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A Review of Pretreatments in Anaerobic Digestion and Biogas Quality Improvement

Milind Kulkarni[1], Dr. P.M. Ghanegaonkar[2]

[1]*Research Scholar, Mechanical Engineering Department, SCOE Vadgaon(Bk), SPPU, Pune.*
[1]*Assistant Professor, SVERI's College of Engineering, Pandharpur.* mbkulkarni1@rediffmail.com
[2]*Principal, Keystone School of Engineering, SPPU, Pune.* pmghanegaonkar@yahoo.com

Abstract— A widespread use of renewable energy sources is necessary to meet ever rising energy demands of the modern world. Biogas has emerged as a promising renewable energy source, especially in rural India, because of the abundant availability of biomass. Dissemination of biogas technology in India faces several barriers and there is a scope for increased applications of biogas in India. Improvement in methane content of biogas by removal of contaminants can enable widespread applications of biogas. A review of techniques for enhanced biogas production using different pretreatments, and the techniques for biogas quality improvement has been presented. The review may be useful for researchers in the field of biogas energy for further propagation of biogas technology in India.

Keywords— Anaerobic digestion, pretreatments, carbon dioxide, hydrogen sulfide, biogas scrubbing, biogas purification.

I. INTRODUCTION

Renewable energy sources like solar energy and wind energy require high capital investments and have the limitation of intermittent energy production. Biogas can thus become a vital energy source in India, due to abundant availability of agricultural waste, industrial waste, and municipal waste materials. Production of biogas offers multi-fold benefits like useful energy generation, reduction in environmental emissions and generation of a useful by-product in the form of digested slurry, which can be used as an organic fertilizer. However, the dissemination of biogas technology in India faces many socio-economic constraints. The actual biogas production in India is merely 7% of its minimum estimated potential (Mittal et al., 2018). Thus more research is necessary to explore low-cost and user-friendly materials and methods for biogas production.

A review of different aspects of anaerobic digestion, enhancement in biogas production, improvement in biogas quality by removal of contaminants etc. is presented in the following text.

II. OVERVIEW OF ANAEROBIC DIGESTION PROCESS

Anaerobic digestion (AD) process produces biogas by carrying out biodegradation of diversified organic waste materials or energy crops, in the absence of air or oxygen. Different stages of AD process comprise hydrolysis, acidogenesis, acetogenesis and methanogenesis, which are carried out by various species of microorganisms. The classification of AD process can be done on the basis of operating temperature range such as mesophilic temperature range (20^oC to 45^oC), thermophilic temperature range (50^oC to 65^oC) or psychrophilic temperature range (below 20^oC).

A bio-digester or bio-reactor is used to carry out AD process with controlled operating parameters inside the digester. The biogas production depends mainly on parameters like hydraulic retention time, carbon-nitrogen ratio in the feedstock, the type of reactor used, temperature and pH of the working medium, type of pretreatment applied to the feedstock and co-digestion of different types of feedstock materials employed. The digesters used for carrying out AD may be in the form of fixed dome or floating drum digester; single stage or two-stage digester, and batch-fed or continuous fed digester. A variety of bio-digesters like KVIC model, Janata model, Ganesh model, Pragati model, Deenbandhu model, TERI model, Chinese model, bag type reactor model and many others are used at different places in India. ("Biogas Technology", B. T. Nijguna).

The operational aspects of AD process include pretreatment, digestion, gas upgrading and digestate treatment (Monnet Fabien 2003). The volume of biogas produced during anaerobic digestion is affected by parameters such as the digester temperature, pH of the slurry, retention time, feeding frequency and the use of catalysts for biogas generation (Sambo et al., 1995; Mandal and Mandal, 1998; Laskari and Nedjah, 2015; Zealand et al., 2017).

III. FEEDSTOCK PRETREATMENTS IN ANAEROBIC DIGESTION

The brochure of International Energy Agency (IEA) mentions the need, different types, advantages and limitations of different pretreatment processes applied to the feedstock (Montgomery and Bochmann, 2014).

Different types of pretreatment methods can be classified on the basis of principles of operation (Table 1). A general composition of lignocellulosic biomass and the effect of pretreatments on the feedstock structure are mentioned in the literature to understand the operational aspects of various pretreatment methods (Mood et al., 2013).

TABLE I
OVERVIEW OF DIFFERENT PRETREATMENT PRINCIPLES AND TECHNIQUES (MONTGOMERY AND BOCHMANN, 2014)

Principle	Technique
Physical	Mechanical, Thermal, Ultrasound, Electrochemical
Chemical	Alkali, Acid, Oxidative
Biological	Microbiological, Enzymatic
Combined processes	Steam explosion , Extrusion, Thermochemical

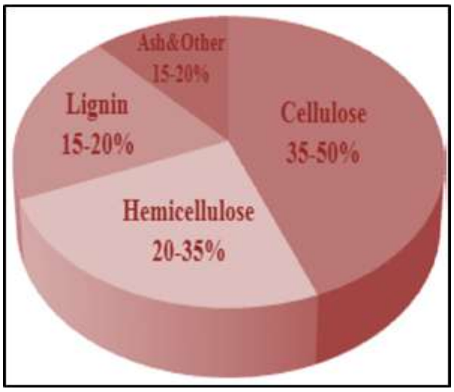

Fig. 1 General composition of lignocellulosic biomass (Mood et al., 2013)

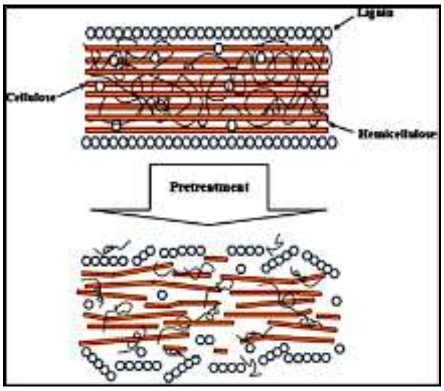

Fig. 2 Schematic pretreatment of lignocellulosic material (Mood et al., 2013)

Lignocellulosic material contains three different types of polymers, namely cellulose, hemicellulose and lignin, which are associated which each other. Use of lignocellulosic materials for biofuel generation is limited due to many factors like lignin content, crystallinity of cellulose, and particle size of the hemicellulose and cellulose. Each pretreatment method has its own effects on the cellulose, hemicellulose and lignin components of lignocellulosic biomass (Hendriks and Zeeman, 2009).

Enzymatic hydrolysis of lignocelluloses without any pretreatment is usually less effective due to high stability of these materials to enzymatic or bacterial attacks. An effective and economical pretreatment should possess characteristics like production of reactive cellulose, minimum energy demand for operation, use of low-cost chemicals etc. (Taherzadeh and Karimi, 2008).

Application of various pretreatments such as mechanical pretreatment, chemical pretreatment, thermal pretreatment or biological pretreatment applied to the feedstock gives enhancement in biogas production. Pretreatment of the feedstock increases its biodegradability by opening its structure, and making it more accessible to the enzymatic attack by microorganisms (Sambusiti et al., 2013).

Improvement in production of biogas, and waste stabilization as well as disposal is obtained by the pretreatment of biomass. Economic analysis, operational cost and the benefits derived is essential while selection of pretreatment methods for large scale application (Sahilu and Alam, 2016).

IV. BIOGAS SCRUBBING AND PURIFICATION

Raw biogas from anaerobic digestion process contains combustible methane gas between 50- 70% and carbon dioxide between 30-50%, along with traces of hydrogen sulfide and moisture. Presence of impurities like carbon dioxide (CO_2), hydrogen sulfide (H_2S) and moisture in biogas lowers its quality and limits its widespread applications. Biogas should be made a transportable fuel and also suitable for other widespread applications such as running of internal combustion engines, vehicular fuel applications or injection into natural gas grids. To achieve this, removal of contaminants from biogas is necessary (Yadav et al., 2016). Removal of carbon dioxide from biogas is known as biogas up-gradation or scrubbing, and removal of hydrogen sulfide from biogas is known as biogas purification or desulfurization. Small-scale biogas plants in India seldom use purification and scrubbing systems, because of cost considerations and inadequate knowledge of these techniques.

Removal of CO_2 from Biogas

Application of biogas as a vehicular fuel is still in an early stage and the worldwide use of biogas for vehicular applications is reported to be less than 1%. Compared with gasoline, the estimated reduction of greenhouse gas (GHG) emissions due to vehicular applications of biomethane (biogas containing more than 90% methane) is around 60-80% (IRENA, 2017).

Following techniques are commonly used for removal of carbon dioxide from biogas (Ryckebosch et al., 2011):

- Physical and chemical absorption
- Pressure swing adsorption (PSA) and vacuum swing adsorption (VSA)
- Membrane separation technique
- Cryogenic separation technique
- Biological methane enrichment

Physicochemical methods of biogas scrubbing are widely used due to high technology readiness levels, while biological scrubbing methods are relatively new and not yet operational at commercial levels (Angelidaki et al., 2018).

Minimization of the operating cost cannot be the only criterion for selection of a biogas upgrading technology. It is also important that the selected technology should meet the quality requirements for the upgraded gas (Sun et al., 2015).

A comparative study of five biogas upgrading methods was simulated and analyzed by Hosseinipour and Mehrpooya (2018). The study reveals that caustic scrubbing method is very efficient, but the recycling of NaOH is energy intensive and expensive. For economical operation of the process it is suggested to use fresh NaOH repeatedly and the residuals can be discarded as waste.

Carbon dioxide removal efficiency upto 99.98% is achieved by using sodium carbonate absorbent, as compared to 30% removal efficiency using water scrubbing method. Also, hydrogen sulfide removal efficiency of 70% is achieved using sponge iron (iron oxide). Regeneration of sodium carbonate effluent from carbon dioxide scrubber is done by using algal treatment (Mohanakrishnan and Joseph, 2016).

Upgraded biogas containing around 95% methane is obtained by using a biogas compression and storage system intended for cooking applications in rural Indian households. Carbon dioxide removal is achieved by using limestone crystals while hydrogen sulfide removal is achieved by using catalyst iron oxide in the form of oxidized steel wool (Ray et al., 2016).

Methane enrichment upto 95% using chemical scrubbing method is achieved and the results of road testing of a vehicle are also presented. The first run comprising a combination of dry lime and potassium hydroxide gives 95.11% methane in upgraded biogas alongwith 102 parts per million (ppm) of hydrogen sulfide. The second run uses a combination of sodium hydroxide and calcium hydroxide and gives 94.69% methane in upgraded biogas alongwith 87 ppm of hydrogen sulfide. Removal of hydrogen sulfide is achieved using steel wool (iron oxide) and silica gel is used for removal of moisture from raw biogas (Shah et al., 2016).

Biogas upgradation with 95% methane content and a total elimination of hydrogen sulfide from raw biogas has been achieved by using porous membrane technique. The porous membrane was obtained from natural zeolite material and activated by different concentrations of sodium hydroxide. The highest purity of biogas was achieved by using 5% concentration of NaOH (Tira and Padang, 2016).

A simple and easy-to-use method in rural areas has been experimented using chemical absorption with the aid of dry absorbent. Methane content of purified biogas got enriched upto 97.7% by using dry sodalime for chemical scrubbing process (Ghatak and Mahanta, 2016).

Biogas flow rates, the type of solution used and concentration of the solution could affect the biogas purification process using calcium hydroxide and monoethanolamine. Maximum CH_4 concentration of 89.3% is obtained in purified biogas using 0.2 molar concentration of calcium hydroxide, solution flow rate of 30 LPM, and biogas flow rate of 5 LPM (Srichat et al., 2017).

Methane enrichment above 95% and hydrogen sulfide removal efficiency between 85-96% is achieved using combined method of absorption and adsorption. Using chemicals iron oxide (Fe_2O_3), zero valent iron (Fe^o), and iron chloride ($FeCl_2$) facilitates hydrogen sulfide removal from biogas. Silica gel, sodium sulfate (Na_2SO_4), and calcium oxide (CaO) are used for water vapour and carbon dioxide removal from raw biogas (Rashed and Torii, 2017).

A method of biogas quality improvement by elimination of CO_2 and H_2S was studied by using limewater solutions in packed columns. The effect of different limewater concentrations and variations in biogas flow rates on CO_2 removal efficiency was studied. Using 14% concentration of limewater at a biogas flow rate of 1 liter per minute (LPM) gives the highest CO_2 removal efficiency alongwith CH_4 enrichment of 21.2% (Mell et al., 2014).

Methane enrichment of biogas was achieved by carbon dioxide fixation using the chemicals calcium oxide, calcium oxide solution/calcium hydroxide and activated carbon (Rashed et al., 2016).

Removal of H_2S from Biogas

Biogas purification or desulfurization process consists of removal of hydrogen sulfide (H_2S) from biogas. Elimination of H_2S from biogas is highly desirable because of the associated health hazards to the users and also the corrosion of burners, storage tanks, and engine components (Shah and Nagarseth, 2015). The origin of hydrogen sulfide in biogas plants is attributed to the degradation of sulfur-containing proteins in the feedstock. Removal of hydrogen sulfide can take place in the digester itself or by using suitable purification system placed after the digester (Muche et al., 1985).

Common techniques for removal of H_2S from biogas include:

- Absorption technique using water or aqueous alkaline solutions
- Adsorption technique using solid materials like iron oxide or activated carbon
- Biological conversion technique for converting sulfur compounds into elemental sulfur

An effective method for hydrogen sulfide removal from biogas comprises in-situ H_2S reduction within the digester. For this purpose addition of reagents like iron chloride, iron oxide or iron hydroxide is directly done to the digester, or along with the feedstock in a pre-storage tank. Another least expensive method of desulfurization consists of biological aerobic oxidation of H_2S. A small amount of oxygen (3-6% air in biogas) is introduced in the biogas digester by using an air pump. Overdosing of air needs to be avoided as biogas in air is explosive in the range of 6 to 12% (Allegue and Hinge, 2014). Another approach for classification of commonly used H_2S removal techniques is the dry oxidation process and liquid phase oxidation process. Effective techniques of biogas desulfurization include the introduction of air/oxygen into the biogas system, adsorption using iron oxide or activated carbon, liquid phase oxidation using NaOH and $FeCl_3$ (Kapdi et al., 2005).

A simplified and cost-effective method for biogas desulfurization uses the reagent iron oxide in the purification columns. Iron oxide is easily available in the form of oxidized (rusted) steel wool or iron chips from workshop.

Regeneration of iron oxide is possible by exposing it to the atmospheric oxygen (Shah and Nagarseth, 2015). Commercially available steel wool packed in polyvinyl-chloride (PVC) columns can give hydrogen sulfide removal efficiency of 95%. Additional advantages like low-cost operation and regeneration of steel wool by exposure to atmospheric air are also mentioned. Effectiveness for H_2S removal of regenerated steel wool is found to be similar to that of fresh steel wool (Magomnang and Villanueva, 2015).

The performance of various oxido-alkaline solutions for H_2S absorption is found to be better than that of amine solutions. Sodium hydroxide (NaOH), monoethanolamine (MEA) and hydrogen peroxide (H_2O_2) solutions were used for capturing H_2S and CO_2 from raw biogas (Dubosis and Diane, 2010).

The removal of hydrogen sulfide using chemical absorption is more effective than water scrubbing under similar conditions. Experimental results demonstrate that complete removal of H_2S is possible from biogas using an iron-chelated process operating at ambient temperature (Horikawa et al., 2004).

V. CONCLUSIONS

The propagation of biogas energy in India is essential to harness useful energy from available biomass. Research work regarding alternate feedstock for biogas generation and improvement in biogas production can be beneficial to reduce the dependency upon the fossil fuels. An increase in the process efficiency of biogas generation is possible by using suitable pretreatment methods. Removal of contaminants from biogas by using suitable scrubbing and purification techniques can upgrade biogas up to natural gas quality and can be used for wider potential applications.

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