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Biogas Upgrading Technologies: State of Art Review in European Region

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Upgrading biogas to high energy biomethane is commonly utilized to produce SNG (substitute natural gas used for injecting into grid) and/or CNG (compressed natural gas employed as a fuel in transportation). In this process the most crucial operation is a separation of CO_2 from biogas, which is carried out by technology based on unit operations like absorption or permeation. Aim of this text is to introduce state of art in development of these technologies within European region: assess their pros and cons in order to alleviate orientation in this issue and point out research tendencies. There were chosen three aspects for the assessment: (1) process-technology, (2) energy-economy and (3) environmental impact. The review is based on research of studies, reports and other informational sources that come from the work of some research institutions and engineering companies. From process-technology perspective specifications like methane purity and flow rate range were evaluated. Aspect regarding energy and economy is mainly focused on assessment of consistency of available data and on utilization of the data for comparative analysis of given technology. From environmental point of view there was considered an important specification called methane losses.
The review clearly suggests that in European region the highest share refers to water scrubbing technology which is followed by PSA method and chemical absorption. All kinds of absorption technology (water scrubbing, absorption with chemical or physical solvents) seem to be well established and conventional. On the other hand PSA method and especially membrane technology offer progressive research potential.

1. Introduction

There are several ways how to utilize biogas as a resource of energy. Application of biogas in a specific way of utilization depends on technical, economic and legislative factors which are moreover limited by locality and social demand. The utilization of biogas for biomethane production represents one of the thriftiest methods. However, share of biomethane in renewable resources market is still tiny. In European region Germany and Sweden are regarded at present as the main forerunners in terms of biomethane support. The actual amount of biomethane plants operating in Germany is around 90 and in Sweden 60. These numbers are several times higher than in any other country of European region (IEA, 2013).
The term biomethane is usually used for biogas upgraded to the level which is accepted for injecting into gas grid and/or for usage as a vehicle fuel. From that fact it is possible to call the upgrading process as a process of improving biogas up to the level of substitute natural gas (SNG) or compressed natural gas (CNG). The input refers to biogas originating from anaerobic digestion either in form of landfill gas or gas from controlled reactor. The quality of biomethane on the output side is set by directives issued by a government in cooperation with relevant organizations or keepers of pipelines (natural gas distributors). Ratio between SNG and CNG production is at present around 2:1 in European region. Around 2.5 % plants combine both types of productions (IEA, 2013).
The biogas that comes from anaerobic digestion is a mixture of two major components – methane (CH_4) and carbon dioxide (CO_2). In addition biogas consists of minor portions of other components like siloxanes or sulfane (H_2S). Presence and fraction of the impurities is variable and depends mainly on types of

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substrates. Any biomethane (biogas) plant can use various combinations of substrates. In European region at present the substrates like manure or energy crops are employed at almost 50 % of all biomethane plants. One quarter of all plants processes sewage sludge and around one third relates to sewage sludge treatment. The lowest number belongs to landfill gas that is processed at 4 % of all biomethane plants (IEA, 2013).

The following text is focused on review and evaluation of technologies related only to separation of CO_2 in biogas upgrading. The concept of this work is based on these aspects: (1) process-technology, (2) energy-economy and (3) environmental impact. The research was carried out by exploration of available literature in form of various research studies, reports, scientific and company articles. Some statistical figures were based on data gathered from (IEA, 2013).

2. Overview of biogas upgrading technologies

In the process of biogas upgrading into biomethane the separation of minor impurities (siloxanes, sulfane, etc.) and especially CO_2 is necessary and crucial operation. Methods primarily used for CO_2 separation are able to some extent remove also minor compounds but in some cases there are installed special pretreatment units for removal of minor compounds. Therefore configuration and presence of pretreatment operations derives from adopted method of CO_2 separation.

In industrial practice there are several methods for CO_2 separation based on these unit operations: (1) absorption (physical – purisol, selexol, rectisol, water scrubbing; chemical – MEA, DEA, MDEA solvents), (2) adsorption (PSA, TSA), (3) permeation (high pressure and low pressure membranes), (4) others (cryogenic and biological approach).

As for biomethane the most significant technologies in European region at present are: (1) water scrubbing (WATS), (2) pressure swing adsorption (PSA), (3) chemical scrubbing (CHEMS), (4) physical scrubbing (PHYS) and (5) membrane separation (MEMS). According to (IEA, 2013) there are more than 200 biomethane plants in European region. The most prevailing technology represents WATS, which is employed at almost 40 % of all biomethane plants. PSA and CHEMS have both around 25 % share. PHYS and MEM are the lowest employed technology with 6 % and 4 % share. All five significant technologies will be discussed in the following chapters.

3. Process-technological aspect

3.1 Water scrubbing

WATS represents process based on physical absorption employing water as a solvent for dissolving CO_2. The reason why absorption in water is employed is that solubility of CO_2 in water is many times higher than solubility of CH_4 in water.

Water scrubbing itself is processed usually in a packed absorption column. Biogas is introduced to the bottom of the column and flows up. Water enters the column at the top and flows downward, so that mass transfer occurs in a counter-flow way. Purified biogas (biomethane) leaves column at the top and water saturated with CO_2 is let out at the bottom. The scrubbed water stream is either regenerated in a desorption column and reused for absorption or scrubbed water is used only for once in a single pass system. CO_2 is released into atmosphere as an off-gas in case of water recirculation system or stays in water in case of a single pass system. The system without recirculation can be suitable for plants with low cost water (e.g. waste water treatment facility). Any CH_4 dissolved in water is captured and recycled in absorption column in order to alleviate methane losses.

WATS also enables to remove simultaneously H_2S, hence pretreatment for H_2S is not necessary. However, it is suitable to treat H_2S and also CO_2 after scrubbing (Beil and Hoffstede, 2010). The range of operating pressure is 6-12 bar (Beil and Hoffstede, 2010). De Hullu (2008) claims that maximum CH_4 yield is 94 %. Typical value of CH_4 purity is around 98 %. Data gained from (IEA, 2013) indicate that WATS is used for wide range of biogas flow rate, although the most preferred category belongs to higher flow rates of 500-2,000 Nm^3/h (see Figure 1).

3.2 Chemical scrubbing

CHEMS like WATS is based on dissolving CO_2 from biogas in a solvent. However, absorption is associated with chemical reaction (between CO_2 and solvent), so that process is called chemical absorption (chemical scrubbing). The most employed solvents are monoethanolamine (MEA), diethanolamine (DEA) or diglycolamine (DEA), which in comparison to water can dissolve considerably much more CO_2 per unit volume.

Technological arrangement of CHEMS is similar to WATS with regeneration. However, the regeneration of solvent is processed under significantly higher temperature and energy demand. So that comparison

between water and chemical scrubbing demands technical-economic analysis regarding solvent consumption, requirements for CH_4 recovery etc. (Gamba and Pellegrini, 2013). Pretreatment of H_2S is recommended (Beil and Hoffstede, 2010) and also by TUV, 2012).
Operating pressure is around 1 atm (Dirkse, 2009). De Hullu (2008) claims that maximum CH_4 yield is 90 %. Typical value of CH_4 purity is 99 %. Data gained from (IEA, 2013) indicate that CHEMS is used for wide range of biogas flow rate, although the most preferred category belongs to medium flow rates of 500 – 1,000 Nm^3/h (see Figure 1).

3.3 Physical scrubbing

PHYS is another variation of technology based on absorption process without chemical reaction. The most employed solvents are for instance selexol, rectisol and genosorb.
Technological arrangement of PHYS is similar to CHEMS. However, the regeneration of solvent is processed under higher temperature and energy demand than WATS but lower than CHEMS. Pretreatment of H_2S is not required (Beil and Hoffstede, 2010).
Operating pressure is 7 - 8 bar (Dirkse, 2009). De Hullu (2008) claims that maximum CH_4 yield is 90 %. Value of CH_4 purity is 93 - 98 %. Data gained from (IEA, 2013) indicate that PHYS is used primarily for category of higher flow rates (500-2,000 Nm^3/h; see Figure 1).

3.4 Pressure swing adsorption

PSA is based on adsorption. Adsorbent materials are able to selectively retain some compounds of a mixture by molecular size. Molecules of CO_2 have smaller size than molecules of CH_4, therefore in the case of biogas only the molecules of CO_2 are captured in a proper adsorbent material and hence separated from CH_4 molecules. Efficiency of adsorption process depends mainly on temperature, pressure and adsorbent. In the case of PSA the temperature is constant and pressure is variable. For commercial applications adsorbents like molecular sieves, zeolites and activated carbon are primarily employed (Grande, 2011).
Conventional PSA is processed in a string of adsorption columns (usually four) packed with adsorbents. Pressure changes in the columns cyclically. One cycle has usually four basic steps: pressure build-up, adsorption, depressurization and regeneration. CO_2 from raw biogas is captured in adsorbent and consequently as off-gas stream released into atmosphere. CH_4 leaves column in a biomethane stream. A bit novel innovation of classic PSA is rapid PSA, which performs cycles in quicker way. That enables to design smaller sized and easier maintained equipment (Electrigaz, 2008).
PSA also enables to remove N_2 and O_2. Since the adsorption of H_2S is hardly reversible (adsorbent is hardly regenerated), pretreatment is required (Beil and Hoffstede, 2010). However, as Pagliai and Felice (2012) shows the effectiveness of simultaneous H_2S and CO_2 capture depends on water content in biogas.
Range of operating pressure is 4 - 10 bar (Ryckebosch et al. , 2011). De Hullu (2008) claims that maximum CH_4 yield is 91 %. Typical value of CH_4 purity is 98 %. Data gained from (IEA, 2013) indicate that PSA is used for wide range of biogas flow rate except high flow rates above 2,000 Nm^3/h (see Figure 1).

3.5 Membrane separation

MEMS is based on selectivity of a membrane that allows different compounds pass through differently. As for biogas: the mixture is split into two streams, the permeate fraction (compounds transferring through the membrane) is represented mainly by CO_2 and the retentate fraction (compounds passing by) is mainly composed of CH_4. There are two types of membrane systems: (1) high pressure, which employs gas flow both in permeate and retentate and (2) low pressure, which employs gas on the retentate side and liquid on the permeate side. Membranes can be made of polymers like silicone rubber or cellulose acetate. Another group of materials comprise polyimide or liquid membranes. The most employed materials for commercial applications are hollow fibres (Ryckebosch et al., 2011).
Due to significant research in membrane development for biogas upgrading that has been done in recent years as Scholz et al. (2013) shows in a very comprehensive study, there are various findings on testing new materials and various membrane system configuration. On the whole there are usually multistage membrane systems, which can be accompanied by another technology like PSA. The appropriate pretreatment is required for any undesirable compound in biogas (Karaszova et al., 2012) and the depth of pretreatment depends on membrane material (Scholz et al., 2013).
Range of operating pressure is for high pressure systems 20-36 bar, for low pressure systems around 1 atm (Ryckebosch et al., 2011). De Hullu (2008) claims that maximum CH_4 yield is 78 %. Value of CH_4 purity is 90 - 97 %. Lower performance of membrane separation (CH_4 purity and recovery) is obtained in single stage systems. But multistage systems can achieve better performance results (CH_4 purity 99 %, recovery 99.5 %) and therefore they are mandatory (TUV, 2012). Data gained from (IEA, 2013) indicate

that MEMS is used for category of low and medium flow rates, especially less than 300 Nm^3/h (see Figure 1).

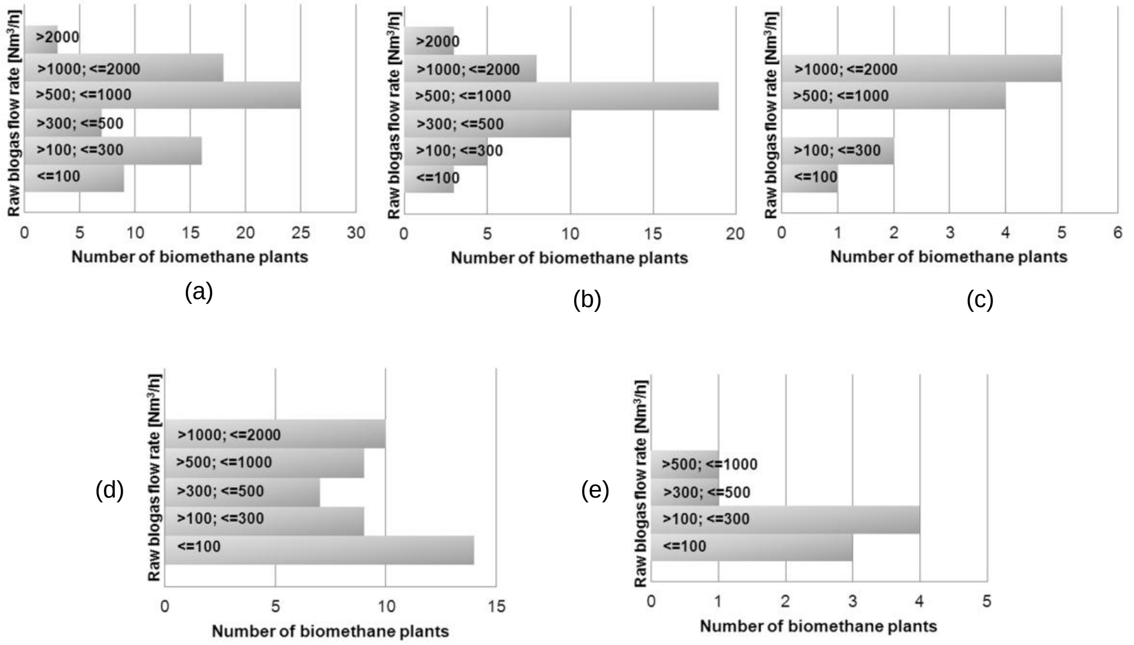

Figure 1: Range of flow rates: (a) WATS, (b) CHEMS, (c) PHYS, (d) PSA, (e) MEMS (data gathered from IEA (2013))

4. Energy-economy aspect

4.1 Energy

In order to compare energy performance there were gathered and examined available data related to energy requirements from five different sources coming from academic and industrial literature issued between 2006 - 2012. Data are summarized in Table 1.

Table 1: Comparison of energy performance of biogas upgrading technologies

Technology	Energy requirements [kWh/Nm^3]				
	TUV (2012)	Beil (2010)	(Electrigaz, 2008)	Gunther (2007)	Berndt (2006)
WATS	0.46	0.2	0.3	0.391	0.28
CHEMS	0.27	0.56	n/a	0.126	0.42
PHYS	0.49-0.67	0.43	0.67	0.511	0.32
PSA	0.46	0.24	0.27	0.285	0.21
MEMS	0.25-0.43	0.19	n/a	n/a	0.5

The well-established and foremost technologies – WATS and PSA – demonstrate both the most numerous and the most consistent data. In case of WATS data range from 0.2 to 0.46 kWh/Nm^3. Data for PSA are a bit more consistent and have range 0.21 - 0.46 kWh/Nm^3. Wider limits occur in CHEMS and PHYS – 0.126 - 0.56 kWh/Nm^3 and 0.32 - 0.67 kWh/Nm^3 – which is caused by excluding or including energy consumption for regeneration of solvent. The lowest amount and weak consistency relate to MEMS – 0.19-0.43 kWh/Nm^3.

Both CHEMS and PHYS can be regarded as the most demanding technologies. But inconsistency of CHEM, PHYS and also MEMS obviously refers to various technological layout (including or excluding regeneration and multistage systems). PSA, followed by WATS, appears to be the least demanding technology. However, the newest comparison in TUV (2012) presents energy requirements for all technologies as quite tight.

4.2 Economy

From the available economic performance data were picked basic general data relating to investment and operating costs. Data originate from three literature sources (see Table 2). In de Hullu (2008) there were carried out comparison of investment and operating costs for flow rate of 250 Nm^3/h. In Beil and Hoffstede (2010) there was carried out only operating costs comparison for flow rate of 1,000 Nm^3. From TUV (2012) there were chosen only data regarding operating costs comparison for flow rate of 250 Nm^3. The original absolute values were recalculated into the relative values in order to clearly suggest ratio of each technology. The reference technology is WATS.

The older sources as (de Hullu, 2008) evidently show that the lowest operational cost relate to WATS followed by MEMS, whereas PSA and CHEMS are the most demanding. The lowest investments costs belongs to WATS, the other technologies are sort of twice more expensive. On the other hand, the newest source (TUV, 2012) presents the economic performance of all technologies much even and tighter.

Table 2: Comparison of economic performance of biogas upgrading technologies

Technology	Economic performance [relative values]				
	250 Nm^3/h – TUV (2012)		1000 Nm^3/h - Beil (2010)	250 Nm^3/h - de Hullu (2008)	
	Investments	Operating cost	Operating cost	Investments	Operating cost
WATS	1	1	1	1	1
CHEMS	0.91	1.16	3.93	1.98	1.50
PHYS	0.91	0.99	2.60	n/a	n/a
PSA	0.98	0.98	3.73	1.83	1.56
MEMS	0.87	0.93	1.67	1.70	1.1

5. Environmental aspect

The most notable criterion for environmental impact of technology is methane losses that express portion of CH_4, which slips away from raw biogas due to upgrading method itself or due to problematic equipment. Besides lower profit, methane losses are significant because methane (as a greenhouse gas) is several times more harmful than CO_2.

Table 3 shows values of methane losses comparison gathered from four different literature sources. Berndt (2006) and Dirkse (2009) represent general limits guaranteed by producers which are considerable lower than values obtained from more independent source like Gunther (2007). On the whole the lowest methane losses are indicated for CHEMS and the highest one relates to MEMS. But the methane slip in MEMS depends on technological layout; so that the value is much more lower in case of multistage systems as TUV (2012) claims.

Table 3: Comparison of methane losses of biogas upgrading technologies

Technology	Methane losses [%]			
	TUV (2012)	Dirkse (2009)	Gunther (2007)	Berndt (2006)
WATS	2	<2	4.7	Medium
CHEMS	0.04	<0.1	0.03	Low
PHYS	4	<2	13,75	High
PSA	2	2	5.5	Medium
MEMS	0.5-20	>10	n/a	High

6. Conclusions

Biogas upgrading is beneficial but its market is still relatively very small. In European region there are at present around 200 biomethane plants that employ five main technologies: (1) water scrubbing (WATS), (2) pressure swing adsorption (PSA), (3) chemical scrubbing (CHEMS), (4) physical scrubbing (PHYS) and (5) membrane separation (MEMS). The most preferable technology is WATS with almost 40 % share, followed by PSA and CHEMS (both around 25 % share). The lowest share has MEMS with around 4 %. All five technologies are able to produce biomethane with required purity.

WATS is well-proven and simple technology, universally applicable for various flow rates. Pretreatment for H_2S is not necessary contrary to other technologies, where some pretreatment of H_2S is strongly recommended. A downside is big consumption of water. PSA can be a very compact technology employing various adsorbents and process configurations. A valuable quality is usage of none chemicals. PSA is used for any category of flow rates except very high ones. CHEMS and PHYS share the same technological feature - necessity for high-energy solvent regeneration. CHEMS can achieve the highest purity of biomethane. CHEMS and PHYS is preferably used for medium or large scale plants. MEMS appears to be a very promising technology. However, the experience with biogas upgrading is still lower and the output is a bit inconsistent. The great asset of technology is ease of operation, employment of various materials and process configurations. Suitable applications for MEMS appear to be at medium and small plants.

The most energy demanding technologies are CHEMS and PHYS, whereas PSA, followed by WATS, appears to be the lowest demanding. MEMS can be low energy demanding. The lowest investment costs relate to WATS, whereas other technologies are twice more expensive. The lowest operational costs relate to WATS followed by MEMS, whereas the highest operational costs belong to PSA and CHEMS. However, the newest research shows that economic performance of all technologies can be quite even and tight.

As for methane losses: due to the very high solubility of CO_2 in chemical solvents, CHEMS indicates the lowest methane leaks. MEMS and PHYS can have the highest methane losses.

Examination of gathered data regarding energy-economy and environmental aspects point out the limits in comparing studies that need to be revised especially with on-site measuring and more sources.

WAT, CHEM and PHYS are proven technologies with possible research on the field of process optimization. PSA and especially MEMS offer more progressive research aiming to develop new adsorbents and membranes and various process configuration.

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