Offshore amine unit optimisation

Robert B. Fedich and Amalia Pantazidis, ExxonMobil Catalysts and Licensing LLC, USA, outline the benefits of a flexible initial process design for an amine unit on an offshore platform.

When an offshore gas platform was designed more than 20 years ago, the engineers knew they had to face many challenges due to its location in about 300 ft of water and the inclement weather conditions in the Central North Sea. The reservoir itself is about 15 000 ft below the sea bed and is a high temperature, high pressure reservoir. A gas treating technology was required to produce export gas offshore which would meet sales gas quality specifications.

This is a joint venture license holder. Design gas production was less than 500 million standard ft^3/d and condensate production was less than 100 000 bpd. The gas export pipeline is a shared pipeline that requires both a low temperature separator and an amine plant to be installed on the offshore platform. The original sweetening duty of the amine plant is to remove hydrogen sulfide (H_2S) from about 53 vppm to less than 1 vppm, while simultaneously controlling the export carbon dioxide (CO_2) content in the sales gas within a limited range. The H_2S specification of less than 1 vppm is very low compared to the typical range of 3 – 4 vppm, depending upon the region. The Wobbe index (heating value) of the export gas must be tightly controlled. The CO_2 must be removed in the amine unit, designed for 3.4 mol% in the feed gas to 1.7 mol% in the treated gas. All of these requirements lead to a very demanding duty of the amine plant, complicated by the fact that the amine plant will be installed in an offshore environment.

The contractor solicited bids from major amine licensors to ensure the final selection of an amine-based solvent was the correct solution for the platform. The final decision was based on life cycle costs and minimisation of platform footprint and weight. ExxonMobil's FLEXSORB SE™ technology offered the lowest circulation rate of all the proposals including the methyl diethanolamine (MDEA) bids. The lower circulation rate results in smaller regeneration facilities and lower energy consumption, as well as a smaller footprint and less weight, which is very important for an offshore platform. The proprietary process utilises a severely hindered amine, offering high selectivity for H_2S removal.

In aqueous amino alcohols, steric hindrance is the dominant factor, resulting in high thermodynamic capacity for acid gases and slower CO_2 reaction rate. The FLEXSORB SE amine has a high basicity (high pKa), resulting in high absorption capacity for acid gases. The high mass transfer rates and high rich loadings allows FLEXSORB SE to achieve the required H_2S specification in a shorter contact time and lower circulation rate than MDEA.[1] Because the mass transfer required for the H_2S removal is so low, additional mass transfer area is added to reliably meet the requirement of the controlled CO_2 in the treated gas. The lower circulation rate and higher rich loadings results in reduced hydrocarbon absorption compared to MDEA.

To achieve the highest selectivity, the more basic the amine, the faster it will react with acid gases. Primary and secondary amines (MEA, DEA, etc.) are more basic and have fast reaction rates. Tertiary amines (MDEA) are less basic and have slower reaction rates. If the amine forms a stable carbamate, it loses capacity (CO_2 consumes two molecules of amine). Primary and most secondary amines (MEA, DEA, etc.) form stable carbamates. Hindered and tertiary amines do not form stable carbamates. Decreasing the CO_2 reactivity reduces the amount of CO_2 picked up, thereby increasing the capacity. Primary and secondary amines react quickly with CO_2 and are non-selective.

Changing the amine structure can change the chemistry. The structures of a tertiary and a hindered amine are given in Figure 1. Hindered amines are formed by placing a bulky substituent group close to the amino nitrogen site to lower the stability of the carbamate ion. This bulky group provides the steric hindrance to the CO_2 molecule and lowers the CO_2 reaction rate. Severely hindered amines (FLEXSORB SE) have

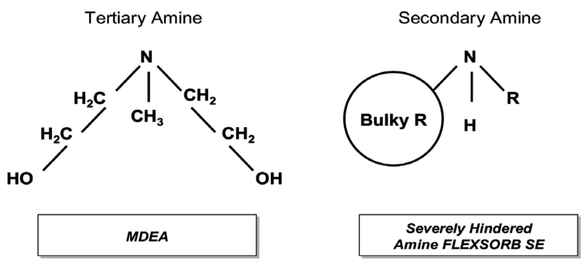

Figure 1. Structure of a tertiary and a hindered amine.

better selectivity for H_2S over CO_2 compared to conventional MDEA.

Steric hindrance reduces carbamate formation. The steric hindrance of the nitrogen atom is the primary factor in H_2S selectivity over CO_2 reaction with the amine. The severe steric hindrance of the amino group is the dominant factor in providing high thermodynamic capacity for H_2S, and slower CO_2 reaction rate.

In order to capture the maximum processing flexibility, the team developed a range of feed compositions. There were 120 possible feed gas compositions to the amine unit, as it was initially fed from five separate wells (either individually or in any combination, depending on the onshore demands). It was also recognised that the production facilities could be used as a future processing centre for other fields in the area. This flexibility was achieved using multiple packed beds with a number of lean amine feed points to the absorber tower. The amine plant was designed for a gas turndown to 30% of the full design and a liquid turndown to 20% of the full design. The ExxonMobil team provided a complete operating envelope and philosophy to guide the operations. The appropriate lean amine injection location and lean amine circulation rate was defined to achieve the treating objectives covering the range of the original five wells. The operator engaged ExxonMobil throughout all project phases including operator training courses, the hazard and operability study (HAZOP), degreasing operations, and tower internal inspections, as well as operating envelopes and operating philosophy documents.

The platform was asked to treat gases from other fields in the area. If the amine feed gas was significantly different from the operating envelope created, the operator contacted ExxonMobil as the technology licensor to offer new recommendations for amine strength, amine flow rate, reboiler duty, and other key operating parameters. ExxonMobil has a kinetic model, rather than a theoretical stage or HETP model, for carrying out FLEXSORB SE amine treating simulations. This model uses the actual feet and type of packing, and tower diameter, to develop the treated gas composition for a specified amine flow rate.

The latest gas nomination for treatment posed several new challenges. The first proposal was to treat the native gas and the new nomination gas to meet a lower export gas specification of less than 2 mol% CO_2, with the CO_2 from the regenerator offgas being vented to the atmosphere. Due to CO_2 emission concerns offshore, slipping more CO_2 from the amine absorber into the export gas is now a requirement. The new CO_2 specification for the treated gas was 1.9 mol%, with this higher CO_2 export gas being sent via pipeline. This CO_2 specification should be achieved as close as possible to the target; it is not a maximum nor a minimum amount. The new H_2S treated gas specification was a maximum of 2 vppm, which is not to be exceeded.

A series of cases was provided with flow rates ranging from a turndown case to the 90% probability case. These gas rates are less than the original design and therefore will have a higher residence time in the absorber tower. The inlet CO_2 concentration varied from 3.4 mol% (less than the original design) to 4.2 mol% (higher than the original design).
The feed gas H_2S concentration was 50 vppm, which is very

similar to the original design. The information requested by the operations group included:

- Recommended lean amine concentration and flow rate.
- Temperature leaving the top of the absorber.
- Rich amine temperature leaving bottom of absorber.
- Rich/lean exchanger duty.
- Lean amine cooler duty.
- Regenerator reboiler duty.
- Overhead condenser duty.

The assessment of the items listed above should be at the limits of the installed equipment, plus any design margins provided in the original design for the flexibility discussed earlier.

Using simulation tools and benchmarking data from actual unit operations, ExxonMobil estimated that the FLEXSORB SE unit may be able to treat a feed gas flow rate of up to 44% of the original design rate at 4.2 mol% CO_2, or 75% of the original design rate at 3.43 mol% CO_2. The new CO_2 specification of 1.9 mol% should be achievable using the existing facilities utilising FLEXSORB SE with a few changes in operation.

Conclusion

The joint venture license holders made the decision to provide a flexible initial process design for the offshore platform. As a result, they have successfully monetised 20 years of reliable operations. The built-in flexibility demonstrated that the current FLEXSORB SE solvent can handle new gas nominations without a solvent changeover. This is important offshore in order to avoid potential environmental impacts. As the operators are already familiar with the current technology, no management of change is required.

The selective removal of H_2S over CO_2 with amine solvents is an important application area for gas treating, as illustrated with this project. Capacity, operational flexibility, reliability, and the ability to achieve treated gas specifications (emissions) at low energy consumption were all considered during the technology selection process. The sterically-hindered amine FLEXSORB SE solvent, with enhanced selectivity for H_2S, has been in commercial use for 39 years in high H_2S selectivity applications such as tail gas clean up (TGCU), acid gas enrichment (AGE), onshore/offshore natural gas treating, and FLEXICOKING™ Flexigas treating.

Table 1. Simulation results summary for offshore platform

Feed gas conditions	Design Case	Case A	Case B	Case C	Case D
Pressure (bara)	88.9	82.5	82.5	82.5	82.5
Temperature (°C)	49.6	45	45	45	45
Rate (million standard ft^3/d)	Base	0.75 x base	0.75 x base	0.12 x base	0.44 x base
H_2S composition (vppm)	53	50	50	50	50
CO_2 composition (mol%)	3.4	3.4	3.4	4.2	4.2
Contactor					
Diameter (mm)	3350	3350	3350	3350	3350
Number of packed beds in operation	2	1	1	1	1
Product conditions					
Pressure (bara)	88.8	82.4	82.4	82.4	82.4
Temperature (°C)	67.9	60.4	60.8	67.2	63.8
CO_2 rate (kgmol/hr)	379.6	308	308	49.4	179.8
H_2S composition (vppm)	< 1	< 2	< 2	< 2	< 2
CO_2 composition (mol%)	1.70	1.90	1.90	1.90	1.90
Lean solution conditions					
FLEXSORB SE (wt%)	50	50	55	50	50
Temperature (°C)	51.7	51.7	51.7	51.7	51.7
Lean solvent rate (m^3/hr @ 15.6°C)	Base	0.90 x base	0.86 x base	0.16 x base	0.67 x base
Rich solution conditions					
Temperature (°C)	53.5	56.4	56.3	58.8	61.5
Regenerator					
Reboiler pressure (bara)	1.7	2.1	2.1	2.1	2.1
Reboiler temperature (°C)	118.9	125.6	125.9	125.6	125.6
Reflux drum pressure (bara)	1.2	1.9	1.9	1.9	1.9
Acid gas temperature (°C)	35	40	40	40	40
Heat exchanger duties					
Rich/lean exchanger	Base	0.78 x base	0.74 x base	0.13 x base	0.53 x base
Lean cooler	Base	1.10 x base	1.02 x base	0.20 x base	0.98 x base
Regenerator reboiler	Base	1.11 x base	1.10 x base	0.24 x base	0.95 x base
Overhead condenser	Base	1.19 x base	1.08 x base	0.27 x base	1.07 x base

Reference

1. VAN SON K . J., CHLUDZINKSI, G. R., CHARLES, P.R., and LIDAL, H., 'Asgard B Process Selection for Hydrogen Sulfide Removal and Disposal,' Gas Processors Association, 78th Annual Convention, Nashville, Tennessee, US, (1 – 3 March 1999).