Distribution of Hydrate Inhibitors in Processing of Gas-Condensate

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"Knowledge is the food of the soul".

- *Plato*

ABSTRACT

The formation of gas hydrates have been known to cause serious problems with blockages in natural gas pipelines, wellbore and natural gas processing units. The offshore sector of the North Sea comes into focus owing to factors such as low temperature, high pressure because of deep water fields, great depth of the subsea environment and remote locations that are factors underlying the increased hydrate formation. Hydrates are formed in multiphase transport comprising gas, condensate and water. Produced water must be cleaned if it is to be re-injected into the formation, or discharged into the sea or other water bodies, hence due to potential recycling of the inhibitor. One of the main purposes of water treatment is to distinguish the previously injected thermodynamic hydrate inhibitor in Gas-Condensate production.

The aim of the thesis is to conduct a simulation study to determine the distribution of various thermodynamic hydrate inhibitors and H_2O, in water treatment, using a Distillation Column. The distribution of thermodynamic hydrate inhibitors between the three phases, Vapour, Liquid and Aqueous Phase was also studied. The software used to complete this task was Aspen Tech HYSYS. The data used are respectively from the Shell operated gas field Ormen Lange at the Norwegian Continental Shelf and the corresponding land-based processing facility; Nyhamna. Three cases have been studied in this thesis; the use of Methanol, Ethanol and Mono-Ethylene Glycol as hydrate inhibitor.

The results show that the use of Distillation Column alone in HYSYS is not suitable for the process of separate water and Methanol due to the dispersed distribution in the column. Distillation process gives a perfect distribution of Ethanol with 100% lean Ethanol leaving the Distillation Column as vapour, but indicates only a small amount of Ethanol left after transportation. The results refer to a perfect distribution of Mono-Ethylene Glycol leading to a simplified process for recycling. The bottom product stream contains pure quantity of Mono-Ethylene Glycol and the process is optimal for the use of Mono-Ethylene Glycol as a thermodynamic hydrate inhibitor.

SAMMENDRAG

Dannelse av gasshydrater har lenge vært kjent for å forårsake alvorlige problemer med blokkering i rørledning, brønnbane og prosesseringsenheter. Offshoresektoren i Nordsjøen kommer i fokus på grunn av faktorer som lav temperatur, høyt trykk på grunn av dypvannsfelt, undervannsmiljø på dypt vann og store avstander, som alle er faktorer bak økt hydrat dannelse. Hydrater dannes i flerfasestrømning som består av gass, kondensat og vann. Produsert vann må renses hvis det skal injiseres tilbake til formasjonen eller slippes ut i sjøen, men også på grunn av eventuell resirkulering av inhibitoren. Et av de viktigste formålene med vannbehandling er å skille ut tidligere injisert termodynamiske hydrat-inhibitor.

Formålet med denne oppgaven er å gjennomføre simuleringer for å kartlegge fordeling av ulike termodynamiske hydratinhibitorer og H_2O, i vannbehandlingen, ved hjelp av en destillasjonskolonne. Fordelingen av termodynamiske hydratinhibitorer mellom de tre fasene, gass, flytende og vannholdigfase vil også bli studert. Programvaren som brukes til å fullføre denne oppgaven er Aspen Tech HYSYS. Dataene som brukes er henholdsvis fra det Shell-opererte gassfeltet Ormen Lange på den Norske kontinentalsokkelen og tilsvarende landbaser prosessanlegg; Nyhamna. Tre tilfeller har blitt studert i denne avhandlingen; bruk av Metanol, Etanol og Mono-etylen Glykol som hydratinhibitor i gass-kondensat produksjon.

Resultatene viser at bruken av destillasjonskolonnen alene i HYSYS ikke er egnet for å separere vann og Metanol på grunn av den dispergerte fordeling i kolonnen. Destillasjonsprosessen gir en perfekt fordeling av Etanol. 100% ren Etanol forlater destillasjonskolonnen som damp, men viser bare en liten mengde Etanol som er igjen etter transport. Resultatene refererer til en perfekt fordeling av Mono-etylen Glykol som fører til en videre forenklet prosess for gjenvinning. Den nederste produktstrømmen inneholder ren mengde Mono-etylen Glykol og prosessen er optimal for bruk av Mono-etylen Glykol som termodynamisk hydrat-inhibitor.

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CHAPTER 1

INTRODUCTION

The oil and gas industry is facing vast number of field development challenges due to its ever changing offshore sector. With the advancement of the technology knowledge comes a higher possibility to operate in deeper waters, more complex reservoirs and harsh environment with longer distance from well to process facilities (Aker Solutions 2013).

Flow assurance, also known as multiphase transport, describes the transport of a mixture of oil, gas, condensate and water in a pipeline (Statoil 2007). The term describes the technology that covers the whole range of design tools, methods, equipment as well as knowledge. All of these factors are needed to ensure safe, uninterrupted and simultaneous transport of oil, gas and water mixtures through wells and pipelines from the reservoir all the way to an offshore or a land-based processing facility. Multiphase flow transfer has become the rule rather than the exception for new offshore developments (Statoil 2007).
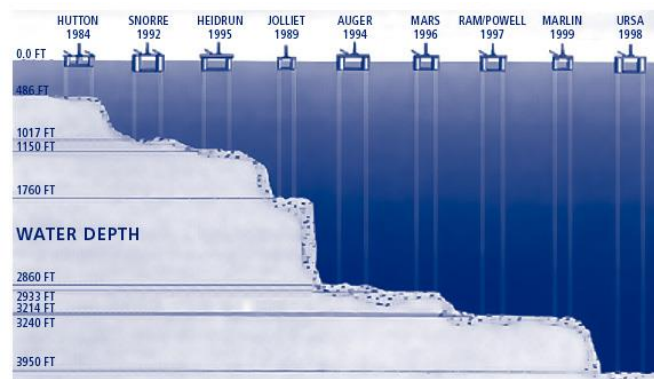
FIGURE 1 DEEP WATER DEVELOPMENT (U.S. MINERALS MANAGEMENT SERVICE 1999).

The flow assurance problems challenged in oil and gas production have become more onerous, leading to an increased overall industry-wide consciousness. This is especially case in the offshore sector. The North Sea sector in particular has come into focus owing to factors such as low temperature, high pressure due to deep water fields, great depth of subsea environment and remote locations that are factors underlying the increased hydrate formation (Watson 2003).

The increase in deep water activities over the years and their potential to expand over the coming years puts a new scope on hydrate inhibitions. Essentially, it increases the importance of lost inhibitors during the processing and the need to further understand the environmental and economic impact relevant thereof. These economics provide the initial motivation to investigate hydrate prevention (Sloan 2000).

Thermodynamic hydrate inhibitors are the most common technique to prevent the formation of natural gas hydrate in oil and gas production. Methanol and Mono Ethylene Glycol (MEG) are the most common hydrate inhibitors and Ethanol used in rare and special cases.

The complexity of water treatment increases, due to increasing environmental standard and increased requirements of commitment to development work. One of the main purposes of the regeneration process in water treatment is to separate off the injected thermodynamic hydrate inhibitor. The reason for this process is to clean the water for further re-injection and potential recycling of the inhibitor.

The inhibitors used in large offshore development are usually recycled and the recycling depends on separation, fractionation, distillation and solids settling. In relation to environmental standards, it will be convenient to recycle all forms of injected hydrate inhibitor. Earlier literature and experiments show that the recycling facilities are expensive, both in CAPEX

and OPEX. The recycling process of alcohol is not economical because the process is advanced and very costly in comparison with the process of glycol.

The aim of the thesis is to conduct a simulation study to determine the distribution of various thermodynamic hydrate inhibitors and H_2O, in the water treatment process, by using a distillation column. The distribution of thermodynamic hydrate inhibitors between the three phases; Vapour, Liquid and Aqueous will also be studied. The thermodynamic hydrate inhibitors are limited to be Methanol, Ethanol and MEG. The software used to complete the task is Aspen Tech HYSYS. The data used are respectively from the Shell operated gas-condensate field Ormen Lange at the Norwegian Continental Shelf and the corresponding land-based processing facility; Nyhamna. The data are modified by the author to test the various simulation parameters for the purpose of this work.
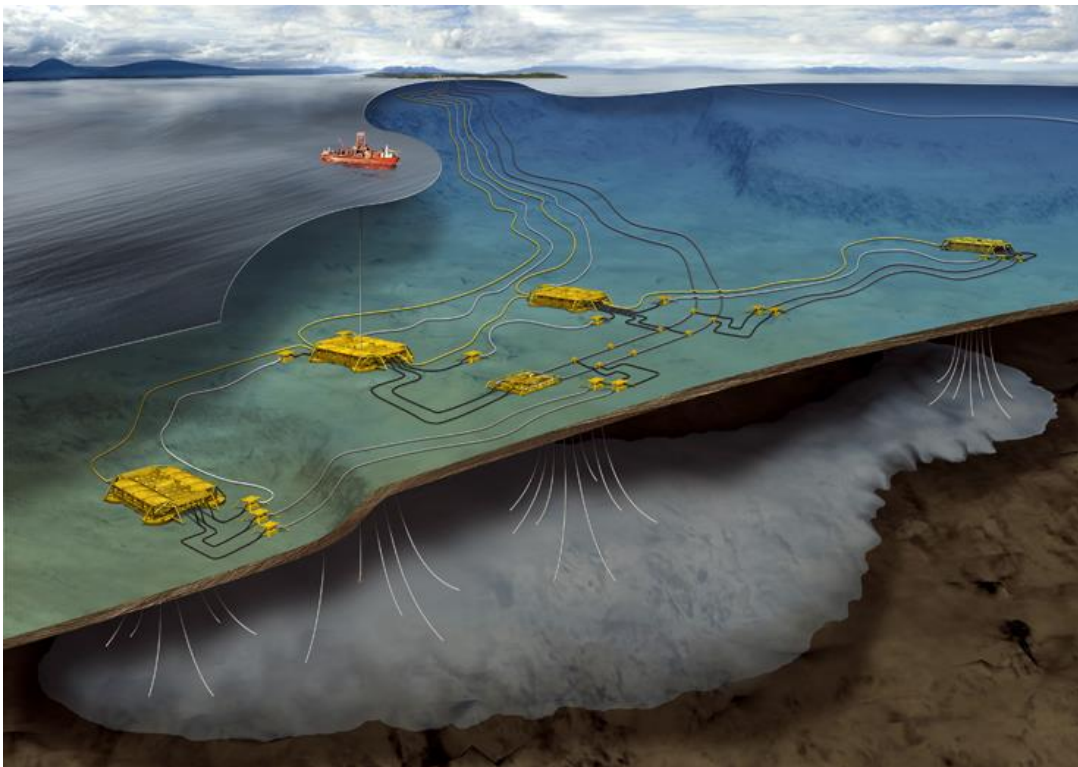
FIGURE 2 THE GAS FILED ORMEN LANGE AND PIPELINES TO LAND-BASED PROCESING FACILITY; NYHAMNA (A/S NORSKE SHELL 2013).

CHAPTER 2

FLOW ASSURANCE

The term "flow assurance" encompasses a range of factors such as fluid flow, heat transfer and production chemistry issues that have important consequences for the transportation of hydrocarbons from reservoir to processing facilities (Pickering 2009). The term was coined by Petrobas in the early 1990s translated from the Portuguese phrase "garantia de fluxo" to "Guarantee the flow", which later became the well-known term "flow assurance" (Watson 2003). Formation of solid deposits in oil and gas constructions such as pipelines and wellbore processing units have been well documented to cause severe problems, such as blockages.

In this chapter, information about the most common issues in flow assurance is studied. The section focuses primarily on hydrate formation but also addresses the issues pertaining to corrosion, scale, paraffin wax and asphaltenes. This is to provide a deeper understanding of the changes of hydrate formation conditions that may act to promote other solid deposits.

FIGURE 3 MULTIPHASE FLOW (G. OWREN 2012).

2.1 HYDRATES IN NATURAL GAS AND CRUDE OIL

Hydrates may occur in multiphase flow when water molecules crystallize around so-called guest molecules. Those guest molecules are the light hydrocarbon components such as methane, ethane, propane and butane, and non-hydrocarbons like CO_2, N_2, and H_2S. The structure of hydrates is very similar to the structure of ice occurred by frozen water molecules. Whereas ice is crystalline frozen water that only occurs at temperature at 0°C or below, hydrates often occur at temperature above the freezing point of water and high pressure (usually 0-25°C and 100 bara).
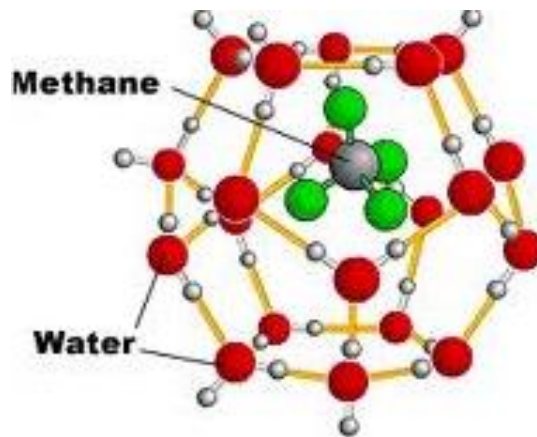
FIGURE 4 EXAMPLE OF THE MOLECULAR STRUCTURE OF METHANE CLATHRATE HYDRATE (TIME 2011).

Gas hydrates are composed of clathrate compounds. Where each water molecule forms hydrogen bonds with its four nearest water molecules to build a solid crystalline lattice structure, this encages gas molecules into interstitial cavities. This study is based on Hammerschmidt's determination from 1934;

"Solid gas hydrates form during transportation of natural gas and cause severe problems of blockage in pipelines".

The word clathrate comes from the Latin clathratus, which means lattice bars and is the reason for hydrates often being called clathrate hydrates (Mokhatab et al. 2006).

The formation of hydrates is also reliant on the composition of the gas in the feed stream. As documented by Katz (1945), the hydrate dissociation curve is displaced towards lower pressure and higher temperatures as the gas gravity or molecular weight increases (Pickering 1998). The two most common conditions are due to temperature and pressure (gas being at or below the water dew point and gas being at the appropriate temperature and pressure). (Mokhatab et al. 2006).

When the temperature and pressure conditions favour the formation of hydrates, the water molecules align in a certain pattern. The host molecule stabilizes the water molecules and hence causes crystallisation. The crystals effectively form a cage, held together by hydrogen bonding, trapping the host molecules. A hydrogen bond is the attractive intermolecular force between the polar water molecules. The two positively charged hydrogen atoms of water molecules attract the negative oxygen atoms from other molecules, forming an intermolecular bond.

In a pipeline, as soon as hydrate crystals are formed, they may continue to travel along with the flow depending on the nucleation site. This is not problematic, so long as the crystals are small. Obviously, larger crystal can damage pipeline equipment such as valves and pumps and need to be accounted for. Irregularities and equipment installed within the pipeline make for good nucleation and can cause the hydrates to deposit (Gudmundsson 2009).

Such conditions, like high pressure and low temperature are common in deep water oil and gas fields. When multiphase flow produced at wellhead flows into pipelines, it cools, which means most subsea pipelines will experience hydrate formation at some point within their operating envelope. The risk of

hydrate formation is highest during shut-in and start-up, when the temperature at shut-in drops to the temperature of the ocean floor so the system is almost always in the hydrate region. At this condition, multiple hydrate plugs can form.

FIGURE 5 CONCEPTUAL ILLUSTRATION OF HYDRATE DEPOSITION ON THE PIPE WALL (SUM 2012).

In case of a hydrate plug, the pressure levels in the pipeline may cause a dangerous situation. The pressure builds up on the one side of the hydrate plug while it remains low on the other side. If the plug detaches from the wall, the pressure will cause the plug to run wild in the low-pressure direction. In areas like pipeline elbows, valves and pumps are especially exposed to such plugs and could result in ruptures or production shutdown (Mokhatab et al. 2006).

2.2 PARAFFIN WAX

Wax depositions and dissociation are important issues in oil and gas transportations and production. Paraffin wax is predominately heavy hydrocarbons, and is prevalent in natural condensate. It may contain following components: Hydrogen sulfide (H_2S), mercaptans, carbondioxid (CO_2), long-chain alkanes (from C_2-C_{12}), cyclohexane and other napthenes, aromatics (benzene, toluene, xylene and ethylbenzene). Paraffin wax crystallises from crude oil and condensate when the temperature is sufficiently low (Gudmundsson 2009).

The first point at which wax formation can be identified is called Wax Appearance Temperature (WAT) as illustrated in Figure 6. The term "cloud point" is also used to determine the first temperature of wax formation. Cloud point occurs typically at 30-40°C. As the temperature is cooled further below the "cloud point", higher amount of paraffin wax is precipitated. The substance is a very thick and gel-like fluid; this is a result of the paraffin wax mixture being cooled down (Gudmundsson 2009).
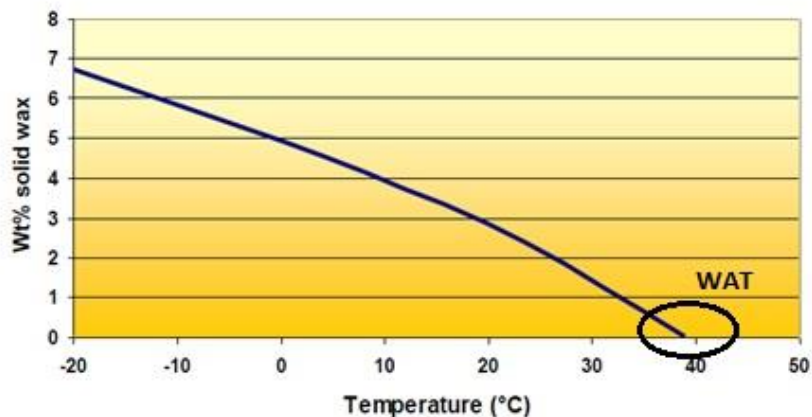
FIGURE 6 EXAMPLE OF WAX PRECIPITATION CURVE FROM NORNE CRUDE AT 1 BAR (GUDMUNDSSON 2009).

Similar to hydrates and scale, the deposits grow as long as the conditions favour continued wax formation. The deposits may well block the pipeline and could also be very hard to remove. Mechanical scraping also called pigging, heating, pipeline insulation and chemical additives are the most common preventive against wax formation (Stokkenes 2012).

The heaviest alkanes are the first to crystallize, followed by lighter and lighter components, during paraffin wax formation. As a result of his process, the hardest waxes are the ones to crystallize first because the molecular weight is closely related to the density of the deposits. If the hard wax has a high molecular weight the alkanes are also less soluble. Hence, the nature of wax deposits will change with distance from the pipeline inlet, as the fluid flow will cause lighter wax to form further downstream.

2.3 SCALE

Oilfield scale is a solid, stone-like substance that can deposit inside pipelines if the conditions are right. Scale is often a derivative of inorganic salts such as carbonates and sulphates of barium which crystallize during petroleum production (Time 2011). When hydrates and wax formations occur as temperature decreases, it is not as "simple" when it comes to scale formation. When sulphates deposit, (as the temperature drops because the liquid is unable to hold in solution) the solubility of calcium carbonate decreases as the temperature increases. Hence, the lower the temperature the more calcium carbonate is kept in solution and prevented from crystallization.

Oilfield scale – formed by brine such as formation water – undergoes PVT changes. This situation generally gives rise to carbonate scale. Another situation where oilfield scale may occur is if incompatible waters mix. For example; formation water rich in calcium, strontium and barium and sea water rich in sulphate generally gives rise to sulphate scale (Time 2011).

Akin to hydrate and paraffin wax, scale is formed by crystallization. Different from hydrate and paraffin wax formation, scale tends to deposit where it first crystallized, known as local deposition.

FIGURE 7 EXAMPLES OF HEAVY SCALE PRECIPITATION (STATOIL 2013).

2.4 CORROSION

Corrosion is the primary means by which metals deteriorate. Most metals corrode on contact with water and moisture in the air, acids, bases, salts, oils, and other solid and liquid chemicals. Corrosion takes place when positive ions break loose from the metal lattice into the surrounds and the term specifically refers to any process involving the deterioration or degradation of metal components. In the case of carbon steel, the iron-alloy surface undergoes an oxidation where it releases electrons and positive Fe^{2+}-ions break loose from the metal surface (Corrosion Doctors 2012).

The net reaction is composed of an anode oxidation and cathode reduction (Ramstad 2012). When electrons transfer to the anode which in this case is the pipe wall, it results in directly reducing of the carbonic acid. This process leads to Fe^{2+}-ions being corroded from the pipeline. The negative carbonate ion can react with Fe^{2+}-ions and cause iron (II) carbonate ($FeCO_3$) precipitation. This substance is a protection film against corrosion, but it is important to take in account that other mechanisms that determine the rate of formation are hard to predict. CO_2 partial pressure, pH and temperature are factors that play an important role when it comes to corrosion formation. If the conditions are not sufficient, the corrosion film may be porous, which does not yield any further protection against corrosion (Daugstad 1998).

FIGURE 8 PIPELINE CORRODED (MERUS 2013).

2.5 ASPHALTENES

Asphaltenes deposition is another well know problem that may block the pipeline and generates a large cost increase in the petroleum industry. Unstable asphaltenes can form a separate phase that might plug the oil-bearing rock formation near a well. The first step toward avoiding any of these problems is the understanding of how to evaluate asphaltene stability (Bukley 2005). It is reported that the substance resin adsorbs on asphaltene particle and then stabilizing the large polar molecule, and it is important to mention the high uncertainty and large discussion regarding the topic.

FIGURE 9 EXAMPLES OF HEAVY SCALE PRECIPITATION (STATOIL 2013).

Asphaltenes have high molecular weight and the structure contains of polycyclic organic compounds with nitrogen, oxygen and sulphur, in addition to carbon and hydrogen. They are among the heaviest molecules in the crude oil with molecular weight that range from 300-1400 g/mole, with an average molecular weight of 750 g/mole. Material in the asphaltene fraction forms aggregates. That is why standard measurements of molecular weight seldom provides an accurate value and produces very high estimates of molecular weight.
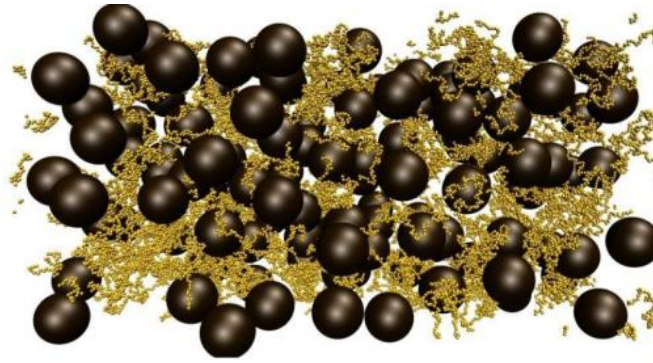
FIGURE 10 STRUCTURE OF ASPHALTENE (BAKER HUGHES 2013).

The important factor about asphaltenes is not the amount of asphaltene in the crude oil but the stability of asphaltenes. Stability depends not only on the properties of the asphaltene fraction, but also on how asphaltenes are affected by the remaining oil as a solvent. It is important to remember that the extent of how well the oil is as a solvent varies from sample to sample. Paradoxically, the asphaltene precipitation is often observed in petroleum fluids that contain very low asphaltene content. Light oils with small amounts of asphaltenes will more likely cause problems than heavy oil with larger amounts of asphaltenes (Goual & Firoozabadi 2002).

Figure 11 illustrates the asphaltene-precipitation envelope that defines the stability zones for asphaltenes in solution. When pressure reaches the upper asphaltene-precipitation envelope, also known as the asphaltene-precipitation onset pressure, the least-soluble asphaltene will precipitate. As pressure continues to decrease, more asphaltenes will precipitate, until the bubble point pressure is reached, and gas is released from solution (Akbarzadeh et al. 2007). With continued pressure decrease, solution gas has been removed from the system; the oil becomes denser and may begin to redissolve asphaltenes at the lower asphaltenes-precipitation envelope (Akbarzadeh et al. 2007).

Asphaltene-Precipitation Envelope

- Liquid
- Example reservoir conditions
- Upper asphaltene envelope
- Liquid and asphaltenes
- Increasing pressure
- Vapor-liquid equilibrium (bubblepoint)
- Liquid, vapor and asphaltenes
- Lower asphaltene envelope
- Liquid and vapor
- Increasing temperature
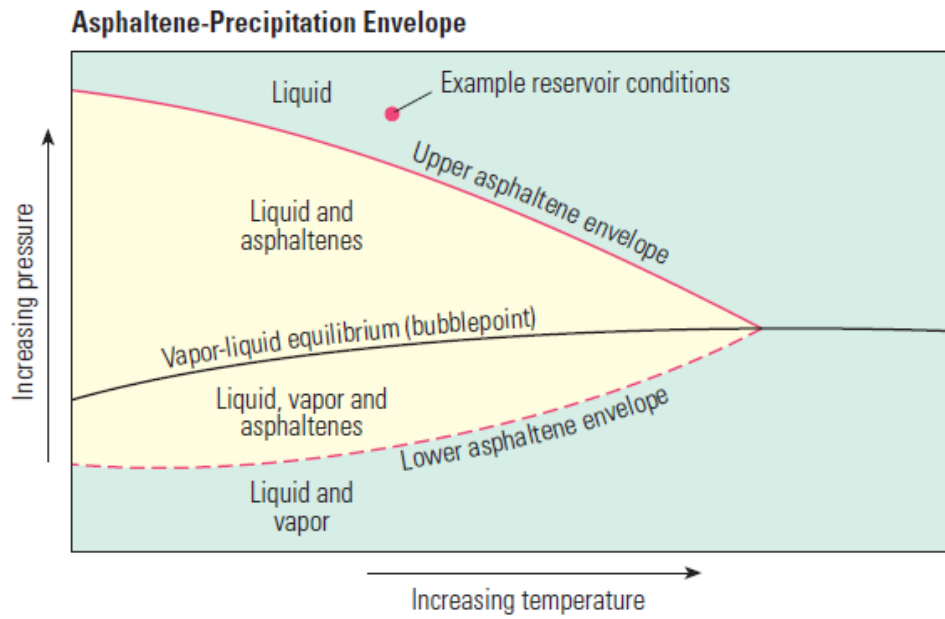
FIGURE 11 ASPHALTENE - PRECIPITATION ENVELOPE (AKBARZADEH ET.AL 2007).

CHAPTER 3

TRANSPORTING OF OIL AND GAS

The following sections will provide an overview of various methods of oil and gas transportation and storage facilities in the petroleum industry. Risk, safety and the environmental impact will be presented as well as these factors are of great importance when it comes to transportation of oil and gas.

3.1 TRANSPORTATION

Safety, security and respect of the environment are important factors weather oil and gas are transported from production sites to refinery by land or by sea. When oil and gas are transported by sea, one of the main issues is to avoid pollution. Pollution may occur not only by accidental oil spill and gas leaks, but also by slowly discharging of polluting products such as residue from tank and bilge cleaning. When oil and gas are transported by land it is important that damage equipment will be replaced and the state of pipelines must be kept under observation (Offshore Centre Denmark 2010: Ch. 6).

Not only oil and gas that is transported over a long distance needs to be stored, also once it is produced it may be stored in tanks and later transported by ship to where it will be sold or enter the transportation system. In some cases and more commonly, produced oil and gas goes from wellhead and direct into a small pipeline and from there into a larger pipeline or a pipeline network (Offshore Centre Denmark 2010: Ch. 6).

3.2 PIPING & PIPELINES

Within the petroleum industry, the definition of piping is a system of pipes used to convey media from one location to another. While the word "piping" generally refers to in-plant piping such as process piping, which is used inside a plant facility, the word "pipe-line" refers to a pipe running over a long distance and transporting liquids or gases. Downstream pipelines most often extend into process facilities such as refineries and process plants. See Figure 12.
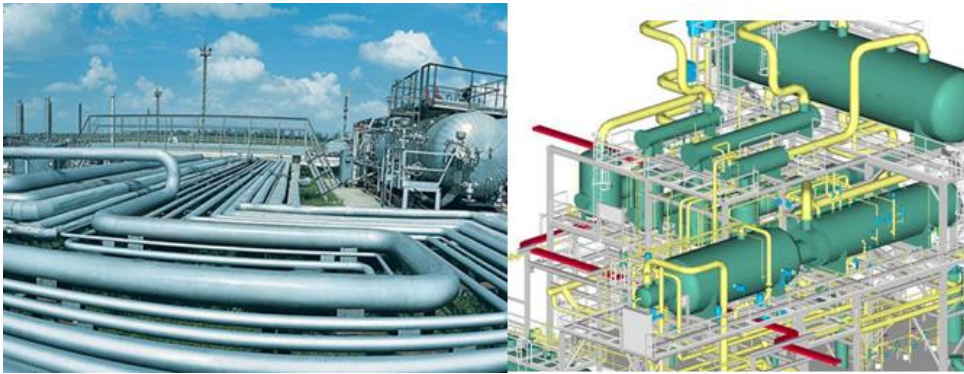
FIGURE 12 TO LEFT: PIPELINES, TO RIGHT: PIPING (TREND NEW AGENCY 2013).

Pipelines are used to transfer production from offshore wells to shore as well as to transfer production from a production field to a tanker loading area for shipping. In addition, pipelines may also transfer oil from a production field to a tanker loading area for shipping or from a port area to a refinery to be processed into petrol, diesel fuel, jet fuel, and many other products (Offshore Centre Denmark 2010: Ch. 6).

Natural gas, on the other hand, is almost always transported through pipeline, either it is onshore or offshore. Due to difficulties in transferring the gas from where it is found to where the potential consumers are located, not all gas deposits are produced. Years ago, the gas would have been wasted, also known as "flared", as an unwanted by-product of oil production. However, the industry is now using the clean-burning natural gas and is working on

improved technologies for the transportation from the reservoir to the consumer (Offshore Centre Denmark 2010: Ch. 6).

In Norway, the state-owned company Gassco is responsible for the natural gas pipeline network as well as managing the system "Gassled" which is the network of international pipeline. The system also contains receiving terminals that exports Norway's natural gas production to the United Kingdom and continental Europe (Offshore Centre Denmark, Ch.6, 2010). The Far North Liquids and Associated Gas System, FLAGS (UK), is linking Norwegian and UK gas line network as explained in more detail in Appendix B.

3.2.1 ENVIRONMENTAL IMPACT

Marine pipeline projects are governed by national authority regulations requiring Environmental Impact Assessment (EIA). The system is not mandatory for offshore pipelines and is most often case for pipelines located close to shore. To carry out a full EIA is time consuming and may take approximately two years, for which reason time scheduling is important. This is especially case in the northern European countries (Offshore Centre Denmark 2010).

A frequent criterion used by authorities for weather EIA is required or not will be regarding the pipeline route and weather it lays within the country's national territorial waters, which is 12 nautical miles. The second criterion will be weather the pipeline project includes landfall, in which case an EIA will normally be required. However, no general guidelines exist, and the evaluation therefore varies from country to (Offshore Centre Denmark 2010).

3.2.2 Risk and Safety

When it comes to the overall safety concern for pipelines located offshore the main focus is to ensure that there is a low probability of damage to the pipeline and of harmful effects on third parties, including the environment. This has to be valid both during operation and construction.

Of this reason, risk and safety activities in relation to offshore pipeline projects includes the main objectives; security of supply, personnel safety and environmental safety (Offshore Centre Denmark 2010).

Of the above mentioned objectives the specific focus depends on the medium to be transported in the pipeline system. In transporting natural gas the environment impact may be less severe compared to system transporting oil, but the safety of the personnel may be more critical due to the potential explosive nature of gas (Offshore Centre Denmark 2010).

Figure 13 shows the gas line from field to refinery in Bahrain, Middle East located uncovered and close to the highway. The location close to the highway leads to reduced safety and the reason why the pipeline is uncovered is assumed to be for easier access in case of maintenance and construction.

FIGURE 13 LACK OF SAFETY AND SECURITY IN BAHRAIN 2013

3.3 GAS TRANSPORTATION AND STORAGE FACILITIES

Since enormous quantities of transported oil and gas are not used immediately, storage facilities ensuring total safety and security have to be available to accommodate both for refinery end products and for produced oil and gas (Offshore Centre Denmark 2010: Ch. 9).

By the large picture, challengers of transporting and storage of gas are the same as for oil. Consumer and producer are far apart, and gas has to be transferred from one to the other. However, when it comes to details, things are quite different. Pipelines are preferred whether over land or under water.

At normal pressure and temperatures gas is in a gaseous state and occupies a volume 600 times greater than of oil for the same quantity of energy. From this reason, gas is always transported through pipelines in the gaseous state and the gas is conveyed under high pressure (Offshore Centre Denmark 2010: Ch. 9).

Some pipelines are underwater pipelines, such as those that link the Norwegian gas field to the European terminal, and other pipelines are overland pipelines like those that bring Russian gas to the European Union. The pipelines overland in European area are buried underground and not visible, for reasons of safety and security and due to strict regulations in over mentioned area. On the other hand, maintenance and construction will be more difficult in this case, as briefly mentioned in the section above (Offshore Centre Denmark 2010: Ch. 9).

CHAPTER 4

HYDRATE PREVENTION

The following sections will provide an overview of hydrate control methods. The health, safety and environmental aspects will be presented, as well as chemical properties of glycols and alcohols of interest in this thesis.

4.1 AN INTRODUCTION TO HYDRATE PREVENTION

Gas hydrates represent a severe operational problem as the hydrate crystals deposited on pipe walls accumulate as large plugs. As mentioned earlier this may result in blocked pipes, over-pressuring and eventually shut down on production facilities.

The removal of hydrate plugs in subsea production or transmission systems poses safety concerns and can be time-consuming and costly. For this reason, the hydrate formation in subsea gas transmission pipelines should be prevented effectively and economically to guarantee operational normality (Mokhatab et al. 2006).

When we talk about hydrate formation as a concern, one of the key factors relates to economics. Even concerns of higher value (e.g., safety or environmentally) relate directly to economics because these concerns can prevent process operations. Most oil and gas companies take earned pride in the number of accident-free days. Safety is related to cost, but company policy invariably is "safety at all costs" or "If we can't operate safely, we can't operate" (Sloan 2000).

The oil and gas production industry in the U.S 1996 used an estimated 400 million lbm of methanol (MeOH). Shell's usage of MeOH was at the same time 500 million lbm. Conventional methods of hydrate control typically cost 50 million USD for one field. Use of conventional inhibitors requires large storage tanks on the platforms and costly system for injection and possible regeneration (Aker Solutions 2012).
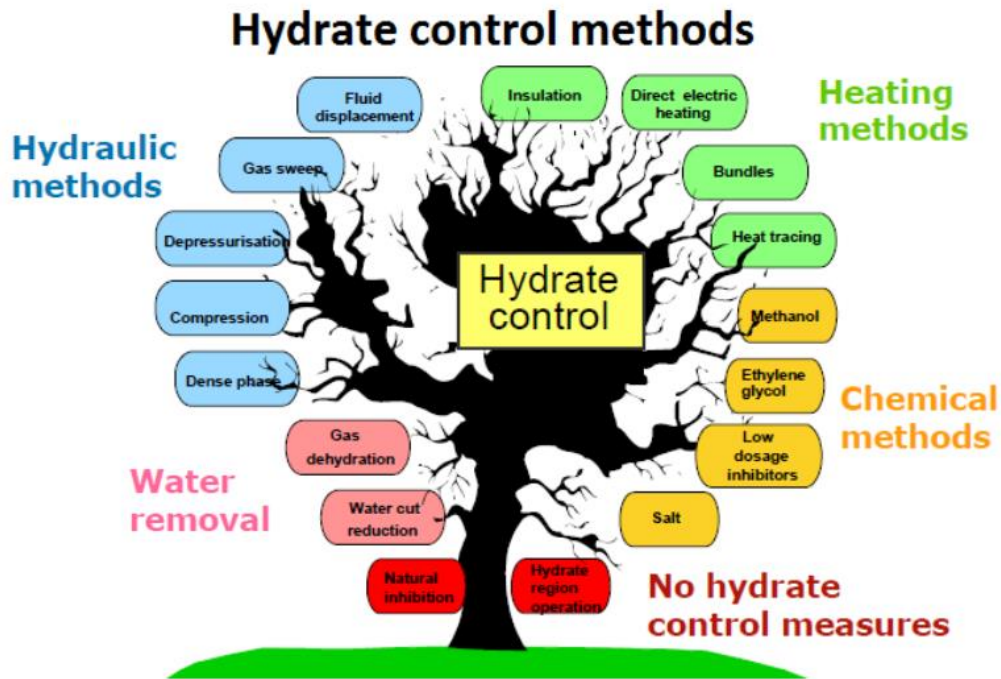
FIGURE 14 HYDRATE CONTROL METHODS (STEINBAKK 2012).

4.2 HYDRATE PREVENTION TECHNIQUES

The permanent solution to prevent hydrate formation is removal of water prior to pipeline transportation, such as using an offshore dehydration plant or subsea separation, which is not often the most cost efficient solution.

Another way to prevent hydrate plugs is to change the pressure and temperature conditions outside the hydrate formation region. By this it means preventing the hydrate envelope (HE), pressure (P) and temperature (T)

production facilities profile from crossing each other during normal production. This can be done by forcing HE to the left using inhibitors such as alcohols and glycol, or by shrinking the P and T production facilities profile to the right by insulation and heating the flow line. As illustrated in Figure 15 below. The figure represents a hydrate formation diagram in the pressure-temperature plane. The region on the right side "No hydrate" covers pressure and temperature at which hydrates are thermodynamically unstable.
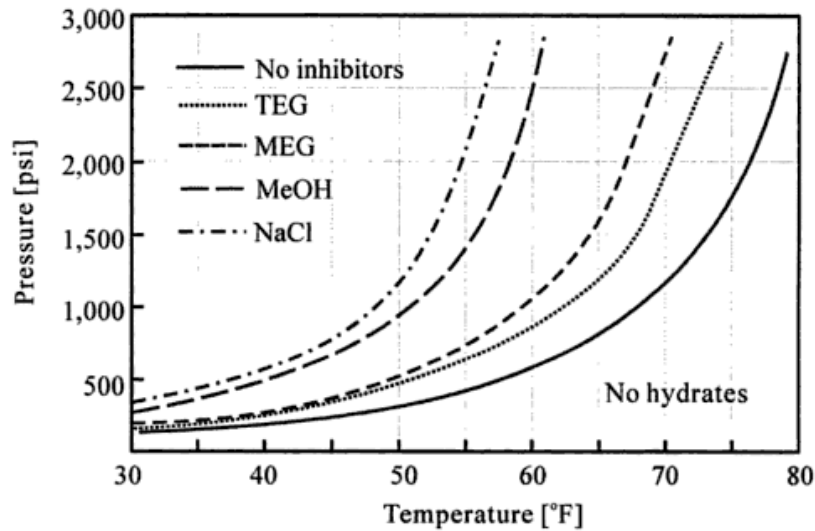
FIGURE 15 HYDRATE PREVENTION BY CHEMICAL INHIBITION (SLOAN 2000).

4.2.1 CHEMICAL INHIBITION

The most common technique in deep water environments is adding chemical compounds that change the behaviour of the mixture. This is to keep pressure and temperature away from hydrate formation region, as briefly explained in the section above. In deep water environments both oil and gas flow lines require hydrate inhibitors. Since typical gas pipelines do not have insulation, chemical inhibition for hydrate formation is continuously required. Oil flow lines are more likely to be insulated but require hydrate inhibitors for start-up and shut-in restarts. Chemical inhibitors are usually injected at the wellhead

and prevent the hydrate formation by decreasing the hydrate temperature below the pipeline operating temperature. If the water production is significant this method is expensive.

For most oil production systems, this cost is prohibitively expensive whereas it can be the least expensive alternative for a gas system. Hydrate inhibition by using chemical inhibitors is still the most widely used method. The development of alternative methods due to cost-effective and environmentally acceptable hydrate inhibitors is a technological challenge for the oil and gas industry (Lederhos et al. 1996).

Thermodynamic inhibitors are chemicals such as methanol, ethanol, ethylene, glycol and triethylene glycol. These have the effect of shifting the hydrate formation area to the left, which causes the hydrate formation point to be displaced to a lower temperature and a higher pressure.

4.3 HEALTH, SAFETY AND ENVIRONMENTAL ASPECTS

The various Health, Safety and Environment (HSE) and technical aspects are important factors to discuss when we talk about chemical inhibition. As well as potential solutions that could improve the possibility of making glycols our preferred hydrate inhibitor when it comes to HSE. However, with increasing focus on HSE in the oil and gas industry, the safety concern of MeOH become more fore frontal.

After the product has been assessed under the HOCNF (Harmonised Offshore Chemical Notification Format), the component level evaluation is undertaken when it is created on the CEMS database and given a colour classification appropriate to its environmental footprint. Table 1 shows an example of the requirement given by HOCNF.

TABLE 1INDEPENDENT ENVIRONMENTAL IMPACT CLASSIFICATION NORWAY

Chemical / Substance	Rating
Water	Green
Chemicals on PLONOR List	Green
Hormone disturbing (1)	Black
Environmental Toxicant (2)	Black
BioDeg < 20% and logPow >= 5	Black
BioDeg < 20% and Tox LC/EC50 = 10 (mg/l, mg/kg)	Black
Chemicals on OSPAR Tainting List	Red
2 out of 3: BioDeg < 60%, logPow >= 3 or Tox LC/EC50 = 10 (mg/l, mg/kg)	Red
Inorganic and Tox LC/EC50 < 1 (mg/l, mg/kg)	Red
BioDeg < 20%	Red
OSPAR Convention, appendix 2	Red
Other Chemicals	Yellow

Green	Allowed to discharge without permission
Yellow	Need discharge permission. Acceptable environmental properties, so applications will usually go through.
Red	Need discharge permission. Chemicals to be phased out. Norwegian authorities are planning to not allow discharging from 2005.
Black	No discharge is permitted (in general)

All chemicals on the PLONOR list are classified as green substances. Methane, ethane and MEG respectively are all classified as green (OSPAR 2008).

An example of Marathon Petroleum's emulsion application for the field "Alvheim" is shown in Table 2. The yearly amount of methanol loss to the ocean is 53 509 kg which contains 0.085 % of total amount. Yearly amount of pH adjusted TEG is calculated to be 0.084% of total.

Kjemikalie-navn (Produksjonskjemikalier)	Funksjon	Miljø-klasse	Forbruk per år (kg)	Utslipp til sjø (kg)
Gyptron SA1170	Scale inhibitor	Gul	243782	24378
Flotron A1670	Asfalthene inhibitor	Gul	97727	7.3
Emulstron CC3295-G	Demulsifier	Gul	166755	1151
Cleartron MRD208SW	Flocculant	Gul	117334	10406
Cortron RN-421	Corrsioninhibitor	Rød	231479	11151
MeOH (Metanol)	Hydrate inhibitor	Grønn	625957	53509
pH adjusted TEG	Hydrate inhibitor	Rød	25875	2174
Bactron B1150	Biocide	Gul	74226	4973
OS2	Oxygen scavenger	Grønn	1567	157
WM1840, Flexoil	Wax inhibitor subsea	Rød	258146	1420
EGMBE	Solvent	Gul	17888	44
Flotron WD1000	Solvent	Rød	33586	0.7
Sum			1894321	109370

In terms of safety, the presence of hydrates can cause serious implications for drilling operations. At the conditions which prevail during drilling, hydrates can form in drilling risers, chokes, kill lines and blowout preventers (Pickering et al. 2001).

In addition, the occurrence of naturally occurring hydrates close to the surface can also present a serious hazard during drilling by releasing gas into the borehole leading to well control difficulties and the potential for blowouts. Furthermore, operations such as fraccing can also suffer from hydrate formation requiring special fluid and inhibitor formulations to prevent blockages (Pickering 1996).

4.4 CHEMICAL PROPERTIES OF GLYCOLS AND ALCOHOLS

TABLE 3 CHEMICAL PROPERTIES OF METHANOL, ETHANOL, MEG AND WATER (KIDNAY & PARISH 2006), (AYLWARD & FINDLAY 2007).

	Methanol	Ethanol	MEG	Water
Empirical formula	CH_4O	C_2H_6O	$C_2H_6O_2$	H_2O
Molecular weight, g/mol	32.042	46.07	62.07	18.02
Boiling point, °C	64.7	78.4	198	100
Vapor press. (at 20°C), kPa	12.5	5.7	0.011	2.3
Melting/Freezing point, °C	-98	-112	-13	0
Density (at 20°C), kg/m³	792	789	1,116	998
Viscosity (at 20°C), cP	0.59	1.2	21	1.002
Surface tension, dynes/cm (at 25°C)	22.07	22.39	48	72
Maximum Recommended Regeneration Temp. [°C]	-	-	163	-

4.4.1 MONO-ETHYLENE GLYCOL (MEG)

Mono-ethylene glycol ($HOCH_2CH_2OH$) is the simplest of the glycols. It is often referred to as just EG or MEG. Common for all glycols is that they contain two hydroxyl (OH) functional groups. MEG is the most widely used glycol, due to its availability, cost and technical efficiency. MEG has a flash point of 116°C and is significantly less flammable than Methanol and Ethanol. Similar to the alcohols MEG has a distinct alcoholic odor and is soluble in water. Referred to Table 3 MEG has a boiling point at 198°C at atmospheric pressure, liquid density of 1116 kg/m³ and a molecular weight of 62 g/mol. At 20°C MEG has a viscosity of 21 cP. The high viscosity is one of the bigger obstacles related to the use of MEG in flow assurance. MEG is moderate toxic to humans. The biggest risks are related to coming in contact with large quantities, as the skin quickly absorbs it. The effect of being exposed to harmful amounts of MEG can be deep and rapidly induced sleep, breathing difficulties and kidney failure (Store Norske Leksikon 2012).

MEG is in environmental classification sector "green" (Marathon Petroleum 2009).

4.4.2 METHANOL

Methanol (CH_3OH) has the simplest alcoholic molecular structure. Due to the availability and price Methanol became one of the most common thermodynamically hydrate inhibitor, compared to other inhibitors, in the oil and gas industry. It is a colourless, toxic and highly flammable substance with a flash point of 11°C. Furthermore, methanol burns with an invisible flame, making fire detection a more difficult problem, combined with the flammability, makes it a very tricky material to handle safely. Similar to ethanol, methanol has a distinct smell of what humans associate with an alcoholic substance.

Methanol has a boiling point of 64.7°C at atmospheric pressure, liquid density of 792 kg/m^3 and a molecular weight of 32 g/mol. At 20°C Methanol has a viscosity of 0, 59 cP. Methanol represents a serious risk to consumers, a dose a small as 7-8 grams and lethal as dose of 30 grams or more are damaging to human beings. It allows less oxygen to be absorbed in the bloodstream and can as a result of this cause permanent blindness, as the retina is one of the first things to suffer from the lack of oxygen (Store Norske Leksikon 2012).

MeOH is toxic and should be prevented from entering the water, and subsequently, the food chain. Such concerns currently are very important in the Norwegian sector of the North Sea and may take precedence over economics. It is assumed that MeOH in the nearest future will be prohibited by environmental concerns (Sloan 2000: p.60). However, methanol is classified as "green" due to HOCNF's environmental classification system (Marathon Petroleum 2009).

4.4.3 ETHANOL

Ethanol (C_2H_5OH) has the second simplest alcoholic molecular structure. It is a colourless substance with a flash point at 14°C. Ethanol has a boiling point at 78, 5°C at atmospheric pressure, liquid density of 789 kg/m^3 and a molecular weight of 46, 07 g/mol. (Shakasiri 2009) Ethanol has been made since ancient time by the fermentation of sugar. Simple sugar is the raw material. The fermentation process is presented by the equation.

$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$$
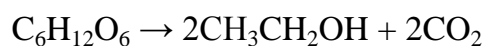
Ethanol is toxic to human beings in a small extend compared to Methanol. Ethanol is common as a hydrate preventing inhibitor in South-America, Brazil. Without further information, it is assuming that ethanol is more easily available because of the sugar production in the region, which is the substance ethanol is made from.

4.5 SOLUBILITY AND PHASE DIAGRAM

Generally, inhibitors are more efficient with decreasing molecular weights. Hence, Methanol is more efficient than Ethanol, which is more efficient than MEG. As a general rule, the anti-microbial activity of alcohols increases with molecular weight and chain length to about C10 (Chandraguptan 2011).

Alcohols have a lower viscosity and their lower surface tension makes effective separation easy at cryogenic conditions. Alcohols with small molecules are volatile, colourless, flammable liquids which are soluble in water. As the molar mass increases, the boiling point, melting point and viscosity also increase, while solubility in water decreases. The boiling point and solubility in water increases by adding hydroxyl groups (OH). These are bonded to a carbon atom and part of the structure for both alcohols and glycols (Martinez 1995).

Methanol, Ethanol and MEG are miscible with water which means they mix in all proportions, forming a homogeneous solution. The term also applies to solids and gases, but the main focus is the solubility of one liquid in another (Martinez 1995).

The figure below illustrates a phase diagram for methanol, ethanol and MEG water solutions.
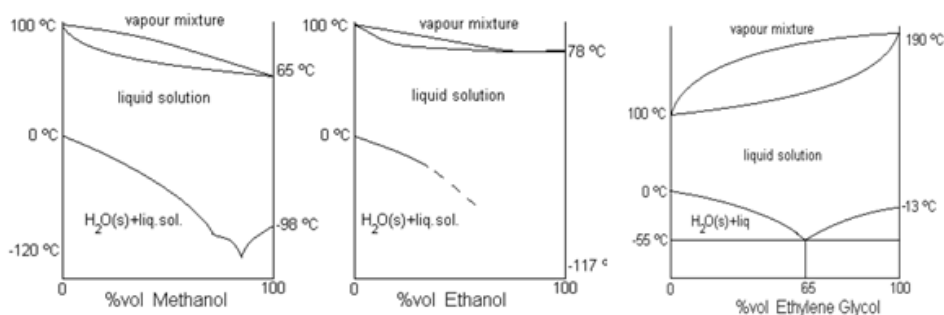
FIGURE 16 PHASE DIAGRAM FOR WATER SOLUTIONS (MARTINEZ 1995).

CHAPTER 5

THEORY ABOUT THE DEHYDRATION AND REGENERATION PROCESS

In the gas dehydration process water is removed from the gas using glycol as a solvent. In the regeneration process water is treated to make it as clean as possible, which is a part of the process called Water Treatment. In the over mentioned process sand, salt and other unwanted chemicals such as THI are removed from the water stream. THI is removed for the reason of recycling if the process is possible or the amount is left for further treatment, which will be discussed in more detail in chapter 6.

The main focus of this chapter will be directed towards regeneration of the water separation system, which also includes methods for sand removal, salt cleaning and hydro cyclones. These processes are included to provide a better understanding of the general process of water separation. The above processes are only included in the regeneration process according to the water treatment and not included in gas drying. Gas dehydration method will be briefly discussed in the first section, because this process is related to the regeneration process in the gas drying situation.

5.1 DEHYDRATION METHOD

The glycol dehydration process can be divided into two parts. First lean glycol dries the wet gas, thereby making the glycol rich. In the second part of the process water is removed from the rich glycol making it lean once again. This process is illustrated in Figure 17.
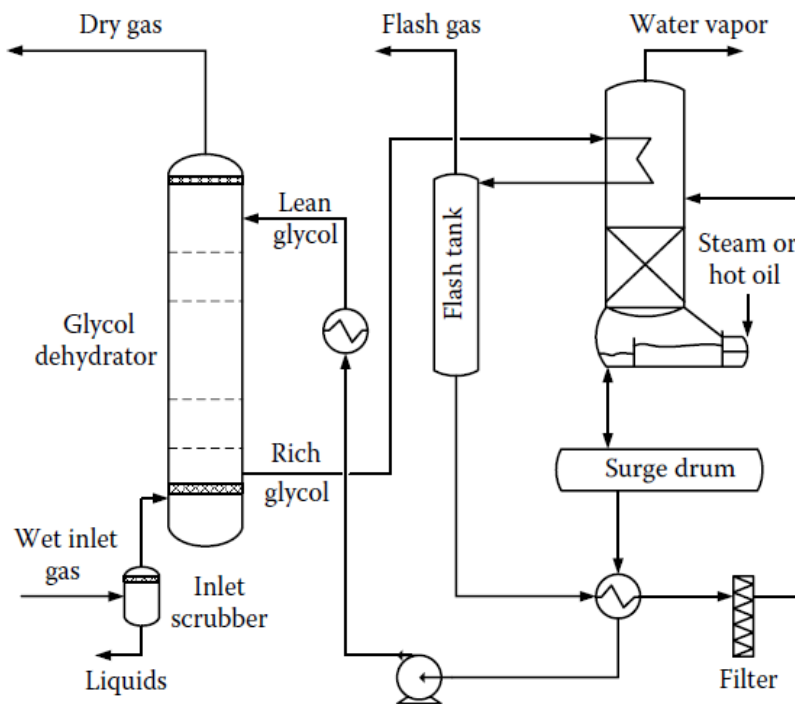
FIGURE 17 SCHEMATIC OF TYPICAL GLYCOL DEHYDRATION UNIT (KIDNAY AND PARRISH 2006).

The most common methods for gas dehydration are absorption, adsorption, membrane processes and refrigeration. Depending on the water content the methods may be combined or be used by themselves (Kidnay and Parrish 2006).

Refrigeration does in many cases not remove enough water from the gas; it is however often used in combination with the other dehydration methods. The

adsorption process yields the lowest water content in the gas, dependent on the adsorbent. Even though the absorption process cannot remove as much water as adsorption process it is still preferable. This is because it removes enough water from the gas that requires for the criteria for the dry gas, as well as it gives a better cost-benefit result than the adsorption process. In some cases where low temperature gas treatment is involved adsorption dehydration is required. In those cases the cost is often reduced by combining adsorption plant with an absorption plant (Christensen 2009).

The efficiency of the dehydration process is evaluated by the water contents in the gas after the dehydration. The water content after dehydration is often given as the water dew-point; this is to ensure that no water will condense in the pipeline. The water dew-point is therefore more practicable because it is directly comparable with the pipeline operating conditions (Christensen 2009).

5.1.1 WATER ABSORPTION IN GAS DEHYDRATION PROCESS

In dehydration by absorption water is removed by a liquid with strong affinity for water, glycols being the most common. The wet gas passes through an inlet scrubber to remove solids and free liquids, and then enters the bottom of the glycol contactor. Dry gas flows upward in the contractor while lean glycol solutions which is glycol with little or no water flows down over the trays. Sometime it might be preferable to lower the gas inlet temperature before the dehydration, so an inlet cooler might also be used. The process is illustrated in Figure 17.

There are certain requirements for absorbents used for gas dehydration, the book *Fundamentals of natural gas processing*; mentions some of the requirements;

- A high affinity for water

- A low affinity for hydrocarbons

- A low volatility at the absorption temperature to reduce vaporization losses

- A low viscosity for ease pumping and good contact between the gas and liquid phases

- A good thermal stability to prevent decomposition during regeneration

- A low potential for corrosion

The most critical property for a good dehydrator is the first point; a high affinity for water. The other criteria are used to evaluate potential absorbents practical applicability in the industry. In practice glycols are the most commonly used absorbents for dehydration.

Referred to Table 3, the most important values are the boiling point, vapour pressure, viscosity and maximum recommended regeneration temperature. The boiling point and the vapour pressure have an influence on the distillation process. The greater the difference for these properties between the top and the bottom product, the easier it is to separate the components. The separation between glycol and water is important because the water contents in the lean glycol determine the amount of water the glycol can remove from the gas.

5.2 WATER TREATMENT

Water is one of the most handled and well used fluids in the petroleum industry. Large volumes of water are used in injection operations, and even larger volumes are a major waste by-product from the production of oil and gas (Ditra and Hoyack 1994). Before produced water can be reused or disposed, the water must be treated to remove the unwanted compounds due to environmental regulations (Ospar Comission 2009).

Displacement water and produced water are the main contributors to the oil discharges from the offshore oil and gas activities in the North Sea, representing 96% of the total amount of oil discharges to the sea in 2009 (Ospar Comission 2009). There is an aim for zero harmful discharge and continuous improvement of water cleaning technology (Ramstad 2013).

The overall reason for water treatment is to be able to either inject produced water back into the reservoir or discharge produced water to the sea or other water bodies. This is done by removing particles and heavy metals and reduces oil in water and bacterial activity and toxic compounds. The reason for water treatment is also to reduce risk of infectivity losses, mechanical failure, environmental impact and reservoir souring (Ramstad 2013).

Figure 18 show the total crude oil and water production by country, in the Asia/Pacific region in 1994. This figure emphasis the large impact water has on oil and gas producers, and the importance of increased focus.

MAJOR CRUDE OIL AND WATER PRODUCTION AREAS
in the Asia/Pacific Region
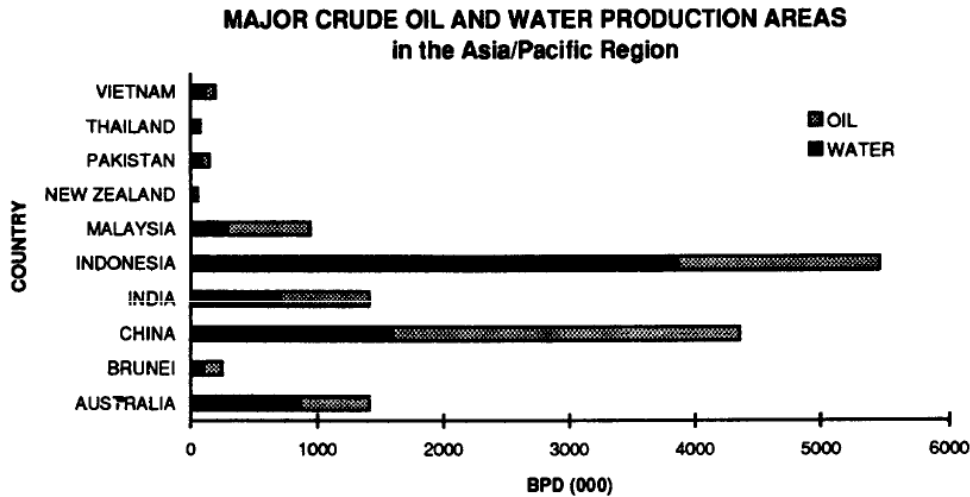
FIGURE 18: MAJOR CRUDE OIL AND WATER PRODUCTION AREAS IN THE PACIFIC/ASIA REGION (DITRA & HOYACK 1994).

Water is always presence in the production of oil and may contain dissolved and dispersed hydrocarbons, dissolved organic and inorganic compounds (Seureau et. al 1994). In addition, produced water may also contain a significant amount of suspended solids of various origins such as precipitation, formation, hydrate inhibitors, corrosion, etc., thus, solids of nature such as clay, sand, sulphates, carbonates, etc.

When water is separated off in the three-phase separator the water stream still contains a small amount of hydrocarbon as well as the over mentioned material. Regardless of the hydrate inhibitor used we want to separate it off the water (Kidnay and Parish 2006).
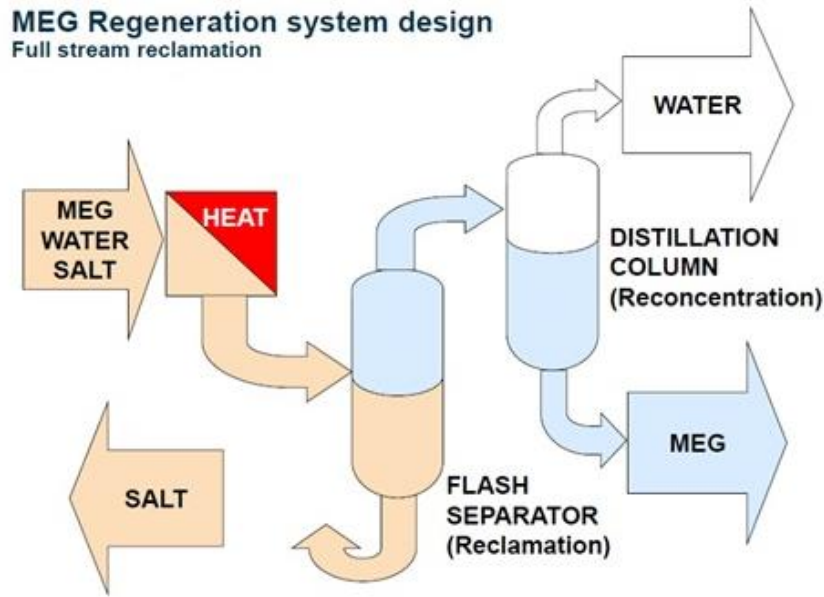
FIGURE 19 MEG REGENERATION SYSTEM DESIGN (SØRLI 2008).

5.2.1 REGENERATION

The regenerator is a distillation column, where glycol/alcohol and water is separated. At the top of the column it is a partly condenser, this provide reflux thus improving the separation between water and glycol/alcohol. The condenser also minimizes glycol loss from the regenerator. The remaining water vapour leaves the condenser and is vented to the atmosphere.

The energy required to separate glycol/alcohol and water is supplied by the re-boiler at the regenerator column. The recommended maximum temperature in the re-boiler is shown in table 1. In the case where glycol is used as THI the lean glycol is taken from the re-boiler and is transferred to a storage tank before it is recycled or in some cases it is recycled directly from the re-boiler. In the case where alcohol is used as THI the alcohol is transferred to a storage tank from the condenser, but is not going through a recycling process since this is a more advanced and costly process. This is explained in more detail in chapter 6.

The pressure in the regeneration system is just above atmospheric pressure, this is to insure that no air can enter the system from the atmospheric vent. A simple way to increase the lean glycol purity is to add a stripping gas to the regenerator or regenerate by vacuum distillation. Stripping gas can be added to the regenerator boiler or in a stripping column after the regenerator column.

5.2.1.1 TRAYS

Tower internals are arguably the most important piece of process equipment since they are hard to maintain because of access after start-up. The technology about trays and the distillations columns internal is complicated and will not be discussed in further detail.
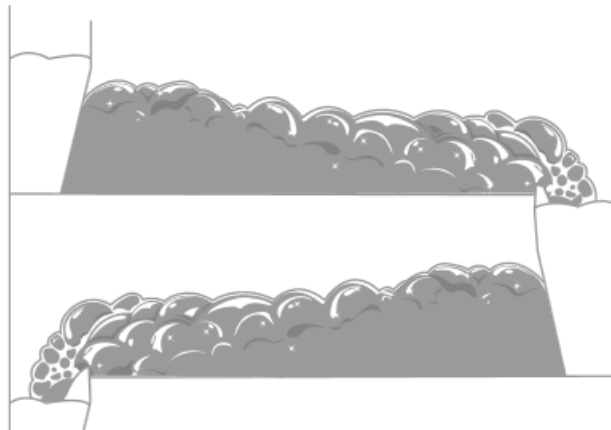
FIGURE 20 TRAYS INSIDE A TOWER ILLUSTRATE VAPOUR BUBBLES DISPERSED IN LIQUID (PILLING AND HOLDEN 2009)

5.2.2 SALT REMOVAL

Salt removal in the regeneration system is a challenge and can be achieved through good chemistry control and proper separation equipment. A closed MEG loop will become contaminated with salt/particles from the gas production. When it comes to chemistry control, low soluble salts like Ca^{2+}, Mg^{2+}, Fe^{2+}, CO_3^{2-} and HCO_3^- must be removed from the phase. Divalent cations will easily precipitate thus forming scale and undesired locations at

low concentrations. The precipitation will be done by alkalinity and temperature control (Seereeram 2008).
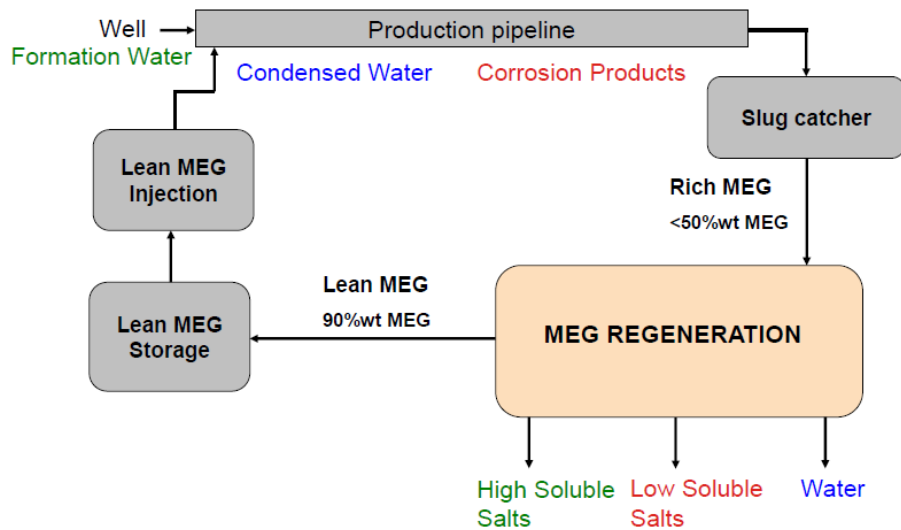
FIGURE 21 CLOSED MEG - LOOP (SØRLI 2010).

Some level of high soluble salts can be tolerated, such as Na^+, K^+ and Cl^-. The precipitation will be done by evaporation and monovalent cations may accumulate up to > 75000 mg/l without precipitation (Seereeram 2008).

Other chemicals: acetat and corrosion inhibitor will not precipitate but accumulates in the Reclaimer.

5.2.3 SAND REMOVAL

The crude and/or water may contain an amount of sand particles when it enters the processing plant. The amount is dependent of the reservoir formation and other factors such as distance from field to shore. As same as salt and THI, sand needs to be removed before water can be reinjected or discharged to the sea.

In a solid-liquid separation the hydrocyclone will be defined as a "desander" and the separation of produced sand from crude and/or water will be defined as "desanding". The dehydration, also called liquid-liquid separation of water

from crude, will be defined as "dewatering" and the hydrocycone will be defined as "dewaterer" (Ditra & Hoyack 1994).

5.2.4 GLYCOL AND ALCOHOL STORAGE TANK

A storage tank is an optimal instalment that ensures a constant glycol flow to the contactor column. Because there will be a loss of glycol in the dehydration system, a storage tank can act as a buffer to prevent insufficient glycol flow, and also be used to measure the glycol contents in the system.

CHAPTER 6

PROCESS SIMULATION

This chapter introduces the process of interest; the separation of water and THI in the regeneration process. Gas dehydration is briefly mentioned because the regeneration process is involved in this operation as well. The rest of the operations in the processing plant are mentioned in appendix B.

To make a basis for comparison for the three cases it is important that the data and procedure are the same for the different cases. To avoid repeating the same procedure three times, this chapter is only explaining the procedure for the case with Methanol as a Thermodynamic Hydrate Inhibitor.

6.1 SIMULATION SOFTWARE

The Software Developer "Lanner" describes a Simulation Software in a following manner:

"Simulation, through the use of simulation software, is the science of creating statistically accurate models to represent the behaviour of real life systems in order to subject them to predictive experimentation. These experiments or scenarios can then enable 'what if?' questions to be answered without risk or disturbance to the real life system." (Lanner 2013).

When using a process simulation program to simulate a process plant there are several things that must be taken into consideration. These considerations include the settings for the simulation program, setting and design for the process plant. When the simulation starts to run additional problems might

arise, because variables need to be defined or values estimated before the simulations converge (Christensen 2009).

6.1.2 THE SIMULATION SOFTWARE HYSYS

Aspen Tech HYSYS is a process modelling software developed by Aspen technologies Inc. AspenTech is a company that develops software exclusively for the process industry that uses thermodynamic models to represent the phase equilibrium behaviour and energy level of pure compound and mixture systems. AspenTech is the world's leading supplier of software that optimizes process manufacturing (Guerra 2006).

"Aspen HYSYS is a market-leading process modelling tool for conceptual design, optimization, business planning, asset management, and performance monitoring for oil and gas production, gas processing, petroleum refining and air separation industries" (AspenTech 2012)

The software HYSYS offer several thermodynamic packages for the calculations involved in the processing plant. A package contains all the thermodynamic equations required to calculate the system. The packages available are the commonly used Equation of State (EOS) like Peng-Robinson, but also more seldom or special packages depending on the components simulated.

6.2 SIMULATION MODEL

The first step using HYSYS is to select a fluid package. Peng-Robinson is selected for the HYSYS simulations, as this is a preferred fluid package for hydrocarbon mixtures. Peng-Robinson is recommended for oil and gas systems because it handles the properties of single-phase, two-phase and three-phase systems with a high amount of accuracy (Aspen HYSYS Simulation Basis Manual 2012). The fluid package contains information

about the physical and flash properties of components, as well as it determines the relation between each component and how they react.

The next step is to input the necessary component needed for the simulation. The Gas Condensate components list from Pedersen o.a (1989) Properties of Oils and Natural Gases, Gulf Publishing Company with some modifications is used in this work. In addition, the components Methanol, Ethanol, EGlycol and H_2O are added to the list. See Table 4.

The input data can be given in several measuring unit sets, depending on the user's choice. In these simulations the units are consistently set to be SI units.

The specifications consist of composition, flow, temperature and pressure for the wet gas and the required purity of the THI. The operation conditions are given in Appendix A. The Gas Condensate component list is illustrated in Table 4. The molar composition is equal in the entire system.

TABLE 4 COMPOSITION OF THE FEED

Molar composition	Molar Mass
Methane	0.7086
Ethane	0.0853
Propane	0.0495
i-n-Butane	0.0200
i-n-Pentane	0.0081
n-Hexane	0.0046
n-Heptane	0.0061
n-Octane	0.0071
n-Nonane	0.0039
n-Decane	0.0028
C_{11}	0.0020
C_{12}	0.0015
C_{13}	0.0011
C_{14}	0.0010
C_{15}	0.0007
C_{16}	0.0005
C_{17+}	0.0037
Water	0.0009
Nitrogen	0.0071
Carbon dioxide	0.0865

The distillation column used in this case is a special type of sub-flowsheet in HYSYS. The operational guide describes a sub-flowsheet to contain equipment and streams, and is used to exchange information with the parent flowsheet through the connected internal and external streams.

The column appears as a single, multi-feed multi-product operation that is ran from the main simulation environment (HYSYS Operational Guide 2003). The most complex unit operations that HYSYS simulates are the multi-stage fractionation towers, such as re-boiled de-methanizer, vacuum and crude distillation units, and extractive distillation columns.

Each one of these towers consists of a series of equilibrium or non-equilibrium flash steps. This process is dependent on the system being simulated. A stage may include one or more feed streams flowing on it, liquid or vapor products withdrawn from it, and can be heated or cooled in a side exchanger.
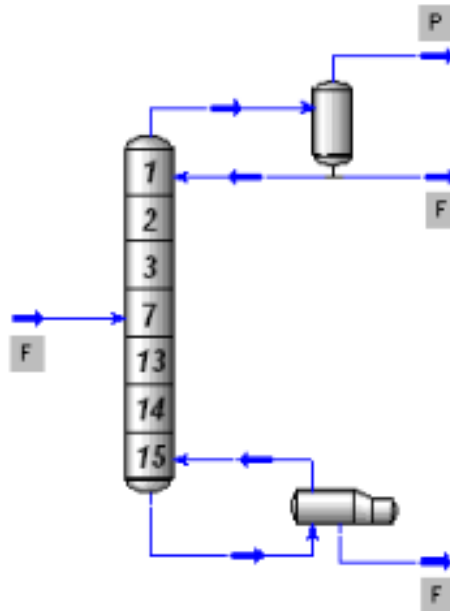
FIGURE 22 STANDARD DISTILLATION COLUMN (HYSYS OPERATIONS GUIDE, 2003).

In this case only one feed stream is entering the tower and no side exchanger involves in the process. A standard distillation column as shown in Figure 22 is used in the process plant.

After the correct tower is chosen, Partial Condenser is set for the case, to give values for vapour flow and water flow that contains salts, solids, alcohol and unwanted chemicals. The next step is to specifying the inlet and the three exit streams which are attached to the main tray section. The number of both inlet and exit streams are depending on the condenser configuration. When used alone, the distillation column has three or four boundary steams but requires four or five pressure-flow specifications; generally one pressure and three or four flow specifications. The extra pressure –flow specification is required due to the reflux stream. The inlet stream is entering the column on the middle tray (HYSYS Operational Guide 2003).

When the streams are defined, HYSYS asks to determine pressure for both condenser and re-boiler.

Pressure in the column is lower than the pressure in the inlet stream, to make the stream boil quicker when it first enters the column. The pressure profile in a Column Tray Section is calculated based on the added specifications.
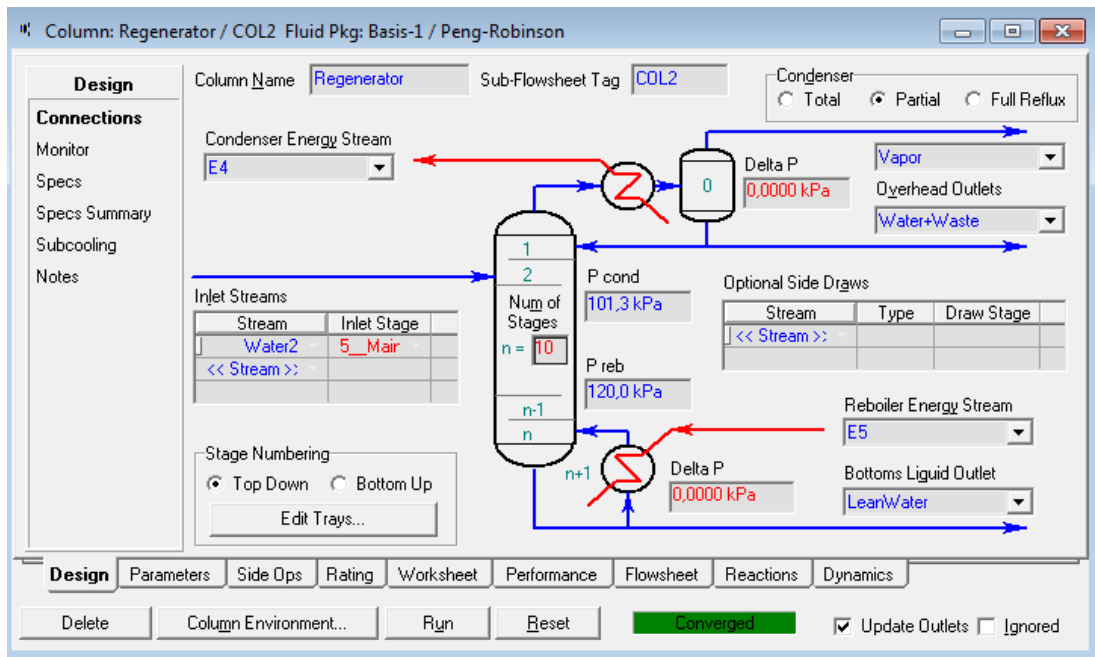
FIGURE 23 "PRINT SCREEN" FROM THE FIRST STAGE OF THE REGENERATOR PROCESS IN ASPEN TECH. HYSYS

The pressure is measured by define the top and bottom tray pressure in an early stage of the simulation. As shown in Figure 23, HYSYS requires pressure at top and bottom of the tower; pressure in the condenser (P cond) and pressure in the re-boiler (P reb). Pressure at the condenser is required to be lower than pressure at the re-boiler to make the stream flow to the top.

HYSYS will then interpolate between the specified values to determine the pressure profile. Simple linear interpolation is used to calculate the pressure on stage which is not explicitly specified Figure 24 illustrates the pressure profile for the case with Methanol as a THI. As shown in Figure 24 pressure in tray at the top (tray number 1) and bottom (tray number 10) of the column is

constant and increases linear from 101.3 kPa to 120kPa from top to bottom (HYSYS Operational Guide 2003).
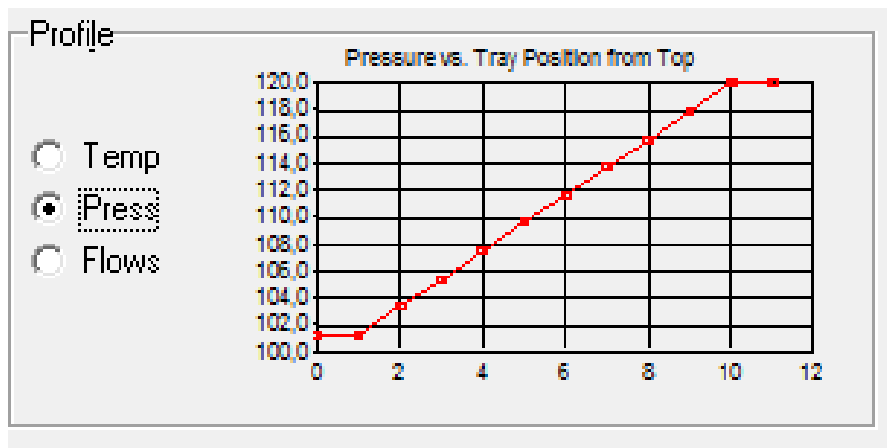
FIGURE 24 "PRINT SCREEN" OF THE GRAPH; PRESSURE VS. TRAY POSITION FROM TOP TO BOTTOM OF THE COLUMN, IN THE CASE WITH METHANOL AS THI

The number of stages in the distillation column is automatically set to be 10 and have to be changed manually. The number that is specified for the tray section does not include the condenser at the top and bottom re-boiler. The vapour that leaves each stage flows to the stage above.
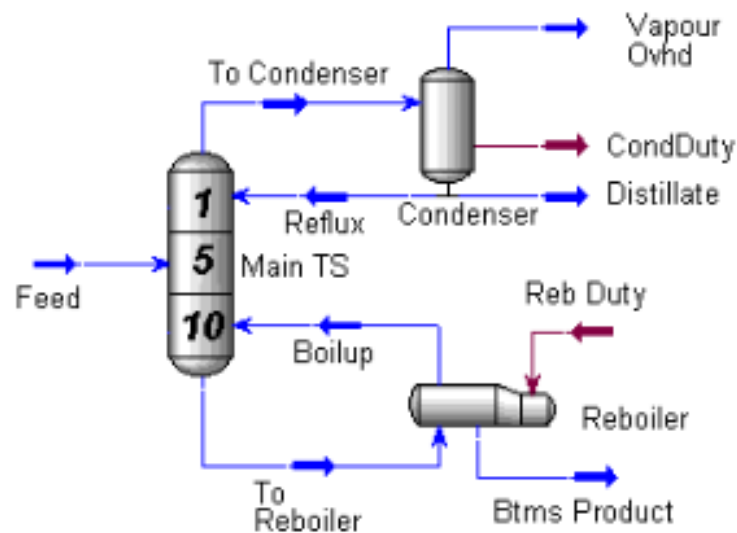
FIGURE 25 STREAM SPECIFICATIONS FOR DISTILLATION COLUMN WITH A CONDENSER AND RE-BOILER (HYSYS OPERATIONS GUIDE)

The partial condenser has three exit streams, as shown in Figure 25 and Figure 26.

- Overhead vapour (P)
- Reflux (F)
- Distillate (F)
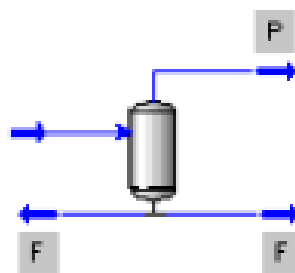
FIGURE 26 PARTIAL CONDENSER IN THE DISTILLATION COLUMN

HYSYS recommends one pressure specification for the Overhead vapour stream, and one flow specification for either of the liquid product streams; reflux flow and Distillate.

The re-boiler has two exit streams:

- Boil-up vapour
- Bottom liquid (F)
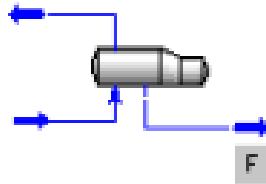
FIGURE 27 RE-BOILER IN THE DISTILLATION COLUMN

In the re-boiler only one exit stream can be specified; the stream of the heavy product. In this process will the exit stream from the re-boiler contain water or a mixture of water and glycol depending of the selected THI used in the particular case. If a pressure constraint is specified elsewhere in the column, this exit stream must be specified with a flow rate. The heavy product is dependent on the products involved in the specific mixture. In the mixture of glycol and water, glycol will be the heavy product, in the mixture of water and alcohol; water will be the heavy product (HYSYS Operational Guide 2003). Refers to Table 3.

TEMPERATURE

The Profile page in the Parameters tab of the Column Property view can also be used for temperature changes in the system. Temperature estimates can be given for any stages in the column, including the re-boiler and the condenser.

Another way to change temperatures in the system is by adding specifications in the Monitor tab. The specified temperature for both the condenser and the re-boiler are defined by the thermodynamic inhibitor used in the specified system. See Table 5. If the overhead product is a subcooled liquid, it is best to

specify an estimated bubble-point temperature for the condenser rather than the subcooled temperature (HYSYS Operational Guide 2003).

TABLE 5 OVERVIEW OF TEMPERATURE IN THE REGENERATION PROCESS

Case	1: Methanol	2: Ethanol	3: MEG
Inlet Temp [°C]	20	20	20
Temp. Condenser [°C]	82	83.5	98
Temp. Re-boiler [°C]	115	101	150

In this case, the overhead product is water, and therefore not a subcooled liquid. The estimated temperature is set to just above the bubble point for water; 102 °C. Temperature for the inlet stream is just below the boiling temperature for the overhead product. The temperature in the condenser should be at or slightly above boiling temperature for the overhead product.

The temperature in the re-boiler should be below boiling point for the heavy components. In this case, the heavy components are either water or MEG in the three cases. The various temperatures for the case with Methanol are shown in Figure 28. Temperature increases from 82°C to 115°C from top of the column to the bottom as shown in Table 5 and Figure 28 (HYSYS Operational Guide 2003).
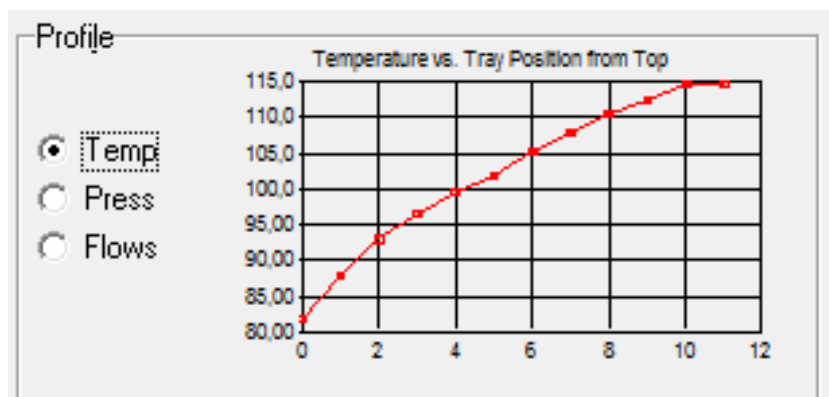

FIGURE 28 "PRINT SCREEN" OF THE PLOT; TEMPERATURE VS. TRAY POSITION FROM TOP TO THE BOTTOM OF THE COLUMN, IN THE CASE WITH METHANOL AS THI

After the input data are given HYSYS requires two variables that need to be defined in this particular case. This is illustrated in the Monitor tab and the picture of Degrees of Freedom. HYSYS is able to run when the Degrees of Freedom is equal to zero. When one specification is made active, the degree of freedom is decreasing by one. Conversely, when you deactivate a specification, the degrees of freedom are increased by one. You can start column calculations when there are zero degrees of freedom. Since two design criteria are given namely to the condenser and re-boiler temperature these are set to be Active. When these criteria are entered into HYSYS the column control screen is shown in Figure 29 (HYSYS Operational Guide 2003).
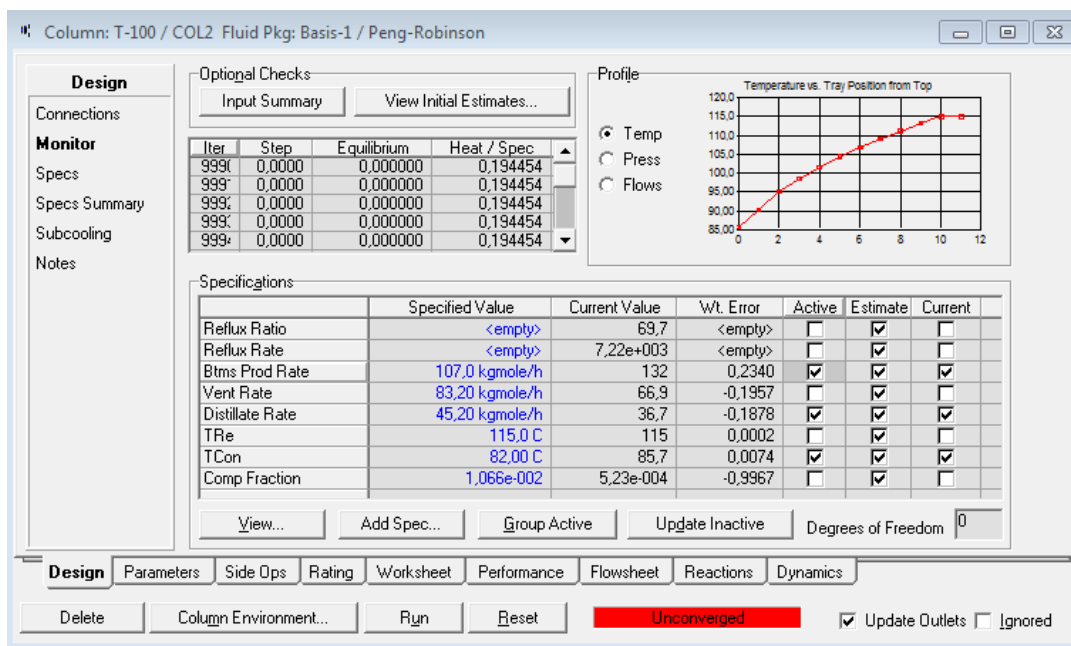
FIGURE 29 "PRINT SCREEN" OF THE UNCONVERGED PROCESS IN THE REGENERATOR PROCESS IN ASPEN TECH. HYSYS

As shown in Figure 29 the simulations are unable to converge with only the condenser and the re-boiler temperature given. More information about the process is required and the design parameters can be supplemented by estimated start values that help to solve the calculations. To make HYSYS

converge quicker, the estimates should be chosen as suitable to the system as possible (HYSYS Operational Guide 2003).

There are three ways to provide the column with initial estimates:

- Provide the estimate values when first build the column.
- Go to the profiles or Estimates page on the Parameters tab to provide the estimate values.
- Go to the Monitor or Spec on the Design tab to provide values for the default specifications or add your own specifications.

In this system, the last option is chosen. Values for the default specifications are provided in the Monitor tab. Obvious estimates are data that are already known or can be easily estimated by the situation. The first estimate is the Bottom Product Rate (Btms Prod Rate) which is calculated by HYSYS to be 107 kgmole/h.

A second estimate is Vent Rate which is calculated by HYSYS to be 83.20 kgmole/h.

A third estimate is in this case set to be Temperature Reboiler (TRe). HYSYS does not require the Re-Boiler temperature to be active and works well with the specified value for Distillation Rate (HYSYS Operational Guide 2003).

The information required to make the simulation converge varies from case to case. The column of Wt. Error gives an indication of the values used. With the added values shown in Figure 30, the column now converges.
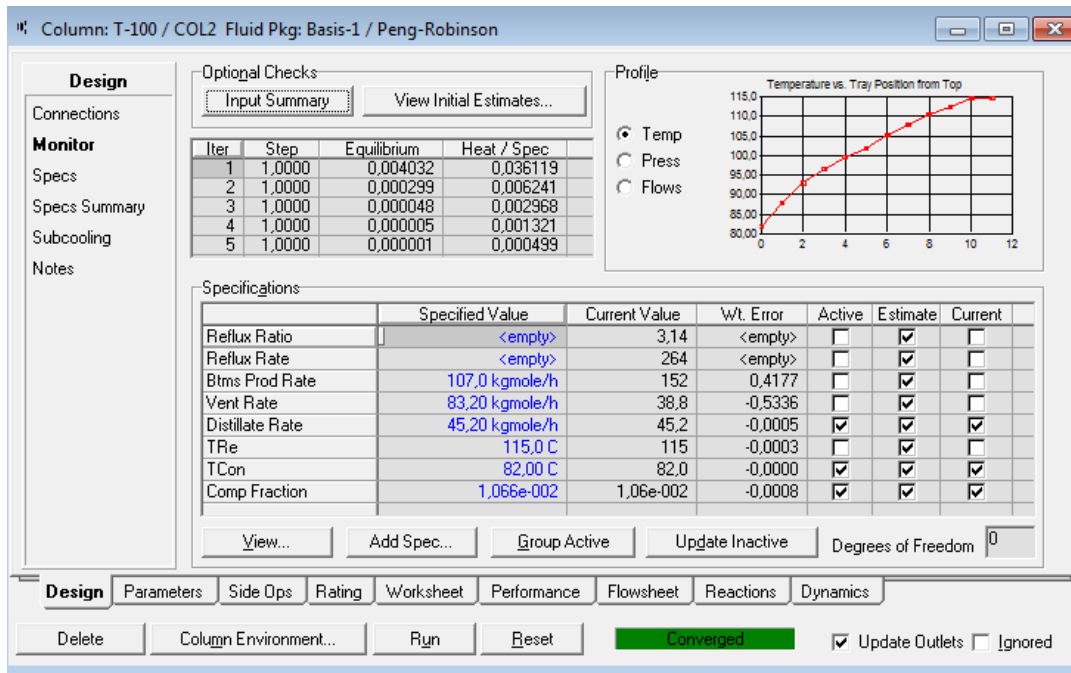
When the distillation column starts to run the simulations for the first time or after the reset function has been used, it is important to take into consideration the specification values are still estimates. If one of the original default specifications (side liquid draw, overhead vapour flow or reflux ratio) has been replaced with a new active specification, the new specification value is used as initial estimates. For this reason HYSYS recommends to provide reasonable specification values initially (HYSYS Operational Guide 2003).

The HYSYS Operational Guide 2006 describes the Regeneration Control Screen in Figure 31. Each specification, along with its specified value, current value, weighted error, and status is shown in the Specifications Group. A specified value can be changed by typing directly in the associated Specified Value cell. Any changes made in one place are reflected in the total system.

FIGURE 31 HYSYS'S DESCRIPTION OF THE REGENERATOR CONTROL SCREEN FROM THE USER GUIDE (HYSYS OPERATIONAL GUIDE, 2012)

6.2.2 THE DEHYDRATION PROCESS
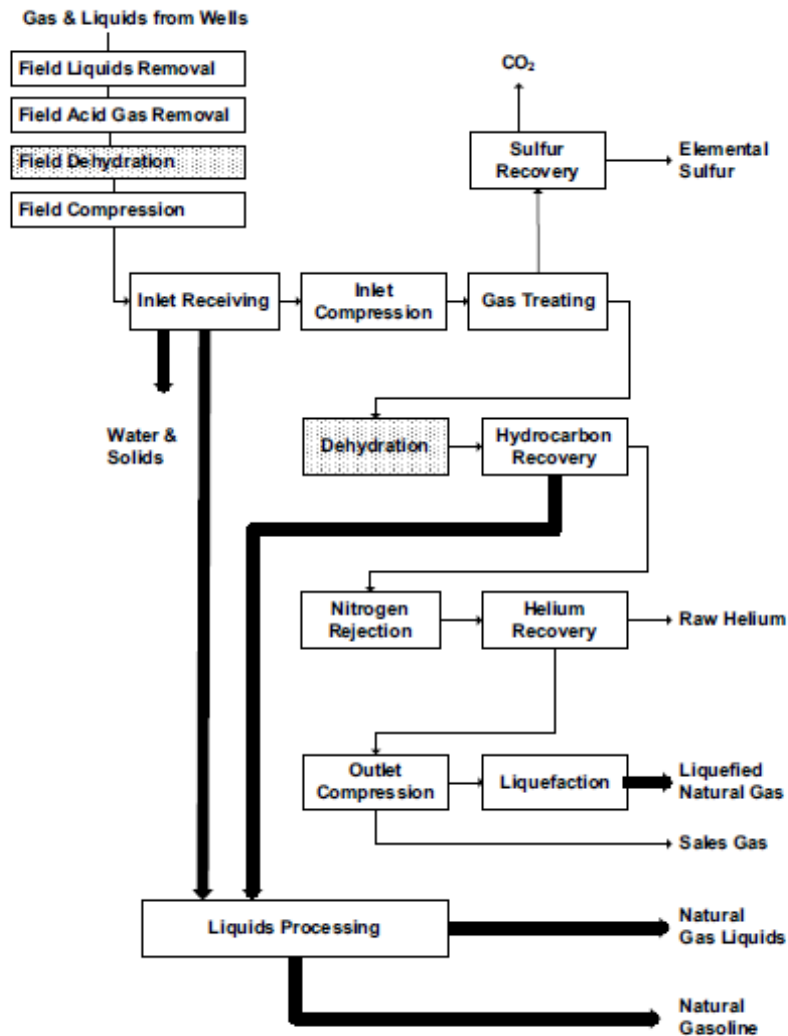
FIGURE 32 OVERVIEW OF THE GAS DEHYDRATION PROCESS (KIDNAY & PARISH, 2003)

Figure 33 shows the recommended flow specifications for an absorber column. The same kind of Absorber is used in the dehydration process and has two inlet and two exit streams. The absorber has four boundary streams and then requires four Pressure Flow specifications. A pressure specification is always required for the liquid product stream leaving the bottom of the column. A second pressure specification should be added to the vapour product of the top of the column, in this case set to be 2000 kPa, and the bottom pressure in this case is set to be 7000 kPa (HYSYS Operational Guide 2003).
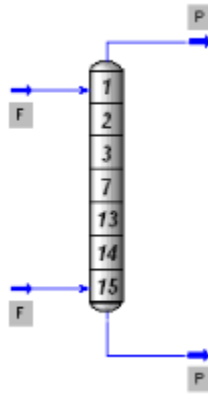
FIGURE 33 STANDARD ABSORBER COLUMN (HYSYS OPERATIONS GUIDE)

The contactor is a column with five trays. TEG is used as an absorbent in the three different cases. The TEG inlet (LeanTEG) and gas outlet (Dry Gas) are placed at the top of the column and the gas inlet (Wet Gas) and the TEG outlet (Rich TEG) are placed at the bottom of the column. The entire process is described in Appendix A.

CHAPTER 7

SIMULATION RESULTS

The HYSYS simulation model developed in section 6.2 has been done in three cases. The simulation model is equal in the different cases and the results differ in the way THI is selected. In this chapter the simulation results from the three cases with Methanol, Ethanol and MEG as THI are presented. The results given in this chapter are limited to the results of interest. All values are taken directly from simulations with an exception of some calculations which are explained in appendix C.

First, the distribution of THI, CO_2 and Water in the four streams that are attached to the Distillation Column is presented.

Second, results from each of the three cases are respectively presented. Four different tables in each case indicate:

1. The total material balance in the Distillation Column; $q_{in} = q_{out}$

2. How the stream is distributed between Vapour, Liquid and Aqueous Phase. The total mass flow [kg/h] in the system and mass flow of THI is also presented.
3. Material balance for THI in the same system.
4. How the total flow is distributed in the system compared to the distribution of THI.

7.1 DISTRIBUTION OF THI, H_2O AND CO_2

Table 6 illustrates only the distribution of water (H_2O), THI and carbon dioxide ($CO_{2)}$, isolated in each of the four streams that are attached to the distillation column. The results only give an indication of the distribution and not the amount of material in the system. To give an understanding of the distributed material in the system the flow rate has to be included. This is illustrated in the next section.

TABLE 6 DISTRIBUTION OF H20, THI AND CO2 IN THE INLET AND THE THREE OUTLET STREAMS IN A DISTILLATION COLUMN (ASPEN TECH HYSYS 2006)

	Methanol [%]	Ethanol [%]	MEG [%]
Water, Inlet:			
H_2O	83.13	99.98	71.60
THI	*16.83*	*0.01*	*28.35*
CO_2	0.04	0.01	0.06
Bottom Product:			
H_2O	98.93	100	22.55
THI	*1.07*	*0.00*	*77.45*
Distillate:			
H_2O	67.43	3.99	100
THI	*32.57*	*95.37*	*0.00*
CO_2	0.00	0.64	0.00
Vapour:			
H_2O	39.68	3.06	93.28
THI	*60.07*	*30.30*	*0.00*
CO_2	0.24	65.37	6.64

7.2 CASE 1: METHANOL

TABLE 7 MATERIAL BALANCE IN CASE 1: METHANOL (ASPEN TECH HYSYS 2006)

1.	Stream	Flow [kg/h]	Total [kg/h]
In :	Water2	4804	4804
Out :	Vapour	1029	
	Distillate	1021	4805
	Bottom Product	2755	

TABLE 8 HYSYS RESULTS FOR CASE 1: METHANOL (ASPEN TECH HYSYS 2006)

2.	Stream 1: Inlet	Stream 2: Vapour	Stream 3: Distillate	Stream 4: Bottom Product
Mass Fraction MeOH [wt%]	0.1683	0.6007	0.3257	0.0106
Mole Flow [kgmole/h]	35.7	38.82	45.20	151.7
Mass Flow [kg/h]	4804	1029	1021	2755
Mass Flow, MeOH [kg/h]	808.5	618.1	332.5	29.2
Mass Fraction, Vapour Phase [wt%]	-	0.6007	-	-
Mass Fraction, Liquid Phase [wt%]	-	-	-	-
Mass Fraction, Aqueous Phase [wt%]	0.1683	-	0.3257	0.0106

TABLE 9 MATERIAL BALANCE FOR THI IN CASE 1: METHANOL (ASPEN TECH HYSYS 2006)

3.	Stream	Flow [kg/h]	Total [kg/h]
In :	Water2	808.5	808.5
Out :	Vapour	618.1	
	Distillate	332.5	
	Bottom Product	29.2	979.8
Difference			171.3 (= 17.5%)

TABLE 10 DISTRIBUTION OF METHANOL IN THE DISTILLATION COLUMN (ASPEN TECH HYSYS 2006)

4.	Stream 2: Vapour	Stream 3: Distillate	Stream 4: Bottom Product
Distribution of Total Flow Rate [%]	21.4	21.3	57.3
Distribution of Methanol [%]	63	33.9	2.9

7.3 Case 2: Ethanol

TABLE 11 MATERIAL BALANCE FOR CASE 2: ETHANOL (ASPEN TECH HYSYS 2006)

1.	Stream	Flow [kg/h]	Total [kg/h]
In :	Water2	3280	3280
Out :	Vapour	1.436	
	Distillate	8.799E-5	3280.436
	Bottom Product	3279	

TABLE 12 HYSYS RESULTS FOR ETHANOL (ASPEN TECH HYSYS 2006)

2.	Stream 1: Inlet	Stream 2: Vapour	Stream 3: Distillate	Stream 4: Bottom Product
Mass Fraction EtOH [wt%]	0.0001	0.3030	0.9537	0.000
Mole Flow [kgmole/h]	182	0.03291	1.958E-6	182
Mass Flow [kg/h]	3280	1.436	8.799E-5	3279
Mass Flow, EtOH [kg/h]	0.328	0.435	8.391E-5	-
Mass Fraction, Vapour Phase [wt%]	-	0.3030	-	-
Mass Fraction, Liquid Phase [wt%]	-	-	0.9537	-
Mass Fraction, Aqueous Phase [wt%]	0.0001	-	-	-

TABLE 13 MATERIAL BALANCE FOR THI IN CASE 2: ETHANOL (ASPEN TECH HYSYS 2006)

3.	Stream	Flow [kg/h]	Total [kg/h]
In :	Water2	0.328	0.328
Out :	Vapour	0.435	
	Distillate	8.391E-5	
	Bottom Product	0.000	0.435
Difference			0.107 (= 24.6%)

TABLE 14 DISTRIBUTION OF ETHANOL IN THE DISTILLATION COLUMN (ASPEN TECH HYSYS 2006)

4.	Stream 2: Vapour	Stream 3: Distillate	Stream 4: Bottom Product
Distribution of Flow Rate [%]	0.1	0	99.9
Distribution of Ethanol [%]	100	0	0

7.4 CASE 3: MEG

TABLE 15 MATERIAL BALANCE FOR CASE 3: MEG (ASPEN TECH HYSYS 2006)

1.	Stream	Flow [kg/h]	Total [kg/h]
In :	Water2	2906	2906
Out :	Vapour	15.89	
	Distillate	1073	2905.89
	Bottom Product	1817	

TABLE 16 HYSYS RESULTS FOR MEG (ASPEN TECH HYSYS 2006)

2.	Stream 1: Inlet	Stream 2: Vapour	Stream 3: Distillate	Stream 4: Bottom Product
Mass Fraction MEG [wt%]	0.3414	-	-	0.7745
Mole Flow [kgmole/h]	95.23	0.8049	59.57	34.85
Mass Flow [kg/h]	2906	15.89	1073	1817
Mass Flow, MEG [kg/h]	992.11	-	-	1407.27
Mass Fraction, Vapour Phase [wt%]	0.0143	-	-	-
Mass Fraction, Liquid Phase [wt%]	-	-	-	0.7745
Mass Fraction, Aqueous Phase [wt%]	0.3271	-	-	-

TABLE 17 MATERIAL BALANCE FOR THI IN CASE 3: MEG (ASPEN TECH HYSYS 2006)

3.	Stream	Flow [kg/h]	Total [kg/h]
In :	Water2	992.11	992.11
Out :	Vapour		
	Distillate		
	Bottom Product	1407.27	1407.27
Difference			415.16 (= 29.5%)

TABLE 18 DISTRIBUTION OF MEG IN THE DISTILLATION COLUMN (ASPEN TECH HYSYS 2006)

4.	Stream 2: Vapour	Stream 3: Distillate	Stream 4: Bottom Product
Distribution of Total Flow Rate [%]	0.55	36.9	62.5
Distribution of MEG [%]	0	0	100

CHAPTER 8

DISCUSSION

Information about the processes involved in water treatment has been presented in the three preceding chapters. The main objective has been the study of regeneration process when injected THI such as Ethanol, Methanol and MEG were used and the analysis of the distribution of the mentioned chemicals.

In this chapter a direct analysis of the three simulated cases will be made. Next, weaknesses and limitations of data and the model used will be discussed. Finally, suggestions to improve the system will be presented.

8.1 BASIS OF COMPARISON

If alcohols are used as THI, the Distillation Column will distil off the alcohol because of their lower vapour pressure compared to water. If glycols are used, then water will be distilled off because water has a lower vapour pressure than glycols. Simulations done in this thesis show how the distillation column works in relation to which products that dissociate either at the top of the column; in the distillation stream or as vapour, or at the bottom of the column; in the bottom product stream.

Table 6 verifies the statement of distribution of alcohols and glycols in the Distillation Column; heavy products dissociate in the bottom of the column and light products at the top of the column as vapour and/or distillate. In a mixture with water, alcohols act as the light product while glycols act as the heavy product.
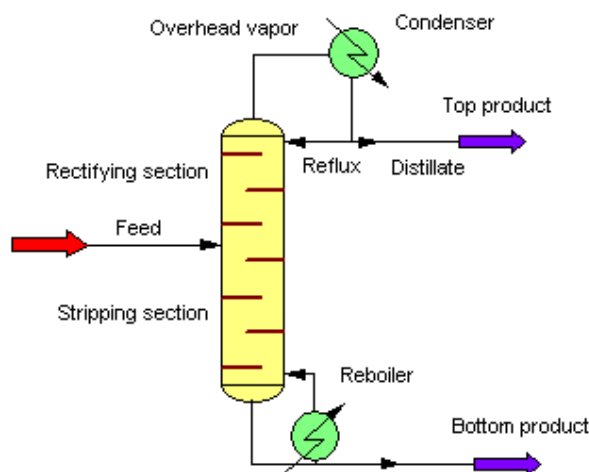

FIGURE 34 SCHEMATIC OF A DISTILLATION COLUMN (ASPEN TECH HYSYS 2006)

In case 1 and 2 the condenser temperatures are much higher than boiling point for both methanol and ethanol and the reason for the high amount of THI in Vapour Stream at the top of the condenser. HYSYS recommends this high temperature in the regeneration process to make the system converge.

8.2 EVALUATION OF CASE 1: METHANOL

Methanol has a lower vapour pressure compared to water and will for this reason be distilled off. See Table 3. The boiling temperature for Methanol, as illustrated in Table 3 is 64.7°C, and temperature for Condenser used in the distillation column is recommended of HYSYS to be slightly above boiling point. See Table 5.

Table 7 illustrates the total Material Balance in the case with Methanol used as THI. The calculations indicate a flow rate higher out of the system than in to the system, with an error of 1 kg/h. An increase of flow rate in a closed system where there is no access to other materials is unrealistic and this error is due to a weakness in the operation. HYSYS calculates the flow rate without decimals, so this may be a reasonable assumption in relation to the error in the case.

The distribution of flow rate in the distillation column is as follow; 21.4% leaves as vapour, 21.3% leaves as distillate and 57.3% leaves as bottom product. The distribution of methanol is as follow; 63% leaves as vapour, 33.9% leaves as distillate and only 2.9% leaves as bottom product. The process does not act properly in terms of distribution since the flow is dispersed and needs to be separated once more before the loop is complete. This leads to a more advanced and costly process.

When methanol is used as thermodynamic hydrate inhibitor the methanol will distribute only in the aqueous phase and gas phase and nothing will be dispersed into liquid phase. This is illustrated in Table 8.

Table 9; Material Balance for THI in Case 1: Methanol indicates a difference in the material balance calculations to be +17.5% which means the amount of methanol increases inside the column. In a closed system where no other material is added and there is no room for chemical reaction to occur in terms

of increase the amount of methanol, the situation is assumed to occur because of weaknesses due to the model and data provided.

Because of the low boiling temperature for methanol, the chemical properties compared to water and the distribution of methanol in the process it is assumed that the use of Distillation Column alone in HYSYS is not suitable for the process of separate water and methanol.

8.3 Evaluation Of Case 2: Ethanol

Similar to Methanol, Ethanol has a lower vapour pressure compared to water and will react in the same manner as Methanol, as described in section 8.2. The boiling temperature for Ethanol, as illustrated in Table 3 is 78.4°C, and temperature for Condenser used in the distillation column is recommended of HYSYS to be slightly above boiling point. See Table 5.

Table 13 illustrates the total Material Balance in the case with Ethanol used as THI. Similar to Case 1: Methanol, the calculations indicate a flow rate higher out of the system than in to the system, with an error of 0.564 kg/h. An increase of flow rate in a closed system where there is no access to other materials is unrealistic and this error is due to a weakness in the operation. HYSYS calculates the flow rate without decimals, so this may be a reasonable assumption in relation to the error in case 2.

The distillation process gives a perfect distribution of ethanol as 100% lean ethanol leaves the Distillation Column as vapour. All amount of ethanol is evaporated to the vapour phase through the condenser because the high temperature in the condenser. However, the Distillation Column works properly in terms of perfect distribution, but the amount of ethanol left after transportation is minimal. As illustrated in Table 13 only 0.328 kg/h out of 2000 kg/h is left when the water stream enters the Distillation Column. In this case I would recommend a simplified method which is less costly.

Differently to case 1, ethanol will distribute mainly in the liquid phase and gas phase and just a small amount will be dispersed into aqueous phase. This is illustrated in Table 12.

Because of the low boiling temperature for ethanol, the chemical properties compared to water and the over mention reason it is assumed, similar to case 1, that the Distillation Column used in HYSYS is not suitable for the process

of separate water and ethanol. Alcohols have different properties than glycols and are usually not preferred as THI in the petroleum industry. Methanol is a better choice than ethanol due to chemical properties.

Table 13; Material Balance for THI in Case 2: Ethanol indicates a difference in the material Balance calculations to be + 24.6%. The reason for the increased amount of ethanol is assumed to be similar to that in Case 1. Compared to Case 1 is the increase of THI slightly higher in Case 2. This is due to the chemical properties of methanol and ethanol and their different solubility in water.

8.4 EVALUATION OF CASE 3: MEG

Table 6 and Table 16 illustrate the distribution of THI in the system and confirm that the distillation column works properly in the situation with MEG as inhibitor, with 100% of MEG dissociates as bottom product.

Compared to case 1 and 2, case 3 works best in terms of the amount THI left after transportation. Table 17 shows the amount of MEG when entering the processing plant; 979.8 kg/h out of 2000 kg/h.

The results refer to a perfect distribution of THI leading to a simplified process for recycling. Since the bottom product stream containing pure quantity of MEG, I will further conclude that the process is optimal for the use of MEG as a THI

Boiling point for MEG is 198°C and Maximum Recommended Regeneration Temperature is 163°C, as illustrated in Table 3. HYSYS recommends the temperature in the Re-Boiler to be 150°C, see Table 5, which is lower than both Boiling Point and Maximum Recommended Regeneration Temperature. The low temperature of the Re-Boiler is the reason for the perfect distribution and no amount of MEG left to the Vapour or Distillation stream.

Table 17; Material Balance for THI in case 3: MEG indicates a difference in material balance calculations to be +29.5%. The value is higher than Methanol and Ethanol respectively and is due to the different chemical properties of alcohols compared to glycols. Refers to Table 3.

8.5 WEAKNESSES AND LIMITATIONS

The simulations done are simplified models designed to obtain a clear view of the processes involved, comparison of the three different cases and an overview of produced fluid composition, flow rates, temperatures and pressures. The simulations do not represent the actual and completed process flow diagram. This error is due to limited data available and data that might not be up to date. In addition to this weakness due to previous work that is not up to date is also a consideration.

The regeneration process involved in the gas dehydration would have given a better understanding of the entire process and should have been included to give a complete overview of the situation. The processes included in water treatment, such as sand and salt removal as explained in section 5.2, should also been included in the simulation. In addition to this, circulation pump, heat exchangers and glycol storage tanks would have given a better understanding of the processes involved. Alcohol will not be recirculated due to economics and the storage process of alcohol is not included in this report. Due to limitations when it comes to time and guidance this part is left out and left for future improvement.

8.6 POTENTIAL IMPROVEMENTS AND SUGGESTIONS FOR FURTHER WORK

The oil and gas industry is still under increasing researching about alternative methods and other hydrate inhibitors that are cost-effective and environmentally acceptable when it comes to multiphase flow to be transported over long distances.

More comprehensive analysis of data from producing fields is required to evaluate conservatism in design producers. This analysis should be performed over a wide range of field types that are possible and should include both successful development and plagued by Flow Assurance issues. By such a methodical approach, it will be possible to accurately quantify the levels of Flow Assurance risk and environmental consequences due to lost inhibitor in the entire system (Watson 2003).

If the produced water is to be re-injected into the formation, it is important that suspended solids are reduced to prevent potential blockage of the receiving medium (Seureau et. al 1994). In this case de-sanding hydro cyclones are commonly used for the separation of two phases. The process can be used to separate solids or liquid from gases, to separate a lighter dispersed liquid from and heavier continuous liquid or as in this case to separate solids from liquid.

The over mentioned process is suggested as the next step in terms of separate water from potential solids. There are some additional features that should be considered and left for future improvements when designing a regeneration plant:

➢ Installing a flash separator before the regeneration column. This separator removes the majority of the hydrocarbon that is dissolved in

the glycol.

- ➢ Integrating heat exchangers, so the lean glycol is cooled by heating the rich glycol, thus minimizing the energy consumption.
- ➢ Glycol/alcohol make-up to replace the glycol/alcohol loss, stored in a storage tank.

Because of these considerations the design of the regeneration process varies with the design of the plant. The integration of heat exchangers is especially important, because this reduces the overall energy consumption of the plant (Christensen 2009).

An important question for further work is what is going to happen with the amount of alcohol that leaves the Distillation Column if the process is too expensive for recirculation.

C HAPTER 9

CONCLUSION

Based on data available and some modifications done it was possible to simulate the regeneration unit in HYSYS. The following conclusions are drawn:

Case 1 Methanol: The process does not act properly in terms of distribution; the flow is dispersed and needs to be separated once more before the loop is complete. This leads to a more advanced and costly process. It is assuming that the use of Distillation Column alone in HYSYS is not suitable for the process of separate water and methanol.

Case 2 Ethanol: The distillation process gives a perfect distribution of ethanol with 100% lean ethanol leaving the Distillation Column as vapour. All amount of ethanol is evaporated to the vapour phase because of the high temperature in the condenser. The amount of ethanol left after transportation is minimal which means a simplified and less costly unit would be recommended in terms of separating ethanol and water.

Case 3 MEG: A perfect distribution of MEG as THI leading to a simplified process for recycling. Since the bottom product stream containing pure quantity of MEG the process is optimal for the use of MEG as a THI.

The HYSYS results verify the theory about a Distillation Column carried out in earlier part of the report; in a mixture with water, alcohol act as the light product and dissociate at the top of the column while glycol act as the heavy product and dissociates at the bottom of the column.

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ABBREVIATIONS

CAPEX	Capital Expenditure
EOS	Equation of State
EtOH	Ethanol
FLAGS	The Far North Liquids and Associated Gas System
HE	Hydrate Envelope
HOCNF	Harmonised Offshore Chemical Notification Format
HSE	Health, Safety and Environment
MEG	Mono-ethylene Glycol
MeOH	Methanol
OPEX	Operational Expenditure
P	Pressure
PLONOR	Pose Little Or No Risk
T	Temperature
THI	Thermodynamic Hydrate Inhibitor

APPENDIX – A

A1 - PROCESS SIMULATIONS HYSYS

Reservoir conditions:

- Temperature T_{Res} = 90°C
- Pressure P_{Res} = 290 bar
- Gas Flow Rate q_g = 1.133 x 10^6 kg/h
- Water Flow Rate q_w = 3000 kg/h

Wellhead conditions are assumed to be 80% of reservoir conditions:

- Temperature T_{WH} = 72°C
- Pressure P_{WH} = 230 bar
- Flow Rate q_g = 1.131 x 10^6 kg/h

Gas Stream to three-Phase separator:

- Flow = 1.133e6 kg/h
- Temperature = - 13.08 C
- Pressure = 21.26 bar

Injected **THI**:

- P = 200 bar
- T = 60 C
- Flow Rate = 2000 kg/h

Glycol

MEG

- Lean MEG flow = 1817 kg/h
- Lean MEG temperature = 150 °C
- Lean MEG pressure = 1.1 bar

Alcohol, Vapour stream out of Distillation Column

Type: **Methanol**

- Mass Flow = 1021 kg/h
- Temperature, T_{MeOH} = 82 °C
- Pressure = 0.8 bar

Type: **Ethanol**

- Mass Flow = 8.799 e(-5) kg/h
- Temperature T_{EtOH} = 51.54 °C
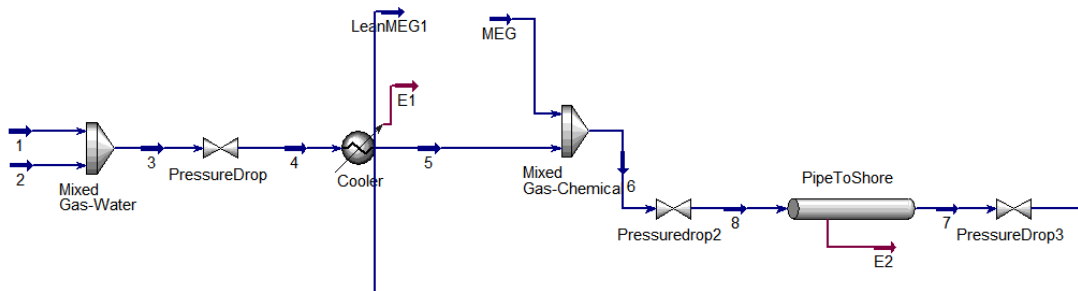- Pressure =1.1 bar

FIGURE 35 "PRINT SCREEN" OF THE GAS PLANT SIMULATION DONE IN HYSYS

The fluid at wellhead is further mixed with hydrate prevention inhibitor with a flow rate at 2000 kg/h ($q_{Inhibitor}$ = 2000 kg/h). The flow rate is equal for injected alcohol and glycol, and the temperature and pressure conditions are equal to fluids at the wellhead. The rate is equal for MeOH, EtOH and MEG related to comparison of the different situations. It should be noted that this is a simplified system. To get accurate values of the needed amount the rate should be calculated from Hammerschimd's equation. This part is left for future improvement. It is in this case assuming 100% lean THI. This is not a

realistic case only a simplified assumption, and will in this report not be studied any further.

The stream is transported to the terminal through a pipeline at the seabed. Specifications for the pipe are given as:

- Length = 100 km
- Elevation = 900 m
- Outer diameter OD = 30"
- Roughness = 4.572 x 10^{-5}
- Ambient Temperature = 2.5°C
- Overall Heat Transfer Coefficient, U = 11 W/Km^2

The pipeline is kept as one segment, which is a simplified view of the topography. The pressure at the terminal is specified to be 120.8 – 90.02 = 30.78 bar and temperature equals to -11.25°C for the gas stream with Methanol as a hydrate prevention inhibitor. The temperature varies with different inhibitor used in the system. It should be noted that this figure does not represent the actual and completed process flow diagram, but is a simplified version designs to obtain correct information about the produced fluid composition, phase envelope, flow rates, temperatures and pressures.

A2 - LOSS OF THERMODYNAMIC HYDRATE INHIBITOR DURING TRANSPORTATION

TABELE 19 HI LOST FROM THE SYSTEM DURING TRANSPORTATION FROM WELLHEAD TO THE THREE-PHASE SEPARATOR AT THE LAND-BASED TERMINAL

	1: Methanol	2: Ethanol	3:MEG
Loss of THI during Transportation			
Amount of lost THI [kg/h]	1433.5	1206.9	1206.9
Lost THI [%]	71.68	60.35	60.35

Table 19 indicates the loss of THI during transportation from wellhead to three-phase separator. THI is injected at the wellhead and mixed with the feed before the mixed stream passes through a 100 km long pipeline to the land-based terminal. At the land based terminal the stream enters a three-phase separator.
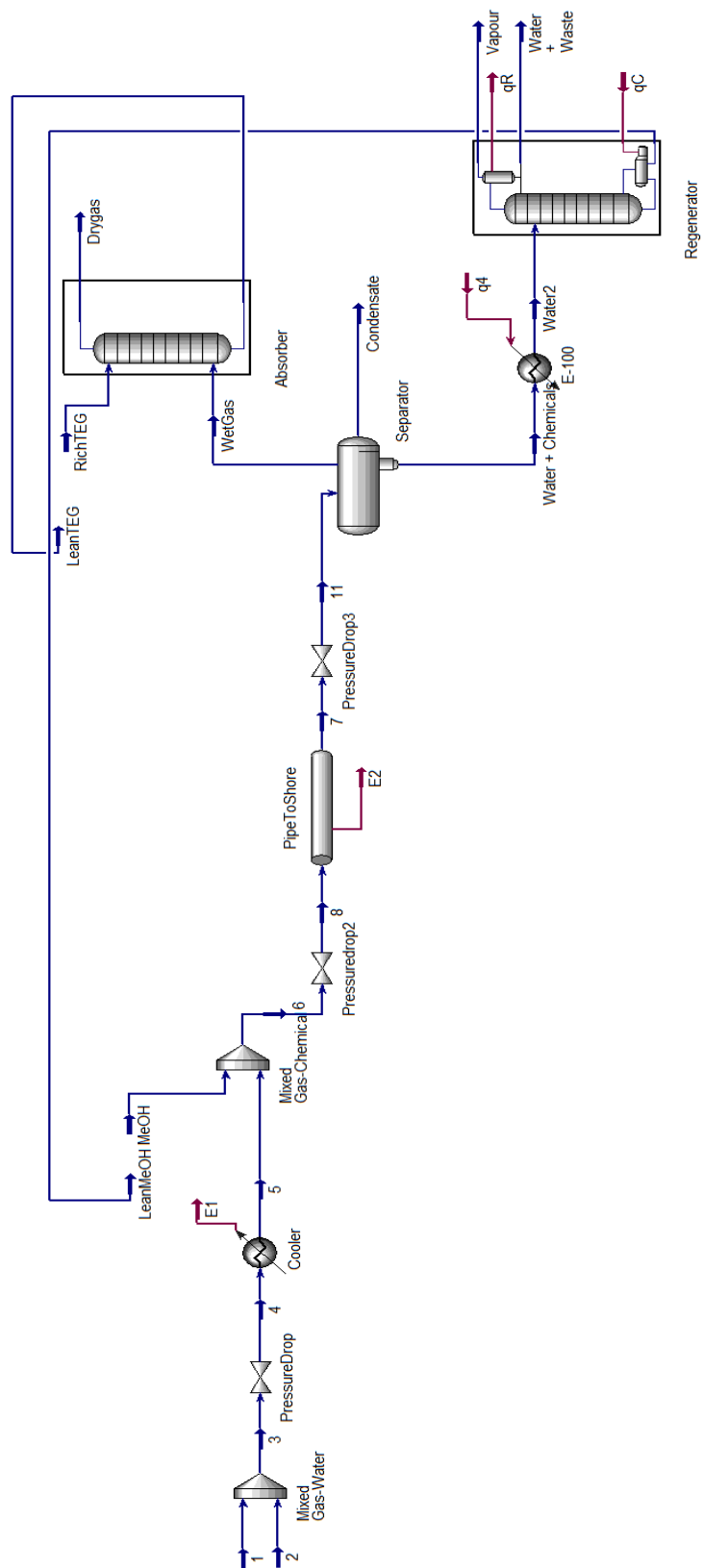
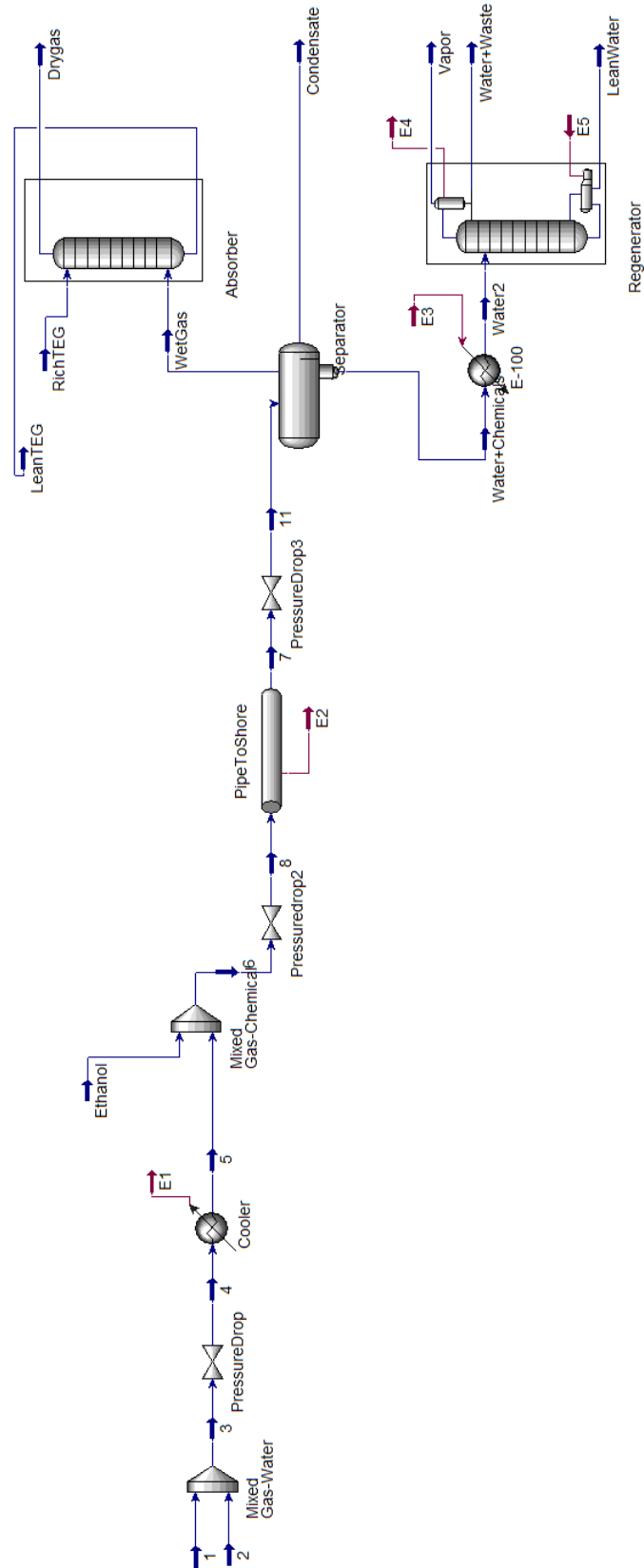**FIGURE 36 "PRINT SCREEN" OF THE ENTIRE SIMULATION PROCESS, FOR CASE 1: METHANOL USED AS THI**

FIGURE 37 "PRINT SCREEN" OF THE ENTIRE SIMULATION PROCESS, FOR CASE 2: ETHANOL USED AS THI
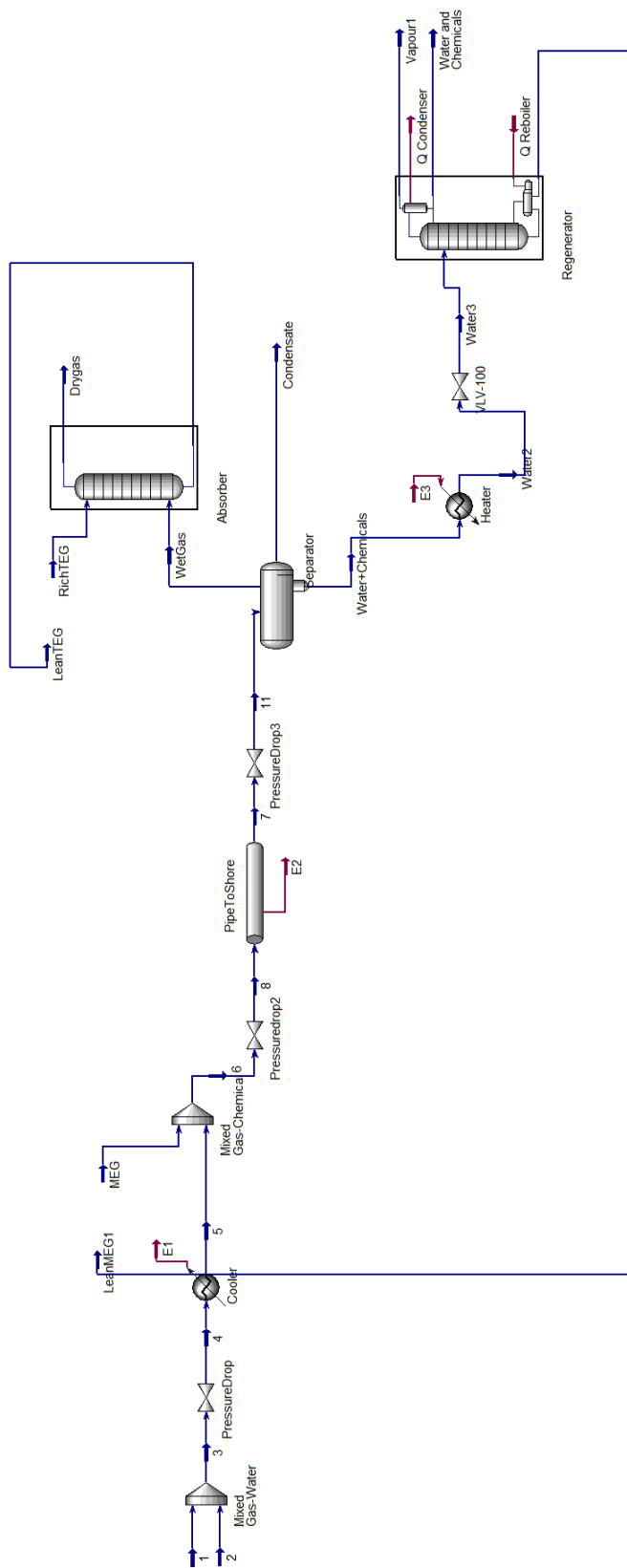
FIGURE 38 "PRINT SCREEN" OF THE ENTIRE SIMULATION PROCESS, FOR CASE 3: MEG USED AS THI

APPENDIX – B

FLAG SYSTEM

The Far North Liquids and Associated Gas System, FLAGS (UK), was developed for the utilisation of associated gas from oil fields located in the northern sector of the North Sea (Maslin et al., 1987). There are four main pipeline systems in the U.K that are transporting natural gas from offshore platforms to coastal landing terminals. Shell operates the 283-mile FLAGS that transports associated gas deposits from the Brent oil system to the receiving terminal at St. Fergus in Scotland.

Once brought onshore, the responsibility for transporting natural gas throughout the country belongs to the utilities operating in the U.K. In 2003, it was reported that the 283-mile, 36-inch FLAGS transported 760 million cubic feet per day (Mmcf/d) of associated gas.

Natural gas from the Norwegian Statfjord Oil and Gas Field is transported through the Tampen pipeline and Gjoa/Vega through the Gjoa pipeline, linking Norwegian and UK gas trunk line networks. Tampen Link runs for 23.1 kilometers from the Statfjord Oil and Gas Field to a Flags tie-in, as illustrated in figure 7 and 8.
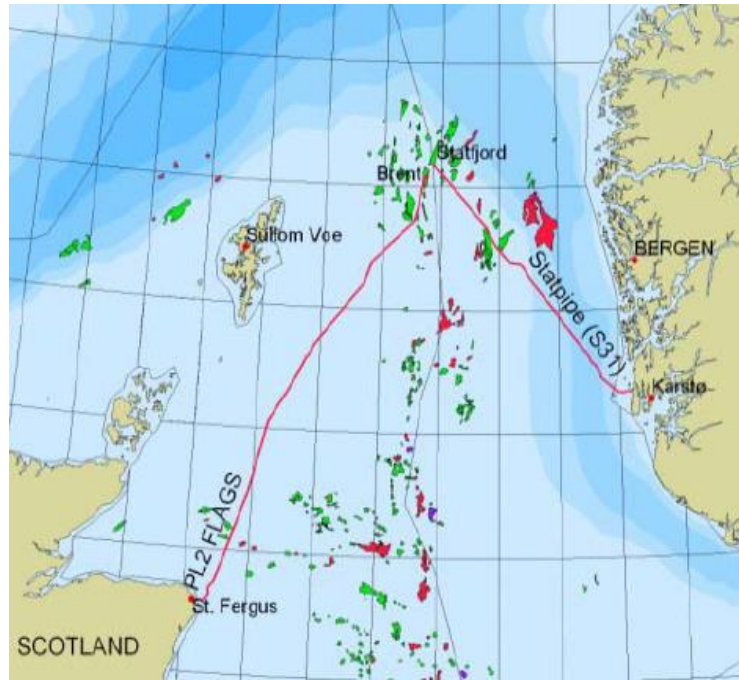
FIGURE 9: FLAG SYSTEM NORTH SEA. (SHELL INTERNATIONAL 2012)

Entry specification made from FLAGS indicates that Shipper gas should be technically free from any objectionable odours and dust or other matters, in a solid, liquid or gaseous state.

It specifies that waxes, gums, gum forming constituent which cause injury to or interference with the operation of the lines, meters, regulator or other appliances through which it flows (Shell, 2012). Table 20 gives an overview of the specifications given for FLAGS.

TABLE 20 SPECIFICATIONS GIVEN FOR FLAGS (SHELL 2012)

Components:	Maximum allowance:
CO_2	1.6 %vol
H_2S	2.5 ppmv
Total Sulphur	15 ppmv
H_2O	35 ppmv
Cricondenbar	105 bar
O_2	10 ppmv
Mercury	0.01 $\mu g/m^3$
Non-hydrocarbon content	5.5 mol%
C_3^+ (propane and heavier)	5.5 mol%
Nominal wet gas capacity	30 million Sm^3/d

APPENDIX – C

CALCULATIONS

Calculation from table no. 2 in chapter 7.2, 7.3 and 7.4:

$$Mass\ Flow, THI\ \frac{kg}{h} = Mass\ Fraction, THI\ \frac{kg}{h} * Mass\ Flow\ \frac{kg}{h}$$

Calculations for Mass Balance THI, table no. 3 in chapter 7.2, 7.3 and 7.4

Case1; Methanol:

$$1 - \frac{808.5}{979.8} = 17.5\%$$

Case 2; Ethanol:

$$1 - \frac{0.328}{0.435} = 24.6\%$$

Case 3; MEG:

$$1 - \frac{992.11}{1407.27} = 29.5\%$$