

# CHALMERS



## Plant Design for the Separation of Various Components from Turpentine Oil

Master of Science Thesis

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Göteborg, Sweden, February 2012

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## Abstract

Due to the increased concern for a climate change caused by the increased CO<sub>2</sub> content of the atmosphere there is a great interest in finding alternate way to produce different chemicals from non-fossil material. Lignocellulosic material is an abundant material which shows potential to at least partial replace fossil raw material both for energy and material production.

The purpose of this Master thesis (Project) is to perform a design and economic feasibility for the separation of different components from thermomechanical pulp (TMP) turpentine. In this project a process for feed of 239.8 Kg/h (based on 24 h/week) of turpentine, with purity of 95wt%, of turpentine has been studied. The turpentine studied in the work is produced by the Ortviken paper mill. The work is carried out with collaboration of Chalmers University of Technology Goteborg with SCA (Svenska Cellulosa Aktiebolaget) Sundsvall.

Based on a separation technique, distillation (packed column), alpha-pinene, beta-pinene, d-limonene and cadinene is separated out from Ortviken turpentine. Östrand mill constitutes with sulphur as methyl mercaptan, is necessary to remove in the beginning because of its affects to process and equipment. Therefore cadinene (Ortviken mill) is replaced by the methyl mercaptan (Östrand) and rest separated components are same. They are purified to 95wt% by using different sizes of the columns. The design process also provides the option of  $\pm 2$  % variation in the feed stream, without affecting purity. Integration of the system is carried out to reduce energy cost. The total investment cost for the process is 1.4 MSEK, out of which 43.2 KSEK is for the packing cost.

In the end, a design is suggested to treat the turpentine of both mills together and also provide an opportunity to select suitable flow. In future, if SCA would receive turpentine from other industries, then able to mix it with after some initial treatment. The total investment cost of this suggested plant is 2.8 MSEK.

## Acknowledgements

Before anything else, I take immense pleasure in thanking Hans Theliander (Examiner) for providing me an opportunity to complete the project in the congenial atmosphere of the department. The guidance and support received from Maria Sedin (Supervisor) was vital for the success of the project. Thanks and appreciation for the patience, advice and unconditional help she offered me. I am highly indebted to Chistian Kugge and Kent Malmgren for their attention, time as well as for providing necessary information regarding the project. Words are inadequate in offering thanks to Magdalena Svanström, who had been a source of inspiration and kind assistance for my scientific endeavours.

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## Chapter 1

### 1.1 Introduction

In the production of thermomechanical pulp (TMP) from spruce some of the volatile compounds found in the extractives are stripped away and can be recovered as a by-product (turpentine) from the pulp production. Today there are large quantities of turpentine available from the Kraft pulping industry. Thus the turpentine from TMP pulping would constitute a substance for material production. The Örtviken paper mill produces coated publication papers, Lightweight coated paper (LWC) and newsprint on four paper machines. The raw material is fresh spruce pulpwood, mainly from SCA's own forests in northern Sweden. Mechanical pulp process is used in the Örtviken mill. In addition to the aforementioned, the Östrand kraft pulp mill production is used for SCA's own manufacturing of publication papers and hygiene products and the remaining volume is sold to external customers. The plant also produces pulp for hygiene, packaging and other products.

Turpentine is a mixture of volatile substances, terpenes, mainly from wood and is always obtained when softwood is used as the raw material for the pulping process. A short overview of how turpentine is produced in the Östrand mill, in form of flow sheet, shown in the Figure 1. The wood chips are first partially softened in a digester by using chemicals and heat. The pulping process is done by mechanical method, on the softened chips. It then moves upward, opposite to the direction of chip column, to remove cooking liquor chemicals and dissolved organic substances. From the digester, the material is feed to the cyclone separator in which centrifugal force is used to remove the volatile extractives which are distilled with the steam evolved. The process is nearly similar for the Örtviken turpentine in which chemithermo-mechanical pulp process (CTMP) is used and the pulp refiner is pressurized. In this process, high preheating temperature is used to produce long fibres with as low energy input.

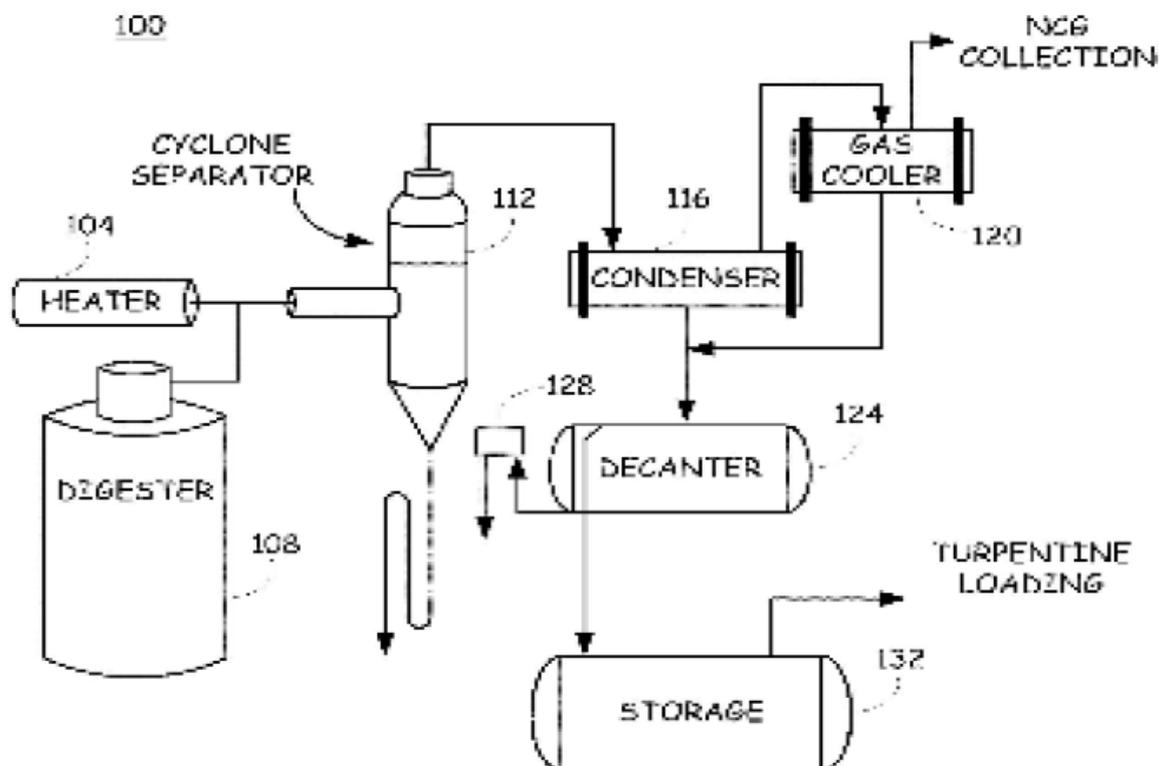


Figure 1: Flow sheet of turpentine production at Östrand mill

After cooling the steam from the refiner, condensate 'TMP- turpentine' is produced in the decanter. As turpentine is lighter and insoluble in water, it will float on top of the water layer in the decanter. About 0.4 kg TMP-turpentine per ton pulp can be collected. Hence, it would be possible to obtain 320 tons of TMP-turpentine from Ortviken each year. Turpentine obtained from the Östrand mill is 700 ton each year. The turpentine produced from the Ortviken is of a high quality compared to turpentine from other industry, e.g Östrand, which due to the nature of the latter process contains sulphur compound mainly (methyl mercaptane).

The goal of the work presented in this thesis, is to make it possible to produce value-added compounds or fractions. The most important component in the turpentine streams are alpha-pinene, beta-pinene, d-limonene, cadinene and methyl mercaptan from both turpentines.

## Chapter 2

### 2.1 Methods/Technology

Separation of the mixture into its constituents, the inverse process of mixing, requires an expenditure of energy. Almost all chemical process requires separation either binary or multicomponent. Binary separation is relative easy to perform and design as compared to the multicomponent separation. The design of multicomponent separation system is a very complex process as it involves the selection of separation method and also the sequence in which the separation equipments are placed. A second phase is created or added before separation, if the feed is single homogeneous phase that is created either by the help of energy separating agent (ESA) or as mass separating agent (MSA), see Table 1.1. ESA involves heat transfer or transfer of the shaft work to or from the mixture which is to be separated where as MSA involves addition of one or more component to the feed to ensure that the proposed separation takes place. Multicomponent separation engaged a number of separation units but generally the minimum number of operation is one less than the number of products.

Table 1.1 Common industrial separation method.

Separation method	Phase of feed	condition	Separating agent	Added phase	Separation property
Liquid-liquid extraction	Liquid		Liquid solvent MSA	Second liquid	Solubility
Liquid adsorption	Liquid		Solid adsorbent MSA	Solid	Adsorbability
Membrane	Liquid / Vapor		Membrane ESA	Membrane	Permeability &/or solubility
Leaching	Solid		Liquid solvent MSA	Liquid	Solubility
Drying	Solid & liquid		Heat transfer ESA	Vapor	Volatility
Distillation (ordinary)	Liquid vapor	and/or	Heat transfer or shaft work ESA	Vapor or liquid	Volatility
Extractive distillation	Liquid vapor	and/or	Liquid solvent & heat transfer MSA	Liquid and vapor	Volatility
Azeotropic distillation	Liquid vapor	and/or	Liquid entrainer & heat transfer MSA	Liquid and vapor	Volatility

Distillation is a process of separating a mixture into its components by virtue of difference in the volatilities. The more volatile component is separated out from the mixture. Separation that used ESA (distillation) is mostly preferred because it has potential for high mass transfer rates, cheapest and good method for separating a liquid mixture to its components [1]. There is an involvement of solvents or solid material present in almost all other separation process. Also, the separating potential (volatility in distillation) tends to be largest for the energy separating cases and can produce very high purity products. Disadvantage of the use of MSA is it needs additional equipment: needs MSA makeup, possible contamination of the product with MSA and more difficult design procedures which consequently affects economy of the

process [2]. Table 1.1 shows different separation techniques. Liquid-liquid extraction may be used when distillation is impractical, the mixture is temperature sensitive or more than 100 stages are often required [2]. The major problem with leaching (liquid-solid extraction) is to enhance the diffusion of solute out of the solid and into the liquid solvent. Adsorption, stripping and absorption are used to remove components present at low concentration [3]. Therefore from afore mentioned processes, distillation would be a good candidate for separation technique to proceed.

## 2.2 Distillation

During the beginning of twentieth century, the purpose of distillation extended from the tool for rectification of alcohol to the prime separation technique in the chemical industry. Distillation is a unit operation that has been around for a long time. It is a primary separation method in various process plants in spite of its low thermodynamic efficiency, still higher than others process. In order to increase efficiency, inter-condensers and inter-reboilers are used. From kinetic standpoint, mass transfer per unit is limited by the diffusional resistances on either side of the vapor-liquid interface in turbulent phases. Thus, it has the potential for high mass transfer rate.

Design of distillation is carried out using commercial process simulation software in order to save time, efforts and cost. The use of computers led to a rapid development in the distillation technique and procedure. This simulation software's based on the working of shortcut and rigorous columns of the selected components for separation are designed. Shortcut simulation or methods are used to generate the preliminary necessary information that forms the basis for the rigorous design. The principal step is to find the feed stage, total stages and reflux requirement, which can be done by using shortcut method, needed for the required separation. The shortcut (SC) program uses the equations of Fenske, Underwood and Gilliland method (FUGM) for estimating the minimum reflux rate, the minimum number of trays and required number of trays for a given reflux rate. This necessary initial information is finally forming the foundation for the rigorous design. In the rigorous simulation when the number of stages and feed points are fixed, distillate or bottom composition becomes the function of reflux rate specification. The purity level of the components is controlled by using the reflux rate specifications. Other variables that can vary reflux-to-distillate ratio, boil-up ratio, distillate-ratio and temperature of the column. Therefore, it's basically a trade-off among several factors.

## 2.3 Flow sheeting

The key role of this section is to define process simulation and its role in assisting the design group in process creation. Flow sheeting is the method to show the existing or hypothetical process in sufficient detail to describe the vital features. It only includes the major part of the system while minor parts or components i.e, piping ratings or piping systems are omitted. Process flow sheet is explained by using analysis or simulation that is used to forecast the process performance. All these things are based upon important factors such as mathematical model, set of equations that are related to process variables, physical and thermodynamic properties setting and so on. Steady state simulation is used to get the unknown variables by

providing certain known values. The engineers have to use this simulation for many important task, i.e from calculation of mass / energy balance, equipment sizing to forecast the performance of process alternatives.

ASPEN HYSSES (by Aspen Technology, Inc.) and CHEMCAD (by ChemStations, Inc.) were the two types of process simulators, provided by the University. During the work, HYSSES was chosen because of its implementation of 'bidirectional information flow' is very proficient in satisfying many specifications, i.e. specification are provided to the product streams and unknown variables of the inlet streams are computed [3]. Whenever a stream variable is changed, the adjacent process units are recalculated thus makes the information to flow in parallel to the material [3]. HYSSES has an exception to show the units such as 'recycle' where as CHEMCAD do not show the convergence unit but it exists and is transparent to the user [3]. These are the benefits for preferring HYSSES over CHEMCAD.

HYSSES, a powerful tool created by Hyprotech, was initially designed for the simulation of oil refineries. As it is efficient software, therefore later it founds its application into large number of industries, used by the process and design engineers. In HYSSES calculations are performed, on the basis of 'degree of freedom' approach. This can be done by providing the minimum required information to the unit operation and property packages. HYSSES cannot calculate the outlet condition until the parameters are provided to it. It includes tools for the calculation of physical properties, liquid-vapor phase equilibria and simulation of many different types of chemical equipments. This information is then used to see how the variation can be made in order to maximize product, minimize energy etc. Whenever a condition changes, the displayed information are automatically updated and HYSSES is affective in doing so. It has a number of unit operations which can be used to form a flow sheet. By careful selection of the proper unit operation and stream properties, enable us to make a model for the desired process. Few unit operations are governed by thermodynamic and mass / energy balance such as heat exchangers, separators etc while some are included specially for dynamic modeling such as controller, transfer function block, selector. Like in our case, separation of component from turpentine oil is designed by the help of proper and accurate properties and unit operation.

Mathematical simulation techniques are used by the industries to improve their products. Main issues attached to it are plant economy and safety, utilities consumption and environmental impacts etc. The most significant steps in these processes are conversion of the components into products by chemical reactions and separation of mixtures to obtain certain purities. They depend on various physical and chemical properties such as volatility, vapor pressure, density, solubility of the components in mixtures. During design or process synthesis, continuous feedback is important to meet the goals that are set in the beginning. Several constraints such as purity of the product, energy consumption, equipment cost are basic steps that are defined in the first design phase known as 'basic engineering'. In the next step the flow sheet is refined in 'detailed engineering' with the exact dimensions of all unit operations such as area of heat exchanger, exact number of plates, dimensions of the packed columns etc. Stationary flow sheeting is an essential tool for all of these tasks. Whereas in some cases the input information is used to calculate the output of the next component. In this

way, output information of the previous is utilized to determine the output information of the next component and so on. Thus the final output information is inter-related to the previous component and thus known as sequential method.

## 2.4 Physicochemical Modelling

At present, it is possible to setup basic simulation specifications in a very efficient way. Physical chemical properties greatly affect the accuracy of the model and consequently simulation. In our case,  $\Delta$ -3-carene and  $\Delta$ -cadinene are included as hypothetical components, and thus we have to define its thermodynamics properties. Models have built-in assumptions and practical limits that should apply. The goal of this section is to outline these assumptions and provide techniques for estimation of missing properties. It can be summarized with the following five steps [4]:

1. Selecting a suitable physical property technique
2. Validating the physical properties
3. Defining non-databank components (chemical species or compound) and missing parameters
4. Obtaining and using physical property data
5. Estimate any omitted property parameters

These sequential steps can be changed according to the situation and decision made at the selection time by the experts. However, each step must be considered with great confidence to make simulation as accurate as possible.

In order to select the right physical property technique a decision tree is a helpful tool. In Figures 2-4, a decision tree in accordance to is shown [4]. If we know the chemical components, their approximate temperature and pressure in the simulated process, the decision tree may be used. Many process such as distillation, evaporation, absorption is based on vapor/liquid equilibrium (VLE) and liquid/liquid equilibrium (LLE) respectively.

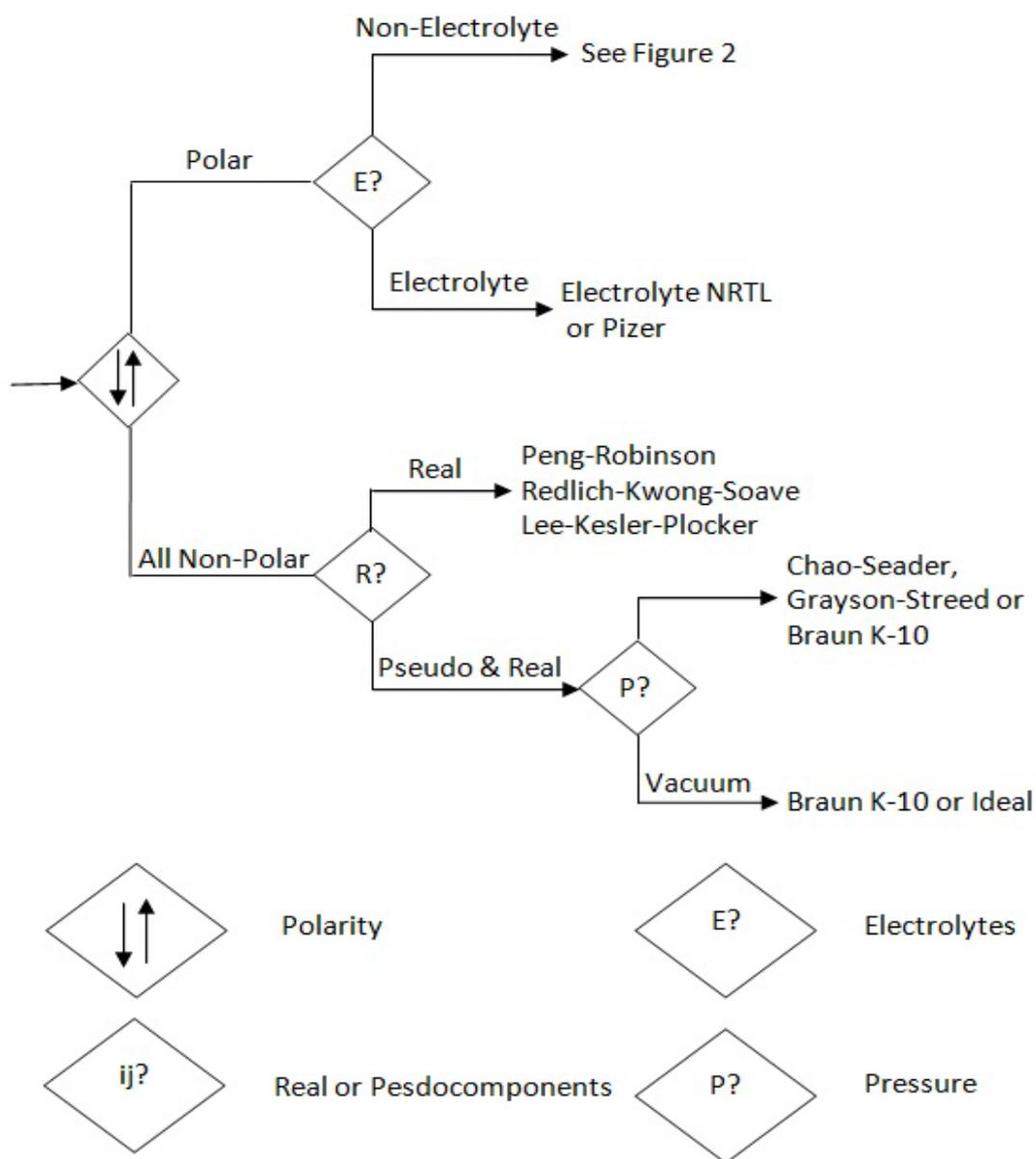


Figure 2: First step to select physical property methods [6].

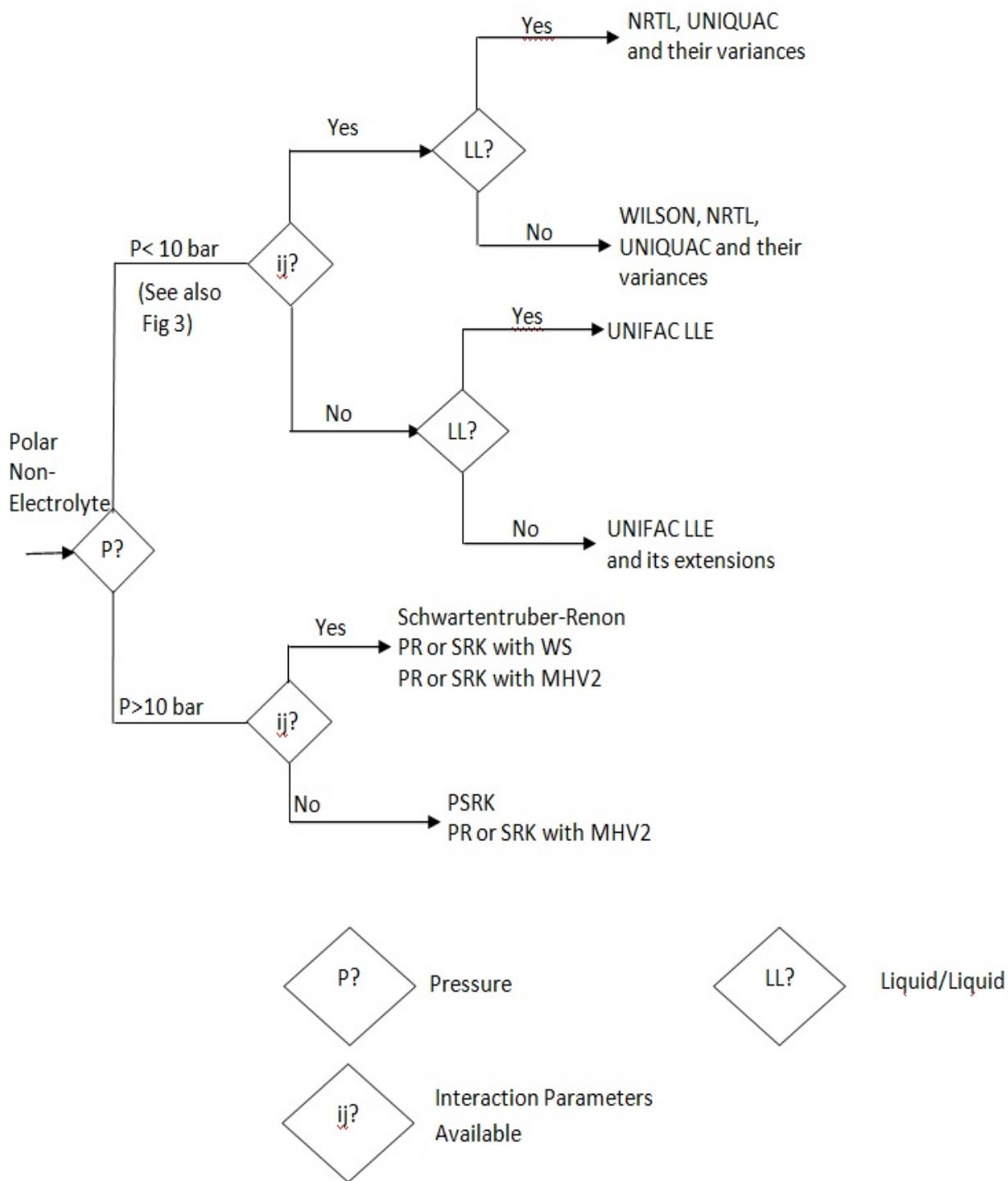


Figure 3: Process for polar and Non-Electrolyte Components [6].

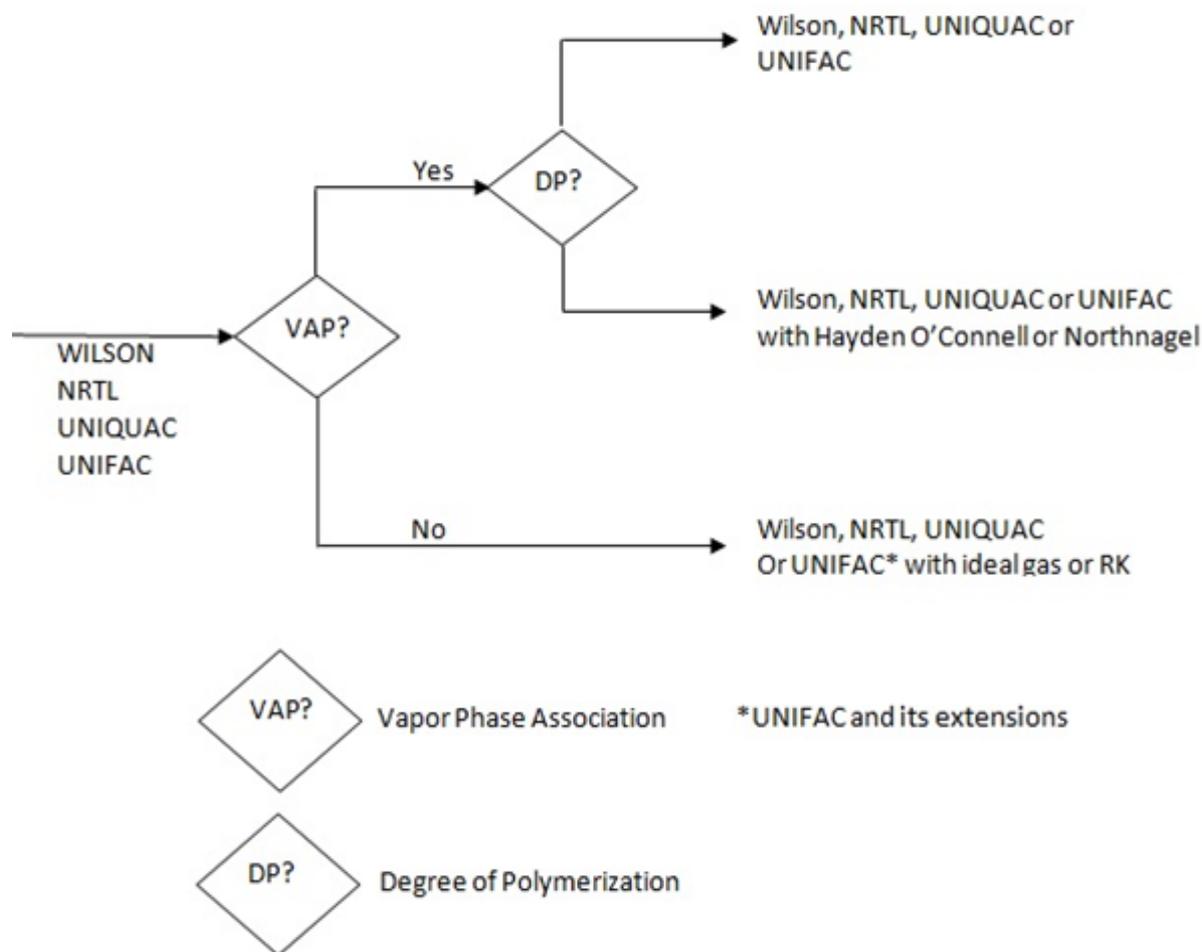


Figure 4: Options for vapor-phase calculations with activity coefficient models [6].

The model selected for the process is ‘Activity coefficient’ as it is used accurately to predict non-ideal liquid behavior such as VLE and LLE [5]. For non-ideal mixtures properties such as density, enthalpy, fugacities and activity coefficients are the functions of temperature, pressure and phase composition. Activity coefficient model is suitable when the pressure in process flow diagram is less than 10 bar [4]. At this pressure level Wilson, NRTL and UNIQUAC gives the best result which is then compared to experimental data (not available in this case) using activity coefficient model. The importance of pure component data must not be underestimated as these are the foundation for both pure component as well as mixture properties. Without pure properties calculation, accurate properties of the mixture are not possible for instance, vapor pressure (pure component properties) is used in phase equilibria calculation. Selection of VLE method using an activity coefficient model also requires a choice of model for the vapor phase properties. Phase equilibria and enthalpy is strongly dependant of association in the vapor phase. Activity coefficient models and Raoult’s law are not used when temperature is higher than the critical temperature of the component and also at high pressure. The UNIFAC method is used, as interaction parameters are not available. The UNIFAC is practiced when there is no experimental data or binary interactive parameters or when approximate values are acceptable.

ASPEN HYSSES have the ability to estimate binary interaction parameters for Wilson, UNIQUAC or NRTL from UNIFAC. Estimated interaction binary parameters are not providing much accuracy, thus only preferred to use in the early stages of the physical property data investigation. Therefore it is vital to enter the known parameters before doing property estimation. Experimental data is more reliable and accurate than estimated values and will be helpful in prediction of the property parameters.

## 2.5 Sequence heuristics

Selection of the most favorable sequence is the vital part of the process design. The higher the number of components in the feed stream, the more difficult to find the best sequence, i.e five components in feed will give fourteen possible column configurations. Therefore, sequence must be selected in an efficient way to make the process feasible. The following heuristics rules were applied to find an optimal sequence [6]:

1. Corrosive component should be removed first to avoid using explosive metallurgy in the whole sequence
2. If solids are present in the feed then it is better to remove the heaviest component first because it requires special plates which reduce plugging.
3. Split any components that cannot be condensed using cooling water from those used early in sequence.
4. Perform difficult separation late in the sequence, i.e. close boiling point components as it requires a large number of stages and high reflux. This sequence will help in reducing the amount of feed to the column and thus the column handles less material.
5. Desired product should be taken as distillate to avoid unwanted material in product.
6. Remove the most plentiful component first to reduce the cost of the subsequent columns by reducing the flow.

In turpentine there is no corrosive or solid material in it. Therefore, performing separation on the basis of boiling point should be used as the guidance in the selection of separation sequence.

## 2.6 Turpentine

The word 'terpene' is derived from 'turpentine' and consists of complex mixtures of monoterpenes hydrocarbon with the general formula of  $C_{10}H_{16}$  and sesquiterpenes  $C_{15}H_{24}$ . Monoterpenes covers alpha-pinene, beta-pinene,  $\delta$ -3-carene and d/l-limonene (isomers) where as sesquiterpenes only consider cadinene. d-limonene or l-limonene are stereoisomers that differ only in the spatial arrangement of atoms.

The composition of turpentine depends on the species used for its production and thus creates considerable difference and different end use. If alpha and beta pinenes contribution is higher than 90 weight % and 30-40 weight % respectively, then it is considered good and excellent turpentine. But, if these contents are less than 70-80 weight % then it is of limited value, for

derivative manufacture [7]. The presence of certain compounds in the turpentine lowers its value such as 3-carene. This product finds little use other than as a solvent.

Alpha-pinene, beta-pinene and d-limonene are the important source of producing different compounds such as anethol, citral, camphene, linalool etc [7,8]. They are mainly used in solvents, paints, varnishes, perfumes as well as in pharmaceuticals. Due to its antiseptic properties, it is widely used in many cleaning and antiseptic products and also has a medical importance as a gum derived from turpentine is to relieve the pain of toothaches [7,8]. Other extracts are used for the treatment of cough and cold symptoms. All of these contain significant quantities of terpenes and their derivatives. Turpentine consisting of alpha and beta pinene is therefore an important source of starting materials for a wide variety of useful flavor compounds.

### (a) Composition

The composition provided by the Ortviken pulp mill is based on the analysis taken from November 14<sup>th</sup> 2011. Thus, it is the current status of the turpentine produced by the mill. The composition is given in Table 1.2

Table 1.2: Ortviken pulp mill composition.

Components	Mass %	Mass Fraction
$\alpha$ -Pinene	42.30	53.58
$\beta$ -Pinene	20.80	26.34
$\delta$ -3- carene	03.00	03.80
d-limonene	10.00	12.66
Cadinene	02.84	03.59
Total	78.94	99.97 $\approx$ 100

In addition, the Östrand kraft pulp mill turpentine composition was provided to run on the current designing for Ortviken, to see what affect it cause, amount of separation, composition etc. Its composition is given in Table 1.3

Table 1.3: Östrand paper mill composition.

Components	Mass %	Mass Fraction
Methyl mercaptan	05.00	05.90
$\alpha$ -Pinene	45.87	54.14
$\beta$ -Pinene	17.35	20.47
$\delta$ -3- carene	08.50	10.00
d-limonene	08.00	09.44
Total	84.72	99.95 $\approx$ 100

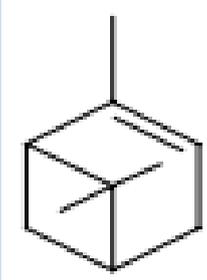
The five most abundant components made up 78.94 % and 84.72 % of the turpentine's respectively, as it consist of large number of other components with minor concentration (less than 2 %). The composition of monoterpenes in the kraft pulp-turpentine is slightly different from that in the TMP-turpentine with the exception of

the presence of methyl mercaptan in the later mill (kraft pulp-turpentine - Östrand). The complete composition of the two turpentine's is given in Tables 1.2 and 1.3.

### (b) Component properties

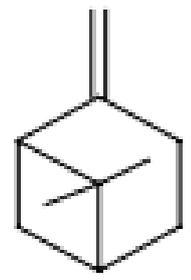
(1) **Alpha-pinene:** Alpha-pinene is a monoterpene and is formed from two isoprene units. It occupies the major proportion of the turpentine, around 50 weight %. Due to its pleasant aroma it is widely used in the perfumery industry and is also used in manufacturing of many chemicals such as camphene, pine oil, rosins and several others. Pinene is extremely strong in geraniol and its derivatives. Its most important properties in Table 1.4

Table 1.4: Alpha-pinene properties.

Properties	Bond distribution		Molecular structure	
Molecular formula	$C_{10}H_{16}$	Ring groups		
Molecular weight	136.2	-CH <sub>2</sub> -		2
Class / Family	hydrocarbon	>C<		1
Density	864.3 kg/m <sup>3</sup>	>CH-		2
Flash point	32.2°C	=C<		1
Boiling point	156.1°C	=CH-		1
CAS registry number	80-56-8	Non-ring groups		
Solubility in water	Insoluble	-CH <sub>3</sub>		3
Vapor pressure (25°C)	3.489 mmHg			
Enthalpy of vaporization	37.83 KJ/mol			

(2) **Beta-pinene:** Like alpha, it is also monoterpene and the second most important constituents of the turpentine. Beta-pinene is the more versatile chemically, although alpha-pinene is usually more abundant. It is used in the production of myrcene, geraniol, citral and in many other organic synthetic industries. The most important information of beta-pinene is shown in Table 1.5

Table 1.5: Beta-pinene properties.

Properties	Bond distribution		Molecular structure	
Molecular formula	$C_{10}H_{16}$	Ring groups		
Molecular weight	136.2	-CH <sub>2</sub> -		3
Class / Family	hydrocarbon	>C<		1
Density	873.2 kg/m <sup>3</sup>	>CH-		2
Flash point	34.9°C	=C<		1
Boiling point	166°C			
CAS registry number	127-91-3	Non-ring groups		
Solubility in water	Insoluble	=CH <sub>2</sub>		1
Vapor pressure (25°C)	2.398 mmHg	-CH <sub>3</sub>		2
Enthalpy of vaporization	38.59 KJ/mol			

- (3) **d-limonene:** Limonene is a chemical compound that are present in two forms, as l-limonene or d-limonene, shown in Figure 5. The two are mirror images of one another chemically, and have the same properties, but different fragrance. The "d" version typically smells like a citrus fruit while "l" tends to have a more sour turpentine-like scent mixed with pine.



Figure 5: d-limonene.

l-limonene[5].

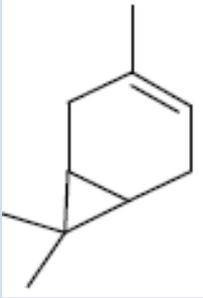
In the structures in Figure 2, the wedge line in the d isomer represents a bond projecting out of the plane of the paper. The dashed line in the L – limonene structure represents a bond projecting behind the plane of the paper. d-Limonene is used in the process as it is present in the HYSES databank. The most important properties of d-limonene are shown in Table 1.6

Table 1.6: d-limonene properties.

Properties	Bond distribution		Molecular structure	
Molecular formula	$C_{10}H_{16}$	Ring groups		
Molecular weight	136.2	$-CH_2-$		3
Class / Family	hydrocarbon	$=CH-$		1
Density	$847.4 \text{ kg/m}^3$	$>CH-$		1
Flash point	$42.77^\circ\text{C}$	$=C<$		1
Boiling point	$176.5^\circ\text{C}$			
CAS registry number	5989-27-5	Non-ring groups		
Solubility in water	Insoluble	$=CH_2$		1
Vapor pressure (25°C)	1.541 mmHg	$=C<$		1
Enthalpy of vaporization	39.48 KJ/mol	$-CH_3$		2

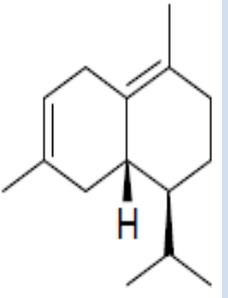
- (4)  **$\Delta$ -3-carene:** It is a bicyclic monoterpene that has colourless to slightly yellowish clear liquid. This material is used as an ingredient in the manufacturing of aromatic bases. fragrance industry, cosmetic industry etc. There is low concentration of  $\delta$ -3-carene present in the TMP turpentine (Ortviken) as compared to the Kraft pulp-turpentine (Östrand). This component is created as it is not present in the Hyses, so called it 'HypoCarene' in process flow diagram (PFD). Its properties are present in Table 1.7

Table 1.7:  $\Delta$ -3-carene properties.

Properties	Bond distribution		Molecular structure	
Molecular formula	$C_{10}H_{16}$	Ring groups		
Molecular weight	136.2	$-CH_2-$		2
Class / Family	hydrocarbon	$>CH<$		1
Density	$879 \text{ kg/m}^3$	$>CH-$		2
Flash point	$46.11^\circ\text{C}$	$=C<$		1
Boiling point	$171.4^\circ\text{C}$	$=C-$		1
CAS registry number	13466-78-9	Non-ring groups		
Solubility in water	Insoluble	$-CH_3$		3
Vapor pressure ( $25^\circ\text{C}$ )	1.861 mmHg			
Enthalpy of vaporization	39.10 KJ/mol			

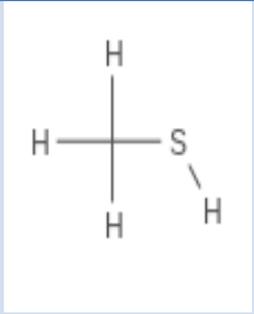
- (5)  **$\Delta$ -cadinene:** Cadinene is a chemical name of many isomeric hydrocarbons and used in the broad sense to refer any sesquiterpenes. They are bicyclic sesquiterpenes which is present both as hydrocarbons and oxygenated ones, in the TMP-turpentine. Like Hypocarene, it is also included as ‘HypoCadinene’ because of its absence in Hyses databank. Table 1.8 depicts vital properties of  $\Delta$ -cadinene.

Table 1.8:  $\Delta$ -cadinene properties.

Properties	Bond distribution		Molecular structure	
Molecular formula	$C_{15}H_{24}$	Ring groups		
Molecular weight	204.3	$-CH_2-$		4
Class / Family	hydrocarbon	$>CH-$		2
Density	$902 \text{ kg/m}^3$	$=C<$		3
Flash point	$110.5^\circ\text{C}$	$=C-$		1
Boiling point	$279.7^\circ\text{C}$			
CAS registry number	483-76-1	Non-ring groups		
Solubility in water	Insoluble	$>CH-$		1
Vapor pressure ( $25^\circ\text{C}$ )	0.007 mmHg	$-CH_3$		4
Enthalpy of vaporization	49.76 KJ/mol			

- (6) **Methyl mercaptan:** A colorless, flammable and volatile sulphur compound with rotten cabbage-like smell is usually known as methyl mercaptan. It is produced as byproduct from paper industry i.e Östrand pulp mill and also released as a decay product of wood in pulp mills. It is also used as an intermediate in the manufacture of jet fuels, pesticides, fungicides, and plastics. Important properties are present in Table 1.9

Table 1.9: Methyl mercaptan properties.

Properties		Molecular structure
Molecular formula	CH <sub>4</sub> S	
Molecular weight	48.10	
Class / Family	Miscellaneous	
Density	863.2 kg/m <sup>3</sup>	
Flash point	-18°C	
Boiling point	5.9°C	
CAS registry number	74-93-1	
Solubility in water	Insoluble	
Vapor pressure (25°C)	1901 mmHg	
Enthalpy of vaporization	23.78 KJ/mol	

## Chapter 3

### 3.1 Distillation column design steps

The design of distillation column is divided into following steps [6]:

- (1) First step is to set product specification
- (2) Set operating condition, i.e batch or continues, pressure etc
- (3) Find the stage and reflux requirement to achieve the efficient separation
- (4) Select either plates or packing with respect to the design condition
- (5) Sizing of column is defined by using diameter, number of real stages
- (6) Internal specification of column is designed: plates, packing support, distributors
- (7) Mechanical design: Vessel & internal fittings

These steps are accomplished by passing through several stages in industrial scale. With respect to thesis work, the first five steps are studied by undergoing through shortcut and rigorous columns in HYSSES which are explained further. Finally cost is calculated for the design.

### 3.2 Process Flow Diagram (PFD)

The design of the distillation column is proceeds stepwise. First, a short cut column is designed to get the basic information such as stages, reflux, feed plate and duties. The obtained information forms the basis of the rigorous column design. In the later step, column designed undergoes through important variations and finally optimized to provide final results. The shortcut and rigorous design column is defined separately for each component. The overall process flow diagram (PFD) is shown in Figure 6.

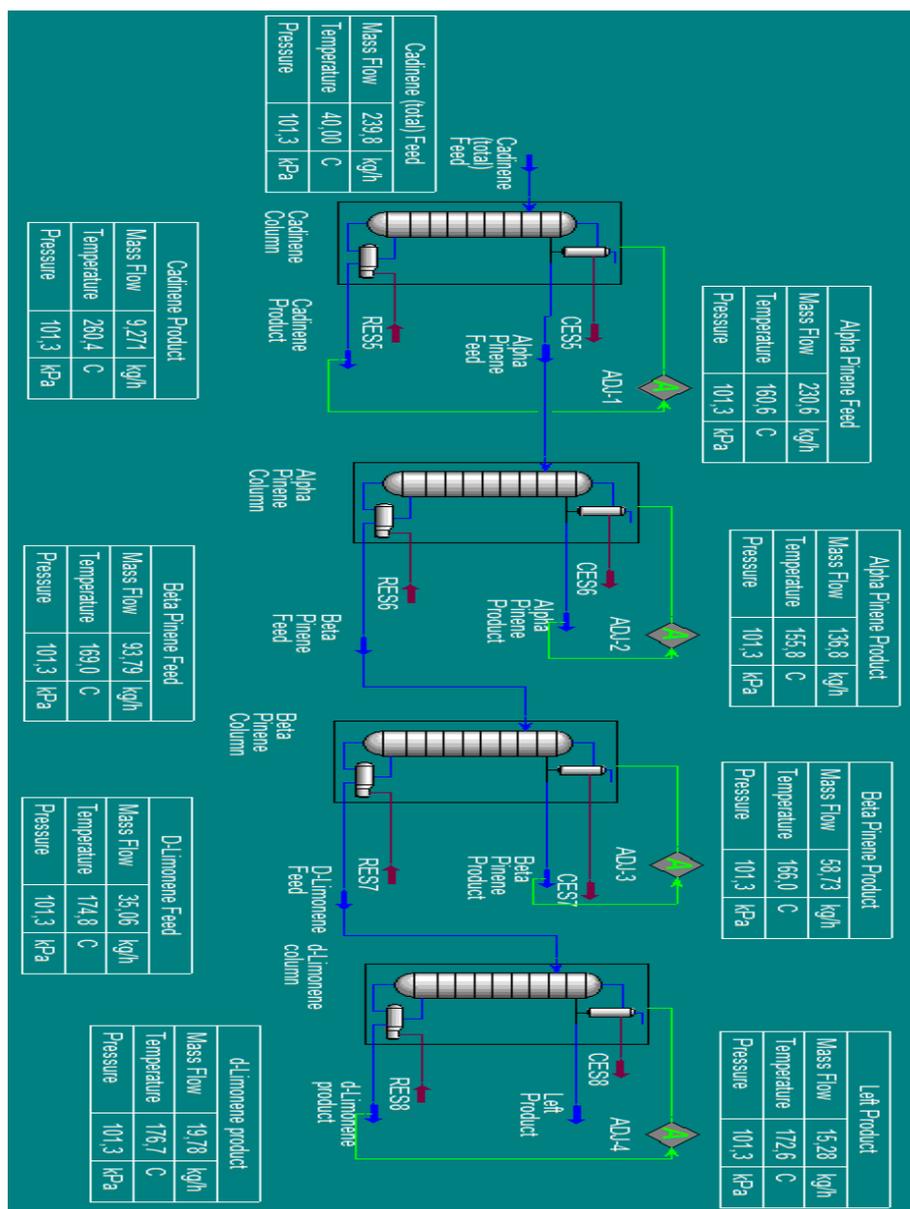


Figure 6: Ortviken PFD for turpentine separation.

The turpentine feed flow is 239.8 kg/h (operating 24 h/week). The operating time 24 h/week is selected because the feed rate is very small if we operate each hour of the week. Also, the selected operating hours will reduce the production cost of the products. The turpentine feed is liquid having temperature 40 °C and pressure is 101.3 kPa. Each column is designed to produce 95 weight % purity of every product.

#### (a) Cadinene distillation columns:

The feed to the column is 239.8 kg/h and the product is withdrawn from the bottom.

**Cadinene shortcut column (T-108):** The above feed is entered to the ‘Cadinene shortcut column’ to determine the necessary information shown in Table 1.10. The light key (LK) is alpha-pinene where as heavy key (HK) is hypocadinene due to their boiling point.

Table 1.10: Shortcut information for cadinene column.

Parameters		Values
Actual number of trays	( $N_T$ )	13.07 $\approx$ 14
Optimal feed stage	( $N_F$ )	7.90 $\approx$ 8
Minimum reflux ratio	( $R_m$ )	0.035
External reflux ratio (1.5* $R_m$ )	( $R$ )	0.052

**Cadinene (Rigorous) column:** The values obtained from the shortcut column are used in the rigorous design. The cadinene product obtained is 9.271 kg/h with 95 % while 230.6 kg/h (alpha-pinene feed) is further processed to the alpha-pinene column. Some of the important parameters are shown in Table 1.11

Table 1.11: Rigorous results for cadinene column.

Parameters		Values
Cadinene (Total) Feed (Kg/h)		239.8
Alpha-Pinene Feed (Kg/h)		230.6
Cadinene Product (Kg/h)		9.271
Component Mass Fraction		0.95
Condenser temp ( $^{\circ}$ C)		160.6
Reboiler temp ( $^{\circ}$ C)		260.4
Condenser duty (kJ/h)		$6.592 \cdot 10^4$
Reboiler duty (kJ/h)		$1.202 \cdot 10^5$
Reflux ratio		0.052
Boilup ratio		40.71

**(b) Alpha-pinene distillation columns:**

This is an important column as alpha-pinene is the main product of the process.

**Alpha-pinene Shortcut column (T-108):** 230.6 kg/h is feed introduced to the alpha-pinene distillation column and product obtained from top shown in Table 1.12. In this column, alpha-pinene is light key (LK) and beta-pinene is heavy key (HK).

Table 1.12: Shortcut information for alpha-pinene column.

Parameters		Values
Actual number of trays	( $N_T$ )	38.34 $\approx$ 39
Optimal feed stage	( $N_F$ )	13.69 $\approx$ 14
Minimum reflux ratio	( $R_m$ )	4.166
External reflux ratio (1.5* $R_m$ )	( $R$ )	6.249

**Alpha-pinene (Rigorous) column:** In rigorous column the data is run with other important changes to make the simulation running. Alpha-pinene 136.8 kg/h is obtained which is 95 % pure, while 93.80 kg/h is used for the separation of other component shown in Table 1.13

Table 1.13: Rigorous results for alpha-pinene column.

Parameters	Values
Alpha-Pinene Feed (Kg/h)	230.6
Alpha-Pinene Product (Kg/h)	136.8
Beta Pinene Feed (Kg/h)	93.79
Component Mass Fraction	0.95
Condenser temp (°C)	155.8
Reboiler temp (°C)	169.0
Condenser duty (kJ/h)	$2.614 \cdot 10^5$
Reboiler duty (kJ/h)	$2.619 \cdot 10^5$
Reflux ratio	06.249
Boilup ratio	10.05

**(c) Beta-pinene distillation columns:**

It is the most sensitive column of the process. Any changes made in previous columns will affect its results. Therefore, care should be taken in this column in order to make any type of changes, improvement etc.

**Beta-pinene Shortcut column (T-109):** The feed of 93.79 kg/h is fed to the T-109 column for the separation of the beta-pinene shown in Table 1.14. It is also removed from the top of the column. Beta-pinene is light key (LK) and hypocarene is heavy key (HK) components.

Table 1.14: Shortcut information for beta-pinene column.

Parameters	Values
Actual number of trays ( $N_T$ )	$64.65 \approx 65$
Optimal feed stage ( $N_F$ )	$19.27 \approx 20$
Minimum reflux ratio ( $R_m$ )	6.191
External reflux ratio ( $1.5 \cdot R_m$ ) (R)	9.287

**Beta-pinene (Rigorous) column:** The feed entered from the twentieth plate to the column. The obtained data when entered the rigorous column, the purity of the beta-pinene is below than the desired result. Thus, changes have been made to the reflux ratio that reaches to 12.79 from 9.29. Beta-pinene separated is 58.73 kg/h shown in Table 1.15.

Table 1.15: Rigorous results for beta-pinene column.

Parameters	Values
Beta-Pinene Feed (Kg/h)	93.79
Beta-Pinene Product (Kg/h)	58.73
d-Limonene Feed (Kg/h)	35.06
Component Mass Fraction	0.95
Condenser temp (°C)	166.0
Reboiler temp (°C)	174.8
Condenser duty (kJ/h)	$2.240 \cdot 10^5$
Reboiler duty (kJ/h)	$2.241 \cdot 10^5$

Reflux ratio	12.79
Boilup ratio	23.00

**(d) d-limonene distillation columns:**

This is the last column where d-limonene is selected to separate out as the product on the basis of initial feed. Maximum amount of the feed is recovered as d-Limonene.

**d-limonene Shortcut column (T-109):** The feed flow rate of 35.06 kg/h is introduced and product is removed from the bottom shown in Table 1.16. Hypocarene is light key (LK) and d-Limonene is heavy key (HK) components.

Table 1.16: Shortcut information for d-limonene column.

Parameters		Values
Actual number of trays	( $N_T$ )	48.61 $\approx$ 49
Optimal feed stage	( $N_F$ )	42.77 $\approx$ 43
Minimum reflux ratio	( $R_m$ )	15.50
External reflux ratio (1.5* $R_m$ )	( $R$ )	23.25

**d-limonene (Rigorous) column:** d-limonene is the final product that are formed in this column. The obtained product is 20.14 kg/h from the total feed of 35.06 kg/h where as 14.93 is the untreated product that is removed from the top. Results are present in Table 1.17

Table 1.17: Rigorous results.

Parameters		Values
d-Limonene Feed	(Kg/h)	35.06
d-Limonene Product	(Kg/h)	19.78
Left Product	(Kg/h)	15.28
Component Mass Fraction		0.95
Condenser temp	( $^{\circ}$ C)	172.6
Reboiler temp	( $^{\circ}$ C)	176.7
Condenser duty	(kJ/h)	1.021*10 <sup>5</sup>
Reboiler duty	(kJ/h)	1.021*10 <sup>5</sup>
Reflux ratio		24.00
Boilup ratio		18.27

An important consideration is given to the four adjusters used in the process flow diagram (PFD). The function of adjuster is to adjust the required value by varying the value of independent variable. If the composition changes with time, it's vital to make a design in such

a way that it can be used when any modification in composition takes place. The design can handle  $\pm 2$  % variation in the feed without affecting the purity of the products, i.e. 95 weight % purity.

Optimization is applied to improve all product and process design at various design stages. In the 'concept stage' approximate models and functions are used to select from numerous alternatives. Later, 'feasibility and development stage' comes that involve better understanding of the models and objectives. When product purity and production cost is fixed then set minimum factors to do the desired job. These factors are balanced against higher cost of labor, energy, reflux and maintenance etc. Optimization involves finding the reflux and boilup minimum to deliver the distillate and bottom purity respectively.

The best set of operating condition is required before making any kind of variation. The first step is to find the ultimate limiting capacity of all equipments such as reboiler, condenser and pumps etc. It can be done by the plant testing and calculations which are then extrapolated to determine operating limits [9]. The search is time consuming and involves many case studies but use of computer simulation makes it possible to achieve the task in a quick, efficient way.

## Chapter 4

### Östrand Mill Composition

In order to investigate if it is feasible to use turpentine from Östrand, the column sequence from Ortviken process flow design is used. First the feed flow is adjusted to 240.9 kg/h  $\approx$  239.8 kg/h (Ortviken Mill feed). The feed is considered at the atmospheric pressure and 25°C. In this case, 5 % sulphur as methyl mercaptan is present and is essential to remove it at first because of its corrosive nature especially to the carbon steel and piping [10]. It is toxic, explosive (presence of sufficient oxygen), and having a low boiling point [10]. Therefore, remove it in the beginning is a good technique to ensure plant, environment and personnel safety.

From the feed of 240.9 kg/h, 13.24 kg/h sulphur is separated as methyl mercaptan, 136.0 kg/h alpha-pinene, 48.58 kg/h beta-pinene, 18.05 kg/h d-limonene are removed. The overall process flow diagram (PFD) for Östrand mill is shown in Figure 7.

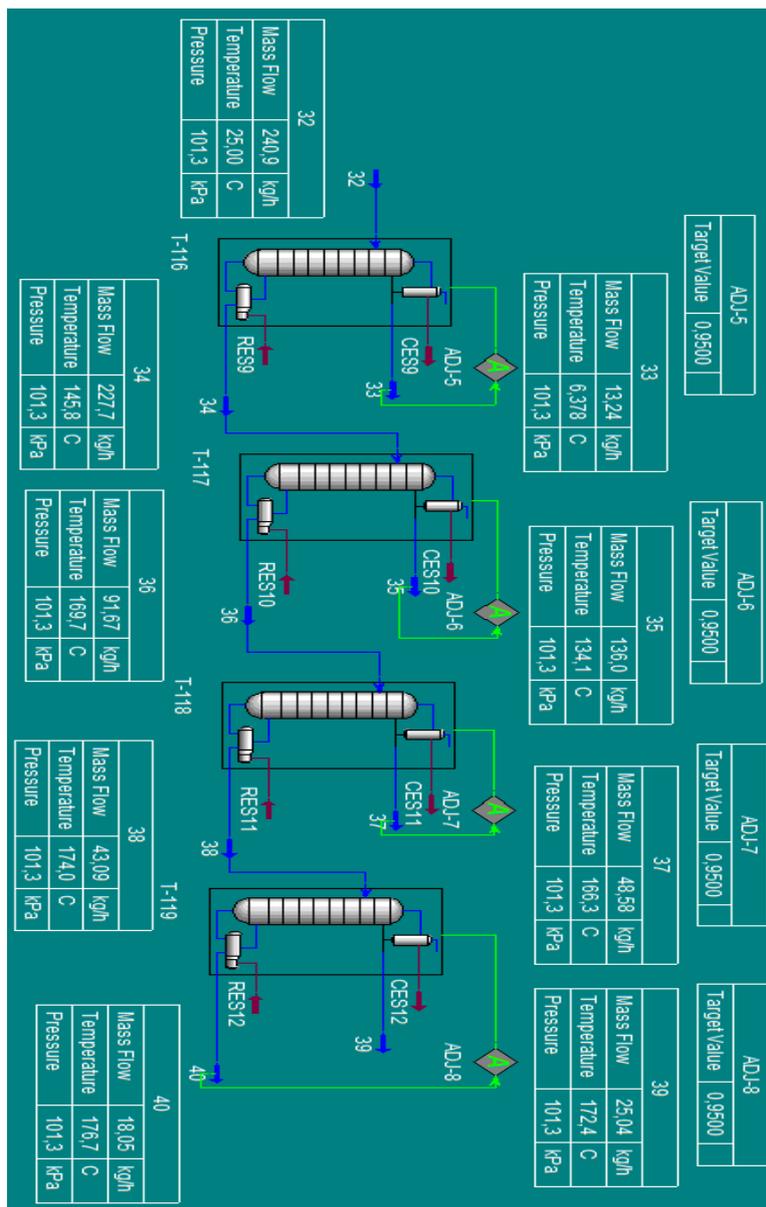


Figure 7: Östrand PFD for turpentine separation.

Except beta-pinene purity (88.7 %), all others column are fulfilling the desired task (95 weight %) without the change in the packed columns conditions (i.e. column diameter, height, packing material). More detail is present in the below Table 1.24

Table 1.18: Östrand mill information.

Components	Actual Plates ( $N_T$ )	Feed plate ( $N_T$ )	Reflux ratio	Purity (%)	Cond T (°C)	Reboil T (°C)	Cond duty (kJ/h)	Reboil duty (kJ/h)
<b>Methyl mercaptan</b>	14	9	0.011	0.959	6.3	145.8	7315.0	$5.282 \cdot 10^4$
<b>Alpha-pinene</b>	39	14	5.526	0.950	134.1	169.7	$2.717 \cdot 10^5$	$2.737 \cdot 10^5$
<b>Beta-pinene</b>	65	20	12.79	0.887	166.4	173.8	$1.850 \cdot 10^5$	$1.850 \cdot 10^5$
<b>d-Limonene (bottom Prod)</b>	49	17	11.39	0.95	172.1	176.7	$8.434 \cdot 10^4$	$8.437 \cdot 10^4$

Beta-pinene purity is less than the desired (present in Italic/Green colour in the Table 1.18). Here the two options used: Either increase the reflux, resulting an increase of the column diameter (change the column dimension) or go for complete new column design of the third column (beta-pinene). The reflux changes to 27 which results into nearly two fold increase in reboiler ( $3.429 \cdot 10^5$  kJ/h) as well as on condenser duty ( $3.429 \cdot 10^5$  kJ/h). The column dimensions, diameter and height changes to 0.4572 m and 29.72 m respectively. Amount separated is 40.11 kg/h of beta-pinene with 95 weight % is obtained.

In the d-limonene (last) column, the feed plate is changes to 17 (present in italic/green colour in Table 1.24). The column produces 18.10 kg/h of the desired component (d-limonene) and from top carene (hypocarene) 24.99 kg/h with the composition of 0.741 carene and 0.207 of d-limonene.

## Chapter 5

### 5.1 Heat-integrated distillation column

Distillation is an energy-intensive technique having low thermodynamic efficiency but is widely used in many process industries. In that case, process integration is a valuable tool used in designing and optimizing stage. Heating and cooling requirements will meet at minimum expense. In the concept stage it is very much feasible to play with fewer parameter such as feed temperature, degree of vaporization or with column pressure.

#### 5.1.1 Impact of operating pressure:

Distillation column pressure is a key design variable as it associates with the reboiler and condenser temperature. Therefore, adjustment can be made in pressure of towers to keep these duties relatively low [3]. Lowering the pressure will also reduce the temperatures and paves the path for heat exchange. General temperature-heat duty diagram is shown in Figure 8.

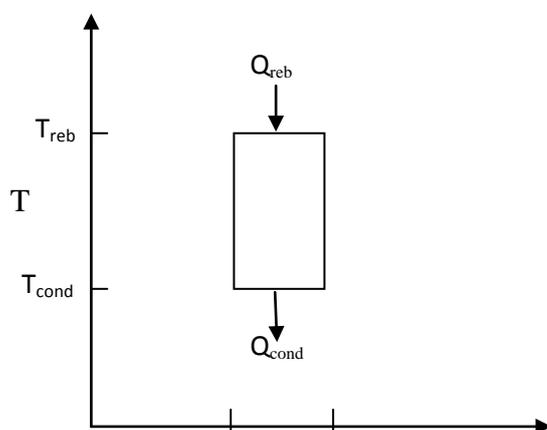


Figure 8: T-Q diagram of distillation column [11].

If the pressure is changed in such a way that heat produced by the condenser of one column is used by the reboiler of the other. Heat provided by the reboiler  $Q_{reb}$  is at temperature  $T_{reb}$  and heat removed by the condenser  $Q_{cond}$  is at temperature  $T_{reb}$ . For possible heat exchange either  $Q_{cond} = Q_{reb}$  or  $Q_{cond} > Q_{reb}$  will be met with a particular value of minimum temperature difference ( $\Delta T_{min}$ ).  $\Delta T_{min}$  is inversely proportional to the heat exchanger area that consequently affects total cost [11]. Minimum temperature difference leads to minimum running cost but higher capital cost due to increase in heat exchanger area. All these factors take into account whenever the integration of the column is done.

From Table 1.19, it is clear a heat exchange is possible between reboiler of the beta-pinene and the condenser of the alpha-pinene columns. It is also supportive as these two pinenes are the main products of the process.

Table 1.19: Temperature and duties of columns.

Variables	Cadinene column	Alpha-Pinene column	Beta-Pinene column	d-Limonene column
Column Pressure (kPa)	101.3	101.3	101.3	101.3
Condenser Temp (°C)	160.9	155.8	166.0	173.4
Condenser Duty (kJ/h)	$6.608 \times 10^4$	$2.554 \times 10^5$	$2.605 \times 10^5$	$9.349 \times 10^5$
Reboiler Temp (°C)	260.6	169.3	175.4	176.7
Reboiler Duty (kJ/h)	$1.206 \times 10^5$	$2.559 \times 10^5$	$2.606 \times 10^5$	$9.350 \times 10^5$

Integration of these two columns allows reducing the running cost of the plant by decreasing the heating as well as cooling duties. The integration will result into higher investment cost but successful in keeping the running cost lower. Therefore, a tradeoff is made between running and investment cost. In the ongoing case, the valve VLV-100, Figure 9, is used for pressure reduction and beta-pinene column is operating (under vacuum) at 70.90 kPa. This decrease in pressure will reduce the boiling point of the mixture to 154.8°C. Beta-pinene column has operating pressure of 131.7 kPa by using pump (P-100) that will raise its temperature to 177.1°C. The details of pump (P-100) is shown in Table 1.20

Table 1.20: Pump results.

Parameters	Values
P reduced (kPa)	60.80
Power (kW)	$2.841 \times 10^{-3}$
Heat flow (kJ/h)	10.23

The function of the other valve, VLV-101, after beta-pinene column (stream 29), is to decrease pressure so that d-limonene column is operate at atmospheric pressure.

The process flow diagram (PFD) is shown in Figure 9

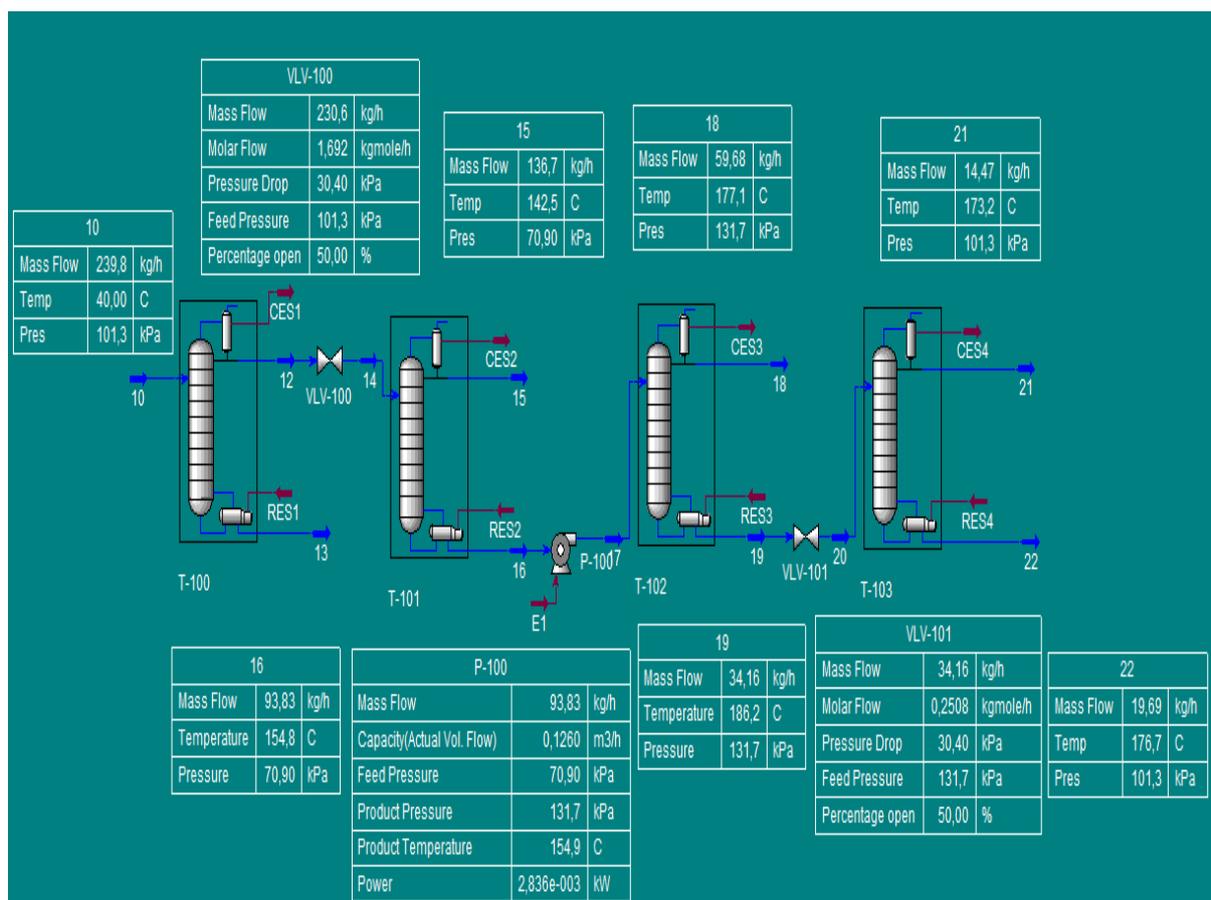


Figure 9: PFD of integrated plant

The final detail of integrated plant is given in Table 1.21

Table 1.21: Integrated plant temperature and duties.

Variables	Cadinene column	Alpha-Pinene column	Beta-Pinene column	d-Limonene column
Column Pressure (kPa)	101.3	70.90	131.7	101.3
Condenser Temp (°C)	160.9	142.5	177.0	172.9
Condenser Duty (kJ/h)	$6.608 \times 10^4$	$2.616 \times 10^5$	$3.299 \times 10^5$	$9.858 \times 10^4$
Reboiler Temp (°C)	260.6	155.2	186.3	176.7
Reboiler Duty (kJ/h)	$1.206 \times 10^5$	$2.553 \times 10^5$	$3.359 \times 10^5$	$9.753 \times 10^4$

From above table, it's clear that beta-pinene condenser will satisfy the heat demand of alpha-pinene reboiler with certain amount of  $\Delta T_{min} = 22.3^\circ\text{C} \approx 22^\circ\text{C}$ . A integrated plant reduce the consumption of hot utility, when the cost of fuel is high then it is an attractive design.

## 5.2 Decision for Heat-Integrated System:

The encouragement behind sequencing integration process is to reduce energy consumption. Sometimes, unfortunately addition of integration system makes the process more complex.

Efficient energy integration is always considered if best possible cost solution is developed by altering the process conditions.

### **5.2.1 Vacuum distillation (Alpha-pinene column):**

The integration of the process leads to operate the alpha-pinene column below atmospheric pressure, i.e vacuum distillation. The purpose of reducing pressure is to reduce the temperature required for distillation. It is a costly process and results in to high capital and operating cost for the following reasons.

1. Column diameter increases due to decrease in vapor density because of low pressure.
2. Thicker walls are needed in order to withstand an external pressure. Thus, the column must be redesigned.
3. Safety precautions and inspection is needed to constantly maintain vacuum in the column.
4. Vacuum column has low pressure drop per tray, low weir height that leads to lower stage efficiency. Thus, packing is suitable for vacuum services.

### **5.2.2 Other necessary equipment:**

To undergo the integrated process, important process equipment such as heat exchanger, pump, valves, control equipments are also needed. It is used to increases the pressure between the process operation. The selection of pump depends on power required, capacity, rate and nature of the process streams.

### **5.3 Outcome of findings**

There is a modest heat saving ( $2.559 \times 10^5$  kJ/h) by the integration of the process, at the expense of high investment and operating cost due to aforementioned factors. Therefore, it is suggested that to operate plant at normal condition.

## Chapter 6

### 6.1 Packed-Type Distillation Column

When packing is used in the column then the stages are referred as packed height and column is called as packed column. It is used when the tower diameter is small i.e less than 3ft [12] in order to provide uniform distribution of vapor liquid throughout the column, for liquids and also where operation requires low pressure drop and low liquid holdup. Normally there are grids, random and structured packing, thus selection of suitable packing affects the operation as well as cost. Pall ring is utilized in the process because of having higher capacity and efficiency with low pressure drop [1]. It belongs to random packing class and is available in metal, plastic and ceramics. For new columns the choice is normally either Pall ring or Berl or INTALOX saddles. Plastic packing are normally for strong alkalis, ceramics for corrosive fluids and metal where the column operation is unstable. Pall (metal) ring 1,5 inch Glitsch is used in all of the columns shown in Figure 10. Its geometry facilitates high gas and liquid transfer rates [6]. The opened cylinder walls and inward bent allow better capacity and lower pressure drop than standard cylindrical rings. The inner and outer walls contacting surfaces of the pall ring offers for an efficient distribution of liquids. This open ring design also maintains a uniform distribution and resists wall-channeling. This problem can also be minimized by providing the diameter of the tower at least eight times the packing size [13]. In packed column, the region of higher void spaces is near the column walls as packing material is loosely nested around the wall as compared to itself. Liquid has a natural affinity to move towards region of greater void spaces near to walls. Thus, careful selection of the packing material is required.



Figure 10: Pall ring (Metal) packing [14].

#### 6.1.1 Column Sizing

The sizing of a column is difficult process which requires lot of factors to be considered before making final recommendations. The height of packed column is determined by multiplying the number of theoretical plates by height equivalent to theoretical plates (HETP) [13]. It is the height of packing section that gives the same separation as achieved by one theoretical plate. The ratio of tower height to packing diameter is to be at least 15 [12]. The height of tower is limited to 200 ft ( $60.96 \approx 60$  m) due to wind load, structural and foundation consideration [3,12]. Increase in reflux ratio will decrease the number of plates but increase

the column diameter which consequently increased duties [2]. Final design should be created by professionals but an engineer often performs preliminary design for studies. This thesis work provides an opportunity to make a good estimate about the final design. Table 1.22 depicts important properties of the packed columns.

Table 1.22: Sizing of packed columns.

Parameters	Cadinene column	Alpha-pinene column	Beta-pinene column	d-limonene column
Actual number of trays ( $N_T$ )	14	39	65	49
Feed Plate ( $N_F$ )	8	14	20	43
Amount separate (kg/h)	9.27	136.8	58.73	19.78
Packing size (inch)	1.5	1.5	1.5	1.5
Section diameter (m)	0.3048	0.3048	0.3048	0.3048
X-sectional area ( $m^2$ )	0.0729	0.0729	0.0729	0.0729
Section height (m)	4.267	11.89	19.81	14.94

## 6.2 Cost Estimation

The chemical engineering design projects are carried out to provide the capital (investment) and operating (running) cost estimates that plays a crucial role in selecting the feasible design alternatives. The role of design of chemical engineer is to make a rough cost estimate of the selected choice as precise and more accurate cost estimation is a specialized subject that requires lot of expertise and efforts. The preliminary investment plant cost is the scope of this thesis project, as accurate cost information is not available. It is necessary in the early stage of the design to determine the profitability of the process. Fixed cost is not easily influenced by operation of the plant, but by making improvements in plant conditions and operating safely with the smaller work force. Therefore it can be controlled at the corporate level than the plant level. Most of the cost calculation used in the project is taken from the book Chemical Engineer Design (Sinnot Towler).

The equation used for basic cost calculation is  $C_e = (a + bS^n)f_m$

Where  $C_e$  = purchased equipment cost on a US Gulf Coast basis, Jan. 2007

$a, b$  = cost constant

$S$  = size parameters

$n$  = exponent for that type of equipment

$f_m$  = material factor (1.3 for stainless steel)

Other important factors that are used in the cost calculations is shown in Table 1.23

Table 1.23: Basic factors

Factors	Values
Wall thickness ( $T_w$ ; m)	0.005 <sup>1</sup>
Specific gravity	8
Density ( $Kg/m^3$ ) Stainless steel	8*1000
Density ( $Kg/m^3$ )	8000

<sup>1</sup> It also includes corrosion allowance (0.002 m).

The choice of material for construction depends on several factors such as mechanical engineers, corrosion engineers, stress experts etc. The most important responsibility lies on corrosion engineer whether the material specified will offer corrosion resistant under all sets of environment during normal operating conditions. The other point that also play a role is that corrosion resistant factor is the chemicals used for cleaning and sanitizing. Cost, strength, fabrication, maintenance makes some primary criteria that is considered in the initial selection process. It's better to use cheap material that will perfectly satisfy the requirement. Selection of stainless steel for the plant design is because it's certain benefits over carbon steel. Stainless steel is good for most hydrocarbon system but carbon steel is good for non-corrosive hydrocarbon system. When all these factors are taken into account, the long list of possible starters will be reduced to maybe one or two.

Since all economic data is given in US\$ for year 2007, it is essential to update it to the current year 2011 in Swedish currency (SEK). This can be done by using the CPE-index and exchange rate. CPE-index for the year 2007 is 525 and for the year 2011 – 575 (obtained by extrapolation of the given data based on previous years). Marshall & Swift (MS) index is used and is shown in Figure 11.

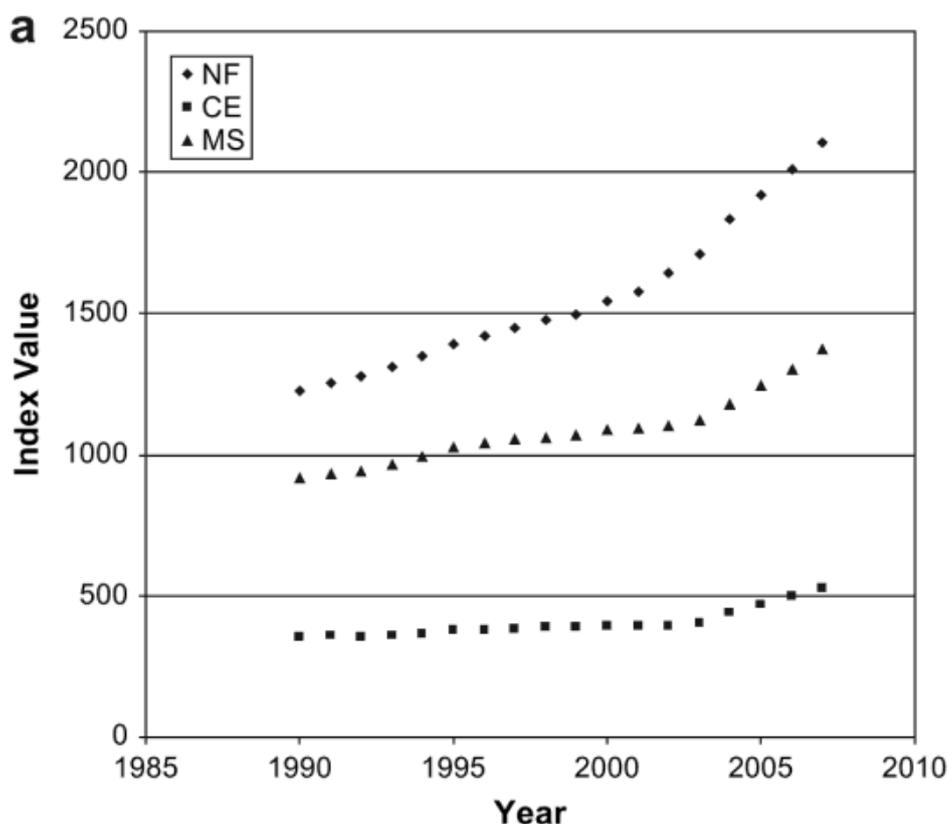


Figure 11: Major cost indices NF=Nelson-Farrer Refinery Construction Index, CE=Chemical Engineering Plant Cost index, MS= Marshall & Swift index

Table 1.24 depicts the major investment cost of the packed columns.

Table 1.24: Data for and result from purchased cost calculations cost given in 2007.

Distillation column	Specifications	a	b	S	n	Ce [US\$ 2007]
Cadinene (Vessel)	Stainless steel	15000	68	239,91	0,85	22170,73
Cadinene (Packing)	1.5" Pall ring (Metal)	0	7700	0.48	1	3721.40
<b>Total Cadinene Packed column cost<sup>2</sup></b>						<b>33659.76</b>
Alpha-Pinene (Vessel)	Stainless steel	15000	68	531.74	0.85	29104.57
Alpha-Pinene (Packing)	1.5" Pall ring (Metal)	0	7700	1.01	1	7799.96
<b>Total Alpha-Pinene Packed column cost<sup>2</sup></b>						<b>47975.88</b>
Alpha-Pinene (Vessel)	Stainless steel	15000	68	834.94	0.85	35697.61
Alpha-Pinene (Packing)	1.5" Pall ring (Metal)	0	7700	1.59	1	12247.46
<b>Total Beta-Pinene Packed column cost<sup>2</sup></b>						<b>62328.59</b>
d-Limonene (Vessel)	Stainless steel	15000	68	648.51	0.85	31697.03
d-Limonene (Packing)	1.5" Pall ring (Metal)	0	7700	1.23	1	9512.69
<b>Total d-Limonene Packed column cost<sup>2</sup></b>						<b>53572.63</b>
<b>Total Purchase cost</b>						<b>US\$ 197536.86</b>

<sup>2</sup> Including factor for stainless steel

The investment cost in 2011 can be calculated using equation

$$(Cost\ in\ 2011) = (Cost\ in\ 2007) * \frac{(Cost\ index\ 2011)}{(Cost\ index\ 2007)}$$

The total investment cost of the plant is 197536.86 US\$ (2007) 216349.89 US\$ (2011). Exchange rate from US\$ to SEK, on January 4, 2012 is 6.84. The cost is 1479833.27 SEK  $\approx$  1.4 Million SEK (Jan 2012).

## Chapter 7

### Suggested design

SCA has two mills, one is Ortviken paper and other Östrand pulp mill, producing turpentine of different qualities with different amount. Nearly 320 tons produced by the Ortviken and 700 ton from the Östrand mill. The paper mill produces turpentine with cadinene while pulp

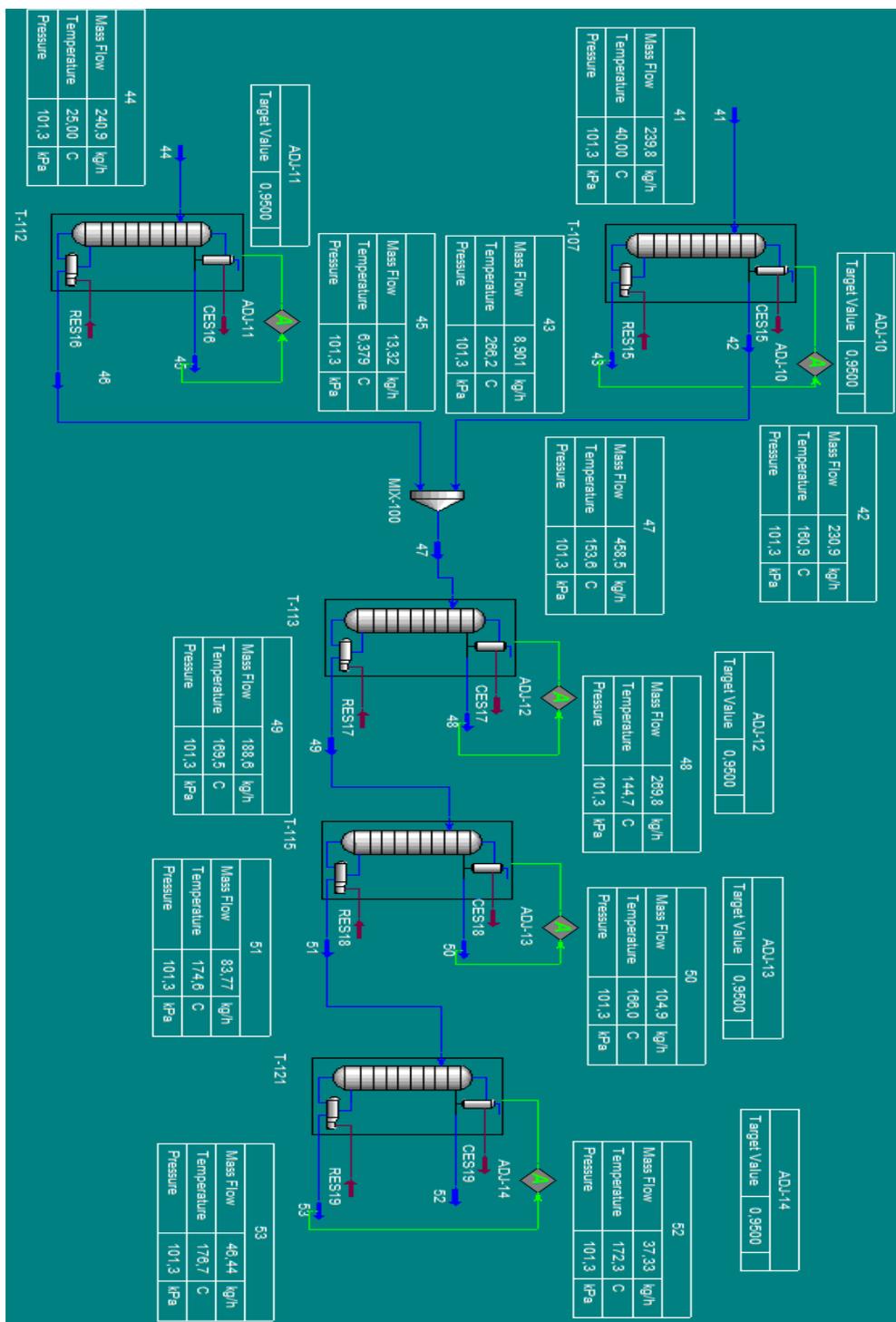


Figure 12: PFD of suggested process

mill produces methyl mercaptan in the turpentine. The flow rate of Ortviken mill (239.8 kg/h) and Östrand mill is (240.9 kg/h) is nearly similar. It is better to separate these two components and then mix both streams. Cadinene (8.9 kg/h) is preferable to remove in the first column because it has high boiling point. Therefore, it is better to remove in the beginning to keep the energy consumption low, where as for methyl mercaptan (13.32 kg/h) it is vital to separate in the initial column for plant, personnel and environment safety. Both these separation should performed in two different columns as shown in Figure 12. After these separations, the feed should be store in the storage tank (458.5 kg/h). It has many benefits. First of all, it enables to adjust the flow rate that affect the column dimension as well as operation. Moreover, plant can be able to run continuously because of having storage amount. Lastly, if in future they are able to get more turpentine from other processes / mills, then they can mix them, after determining what kind of component are present in it.

Next to these columns, alpha-pinene (269.8 kg/h), beta-pinene (104.9 kg/h) and d-Limonene (46.44 kg/h) is removed in the subsequent columns. Important properties are shown in the Table 1.25

Table 1.25: Suggested design information.

Components	Actual Plates ( $N_T$ )	Feed plate ( $N_T$ )	Reflux ratio	Purity (%)	Cond T ( $^{\circ}\text{C}$ )	Reboil T ( $^{\circ}\text{C}$ )	Cond duty (kJ/h)	Reboil duty (kJ/h)
<b>Cadinene</b>	14	8	0.052	0.95	160.9	266.2	$6.613 \times 10^4$	$1.208 \times 10^5$
<b>Methyl mercaptan</b>	14	8	0.011	0.959	6.3	146.4	7355.0	$5.313 \times 10^4$
<b>Alpha-pinene</b>	39	14	5.844	0.950	134.1	144.7	$5.281 \times 10^5$	$5.300 \times 10^5$
<b>Beta-pinene</b>	63	22	25.0	0.95	166.0	174.6	$7.541 \times 10^5$	$7.543 \times 10^5$
<b>d-Limonene (bottom Prod)</b>	55	45	25.79	0.95	173.3	176.7	$2.725 \times 10^5$	$2.725 \times 10^5$

Column dimension and other parameters are changes as the feed rate is changes. Important parameters and there values are shown in the Table 1.26.

Table 1.26: Suggested mill information.

Parameters	Cadinene column	Methyl mercatan column	Alpha-Pinene Column	Beta-Pinene Column	d-Limonene Column
Actual trays ( $N_T$ )	14	14	39	63	55
Feed Plate ( $N_F$ )	8	8	14	22	45
Amount separate (kg/h)	8.901	13.3	269.8	104.9	46.44
Packing size (inch)	1.5	1.5	1.5	1.5	1.5
Section diameter (m)	0.3048	0.3048	0.4572	0.6096	0.3048
X-sectional area ( $\text{m}_2$ )	0.0729	0.0729	0.164	0.2919	0.0729
Section height (m)	4.267	4.267	17.83	27.15	16.76

## Chapter 8

### Summary of results

The summary of the thesis work is given as

- (1) Orviken mill composition is used for the design case.
- (2) Components are separated by the virtue of their boiling points.
- (3) Distillation (packed column) is used to separate selected components.
- (4) Plant is operated for 24 h/week with a feed flow rate of 239.8 kg/h. 9.27 kg/h cadinene, 136.8 kg/h alpha-pinene, 58.73 kg/h beta-pinene and 19.78 kg/h of d-limonene is separated out with 95 % purity level.
- (5) Energy saving can be achieved by integrating plant. It is done by performing vacuum distillation, but is not feasible at for this design case.
- (6) The Östrand mill data is used in the present design (Ortviken) with a feed of 240.9 kg/h. This will separate 13.4 kg/h methyl mercaptan, 136.00 kg/h alpha-pinene, 48.57 kg/h beta-pinene and 18.10 kg/h d-Limonene. The major affect is seen on the beta-pinene as it gives purity of 88.7 % where as the rest are producing the desired purity percentage (95 %). Reflux ratio is changes from 12.78 to 27 in order to get the 95 % of the beta-pinene. The feed plate of d-limonene in this case is 17.
- (7) The Pall rings (packing) of 1.5" and stainless material of construction is used for the design of the packed columns that results into the investment cost of 0.22 million US \$  $\approx$  1.4 million SEK (Jan 4, 2012).
- (8) The suggested design to use both mill turpentine's separately used the same Pall rings (packing) of 1.5" and stainless material of construction results into the cost of 0.41 million US \$  $\approx$  2.83 million SEK (Jan 4, 2012).

## Chapter 9

### Conclusions

The cost calculations show that the plant design for the separation of various components from the turpentine oil could be of interest. There are various factors that have to be considered, to make it successful. The utmost care is taken in order to increase of feed. The present design can able to handle a  $\pm 2$  % variation in the feed which means that variation in the feed, either due to mixing or some other reasons, would not increase the fixed cost. Now the plant is running 24 hours / week because of the small flow rate of feed and it's better to run the plant continuously by overcoming this barrier. If SCA Sundsvall wishes to continue it, then there are some recommendations. First to calculate the running cost, selling cost of the separated components and then calculates the pay-back time (PBP). These factors need to be including before building the plant and to make it more beneficial.

Integration of the plant would be a choice if in the future the cost of production of steam would be expensive. It means that the both (alpha-pinene and beta-pinene) columns are run at the expense of the single stream, leads to save running (operating) cost. Also, there might be some better way to further optimize the plant. This master thesis should act as a base case design and thus provides an opportunity for the future research.

The feasibility of the ongoing research depends on future economic conditions. Presently, the turpentine oil is exported to abroad for further treatment which consequently includes export cost. Running cost, land cost, contingency charges, working capital etc must be overlooked to give final recommendations.

## Chapter 10

### Future Work

Following work can be carried out as the future studies.

- (1) The two mills, Ortviken & Östrand, differ in composition as Östrand mill contains 'Sulphur' in the form of methyl mercaptan. It should be removed in the beginning and is then mixed with the Ortviken mill to increase the feed. This mixing will make the process more efficient.
- (2) An integrated option is designed, which will be helpful in future, if the plant management considers a steam generation process is a costly business. Also, the designed plant can be integrated by the grand composite curve GCC (heating and cooling demand) of the current industry.
- (3) An extractive distillation can be used, instead of 'd-limonene packed' (last) column, to separate d-limonene from carene. For this purpose, extractive agent nonyl phenol, ethyl salicylate, 4-ethyl phenol, 2-phenoxy ethanol, diethylene glycol phenyl ether or tripropylene glycol methyl ether can be used. This study is not suitable in current situation as the feed in the last column is 35.06 kg/h so, if extractive distillation is to perform then there is a need of a pure extractive agent, additional equipment is required. It also enhances the energy demand as extractive agent is to boil 20°C higher than the components. But, if in future the feed increase then it might be an interesting option.
- (4) In the last column there is an option to take 'carene' as the product instead of 'd-limonene'. It is an attractive opportunity that is strongly related to the demand and selling price of these products. Also, cost studies should be performed to determine various factors which affect the process. This study will include factors such as pumping, piping, running (operating) and selling price of the separated components.

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