QATAR UNIVERSITY

COLLEGE OF ENGINEERING

DESIGN AND PROCESS ECONOMICS OF A MONOETHYLENE GLYCOL (MEG) RECOVERY SYSTEM FROM PRODUCED WATER

BY

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ABSTRACT

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Title:_Design and Process Economics of a MEG Recovery System from Produced Water

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Monoethylene glycol (MEG) is a widely used hydrate inhibitor in the oil and gas industry to reduce the risk of hydrate formation in pipelines that could cause a blockage. Large volumes of MEG are used annually as an effective hydrate control strategy adding an extra cost on oil and gas industries. The spent MEG is disposed of afterward by injection in wells. The environmental impact of the disposal of MEG has not been well studied yet, but it is expected to gain importance in the near future. The development of an effective process for MEG recovery has been gaining importance to reduce its purchase cost and eliminate the environmental concern of its disposal after use. Hence, the present study was performed to develop and optimize MEG recovery process based on a simulation method and to evaluate the economic feasibility of recycling and reusing the recovered MEG. The simulation process was carried out using Aspen Plus and a built-in ELEC-NRTL thermodynamic package, while the process economics was investigated using the economic analyzer tool add-in to estimate the cost of the design developed. The process simulation was conducted in two distinct designs with four scenarios. The results revealed that an optimized process consists of a flash separator and a distillation column operated under vacuum pressure recovering 99.7% of high purity (99.7wt%) MEG. The capital expenditures (CAPEX) and operating expenses (OPEX) associated with the optimized process reported as present worth, project lifetime of 20 years and annual interest rate of 8%, were estimated to be 11.5 and 35 MMUSD, respectively. All studied scenarios achieved the required MEG recovery and purity reaching values up to 99.7% as per the requirement of the Qatari industry in general and ConocoPhillips in specific. The similarity in the trends for all scenarios is due to the homogenous water chemistry as well as the low amount of total dissolved solids (TDS). Applying the proposed MEG recovery system can save at least 50% of the MEG purchase cost if MEG passes through one regeneration cycle in the unit. Moreover, this study shows that 80% of MEG purchase cost can be saved when MEG is regenerated up to 5 times. Finally, an environmental benefit is achieved due to the considerable reduction in the disposal of spent MEG.

ABSTRACT (IN ARABIC)

يُعتبر احادي جلايكول الإيثلين (MEG) من مثبطات هيدرات الغاز الأكثر استعمالاً في قطاع صناعة النفط والغاز للحد من مشاكل تكون هيدرات الغاز التي تؤدي إلى انسداد خطوط نقل الغاز . يتم استخدام كميات كبيرة من احادي جلايكول الإيثلين سنوياً كاستراتيجية فعالة للتحكم في تكون هيدرات الغاز مما يضيف تكلفة إضافية على صناعات النفط والغاز. يتم التخلص من احادي جلايكول الإيثلين المستهلك بعد ذلك عن طريق الحقن في الآبار . إلى الآن، لم يتم دراسة الآثار البيئية الناتجة عن التخلص من احادي جلايكول الإيثلين المستهلك بشكلٍ جيد، ولكن من المتوقع أن تكتسب أهمية في المستقبل القريب. لقد ازدادت أهمية تطوير عملية فعالة لاسترجاع احادي جلايكول الإيثلين لتقليل تكلفة الشراء و تجاهل القلق الخاص بعملية التخلص منه بعد الاستعمال. وبالتالي، تم إجراء هذه الدراسة لتطوير وتحسين عملية استرجاع احادي جلايكول الإيثلين باستخدام برنامج محاكاة وتقييم الجدوى الاقتصادية لإعادة تدوير واستخدام احادي جلايكول الإيثلين المسترجع. تم تنفيذ عملية المحاكاة باستخدام برنامج Aspen Plus و حزمة الديناميكا الحرارية ELEC-NRTL، في حين تم فحص اقتصاديات العملية باستخدام أداة التحليل الاقتصادي المدمجة بالبرنامج لتقدير تكلفة التصميم الذي تم تطويره. تم إجراء محاكاة العملية من خلال تصميمين مختلفين مع أربعة سيناريوهات. كشفت النتائج أن العملية المحسنة تتكون من فاصل حراري وعمود تقطير يعملان تحت ضغط التفريغ ينتُج عنها استعادة ٩٩٫٧٪ من احادي جلايكول الإيثلين عالي النقاء (٩٩٫٧٪ بالوزن). تم تقدير القيمة الحالية للنفقات الرأسمالية (CAPEX) و المصروفات الجارية (OPEX) للعملية المحسنة لمدة ٢٠ عاماً للمشروع و سعر الفائدة السنوية المقدرة ب ٨٪ بمبلغ ١١٫٥ و ٣٥ مليون دولار أمريكي على التوالي. حققت جميع السيناريوهات التي تمت دراستها معدل نقاء ونسبة استرجاع لاحادي جلايكول الايثلين

تصل إلى ٩٩٫٧٪ وفقًا لمتطلبات الصناعة القطرية بشكل عام و شركة ConocoPhillips بقطر بشكل خاص. يرجع التشابه في نتائج جميع السيناريوهات إلى كيمياء المياه المتجانسة بالإضافة إلى انخفاض كمية الأملاح الذائبة (TDS). يمكن لتطبيق نظام استرجاع احادي جلايكول الإيثلين المقترح أن يوفر حوالي ٥٠٪ على الأقل من تكلفة شراء احادي جلايكول الإيثلين إذا مرت بدورة تجديد واحدة في وحدة الاسترجاع. علاوةً على ذلك ، توضح هذه الدراسة أنه يمكن توفير ٨٠٪ من تكلفة شراء احادي جلايكول الإيثلين عندما يتم تجديده حتى ٥ مرات. أخيرًا ، يتم تحقيق فائدة بيئية من عملية الاسترجاع بسبب الانخفاض الملحوظ في التخلص من احادي جلايكول الإيثلين المستهلك.

DEDICATION

This thesis is dedicated to my beloved parents who has provided me with continuous support and motivation throughout the two years of my Master's study. The achievement of this thesis would not have been possible without their patience.

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Last but not least, I would like to thank my parents and my beloved friends for giving me the strength to finish my master's degree and helping me to stay calm and sane during the critical times in the past two years.

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CHAPTER 1: INTRODUCTION

1.1 Background of the study

As the world's energy demand is in a continuous surge, oil and gas exploration processes have been moving to offshore and deep subsea environments in order to maximize their production and profitability. The world has been relying recently on offshore oil and gas production which was stated to represent 33% of the total production in 2014, and that might surge due to the abundance of deep offshore oil and gas fields in addition to the exhaust of shallow water reservoirs [1]. With the increasing exploration and production of natural gas in offshore fields, the emergence of production challenges is inevitable. One major concern in natural gas production is flow assurance that is associated with ensuring the safe production and transportation of natural gas from production sites to the processing facilities. Being placed in cold deep-water at high pressures, the transportation pipelines are susceptible to the formation of gas hydrates due to the gas's water content, which ends up causing a blockage in pipelines leading to severe problems. These hydrates can cause huge safety and economic issues on gas processing, and production as the hydrate plugging can be simple stopping the production for days or even months, or severe causing potentially hazardous pipeline explosion [2]. The formation of these gas hydrates is becoming a huge challenge in the production of natural gas that needs to be stopped. As the remediation of these plugs has economic and time constraints, hydrate prevention mechanisms become necessary to be implemented. Conventionally, hydrate formation is avoided by the continuous injection of some field chemicals known as hydrate inhibitors that work on reducing the water activity in pipelines during transportation which in turn reduces the likelihood of gas hydrate formation. In Qatar, hydrate inhibitors are usually injected in natural gas wells during the winter months between

December and March [3]. Furthermore, Qatargas has been leaning on the injection of kinetic hydrate inhibitors and monoethylene glycol (KHI/MEG) in order to prevent hydrate formation during the winter season, but due to several issues, a decision was made in order to replace KHI with MEG for hydrate control purposes [4,5]. Numerous gas fields operators have been leaning on MEG as the main hydrate inhibitor utilized due to its relatively simple recovery process compared to other hydrate inhibitors [6–8]. The process of MEG recovery is increasingly becoming of considerable importance since MEG is expensive and significant volumes are required for effective hydrate inhibition which in turn raises economic, environmental, and logistics concerns in terms of their supply and disposal after use[8–10]. Thus, a process that can be used to recover and reuse MEG several times is highly required. It was stated that MEG recovery/regeneration has numerous benefits including the reduction in the purchased amount of fresh MEG, the protection against hydrate formation due to utilizing more pure MEG with less water content, and the reduction in corrosion, scaling and fouling issues [11]. Since MEG after being used and separated from the gas stream at the processing facility is obtained as rich MEG loaded with water, the proposed recovery process should focus on the removal of water and dissolved solids to obtain highly pure lean MEG that can be reused as a hydrate inhibitor.

1.2 Main objectives of the thesis

The scope of this thesis focuses on the design of a MEG recovery process from produced water to permit its reuse with minor losses. The study also focused on the economic feasibility of the designed process based on CAPEX and OPEX. The process design and economic evaluation was carried out using Aspen plus simulation software. Different scenarios were evaluated to select an optimum design with maximum percentage recovery and high MEG purity. The overall project cost justifying the establishment of a MEG recovery was presented. Other specific objectives are:

1. Develop a simulation model for different processes, assess and compare the energy requirement for each process using Aspen Plus.
2. Prepare and study the change in capital expenditures (CAPEX) and operational expenses (OPEX) for each process using Aspen Plus economic analyzer
3. Compare the economic and environmental benefits of each process with respect to the current MEG disposal practice.

1.3 Justification of the study

For hydrate inhibition purposes, large volumes of MEG are required in order to suppress the hydrate formation conditions. Besides, when MEG is separated from the natural gas, the industrial practice for its disposal is through injection in deep onshore wells having considerable costs and posing environmental concerns if it finds its way through aquatic environments. Furthermore, since hydrate inhibition is a critical requirement during gas production, the purchase of fresh MEG is a necessity. Taking into consideration all the formerly mentioned reasons, it is necessary to establish a MEG recovery unit in order to facilitate its re-injection in transportation lines. The results achieved from this study will help policymakers and industries decide whether to implement the MEG recovery process or keep on with the current disposal practice.

1.4 Thesis outline

This thesis is organized as follows: Chapter 2 provides a general background about gas hydrates, hydrate inhibitors and the selection of MEG as a hydrate inhibitor. Followed by a description of MEG recovery processes and past studies conducted in the design of the MEG recovery unit and the associated process economics highlighting the gaps found in the literature. Chapter 3 describes in detail the exact methodology followed in order to achieve the study objectives. In chapter 4, the results of the designed process are presented with details on the design parameters and the cost analysis study performed. Finally, chapter 5 summarizes the main conclusions of this thesis and highlights some recommendations for the future outlook.

CHAPTER 2: LITERATURE REVIEW

2.1 Gas hydrates

Gas hydrates are ice-like clathrates of crystalline structure that form when the water content of the gas freezes and solidifies causing a pipeline plug that stops the gas flow and causes pressure build-up upstream the plug which ends up causing a pipeline rupture [9,12]. Gas hydrates can form at temperatures above the freezing point of water at high pressures; eventually, hydrate formation is triggered at temperatures lower than $20°C$ and pressures higher than 30 bar [13]. These hydrates have significant safety risks, and economic challenges in gas production as this issue ends with up with a complete operational shut-down for an extended period in order to remove or remedy these plugs (Figure 1). Since the remediation of these plugs can be of a considerable cost and time-consuming, it is necessary to provide a better alternative for the remediation process. In offshore production, measures for avoiding, mitigating and control of these hydrates is necessary. The formation of gas hydrates can be avoided by either dehydrating the gas, maintaining the temperature of the pipelines above the hydrate's formation temperature by heating or thermal insulation, depressurization of the pipelines, or injecting a hydrate inhibitor. In most of the cases, the first three options may not be practical or feasible due to their limitations in their applicability and flexibility. Therefore, it becomes necessary to inject a hydrate inhibitor.

Figure 1. Remediation of a hydrate plug in natural gas transportation pipeline [14].

2.2 Hydrate inhibitors

Hydrate inhibitors are chemicals added to pipelines to prevent the formation of gas hydrates during transport between the production wells and processing sites. The continuous injection of hydrate inhibitors in transportation pipelines is a promising alternative to prevent, retard, or reduce the chances of gas hydrate formation. Hydrate inhibitors can be classified into two main categories based on their working mechanisms: Thermodynamic hydrate inhibitors (THIs) and low dosage hydrate inhibitors (LDHIs). THIs are preventive inhibitors as they reduce water activity by shifting the hydrate formation equilibrium to lower temperatures and higher pressures as shown in figure 2. The more the equilibrium curve is shifted to the left, the better the inhibition is. The most common THIs used in industry are glycols (monoethylene glycol (MEG), diethylene glycol (DEG), and triethylene glycol (TEG)), ethanol and methanol. LDHIs do not lower the hydrate formation temperature as in THIs' case; instead, they diminish the effect of hydrate formation. LDHIs can be classified into two different categories: kinetic hydrate inhibitors (KHIs) and anti-agglomerating hydrate inhibitors (AAHIs). KHIs are polymer-based chemicals that act as retarding inhibitors that slow down the kinetics of crystal growth and hydrate formation inhibiting its development for a defined period. Typical examples of KHIs are polyvinyl caprolactam and polyvinylpyrrolidone [15]. AAHIs are merely dispersing agents of quaternary salts or surfactants that hinder the small crystals from agglomerating into large structures of gas hydrates[15]. In terms of global consumption, THIs are the most commonly used hydrate inhibitors among the other types because of their effectiveness and reliability[16–18]. The reason behind that is the limitation in using AAHIs and KHIs as AAHIs work effectively only there is a specific amount of condensate/ oil phase along with the gas while KHIs are limited in their ability to suppress hydrate formation in addition to its low efficiency at high pressures[19]. Generally, THIs are commonly injected at large dosages ranging from 20% up to 70% of the total water produced in a typical offshore deepwater system raising concerns regarding their management after utilization [20].

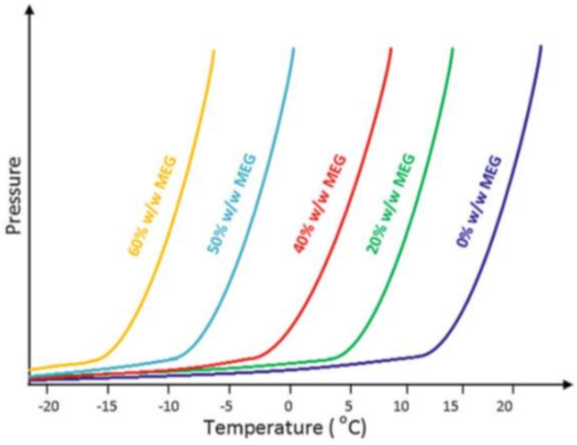


Figure 2. Hydrate equilibrium shift with increasing MEG(THI) concentration [21].

2.3 MEG vs. methanol

For continuous injection, glycols are preferred with systems at low temperatures up to – 40°C. The reason behind that is their economic advantage in terms of their recovery by distillation. However, below this temperature, methanol is preferred because the glycol's viscosity makes the separation less effective than methanol's separation[22]. The most common THIs used in industry are methanol and MEG due to their high performance and relatively low cost [19]. Methanol is advantageous in terms of being less expensive compared to MEG, requiring lower concentration for inhibition and inhibiting to lower temperatures than MEG; as smaller volumes of methanol than MEG are required for the same hydrate inhibition effect[8]. Besides, during its regeneration, the dissolved salts are more soluble in water than in methanol leaving it pure. Despite these advantages, methanol is profoundly lost with hydrocarbons vapor and liquid, in addition to the aqueous stream that is difficult to recover methanol from posing some economic concerns in the recovery process [19,21]. Moreover, it is not as safe as MEG since it is more toxic and flammable than MEG. For these reasons, the industry is starting to divert towards MEG as a potential hydrate inhibitor for use. MEG is characterized by having low solubility in the liquid hydrocarbon phase, being effectively recovered from the aqueous phase after use with minor losses, and possessing a huge potential of hydrate depression temperature; in addition to having an advantageous feature of providing corrosion inhibition in pipelines saving operational costs associated with supplying corrosion inhibitors [2,19,23]. Another advantage of MEG over methanol is that it can be used for continuous inhibition while methanol can be used only when occasional inhibition is required [24,25]. Another driving criterion for MEG selection is that MEG recovery units are easy to operate, safe, reliable, cost-effective, of high MEG recovery, low energy consumption and carbon emissions, and moderate disposal of salts within the acceptable levels of HSE standards[26]. Finally, the water obtained from MEG recovery poses less environmental hazards compared to that obtained from methanol recovery [10].

2.4 MEG Recovery

After injection in pipelines, MEG flows with the gas along with produced water ensuring its safe delivery without any hydrate blockage. As soon as the production fluids reach the processing facilities, they pass through the slug catcher and then they are separated in a 3-phase separator to an upper gas stream – natural gas, intermediate condensate stream – liquid hydrocarbons, and a bottom aqueous stream – rich MEG along with produced water and dissolved salts. The gas and the condensate streams are passed to further processing and sales unit onshore while rich MEG is passed to the regeneration unit. Before MEG can be reused for hydrate inhibition, re-concentration (water removal) and reclamation (salt removal) are necessary in order to obtain pure MEG to be effective in hydrate inhibition. In addition, the continuous use of MEG in hydrate inhibition might cause its contamination and degradation if the impurities are not removed regularly in a controlled manner. After MEG is separated from its impurities, water, and salts, it is produced as a concentrated stream known as lean MEG which returns to the injection point as a recycled hydrate inhibitor.

The underlying reason behind developing MEG recovery systems is that the prices for glycol have been increasing significantly in recent years necessitating the need for recovery systems for a cost-efficient application of hydrate inhibition [27]. PUREMEG process is one of the well-known MEG recovery units globally having an overall MEG recovery of 99.5% [28]. MEG recovery units (MRUs) are characterized by being a small unit and having a simple design. Usually, MEG recovery units are comprised of 2 stages which are regeneration and reclamation. Regeneration is concerned with water removal while reclamation is concerned with salt removal. One challenge encountered in most MEG recovery units is the presence of salts, their accumulation within MEG loops and scaling problems that lead to equipment failure. Hence, special regeneration and reclamation designs are implemented in MRUs, usually vacuum systems [24]. Vacuum systems are usually essential in order to vaporize MEG from salts stream which is not achievable at the atmospheric boiling point 197 ℃ since MEG thermally degrades at around 160 ℃, and major losses are expected when vaporized at atmospheric conditions [12,29]. Hence, a vacuum pressure of 0.1 – 0.3 bara is used in order to lower MEG’s boiling point below its degradation point avoiding from one side its degradation and from the other side its contamination with salts [30].

Of special concern in MRUs is the presence of divalent ions, such as calcium and magnesium as they tend to precipitate out of the aqueous stream and deposit on pipelines and equipment easily. Hence, some systems employ a pretreatment stage in order to remove the potentially hazardous divalent salts that induce scaling leaving behind monovalent salts to be removed by reclamation. Generally, three modes of MEG recovery can be implemented: traditional process (TP), full-stream reclamation process (FS), and slip-stream reclamation process (SS).

2.4.1 Traditional process (TP)/Regeneration

This process is comprised only of a single distillation column that separates MEG from water at atmospheric conditions obtaining lean MEG as a bottom product with concentrations up to 90wt% [31]. Typical regeneration unit in Minerva Gas Plant is shown in figure 3. At atmospheric conditions, only 90wt% lean MEG can be achieved since the distillation column is operated at a temperature around 130 °C that is enough to boil off water and keep MEG in the liquid phase [8]. The advantages of this process are simple, low process economics, and low energy requirements making it economically attractive for MEG regeneration.

Nevertheless; this process is effective when rich MEG contains no/low total dissolved solids; however, any increase in the salt levels within rich MEG beyond the tolerable limits, the salts end up accumulating and precipitating in the processing facilities leading to salt deposition and equipment fouling [10,26]. Thus, this process is the least employed process in MEG recovery since rich MEG streams are usually expected to be loaded with salts. Another disadvantage of this process is that it is not capable of producing MEG with purity > 90wt% as this requires additional heating increasing the temperature profile of the column. At elevated temperatures, MEG undergoes thermal degradation where it breaks down forming organic acids such as glycolic, formic, and acetic acid which in turn accelerates pipelines corrosion, deteriorates hydrate inhibition performance, and requires further MEG makeup which increases the operating costs [32,33]

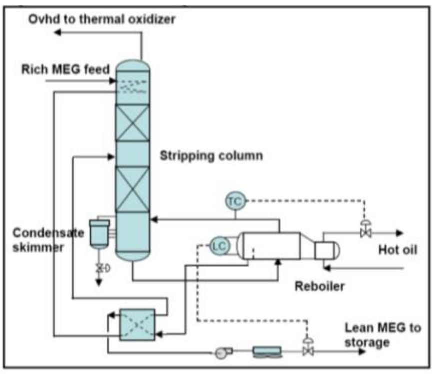


Figure 3. Typical regeneration unit [34].

2.4.2 Full-stream reclamation process (FS)

Full-stream reclamation process (FS) is comprised of a distillation column imitating the one present in TP followed by a reclaimer vessel. The reclaimer is a flash separator that is usually operated under vacuum conditions (10-15 kPa) in order to vaporize MEG-water completely removing both monovalent and divalent salts leaving them behind as a concentrated brine stream which is usually separated using a centrifuge [19,29]. Sometimes, the flash separator is followed by another sub-atmospheric distillation column for further water removal where the first distillation column is omitted [35]. It was reported that the FS process is necessary whenever high formation water rates are expected [36]. Figure 4 shows a typical FS reclamation process.

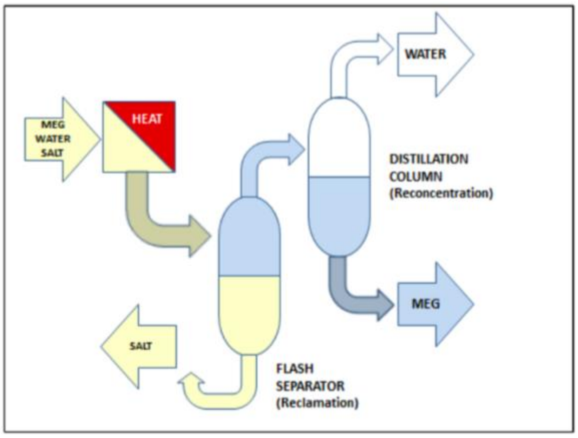


Figure 4. Typical process flow diagram for the full-stream reclamation process [10].

2.4.3 Slip-stream reclamation process (SS)

Slip-stream reclamation process (SS), as shown in figure 5, has the same design as FS but it only treats a fraction of rich MEG stream in the vacuum flash separator, either upstream or downstream the regeneration column, where the rest is bypassed to be combined later with the final product [38]. This is usually done as the ionic salts present in the rich MEG stream could be used in order to enhance the hydrate inhibition efficiency when injected along with MEG [32]. The amount of bypassed MEG is necessary to be controlled and monitored as increasing the bypass reduces the size of the reclaimer unit and its energy requirement but increases the salt loading causing operational issues in the MEG recovery system [38]. This process usually has a pretreatment step, mainly pH adjustment using caustic soda (sodium hydroxide NaOH), that is required for the removal of divalent salts (low-soluble salts) before regeneration and reclamation are performed as these are highly prone to be deposit out of the solution, cause scaling problems, and jeopardize the performance of the equipment [23]. SS process is usually applied for the cases of having low or medium formation water rates as it minimizes the total cost of the recovery unit [36]. The selection between FS and SS process depends on the required amount of salts in the final lean MEG product for reinjection for hydrate inhibition. Table 1 shows the main differences between these two reclamation processes.

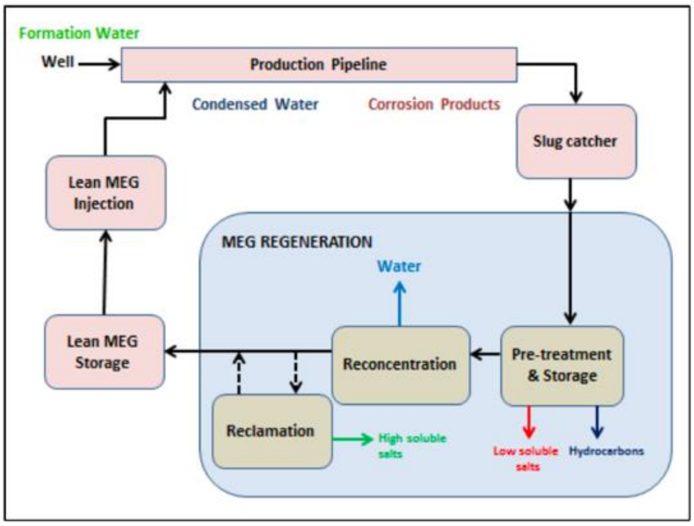


Figure 5. Typical process flow diagram for slip-stream reclamation [10].

Table 1. Differences between Full-stream Reclamation and Slip-stream Reclamation Processes

	Full-stream reclamation (FS)	Slip-stream reclamation (SS)
Mode of operation	Complete reclamation of rich MEG removing all dissolved salts.	A portion of rich MEG stream enters the reclaimer for salt removal leaving some salts behind in the bypassed stream.
Advantages	• Complete salt removal from rich MEG avoiding any scaling or equipment fouling issues in addition to having salt-free MEG at injection points. • It is effective when the total dissolved salts (TDS) is high [39]. • It has a smaller footprint compared to SS due to the reduction in the number of equipment making it favorable for off-shore applications [30].	Lean MEG contains some inhibitors and pH stabilizers that are entirely lost in the FS process along with the brine stream [29]. These compounds are usually useful to be injected in pipelines for corrosion control purposes.

	Full-stream reclamation (FS)	Slip-stream reclamation (SS)
Disadvantages	High energy requirements due to the complete vaporization of MEG and water in the reclaimer vessel leading to elevated operational costs associated with the vaporization process	• It has a potential of equipment fouling due to the build-up and accumulation of salts with time leading to detrimental failure in the MEG loop [38]. • It cannot handle high levels of TDS in rich MEG especially if MEG is alkaline and is loaded with calcium and iron [39,40]. • This configuration is difficult to be handled if MEG is alkaline and contains a significant amount of calcium and iron [40].

The major challenge in MEG recovery is the presence of salts and the issues associated with their deposition and precipitation within equipment that causes their fouling; hence, it is crucial during the design of the MEG loop to assure that the flow of MEG from the injection point up to downstream the recovery unit is unrestricted by scaling/deposition and force precipitation at the intended locations, i.e. reclaimer vessel [40].

2.5 Past studies in MEG Recovery

Through the literature review process, it was found that the number of studies conducted focusing on MEG recovery is limited with a weak focus on the design details. In addition, all the studies conducted are published recently indicating that this kind of work is still new and requires extended research work. There were only five published papers studying the MEG recovery which will be summarized and criticized below.

The first paper published approached the design using the concept of exergy analysis in order to determine the amount of energy degraded in MEG recovery process. Teixeira [2] carried out a comparative study between TP, FS, and SS in terms of energy consumption, carbon dioxide emissions and exergy performance through simulation using Aspen HYSYS as a software and glycol thermodynamic property package for a rich MEG feed of 100 ton/day of 55wt% MEG. In their design, TP process was comprised of a single atmospheric distillation column while the FS and SS process started with an atmospheric distillation to remove a fraction of the water; then it was followed by a flash separator and another distillation column that were operating under vacuum conditions. In their study, they set an operating pressure of 0.2 bar with process feed containing NaCl as the main salt constituent representing 1-3wt% of rich MEG as other salts did not contribute significantly to the thermal effects due to their low concentrations. However, they did not consider any salt presence in their simulation justifying that it does not affect energy consumption since it settles after MEG-water evaporation beside the fact that the trial of salt inclusion differed by 1-2% in terms of heat duty. The outcomes of their study included a maximum MEG purity of 93% obtained from FS process compared to 85% maximum purity obtained from TP and SS process with the energy consumption highest in FS followed by SS and TP having reduced energy consumption of 18.75% and 27.5%, respectively. The study has come up with good results; however, it could have been enhanced if salt inclusion was done and providing more details on their design.

Another study conducted by Zaboon [36] comparing the output from MEG recovery design on an experimental basis and a simulation basis. Experimentally, they operated a distillation column at different trials salt-free and salt-inclusive at operating conditions of 30 ℃ and 140 kPa coming to the conclusion of designing a 6-stage distillation column obtaining a MEG purity of 80-90wt% for salt-free rich MEG and 70-80wt% for salt-laden rich MEG. On a simulation basis, they conducted different trials one using Aspen HYSYS with PENG-ROBINSON (PR) property package, one using Aspen HYSYS also but with glycol property package and finally using Aspen plus with ELEC-NRTL property package. In their simulation, they have only considered monovalent cations sodium and potassium; however, they did not simulate them. Operating with the same conditions as the experimental conditions, they come to a conclusion that glycol property package failed to match the experimental results while using PR they obtained MEG purity of 78-86wt% and using ELECNRTL they obtained 71-80wt%. Although their study was successful in comparing different trials through different methods, they did not go into the detail of the design in addition to the poor purity obtained.

Son [37] studied the process modeling and simulation of a MEG recovery unit using a combination of simulators. The simulation for the re-concentration stage was done using a commercial simulator called “Unisim Design” with PENG Robinson and NRTL as the thermodynamic package while the simulation for reclamation stage was done on Aspen plus interface using ELEC-NRTL as a property model for the salts present, mainly sodium, calcium, and chloride. By operating the reclaimer at Full-stream reclamation mode with an operating pressure of 35 kPa and a distillation column having 26 stages and operating a reflux ratio of 0.56, they obtained an overall MEG recovery of 99.42% and MEG purity of 80wt%. The only comment on this study that the results might not be accurate as they simulated each sub-unit of the MEG recovery unit in different software without providing a logical justification for their approach.

Finally, the two studies that have made significant contributions to this field and have provided a detailed design with a focus on the economic part as well. Kim [41] proposed a modified design for the slip-stream reclamation process having two distillation columns: an atmospheric column before reclamation and a vacuum column after reclamation. This modification was done in order to compare it to the conventional reclamation in terms of salt precipitation incidence and total project cost on a simulation basis using Aspen plus software and ENRTL-RK property package. In their simulation, the salts simulated was obtained using electrolyte wizard for salt precipitation of sodium, calcium, chloride, and bicarbonate ions. They concluded that their modified design provided a reduced cost compared to the conventional design with more tolerance to the salts present and fewer precipitation incidences. In addition, their design achieved an overall MEG recovery of 99.5% with a purity of 97wt%. Assuming a project lifetime of 15 years, the design had an economic benefit with 9.8% reduction in its capital cost (CAPEX) and 8.6% reduction in the operating cost (OPEX) having values of 5.88 MMUSD and 101.84 MMUSD, respectively.

Similarly, the main author conducted another work using Aspen HYSYS and PR property package without considering the salt presence using full-stream reclamation concept operating the reclaimer and distillation column at vacuum conditions. Kim [25] obtained 99.5% MEG recovery but a purity 90wt% with a CAPEX of 8.5 MMUSD and OPEX of 47.33 MMUSD. Comparing this study to the former one, although they obtained a purity of 90wt% instead of 97wt%, the overall project cost was reduced by 50% approximately making the second design considering that 90wt% MEG can provide an effective hydrate inhibition for many injection cases [42].

Taking an overall look in the past studies in literature review; there was no uniform approach for designing a MEG recovery unit in addition to having numerous designs developed, so the process of comparing designs and outcomes was redundant. Moving to the equipment design, even though all the studies agreed on the design of the reclaimer operating at vacuum conditions, there were discrepancies in distillation column design. To illustrate, looking into the distillation column design, Zaboon [36] stated that 6-stage distillation is adequate for obtained 80-90wt% MEG compared to 26 staged-distillation for 80wt% MEG obtained by Son [37]. Considering that the reflux ratio for both columns was in a close agreement, having a quadruple number of stages make the design process debatable. Moving to the economic aspect, minimum studies were done to be looked upon. To conclude, there is a huge gap in literature that needs to be filled by looking at the approach of design, the design itself, salt precipitation and deposition issues and how to troubleshoot/overcome them, the optimum product purity, and the economics of the recovery process justifying its establishment instead of purchasing fresh product.

2.6 Gap in literature

As mentioned earlier and after a thorough investigation of existing literature about the design of a reliable MEG recovery unit with attractive outputs, there has been limited work investigating the recovery of MEG in oil and gas production processes which also had significant discrepancies in the equipment designs, outcomes, and design considerations. Although there are many MEG recovery technologies beyond the formerly mentioned studies that are applied and exist in different plants around the world, this information was not accessible, and the available ones were of minor details because of being companies' confidential information. To the best knowledge, it has not been discussed in detail the operating conditions of different equipment in the process and how they affect the output of the project. In addition, no one has addressed with numbers how much would MEG recovery save from its purchase cost. Accordingly, there will be an in-depth discussion regarding these two aspects of this thesis work. Another contribution to the literature from this work is considering all the salts present in rich MEG and evaluating their effect on the unit performance and product recovery.

CHAPTER 3: APPROACH AND METHODOLOGY

The main objective of this study is to design a MEG recovery unit in order to recover pure MEG from produced water and determine the associated cost with the recovery process. The objective was approached by designing the unit with equipment that is selective to the impurities that need to be removed. During this stage, different scenarios and designs were obtained for the MEG recovery unit depending on the feed quality and the final lean MEG requirement.

3.1 Data collection

The specifications for the rich MEG sample under study was obtained from ConocoPhillips Global Water Sustainability Center (GWSC) based on on-site analysis conducted by them. Table 2 shows the quality of the produced water (PW) associated with MEG in the rich MEG stream. This PW was collected from a treatment facility in the North Field in Qatar sampled downstream the slug catcher. A design basis was developed for the MEG recovery unit where it is designed to treat 50 m^3/hr of rich MEG at a temperature and pressure of 30 ℃ and 3 bar containing 50wt% MEG and 50wt% produced water. The target for the final product was set with a minimum purity of 90wt% up to 99wt% with an overall MEG recovery of 99.5% and above.

Table 2. Properties and Composition of The PW Sample

PRODUCED WATER PROPERTIES	
COD	1600 mg/L
TOC	500 mg/L
CHLORIDE (CL^-)	2300 mg/L
SODIUM (NA^+)	1000 mg/L
CALCIUM (CA^{2+})	350 mg/L
SULFIDE (S^{2-})	800 mg/L
MAGNESIUM (MG^{2+})	60 mg/L
BROMIDE (BR^-)	50 mg/L
SULFATE (SO_4^{2-})	50 mg/L
POTASSIUM (K^+)	40 mg/L
ACETATE (CH_3COO^-)	350 mg/L
TOTAL DISSOLVED SOLIDS	5000 mg/L

3.2 Assumptions

1. The sulfide content was not included in the simulation as it is typically stripped out upstream the MRU [43].
2. The scope of the design starts downstream rich MEG storage tanks and ends upstream the lean MEG storage tanks.
3. The target concentration of the recovered MEG was set at 99wt% with an overall loss of MEG within the unit premises not exceeding 0.5%.
4. The total cost of the project includes the capital cost (CAPEX) and the operating costs (OPEX) as per Aspen Plus economic analyzer tool estimation.

5. The utilities used in this process include only electricity, steam for heating purposes and either refrigerant Freon R-12 or cooling water for cooling purposes depending on the scenario requirement.
6. As per the industrial regulations, the maximum alkalinity of the product should be 20 mmol/kg.
7. The economic evaluation was based on a project life of 20 years with an interest rate of 8% per year.

3.3 Process design and simulation

The design process was carried out on a simulation basis using Aspen Plus software. The selection for this software is attributed to its reflection upon different parameters that could be interpreted from an industrial perspective. In addition, Aspen Plus is a reliable software that has an advantageous feature of handling the presence of solids and salts that other simulation software such as HYSYS and Promax cannot simulate.

The initial procedure was to assess the system under study and define its chemical components (MEG, water and dissolved ions) on the Aspen interface; different scenarios were suggested in order to see how the system reacts to any alteration to the quality of the dissolved ions present. Four scenarios were tested as shown in figure 6:

1. The salts present include monovalent and divalent ions with no salt precipitation.
2. The salts present include monovalent ions only with no salt precipitation.
3. The salts present include monovalent and divalent ions with salt precipitation.
4. The salts present include monovalent ions only with salt precipitation.

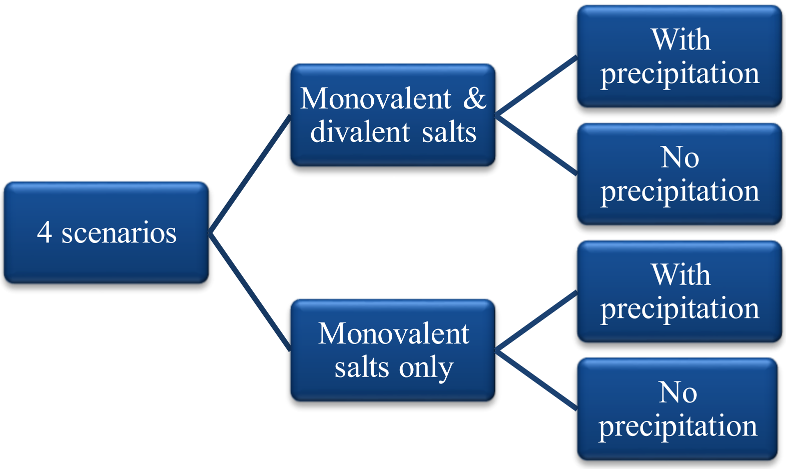


Figure 6. Illustration for the scenarios under study.

These scenarios were suggested in order to assure that the salts remain dissolved in the aqueous stream and do not precipitate out; this is the reason behind simulating scenarios without precipitation and scenarios with precipitation. In overall, these scenarios were implemented in order to analyze how the process performance, operating conditions, and process economics could change for each scenario. Highlighting that scenario 3 is the case that imitates the real-life application in industry, so it is the scenario with the most expected results to be endorsed.

After defining all the components associated with MEG recovery unit, it was essential to select the most appropriate thermodynamic property package to use with the simulation. By using the methods assistant tool in Aspen Plus and defining the case under study, which mainly is an electrolyte system, the most convenient thermodynamic property packages selected for this system were ENRTL-RK and ELEC-NRTL due to their capability of simulating electrolytes as it is the case experienced in the industry during MEG recovery.

Following that, the simulation design was initiated by defining the feed as per the specifications provided earlier in table 2, and the electrolyte wizard was used in order to simulate the scenarios that include salt precipitation. Figure 7 shows the process flow diagram (PFD) developed for the recovery unit on Aspen interface based on equipment selection; each is selective to one type of contaminant. This will be elaborated more in the upcoming sections with the design details.

To start with, since the produced water has a considerable COD and TOC values, a flash drum (FLASH) operating at 55 ℃ was added in order to flash off any traces of hydrocarbons in the rich MEG stream that could contribute to the COD and TOC content. The presence of hydrocarbons could cause damage to the regenerator internals and packings leading as well as foaming issues [44,45]; preceding that, the feed is passed through a pressure reducing valve (PRV) in order to reduce the pressure of rich MEG to 1 atm in order to accelerate the vaporization of the dissolved hydrocarbons. Since the solubility of monovalent salts, which are the main ionic species in rich MEG stream, decreases with increasing MEG concentration [41,46], it was decided to find a method to remove the salts/ions first and then separate MEG from water. This was achieved by using a reclaimer vessel/flash separator (FLS) that works on vaporizing MEG completely from the accompanying salts. One obstacle faced during this process is that MEG can be vaporized at 1 atm if it is heated up to 197 ℃, but it is commonly known that MEG thermally degrades if it is heated to around 163 ℃ where it breaks down to its organic acids such as acetic acid, glycolic acid, and formic acids and become hugely lost [12,29]. Hence, the reclaimer vessel was operated at vacuum conditions in order to vaporize MEG at a lower temperature than its degradation temperature. Vacuum pumps were added to the outlet streams of the reclaimer vessel to guarantee that the vacuum pressure inside the reclaimer is well maintained.

Numerous operating temperatures and pressures were tested and varied in order to decide which operational condition is the ideal one that could cause MEG-water mixture to vaporize completely leaving the salts behind a concentrated brine stream and at the same time does not cause MEG degradation. After a lengthy procedure of trying different temperatures and pressures, it was decided that in order to satisfy the formerly mentioned criteria, the reclaimer should be operated at a temperature range from 100 ℃ to 130 ℃ and a pressure range from 0.05 bar to 0.25 bar. This range of data could be used where the lower limits for temperature and pressure should be used together and the higher limits to be used together. The exact operating conditions for the reclaimer vessel are present in table 3. For the design to be ideal, these operating conditions were tested to see the final temperature for the end product obtained and ensure that this temperature as well is below the degradation temperature. It is important to highlight that operating at any combination of temperature and pressure presented in table 3, leads to complete salt removal with a minimum of 99.5% MEG recovery. Any slight deviation from one row of data by either reducing the vacuum pressure or reducing the temperature would cause around 50% MEG loss along with the salts stream, so it is important to keep monitoring and maintaining the operating conditions. It was decided that the unit is to be operated at 0.05 bar and 100 ℃ to remain far as much as possible from degradation conditions. Besides, it was hypothesized at this condition, the unit will have the least cost as less heating is required, and the amount of steam is reduced reducing the OPEX of the unit. This hypothesis is to be checked and clarified later.

Table 3. Set of Operating Pressures and Temperatures for The Reclaimer Flash Vessel

P (bar)	T (℃)	Lean MEG temperature (℃)
0.05	100	121
0.1	110	136
0.15	120	146
0.2	125	152
0.25	130	158
0.3	135	**162**

The next step was to find a method to separate MEG from water which was selected to be distillation since there is a huge difference in their boiling points (100 ℃ for water compared to 197 ℃ for MEG at 1 atm) that could make the separation process easy. Hence, the separation was tested in Aspen using ‘DSTWU’ shortcut distillation model by setting the water as a light key with a recovery of 99.9% and MEG as a heavy key with a. recovery of 0.1%, both in the distillate stream in order to ensure the complete separation. In addition, the operating pressures for the condenser and reboiler were set to be the exact vacuum pressure (= 0.05 bar) of the reclaimer since aiming for a highly pure MEG would require a complete separation which at atmospheric conditions is achievable at high temperatures that could cause thermal degradation of MEG. Hence, vacuum distillation was used in order to increase the relative volatility and obtain the desired separation of the key components at lower temperatures. The vacuum pressure was also maintained here by adding vacuum pumps at all the outlet streams of this equipment in order to ensure that the design has excellent preservation of the vacuum pressure. After running the simulation, the design parameters for the distillation column such as the reflux ratio, number of stages, feed stage, and distillate-to-feed ratio. These parameters were used later to run ‘RadFrac’ full distillation column model obtaining lean MEG as a bottom product.

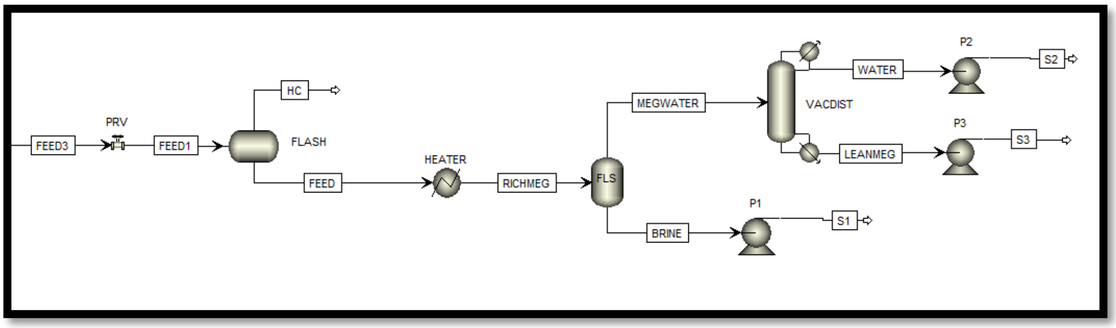


Figure 7. PFD for design 1 for MRU.

In order to ensure the smooth operation of the process, some important considerations were taken in the simulation:

1. Salt precipitation scenarios were simulated after defining all the salts that can form from the combination of ions present in the feed. In addition, the formation reaction of each salt was defined using the chemistry environment in order to check if the process is to be encountered with any salt precipitation incidence.
2. The maximum temperature for the preheater was set to be at 130°C in order to avoid any high temperatures occurring during the process that could cause MEG degradation and loss. Furthermore, it was stated that higher operating temperatures might cause salt precipitation, especially calcium salts, and equipment failure that could adversely affect the separation efficiency [36]. The maximum limit was selected after testing different operating temperatures and monitoring the product’s temperature concluding that the final product reaches

the degradation temperature when the system is operating at 135°C. Hence, the maximum operating temperature was set to be 130°C.

3. The distillation column pressure was set at the same pressure of the flash separator in order to avoid additional equipment duty and operational costs.
4. Vacuum pumps were added to all the outlet streams from the flash separator and the distillation column in order to maintain vacuum pressure within these units.

After obtaining the desired effluent quality specifications, the Aspen Economic Evaluation Add-in was used in order to determine the capital (CAPEX) and operating (OPEX) costs as well as the utilities and equipment costs. This was useful in order to decide if establishing a MEG recovery unit can reduce the costs associated with purchasing fresh MEG to be injected in wells for hydrate inhibition.

3.4 Sensitivity analysis and optimization studies

Besides the approach stated earlier, additional simulation trials were done as a sensitivity analysis step in order to optimize the performance of the unit and check how the CAPEX and OPEX change. First of all, different sets of temperatures and pressures were tested for the heater and flash separator to monitor at what conditions MEG and water vaporize from the brine stream taking into consideration that MEG loss with brine does not exceed 0.5%. The obtained set of temperatures and pressures were tested against the purity of the product, the recovery, and the cost. In addition, the distillation column performance was altered and tested against producing MEG at different purities of 99wt%, 95wt%, 92wt%, and 90wt% and monitor how the total cost of the unit reacts to this alteration.

3.5 Comparing the designs

During the process of developing the first design and carrying out the optimization process, another design was developed for the MEG recovery unit but with a different product quality specification. Figure 8 presents the PFD for this developed design which differs from the first design in the fact that it is selective to the type of salt it removes. In this design, after flashing the hydrocarbons, caustic soda (NaOH) is injected in order to precipitate divalent ions, mainly calcium and magnesium, as hydroxides and remove them. These divalent salts can be removed completely in a pretreatment unit as these types of salts tend to precipitate out easily and then the monovalent salts can be removed later. Also, this design tests operating the distillation column at atmospheric pressure and determine the purity of MEG that could be obtained without losing it due to degradation. After various trials, it was found that rich MEG can be distilled increasing its concentration up to 90wt% MEG as lean MEG is obtained at a final temperature of 140 ℃. Finally, it was found that this stream can be vaporized only under a vacuum pressure of 0.1 bar to remove the monovalent salts.

Generally, design 1 follows the FS concept while design 2 follows the SS concept. Both designs were compared to each other based on the final product obtained at purity 90wt% as it is the maximum limit for design 2 in addition to the associated economics in order to determine which design is more cost-effective.

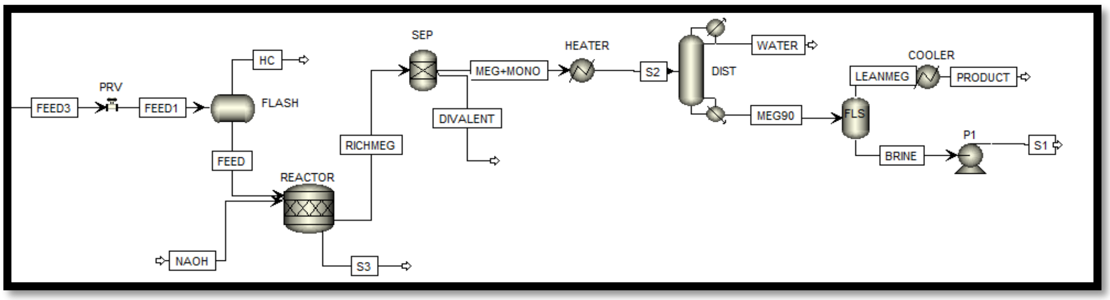


Figure 8. PFD for design 2 for MRU.

Finally, after determining the costs associated with MEG recovery units, the prices for purchasing fresh MEG for injection was compared to the cost of establishing this unit based on a project life of 20 years and an interest rate of 8% per year.

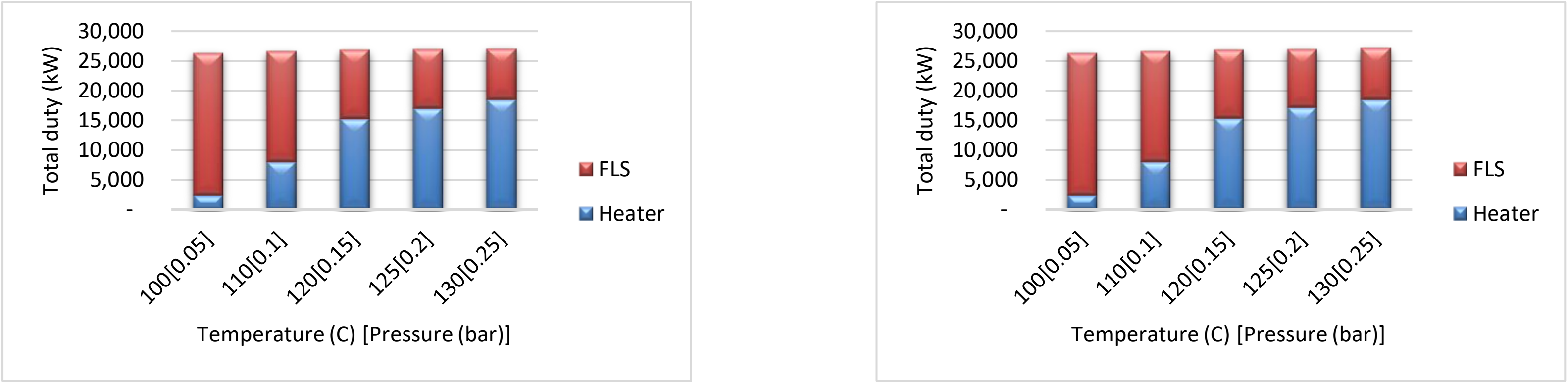
CHAPTER 4: RESULTS AND DISCUSSION

4.1 Design 1 simulation results

The MEG recovery unit was successfully simulated through Aspen plus with MEG recovery and final lean MEG purity exceeding 99.7% in all scenarios implemented. In the design process, all the equipment was sequentially optimized in the order they appear in the flowsheet. To start with, in the reclamation design the heater and flash separator temperature and pressure were varied simultaneously to obtain the optimum operating conditions that could vaporize at least 99.5% of the MEG present in the feed from the accompanying salts leaving behind a concentrated brine stream. This was accomplished in all four scenarios, presented earlier in figure 6, at a set of optimized pressures and temperatures for flashing as shown previously in table 3. The last set of data in that table was not considered in the simulation since at these conditions the lean MEG product is obtained at 162 ℃ where MEG starts to degrade thermally. As the values in table 3 demonstrate, if rich MEG is to be passed down to the flash separator (FLS) at a lower temperature, more vacuum is required since the vaporization of MEG can be achieved either by heating at a high temperature or reducing the pressure but since MEG degrades at a temperature lower than its boiling temperature, extreme vacuum conditions were used. Since each set of temperature and pressure has produced MEG at the same purity (>99wt%) and recovery (>99.7%) for all four scenarios, the set of data was tested in all four scenarios against its effect on the energy requirement of the process. Analyzing the energy requirement for each equipment in all four scenarios as shown in figure 9, the overall conclusion that can be made is that there is no considerable discrepancy in the energy requirement at any of the reported operating conditions between any of the scenarios. This is due to the low amount of total dissolved salts and the water chemistry that does not contribute majorly to the vaporization energy required; however, there were minor differences in the obtained duties where the exact values are presented in Appendix A. In addition, it can be deduced from the figure that at extreme vacuum condition the FLS duty outweighs the heater duty, and as the vacuum is reduced and the heater's temperature is increased, the heater's duty increases making the net duty in overall constant.

Looking closely at any of the scenarios in figure 9 (i.e. scenario 1), it can be observed that when the temperature increases from 100 ℃ to 110 ℃, the heater's duty triples. Simultaneously, the vacuum pressure is reduced by increasing the pressure from 0.05 bar to 0.1 bar causing around 22% reduction in FLS duty; however, in overall, the net duty for both equipment remains constant. As the temperature is furtherly increased and vacuum pressure is reduced, the heater's duty increases but by a small factor compared to moving from 100 ℃ to 110 ℃, while the FLS duty decreases making the net duty at all conditions exactly the same.

a) Scenario 1 **b) Scenario 2**



c) Scenario 3 **d) Scenario 4**

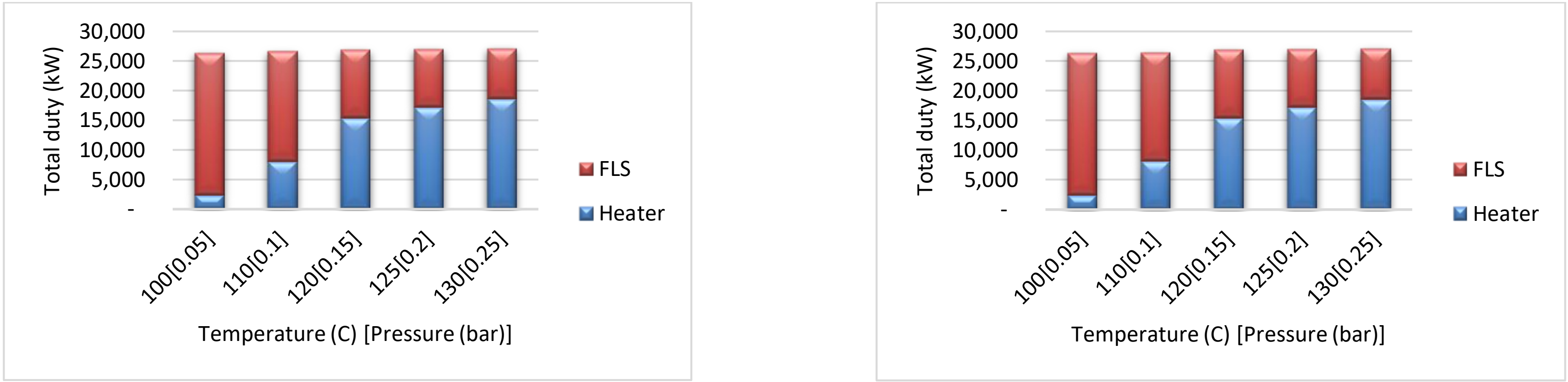


Figure 9. Variations in heater's and flash separator's duties for all scenarios with varying operating conditions. The scenario includes a) monovalent and divalent ions with no salt precipitation. b) monovalent ions only with no salt precipitation. c) monovalent and divalent ions with salt precipitation. d) monovalent ions with salt precipitation.

Finally, the distillation column was simulated successfully by operating it at the same vacuum condition of the flash separator (FLS) for simplicity and flexibility. Using the shortcut distillation model 'DSTWU' to design a distillation column producing at least 99wt% MEG, the obtained design parameters were as shown in table 4. Running the distillation column was done based on the obtained values of 0.774 as a distillate-to-feed ratio, 0.305 as a minimum reflux ratio and three stages as a minimum value. However, at these conditions, the column has a drying up error and failed to converge, so the reflux ratio was increased. Many trials were carried out to see which reflux ratio was enough to eliminate the problem of drying stages and it was found to be 0.5 but having three stages only in the distillation column produced lean MEG with a purity of 96.8% and recovery 90% that was required to be further increased. Thus, the number of stages was continuously increased and the feed stage was continuously lowered to be close to the reboiler, which were found to be enhancing the recovery and purity of MEG. After plugging in a vast number of values for reflux ratios, number of stages and feed stage, it was found that the optimized distillation column should be run at a reflux ratio of 0.562 and six stages with the feed stage 5. Any further increase in the reflux ratio and number of stages would only increase the cost with no significant benefit, as these were the optimum conditions that had the maximum purity and recovery and the minimum condenser and reboiler duty. It is important to note that the exact design parameters were used in all four scenarios having the same output since at the stage of distillation all four scenarios behave the same with negligible differences.

Table 4. The Design Parameters for The Distillation Column in Design 1

Purity (wt%)	99.9
R_{min}	0.305
R	0.562
N_{min}	3
N	6
N_F	4
D/F	0.774

In overall, this design has shown good performance with favorable outcomes in terms of the purity and MEG recovery in all four scenarios implemented as shown in table 5. The net duty requirement for the unit was found to be around 55 MW producing 99.9wt% MEG with a minimum overall recovery of 99.7% for all four scenarios.

Table 5. Purity and Recovery Obtained in Design 1 from All Four Scenarios with The Corresponding Net Duty

	Scenario 1	Scenario 2	Scenario 3	Scenario 4
Purity (wt%)	99.90	99.89	99.95	99.94
Recovery (%)	99.72	99.73	99.93	99.99
Net duty (kW)	55,776	55,797	55,845	55,864

4.2 Design 2 simulation results

As the design shows in figure 8 presented earlier, after flashing off the hydrocarbons, rich MEG is mixed with sodium hydroxide in order to precipitate out the divalent cations, mainly calcium and magnesium. For that, some calculations were made to determine the exact amount of NaOH required since it is unfavorable to inject it more than required. The reason behind injecting the minimum amount of NaOH is that it is highly alkaline and will increase the alkalinity of the lean MEG if injected more than required which in turn is not recommended as it increases the risk of calcium carbonate precipitation and scale formation in pipelines downstream MEG injection points [40,47–49]. Thus, based on the concentration of these ions given in table 2, the exact amount of NaOH required was calculated as shown in Appendix B. It was found that NaOH should flow at a rate of 40 kg/hr in order to completely precipitate out the divalent salts. Then, in a similar manner rich MEG was passed down to a distillation column which was run in shortcut model first to obtain the design parameters where the light key set as water with a recovery of 90% in the distillate and MEG as a heavy key with a recovery of 0.1% in the distillation. Water recovery was set as 90% since any increase in water recovery for a distillation column operating under atmospheric conditions would cause an increase in the temperature profile of the column which is known to cause MEG degradation. The condenser and reboiler's pressure were set as 1 bar to test the distillation at atmospheric conditions. The values obtained are present in table 6 and they were tested and used similarly as in design 1. The column was found to be having six stages as in the first design with feed stage 5, which provides the required separation operating at a reflux ratio of 0.1. This reflux ratio is lower compared to the first design since less water has to be evaporated as the first design produces 99.9% pure MEG while the second design obtained a maximum purity of 90wt% since any attempt to increase the purity would cause MEG degradation and loss due to elevated temperatures in the distillation column. Finally, lean MEG was vaporized in a flash separator operating at 140 ℃ (the temperature of the bottom product from distillation column) and 0.1 bar in order to remove the monovalent salts. The selection of the extreme vacuum pressure was made since it was the only condition achieving monovalent salts separations.

It is important to highlight that in both designs, there were minor traces of acetic acid/acetate ions present in the final product. A critical check that had to be done on the final product from both was the acetate level since it was reported that the acetate concentration should be kept below 2.36 g/l in order to control the corrosion rates [19]. The maximum acetate concentration obtained in all the designs and scenarios was 6.75×10^{-6} g/l which is also too small to be considered. Another critical parameter that had to be checked was the level of alkalinity to avoid any scaling issues as stated earlier. The alkalinity found was much lower than the maximum limit set with a value not exceeding 0.00002 mmol/kg at all designs and scenarios, so it was not of major concern.

Table 6. Atmospheric Distillation Column Design Parameters in Design 1

Purity (wt%)	90
R_{min}	0.024
R	0.12
N_{min}	3
N	6
N_F	5
D/F	0.698

4.3 Economic evaluation for design 1

To determine and assess the cost associated with establishing a MEG recovery unit, Aspen Process Economic Analyzer Add-in tool embedded in Aspen Plus environment was used to provide an estimate for the capital cost (CAPEX) and operating cost (OPEX) for the MEG recovery unit simulated earlier for all the four scenarios. Assuming a project life of 20 years and interest rate of 8% per year, the capital (CAPEX) and operating costs (OPEX) for all four scenarios are obtained and calculated as a present worth that can be seen in figure 10. As it can be observed, the same cost was obtained for all four scenarios which were expected since all the scenarios have behaved similarly. In overall, it was deduced in the cost estimation process that there was no significant difference in the obtained values for all the scenarios; thus, from now on, only one scenario is adopted, analyzed and discussed as a representative. On average, the cost associated with design 1 producing 99.9wt% MEG is 11.5 MMUSD as a CAPEX and 35 MMUSD as OPEX which equates to an annual cost of 3.5 MMUSD.

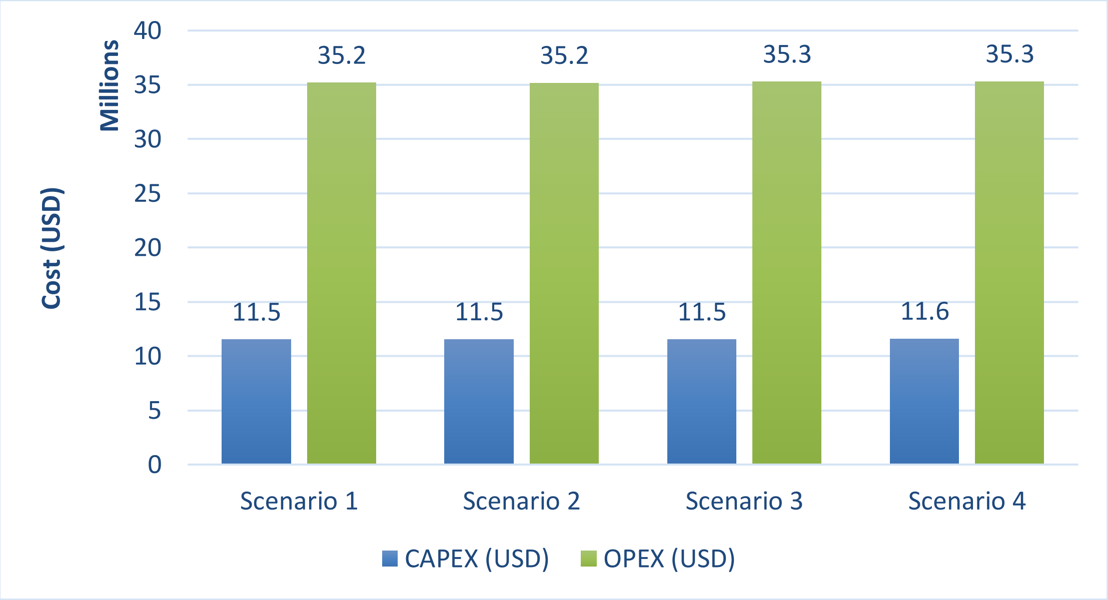


Figure 10. CAPEX and OPEX present worth for the four scenarios for design 1 at an operational pressure of 0.05 bar.

Looking at the breakdown of the total cost for design 1, for the CAPEX, around

50% of the cost is dedicated to the purchase and installation of the equipment with an average total installed cost 5.2 MMUSD for all four scenarios. Figure 11 presents the contribution of each equipment to the total equipment cost for design 1 where there is no significant difference in the reported values for all scenarios; thus, one scenario has been adopted and discussed. As it can be seen, the vacuum distillation has the dominant cost of all the equipment with 85% contribution which is expected since distillation columns are usually expensive adding to that the fact that this column runs at extreme vacuum conditions which generally indicates high vapor loads in the column and having the column of huge size due to increased diameter [50]. Furthermore, it was stated that running under vacuum conditions involves additional overhead equipment to maintain the vacuum which also requires a large diameter column in order to prevent flooding [38]. The vacuum flash separator has also contributed with almost 10% of the cost due to its increased size. Regarding the remaining of the CAPEX aside from the equipment, these costs could be related to piping, instrumentation, insulation, paint, contract fees, escalation, contingencies, General and Administrative (G&A) expenses.

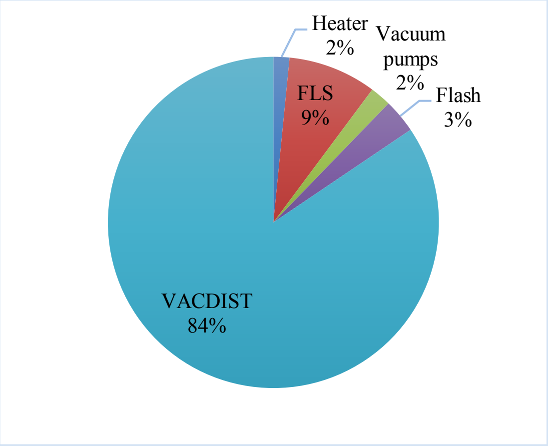


Figure 11. The contribution of each equipment to the total equipment cost in design 1.

Moving to the OPEX which was found to be around 3.5 MMUSD/yr, this cost is mainly comprised of utility cost and some other costs, such as operating labor costs, maintenance costs, operating charges, plant overhead, General and Administrative Expenses (G&A). As per Aspen's estimation, the main utilities that would be required in this case is electricity, refrigerant freon-12 (R-12), and medium-pressure (MP) steam (100 psi). Figure 12 shows the contribution of the utility cost to the operating cost. As demonstrated, the utility cost has a 63% contribution to the OPEX with an average of 2.25 MMUSD/yr while the others category refers to the additional operational expenses mentioned earlier. The utility cost was mainly due to the MP steam used as a heating utility stream for the preheater and the reboiler in the distillation column as well as Freon-12 used as a cooling utility stream for the condenser in the distillation column. The refrigerant was necessary as in the vacuum distillation column the boiling point of water is reduced at a much lower temperature than 100 °C necessitating the need for a low-temperature cooling medium [50].

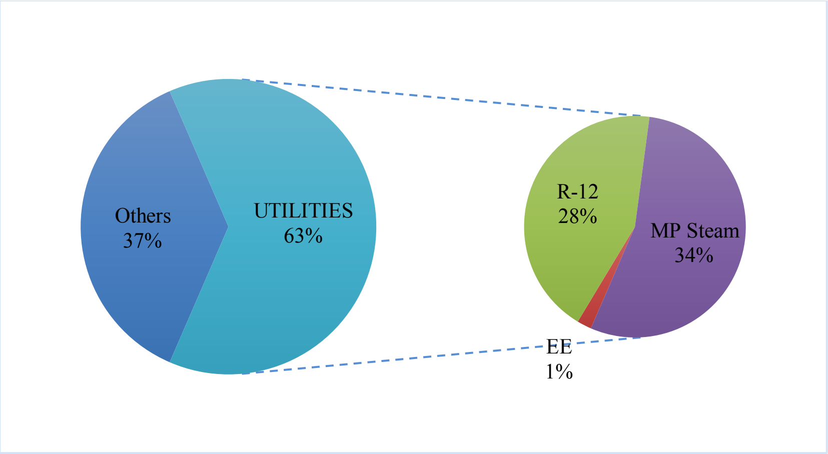


Figure 12. The contribution of utilities to the operating cost in design 1.

4.4 Economic evaluation for design 2

Similar to the first design, the economic evaluation for the second design was conducted in the same manner. The CAPEX and OPEX obtained for this design were

6.5 MMUSD and 8.2 MMUSD/yr, respectively. For the capital cost, the total equipment installation cost was around 33% of the capital cost with an investment of 2.2 MMUSD divided on the unit's equipment as shown in figure 13. As shown the distillation column has the highest cost as expected with a share of almost 50%. Then, it is followed by the divalent ions' precipitator with a share of 20% as it does the job of a reactor (reacting caustic soda with divalent ions) and settler (allow the formed the solids from the reaction to settle down by gravity). Also, the vacuum flash separator has a contribution of 10% as it works under vacuum indicating its large size while the remaining other equipment has shares <10%.

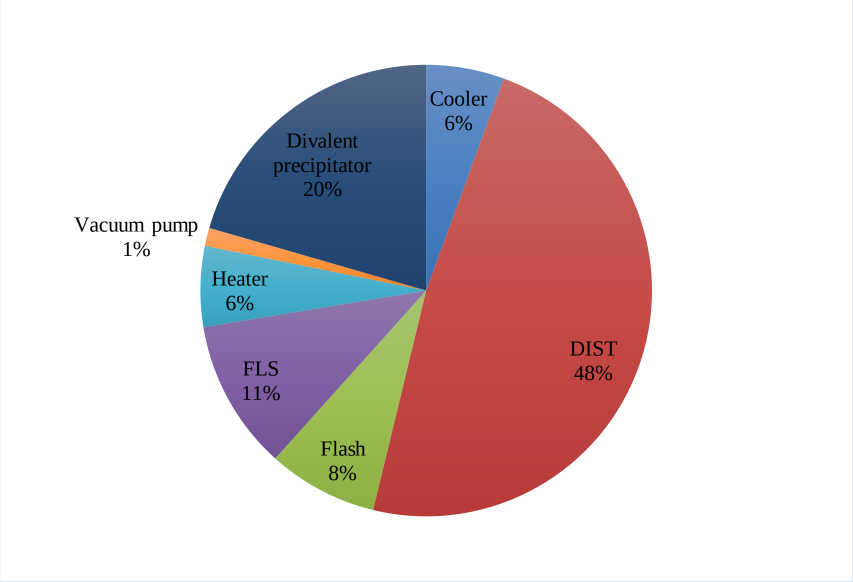


Figure 13. The contribution of each equipment to the total equipment cost in design 2.

Moving to the operational costs, it can be realized from figure 14 that the utility cost represents 78% of the OPEX mainly influenced by the steam cost as this design carries out the vaporization at atmospheric conditions having high temperatures requiring a tremendous amount of steam. For cooling purposes, some amount of cooling water was required having a share of 7% to the total operational cost.

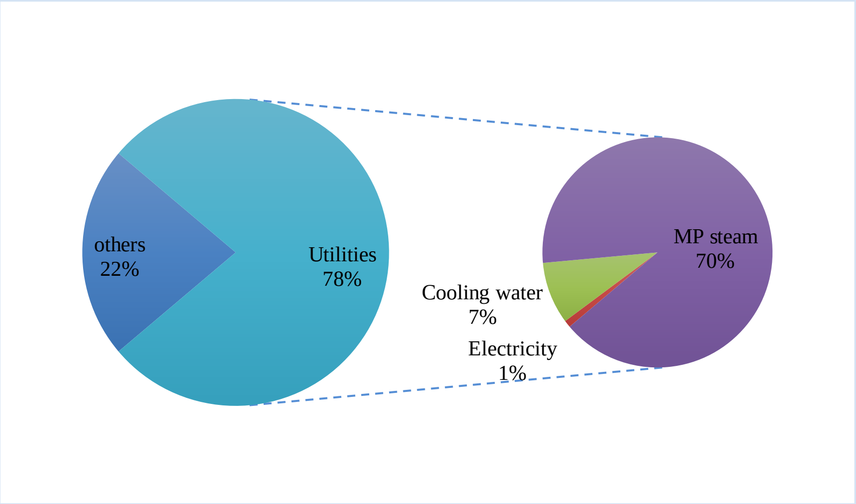


Figure 14. The contribution of utilities to the operating cost in design 2.

4.5 Sensitivity analysis on the performance of the unit

In order to determine if the unit is flexible to any operational changes, it was essential to conduct the sensitivity analysis to see how the performance of the unit is affected by the variation of different parameters. In principle, the sensitivity analysis was performed on the first design only as the second design was not flexible to the variation in the operational conditions or feed conditions because its design is specific to the conditions provided and any minor changes in that would cause significant MEG loss and to confirm that three conditions were tested in Aspen plus and the simulation has failed to converge. Besides, the sensitivity analysis presented here is based on design 1. In addition, it is important to highlight that scenario 3 shows the most realistic case with both types of salts are present and taking into consideration the chances of salt precipitation incidence, so most of the sensitivity analysis studies are based on this scenario.

4.5.1 Variation of rich MEG feed flow rate

The variation in the feed's flow rate was tested against different parameters, such as equipment duties, salt precipitation, salt carryover with MEG, MEG recovery, and purity. Figures 15 & 16 show an increasing linear trend for the duties of the heater, vacuum flash separator (FLS), condenser, and reboiler of the distillation column with increasing feed flow rate which indicates increasing cost. However, there were no incidences of severe salt precipitation or salt carryover with the product which indicates the excellent performance of the unit even at high loads of double the design flow rate; adding to that; there was no deterioration either in the quality of the product nor its purity. Looking closely at the figures below, in figure 15 it can be observed that the variation in the FLS duty is much higher than the heater's duty because of the extreme vacuum the unit is operated at. In figure 16, it is observed that the condenser's duty is increasing considerably compared to the reboiler's duty and this is due to the same reason of operational vacuum condition that increases the cooling requirements due to low operating temperatures.

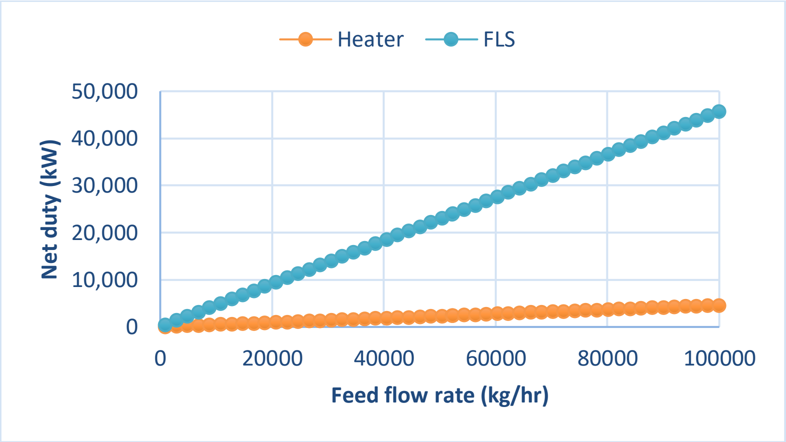


Figure 15. Variation of the heater and FLS duty with the feed flow rate.

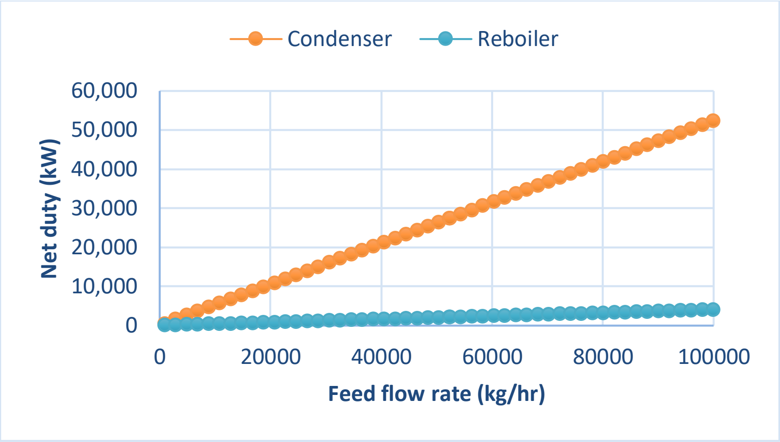


Figure 16. Variation of the condenser and reboiler duty with the feed flow rate.

4.5.2 Variation of rich MEG concentration

The variation in the inlet rich MEG concentration at the same inlet flow rate was mainly looked upon its effect on the product purity and recovery as it did not affect other parameters. Figure 17 shows the effect of increasing MEG concentration on the purity and recovery of the product obtained. It can be realized from the trend that there is a behavior for the unit at rich MEG concentrations < 50wt% and another behavior at rich MEG concentrations > 50wt%. If the feed has rich MEG concentration < 50wt%, the recovery of the product remains unchanged, but the purity of lean MEG is reduced which increases with increasing rich MEG concentration. This is mainly due to the operating conditions of the distillation column which was designed for a feed of 50wt% which if reduced, the purity of the product is reduced due to the poor separation occurring that requires a change in the operational conditions of the column. On the other hand, at rich MEG concentrations above 50wt%, the situation is reversed where the purity obtained remains unchanged as 99.9 wt%, but the recovery starts to get reduced reaching 60% at an inlet rich MEG concentration of 65wt%. This is mainly due to the loss in the distillation column with the top product for the same reason stated earlier.

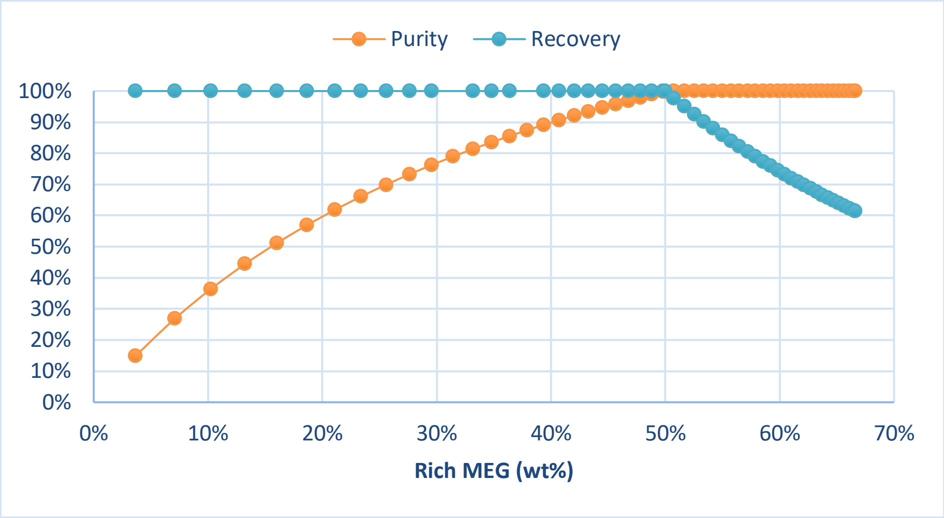


Figure 17. Variation in the MEG purity and recovery with varying inlet MEG concentration.

4.5.3 Variation of inlet salt concentration

The variation in the inlet salt concentration was mainly studied by varying the main ionic species present in the feed which are sodium, chloride, and calcium. For sodium and chloride ions, their concentrations were increased at least up to 3 times the design concentration, and it has not affected the performance of the units in terms of salt precipitation incidences, or product recovery and purity. On the other hand, for calcium ions, with increasing concentration, there were minor chances of the formation of $CaSO_4$ upstream the vacuum flash separator with concentrations less than 40 ppm which can be resolved by adding a vessel upstream the unit and allow these salts to precipitate and settle down by gravity if needed.

4.5.4 Variation of the design parameters of the distillation column

In this analysis, the number of stages and the reflux ratio were studied to determine if the performance of the distillation could be enhanced any further. Regarding the stages of the column, a minimum of 3 stages was required to have MEG-water separation, but with stages between three and six, the column has shown an enormous load on the condenser and reboiler duty in addition to having high temperatures in the column that could cause MEG degradation. Having 6-staged distillation has shown an acceptable operational temperature with obtaining the maximum separation which was ideal for the design. Further increase in the number of stages has not demonstrated any enhancement in the performance as well as increasing the capital cost of the column; thus, the column was designed to have six stages. Moving to the reflux ratio, the selected value for the design was around 0.56, below that the simulation has failed to converge due to the drying up of the column. On the other hand, operating the column above the designed reflux ratio with an attempt to reduce the number of stages has shown no favor as the utility requirement increased tremendously with a minor reduction in the initial cost of the column. This can be affirmed by observing figure 18.

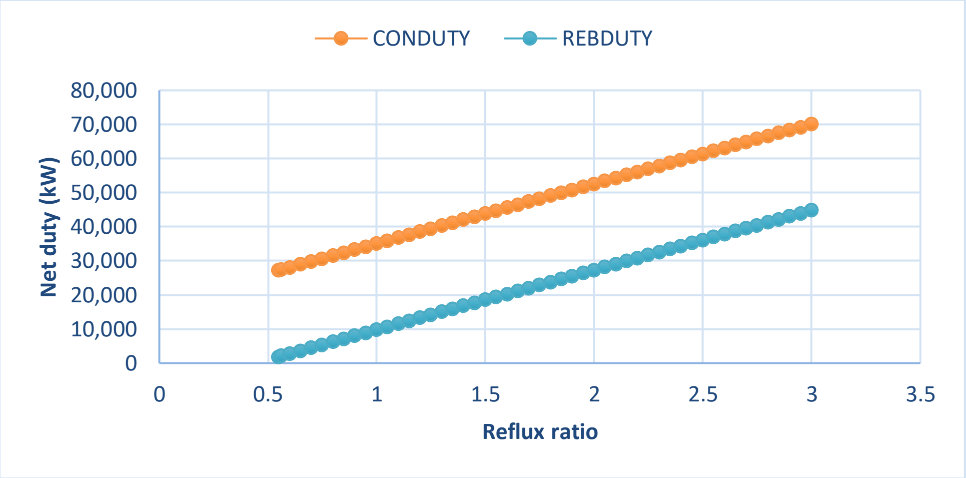


Figure 18. Variation in the condenser and reboiler duty with varying reflux ratio.

4.6 Sensitivity analysis on the economics of the unit

As mentioned earlier, the sensitivity analysis was conducted on the first design only, and this was done to test two aspects only. The first aspect was to examine the different temperatures and pressures for design 1 reported earlier in table 3 as all have shown the same performance, so it was essential to test their economics. The second aspect was to examine the variation in the overall cost of the project at different product purity, which was useful to compare to design 2.

4.6.1 Effect of different operating conditions on the process economics

Changing the operating conditions was mainly done by varying the temperature of the preheater and the pressure of the FLS vessel and distillation column between the values reported in table 3 and shown in figure 19. It is important to highlight that that the cost was converted to its equivalent of present worth using PV function in excel assuming a project life of 20 years and an interest rate of 8% per year. As shown, if the preheater increases the temperature of rich MEG stream to higher temperatures, less vacuum is required which is presented in figure 19 on the X-axis moving from the left to the right. With this behavior, the CAPEX was slightly reduced from 12 MMUSD at 0.05 bar up to 7 MMUSD at 0.25 bar while the OPEX was increasing significantly from 35 MMUSD at 0.05 bar up to 78 MMUSD at 0.25 bar. The reduction in the capital cost is explained by the reduction in the vacuum condition which caused a reduction in the size of the distillation column which in turn has reduced the capital cost. On the other hand, the OPEX was increasing due to the increasing temperature of the preheater and the distillation column due to the reduction in the pressure; this increase has amplified the requirement of steam supply as a heating utility from 8 ton/hr MP steam at an operating pressure of 0.05 bar up to 37 ton/hr at a pressure of 0.25 bar causing the considerable surge in OPEX as shown below. The exact cost values and utility requirements are presented in Appendix C for further understanding. In general, operating at the unit at any of these conditions is feasible and shows the same performance. The selection of any of them has a major trade-off between maintaining the extreme vacuum conditions and the higher economics at lower vacuum conditions. The concern of operating at 0.05 bar can be resolved by knowing that in the industry up to 2 mbar pressure levels are already applied [50]. As can be seen in figure 19 below, the hypothesis of operating at 100 °C and 0.05 bar would have the lowest cost has been clarified.

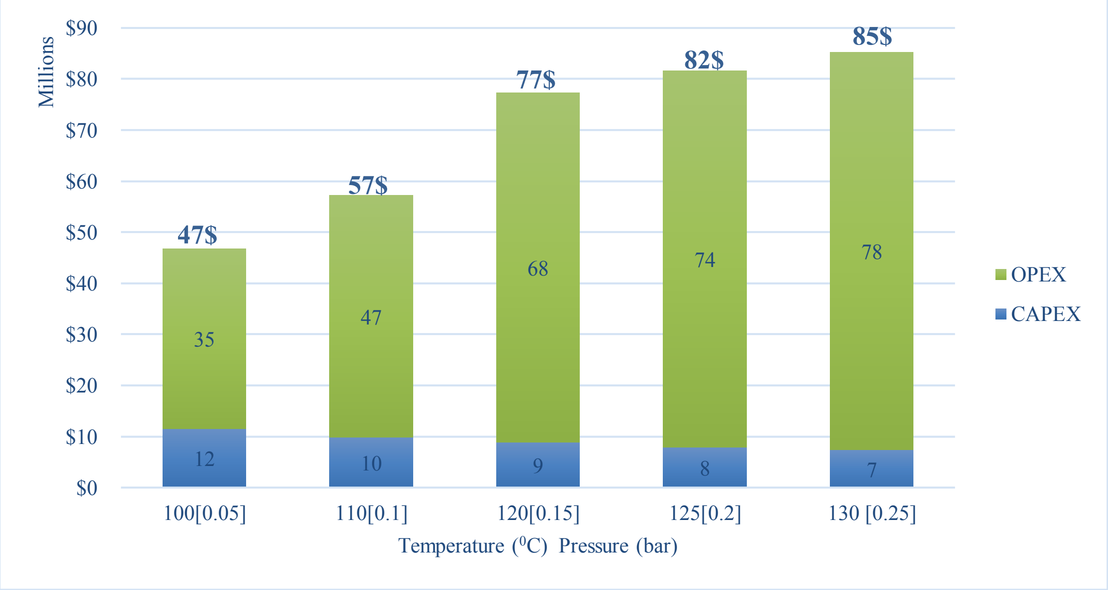


Figure 19. Effect of different temperature and pressure on the CAPEX and OPEX of design 1.

4.6.2 Economics of the unit at different product purities

In order to test the flexibility of the design and compare its economics to the economics of the second designs, the design was tested against producing four different MEG purities (99wt%, 95wt%, 92.5wt%, and 90wt%). This analysis was successfully conducted by changing the design parameters of the distillation column, mainly the reflux ratio and the distillate-to-feed ratio at the same number of stages. This analysis was done at an operating pressure of 0.05 bar as it shows the minimum overall cost based on the previous analysis. Generally, all the four scenarios have produced the same output in this analysis with the same reflux ratio and the distillate-to-feed ratio at a given purity. The values obtained are present in table 7. Generally, the change in these parameters has reduced the reboiler's duty four times with decreasing purity from 99.9wt% to 90wt%. This is because less water has to be evaporated from MEG which in turn reduces the load on the reboiler of the column. Figures 20 to 22 show the variation in capital cost, operational cost, and the total project cost for all four scenarios whose trends are the same at each scenario. From figure 20, it can be seen that there is a slight reduction in the capital cost with decreasing purity which is mainly due to the reduction in the size of the distillation column. Figure 21 shows the variation in the OPEX with purity which mainly tends to reduce with decreasing purity. This is mainly due to the reduction in the steam requirement as the reboiler's duty has been reduced. In overall, figure 22 shows the reduction in the total project cost from 47 MMUSD at a purity of 99.9 wt% to 40 MMUSD at a purity of 90 wt%. Generally, from this analysis with decreasing purity, the following was obtained:

1- 2.5% reduction in the refrigerant requirement.

2- 35% reduction in the steam requirement.

3- 10% reduction in the distillation column purchase and installation cost.

Table 7. Data Table for Distillation Column Design Parameters at Different Purities for Design 1

Purity	Reflux ratio (R)	Distillate-to-feed ratio (D/F)
99.9wt%	0.56	0.774
95wt%	0.59	0.736
92.5wt%	0.65	0.713
90wt%	0.71	0.69

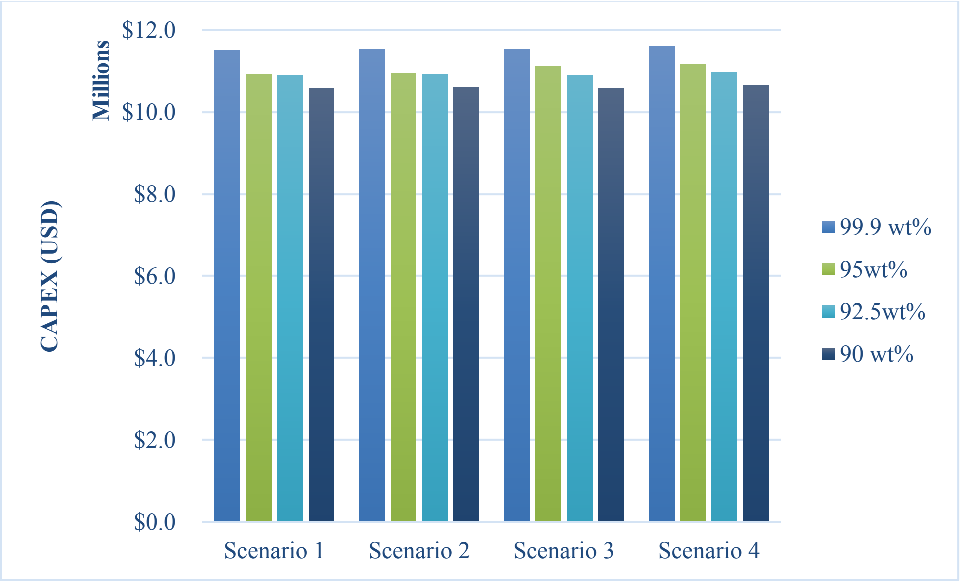


Figure 20. Varying CAPEX with product purity for all four scenarios in design 1.

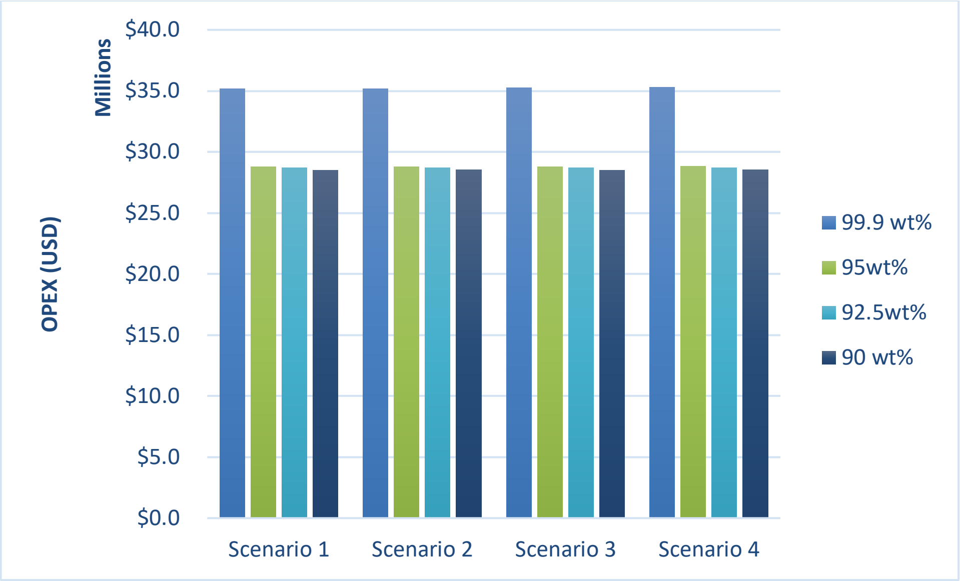


Figure 21. Varying OPEX with product purity for all four scenarios in design 1.

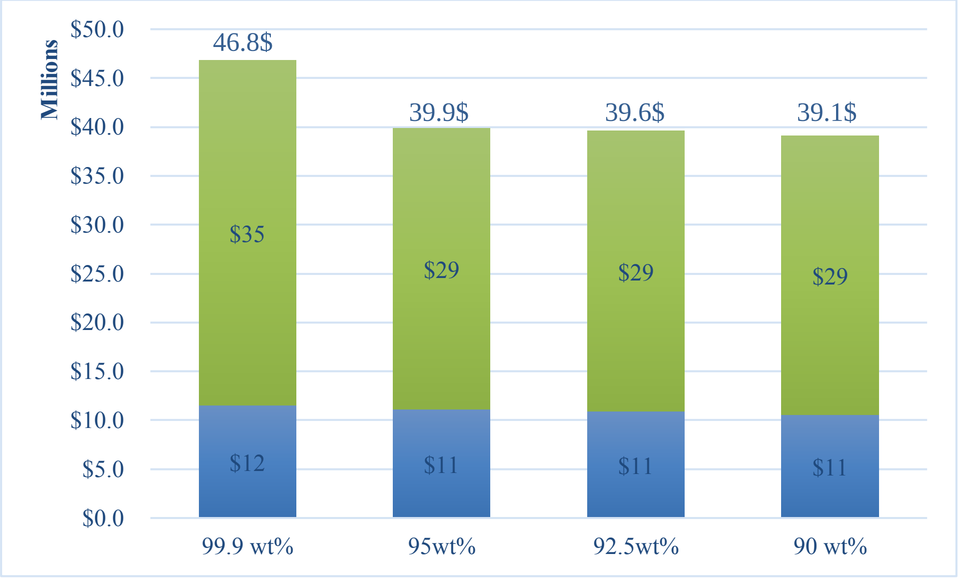


Figure 22. Varying total cost with product purity for scenario 3 in design 1.

4.7 Economic comparison between the two designs

To select the best of the two designs, an economic comparison was conducted between them based on a similar performance. Since the second design produces MEG with a purity of 90wt%, so it is compared to the first design at the operating conditions that produce 90wt% MEG. Figures 23 & 24 present the difference in equipment cost and utilities cost for both designs. It can be observed in figure 24 that the distillation column has significantly higher costs than other equipment being four times higher in the first design compare to the second design. The reason behind that is that the distillation column in the first design is operated under vacuum while in the second design is at atmospheric condition making the column in design 1 of a huge size compared to that in the second design. On the other hand, looking at the utilities cost present in figure 24, which shows that the steam cost is the primary controller in the utility cost being five times higher in the second design compared to the first one. This is due to the same reason mentioned earlier; the second column operating under atmospheric pressure has higher operational temperatures requiring vast amounts of the steam. In overall, analyzing the results present in figure 25, although the CAPEX of design 2 is lower than design 1, the high OPEX associated with the second design as steam accounts for 70% of this cost makes the overall project cost comparably higher than the first design for a project life of 20 years and interest rate 8% per year. The OPEX is around 12 times the CAPEX in the second design, as MP steam is used to increase the operational temperatures of the distillation column. Thus, design 1 is more attractive as it has lower cost and higher flexibility to changes in operational conditions, so it is recommended to adopt the first design with an overall project cost of 39 million USD for 90wt% MEG production or 47 million USD for 99wt% MEG production. If this design is compared to past studies in literature, this design has the least cost of all.

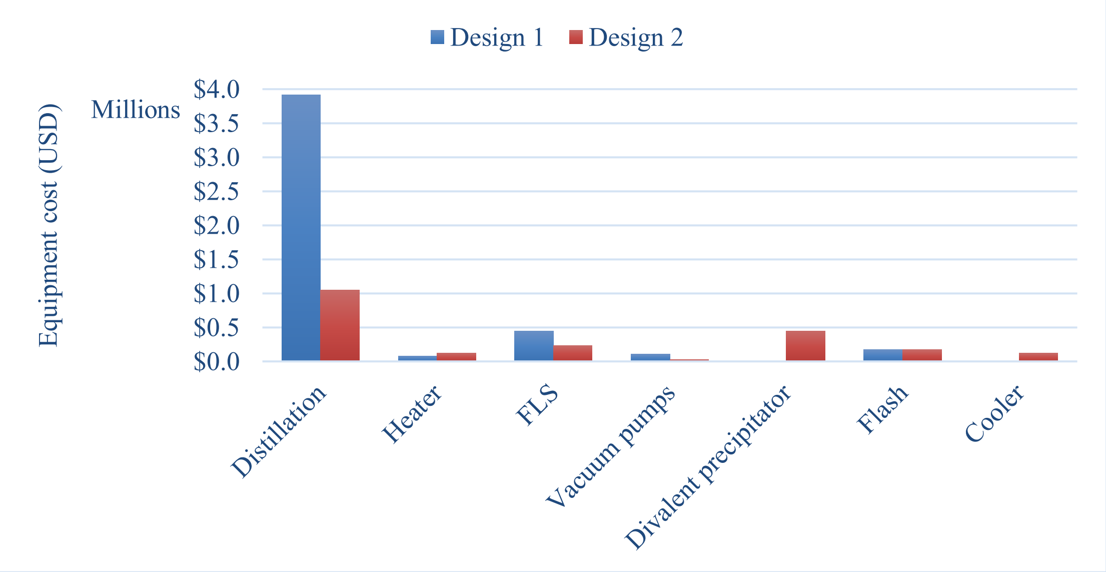


Figure 23. Equipment cost comparison between the two proposed designs.

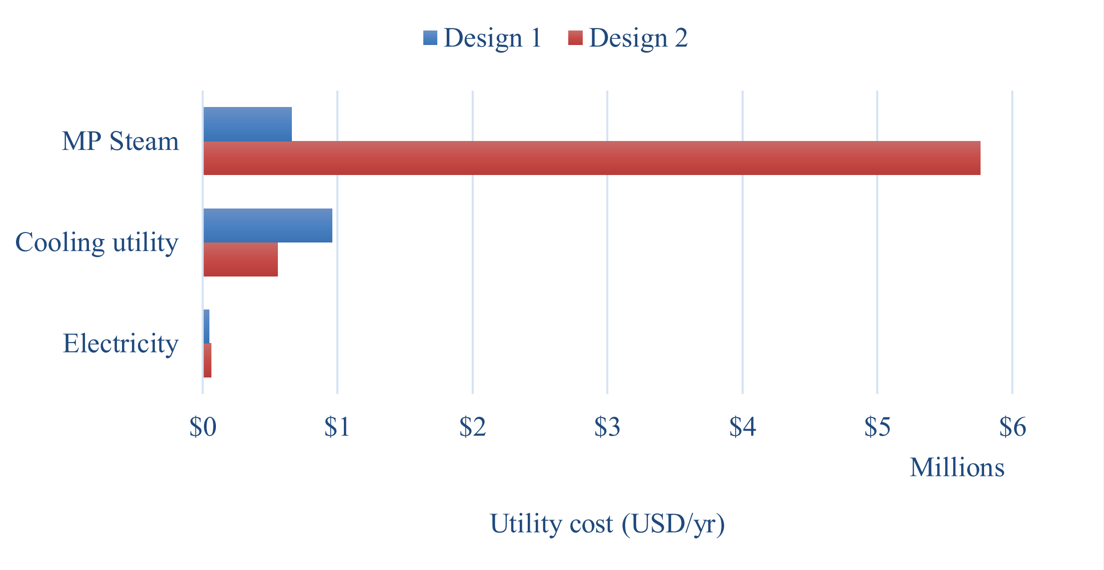


Figure 24. Utility cost comparison between the two proposed designs.

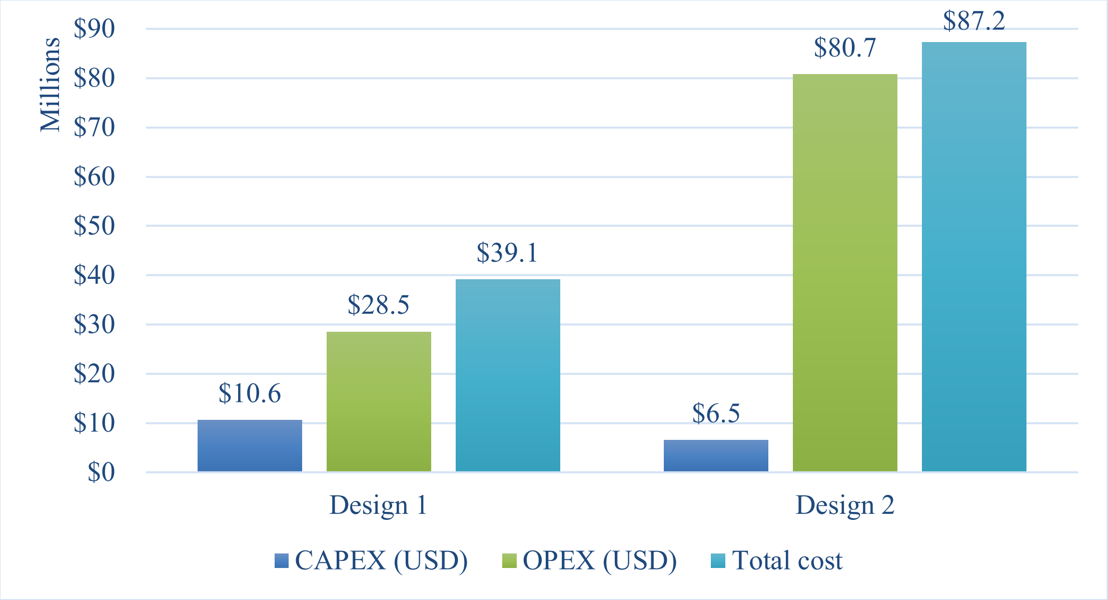


Figure 25. Overall project cost comparison between the two proposed designs.

4.8 The Engineering solution in establishing a MEG Recovery unit

The idea of establishing a MEG recovery unit seems promising as the hydrate inhibitor is purified and recycled for injection. However, this will not be attractive unless there are benefits to be drawn and MEG purchase costs are reduced or saved. Hence, after deciding to adopt design 1, it was necessary to conduct an additional economic study to compare the prices of purchasing fresh MEG and the costs of establishing a MEG recovery unit and come to a conclusion if the cost of MEG recovery unit is justified or not.

A basis of 28% MEG in the aqueous phase is assumed, and this dosage is correlated to a produced water flow of 60 m^3/hr in an LNG train having a natural gas production of 7.8 million tons annually. Also, it is assumed that the MEG injected is pure with a density of 1,110 kg/m^3 at 25 ^{o}C and an approximate cost of 700 USD/ton [24]. Based on this information, the annual cost associated with MEG purchase was estimated to be around 175 million USD as shown in the calculations present in Appendix D. It is important to recall that the overall project cost of a MEG recovery unit producing 99wt% MEG based on a present worth calculation for a project life of 20 years and interest rate 8% per year was estimated to be around 47 MMUSD.

Assuming that the purchase prices of MEG are to be reasonably stable over 20 years [6], the present worth of the annual costs of MEG purchase estimated earlier was estimated as a present worth with an approximate value of 1.9 billion USD. Hence, this amount represents the cost of MEG purchase for 20 years without recovery/regeneration. This cost was used as a basis of comparison to the purchase cost of MEG if it is to be regenerated. For that, it was assumed that MEG could be regenerated up to 5 times comparable to 9 regeneration cycles for MEG that was reported to perform well in hydrate inhibition as per an experimental analysis[42]. Thus, this analysis was done on MEG if it is to be regenerated once, twice, thrice, quadruple, and five times before being disposed of. Figure 26 presents the cost savings associated with MEG regeneration; the exact values are given in Appendix E. To start with if MEG is regenerated once after being utilized and then disposed of, almost 50% of its purchase cost can be saved based on a lifetime of 20 years. The savings percentage increases exponentially with increasing number of regeneration cycles reaching up to 80% saving in purchase cost for five regeneration cycles. Based on this analysis, the installation of a MEG recovery unit can be justified economically.

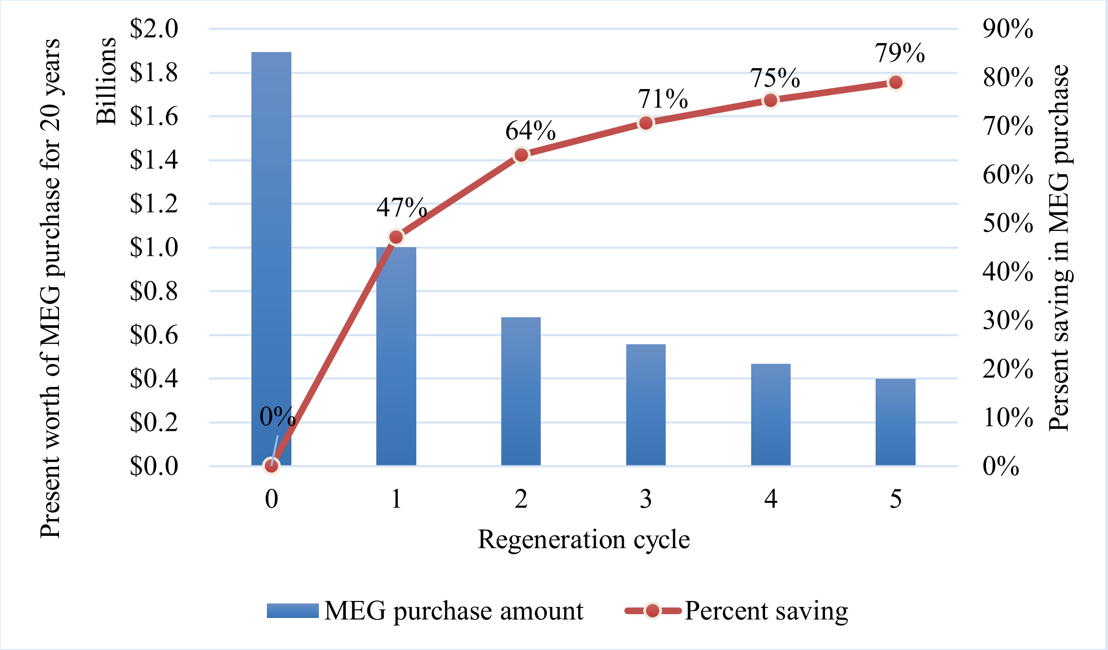


Figure 26 Variation in MEG purchase cost and percent savings with the number of regeneration cycles.

4.9 Environmental benefit of establishing MEG recovery unit

An important aspect to look at is the environmental concern associated with the installation of a MEG recovery unit. Regularly, if a plant does not have a MEG recovery unit, the fate of spent MEG after separation from natural gas is the disposal through injection into deep onshore wells. If it is decided to install a MEG recovery unit, it is essential to have an idea regarding the waste streams produced within the unit. In this unit, there are two main wastes in the process which are the concentrated brine from the reclaimer vessel and the water from the regeneration distillation column. For the concentrated brine/slurry, different treatment methods can be used. A salt handling system can process the salts by sending them to a centrifuge or a hydrocyclone to obtain a clean salt that can be sent for sales or disposed of as a solid waste [28,38]. Another treatment is its redissolution and dilution with seawater to be disposed to the sea if the appropriate regulations are set [12]. For the PW coming out of the regeneration column, it is clean enough to be sent for re-injection [26]. Hence, the wastes coming from a MEG recovery unit does not pose a substantial environmental concern adding to that the significant reduction in the disposal of spent MEG through injection into deep wells. Finally, concluding that the disposal is avoided by investing in the regeneration system removing the burden of the environmental concern.

4.10 Comparing the results of this work to the results in literature

Looking into the details, this work has included the salts/ions present in rich MEG in the simulation which was ignored by some other studies [2,25] making the designs presented in this study unique, effective and reliable. Other studies have considered the presence of salts/ions in their simulation [36,37], but there was no detailed information regarding the designed process, approach, and performance. Moreover, MEG recovery process was optimized for high purity and low cost in terms of operating pressure and distillation column design parameters, which was ignored in previous studies as presented by Zaboon [36] and Son [37].

Distillation column configuration is another aspect that can be compared with results from literature. The present study showed an effective MEG recovery with a distillation column of six stages, operated under a reflux ratio of 0.562 and a pressure of 0.05 bar. These operational conditions resulted in almost pure MEG with a recovery of 99.9%. The recovery percentage achieved in this study is better than the value (86wt%) reported by Zaboon et al. [36] who have tested MEG recovery experimentally and using simulation in a 6-staged distillation column operated at 1.4 bar. On the other hand, Son [37] designed a distillation column operated at 0.35 bar with a reflux ratio of 0.56 and producing MEG with a purity not exceeding 80wt% in 26 stages distillation column.

In addition, the results in this work are comparable to all other studies where a design was obtained producing 99.9wt% MEG with an overall project cost of 46 MMUSD for a lifetime of 20 years. Kim [41] developed a MEG recovery process that consists of a flash drum, two distillation column in parallel, a vacuum flash separator, and another vacuum distillation column. This design was capable of recovering 97wt% MEG with an overall project cost of 110 MMUSD for a project lifetime of 15 years. In another study, Kim [25] showed a design having a vacuum flash separator and a vacuum distillation similar to design 1 in this work with a total project cost of 55 MMUSD, yet, the maximum purity obtained was 90%. Based on the previous comparison, it can be concluded that the design presented in this study is cost-effective and of a recognizable performance.

To summarize, if all the results of this work are well studied and compared to all the research work and studies in literature, it would be observed that this work covers many aspects that other studies failed to include. The only one research work that was published with considerable results that could be compared with this study is the one conducted by Kim [41], but even this work did not consider different scenarios or having a design that is flexible to change the product purity or optimizing distillation columns with detailing design parameters. Thus, in overall, this work can have a significant contribution in literature for MEG recovery field.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

In this thesis, a MEG recovery unit was designed employing Aspen Plus simulation software, which was a suitable means of assessing different process configurations. After developing 2 designs, carrying out an optimization process for the operating conditions, conducting sensitivity analysis studies to determine the ideal conditions, and evaluating the process economics for all designs and scenarios implemented, it was found that design 1 operating under a vacuum pressure of 0.05 bar has shown the best performance obtaining the maximum purity and recovery with values of 99.9% for both and the minimum project cost with CAPEX and OPEX values of 11.5 and 35 MMUSD, respectively. To the best knowledge, the novelty of this thesis is filling the gaps in the literature related to the lack in a detailed analysis of the optimum operational conditions for MEG recovery and their effect on product purity, energy consumption, and cost. This study, therefore, has provided a sequential optimization on each equipment within MEG recovery process to obtain the best performance with the minimum cost. It was observed that MEG could be recovered at high purity if the OPEX and energy footprint of the process are optimized. The study also showed that being a distillation-based process, MEG recovery is combined with high and intensive heat requirements. In other words, the decision to install a MEG recovery unit is driven by an economic trade-off between the capital cost and operational costs. For these reasons, as a future perspective, it is recommended to conduct a sensitivity analysis on the effect of changing utility prices on the decision of installing the recovery unit and whether it would be economically justified if the utility cost surges in the future. Furthermore, in order to proceed with this study and test it in the industrial field, it is recommended to test the salt precipitation incidences and include in the investigation any scale inhibitors or corrosion inhibitors that could be injected in the pipelines along with MEG. Finally, It is also important to consider that during real-life application in Qatar, MEG is commonly injected 4-5 months per year during the winter season; thus, a study can be conducted to analyze if this would affect MEG recovery, cause significant changes in the cost and have positive outcomes.

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APPENDIX A: DUTIES FOR THE HEATER AND FLASH SEPARATOR FOR ALL SCENARIOS AT DIFFERENT OPERATING CONDITIONS

Scenario 1

T (℃)	P(bar)	Heater duty (kW)	FLS duty (kW)	Net duty (kW)
100	0.05	2,405	23,912	26,317
110	0.1	8,039	18,534	26,573
120	0.15	15,306	11,536	26,843
125	0.2	17,094	9,879	26,973
130	0.25	18,514	8,592	27,106

Scenario 2

T (℃)	P(bar)	Heater duty (kW)	FLS duty (kW)	Net duty (kW)
100	0.05	2,407	23,929	26,336
110	0.1	8,264	18,113	26,377
120	0.15	15,408	11,438	26,846
125	0.2	17,172	9,743	26,915
130	0.25	18,576	8,482	27,058

Scenario 3				
T (℃)	**P(bar)**	**Heater duty (kW)**	**FLS duty (kW)**	**Net duty (kW)**
100	0.05	2,405	23,930	26,335
110	0.1	8,043	18,554	26,597
120	0.15	15,387	11,477	26,864
125	0.2	17,210	9,786	26,996
130	0.25	18,622	8,507	27,130

Scenario 4				
T (℃)	**P(bar)**	**Heater duty (kW)**	**FLS duty (kW)**	**Net duty (kW)**
100	0.05	2,407	23,929	26,336
110	0.1	8,264	18,113	26,377
120	0.15	15,408	11,438	26,846
125	0.2	17,172	9,743	26,915
130	0.25	18,576	8,482	27,058

APPENDIX B: CALCULATIONS FOR THE AMOUNT OF SODIUM HYDROXIDE REQUIRED FOR INJECTION IN DESIGN 2

$$[Ca^{2+}] = 350\frac{mg}{L} \quad , \quad [Mg^{2+}] = 60\frac{mg}{L}$$

$$Ca^{2+} + 2NaOH \rightarrow Ca(OH)_2 + 2Na^{+} \rightarrow (1)$$

$$Mg^{2+} + 2NaOH \rightarrow Mg(OH)_2 + 2Na^{+} \rightarrow (2)$$

- $NaOH$ required in reaction 1:

$$350\frac{mg\ Ca^{2+}}{L} \times \frac{1\ mmol\ Ca^{2+}}{40.078\ mg\ Ca^{2+}} \times \frac{2\ mmol\ NaOH}{1\ mmol\ Ca^{2+}} = 17.5\frac{mmol}{L}\ NaOH$$

- $NaOH$ required in reaction 2:

$$60\frac{mg\ Mg^{2+}}{L} \times \frac{1\ mmol\ Ca^{2+}}{24.305\ mg\ Ca^{2+}} \times \frac{2\ mmol\ NaOH}{1\ mmol\ Ca^{2+}} = 5\frac{mmol}{L}\ NaOH$$

$$[NaOH] = 17.5 + 5 = 22.5\frac{mmol}{L}$$

Since the feed flow rate id 50 m^3/hr

$$[NaOH] = 22.5\frac{mmol}{L} \times \frac{1000\ L}{1\ m^3} \times 50\frac{m^3}{hr} = 1.125 \times 10^6\frac{mmol}{hr} = 1.125\frac{kmol}{hr}$$

$$\dot{m}_{NaOH} = 1.125\frac{kmol}{hr} \times 40\frac{kg}{kmol} = 45\frac{kg}{hr}$$

APPENDIX C: DATA TABLE FOR THE COST AND UTILITY REQUIREMENT FOR DESIGN 1 AT DIFFERENT OPERATIONAL CONDITIONS

T (0C) [P(bar)]	**100[0.05]**	**110[0.1]**	**120[0.15]**	**125[0.2]**	**130 [0.25]**
Purity (wt%)	99.9	99.9	99.9	99.9	99.9
Recovery (%)	99.9	99.9	99.8	99.8	99.7
Total capital cost (USD)	11,526,700	9,847,390	8,911,620	7,848,610	7,380,720
Total operating cost (USD/yr)	3,592,970	4,829,820	6,969,940	7,516,140	7,931,210
Total utilities cost (USD/yr)	2,267,780	3,459,040	5,470,540	5,986,800	6,380,000
EE (kW)	70	70	70	70	70
EE (USD/yr)	47,738	47,738	47,738	47,738	47,485
Cooling medium (m3/hr)	598 ton/hr	2,096	2,081	2,069	2,060
Cooling medium (USD/yr)	R-12 982,066	CW 582,095	CW 577,870	CW 574,674	CW 572,170
Steam (ton/hr)	8	18	31	34	37
Steam (USD/yr)	1,236,430	2,826,834	4,841,188	5,360,297	5,755,977
OPEX (USD)	35,276,309	47,419,885	68,431,898	73,794,570	77,869,789
Total cost (USD)	46,803,009	57,267,275	77,343,518	81,643,180	85,250,509

APPENDIX D: CALCULATIONS FOR THE ANNUAL PURCHASE COST OF MEG

Given:

- $MEG\ concentration\ in\ the\ aqueous\ phase\ (vol\%) = 28\%$
- $LNG\ production = 7.8 \times 10^6 \frac{ton}{yr}$
- $PW\ flow = 60 \frac{m^3}{hr}$
- $MEG\ purity = 100\%$
- $MEG\ cost = 700 \frac{USD}{ton}$

$$PW\ flow = 60 \frac{m^3}{hr} \times \frac{24\ hr}{1\ day} \times \frac{365\ day}{yr} = 525{,}600 \frac{m^3}{yr}$$

$$Aqueous\ phase\ flow = \frac{525{,}600 \frac{m^3}{yr}}{1 - 28\%} = 730{,}000 \frac{m^3}{yr}$$

$$MEG\ flow = 28\% \times 730{,}000 \frac{m^3}{yr} = 204{,}400 \frac{m^3}{yr}$$

$$Density\ of\ MEG\ @\ 25℃ = 1{,}110\ kg/m^3$$

$$MEG\ annual\ consumption = 204{,}400 \frac{m^3}{yr} \times 1{,}110 \frac{kg}{m^3} = 2.27 \times 10^8 \frac{kg}{yr}$$

$$MEG\ annual\ cost = 2.27 \times 10^8 \frac{kg}{yr} \times \frac{1\ ton}{907.185\ kg} \times \frac{700\ \$}{ton} = 175 \times 10^6\ USD$$

APPENDIX E: DATA TABLE FOR MEG SAVINGS PER REGENERATION CYCLES

Regeneration cycle	MEG purchase amount	Percent saving	Cost saving
0	$1,893,908,287	0%	$0
1	$1,001,433,372	47%	$845,671,906
2	$680,462,859	64%	$1,166,642,419
3	$556,514,193	71%	$1,290,591,085
4	$468,055,180	75%	$1,379,050,098
5	$398,722,383	79%	$1,448,382,895

APPENDIX F: PUBLISHED WORK FROM THE THESIS

- **Conference presentation**

The work produced in this thesis has been used as a contribution to the 8th Global Conference on Global Warming (GCGW) held in Qatar, where two abstracts have been submitted and accepted in the conference to be presented and published through high-impact journals. The details for the two abstracts are as follows:

Abstract 1:

- **Title:** Design and simulation of mono-ethylene glycol (MEG) Recovery unit
- **Authors:** Asmaa Othman, Fares AlMomani, Majeda Khraisheh, Ahmed AlNouss.
- **Abstract:**

The world has been relying recently on offshore oil and gas production which was stated to represent 33% of the total production in 2014 and that might surge due to the abundance of deep offshore fields and the exhaust of shallow water reservoirs. One major concern in natural gas production is flow assurance that is associated with ensuring the safe production and transportation of natural gas from production sites to processing facilities. Being placed in cold deep-water at high pressures, the natural gas within the transportation pipelines is likely to form gas hydrates due to the stimulating surrounding conditions. Gas hydrates form when the water content of the gas freezes and solidifies causing a plug in pipelines that stops the gas flow and the pressure builds up leading to its rupture. Hydrate inhibitors are chemicals added to pipelines in order to prevent the formation of gas hydrates during transport between offshore wells and onshore processing sites. In Qatar, hydrate inhibitors are usually injected in natural gas wells during the winter months between December and March. The present study was conducted in order to design a mono-ethylene glycol (MEG) recovery unit in order to

extract and recover MEG from produced water to permit its reuse. This study was carried out in a simulation basis using Aspen plus software with the support of the economic evaluation tool add-in for the economic analysis. The process was designed using Aspen plus environment using ELEC-NRTL as a property package, the recovery of MEG was successfully achieved by the separation of MEG-water vapor mixture from the salts present in produced water using vacuum followed by the vacuum distillation of MEG-water vapor mixture in order to obtain lean MEG as a bottom product. It was observed that a vacuum pressure of 0.05 – 0.4 bar provides a complete salt separation from MEG. In addition, it was found that six stages are required in the distillation column in order to obtain at least 99% MEG recovery and purity. Different scenarios were implemented in order to see how the system responds to susceptible alterations to the salts present in rich MEG stream. The scenarios were subjected to changes in the quality of the salts and the incidence of salt precipitation. In overall, it was realized that the main challenge in this process is the presence of dissolved salts and how to remove that at earlier stages in order to avoid their deposition on the equipment that could lead to their failure with time. One realization made is that there might be a risk of calcium sulphate (CaSO4) precipitation in the feed that might require a pretreatment step for this removal for the case of long-term operation.

Keywords: offshore oil, transportation of natural gas, Gas hydrates

Abstract 2:

- **Title**: Conceptual Process Design and Economic Analysis of MEG Recovery System Based on sequential salt precipitation and vacuum distillation
- **Authors:** Asmaa Othman, Fares AlMomani, Majeda Khraisheh, Saad Ali AlSobhi, Ahmed AlNouss.
- **Abstract:**

The recovery of monoethylene glycol (MEG) from aqueous streams via sequential salt separation followed by the vacuum distillation is evaluated as an alternative technology to conventional recovery methods. In this study, MRU is simulated in Aspen plus environment using ELEC-NRTL convenient thermodynamic to accommodate the presence of salts using the electrolyte wizard. Four different scenarios were considered

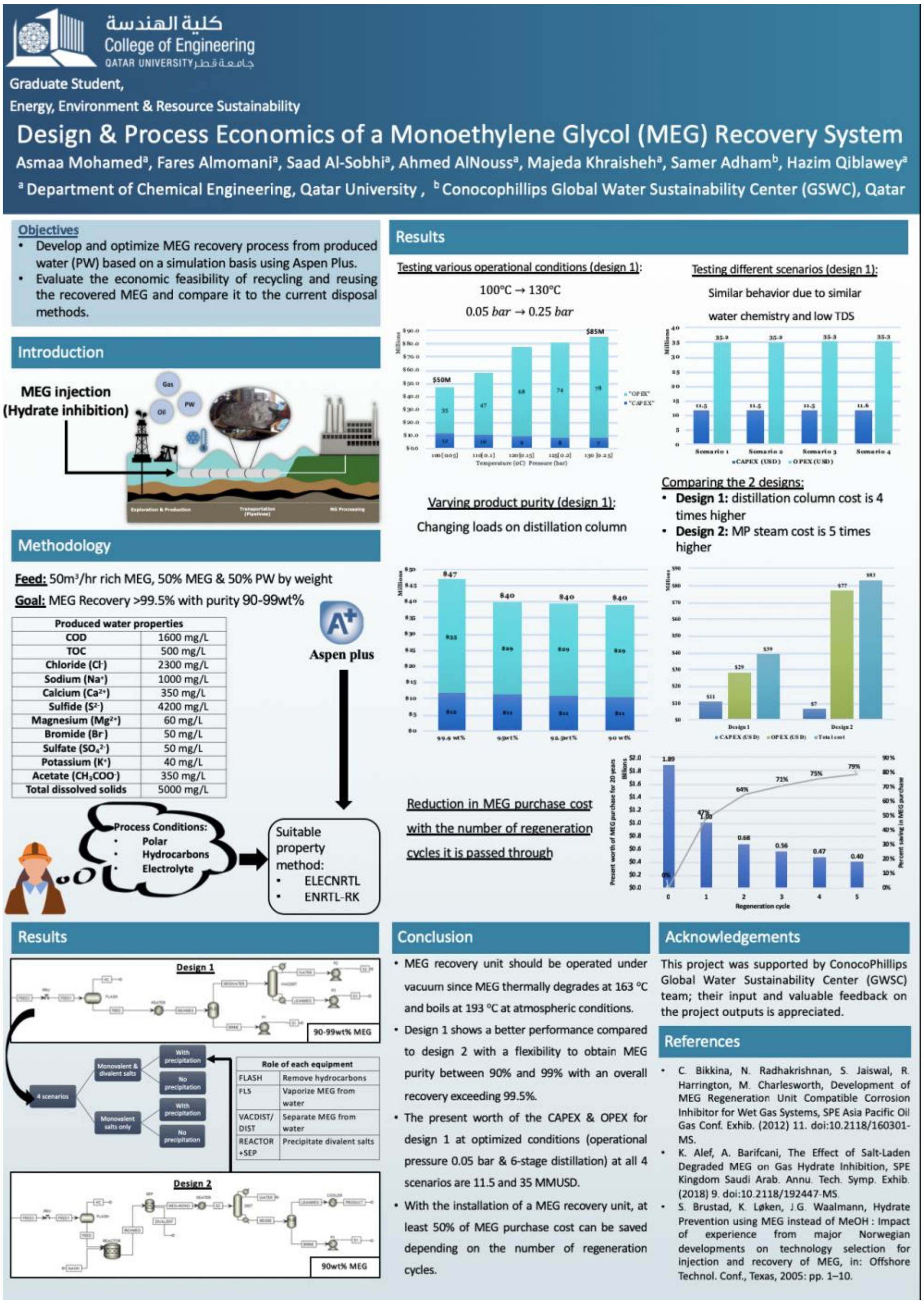
1- Monovalent and divalent salts without precipitation.
2- Monovalent salt alone without precipitation.
3- Monovalent and divalent salts with salt precipitation.
4- Monovalent ions only with salt precipitation.

The presence of monovalent salts only without divalent salts was studied in order to determine how the process would react to that change. In addition, it is common for divalent salts to be removed in an initial pretreatment vessel through pH adjustment with sodium hydroxide or caustic soda in order to avoid the associated problems of precipitation, scaling and equipment failure. Hence, it was necessary to simulate a case with monovalent salts. The third and fourth scenario were simulated to see how the process reacts in case salt precipitation occurs within MEG loops either when all salts are present or when monovalent salts only are present. In overall, these scenarios were implemented in order to analyze how the process performance, operating conditions, and process economics could change for each case. In order to ensure the smooth operation of the process, some important considerations were taken in the simulation. The results show that sequential salt separation followed by the vacuum distillation technology offers high energy savings, around 99% of MEG was recovered. Another outcome from this study using the economic evaluation analysis tool in Aspen, the CAPEX and OPEX estimated for the most industrial-imitating scenario were around $11.5 MM and $35MM, respectively.

Keywords: Produced water, hydrate, CAPEX, OPEX

- **Poster presentation**

Another contribution was made from this work by a poster to be presented in The Annual Research Forum & Exhibition 2019 held in Qatar University. A snapshot for the poster is presented below.



Graduate Student,
Energy, Environment & Resource Sustainability

Design & Process Economics of a Monoethylene Glycol (MEG) Recovery System

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Objectives

- Develop and optimize MEG recovery process from produced water (PW) based on a simulation basis using Aspen Plus.
- Evaluate the economic feasibility of recycling and reusing the recovered MEG and compare it to the current disposal methods.

Introduction

Methodology

Feed: 50m³/hr rich MEG, 50% MEG & 50% PW by weight

Goal: MEG Recovery >99.5% with purity 90-99wt%

Produced water properties	
COD	1600 mg/L
TOC	500 mg/L
Chloride (Cl^-)	2300 mg/L
Sodium (Na^+)	1000 mg/L
Calcium (Ca^{2+})	350 mg/L
Sulfide (S^{2-})	4200 mg/L
Magnesium (Mg^{2+})	60 mg/L
Bromide (Br^-)	50 mg/L
Sulfate (SO_4^{2-})	50 mg/L
Potassium (K^+)	40 mg/L
Acetate (CH_3COO^-)	350 mg/L
Total dissolved solids	5000 mg/L

Process Conditions:
- Polar
- Hydrocarbons
- Electrolyte

Suitable property method:
- ELECNRTL
- ENRTL-RK

Results

Role of each equipment	
FLASH	Remove hydrocarbons
FLS	Vaporize MEG from water
VACDIST/ DIST	Separate MEG from water
REACTOR +SEP	Precipitate divalent salts

Results

Testing various operational conditions (design 1):

100°C → 130°C

0.05 *bar* → 0.25 *bar*

Testing different scenarios (design 1):

Similar behavior due to similar water chemistry and low TDS

Varying product purity (design 1):

Changing loads on distillation column

Comparing the 2 designs:

- **Design 1:** distillation column cost is 4 times higher
- **Design 2:** MP steam cost is 5 times higher

Reduction in MEG purchase cost with the number of regeneration cycles it is passed through

Conclusion

- MEG recovery unit should be operated under vacuum since MEG thermally degrades at 163 °C and boils at 193 °C at atmospheric conditions.
- Design 1 shows a better performance compared to design 2 with a flexibility to obtain MEG purity between 90% and 99% with an overall recovery exceeding 99.5%.
- The present worth of the CAPEX & OPEX for design 1 at optimized conditions (operational pressure 0.05 bar & 6-stage distillation) at all 4 scenarios are 11.5 and 35 MMUSD.
- With the installation of a MEG recovery unit, at least 50% of MEG purchase cost can be saved depending on the number of regeneration cycles.

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