# Pretreatment of Acid Gas in feed for Petronas floating LNG facility

Zainab Kayat - PETRONAS Mark Schott, Shain Doong, Ron Subris, David Farr - UOP LLC, A Honeywell Company

### Abstract

The pretreatment system for Petronas' first FLNG project has been designed using advanced onshore pretreatment technology. This technology has been modified for use in a floating service environment to minimize plot, weight and cost, while improving reliability, resistance to rocking motion and expanding the operating envelope. Additionally, proven FPSO technology has been incorporated into these systems for additional reliability. These systems have been designed in cooperation between Petronas and UOP, a leading technology provider for Gas Processing Technology.

The paper will discuss the choices in FLNG Acid Gas Removal Unit (AGRU) design and review the selection for the Petronas FLNG project and future projects.

## INTRODUCTION

Growing global demand for natural gas is pushing the industry to consider development of remote offshore fields, once considered impractical to develop. Liquefied Natural Gas (LNG) production on a floating, ship-based platform offers a cost effective alternative to develop remote reservoirs where it is not economical to install pipelines and related infrastructure to support land-based conditioning and offloading facilities.

Off-shore liquefaction of natural gas, or Floating Liquefied Natural Gas (FLNG), is expected to be the next technological breakthrough for monetizing remote, offshore natural gas resources. It is estimated that over 30% of the world's natural gas reserves are located in offshore fields. This volume is an impressive 2,000 trillion cubic feet of natural gas reserves which is equivalent to 100 years of demand in the United States <sup>1</sup>.

Carbon Dioxide  $(CO_2)$  is a common acid gas in natural gas streams, with levels as high as 80%. In combination with water,  $CO_2$  is highly corrosive and can rapidly destroy pipelines and equipment unless partially removed.  $CO_2$  also reduces the heating value of a natural gas stream and reduces pipeline capacity. Other contaminants that need to be removed to very low levels include water, hydrogen sulfide (H<sub>2</sub>S) and Mercury (Hg). In order to achieve these specifications, several technology options must be integrated for acid gas and trace contaminant removal for pretreatment in LNG facilities. An additional concern is mitigating the effects of rocking motion and permanent tilt on the pretreatment system in a floating environment.

Drawing on UOP's & Petronas's extensive land-based LNG pretreatment experience the pretreatment train has been designed in cooperation between Petronas and UOP to meet the challenges in this new frontier of gas treating and conditioning.

### OBJECTIVES

A key technical challenge in this project is the scalability of the Acid Gas Removal Unit (AGRU) over time as the FLNG vessel is shifted from field to field to meet its targeted 20-year deployment life. The objectives of this paper are to discuss the technology selection process and review the methodology used to offer a robust pretreatment scheme in a floating environment subject to rocking motion, while ensuring project economics are not compromised and the project can achieve final investment decision.

### PRETREATMENT REQUIREMENTS

There are three principle contaminants in the raw feed gas considered potentially damaging in the liquefaction process of condensing methane to produce LNG: mercury, carbon dioxide and water.

### Mercury Removal

Mercury is known to cause stress cracking in brazed aluminum heat exchangers that are utilized in the cryogenic section. To prevent the stress cracking, the typical LNG Mercury specification is <0.01  $\mu$ g/Nm<sup>3</sup>. Mercury can be easily removed by conventional methods such as a non-regenerable metal oxide guard bed. The optimal location of the Mercury guard beds is upstream of the acid gas removal unit to minimize mercury contamination in the AGRU, prevent mercury-contaminated side streams and reduce HSE concerns during plant maintenance.

#### Water Removal

Water causes hydrates and freezing in the cryogenic section of the LNG train. Typical water specifications are <0.1 ppmv. Molecular sieves are the proven technology to achieve these low water content specifications.

#### CO<sub>2</sub> Removal

 $CO_2$  removal to very low levels is required to prevent freezing in the low-temperature cryogenic unit in the liquefaction section. There are numerous technology options than can be utilized for  $CO_2$  removal and two of these will be discussed below, based on a  $CO_2$  feed inlet ranging of up to 20 mol %. The typical outlet  $CO_2$  specification in LNG pretreatment is less than 50 ppmv.

The pretreatment unit is intended to remove these contaminants to enable downstream liquefaction of the treated natural gas for LNG production. Apart from an efficient treatment system design, the most challenging considerations for pretreatment systems designed for floating facilities are the space and weight constraints encountered in a floating environment.

 $CO_2$  removal from natural gas using amines is a mature and widely used technology. In a typical commercial amine process, an aqueous alkanolamine solution is in counter-current contact with natural gas containing  $CO_2$  in an absorber column. The basic amine reacts with the acidic  $CO_2$  vapors to form a dissolved salt, allowing purified natural gas to exit the absorber. The rich amine solution is regenerated in a stripper column to produce an acid gas stream concentrated with  $CO_2$ . The lean solution is then cooled and returned to the absorber so the process is repeated in a closed loop. Amine technology is able to remove the  $CO_2$  to a low level concentration of 50 ppmv.

Membrane technology has been applied in natural gas processing for over 20 years<sup>2</sup>. Membranes are frequently used for bulk  $CO_2$  removal from natural gas at processing rates from 1 to 1000 MMSCFD. Many of these units are used for off-shore service either on a platform or Floating Production Storage and Offloading vessel (FPSO). Because of their modular design, membrane systems can offer flexibility to treat an array of acid concentrations and offer greater turndown capability than amine systems. Membranes are not affected by rocking motion or static tilt conditions encountered in marine environments.

Membrane separation is based on different gas permeation rates or permeabilities among different gas components. For example,  $CO_2$  permeates faster than methane ( $CH_4$ ) or other hydrocarbon gases in a commercial  $CO_2$ -selective membrane. The driving force for membrane separation is the partial pressure differential between the feed side and the permeate side of the membrane for each gas component. The reduced  $CO_2$  treated gas stream contains mostly slow-permeating components and is at a pressure slightly lower than the feed. The enriched  $CO_2$  permeate stream contains mostly fast-permeating species and is at a pressure much lower than the feed.

Removing  $CO_2$  to very low levels in membranes requires exponentially more membrane area because the low  $CO_2$  concentration results in low  $CO_2$  partial pressure and hence very low driving force for permeation. Using membranes to achieve the 50 ppm  $CO_2$  LNG specification would require a prohibitively large membrane area, so they are proposed only for bulk removal of  $CO_2$ .

### INTEGRATED FLNG PRETREATMENT SCHEMES

Based on the two  $CO_2$  removal technologies discussed above, three FLNG pretreatment schemes can be configured, as shown in Figure 1, to achieve the desired LNG specifications as the feed  $CO_2$  increases during the life the project.

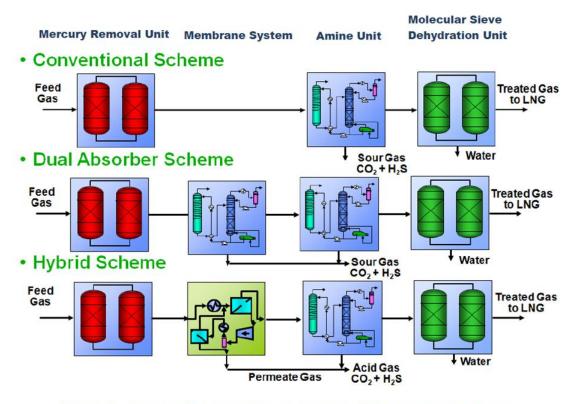


Figure 1. - Three FLNG pretreatment schemes, 1) Conventional Scheme, 2) Dual Absorber Scheme and 3) Hybrid scheme

The first pretreatment scheme is the conventional scheme, where an amine unit is followed by a molecular sieve dehydration unit. This scheme is preferred for the initial phase of the project since there is a relatively low  $CO_2$  content in the raw feed gas. At a future time, the ship is expected to be relocated to a field with concentrations as high as 20 mol%  $CO_2$  in the feed gas. To utilize a single amine train for this range of  $CO_2$ , the large unit would have to operate at turndown ratios up to 20:1 for the solvent. This would be a very inefficient set of conditions and would result in significant over-circulation of the solvent and higher reboiler duties than actually required for the process conditions.

The second scheme therefore utilizes two amine absorbers in series, a bulk CO<sub>2</sub> Absorber that would be installed in the second phase of the project, and a trim amine Absorber to meet final product specifications that will be installed in the first stage of the project. Solvent from the bulk removal absorber is flash regenerated to form a semi-lean stream dedicated to the bulk removal absorber (see Figure 2). A conventional amine unit polishes the gas stream to achieve <50 ppmv CO<sub>2</sub> and the downstream molecular sieve unit removes water to <1 ppmv H<sub>2</sub>O. The CO<sub>2</sub> composition after the bulk absorber and before the trim amine absorber are optimized to minimize the semi-lean solvent rate and corresponding size of the bulk removal absorber during Phase 2, while avoiding significant oversizing of the trim removal absorber and regenerator during Phase 1. Since the additional amine absorber is not required for several years, investment can be delayed. However, infrastucture for the added weight of the absorber, flash column and solvent inventory would need to be pre-invested to allow for the future installation of this equipment.

The third scheme, known as a hybrid, first uses a membrane unit for bulk removal of  $CO_2$  and conventional amine and dehydration units for polishing of the gas stream to achieve <50 ppmv  $CO_2$  and <1 ppmv H<sub>2</sub>O. As in the second scheme, the amine absorber, along with the second phase infrastructure, would be installed in the first phase of the project to minimize initial investment. The membrane system would be installed during the second phase. The  $CO_2$  composition after the membrane and before the amine can be optimized based on footprint, weight and cost considerations.

Fuel gas requiremens and acid gas disposal options can also be considered when optimizing the membrane system.

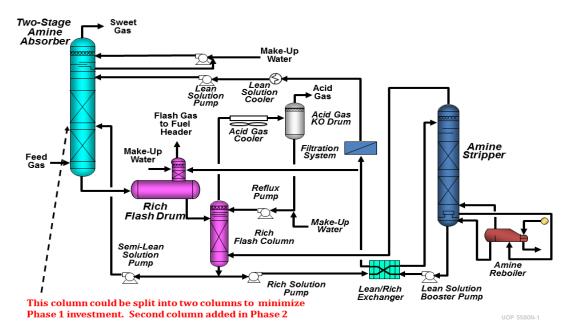


Figure 2. Two-Stage Amine Absorber with Rich Flash Column

# AMINE TREATING IN ROCKING MOTION

Use of the amine process for FLNG service has raised concerns with respect to the sea motion effect on the column performance. While amine units have been installed on FPSO applications for product gases with a  $CO_2$  specification of 2-3%, there is no amine unit currently operating for FLNG service. The motion effect will be more pronounced for an amine unit meeting 50 ppmv  $CO_2$  product specification. Column efficiency reductions for distillation or absorption processes under rocking conditions due to sea motion have been well documented in the literature<sup>3-9</sup>. Rocking motion generally affects the amine column performance by creating gas/liquid mal-distribution within the column, with the liquid preferentially moving towards one side of the column leaving the other side of the column depleted of the liquid, as shown in Figure 3. As a result, the gas will have a tendency to flow to the region with the deficit of the liquid while the region with the surplus of liquid will encounter less gas flow. The non-uniform distribution of the liquid and gas over the cross section of the column leads to a performance drop or decrease in column efficiency. Prior studies show that column performance suffers most with permanent tilt and the taller the bed height, or height/diameter ratio, the higher the loss in efficiency<sup>5-6</sup>.

PETRONAS together with UOP has conducted detailed marinisation studies on amine columns for FLNG application and found that depending on the sea motion conditions, significant margins need to be added to the solvent circulation rate and the and equipment sizes in the regeneration loop. This has a negative impact on the amine system size, weight and cost.

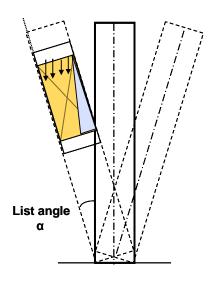


Figure 3. - Amine column under tilt or rocking condition, showing preferential liquid flow toward one side of the column

A basic flowchart depicting the process for the marinisation study is depicted in Figure 4. The implementation of marinisation margins begins with a "land-based" AGRU design. Project specific motion data provided by the customer is an input to the CFD model, as well as internal and published pilot plant rocking data. The CFD model determines the maldistribution factors, which are then input into a proprietary heat and mass transfer model to determine the design margins (marinisation margins) required for AGRU design to meet product guarantees. Numerous iterations may be required to confirm the marinisation factors and develop the final AGRU design and to confirm which rocking motion is the governing case.

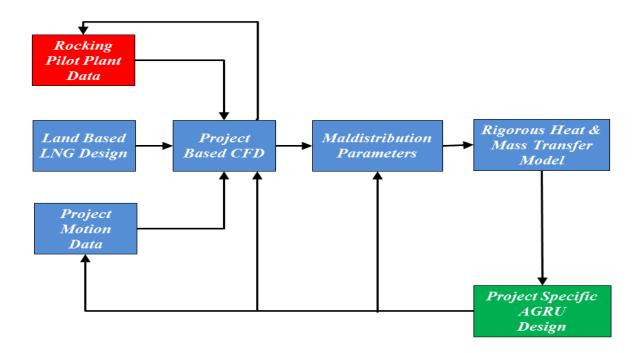


Figure 4. Marinisation Process Methodology.

Commercial CFD programs do not have the proper codes to adequately model motion effects in a packed column. Specific models and codes were developed to be used by the CFD models for solvent systems in FLNG and FPSO applications. These models and codes have been benchmarked against test data. Figure 5 Shows the liquid rates collected at the bottom of a test column under two different tilt angles as compared with the CFD results. As can be seen, the liquid is predominantly collected on one side of the column while the other side is almost dry. This picture is completely captured by the CFD results on the right side of Figure 5. CFD modeling can also be applied to columns under rocking conditions and combinations of static tilt and oscillating states. CFD modelling generally confirms that same angle static tilt is the most severe design condition with the highest maldistribution factors.

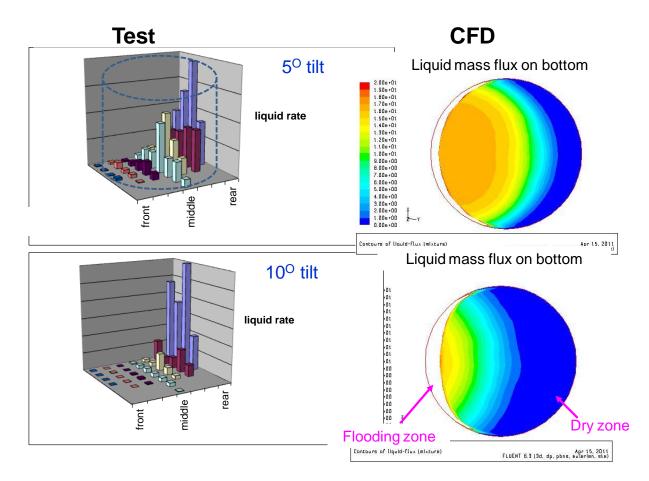


Figure 5. CFD modeling results compared to a Test Case.

Using the maldistribution parameters estimated from CFD in the heat and mass transfer equations, the amine process simulator estimates the impact of maldistribution on the amine absorber performance. Figure 6 provides an example showing the  $CO_2$  compositions in the treated gas for three different solvent circulation rates. For each case evaluated, a slight increase in the maldistribution results in a significant increase in  $CO_2$  slip. At higher liquid rates, the absorber is less sensitive to maldistribution. Depending on the maldistribution parameters obtained from the CFD, an appropriate solvent circulation rate can then be determined for the amine column to mitigate the effects of rocking motion and static tilt.

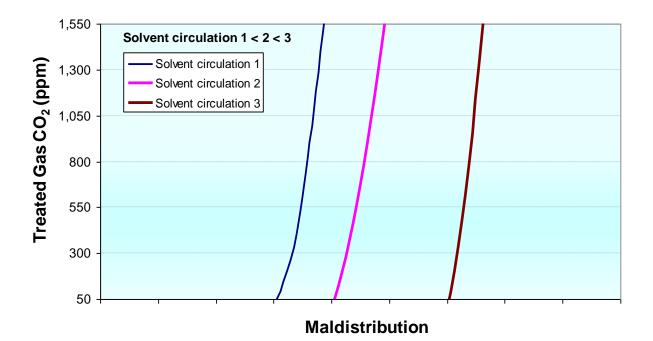


Figure 6. CO<sub>2</sub> slip versus degree of maldistribution.

### **EVALUATION OF PRETREATMENT SCHEMES**

When designing for the deployment life of the ship with varying feed gas conditions, there will always be tradeoffs in the amount of pre-investment that should be made. Due to space and weight constraints on the ship, upfront technology decisions need to be made to ensure that future expansion is possible. The final design must provide a minimized footprint and weight, low capital cost yet have easy scalability based on feed gas impurity concentrations and flowrates.

For this evaluation the acid gas removal unit would be required to meet the product gas specifications at capacities between 30% and 100% at widely varying acid gas levels. A detailed configuration study was conducted to evaluate the three pretreatment flowschemes presented in Figure 1 across the expected range of feed gas cases. A marinisation study that implemented advanced CFD modeling was conducted to assure that the rocking effects and static tilt due to marine environment would be mitigated for each configuration that was considered. The desired result was a robust and optimized pretreatment design that would meet the desired LNG specifications in all expected sea states. Two other important considerations for the AGRU are to minimize the complexity of the process and increase the flexibility of the proposed design for the proposed project phases.

The configuration study evaluated:

- Overall footprint and weight of each configuration
- Flexibility of design to treat the expected range of acid gas in the various project stages
- Ease of revamping the AGRU (future addition of equipment)
- · Ability to operate at design rocking conditions and permanent tilt
- CAPEX and OPEX evaluations to determine the tradeoffs between the conventional and hybrid flowschemes

A customized acid gas removal unit was developed addressing field production and LNG processing requirements, and incorporating a robust amine design that is scalable and able to satisfy product specifications for the varying design conditions and the broad design envelope. For such purpose, the amine-only configuration is economically feasible up to a certain  $CO_2$  concentration and flowrate. This  $CO_2$  concentration may vary from project to project as it is also influenced by such factors as feed flow rate, design rocking motion requirements as well as waste heat availability in the entire facility. Above the threshold  $CO_2$  concentration, the hybrid configuration offers a significant space, weight and CAPEX advantage over standalone amine units.

### **EVALUATION RESULTS**

The hybrid configuration potentially provides an advantage over standalone amine units by allowing deferment of investment and high scalability as acid gas content increases in the feed gas. Results summarised in Figures 7 and 8 indicate the hybrid configuration offers significant weight and plot area savings versus comparable sized bulk amine absorbers. The hybrid configuration reduces complexity in future revamp activities and offers flexibility to treat an array of acid gas concentrations. At higher  $CO_2$  concentrations and higher natural gas flow rates, amine units begin encountering lifting weight limitations - these concerns are not present for the hybrid configuration. The downside of the hybrid configuration is the hydrocarbon loss but this can be mitigated by using a multi-stage membrane system or incorporating the permeate gas into the fuel gas system.

Hybrid Option I depicted below represents a module with a single stage membrane system. Hybrid Option II represents a multi-stage membrane system.

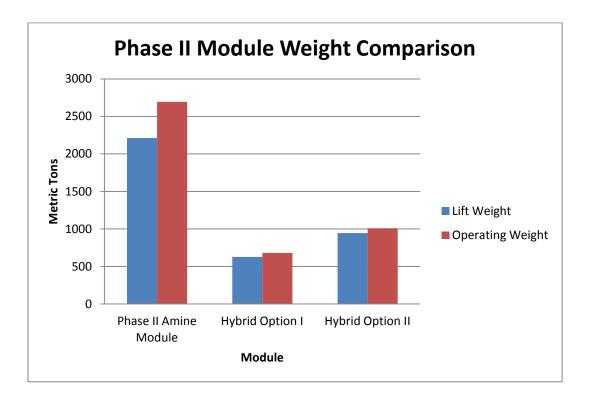


Figure 7. – Module Weight Comparison

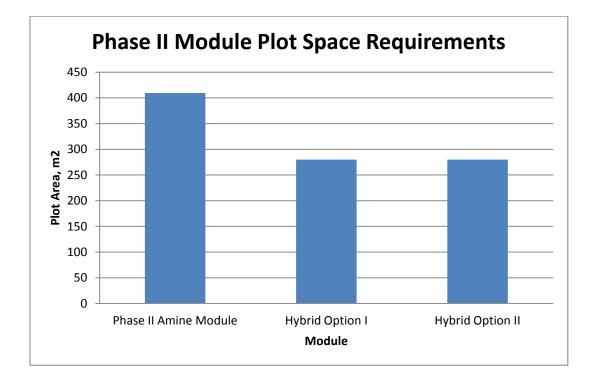


Figure 8. – Module Plot Space Comparison

### CONCLUSION

Many factors contribute to the selection of the optimal pretreatment design configuration, including rocking motion effects, flexibility to treat a wide array of feeds and flows, as well as the expected range of the feed  $CO_2$  and  $H_2S$  content. Commercial technologies for removing mercury, acid gas ( $CO_2/H_2S$ ) and water from natural gas can be integrated and configured into various FLNG pretreatment schemes. The amine system with liquid circulation is negatively affected by tilting and rocking due to motion of the sea. The impact of rocking motion on the amine system can be mitigated by conducting detailed marinisation studies that include sophisticated computer modeling, such as CFD, to determine the proper design margins that should be incorporated into equipment design and solvent circulation rates.

Evaluation of the three pretreatment schemes shows that as the  $CO_2$  levels increase beyond a certain, project specific limit, the hybrid process has a more attractive cost and weight among the three options studied, based on modular design. By reducing the  $CO_2$  levels entering the amine unit, the ultimate impact of static tilt and rocking motion are reduced, thus decreasing the required design margins required for marinisation. The size of equipment required in the amine unit is therefore reduced, resulting in the desired minimization of weight and plot space for the FLNG vessel.

# REFERENCES

- 1. Nexant PERP Report 07/08S10, "Floating LNG Production", December 2008
- 2. P. Bernardo, E. Drioli, and G. Golemme, "Membrane Gas Separation: A Review/State of the Art" Ind. Eng. Chem. Res. 2009, 48, 4638–4663
- 3. Pluss R.C. and Bomio P., 1992, "Design aspects of packed column subjected to wave induced motions", I.CHEM.E. Symposium Series No. 104, A259

- 4. Baker S.A., Tanner R.K. and Waldie B., "Comparison of packing types in a water deaeration column under vertical, tilt and motion conditions", Trans IChemE, Vol 70, Part A, September, 509
- 5. Tanner R.K. and Waldie B., 1992, "Liquid distribution in a packed column", The 1994 ICHEM Research Event, 1084
- 6. Tanner R.K, Baker S.A., Millar M.K. and Waldie B., 1996, "Modelling the performance of a packed column subjected to tilt", Trans ICheE. Vol 74, Part A, March, 177
- White V., Kalbassi, M.A., Waldie B. and Wilson, J., 2007, "Structured packing and use thereof" US Patent 7673857
- Kalbassi, M.A, Waldie B., White V., and Bell C., 2008, "Liquid distribution from structured packings and distributors under tilt and motion relevant to floating cryogenic air separation plants", Proceedings of the 2008 International Symposium on Safety Science and Technology, September, 2008 Beijing China, p151
- 9. Hoerner B.K., Wiessner F.G. and Berger E.A., 1982, "Effect of irregular motion on absorption/distillation processes", CEP, November, 47