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Bibliographic Review

Main technologies available for biogas purification

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Abstract

This study aims to investigate, gather and clearly explain the main methods used to clean and purify biogas, with the removal of compounds such as hydrogen sulfide, carbon dioxide and water, highlighting the techniques which present higher efficiency in the treatment of gas, increasing the calorific value of biogas, thus avoiding corrosion and damage to metal parts and making this gas with characteristics closest as possible to natural gas. Through this information, it is possible to conclude that there are several technologies in development based on the main techniques which are already widespread for the natural gas, aiming a better harnessing of biogas, in a way that it can be appropriately used without restriction in the energy matrix. However, further research should be conducted aiming to reconcile the efficiency factor with the cost-benefit of these purification processes.

Keywords: renewable energies; hydrogen sulfide; methane.

Detalhamento das principais tecnologias disponíveis para purificação de biogás

Resumo

O presente trabalho visa investigar, reunir e explicar de forma clara os principais métodos empregados na limpeza e purificação do biogás retirando compostos como sulfeto de hidrogênio, dióxido de carbono e água, evidenciando as técnicas que apresentam maior eficiência neste tratamento aumentando o poder calorífico do biogás, evitando a corrosão e os danos em peças metálicas tornando este gás com características mais próximas o possível do gás natural. Através do apanhado de informações é possível concluir que existem diversas tecnologias em desenvolvimento com base principal em técnicas já difundidas para o gás natural visando melhor aproveitamento do biogás, de modo que ele possa ser utilizado apropriadamente sem restrições na matriz energética. No entanto mais pesquisas devem ser desenvolvidas visando conciliar o fator eficiência com o custo beneficio destes processos de purificação.

Palavras-chave: energias renováveis; sulfeto de hidrogênio; metano.

Detallamiento de las principales tecnologías disponibles para la purificación de biogás

Resumen

El presente estudio tiene como objetivo investigar, recopilar y explicar claramente los principales métodos utilizados en la limpieza y la purificación del biogás retirando compuestos como el sulfuro de hidrógeno, dióxido de carbono y agua, poniendo en evidencia las técnicas que tienen una mayor eficiencia en este tratamiento, aumentando el pode calorífico del biogás, la prevención de la corrosión y los daños en las partes metálicas, tornando este gas con características más cercanas a el potencial del gas natural. A través del ayuntado de informaciones se puede concluir que hay varias tecnologías en fase de desarrollo con base principal en las técnicas ya existentes para el gas natural, visando mejor utilización del biogás, de modo que pueda ser utilizado adecuadamente sin restricciones en la matriz energética. Sin embargo, adicionales investigaciones deben ser desarrolladas para conciliar el factor de eficiencia con el costo beneficio de estos procedimientos de purificación.

Palabras clave: energía renovable; sulfuro de hidrógeno; metano.

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Introduction

The search for alternative sources of energy puts the society in face of a challenge towards the massive participation of non renewable sources in world energy supply. Nowadays, some new sources of energy that may perform an interesting role in the future stand out, such as the energy originated from biomass (MAGALHÃES et al., 2004).

The energy derived from biomass presents great possibilities of research and use, since the firewood and coal (traditional forms) are giving way to the modern biomass (bioethanol, biokerosene, biodiesel and biogas), presenting more efficient ways of energy generation (MIURA et al., 2011).

The biogas is a clean, renewable form of energy, produced from the anaerobic fermentation and consisting between 40% and 70% of methane, being the remainder carbon dioxide, hydrogen, sulfide and trace of some other gases (SINGH and SOOCH, 2004). Biogas is produced mainly from raw materials which are available in the location and can be harnessed in manageable quantities. In sum, the energy production through biogas actually transforms an expensive problem into a profitable solution (WALEKHWA et al., 2009).

Biogas is an important carrier of renewable energy, which can be used either directly as fuel or as raw material for production of gas of synthesis and hydrogen. Yet, depending on its origin, it may contain significant quantities of undesired compounds, such as hydrogen sulfide (H_2S), some halogenated hydrocarbons, ammonia (NH_3) and siloxanes. These compounds might pose technical problems of combustion, besides of forming corrosive acid compounds and emitting noxious gases to the environment (DEWIL et al., 2006).

Aiming allocation of biogas as fuel for boilers and engines, it becomes necessary a minimum treatment of this gas, now, for gas pipelines it is necessary a more rigorous purification in order to remove most of the undesired compounds which may damage and reduce the efficiency of the system (TOLMASQUIM, 2003).

Different methods can be used aiming the cleaning and purification of biogas, although these differ in their functioning, condition and minimum required quality of inlet gas, besides of the efficiency of purification and operational bottlenecks. Among these are mentioned the methods of condensation and drying, air compression and use of membranes (RYCKEBOSCH et al., 2011). The technologies for biogas purification are well established, however they present some disadvantages, such as the wide dimension of necessary equipments and its elevated demand for energy (SCHOLZ et al., 2013).

This study aims to gather and clearly explain the main methods used to clean and purify biogas, with the removal of compounds such as hydrogen sulfide, carbon dioxide and water, highlighting the techniques which present higher efficiency in gas treatment.

Removal of Hydrogen Sulfide (H_2S)

The hydrogen sulfide is a corrosive acid found in stagnant water, drains and sewers. Besides of being part of the chemical composition of fuels derived from petroleum, natural gas and biogas, which over time can proportionate serious damage to equipments and accessories used in the process of energy obtainment. This contaminant is highly undesired in combustion systems, because it converts into corrosive compounds and is highly hazardous to the environment, having a certain odor and bringing toxicity to human health. Depending on the organic matter composition, the H_2S content in the biogas can vary from 100 to 10.000 ppm, being its removal essential before any potential use of biogas (PÉREZ et al., 2008; FIERRO, 2012; TRUONG and ABATZOGLOU, 2005; ABATZOUGLOU and BOIVIN, 2009).

The choice of a certain technique for hydrogen sulfide removal is dependent on factors, such as: gas concentrations; treatment cost; and H_2S content in the biogas. The simplest method for H_2S removal from the biogas is through air addition in the digester or in the gas storage dome. The addition varies from 2% to 6% and can ensure a hydrogen sulfide reduction of up to 95% (NAGL, 1997; CCE, 2000).

Processes through Absorption

The purification methods through absorption are widely used due to the high efficiency and reactivity of sulfur with most of metals (HORIKAWA et al., 2004). The chemical absorption is shown as an efficient technology for removal of CO_2 and H_2S from the gaseous mixture, where in an absorption column, the pollutant is transferred from gas into a gas/liquid interface, and then, for most of the liquid phase, where the reactions occur. Absorbents are used aiming to raise the surface area and optimize the contact time of the gas. The alkaline and alkanolamines are among the most popular reagents for this type of practice (GEORGIOU et al., 2007; ZICARI, 2003; TIPPAYAWONG and THANOMPONGCHART, 2010).

The most commonly used absorption systems are composed by iron, absorption though organic compounds and through water. In the absorption with iron, it is used iron filings accommodated in purification columns, which are discontinuously, being moistened with water and filled with other materials, such as sawdust, in order to assist the hydrodynamic system (ARIAS, 2010). This system works with different pressures, removing the hydrogen sulfide efficiently either in room temperature or higher.

Several compounds have been used in biogas purification. Amines solutions combine with an amino group with CO_2 and H_2S aiming to obtain hydrogen carbonate and ammonium or ammonium sulfide. These processes are normally operated at temperatures of up to 48° C. The hydroxylamino ethyl ester presents an even lower corrosively, reason why it is preferable for the gases purification (FERNANDEZ, 2004).

The process of absorption with water, also known as wet cleaning, uses water in contact with the biogas in towers or columns, performing the masses transference of CO_2 and H_2S, from gas into water, which follow in counter-current. The operation temperature of the columns normally is between 5° C to 10° C, however, this procedure is also liable of operation at room temperature, if using pressure above 1726 kPa (VARNERO et al., 2012).

Processes through Adsorption

The purification techniques by adsorption are performed in fixated solid material, where the hydrogen sulfide tends to be adsorbed by adhesion. The process is normally used in smaller sized installations, where adsorbents depend of the physical adsorption of a molecule in the gaseous phase in a solid surface, not occurring chemical transformation. The desired characteristics of good adsorbents are high porosity and large surface areas (YANG, 1987).

As in the adsorption process the molecules are retrieved by weak electrostatic forces, the reaction can be easily affected by moisture, selectivity, temperature and pressure. The process demands less quantity of energy when the activated carbon is used, as it operates under conditions of temperature and pressure, where the reaction occurs in the pores and the hydrogen sulfide reacts with oxygen producing sulfur and water (Reaction 1) (LLANEZA et al., 2010).

Zeolites are natural or synthetic silicates often used in gas purification, for having uniformity of pores size, moreover being used as absorbent in dehydration processes (KOHL and NEILSEN, 1997).

As stated by KOHL and NEILSEN 1997, some alkaline solids also react with acid gases in neutralization reactions, and despite the use of scrubbers with liquids in the gases filtering processes, fixed beds of solids alkaline granules can be also used, with a box of standard drying, having upward flow of gas. The main alkaline solids used are the sodium hydroxide (Reaction 2) and the calcium hydroxide (Reaction 3).

According to a study made by TRUONG and ABATZOGLOU (2005), the procedure of hydrogen sulfide removal through adsorption appears to be promising, through a unity in pilot-scale constructed and tested in a pig farm in Quebec, Canada.

In addition to these methods, it is still found purification via filtration through membrane, where the gas stream goes through a selective membrane resulting from the driving force generated by the pressure difference. The factor that determines the process is the permeability, which posses the molecules that form the stream of biogas to be purified (VARNERO et al., 2012).

Removal of Carbon Dioxide (CO_2)

Among the ways to improve the biogas harnessing, it can be decreased the concentration of substances that reduce its calorific value, such as the CO_2, having effect of biogas dilution. The biogas purification with carbon dioxide removal enables its better use in generation of electric energy and in vehicles (MAGALHÃES et al., 2004; LASTELLA, 2002).

Several technologies were developed aiming CO_2 separation from the gases currents. Among these it is included the absorption by chemical solvents, physical absorption, cryogenic separation, separation through membrane and CO_2 fixation by other chemical and biological methods. Amongst the methods for CO_2 removal, the oxygen introduction in small quantities (2-6%) through air pumps is found as the simplest, and may provide efficiency of carbon dioxide removal, within the range of 80% to 99% (ABATZOGLOU et al., 2009; GRANITE and O'BRIEN, 2005; KRICK et al., 2005).

Absorption

The carbon dioxide removal through absorption is considered a unitary operation where one of the mixture components is dissolved in a liquid, being that this operation can involve some chemical reactions or be simply physical. Many chemical methods may be mentioned, among them there is the absorption in potassium carbonate, calcium hydroxide, sodium hydroxide, TNG, etc. Nevertheless, the physical methods, such as molecular sieves, separation through membranes and columns of absorption are best known and used, due the easy regeneration of used components in the processes. These methods are very alike to the used in natural gas in petrochemical industries and present advantage of demanding low quantity of energy, however the CO_2 must be with a partially elevated pressure (WONG and BIOLETTI, 2002; SUZUKI et al., 2011).

The water scrubbing method for cleaning of biogas is used with elevated efficiency even at low gas productions. The biogas is fueled upwards in the absorption column and pressurized water is pulverized in small droplets in the opposite direction to facilitate the carbon dioxide absorption. Thus, the CO_2 is dissolved and carried by water, forming H_2CO_3. This mixture follows into a box of elimination where the CO_2 is separated from the water and liberated into the atmosphere. This method presents reduced cost involving only pressurized water and little infrastructure (SILVA, 2009; COSTA, 2006).

Adsorption

The adsorption processes became very common and are often used in industries which aim the separation of the air present in biogas, besides of the hydrocarbons separation, mainly in petrochemical industries as well as processes for organic synthesis (ACKLEY, 2003).

Among the technologies for adsorption, the Pressure Swing Adsorption (PSA) has gained interest in the separation and capture of CO_2, due to its reduced costs in energy and resources, when compared to conventional separation methods, such as absorption and distillation (KAPDI et al., 2005; HUANG et al., 2006).

PSA is based on the undesired gas adsorption in a porous adsorbent in high pressure and recuperation of gas in low pressure, with continuous modulation of pressure during the process. The porous absorbent can be reused in a subsequent adsorption cycle. Processes of membrane separation and CO_2 liquefaction are also highly indicated for CO_2 separation, such as the Zeolites, which have high capacity of selectivity (MADEIRA, 2008; PANDE et al., 1989).

The dynamic of the process takes place by adsorbent beds or through combinations of these in different regions of a column, process similar to a chromatography. These different zones that are responsible by the reversibility and selectivity of the gas removal process (STÖCKER et al., 1998).

In the procedure of cleaning and purifying biogas, the optimal is that the CO_2 is removed until the methane percentage gets near to natural gas, in a way that it is designed the same use. According to the Agencia Nacional do Petróleo (ANP), as per Ordinance 128, of August 28 of 2001, the minimum percentage of methane in natural gas must be of 68% and maximum CO_2 of 18%, being this for the north region of the country, while in other regions the minimum percentage of methane is 86% and 5% of CO_2 (MAGALHÃES et al., 2004).

Many of the used techniques for carbon dioxide and hydrogen sulfide removal from biogas also remove many traces of other compounds. The biogas generated in the biodigestion process presents certain humidity and needs to be dry before its use. The most used techniques of water removal of the biogas are condensation and through adsorption by silicagel, activated carbon and aluminum oxide, besides the water absorption in glycol or hygroscopic salts (URBAN et al., 2008; RASI et al., 2011).

Membranes Use

As regards the biofuels purification, the use of membranes is a recent process, mainly targeting the biogas enrichment. The principle of the technique is the passage of gas through a membrane (<1 mm) where some components are transported and others are retained, thus separating unwanted compounds by means of the selective membranes. Each component has a different permeability to the material and the partial pressure difference promotes transportation by the membrane. The methane presents high permeability to cellulose acetate polymers if compared to the CO_2 and H_2S, ensuring a good separation of these components (SILVA, 2009).

The use of membranes treats most part of the problems caused by the CO_2 and hydrogen sulfide presence, which cause reduction of calorific value and damage metallic components, storage tanks, pipe networks of gas and engines, moreover presents viability when compared to chemical procedures that require much energy and great facilities for gas treatment (HOFMANN, 2006; SCHOLZ, 2013).

Biological Removal

Certain species of cyanobacteria present in effluents produce biomass and at the same time remove organic pollutants. Some of these microorganisms present advantages if compared to conventional treatments, for being more ecological it can be recycled, thus reducing secondary causes of pollution, such as heavy materials present in the effluent (MARTÍNEZ et al., 1999; PROULX et al., 1994).

The *A. platensis* cyanobacteria offer several advantages on microalgae and other cyanobacteria in the treatment of residual waters. Presents preference for basic means and allows the use of the mixotrophic metabolism, removing CO_2 and others pollutants, besides of preventing external contamination (DE-BASHAN et al., 2002; CONVERTI et al., 2006; LODI et al., 2005; CONVERTI et al., 2009).

Conclusion

Through these information it is possible to conclude that exist several technologies in development, with emphasis in already widespread techniques for the natural gas, aiming better biogas harnessing, in a way that it can be appropriately used without restrictions in the energy matrix. However, more researches must be developed aimed at conciliating the efficiency factor with the cost-benefit of the process.

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