CHALMERS

Implementation of an ASA catalyst in the catalytic polymerisation unit at Preem refinery in Lysekil.

Simulation and re-design of an existing C3/C4 splitter

Master Thesis within the Innovative and Sustainable Chemical Engineering programme

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CHALMERS UNIVERSITY OF TECHNOLOGY
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MASTER’S THESIS

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Abstract

The use of solid phosphoric acid catalyst (SPA) for production of polymerized fuels is an old invention. At the Preem oil refinery the technology of SPA has been used since the polymerisation unit was built in 1982. There are several problems with the operation of the plant and handling of the catalyst during replacement that are related to the characteristics of the catalyst. The refinery has several times looked for other potential types of catalysts for this operation, but so far none have had sufficient compatibility with the current plant. In this thesis, the potential of using an amorphous silica alumina catalyst (ASA) has been investigated.

According to information received from the catalyst vendor it was concluded that the product obtained with the ASA catalyst could not be blended directly into the gasoline pool without further separation. Consequently, the implementation of the ASA catalyst required a split between gasoline and diesel components due to the increased production of heavy hydrocarbons with the ASA catalyst compared to the current SPA catalyst. A main task in this thesis has been to evaluate the feasibility of utilizing an existing C3/C4 splitter column to perform the split between poly-gasoline and poly-diesel.

Even though the increased formation of diesel components requires re-design of the polymerisation unit the case is still interesting. An increased production of diesel fuels is included in the long term strategy of Preem due to increasing demands for diesel in Europe in the recent years.

The simulation of the existing distillation column was done with ASPEN HYSYS in combination with the tray hydraulic software SULCOL. The simulations have shown that the column most probably cannot be used for the split between gasoline and diesel without re-design of the internals. However, the size of the existing column should be sufficient meaning that it might be used with modified internals.

Key words: Oligomerisation, Polymerisation, Olefins, Butene, Amorphous silica alumina, Solid phosphoric acid, hydraulic simulation,

It is recommended to have the process flow diagrams (PFD) available when reading the report in order to facilitate understanding. The PFD´s are given in appendix 2 and 3.

This report is written in English.

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Abbreviations and symbols list

- Cx – Correspond to a hydrocarbon paraffin or olefin with x carbon atoms in the molecule.
- FCC – Fluidized catalytic cracker
- ASA – Amorphous silica alumina
- SPA – Solid phosphoric acid
- TBP – True boiling point
- IBP – Initial boiling point
- FBP- Final boiling point
- ASTM – American Society for Testing and Materials
- ASTM D86 – ASTM standard distillation range test method corresponding to one stage batch distillation.
- MON – Motor octane number
- RON – Research octane number
- LPG – Liquefied petroleum gas
- HCO – Heavy cracker oil
- HK – Heavy key component i.e. the most volatile component in the bottoms.
- LK – Light key component i.e. the least volatile component in the distillate.
- MHC – Mild hydro cracker (performs mainly saturation and desulphurisation).
- HAGO – Heavy atmospheric gas oil
- VGO – Vacuum gas oil

1. Introduction

1.1 Background

From the fluidized catalytic cracker (FCC) a stream containing C4 paraffins and olefins (n-butane, iso-butane, n-butene & iso-butene) is fed to a polymerisation plant where the olefins are converted to C8 or C12 products in an oligomerisation reaction catalyzed with a phosphoric acid catalyst. After this reaction the components are fractionated and used as gasoline components. The reaction takes place in three parallel reactors where two are running at the same time. Each reactor contains five catalytic beds. The reaction is exothermic meaning that cooling is needed between each bed.

The catalyst that is used today is based on phosphoric acid with several problems related to the catalyst. Firstly, a large pressure drop is built up over the catalytic beds limiting the reaction and requiring frequent replacement of the catalyst. This is a problem since the reaction is controlled by the temperature and pressure but the need for catalyst replacement may also arise due to decreased activity caused by gum deposits on the catalyst. Secondly, the replacement procedure is quite time consuming since the catalyst particles are often strongly attached to each other giving a massive structure that often must be removed using a jackhammer and a vacuum cleaner. In addition the replacement is performed in a nitrogen atmosphere and is fairly expensive and dangerous. Due to the cost of catalyst replacement it is favourable to find an alternative catalyst with longer cycle lengths and easier handling during replacement. Today each reactor can operate about 6 months or at best up to 8 months.

Preem wants to investigate if the catalyst can be replaced with a silica-alumina based catalyst giving the same reaction but a larger amount of heavier products (diesel components). The new catalyst is a bit more expensive, but the catalyst cycle might be considerably increased. In addition the catalyst is easy to dump from the reactor so there will be fewer problems related to the replacement procedure.

The major problem related to the new catalyst is the increased amount of distillates which cannot be separated from the gasoline with the existing configuration of the separation equipment. According to the initial contacts with the catalyst vendor the amount of distillates can be decreased to some extent, but they cannot guarantee the same specifications as the Poly-gasoline that Preem produces today.

According to the vendor the catalyst is very flexible, enabling the possibilities to shift the production towards more diesel components. This is favourable due to the increased demands for diesel fuels in the recent years. In addition an increased diesel production is included in the long-term strategy of Preem. But as stated above, the production unit does not have the required distillation columns to separate the poly-gasoline and poly-diesel products. The separation of poly-gasoline and poly-diesel is a prerequisite for maximum utilization of the catalyst benefits. However, there is a distillation column that is currently not in operation which might be possible to use.

1.2 Objectives

The purpose of this project was to investigate different possibilities to operate the polymerisation process with the new catalyst. The first intention was to look into the possibilities to operate the process with the existing equipment. In other words, the task was to check if it is possible to only change the catalyst and reactor operating conditions and still obtain an acceptable poly-gasoline product. Since the new catalyst is designed to produce poly-diesel in addition to the poly-gasoline, an additional task was to investigate the possibilities to utilize an existing distillation column for the separation of the poly-gasoline and the poly-diesel. During the literature study in the beginning of the project, searching in research literature and reports by catalyst manufacturers has been done in order to find information about reaction characteristics and if there are other suitable catalysts available for this purpose.

The expected results after project completion was to obtain sufficient information from the catalyst vendor in order to assess if it is possible to authorize a “test run” of the new catalyst in one of the reactors with existing subsequent separation units. This means that the new catalyst must be able to operate under such conditions that the product meets the current specifications or at least ensure that the refinery obtain a useful product. A “test run” will be too expensive if the products cannot be used in an appropriate way.

The investigation regarding the utilization of the existing unused distillation column, to separate the diesel and gasoline fractions, was intended as an evaluation aimed to determine if the column can be used for this purpose without re-design of the internals. This evaluation includes both flow sheeting simulation and tray hydraulics simulation.

1.2.1 Problem statement

- Regarding the new catalyst: Is it possible to inhibit the reaction or operate the reactors at such conditions so that the product meets the current specification of the poly-gasoline?
- If the new product cannot be blended directly into the gasoline pool. Is it possible to separate the product with the existing distillation column which is currently not in use?

1.3 Delimitations

A test of the operation with the new catalyst was not performed within this project depending on the requirements for preparation and the delivery time of the catalyst.

Energy integration of the redesigned distillation column was not considered in this project nor the size calculation of heat exchangers needed to cool the products from the column.

One possibility is to include larger alkenes e.g. C5 in the feed to the polymerisation unit if the new catalyst is implemented. But in this case even more diesel products will be produced.

Due to limitations in the maximum capacity of the polymerisation unit this alternative was not considered.

Another possibility is to have a recirculation of either poly-gasoline or poly-diesel or both to the FCC unit in order to increase the propylene yield. The capacity of the propane/propylene separation is also on its maximum limits meaning that a recirculation of the oligomerisation products was not considered in this project.

1.4 Methodology

1.4.1 Literature review and information from catalyst vendor

In the beginning of the project a literature study was performed. In order to get information about the polymerization plant Preem´s internal documentation was mainly used. In addition a literature search in research reports and reports by other catalyst vendors was performed in order to find information about oligomerisation with similar catalysts including other ASA catalysts or zeolite catalysts.

In order to investigate whether the ASA catalyst can be used to produce poly-gasoline within the current specifications, the reference information comes from the department of hydroprocessing and olefins technologies at the manufacturing company. A technical offer has been provided from the vendor based on the operating conditions at Preem. Further contacts have also been taken with the technology manager for hydroprocessing and olefins technologies at the catalyst manufacturing company. The initial discussions have been focused on reactor operating variables in order to find possibilities to obtain a gasoline with a sufficiently low final boiling point (FBP).

When the information was provided it was up to the refinery’s department of production planning to decide if the new product could be blended in the gasoline pool.

1.4.2 Process simulation

The information from the vendor showed that it is unlikely that the catalyst can be implemented without any separation of the oligomer product. If the new catalyst will be implemented it is probable that the plant will start to produce larger amounts of poly-diesel in the future.

In order to separate the gasoline and diesel fractions, possibilities to utilize an existing distillation column were investigated. The evaluation has been done by using design methods in relevant literature such as “Coulson & Richardson´s Chemical Engineering Design” and “Separation Process principles” together with computer software design programs. Aspen HYSYS has been the main software used for the simulation of the column and heat exchangers. Another program named SULCOL has been used for the hydraulic simulation of the flows on trays and in the downcomers. This program is provided by Sulzer which is the manufacturer of the trays in the existing column. A more detailed description of the simulation procedure is given in chapter 3.

2. Literature review

Firstly, a process description is presented in order to give deeper understanding of the conditions and functionality of the polymerisation unit and the problems related to the catalyst.

Secondly, the literature review is focused on various oligomerisation catalysts for conversion of light olefins to gasoline and distillate products. Since the new catalyst is based on amorphous silica alumina (ASA) similar catalysts has been primarily studied. Another type of catalysts that can be used for these purposes are zeolite catalysts often composed of silica alumina as well but unlike the ASA catalyst the zeolite have an ordered pore structure. The use of zeolite catalysts in commercial processes have been studied to some extent. The whole literature review is primarily focused on research that fits the situation, such as reactor conditions and design limitations, at Preem as much as possible.

2.1 Process Description

The purpose of the polymerisation unit is to couple light olefins via a cationic polymerization reaction in order to increase the production of high quality gasoline. The feed to the unit is the C4 cut coming from the catalytic cracker and has the approximate composition according to table 1 [1].

Table 1. Approximate feed composition to the polymerisation unit.

Compound	Composition (mole %)
Iso-butane	45
Iso-butene	15
n-butene	30
Butane	10
1,3-butadien	0,07

Small amounts of impurities like sulphur, oxygenates, nitrogen and sodium are present as well.

A process flow diagram of the catalytic polymerization unit is given in figure 1.

The feed enters a washing column T1601 where a water washing mixture containing phosphate as sodium hydrogen phosphate NaH_2PO_4 is added. The purpose of the washing stage is to remove alkaline components that will neutralize and deactivate the acidic catalyst [1].

After the washing column T1601 the feed enters the vessel D1603. The purposes of this vessel are mainly two. The water added in the washing column is separated from the hydrocarbons and the mixture is diluted with paraffins in order to receive an olefin concentration of approximately 25 %. The dilution is done to decrease the ability for reaction of the olefins. If the olefin concentration becomes higher, “over reaction” of the olefins will be obtained in the reactor resulting in extensive deactivation of the catalyst and production of too high molecular weight products. In addition to diluents the paraffins are used to achieve the correct pressure in the unit [1].

From the vessel the mixture is heated in a couple of heat exchangers to a temperature of about 165 °C, depending on the time in the catalyst cycle, and is then fed to the reactors from the top. If the operation temperature is below 150 °C, phosphoric acid esters can be formed in the reactors and cause downstream corrosion in the process. On the other hand if the temperature is too high, tars are formed and over reaction of the olefins take place resulting in deposition of heavy hydrocarbons on the catalyst (coke). The reactor feed enters from the top and flows downwards passing five catalytic beds with increasing size (length). Under normal operation two reactors are operating at the same time while the third one is on stand-by for catalyst replacement. Between each of the catalytic beds quench nozzles are placed for injection of C4 (paraffins). Both the quench nozzles and the variation of bed size allow for temperature control [2].

The oligomerisation reaction is catalyzed by phosphoric acid in gas phase located around the catalyst particles. An important factor for the catalyst to remain active is the hydration. Hydroxyl groups are required in order to have an active catalyst since the reaction mechanism is based on cationic polymerization. The catalyst can be both too much and too little hydrated, resulting in various operation problems. The over hydration arises when too much water is present in the reactors or if the temperature is too low resulting in a too low acid concentration around the catalyst particles. This behaviour might cause a low conversion of olefins and corrosion problems after the reactors. On the other hand if too little water is present or if the temperature is too high the catalyst will be under hydrated. This will result in an increased acid concentration around the catalyst particles, possibly causing increased conversion of olefins. A higher catalytic activity also causes formation of heavier hydrocarbons and coke that will be deposited on the catalyst surface and in the catalyst pores resulting in cracking of the catalyst particles giving a denser structure of the particles and therefore a higher pressure gradient over the reactor [1].

After the reactor outlet the products are cooled with the reactor feed in three parallel heat exchangers (one for each reactor outflow) and then fed to the flash rectifier T1602 which performs the first separation of the C4 and the reaction products. The C4 is the top product and is recycled to the reactor feed. The quench flow of C4 to the reactors is taken from this stream as well [1].

The bottom stream from the flash rectifier is fed to the stabilizer T1603 where the poly-gasoline C5+ fraction is separated from the rest of the C4. From the stabilizer overhead, one stream is recycled back to the feed surge drum and the rest is cooled down and then sent to cavern storage. Previously this stream was a mixture of mostly propane and butane which required further separation in a subsequent distillation column T1604 but now the feed to the polymerisation unit almost completely consist of C4 molecules [1].

This means that T1604 does not perform any separation and will be shutdown in 2013. However, if the new catalyst requires a split between gasoline and diesel T1604 might be possible to use.

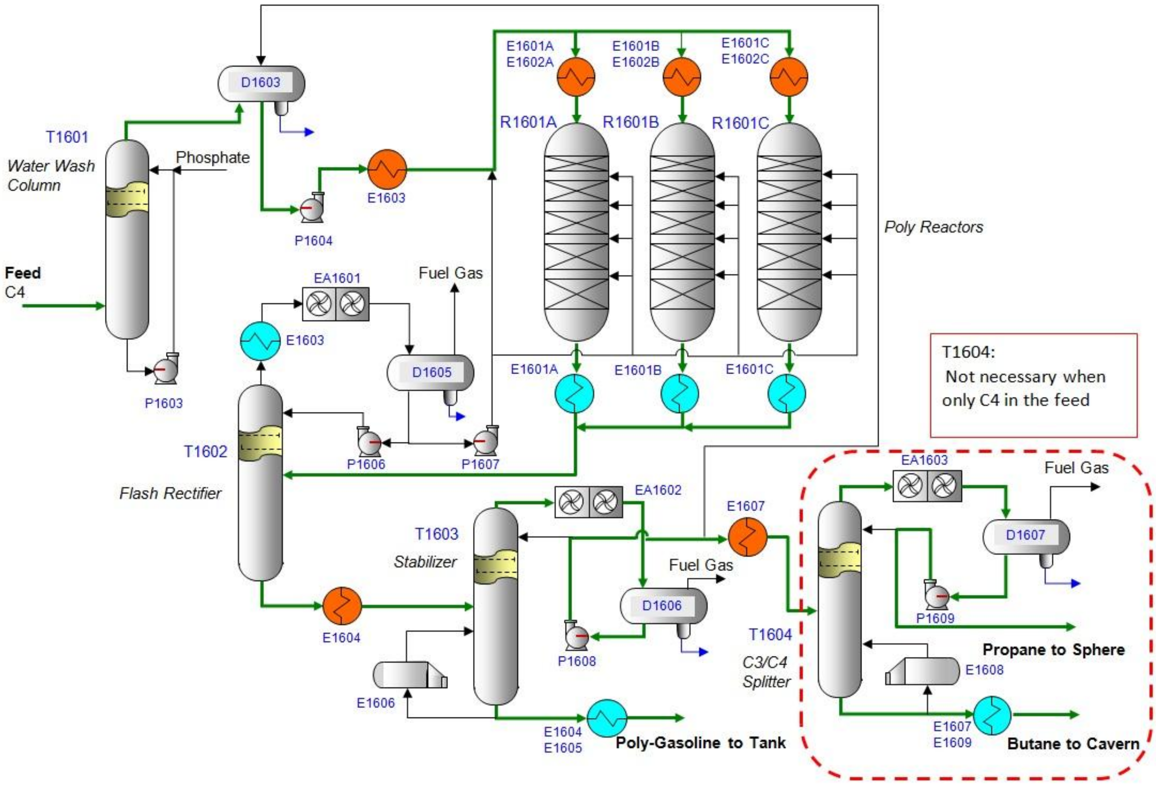

Figure 1. Process flow diagram of the polymerisation unit at Preem refinery in Lysekil.

2.1.1 Important Reactions

The major reactions in the polymerisation unit with C4 as feed are dimerisation and trimerisation of the butene molecules i.e. formation of C8 and C12 olefins. A principle illustration of the reaction mechanism for dimerization of 1-butene to a C8 olefin is shown in figure 2. Further polymerisation occurs to a minor extent and this explains the formation of heavy hydrocarbon on the catalyst that is found when it is dumped for replacement [2].

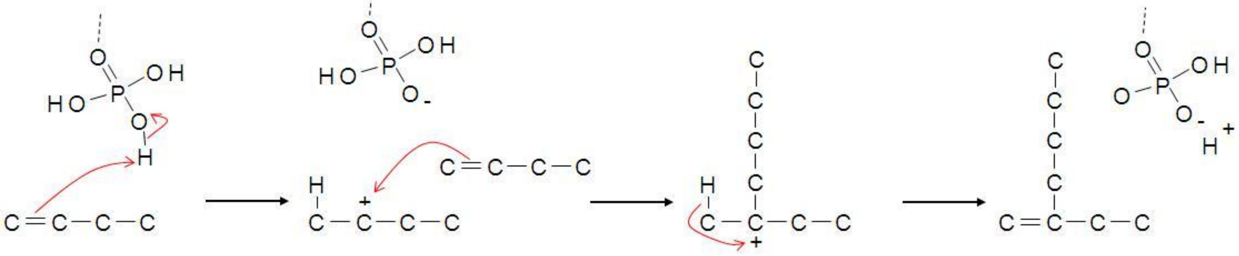

Figure 2. Reaction mechanism for dimerization of 1-butene over SPA catalyst.

Decomposition of the oligomers does also occur by cracking reactions giving a continuum of hydrocarbon chains. However, the operating temperature is fairly low meaning that the cracking reactions only occur to a minor extent. Hydrogen transfer is another reaction that occurs to a minor extent. The hydrogen transfer reaction produces paraffins when hydrogen is transferred particularly from heavy oligomers to lighter species [2].

2.1.2 The current poly-gasoline quality

The poly-gasoline has a unique quality and has an important contribution in the gasoline pool. Due to its high olefin content and high degree of branching it is a mixture of components with particularly high octane number. The amount that is mixed into the gasoline pool is relatively small, up to 10 %, but the poly-gasoline still has a crucial role for improvement of the octane number. The boiling point range of the poly-gasoline is analysed by the laboratory at the refinery with gas chromatography and the result is presented as a TBP-curve. The boiling point range of the product obtained from simulations done by the catalyst vendor is provided according to the ASTM D86 method meaning that the result cannot be compared directly with the TBP-curve. Therefore the TBP-curve is translated to ASTM D86 by using correlations. This work was done by the laboratory. The current poly-gasoline boiling point range according to ASTM D86 is shown in figure 3. The figure shows the cumulative volume fraction versus the corresponding boiling point. A more detailed explanation of distillation curves is given in appendix 4. The poly-gasoline is composed of a lot of components resulting in a relatively wide boiling point range for the mixture. The maximum final boiling point (FBP) of the gasoline pool is 210 °C (ASTM D86) and the FBP of the poly-gasoline is about 220 °C. As a result, the FBP of the poly-gasoline is already at its highest limit. Since the poly-gasoline corresponds to a smaller part of the gasoline pool, the effect of the FBP can be offset to some extent by mixing with lighter components. However, a significant increase in FBP cannot be accepted.

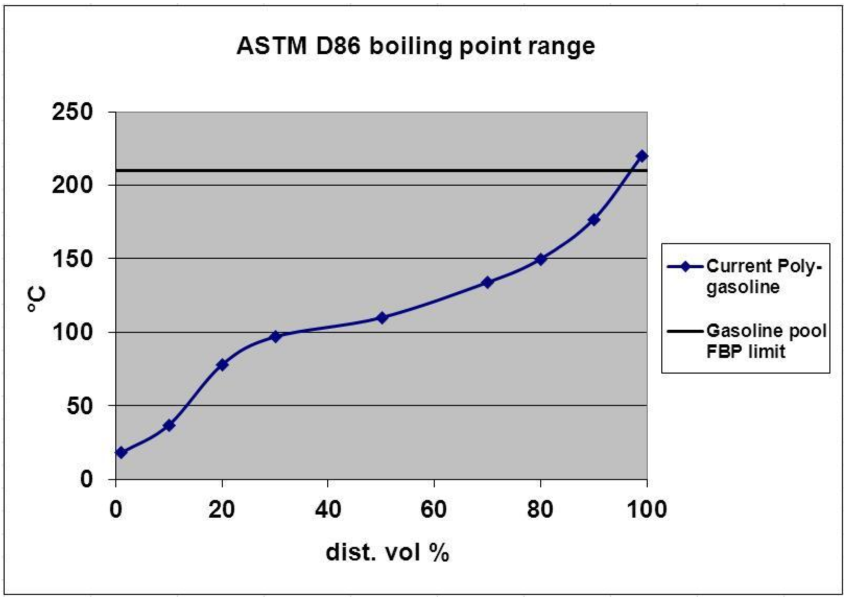

Figure 3. Boiling point range for the current quality of the poly-gasoline.

2.2 Oligomerization catalysts

The technology of the solid phosphoric acid catalysts (SPA) for oligomerisation of C3 and C4 olefins is an old invention while the use of zeolites for this purposes has emerged in comparison relatively recently. Several processes using various types of zeolite catalysts have been developed for this purpose [3]. Unfortunately there is little information present regarding the conversion of olefins over ASA catalysts [4].

The SPA catalyst has a high selectivity towards C8-C9 oligomers. This is probably due to the easy desorption of the relatively hydrophobic C8-C9 olefins from the hydrophilic catalyst surface. If the oligomerisation is performed with a zeolite the degree of branching can be effectively controlled by the size and diameter of the micro porous structure. This term is named as the shape selectivity of the zeolite. However, zeolites in general are not particularly effective in controlling the degree of oligomerisation, but ZSM-57 is one example of a zeolite structure that has shown quite high selectivity towards C8-C9 olefins [3]. Unfortunately, no commercial examples or suppliers for such a catalyst for that purpose have been found in this research.

2.2.1 Reaction characteristics of ZSM-5 zeolits in oligomerisation

For a zeolite catalyst the pore size determines the product structure, while the reaction conditions; temperature, pressure and space velocity determines the molecular weight of the product. For the ZSM-5 catalyst the structure of the higher hydrocarbons is mostly methyl branched since the maximum cross section of the molecules is limited by the pore dimensions of the catalyst. The reaction window in terms of temperature, pressure and space velocity for the oligomerisation reactions is very large but the interesting area of reaction is where the conversion of light olefins is almost complete. The conditions that can be used for oligomerisation of light olefins overlaps with the conditions for cracking of large paraffins and olefins. This means that equilibrium considerations must be taken into account under these conditions. The condition where this effect has significance is at temperatures above 350 °C. If the reaction temperature exceeds this region cracking reactions will be important resulting in a continuous carbon number distribution from the light olefins to the heaviest products. This arises since both the cracking reaction and oligomerisation reaction occur at the same time [5]. However, this is not the purpose of the reaction at Preem and such high temperatures cannot be obtained in the reactors since they are limited to 232 °C as a design restriction.

As mentioned before the temperature, pressure and space velocity are the primary variables determining the average molecular weight of the product. A high initial conversion is obtained when the temperature and pressure is high and the space velocity is low. A higher pressure will always favour the formation of heavier products.

One process for oligomerisation of olefins to motor fuels is presented by the Mobile Company and is called Mobile Olefin to Gasoline and Distillate (MOGD). In this process light olefins are converted to gasoline and distillate products over a ZSM-5 zeolite catalyst. In the commercial example, presented by S. A. Tabak, et.al. a mixture of C3 and C4 olefins is converted to oligomers in a fixed bed reactor process with three reactors operating in series and one on stand-by for regeneration. The product yields are shown in table 2. Selectivity towards gasoline and distillate is greater than 95 %. In 1981 a systematic test run was made in a mobile refinery. The feed consisted of C3 and C4 paraffins and olefins directed from an FCC unit with 62 % olefins. The test run showed that the process could be scaled up to a commercial size plant since the products showed the same yield and selectivity that were previously showed in a pilot plant.[6]

Table 2. Product yield for the diesel and gasoline mode using ZSM-5 catalyst.

	Diesel mode [%]	**Gasoline mode [%]**
C1-C3	1	4
C4	2	5
C5-165 °C Gasoline	18	
165 °C -Distillate	79	
C5-200 °C Gasoline		84
200 °C -Distillate		7

Another process presented by PetroSA is the process called “Conversion of Olefins to Distillate”. According to the research program on this process the process feed can be a mixture of C3, C4 olefins but also C5 and C6 can be used. In the plant of the commercial example located in Mossel Bay the unit consists of three parallel reactor trains where each train consists of three reactors in series. Two trains are operated at the same time while the third is regenerated. The catalyst is named COD-9 which is a ZSM-5 zeolite type catalyst manufactured by Süd-Chemie. PetroSA has also done some further investigation of the COD process in a pilot plant [7].

Results from the pilot plant:

The pilot plant was operated at a pressure of 55 bar, the temperature was varied between 150 °C and 360 °C and the Weight Hourly Space Velocity (WHSV) was between 0,2 and 6 h^{-1}. The feed was a mixture of C3-C6 olefins [7].

The conversion of butene was almost 100 % and the conversion of propene was slightly lower but over 90 %. The product is fractionated in gasoline and diesel fractions with the initial and final boiling points analyzed according to ASTM D86 and showed in table 3 [7].

Table 3. Approximate initial and final boiling points of the gasoline and diesel fractions.

	IBP °C	**FBP °C**
Gasoline fraction	30-40	80-130
Distillate fraction	50-100	250-350

Common for both the MOGD and COD process using the ZSM-5 zeolite is the production of a high quality distillate product but a gasoline product with a lower quality. The motor octane number is favoured by a product with a high amount of highly branched and unsaturated molecules unlike the cetane number which is favoured by molecules with a saturated and linear structure.

2.2.2 ASA catalysts

One manufacturer of ASA catalysts claims that the ASA catalyst is more robust and less expensive compared to a corresponding zeolite catalyst [8, 9]. The catalyst has significantly longer operating cycles compared to the present SPA catalyst and long total life time, since the catalyst can be regenerated several times. This makes the catalyst very cost effective compared to the SPA catalyst which has an extensively shorter life cycle and cannot be regenerated. In addition the ASA catalyst has a high mechanical strength and is robust to the presence of water and other impurities [8, 9]. According to the vendor the pressure build up problems related to this catalyst is almost absent which is the dominating reason for the short cycle time of the present catalyst [10].

A. de Klerk presented a research report regarding the oligomerization of Fisher Tropsch olefins over an ASA catalyst. The investigation was made with similar reactor conditions as the conditions at Preem but the concentration of olefins in the feed was extensively higher about 85 % by weight compared to about 25 % currently at Preem. The feed contained olefins in the range C3 to C6 which is a difference compared to Preem where the feed primarily consists of C4 hydrocarbons. The report is primarily focused on the conversion of olefins to distillate [4].

One of the experiments was performed at 60 bar. At this pressure the distillate selectivity seemed to be almost independent of the temperature in the interval 140-235 °C. The distillate selectivity was between 65-70 % and the olefin conversion between 75-99 %. An important factor for the distillate selectivity seems to be the molecular weight of the feed [4].

The ASA catalyst has an order of magnitude higher activity for the hydrogen transfer compared to the ZSM-5 zeolite. Hydrogen transfer reactions were observed at all investigated temperatures but increases with increased temperature. The hydrogen transfer also contributed to the formation of aromatic compounds which increased the density of the distillate product [4].

Since polymerisation units using a SPA catalyst are often operating at a lower pressure than 60 bar the effect of pressure was investigated in order to investigate retrofit possibilities of such a plant. At 160 °C the pressure was decreased from 60 bar to 40 bar giving a decreased conversion and distillate selectivity [4].

2.2.3 Conclusions about alternative catalysts

As presented in previous sections it is probably not possible to produce a gasoline product with the same distillation range as with the SPA catalyst. The zeolite catalyst uses the same reaction mechanism but the reaction takes place inside the catalyst pores, unlike the SPA catalyst where the reaction takes place outside the surface using the free phosphoric acid in the gas phase. This seems to be an important difference when it comes to the ability of the catalyst to be selective towards gasoline components. According to S. Kulprathipanja, zeolites are in general not particularly effective in controlling the degree of oligomerisation. On the other hand, S.A. Tabak et. al. means that the catalyst pore size determines the product shape and degree of branching while the reaction conditions including temperature, pressure and space velocity determines the molecular weight of the product. However, it seems like the structure of the zeolite has some significance to the degree of oligomerisation but there are still no zeolites available on the market that can accomplish the production of a gasoline quality similar to the quality produced by the SPA catalyst. On the other hand it is probable that the refinery wants to shift the production from poly-gasoline to poly-diesel since the diesel demand has increased in the recent years.

3. Evaluation of the separation section for production of a poly-diesel product

This chapter includes the evaluation of the separation section aiming for production of a gasoline and a distillate product. Firstly a description of the operation and characteristics of the existing column T1604 is given. Secondly the simulation procedure is described in order to analyse the possibilities to utilize the existing column for the separation of the oligomer product in a gasoline and a distillate fraction. This evaluation includes a simulation of the columns T1603, T1604 and related heat exchangers in HYSYS. A detailed hydraulic simulation of the rectifier part of T1604 is performed in SULCOL.

3.1 Description of existing distillation column (T1604)

As mentioned in the description of the oligomerisation process the distillation column T1604 does not currently perform any separation. The column was previously used to split the C3 and C4 fractions mainly composed of propane and butane. The column is equipped with a u-tube heat exchanger reboiler and partial condenser. The top product normally leave the system almost completely as liquid in the propane stream but a fuel gas stream is needed in order to take care of small amounts of methane and ethane that might be present in the system. Minor amounts of water might be present as well which leave the system from the boot in the bottom of D1607 (overhead receiver).

Since the separation of C3 and C4 was almost complete the column is composed of 40 trays with the feed entering on tray 20. In the stripper part of the column a special type of trays called Consep trays are installed. The Consep trays are in particular adapted to handle a high vapour velocity while avoiding liquid entrainment [11]. In the column rectifier part MVG valve trays are installed. A summary of the column characteristics are shown in table 4.

Table 4. Summary of T1604 characteristics.

Height TL/TL	27 300 mm
Internal diameter	982 mm
Number of trays (Feed tray)	#40 (20)
Tray type (1-19)	MVG fixed valve trays
Tray type (20-40)	ConSep trays
Overhead receiver	Horizontal cylinder 1000 x 3000 mm water boot 276 x 650 mm

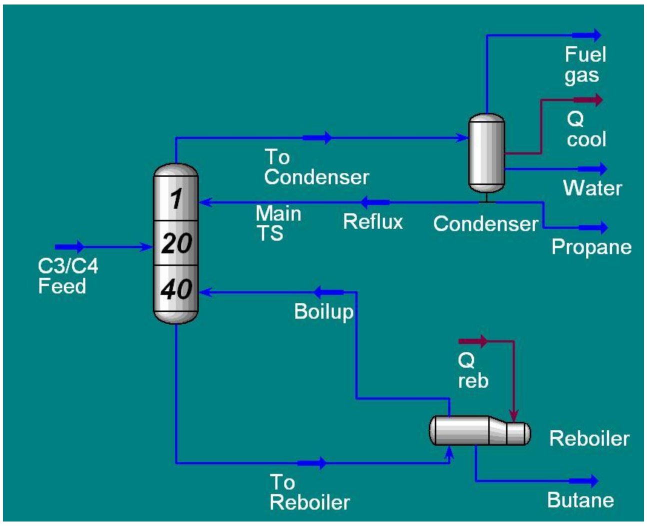

Figure 4. HYSYS flowsheet of the existing C3/C4 splitter (T1604).

3.2 Simulation of existing distillation column by using real plant data

In order to get some ideas of the accuracy of the result from the HYSYS simulation the column was first implemented in HYSYS by using real plant data. The composition of the butane and propane products are analysed by the refinery laboratory regularly meaning that a mixture of the products can be used as a feed to the column. For this simulation, old data was used when the column still performed the split between C3 and C4. Together with additional stream data as feed stream size and reboiler duty obtained from the process explorer program the column was simulated according to a real case. In this simulation a stage efficiency of 1.0 has been used for all trays. The result of this simulation turned out to be very accurate when it was compared to "reality". The deviation of the distribution of the different components was less than 1 % compared to the laboratory analysis but the reboiler duty was about 6 % larger compared to the measured value. However, the measured value is obtained from a steam flow measurement which has an accuracy of about 5 %. This simulation also gives knowledge about the internal flow rates of liquid and vapour on the trays which can be of interest for the tray hydraulics as a comparison to the new system.

3.3 HYSYS simulation of existing distillation columns with the new oligomerisation product as feed.

3.3.1 Product requirements

If the oligomerisation product is separated into diesel and gasoline fractions, the limiting factor is the IBP (initial boiling point) of the diesel (bottom) product. The desired IBP for the diesel fraction is approximately minimum 165 °C (ASTM D86). The FBP for the gasoline is not that critical since it will be lower compared to the present case where no separation is performed.

According to the catalyst vendor the gasoline product will be a greatly branched and olefinic molecule giving good gasoline properties in terms of motor octane number (MON) and research octane number (RON). RON and MON seem to be in the same range with the ASA catalyst compared to the present SPA catalyst. However, high octane numbers means low cetane numbers meaning that the diesel fraction will not fulfil the requirements of a high quality diesel fuel without further treatment. In order to increase the cetane number the diesel fraction should undergo saturation reactions in a hydrotreater in order to remove the olefin structure.

The current gasoline product contains significant amounts of C4 (mainly butane and i-butane). The amount of C4 in the gasoline product is controlled in the stabilizer T1603. The C4 content has mainly two effects on the gasoline. Firstly, it is used to control the vapour pressure of the gasoline mixture. Secondly, a high C4 content is favourable for the octane number. In addition it is usually more economically beneficial to sell the C4 as gasoline than ordinary C4. In the current poly-gasoline product the C4 content is about 15 wt%.

3.3.2 Simulation of the Stabilizer T1603

In order to keep the C4 content at approximately 15 wt% in the gasoline product from T1604 the C4 content must be decreased in the bottom stream from the stabilizer T1603. For that reason the stabilizer is included in the HYSYS simulation as well. The trays in this column will be replaced in the FCC revamp in 2013 in order to meet a higher capacity of the unit. However, it is not expected that the separation of C4 would be a problem, consequently a thorough simulation of the stabilizer was not done in this project. The stabilizer was included in the HYSYS simulation in order to obtain an expected bottom product with the desired C4 content. The C4 content is specified to meet approx. 15 wt% in the gasoline product from T1604. This means that the C4 content in the bottom stream from T1603 depends on the cut point in T1604 and the relative amount of gasoline and diesel in the oligomer product.

3.3.3 Distillation column parameters

Usually when a new distillation column is going to be designed there is a compromise between the number of separation stages and the reflux ratio. A higher reflux ratio means that fewer stages are required to achieve the same separation but at the same time the energy requirements in the reboiler is increased due to increased reflux. In other words there is a compromise between high investment costs or high operating costs. However, in this particularly case the column is already built meaning that the investment cost for the column does not exist. On the other hand, the separation must be adapted to the existing column in order to avoid redesign. Since the diameter of the column is fixed the vapour and liquid loads must be kept within the feasible operating window i.e. avoiding liquid entrainment, flooding and weeping. These factors together with the distillation specification of the products establish if the column can be used for this purpose or not.

The choice of column pressure is dependent on which are the suitable temperature levels in the condenser and the reboiler but also practical limitations because it is unsuitable to have vacuum in the column. As a result of the feed composition to the column it is not favourable to have a high pressure since that would give a very high reboiler temperature. However, it is interesting to have as low temperature as possible since it usually is economically feasible to avoid high temperature levels in the reboiler. In this case there is a heavy cracker oil (HCO) stream used as reboiler medium to the stabilizer (T1603). That stream is available at minimum 250 °C and is located very close to T1604.

A frequent limitation of the minimum pressure is the condenser cooling temperature since the cooling is performed with air coolers. In a hot summer day the air cooling temperature might be 30 °C. In this case the limiting factor for the column pressure is the minimum reasonable pressure in the top section of the column which is considered to be 1,0 barg. This determination arises since the bubble point of the expected top product is about 58 °C at that pressure, thus far above 30 °C. By assuming a column pressure drop of approximately 1250 Pa per tray the reboiler pressure is estimated to 1,5 barg. This estimation might be revised with information from the thorough hydraulic simulation program.

3.3.4 Description of the HYSYS simulation procedure

Feed stream specification

The theoretical poly-gasoline product was specified by the catalyst vendor as a distillation curve according to ASTM D86. Since no specific components were specified pseudo components (hypocomponets) were used in HYSYS to specify the feed. For this type of mixture the number of possible components can be from 10^4 to 10^6. Consequently it is unrealistic to specify that many components in the simulation program. For that reason a number of possible components in a boiling point range are lumped together into a single pseudo component corresponding to a single boiling point. In this way every petroleum assay can be adapted to a set of pseudo components which can be used for modelling of that oil [12].

As default option in HYSYS the pseudo components are evenly distributed over the boiling point range but in order to increase the accuracy of the IBP and FBP of the products distillation curves, pseudo components are defined with a higher density near the cut point. Since the component mixture is composed of hydrocarbons, the Peng-Robinson equation of state has been used in all HYSYS simulations.

The C4 components, mainly i-butane and n-butane, are specified as a separate stream and then mixed with the oligomer stream and used as the feed to the stabilizer T1603. The feed stream conditions as temperature and pressure are taken from plant measurements or estimated by using relevant plant measurements. The temperature is measured at the bottom of T1602 and the pressure is measured at the top of T1602. The pressure drop is assumed to be approximately 1,25 kPa per tray giving the feed stream conditions for E1604.

Short-cut model

Modelling of distillation columns can be done with different degrees of accuracy. As a first approximation of the requirements in terms of number of equilibrium stages, reflux ratio, bottoms and distillate product rate, short cut models were used. This model uses the Fenske-Underwood-Gilliland method for these approximations. There are some problems related to the short cut model e.g. the assumption of constant relative volatility which is a major problem if there are significant liquid- or vapour-phase non-idealities [12]. However, since the system almost exclusively is composed of hydrocarbons the short cut method is expected to give a reasonable approximation of the requirements of the separation. The advantage of short cut models is that they are robust and easy to converge. The result is not very accurate but it is valuable as an initial guess for rigorous distillation models which can be much harder to converge.

In this case the product target specification is an IBP and FBP in a distillation curve and not a composition of a particular component. Usually the target for separation is determined by a minimum fraction of a light key component and a heavy key component in the bottoms and the distillate respectively. This means that it is difficult to use fixed specifications on the light and heavy key in the Short-cut model. Therefore the fraction of light and heavy key components in bottoms and distillate respectively are specified as very low numbers. The external reflux ratio is then specified to meet the actual number of stages in the real column e.g. 40 stages. If the fractions of the key components are specified too low the result will be a very sharp cut and an unnecessarily large reflux ratio. However, in order to meet the specifications of the IBP and FBP of the products the reflux ratio and distillate rate is tuned in the rigorous model. This procedure gives a good initial guess for the rigorous model.

Rigorous model

The rigorous model performs a complete stage by stage calculation of the column by solving the MESH-equations. The MESH- equations represent Material balances, Equilibrium conditions, Summation equation and Heat balance. The HYSYS program uses an equilibrium stage model where full vapour-liquid equilibrium is assumed on each stage if not a stage efficiency is entered by the user. Unfortunately, the stage efficiency is an uncertain parameter. As an estimation of the overall column efficiency the O'Connell's correlation was used [12]. This estimation resulted in a plate efficiency of 70 %. The calculation procedure is given in appendix 1.

The equilibrium stage model in HYSYS requires that the pressure profile is given. As a rough estimate the pressure drop was assumed to be 1,25 kPa per tray. The real pressure drop is mainly dependent on two sources of pressure loss. Firstly, the pressure loss due to the flow of vapour through the valves which is an orifice loss. Secondly, the head of liquid on the plate which is a static pressure loss [12]. Consequently, the pressure drop is greatly dependent on the vapour flow velocity. From the hydraulic simulation both the dry pressure drop and the total pressure drop is calculated for the rectifier part of the column. Since the pressure drop for the stripper part is still unknown the assumed pressure drop of 1,25 kPa is used through the whole column. This is done to avoid underestimation of the reboiler temperature. For the final design a more accurate pressure drop is used in the HYSYS simulations as well.

From the short cut model the estimated parameters are used as an initial guess to ease convergence of the rigorous model. The specified parameters are the reflux ratio and the distillate rate with the assumption that all the distillate leaves the overhead receiver as liquid. This assumption specifies that the mixture is at its bubble point temperature. In order to meet the specifications of the products, the reflux ratio and distillate rate are altered. It is of interest to minimize the reflux ratio in order to favour a minimum energy demand in the reboiler. The reflux rate is also an important parameter in order to fit the column internal vapour and liquid flow rates to receive satisfactory plate hydraulics. When proper top and bottom products are achieved, relevant data are extracted from HYSYS in order to make a more detailed estimate of the plate hydraulics. An illustration of the simulation procedure in HYSYS is shown in figure 5.

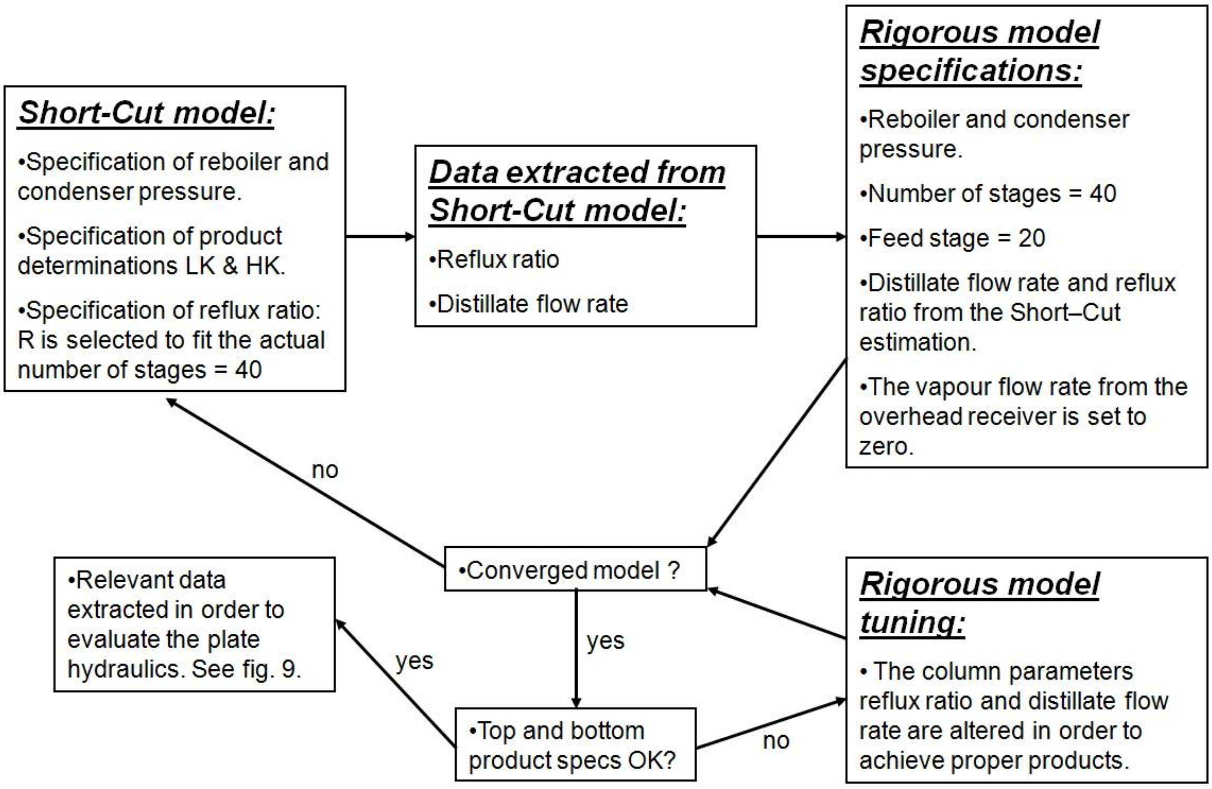

Figure 5. Simulation procedure for the existing column T1604 in ASPEN HYSYS.

3.4 Heat exchanger simulation

It is important for the hydraulic evaluation of T1604 to get a reasonable estimation of the condition of the feed. Therefore the heat exchangers related to T1603 and T1604 must be included in the simulation. In order to avoid extensive reconstruction it has been assumed that the bottom stream from T1603 enters the heat exchanger E1604 and then E1607. The new suggested PFD is shown in appendix 3. A discussion about a suitable heat exchanger configuration is given in chapter 4.6.

For the HYSYS simulations the existing heat transfer data from the manufacturer’s datasheet has primarily been used. This is considered to give a good estimate for E1604 since the streams will not deviate significantly from the original design. However, in the case of E1607 the stream composition and flow rate will change significantly affecting the overall heat transfer coefficient. E1607 is designed for a maximum temperature of 120 °C meaning that it is not likely that this heat exchanger can be used for the required temperatures which are significantly higher. In this case it seems unnecessary to calculate a new heat transfer coefficient for that heat exchanger. Instead a new heat exchanger should be placed at this position. For the HYSYS simulation this heat exchanger is simulated by assuming a minimum temperature difference of 20 °C in order to obtain a reasonable heat recovery from the bottom stream from T1604.

3.5 Plate Hydraulic simulation

3.5.1 Fundamentals about plate hydraulic design

The satisfactory operating range in terms of vapour and liquid flow rates is specific for each column and each system in terms of composition, operating pressure and temperature. The area of satisfactory operation is mainly determined by four conditions that can apply if either the vapour or liquid flow rates become too high or too low. Flooding is caused by two reasons, either by carry-over of liquid to the next plate by high vapour velocities or by liquid backing up in the downcomers by high liquid flow rates. Weeping occurs when liquid starts to flow down through the valves caused by insufficient vapour flows. Insufficient liquid flow rates may give a condition named coning which is when the vapour pushes the liquid back from the holes giving a poor liquid vapour contact [12]. A principle illustration of a performance diagram is shown in figure 6.

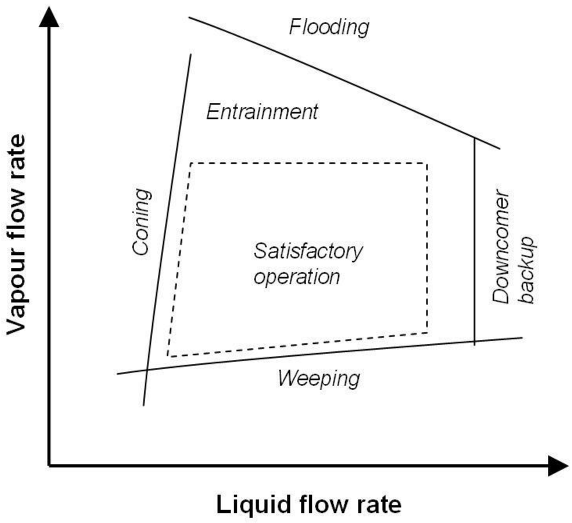

Figure 6. Principle illustration of a tray performance diagram.

In order to investigate whether the new vapour and liquid flows in T1604 are feasible a simulation program named SULCOL, provided by the tray manufacturer Sulzer, has been used. Unfortunately, only the rectifier part containing the MVG valve trays can be simulated by using this program. The evaluation of the stripper part of the column, containing the ConSep trays, needs to be performed by the manufacturer. As a result of the restricted simulation opportunities the liquid and vapour loads can only be adapted to the performance of the rectifier trays.

In this case the problem is related to an already existing column, meaning that a conventional tray hydraulic optimisation is not relevant. As a first step the plate hydraulics were analysed by using the plate characteristics related to the existing case i.e. avoiding redesign of the trays and downcomers. This means that the internal liquid and vapour flow rate must meet the requirements of the existing tray design.

In principle there are two main parameters that determine the internal vapour and liquid flow rates. These parameters are the feed quality, which is the fraction of liquid in the feed, and the reflux ratio. The feed quality is dependent on the temperature, pressure and the content of C4 which most probably will be present in vapour phase at the feed conditions. The second parameter affecting the internal flow rates is the reflux rate. If the cut point is fixed the boil-up rate is determined by the reflux rate giving a change of the internal vapour and liquid flows. On the other hand, the reflux rate also has an effect on the product quality in terms of the performance of the separation between gasoline and diesel. However, these two parameters can be used to achieve appropriate flows and plate hydraulics adapted to the existing tray configuration. An illustration of the effect of the feed quality and reflux rate on the column internal flows is shown in figure 7.

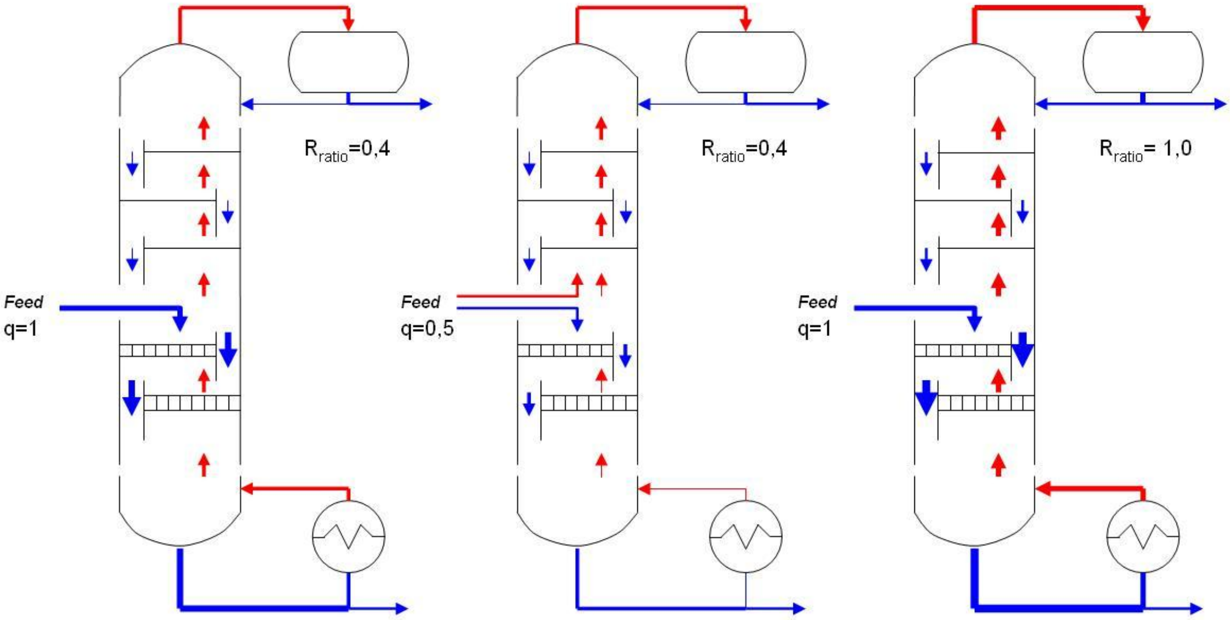

Figure 7. The effect of feed quality and reflux rate on the column internal flows. Red streams mean vapour flows, blue streams mean liquid flows and the thickness of the lines illustrate the size of the flow.

3.5.2 Hydraulic evaluation using the SULCOL software

The SULCOL program is a hydraulic design software provided by the tray manufacturer SULZER. The purpose of the use of the program is to obtain a thorough analysis of the internal flows on the trays through the column. There are some basic requirements that should be fulfilled on the trays for good liquid/vapour contact on the trays. As discussed previously the vapour and liquid flows should be within acceptable limits in order to avoid flooding, weeping, coning and downcomer backup. For that reason it is necessary to check both the maximum and minimum vapour and liquid loads that can be obtained on the trays.

The input data required in the program is related to the geometry of the trays and the characteristics of the vapour and liquid fluid flows that pass the trays. The data required for the fluids are the vapour and liquid loads, densities, viscosities and the liquid surface tension. These data can be extracted from the HYSYS simulation and implemented into SULCOL. The data related to the tray geometry is more extensive. The most important parameters and their value for T1604 are shown in table 5. From the hydraulic simulation a more accurate value for the pressure drop of the rectifier part is calculated. Therefore this pressure drop is implemented in HYSYS in order to obtain more accurate results for the distillation. This procedure requires some degree of iteration of data between the simulation programs. A description of the most important calculated parameters, that determines the feasible design, is given in next chapter (3.5.3).

Table 5. Required characteristics of the tray geometry for the hydraulic evaluation.

Tray type	*MVG*
Tray diameter [d]	*982 mm*
Number of tray passes	*1*
Tray thickness [thk]	*2 mm*
Tray spacing [TS]	*600 mm*
Percentage open area	*12,19 %*
Valve lift	*8 mm*
Downcomer top width [wt]	*250 mm*
Downcomer bottom width [wb]	*250 mm*
Downcomer Clearance [cle]	*40 mm*
Outlet weir height [hw]	*50 mm*

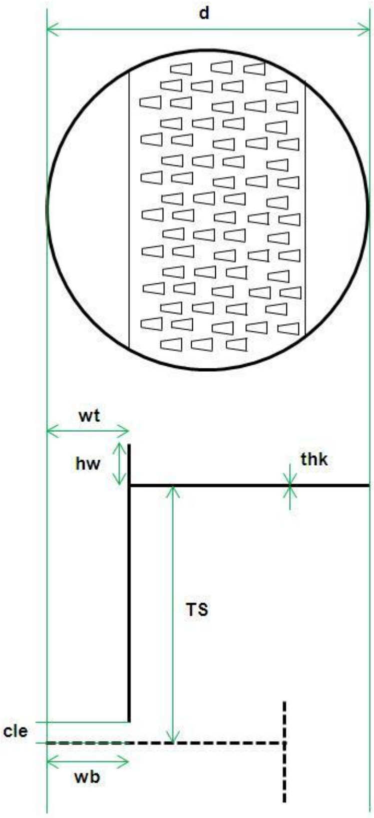

Figure 8. Tray geometry illustration

An illustration of the SULCOL simulation procedure and the exchange of data between the simulation programs are described in figure 9.

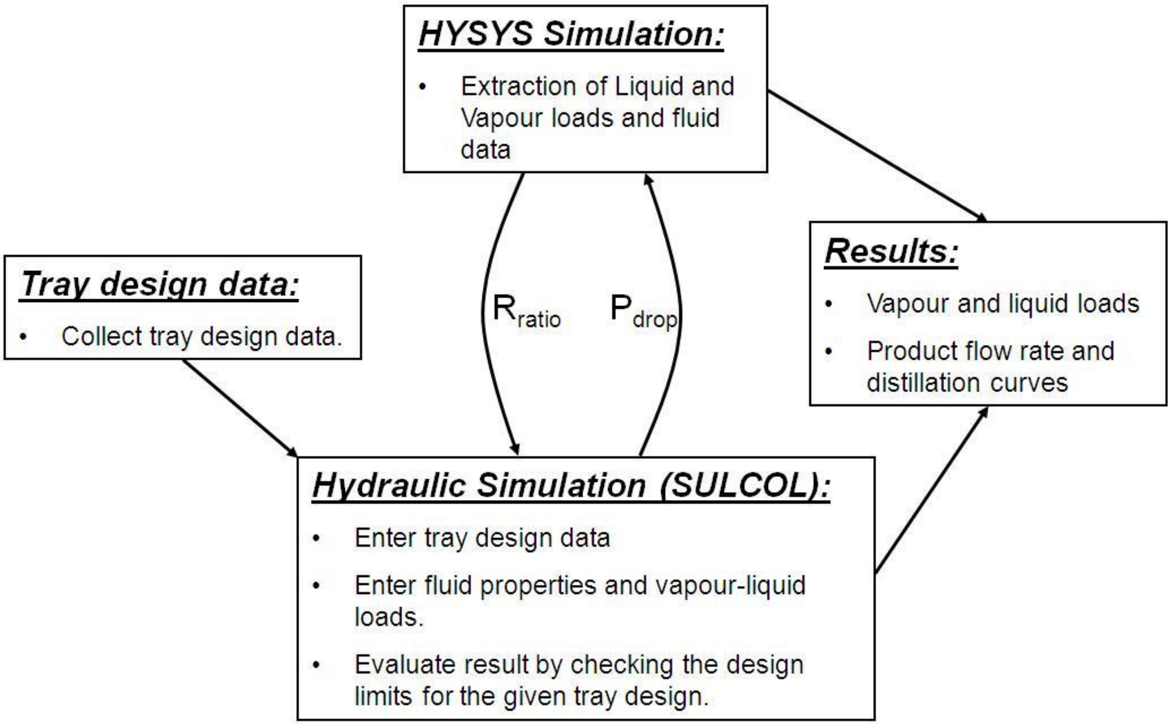

Figure 9. Simulation procedure of the tray hydraulics.

3.5.3 SULCOL output design parameters

In order to obtain a feasible and effective tray design there are parameters related to the flow on the trays and in the downcomers that are used in the SULCOL program. The most important parameters are described below and the limits related to the tray configuration in the rectifier part of T1604 are presented in table 6.

Useful capacity % and Flood %:

- These are two measurements of vapour capacity adapted to different tray types. For the MVG valve trays the useful capacity measurement should be used [13].

Weir loading:

- Measure of the amount of liquid that passes the outlet weir. The unit is area per time which is the same as volumetric flow rate per weir length [13].

Pressure drop:

- The total pressure drop is the sum of the dry pressure drop caused by the vapour flow through the tray open area and the head of clear liquid on the tray. This parameter may be a limiting criterion especially in low pressure columns [14].

Downcomer froth backup %:

- This limitation is related to aerated liquid (froth) stack-up in the downcomer. The head of liquid in the downcomer is a balance between the pressure drop across the tray and the head loss under the downcomer [14].

Downcomer head loss:

- The head loss is equivalent to the pressure loss that arises when the liquid from the downcomer passes through the downcomer clearance. As a consequence the head of liquid in the downcomer is related to the head loss. There is a minimum head loss required for good liquid distribution over the tray [13].

Downcomer flood:

- Occurs when the liquid loads are high or when the downcomers are too small giving high liquid velocity and short residence time. This leads to vapour entrainment through the downcomer to the tray below which in turn might give rise to foaming and downcomer froth back-up. The limiting value is primarily a function of the vapour-liquid density difference [14].

Spray factor:

- The spray regime is defined as a continuous vapour phase with liquid droplets. It is like a fluidization on the tray that arises when the weir loading is low in combination with high vapour flows [13]. The consequence is that the trays are blown dry. There are in principle four ways to increase the spray factor; increase weir height, increase open area, decrease opening size and decrease weir length. The most effective is to decrease the weir length which can be done by using a Picket-Fence outlet weir [15].

Table 6. Design limits of tray related flow characteristics

Parameter	Min	Max
Useful capacity [%]	10	95
Weir loading [m^3/mh]	5,37	116,24
Dry drop [mmH_2O]	7,62	60,85
Pressure drop [mbar]	0	20
D.C. froth backup [%]	5	90
D.C head loss [mm]	2,54	38,1
D.C flood [%]	0	80
Spray factor	2,78	N/A

4. Results and discussion

4.1 Maximum gasoline mode

The maximum gasoline mode is primarily interesting if it is possible to avoid reconstruction of the plant separation section meaning that the new oligomer product must meet the requirements of the current poly-gasoline in terms of the heavy end of the boiling point range. If re-construction is necessary it might be more interesting to adapt the unit for maximum diesel production.

With the ASA catalyst, there is no mechanical degradation during the run and thus no pressure drop issues thanks to its high mechanical strength. The temperature is gradually increased during the cycle to compensate deactivation of the catalyst linked to impurities in the feed. The operation is stopped when the end of run temperature is reached. The catalyst is regenerable and is thus sent to regeneration. Regenerated catalyst is reloaded to proceed with the next runs. Numerous regenerations can be performed while maintaining similar performances of the unit [10].

According to the vendor of the ASA catalyst the catalyst life cycle length can be increased to 1,5 to 2 times the cycle length of the SPA catalyst.

The octane numbers (RON and MON) which are important parameters for the gasoline product is estimated by the catalyst vendor to remain on the current level.

According to the vendor, the expected oligomer produced is composed by 91% gasoline boiling range material and 9% diesel boiling material. The oligomers produced with the SPA catalyst is composed of 98% gasoline boiling range material and 2% kerosene boiling material. This is obtained for an overall conversion ≥ 90%. However, with the ASA catalyst it is possible to tune the product slate from maximum gasoline to maximum distillates by varying operating severity. It provides an additional flexibility in this respect as compared to alternate technologies that can only produce gasoline.

For a given feed composition and within an existing unit design, it is mainly the temperature and internal recycle that can modify the selectivity towards gasoline. It is possible to increase the gasoline selectivity by decreasing the temperature but the conversion will be decreased as well, all the other parameters being fixed by existing design. Within the existing unit design, the selectivity towards gasoline cannot be pushed to more than 91% without extensively decreasing the conversion [10]. The amount of diesel boiling range components is considered to be too large for usage directly in the gasoline pool. Therefore it is probably not possible to perform a test run of the catalyst in the present plant i.e. without any separation of the oligomer product.

4.2. Simulation results for maximum gasoline mode

An illustration of the process flow sheet created in HYSYS is shown in appendix 6. In this chapter the extracted results from HYSYS are presented. The results from the hydraulic analysis are presented here as well.

HYSYS results

When the unit is operated in maximum gasoline mode the amount of diesel produced, (TBP>170 °C), is fairly small. The distillate and bottoms flow rate are presented in table 7. The reflux ratio was altered between 0,1 and 0,5 in order to generate various flow distribution within the column. It should be noted from the table that the amount of distillate and bottoms is about 65 % and 35 % respectively. This uneven product distribution in combination with a low reflux ratio contributes to a deviation of internal flows of the column compared to the current operation. When the column worked as a C3/C4 splitter the amount of distillate and bottoms was about 10 % and 90 % with a reflux ratio of about 5-8. Due to this fact it is not probable that the hydraulic parameters can be approved for the present tray and downcomer design. This is both due to the required change of product distribution, reflux ratio and column pressure. This will be explained in more detailed later in the results.

Hydraulic evaluation

The hydraulic evaluation was done according to the principle described in chapter 3.5.2. The results are shown in tabular form in the bottom part of table 7. The red numbers represents calculated results that appear to be outside the allowable design limit. As can be seen in the table, there are no feasible alternatives that fulfil the requirements of the size of liquid and vapour flow. For the highest reflux ratio the useful capacity exceeds the allowable 95 % indicating a too large vapour velocity. Also the dry pressure drop exceeds the maximum value of 60,85 mmH_2O indicating a too large vapour velocity as well. However, at the same reflux ratio the downcomer head loss and spray factor are less than the required minimum indicating a too low liquid load. When the reflux ratio is decreased the vapour related design restrictions appear to be inside the limit but the liquid related restrictions becomes even worse. This means that it is impossible to find a case that meet the current column design for the maximum gasoline mode. The general problem is that the column pressure must be decreased in order to avoid mechanical design limitations of the column. A decreased column pressure causes lower vapour density and higher vapours velocity. Therefore the hydraulic parameters related to vapour velocity appear to be outside the limits. When the reflux ratio is decreased in order to decrease the vapour velocity, low liquid flows becomes the limiting factor instead.

Table 7. Results from HYSYS simulations and hydraulic simulation of T1604 for various reflux ratios.

Calculated output HYSYS	**Case 1**		**Case 2**		**Case 3**		**Case 4**		**Case 5**	
Distillate flow rate (kg/h)	8640		8640		8640		8640		8640	
Bottoms flow rate (kg/h)	4700		4700		4700		4700		4700	
Feed quality (vap. frac.)	0,26		0,26		0,26		0,25		0,25	
Feed temperature (°C)	131,1		131,1		130,8		130,4		129,5	
Feed pressure (kPa)	250		250		250		250		250	
Reflux ratio	0,5		0,4		0,3		0,2		0,1	
Reboiler temp (°C)	248,6		248,3		247,8		246,7		244,3	
Reboiler duty (kW)	1493		1384		1276		1171		1071	
Condenser temp. (°C)	58,4		58,4		58,4		58,4		58,3	
Condenser duty (kW)	1728		1619		1511		1405		1304	
Calculated output SULCOL	**max**	**min**	**max**	**min**	**max**	**min**	**max**	**min**	**max**	**min**
Useful capacity [%]	111,3	104,0	102,7	95,7	94,1	88,0	86,6	80,8	79,9	75,2
Weir loading [m^3/mh]	11,13	10,41	8,80	8,04	6,42	5,73	4,17	3,48	1,96	1,39
Dry drop [mmH_2O]	89,15	76,75	75,19	64,42	62,44	53,45	50,92	43,63	41,34	35,56
Pressure drop [mbar]	9,60	8,39	8,19	7,13	6,88	5,99	5,66	4,93	4,59	3,98
D.C. froth backup [%]	44	40	38	35	33	30	28	25	23	20
D.C head loss [mm]	0,85	0,75	0,53	0,44	0,28	0,23	0,12	0,08	0,03	0,01
D.C flood [%]	11	11	9	8	7	6	4	4	2	1
Spray factor	1,27	1,38	1,31	1,42	1,34	1,43	1,31	1,37	1,15	1,14

4.3 Alternatives for re-design

There are several alternatives to change the operating conditions in order to decrease the vapour loads and at the same time increase the liquid loads. There are also re-design possibilities to overcome the spray factor and downcomer head loss problem.

4.3.1 Process operation changes

- <u>Higher pressure in T1604.</u>

The simulations were done with a condenser pressure of 1,0 bar(g), a higher pressure gives higher vapour densities and therefore lower vapour volumes giving a decreased vapour velocity. However, a higher pressure means higher temperatures in the whole column including the reboiler that needs to be heated with a heat source on a higher temperature level. In addition problems may arise regarding the design restrictions in terms of temperature and pressure of the column.

- Lower C4 content in the feed.

Another way to decrease the vapour loads is to reduce the C4 content in the feed to T1604. In the simulations for the maximum gasoline mode the C4 content is about 10 wt % in the bottom stream from T1603 in order to meet the C4 content in the current poly-gasoline. However, if the C4 content is reduced in the feed to T1604 the corresponding amount needs to be separated in T1603. This requires a careful split between the C4 and oligomer components which might not be achievable by T1603. The most obvious problem that might arise if almost all C4 is to be separated is that gasoline components end up in the C4 stream from T1603.

4.3.2 Tray design changes

In order to adapt the tray design to the new operation, there are in principle two things that must be done. The trays must be adapted to handle higher vapour flows and at the same time be able to handle lower liquid flows. In this case three design changes were considered to be required in order to meet the vapour and liquid loads for the new separation.

- Decrease downcomer clearance.

The downcomer clearance can be decreased in order to increase the downcomer head loss. This must be done in order to obtain a feasible liquid distribution on the tray.

- Use Picket-Fence outlet weirs on the trays.

A picket-fence weir can be used for designs with low liquid loads. The purpose is to retain more of the liquid on the tray and slowing down the velocity to prevent the tray from being blown dry [15]. However, the use of a picket weir will result in a certain degree of vapour blockage when the outlet weir decreases the possibilities for vapour expansion over the downcomer.

- Decrease the bottom width of the downcomers.

By decreasing the bottom with of the downcomer the inner wall of the downcomer will be angled giving a larger volume for vapour expansion over the tray deck resulting in lower vapour velocity. High vapour velocity is a major problem in this case, therefore this action has an important impact on the performance factors. By decreasing the vapour velocity the capacity condition related to flooding decreases, as well as the dry pressure drop which both pose problems at the highest vapour loads. In addition the spray factor is favoured by the lower vapour velocities as well.

With the new tray design a new set of data were obtained presented in table 9. The tray design changes are given in table 8. There are different sources of minimum allowable effective weir length. Exxon mobile has 70 % as acceptable blockage and DOW has 80 %. Also 55 % has been suggested as the maximum blockage of the outlet weir [15]. In this case the design is based on a blockage of almost 60 % of the total weir length. A very high blockage increases the risks for creation of stagnant zones close to the weir giving a poor liquid flow pattern [15].

As can be seen in the table the low liquid loads are still a limiting factor for cases 3-5 related to the lower reflux ratios. The downcomer clearance should be further decreased in order to allow lower liquid loads. However, the decreased downcomer bottom width had a significant effect of the vapour velocity giving an acceptable capacity parameter below 95%. The reduced vapour velocity together with the use of a picket-fence outlet weir resulted in a spray factor within the allowable limits. The reason why the spray factor is too low for case 1 is because of the highest reflux ratio gives higher vapour loads. The spray factor for the maximum load of case 2 is exactly on the lower limit meaning that a reflux ratio of 0,4 corresponding to case 2 should be acceptable for the new design.

Table 8. Changes of tray design parameters.

	New design	*Original design*
Effective outlet weir length	*350 mm (59,1 %)*	*856 mm (100 %)*
Downcomer bottom width [wb]	*100 mm*	*250 mm*
Downcomer Clearance [cle]	*20 mm*	*40 mm*

Table 9. Hydraulic simulation results of the new tray design.

Calculated output SULCOL	**Case 1**		**Case 2**		**Case 3**		**Case 4**		**Case 5**	
	max	**min**	**max**	**min**	**max**	**min**	**max**	**min**	**max**	**min**
Useful capacity [%]	89,2	83,3	81,5	75,9	73,5	68,6	66,4	61,9	60,9	57,5
Weir loading [m^3/mh]	27,22	25,45	21,52	19,65	15,70	14,00	10,20	8,50	4,79	3,40
Dry drop [mmH_2O]	57,45	49,46	48,45	41,52	40,24	34,44	32,81	28,12	26,64	22,92
Pressure drop [mbar]	7,10	6,32	6,14	5,46	5,24	4,64	4,35	3,84	3,49	3,05
D.C. froth backup [%]	35	32	30	27	25	23	21	19	17	15
D.C head loss [mm]	7,08	6,19	4,42	3,69	2,36	1,87	0,99	0,69	0,22	0,11
D.C flood [%]	11	11	9	8	7	6	4	4	2	1
Spray factor	2,69	2,92	2,78	3,00	2,82	3,00	2,73	2,85	2,36	2,32

4.4 Thorough analysis with re-designed trays

In order to obtain a more accurate result for case 2, the calculated pressure profile was implemented in HYSYS and a new set of vapour and liquid loads were obtained and implemented in SULCOL. This procedure was performed until constant data were obtained. The pressure drop for the stripper part was also in this case assumed to be 1,25 kPa per tray.

After the third iteration the pressure drop and internal vapour and liquid flows did not change significantly. The mean pressure drop for the rectifier part was therefore set to 588 Pa per tray according to table 9. The internal liquid and vapour loads and properties obtained from HYSYS are given in appendix 6. The final result of the simulation according to case 2 is presented in table 10. The expected TBP distillation curves for the gasoline and diesel product related to case 2 are presented in figure 11 and in tabular form in table 11.

The cut obtained between the gasoline and diesel fractions are relatively good despite the low reflux ratio. However, this separation should be sufficient since it is only the diesel fraction that might have an IBP restriction close to the cut point. If this becomes a problem the cut point can easy be moved a few degrees. It should be noted that the spray factor is obtained just under the minimum limit (2,78) for the tray with the highest flow. However, since such a low number is obtained only on one or two trays it should not cause any major problems.

Table 10. Simulation results for the thorough simulation with re-designed trays

Calculated output HYSYS	***Case 2***	
Distillate flow rate (kg/h)	*8640*	
Bottoms flow rate (kg/h)	*4700*	
Feed quality (vap. frac.)	*0,25*	
Feed temperature (°C)	*130*	
Feed pressure (kPa)	*250*	
Reflux ratio	*0,4*	
Reboiler temp (°C)	*246*	
Reboiler duty (kW)	*1385*	
Condenser temp. (°C)	*58*	
Condenser duty (kW)	*1619*	
Calculated output SULCOL	***max***	***min***
Useful capacity [%]	*81,7*	*77,0*
Weir loading [m^3/mh]	*21,56*	*19,87*
Dry drop [mmH_2O]	*48,67*	*42,91*
Pressure drop [mbar]	*6,16*	*5,59*
D.C. froth backup [%]	*30*	*28*
D.C head loss [mm]	*4,44*	*3,77*
D.C flood [%]	*9*	*8*
Spray factor	*2,77*	*2,94*

Table 11. Boiling point range of the gasoline and diesel products

wt %	*TBP gasoline (°C)*	*TBP diesel (°C)*
1	*-19,6*	*164,4*
5	*-9,9*	*171,2*
10	*-3,7*	*176,1*
20	*89,3*	*184,5*
30	*107,7*	*193,8*
40	*113,5*	*204,1*
50	*117,3*	*215,3*
60	*123,6*	*226,6*
70	*132,0*	*239,5*
80	*143,4*	*252,9*
90	*156,7*	*284,2*
95	*163,7*	*311,4*
99	*173,2*	*334,9*

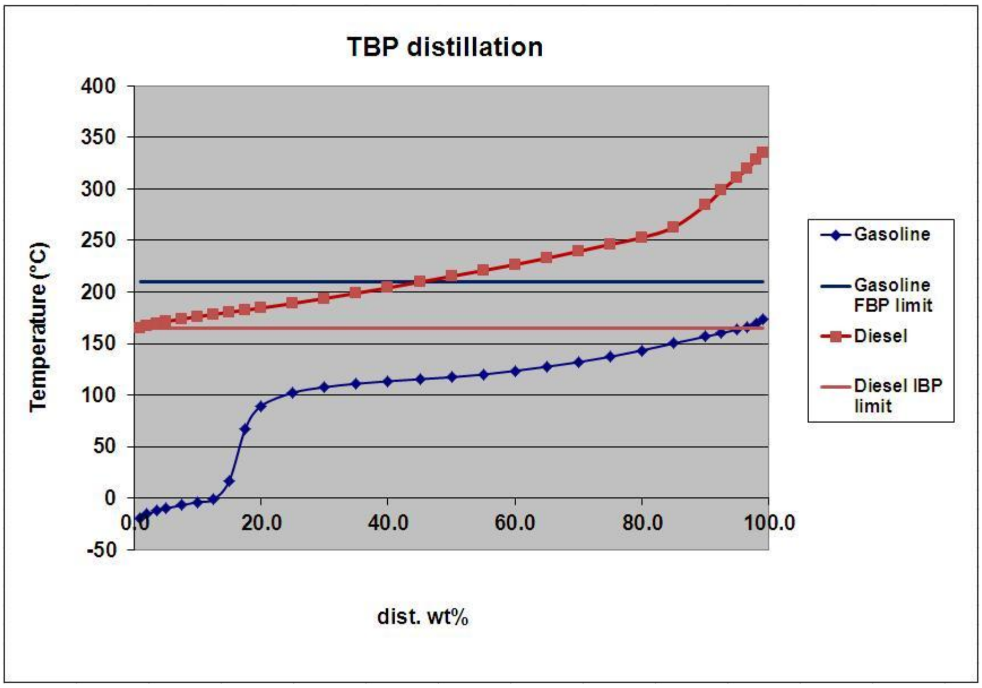

Figure 10. Distillation curves for the gasoline and diesel products

4.5 Maximum distillate mode

Unfortunately, the input data required for the evaluation of T1604 in maximum distillate mode was not provided from the catalyst vendor on time in order to perform the evaluation on the same basis as for the maximum gasoline case. However, some comments and discussion is given here related to the utilization of T1604 and operation of the unit in maximum distillate mode.

According to the catalyst vendor the typical product ratio can be pushed to 40 % gasoline and 60 % middle distillate depending on the severity and cut point. From the previous results discussion it is clear that an increased amount of middle distillate favours the possibilities of utilization of T1604. However, it is still unclear if the column can be used without reconstruction of the internals. Another aspect is the C4 amount that must be even more decreased when the amount of gasoline in the oligomer mixture is decreased. This might cause problems in the stabilizer T1603.

4.6 Hydro-treatment of the distillate fraction

Due to the high content of olefins and branched molecules the distillate fraction does not fulfil the specifications of a diesel fuel. In order to adapt the properties of the diesel fraction the stream needs to undergo hydro-treatment in the mild hydro cracker unit (MHC). This hydro-treatment is necessary in order to saturate the molecules and thereby increase the cetane number. The hydro-treatment must be done for the diesel fraction produced from the polymerisation unit regardless of maximum gasoline or maximum diesel production.

The distance between the polymerisation unit and the MHC unit is quite large, approximately 500-600 m. Fortunately, there is an existing pipe previously used for another purpose that can be used for transportation of the poly-diesel between the units.

The MHC unit normally operates in two different modes which are related to different feed heavy atmospheric gas oil (HAGO) and vacuum gas oil (VGO). Most of the time the MHC unit operates in HAGO mode but it is of interest to include the poly-diesel as a sub-feed in both HAGO and VGO mode.

According to the information given from the vendor of the hydro-treatment catalyst, there should be no problems including the poly-diesel as a sub-feed to the MHC unit in both HAGO and VGO mode. The total feed to the MHC unit is normally between 280-350 m^3/h meaning that the poly-diesel corresponds to approximately 3 % of the total feed. Consequently, the effect on the product will be minimal. However, according to the vendor the bromine number, corresponding to the amount of olefins in the feed, will be slightly increased which might result in a few degrees higher temperature difference over the first bed in the first reactor. A more problematic factor according to the vendor might be the amount of di-olefins in the poly-diesel. The di-olefins might cause fouling problems in the process furnace prior to the reactors in the MHC unit. However, the di-olefins are very reactive in the polymerization plant so it is likely that the amount of di-olefins in the poly-diesel will be very low.

4.7 Heat exchanger configuration

A thorough evaluation of necessary heat exchangers has not been done in this project. However, a discussion regarding the feasibility and re-use of existing heat exchangers is given here. Heat exchangers that are affected by a possible reconstruction of the unit are: E1605, E1607, E1608 and E1609. The new proposed configuration is shown in appendix 3. It should be mentioned that the cooling media in E1605 and E1609 is water meaning that there is no major problems resulting from slight changes in the transferred effect.

E1605: In the current design E1605 is used as a cooler for the poly-gasoline stream to tank. From a piping construction point of view it is feasible to keep this heat exchanger as a gasoline cooler in order to decrease the needs for pipe reconstruction. However, this heat exchanger will probably have a bit over-dimensioned due to the decreased gasoline flow and lower temperature of the gasoline entering the heat exchanger. Since the temperature in the overhead receiver D1607 is fairly low (58° C) for the new design, it should be checked if a heat exchanger is necessary at all at this position.

E1607: Can probably not be used at the current position for the new operation mainly due to limitations in design temperature. However, it is feasible to have a heat exchanger at this position also in the future in order to favour energy recovery from the hot bottom stream from the column. By installing a new heat exchanger the size can be adapted in order to achieve desired conditions.

E1608: The splitter reboiler must probably be replaced as well. This is both due to temperature design limitations but also an increased power demand for the new separation. In addition the temperature driving force will be significantly decreased if HCO is used as the heating medium, meaning that the required effect probably requires a larger heat transfer area.

In the current design the condensation of medium pressure steam is used as heating medium which requires significantly smaller heat transfer area.

E1609: This heat exchanger is probably most feasible to use as butane cooler. The conditions as flow and required temperature change are quite similar to the current design. In addition, this configuration decreases the need for pipe reconstruction.

5. Conclusion

It is clear that there several potential advantages with the ASA catalyst compared to the current SPA catalyst. However, due to the increased amount of heavier hydrocarbon produced, the ASA catalyst is not feasible to be implemented in the current unit configuration. The gasoline-stream produced cannot be blended directly into the gasoline pool without complications.

In order to use the ASA catalyst the oligomer product requires further separation. In this thesis the possibilities to utilize an existing column (T1604) has been investigated. The conclusion is that it is probably possible to utilize T1604 as a gasoline/diesel splitter for the maximum gasoline case but the column internals in the rectifier section need to be replaced. The maximum diesel case has not been simulated but this case should have an increased applicability of using T1604. This is due to the increased amount of bottoms in the maximum diesel case. However, it is likely that the column trays require reconstruction also in the maximum diesel mode, mainly due to high vapour velocities in combination with low liquid loads. As mentioned in the discussions, the column pressure can be increased in order to decrease the vapour velocities. An increased pressure decreases the vapour density and thereby the vapour velocity but the temperature level in the reboiler is increased as well. A higher temperature decreases the possibilities that HCO can be used as heating media. Another restriction is due to mechanical design limitations. Consequently, the possibility of utilize T1604 with minor reconstruction and maximum adaption to the current polymerisation unit is a trade off between different parameters.

5.1 Suggestions for further investigation

In order to complete the investigation the evaluation of T1604 in max diesel mode should be done. When the preferred conditions related to the column are fixed the heat exchanger design can be done. After that an economic evaluation including all reconstruction costs and benefits related to the new catalyst should be carried out in order to assess the value of a potential project.

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Appendix 1. Estimation of plate efficiency

This appendix includes the calculation procedure of the estimation of the plate efficiency by using O'Connell's correlation for overall column efficiency. The procedure follows the instructions given in C&R Chemical Engineering Design chapter 11.10.2. The O'Connell correlation is based mainly on data from hydrocarbon systems and bubble cap trays.[A] However, since the AIChE method seemed to be too complex for this system the O'Connell correlation was considered to be most accurate as an approximation. The AIChE method is given in C&R as well.

O'Connell's correlation is given in equation 1.

$$E_0 = 51 - 32{,}5 \cdot \log(\mu_a \alpha_a) \qquad (1)$$

Where

μ_a = The molar average liquid viscosity of the feed (mNs/m^2)

α_a = Average relative volatility of the light key to the heavy key

In this case the column efficiency has been calculated at each stage in the column. The relative volatility has been calculated as the ratio of the K-values for the pseudo components with a boiling point closest to the cut point. The overall column efficiency is related to the Murphree plate efficiency according to equation 2.

$$E_0 = \frac{log\left[1+E_{mV}\left(\frac{mV}{L}-1\right)\right]}{log\left(\frac{mV}{L}\right)} \qquad (2)$$

Where

E_{mV} = Murphree plate efficiency

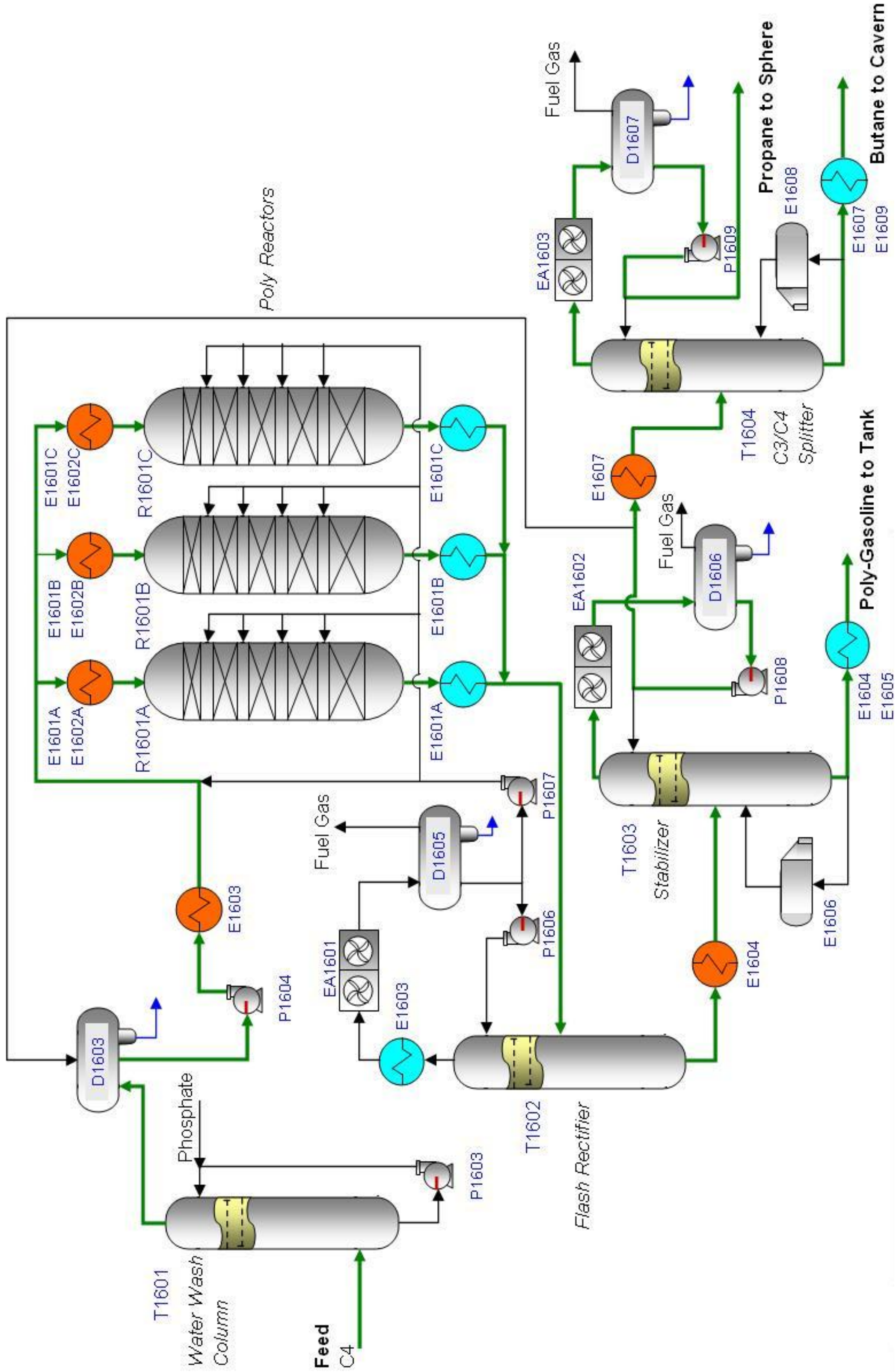
m = Slope of the equilibrium curve

V = Molar vapour flow rate

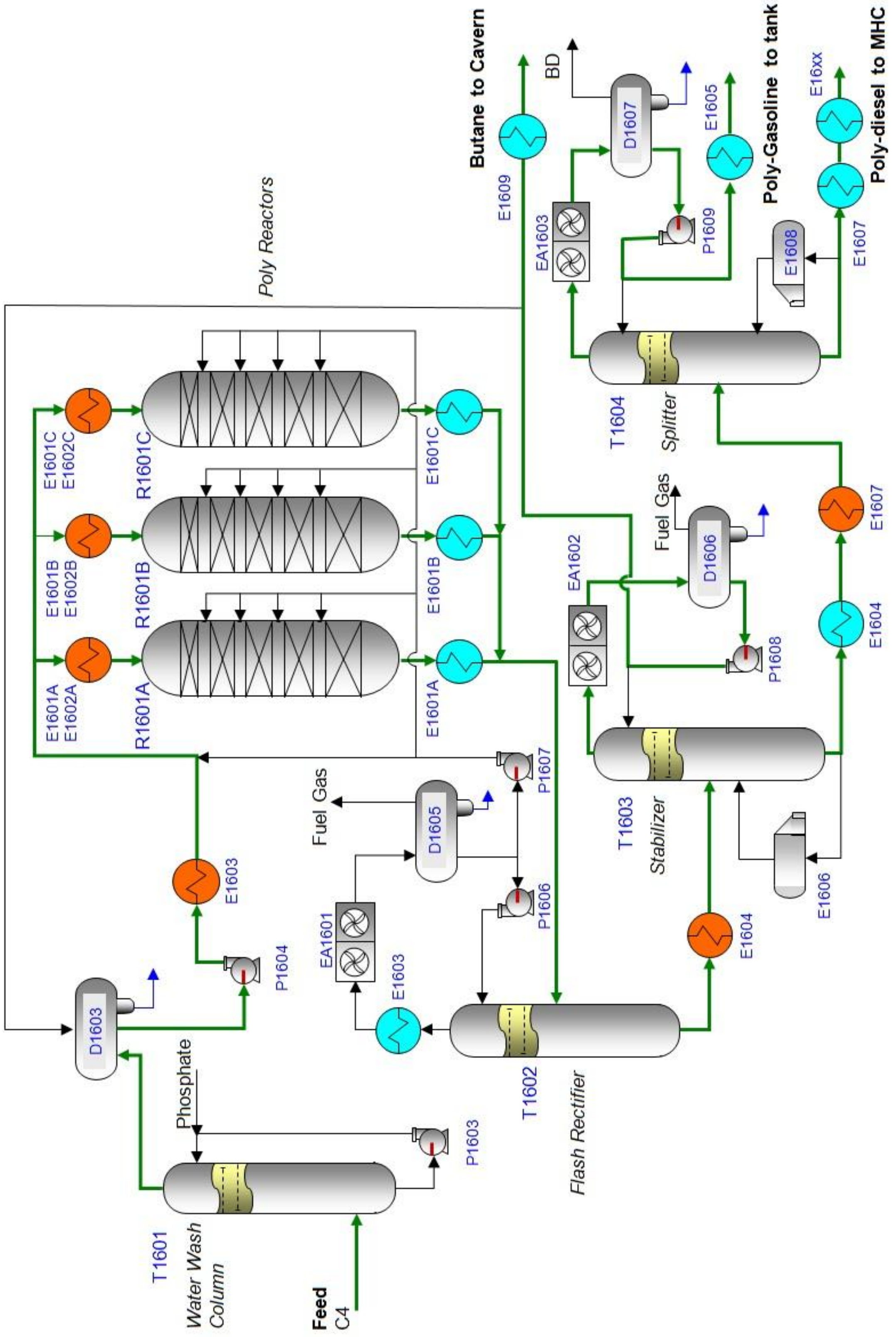
L = Molar liquid flow rate

The equilibrium curve is approximated with data from HYSYS for the fraction of the light key component in the gas and liquid phase at each stage in the column. For this approximation it is assumed that the stage efficiency is 1,0. Since the slope of the equilibrium curve differs throughout the column the stage efficiency is approximated as a mean value at the top bottom and feed stages.

Appendix 2. PFD of the existing polymerisation unit



Appendix 3. PFD of the modified polymerisation unit



Appendix 4. Basic theory about distillation analysis

Usually the number of components in an oil mixture is extremely high resulting in it being unfeasible to characterise the mixture with compositions corresponding to specific components. An ordinary way to characterise a petroleum mixture is to use petroleum assays also called distillation curves. A distillation curve relates the fraction of the total mixture to different boiling points, e.g. 5 vol% of the mixture has a boiling point less than 50 °C and 10 vol% of the mixture has a boiling point less than 70 °C. If the analysis is done over the whole mixture of components a distillation curve is created.

However, there are different types of distillation analysis methods. The oldest method was invented when the first refineries started with petroleum fractionation. This method is referred to as ASTM D86 which was developed to analyse jet fuels and diesel (which is included in group 4 fuels). However this method can also be used for lighter hydrocarbon fractions but it must be calibrated for loss of light material during the analysis. The definition of ASTM D86 is one stage batch distillation at atmospheric pressure.

Another standard measurement of distillation is the True Boiling Point (TBP) analysis. The definition of the TBP analysis is distillation in a 15 theoretical stage column with a reflux ratio of 5:1. This analysis gives a more wide-ranging temperature interval since the separation becomes better with more equilibrium stages.

Actually, the analysis is usually not performed in the previously mentioned equipment. Nowadays the normal method is to perform the measurement by GC-analysis which is faster and more convenient.

An example of a comparison between the TBP curve and ASTM D86 is shown in figure 1.

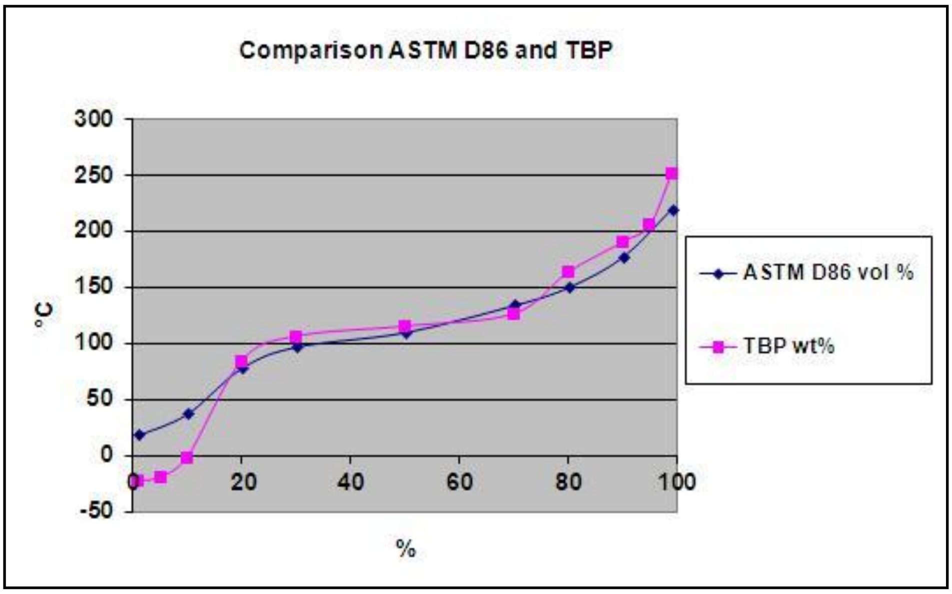
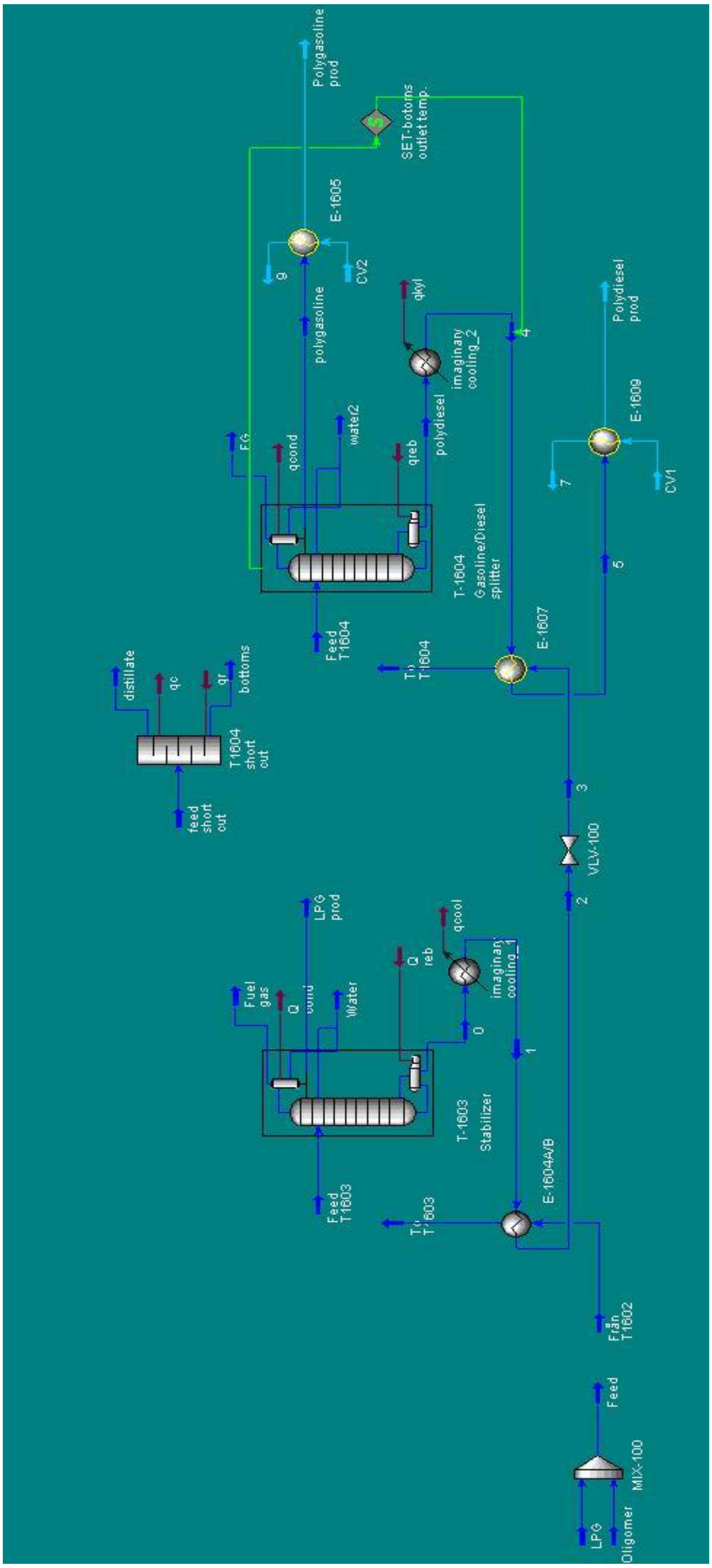


Figure 1. Comparison between TBP and ASTM D86

Appendix 5. HYSYS process flow diagram



Appendix 6.Internal vapour and liquid loads and properties

The internal vapour and liquid loads and properties for each stage in the column T1604 are presented in table 1 and 2.

Table 1. Internal flows and properties for vapour to each tray

Tray	Mass Flow [kg/h]	Gas Flow [ACT_m3/h]	Mole Wt.	Temperature [C]	Density [kg/m3]	Viscosity [cP]
1__Main TS	13260	2093	103.40	151.1	6.33	0.00827
2__Main TS	13427	2104	104.48	154.3	6.38	0.00830
3__Main TS	13413	2091	104.90	155.9	6.41	0.00832
4__Main TS	13386	2077	105.11	156.9	6.44	0.00833
5__Main TS	13361	2064	105.23	157.6	6.47	0.00835
6__Main TS	13338	2052	105.31	158.2	6.50	0.00836
7__Main TS	13317	2040	105.36	158.6	6.53	0.00837
8__Main TS	13297	2029	105.39	159.0	6.55	0.00838
9__Main TS	13278	2017	105.42	159.4	6.58	0.00838
10__Main TS	13259	2006	105.44	159.7	6.61	0.00839
11__Main TS	13241	1995	105.46	160.1	6.64	0.00840
12__Main TS	13221	1984	105.48	160.4	6.66	0.00841
13__Main TS	13200	1973	105.50	160.8	6.69	0.00842
14__Main TS	13176	1962	105.52	161.2	6.72	0.00843
15__Main TS	13148	1950	105.55	161.7	6.74	0.00844
16__Main TS	13114	1938	105.58	162.2	6.77	0.00845
17__Main TS	13071	1925	105.63	162.9	6.79	0.00847
18__Main TS	13035	1912	105.74	163.5	6.82	0.00848
19__Main TS	13143	1907	106.14	162.8	6.89	0.00846
20__Main TS	13152	1696	121.43	178.5	7.75	0.00807
21__Main TS	14772	1847	126.87	187.6	8.00	0.00804
22__Main TS	15763	1929	130.51	193.8	8.17	0.00803
23__Main TS	16435	1977	133.32	198.4	8.31	0.00803
24__Main TS	16944	2009	135.48	201.8	8.43	0.00802
25__Main TS	17339	2032	137.14	204.5	8.53	0.00802
26__Main TS	17643	2046	138.44	206.7	8.62	0.00801
27__Main TS	17881	2055	139.52	208.5	8.70	0.00801
28__Main TS	18072	2060	140.44	210.1	8.77	0.00802
29__Main TS	18233	2063	141.26	211.5	8.84	0.00802
30__Main TS	18372	2063	142.04	212.9	8.91	0.00802
31__Main TS	18498	2062	142.80	214.2	8.97	0.00803
32__Main TS	18615	2060	143.56	215.6	9.04	0.00803
33__Main TS	18726	2057	144.37	217.0	9.11	0.00803
34__Main TS	18834	2053	145.25	218.6	9.18	0.00804
35__Main TS	18938	2047	146.26	220.3	9.25	0.00805

36__Main TS	19039	2040	147.48	222.4	9.33	0.00806
37__Main TS	19132	2030	149.02	225.1	9.43	0.00807
38__Main TS	19201	2014	151.09	228.7	9.53	0.00808
39__Main TS	19168	1985	154.02	234.3	9.66	0.00812
40__Main TS	18614	1920	158.40	245.6	9.70	0.00822

Table 2. Internal flows and properties for liquid from each tray

Tray	Mass Flow [kg/h]	Liq Flow [m3/s]	Mole Wt.	Temperature [C]	Density [kg/m3]	Viscosity [cP]	Surf Ten [dyne/cm]
1__Main TS	4620	0.00200	116.61	139.2	640.9	0.21032	11.72
2__Main TS	4787	0.00210	119.99	151.1	634.5	0.20105	11.16
3__Main TS	4773	0.00209	121.60	154.3	633.6	0.19994	11.06
4__Main TS	4746	0.00208	122.53	155.9	633.3	0.19975	11.02
5__Main TS	4721	0.00207	123.10	156.9	633.1	0.19966	11.00
6__Main TS	4698	0.00206	123.50	157.6	632.9	0.19957	10.98
7__Main TS	4677	0.00205	123.79	158.2	632.8	0.19946	10.96
8__Main TS	4657	0.00204	124.02	158.6	632.6	0.19936	10.95
9__Main TS	4638	0.00204	124.22	159.0	632.5	0.19924	10.93
10__Main TS	4619	0.00203	124.40	159.4	632.3	0.19912	10.92
11__Main TS	4600	0.00202	124.57	159.7	632.2	0.19901	10.90
12__Main TS	4581	0.00201	124.74	160.1	632.1	0.19890	10.89
13__Main TS	4560	0.00200	124.92	160.4	632.0	0.19881	10.87
14__Main TS	4536	0.00199	125.13	160.8	631.9	0.19876	10.86
15__Main TS	4508	0.00198	125.38	161.2	631.8	0.19877	10.85
16__Main TS	4474	0.00197	125.70	161.7	631.8	0.19887	10.84
17__Main TS	4431	0.00195	126.15	162.2	631.8	0.19913	10.83
18__Main TS	4395	0.00193	126.82	162.9	631.9	0.19973	10.83
19__Main TS	4503	0.00198	127.88	163.5	632.5	0.20122	10.85
20__Main TS	17854	0.00778	131.87	162.8	637.3	0.21218	11.08
21__Main TS	19474	0.00862	135.69	178.5	627.7	0.19714	10.33
22__Main TS	20465	0.00913	138.40	187.6	622.4	0.18928	9.92
23__Main TS	21136	0.00948	140.58	193.8	619.1	0.18469	9.68
24__Main TS	21646	0.00975	142.27	198.4	616.8	0.18149	9.51
25__Main TS	22040	0.00995	143.57	201.8	615.1	0.17914	9.38
26__Main TS	22345	0.01011	144.61	204.5	613.7	0.17737	9.28
27__Main TS	22583	0.01024	145.46	206.7	612.7	0.17600	9.20
28__Main TS	22774	0.01034	146.20	208.5	611.8	0.17491	9.13
29__Main TS	22935	0.01043	146.87	210.1	611.0	0.17398	9.08
30__Main TS	23074	0.01050	147.51	211.5	610.4	0.17317	9.03
31__Main TS	23200	0.01057	148.12	212.9	609.7	0.17243	8.98
32__Main TS	23317	0.01063	148.75	214.2	609.2	0.17172	8.94

33__Main TS	23428	0.01069	149.42	215.6	608.6	0.17104	8.89
34__Main TS	23536	0.01075	150.15	217.0	608.0	0.17037	8.85
35__Main TS	23640	0.01081	150.99	218.6	607.4	0.16969	8.81
36__Main TS	23741	0.01087	152.01	220.3	606.8	0.16898	8.76
37__Main TS	23834	0.01092	153.30	222.4	606.2	0.16824	8.70
38__Main TS	23903	0.01097	155.04	225.1	605.5	0.16742	8.64
39__Main TS	23870	0.01097	157.52	228.7	604.7	0.16641	8.56
40__Main TS	23316	0.01074	161.25	234.3	603.1	0.16464	8.43