicty of the reactions of hydrodesulfurization, a cool hydrogen quench is added to the inter bed areas. When the reaction mixture exits the reactor, it is cooled in a series of heat exchangers from E-101 to E-104 and next in air cooler E-105. Once the temperature is significantly lowered it is flashed into high-pressure separator (V-102).

Condensate is injected into the reactor effluent just before air cooler E-105 to dissolve and remove ammonium salts, that result from the reaction between ammonia and H_2S (problems in pipes for possible blockage of them). The separation of ammonium salt solution happens in high pressure separator drum V-102 and it's recovered in the refinery wastewater system.

The hydrogen-rich gas from the HP separator (almost pure hydrogen), enters H_2S absorber V-107, where with an amine washing (diethanolamine, DEA, solution) the H_2S is removed. The H_2S-free gas is mixed with makeup hydrogen coming from the hydrogen plant. We have and intermediate compression made by centrifugal compressor C-101. As stated before part of the recycled gas is used as an inter bed quench in the reactor, while the remaining hydrogen (heated in heat exchanger E-102 and fired heater H-101), joins the hydrocarbon feed before entering the reactor V-101.

The liquid hydrocarbon stream from separator V-102 is flashed in V-103. The flash gas is sent for H_2S removal before going to refinery fuel system, while the bottoms liquid stream from V-103 is preheated in the reactor heat exchanger E-104 before flowing into the stabilizer column V-104. This column separates the gases, light ends, and naphtha formed as a result of HDS reactions in the reactor. The stabilizer overhead vapors are condensed in air-cooled exchanger E-109 and then sent to accumulator drum V-105; while this liquid (the so called unstabilized naphtha) is used as a reflux to the column itself, and the excess is recovered as naphtha product. Heat is supplied through medium-pressure steam. The stabilizer bottoms is the desulfurized diesel product. The product is cooled in heat exchangers E-110 and E-111 before being stored.

Table 5: Operative Conditions Gas Oil Unit, SURINDER PARKASH , *Refining Processes Handbook*, Gulf Professional Publishing, 2003

OPERATING PARAMETERS	UNITS
Reactor Inlet Temperature	614 [K]
Reactor ΔT	30 [K]
Reactor inlet pressure	15.7 [MPa]
H_2 partial pressure	11.9 [MPa]
Reactor ΔP	0.2 [MPa]
H_2 consumption	422.3 [scf/bbl]
Recycle Ratio	5065 [scf/bbl]
% Desulfurization	98.9
% Denitrification	73.9

3.4 PLANT SCHEMES

We start now the study of the project plant and the modifications put in act in order to simulate the most realistic possible a HDS unit. The project has been built in Aspen Hysys®.

For what regards our study the goal has been focused on the gas oil plant. For the most realistic project as possible a model from literature has been selected and then subsequently modified in order to make it possible a good design with the possibility to have a feasibility in the modeling.

The essential modifications applied to the model from literature are the sequent:

- Heat-exchangers
- Stabilization column
- Kinetics

For what concerns the first two modifications the main reason has been to make as easy as possible the optimization of the plant: all the equipments have been evaluated based on their real effectiveness on the plant specification and on their impact on optimization time. Each train of heat-exchangers make the calculation slow in terms of numerical solution, they burden cause every loop forces the simulation program to calculate (in the built-in algorithms) energy balances, pressure drops and velocities. The stabilization column instead is guilt to an inadequate solution, when it has been found; because of a instability in evaluation counts, while the optimization program is running and it's changing the initial evaluation point. The first has been substituted either with simple heater or cooler.

In other words we have to considered what is extremely necessary to make a process plant feasible without losing reliability or without losing ourselves in too much expensive calculations.

On the same idea are based the considerations on the kinetics and the problem here is purely numerical; as we will analyze next, a set of different kinetics equations[31][32] has been tested and compared with data on literature in order to see what is the best solution with regard on time and accuracy.

Now in order to understand what is the real reason for what we have so much interest in a "speedy" evaluation we have to analyze our purpose and in particular we have to remember that the so-called "Self Optimizing Control" is a technique developed by Prof. Sigurd Skogestad dealing with the possibility to operate a solid and robust control on a selected plant having chosen some "magical" variables that even if we have some modifications on the feed or other external parameters (so called *disturbances*) they don't get far from the optimal operating point. In order to find this theoretical optimal point (and in this case we have to point out that we speak about an optimal point that is the best considering the whole parameters affecting the simulation in that moment. It's the optimal solution with that set of variables and disturbances but it's always the optimum. A wide speech could be faced if we consider the problem of a "moving optimum" or something that would have to update every iteration with every different set of parameters. It could be a philosophical digression on what's the real meaning of optimal solution); a Matlab® code has been written in order to find the best solution at a given set of parameters, working on what has been selected as the best approximation of an HDS scheme plant.

The basis on which the scheme has been selected is a Gas Oil scheme plant whose design has been found in literature. The project built in Aspen Hysys® and has been modified in different versions in order to make the finding of a feasible solution possible with the Matlab® code.

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[31] GILBERT F. FROMENT, GUY A. DEPAUW, AND VALÉRIE VANRYSSELBERGHE, *Kinetic Modeling and Reactor Simulation in Hydrodesulfurization of Oil Fractions*, Amercan Chemical Society 1994.

[32] AYSAR T. JARULLAH, IQBAL M. MUJTABA, ALASTAIR S. WOOD, *Kinetic parameter estimation and simulation of trickle-bed reactor for hydrodesulfurization of crude oil*, Chemical Engineering Science 2011, vol. 66, pp. 859-871, 2011

3.4.1 FIRST MODEL: HDS from literature

As seen previously literature provides us some valid models and plant projects that are representing the common way to process a certain kind of feed and treating it to remove undesired compounds.

In this case, to make it possible reliable configuration of a scheme plant, it has been chosen the one dealing with the treatment of a gas oil feed.

This layout of plant scheme is complete with all equipments and is presented in its first realization on Aspen Hysys® program:

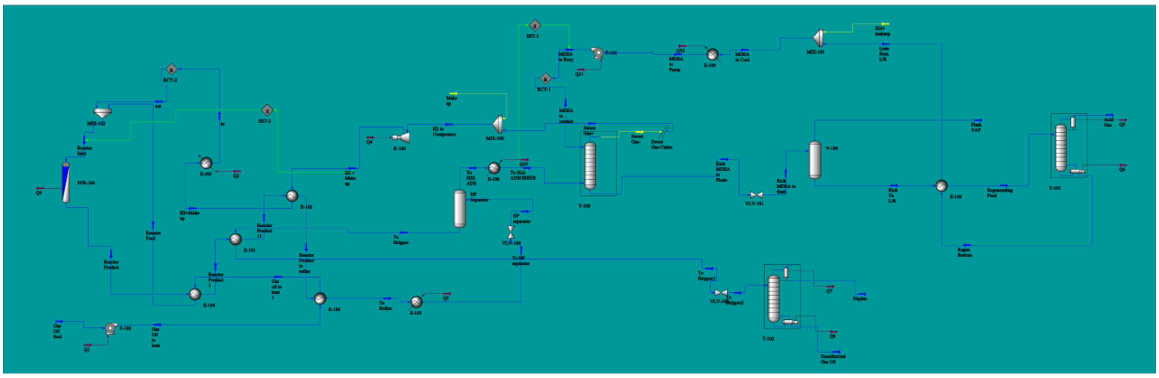

Figure 17: Aspen HYSYS® model adapted from Surinder Parkash , Refining Processes Handbook, Gulf Professional Publishing, 2003

As explained before we can subdivided the HDS process in two main loops: the part dealing with the hydrogenation (and then we consider the part with the reactor and its train of heat exchangers in order to make it possible the reaching of operative conditions for the reaction); and the post treatment of H_2S as by-product of the reaction and its treating in the amine washing loop and the regeneration of this last one.

As you can see in the picture before we have both the part regarding the real hydrogenation process (the heart of the HDS treatment) and the loop of amine treatment-regeneration.

In the final part it has been also introduced the stabilizer column in order to obtain the different specification products.

3.4.1a Considerations

Even if this is a project working and reliable in its features we have to consider two main things, which will be our guideline during all the optimization analysis of the plant:

1. CALCULATION TIME: in the perspective of an optimization evaluation on all the plant, more variables are considered (that is more equipments in the scheme) more

time is spent on calculations on every loop made by simulation program to converge to a numerically correct and feasible solution while the optimization program is running to find the optimum that is the optimal solution. We could assert that we two calculation loops, one subjected to the other, both subjected to our specification made by feasibility of the solution. That is why we want to obtain the fastest solution possible from the simulation program because it is moved by the optimization program on solutions surface in order to find the optimum (in this sense we could see it as a master-slave controller: some control systems arrange PID controllers in cascades or networks, that is a "master" control produces signals used by "slave" controllers).

2. ACCURACY: and in this sense we want to underline the possibility to obtain solution with a certain grade of compatibility with specification we set at the beginning of each simulation.

As we can observe directly on the plant scheme we note first of all the complexity present among the different parts of the plant itself; we could individuate the two main loops and we can analyze them differently: the main loop where we have the reactor and the reaction takes place is characterized by a series of train of heat-exchangers whose duty is to raise the feed temperature till almost the reactor level and operate a thermal recover from the product line in order to decrease the costs of the calories in all the process. Then we see the loop of amine treating and the regeneration of the same itself: it's particularly highlighted by the presence of the scrubber and by the regeneration column which is responsible both for water make-up and indirectly for the H_2 make-up, if we consider that higher is the efficiency of an amine washing higher is the amount of H_2 that could be recycled to the reactor, that means less cost of raw materials in that case H_2 itself.

Although this scheme is incredibly faithful to reality, we face with two problems: the first is that mentioned before of a too expensive calculation time. By the clock if we change some input data (in this case fixed the composition of the feed and having set all the parameters regarding temperatures and pressures allowing the simulation program to evaluate the remaining ones) we can see that every try takes about one minute (45/50 [s]) in order to reach the solution, or better in order to converge to a solution. Considering this particular we can note that if we have the necessity of changing in a range of 1000 of values per variable set to be optimized, calculation time reaches too high values without having the certainty of a correct solution (in terms of optimized solution).

The other problem is represented by the stabilization column. While calculation time, although high and unfeasible if we want to make an optimization usable directly in a RTO, always bring to a solution; the equipment represented by the column is often guilt of a non-correct solution or in some cases it doesn't make it possible the finding of a solution. Aspen HYSYS® column environment is really susceptible of initial value and initial estimation of the solution of the column itself and great changing in them make impossible finding A solution. Moreover we have to take in account that for the same reason it has a environment apart, counts to reach the solution are made in a loop apart. In this sense besides having an unfeasible or impossible solution it could take too much time without finding it.

The approach followed to build a realistic model and at the same time feasible in terms of time taken for evaluation and solution, has been based on the assertion "keep it easy".

Starting from the simplest plant design, it has been added different equipment to make it realistic and at the same time without prejudging solution time.

The different version of the scheme will be shown and briefly commented, regarding with the modification added and parts substituted.

3.4.2 THE SIMPLEST MODEL: "naked" HDS

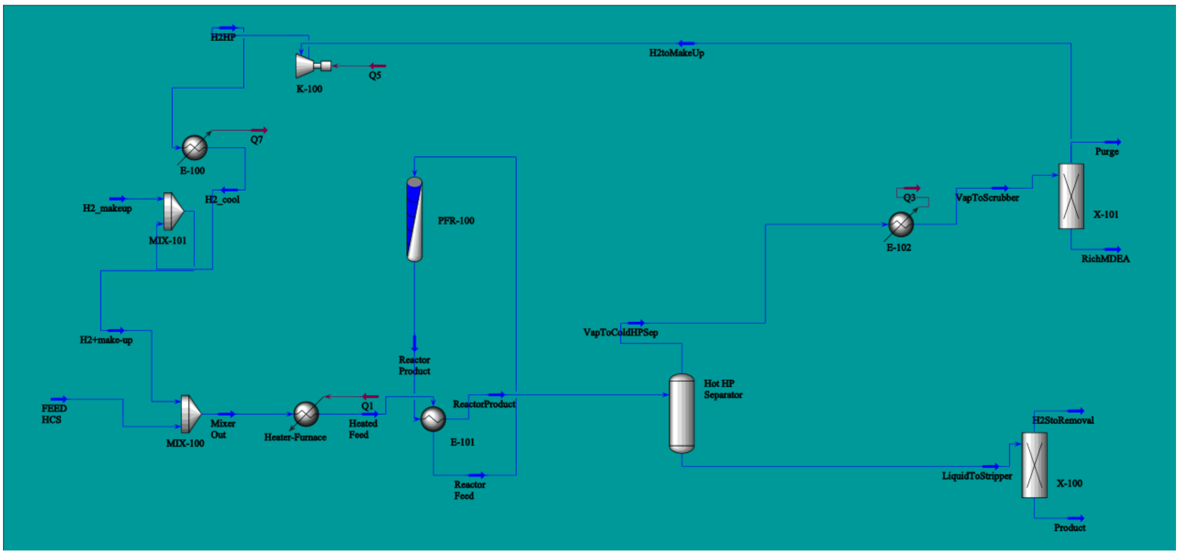

Figure 18: the easiest way to configure an HDS unit

Starting from the simplest one, without considering the two mentioned before loops, excluding all equipments more complex than a vessel, this is the result. It's a poor scheme plant whose core is the reactor and where we had the stripper and the scrubber their place has been substituted by two splitter.

Even if this work could seem useless and without any sense, we can observe instead the real effectiveness of every single part of a chemical unit and its weight in a more complex system.

In this case amine washing has been changed with a splitter and instead the regeneration we split the fractions of H_2S and H_2 in order to send the last one to the reactor.

This preliminary analysis has underlined how important is the loop regarding scrubber and its regeneration. The calculation time has dropped down reaching 1.2 [s] at the maximum, while the solution was always acceptable.

Stripper itself has been changed with a splitter and we have a kind of flash in this section.

Also heat-exchangers train has been taken away, keeping only the product/feed one.

The compressor absolve the role to compensate pressure drops and no recycle as been introduced.

The system is working and data coming from the exit of the reactor are acceptable.

This isn't a real unit yet. It has been useful to evaluate and understand at the basis the process and how the different level of detail could affect the behavior of a chemical unit. In this simple case we can analyze the role of the reactor and how it responds to different changing in feed flow or inlet reactor temperature or different pressure/pressure drops. It's a preliminary analysis on one of the two loops involved in the real process. Pointing out how important is the choice of a right kinetics, because every added equipment has been set to the simplest one possible.

3.4.3 THE FIRST MODIFICATIONS

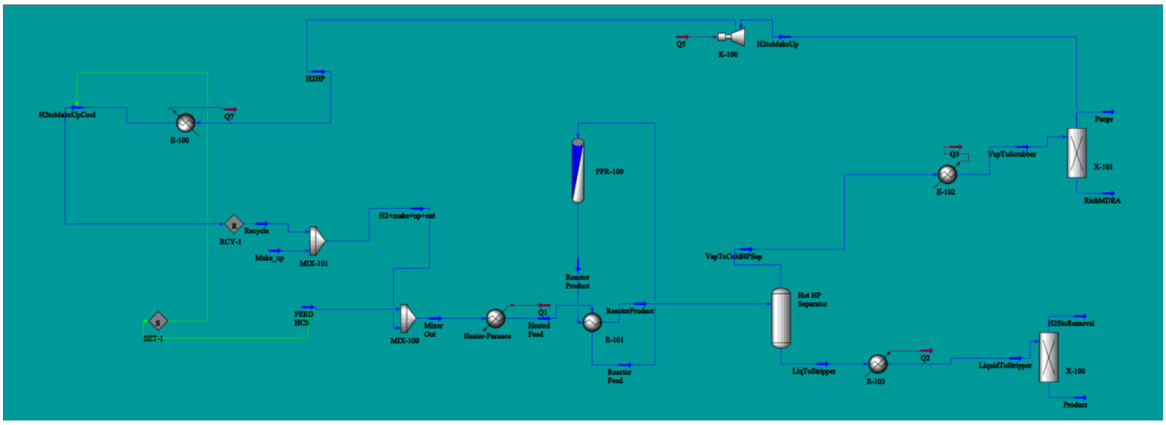

Figure 19: HDS unit with a previous selection of the desired layout

Having clear in mind how the process and the reaction takes place, some little modifications have been inserted in order to control and set some variables; in particular it has been put the recycle of H2 to reactor and the set for the pressure assuming that the major contribute of pressure drop is only in the reactor (as documented in literature[33]) and obviously in HP separator which acts like a flash at high temperature. Ideal behavior of heater and cooler has been hypothesized that is in this case no pressure drops.

For what concerns scrubber and stripper the two units has been simulated treating them as splitter as the case before.

In this simulation the importance was put on the recycle that has to make it converge in order to evaluate correctly the necessary supply of H_2 in reaction loop and directly the make-up.

Conditions, taken from literature too, are what resumed in Table 3.

The composition is a typical gas-oil blend with a sulfur content variable from 1 to 2 wt %[34].

3.4.4 AMINE LOOP STRIPPER

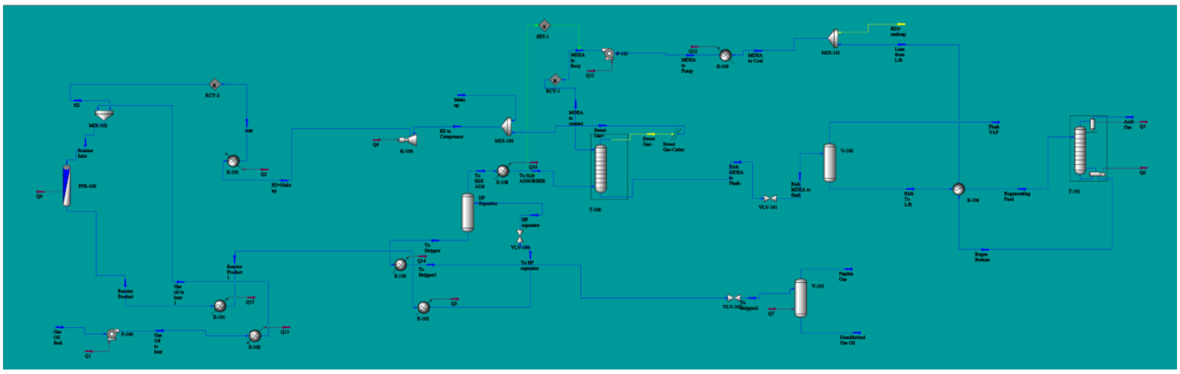

Figure 20: HDS unit with the regeneration unit

After all considerations regarding the reaction loop and its recycle, it has been possible introduce some modification useful to make more realistic the model. In this sense the two splitters set before instead of scrubber column and stripping one, it has been inserted the "*amine loop*" and a simple flash separator with a steam stream to supply the necessary duty to make possible a best separation between the gas-oil stream and gas phase of non-condensable.

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[33] SURINDER PARKASH , *Refining Processes Handbook*, , Gulf Professional Publishing, 2003.

[34] 1.82 wt %; GILBERT F. FROMENT, GUY A. DEPAUW, AND VALÉRIE VANRYSSELBERGHE, *Kinetic Modeling and Reactor Simulation in Hydrodesulfurization of Oil Fractions*, Amercan Chemical Society 1994.

When we speak using the expression “amine loop”, we want to underline the importance of this sub-unit of an HDS plant for what concerns the specifications we want to obtain; such an importance that we can describe a self standing loop. We must note in this sense that amine loop is all the equipment tied to scrubber and amine washing: starting from scrubber column, in cascade we have a flash separator then the regeneration column with the make-up of water lost as vapor in gas phase in head stream.

It’s important to make clear the reason for such a particular attention given to this part of the plant. In the amine loop we recover H2 that is sent then to the recycle in order to keep the reaction at its optimal value. Therefore it’s evident that if we have a correct workable unit in this section we can achieve best results in all the plant.

In order to design a correct project for this loop, the starting point has been taken from tutorials available for this commercial software[35] . With this raw scheme it has been possible realize a workable unit useful to simulate the correct behavior of this loop.

For what concerns the amine used in the amine-washing unit, it has been selected DEA instead MEA for its major absorption capability; while operative conditions adopted for the simulation have been selected in order to achieve the best result[36]. These value are comparable with the literature ones used for the plant project.

Stripper column, instead, has been substituted in the simulation with a simple flash whose duty has supplied by an external source. The main reason why this solution has been selected is found in the potential instability during calculations introduced by a stripper column. Generally besides problems dealing with slowness of every iteration, we have to face the possibility of some numerical inconsistencies and subsequently a non feasible solution.

Before doing this radical simplification, different results in specification has been taken in consideration and compared in order to see if it was acceptable or it could be result in something completely wrong. For what concerns the concentration in sulfur compounds in gas oil desulfurized stream we have the same results, within a less than 1% of tolerance. In this way it has been possible to build a realistic and faster model than if we adopted the real configuration.

Global operative conditions are the same seen for the previous models.

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[35] *HYSYS 3.0*, HYPROTECH LTD., 2002.

[36] LUKE ADDINGTON AND CHRIS NESS, *An Evaluation of General “Rules of Thumb” in Amine Sweetening Unit Design and Operation*, GPA 89th Annual Convention March 21-24, 2010.

3.4.5 SETTING PRESSURES and TEMPERATURES

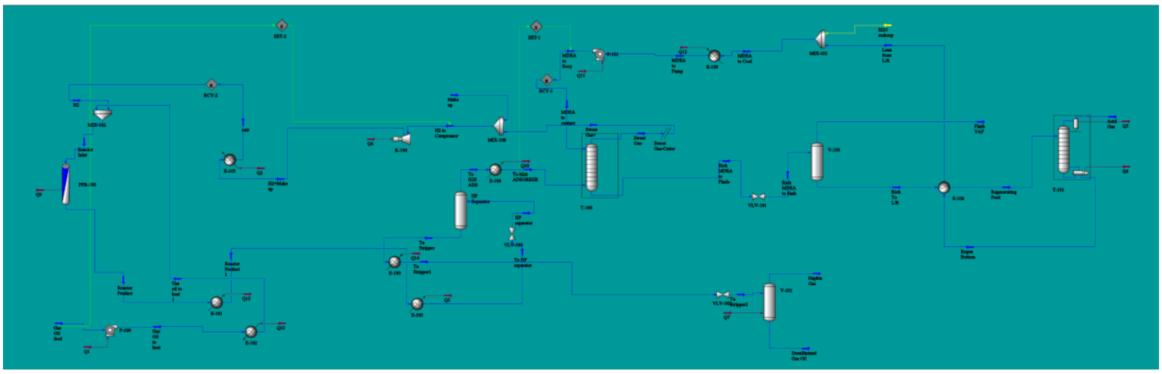
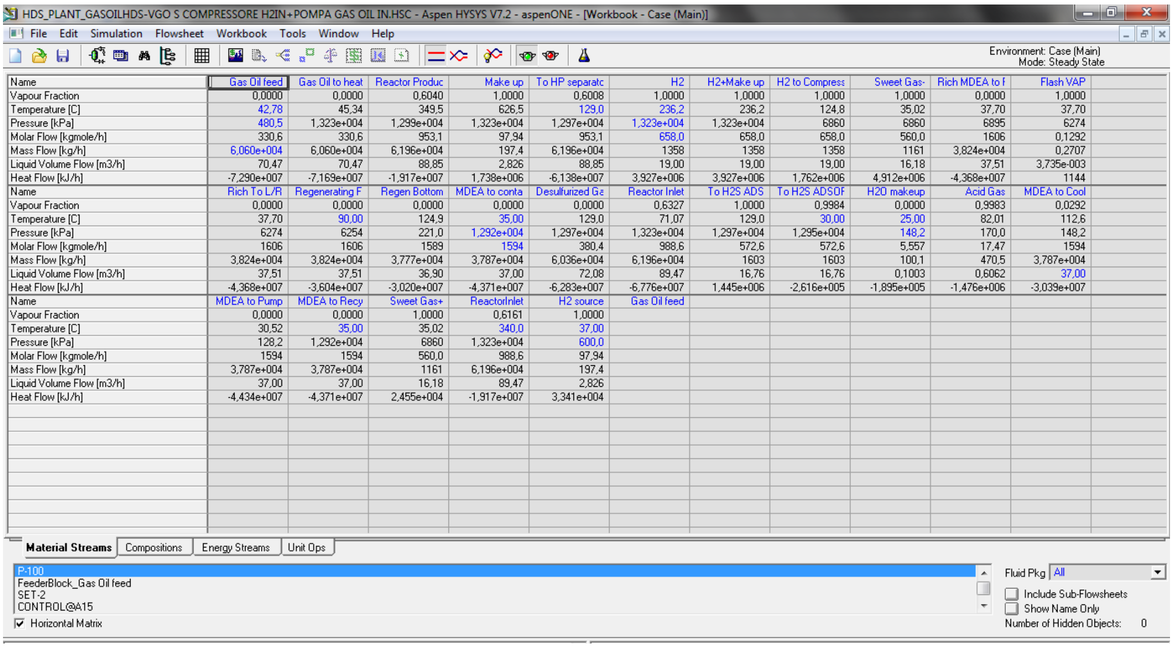


Figure 21: HDS unit with the optimal configuration of the equipment

At this point, it has been useful to introduce some small details in order to simplify the procedure of optimization of the plant. As it can be possible observe, among the main stream, it has been inserted different set instruments. Thank to this approach different line where controlled setting a value of reference that is then responsible of the optimization value we will obtain from the optimization system.

Before doing this, trough the "workbook" command in Aspen HYSYS®, all over specified values has been deleted in order to make the program evaluate them. In this way it has been possible avoid some unwanted error due to inconsistencies.



Name	Gas Oil feed	Gas Oil to heat	Reactor Produc	Make up	To HP separatc	H2	H2+Make up	H2 to Compress	Sweet Gas-	Rich MDEA to F	Flash VAP
Vapour Fraction	0,0000	0,0000	0,6040	1,0000	0,6008	1,0000	1,0000	1,0000	1,0000	0,0000	1,0000
Temperature [C]	42,78	45,34	349,5	626,5	129,0	236,2	236,2	124,8	35,02	37,70	37,70
Pressure [kPa]	480,5	1,323e+004	1,299e+004	1,323e+004	1,297e+004	1,323e+004	1,323e+004	6860	6860	6895	6274
Molar Flow [kgmole/h]	330,6	330,6	953,1	97,94	953,1	658,0	658,0	658,0	560,0	1606	0,1292
Mass Flow [kg/h]	6,060e+004	6,060e+004	6,196e+004	197,4	6,196e+004	1358	1358	1358	1161	3,824e+004	0,2707
Liquid Volume Flow [m3/h]	70,47	70,47	88,85	2,826	88,85	19,00	19,00	19,00	16,18	37,51	3,735e-003
Heat Flow [kJ/h]	-7,290e+007	-7,169e+007	-1,917e+007	1,738e+006	-6,138e+007	3,927e+006	3,927e+006	1,762e+006	4,912e+006	-4,368e+007	1144
Name	Rich To L/R	Regenerating F	Regen Bottom	MDEA to conta	Desulfurized Ga	Reactor Inlet	To H2S ADS	To H2S ADSOF	H20 makeup	Acid Gas	MDEA to Cool
Vapour Fraction	0,0000	0,0000	0,0000	0,0000	0,0000	0,6327	1,0000	0,9984	0,0000	0,9983	0,0292
Temperature [C]	37,70	90,00	124,9	35,00	129,0	71,07	129,0	30,00	25,00	82,01	112,6
Pressure [kPa]	6274	6254	221,0	1,292e+004	1,297e+004	1,323e+004	1,297e+004	1,295e+004	148,2	170,0	148,2
Molar Flow [kgmole/h]	1606	1606	1589	1594	380,4	988,6	572,6	572,6	5,557	17,47	1594
Mass Flow [kg/h]	3,824e+004	3,824e+004	3,777e+004	3,787e+004	6,036e+004	6,196e+004	1603	1603	100,1	470,5	3,787e+004
Liquid Volume Flow [m3/h]	37,51	37,51	36,90	37,00	72,08	89,47	16,76	16,76	0,1003	0,6062	37,00
Heat Flow [kJ/h]	-4,368e+007	-3,604e+007	-3,020e+007	-4,371e+007	-6,283e+007	-6,776e+007	1,445e+006	-2,616e+005	-1,895e+005	-1,476e+006	-3,039e+007
Name	MDEA to Pump	MDEA to Recy	Sweet Gas+	ReactorInlet	H2 source	Gas Oil feed					
Vapour Fraction	0,0000	0,0000	1,0000	0,6161	1,0000						
Temperature [C]	30,52	35,00	35,02	340,0	37,00						
Pressure [kPa]	128,2	1,292e+004	6860	1,323e+004	600,0						
Molar Flow [kgmole/h]	1594	1594	560,0	988,6	97,94						
Mass Flow [kg/h]	3,787e+004	3,787e+004	1161	6,196e+004	197,4						
Liquid Volume Flow [m3/h]	37,00	37,00	16,18	89,47	2,826						
Heat Flow [kJ/h]	-4,434e+007	-4,371e+007	2,455e+004	-1,917e+007	3,341e+004						

P-100
FeederBlock_Gas Oil feed
SET-2
CONTROL@A15

Figure 22: Aspen HYSYS® workbook

Having complete this preliminary part some test changing feed flow and condition of pressure as been tested to verify the feasibility of the system and if there weren't some numerical problem of evaluation.

3.4.6 THE LAST MODEL

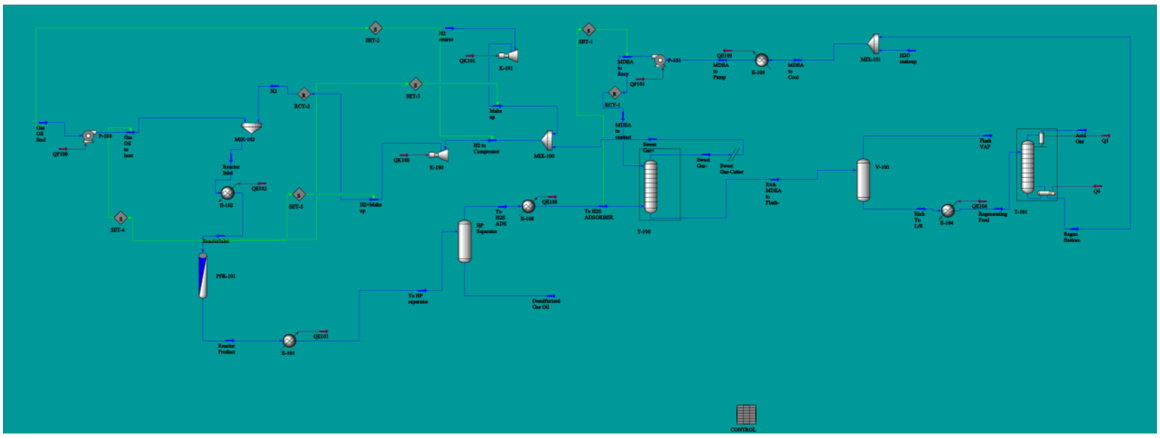


Figure 23: final HDS unit layout

This last version of the scheme plant is the outcome of a discussion with professor Skogestad about the possibility of making more reliable and credible the project. In the make-up line it has been inserted a compressor to simulate the real supply of H_2 in a real plant: the line before the plant is typically at about 6 [bar], while the system is working at about 100 [bar].

With this modification, also the flash column at the end of treatment plant has been removed to make the plant easier to work and faster than before.

Beyond this all throttling valves used to flash the mix inside the different vessels (e.g. HP separator and scrubber) have been substituted by direct expansion inside the equipment cited before.

The number of fixed variables have been lowered more than the previous model, allowing the simulation program evaluate them. The reason of this procedure is the same expressed before.

A "spreadsheet" has been introduced in order to monitor more accurately the operative parameters and working conditions.

What is possible to observe directly on the PFD is how clearer is compared with the previous models; but even if the equipment has been modified or changed in order to make calculations easier and maybe without any numerical error, the model follows as best as its possibility (that is optimally as well) a real hydrodesulfurization unit.

At the end of this preliminary part professor Skogestad has verified the real feasibility and rightness of the system. The model was proved to be functional and able to reproduce different situation of loading and at various operative conditions.

3.5 KINETICS

In order to evaluate the right behavior of the reactor and subsequently its performance on sulfur compounds' abatement, a series of different kinetics have been tested. Here it will be shown simple graphs to give an idea how they work and why the choice has been done on one instead of another one.

The best way to test them has been to build some models in C++ code and make it to plot the graphs used to compare with the example taken in literature and with our goal. We have to note that among the different possibilities offered by AspenHYSYS® simulation program there is the possibility to insert and adopt different kinetic scheme from equilibrium to heterogeneous catalytic provided that the right parameters are used.

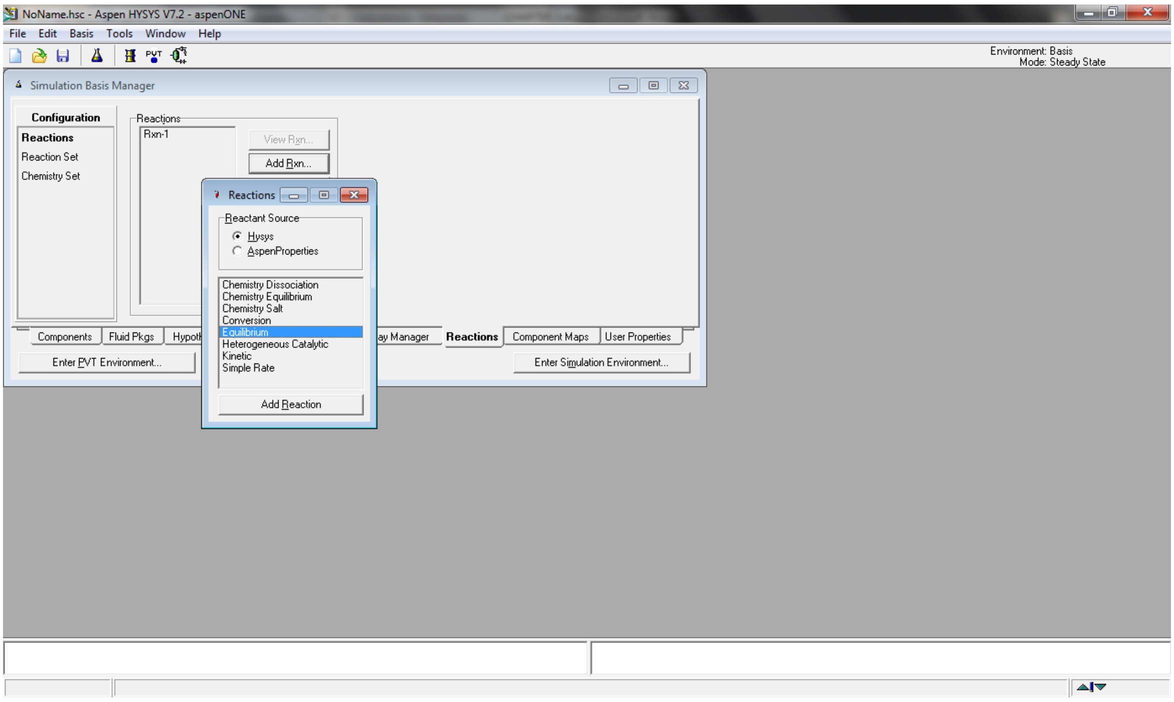


Figure 24: how to select the reaction set in Aspen HYSYS®

3.5.1 FIRST KINETICS: FORMENT et al.

In order to make it possible the right operation of the reactor, as stated before, it's necessary to introduce a right kinetic model and see if it's capable to represent every situation that could be verify during the normal activity of a plant. First kinetic scheme is that proposed by Froment et al.[37].

In this paper the HDS reactions was analyzed one by one considering all the possible way through which the reaction could happen. The main compounds treated were benzothiophene and dibenzohiophene those are the major contribute for what concerns the total sulfur presence in a typical diesel feedstock.

This scheme was proved only for T = 533 [K] as it was in isothermal conditions even if it is unreal as hypothesis, but that was the only temperature available: all kinetic expressions are patented and "that is now part of a commercial software" (G.Froment, 12/03/2013).

The rate of H_2 consumption and sulfur compounds, with the production of hydrogen sulfide too were in agreement with literature data and also in test with the corresponding graphs of the article from which the scheme was taken there was good respect.

But the impossibility to verify the workability of a system on a range of temperature different from the one used before, has made necessary the goal to find a new kinetic scheme which it could be fully defined and completely functional.

3.5.2 SECOND KINETICS: D. TSAMATSOULIS and N. PAPAYANNAKOS

In this second case the possibility to choose a kinetic model with an expression rate unique for all the compounds taken in consideration, has been verified. For this analysis a paper of D. Tsamatsoulis et al.[38] has been used.

In the article the hydrodesulfurization of a VGO has been taken into consideration and there have been estimated kinetic equations in order to evaluate the behavior of the system; two kinetics have been analyzed:

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[37] GILBERT F. FROMENT, GUY A. DEPAUW, AND VALÉRIE VANRYSSELBERGHE, *Kinetic Modeling and Reactor Simulation in Hydrodesulfurization of Oil Fractions*, Amercan Chemical Society 1994.

[38] D. TSAMATSOULIS AND N. PAPAYANNAKOS, *Investigation of intrinsic hydrodesulphurization of a VGO in a trickle bed reactor with backmixing effects,* Chemical Engineering Science, Vol. 53, No. 19, pp. 3449-3458, 1998.

$$r_{HDS} = \frac{k_{HDS} \cdot P_{H_2}^{np} \cdot C_S^n}{1 + K_{H_2S} \cdot P_{H_2S}}$$

$$r_{HDS} = \frac{k_{HDS} \cdot P_{H_2}^{np} \cdot C_S^n}{1 + K_{H_2S} \cdot P_{H_2S} + K_H \cdot P_{H_2}}$$

with $k_{HDS} = k_{HDS}^0 \exp\left(\frac{E_{HDS}}{RT}\right)$ and $k_H = k_H^0 \exp\left(\frac{E_H}{RT}\right)$

The research has brought to find some different parameters based on the type of catalyst; and these parameters have been evaluated for the catalyst used in the process and they are found to equal to:

Table 6: HDS kinetic parameters of D. TSAMATSOULIS AND N. PAPAYANNAKOS

HDS kinetic parameters	VALUE
n	2.13
np	0.92
k_{HDS}^0	$1.5x10^8$
E_{HDS}	142,950
K_{H2S}	$0.36x10^{-5}$

3.5.3 THIRD KINETICS: AYSAR T. JARULLAH, IQBAL M. MUJTABA, ALASTAIR S. WOOD

Having noted that a kinetic equation able to describe the overall behavior of this unit is more appreciable also in the results it gives us; the analysis of a "near optimal" kinetics have brought to the paper of Aysar T. Jarullah et al[39]. The HDS I described by an equation based on Langmuir-Hinshelwood model:

$$r_{HDS} = K_{HDS} \frac{\left(C_{H_2}^S\right)^m \cdot (C_S^S)^n}{(1 + K_{H_2S} \cdot C_{H_2S}^S)^2}$$

Where $k_{H_2S} = 41769.8411 \exp\left(\frac{2761}{RT}\right)$

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[39] AYSAR T. JARULLAH, IQBAL M. MUJTABA, ALASTAIR S. WOOD, *Kinetic parameter estimation and simulation of a trickle-bed reactor for hydrodesulfurization of crude oil*, Chemica Engineering Science, vol. 66, pp. 859-871, 2011.

$$K_{HDS} = A^0_{HDS} \exp\left(-\frac{EA_{HDS}}{RT}\right)$$

While the other parameters are summarized in table below:

Table 7: HDS kinetic parameters of AYSAR T. JARULLAH, IQBAL M. MUJTABA, ALASTAIR S. WOOD

HDS kinetic parameters	VALUE
n	1.147
m	0.4749
A_{HDS}^0	2,026.23
EA_{HDS}	50,264.10

Seeing in comparison the simulation results (evaluated by Aspen HYSYS®, on the basis of the above mentioned kinetics[40]) and the paper used as reference to study the process[41], with the feedstock to treat, we can observe a good prediction of the performance of this unit:

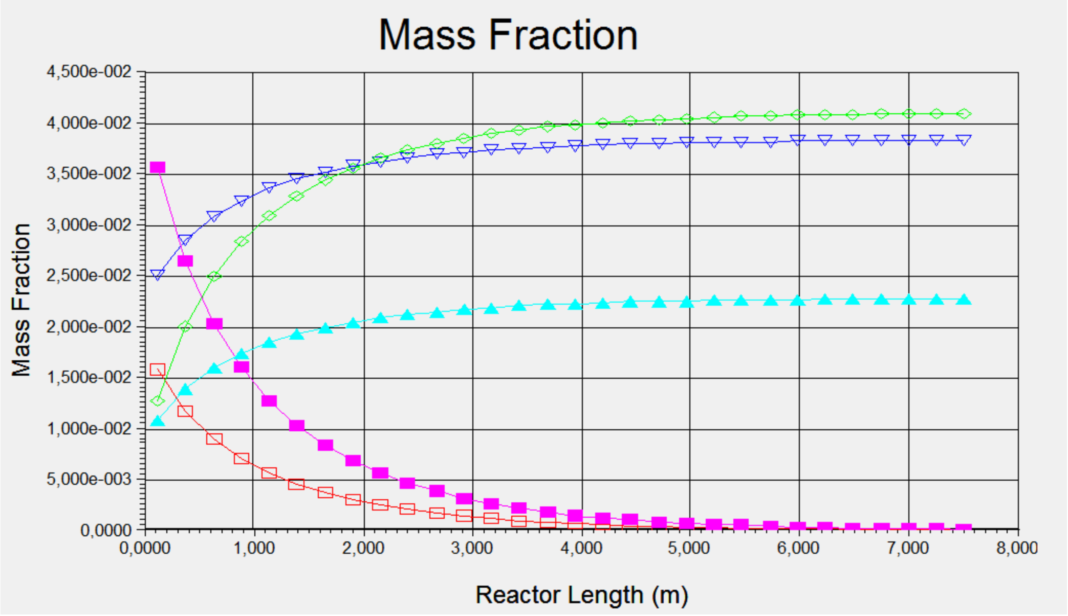

Figure 25: results from Aspen HYSYS®

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[40] AYSAR T. JARULLAH, IQBAL M. MUJTABA, ALASTAIR S. WOOD, *Kinetic parameter estimation and simulation of a trickle-bed reactor for hydrodesulfurization of crude oil*, Chemica Engineering Science, vol. 66, pp. 859-871, 2011.

[41] GILBERT F. FROMENT, GUY A. DEPAUW, AND VALÉRIE VANRYSSELBERGHE, *Kinetic Modeling and Reactor Simulation in Hydrodesulfurization of Oil Fractions*, Amercan Chemical Society 1994.

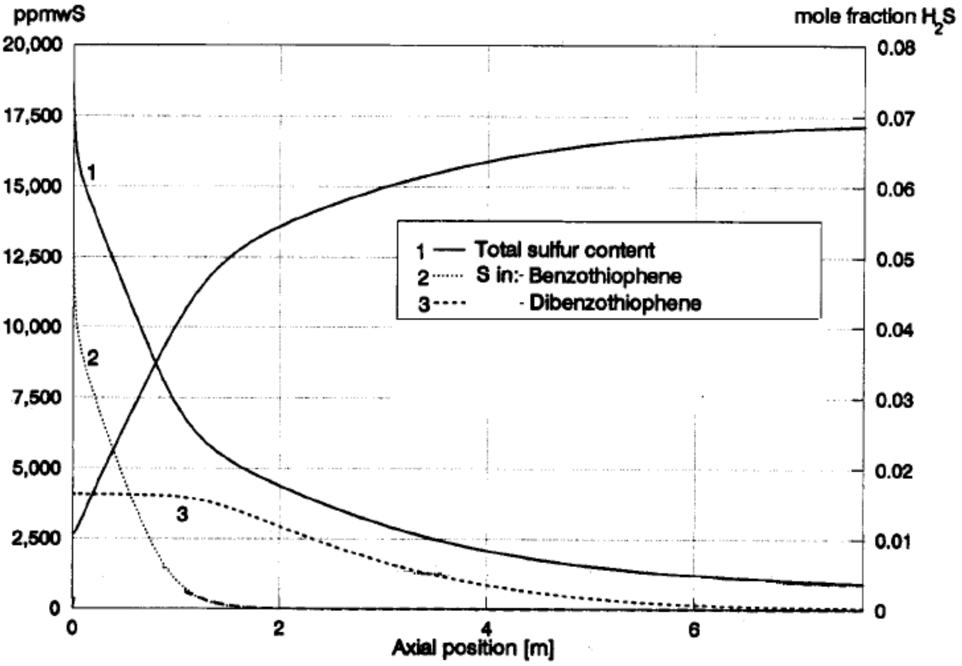

Figure 26: Gilbert F. Froment results

With a percentage of desulfurization equal to 99.04%, value that is comparable with the literature previous one.

3.6 THE FEEDSTOCK

As seen previously, there are different kind of HDS unit, everyone optimal and "specialized" for a certain type of feedstock. In particular for a certain raw feed to treat. It's quite clear that the characteristics of the feed, in terms of sulfur and nitrogen content, depend on first of all the geographical position; then obviously it's tied with the type of the lump taken in consideration.

For this simulation the focus was pointed on a synthetic diesel feed[42]. Although there are various possibilities cause the extreme variation also in composition and the different ratio between PAN in the same raw feed; the choice has been done in order to make some direct considerations on this fuel that in these last years has been put under the direct observation of the various environmental agencies in order to control the worldwide toxic emission, among those: SO_x and NO_x. The composition used is reported in the table below:

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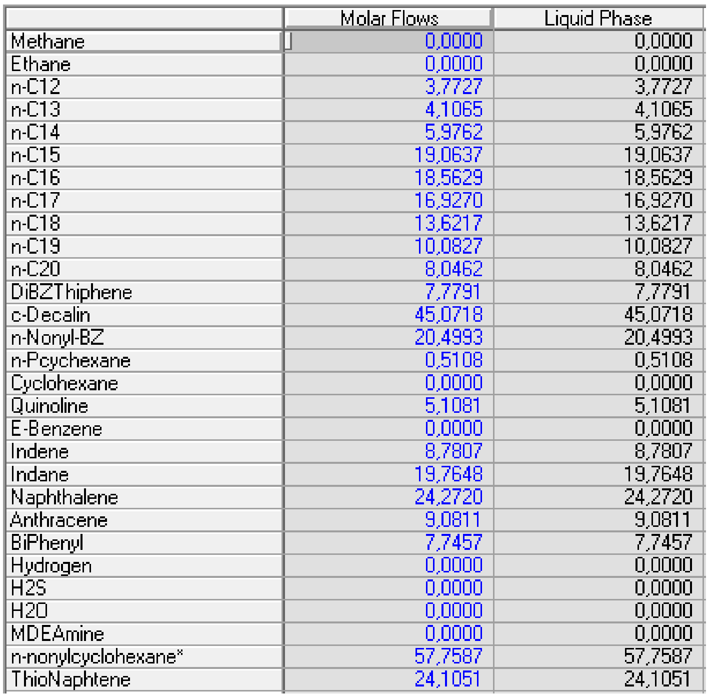
[42] GILBERT F. FROMENT, GUY A. DEPAUW, AND VALÉRIE VANRYSSELBERGHE, *Kinetic Modeling and Reactor Simulation in Hydrodesulfurization of Oil Fractions*, Amercan Chemical Society 1994.

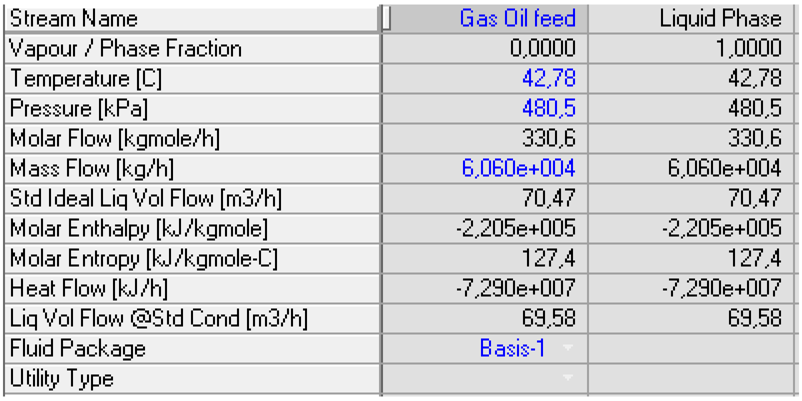


	Molar Flows	Liquid Phase
Methane	0,0000	0,0000
Ethane	0,0000	0,0000
n-C12	3,7727	3,7727
n-C13	4,1065	4,1065
n-C14	5,9762	5,9762
n-C15	19,0637	19,0637
n-C16	18,5629	18,5629
n-C17	16,9270	16,9270
n-C18	13,6217	13,6217
n-C19	10,0827	10,0827
n-C20	8,0462	8,0462
DiBZThiphene	7,7791	7,7791
c-Decalin	45,0718	45,0718
n-Nonyl-BZ	20,4993	20,4993
n-Pcychexane	0,5108	0,5108
Cyclohexane	0,0000	0,0000
Quinoline	5,1081	5,1081
E-Benzene	0,0000	0,0000
Indene	8,7807	8,7807
Indane	19,7648	19,7648
Naphthalene	24,2720	24,2720
Anthracene	9,0811	9,0811
BiPhenyl	7,7457	7,7457
Hydrogen	0,0000	0,0000
H2S	0,0000	0,0000
H2O	0,0000	0,0000
MDEAmine	0,0000	0,0000
n-nonylcyclohexane*	57,7587	57,7587
ThioNaphtene	24,1051	24,1051

Figure 27: Aspen HYSYS® composition

As you can note in the table there is a compound over star-signed: the n-nonylcyclohexane has been introduced in the simulation building the molecule through UNIFAC structure; all data for this compound are those from the same theory and in order to have a good approach to simulation these data have been compared with those coming from literature matching perfectly.

For what concerns the conditions of this stream are those one:



Stream Name	Gas Oil feed	Liquid Phase
Vapour / Phase Fraction	0,0000	1,0000
Temperature [C]	42,78	42,78
Pressure [kPa]	480,5	480,5
Molar Flow [kgmole/h]	330,6	330,6
Mass Flow [kg/h]	6,060e+004	6,060e+004
Std Ideal Liq Vol Flow [m3/h]	70,47	70,47
Molar Enthalpy [kJ/kgmole]	-2,205e+005	-2,205e+005
Molar Entropy [kJ/kgmole-C]	127,4	127,4
Heat Flow [kJ/h]	-7,290e+007	-7,290e+007
Liq Vol Flow @Std Cond [m3/h]	69,58	69,58
Fluid Package	Basis-1	
Utility Type		

Figure 28: Aspen HYSYS® feed conditions

Chapter 4

Steady State simulation: theory, analysis and results

“*Ready Steady Go*”
Paul Oakenfold

4.1 INTRODUCTION

The previous chapter has been useful to introduce and specify the scheme-basis on which it will be possible to apply the procedure of control that is the so-called Self Optimizing Control based on a more general approach of the Economic Plantwide Control. This procedure found its basis in the theory developed by Professor Sigurd Skogestad.

We must consider that a chemical plant has thousands of measurements and control loops. If we thought to adjust and control each of these measurements maybe we couldn’t have reason of what a plant is and how it acts during its work. So the term plantwide control

“does not imply the tune and behavior of these loops, but rather the CONTROL PHILOSOPHY of the overall plant with emphasis on the structural decisions”[43].

The analysis brings to a control system divided in several layers each for a different timescale level, as you can see in Figure 1.

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[43] SIGURD SKOGESTAD, *Plantwide Control, Recent Developments and Applications*, Wiley 2012

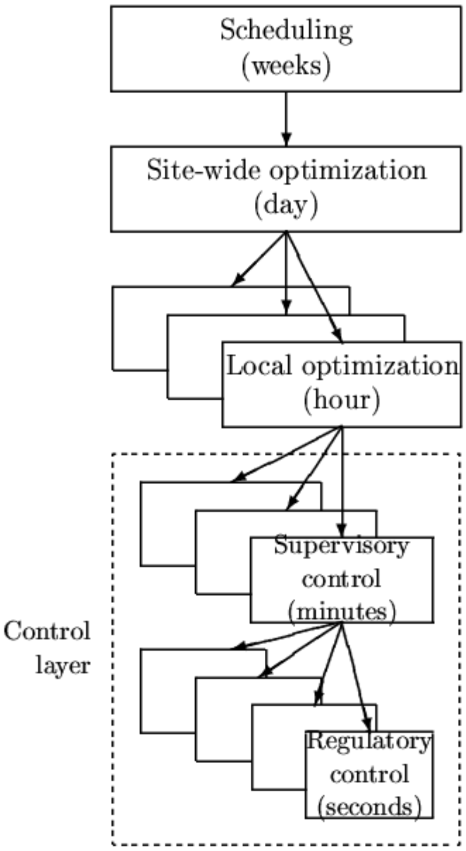

Figure 29: hierarchical control

This theory was born in 1983 when for the first time Skogestad started to search a correct structure for a column control. Taking his inspiration from a famous article by Foss (1973)[44] in which he stated that the determination of control system structure is the "central issue to be resolved in control" he went on this way. In 2004 he published his work[45] where he explained the basis and the rules of the procedure; procedure that is split in two parts: a top-down, based on economics and a bottom-up which aims to reach a simple and robust "stabilizing" or "regulatory" control.

This philosophy aims to reach control as simplest as possible, "PhD Control" (Figure 2):

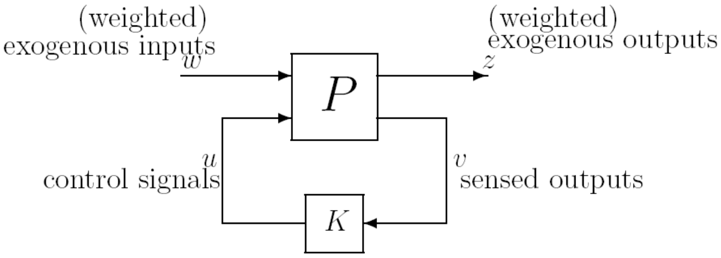

Figure 30: PhD control

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[44] FOSS, A. S., *Critique of Chemical Process Control Theory, IEEE Transactions on Automatic Control, AC-18*(6), 646-652, 1973.

[45] SIGURD SKOGESTAD, *Control structure design for complete chemical plants*, Computers & Chemical Engineering, Volume 28, Issues 1–2, 15 January 2004, Pages 219-234.

that is an idealized way to see the control structure in a process; because what we have in reality is something more complex and sometimes unforeseeable, something like this (a classical “PID control”):

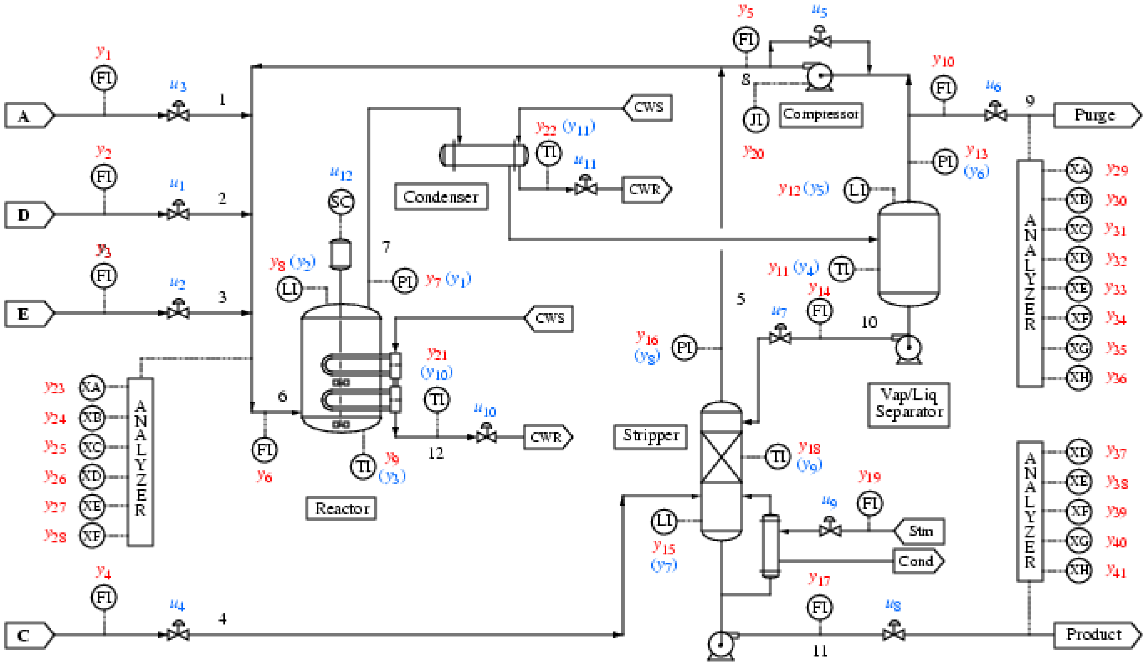

Figure 31: Tennessee Eastman challenge problem (Downs, 1991)

where the choice of decide what and where to put the different controllers becomes really difficult, especially if our intent is reach an intelligent way to control, taking into account of the fastness of response of the diverse controllers and the possibility to avoid redundant measurements.

The right question become how do we get from a PID to a PhD control? Is it possible to achieve a systematic procedure to pursue this goal?

To these questions we can find an initial response if we consider the previous referring to Alan Foss[46]:

> *The central issue to be resolved ... is the determination of control system structure.* ***Which variables should be measured, which inputs should be manipulated and which links should be made between the two sets?*** *There is more than a suspicion that the work of a genius is needed here, for without it the control configuration problem will likely remain in a primitive, hazily*

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[46] Foss, A. S., *Critique of Chemical Process Control Theory, IEEE Transactions on Automatic Control, AC-18*(6), 646-652, 1973.

> *stated and wholly unmanageable form. The gap is present indeed, but contrary to the views of many, it is the theoretician who must close it.*

Or as stated by Carl Nett[47]:

> *Minimize control system complexity subject to the achievement of accuracy specifications in the face of uncertainty.*

So when the purpose is to control a process the objective is *not* the tuning and behavior of each control loop, rather the *control philosophy* of the overall plant with emphasis on the structural decisions:

- *Selection of controlled variables ("outputs")*
- *Selection of manipulated variables ("inputs")*
- *Selection of (extra) measurements*
- *Selection of control* ***configuration*** (structure of overall controller that interconnects the controlled, manipulated and measured variables)
- *Selection of controller type* (LQG, H-infinity, PID, decoupler, MPC etc.).

If we proceed in this way we can easily achieve the previous goal: to get from ``PID control'' to "PhD" control.

Summarizing all the previous idea the concept on which work in order to reach the control of a process is that: *plantwide control* is *control structure design for complete chemical plant*.

Now we can begin with the analysis of Skogestad theory.

4.2 THE THEORY

When we thin to the term *plantwide control* we have to focus on a definition like this: control structure design applied to chemical plants. If we concentrate on this assertion we can highlight how this definition doesn't imply directly neither the tuning of the control system nor the behavior of the various loops naturally present in a plant. What is expressed in reality is a "control philosophy" whose horizon is the overall plant; and the fulcrum of all this dissertation are the structural decision.

In a schematic view of the procedure:

- Selection of Controlled Variables (CVs), i.e. OUTPUTS
- Selection of Manipulated Variables (MVs), i.e. INPUTS
- Selection of extra measurements

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[47] HADDAD, WASSIM M., BERNSTEIN, DENNIS S., NETT, CARL N., *Decentralized H2/H∞ controller design: The discrete-time case*, Proceedings of the IEEE Conference on Decision and Control, 2, pp. 932-933, 1989

- Selection of control configuration (that is overall controller)
- Selection of controller type (P, PI, PID, MPC, LQC etc.)

When we speak of plant-wide control, we mean all the decisions necessary to understand and make us possible to represent the plant in a diagram: from the simplest possible PF to the most complete one P&I. If we consider this problem from the mathematical point of view, we could abandon the hope to find a solution, because it's a very huge system made by a large number of discrete decision variables; problem that has its objective in keeping the CVs near to the set point. But the real question is what must we control? That is said more precisely and in a different manner: What are the CVs?

If we consider AS WE MUST DO the overall plant, the answer is minimize cost or maximize profit satisfying at the same time the constraints imposed by the market or equipment.

Speaking in a mathematical manner this is a simple way to formulate the problem: we have a constrained problem whose solution could be found in some particular cases, with the right assumptions (this has been possible thanks to the recent development in technology and in particular in the numerical calculus). In practice what it's necessary to do is obtain a complete plant, detailed in both dynamic and steady-state model, defining:

- Operational constraints
- All measurements and manipulations
- All expected disturbances
- All expected, allowed or desirable ranges for variables

and finally design a controller to keep variables close to set points. That is a controller that in any time collects all the information coming from the plant and consequently provides an optimizations of the Manipulated Variables.

That could be possible I some cases (very simple one), but practically it's being considered impossible. Moreover if we consider that acceptable control is achieved with simple structures and that the same structures made possible a good operation for most real plants, then the right conclusion is that we need to use a simple, but effective, control strategy.

How could be possible to control a real system? Sometimes as usual a decomposition of the global problem into many simpler problems could be useful to highlight and find the solution. During the decomposition we take into account two different phases:

1- Decentralized control: it's the "horizontal decomposition", where the advantage we obtain is based on spatial separation, i.e. the control of individual process units.

2- Hierarchical control: it's the "vertical decomposition", whose subdivision is made analyzing the timescale of the process (Figure 1); in order to have an idea of what concerns with the timescale of a real chemical plant, you can observe that:
  - ✓ SCHEDULING is in the order of the weeks;
  - ✓ SITE-WIDE OPTIMIZATION takes days;
  - ✓ LOCAL OPTIMIZATION, we talk about ours;
  - ✓ SUPERVISORY CONTROL, just minutes;
  - ✓ REGULATORY CONTROL, whose characteristic time is about seconds;

Such a cascade decomposition that operates on different timescale is at the basis of the control of all complex systems, e.g. biological systems, airplanes, plants and so on.

Considering the previous picture, and referring to the precedent bulleted list in particular to the first three points, we have to precise that those are part of an economic optimization of the plant or structure we want to control. What is the real interest of this work is focused on the last two points, or layers, i.e. the supervisory control and the regulatory control one, with the goal to track the set points coming from the previous layers. And before this, a very important decision is the choice of the Controlled Variables (CVs), for which the set points are given: in the supervisory control we select the CVs useful for an economic vision of the plant. For what concerns the selection of the TYPE of the controller, there's no a unique choice, the most used one is the PID controller, able to grant rapidity, precision and robustness to the control action.

Independently from the choice, it's necessary work and think about the sequent decisions:

- ❖ Decision 1: we must individuate the primary CVs (CV_1) based on an economic analysis of the plant → supervisory control. Their set points are the bridge between the optimization layer and the control one;
- ❖ Decision 2: we must select the secondary CVs (CV_2), i.e. the stabilizing variables → regulatory control. Their set points link the two control layers;
- ❖ Decision 3: we need to locate the throughput manipulator (TPM);
- ❖ Decision 4: we have to select pairings for the stabilizing layer, i.e. pair inputs (valves) and controlled variables, those coming from Decision 2.

The first and the second decision we can see in Figure 2, where CV_1, CV_2 are matrices and they are defined by $\mathbf{H_1}\ \underline{y}$ and $\mathbf{H_2}\ \underline{y}$ (both H are matrices themselves) while $\underline{y}$ are the measurements available.

So that’s the previous picture with the respect of the choice made for the different CVs and how they act on the plant:

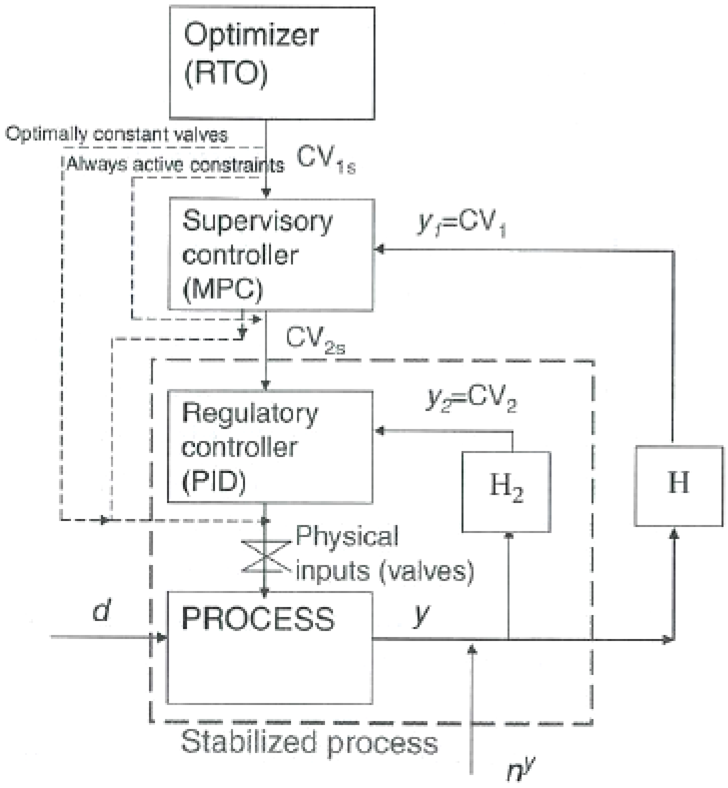

Figure 32: different control levels

4.3 THE PROCEDURE

This project has been made possible thanks to the previous work by Sigurd Skogestad. One of the first approach to the plantwide control was made by Buckley[48] (1964), then what we can obtain from literature is relatively scarce.

A recent review of the literature on plantwide control can be found in Skogestad and Larsson in 2000[49] who proposed a systematic subdivision and a good review of the previous works and approaches proposed.

On the basis of their work it’s possible to distinguish and join the different articles into two classes:

- the *process-oriented approaches* (that are engineering or simulation-based), among those we can find the ones proposed by Buckley[50], Douglas[51], Downs[52], Luyben *et*

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[48] PAGE S. BUCKLEY, *Techniques of Process Control*, Wiley, New York (1964)

[49] TRULS LARSSON, SIGURD SKOGESTAD, *Plantwide control - A review and a new design procedure*, Modeling, Identification and Control, 21 (4), pp 209 – 240 (July 1, 2000)

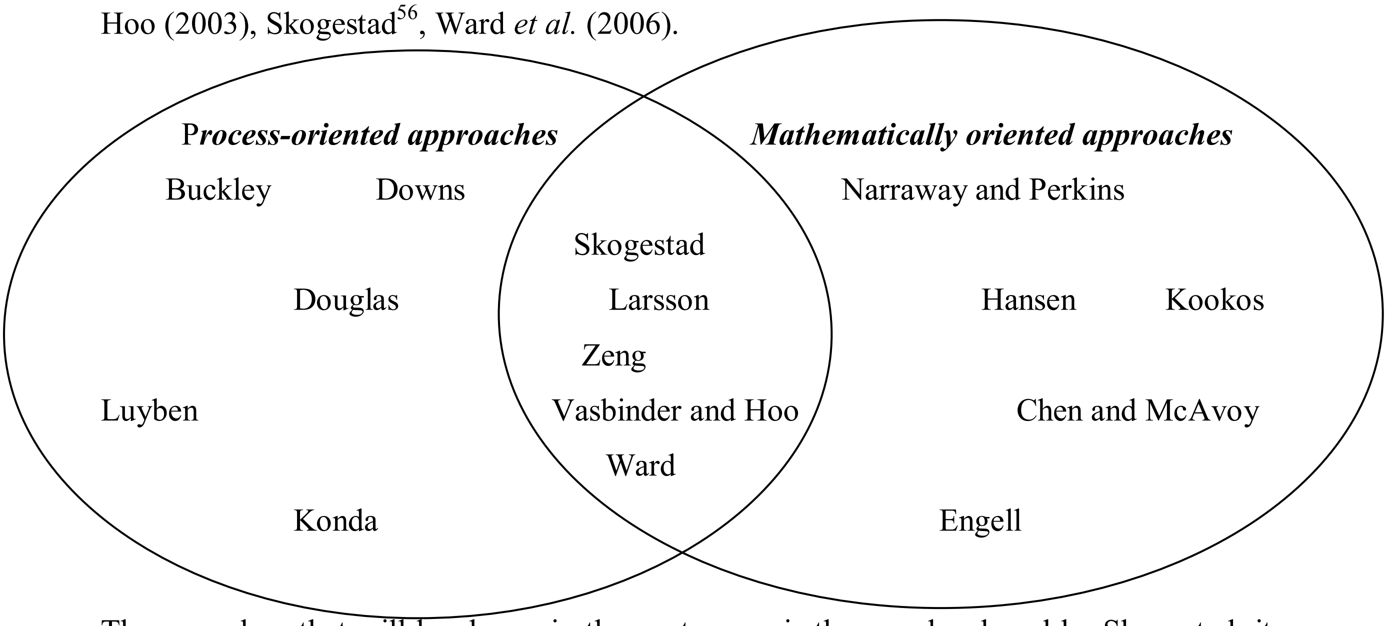
[50] PAGE S. BUCKLEY, *Techniques of Process Control*, Wiley, New York (1964)

[51] JAMES MERRIL DOUGLAS, *Conceptual Design of Chemical Processes*, New York: McGraw-Hill (1988)

al. (1997, 1998) and Konda *et al.* (2005). They are characterized by a non sufficient systematic procedure and their goal is reached without giving importance to economics.

- the *optimization* or *mathematically oriented approaches* (academic in a certain way), with works of Narraway and Perkins[53], Hansen *et al.* (1998), Kookos and Perkins[54], Chen and McAvoy (2003) and Engell (2007). With the term of academic here, we mean that these approaches lead to optimization problems those are insoluble for what concerns the plantwide application, i.e. their use is purely academic without any correspondence in real life.

So the right way to move on is a hybrid approaches between the previous ones: and in this sense we find the works of Zheng *et al.*(1999), Larsson and Skogestad[55], Vasbinder and Hoo (2003), Skogestad[56], Ward *et al.* (2006).



The procedure that will be shown in the next pages is the one developed by Skogestad; it was inspired by Luyben, but we'll able to note that the former is divided in two different parts: one concerned with steady-state economics, while the second one is involved in the stabilization loops.

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[52] J.J. DOWNS, *Distillation Control in a Plantwide Control Environment,* In: Practical Distillation Control, W.L Luyben (ed.), Van Nostrand Reinhold, 413-439 (1992)

[53] L. T. NARRAWAY, J. D. PERKINS, *Selection of process control structures based on Economics,* Comp. Chem. Eng. 18, S511, (1993a)

[54] **KOOKOS, I.K.,** PERKINS, J.D., *An algorithmic method for the selection of multivariable process control structures*, *Journal of Process Control,* 12 (1) , pp. 85-99, 2002

[55] TRULS LARSSON, SIGURD SKOGESTAD, *Plantwide control - A review and a new design procedure*, Modeling, Identification and Control, **21** (4), pp 209 – 240 (July 1, 2000)

[56] SIGURD SKOGESTAD, *Control structure design for complete chemical plants*, Computers & Chemical Engineering, Volume 28, Issues 1–2, 15 January 2004, Pages 219-234.

In order to evaluate the differences between these two configurations we start analyzing Luyben's procedure and then we'll compare with Skogestad's one.

4.3.1 LUYBEN'S PROCEDURE

- **Step L1.** *Establish control objectives*
- **Step L2**. *Determine control degrees of freedom*
- **Step L3**. *Establish energy management system*
- **Step L4.** *Set the production rate* ***(Decision 3)***
- **Step L5**. *Control product quality and handle safety, environmental and operational constraints*
- **Step L6**. *Fix a flow in every recycle loop and control inventories*
- **Step L7**. *Check component balances*
- **Step L8.** *Control individual unit operations*
- **Step L9.** *Optimize economics and improve dynamic controllability*

Now we have to note some things:

- "Establish control objectives" in step L1 doesn't lead directly to the choice of controlled variables (i.e. what we find in **Decisions 1 and 2**). Thus, in Luyben's procedure, **Decisions 1, 2 and 4** aren't explicit, but are included implicitly in most of the steps.
- Even though the procedure is systematic, we have a cascade of different steps, it is still heuristic and *ad hoc*: as it is not clear how the authors arrived at the steps or their order.
- A major weakness is that the procedure doesn't include economics, except as an afterthought in step L9 where we find the expression "Optimize economics", but it's loosely implied in all the procedure, or better there's no a clear link between economics and the optimization of a plant.

4.3.2 SKOGESTAD'S PROCEDURE

I **Top Down** (focused on steady-state optimal operation)

- Step S1: Define operational objectives (optimal operation)
  - Cost function *J* (to be minimized)
  - Operational constraints
- Step S2 (optimization):
  - (a) Identify degrees of freedom (MVs).
  - (b) Optimize for expected disturbances and find regions of active constraints
- Step S3 (implementation): Select primary controlled variables c = y_1 (CVs) (**Decision 1).**
- Step S4: Where set the production rate? Where do I collocate the TPM? (Inventory control) (**Decision 3)**

II **Bottom Up** (focused on the control layer structure)

- Step S5: Regulatory / stabilizing control (PID layer)
  - What more to control (y_2; local CVs)? y (**Decision 2**)
  - Pairing of inputs and outputs y (**Decision 4**)
- Step S6: Supervisory control (MPC layer)
- Step S7: Real-time optimization (Is it necessary?)

As we can observe from the very first point of the overall procedure we have to note that economics is at the basis of all the process: in other words we have collocate economics into basic control layer.

Table 8: top-down/bottom up procedure

STEP	**Comments, analysis tools and model requirements**
I. TOP-DOWN ANALYSIS:	
1. MANIPULATED VARIABLES Select manipulated variables **MV** (valves and actuators) for control.	May need extra equipment if analysis shows there are too few DOFs.
2. DEGREE OF FREEDOM ANALYSIS Identify dynamic and steady-state degrees of freedom (DOF)	
3. PRIMARY CONTROLLED VARIABLES: Which (primary) variables c should we control? • Control active constraints • Remaining DOFs: Control variables for which	*Steady-state economic analysis:* • Define cost and constraints • Optimization w.r.t. steady-state DOFs for various disturbances (gives active

constant setpoints give small (economic) loss when disturbances occur.	constraints) • Evaluation of loss with constant setpoints
4. PRODUCTION RATE: Where should the production rate be set? (Very important choice as it determines the structure of remaining inventory control system.)	Optimal location follows from steady-state optimization (step 3), but may move depending on operating conditions.
II. BOTTOM-UP DESIGN: (With given controlled and manipulated variables)	*Controllability analysis*: Compute zeros, poles, pole vectors, relative gain array, minimum singular values, etc.
5. REGULATORY CONTROL LAYER. *5.1 Stabilization* *5.2 Local disturbance rejection* *Purpose:* “Stabilize” the plant using single-loop PID controllers to enable manual operation (by the operators) *Main structural issue*: What more should we control? • Select secondary controlled variables (measurements) y_2 • Pair these with manipulated variables m, avoiding m’s that saturate (reach constraints)	*5.1 Pole vector analysis* (Havre and Skogestad, 1997) for selecting measured variables and manipulated inputs for stabilizing control. *5.2 Partially controlled plant analysis*. Control secondary measurements (v) so that the layer above (or the operators) can handle the effect of disturbances on the primary outputs (c). *Model:* Linear multivariable dynamic model. Steady state usually not important.
6. SUPERVISORY CONTROL LAYER. *Purpose:* Keep (primary) controlled outputs c at optimal setpoints c_s, using unused manipulated variables and setpoints v_s for regulatory layer as degrees of freedom (inputs). *Main structural issue*: Decentralized or multivariable control? *6a. Decentralized (single-loop) control* Possibly with addition of feed-forward and ratio control. • May use simple PI or PID controllers. • Structural issue: choose input-output pairing *6b. Multivariable control* Usually with explicit handling of constraints (MPC) • Structural issue: Size of each multivariable application	*6a. Decentralized*: Preferred for noninteracting process and cases where active constraints remain constant. *Pairing analysis:* Pair on RGA close to identity matrix at crossover frequency, provided not negative at steady state. Use CLDG for more detailed analysis *6b. Multivariable:* 1. Use for interacting processes and for easy handling of feedforward control 2. Use MPC with constraints handling for moving smoothly between changing active constraints (avoids logic needed in decentralized scheme 5a) *Model*: see 5
7. OPTIMIZATION LAYER *Purpose:* Identify active constraints and compute optimal setpoints c_s for controlled variables. *Main structural issue*: Do we need real-time optimization (RTO)?	*Model:* Nonlinear steady-state model, plus costs and constraints.

8. VALIDATION	Nonlinear dynamic simulation of critical parts

Now we will analyze the procedure in each of the above point (steps), in order to give the right visual of what they mean and to make possible understanding the overall project.

4.4 SKOGESTAD'S PROCEDURE

Before the analysis of each points previously stated, it's necessary to introduce the concept of *degrees of freedom* for operation.

4.4.1 DEGREES OF FREEDOM

The idea of degrees of freedom for an operation is often not as simple as it would be expected. First of all when we consider an operation we have to think that the equipment is assumed fixed; and then that the degrees of freedom (our MVs or DOFs, and from this point on *u* in the sequent explanation) change during the passage through the hierarchy (as you can see in Figure 1and 4). We can have three different kind of degrees of freedom:

- DOFs for optimization (i.e. steady-state DOFs, $\underline{u}$), $MV_{opt}=CV_1s$
- DOFs for supervisory control, $MV_1 = CV_{2s}$ + unused valves
- DOFs for stabilizing control (physical), MV_2 = valves (for the dynamic process)

For this application, the economics of overall the plant is determined and evaluated at steady-state behaviour (Morari *et al.* 1980), and the former steady-state degrees of freedom are the same of the economic DOFs.

A brief explanation of what we consider as valves: this term is adopted here because this is their nature when we speak of process control. The stabilizing control layer usually doesn't use all the valves: e.g. some valves may not be used dynamically because they are optimally constant (for example a relief valve); while other valves may not be needed for stabilizing control and they can be used by the supervisory control layer to improve the dynamic performance of the control system itself.

4.4.1a Steady-State DOFs

This is the first class of DOFs. And while the individuation of the physical degrees of freedom in quite absolute (in the sense that they represent the valves and in this sense it's easier to collocate their position and number inside the process); it is more difficult to find the steady-state DOFs (our *u*, as seen before).

Yet what is useful to find is the *number* of the DOFs, here n_u and not really the variables themselves, because this is the number that individuate the CV_1 that will be used in Step 3. In this sense it's important to note and keep in mind that with this counting we will be able to understand and identify the number of primary controlled variables, i.e.:

N° of primary CVs = N° of steady-state DOFs, n_u

It's important to find a independent and simple way to find n_u because it's useful to check and then to reduce the time spent on optimizing the process.

Actually there are three ways to identify and evaluate the number of them:

- Equation-counting
- Valve counting
- Potential degrees of freedom

EQUATION-COUNTING

Among all the possibilities this is certainly the most difficult to apply without encountering in an error. It's the most "brutal" method and concerns with the evaluation of all equations in the model; but if we think that is really difficult have a correct model for the process, the idea of identify all the equations seems to become unreal and almost fantastic.

In practice we have:

$$n_u = \text{n° of variables} - \text{n° of equations/specifications}$$

and it's difficult and not used in everyday practice.

VALVE COUNTING

The first approach is identify all physical degrees of freedom (the so called dynamic), valves ("valves" also includes adjustable compressor power for example, in other words anything we can manipulate). But as the economics is usually depending on only steady-state, we have to take into account valves with steady-state effect and avoid inserting variables without or with negligible effect on economics, i.e. variables with dynamic effect. So:

#steady-state DOFs, n_u = #valves - #variables without steady-state effect

Or if we want to be more precise:

$$n_u = N_{valves} - N_{0ss} - N_{specs}$$

where:

N_{valves} = n° of dynamic (control) DOFs (valves)

$N_{0ss} = N_{0y} + N_{0,valves}$ = n° of variables with no steady-state effect

$N_{0,valves}$ = n° purely dynamic control DOFs

N_{0y} = n° controlled variables (e.g. liquid levels) with no steady-state effect

N_{specs} = n° of equality specifications (e.g. given pressure)

Let's now see some examples in order to understand better the meaning of the above mentioned method usable to identify the different steady-state degrees of freedom. In particular we analyze a typical simple equipment (heat exchanger) and more complex one, very important in whatever plant we are concerning with studying, that is the distillation column.

Examples:

Heat exchanger = 3 valves (bypass valves on both hot and cold side and a valve on cooling water) – 2 bypass valves = 1 n_u, i.e. the amount of heat transferred.

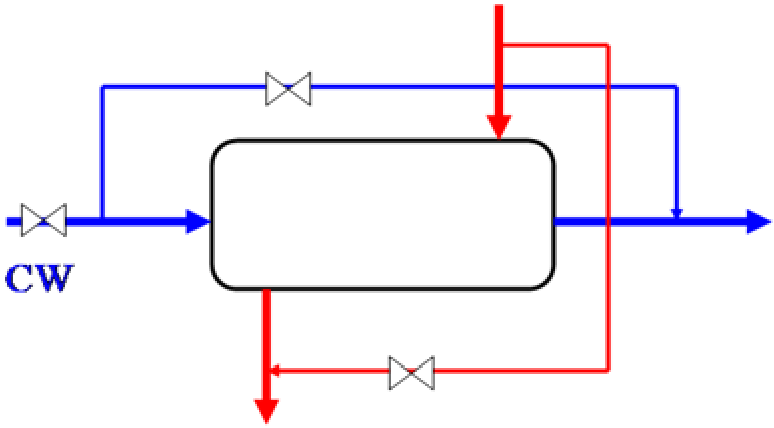

Figure 33: a heat exchanger

Distillation columns = 6 valves (feed, F + bottom product, B + distillate product, D + cooling, C + reflux, R + heat input Q → it determines the boil-up V) – 2 specifications on product (B + D) = 4 $\boldsymbol{n_u}$.

It's usual to exclude liquid levels because they have no steady-state.

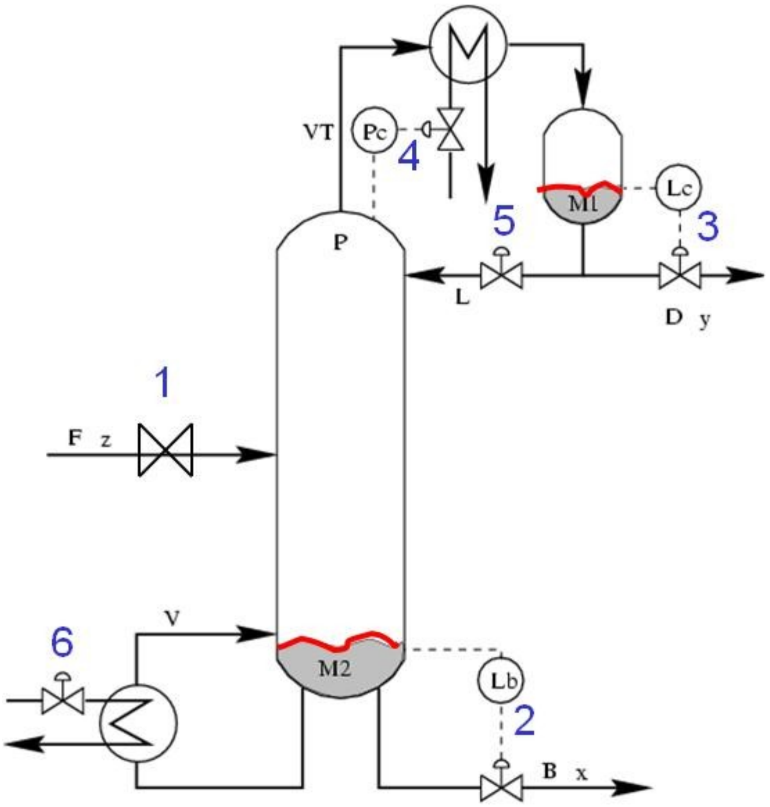

Figure 34: DOFS of a distillation column

POTENTIAL STEADY-STATE DOFs

Another way to identify the different degrees of freedom of an equipment is to adopt the sequent table (Table 1). When you use the word "potential" you have to take into account that there isn't always a valve to adjust the DOF: in the previous example when we speak about the heat exchanger we have said that it has 1 DOF, but if there's not a bypass then it cannot be used.

Table 9: Potential steady-state degrees of freedom

Equipment	n_u	
Each external feed stream	1	Feed rate
Splitter	n-1	Split fractions
Mixer	0	[-]
Compressor, turbine, pump	1	Work/speed
Adiabatic flash tank	0*	[-]
Heat exchanger	1	Bypass/flow
Liquid phase reactor	1	Holdup reactant
Gas phase reactor	0*	[-]
Column (no heat exchanger)	0*+n° side streams	[-]

Note: pressure*: we need to add 1 DOF at each extra place you set the pressure (that means to use an extra valve, compressor or pump).

Considering again the previous examples we obtain:

Examples:

Heat exchanger = 1 $\boldsymbol{n_u}$, as we can evidence from Table 1.

Distillation column = the column itself has 0 DOFs (steady-state), but I's necessary to take into account other potential DOFs: feed rate count for 1, splitter (reflux) is 1 again and we have 2 DOFs coming from heat exchangers (condenser and reboiler). The total is another time 4 $\boldsymbol{n_u}$ as previously obtained from valves counting.

We can start now the analysis of Sigurd Skogestad approach, going to analyze all the steps more in detail.

4.4.2 TOP-DOWN

This part as said before is particularly concerned with economics and economics is the basis on which building the control structure. For this part of the analysis a steady-state of the model is sufficient for a complete study and selection of the CVs.
The model built previously it would be the canvas for our project.

4.4.2a Step 1: Define Operational Objectives (Cost J and constraints)

If our intent is approaching a plantwide control we need first of all to quantify and evaluate the operational objectives as scalar cost function J ([money/time] →[€/h]) which has to be minimized or, that is the same thing, evaluate the profit function, which has to be maximized (P= -J).
For this point all we have to consider is:

J = cost feed + cost utilities (i.e. energy) – value products [money/time]

But what are we going to use our degrees of freedom $\boldsymbol{u}$ (MVs), previously determined, for? The answer is just here. The scalar function we define is a function defined in this way:

$$J = J(\boldsymbol{u}, \mathbf{x}, \underline{\mathrm{d}})$$

where:

u: degrees of freedom (usually steady-state)

x: states (internal variables)

d: disturbances

We have to pay attention to some critical points:

- Fixed costs and capital costs aren't included: indeed they aren't affected by plant operation on timescale we consider (i.e. usually 1 [h]).
- We want to minimize *J*, subject to satisfying the operational constraints (safety, environmental constraints and also some physical measurements whose negative value would be a nonsense, e.g. flows and concentration, and so on).

4.4.2b Step 2: Determine the steady-state Optimal Operation

In order to achieve a reliable and efficient control system we have to find the optimal way of operating process, and this has to be done before design the control system itself.

Consider that we can find that a valve should be closed (e.g. a bypass valve); then this device couldn't be used for stabilizing control unless we accept the loss of "back-off" coming from the optimal operating conditions. And to determine this plant condition we have to work on a steady-state model, then identify DOFs (as explained previously) and optimize it for expected disturbances.

Summarizing:

1- **Identify steady-state DOFs *u***: we must identify them as seen before this explanation of the first two steps. In this case actually we are concerned into the number of ***u*** and what's the nature of this variables. Indeed they make an independent set.

2- **Identify important disturbances d and their expected range**: they are usually concerned into the feed rate (throughput) and feed composition, for what regards internal disturbances; and they are related to temperature and pressure when we consider external variables. We have to add also disturbances from the possible change in specifications and active constraints (e.g. purity specification) and in parameters (equilibrium constants or rate constants for example); moreover we have to include the expected range in prices of products, feed and energy.

3- **Optimize the operation for the expected disturbances**: in this passage we specify the disturbances d and we vary the degrees of freedom in the optimal way as possible $\boldsymbol{u}_{opt}$ (d) in order to make it possible the minimization of the cost function *J*, with the respect of the constraints. Our goal is the achievement of the individuation of the constraint regions and the optimal set-points in regions themselves.

With the scalar function we define:

$$J = J(\boldsymbol{u}, \mathbf{x}, \underline{d})$$

we optimize operation with respect to *u* for given d (usually steady-state):

$$\min_u \; J(\boldsymbol{u}, \mathbf{x}, \underline{d})$$

subject to:

- Model equations: $f(\boldsymbol{u}, \mathbf{x}, \underline{d}) = 0$
- Operational constraints: $g(\boldsymbol{u}, \mathbf{x}, \underline{d}) \leq 0$

Example:

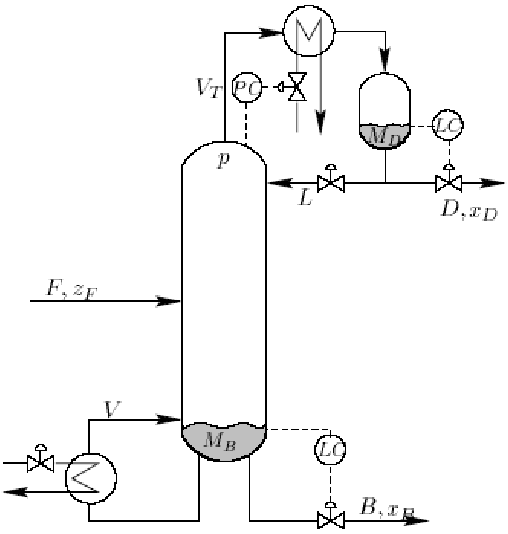

Figure 35: a distillation column

We proceed now analyzing a distillation column at steady-state with given p (i.e. pressure) and F (that is the feed fed to the column): we have $\boldsymbol{n_u} = 2$, e.g. L and V ($\boldsymbol{u}$).

What must be minimized is the cost:

$$J = -P$$

$$\text{where } P = p_D \cdot D + p_B \cdot B - p_F \cdot F - p_V \cdot V$$

with p_D, p_B, p_F, p_V = prices of Distillate, Bottom, Feed and Energy (p_V)

and the following constraints:

Purity D: $x_{D,\ impurity} \leq \max$

Purity B: $x_{B,\ impurity} \leq \max$

Flow constraints: $\min \leq$ D, B, L etc. $\leq \max$

Column capacity (flooding): $V \leq V_{max}$

Pressure: 1) p given (d)

2) p free (u): $p_{min} \leq p \leq p_{max}$

Feed: 1) F given (d)

2) F free (u): $F \leq F_{max}$

Our goal is to minimize *J* with respect to steady-state DOFs (*u*)

That is the mathematical expression of the steady-state optimization problem. Remembering what has been explained previously, we have *u* those are our degrees of freedom, x are the internal variables (states) and d are the disturbances cited before.

When we put the equality f = 0 it's our intent to express the mathematical model equations and some equality constraints (e.g. the feed flow or a pressure, whatever has the necessity to be set with a certain value); on the other hand when we state $g \leq 0$, we want to represent the operational constraints (for example a product composition or maybe a liquid/vapour ratio).

When we speak about active constraints[57], we refer to the expression used in mathematical optimization, where we have a problem defined using an objective function that has to minimize or maximize, and in parallel we have a set of constraints, usually some equalities and inequalities:

$$g_1(x) \geq 0$$
$$g_2(x) \geq 0$$
$$g_3(x) \geq 0$$
$$\dots$$
$$g_n(x) \geq 0$$

that define the feasible region, that is, the set of all **x** to search for the optimal solution. So given a point x in the feasible region, one of the previous constraints,

$$g_i(x) \geq 0$$

is called *active* if we have the following equality:

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[57] NOCEDAL, JORGE; WRIGHT, STEPHEN J., *Numerical Optimization,* Berlin, New York: Springer-Verlag, 2nd ed. 2006

$$g_i(x) = 0$$

One of the most important results we want to obtain from the optimization is to find the region of active constraints; this is the most time-consuming step of the entire procedure both obtaining the model from literature or building up from a previous P&I diagram and the optimization itself with the mathematical numerical resolution.

In case of necessity (when the model may not be available or there no material time to operate the optimization) it could be possible perform a simplified version of the Step 1 and Step 3 using a process insight to operate the individuation of active constraints themselves and the possible self-optimizing variable (CV_1) for the remaining DOFs.

It's important to understand that there is not a unique control structure defined as optimal and that is due to the fact that the set of active constraints will vary and depend on disturbances and on prices of market. Generally the control system should be able to supply reliability in case of future variations. What should be done in order to increase the performance of the control system, it would be the offline analysis and optimization to identify expected regions of active constraints.

As we stated before the optimal active constraints change depending on disturbances (feed, composition, temperature and so on) and on market conditions (i.e. price). For this latter cause there are two mode of operation, function of market condition: *given throughput/feed-rate* (Buyer's Market) or *maximum throughput/product* (Seller's Market).

The former (*given throughput/feed-rate*) is usually the nominal mode for which the control system is set up to handle. It's the typical situation tending to maximize the efficiency, where we have some tradeoff among the utilities (consumption of energy) and the recovery of the product. It a situation providing an unconstrained optimum.

What we have is the sequent situation:

$$J = \text{cost feed} - \text{value product} + \text{cost energy}$$

where the first two terms of the previous equality (cost feed – value product) are considered often constant; and usually, as said before, optimal operation is usually *unconstrained*. The control is going to operate at optimal trade-off, but this is not obvious what to control to achieve this.

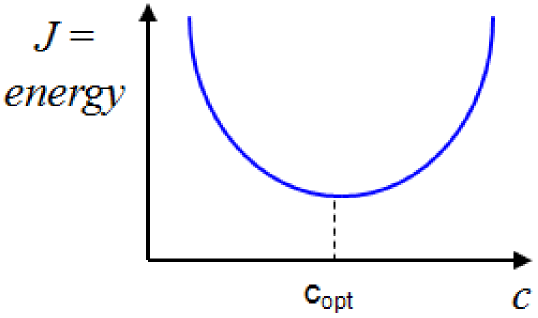

Figure 36: objective function *J* versus cost energy

The latter (*maximum throughput/product*) could be applied when the product price is higher if compared to price of raw material (feed) and energy (utilities) and tends to increase the throughput as much as possible. In contrast with the previous situation here the efficiency falls and it usually happen that constraints reach the bottleneck and in this state any further increase results in an infeasible solution.

The situation is similar to the previous one:

$$J = \text{cost feed} - \text{value product} + \text{cost energy}$$

but in this case the assumptions regard the feederate that is now a degree of freedom and that the product is much more valuable than the feed: the optimal operation is then as stated before to maximize product rate (and always as seen before, remaining in the feasible region). Here what has to be controlled is the “bottleneck” and it’s obvious for sure.

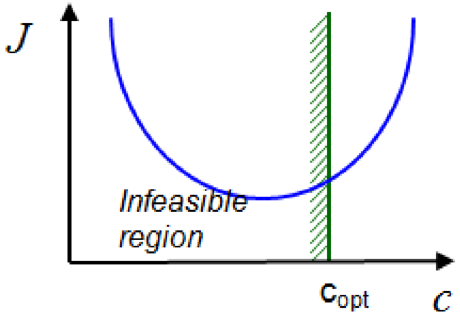

Figure 37: objective function *J* versus DOFs

4.4.2c Step 3: Select Economic (Primary) Controlled Variables, CV_1

In this point we will deal with the implementation of optimal points found in the previous two steps. Our goal is tend to organize them in a robust and simple manner in order to make it possible to create a *praxis* useful to anyone is going to apply this procedure.

What we have obtained from the previous analysis is the economic degrees of freedom (u), and now what we want to reach is identify the economic controlled variables (CV_1) those are responsible for the first controlling layer of the hierarchical structure we have see at the beginning of this chapter. Remember that the number of first controlled variables is equal to steady-state degrees of freedom one.

The question we have to answer is: What should we control? And how should we adjust the degrees of freedom ($\boldsymbol{u}$)?

So the optimal operation for given d^*:

$$\min_u \ J(\boldsymbol{u}, \mathbf{x}, \underline{d})$$

subject to:

$$\text{Model equations:} \qquad f(\boldsymbol{u}, \mathbf{x}, \underline{d}) = 0$$

$$\text{Operational constraints:} \qquad g(\boldsymbol{u}, \mathbf{x}, \underline{d}) \le 0$$

The result of this study is u_{opt}, whose values however usually cannot be kept constant because disturbances d change, and in this way the optimal results change too.

By the way for the economical optimal operation, we have two rules:

- **CV_1 – rule 1**, that is control active constraints
- **CV_1 – rule 2**, i.e. for the remaining unconstrained DOFs, we must control self-optimizing variables, where the ideal self-optimizing variable c is the gradient is

$$\mathbf{c} = \partial J / \partial \mathbf{u} = J_u$$

As seen previously for each steady-state degree of freedom, *u*, there is one CV_1. There is a unique match between the variables and the DOFs. For what regards the so-called “self-optimizing” variables we mean variables “for which close-to-optimal operation with constant setpoints can be achieved, even when there are disturbances”[58].

Thinking about active constraints, instead, they are self-optimizing variables in the wider sense, because operation is optimized keeping their values constant (usually they are referred as unconstrained self-optimizing variable, highlighting the difficulty to find them).

CV_1 – rule 1

As anticipated in the previous section of this paragraph we have to control active constraints for first, because they are the obvious self-optimizing variables to be kept constant. Active constraints are evaluated by analysis in Step 2. It’s important to identify if an active constraints is an input constraints or an output one. What’s the difference? The former are trivial to implement cause we could only set the minimum or the maximum value for this variable and because this reason no control is then needed.

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[58] TRULS LARSSON, SIGURD SKOGESTAD, *Plantwide control - A review and a new design procedure*, Modeling, Identification and Control, **21** (4), pp 209 – 240 (July 1, 2000)

For example, if we are dealing with an optimal operation of a runner (a sprinter on 100 [m]), assuming that the optimal operation itself is time (J = T), we could achieved the solution for this problem with maximum speed for the athlete (no thinking is then required). In this case the active constrained "controlled" is the speed of the athlete or better the power he's able to use to run that distance.

Instead, if we are dealing with an output constraints (the latter of the previous distinction) we need a controller, where it's often sufficient a simple single-loop to achieve the desired result. Take into consideration the previous example: if now we have to face a marathon (42.195 [km]), it's impossible to require an athlete to run at his maximum speed for such a long race. Even if time is our optimal operation that has to be minimized we can achieve the result in a better way. The question here is which self-optimizing variable c do we need to control at constant setpoint?

- c_1 = distance to leader of race
- c_2 = speed
- c_3 = heart rate
- c_4 = level of lactate in muscles

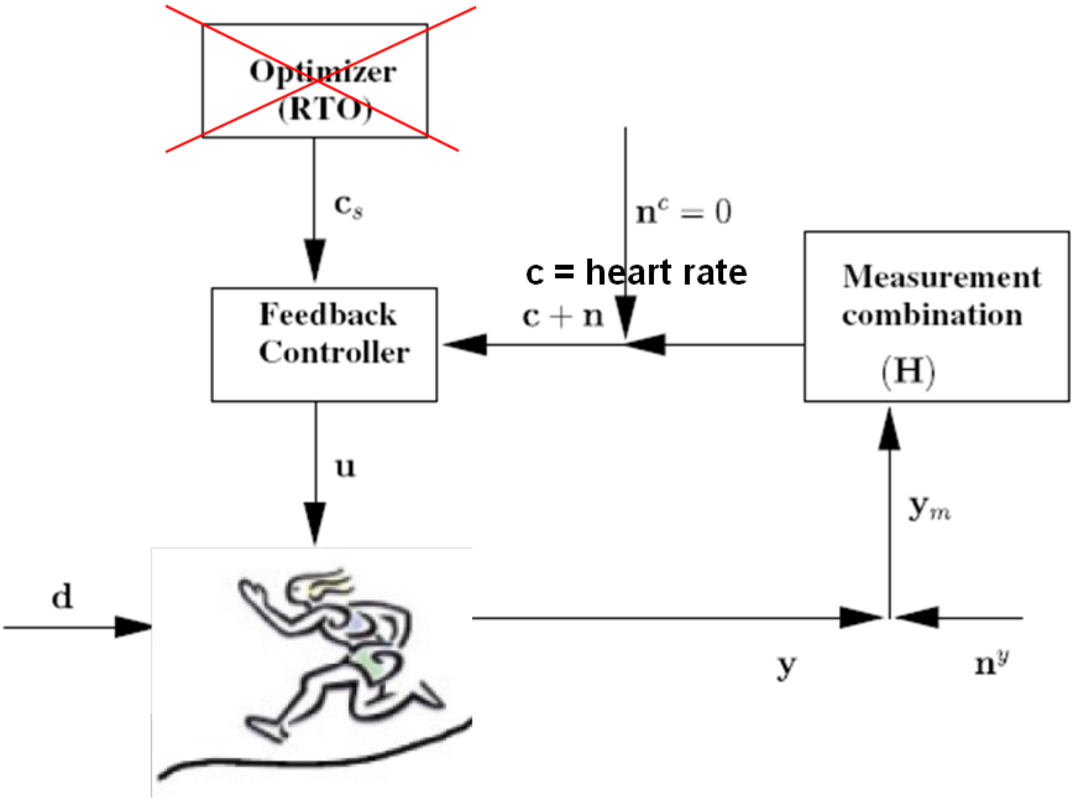

Figure 38: self-optimizing control of a marathon runner

Thinking in this way the problem is now reduced into a simple and robust implementation, where disturbances are indirectly handled by keeping a constant heart rate (our variable controlled) which *may* have infrequent adjustment of setpoint (heart rate itself).

BACK –OFF and LOSS

Let's now consider another example in reference to the previous one about marathon. In this case think about a car and consider that the maximum speed limit is like an active constraint (suppose that the maximum speed limit is 80 [km/h]) and because of this nature we should be selected as controlled variable (CV_1). In order to reach this control we may use the cruise controller, which is able to adjust the engine power, keeping the car velocity near to the setpoint. But either in the case there is a steady-state measurement error ($n^y = 5$ [km/h]) or there is a dynamic control error (3 [km/h]), we have to recede from the speed limit to avoid exceeding the speed limit itself (and for this reason put the setpoint at 72 [km/h]). So in general we want to minimize the back-off because larger is the back-off itself greater is the loss (i.e. larger J = T).

The *back-off* is the limit, the safety margin from the active constraints and it can be defined as the difference between the active constraints value and the chosen setpoint, i.e.:

$$\text{Back-off} = |\text{Constraint - Setpoint}|$$

In our example we have a back-off equal to 8 [km/h] (|80 [km/h] – 72 [km/h]|) if we must not exceed the speed limit (i.e. a hard constraint); while it can be reduced to 5 [km/h] if we consider that the dynamic error will average out if control has an integral action (80 [km/h] – {72 [km/h] + 3 [km/h]}), i.e. soft constraint.

Why do we have to control the active constraints? They must be selected as CV_s because the optimum doesn't reach a flat point with the respect of this variables.

Moreover, as mentioned before, there is an economic penalty if we recede from an active constraint: if a constrained optimization method is used for the optimization, then we can quantify the loss using the Lagrange multiplier λ, associated to the constraint itself:

$$\text{Loss} = \lambda \text{ x back-off}$$

Because of the direct dependence (linearity) from the Lagrange multiplier, we can note that bigger is the multiplier, greater is the economic loss unless the back-off is very small.

What's the right value for a back-off?

In case of input constraints, it's obvious we do not have any back-off unless the goal is to use the input for stabilization in the lower regulatory layer (the stabilizing one); in that case then we need a range in order to make possible the control.

If, instead, we deal with output constraints, we have to face two different cases:

- soft output constraints (only average value matters):

  back-off = measurement error (bias, n^y)

- hard output constraints (has to be satisfied at all time):

  back-off = measurement error (bias, n^y) + control error (dynamic)

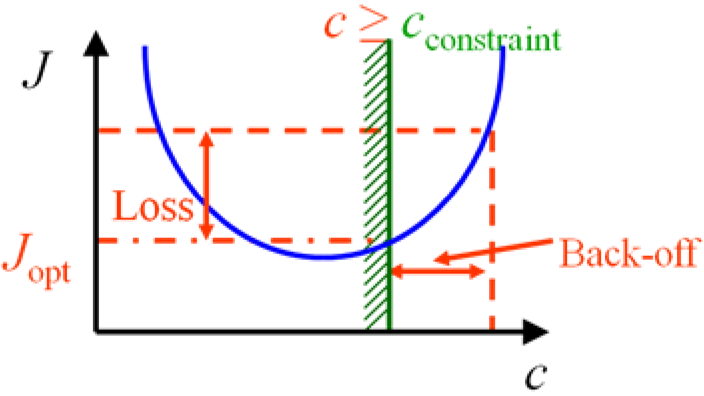

Figure 39: active output constraints

It's quite clear that a method to reduce the back-off is to have the possibility using accurate measurements of output constraints; then for hard output constraints we need:

- tight control with a small dynamic control error
- "squeeze and shift rule":by squeezing the output variation (with control), we can shift the setpoint closer to its limit value.

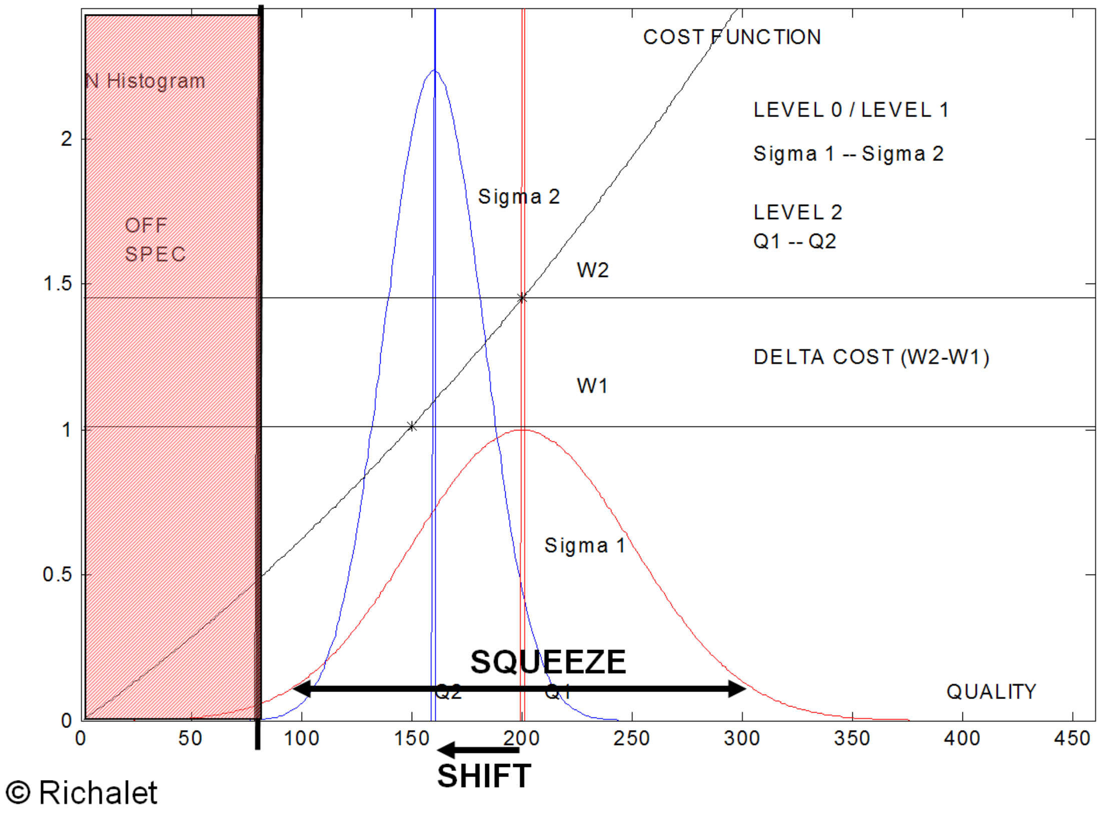

Figure 40: "squeeze and shift" rule, Richalet©

In summary and other simple thumb rules:

1. Always control active constraints
2. Purity constraint on expensive product are always active (we don't need overpurification), i.e.:
    (a) "Avoid product give away" (e.g. selling water as expensive product)
    (b) Save energy (costs energy to overpurify)
3. In case of an unconstrained optimum, we NEVER try to control a variable that reaches maximum or minimum at the optimum (never try to control directly the cost J).
4. Exception to CV_1 – rule 1: if the Lagrange multiplier is small for some active constraint, then it may be better to select some other unconstrained CV_s, because of simplicity, but one then needs to *back off* from optimal point to guarantee feasibility.

CV_1 – rule 2

This second rule is concerning the selection of the unconstrained self-optimizing variables. In order to accomplish this goal, we have to follow the next steps:

1. **Identify candidate measurements y**: first of all we must identify all the candidate measurements y, with their expected *static* measurements error (bias, n^y). In y we take into account both the inputs and the measurements used to control the active constraints.
2. **Select primary (economic) controlled variables $\mathbf{CV_1 = H \cdot y}$ (Decision 1)**: in the most optimistic vision we would like to control all single measurements for simplicity and (in this case) H is a selection matrix. More generally we may control measurement combination and in this case H is the "full" matrix. This step must be repeated for each constraint region. In order to reduce the necessity to switch between regions, it could be possible to use the same CV_1s, although it'd be responsible of infeasibility.

As we can understand it's easy to identify and control the active constraints; the most difficult thing is to work on and with the other degrees of freedom, and if our question is if it makes a difference what we control with the remaining DOFs, we have to expect that the answer is clearly "yes". In order to understand better we can take as example the previous one about a marathon runner: that is a clear problem that it couldn't be solved as the sprinter one. We have to use a self-optimizing approach.

It's now useful introducing some **qualitative approaches** to identify a *good* $\mathbf{c} = \mathbf{H} \cdot \underline{y}$, most of all if our intention is to control a single measurement (i.e. $\mathbf{c}$ = selected $\underline{y}$):

1- The *optimal* value of our controlled variable c is insensitive to disturbances, that is the derivative $d\mathbf{c}_{\mathbf{opt}}/d\underline{d}$ should be small, but it doesn't mean that the sensitivity of c to disturbances is small: $d\mathbf{c}/d\underline{d}$ must be not too large, because in this case the control would be difficult. On the other hand the same ratio doesn't have to be too small (that is $dc/d\underline{d}$ tends to 0), because in this case it would be impossible to control acting on the variable c and the disturbance cannot be deleted. In summa we weant $d\mathbf{c}_{\mathbf{opt}}/d\underline{d}$ to small.

2- The variable c has to be easy to measure and control in an accurate manner.

3- The value of c is insensitive to disturbance (see point 1), but is sensitive to manipulated variable $\boldsymbol{u}$: the gain $\mathbf{G} = d\mathbf{c}/d\boldsymbol{u}$ from u to c is large (i.e. a large error in controlled variable $\mathbf{c}$ results in a small change of $\boldsymbol{u}$). we could say equivalently that the optimum with respect to variable c should be "flat".

4- In case of two or more controlled variables **c**, they don't have to be loosely correlated in order to avoid impracticability of control due to dependencies among them.

Note that all four point above mentioned should be satisfied.

How can we find the matrix **H**? In practical there are two main approaches for finding it, i.e. to identify self-optimizing CV$_1$s associated with the unconstrained DOFs: the *"brute force" approach* and the *"local" approaches*.

1- **"Brute force" approach**: given a set of controlled variables CV$_1$ = **c** = **H** · $\underline{y}$, we compute the cost J (**c**, $\underline{d}$) when we keep c constant (**c** = **c$_s$** + **H**· $\underline{n^y}$) for various disturbances $\underline{d}$ and measurements error $\underline{n^y}$. With this procedure we want to cover the expected future operation. Generally expected extreme values in the parameter space ($\underline{d}$ and $\underline{n^y}$) are used to compute the cost for alternative choice in the controlled variable (matrix **H**). this method although is simple to understand and apply and it works for non-linear plants and for changes in active constraints too (only one nominal optimization is required to find the setpoints); it's very time consuming and it cannot guarantee that every case is covered (there are infinite choices for matrix H and we are not sure that the best c$_s$ are found).

2- **"Local" approaches**: the basis is on quadratic approximation of the cost[59], and the main ones are pointed out here:

   a. **Maximum gain rule**: this is a quantitative version of the previous requirements 1 and 3, i.e. that "sensitive" variables should be controlled with a large gain, |**G**| from ***u*** to **c** = **H**· $\underline{y}$. With this rule we can have a clear insight of our variables. In words we want to **maximize** $\underline{\sigma}(G_s)$, where:

$$G_s = S_1 G J_{uu}^{-\frac{1}{2}}$$

$$S_1 = diag\left\{\frac{1}{span\ (c_i)}\right\}$$

$$span\ (c_i) = |n_i^c| + |\Delta c_{i,opt}(d)|$$

   In words, select controlled variables c for which the gain G (= "controllable range") is <u>large</u> compared to its span (= sum of optimal variation and control error).

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[59] ALSTAD, V., SKOGESTAD, S., HORI, E.S., *Optimal measurement combinations as controlled variables*, Journal of Process Control, 19 (1), pp. 138-148 (2009)

b. **Nullspace method**: we know that the optimal measurement sensitivity, defined as $\mathbf{F} = d\underline{y}^{opt}/d\underline{d}$, is obtained when we select matrix **H** in order to have $\mathbf{HF} = 0$. This method reach its best results and optimal measurement combinations in case of no noise, that is $\underline{n}^y = 0$. Each column of **F** express the optimal change in y when the unconstrained variable $\boldsymbol{u}$ is adjusted in order to have a system remaining optimal with respect to disturbances $\underline{d}$. Active constraints are assumed to be constant. With a model of the process is straightforward to obtain **F** numerically. Assuming that we have at least as many independent measurements $\underline{y}$ as the sum of the number of independent inputs $\boldsymbol{u}$ and disturbances $\underline{d}$, the optimal $\mathbf{c} = \mathbf{H} \cdot \underline{y}$ is selected to have $\mathbf{HF} = 0$, that doesn't require that $\mathbf{H} = 0$, because **H** is a non-square matrix, but rather that **H** is in the Nullspace of $\mathbf{F}^\mathbf{T}$.

The assumption is that we want optimal value of c to be independent of disturbances $\underline{d}$, that is:

$$\Delta c_{i,opt} = 0 \cdot \Delta \mathrm{d}$$

so, we find optimal solution as a function of d: $\mathbf{u_{opt}}(\underline{d})$, $\underline{y}_{\mathrm{opt}}(\underline{d})$ firstly, then we linearize this relationship and in this sense we obtain

$$\Delta \mathrm{y_{opt}} = \mathbf{F} \cdot \Delta \mathrm{d}$$

where, as stated before F is the optimal sensitivity matrix. In order to achieve this we want then:

$$\Delta c_{opt} = \mathbf{H} \cdot \Delta \mathrm{y_{opt}} = \mathbf{HF}\, \Delta \mathrm{d} = 0$$

That is to have $\mathbf{H} \in \mathcal{N}(\mathbf{F}^\mathbf{T})$. It is always possible if the number of measurements is greater than the sum of disturbances and the number of DOFs, i.e. $\#\underline{y} \geq \#\mathbf{u} + \#\underline{d}$[60].

Moreover if we consider the derivative of the cost function with respect to the degrees of freedom, J_u, what we obtain is that this is equal to 0; indeed if we consider the following simplification of a transfer function of the system:

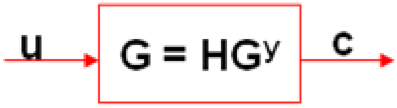

Figure 41: simple scheme for transfer function

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[60] V. ALSTAD AND S. SKOGESTAD, *Null Space Method for Selecting Optimal Measurement Combinations as Controlled Variables*, Ind.Eng.Chem.Res, 46 (3), 846-853 (2007)

we have:

$$J_u = J_u(\boldsymbol{u}_{\boldsymbol{opt}}) + J_{uu}(\boldsymbol{u} - \boldsymbol{u}_{\boldsymbol{opt}}) = 0 + J_{uu}(\boldsymbol{u} - \boldsymbol{u}_{\boldsymbol{opt}})$$

$$(u - u_{opt}) = (\mathbf{H}G^y)^{-1}(\boldsymbol{c} - \boldsymbol{c}_{\boldsymbol{opt}})$$

perfect control $\mathbf{c} = 0$ (no noise)

$$c_{opt} = \mathbf{H}y_{opt} = \mathbf{HF}\underline{\mathrm{d}}$$

$$J_u = -J_{uu}(\mathbf{H}\boldsymbol{G}^y)^{-1}\mathbf{HF}\underline{\mathrm{d}}$$

And because we state that H is in the Nullspace of $\mathbf{F}^T$, we have $\mathbf{HF} = 0$, and then $J_u = 0$ for any disturbances, $\underline{d}$.

c. **Exact local method**: called also loss method, it extends the Nullspace method to the case with noise and to any number of measurements[61, 62].

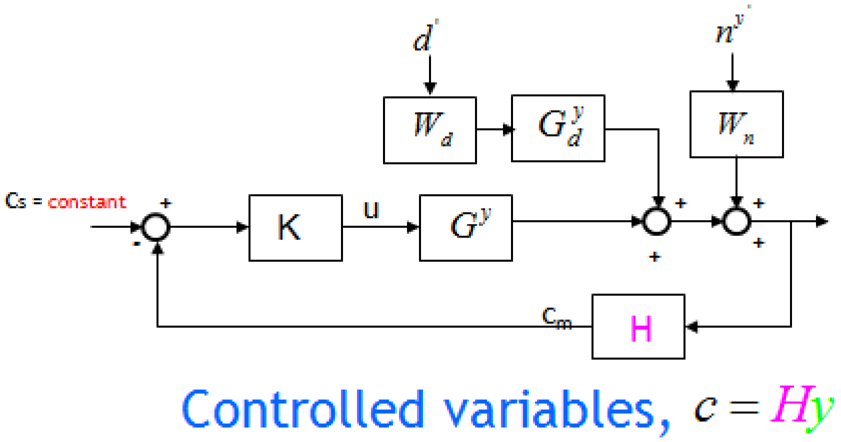

Figure 42: control scheme for the exact local method

In this case for any disturbance $\underline{d}$, we have to choose u in such a way that

$$\boldsymbol{c}_{\boldsymbol{m}} = \mathbf{H}\underbrace{(y + n^y)}_{y_m} = \boldsymbol{c}_{\boldsymbol{s}}$$

where c_S is constant, equal to 0 nominally. Our intent with this approach is to find the optimal H in order to minimize the magnitude of the loss, L, for the expected d and n^y, i.e.:

$$\mathrm{L} = J(u, d) - J_{opt}(u_{opt}, d),$$

Where:

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[61] ALSTAD, V., SKOGESTAD, S., HORI, E.S., *Optimal measurement combinations as controlled variables*, Journal of Process Control, 19 (1), pp. 138-148 (2009)

[62] KARIWALA, V., *Optimal measurement combination for local self-optimizing control*, Industrial and Engineering Chemistry Research, 46 (11), pp. 3629-3634 (2007)

$$d = W_d d'$$,

$$n^y = W_{n^y} n^{y\prime},$$

$$\left\| \begin{matrix} d' \\ n^{y\prime} \end{matrix} \right\|_2 \leq 1.$$

In order to evaluate the magnitude there are two solutions:

1- Worst case loss, i.e. L_{wc}

2- Average loss, i.e. L_{avg}

Considering only the second case as example, we have:

$$\mathrm{L} = J(u, d) - J_{opt}(u_{opt}, d),$$

$$J(u, d) = J(u_{opt}, d) + J_u(u - u_{opt}) + \frac{1}{2}(u - u_{opt})^T J_{uu}(u - u_{opt}) + \zeta^3$$

$$L_{avg} = \left\| J_{uu}^{\frac{1}{2}} (\mathrm{H}G^y)^{-1} \mathrm{H}Y \right\|_F^2,$$

with:

$Y = [\mathrm{FW_d}\ \mathrm{W_n}]$

$\mathrm{F} = \mathrm{G}^y J_{uu}^{-1} J_{ud} - \mathrm{G}_d^y$

So the optimal H is such a solution that minimize the following expression:

$$min_H \left\| J_{uu}^{\frac{1}{2}} (\mathrm{H}G^y)^{-1} \mathrm{H}Y \right\|_F = \left\| J_{uu}^{\frac{1}{2}} (\mathrm{H}G^y)^{-1} \mathrm{H}[\mathrm{FW_d}\ \mathrm{W}_{\mathrm{n}^y}] \right\|_F$$

The general analytical solution is the following (indeed "full" H):

$\mathrm{H} = \mathrm{G}^{yT} (YY^T)^{-1}$,

While in case of no disturbances (i.e. $W_d = 0$) and with the same noise for all measurements ($W_{ny} = 1$), we obtain that $H = G^{yT}$; and if we have no noise we achieve again the solution of Nullspace method, i.e. HF = 0. This is always true only if we can have a sufficient number of measurements.

NOTE: as explained before, the new self-optimizing variables must be identified (offline) for each region, and when you find a new region (online) it's necessary to switch controlled variables. So it's easy to identify when to switch when a constraints is encountered. It's less clear when to switch out a constraint, but monitoring the value of the unconstrained CVs from the neighboring regions and then switch out of the constraint region when the unconstrained CV reaches its setpoint.

4.4.2d Step 4: Select the Location of TPM (Decision 3)

As basis idea a process plant aim to transform some raw materials into products whose value is higher than the feedstock, and to do this it involves the passage of mass through the plant. This amount is expressed by the feed rate or product rate and it's determined by specifying one DOF which we are usually to refer as the throughput manipulator (TPM). Where does the TPM have to be collocated? This is an important decision and it's the link between the TOP DOWN and the BOTTTOM UP of the procedure. In a certain sense it's the "gas pedal" of the process deciding how much matter has to be transformed per hour, it's usually a flow and it's set by the manual control.

> *A TPM is a degree of freedom that affects the network flow and which is not directly or indirectly determined by the control of the individual units, including their inventory control.*[63]

The TPM is not unique: some plant with parallel units may have more than one TPM. It's usually placed at the feed of the plant and this is due to the fact that most of the control structure decision are made during the design stage, i.e. before the plant is build, and when the feed rate is considered constant and fixed. But focusing on the future operation of the plant it's probable that we want to maximize the feed in order to achieve better performance and it could be a reasonable choice to move the TPM.

The question now is where should the TPM collocated? Generally the TPM may be collocated anywhere in the plant, even if operators prefer to have at the feed and this is usually the default choice. But what doesn't affect from the steady-state point of view, it's instead very important if we consider the dynamic behavior of the plant. We have to consider two principles to set it:

1- **Economics**, as usual, covers a great importance in all decisions: in fact there could be a possible back-off if active constraints are not tightly controlled. The economic loss, moreover, could be large if the bottleneck unit is not tightly controlled. If this would be the case, then the TPM should be located close to the bottleneck in order to reduce the back-off from the active constraint (largest effect on the production rate).

2- **Structure of regulatory control system**: because of the radiation rule[64], the location of the TPM has a great importance on the structure of the regulatory

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[63] *ibidem*

[64] PRICE, R.M., GEORGAKIS, C., *Plantwide regulatory control design procedure using a tiered framework*, Industrial and Engineering Chemistry Research, 32 (11), pp. 2693-2705 (1993)

control structure for the entire plant. Inside this assumption there is the will of "local" consistency of the inventory control system[65]. This rule may not be adhered to by allowing for "long" inventory loops: but this is not common for operational reasons (i.e. emptying or overfilling tanks, startup, tuning and increasing complexity).

Some TPM collocation's examples, we can find in the following pictures (Figure 13, 14, 15):

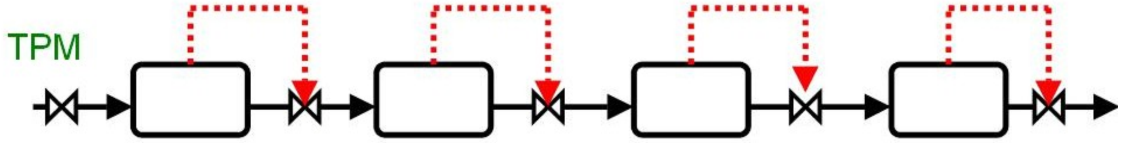

Figure 43: TPM at inlet (feed), inventory control in direction of flow

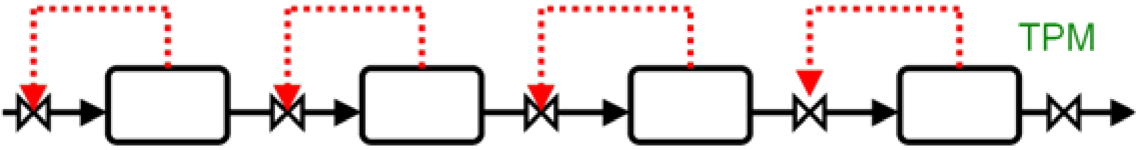

Figure 44: TPM at outlet, inventory control in direction opposite the flow

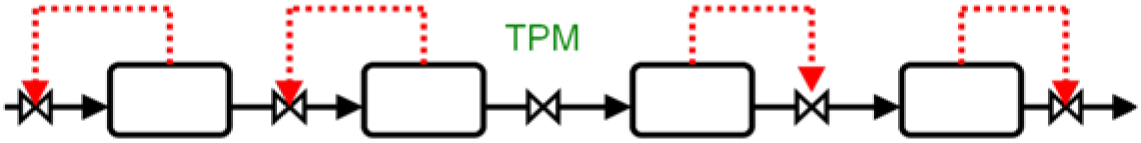

Figure 45: general case with TPM inside the plant, Radiation Inventory Control

If we consider only a part of the plant, there could be the possibility that this part doesn't have a TPM. There will be instead a given flow that acts as a disturbance which the control system has to set up and handle. In other words it is as having the TPM at a fixed location. And this is the preferable solution: first of all in fact it makes it simpler for operators (they are responsible for adjusting the TPM); then it avoids switching the inventory structure, which should be "radiating" around the TPM. Anyway because there is not a specific location (or better, just common preferable location), the tempting to consider its collocation as degree of freedom, and the moving of it in order to improve performance,

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[65] ALSTAD, V., SKOGESTAD, S., HORI, E.S., *Optimal measurement combinations as controlled variables*, Journal of Process Control, 19 (1), pp. 138-148 (2009)

reduce back-off as disturbances cause the optimal constraints to change. Skogestad proposed this rule[66]:

> *To get tight control of the new active constraint and achieve simple switching, locate the TPM "close" to the next active constraint (such that the TPM can be used to achieve tight control of the constraint when it becomes active).*

The basis to this rule can be found in economics and it aims to simplify the required switching when the next capacity constraint becomes active. We have to note, however, that when we move the TPM, we may have to switch regulatory loops, and this is not a desirable thing.

Come at this point we pass through the hierarchical structure and we proceed to the bottom up control procedure. We are now going to deal with the real control layer: regulatory and supervisory layers. They are responsible of the action on the plant devices set up, and they are "children" of all the previous analysis done till this point.

4.4.3 BOTTOM-UP

4.4.3a Step 5: Select the Structure of Regulatory (Stabilizing) Control Layer

As it is clear from the name itself, the main purpose of the regulatory layer is to "stabilize" the plant, preferring a simple control structure with single-loop PID controller (reliable of a more robust control). In this case stabilize means that the process doesn't drift too far away from acceptable operation even if there are some disturbances (indeed it's this one the goal of a regulatory layer).

Among all the control layer the regulatory is the fastest one and it's used to control variables which need a fast and a tight control (i.e. the economically important active constraints). Note that this layer uses setpoint coming from the Step 3, but it should follow the ones given by the supervisory layer.

In this step there are two faced two main decision:

1- Select controlled variables (CV_2), i.e. Decision 2
2- Select inputs (that is valves) and "pairings" in order to control the above mentioned variables (CV_2), i.e. Decision 4

It's worth of noting that while the selection of controlled variable can be done on steady-state considerations, dynamics is the primary concern when we select inputs and pairings.

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[66] SIGURD SKOGESTAD, *Control structure design for complete chemical plants*, Computers & Chemical Engineering, Volume 28, Issues 1–2, 15 January 2004, Pages 219-234.

We have not to add any degrees of freedom because the setpoints CV_{2s} are left as manipulated variables (MVs) for the supervisory layer.

If we consider to allow for cascade loops, then the stabilization layer may be designed independent of the supervisory control layer (i.e. the economic one). But when we use cascade loops, we add complexity and when closing a stabilization loop, we use up some of the time window as given by the closed-loop time response (bandwidth) of the stabilization loop. This is why it'd be better to simplify and reduce the need of cascade loops.

SELECT STABILIZING CV_2 (Decision 2)

Firstly we have to stabilize the process by controlling drifting variables such level and pressure (i.e. inventories), reactor temperature and temperature profile in the distillation column. More precisely we want to control:

1. **Levels** (inventory liquid)
2. **Pressures** (inventory gas/vapor) (note: some pressures may be left floating)
3. **Inventories of components** that may accumulate/deplete inside plant
    - E.g., amount of amine/water (deplete) in recycle loop in CO_2 capture plant
    - E.g., amount of butanol (accumulates) in methanol-water distillation column
    - E.g., amount of inert N_2 (accumulates) in ammonia reactor recycle
4. **Reactor temperature**
5. **Distillation column profile** (one temperature inside column)
    - Stripper/absorber profile does <u>not</u> generally need to be stabilized

This simplifies the supervisory control layer and its tasks because it provides for local/fast disturbances rejection and reducing the non-linearity in the model. Then we should include active constraints (CV_1) those need a tight control (they are usually hard output constraints) in $CV_2$for the regulatory layer. In this way we reduce the required back-off. Because of all these reasons it is usually not necessary for tight control of unconstrained CV_1, indeed the optimum is quite "flat".

We have to take into consideration two main objectives of the regulatory layer, in order to select systematically select the stabilizing $CV_2 = \mathbf{H_2} \cdot \underline{y}$:

- **Local disturbance rejection** (indirect control of primary variables CV_1). If we control variables CV_2, the effect of any disturbance on the primary CV_1 should be small. This is to get fast control of the CV_1, which are important to reduce the control error (and then the back-off) for some variables such as active output constraints.
- **Stabilization** (minimize state drift). Because more generally the objective is to minimize the effect of the disturbances on the internal variables (states, **x**). Why? The main reason is to keep the process in the linear region and in this way (we want it close to the nominal steady-state) to avoid the process itself drift into a region where it's impossible to control it. The advantage of considering some measurements of all the states **x**, is that the regulatory control layer isn't tied to a particular control objectives (CV_1), that could be change with time on the basis of disturbances and prices.

When we consider disturbance rejection and stabilization in this layer of control (i.e. regulatory), it's the behaviour at the closed-loop time constant of the above supervisory control layer which is of main interest; moreover the supervisory layer is usually relatively slow and for this reason is sufficient consider the steady-state behaviour when we select CV_2.

SELECT INPUTS (i.e. valves) FOR CONTROLLING CV_2 (Decision 4)

Now we have to find inputs (valves) to use to control CV_2. Usually and in practice single-loop, decentralized, controllers are used in the regulatory layer and in this way the objective is to identify pairings. The main rule is to "pair close" so that the dynamic controllability is good and at the same time affecting in small measure the delay (i.e. small interactions between the loops). Then we have to note that:

- ✓ Local consistency for the inventory control[67]; this means that the inventory control system is radiating around the given flow (remember the radiation rule[68] mentioned before)
- ✓ Tight control of important active constraints (we want to avoid the back-off)

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[67] E.M.B. ASKE AND S. SKOGESTAD, *"Consistent inventory control"*, Ind.Eng.Chem.Res, 48 (44), 10892-10902 (2009)

[68] PRICE, R.M., GEORGAKIS, C., *Plantwide regulatory control design procedure using a tiered framework*, Industrial and Engineering Chemistry Research, 32 (11), pp. 2693-2705 (1993)

- ✓ Avoid selecting variables that could be optimally saturate (steady-state) as MVs in this layer, because this would require either reassignment of regulatory loop or back-off for the same manipulated variables
- ✓ Derivation from the previous note is that we need to avoid the reassignments in the regulatory layer

In a more schematic visual of the problem we may divide this second step (selection of inputs → valves), in to two different passages, those are:

- ➢ Structure of inventory control layer (we find some analogies with Step 4)
- ➢ Structure of remaining regulatory control system

Because of its nature, this layer of control should be independent from economic control objectives. This means that CV_1 and CV_2 are independent each other. But to simplify and reduce the need for cascade loops, it's an advantage if we have $CV_1 = CV_2$, or at least some of their variables.

4.4.3b Step 6: Select Structure of Supervisory Control Layer

This control layer, often called "advanced" control layer, has three main tasks:

1- It must control the primary (economic) CV_1 using the setpoints to the regulatory layer plus any remained *unused* valves as MVs.

   Considering that at this timescale interactions are significant, then MPC (i.e. a kind of multivariable control) should be taken into consideration. To improve dynamic response this layer uses level setpoints or other additional dynamic degrees of freedom. At steady-state condition these variables should stay to their ideal value. It could use also feedforward control (i.e. the use of disturbances).

   For the estimation of the CV_1 not measured, there could be used "soft sensors" for their estimation. These sensors are static, although dynamic estimators. But their use is quite small cause the slowness in response time of this control layer.

2- Supervise the performance of the regulatory layer: this layer should take action to avoid saturation of MVs used for regulatory control. In fact we must note that if a MV in the regulatory layer saturates, then the control of the corresponding CV2 is resulting in a large drift away from the desired operating point.

3- Switch controlled variables and control strategies when we have disturbances on prices that could cause the process to change the region of active constraints.

The controller those are possible to use in this layer are essentially two:

- **Advanced single loop control**, i.e. PID control, with some additional “fixes”, for example feedforward ratio, decouplers, logic, selectors and split range control. With this kind of control it’s extremely important to select the pairings. Moreover we must to note that finding the right pairings is more difficult because slower the timescale stronger are the interactions.
- **Multivariable control (MPC)**. Although the use of MPC can reduce the use of switching and logic, this cannot be completely avoided. Generally when we switch regions it may be necessary to change the performance objective of the MPC controllers.

4.4.3c Step 7: Structure of Optimization Layer (RTO) (related to Decision 1)

Now, the goal of the RTO layer is to update the setpoints for CV_1 and to detect changes in active constraints regions that should be required the switching of the same CV_1.

We have to note that in most of cases with a self-optimizing choice for the choice of the primary controlled variables, what we can obtain from this kind of system is too low to justify the cost of creating and then sustaining the detailed steady-state model required for this layer.

If we add the numerical issues related to the optimization (difficult) and then the offline optimization (difficult too), the use of this last layer can be reasonably avoided. That said in other word present the possibility to reach the same result of a RTO with an only stable, simple and robust control, not always, but for sure in those cases for which the costs for this solution are not comparable with the advantages we can obtain.

This is an appendix of all the procedure, that could be useful but it doesn’t have to be a “must”. It’s for this reason that the last word on this chapter should be left another time to economics, which rules from the very for step till the last one.

After the analysis of the procedure proposed and applied by Sigurd Skogestad, it will be interesting verify this systematic approach to a process which for a long time has been used and exploited, but relatively to its performance hasn't been optimized and searched for an optimal solution: the hydrodesulfurization process.

Starting from the very first step of the above descript procedure, it will developed in order to reach and develop a simple and robust control structure. It's interesting to note that although the process is dated and it started working online in the refining process industry during the '20s of the last century, neither it has received nor it has been modified a lot during this lat period. Till the very recent years. In this last period cause the more severe and stringent rules on the environment pollution has given the right propulsion to an improvement for this process and under some points of view a new "life" for an, otherwise, outdated plant unit.

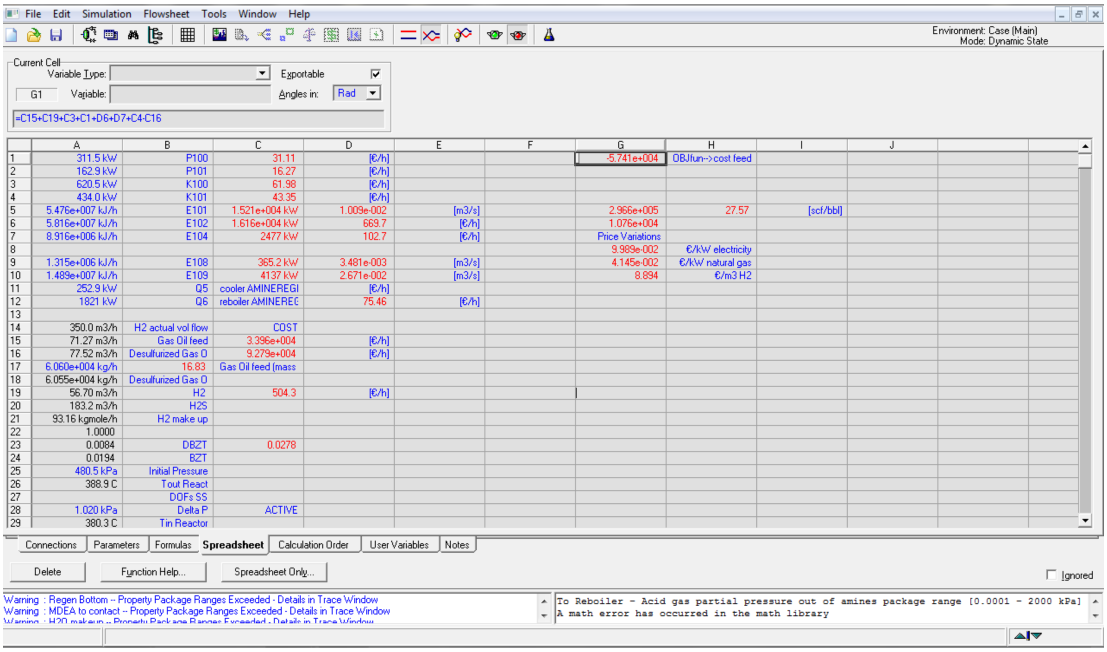
4.5 ANALYSIS AND RESULTS

It's time to analyze the previous process plant and then operate on this one in order to have the possibility to search for a stable and robust control structure. The procedure is followed from the beginning till the last point; leaving at the end of all the systematic procedure the possibility to apply or not to, a RTO.

In this part, the looking for application of the previous steps will follow. We can now start.

4.5.1 Step 1:Define Operational Objectives

Standing on the basis of the previous description of this step, we have to evaluate the operational objectives in terms of a "scalar cost function" J, in this case [€/h], that has to be minimized. To build this function it has been conducted a search in different ways (meaning in that case the different possibilities used to calculate it) in order to find a correct evaluation for this goal. First of all after having build a reliable model of the plant it has been used a spreadsheet in which has been collected the main factors those are responsible for a certain cost in the plant. In this selection has been taken into consideration all the contributes those affected in a certain way the cost of a plant. We must note, as it highlighted previously, that in this case and for this economic evaluation, all the costs of devices and instrumentation (pipes, vessels, reactors, columns and tanks too) are not of our interest cause they can be considered as sunk costs and for this reason not worth for an analysis that aims to model a structure around something that has subject to variation due to changes of economic nature.



Environment: Case (Main)
Mode: Dynamic State

G1
Variable Type:
Variable:
Exportable ☑
Angles in: Rad

=C15+C19+C3+C1+D6+D7+C4-C16

	A	B	C	D	E	F	G	H	I	J
1	311.5 kW	P100	31.11	[€/h]			-5.741e+004	OBJfun-->cost feed		
2	162.9 kW	P101	16.27	[€/h]						
3	620.5 kW	K100	61.98	[€/h]						
4	434.0 kW	K101	43.35	[€/h]						
5	5.476e+007 kJ/h	E101	1.521e+004 kW	1.009e-002	[m3/s]		2.966e+005	27.57	[scf/bbl]	
6	5.816e+007 kJ/h	E102	1.616e+004 kW	669.7	[€/h]		1.076e+004			
7	8.916e+006 kJ/h	E104	2477 kW	102.7	[€/h]		Price Variations			
8							9.989e-002	€/kW electricity		
9	1.315e+006 kJ/h	E108	365.2 kW	3.481e-003	[m3/s]		4.145e-002	€/kW natural gas		
10	1.489e+007 kJ/h	E109	4137 kW	2.671e-002	[m3/s]		8.894	€/m3 H2		
11	252.9 kW	Q5	cooler AMINEREGI	[€/h]						
12	1821 kW	Q6	reboiler AMINEREC	75.46	[€/h]					
13										
14	350.0 m3/h	H2 actual vol flow	COST							
15	71.27 m3/h	Gas Oil feed	3.396e+004	[€/h]						
16	77.52 m3/h	Desulfurized Gas O	9.279e+004	[€/h]						
17	6.060e+004 kg/h	16.83	Gas Oil feed (mass							
18	6.055e+004 kg/h	Desulfurized Gas O								
19	56.70 m3/h	H2	504.3	[€/h]						
20	183.2 m3/h	H2S								
21	93.16 kgmole/h	H2 make up								
22	1.0000									
23	0.0084	DBZT	0.0278							
24	0.0194	BZT								
25	480.5 kPa	Initial Pressure								
26	388.9 C	Tout React								
27		DOFs SS								
28	1.020 kPa	Delta P	ACTIVE							
29	380.3 C	Tin Reactor								

```
Warning : Regen Bottom -- Property Package Ranges Exceeded - Details in Trace Window
Warning : MDEA to contact -- Property Package Ranges Exceeded - Details in Trace Window
Warning : H2O makeup -- Property Package Ranges Exceeded - Details in Trace Window
```

```
To Reboiler - Acid gas partial pressure out of amines package range [0.0001 - 2000 kPa]
A math error has occurred in the math library
```

Figure 46: spreadsheet with all contributes to the final cost function

As possible to individuate in the previous shot of the spreadsheet, the different contributions of all elements in the plant has been individuate and selected weighting the different contribution in terms of power required to work properly. It means that for this passage has been done a research on the different costs and it has been possible evaluating all the different values.

First of all it has been done a selection of the different contributions on the basis of their impact on real costs. Utilities are studied and analyzed to see how strong was their importance in this first step. For example not all pumps have been considered for the overall count of costs because some of them had a very small impact on this balance; they have been considered instead:

- Compressor (K-100 – K-101 on the process flow diagram)
- Heaters (E-102 – E-104)
- Pump (P-100)

In order to have the same calculation basis, the work necessary to make possible the right working of this device has been converted in cost per hour: that means the work evaluate by the simulation program, expressed in [kW] has been multiplied per the cost of electric energy for what regards compressors and pumps; while for what is dealing with heaters, their power has been estimated multiplying this value for the cost of natural gas used to feed to furnace. This has been done without considering effectiveness factors or other different corrections because the importance in this economical analysis of the plant what it is really important is a global visual of all costs and how much they affect plant economics. This assumption however does not compromise the effectiveness of the results. So electricity and natural gas prices have been found on *Europe's Energy Portal*[69], and in order to obtain a unique value it, it has been necessary to average the different value.

On the same site in has possible then to evaluate the costs for crude to treat and the value for the product, considering diesel price without VAT. Hydrogen cost has been estimated on the basis of industrial gases market, referring to values reported by industries dealing with selling gases with different specification in accordance to their use (medical, industrial or laboratory)[70]. The different values for energy utilities are reported in the following tables.

Table 10: costs of electricity and natural gas

Country	€ per kWh Natural Gas	Country	€ per kWh Electricity
Austria	0.04021	**Austria**	0.11845
Belgium	0.04022	**Belgium**	0.09899
Bulgaria	0.03294	**Bulgaria**	0.06326
Czech Rep.	0.03774	**Cyprus**	0.16953
Denmark	0.08427	**Czech Rep.**	0.09993
Estonia	0.0316	**Denmark**	0.09774
Finland	0.04622	**Estonia**	0.07686
France	0.04137	**Finland**	0.07443
Germany	0.04966	**France**	0.07768
Hungary	0.04122	**Germany**	0.11417
Italy	0.0417	**Greece**	0.08994
Latvia	0.03363	**Hungary**	0.09593
Lithuania	0.03832	**Ireland**	0.09618
Luxembourg	0.04769	**Italy**	0.14438
Netherlands	0.04434	**Latvia**	0.09716
Poland	0.03428	**Lithuania**	0.10696
Portugal	0.04193	**Luxembourg**	0.07482
Romania	0.02386	**Malta**	0.16313
Slovakia	0.04011	**Netherlands**	0.09138
Slovenia	0.05574	**Poland**	0.08768
Spain	0.03675	**Portugal**	0.10086
United Kingdom	0.0286	**Romania**	0.07348
AVERAGE [€/kWh]	0.041472727	**Slovakia**	0.12163
		Slovenia	0.08673
		Spain	0.09927
		Sweden	0.07764
		United Kingdom	0.09895
		AVERAGE [€/kWh]	0.099894815

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[69] http://www.energy.eu/fuelprices/, accessed on February 2013

[70] PRICE SCHEDULE –INDUSTRIAL GASES 49009.XLS, accessed on February 2013

While for the raw material prices and for the product value in the next table there is the summa of what the above mentioned survey:

Table 11: price and value of raw materials

EU [$/bbl]	**CRUDE OIL [€/bbl]**	**[€/l]***	**[€/m^3]**
160.6	75.764	0.476504	476.5035
	PRODUCT VALUE [€/bbl]	[€/l]	[€/m^3]
with VAT	230.550	1.45	1450
without VAT	190.323	1.197	1197
	HYDROGEN COST [€/m^3]		
INDUSTRIAL	8.8937665		
***note that all prices have been converted on the basis of actual $/€ change, February 2013**			

Because we want to evaluate:

$$J = -\mathrm{P}$$

in order to minimize it, we have to determinate

J = cost feed + cost utilities (i.e. energy) – value products [money/time]

in this case[71]:

cost feed = actual volume flow feeds [m^3/h] * cost [€/m^3]

= Gas Oil Feed [m^3/h] * Crude Oil [€/m^3] + H_2 [m^3/h] * Hydrogen Cost [€/m^3]

= 72.27 [m^3/h] * 476.50 [€/m^3] + 70.62 [m^3/h] * 8.89 [€/m^3]

= 34516.17 [€/h]

value products = actual volume flow product[72] [m^3/h] * cost [€/m^3]

= Desulfurized Gas Oil [m^3/h] * Product Value [€/m^3]

= 74.32 [m^3/h] * 1197.00 [€/m^3]

= 88961.04 [€/h]

cost utilities = compressors' power [kW] * Electric Energy cost [€/kWh] + heaters' power [kW] * Natural Gas cost [€/kWh] + pump's power [kW] * Electric Energy cost [€/kWh]

---

[71] Note that all reference are taken from Aspen HYSYS® flow sheet, i.e. values for floods, properties of feedstock and so on

[72] Take into consideration that for product in the overall discussion it will be considered only the desulfurized charge, while for the main other by product we are not concerning in, i.e. hydrogen sulfide. Note that in case of more precision and maybe an improvement to this simulation, this value could be, for example, evaluated in order to feed it to a Klaus process to recover sulfur.

= 1287.11 [kW] * 0.10 [€/kWh] + 33020.10 [kW] * 0.042 [€/kWh] + 328.10 [kW] * 0.10 [€/kWh]

= 1548.35 [€/h]

$$J = -51896.52\ [€/h]$$

In this way it has been possible to evaluate simply and clearly our objective function. If under some points of view it could be seemed too much simple, we have to consider that for an economical evaluation all the more important contributes have been taken into consideration and the important in this step is not to lose sight of the general goal: to optimize a complete unit.

At this point we have completed the first step of the procedure: all the important terms have been collected and it has been evaluated the objective function.

4.5.2 Step 2: Determine the steady-state Optimal Operation

As stated before, "in order to achieve a reliable and efficient control system we have to find the optimal way of operating process".

To determine the optimal plant condition we have to work on a steady-state model (the one determined and built in Aspen HYSYS®), then identify DOFs and finally optimize it for expected disturbances (having considered previously what are the most important ones and their range of variation). That is:

$$J = J(\boldsymbol{u}, \mathbf{x}, \underline{d})$$

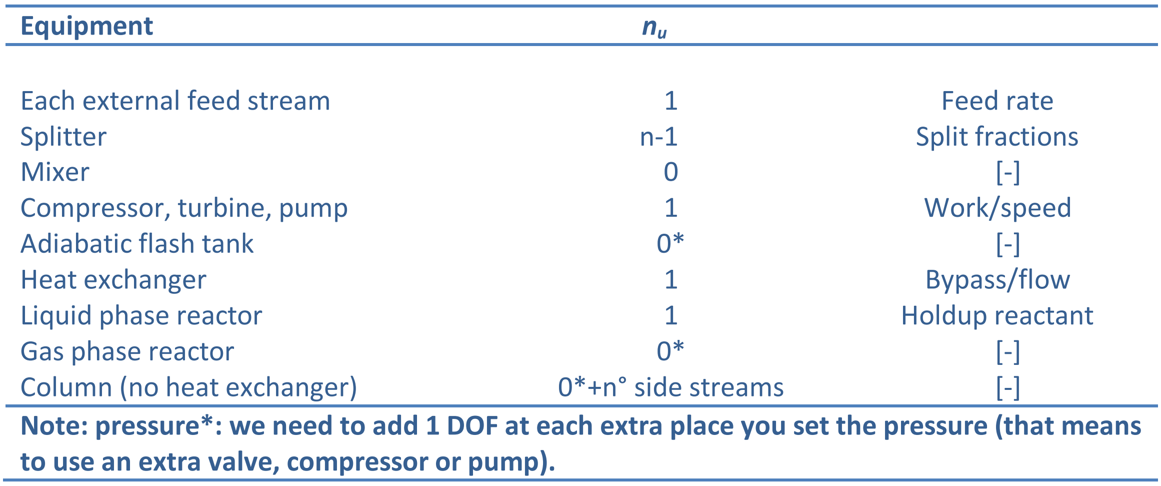
we optimize operation with respect to u for given d (usually steady-state):

$$\min_u \; J(\boldsymbol{u}, \mathbf{x}, \underline{d})$$

subject to:

- Model equations: $f(\boldsymbol{u}, \mathbf{x}, \underline{d}) = 0$
- Operational constraints: $g(\boldsymbol{u}, \mathbf{x}, \underline{d}) \leq 0$

So in order to achieve this result we have first of all to identify the steady-state degrees of freedom. Actually we are concerned into the number of u and what's the nature of this variables. It's important to find a independent and simple way to find n_u because it's useful to check and then to reduce the time spent on optimizing the process. Even if there are the above mentioned three methods to individuate them, we will eventually find them when we perform optimization, i.e. analyzing the system and its behavior it is possible to highlight some variables that have a great impact on all the structure, while for other there is not the same emphasis. This is useful to understand which are the "real" degrees of freedom to take into account. With respect to methods explained before, because the dimension of the plant is reasonably big, it is useful to evaluate the DOFs counting with the "Potential Degrees of Freedom". That has been done because the idea to consider the equations counting was impossible, practically because working on the Aspen HYSYS® we are not able to evaluate all the ones the program is using to simulate the unit. Because the other two methods are quite similar, in order to reach the easiest way to evaluate them we have done it considering the Table 2 (here reported in order to make it easy the evaluation of the next step), that is perfectly analogue to the valve counting method:



Equipment	n_u	
Each external feed stream	1	Feed rate
Splitter	n-1	Split fractions
Mixer	0	[-]
Compressor, turbine, pump	1	Work/speed
Adiabatic flash tank	0*	[-]
Heat exchanger	1	Bypass/flow
Liquid phase reactor	1	Holdup reactant
Gas phase reactor	0*	[-]
Column (no heat exchanger)	0*+n° side streams	[-]

Note: pressure*: we need to add 1 DOF at each extra place you set the pressure (that means to use an extra valve, compressor or pump).

Figure 47: Table 2

Analyzing the plant scheme of the hydrodesulfurization unit, we can start to evaluate all the device and equipment, we have the following degrees of freedom:

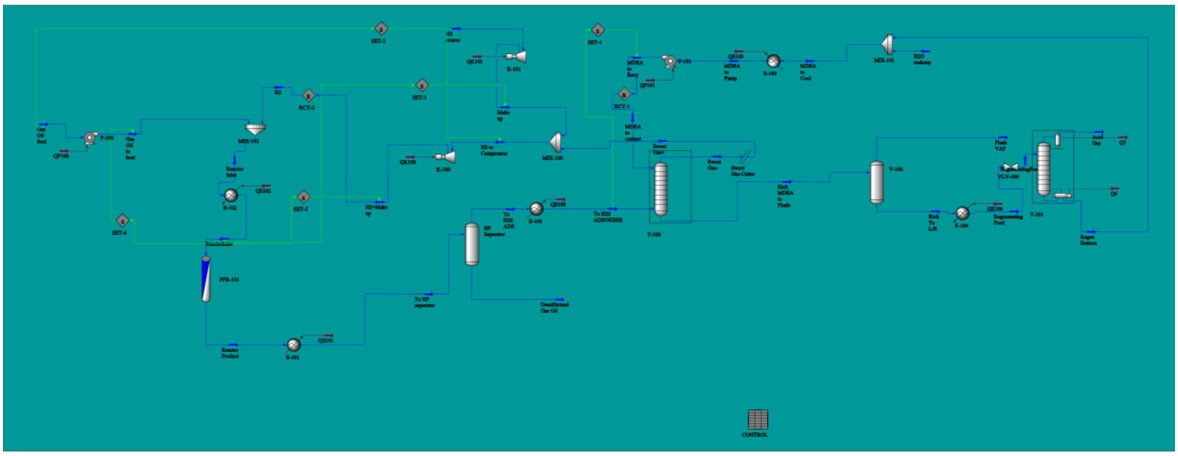


Figure 48: the plant

Table 6: DOFs counting

Equipment	n_u	**name**	**DOFs**
Each external feed stream	1	Gas Oil Feed, H2 source, H2O makeup	3
Mixer	0	MIX-100/101/102	0
Compressor, turbine, pump	1	K-100/101, P100/101	4
Adiabatic flash tank	0	HP Separator, V100	0
Heat exchanger	1	E-101/102/104/108/109	5
Liquid phase reactor	1	PFR 101	1
Column	2	T-100/101	4
		TOTAL	17

It could seemed finished here the counting step, but it is necessary to make some observations useful to reduce, without losing precision and effectiveness, the number of these degrees of freedom. First of all is important as explained before having clear in mind the purpose of all the project: the optimization of an HDS unit. In order to achieve this goal is fundamental knowing the plant: the key issue is understand how it works and which are the DOFs responsible for great changing in plant working. For this reason the previous number of DOFs has been reduced and modified, till the value of 11 degrees of freedom, considering and taking into consideration the importance of the different variable per each equipment.

Table 7: list of degrees of freedom

DOFs' name	***in***	n_u
Inlet Pressure	P-100	1
Reactor Temperature	PFR-100	1
Cooling Temperature	E-101	1
HP Separator Pressure	HP Separator	1
Absorption Pressure	T-100	1
H2/Gas Oil Ratio	MIX-100	1
Molar Flow Absorption	T-100	1
Reboiler Duty	T-101	1
Inlet Temperature Regeneration	E-104	1
Outlet Temperature Regeneration	E-109	1
Regeneration Column Pressure	T-101	1
	TOTAL	**11**

After the identification of the degrees of freedom it has been possible to recognize and then select the important disturbances, with their expected range.

Because the unit is designed to work with an expected feed, the most important disturbs will come from it; while without losing in generality the disturbances in feed temperature or pressure could be neglected because of their not so important impact.

For the optimization the disturbances have been selected as follows:

- Changing in **feed flood** :
  50000 [kg/h] < 60600 [kg/h] < 80000 [kg/h]
- Changing in composition, meaning the **total sulfur content**:
  4.01 % [mol/mol] < 9.55 % [mol/mol] < 14.97 % [mol/mol]
- Changing in one compound composition, **double** DBZT content:
  2.33 % [mol/mol] < 4.5 % [mol/mol]

At this point it has been possible to start the optimization of the system, firstly optimizing the nominal point of working (the "normal" operative conditions), then disturbing the system and optimizing it for the expected disturbances. In this way it has been possible evaluate the optimal sensitivity of the system.

In order to solve this problem it has been built a program using Matlab®: in particular the .m file it would be result in an optimization code, which calling inputs directly from Aspen HYSYS® tries to optimize the previous objective function acting on the above mentioned DOFs; the values find in this way are then sent again to Aspen HYSYS® which evaluates another time the objective function. All this procedure is repeated till a feasible solution is found with the respect of the operative constraints and equalities set for the model.

In this case the operational constraints has been set to stream:

Table 12: operational constraints set to the system

Lower bound value	≤ Constraints ≤	Upper bound value
1	Delta Pressure [kPa]	10
300	Inlet Temperature Reactor [°C]	500
10	Cooling Temperature [°C]	110
1.2959E+04	Inlet Pressure [kPa]	2.5E+04
1.919	H2/Gas Oil Ratio [-]	3
5.10E+03	Absorption Pressure [Pa]	7.0E+03
1E+07	Reboiler Duty [kJ/h]	1E+08
0.278	Molar flow ABS column [kgmol/h]	0.556
40	Inlet Temperature Regeneration [°C]	99
30	Outlet Temperature Regeneration [°C]	60
130	Regeneration Column Pressure [kPa]	190
	the total sulfur content "Desulfurized Gas Oil" [% wt/wt] ≤ 0.007	
	title of stream "H2 to Compressor" = 1	

Note that title of “H2 to Compressor” = 1 is fixed to be equal to 1(i.e. in order to avoid the compressor’s collapse; because for this purpose it is usually selected an axial-flow compressor, whose fan-like airfoils are susceptible of damage and failing in case of presence of liquid fluids) and the non correct working of the plant; and the total sulfur content “Desulfurized Gas Oil” [% wt/wt] ≤ 0.007 (at the exit of the unit it has to be in accordance with the environmental specification).

The function called by Matlab® for this purpose is `fmincon`[73], which attempts to find a constrained minimum of a scalar function of several variables starting at an initial estimate (the initial point). This is generally referred to as *constrained nonlinear optimization* or *nonlinear programming*.

$$\min_{x} f(x) \text{ such that } \begin{cases} c(x) \le 0 \\ ceq(x) = 0 \\ A \cdot x \le b \\ Aeq \cdot x = beq \\ lb \le x \le ub \end{cases}$$

Figure 49: fmincon function, MATHWORKS, *fmincon*, http://www.mathworks.it/it/help/optim/ug/fmincon.html, accessed on March 2014

What it is worth of noting is that this function uses optimizers which are not very robust. This results in a not unique solution, which is instead function of the initial estimate of it. For this reason to obviate to this problem the optimization has been repeated again and again, with the disturbances selected in order to see what was the solution or the solutions able to “absorb” better them and with a greater value of optimum. Anyway this is not a huge problem, because we have to consider another particular i.e. that we are looking for a solution, an optimal solution, which won’t be the absolute optimum. This will be a relative optimum that is in turn function of disturbances, and it will be the control of the system which will have the duty to move it to the optimum. So for this reason it is important to find the optimal point, but not so necessary that it has to be the absolute one.

4.5.2a Results of the Optimization

The simulations have been done on a laptop with Windows 7, operative system 32 bit, RAM 2GB and Intel® Pentium® Dual CPU T2370 @ 1.73[GHz] 1.73 [GHz].

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[73] MATHWORKS, *fmincon*, http://www.mathworks.it/it/help/optim/ug/fmincon.html, accessed on March 2014

Matlab® version was R2011b (7.13.0.564).

Here it follows the result of the optimization. Note that have been found 6 different "configurations", that means six possible combinations of different value for the degrees of freedom that result in an optimal solution starting from different initial values.

Each configuration is composed by the following "parameters":

Table 13: DOFs with their unit of measurement

DOFs' name	[Unit of Measurement]
Inlet Pressure	[kPa]
Reactor Temperature	[°C]
Cooling Temperature	[°C]
HP Separator Pressure	[kPa]
Absorption Pressure	[kPa]
H2/Gas Oil Ratio	[-]
Molar Flow Absorption	[kgmole/h]
Reboiler Duty	[kJ/h]
Inlet Temperature Regeneration	[°C]
Outlet Temperature Regeneration	[°C]
Regeneration Column Pressure	[kPa]

So when there is the reference to "configuration" we have to understand that it is a generalized way to consider the different optimal values found by the optimization program.

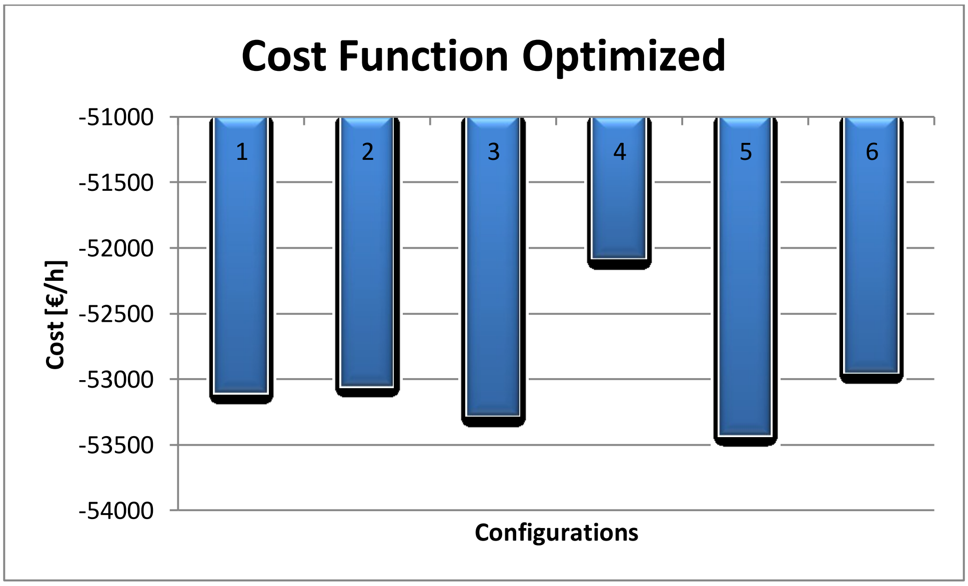

Figure 50: cost function optimized, no disturbances

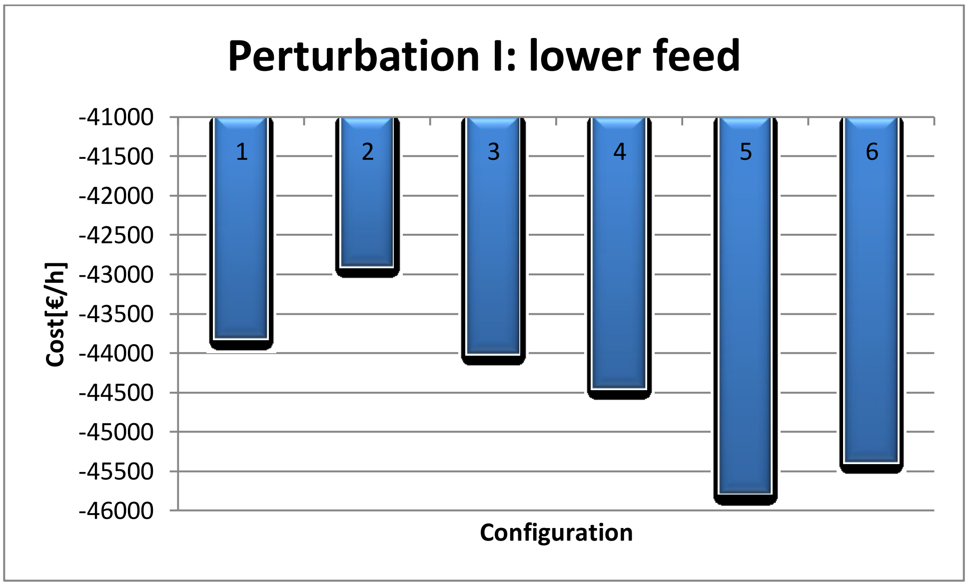

Figure 51: changing in feed flood

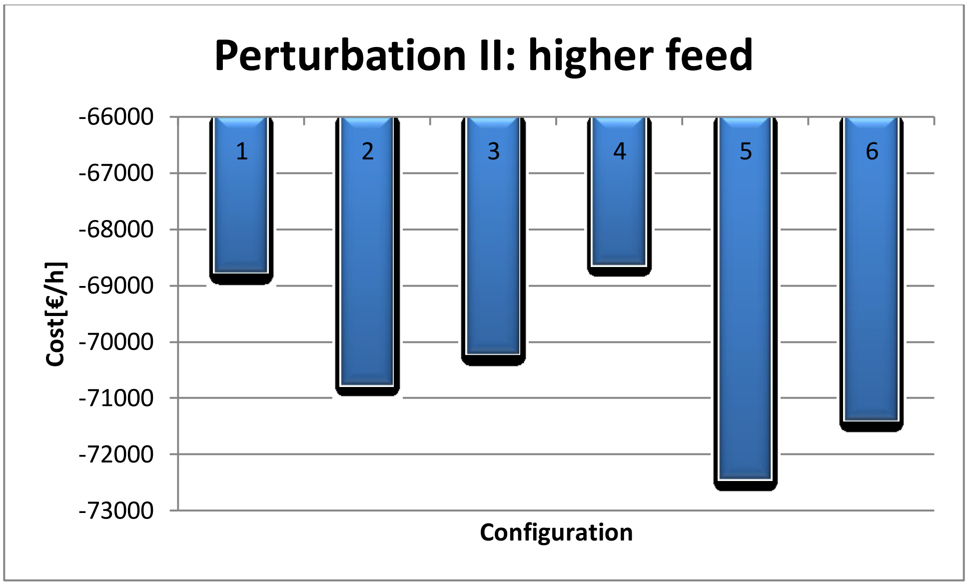

Figure 52:changing in feed flood

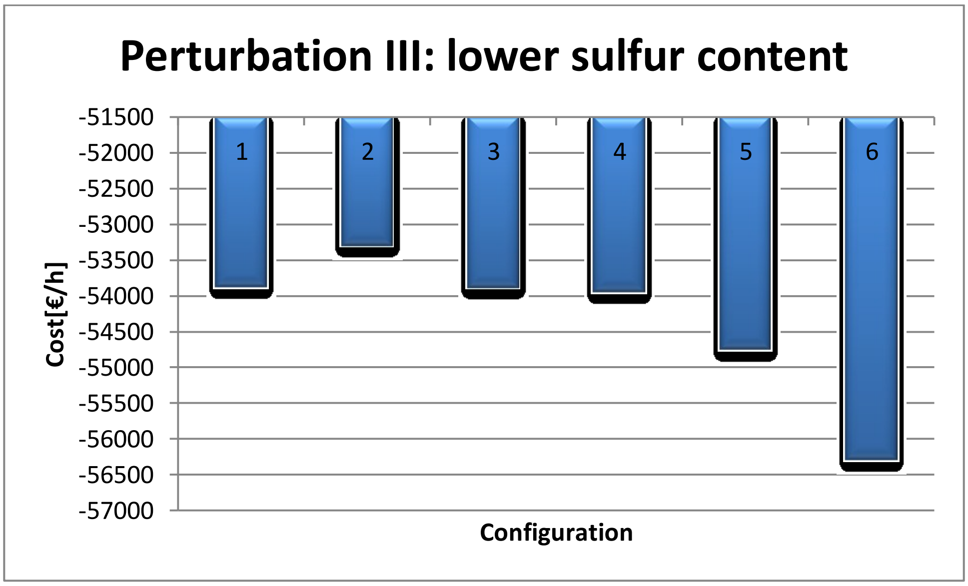

Figure 53: changing in feed composition

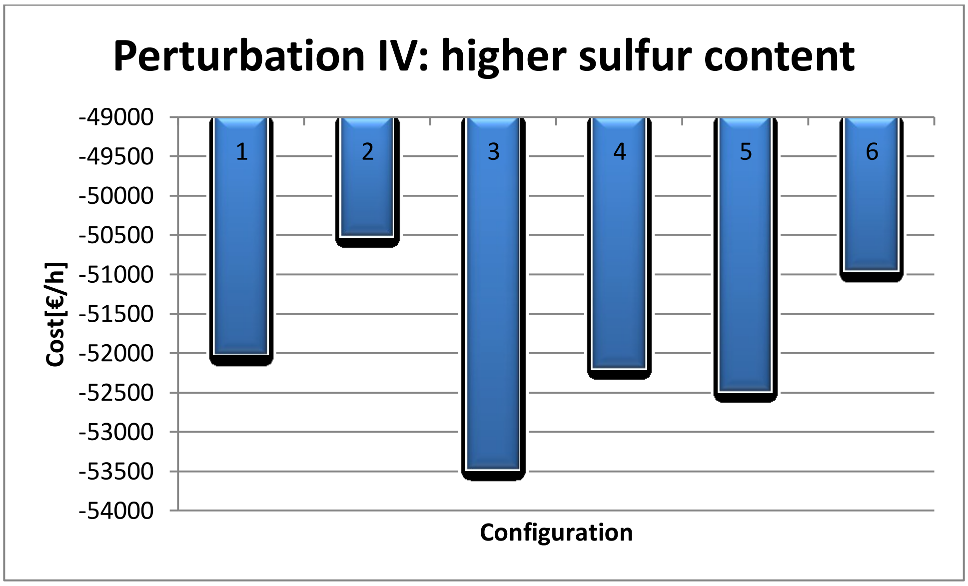

Figure 54: changing in composition

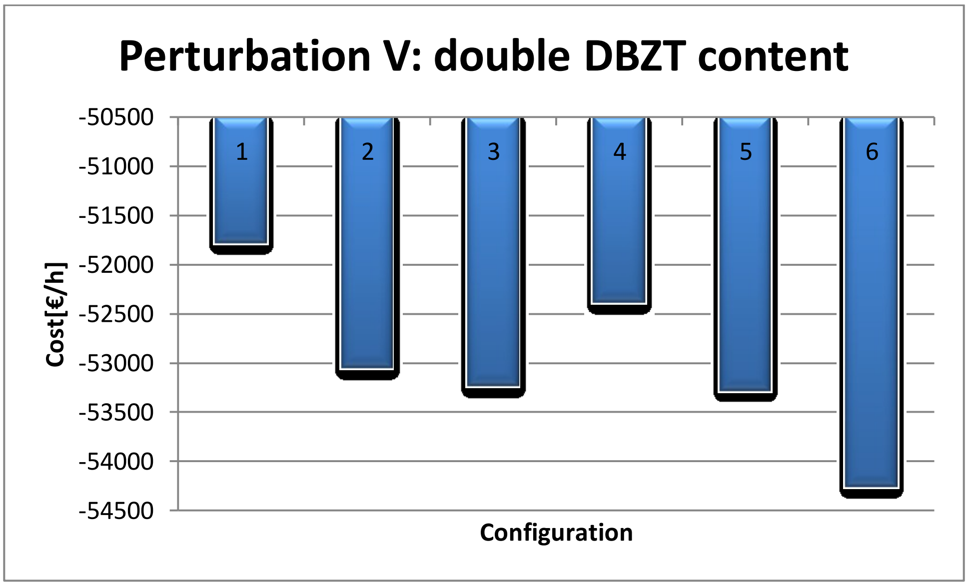

Figure 55: changing in one feed's compound's composition

After this re-optimization due to disturbances, all results have been collected in order to see what was the best solution, here meant as the best combination of different degrees of freedom's values. It has been a quite empirical method on the way of the "brute force" system, but it has responded in a good way.

Time consuming of each optimization was about three hours and a half; time that could be reduce significantly maybe changing the machine or finding a best optimizer. Anyway the problem remains that those are very time consuming simulations.

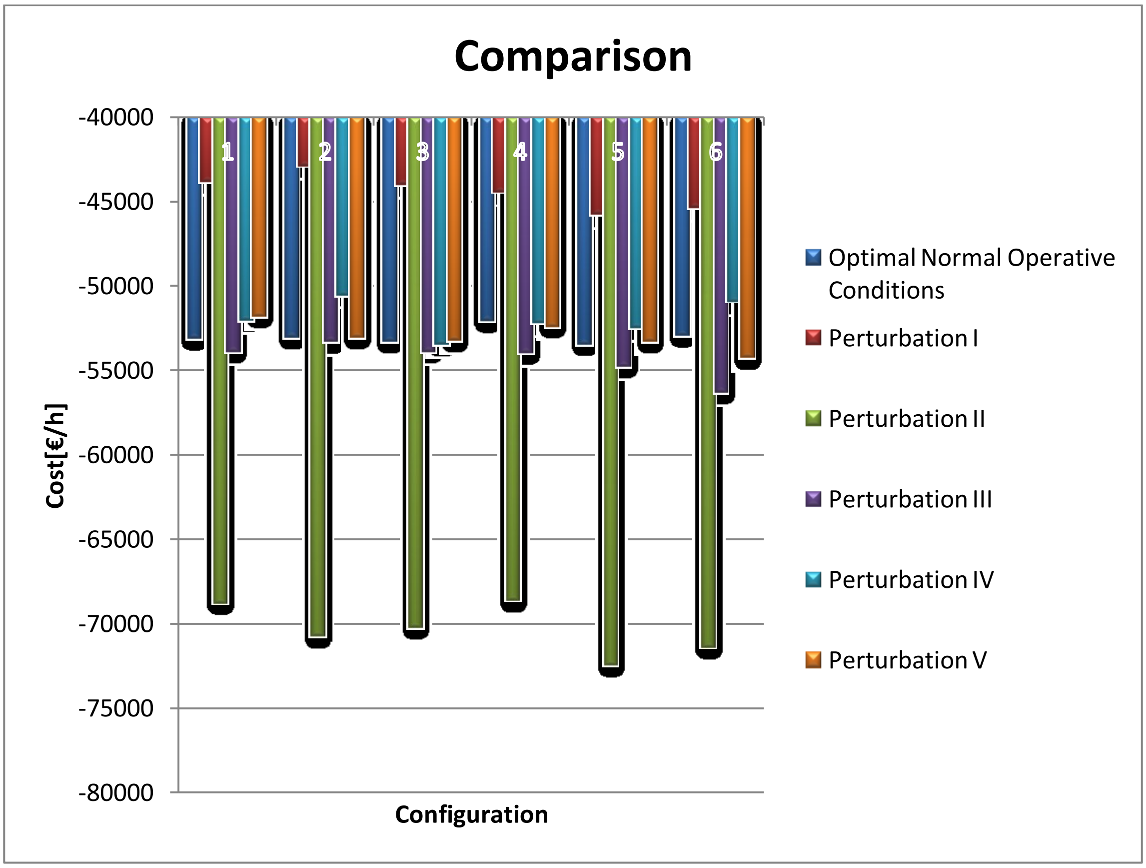

Figure 56: comparison between the different optimizations with the respect of disturbances and their expected range

As you can see there is not a great difference among all the simulation/configuration, that is due to the fact that all are relative optima of the objective function. But analyzing with more attention configuration 3 and 4 we can note that those are the best in terms of less loss from the optimal normal operative conditions.

At this point we have completed the second step.

And here we report the results of this simulation:

Table 14: results of the third configuration

RUN			
Initial Value	**Optimal result**	**DOFs**	**Cost Function, *J***
3	1,123185427	Delta Pressure [kPa]	-53274,30429
350	350,0028264	Inlet Temperature Reactor [°C]	
50	64,51189265	Cooling Temperature [°C]	
1,30E+04	12958,68577	Inlet Pressure [kPa]	
2,43	2,400512383	H2/Gas Oil Ratio [-]	
6,10E+03	6100,019689	Absorption Pressure [Pa]	
13888,88889	50000015,72	Reboiler Duty [kJ/h]	
0,430555556	1159,504081	Molar flow ABS column [kgmol/h]	
60	50,00011585	Inlet Temperature Regeneration [°C]	
35	30,93073656	Outlet Temperature Regeneration [°C]	
150	150,294351	Regeneration Column Pressure [kPa]	

4.5.3 Step 3: Select Economic (Primary) Controlled Variables, CV_1

This is the part which is dealt with the implementation of optimal points found in the previous two steps and their organization in a robust and simple manner.

What we have obtained from the previous analysis is the economic degrees of freedom ($\boldsymbol{u}$), and now what we want to reach is identify the economic controlled variables (CV_1). Or better in this case we want to verify also if those are the right variables for the degrees of freedom.

Remember that the number of first controlled variables is equal to steady-state degrees of freedom one. But what is needed to control?

So the optimal operation for given d:

$$\min_u \; J(\boldsymbol{u}, \mathbf{x}, \underline{d})$$

subject to:

$$\text{Model equations:} \qquad f(\boldsymbol{u}, \mathbf{x}, \underline{d}) = 0$$

$$\text{Operational constraints:} \qquad g(\boldsymbol{u}, \mathbf{x}, \underline{d}) \leq 0$$

The result of this study has been the $\mathbf{u_{opt}}$, whose values however usually cannot be kept constant because disturbances d change, and in this way the optimal results change too.

However for the economical optimal operation, we have two rules, the ones mentioned before:

- **CV_1 – rule 1**, that is control active constraints
- **CV_1 – rule 2**, i.e. for the remaining unconstrained DOFs, we must control self-optimizing variables.

From the analysis previously conducted, we have found that *inlet pressure* is an active constraint of the plant, that means that it is not susceptible for changing and that it has to be set to its maximum (in this case, but it depends on the nature of the variable) value. Together with this degree of freedom we have to take into account, seen from the previous analysis of the results of the optimization the temperature the *H2/Gas Oil ratio* and the *temperature out* from the *regeneration column*. These considerations make possible to reduce the remaining degrees of freedom for which is then necessary to select a controlled variable. So as stated by rule 1, we must control active constraints; the reason is quite obvious because we have to understand that usually the optimum is not “flat” with respect to these variables: this means that there is often an economic penalty if we back off from those variables and we must add a tight control of them.

In summa our active constraints could be assumed as (observing the precedent constraints when they become active):

- Inlet pressure
- Outlet temperature regeneration
- H2/Gas Oil ratio

So we have assigned three CVs to the same number of degrees of freedom. And for the other ones? The solution lies in controlling of the self-optimizing variables. At this step 10 degrees of freedom remain to be assigned. It is now necessary identify the candidate measurements and then select them on the basis of $CV_1 = \mathbf{H} \cdot \underline{y}$, as explained before.

In order to accomplish this goal we have to follow the procedure seen previously.

From the analysis of the system we can use the previous measurements associated with the DOFs to see if they were good candidate to be self-optimizing variables. To achieve this it has been used one of the main approaches developed to find the matrix H; having excluded the "brute force" approach, the problem has been solved with the "local" approach: the so called *Nullspace method*[74,75]. Let we see a brief theoretical explanation.

4.5.3a The Nullspace Method

We consider the unconstrained optimization problem as given in the following form, the same seen previously:

$$\min_u \ J(\boldsymbol{u}, \underline{d})$$

that is, we assume "active constraint control", where all optimally constrained variables are assumed to be kept constant at their optimal values. Our goal is to find a linear measurement combination $\mathbf{c} = \mathbf{Hy}$ to be kept at constant setpoints c_s. Here, $\mathbf{H}$ is a constant $n_u \times n_y$ matrix and $\mathbf{y}$ is a subset of the available measurements.

To make possible to apply this procedure we have to make some assumptions:

1- *Steady state*: We consider only steady-state operation. The justification for this is that the economics of operation is primarily determined by the steady state; directly from this assumption is that a control system in place that can quickly bring the plant to its new steady state.

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[74] See it on pages 27-28, and VIDAR ALSTAD, SIGURD SKOGESTAD, EDUARDO S. HORI, *Optimal measurement combinations as controlled variables*, Journal of Process Control 19, 138–148, Elsevier Ltd., 2009

[75] V. ALSTAD AND S. SKOGESTAD, *Null Space Method for Selecting Optimal Measurement Combinations as Controlled Variables*, Ind.Eng.Chem.Res, 46 (3), 846-853 (2007)

2- *Disturbances*: Only disturbances that affect the steady-state operation are included (in this case we assume the disturbances seen before → Feed flow and feed composition).

3- *Active constraint control*: the same active constraints remain active for all values of the disturbances and that we control these constraints (see CV_1 – rule 1).

4- *No implementation error*: The implementation error is the sum of the control error and the effect of the measurement error.

It is a more serious assumption to neglect the measurement error, so the method implicitly assumes that the measurements have been carefully selected (this is the limitation that the *exact local method* tries to eliminate).

So firstly has been obtained the optimal measurement sensitivity **F**, defined as **F** = $d\underline{y}_{opt}/d\underline{d}$

$$F = \begin{bmatrix} \frac{\partial y_{1,opt}}{\partial d_1} & \cdots & \frac{\partial y_{1,opt}}{\partial d_{n_d}} \\ \vdots & \ddots & \vdots \\ \frac{\partial y_{n_y,opt}}{\partial d_1} & \cdots & \frac{\partial y_{n_y,opt}}{\partial d_{n_d}} \end{bmatrix}$$

However, in practice, it is usually easier to obtain **F** directly, by optimizing for the selected disturbances using a nonlinear steady-state model of the plant: because we are going to find **F** numerically we use a commercial steady-state process simulators, i.e. Aspen HYSYS®. Just to note that in theory, one may even obtain **F** from experiments on a real operating plant, but this method is sufficiently accurate.

So numerically, the n_y x n_d matrix **F** may be obtained by perturbing the disturbances $\underline{d}$ and re-solving the optimization problem with the active constraints being constant, that is:

1- Under nominal conditions ($\underline{d} = \underline{d}^*$), use the steady-state model to obtain the nominal optimum $\underline{y}_{opt}(\underline{d}^*)$ and identify the active constraints (finding the nominal optimum may be difficult, because the optimization problem is generally nonconvex) → Step 2.

2- For each of the n_d disturbances, make a small perturbation and resolve the optimization with the constant active constraints to obtain $\underline{y}_{opt}(\underline{d})$.

3- Compute $\Delta y^{opt} = y^{opt}(\underline{d}) - y^{opt}(\underline{d}^*)$ and obtain **F** numerically (note that a minimum of $n_d + 1$ optimization runs are required.

The next step is to obtain **H**. Numerically, **H** may be obtained from a singular value decomposition of $\mathbf{F}^T$. We have $\mathbf{HF} = 0$ or, equivalently, $\mathbf{F}^T\mathbf{H}^T = 0$. Thus, selecting $\mathbf{H}^T$ as the input singular vectors of $\mathbf{F}^T$, corresponding to zero singular values in $\mathbf{F}^T$, gives an orthogonal basis: then the matrix **H** is find because it has to be respected the condition **HF** = 0. Note that, as stated before, because of **H** is a non-square matrix, it is not necessary that **H** is equal to 0, rather that **H** is in the Nullspace of $\mathbf{F}^\mathbf{T}$.

$$\mathbf{H}^{\mathbf{T}} = nullspace\ (\mathbf{F}^{\mathbf{T}})$$

The corresponding optimal change in the controlled variables is

$\mathbf{c}^{opt}(\underline{d}) - \mathbf{c}^{opt}(\underline{d}^*) = \mathbf{H}(\underline{y}^{opt}(\underline{d}) - \underline{y}^{opt}(\underline{d}^*)$

and by the previous explanation we get that

$\mathbf{c}^{opt}(\underline{d}) - \mathbf{c}^{opt}(\underline{d}^*) = \mathbf{HF}(\underline{d} - \underline{d}^*)$

From which we know that the constant setpoint policy is optimal if:

$\mathbf{c}^{opt}(\underline{d}) - \mathbf{c}^{opt}(\underline{d}^*) = 0$

As usual remember that:

- → This method reach its best results and optimal measurement combinations in case of no noise: $n^y = 0$.
- → Each column of F express the optimal change in y when the unconstrained variable ***u*** is adjusted in order to have a system remaining optimal with respect to disturbances $\underline{d}$.

In this sense it has been calculated the optimal sensitivity first of all optimizing the system (in order to obtain the "nominal point", $y_{nominal}$) then with the re-optimizing the system after the disturbances, it has possible to evaluate the new working value of the variables , y_{ddi}. Considering the *step* as ddi = $ddi_{nominal}$ + step, where ddi is the value of the disturbance and $ddi_{nominal}$ the value of the disturbed variable associated with the nominal point ($y_{nominal}$); it is possible define the optimal sensitivity, F approximating the differentiation as ratio between difference of the two optimal measurements ($y_{nominal}$ and y_{ddi}) and the value of the step. This is a valid numerical approximation which can give optimal results in short time. That is:

$$F_{i,:} = \begin{bmatrix} \frac{y_{ddi} - y_{nominal}}{step} \\ \vdots \end{bmatrix}$$

This matrix will be then transposed in order to have the desired H^T matrix; numerically the operation has been done with Matlab®, using `null`[76] function.

In order to relevance, first of all it has been necessary to identify the candidate measurements in a number that has to be at least equal to the sum of disturbances and DOFs (unconstrained, because the active constraints have been set to be constant),

$$\#y \geq \#d + \#u$$

$$\#y \geq \#2 + \#8$$

$$\#y \geq 10$$

So a number of minimum 10 measurements are required, but we have to take into consideration, in general, the inputs (for example the flow rates), with those used to control active constraints; remember that to make possible to use this method we have to use a number equal to the sum of disturbances and unconstrained degrees of freedom (that will result in a matrix of the same dimensions). That is quite clear if we think that this control has to avoid the system drift away from the optimal nominal point. We consider two sets of measurements in order to see what are the best candidates to be the self-optimizing variables.

Table 15: first candidate measurements

y
gas oil to heat temperature [°C]
reactor inlet mass flow [kg/h]
reactor product temperature [K]
H2O make up mass flow [kg/h]
flash VAP mass flow [kg/h]
rich MDEA to flash temperature [°C]
sweet gas temperature [°C]
regeneration bottom temperature [°C]
H2 to compressor temperature [°C]
desulfurized gas oil total sulfur content [% wt/wt]

---

[76] Z = null `(A)` is an orthonormal basis for the null space of `A` obtained from the singular value decomposition, MATHWORKS, *null*, http://www.mathworks.it/it/help/matlab/ref/null.html, accessed on March 2014

Table 16: second candidate measurements

y
reactor inlet temperature [K]
cooling temperature [°C]
inlet pressure [kPa]
absorption pressure [kPa]
reboiler duty [kJ/h]
molar flow ABS column [kgmol/h]
inlet temperature regeneration [°C]
regeneration pressure [kPa]
H2 actual volume flow [m^3/h]
k-100 power [kW]

Then the system has been disturbed taking into consideration the main two disturbances associated with this kind of process, that are: the mass flow of the feed and the total sulfur content in the feedstock that has to be removed during the processing of the charge.

Table 17: disturbances and their value after small perturbation

Disturbance	
Mass Flow [kg/h]	60,600
3000	63600
-3000	57600
Composition [% wt/wt]	0.077
0.005	0.082
-0.005	0.072

And it has been evaluated the F matrix in order to have an idea of the “impact” of disturbances on the process unit:

Table 18: positive disturbance in mass flow, first candidate measurements

Mass Flow +			
y(d*)	y(d)	Δy	y
45.29123785	45.2912378501	0.0000000000	gas oil to heat temperature
62737.70802687	65758.63656	3,020.9285334023	reactor inlet mass flow
630.01178930	636.2049418	6.1931525538	reactor product temperature
40.71074626	36.94205737	-3.7686888891	H2O make up mass flow
0.32926267	0.309765347	-0.0194973191	flash VAP mass flow
33.63208048	33.55132885	-0.0807516310	rich MDEA to flash temperature
35.05421281	35.03825373	-0.0159590843	sweet gas temperature
122.89776011	122.8977601	0.0000000000	regen bottom temperature
124.46109664	123.3321516	-1.1289450488	H2 to compressor temperature
0.00145463	0.001170	-0.0002849289	desulfurized gas oil total sulfur content

Table 19: negative disturbance in mass flow, first candidate measurements

Mass Flow -			
y(d*)	**y(d)**	**Δy**	**y**
45.29123785	45.2912378501	0.0000000000	gas oil to heat temperature
62737.70802687	59667.63157	-3,070.07646175	reactor inlet mass flow
630.01178930	682.0213114	52.0095221169	reactor product temperature
40.71074626	42.72250998	2.0117637245	H2O make up mass flow
0.32926267	0.339320942	0.0100582768	flash VAP mass flow
33.63208048	33.6740639	0.0419834128	rich MDEA to flash temperature
35.05421281	35.02923462	-0.0249781930	sweet gas temperature
122.89776011	122.8977601	0.0000000000	regen bottom temperature
124.46109664	126.012413	1.5513163739	H2 to compressor temperature
0.00145463	0.000437	-0.0010180343	desulfurized gas oil total sulfur content

Table 20: positive disturbance in composition, first candidate measurements

Composition +			
y(d*)	y(d)	Δy	y
45.29123785	45.29108239	-0.0001554604	gas oil to heat temperature
62737.70802687	62721.48632	-16.2217034520	reactor inlet mass flow
630.01178930	558.7717489	-71.2400404310	reactor product temperature
40.71074626	39.87849367	-0.8322525828	H2O make up mass flow
0.32926267	0.32499145	-0.0042712157	flash VAP mass flow
33.63208048	33.60282563	-0.0292548581	rich MDEA to flash temperature
35.05421281	35.03474995	-0.0194628602	sweet gas temperature
122.89776011	122.8977601	0.0000000000	regen bottom temperature
124.46109664	123.8306725	-0.6304240880	H2 to compressor temperature
0.00145463	0.005795	0.0043403701	desulfurized gas oil total sulfur content

Table 21: negative disturbance in composition, first candidate measurements

Composition -			
y(d*)	**y(d)**	**Δy**	**y**
45.29123785	45.2914444714	0.0002066212	gas oil to heat temperature
62737.70802687	62717.13668	-20.5713466485	reactor inlet mass flow
630.01178930	631.0971491	1.0853598516	reactor product temperature
40.71074626	39.70022117	-1.0105250844	H2O make up mass flow
0.32926267	0.325021184	-0.0042414817	flash VAP mass flow
33.63208048	33.59593921	-0.0361412732	rich MDEA to flash temperature
35.05421281	35.03684367	-0.0173691445	sweet gas temperature
122.89776011	122.8977601	0.0000000000	regen bottom temperature
124.46109664	121.4552614	-3.0058352328	H2 to compressor temperature
0.00145463	0.001087	-0.0003674347	desulfurized gas oil total sulfur content

Table 22: positive disturbance in mass flow, second candidate measurements

Mass Flow +			
y(d*)	**y(d)**	**Δy**	**y**
613.00282639	620.207308	7.2044816892	reactor inlet temperature [K]
64.51189265	49.308238	-15.20365467	cooling temperature [°C]
12958.68577127	12958.685771	0.0000000000	inlet pressure [kPa]
6100.01968930	6099.996326	-0.02336339	absorption pressure [kPa]
50000015.715747	49999995.8515	-19.8642330	reboiler duty [kJ/h]
1159.50408148	1159.504081	0.00000000	molar flow ABS column [kgmol/h]
50.00011585	59.718520	9.71840443	inlet temperature regeneration [°C]
150.29435100	150.503542	0.20919095	regeneration pressure [kPa]
44.78198883	72.413558	27.63156914	H2 actual volume flow [m^3/h]
775.33290728	880.861136	105.528229	k-100 power [kW]

Table 23: negative disturbance in mass flow, second candidate measurements

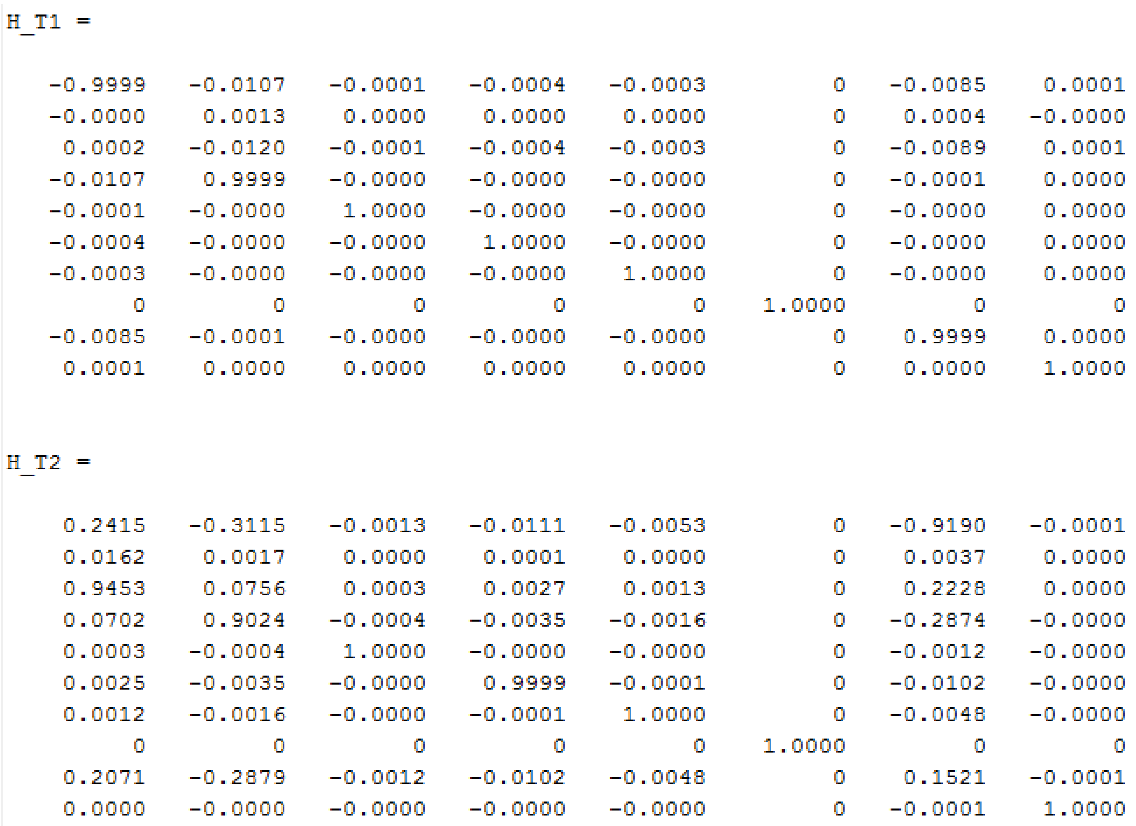
Mass Flow -			
y(d*)	**y(d)**	**Δy**	**y**
613.00282639	666.4425025	53.4396761375	reactor inlet temperature [K]
64.51189265	71.21896752	6.7070748660	cooling temperature [°C]
12958.68577127	12958.68577	0.0000000000	inlet pressure [kPa]
6100.01968930	5747.715073	-352.3046161195	absorption pressure [kPa]
50000015.715747	50615149.98	615,134.267744	reboiler duty [kJ/h]
1159.50408148	1159.504081	0.0000000000	molar flow ABS column [kgmol/h]
50.00011585	50.00000093	-0.0001149250	inlet temperature regeneration [°C]
150.29435100	150.0000029	-0.2943480889	regeneration pressure [kPa]
44.78198883	67.63310187	22.8511130392	H2 actual volume flow [m^3/h]
775.33290728	873.2714304	97.9385231524	k-100 power [kW]

Table 24: positive disturbance in composition, second candidate measurements

Composition +			
y(d*)	y(d)	Δy	y
613.00282639	542.038878	-70.9639485548	reactor inlet temperature [K]
64.51189265	61.480053	-3.0318398951	cooling temperature [°C]
12958.685771	12958.685771	0.0000000000	inlet pressure [kPa]
6100.0196893	6097.764008	-2.2556810765	absorption pressure [kPa]
50000015.7157	50011629.9247	11,614.20903	reboiler duty [kJ/h]
1159.504081	1159.504081	0.0000000000	molar flow ABS column [kgmol/h]
50.00011585	51.725190	1.7250743287	inlet temperature regeneration [°C]
150.29435100	150.000311	-0.2940404841	regeneration pressure [kPa]
44.78198883	69.501676	24.7196875204	H2 actual volume flow [m^3/h]
775.332907	841.512105	66.1791973661	k-100 power [kW]

Table 25: negative disturbance in composition, second candidate measurements

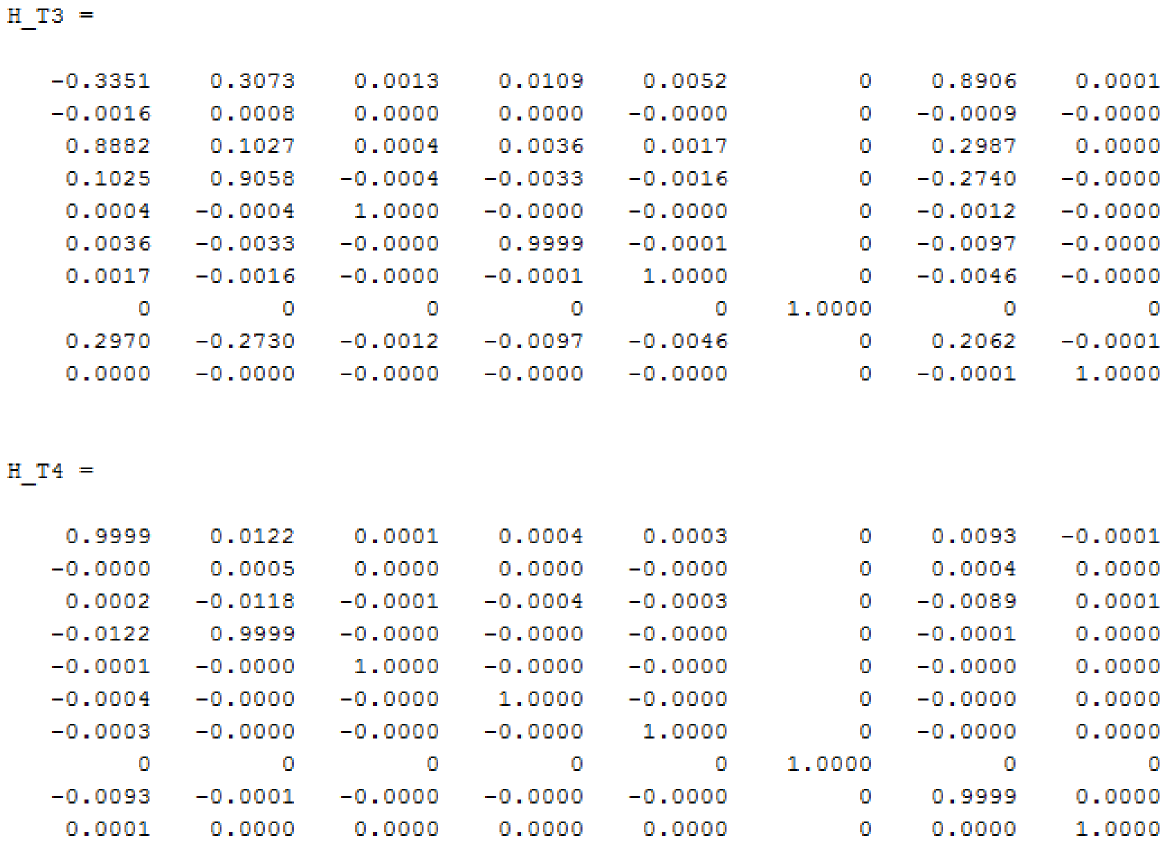
		Composition -	
y(d*)	y(d)	Δy	y
613.00282639	615.7160074	2.71318098	reactor inlet temperature [K]
64.51189265	66.05463659	1.54274394	cooling temperature [°C]
12958.68577127	12958.68577	0.00000000	inlet pressure [kPa]
6100.01968930	6104.307174	4.2874843925	absorption pressure [kPa]
50000015.71574	50008574.84	8,559.128937	reboiler duty [kJ/h]
1159.50408148	1159.504081	0.0000000000	molar flow ABS column [kgmol/h]
50.00011585	50.01475998	0.0146441283	inlet temperature regeneration [°C]
150.29435100	150.0047448	-0.2896062309	regeneration pressure [kPa]
44.78198883	67.52268825	22.7406994	H2 actual volume flow [m^3/h]
775.33290728	833.7486652	58.4157578	k-100 power [kW]



```
H_T1 =

   -0.9999   -0.0107   -0.0001   -0.0004   -0.0003         0   -0.0085    0.0001
   -0.0000    0.0013    0.0000    0.0000    0.0000         0    0.0004   -0.0000
    0.0002   -0.0120   -0.0001   -0.0004   -0.0003         0   -0.0089    0.0001
   -0.0107    0.9999   -0.0000   -0.0000   -0.0000         0   -0.0001    0.0000
   -0.0001   -0.0000    1.0000   -0.0000   -0.0000         0   -0.0000    0.0000
   -0.0004   -0.0000   -0.0000    1.0000   -0.0000         0   -0.0000    0.0000
   -0.0003   -0.0000   -0.0000   -0.0000    1.0000         0   -0.0000    0.0000
         0         0         0         0         0    1.0000         0         0
   -0.0085   -0.0001   -0.0000   -0.0000   -0.0000         0    0.9999    0.0000
    0.0001    0.0000    0.0000    0.0000    0.0000         0    0.0000    1.0000


H_T2 =

    0.2415   -0.3115   -0.0013   -0.0111   -0.0053         0   -0.9190   -0.0001
    0.0162    0.0017    0.0000    0.0001    0.0000         0    0.0037    0.0000
    0.9453    0.0756    0.0003    0.0027    0.0013         0    0.2228    0.0000
    0.0702    0.9024   -0.0004   -0.0035   -0.0016         0   -0.2874   -0.0000
    0.0003   -0.0004    1.0000   -0.0000   -0.0000         0   -0.0012   -0.0000
    0.0025   -0.0035   -0.0000    0.9999   -0.0001         0   -0.0102   -0.0000
    0.0012   -0.0016   -0.0000   -0.0001    1.0000         0   -0.0048   -0.0000
         0         0         0         0         0    1.0000         0         0
    0.2071   -0.2879   -0.0012   -0.0102   -0.0048         0    0.1521   -0.0001
    0.0000   -0.0000   -0.0000   -0.0000   -0.0000         0   -0.0001    1.0000
```

Figure 57: results of the Nullspace method applied to the previous optimal configuration, first two matrices

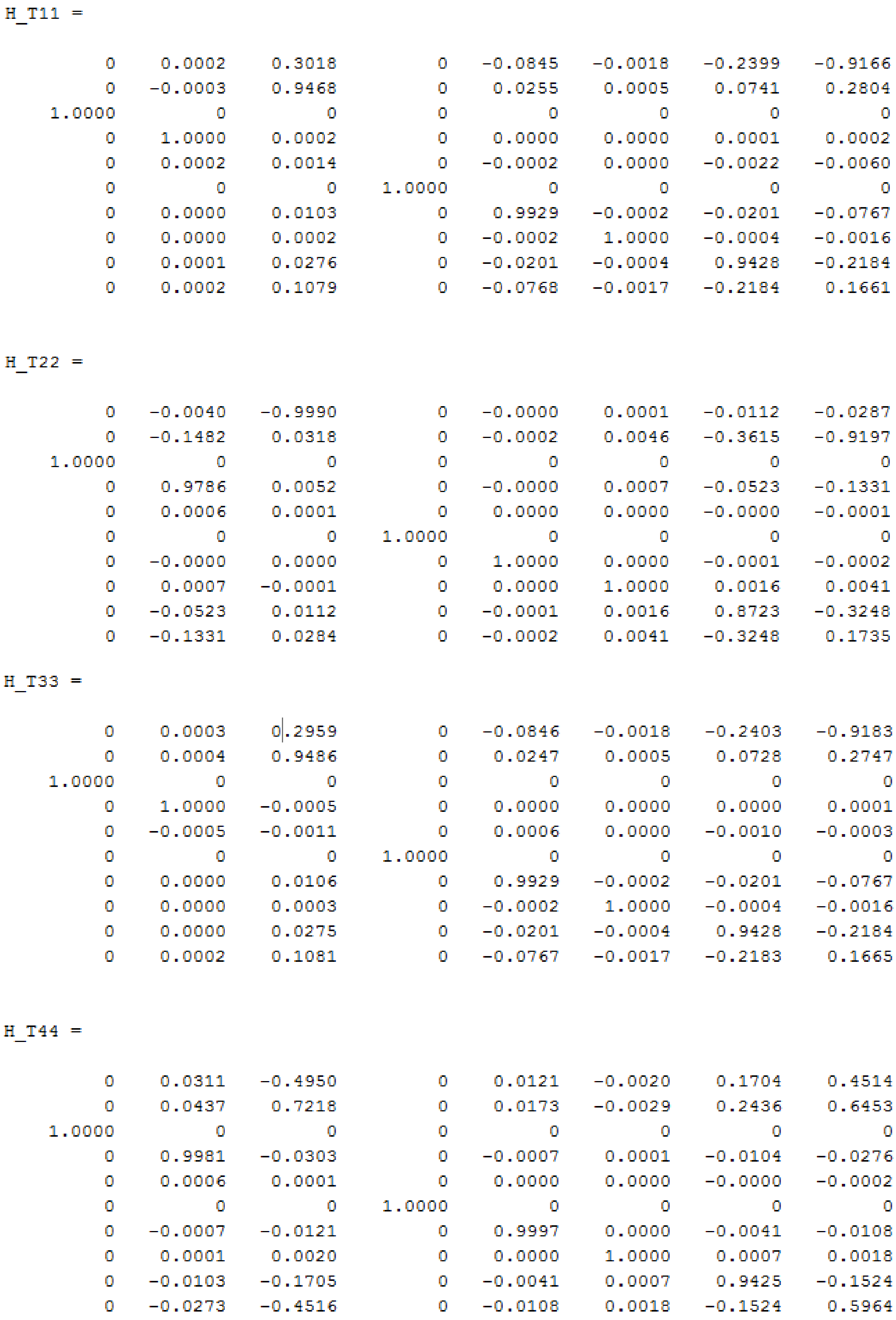
Where H_T1 and H_T2 are the matrices dealing with positive (the first one) disturbance in feed flow and composition too, while the second one has undergone to a negative disturbance in composition and feed flow. Both are the **H** matrix in which we could "see" how the remaining unconstrained DOFs are connected to some variables. They are 10x8 matrices that means we have in row the different measurements and in column the unconstrained degrees of freedom, where the self-optimizing variables are meant as possible combination of measurements. An increasing prediction could be done trying to increasing the measurements or selecting them with more accuracy.



```
H_T3 =

   -0.3351    0.3073    0.0013    0.0109    0.0052         0    0.8906    0.0001
   -0.0016    0.0008    0.0000    0.0000   -0.0000         0   -0.0009   -0.0000
    0.8882    0.1027    0.0004    0.0036    0.0017         0    0.2987    0.0000
    0.1025    0.9058   -0.0004   -0.0033   -0.0016         0   -0.2740   -0.0000
    0.0004   -0.0004    1.0000   -0.0000   -0.0000         0   -0.0012   -0.0000
    0.0036   -0.0033   -0.0000    0.9999   -0.0001         0   -0.0097   -0.0000
    0.0017   -0.0016   -0.0000   -0.0001    1.0000         0   -0.0046   -0.0000
         0         0         0         0         0    1.0000         0         0
    0.2970   -0.2730   -0.0012   -0.0097   -0.0046         0    0.2062   -0.0001
    0.0000   -0.0000   -0.0000   -0.0000   -0.0000         0   -0.0001    1.0000


H_T4 =

    0.9999    0.0122    0.0001    0.0004    0.0003         0    0.0093   -0.0001
   -0.0000    0.0005    0.0000    0.0000   -0.0000         0    0.0004    0.0000
    0.0002   -0.0118   -0.0001   -0.0004   -0.0003         0   -0.0089    0.0001
   -0.0122    0.9999   -0.0000   -0.0000   -0.0000         0   -0.0001    0.0000
   -0.0001   -0.0000    1.0000   -0.0000   -0.0000         0   -0.0000    0.0000
   -0.0004   -0.0000   -0.0000    1.0000   -0.0000         0   -0.0000    0.0000
   -0.0003   -0.0000   -0.0000   -0.0000    1.0000         0   -0.0000    0.0000
         0         0         0         0         0    1.0000         0         0
   -0.0093   -0.0001   -0.0000   -0.0000   -0.0000         0    0.9999    0.0000
    0.0001    0.0000    0.0000    0.0000    0.0000         0    0.0000    1.0000
```

Figure 58: results of the Nullspace method applied to the previous optimal configuration, second two matrices

In these two second matrices the value represented are in H_T3 and H_T4 a positive (the first one) disturbance in feed flow and a negative disturbance in composition, while the second one has undergone to a negative disturbance in feed flow and a positive disturbance in composition (we have to remember that each **H** matrix is considering the possible disturbances and so each of them has a feed and composition disturbance). The same work has been done with the second candidate measurements (we report them in order to see the most significant changing in their value).



```
H_T11 =

         0    0.0002    0.3018         0   -0.0845   -0.0018   -0.2399   -0.9166
         0   -0.0003    0.9468         0    0.0255    0.0005    0.0741    0.2804
    1.0000         0         0         0         0         0         0         0
         0    1.0000    0.0002         0    0.0000    0.0000    0.0001    0.0002
         0    0.0002    0.0014         0   -0.0002    0.0000   -0.0022   -0.0060
         0         0         0    1.0000         0         0         0         0
         0    0.0000    0.0103         0    0.9929   -0.0002   -0.0201   -0.0767
         0    0.0000    0.0002         0   -0.0002    1.0000   -0.0004   -0.0016
         0    0.0001    0.0276         0   -0.0201   -0.0004    0.9428   -0.2184
         0    0.0002    0.1079         0   -0.0768   -0.0017   -0.2184    0.1661


H_T22 =

         0   -0.0040   -0.9990         0   -0.0000    0.0001   -0.0112   -0.0287
         0   -0.1482    0.0318         0   -0.0002    0.0046   -0.3615   -0.9197
    1.0000         0         0         0         0         0         0         0
         0    0.9786    0.0052         0   -0.0000    0.0007   -0.0523   -0.1331
         0    0.0006    0.0001         0    0.0000    0.0000   -0.0000   -0.0001
         0         0         0    1.0000         0         0         0         0
         0   -0.0000    0.0000         0    1.0000    0.0000   -0.0001   -0.0002
         0    0.0007   -0.0001         0    0.0000    1.0000    0.0016    0.0041
         0   -0.0523    0.0112         0   -0.0001    0.0016    0.8723   -0.3248
         0   -0.1331    0.0284         0   -0.0002    0.0041   -0.3248    0.1735

H_T33 =

         0    0.0003    0.2959         0   -0.0846   -0.0018   -0.2403   -0.9183
         0    0.0004    0.9486         0    0.0247    0.0005    0.0728    0.2747
    1.0000         0         0         0         0         0         0         0
         0    1.0000   -0.0005         0    0.0000    0.0000    0.0000    0.0001
         0   -0.0005   -0.0011         0    0.0006    0.0000   -0.0010   -0.0003
         0         0         0    1.0000         0         0         0         0
         0    0.0000    0.0106         0    0.9929   -0.0002   -0.0201   -0.0767
         0    0.0000    0.0003         0   -0.0002    1.0000   -0.0004   -0.0016
         0    0.0000    0.0275         0   -0.0201   -0.0004    0.9428   -0.2184
         0    0.0002    0.1081         0   -0.0767   -0.0017   -0.2183    0.1665


H_T44 =

         0    0.0311   -0.4950         0    0.0121   -0.0020    0.1704    0.4514
         0    0.0437    0.7218         0    0.0173   -0.0029    0.2436    0.6453
    1.0000         0         0         0         0         0         0         0
         0    0.9981   -0.0303         0   -0.0007    0.0001   -0.0104   -0.0276
         0    0.0006    0.0001         0    0.0000    0.0000   -0.0000   -0.0002
         0         0         0    1.0000         0         0         0         0
         0   -0.0007   -0.0121         0    0.9997    0.0000   -0.0041   -0.0108
         0    0.0001    0.0020         0    0.0000    1.0000    0.0007    0.0018
         0   -0.0103   -0.1705         0   -0.0041    0.0007    0.9425   -0.1524
         0   -0.0273   -0.4516         0   -0.0108    0.0018   -0.1524    0.5964
```

Figure 59: results of the Nullspace method applied to the previous optimal configuration, with the second set of measurements

As we can see from the previous results (all **H** matrices) we can note how values of the first row are higher (absolute value) with respect to the other one and that is because it is dealing with the variation of reactor inlet temperature and gas oil to heat temperature, those affect the behavior of all the unit. So they are to be measured the former and control the latter one variable. Same speech could be done about the fourth row, “absorption pressure”, because it significantly affect the grade of purification of the hydrogen to be recycled to the plant. All these variables have to be considered self-optimizing and in this sense they have to be controlled or in a different way measured and used to make more robust the control.

4.5.4 Step 4: Select the Location of TPM (Decision 3)

For this point as discussed previously, there are different approaches and solution on which could be the best location for the TPM. In this case, because the basis idea of the process is to transform some raw materials into products whose value is higher than the feedstock, in an amount that could be justify the expense of the same plant, it is clear that the easiest and the most reliable position of the throughput manipulator is at the beginning of the plant on the feeding line.

It is reasonable acting in this way instead moving it through the plant because in this case as in almost all the other the easiest solution is quite always the best.

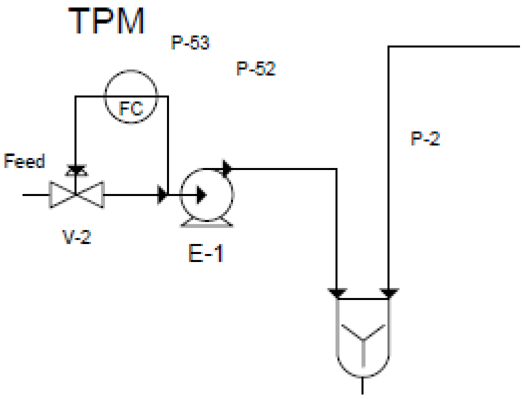


Figure 60: location of the TPM, select at the beginning of the plant

4.5.5 Step 5: Select the Structure of Regulatory (Stabilizing) Control Layer

With this step we aim to stabilize the plant, preferring a simple control structure with single-loop PID controller (reliable of a more robust control). As seen in the previous explanation "stabilize" means that the process doesn't drift too far away from acceptable operation even if there are some disturbances.

In this step there are two faced two main decision:

1- Select controlled variables (CV_2), i.e. Decision 2

2- Select inputs (that is valves) and "pairings" in order to control the above mentioned variables (CV_2), i.e. Decision 4

We have not to add any degrees of freedom because the setpoints CV_{2s} are left as manipulated variables (MVs) for the supervisory layer.

If we consider to allow for cascade loops, then the stabilization layer may be designed independent of the supervisory control layer (i.e. the economic one).

SELECT STABILIZING CV_2 (Decision 2)

Firstly we have to stabilize the process by controlling drifting variables such level and pressure, reactor temperature and temperature profile in the distillation column. In this case we want to control:

1- Levels: the HP Separator, in the Absorption Column (T-100) and in V-100.

2- Pressures/Temperatures, in case of necessity

This simplifies the supervisory control layer and its tasks because it provides for local/fast disturbances rejection and reducing the non-linearity in the model. Then we should include active constraints (CV_1) those need a tight control (they are usually hard output constraints) in $CV_2$for the regulatory layer. In this way we reduce the required back-off. Because of all these reasons it is usually not necessary for tight control of unconstrained CV_1, indeed the optimum is quite "flat".

4.5.6 Step 6: Select Structure of Supervisory Control Layer

At this point of the explanation we remember that this control layer has three principal tasks: firstly it has to control the CV_1 in such a way that it is dealing with the exploitation of the set points to the regulatory layer and using the remained unused valves (meant as MVs); then it has to supervise the performance of the previous layer of control, i.e. the regulatory one, and finally it is involved in switching controlled variables and control strategies when we have some disturbances on price: this means that in some cases we have the possibility to have a switch from a region of active constraints to another one.

Among the two possibilities of controller, advanced single loop control and multivariable control, we will privilege the first one (PID) instead of the second (MPC); and the reason is quite intuitable: we want to grant robustness and at the same time to improve the response of the dynamic system; so when it could be possible we must select and adopt the easiest solution, that is not always so banal to be refused.

We now analyze the control structure proposed to obtain the no-drifting away of the unit during its working. The first structure was proposed by Professor Skogestand and it has been then modified with Professor Manenti in order to be more significant of the real meaning of this process, taking into consideration all the previous dissertations and trying to apply all of them.

In red we can see the CV_1 and the regulatory control acting on them, while in green the remaining CV_2 those are the stabilizing CV_2.

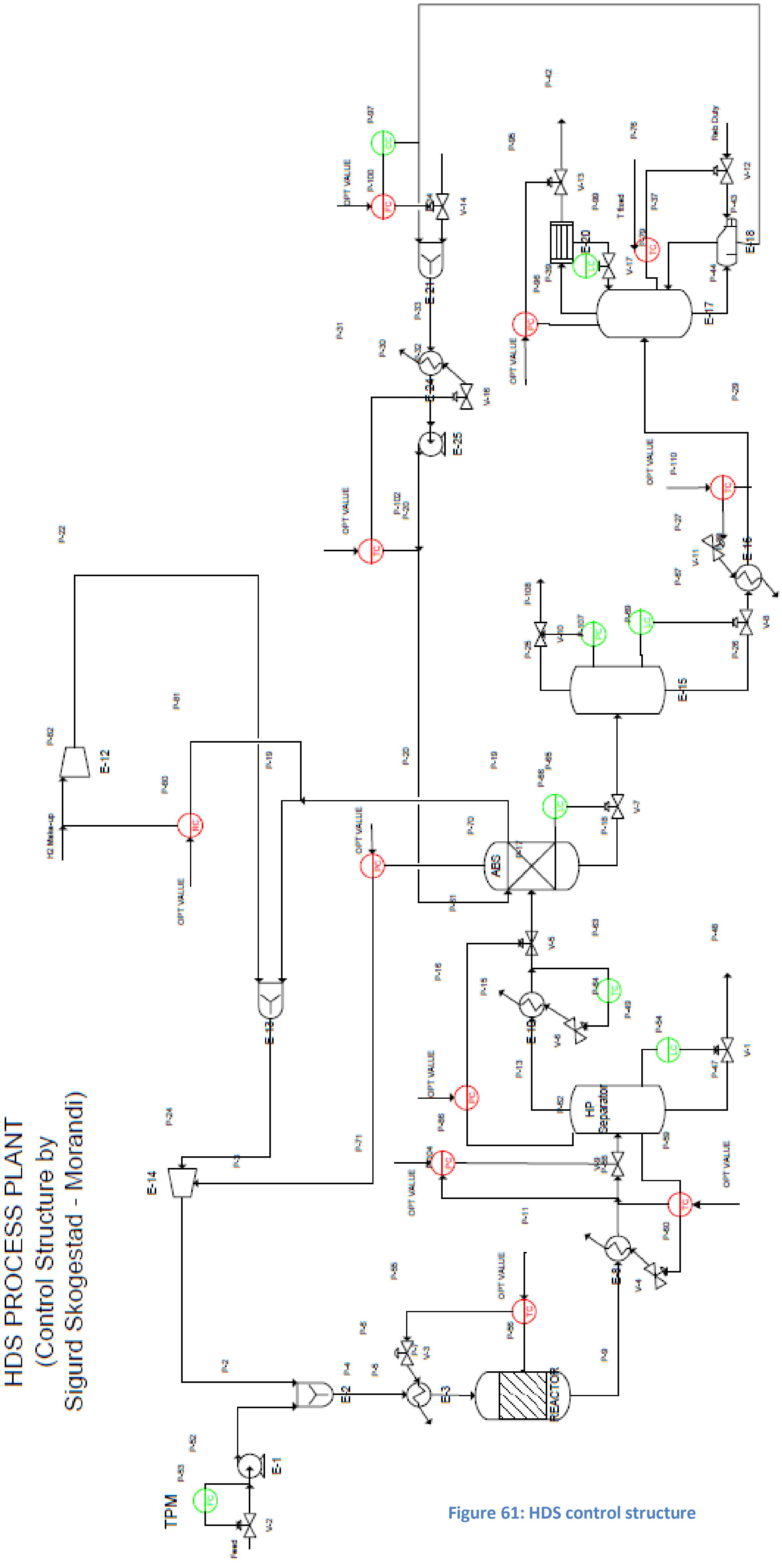


Figure 61: HDS control structure

This is the structure proposed in order to compensate the disturbances and operate always near to the optimal working point, granting stability and at the same time the less loss possible. To the complete explanation of all the system, please refer to Chapter 5.

4.5.7 Step 7: Structure of Optimization Layer (RTO) (related to Decision 1)

For this last point we have to understand that it could be the normal way to conclude such a kind of optimization, nut it has not to be the only reason to guide such an analysis. This is due because the goal of the RTO layer is to update the setpoints for CV_1 and to detect changes in active constraints regions that should be required the switching of the same CV_1; but in most of cases with a self-optimizing choice for the choice of the primary controlled variables, what we can obtain from this kind of system is too low to justify the cost of creating and then sustaining the detailed steady-state model required for this layer.

For this project this choice to make use of the RTO layer has been refused instead a dynamical simulation based on the response to different disturbances.

Moreover for this system it was quite impossible to propose, having seen the slowness of the optimization step. It could be useless such a kind of device if it could not be used properly because the system did not permit such a rapid optimization. If we add the numerical issues related to the optimization (difficult) and then the offline optimization (difficult too), the use of this last layer can be reasonably avoided.

Chapter 5

Dynamic Simulation: tuning and scenarios

“*Run*”
Snow Patrol

5.1 INTRODUCTION

It is now time to face the control structure derived from the previous analysis and the previous assumptions. For this project it has been assumed the possibility to control ll with a PID control. That means for the supervisory control layer the choice between MPC and PID it has been guided to the second one; for simplicity and for the robustness it is at the same time to grant.

In this sense we have to control the CV_1 in such a way that it is dealing with the exploitation of the set points to the regulatory layer and using the remained unused valves (meant as MVs). We now proceed with a brief explanation of what does it mean to use a PID control and then the result of the dynamic simulation will be presented.

5.2 PID[77]

Commonly used in industrial control systems the PID is a control loop feedback mechanism (controller). This device of control works because it is able to calculate an "error" value as the difference between a measured process variable and a desired setpoint. This controller aims to minimize the error by adjusting the process control outputs.

In this way the controller exercises three actions:

- **the proportional one (P)**, where the signal emitted by the regulator is “proportional” to the error and we have such an action that:

  $$c(t) = K_c \cdot \varepsilon(t) + c_s$$

  where K_c is the static proportional gain, c_s is the bias (signal when $\varepsilon = 0$)

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[77] PIO FORZATTI, LUCA LIETTI, *Strumentazione chimica industriale*, Volume 1, Milano: CUSL, 2003

- **the integral action (I)**, because the only proportional action involves a residual error (i.e. the offset), this could be deleted with the integral action:

$$c(t) = \frac{K_c}{\tau_I} \cdot \int_0^t \varepsilon(t)dt$$

Usually these two actions are combined to reduce completely the error and avoid its persistence as offset (which means that the regulating signal is proportional to the error and to its integral in time), that is the **PI** control:

$$c(t) = K_c \cdot \varepsilon(t) + \frac{K_c}{\tau_I} \cdot \int_0^t \varepsilon(t)dt + c_s$$

- **the derivative action (D)**, it is requested when we have to prevent and anticipate the error effect, we introduce the derivative action, where the action is proportional to its derivative. Derivative action predicts system behavior and thus improves settling time and stability of the system, even if it is rarely used in the practice.

$$c(t) = K_c \tau_D . \frac{d\varepsilon(t)}{dt}$$

More often its action is combined with the above mentioned control inputs, the so called **PID** control:

$$c(t) = K_c \cdot \varepsilon(t) + \frac{K_c}{\tau_I} \cdot \int_0^t \varepsilon(t)dt + K_c \cdot \tau_D . \frac{d\varepsilon(t)}{dt} + c_s$$

In a more general sense we can state that the above mentioned actions are able to grant a particular response of the system; in particular the readiness and quickness of the regulation operated by the proportional action, while the integrative one is responsible of the precision and the accuracy. The derivative action instead is the term able to grant robustness to the response.

Even if all of them seems desired actions in all kind of control (in this sense in every variable to be controlled), more often we prefer the control acts with one or maybe a combination of them, without using them all in an aprioristic way.

5.3 TYPICAL REGULATOR CHOICE

We have usually to consider that the choice is made on the basis of the characteristics of the control action (in this sense, P, PI, PID, seldom PD) and on the dynamics of the process. Here reported there are some considerations about the kind of regulator.

In some cases it is preferable to use a different control and we could take into consideration MPC controller, or some adaptive controller. But in order to show the easiness of this control procedure it will be used a simple controller too.

5.3.1 FLOOD

This is a variable with a rapid response, with some disturbances due to turbulence and pressure's pulsations (linked to pumps' work). In this case it is preferable to use a proportional regulators with the integral action too. That is suddenly explained: we have to grant a rapid action (proportional contribute, **P**) and at the same time, because we have to deal with disturbances that would remain uncontrolled otherwise, we have an accurate response (integral contribute, **I**). This coupled action is reliable of rapidity and precision without leaving offset at transient spent, **PI**.

5.3.2 PRESSURE

In this case we have to make a distinction among the phase of the fluid has to be controlled; in particular:

- ✓ *Liquid*: because liquid pressure is going to change with the square of the flood (i.e. $P \propto Q^2$) and as stated before noise due to pumping machines are always present we have to control them with only PI control.
- ✓ *Gas*: we can consider as general rule the use of the only proportional, P, action, that is due to the fact that usually it is necessary "only" to keep this variable between two different values (upstream and downstream) at a constant value.
- ✓ Vapor: in this last case we have to consider the processes involved and more precisely we have that for a tank with vapor to storage or a simple pipeline we have to use a proportional and integral action (PI), to grant precision and a certain rapidity of response; if we have, instead, to control the pressure of a partial condenser it is preferable to have a PID controller: that is because the process of heat transmission is slow and we have to grant, and most of all, increase the response fastness.

5.3.3 LEVEL

Also in this case we have to make some considerations in order to give some thumb rule to grant a reliable response of the controller. In particular we have to deal with the dimensions of the vessel, that for practice are considered as cylinder:

- ✓ Great diameter: in this case is more than sufficient a proportional, P, controller (we have a high process time constant, i.e. slow dynamics).
- ✓ Small diameter: because we have a smaller process time constant and we need more precision it is usually accepted the use of a proportional and integral action, PI.

The derivative action is rarely used and it has to be refused if we have to treat with boiling or agitated liquids.

5.3.4 TEMPERATURE

As mentioned before for pressure control, we have to consider first of all the process at the basis of what we are going to control. In this case because we are dealing with the control of temperature and the process we have to consider is heat transmission, typical of systems with slow response, we need (or better it is preferable to use) the combination of all the three above mentioned actions, that is PID controller. That is resulting an robustness of the regulation without too many oscillations among the set point.

5.3.5 COMPOSITION

At the basis of these processes we have usually mixing or separation processes. But because this kind of analyzers are dealing with dead time and their regulation is sometimes critic, their use is limited to supervisor function instead of a direct control. For all these reasons the main and more sensate control it is normal to use a combination of PID action, granting all the necessary actions involved with this kind of regulators.

5.4 THE PLANT CONTROL

After having disserted about the different action of a PID regulator, we can now see the control applied to the process with all the previous assumptions derived by the self-optimizing control procedure; and In particular we have the optimal set points coming from the optimization of the system unit (those are fixed and for whose we have to grant an accurate control and in the case of the active constraints a tight control too). Remembering the previous control diagram we can see that all active constraints (the one which have been found to be active) are controlled tightly. That is possible in practice fixing a short range for PV (i.e. process variable) and controlling with accuracy the different PID parameters, each of the three actions usable. The control has been done in order to control all the DOFs encountered during the analysis (useful for CV_1 layer) and then introducing more control in order to improve and avoid the drifting away of the system.

Here the control structure:

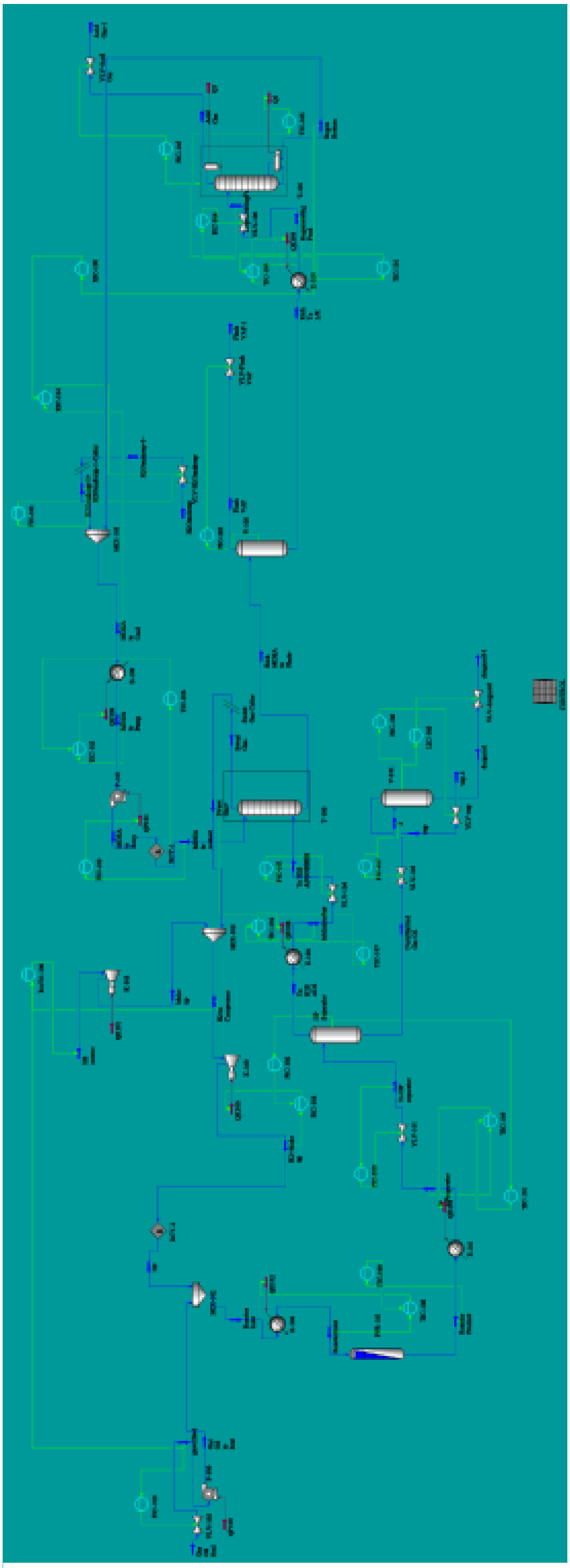

Figure 62: the HDS control

As it is possible to note all streams have been controlled, with a flood control (FC) in the previous control scheme (see Chapter 4). That give reason to the main disturbances take into considerations, and make possible a good control in order to achieve the steady state operative conditions. A point that has to be highlighted is the fact that to store the feed and flash it at right conditions (i.e. to atmospheric pressure and reasonable temperature) it has been introduced a tank out of the line of processed gas oil charge. It is only a little modification that does not affect the results obtained previously, but it is more correct under the perspective of a real processing unit (with this shrewdness it is possible to better control the level of the treated charge).

Anyway, the control of the system has been introduced in order to smooth disturbances and make it possible the right working in conditions as nearest as possible to the optimal point of the unit.

For the optimal values found during the optimization of the system have been selected as optimal set points, that have to be linked during the normal working of the process unit; in this way the best solution is desirable to be found. So first of all the active constraints have been controlled with a tight control and in this sense we have the control on “gas oil ratio”, realized by a ratio control between the “gas oil feed” and the H_2 coming from the regeneration loop; the inlet pressure given by a pressure controller set on line of the regenerating mixtures, but no one pressure controller is present on the feed line acting on the pump, P-100, because the inlet pressure is already set here. The last active constraint, the temperature out from the regenerating column, has been doubly controlled with an indicator on line and a controller acting on the coolant flood.

This means reason for a robust control on the active constraints. Then the remaining degrees of freedom has been set under control with some shrewdness: in particular having notice that, from the previous search for self-optimizing control, the H_2O is influencing the behavior of the plant, particular attention has been give to this variable and in particular a composition control (CC) has been put in order to evaluate the mass fraction of water in regenerating product, and then link to the set-point given by this controller a flood control has been disposed to adjust that value replacing water lost by evaporating during the process of regeneration; in order to have some negative values in H_2O make-up line another flood control has been put in act.

Moreover every “external” feed and in this case it is necessary to take into account the “H2 source”, the feed and the make-up water itself, has been controlled by a flood control (FC). Then it was time for pressures in the different lines, and in particular in the absorption and in the regenerating columns. The former is controlled by flashing the feed at the entrance of the column (4th tray), while the latter is performed controlling the acid gas pressure which is linked to condenser pressure. Another pressure controller has been put before the “HP separator” to provide the necessary difference of pressure for the flashing operation. Another issue has been the temperature control: first of all on the reactor, that aims to avoid some runaway reaction and then on the coolers in order to grant the best optimal working conditions; and in this sense all heaters/coolers have been put under the control of a temperature controllers (TC), verifying in parallel the result with other controllers/indicators. That means reason of a good control on the main self-optimizing variables too, identified as “gas oil to heat” temperature, its pressure, “H2O make-up” mass flow, and linked to this the water mass fraction. In order to face in a first approximation these variables have been selected because of their greater impact on the disturbances’ smoothing. It is reasonable to believe that more alternatives could be adopted and maybe they could be more effective, but in this case with this control good results have been obtained. Here the main and relevant out coming from the dynamic simulation with disturbances acting on the feed flow and on its composition, as studied before.

In order to accomplish the result the control structure has been developed in cascade, adopting a controller on-line, reliable to measure the CV and acting on the relative DOF, whose set-point is given by the master controller which measure the same variable in a critical point maybe more susceptible of variance, i.e. in a more sensitive point; this method has been applied in reactor temperature control, in pressure control (for line coming from amine loop) and for all the temperature measured (and in particular on the 4th tray of both the absorption column and the regenerating column, because it was the most susceptible of changing) and controlled in the unit process plant.

Moreover we have to note that for simulation the integration time has been reduced in order to make it possible the integration itself, because the pre-chosen span-time was too big and it was not possible to achieve a correct simulation.

5.5 RESULTS

As seen previously the control acted on flood has been selected with only proportional action (P), in this sense it is possible to note the presence of the offset. Same thought is valid for pressure control for which it is avoid the use of integrative action because of the noise caused by control valves themselves.

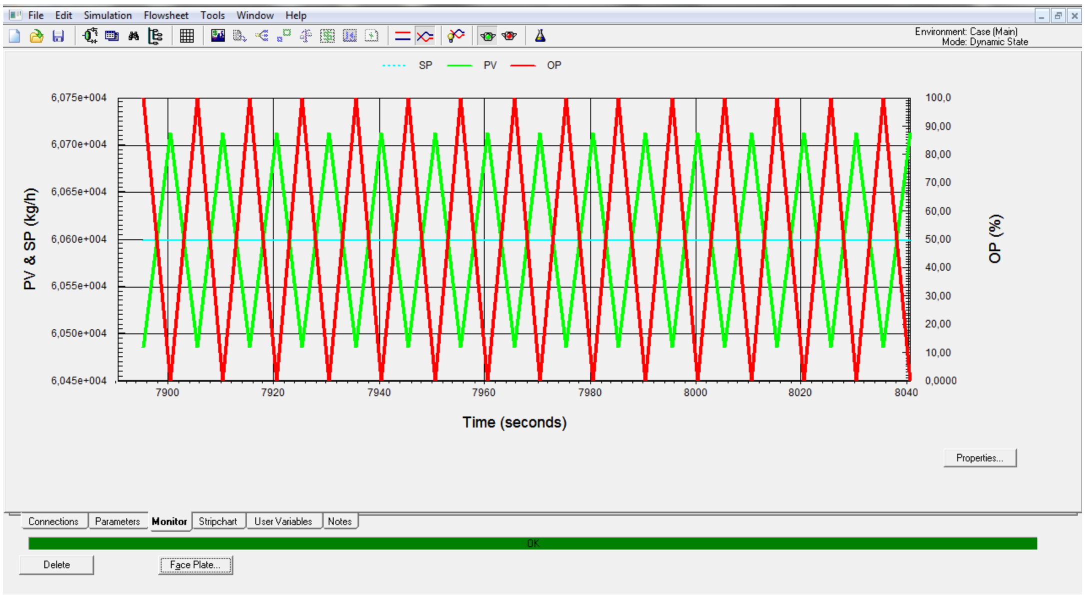

Figure 63: valve signal on feed control valve

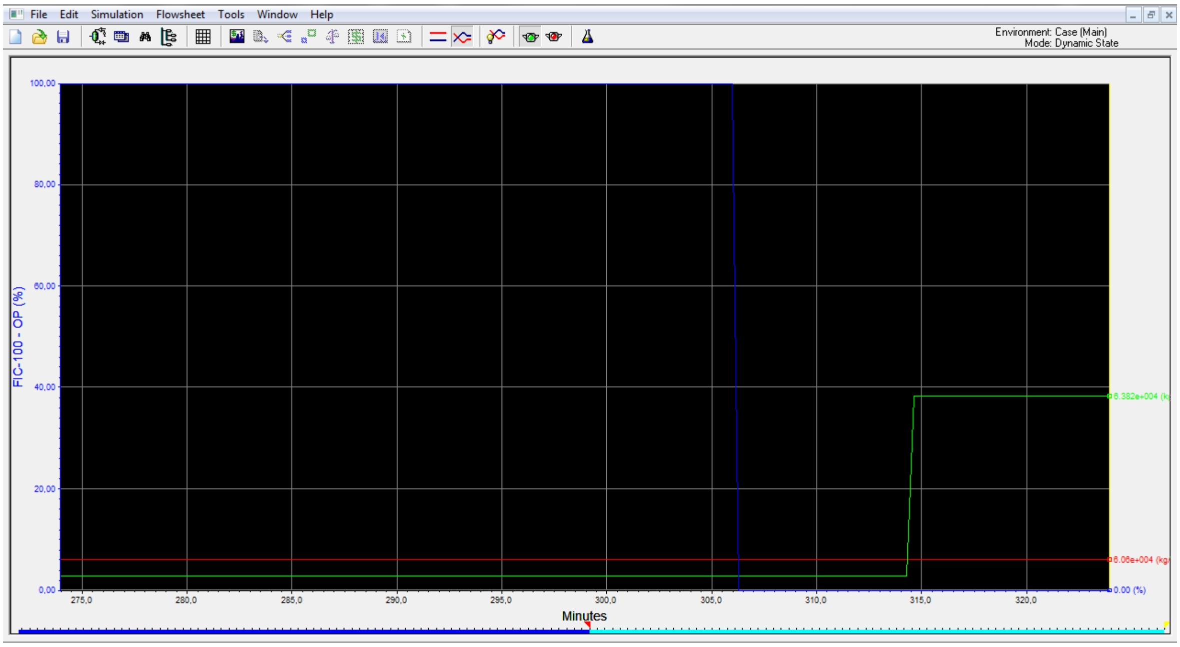

Figure 64: feed flood control and its disturb with increase in flood value from 60600 [kg/h] to 63600[kg/h]

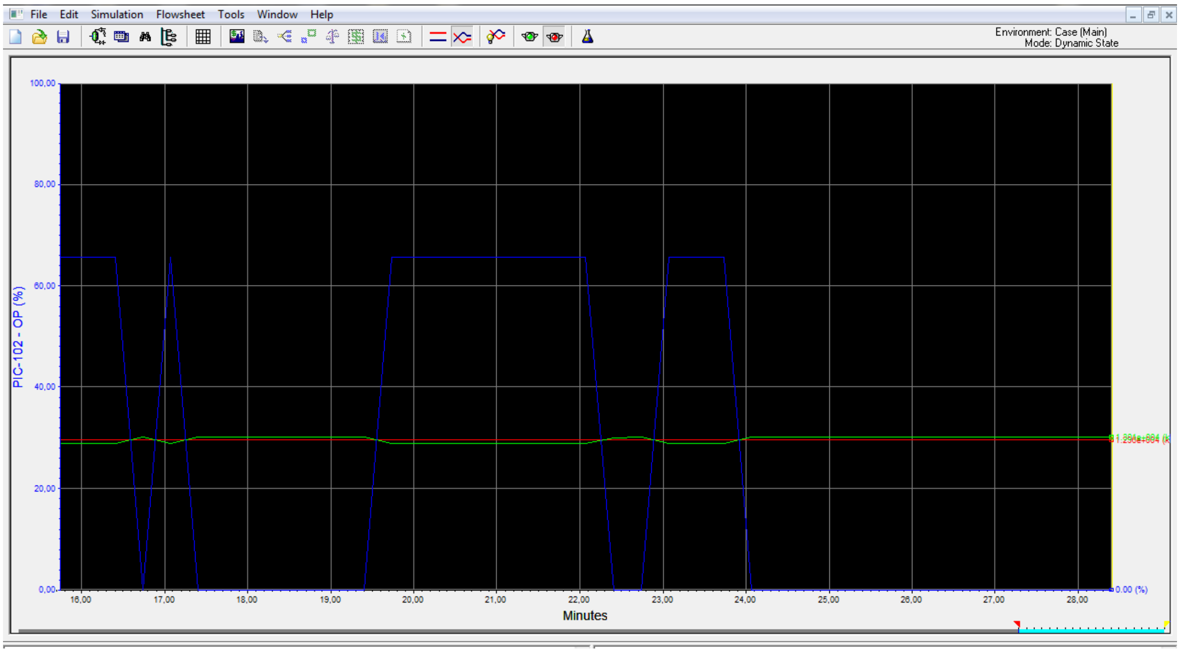

Figure 65: inlet pressure and its control

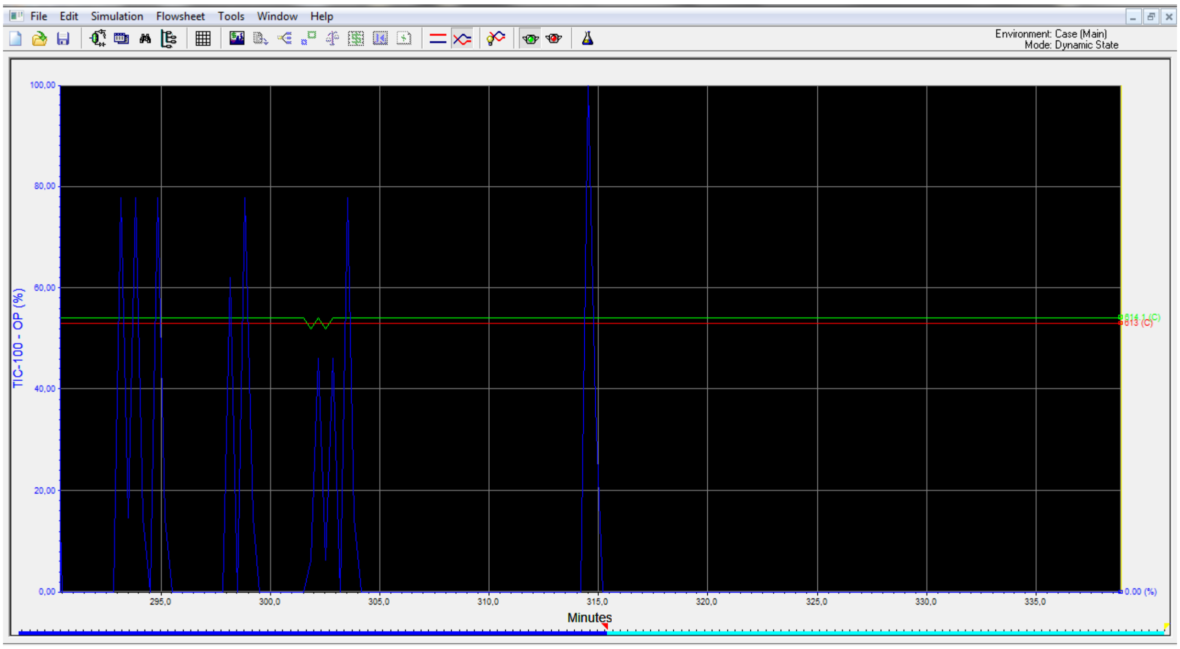

Figure 66: reactor temperature control (slow dynamics) and its response after the disturbance

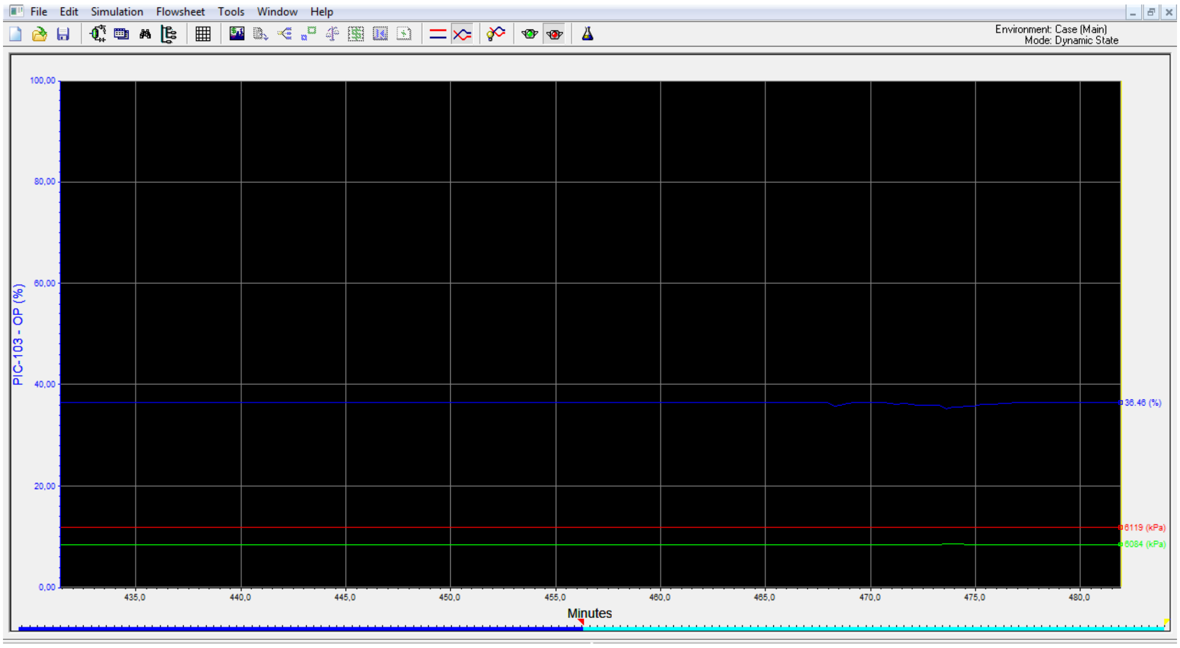

Figure 67: absorption column pressure control and the disturbance effect

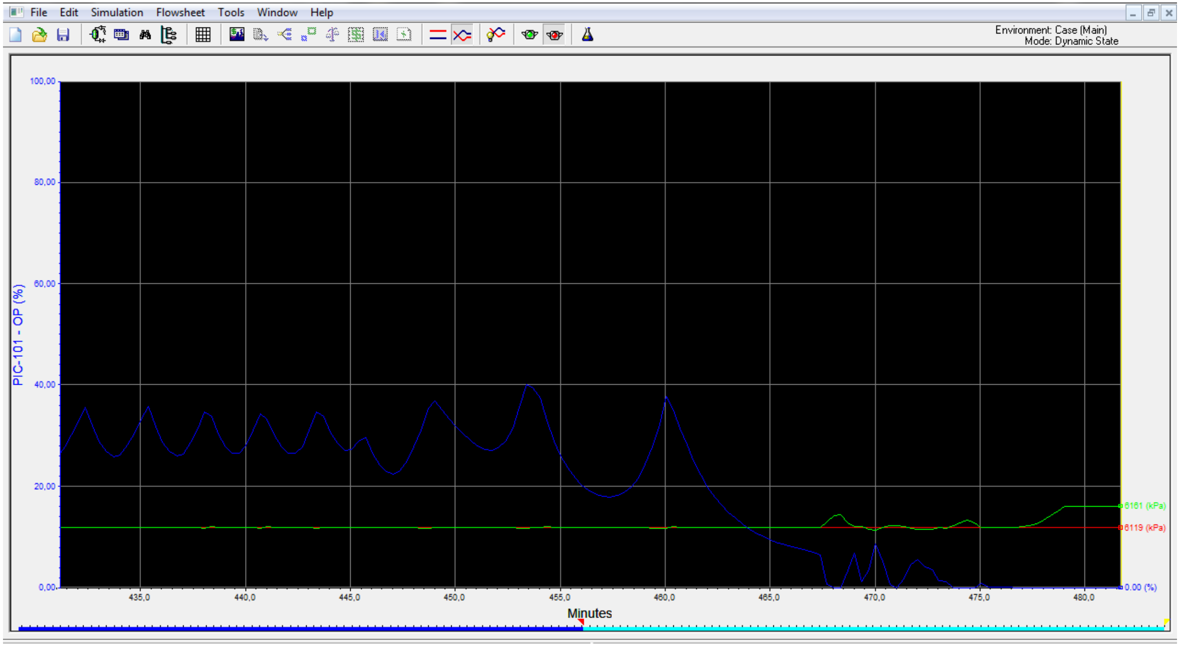

Figure 68: absorption column pressure control with autotuning results

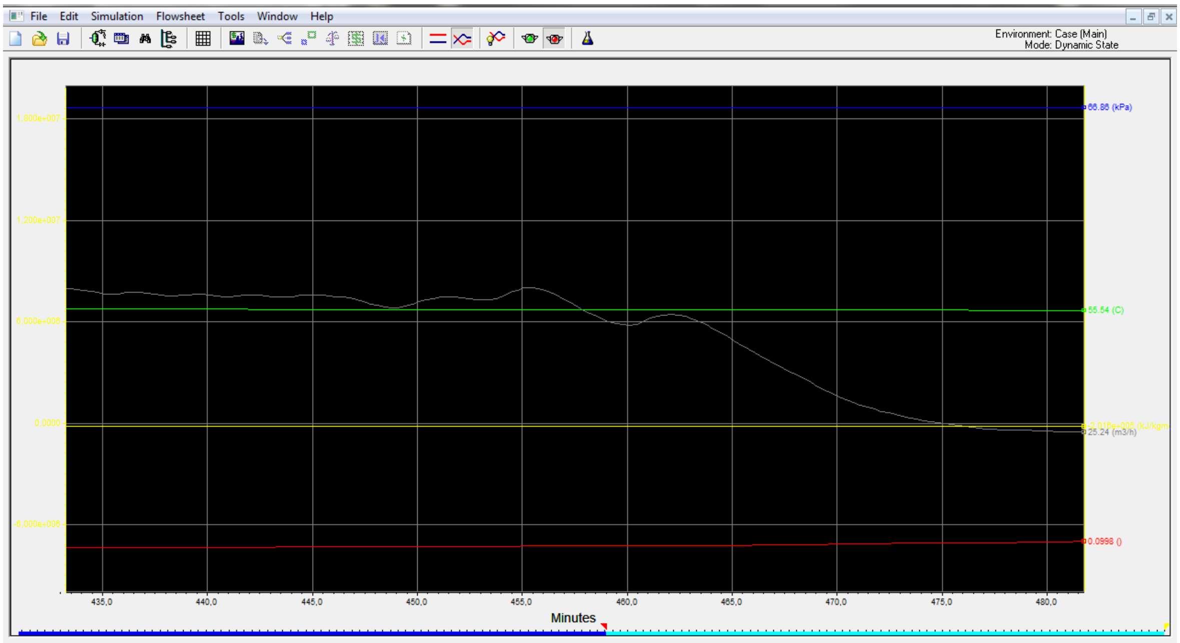

Figure 69: desulfurized conditions

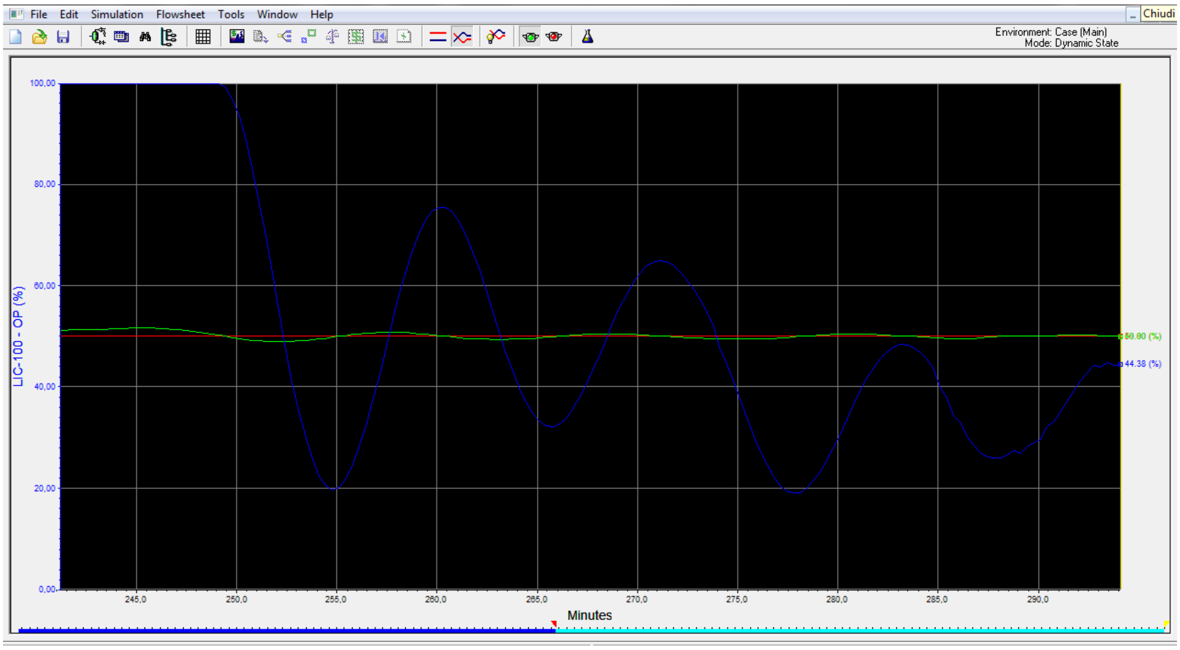

Figure 70: level control of the desulfurized charge, with the result after the disturb in feed flood

As it is possible to observe the system is stopped drifting away from its optimal point. Values are kept almost constant, even if the control it could seem too simple. With some shrewdness there is the possibility to imply a better control maybe using a autotuning controller. After disturbances in composition too, it is possible to note how the system is pointing to its normal working point.

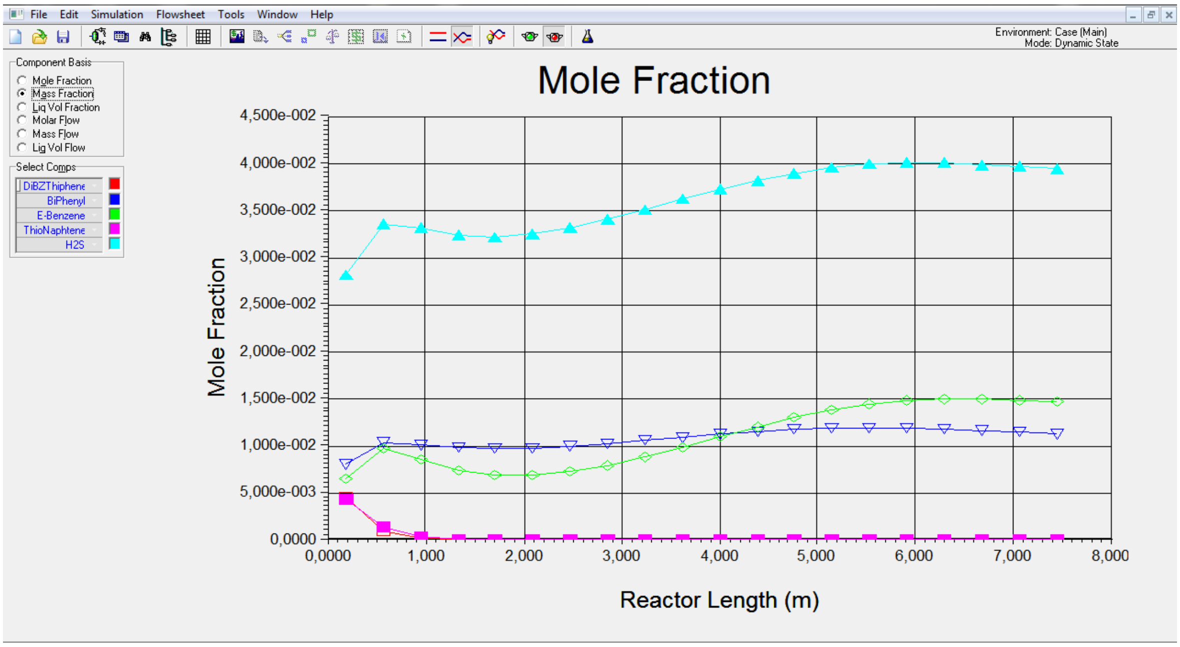

Figure 71: composition after disturb in total sulfur content

Chapter 6

Conclusions and future perspectives

"The end of this chapter"
Sonata Arctica

6.1 CONCLUSIONS

At the end of this procedure it is now time to draw the conclusions and trace a general guideline for next future applications. In this sense it is important to have found it possible to control in a systematic manner a complex process plant, like a HDS unit; the systematic of all the method is however based on the economics, and in this way it is important understand how correct ideas and assumptions are able to grant good result in accordance with the reality.

During path, ideally recognized in the step-by-step procedure and realistic meant as passage through the Northern Lands, it has been possible to me understand how simplicity and accuracy can be the best companions for simulations. All this procedure, even if young and really complete, found its basis in an incredibly long gestation and its hermeneutics has been responsible of a great innovation in chemical engineering plantwide control. Through the overall project, assumptions have been done and suppositions have found reasons to be introduced, in order to improve the feasibility of the system without, at the same time, losing in reliability for results obtained.

In this project the procedure above mentioned has found its reason to be applied: even if, it is important to show, this systematic approach has been seldom applied on chemical plant (instead of single equipments); positive results have been obtained.

What has been done in this project has been to face a real problem with very modern and felt close implications, like environmental pollution, and working on a system set up to solve it partially (we have to remember that refineries at standing conditions are not able to overcome 15 [ppm wt/wt] sulfur content limit, in this case we can reach the level of 70 [ppm wt/wt], and so this system is reliable if in parallel there are downstream processes to accomplish the previous request); trying to find its optimal way of work without basing the control operation on the classical way to operate this, but on the basis of economics building a robust and simple control structure. The model have been manipulated, transformed and the tested. There did not have been a unique project: a lot of tries have been studied with different kinetics. After the choice of the model it has been time for optimization: this part of the project has been developed and performed by Matlab®. While the writing (meant literally) of the program has been simple, the different optimization's runs have been long and not always correct: there have been tested some cost functions (changing the different contributes given by the equipment and taking into consideration different DOFs) in order to give reason to the really important contributes in this process, trying to find the real key parameters able to influence it either positively or negatively.

After the optimization there has been the necessity to find the self-optimizing variables, key role in this procedure, and with the "Nullspace method" it has been possible to verify what variables have a concrete impact on process' operation. Results have given different possibilities to apply a control structure, and so the easiest one has been chosen. No doubt there could be more and significantly different choice, but the structure at the basis had to be controlled in this way.

As mentioned before the project has been "subjected to" different simplifications and assumptions those have made possible the outcome of this project. The most important simplifications, in this sense, have dealt with the kinetics and the reaction involved. So it has been possible to work with a realistic model with such a fastness that could work in acceptable time. The kinetics itself has demonstrated to be in accordance with practical results; but it is right to say that, in this sense, all these simplifications can be removed introducing some more complex models both for kinetics and for the simulation of the catalyst's particle (omitted in this case because the difference in the "order of magnitude" of the process scale; all of this would be result in a perfect model with at the same time really heavy calculation because this is a typical scale up problem: catalyst dimensions vs. plant extension). So a better simulation could introduce longer time to optimize the system which could be now described more accurately with the problem to have more heavier calculation load. Following the same guideline, for what concerns the reaction path involved, for kinetics a single rate has been selected in order to have rapidity and promptness of the system simulated while for typical sulfur compounds it has been chosen the main two present in a common gas oil feedstock (thionaphtene and dibenzothiophene).

On the same direction we can find the considerations about plant's control typology: PID vs. MPC or RTO. The choice has been made on the previous one because there were the right conditions to be applied and then because a receiving horizon approach could result impossible cause the too slowness of the system itself.

There no doubt that an improving effort on calculations (meant as power to solve them) and maybe a more detailed model with other assumptions on some small shrewdness, that is why a case study parallel with a real plant could be very useful, can solve this problem and grant more precision and more reliability.

Standing on calculations it is worth to note that great problems are dealing with the optimizer used to solve the constrained problem associated with the control procedure: it has been demonstrated less robust than it was thought. In this sense it could be useful to introduce a more robust one and then trying to find a more detailed optima, even if the result obtained in this work are not affected, because we have to consider that the optimum is always relative in the condition we are working. It is worth to note that it would be better to have an optimum as nearest as possible to the absolute one (i.e. find one solution more stable and defined with more accuracy the region of active constraints and their actual values); a try has been done in order to verify if some changes there could be obtained, and in this sense it has been selected another criterion of optimization (i.e. the algorithm): the switch has been done between `interior point` and `active-set`, both of `fmincon`. The result of this choice it has been an increasing velocity per each iteration step to the optimal solution (the "main" difference between the two algorithms is the step used to find the optimum), with a small precision on the nature of the optimum itself (even if a huge number of iteration admitted, it is reached without a real solution found).

Then during the analysis of this unit it has been possible to suppose some problems tied to bottleneck conditions and in this sense this is been thought to be when we overpass the sulfur content limits posed by environmental laws. The model has overcome this point with an increasing temperature that for the kinetics is feasible, but that in reality could be useful to verify specially in parallel with a real process data.

Anyway what it is important to note till the first moments the extreme simplicity and reliability of the procedure described in the previous chapters and followed during all this analysis of a process. The results highlighted during this analysis, beyond the control itself, are the schematization and the linearity of the way to control a plant: we started with a procedure and we end with a method. It is a ductile system and in this sense very accessible.

It is important to understand that this is and remain a complex system in which better results can be achieved with time and maybe implementing different strategies of control. In this sense it has to be though that self-optimizing control has shown its best results in controlling single equipment of a process plant and single unit operation. Some optimal results have been proved to be reached when the control is applied to single processes and with more data available[78].

Moreover it is worth to note that this particular approach directed to plantwide control is today too, subject of lot of publications both in chemical engineering papers[79] and innovative control strategies of MSc Thesis and PhD thesis too. As example we can consider that in this date, while I'm concluding this project Springer is receiving overview for other publications. There no reason to doubt that this could be the next way to approach to the chemical process plant.

If we consider that before the last two decades the control was made with some thumb rules, this systematic procedure is able to improve results that have been obtained previously and understand better the real effect and importance of a clear and methodic approach. That means in the very next future the possibility to increase precision and introduce new strategies of control will be real and in this sense a kind of control philosophy could be introduced as new way to think and to approach to problems.

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