



## Industrial case studies in the petrochemical and gas industry in Qatar for the utilization of industrial waste heat for the production of fresh water by membrane desalination

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#### ABSTRACT

An investigation into the potential of using industrial low-grade waste heat in desalination using membrane distillation (MD) has been carried out. This investigation highlighted the need to work on fresh water production using economic and environmentally friendly techniques. Using an approach based on heat integration and heat recovery principles, process streams in three industrial processes, namely the liquified natural gas (LNG), Ethylene and Vinyl Chloride Monomer (VCM) were screened to eliminate unsuitable sources of low-grade heat. This approach is appropriate to Qatar, being one of the countries that have large natural gas reserves and an emerging petrochemical industry. The criteria for selecting suitable low-grade heat sources led to the elimination of LNG and Ethylene processes for further consideration. The VCM process on the other hand showed a promising outlook, in particular in the direct chlorination section where a major vapor stream is condensed through the temperature range 118–46°C. This is precisely the ideal range for low-grade heat recovery for the MD application. A method for the implementation of low-grade heat recovered from the VCM process in a MD application was presented.

*Keywords:* Membrane distillation desalination; LNG; VCM; Pinch technology; Industrial waste heat

#### 1. Introduction

Through continual improvements, particularly in the last decade, desalination technologies can be used reliably to desalinate sea-water as well as brackish waters from saline aquifers and rivers. Reverse osmosis (RO) is currently the state-of-the-art desalination technology, but there are still major challenges to be resolved, such as: membrane fouling; relatively low

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recovery for seawater desalination; and relatively low removal of low molecular weight contaminants. But, desalination technologies used in the Arabian Gulf are mostly based on distillation. For example, the 1,025 MW Ras Laffan B combined-cycle power plant in Qatar has a seawater desalination plant that will produce around 27,500 m<sup>3</sup> of drinking water per day. Water desalination technologies can be categorized on the basis of the energy used to run them, usually thermal or electric. The technologies utilizing thermal

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energy are known as the multi-stage flash, multipleeffect distillation and vapor compression (VC). The desalination technologies that use electric energy rely on a membrane system, such as RO and electro dialysis. There also are other technologies that rely on solar energy or combined electric and thermal energy.

Membrane distillation (MD) is an emerging technology for desalination [1]. MD differs from other membrane technologies in that the driving force for desalination is the difference in vapor pressure of water across the membrane, rather than total pressure. The membranes for MD are hydrophobic, which allows only water vapor (but not liquid water) to pass. Fig. 1 depicts the water intrusion prevention using a hydrophobic membrane.

The vapor pressure gradient is created by heating the source water, thereby elevating its vapor pressure. The major energy requirement is for low-grade thermal energy. The advantages of MD are:

- It produces high-quality distillate.
- Water can be distilled at relatively low temperatures (0–100°C).
- Low-grade heat (solar, industrial waste heat, or desalination waste heat) may be used.
- The water does not require extensive pretreatment as in pressure-based membrane treatment.

Moreover, the Qatari economy is based on its massive hydrocarbon industry. In such industries water is routinely used in a number of applications in the form of process or cooling water. In a number of cases the water used can be seawater but with certain restrictions due to corrosion, fouling and water composition, large volumes of fresh water are required around the chemical plants. As mentioned above, low-grade heat can be utilized to produce water via MD [2]. One such source of low-grade heat is industrial waste heat. It is well known that many processes produce large amounts of excess heat—i.e. heat beyond what can be



Fig. 1. Mechanism for preventing water flowing in a hydrophobic membrane.

efficiently used in the process. The strategy of how to recover this heat depends in part on the temperature of the waste heat gases and the economics involved. Industrial waste heat recovery methods attempt to extract some of the energy as work that otherwise would be wasted. Typical methods of recovering heat in industrial applications include direct heat recovery to the process itself, economizers, regenerators, and waste heat boilers. In many applications-especially those with low-temperature waste heat streams, such as automotive applications-the economic benefits of waste heat recovery do not justify the cost of the recovery systems. This opens the door for the possibility of using this heat to preheat the water as part of the MD process which requires the water to be at a temperature of about 50-80°C. This has the potential of offering an efficient and cost-effective heat recovery method applicable to waste streams from which heat cannot be recovered easily with conventional methods. The utilization of this waste heat and the production of process water in the Qatari industry will have a dual benefit of reducing the amount of water imported which inevitably will contribute to cost and greenhouse gas reduction [3].

The main aim is to investigate the feasibility of utilizing industrial waste heat to produce quality fresh water by MD by applying heat integration and waste heat techniques to assess the forms of waste heat and feasibility of heat recovery for some Qatar-based industries that can be used as a case study. These processes included the liquified natural gas (LNG), Ethylene, and Vinyl Chloride Monomer (VCM).

#### 2. Heat integration and waste heat recovery

Heat is one of the most important forms of energy in any process and the percentage of its need in the chemical plants is high especially in fired furnaces and all types of steam. Heat integration has become one of the main issues in process synthesis as it allows considerable energy savings in process industry, particularly in the production of bulk chemicals from natural gas [4].

Many processes, especially in industrial applications produce large amounts of excess heat and this surplus heat could be reused in order to increase the energy efficiency of industrial processes and thus improve economics. It is important to know that, the quantity of heat is not as essential as its quality. The following shows some sources of waste heat recovery and their quality.

Source	Quality
Heat in flue gases	The higher the temperature, the greater the potential value for heat recovery
Heat losses in providing chilled water or in the disposal of chilled water	High grade: if it can be utilized to reduce demand for refrigeration Low grade: if refrigeration unit used as a form of heat pump
Heat in gaseous and liquid effluents leaving process	Poor if heavily contaminated

Heat integration is the state-of-the-art technique for design of energy-efficient processing plants. It is used to compute the minimum utilities consumption for a process based on the thermal data of process streams like, the temperatures and heat duties in the process. This analysis creates the Grand Composite Curve of the process which represents the net deficit or surplus of heat in the process as a function of temperature. Additionally, the Pinch Point is defined as the temperature where the net deficit or surplus is zero. The main objective of pinch analysis is to achieve the minimum requirement of external energy by applying the heat integration and the following represents the basic steps for pinch analysis. This is applied from to process to process. However, for potential application to MD additional criteria were considered, namely the temperature range within the definition of "low grade" heat of streams that need cooling and minimal "interference" with the process. After applying these criteria, the LNG and Ethylene processes were eliminated from further consideration. Only the VCM process was considered further owing to its broad range of temperatures in the process side as well as utility side.

#### 3. The industrial case study: the VCM process

The availability and the relatively low cost of natural gas and ethylene feedstock in Qatar makes VCM plant a competitive world class plant. VCM has gained worldwide importance because it produces primarily polyvinyl chloride (PVC) which is then used to manufacture a number of industrial and consumer products. The special properties of PVC made it a significant industrial chemical. The production of VCM involves the following processing sections:

- (1) Direct chlorination
- (2) Oxychlorination
- (3) EDC cracking
- (4) EDC purifications
- (5) VCM purification

The process is based on the "balanced" VCM process as the dichloethane intermediate is produced in the direct chlorination as well as from oxychlorination section that utilizes the Dichloroethane (EDC) cracking by-product hydrochlorine acid HCl. It comprises three reaction sections, a purification section for the intermediate EDC and a purification section for VCM (Fig. 2).

#### 4. Results and discussion

#### 4.1. The heat audit in the VCM plant

In this investigation the VCM process plant (with a hypothetical production rate of 600,000 Metric ton/ yr) has been audited for heat integration and waste heat recovery given the constraints for MD (the temperature of low-grade heat must be less than around 200°C and the brine temperature must be heated to 60–80°C). The process considered had heat integration studies carried out and its material and energy



Fig. 2. A simplified block diagram for the production of VCM.



Fig. 3. Grand composite curve for the VCM process.

balance established. The task then consisted of auditing the vast amount of information available. First, the concept of "cooling" curve was considered for the process. This is simply the temperature of the process streams from the front end of the process down to the product storage.

In order to exploit the process cooling curve (which has all streams that also include phase change streams), the heat integration composite curves is used to identify and eliminate the single-phase streams from the cooling curve, leaving phase change streams and "unmatched" hot streams. These would be more suited for MD application in preheating the feed brine. It was found that the VCM process displayed a broad range of temperatures in its cooling curve.

The composite curves for hot and cold stream for the VCM process are given in Fig. 3. It shows streams with no phase change and therefore can be utilized within the process itself. This will not be suitable for low-grade heat recovery in MD applications. It is therefore advisable to target streams not used in heat integration, namely streams with PHASE CHANGE as indicated above. An inspection of the energy balance in the VCM process indicates that some enthalpy can be in the vapor phase EDC stream produced in the direct chlorination reactor (EDC flow rate in this stream is 60,710 kg/hr, EDC latent heat of evaporation is 3,200 kJ/kg). In the actual process, EDC vapor is condensed over the temperature range 118-46°C. An air cooler is used in the process and the low-grade heat extracted to condense EDC is actually wasted directly to the atmosphere.

# 4.2. Low-grade heat utilization for MD application to produce fresh water

In order to work on the VCM case study, work on the MD feed was carried out. This consisted of extracting physical properties that will be used in the simplified MD model which in turn will provide an indication of how much fresh water potentially can be produced from the VCM waste heat in stream (EDC vapor to be condensed). The choice of the MD feed was shortlisted to seawater or brine (possibly reject brine from a desalination plant).

MD can be likened to a counter-current flow heat exchanger divided by a computational grid. There will be a hot fluid and a cold fluid flowing through the grid. The terminal temperature differences may be stated as:

$$\Delta T_{\rm A} = T_{\rm h,0} - T_{\rm c,0}$$

$$\Delta T_{\rm B} = T_{\rm h,n} - T_{\rm c,N}$$

where  $T_{h,0}$  is hot inlet temperature and  $T_{c,0}$  is cold inlet temperature; and  $T_{h,n}$  is hot outflow temperature and  $T_{c,N}$  is the cold outflow temperature.

Fig. 4 shows the grid flow pattern between the hot and cold streams and the heat balance control volume used in modeling MD units with a flat sheet membrane.

The work of Morrow et al. [4] constitutes a good reference for the model building. Starting with the diagram in Fig. 1 a mass and heat balance can be



Fig. 4. Heat balance control volume in MD modeling.

established over the gridded membrane system. The mass flux of fresh water produced will be obtained from the following equation:

$$m = AK(P_{\rm vh} - P_{\rm vc})$$

where *m* is the flux, *A* is the total area of the membrane,  $P_{vh}$  is the vapor pressure of water on the hot side, and  $P_{vc}$  is the vapor pressure of water in the cold side. *K* is a proportionality factor that represents the system, namely the membrane morphology and condition on both sides of the membrane. *K* may be assumed to be constant if the membrane is reasonably uniform in structure.

 $P_{\rm vh}$  and  $P_{\rm vc}$  must be calculated at average temperatures in the membrane computational grid. The heat transferred per unit area from the hot stream of the membrane to the cold stream of the membrane is given by the equation:

$$Q = U(T_{\rm h} - T_{\rm c})$$

where  $T_{\rm h}$  and  $T_{\rm c}$  are average temperatures of the hot and cold streams on either side of the membrane. *U* is the overall heat transfer coefficient represented by the well-known equation:

$U = \left[ \begin{array}{c} \\ \\ \end{array} \right]$	[ 1 ]	
	$\left[\frac{\frac{1}{h_{\rm h}} + \frac{t_{\rm m}}{k_{\rm m}} + \frac{1}{h_{\rm c}}}{\right]$	

where  $t_{\rm m}$  is the membrane thickness,  $k_{\rm m}$  is the thermal conductivity of the membrane,  $h_{\rm h}$  and  $h_{\rm c}$  are the convective heat transfer coefficients on the hot and cold sides respectively.

These coefficients can be estimated using traditional heat exchanger design correlations and dimensionless numbers.

In our case study, a hypothetical MD plant is designed next to the direct chlorination reactor of the VCM plant and its process flow diagram is shown in Fig. 5.

In the design of the MD plant, realistic conditions as well as actual process conditions from the VCM plant were used. Amongst the important conditions adopted were the stream temperatures for the feed and product of the MD plant shown as terminal temperatures in Fig. 6(a). Since it was assumed that our MD plant uses a direct contact membrane sheet, the cooling will have to be done by the fresh water product itself. In order to have realistic approach temperatures, the feed and reject brine were assigned 80 and 40°C. However, the  $\Delta T$  on the hot side may



Fig. 5. Proposed MD desalination plant using VCM generated low-grade heat.



Fig. 6. (a) Terminal temperature profiles around the MD unit; (b) terminal temperature profiles for the MD cooling circuit with seawater.

be on the high side and may put the cold side under strain to achieve this level of cooling. Perhaps a more appropriate outlet temperature for the hot side (brine would be 70°C giving a temperature approach of 10°C). But this may cause a temperature cross between the EDC and brine streams. On the other hand, the cold side of the membrane requires some fresh water product cooling. This is achieved by installing a seawater cooler taking into account the constraint put by the Ministry of Environment in the state of Qatar on seawater cooling, namely a 3°C  $\Delta T$ between inlet and outlet. Consequently, the terminal temperatures adopted in this case study are shown in Fig. 6(b).

### 5. Conclusions

This investigation highlighted the need to work on freshwater production using economic and environmentally friendly techniques. Indeed, this work showed that Qatar may face a shortage of fresh water in the future, without additional investment in desalination capacity. The idea of looking into alternative desalination technologies exploiting the availability of low-grade heat has been clearly demonstrated in our industrial case study, namely on the VCM process. Our approach using heat integration and waste heat recovery helped in eliminating unsuitable sources of heat in chemical processes using temperature and process interference criteria. The enthalpy of the EDC vapor produced in the direct chlorination in the EDC process seemed to be a satisfactory source of lowgrade heat since it is currently dissipated in the atmosphere using air coolers or seawater coolers. Our proposed MD (Fig. 1) plant complied with the requirements of preliminary design of such units in terms of process condition. Additional optimization would be required and the sizing of retrofitted equipment will be necessary for a proper costing of such facility.

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