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Biomethane Production from Distillery Wastewater

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Abstract

Distillery wastewater treatment is a great ecological problem, for example, India produces 2.7 billion liters of alcohol that results in 40 billion liters of wastewater. However, this material can be seen as a resource since 11 million cubic meters of biogas at 60% methane could be produced in addition to cleaning the water. The distillery has two options of what to do with the biogas. The first is to use the biogas to fuel the distillery making the production plant more energy efficient and removing some of the need to buy natural gas. The other is to upgrade the biogas into biomethane and sell it on the market. In this article the reader is walked through the process from raw distillery wastewater to pretreatment, digestion and finally upgrading using a membrane separation of methane from carbon dioxide.

Introduction

The production of alcohol by an average distillery yields 9 to 14 liters of wastewater per liter of alcohol produced. The wastewater is highly acidic with a pH in the range of 4 to 5. Another issue that needs to be handled is the wastewater has a high chemical oxygen demand (COD) in the range of 50 to 100 g/L.[3]

COD is the measure of how much oxygen it would take to decompose organic material that is in solution. This is important because if high strength wastewater is discharged into a nearby waterway the oxygen level would drop leading to the death of aquatic organisms such as fish.[10]

Distillery wastewater is a dark brown liquid that is composed of about 90 to 93% water, 7 to 10% solids, 2 to 20% sugar and 10 to 11% proteins. The characteristics of the wastewater vary considerably from one location to the next due to feedstock and fermentation process. Due to the high cost of treating the wastewater it is commonly dumped into bodies of water or sprayed on fields surrounding the distillery. However, both approaches have serious consequences to soil and water quality. For example, India produces 2.7 billion liters of alcohol that results in 40 billion liters of wastewater. The wastewater can be turned into a valuable resource if the proper water treatment facility was constructed.[4]

An organism that requires oxygen to function and grow is known as being aerobic, whereas an organism that can perform biological activities without oxygen is functioning anaerobically. The advantage of an organism using anaerobic digestion is that the organism can produce an energy rich gas composed mostly of methane and carbon dioxide commonly called biogas.

The distillery wastewater mentioned above has the potential to produce 11 million cubic meters of biogas at 60% methane. The biogas can then be used to power and heat the distillery to save on energy costs. Otherwise, the biogas can be enriched and bottled in cylinders to be sold within the transportation industry.[4]

Compressed Natural Gas (CNG) is composed of 75 to 98% methane with a small amount of other hydrocarbons such as propane and butane. Upgraded biogas can be used for the same purposes that CNG currently is, such as operating trucks, buses and trains. After removal of hydrogen sulfide, biogas is composed of about 60% methane and 40% carbon dioxide. Using biogas has lower emissions than either diesel or natural gas as seen in table 1 below.[9]

Table 1. The varied pollution levels that is associated with 3 different kinds of fuel.[9]

g/km	CO	HC	NO_X	CO_2	Particulates
Diesel	0.20	0.40	9.73	1053	0.100
Natural gas	0.40	0.60	1.10	524	0.022
Biogas	0.08	0.35	5.44	223	0.015

Source: A report on biogas technology and biogas use in Sweden, Traffic and Public Transport Authority, City of Gothenburg, November 2000.

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Another advantage of using biogas is that the material does not contain any hazardous petroleum byproducts such as toluene or benzene. Upgrading the biogas into biomethane has the advantage of boosting the energy value of the end product as well as saving space within the cylinder since carbon dioxide has been removed.[5]

Raw biogas is normally used for heating or generating electricity. However, as much as 60% of the energy is wasted in this practice. Upgrading the biogas allows for higher efficiency as well as increasing the possibilities for use such as vehicle fuel or as a feedstock for chemical industries.[2]

Unlike other renewable energy sources biogas can be produced and used regardless of the time or geographic location. The needed feedstock for biogas, commonly organic waste, is evenly distributed across the world. These factors allow for the development of energy security on a local and national scale.[8]

Comparison of Mesophilic and Thermophilic Reactors

There are two main types of anaerobic digesters that are divided by temperature range. Mesophilic digesters operate the most efficiently in a temperature range of 25 to 40^{o}C. A thermophilic digester works at a temperature range of 55 to 60^{o}C.

In a particular study the use of wastewater from a molasses distillery was used and digested in an Up-Flow Anaerobic Sludge Blanket (UASB). One of the main features of a UASB is the formation of active granules that sink to the bottom of the reactor. The granules are made of self-immobilized anaerobic bacteria that provide effective retention of bacteria in the reactor. The biogas was stored in a dome shaped containers on top of the reactors. When sufficient gas had been generated, it was sent to a boiler for steam generation.[4]

The pH was maintained between 6.5 and 7.0 by adding lime (A mixture of calcium oxide and/or calcium hydroxide) to the reactor. This was done because the optimum pH for methane production is between 7.0 and 7.5. Sulphide concentration should be less than 1 g/L because at this concentration it has toxic effects on the microbial community, decreases the ability to decompose COD as well as lowered biogas production.[4]

For both mesophilic and thermophilic there is a strong correlation between biogas production and COD reduction. The methane content of the biogas is related to COD reduction as well as the hydraulic retention time (HRT). HRT is the average length of time a soluble compound remains in a bioreactor usually as a result of the chamber volume and inlet flow rate.[4]

The report stated the thermophilic reactor showed the following advantages:

1. The thermophilic reactor had higher efficiency with different organic loading rates (OLR) than the mesophilic reactor.[4]

2. The thermophilic reactor was more flexible and had greater stability with variations of OLR and temperature.[4]

3. The thermophilic reactor can be used for wastewater with high OLR and COD without pretreatment or water dilution. Also this reactor could be fed wastewater at a pH of 4 without prior dilution or neutralization.[4]

Aerobic-anaerobic method

The anaerobic digestion of distillery wastewater is challenging because of inhibitory substances within the liquid. One example is phenolics; these compounds interfere with the biological activities of bacteria, therefore the overall rate of decomposition and methane production is slowed down. The need for long hydraulic retention time (HRT) is partially due to the phenolic content of the wastewater.[3]

In this method the researchers used sugar beet molasses fermentation wastewater they obtained from a alcohol factory in el Puerto de Santa Maria, Spain. As a pretreatment the fungal species *Penicillium ignorum* IFJM-B 22 isolation 0.46 Rio Tinto, *Penicillium decumbens* and *Penicillium sp.* isolated from molasses and *Aspergillus niger* IJFM-A570 from a Portugal collection LNETI. Potato dextrose agar was used to maintain the cultures and to provide an active population.[3]

The aerobic vessel conditions are 22°C and circulated at 100 rpm. The fermentation wastewater was diluted to 50% and sterilized before inoculation with spores suspended in a saline solution of (10^7 viable spores per ml). Air input was 3 L/h per 1 L of molasses. The fungal species used in this experiment are active within the pH of 5.2, meaning the fermentation wastewater did not need pH adjustment.[3]

The anaerobic reactors used in this study have a working volume of 1 liter, constantly stirred and kept at a temperature of 350°C. The reactor was initially charged with 750 ml of solution containing peptone (1%), yeast extract (0.5%), sodium chloride (0.5%) and 135 ml of inoculate. The inoculate was biomass collected from an industrial anaerobic contact reactor that was fed vinasse. Vinasse is a vague term used to describe wastewater from either a sugarcane or wine distillery.[3]

All fungal species decreased the coloration of the fermentation wastewater within 5 days with *P. decumbens* showing the best results (41% removal). The COD removal was the highest with *Penicillium sp.* (52.1% removal) with *P. decumbens* at (50.7% removal). As a side benefit of fungal pretreatment, *P. decumbens* also removes heavy metals from the solution as can be seen in the table below.[3]

Table 2. The table shows the removal of several different heavy metals and salts from distillery wastewater before and after pretreatment with P. decumbens.[3]

Cation	Molasses	Pretreated molasses
Na	2500	1875
K	3550	2540
Ca	985	833
Mg	510	500
Fe	83	6.8
Mn	85	0.7
Zn	20	1.0
Cu	7	0.3
Co	2	0.1
Ni	4	0.3
Cr	2	0.2

The methanogenic bacteria had better methane to COD ratio when the fermentation wastewater was pretreated with a fungal species. Also, at organic loading rate (OLR) of 7.5 there was no methane production inhibition as was seen with the untreated control.[3]

Table 3. The table below shows the production of methane after different Organic Loading Rates (OLR).[3]

OLR (g COD per l day)	Untreated molasses l CH_4 STP per g COD	Pre-treated molasses l CH_4 STP per g COD
1.5	0.197	0.224
2.5	0.198	0.218
3.5	0.200	0.203
4.5	0.186	0.193
5.5	0.168	0.183
6.5	0.167	0.170
7.5	0.101	0.177

A combined aerobic - anaerobic system allows for more rapid processing of wastewater than a purely anaerobic system while reducing the costs associated with a completely aerobic system.[3]

Ozonation Pretreatment in Two-phase Anaerobic Digester

When high levels of organic or toxic materials are present a physicochemical pretreatment may be necessary. An example is ozonation where the strong oxidant ozone (O_3) reacts with organic material causing their degradation.

Ozonation allows for greater biodegradability since molecules that would normally take long periods of time have been partially digested. An example of this is the decrease in pH from the formation of organic acids that are easily biodegraded by microorganisms. The formation of hydroxyl radicals are also formed during ozonation; hydroxyls further increase the oxidation reaction within the solution. Ozone is soluble in water, readily available and does not contribute to the waste stream by creating materials that need further disposal.[7]

Ozonation was performed on raw distillery wastewater with concentration of 6063 +/- 806 ml/L. The wastewater did not have any pH adjustment before treatment. The pre-ozonation pH was 4.5; the pH after treatment was 3.5 indicating a release of organic acids. A laboratory scale ozone generator was used in this study using an oxygen cylinder that was also used as a fed gas. The ozone was passed through a glass tube submerged in a rectangular column. The bubbling ozone was allowed to react with the wastewater for 30 minutes. The excess ozone passes through a silicon tubing connected to 2, 1 liter Erlenmeyer flasks with potassium iodide solution. The ozonation chamber was filled with 10 liters of wastewater at room temperature. The oxygen gas flow rate was 2 L/min with 4 g/h of generated ozone.

Seed sludge was taken from a full scale UASB treating distillery wastewater. In order to stabilize the sludge water containing 500 mg/L urea and potassium hydrogen orthophosphate with trace elements was added. The pH of the distillery wastewater was adjusted to 7-7.5 by adding sodium hydroxide solution. The first phase was fed with a centrifugal pump at a rate of 20 Liters per three days. The effluent was then stored in a plastic tank until there was a sufficient amount to be pumped into the second phase.[7]

The ozone treatment reduced COD by an average of 57 +\- 7% and color by 51 +\- 7%. In comparison, a two phase anaerobic digester without pretreatment reduced COD by 38 +\- 14%. Lower sludge production was seen after ozonation possibly due to the reduction of suspended solids in the influent. The biogas generated was 9.0 L for the ozonated wastewater; while untreated wastewater had a biogas production of 9.5 L.[7]

Table 4. The table below shows the results of anaerobic digestion without pretreatment and with ozonation in terms of COD removal.[7]

DAYS	ANAEROBIC TREATMENT ONLY			COMBINED OZONATION AND ANAEROBIC TREATMENT			
	Influent COD (mg/L)	COD after AD I (mg/L)	COD after AD II (mg/L)	Influent COD (mg/L)	COD AFTER O3 (mg/L)	COD after AD I (mg/L)	COD after AD II (mg/L)
3	5450	2532	3216	6403	4323	3446	2254
6	4966	3138	4364	5157	4477	3610	2497
9	6050	3903	2632	6516	5457	3953	2493
12	4948	3524	2939	7129	4671	3501	2585
15	4726	2273	2998	5080	4460	3535	2594
18	5552	3924	3424	6096	4071	3507	3083

Removal of Contaminants in Biogas

Since biogas is a mixture of components some pretreatment is necessary before upgrading the biogas into bio-methane can occur. The water content of the gas is decreased by a two-step refrigeration process to allow the water vapor to condense. This is done to protect downstream equipment and maintain the integrity of the membrane.[6]

Hydrogen sulfide needs to be removed to prevent corrosion in the compressor, gas storage tanks and engines. Hydrogen sulfide is a poisonous and corrosive material that changes into the environmentally hazardous sulfur dioxide when burned.[6]

There are two methods of removing hydrogen sulfide. The dry process is passing biogas through iron oxide pellets or wood chips coated with iron oxide. About 20 grams of hydrogen sulfide can be trapped in 100 grams of iron oxide wood chips. Iron oxide wood chips are a low cost input, however special care must be taken since the powder that comes off used chips and pellets is dangerous to human health.[6]

The second way of removing hydrogen sulfide is liquid based processes. The addition of iron chloride to a digester will combine with the hydrogen sulfide. The resulting chemical reaction produces iron sulfide that precipitates out of solution. Another approach is using an iron-chelated solution composed of ferric ethylenediamine tetraacetic acid (Fe/EDTA). The chemical absorption converts the hydrogen sulfide into elemental sulfur. The elemental sulfur can be easily removed by sedimentation or filtration at ambient temperature.[5]

Membrane Upgrading of Biogas

Operational characteristics of a membrane based system:

1. Lower capital cost than a Pressure Swing Adsorption (PSA) method of upgrading.[5]

2. Operational simplicity and high reliability because of no moving parts and low mechanical wear.[5]

3. The low level of methane that is present in the waste gas can be used for heating.[5]

4. The system is modular and can be scaled easily to fit the volume of biogas produced.

5. If proper pretreatment of the biogas is not carried out it will decrease the lifespan of the membrane. For example, hydrogen sulfide will cause the membrane to soften or have weak spots.[5]

6. The energy requirement of the system is determined by the compressor size.[5]

7. The membrane area is a big part of determining pressure in the system. A large surface area reduces the pressure needed in the system since a lower flux through the membrane can be accepted.[5]

A membrane upgrades the biogas by using a thin semi-permeable barrier. Polymeric membranes separate gases by selective permeation of one or more gaseous compounds from one side of a membrane barrier to the other side. A membrane does not function like a filter where inputs are sorted by pore size. The input gas dissolves on the surface of the membrane and due to the concentration gradient is pushed through by diffusion. The concentration gradient is maintained by having a high partial pressure on one side while having a low partial pressure on the other side.[5]

The membrane is commonly in the shape of a tube. The high pressure feed is on the inner side of the tube and the low pressure permeate waste stream on the outside. This can be seen in figure 1 below.[6]

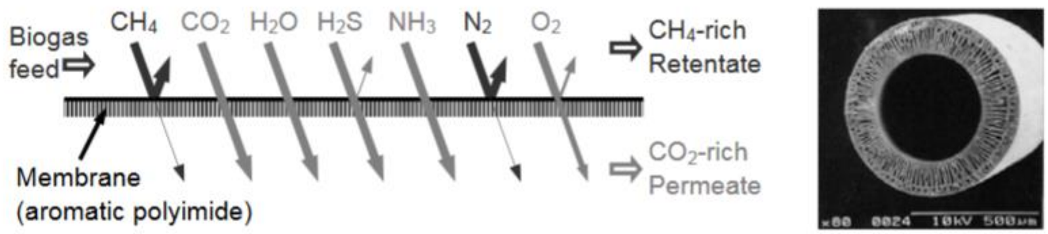

Figure 1. A diagram showing how a biogas membrane works to separate methane from carbon dioxide.[6]

Membranes come in two types: high pressure gas separation and gas-liquid adsorption technique. The high pressure separation is a three stage process where carbon dioxide is separated from methane. Gas-liquid adsorption operates at a low pressure and uses micro-porous hydrophobic membranes as an interface between the biogas and a liquid. With this configuration carbon dioxide and hydrogen sulfide dissolve in the liquid while methane remains in a gas state that is collected.[2]

Storing Upgraded Biogas

Biogas that has been upgraded is called by several names such as Bio-methane, Renewable Natural Gas (RNG) and Bio-CNG. In each of these terms biogas has the impurities removed and the methane concentration enriched to about 90% or more.[6]

The storage of biogas is essential in order to provide a supply of energy when it is needed by the industry. Without a storage system the industry would be restricted by how much biogas was produced at that moment; also an excess of biogas leads to flaring and exhaust to the atmosphere. A low pressure storage unit is an inflatable top to the digester which holds the biogas after it is produced. Low pressure units can be made from a large variety of materials such plastics as well as steel. For intermediate onsite use of biogas a medium pressure unit is used. A medium pressure unit compresses the biogas to approximately 17 Bar. To compress a 60% methane biogas, the energy equivalent 10% of the cylinder is used during compression. A high pressure system always uses upgraded biogas to maximize the energy used for compression. Also, water vapor and hydrogen sulfide will separate out and condense on the cylinder walls if they are not removed. High pressure storage systems are commonly used in the transportation sector. The biomethane inside these tanks are pressurized to 137.89 Bar to 344.73 Bar. This compression requires the energy equivalent to 17% of the gas in the cylinder.[1]

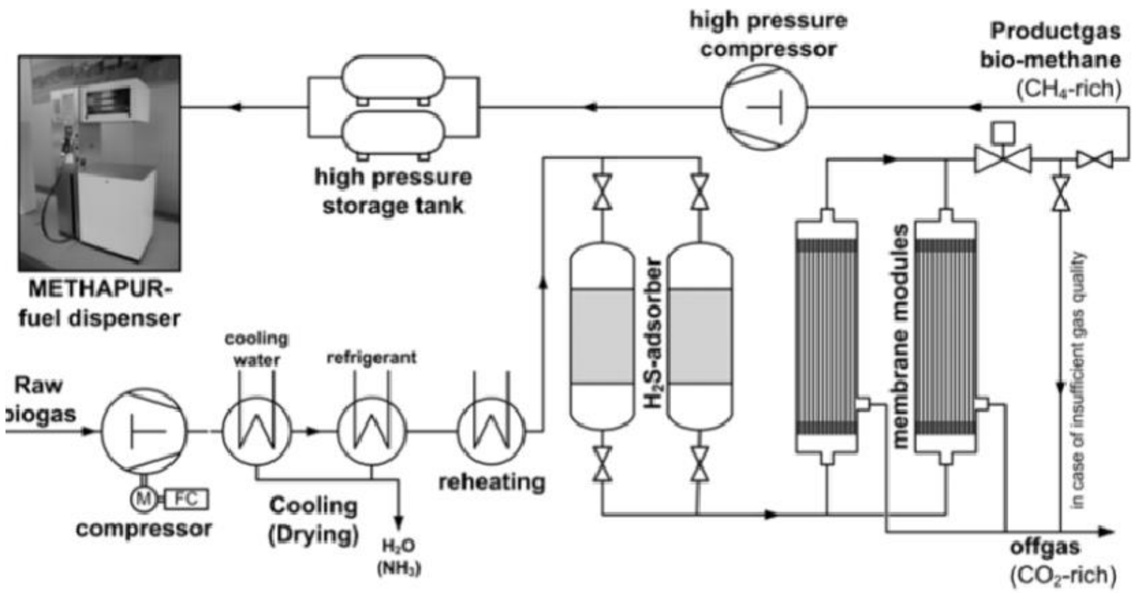

Figure 2. Austria's membrane upgrading Bio-CNG fueling station diagram.[6]

Summary

The process of converting distillery wastewater into biomethane begins with pretreatment. Ozone is used to breakdown hard to digest materials for easier processing by micro-organisms. In order to reduce salts, heavy metals and to breakdown phenols a fungal pretreatment is performed. The resulting wastewater is then pumped into an anaerobic digester for methane production. The biogas is purified of contaminates and passed through a membrane to obtain methane rich fuel gas.

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