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Methanol production FPSO plant concept using multiple microchannel unit operations

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Abstract

Remote, offshore gas reserves have long been a challenging deepwater petroleum resource to tap. Natural gas in many offshore regions is plentiful, but lacks access to the market because of the logistical challenges and costs. Most large offshore gas discoveries are capped, and gas associated with oil production is re-injected into the reservoir or is flared. A more attractive option is to convert the gas into a liquid product on a floating production, storage, and offloading (FPSO) vessel. However, some conventional process technologies are not well suited for operation on floating vessels that are highly space and weight constrained and may challenge vessel stability during inclement weather. Microchannel process technology units under development offer intensified processes that are suitable for offshore production of methanol from natural gas; thereby capitalizing on vast, untapped natural gas reserves. Microchannel process technology is typically applied to individual or a few unit operations, but rarely to an entire chemical plant – inclusive of multiple reactors, phase separation, and distillation for product purification – where each is a microchannel-based unit operation configured into a novel system.

Keywords: FPSO; Microchannel; Methanol synthesis; Distillation; Chemical Plant

1. Introduction

Methanol technologies for offshore applications must meet the requirements associated with operating in a marine environment. Primary challenges include accounting for motion from high-intensity waves, meeting constraints on space and weight, and minimizing freshwater consumption. The process intensification capabilities of microchannel devices are well documented in the literature, but their small channels also offer another distinct advantage for offshore operation—reduced sensitivity to motion. The reagent inventory in the microchannel devices is low and flow travels at high velocities, reducing the effect of external gravitational forces and making these devices more suitable for offshore operation. This includes using very short distillation towers to minimize the impact on flow hydrodynamics as a vessel sways.

In contrast to rural areas where traditional chemical plants are constructed, FPSO deck space is extremely limited and valuable. The process intensification possible in microchannel architecture allows smaller, lighter reactors to produce quantities of chemicals comparable to larger reactors. This means that commercially significant quantities of methanol can be produced on a ship's deck, which is far smaller than the footprint of a terrestrial plant. Another important consideration of offshore is the consumption of freshwater. Microchannel steam methane reforming (SMR) requires substantially less water than traditional SMR units because they can be operated with a lower steam to carbon ratio; thereby minimizing the water that must be desalinated for the methanol process. In addition, the use of a steam reformer to produce synthesis gas eliminates the need for oxygen, as required for partial oxidation or autothermal reforming. Again, this reduces the amount of valuable deck space for offshore applications.

2. Background

Today methanol production technology is supplied by three key players: Synetix (formerly ICI), Lurgi, and Mitsubishi Gas Company. Synetix has held a dominant position as a result of a simple, efficient process that has been incrementally improved over the years. However, new generations of production technology are nearing the market.

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Methanol technology is moving in two directions, both aimed at lower cost. One direction is exploiting increasingly large economies of scale to decrease operating costs. These include Lurgi's Mega-Methanol process and Foster Wheeler's Starchem Methanol process. The other direction is to target underutilized and therefore low-cost gas reserves offshore.

Two companies claim to be pursuing the low-cost feedstock strategy: Synetix, with its Leading Concept Methanol (LCM) process, and Heatric, with the printed circuit heat exchanger architecture for steam reforming and methanol synthesis [1]. The LCM process couples the Synetix Advanced Gas Heated Reformer and Low-Pressure Methanol process to synthesize methanol. Synetix (*Methanol Plant Technology Information Sheet*) describes its process as safe and practicable for offshore applications. The attributes of LCM that enable offshore use are that it is compact, resistant to motion, and self-contained. However, the LCM process requires an oxygen separation system unlike the multiple microchannel concept described presently.

Heatric's compact reforming technology simplifies control and operation, reduces size significantly, has cost advantages, and is close to being industrially proven. However, the cited capacity of the Heatric methanol plant is well below that of the presented study of the multiple microchannel plant.

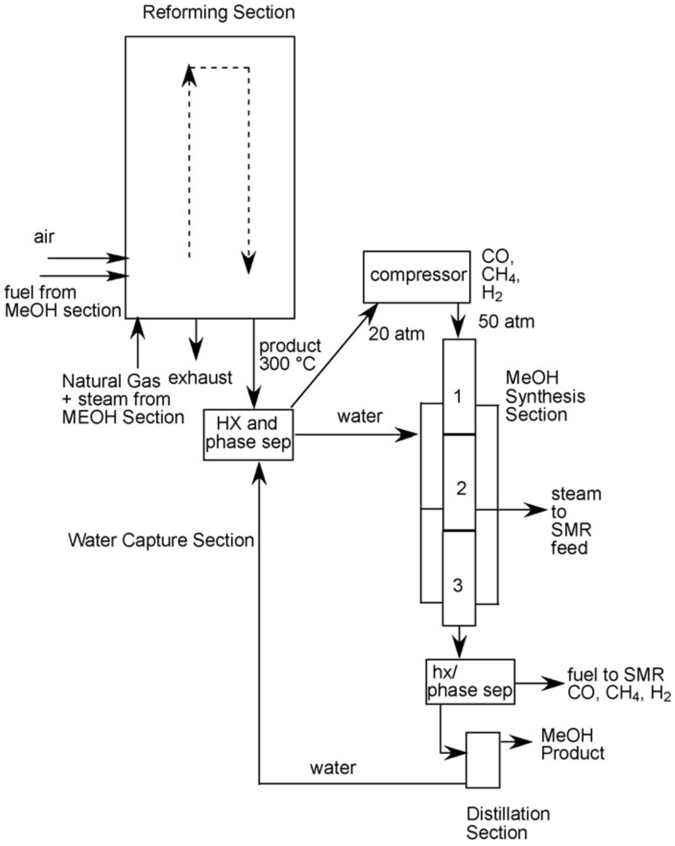

Fig. 1. Integrated methanol production flowsheet.

3. Microchannel plant based on multiple unit operations

A compact microchannel plant, suitable for installation on a FPSO, consists of multiple reactor and separation modules integrated to follow a novel flowsheet (Fig. 1) that eases its integration into an offshore environment. Its salient qualities for offshore use are (1) its compact hardware with a reduced number of discrete components to minimize deck space, (2) short distillation towers to accommodate for vessel sway, (3) minimal requirements for freshwater, and (4) competitive carbon efficiency and overall economics.

The plant is based on using natural gas and air to produce a liquid methanol product. Natural gas is converted to synthesis gas using steam reforming. Air is required for the integrated combustion of the methanol reactor tail gas to drive the endothermic methane reforming reaction. Water for the reformer is taken from the steam generated while removing the exothermic heat of reaction in the methanol synthesis section. Water from the reformer product effluent is captured and recycled along with the collected water from the distillation unit. Collection of water from the exhaust effluent is an option. Water capture and reuse minimizes the total amount of freshwater required. The total water fed to the SMR reactor section is 82 metric tonnes/h. Of this, only 48 metric tonnes/h are from freshwater because of the water capture and reuse within the system. If the water from exhaust was also captured, the total amount of freshwater required would be 28 metric tonnes/h—this represents a net reduction in the total water required of 65%.

After reforming, the dry product gas is compressed to 50 bar for the methanol synthesis reactor. The methanol synthesis reactor is exothermic and strongly equilibrium-limited. Conventional methanol synthesis reactors require a significant reactor recycle to achieve high overall carbon utilization. The microchannel plant concept provides a novel approach to heat integration that eliminates the recycle compressor and the associated deck space, energy requirements, and carbon utilization to drive the compressor. The methanol synthesis reactor uses an isopotential microchannel reactor [2] with only three isothermal reactor stages instead of a continuously dropping temperature profile in the reactor [2]. The first stage of the reactor operates at 250 °C, the second stage at 225 °C, and the final stage at 210 °C. The net conversion for a single pass through the three-stage reactor is 70.5%, which allows operation without a costly recycle compressor. A higher net conversion per pass would require lower temperature reactions and possibly more active catalysts to maintain modest reactor volumes.

Water is co-produced with the methanol and is subsequently removed from the methanol through a microchannel-based distillation module. Non-condensable gases are first separated from the mixture and distilled while remaining at the reaction pressure. Methanol is purified to greater than 95%, and the water is captured for reuse within the system. High-pressure distillation allows for a higher temperature separation and better use of waste heat within the process.

Water is recycled within the system for the steam-reforming reactor from three sources: from the synthesis gas stream after the SMR, from the methanol distillation unit, and optionally from the combustion exhaust stream. In all cases, the small amounts of alcohols, hydrocarbons, ethers, etc. in the water stream are readily reformed in the SMR and do not build up in

Table 1
Summary of mass flows and heat duties for all major unit operations

Section	Unit operation	Stream	Temperature (°C)	Pressure (bar)	Mass flow (kg/h)	Heat duty (MW)
Reforming section	Reformer	Air inlet	129	2.1	161,202	
		Fuel inlet	28	2.1	15,657	
		Exhaust	250	1	176,859	
		Feed (2:1 S:C) inlet	201	23.5	119,574	
		Product outlet	300	21.9	119,574	
		At reaction conditions	900	22	119,574	113
Methanol synthesis section	Reactor	Feed inlet	222	50	83,497	
		Product outlet	190	48.8	83,497	
		Water, section 1	250	40	114,497	29
		Water, section 2	225	27	19,216	5
		Water, section 3	200	22	17,415	4
		Subtotal water	103	35	151,127	38
Distillation section	Distillation unit (no. of stages = 20)	Feed inlet	30	48.5	47,222	
		Methanol outlet	200	48	43,860	
		Water outlet	242	49	1,330	
	Phase separation with HX	Inlet	30	48.5	83,497	
		Gas	30	48.5	36,275	
		Liquid	30	48.5	47,222	
		Overall duty in unit				25
Water capture section	Product HX and heat exchanger	Product in	300	21.9	119,573	
		Water inlet (from distillation)	96	25	36,564	
		Water outlet (to reactor)	188	24.7	36,564	
		Product out to compressor	198	21	119,573	
		Overall duty in unit				10

the system. Water capture in the microchannel hardware is based on the principle of capillary exclusion, where liquid water wets a small pore, making the available gas pressure for breakthrough less than the capillary pressure.

The heat and energy balance for a process simulation was completed using ChemCad Version 5.5.0. The overall system is designed to produce 1000 metric tonnes per day of methanol, with economics competitive with world-scale methanol plants. Table 1 details the flows and heat duties of the major unit operations.

The integrated plant would be a balance between assemblies containing multiple microchannel unit operations and conventional technology to globally optimize their carbon efficiency, plot size, and plant economics. Individual microchannel-based unit operations have been demonstrated, but a fully integrated plant has not yet been assembled.

3.1. Steam methane reforming module

Reforming natural gas in a microchannel reactor has been the subject of nearly 10 years of development, and the process is poised for an independent commercial-scale demonstration. Reforming natural gas involves premixing it with steam and feeding it at modest temperatures (around 250 °C) to the SMR assembly where flow is distributed in a piping network to multiple passively manifolded reactor blocks [3]. After feed distribution from a flange connection to an individual reactor block and then to many thousands of parallel microchannels, the feed stream is preheated in a recuperative microchannel heat exchanger that is integral to a high-temperature reaction channel. The heated feed is catalytically converted to synthesis gas at a temperature between 850 and 900 °C. The reforming catalyst is Rh/Mg-Al_2O_3 [4] and is washcoated on the microchannel walls. Heat is supplied by the catalytic combustion of a fuel stream with air. The noble metal combustion catalyst is also applied on the microchannel walls. The fuel contains natural gas, hydrogen, carbon monoxide, and all non-condensable combustible and non-combustible gases emitted from the methanol synthesis reactor outlet. No additional natural gas as a fuel is required. Air is carefully distributed into the fuel along the length of the reaction section to control the local hot spot and drive the catalytic combustion process [4]. Just as the synthesis gas product follows a U-bend in an adjacent channel to preheat the incoming reactant, the combustion air and fuel are similarly and separately preheated with the exiting exhaust stream to provide a high thermal efficiency.

The size of an experimental plant with 30 full-scale reactor blocks housed within six assemblies would be 3.9 m × 5.8 m × 3.9 m [4]. The complete system for this 1000-metric-tonne-per-day methanol plant, at the performance values of 18 W/cm^2 heat flux in the reforming reaction section and roughly 14 m^2 of area for reaction heat transfer per reactor, would require nine SMR assemblies of five reactors per assembly. Each assembly as integrated for an offshore methanol synthesis reaction system would be roughly 3.9 m (long) × 3.9 m (high) × 1 m (wide). Advanced designs are being developed to reduce the number of assemblies by more than a factor of 2.

3.2. Water capture section

To capture water synthesis, gas at 20 atm exits the SMR reactor and is cooled to 30 °C, where the condensed water is removed by capillary exclusion through a capillary capture structure. Following this step, a compressor boosts the synthesis gas pressure from 21 to 50 bar, upstream of the methanol synthesis reactor.

Capillary capture structures described in the literature have several physical forms [5–7]. Each have a similar attribute—a small pore radius that increases the capillary force for retaining water. The differential pressure of a gas is insufficient to overcome the capillary pressure of the liquid film as water is pulled from the system, as shown in Fig. 2 and in the following equation:

$$P_1 \leq P_2 + \frac{2\sigma}{r} \tag{1}$$

Water from the synthesis gas is removed at pressure and sent to a collection header for the water coolant stream of the methanol synthesis reactor. Water is also captured from the off-gas from the methanol synthesis reactor. Again, the separation is performed at pressure, where the condensed stream is sent to the water header for the methanol reactor coolant feed, and the non-condensed stream is sent to the microchannel distillation unit. Water from the exhaust stream may be collected.

For water capture from the exhaust stream, P_1 is roughly 103.1 kPa. The surface tension of water is 0.0728 N/m. A pore radius of roughly 25 μm would allow for a P_2 pressure as low as 101.4 kPa gauge. For water capture at pressure, a pore radius again of roughly 25 μm would allow for a differential pressure of roughly 5000 Pa to move the liquid to a liquid collection reservoir and pumping station.

The heat duty for the combined heat exchanger and phase separation unit after the methanol synthesis reactor is 25 MW. Using microchannel heat exchangers with embedded phase separation channels, the entire process is sized to fit within one assembly of roughly 1 m (wide) × 1.2 m (high) × 3.9 m (long). The heat duty for the product phase separation unit is 10 MW and is also sized to fit within one assembly of slightly smaller size.

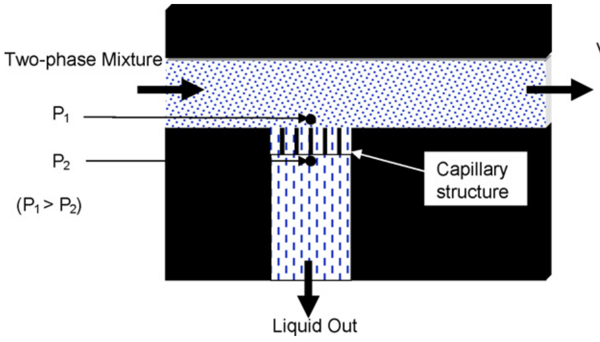

Fig. 2. Phase separation based on capillary exclusion using a capillary capture structure.

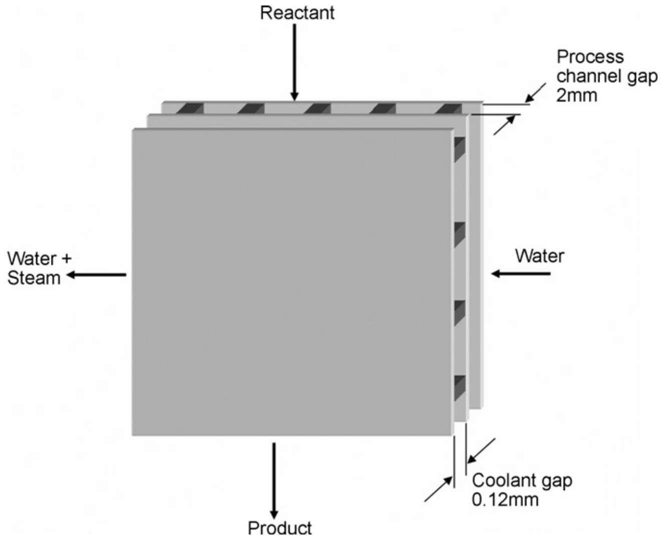

Fig. 3. Schematic of a microchannel methanol synthesis reactor: the process reaction channels contain a particulate catalyst and are cross flow to the partial boiling coolant channels.

3.3. Methanol synthesis reactor

An isopotential microchannel reactor is one way to achieve a high single-pass conversion for an equilibrium-limited reaction. The temperature is dropped as the reaction proceeds to increase the equilibrium potential for conversion. Tonkovich et al. [2] described a continuously dropping temperature profile along the reactor length. The current work proposes a three-stage series reactor constructed within a single reactor module to approximate the more optimized continuously changing temperature profile. The reactor volume and temperatures for three stages were optimized based on the kinetics of a commercial methanol synthesis catalyst [8] to minimize total reactor volume and contact time for the required inlet flowrate. The catalyst is packed in granular form within the open process channels shown in Fig. 3. Contact time is defined by the total reactor volume inclusive of a particulate form catalyst divided by the total volumetric flowrate of reactants at standard conditions. The resulting minimized contact time of 750 ms gives a total CO conversion of 70.5% in the three-stage reactor. Heat from the exothermic reaction generates steam in microchannels adjacent and cross flow to the process channels, as shown in Fig. 3.

Temperature control for a continuously changing temperature profile with a boiling fluid represents significant challenges. A practical alternative is to divide the reactor into three zones, each with isothermal temperature control. Table 2 details the temperature and duty for each stage.

Table 2
Multi-stage methanol synthesis reactor

Zone	Temperature (°C)	Pressure (bar)	Relative volume (%)	Heat duty (MW)
1	250	40	20	29
2	225	27	30	5
3	210	20	50	4

The methanol synthesis microchannel reactor is based on a cross flow of process fluids and heat exchange fluids. Three distinct heat exchange zones are designed down the length of the reactor. The first heat exchange zone is 20% of the total reaction channel length, or 0.2 m of the 1-m length channel. The second heat exchange zone extends to the midpoint of the channel length. The third and final heat exchange zone extends from the midpoint to the channel end. The repeating unit geometry of the methanol synthesis reactor unit is shown in Fig. 3. The design increases the catalyst volume fraction of the reactor to greater than 70%. This high catalyst volume ratio offsets the longer reaction times for methanol synthesis as compared to SMR and generates a modest number of reactor assemblies. Based on these design dimensions, a total of 18 assemblies are required for 1000 metric tonnes per day methanol. Two sets of methanol synthesis assemblies would be stacked high and on top of each SMR assembly to limit deck space requirements for installation on a FPSO. Each methanol synthesis assembly is 1 m (wide) × 1.2 m (high) × 3.9 m long—identical to the size of the SMR assembly. The resulting stack height of three assemblies is less than 7 m.

3.4. Methanol distillation unit

The use of microchannel technology for distillation applications is rapidly emerging. Tegrotenhuis et al. [9] first described an acetone–water separation in 1999 with a height equivalent to a theoretical plate (HETP) of 0.22 in. and followed up with additional work [5]. Micro ChemTec in 2003 made a presentation [10] for a microchannel distillation concept with varying temperature profiles. Silva et al. [11] described the experimental results for a 15-stage microchannel distillation unit with an HETP for cyclohexane–hexane distillation of roughly 0.83 cm. Cypes [12] described a single-stage microdistillation unit in 2006.

Each of the published concepts was based on maintaining a thin liquid film in contact with a thin gas film to allow rapid transfer of mass between the two phases. The physical structure of the liquid film varies, but in all cases the liquid thickness was less than 500 μm. Published values of HETP range from 0.5 to 10 cm and are significantly less than a commercial distillation tower with an HETP in the range of 30–60 cm. The implications of a short HETP are profound for offshore applications. A tall tower is subject to vessel sway and is a significant cost barrier to implementation. With an HETP of 1 cm, a 20-stage separation unit for methanol distillation conveniently fits within a complete distillation assembly less than 1 m high.

The proposed methanol distillation unit is operated under pressure to improve thermal integration for the overall plant. The range of temperatures for the 48-bar distillation unit is from 200 to 242 °C. This compares to a distillation temperature range of 80–120 °C at ambient pressure. The distillation of methanol and water at either ambient or elevated pressure has not yet been demonstrated in a microchannel distillation unit, but has been scaled based on the principles described by Silva et al. [11].

The non-condensable gas stream is separated from the liquid before entering the center of the microchannel distillation unit against a counterflow of liquid and gas. Methanol is recovered from the top of the distillation unit with a purity greater than 95% after 20 stages, and water is recovered from the bottom of the unit with a purity greater than 99%. The water is recycled to the coolant of the methanol synthesis reactor before moving to the SMR feed stream.

The work presented by Silva et al. [11] allowed for scaling a microchannel distillation unit for other applications. While the goal of their development efforts is a commercial-scale ethane–ethylene fractionator, the first proof-of-principle demonstration was the separation of hexane–cyclohexane. The liquid inlet contained 84% hexane and 16% cyclohexane, while the vapor inlet at the opposite end of the 5-in. microchannel was 9% hexane and 91% cyclohexane. The outlet gas stream was removed at a point slightly higher than the liquid inlet within the single-channel device and contained 80% hexane and 20% cyclohexane. The outlet liquid product stream was removed at a point slightly below the inlet vapor stream and contained 7% hexane and 93% cyclohexane. The channel generated 15 equilibrium stages in a 5-in. channel length. The temperature range over the unit varied from 69 to 83 °C.

The estimation of HETP as shown in Eq. (2) is based on balancing the convection time and diffusion time within a laminar flow microchannel. The characteristic time for convection in a single stage is defined by the stage length divided by the average fluid velocity. The characteristic time for diffusion in a single stage is defined by the square of the diffusion distance divided by the fluid diffusivity. Setting the two characteristic times equal allows solving for a simple estimate of the required HETP for phase equilibration. Similar methodologies have proven successful for diffusion to catalytic walls in laminar flow chemical reactions, and by analogy were evaluated for distillation:

$$\frac{\mathrm{vel}_{\mathrm{vap}} t_{\mathrm{vap}}^2}{D_{\mathrm{AB}_{\mathrm{vap}}}} \propto \mathrm{HETP}_{\mathrm{vap}} = \mathrm{HETP}_{\mathrm{liq}} \propto \frac{\mathrm{vel}_{\mathrm{liq}} t_{\mathrm{film}}^2}{D_{\mathrm{AB}_{\mathrm{liq}}}} \qquad (2)$$

For the experiments described by Silva et al. [11] and conducted in a microchannel distillation device as shown in Fig. 4,

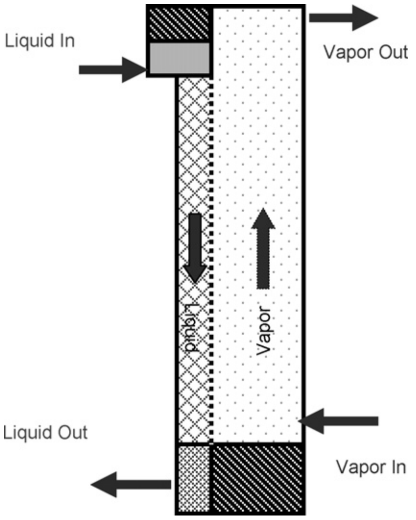

Fig. 4. Schematic of microchannel distillation unit.

a liquid film of 0.178 mm was created by flowing liquid over a woven stainless steel mesh adjacent to a 1.35-mm gas channel. The liquid velocity was 1 mm/s and the liquid diffusivity was 5×10^{-5} cm^2/s. The resulting predicted HETP for the liquid side was on the order of 0.63 cm, using Eq. (2). The gas phase diffusivity was 0.0342 cm^2/s, the average gas velocity was 0.015 m/s, and the gaseous channel gap was 1.35 mm. The resulting predicted gas phase HETP was 0.8 cm. It was somewhat surprising that the predicted HETP in the gas phase was higher than the liquid phase, which demonstrates the importance of balancing the channel design for both fluids. Based on the change in composition, the experimental HETP was calculated at 0.83 cm. Additional experiments performed at higher velocities confirmed that the HETP was roughly inversely proportional to velocity. This is remarkable agreement for an approximate prediction of HETP and is considered a good qualitative predictor of HETP in other microchannel distillation units.

An HETP of 1 cm is projected for the methanol distillation unit based on the separation principles where HETP for a thin liquid film in contact with a thin gaseous film is approximated by Eq. (2). For a film thickness of 25 μm and a velocity of 0.015 m/s, the HETP approaches 1 cm. The gaseous channel has a predicted HETP less than 0.1 cm by maintaining a gas-to-liquid channel gap ratio less than 10. By doing so, the square of the diffusion distance in the gas channel is more than offset by the three orders of magnitude reduction in the gas phase diffusivity over that in the liquid phase.

The methanol distillation unit uses six microchannel assemblies, where each assembly is 1.2 m (high) × 1 m (wide) × 3.9 m (long).

4. Carbon efficiency

The overall carbon efficiency from natural gas to methanol is slightly more than 56%. This carbon efficiency is competitive with other offshore stranded gas upgrading schemes for methanol, but lower than a conventional onshore methanol plant. The lower efficiency is a trade-off for a reduced footprint and minimized plant complexity for offshore production. Improvements in the overall carbon efficiency will primarily come from improved conversion efficiency from the methanol synthesis unit. Work is underway to develop compact hardware with a carbon efficiency greater than 65%.

5. Offshore plant results

A plot plan for an integrated methanol production unit of 1000 metric tonness per day has been designed to fit within an 18 m × 15 m deck, as shown in Fig. 5. Each of the nine SMR assemblies has two methanol synthesis assemblies stacked on top for a total height of less than 7 m. The deck size for each set of one SMR and two methanol reactor assemblies stacked on top of each other is 3.9 m × 1 m × 6.3 m high. The nine assembly stacks fit across 18 m of deck space, where roughly 1 m is allowed between assembly stacks for maintenance access.

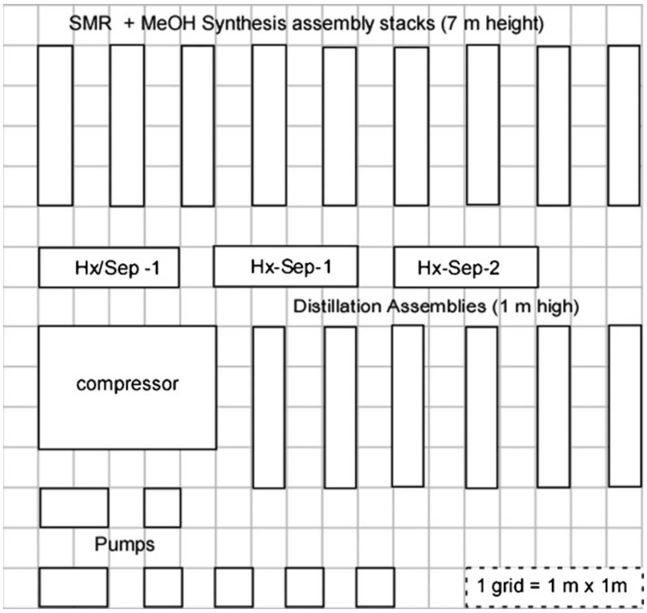

Fig. 5. Deck layout for 1000 metric tonnes per day offshore methanol synthesis plant.

The set of six distillation assemblies requires an approximately 3.9 m × 12 m footprint and is roughly 1 m high. Again, 1 m of deck space is allowed between distillation assemblies for maintenance access. The resulting combination of microchannel units and conventional equipment easily fits within an 18 m × 15 m deck footprint.

6. Conclusion

Microchannel process technology has many advantages over conventional reforming, methanol synthesis, and distillation technologies. These advantages will allow smaller, less expensive equipment to produce commercially significant quantities of methanol on FPSOs. The integration of microchannel technology into multiple unit operations within a chemical plant allow for greater plant flowsheet optimization and size reduction.

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