Investigation of variations in hydrogenation using Multivariate data analysis

Master Thesis
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Abstract

In the mid 1990´s Sweden legislated that the aromatic content in diesel may not exceed 5.0 vol %. To meet this new environmental legislation Preemraff (former Scanraff) constructed a desulphur- and dearomatization plant also called SynSat. Thru the years SynSat have had problems maintaining a constant feed flow whilst still keeping the aromatic concentration on spec. The goal is to find variables that affect the variations in production rate and give suggestions on how to maximize the production rate. The scope for this master thesis has been to identify possible causes to the problem stated above with the help of multivariate statistical analysis. The datasets has been taken from testruns and from logged process data. The MVDA analysis together with physical and experimental data points out three possible causes for the variations; hydrogen purity, feed composition and lighter carbons diluting the hydrogen gas around the catalyst particle. The study has also indicated that there are no equilibrium limitations.

The results show that more has to be learned about the feed composition in order to make accurate conclusions about the variations.

Theory

Process description

Heterogeneous desulphurisation and dearomatisation are the main purposes for SynSat. Below is a schematic figure of the process with important flows, temperatures and pressures.
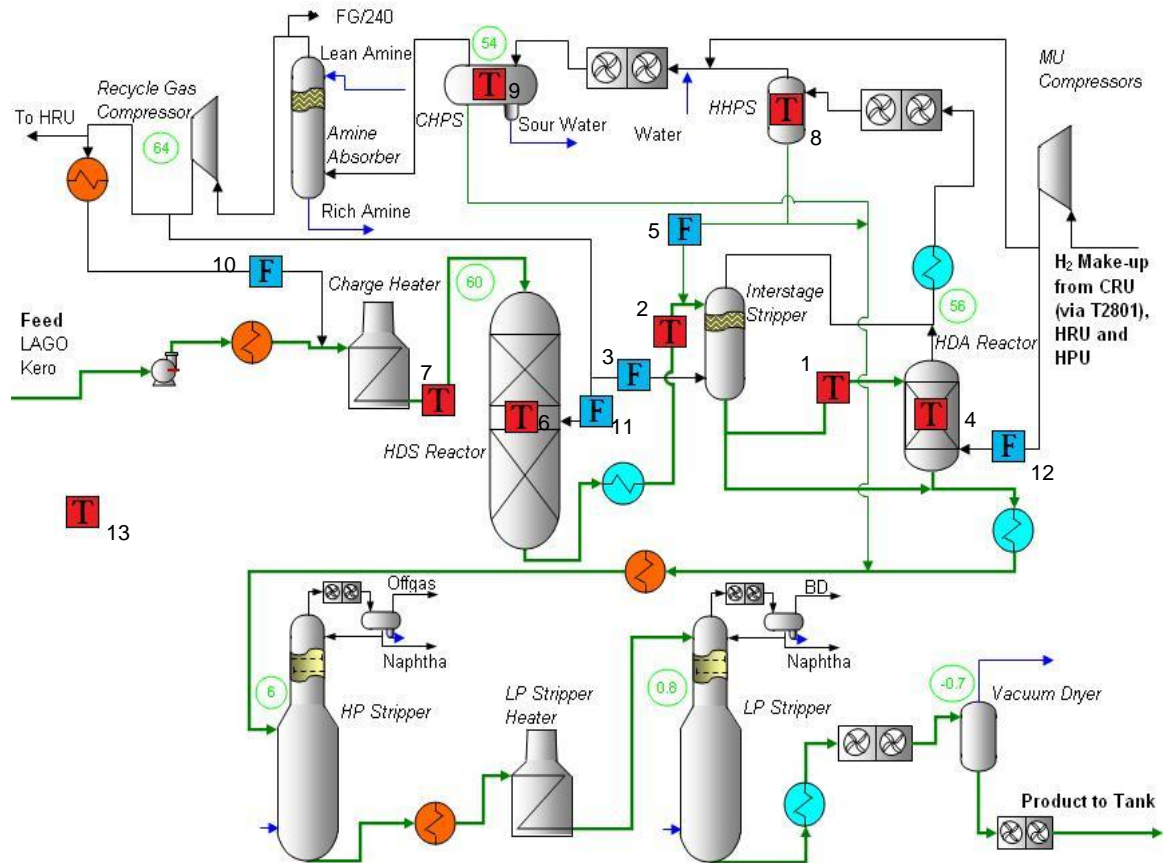
Fig 1. PFD of SynSat

1. Temperature in to the Hydrodearomatization reactor (HDA)
2. Temperature in the Interstage Stripper
3. Hydrogen flow to the Interstage Stripper
4. WABT HDA reactor
5. Flow from the HHPS to the Interstage Stripper
6. WABT HDS reactor
7. Temperature in to the Hydrodesulfurization reactor (HDS)
8. Temperature in the HHPS
9. Temperature in the CHPS
10. Hydrogen flow to the heater
11. Quenchflow
12. Hydrogen flow to the HDA reactor
13. Outside temperature

It's possible to divide the system into three parts; the reactor section, the stripper section and the hydrogen separation section.

1. **The reactor section** consists of the following equipment
   - Charge Heater
   - HDS Reactor
   - Interstage Stripper
   - HDA Reactor

2. **The stripper section** consists of the following equipment
   - High Pressure Stripper
   - Low Pressure Stripper Heater
   - Low Pressure Stripper
   - Vacuum Dryer

3. **The hydrogen separation section** consists of the following equipment
   - Hot High Pressure Separator
   - Cold High Pressure Separator
   - Water wash
   - Amine absorber

Besides these sections there are heat exchangers and other utility and also 2 compressors which task is to compress hydrogen gas.

Correlation problem

Flows and temperatures are often highly correlated inside SynSat. The most important correlations are shown in the table below. Be observant to the red feedback line since this explains the most difficult obstacle in statistical analysis of this system. The red line symbolize the process operator who reduces the feed when the aromatic concentration in the product exceeds 5 vol %. Looking at the picture it is obvious that this will have a lot of side effects.
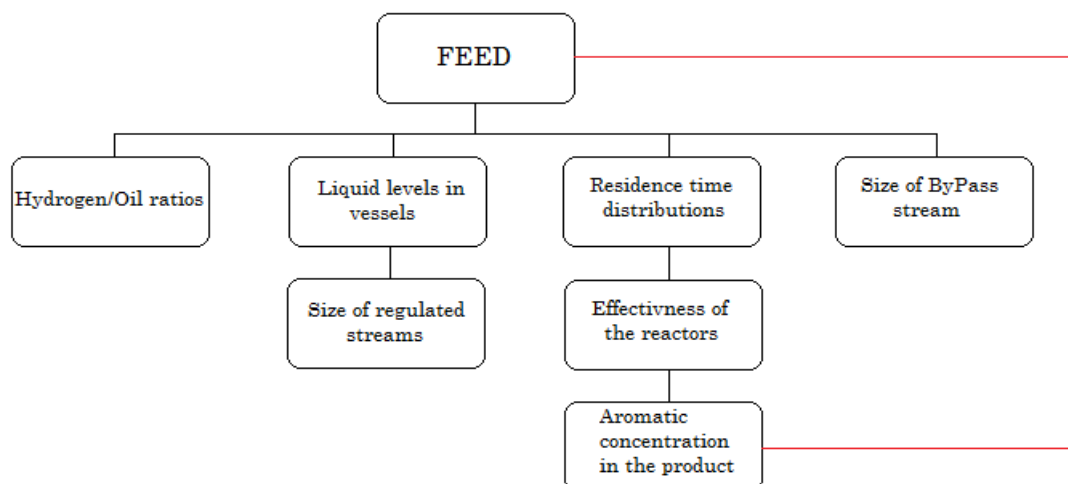
Fig. 2. Correlation pathways

Temperature can also be an indicator of good turnover, since the reaction is exothermic. Below, the figure highlights the most important correlations.

High hydrogen purity

Better reaction in HDS reactor

Higher temperature in HDS reactor (WABT HDS)

High Temperature in HDA reactor

High Temperature in HHPS

High Temperature in CHPS

Higher Temperature in Interstage Stripper

Fig 3. Coupling of variables

Known sources of errors

The process has a major problem area that can, at least partially explain the difficulties in maintaining the specified aromatic concentration in the product.

- The stream marked "Bypass Problem" is a well known source of error as it contains approx. 11 vol. % aromatics and it bypasses the HDA reactor. A quick estimation shows that this str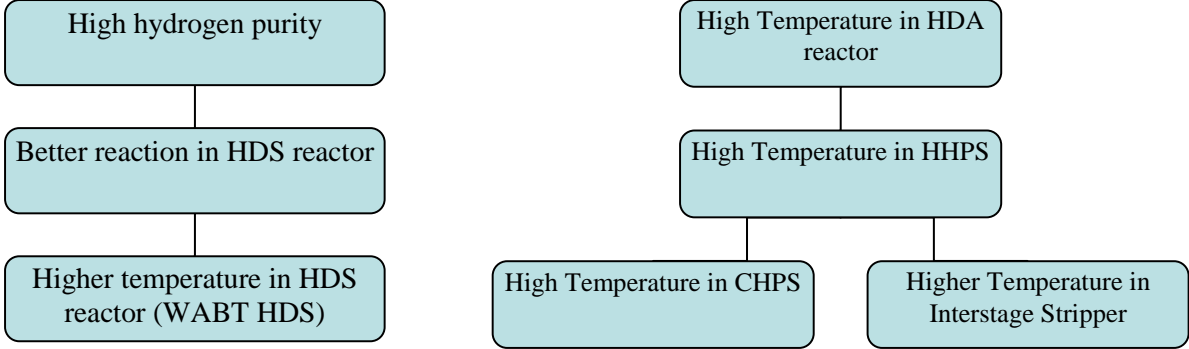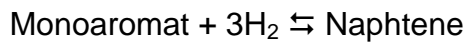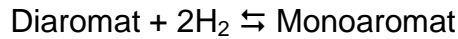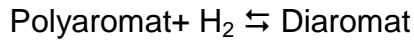eam could significantly increase the aromatic content in the product. Preem has decided to reroute this stream to the MHC plant, constructions are underway.

- Equilibrium is not achieved in the HDA reactor since the aromatic content in the product are totally dependent on the feed flowrate. Knowing this, the need for equilibrium data was evident. Criterion made some testruns in their pilot plant of the HDS reactor with both SynCat-50 and SynCat-40. Results from these pilot runs are explained later on.

- Experiences has shown that so called low sulphur oils (LS) which almost exclusively is oil from the North Sea is harder to dearomatize then so called High Sulphur oil (HS).

- The crude oils Nigeria Forcados and Troll is infamous for their reluctance to be dearomatized.

- There are some thoughts and indications that lighter carbons leaves the Interstage Stripper in the gas stream which could affect the purity of the hydrogen gas. It is also possible that lighter aromatics also go over top and end up in the bypass stream.

- The same problem as mentioned above can also occur in the HDA reactor.

Kinetic theory

Reactions

Aromatic species can be divided into three groups, polyaromatics, diaromatics and monoaromatics. The prefixes poly, di and mono informs about the numbers of aromatic rings in the specie, Poly beeing used when lumping together tri and higher order aromats in one name. The reactions for hydrogenation are exothermic and are listed below.

$$Polyaromat + H_2 \leftrightharpoons Diaromat$$

$$Diaromat + 2H_2 \leftrightharpoons Monoaromat$$

$$Monoaromat + 3H_2 \leftrightharpoons Naphtene$$

Analysis has shown that the feed to SynSat contains aromats of different orders (mono, di, tri etc.). Hydrogenation of polyaromats down to monoaromats isn't a problem for the process since the product almost only contains monoaromats.

The reactions are reversible and are limited by equilibrium constraints. Since the reactions are exothermic it is preferred to keep a temperature where the overall reaction rate is maximized. This is easier done when only dealing with one specie, diesel oil consists of a wide range of aromatic species.

Catalyst

The HDS reactor contains the SynCat-50 catalyst which is a NiMo catalyst on an aluminium-molybdenum oxide support. Besides removing sulphur from the diesel it accounts for a significant part of the dearomatization, approximately 30 vol% aromats are saturated in the HDS reactor.

The catalyst in the HDA reactor is a bimetallic PtPd catalyst on an aluminium- boron oxide support with the trade name SynCat-40. Using boron oxide as support has its advantages which will be briefly discussed.

Since the SynCat catalysts are commercial catalysts it is not possible to retrieve any detailed information of their compositions. Literature also shows that the precise composition of a catalyst is of great importance for its performance under given conditions. Due to this the following chapter gives a comprehensive explanation of phenomena that can play an important role for the problem at hand.

Deactivation

Hydrogenation of diesel oil is always interconnected with catalyst deactivation, or poisoning. Poisons especially relevant for hydrogenation catalysts are listed below[1]

- Sulphur
- Potassium
- Nickel
- Vanadium
- Arsenic
- Zinc
- Quicksilver
- Halides
- Pb
- Ammonium (NH_3)
- C_2H_2

These species adsorb more strongly to the catalyst surface, thereby competing with the reactants.

Another cause for activity loss is coke and carbon formation on the catalyst. Hydrocarbons can condense and chemisorb to the catalyst surface, blocking the metal sites for the reactants.

Aspects of the supporting material

Catalysts of noble metals have an increased sulphur tolerance if supported on an acidic material.[2] The acidity and amount of acidic sites affects undesired hydrocracking and coke formation. High acidity increase hydrocracking but it is also desired to have some acidity to protect the catalyst from sulphur poisoning. Research has shown that it is desirable to have many moderate acidic sites to get a compromise between the two phenomena.

According to literature[3] the noble metals forms clusters on the catalyst surface which becomes electron deficient and weakens the sulphur-metal bond, thereof increasing the sulphur tolerance for the catalyst.

In the production guidelines there is a limit for the total sulphur content of 25 ppm for the HDA reactor. Consulting weekly lab data for a year back the mean concentration of sulphur in the inlet to the HDA reactor is 2.1 ppm. Knowing this, sulphur poisoning isn't a plausible cause for the problem since the sulphur concentration is so low.

[1] . Bartholomew. C.H, Farrauto. R.J, *Fund. Ind. Catal. Proc.* (page 263), Wiley & Sons
[2] . Yasuda H et.al, *Appl. Catal.* 185 page 199-201 (1999)
[3] . Fujikawa T et.al, *Sekiyu Gukkasishi* 42(4) page 271-274 (1999)

Aspects of the noble metals

Different concentrations between the two noble metals Platinum and Palladium gives the catalyst different dearomatization capabilites. Experiments done by Fujikawa and Chang[4] shows a linear relationship between concentration of palladium on the catalyst and dearomatization, an increase in palladium will increase the dearomatization.

Comparison between an Al_2O_3 and an Al_2O_3-B_2O_3 catalyst with the same concentrations of noble metals shows a significant better dearomatization for the Al_2O_3-B_2O_3 catalyst.

Different reaction rate for different catalysts

As mentioned earlier, the two reactors have two different types of catalysts. The HDS reactor consists of a so called sulphide catalyst and the HDA reactor of a so called noble metal catalyst. According to work gathered and analysed by Stanislaus and Cooper[5] these two types of catalysts has completely contrarily rate constants for the same specie. Below, the relative reaction rates are visualized for the HDS and HDA reactors.

HDS reactor: Xylen > Toluen > Bensen

HDA reactor: Bensen > Toluen > Xylen

Due to this, if the efficiency of the HDS reactor decreases the HDA reactor will have problems converting the additional concentration of aromats.

[4] . Chang et.al, *Ind.Eng.Chem.Res*, 34 4285 (1995)

[5] . Stanislaus, A., Cooper, B.H., *Catal. Rew. Sci. Eng.,* 36, 87(1994)

Equilibrium

Equilibrium is not achieved in the HDA reactor since the aromatic content in the product are totally dependent on the feed flowrate. The variable used to abbriviate the ratio between feed and catalytic volume is LHSV[6]. The LHSV for SynSat usually lies between *"confidential"* and *"confidential"*.

One should also remember that the equilibrium is not the only limitation; the hydrogenation is also limited by the reaction kinetics. Since the kinetics is favoured by higher temperatures the reaction rate has its optimum just below the equilibrium temperature, see fig below. It is important to remember that the kinetic parameters are different for different catalysts.
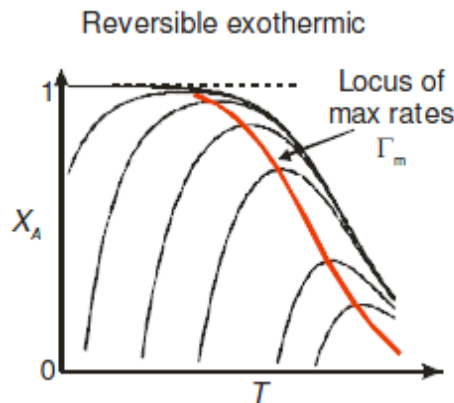

Fig 4. Reversible exothermic reaction

Due to confidential reasons Criterion can´t release the kinetic parameters or the rate constants which makes modelling of the reactor difficult. It would be possible to fit a polynomial to data obtained from testruns where only the temperature is altered. Unfortunately, it is not possible to perform a testrun where only the temperature is altered without affecting other variables which in turn affects the HDA or HDS reactor.

Due to this problem Criterion was very helpful and used data from the process and ran it through their computer model of the HDS reactor.

They also presented a temperature at which they believe the aromatic saturation rate begins decreasing for the SC-40 (HDA reactor), this temperature is here on abbreviated T_{crit}. Equilibrium data is hard to retrieve since not many experiments are done with an MK I matrix. Therefore we are limited to equilibrium charts for hydrogenation of aromats without any additional coal chains.

Since its not clear which exact species the MK I contains it's also hard to make an estimate based on interpolation out of different species equilibrium data.

Criterion made a feed/product specification study a couple of years ago. The result can be viewed in fig 5. Unfortunately the result only shows the concentration of species with the same numbers of carbon atoms. The result doesn't answer the question about the structures of the species.

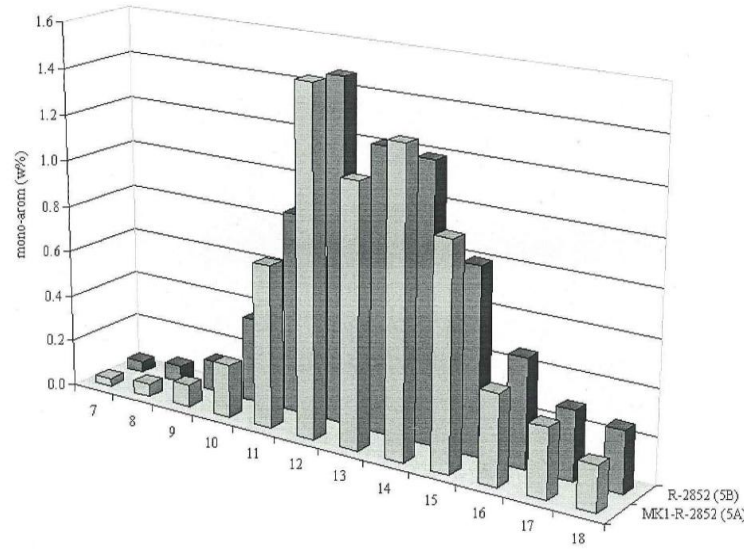[6] . LHSV=Feedflow/Catalytic volume [1/h]

Fig 5. Carbon numbers for monoaromats in the HDA reactor outflow..

Since the reaction is exothermic heat is generated throughout the reactor, therefore the highest temperature can be found in the bottom of the reactor. Fig 6 shows that the bottom of the reactor has a temperature higher than T_{crit}. In this region the hydrogenation rate is very low.
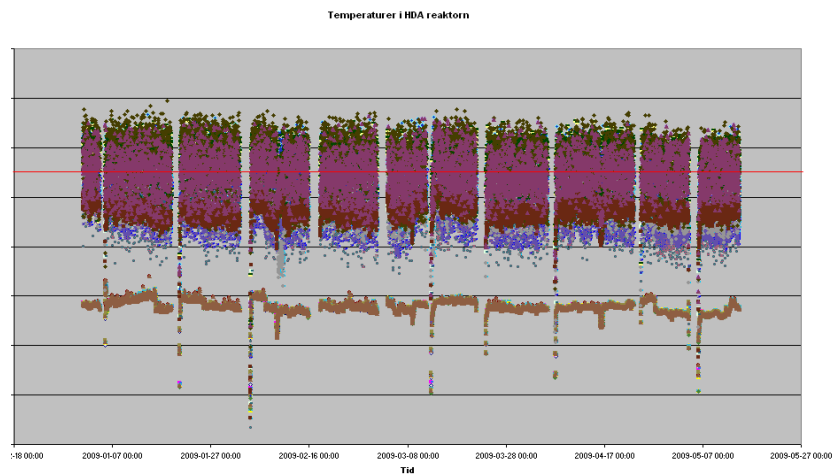

Fig 6. Temperature distribution over the HDA reactor from Dec-08 to May-09 (the red line indicates T_{crit})

Experience says that Nigeria Forcados and Troll are hard to dearomatize. After a quick inspection of the assays the concentration of naphthenes in the two oils where considered remarkable high in comparison with other oil assays. Fig. 7 shows the difference in aromatic and naphthenic concentrations for Ural and Nigerian Forcados.
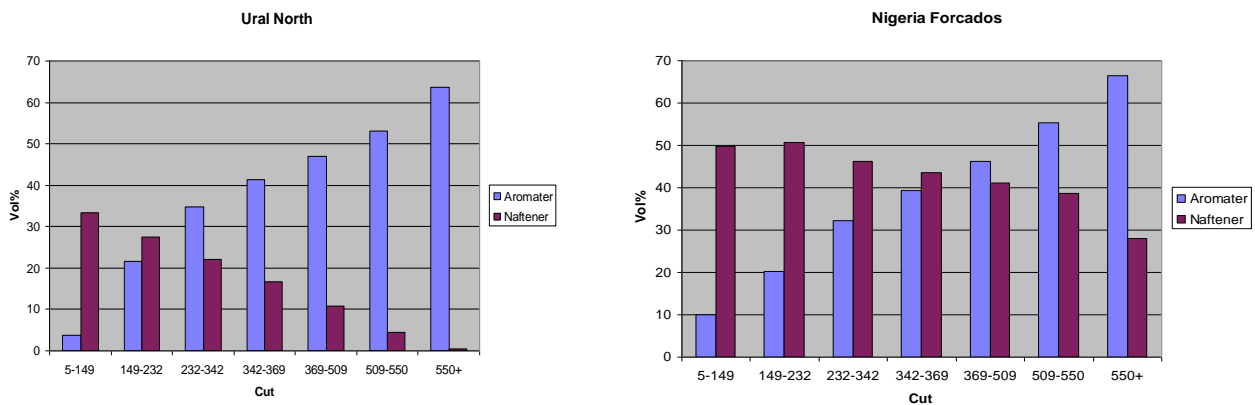
Fig 7 Aromatic and naphthenic concentrations for different cuts of Ural North and Nigeria Forcados.

As mentioned earlier the hydrogenation of aromats is an equilibrium limited reaction between an aromat and its corresponding naphtene. It is not likely that the increased naphtenic concentration will affect the thermodynamic equilibrium. However, if the naphtenes has low boiling points it is possible that they will dilute the gas phase in the reactor causing the reaction to slow down.

Multivariate Data Analysis

Theory

This chapter will briefly explain two types of multivariate data analysis, *principal component analysis* (PCA) and *partial least square* (PLS). SIMCA P+ 12 from Umetrics where used for the data analysis. The following MVDA analysis is made solely using the PLS technique.

PCA

Principal component analysis finds the largest variance in the dataset and creates a pseudo variable, explaining this variance. The pseudo variable is abbreviated principal component 1 (PC1). PCA reduces the numbers of variables (dimensions) in the dataset, producing a more comprehensive representation of the dataset. Below is brief crash course in PCA focusing on giving an understanding of how SIMCA reduces the variables and try to find which variables that explains most of the variance.

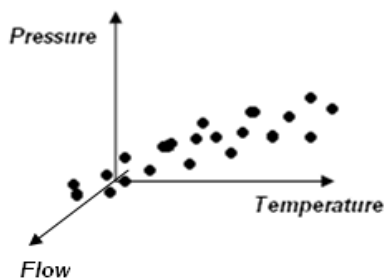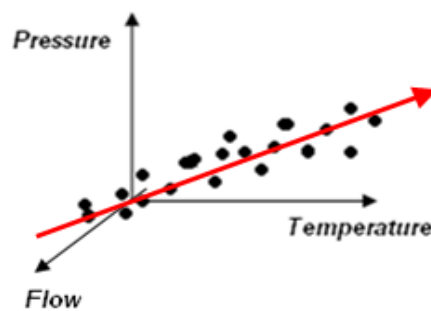Fig 8. Observations   Fig 9. Principal Component 1

Thereafter the second principal component is added in a 90 degree angel from the first component, trying to explain the rest of the variance in the data.
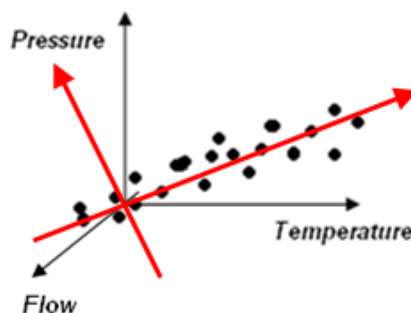
Fig 10. Principal component 1 & 2

The two components form a separate two dimensional plane which can be seen as a piece of paper. The score plot in SIMCA is exact this piece of paper, e.g. fig 13.

However, the user needs to know which variables that explain most of the variance in the dataset. By measuring the angles between each variable and each component, each variables contribution to the variance can be determined.
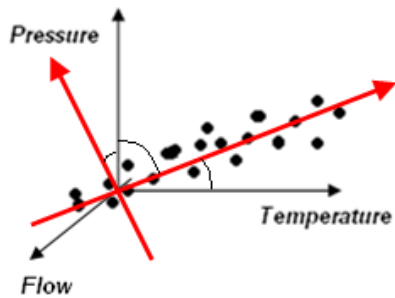

Fig 11. Loading values

The smaller the angel between a component and a variable the larger influence this variable has on the component, i.e. the variance.

Example: If the first component is almost in line with one of the variable axes, lets say Temperature. Then temperature explains almost all variance in the dataset.

Using the angels, SIMCA presents the variable contribution on a so called loading plot, e.g. see Fig 14.

PLS

PLS as many similarities with PCA, for example the first component are calculated to explain the largest variance in the dataset but also to give a good correlation with the Y vector. The Y vector contains the response values, which in this case are aromatic concentration in the product. However, the score plot is calculated in a somewhat different way. The score values is the distance between an observation and a principal component, see fig 12.
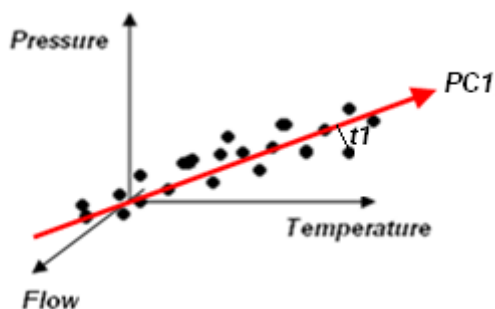

Fig 12. Score value, t1.

During the first week after processing a lot of data it stood clear that the plant is overregulated. Since the aromatic concentration in the product answers directly to the feed flowrate, the process operator controls a runaway aromatic concentration by decreasing the feed flow.

Fortunately, logged process- and lab data where available from an earlier series of testruns. In these testruns the feed flowrate and the quality of the feed where kept constant. This set of data, from here called "Testruns 2005" is a result of a thorough investigation of how certain parameters affect the dearomatisationrate (Appendix I).

Results obtained from the analysis of "Testruns 2005" where then cross examined with another data set called "High and Low" (Appendix I). "High and Low" consists of logged process data divided in an equal amount of high and low aromatic content in the product feed.

Online analysis where proved impossible due to no variance in the parameters and the fact that the system is overregulated.

Pre-Processing

Process data are sampled from Info Plus which is the online process surveillances software. Data collected from the process sensors are being stored in three months in its whole, after this a fraction of the measure points are deleted. An unfortunately effect of this is that large variances in parameters are being flattened.

Analysis and Validation

SIMCA scaled the data sets by default with unitvariance scaling.

Datasets

- **Testruns 2005**

  In 2005 an investigation was done trying to determine which parameters that affect the SynSat plant. Some conclusions could be done but only one parameter where tested at a time at specific testruns over a three month period which made it hard to see any correlations. SIMCA could however see some significant parameters that weren't obvious just looking at the raw data.

- **High and Low 1**

  Due to the fact that the plant is overregulated a dataset containing process conditions when the concentration of aromats in the product stream was either high or low where created. By doing this all dynamics of the system are being lost, but due to the problem stated above it is impossible to catch the dynamics whilst the system is regulated. This set of data has the largest variation in response variable (aromatic concentration).

- **High and Low 2**

  Is based on the same template as its predecessor but its variation in response variable is more moderate and representative for the normal operation.

Results from "Testruns 2005"

Relevant information such as additional plots and datasets can be found in Appendix 1.
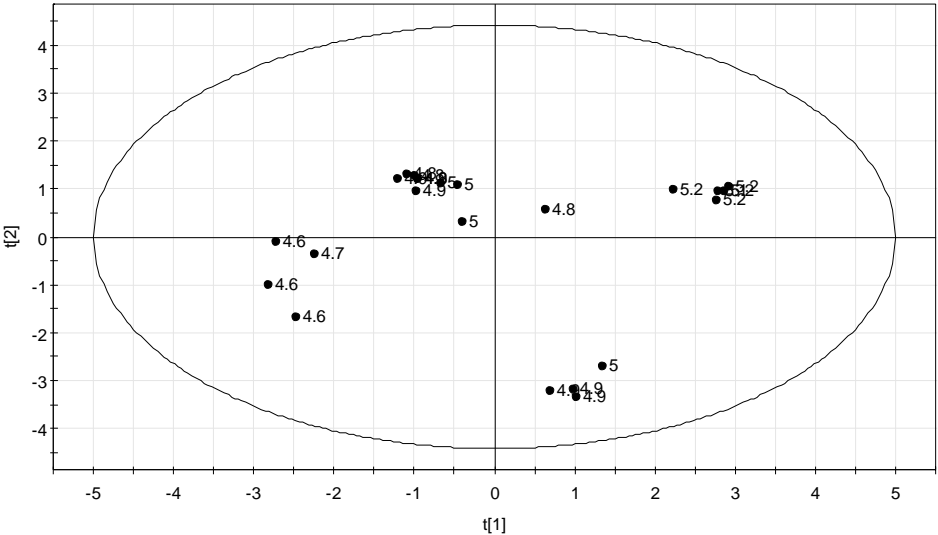
Fig 13. Score plot for the two components with aromatic concentration as labels. Aromatic concentrations above 4.8 are considered as unacceptable.

The score plot shows that it is favourable to run the process in the southwest quadrant and unfavourable in the east part of the plot. It is very important to remember that these observations come from the same testrun, namely the one performed 2005-10-28.

Fig 14. Loading plot with the Y variable (Aromatic concentration) marked with red.

The loading plot shows that the following parameters have a large influence on the model (Note that the table only contains variables that directly can be adjusted.):

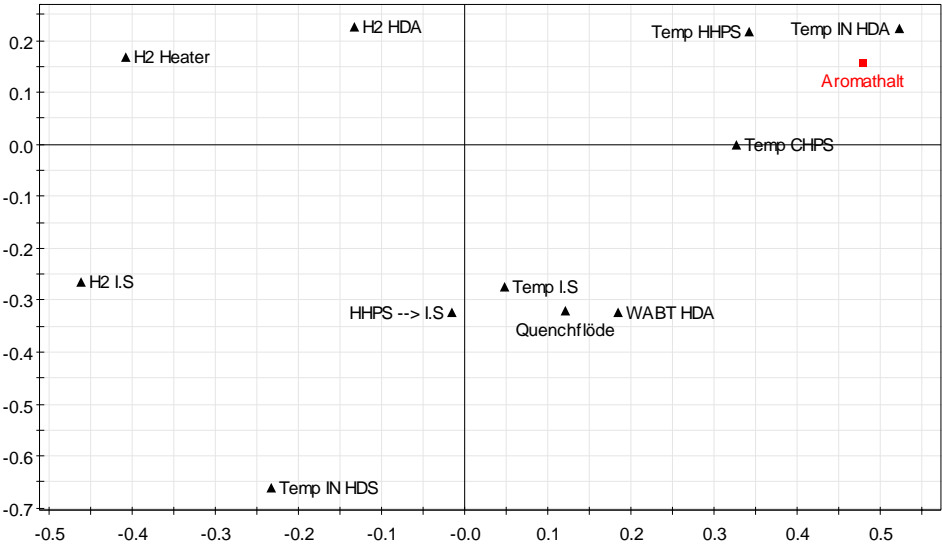| 1. Temperature Into HDA reactor	"Minimize"
2. Temperature Into HDS reactor	"Maximize"
3. Hydrogen gas flow to Interstage Stripper	"Maximize"
4. Hydrogen gas flow to heater	"Maximize"

This reasoning can be clearer by comparing aromatic concentrations below 4.8 with concentrations above. Fig 15. shows the difference in variable settings between the groups of observations to the right with the observations in the southwest quadrant.

The temperatures in HHPS and CHPS have a larger effect on the model then the temperature in the inlet to the HDS reactor. However, these variables are coupled with the temperature in the HDA reactor (see PFD), so a low temperature in the HDA inlet would give a low temperature in the HHPS and consequently CHPS. These variables are still part of the dataset because the temperatures could still, independently affect the response, see "Known source of error".
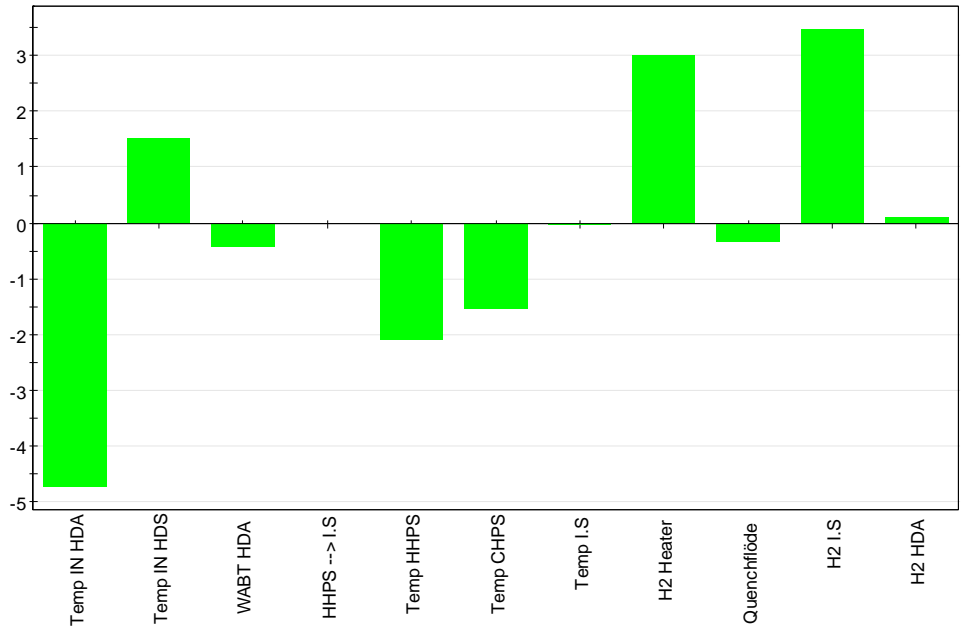
Fig 15. Contribution plot showing how to minimize Y.

Largest difference between the two groups is in the inlet temperature to the HDA reactor. If this is a direct or a secondary affect isn't explained by the model. Since this results goes hand in hand with the limited equilibrium data obtained from Criterion. Chances are that the temperature dependent is a direct affect.

Hydrogen gas is one of the reactants and a a large supply of hydrogen will be favourable for the dearomatization.
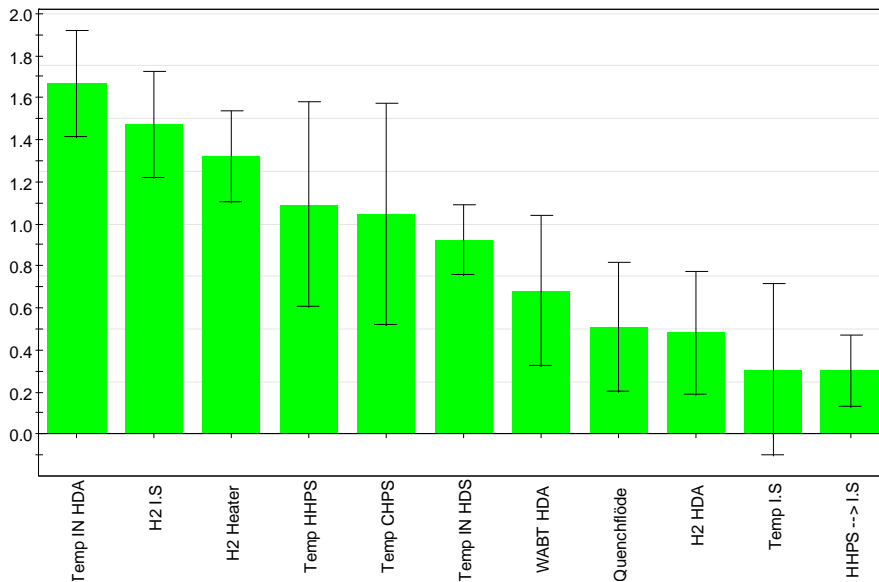

Fig 16. Variable Importance of each variable.

Note that the variable Temp I.S is still a part of the analysis despite its lower limit standard deviation is less than zero. Models where this variable is excluded has been built but proven less reliable when validated.

Results from "High and Low 1"

Relevant information such as additional plots and datasets can be found in Appendix 1.

High and Low's dataset is based on very high and very low values on the aromatic concentration in the product. Two datasets where created for the reason that only very high values of aromatic content could be found right after a change of catalyst. The new catalyst was however very effective and the dearomatization (Feed) where unusual high the first six months. The second dataset was built with the same low observations but with high observations not taken within 6 months after the catalyst change. The two models will be named "High and Low 1" and "High and Low 2".

Fig 17. Score plot for the two components with aromatic concentration as labels. Aromatic concentrations above 4.8 are considered as unacceptable.

According to the score plot it is favourable to run the process in the western quadrant whilst it is less favourable at the east side.
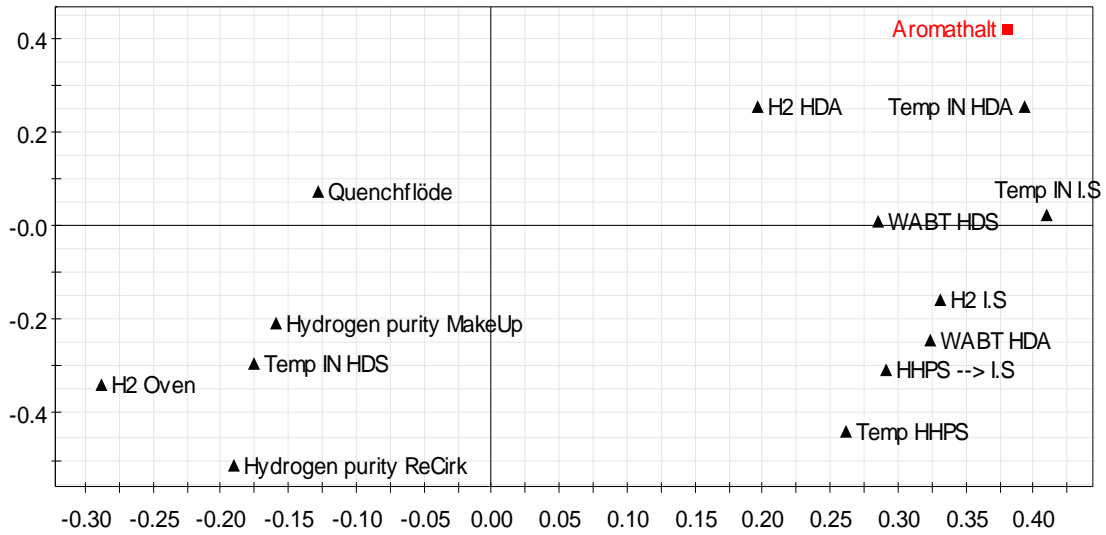
Fig 18. Loading plot with the Y variable (Aromatic concentration) marked with red.

Comparing observations to the east with observations in the west quadrant generates the following plot.
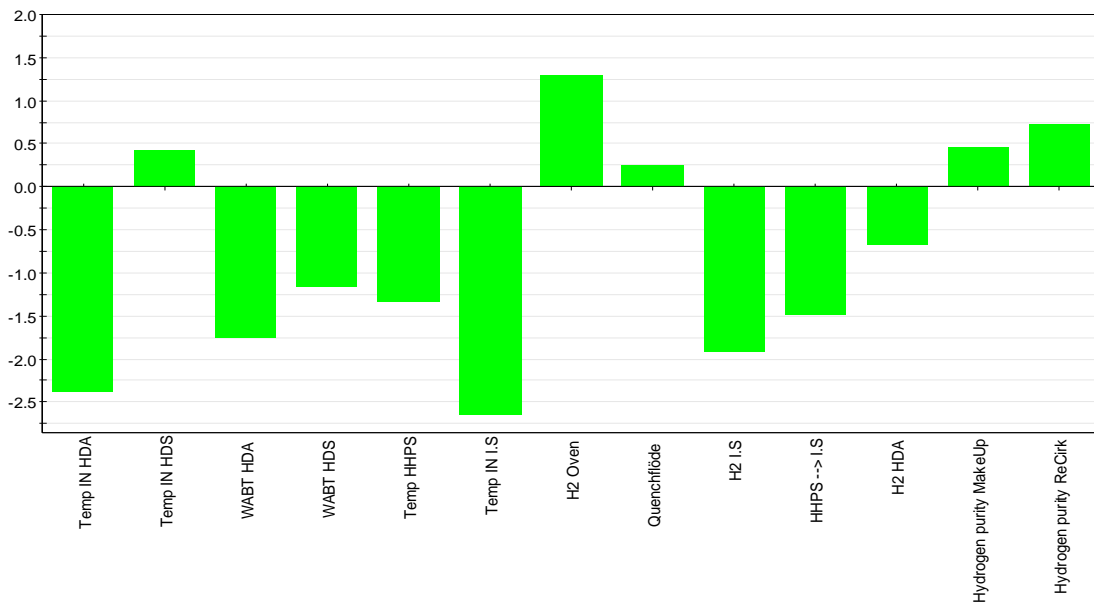
Fig 19. Contribution plot showing how to minimize Y (aromatic concentration).

Fig 19. differs significantly from the same plot for "Testruns 2005" in the following variables:

Variabel	Std. Dev. Testruns 2005	Std. Dev. High and Low 1
Temp in HDS	4.059	0.17
WABT HDA	4.10	4.94
Temperature in Interstage Stripper	2.59	5.11
Flow from HHPS to Interstage Stripper	3.03	5.16

Table 1. Differences in Std. Dev.

Table 1. partially explains the difference in importance between the two models variables. Less or no variance for a significant parameter will vastly affect its importance in the model, thereof the seemingly insignificance for the temperature in to the HDS reactor. The same reasoning goes for all of the above variables. Testruns 2005 however contains only 23 observations compared to High and low which contains 48 observations, this can also explain some of the differences in results.

Temperature In to HDA reactor	"Minimize"
Temperature In to HDS reactor	"Maximize"
Temperature in Interstage Stripper	"Minimize"
Hydrogen gas flow to oven	"Maximize"
Hydrogen gas flow to Interstage Stripper	"Minimize"
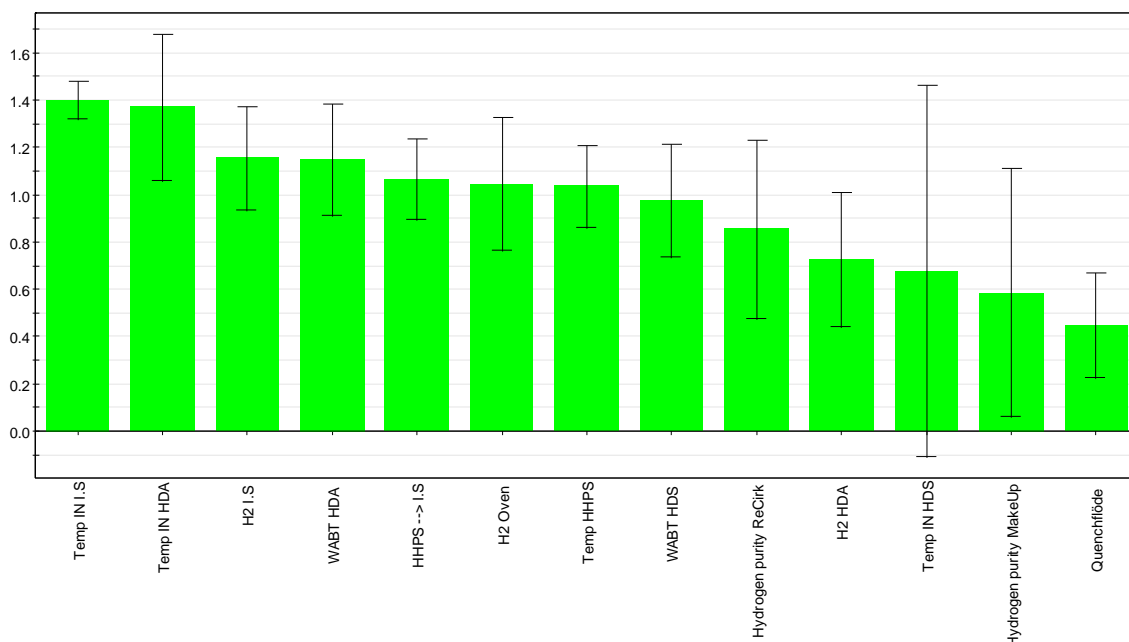
Fig 20. Importance of the parameters in decreasing order.

Results from "High and Low 2"

Relevant information such as additional plots and datasets can be found in Appendix 1.

High and Low 2 have less variation in the observed variable then High and Low 1, but the results is almost the same.
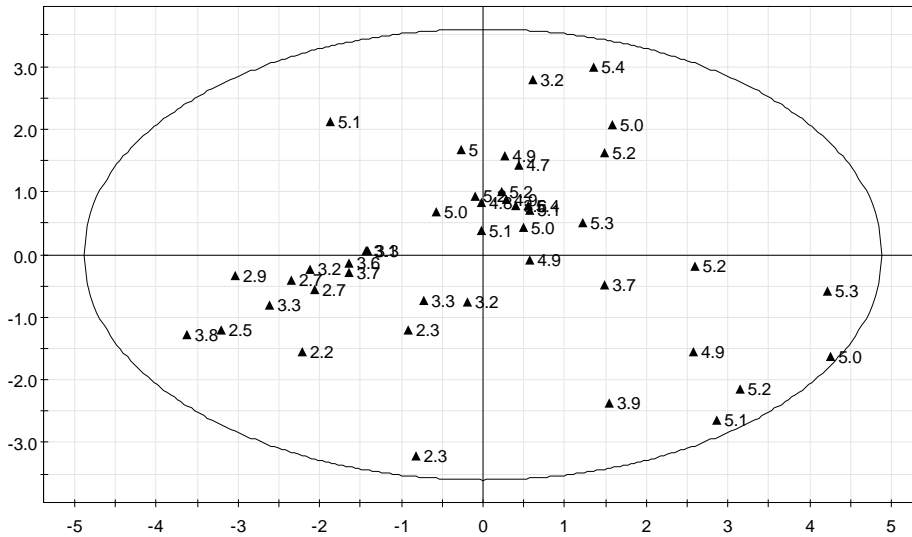
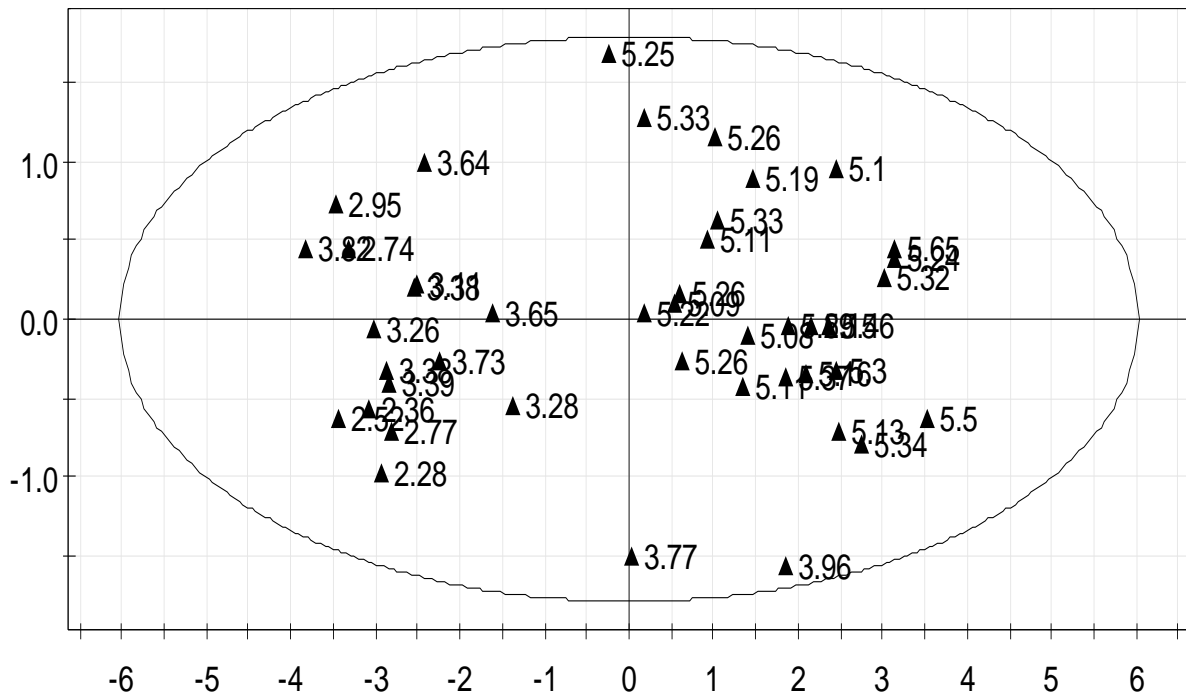*Fig 21. Score plot for the two components with aromatic concentration as labels. Aromatic concentrations above 4.8 are considered as unacceptable.*

The score plot shows almost the same patterns as the previous. High concentrations are located in the northeast quadrant and the low concentrations are consequently located in the opposite quadrant.
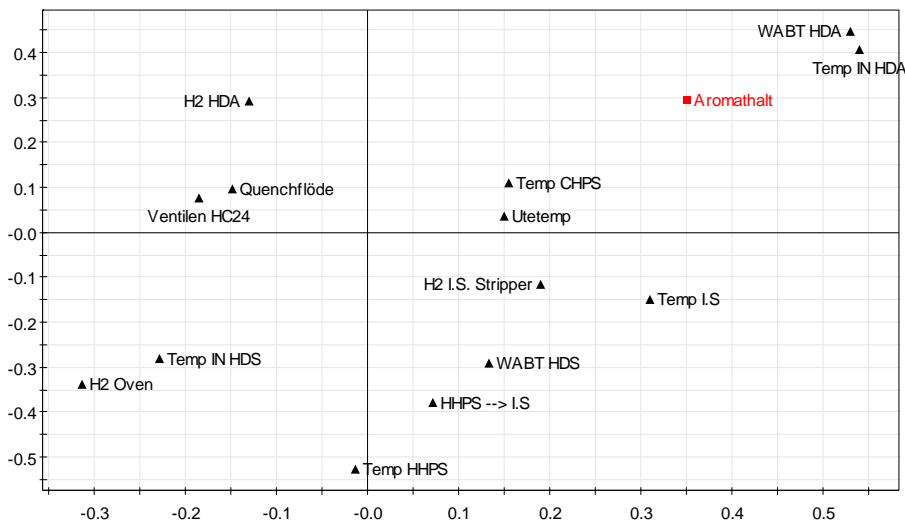
Fig 22. Loading plot with the Y variable (Aromatic concentration) marked with red.

The importance's of the variables are further discussed in the following chapter.

Fig 23. Contribution plot showing how to minimize Y.

Fig.24 Important parameters in decreasing order.

Comparison between the the models

1. **Temperature into the HDA reactor** is the most important variable in all of the models. Decreasing the temperature should improve the dearomatization according to the models. Consulting equilibrium information, discussed in the section "Equlibrium" gives the MVDA models physical meaning in this variable.
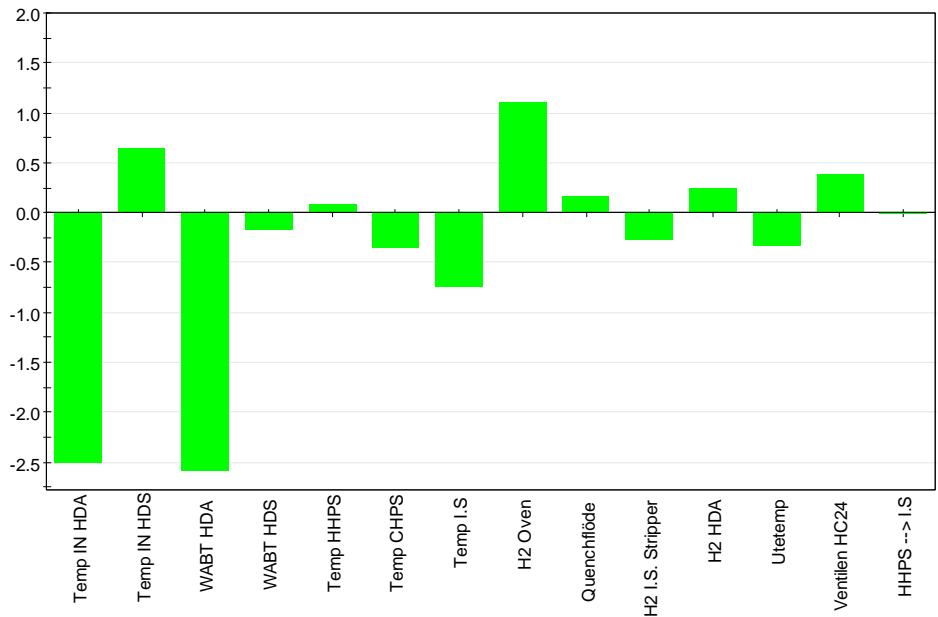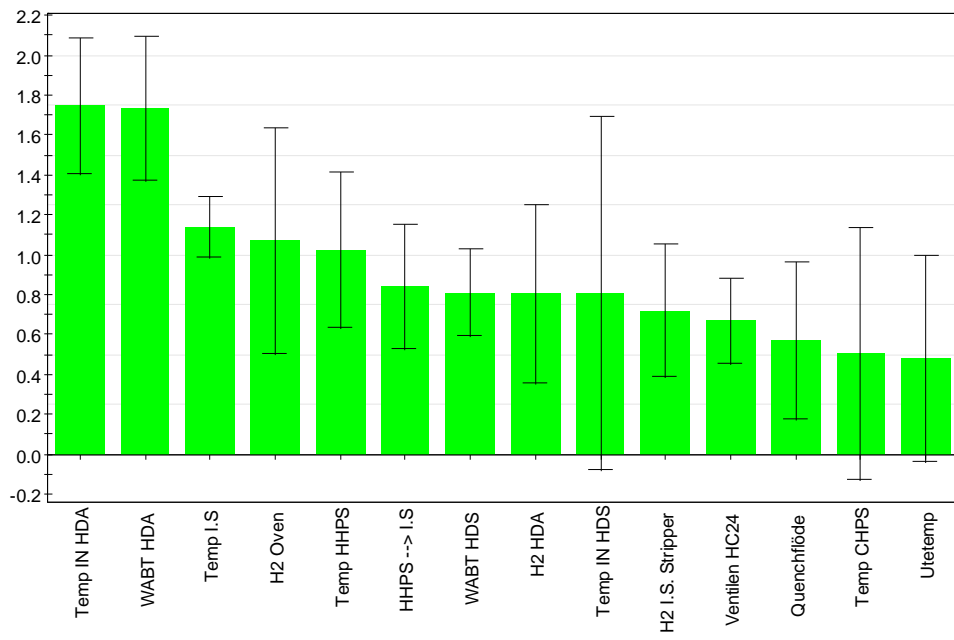A lower temperature would also decrease the vapour pressure of lighter hydrocarbons, increasing the hydrogen purity. Lighter hydrocarbons can enter the HDA reactor from the Interstage Stripper or be produced by cracking in the reactor.

2. **Temperature in the Interstage Stripper** differs in variance between the Testrun 2005 and the other two datasets. Probably making the importance of the variable smaller in the Testrun 2005 model. However, all observations are higher than 245 °C which later on will be proven an interesting temperature.

3. **Hydrogen flow to the Interstage Stripper** is important in Testruns 2005 and High and Low 1 but has opposite signs. This behaviour can be explained by looking at the variable plot for each of the models where the reason for this behaviour is explained. There are too little variance in the "Testruns 2005" to be able to estimate its importance. (However the std. dev. for both of the datasets are almost the same which can be misleading)
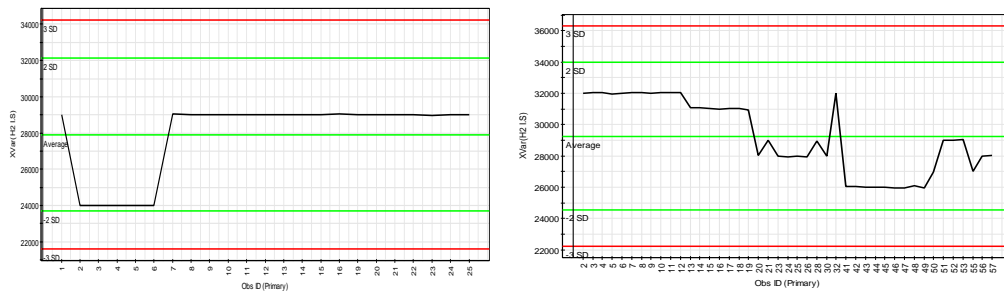
Fig 25. a)Variable plot for Hydrogen flow to the Interstage Stripper from "Testruns 2005". b)) Variable plot for Hydrogen flow to the Interstage Stripper from "High and Low".

4. **Weighted Average Bed Temperature in the HDA reactor** should be reduced to improve dearomatization. "Testruns 2005" show a smaller significance for WABT HDA then "High and low 1 & 2" does. One should be careful when evaluating this variable as the equation for WABT HDA in the HDA reactor is rather simplified. The ordinary equation for calculating WABT is suited for a co current flow reactor, since the HDA reactor is a counter current trickle bed reactor the temperature profile is different.
The variable is also rather ambiguous since a high temperature can reflect a high conversion (exothermic reaction) and a high temperature can also reflect a temperature too high according to equilibrium data. Since the hypothesis is that the temperature in the reactor is too high and that the MVDA analysis indicates a reduction in temperature it is likely to believe that the temperature reflects the reactors position on the equilibrium curve.

5. **Flow from the HHPS to the Interstage Stripper** shows a big significance in the "High and low 1" and almost no significance in the "Testruns 2005". Examining the dataset for "High and low 1" and calculating the means of the feed flow going to the plant when the aromatic concentration is high versus low indicates a quite large difference. In other words, there is more variance in the feed flow in the "High and Low 1" dataset then in the "Testruns 2005".
Since the residence time in the reactor is too short for equilibrium to be reached there is a link between a high feed and high concentrations and when the feed is high there will be more MK I in the system. This in turn leads to larger recirculation streams, giving this variable a false significance.

6. **Weighted Average Bed Temperature in the HDS reactor** is only available in the datasets "High and Low" since this function wasn't available in InfoPlus in 2005. According to the "High and Low 1" model, a decrease in temperature should favour the dearomatization whilst in "High and Low 2" the variable is insignificant for the dearomatizationrate. Taking a look at the standard deviation for the different models:
High and Low 1….. 1.35
High and Low 2….. 1.52

The variance is therefore smaller for the first model, which shows a significance in the WABT HDS variable whilst the second with larger variance shows none and the fact that the variance in either way is small leads to the conclusion that the variable significance in model one is only by chance.

7. **Temperature in to the HDS reactor** has nearly no variance since this is a highly regulated variable. The standard deviation is 0.17 and 0.16 for the respective models. According to equilibrium data the HDS reactor has a too low temperature and the dearomatization rate should be favoured by a temperature increase. The MVDA analysis shows the same result but this is not a significant result due to no variance.

8. **Temperature in the HHPS** is regulated by a pair of air coolers and a heat exchanger. The air coolers can only cool away a certain amount of energy, depending on the outside temperature. Therefore the temperature in the HHPS is also dependent on the temperature in the HDA reactor. Using the same reasoning as with the temperature in the HDA reactor it follows that a low temperature in the HDA reactor will give a low temperature in the HHPS which gives the variable significance.
High and Low 2 however contradicts the other models by telling us that the variable lack any significance for the dearomatization. Increasing the number of observations and the lack of significance would probably disappear.
There is a hypothesis that aromatic species would go over top in the HDA reactor and that a low temperature in the HHPS would place the aromats in the recycle stream. Data however tells us that independent of the temperatures in the vessels, aromats will reach the bypass stream from the CHPS.

9. **Temperature in the CHPS** shows very little significance for the overall model and are even excluded from one model due to lack of significance.

10. **Hydrogen flow to the heater** shows large significance in all of the models. This behaviour is expected since this flow is the main provider of hydrogen gas to the process. See the "Kinetic" section for more detailed information about hydrogen's role in the process.

11. **Quenchflow** shows little effect on the process which can be explained by far less variation in data compared with the hydrogen stream to the heater. The quenchflow however is only a third in size compared to the heater stream.
The quenchflow doesn't only add hydrogen to the process, it regulates the temperature in to the last bed in the HDS reactor, it regulates the temperature in to the HDA reactor and it also regulates the temperature in the interstage stripper. These four properties may be the cause of the insignificance and there would have to be many more observations to declare its affect.

12. **Hydrogen flow to the HDA reactor** is not a significant variable but its variance is also quite small. The hydrogen added do the process through the HDA reactor contributes to approximate 21 % of the total hydrogen consumption.

13. **Outside temperature** didn't show any significant effect. Since the entire process is located outdoors and the fact that heat exchanging to the surroundings is common this is an unexpected result. However, the heat exchanging to the surroundings through fan coolers are regulated with fan speeds and louvers, which will vastly decrease the variables statistical significance.

Source of error

Important to know is that the aromatic analyst mounted on the product feed was not installed at the time of the testruns in 2005. This means that there are no continuous measurements of the aromatic content so we are limited to isolated lab results from samples taken before, under and after the specific test. These samples may not be collected exactly at the time specified in the report which makes the coupling between the other logged processdata and the aromaticcontent in the product vague.

Since the observations aren't gathered in chronology with small time steps dynamic in the system is lost. There is also a risk of collecting bad data, e.g. a temperature has just been changed and the rest of the system hasn't had time to respond. The instantaneous picture of the process given by that observation isn't a representative one. Together with other observations the temperature will act like an outlier. Therefore are every outlier, even moderate ones put aside to not give a corrupt picture of the system.

Both the models High and Low 1 and Testruns 2005 look to be able to explain the variation in data quite well. However this is only a false perception since almost all of the variables is dependent on the feed flow. The response variable is even more dependent on the feed flow then the other variables which make all variables to a certain degree dependent of one variable. Including this variable (the feed flow) in to the models only makes it harder to notice the smaller variations in the data. It is however important to remember that much of the variation explained by the model is just a false perception. This doesn't make the models bad, important information can still be extracted from them. It is just not suitable to use the models in trying to predict future response variables.

Hydrogen purity

Multivariate data analysis has shown that the amount of hydrogen in the process is crucial for the dearomatizationrate. There are two ways in affecting the amount of hydrogen that goes in to the process. Either increasing the flow of hydrogen or increase the purity. The first method has its drawbacks as it would decrease the residence time in the reactor and "inerts" would dilute the reaction mixture and compete with the hydrogen on the catalyst. Left are to increase the purity of the hydrogen. To better understand which variables that affect the purity of the recycled hydrogen an MVDA analysis was performed, using the same dataset as for High and Low 1 the result is presented below.
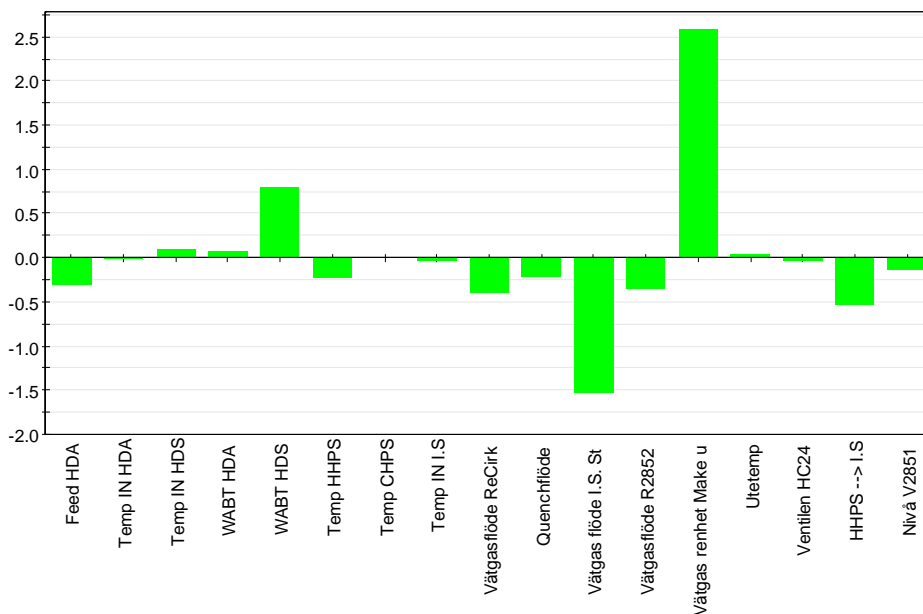

Fig 26. Contribution plot explaining how to maximize the purity of hydrogen.

As the plot shows it is important to maintain a high purity in the makeup gas do be able to maintain a high purity in the recirculation system. The next parameter is however quite interesting, as it suggest that a high hydrogen flow in the interstage stripper causes a draft, taking hydrocarbons over top and contaminating the hydrogen. This means that the significance showed by the same variable in the "High and low 1" doesn't necessary have to come from a direct effect of this variable on the HDA reactor. It's more likely that the variable affects the hydrogen purity, and this variable in turn affects the dearomatizationrate. WABT HDS is a totally dependent variable caused by the increase in reactants to the exothermic reaction.

HYSYS calculations

Lighter carbons

HYSYS have been used to verify the assumptions that lighter carbons go over top in the Interstage Stripper and HDA reactor. Lab analysis concur that this is the case (Appendix II). Taking properties from HYSYS gives the advantage to simulate the oil stream, see Appendix II for details.

NBP is short for Natural Boiling Point which is the species boilingpoint at 1 atm. In HYSYS it is also the name for a pseudo specie predicted by HYSYS based on a boiling point curve from the laboratory.

Composition of the simulated vapour stream (Draft) (const. Pressure=53 bar)						
	T=230	T=235	T=240	T=245	T=250.	T=255	T=260
Hydrogen	0.90296	0.90168	0.90038	0.89909	0.89834	0.89834	0.89834

Table 2.

It seems that the maximum purity is reached between 245 °C and 250 °C. This finding is especially interesting since that can also be an explanation to the results from the MVDA analysis regarding the temperature in the HDA reactor. Since the temperature in the Interstage Stripper and the temperature in to the HDA reactor is in fact the same temperature.

Composition of the simulated vapour stream from the HHPS (const. Pressure=53 bar)						
	T=145	T=135	T=125	T=100	T=90	T=80	T=70
Hydrogen	0.91737	0.91819	0.91886	0.92004	0.92037	0.92066	0.92092

Table 3.

As seen in table 3 the purity could be increased by reducing the temperature in the HHPS. The exact increase and decrease in purity should not be over interpreted since the oil and hydrogen streams used in the simulation isn't totally coherent with reality. However, the simulation indicates an interesting suggestion that the vapour phase contains all the lighter carbons possible to boil of at the current pressure above a certain temperature, which lies very close to the normal operating temperature. This is further discussed in the chapter Results.

Important to know is that when the outside temperature gets low, the fan coolers need to be shut down to maintain the set temperature in the HHPS. If the temperature continues to decrease the temperature in the HHPS continues to decrease, leaving the HHPS without any temperature control.

Testruns 2010

Based on the multivariate data analysis and data retrieved from Criterion the following test runs where planed and performed during two days in early February 2010.

Test 1
Increase and decrease the temperature into the HDS reactor, but maintaining a constant outlet temperature. This is achieved with the help of the quenchgas flow, situated between the beds in the HDS reactor. This is done to maintain a constant temperature in the HDA reactor.

Test 2
Increase and decrease the temperature into the HDS reactor, but this time no other changes is done on the system. The result of this is a temperature increase and decrease in the whole system, including the inlet temperature to the HDA reactor.

Results from the Testruns 2010

Unfortunately, though only a few variables where manipulated it was impossible to maintain all the other variables constant depending on two factors. One, changing one variable almost always affects another variable.

- Hydrogen streams – The hydrogen compressors have a set value and are indifferent of how the hydrogen is divided between consumers downstream. In the first test, when we try keeping a constant temperature out from the HDS reactor, we control the outlet temperature with the hydrogen quench. In doing so, we indirect affect the hydrogen stream into the furnace upstream the HDS reactor.

The second source of error is process operators different views on different variables, especially the valve 28HC24, see fig 27. This valve isn't printed on the PFD since it isn't meant to be used in the daily operation. The best guess is that is it meant to be a handle for emergency cooling of the HDA reactor.
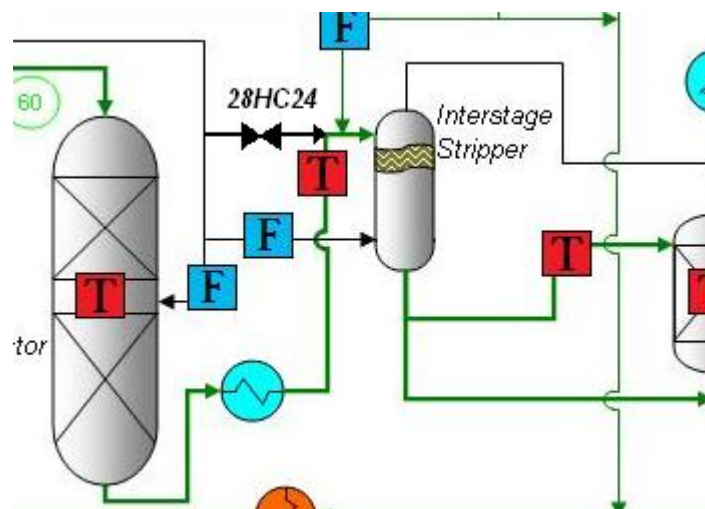

Fig. 27 . 28HC24

When starting the second test we realized that the valve 28HC24 had been opened to some extent (7 %) during the first test. The valve where also open 18 % the second test day and we were forced to close it during the test to accomplish a sufficient temperature increase in the HDA reactor.
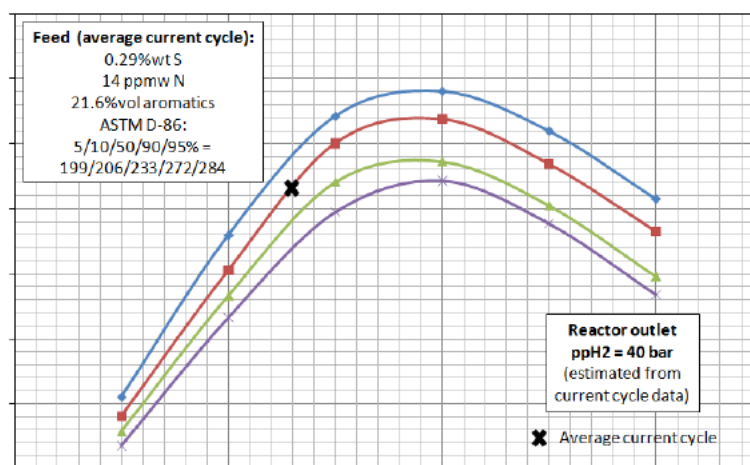
The HDS reactor

Fig 28. Modelled operating lines for the HDS reactor, Temperature = WABT Temperature

According to this graph obtained from Criterion it would be beneficial to increase the WABT temperature in the reactor to obtain a higher conversion.

The results from the testruns are gathered below.

- Criterions model predicted a 39% conversion at a WABT at *"confidential"* °C
- At a WABT of *"confidential"* °C a conversion of 29 % was achieved.
- The highest conversion was 33% at a WABT of *"confidential"* °C

Unfortunately, the reactor doesn't respond to changes in WABT as the model has predicted. Conclusions drawn from these testruns are that the temperature in the HDS reactor should be maintained at *"confidential"* °C and a constant WABT of *"confidential"* °C.

Since the compressors are operated at a constant shaft speed the flow of hydrogen provided by the recirculation compressor are relatively constant. Regulating the outflow temperature of the HDS reactor with the gasquench causes the two other streams from the recirculation compressor to increase. However, the flow in to the Interstage Stripper is regulated to a set value, causing the hydrogen flow in to the furnace increase the same amount as the gasquench is decreased.

The HDA reactor

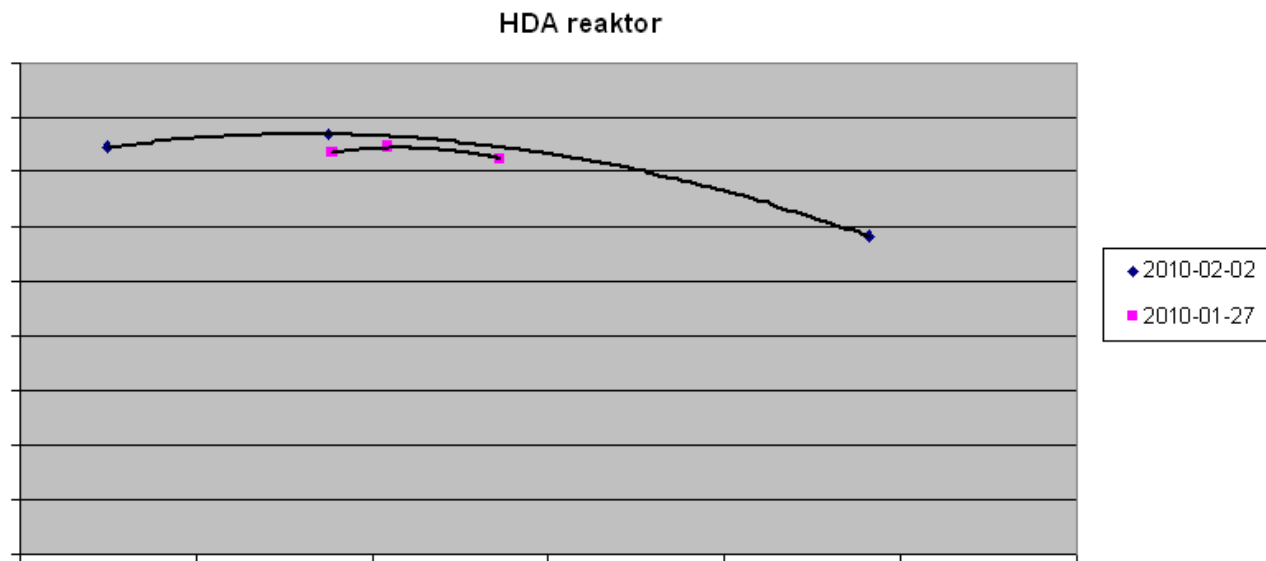Fig 29. shows the conversion of the HDA reactor during the two tests.

Fig 29. Conversion of the HDA reactor during the Testruns 2010.

As seen in the figure, the different operating conditions alter the reactors operating characteristic. Possible causes for this behaviour can be:

1. Purity of the hydrogen entering the bottom of the HDA reactor.
2. The flow of hydrogen entering the bottom of the HDA reactor.
3. The effectiveness of the HDS reactor

Hydrogen purity

During the test we noticed a significant change in hydrogen purity in the recirculation stream. Fig 30 shows that the hydrogen purity is dependent on the temperature in the Interstage Stripper, the temperature in the HDA reactor and the temperature in the HHPS vessel. Fig 30 also verifies the simulation done in HYSYS that all lighter components leaves the Interstage Stripper at a temperature above 245 °C. The following temperature increase doesn't affect the hydrogen purity since all lighter components are already in the vapour stream.
The purity of the recirculation gas is however vastly dependent on the purity of the makeup gas, all this in consensus with the MVDA analysis.

The observant reader has noticed that the MVDA analysis shows no effect of the temperature in the Interstage Stripper on the hydrogen purity. This can be explained by looking at the temperature interval for the Interstage Stripper in the High and Low 1 dataset (Appendix I). The lowest temperature in the Interstage Stripper is 300 °C and is above the interval mentioned earlier.
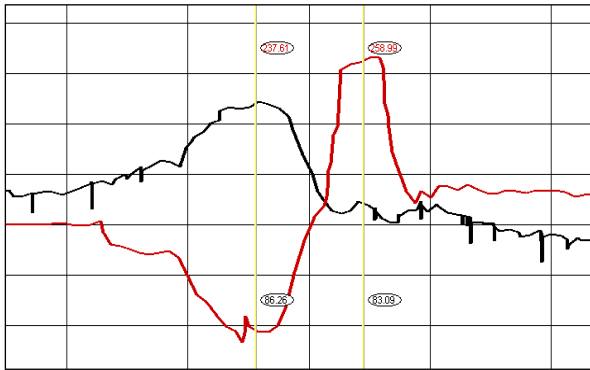

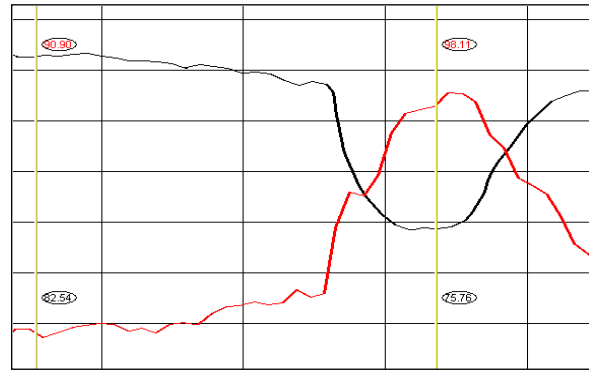*Fig. 30. Temperature in Interstage Stripper(red) and hydrogen purity in ReCirk. Stream (black).*

Fig. 31. Temperature in HHPS(red) and hydrogen purity in ReCirk. Stream (black).

The purity of the hydrogen in the makeup gas, which provides the HDA reactor with hydrogen and acts as make up gas for the recirculation stream is delivered from the CRU CCR unit.

The flow of gas from the makeup compressor to the HDA reactor is fairly constant with an average flow of *"confidential"* m^3/h.
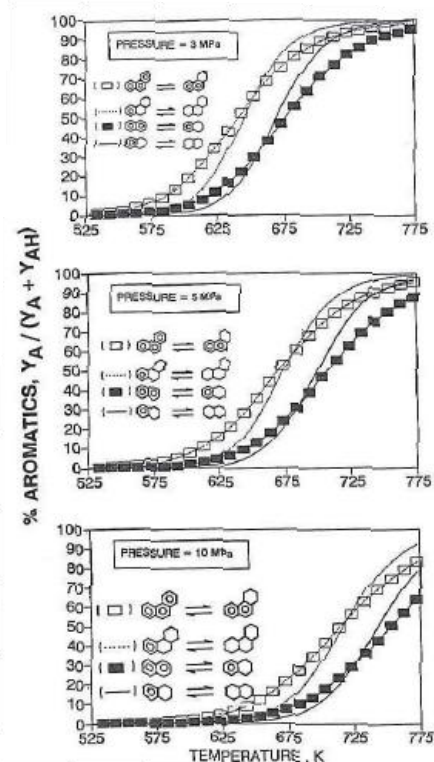
The Reactors

The effectiveness of the HDS reactor varies in both of the tests. SynSat current design is to have two types of catalysts that "cover up" for each other. The cause for this is the use of two different types of catalysts, a Nickel Molybden (NiMo) in the HDS reactor and a noble metal catalyst in the HDA reactor. I refer to the Theory chapter under the section Catalyst for a more detailed explanation.

Consequently if the HDS reactors operating conditions changes negatively, as they did in both of the tests the reactor will leave some additional aromatics in the outflow stream. Unfortunately the HDA reactor, which consists of a noble metal catalyst have problems dealing with these sorts of aromatics. Consequently, the feed to the HDA reactor hasn't been constant adding another uncontrolled variable.

Low feed conversion

During the last days of the study an additional testrun where conducted to evaluate SynSats capability of receiving extra pure make up gas. During the test the feed to SynSat where reduced with 64% and an aromatic sample where taken in the outflow from the HDA reactor. This sample showed an aromatic concentration of 0,7 vol% out from the HDA reactor. This result indicates that there are no equilibrium restraints limiting the reaction. However, it should be taken in to account that the partial pressure of hydrogen were larger during the test, pushing the equilibrium to higher temperatures, see fig 32. During normal operation the partial pressure of hydrogen is approximately 5 MPa and a good approximation of normal operation temperature is *"confidential"* K to *"confidential"* K. Consulting the graphs in fig.32 it is clear that there is no equilibrium limitation.

Fig 32. Equilibrium curves at different partial pressure of hydrogen.[4]

[4] . Stanislaus, A., Cooper, B.H., Catal. Rew. Sci. Eng. 36, 82(1994)

Results

Lighter carbons

When processing oils with high concentrations of naphtenes, the reaction rates decreases. The decrease in reaction rates could be caused by low boiling naphtenes, diluting the hydrogen gas around the catalyst particles. If this is the case, it is also most likely that the efficiency drop occurs in the HDS reactor since low boiling naphtenes are stripped from the oil stream in the Interstage Stripper. The HDS reactor contributes under normal operation to approximate 30 % of the hydrogenation.

It´s also important to remember that Ural also contains naphtenes, and that these concentrations probably variate.

It is also a possibility that there is another significant difference between crude oils with high and low naphthenic concentrations that the current assay data doesn't show. This reasoning leads to the next claim, that a thorough analysis of different feeds should be conducted.

The feed composition

During the study it has been more and more clear that a thorough analysis is necessary to make good predictions of the dearomatization in the different reactors. At the present it is known that the outflow from the HDA reactor contains a significant amount of a monoaromatic specie built up by 12 carbons. The shape and number of entanglements are not known and therefore makes equilibrium data for species represented in the Equilibrium chapter unusable for this specie.

A more thorough investigation regarding the species in and out from the two reactors would result in a significant better way to explain and try to avoid variations in the dearomatization rate.

Important to notice is that the composition of the feed are totally dependent on which crude oil being used. The amount of lighter carbons in the oil stream is also dependent on the magnitude of cracking in the reactors.

Since the reactors have different reaction rates for the same specie, a feed composition study will also answer the question which reactor that are limiting the dearomatization.

During normal operation and normal feed there is no evidence that there is an equilibrium limitation. However, the reaction rate for the above mentioned 12 carbon specie could be very low.

The hydrogen purity

In High and Low 1 the variables hydrogen purity for the recirculation gas and the makeup gas is included. According to the MVDA analysis these should be high to perform a good hydrogenation. Of course this is also what is expected.

The MVDA analysis argues that the feed of hydrogen gas should be high into the furnace for all the models. Increasing the flow of hydrogen to the furnace would increase the amount of hydrogen that could react in the HDS reactor. However, to increase the flow of hydrogen to the furnace to compensate for a low purity would decrease the residence time in the reactors and dilute the reactants with additional lighter carbons from the recirculation gas.

The temperature in the Interstage Stripper and the HDA reactor has proven interesting. Simulation of the equilibrium between phases in HYSYS indicates that all lighter carbons exists the Interstage Stripper in the vapour stream in the interval 245 °C and 250 °C. It is possible that this phenomenon could explain the result from the MVDA analysis regarding the temperature in the HDA reactor. Since the temperature in the top of the HDA reactor and the temperature in the Interstage Stripper could describe the same phenomenon.

The temperature in the HHPS can of course also affect the amount of lighter carbons in the hydrogen stream. However, there is a limitation in lowest temperature allowed in the HHPS since the oilstream contains ammonium bisulphide which can form crystals and cause fouling.

Consequently the temperature in the Interstage Stripper controls the amount of lighter carbons delivered to the HHPS. However, lowering this temperature has no effect until below the interval 245 °C - 250 °C.

The MVDA analysis performed regarding hydrogen purity shows that the variable with the next largest impact is the strip flow of hydrogen in the Interstage Stripper.

Appendix I

Testtruns 2005

Variable	Date
Temperature decreased in Hot High Pressure Separator	2005-10-28
	2006-01-23
Outflow temperature from HDS reactor decreased	2005-11-01
Inflow temperature increase to HDS reactor	2005-10-06
Flow rate decrease and temperature decrease in Interstage Stripper	2005-09-20
Increase hydrogen flowrate to HDA reactor	2005-10-25

Important to know is that the Aromaticanalyst mounted on the product feed was not installed at the time of the test runs. This means that there are no continuous measurements of the aromatic concentration so we are limited to isolated lab results taken before, under and after the specific test.

List of variables originally in the dataset
- Feed temperature in to HDA (Temp in HDA)
- Feed temperature in to HDS (Temp in HDS)
- Weighted Average Bed Temperature in the HDA reactor (WABT HDA)
- Flow from HHPS to Insterstage Stripper (HHPS $\rightarrow$ I.S)
- Temperature in HHPS (Temp HHPS)
- Temperature in CHPS (Temp CHPS)
- Temperature in Interstage Stripper (Temp I.S)
- Hydrogen gas flow in to the oven (Vätgasflöde ReCirk)
- Hydrogen gasflow in the HDS quench (Quenchflöde)
- Hydrogen gas flow in to the Interstage Stripper (Vätgasflöde I.S)
- Hydrogen gas flow in to R2852 (Vätgasflöde R2852)
- Outside temperature (Utetemp)

High and Low 1

List of variables originally in the dataset

- Feed temperature in to HDA (Temp in HDA)
- Feed temperature in to HDS (Temp in HDS)
- Weighted Average Bed Temperature in the HDA reactor (WABT HDA)
- WABT HDS
- Temperature in HHPS (Temp HHPS)
- Temperature in Interstage Stripper (Temp I.S)
- Hydrogen gas flow in to the oven (H2 Oven)
- Hydrogen gasflow in the HDS quench (Quenchflöde)
- Hydrogen gas flow in to the Interstage Stripper (H2 I.S)
- Flow from HHPS to Insterstage Stripper (HHPS → I.S)
- Hydrogen gas flow in to R-2852 (H2 HDA)
- Flow from HHPS to Insterstage Stripper (HHPS → I.S)

High and Low 2

List of variables originally in the dataset
- Feed temperature in to HDA (Temp in HDA)
- Feed temperature in to HDS (Temp in HDS)
- Weighted Average Bed Temperature in the HDA reactor (WABT HDA)
- WABT HDS
- Temperature in HHPS (Temp HHPS)
- Temperature in CHPS (Temp CHPS)
- Temperature in Interstage Stripper (Temp I.S)
- Hydrogen gas flow in to the oven (H2 Oven)
- Hydrogen gasflow in the HDS quench (Quenchflöde)
- Hydrogen gas flow in to the Interstage Stripper (H2 I.S Stripper)
- Hydrogen gas flow in to R2852 (H2 HDA)
- Outside temperature (Utetemp)
- Valve 28HC24 (HC24)
- Flow from HHPS to Insterstage Stripper (HHPS → I.S)

Additional plots from SIMCA

Testruns 2005
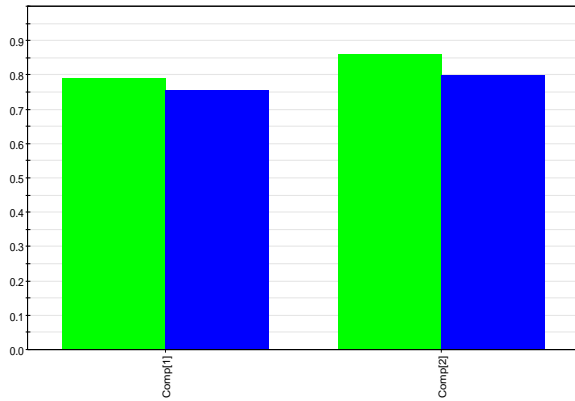
Fig. App.1.1. The two components generated.
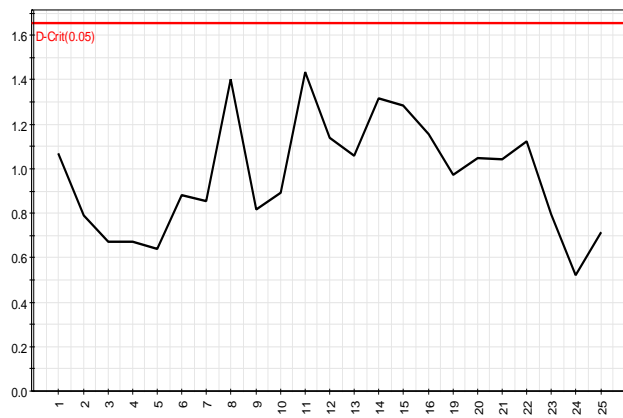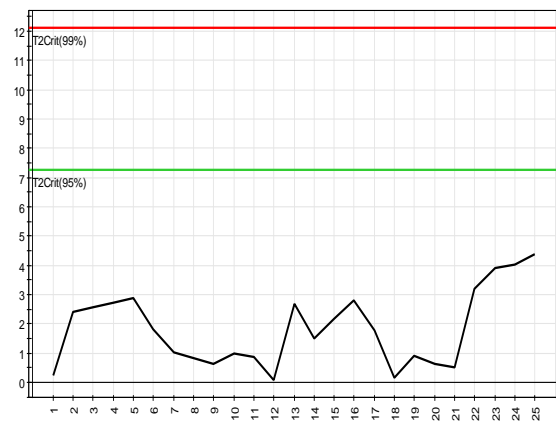

Fig.App.1,3 DModX

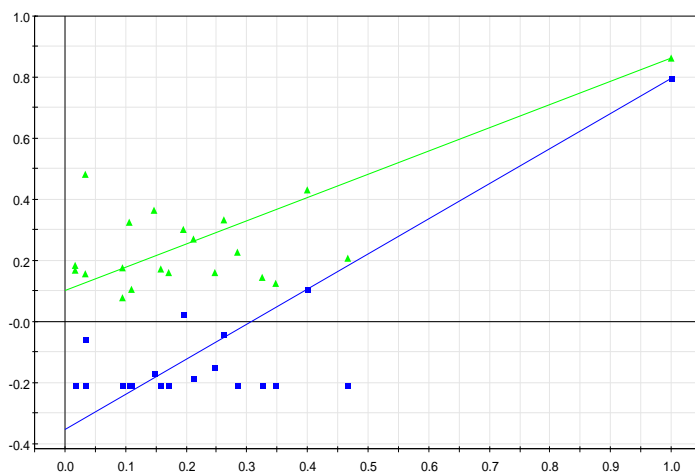*Fig.App. 1,4 Hotelling´s T2 Range*

Fig.App.1,5 Validation with 20 permutations.
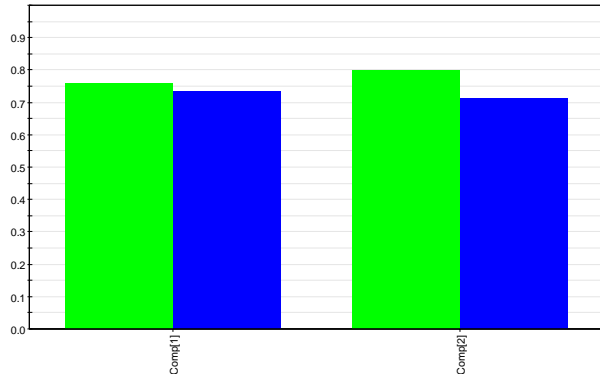
High and Low 1

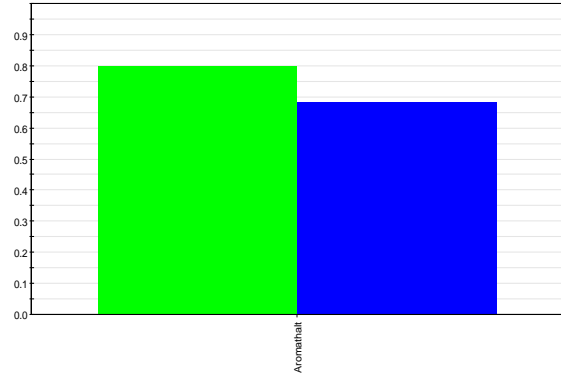
FIG. App11,6. The two components generated.
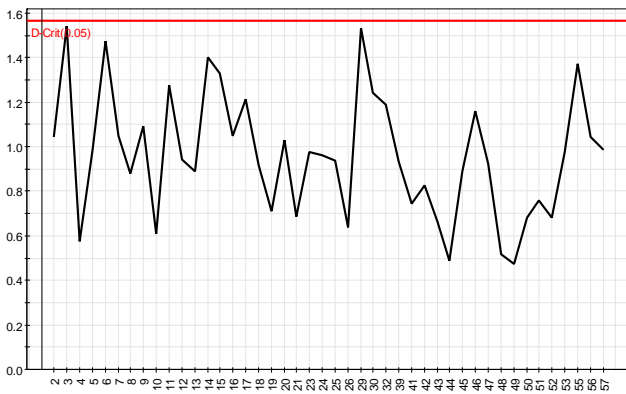

Fig.App.1,7. Model Y
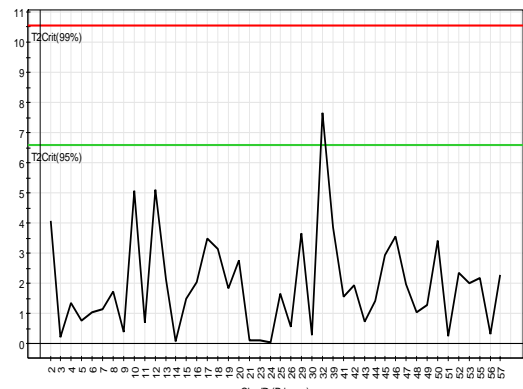

Fig.App.1,8 DModX

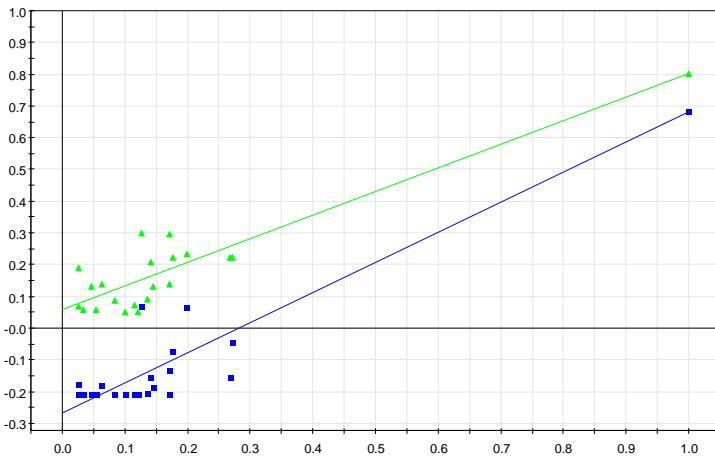Fig.App.1,9 Hotelling´s T2 Range

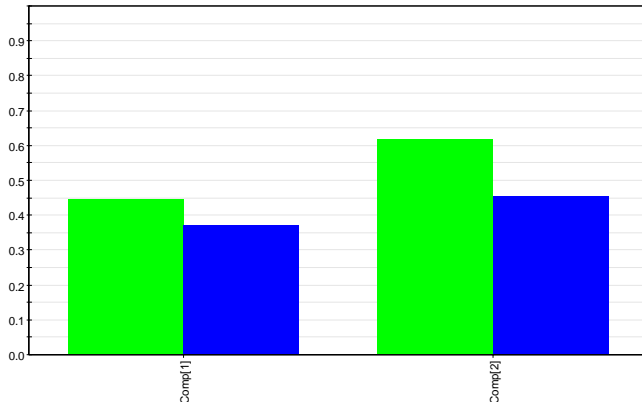Fig.App.1,10 Validation with 20 permutations

High and Low 2

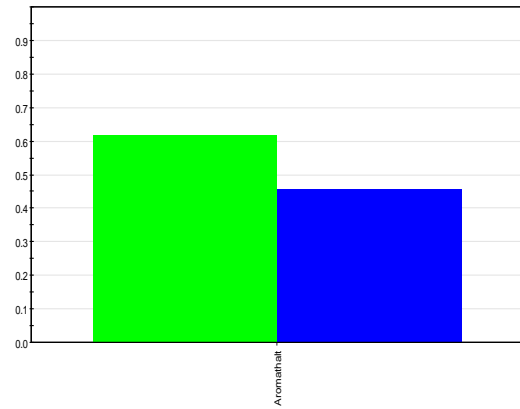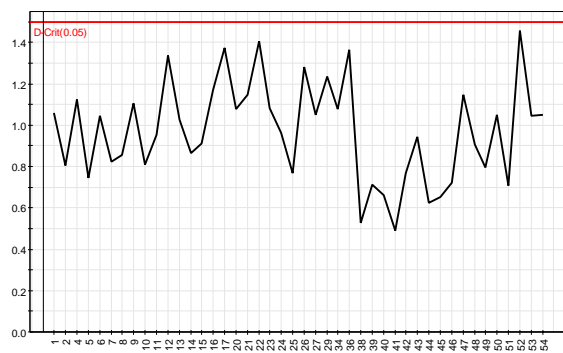FIG. App.1,11. The two components generated.
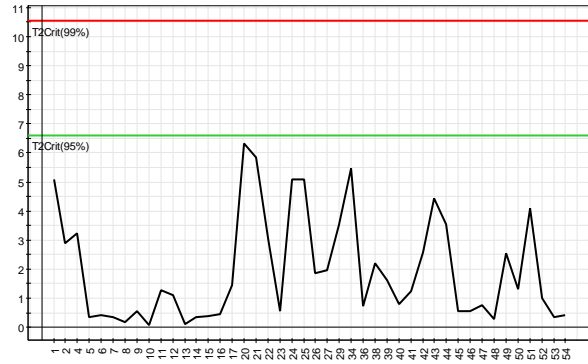

Fig.App.1,12. Model Y

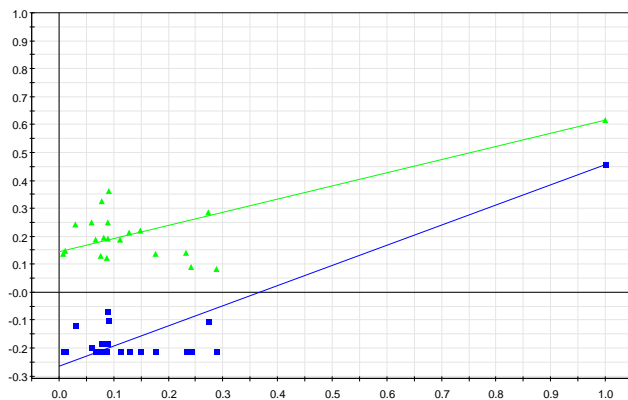
Fig.App.1,13 DModX

Fig.App.1,14 Hotelling´s T2 Range

Fig.App.1,15 Validation with 20 permutations

Appendix II

Composition of the simulated vapour stream (Draft) (const. Pressure=56 bar)

	T=230	T=235	T=240	T=245	T=250.	T=255	T=260
Methane	0.04316	0.04311	0.04305	0.04299	0.04296	0.04296	0.04296
Ethane	0.02352	0.02350	0.02347	0.02345	0.02343	0.02343	0.02343
Propane	0.00979	0.00978	0.00978	0.00977	0.00976	0.00976	0.00976
i-Butane	0.00101	0.00101	0.00101	0.00101	0.00101	0.00101	0.00101
n-Butane	0.00101	0.00101	0.00101	0.00101	0.00101	0.00101	0.00101
Hydrogen	0.90296	0.90168	0.90038	0.89909	0.89834	0.89834	0.89834
147	0.00051	0.00052	0.00052	0.00053	0.00053	0.00053	0.00053
161	0.00075	0.00077	0.00078	0.00079	0.00079	0.00079	0.00079
174	0.00125	0.00127	0.00130	0.00132	0.00133	0.00133	0.00133
189	0.00198	0.00204	0.00209	0.00214	0.00216	0.00216	0.00216
204	0.00269	0.00280	0.00289	0.00297	0.00302	0.00302	0.00302
216	0.00281	0.00296	0.00309	0.00321	0.00327	0.00327	0.00327
229	0.00243	0.00260	0.00275	0.00289	0.00297	0.00297	0.00297
243	0.00207	0.00226	0.00244	0.00260	0.00269	0.00269	0.00269
257	0.00163	0.00182	0.00201	0.00220	0.00230	0.00230	0.00230
271	0.00124	0.00143	0.00163	0.00183	0.00195	0.00195	0.00195
285	0.00065	0.00078	0.00092	0.00108	0.00117	0.00117	0.00117
299	0.00030	0.00038	0.00047	0.00058	0.00065	0.00065	0.00065
312	0.00014	0.00019	0.00024	0.00032	0.00037	0.00037	0.00037
328	0.00008	0.00011	0.00015	0.00022	0.00027	0.00027	0.00027

Table App. 2,1

Simulation of Draft in the Interstage Stripper

Properties for the Hydrogen stream from C-2851

Temperature	66 °C
Pressure	60 bar

Properties for the Oilstream

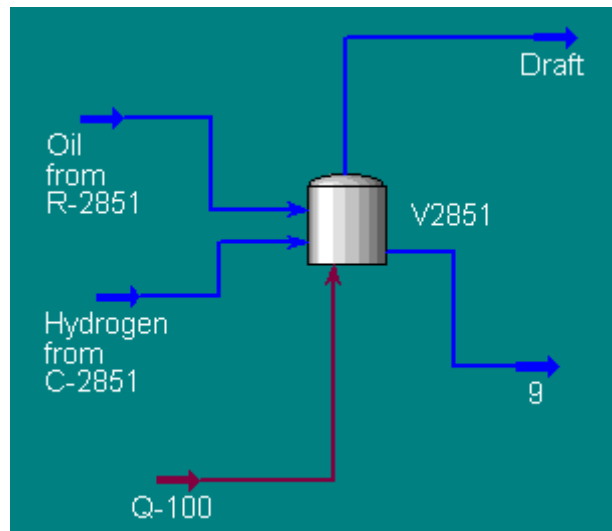|	
Temperature	300 °C
Pressure	59 bar

Table App. 2,3

Fig App 2,1. Simulation setup in HYSYS

Simulation of draft in the HHPS

This simulation is an extension of the previous simulation.

Composition of the simulated vapor stream from HHPS (Stream 10)
(const. Temp in Interstage Stripper = 245°C)

|	T=145	T=135	T=125	T=100	T=90	T=80	T=70
Methane	0.04376	0.04380	0.04382	0.04386	0.04386	0.04387	0.04387
Ethane	0.02373	0.02373	0.02372	0.02369	0.02367	0.02364	0.02360
Propane	0.00979	0.00977	0.00975	0.00968	0.00964	0.00959	0.00953
i-Butane	0.00100	0.00100	0.00099	0.00098	0.00097	0.00095	0.00094
n-Butane	0.00100	0.00099	0.00098	0.00096	0.00095	0.00093	0.00091
Hydrogen	0.91737	0.91819	0.91886	0.92004	0.92037	0.92066	0.92092
147	0.00028	0.00024	0.00020	0.00011	0.00009	0.00006	0.00004
161	0.00035	0.00029	0.00023	0.00012	0.00008	0.00006	0.00004
174	0.00047	0.00037	0.00029	0.00014	0.00009	0.00006	0.00004
189	0.00057	0.00044	0.00032	0.00014	0.00009	0.00006	0.00004
204	0.00060	0.00045	0.00032	0.00013	0.00008	0.00005	0.00003
216	0.00046	0.00032	0.00023	0.00008	0.00005	0.00003	0.00002
229	0.00028	0.00019	0.00013	0.00004	0.00003	0.00002	0.00001
243	0.00017	0.00012	0.00008	0.00002	0.00001	0.00001	0.00000
257	0.00009	0.00006	0.00004	0.00001	0.00001	0.00000	0.00000
271	0.00005	0.00003	0.00002	0.00001	0.00000	0.00000	0.00000
285	0.00002	0.00001	0.00001	0.00000	0.00000	0.00000	0.00000
299	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
312	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
328	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

Table App. 2,4
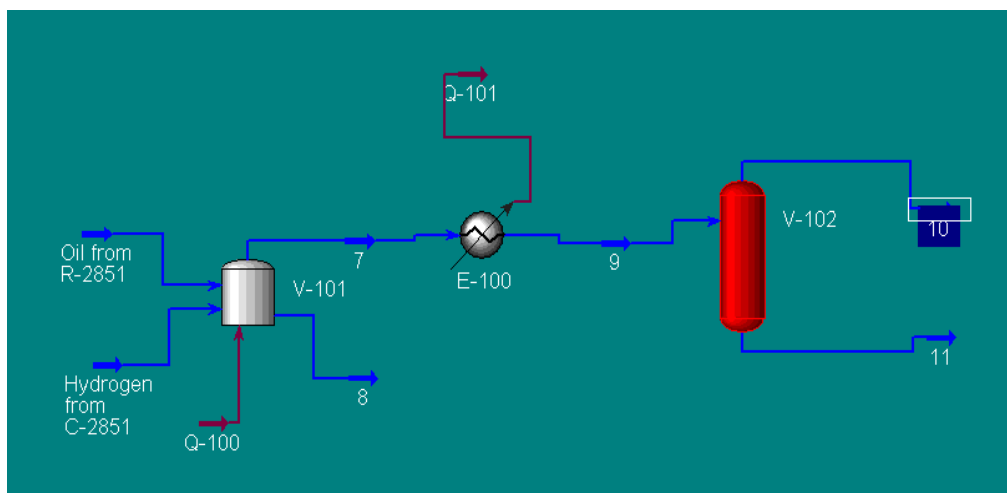
Fig. App. 2,2.
Simulation of draft
in the HHPS (V-102)