Biogas to biomethane

Chemical absorption is both technically and economically feasible for biogas upgrading under atmospheric conditions, thereby avoiding the need for compression

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In its final processed form, biogas is essentially methane, sometimes referred to as biomethane, produced by the anaerobic digestion of organic waste. As produced by digestion of biomass, however, the raw gas contains substantial concentrations of carbon dioxide (CO_2) as well as other gases such as hydrogen sulphide, mercaptans, and sundry other species. It is also water saturated.

One of the most common and accepted ways to upgrade biogas is by absorption of the CO_2 and sulphur compounds into alkaline solvents. As shown in **Figure 1**, with more than 100 upgrading plants, chemical absorption ranked third in IEA Bioenergy Task 37 member countries in 2019 behind water scrubbing and membranes.

However, new and better solvents are still sought in an effort to reduce the cost of CO_2 removal. The industry standard or benchmark is high strength (~30 wt%) MEA (monoethanolamine), but by no means does this produce the most advantageous economics. Given the biogas characteristics (such as high CO_2 concentration and low pressure), solvents with higher capacities are necessary. A whole host of solvents has been proposed with superior characteristics. For example, blends of promoted tertiary amine (Mitsubishi MH-1, Eastman AdapT 200-series) are commercially used cases in-point.

There are two main concerning factors with chemically reactive alkaline solvents in CO_2 removal:

❶ CO_2 reacts only slowly if the solvent lacks sufficient alkalinity

❷ If the solvent is sufficiently alkaline to achieve good absorption rates, it tends to require a lot of energy to reverse the CO_2-solvent reaction and to release the absorbed CO_2, to allow the solvent to be repeatedly reused in a closed-circuit process.

These can be viewed as competing characteristics of any alkaline solvent in this kind of application.

This article shows that chemical absorption is both technically and economically feasible for biogas upgrading. It also shows that:

• The process can operate under atmospheric conditions, thereby avoiding the need for compression

• If post-purification compression of the biomethane is necessary, it can be achieved with about 40% less gas volume than pre-purification, saving compression costs

• Chemical absorption is highly selective, and methane slip is below 0.1%. If absorption is performed under atmospheric conditions, methane slip is below 0.04%

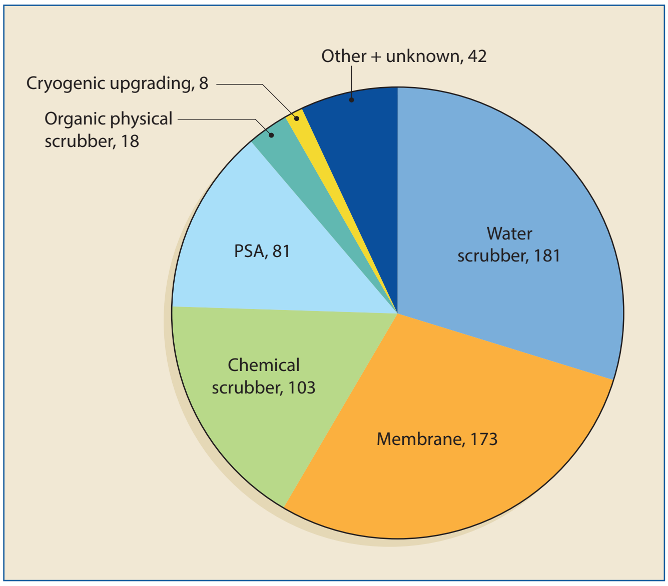

Figure 1 Upgrading plants in IEA Bioenergy Task 37 member countries in 2019[1]

• Methane losses appear to be directly proportional to the pre-flash pressure (flash following the absorber)

• For cases in which excess thermal energy is available, such as ethanol production from sugar cane, a chemical absorption process is very advantageous.

The process

There are a host of processing schemes using chemical solvents, some in actual use but many more proposed, for removing CO_2 and generally upgrading biogas to make it suitable for use as a fuel. But at the heart of them all is a packed absorber, a thermal regenerator, and assorted pots and pans, such as flash and level control drums, pumps, and flow control valves.

Figure 2 is a simplified schematic of the generic process. In general terms, the water-saturated biogas needs a certain amount of compression to overcome the pressure drop generated by the gas flowing through the packed column where CO_2 is absorbed. For this simulation study, on a dry basis, the raw gas is assumed to be 10 kNm^3/h of 60 mol% methane and 40 mol% water.

Following compression and cooling of the gas, a small amount of water condenses out and is removed via Stream 20. The block labelled “S” is a Solver that controls the calculations so that the solvent flow (Stream 24) is just enough

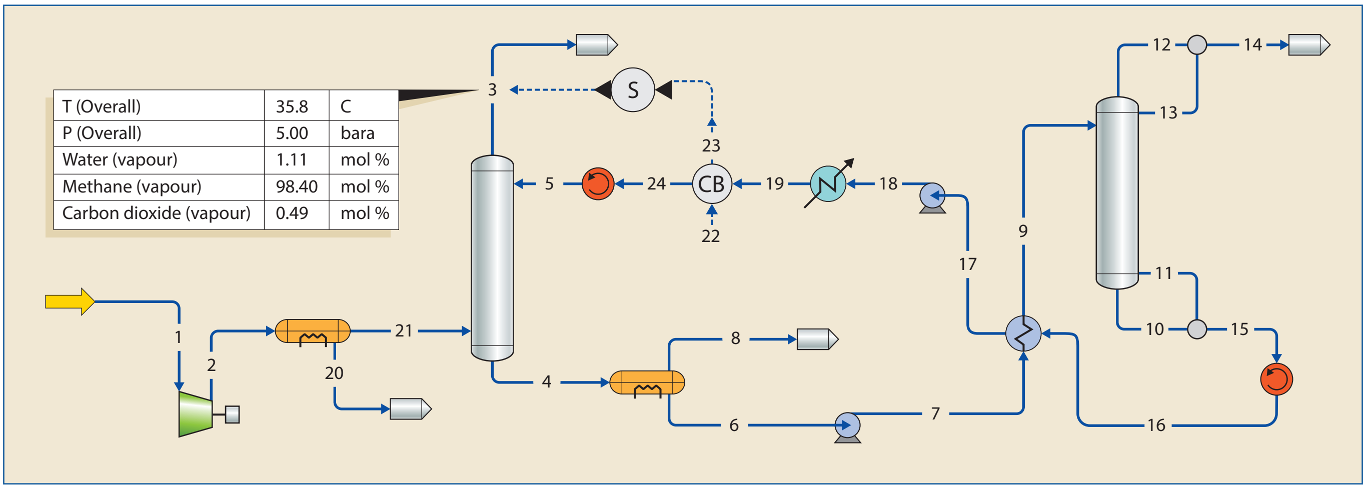

Figure 2 Schematic of biogas upgrading process

to upgrade the biogas to 0.5% ± 0.01% CO_2. Both absorber and regenerator contain Mellapak M250.X structured packing with bed heights of 8 m and 5 m, respectively.

In all simulations, the reboiler's molar boil-up ratio was held constant at 0.1 (ratio of molar vapour flow produced by the reboiler to molar flow of liquid withdrawn from it). The solvent is 35 wt% MDEA with 5 wt% piperazine, and its flow rate is whatever the Solver calculates is necessary to produce biomethane with 0.5 mol% CO_2 (water-saturated basis).

A CO_2 content of 0.5 mol% is not an especially stringent requirement for the performance of a piperazine-promoted solvent, so a very low lean solvent CO_2 loading is not needed to reach it.

Case study

In this discussion, we show the influence of pressure in the upgrading unit. With the fixed plant design as already described, the inlet gas and the flash pressures were varied, and the solvent flow rate was optimised to reach 0.5 vol% CO_2 in stream 3. All other parameters were kept constant.

The simulations were performed in ProTreat using the flowsheet shown in Figure 2.

A total of 16 cases were run where the sulphur-free biogas pressure ranged from 1.05 to 6 bar(a). After the absorber, the solvent was fed to a flash unit so soluble CO_2/CH_4 could be flashed out prior to the regeneration section. The pressure of the flash unit was also varied to see the effect on process performance. **Table 1** shows the varied operating parameters (such as gas and flash pressures) and the main results of the simulations for each case.

The solvent circulation rate, indicated by the liquid over gas ratio, decreases with increasing gas pressure independently of the flash pressure. This indicates that the size of the equipment could be reduced for plants operating pressurised. As shown in **Figure 3** Case 16 (about ambient pressure), the absorber is used at its full height, whereas in Case 1, about half of the absorber is not performing any separation (pinched in the upper half of the packing).

The specific reboiler duty (SRD), the ratio between the reboiler duty (MW) and the total mass flow of CO_2 removed (flash and stripper, kg/s), also decreases with the

Case	Gas pressure, bara	Flash pressure, bara	L/G, kg/kg	SRD, MJ/kgCO_2	CH_4 loss, %	CO_2 flash out, %
1	6	1.5	7.4	1.9	0.08	9.2
2	5	1.5	7.7	2.0	0.07	5.9
3	4	1.5	8.1	2.1	0.06	1.8
4	3	1.5	8.6	2.2	0.05	0.2
5	2	1.5	9.4	2.3	0.04	0.0
6	6	2	7.4	2.0	0.08	3.7
7	5	2	7.7	2.0	0.07	1.1
8	4	2	8.1	2.1	0.06	0.2
9	3	2	8.6	2.2	0.05	0.0
10	2	2	9.4	2.	0.04	0.0
11	6	3	7.4	2.0	0.08	0.3
12	5	3	7.7	2.0	0.07	0.1
13	4	3	8.1	2.1	0.06	0.0
14	3	3	8.6	2.2	0.05	0.0
15	2	2	9.4	2.3	0.04	0.0
16	1.05	1.05	11.2	2.8	0.02	0.0

Table 1 Simulation results

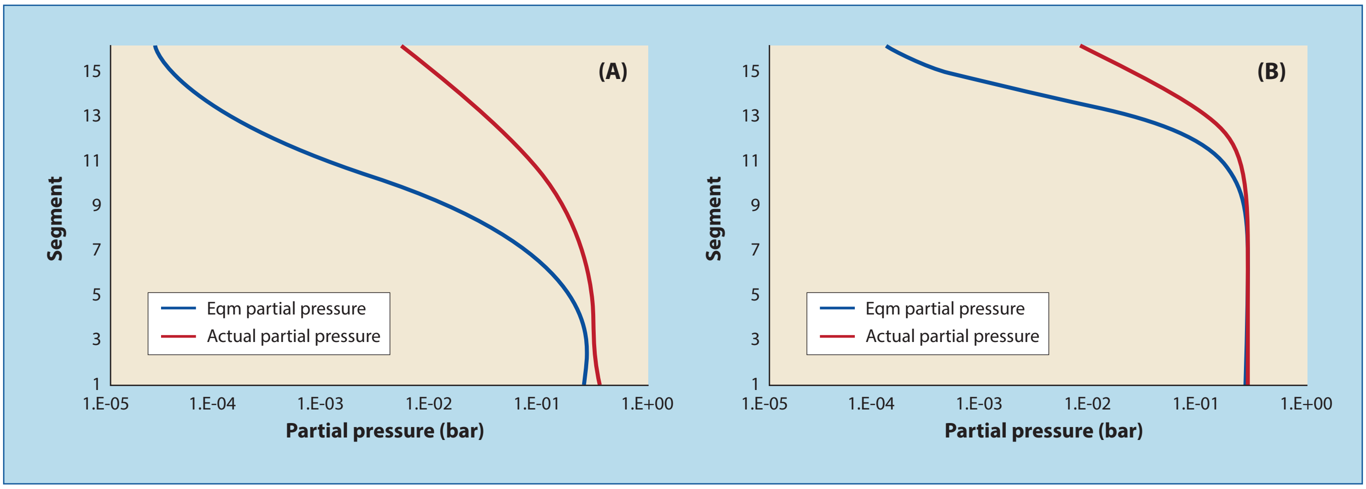

Figure 3 Actual and equilibrium partial pressures calculated with ProTreat for: (A) case 16; and (B) case 1

increase in the gas pressure, and it is almost independent of the flash pressure. However, the CH_4 loss increases almost linearly with the increase in pressure, as shown in **Figure 4**.

Nevertheless, methane loss is still negligible compared to other processes such as water scrubbing and membranes, which can show methane losses up to 20%.[2] If the upgrading plant is operated under atmospheric conditions, CH_4 loss is lower than 0.02%. This benefit is also enhanced by the fact that gas compression is avoided in the upgrading phase, and the final biomethane volume to be further compressed for transportation is reduced by about 40%, significantly saving compression costs.

Chemical absorption with amine-based solvents can be used for biogas upgrading. The process can take advantage of working at nearly ambient pressure and avoid compression costs. However, operations at elevated pressures can also be performed. The operating pressure depends on the chosen pretreatment (such as H_2S removal technology). When operating under pressure, the size of the upgrading unit can be reduced. In our example, for a process operating at 6 bar, the absorber and stripper columns could be reduced by almost half compared to operations under atmospheric conditions.

The design of biogas upgrading plants should be performed on a case-by-case basis. Plants where biogas pretreatment is done under atmospheric conditions require larger equipment while equipment size reduces as the operating pressure increases. Larger equipment, most likely, increases the Capex, while operating at elevated pressures increases the Opex. This trade-off should be evaluated, and the optimal plant should be designed to avoid oversized or undersized equipment.

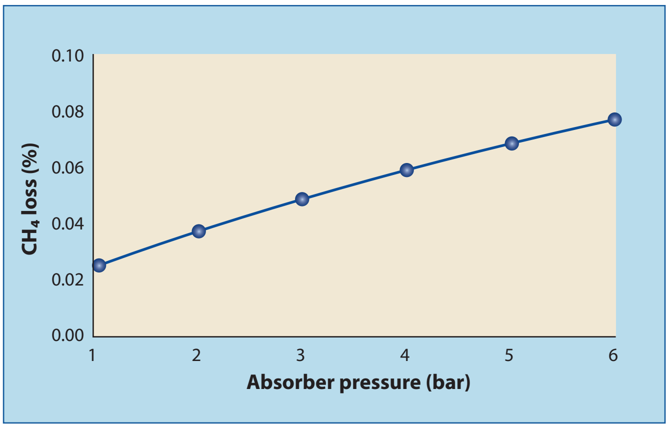

Figure 4 CH_4 loss variation with inlet gas pressure

Targeted CO_2 residual vs targeted CO_2 rejection

The challenge in conventional CO_2 removal operations is to reach sufficiently low CO_2 remaining in the treated gas to meet fairly stringent specifications. This requires sufficient solvent regeneration, so that absorber performance is controlled by events at the absorber's lean end. In other words, the absorber should be operated lean-end pinched.

The solvent flow rate needs to be high enough to eliminate the solvent capacity for CO_2 as a limiting factor. Exceptions tend to be piperazine-promoted MDEA-based solvents because piperazine is so highly reactive that even modest regeneration yields a solvent lean enough for the treated gas to meet (CO_2-residual) specifications even with a modest reboiler steam flow.

Figure 5 Case 16 shows the loading profile with high reboiler energy flow. Figure 5 Case 1 shows what happens when reboiler energy flow is low – the upper half of the regenerator enters into an idling state, and the CO_2 loading

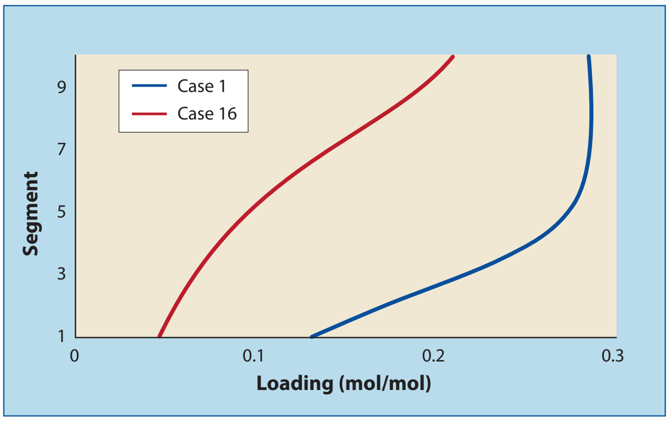

Figure 5 Lean solvent loading at stripper height for: (orange line) Case 16; and (blue line) Case 1. Calculations from ProTreat

of the regenerated solvent remains quite high (0.13 vs 0.05). This translates into an absorber CO_2 profile that is seriously rich-end pinched.

As a general observation, solvent regeneration adequate to achieving targeted CO_2 rejection can be had with quite low steam flow rates to the reboiler. This results in CO_2 removal by the absorber being controlled by a modestly loaded lean solvent flow rate rather than very lightly loaded lean solvent at a high flow rate.

When treating is to be measured in fractional CO_2 removal rather than final CO_2 concentration in the treated gas, the absorber is purposefully operated rich-end pinched by throttling back the solvent flow and using minimal regenerating steam (Case 1 conditions).

How one thinks about solvent flow and regeneration energy in limited CO_2 removal applications is inverted from how one meets stringent requirements in applications such as LNG production and ammonia synthesis gas. Low flow rates of highly loaded solvents also show opposite extremes in corrosivity from high flow rates of lightly loaded solvents.

Corrosion

ProTreat's acid gas corrosion model accounts for the effect of turbulence level (flow regime), temperature, acid gas loading, amine strength, surface roughness, and metallurgy on the expected corrosion rate. Measured corrosion rate data taken under commercial conditions have been correlated against turbulence parameters and corrosion kinetics, as well as piping metallurgy. Heavily-loaded, hot amine solvents turn out to be very corrosive, as are hot solvents that are lightly loaded, especially without enough sulphur content to mitigate against corrosion via passivation.

References

1 Upgrading plant list. Available at: http://task37.ieabioenergy.com/plant-list.html. Accessed on 16 June 2022.

2 Niesner J, Jecha D, Stehlik P, 2013, Biogas upgrading techniques: state of art review in European region, *Chemical Engineering Transactions*, 35, 517-522 DOI:10.3303/CET1335086

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