

- drying systems such as molecular sieves or silica gel are most commonly used.

Usually, no final drying is required when using glycol compounds as the absorbent in the scrubber column. In these systems, simultaneous absorption of humidity takes place.

### *Desulphurization*

Depending on the composition of the fresh substrate, raw biogas may contain hydrogen sulphide (H<sub>2</sub>S) in concentrations of <100 mg/m<sup>3</sup> up to 10,000 mg/m<sup>3</sup> – in exceptional cases up to 30,000 mg/m<sup>3</sup>. During oxidation (burning) sulphurous acid can be formed. To avoid corrosion effects in plant components and to ensure the quality requirements for grid injection or use as vehicle fuel, desulphurization is required. Basically, two steps of desulphurization can be differentiated – primary and precision desulphurization; the first reduces the H<sub>2</sub>S level to <500 ppm (mostly down to ~100ppm) while the second is for fine tuning according to the specifications of the upgrading plant and/or the requirements for gas utilization or grid injection. Furthermore, desulphurization methods can be also divided into internal/external methods (inside or outside of the digester) with or without addition of oxygen.

For primary desulphurization in agricultural biogas plants without biogas upgrading, the internal method is used as a standard application and involves dosing of air into the gas space of the digester. The H<sub>2</sub>S is then biologically oxidized to elementary sulphur. The main advantage of this sulphur reduction step is that it is a very cheap technique because only air and a simple membrane pump combined with a flow meter are needed. At the same time, this economic advantage becomes the main disadvantage because N<sub>2</sub> is inert and does not react in the gas flow. As a consequence of this, N<sub>2</sub> is accumulated in the raw gas. Because most upgrading technologies are not able to separate N<sub>2</sub> it will be found in nearly the same amounts but in higher concentrations in the biomethane. Air addition for desulphurization is thus commonly not the method of choice before gas upgrading. There are two exceptions, as follows:

- If biomethane is injected into natural gas grids with low heating values (L-gas grids), it will be necessary to decrease the CH<sub>4</sub> concentration, and respectively the heating value of the biomethane, by mixing with air. In that case it can be advantageous to apply this cost-efficient desulphurization method.
- If using pure oxygen instead of air for dosing into the raw gas flow, the above-described dilution effect by N<sub>2</sub> does not occur. Pure oxygen can, for example, be provided directly at the plant by a small PSA system.

In both cases (using air or pure oxygen), added oxygen will be found in the gas flow after the biological desulphurization. This becomes an advantage if using an activated carbon filter for the subsequent precision desulphurization. Because this filter needs a small amount of oxygen for the catalytic oxidation of H<sub>2</sub>S, this oxygen can be provided automatically by the former dosing. To avoid the dilution effects with air or oxygen, the primary desulphurization techniques mostly applied when biogas is upgraded to biomethane are

- external biological H<sub>2</sub>S reduction with separated absorption/oxygenation steps
- combination of external biological H<sub>2</sub>S reduction with a basic scrubber
- chemical precipitation using iron salts (sulphide precipitation)
- chemical precipitation using iron hydroxide.

For precision desulphurization, impregnated or doted activated carbon is normally used (catalytic oxidation and following adsorption).

Alternatively, chemisorption on iron oxide- or hydroxide-coated materials in an external column can be applied for precision desulphurization. Chemisorption using zinc oxide in external columns is basically also applicable, but currently not state-of-the-art for precision desulphurization of biogas.

The six most widespread technologies are

1. pressure swing adsorption,
  2. water scrubber,
  3. physical absorption (using organic solvents),
  4. chemical absorption (using organic solvents),
  5. high-pressure membrane separation and
  6. cryogenic upgrading.
- chemical precipitation using iron hydroxide.

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