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Production and Areas of Use of Gas Biofuels and Optimization of Bioprocess Parameters Affecting the Production Efficiency

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ABSTRACT

The importance of renewable energy sources is increasing day by day due to the reasons such as fossil fuel reserves being on the point of exhaustion and trying to minimize the negative effects thereof on the environment. In biogas processes, hydrogen and carbondioxide gases are released through the degradation of organic matters by acidogenic bacteria with fermentation and the conversion thereof into organic acids. In the second stage, organic acids are transformed into acetic acid, hydrogen and carbondioxide by acidogenic bacteria. While methane bacteria use the hydrogen they need, they also remove the hydrogen that affects the acidogenic bacteria negatively. Biohydrogen production processes, on the other hand, the system is processed by applying heat pretreatment to anaerobic fermentation bacteria for 20-45 mins and between 90-105 ^{0}C. In the first stage, organic wastes with high carbohydrate ratio are degraded by heat pretreated anaerobic fermentation bacteria into organic acids, hydrogen and carbondioxide. In the second stage, the organic acids produced in the first stage are degraded to hydrogen and carbondioxide with fermentative bacteria. In this study, optimization of the bioprocess parameters affecting the production, use and production efficiency of gas biofuels is presented.

Keywords: Biogas, Biohydrogen, Renewable Energy

Gaz Biyoyakıtların Üretimi, Kullanım Alanları ve Üretim Verimini Etkileyen Biyoproses Parametrelerinin Optimizasyonu

ÖZ

Fosil yakıt rezervlerinin tükenmek üzere olması ve çevreye olumsuz etkilerini azaltabilmek gibi nedenlerden dolayı yenilenebilir enerji kaynaklarının önemi gün geçtikçe artmaktadır. Biyogaz proseslerinde, organik maddelerin asidojenik bakteriler tarafından fermantasyonla parçalanarak organik asitlere dönüştürülmesi ile hidrojen ve karbondioksit gazları açığa çıkmaktadır. İkinci aşamada, organik asitler asidojenik bakteriler tarafından asetik asit, hidrojen ve karbondioksite dönüşür. Metan bakterileri ihtiyaç duydukları hidrojeni kullanırken, asidojenik bakterileri olumsuz etkileyen hidrojeni de uzaklaştırmış olurlar. Biyohidrojen üretim proseslerinde ise, anaerobik fermantasyon bakterilerine 20-45 dak ve 90-105 ^{0}C aralığında ısıl ön-işlem uygulanarak sistem işletilmektedir. İlk aşamada karbonhidrat oranı yüksek organik atıklar, ısıl ön işlem uygulanmış anaerobik fermantasyon bakterileri tarafından organik asitler, hidrojen ve karbondioksite parçalanır. İkinci aşamada ise birinci aşamada üretilen organik asitler fermantatif bakteriler ile hidrojen ve karbondioksite kadar parçalanır. Bu çalışmada, gaz biyoyakıtların üretimi, kullanım alanları ve üretim verimini etkileyen biyoproses parametrelerinin optimizasyonu sunulmuştur.

Anahtar Kelimeler: Biyogaz, Biyohidrojen, Yenilenebilir Enerji

1. INTRODUCTION

Fossil fuels still being used in the world can be classified as coal, wood, petroleum and natural gas, which are about to exhaust. Almost all of our energy need is supplied from fossil fuels. The toxic gases such as NOx, SOx, COx produced by the combination of these fossil fuels with oxygen gas and the combustion thereof cause environmental pollution. Due to the spread of these toxic gases to atmosphere, the fact that living beings breathe and the world gets warmer with greenhouse effect lead to negative effects such as melting of glaciers, floods, change of climates. Depletion of fossil fuels and pollution of the environment have become an important problem both in the world and in our country. For these reasons, renewable energy sources should be given importance.

Renewable energy sources can be listed as biomass energy (bioenergy), solar energy, geothermal energy, wind energy and hydraulic energy. When assessed from an environmental standpoint, biomass energy is advantageous taking the use of waste products into consideration. Biomass is generally referred to as the whole of biological sources of various organic origin. About 90% of the biomass in the world is in the forests. Energy from forests can reduce problems such as climate change, erosion and desertification. 150 billion tons of biomass is produced annually. Only 10% of this is used commercially (Demirer, 2012). Biomass derived from non-fossil organic (carbon-based) wastes such as urban wastes, wastewater, animal wastes, vegetal wastes and agricultural wastes are important in the production of renewable biofuels. Biofuels (bioethanol, biodiesel, biohydrogen and biomethane), sustainable and environmental negative effects compared to fossil fuels are the advantages of these types of fuel. In addition, the use of hydrogen gas, a gas biofuel, as a single fuel in space vehicles makes this fuel privileged. Gas biofuels (biogas, biohydrogen) are produced by anaerobic digestion of organic wastes. The raw biogas contains approximately 55-65% methane (CH_4), 30-45% carbon dioxide (CO_2), hydrogen sulfide traces (H_2S) and water vapor fractions (Porpatham et al., 2007 ; Xu et al., 2009). Hydrogen gas is obtained in the biogas production stage. In order to obtain this gas biologically, microorganisms must be pretreated (heat). Thus, although the methanogenic microorganisms cannot be totally destroyed, their populations can be reduced. In this context, it is necessary to discuss the parameters affecting the production of gas biofuels in the development and use of alternative energy sources in our country, and to put the studies in this area into practice as soon as possible.

Gas biofuels processes have some advantages such as reducing the dependence on fossil fuels, limited as a source, recycling waste/wastewater and reducing the threat of climate change with positive environmental effect. In these processes, the disadvantage is that they are quickly affected by sudden temperature changes.

2. GAS BİOFUELS

2.1. Production Stages

Biogas production occurs in three stages. In the first stage, the complex organic compounds are fermented and degraded into long-chain fatty acids by acidogenic bacteria, and carbon dioxide and hydrogen gases are produced in the process. Most of the organic waste/wastewater becomes water soluble at this initial stage. In the second stage, the organic acids are transformed into carbon dioxide (CO_2), hydrogen (H_2) and acetate (CH_3COOH) by acidogenesis bacteria. However, when this hydrogen is removed from the medium, this stage becomes possible. Methane bacteria using hydrogen make this process. Thus, while methane bacteria consume the hydrogen they need, they also remove the agent affecting the acidogenesis bacteria negatively from the medium. The third stage is carried out by methanogenic bacteria. These bacteria can survive at the temperatures above 70 ^{0}C at which a lot of living beings cannot live (İlkilic and Deviren, 2011).

Thirty percent and the remaining 70% of the methane occurring in biogas processes form the result in Equation (1) and Equation (2), respectively (İlkilic and Deviren, 2011).

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ **(1)**

$CH_3COOH \rightarrow CH_4 + CO_2$ **(2)**

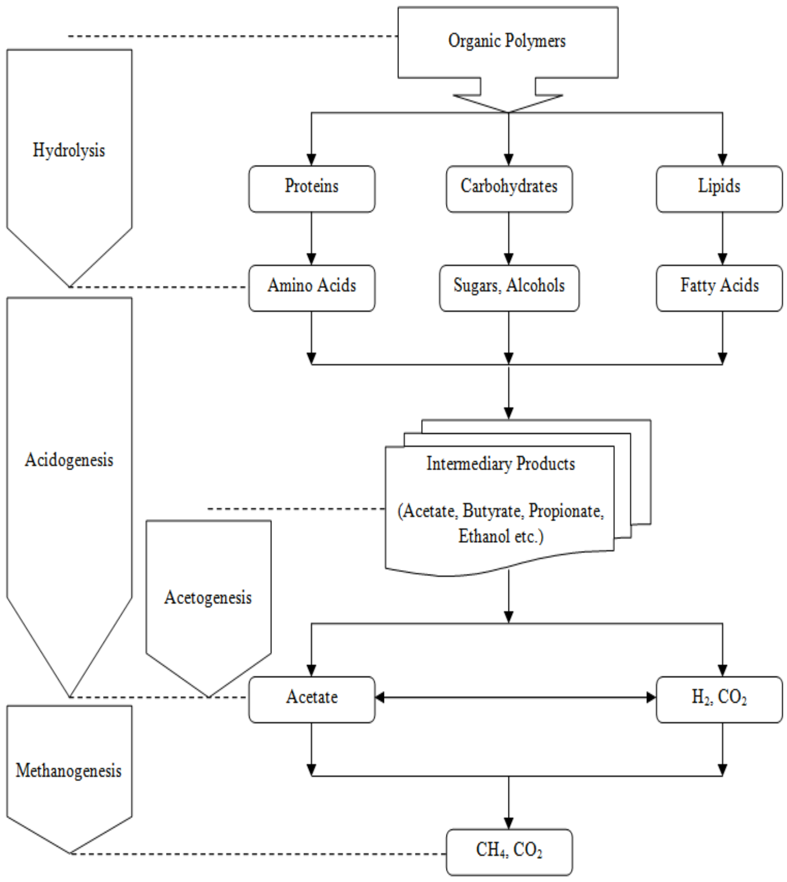

Figure1. Stages of anaerobic fermentation (Lam and Lee, 2011)

In the two-stage biological hydrogen production processes, however, biohydrogen processes are operated by applying heat pretreatment to anaerobic fermentation bacteria for 20-45 mins and between 90-105 ^{0}C. In the first stage, organic wastes with high carbohydrate ratio are degraded by heat pretreated anaerobic fermentation bacteria (*Clostridium* species, mixed vaccine obtained from anaerobic treatment sludge, soil) into organic acids, H_2 and CO_2. In the second stage, the organic acids produced in the first stage are degraded to H_2 and CO_2 with fermentative bacteria.

Acetic acid and butyric acid are used as indicators in hydrogen production in acidogenic systems. In general, the higher ratio of acetic acid and butyric acid gives a higher theoretical hydrogen yield than the stoichiometric equations. The reaction equations are simply shown below (Cavalcante De Amorim et al., 2009).

$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH$ (acetic acid) $+ 2CO_2 + 4H_2$ **(1)**

$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH$ (butyric acid) $+ 2CO_2 + 2H_2$ (**2**)

2.2. Factors Affecting Production

Anaerobic Environment and Bacteria: Obtaining good gas production efficiency depends on the environment being under anaerobic conditions in biogas and biohydrogen processes. In order to provide a good efficiency to biogas systems, the environment should be kept dark. In biohydrogen systems, however, there are production processes that require and do not require light (İlkilic and Deviren, 2011 ; Öztürk, 2008). However, since hydrogen production efficiency obtained in the dark environment do not require sunlight or artificial light as a source of energy, it is the most effective process to be used among the biohydrogen production methods. In biohydrogen production works, due to the economic difficulties, sterilization and the difficulty to work with pure species, the mixed consortium obtained from different sources (compost, soil, anaerobic treatment sludge, municipal sewage sludge) in general has become the most frequently used vaccine type. The system is processed by applying heat pretreatment to these vaccine types for 20-45 mins and between 90-105 ^{0}C in general. In biogas production works, on the other hand, the system is processed generally without applying pre-treatments to vaccine types.

Organic Loading Rate and Hydraulic Retention Time: Biohydrogen production rate can be determined by testing the parameters such as HRT and OLR at suitable intervals. In particular, high organic loading rates and low hydraulic retention times are determined to increase the speed of volumetric hydrogen production (Genc, 2010). Biogas processes, since feeding would be made more than the methane bacteria can use at high organic loading rates, cause pH value to fall and thus can result in negative effect. HRT can change depending on the type and temperature of the organic matter (İlkilic and Deviren, 2011).

Substrate Resources: Biofuel production efficiency can be increased by using high carbohydrate content waste or wastewater as substrate. While substrate source is determined, the cost, availability, degradability and carbohydrate content thereof are considered (Azbar et al., 2009). According to the literature, hydrogen production potential of carbohydrate-rich wastes is 20 times larger than the wastes with high protein and fat ratio (Genc, 2010). In biofuel production, the use of biomass with high organic carbohydrate content (fruit processing plant wastes, kitchen wastes, confectionery plant wastewater etc.) is the most important criterion. Carbohydrate rich biomass (substrate) resources are presented in Figure 2.

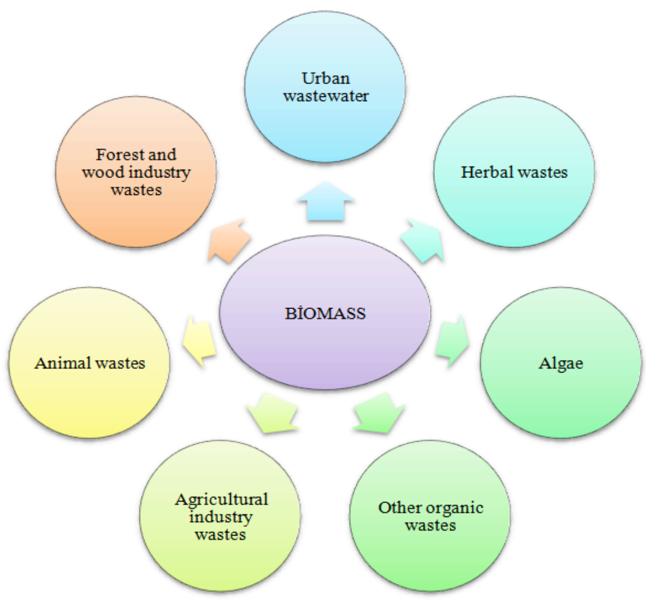

Figure 2. Biomass resources

Nutrients: The bacteria active in biogas production need nitrogen, phosphorus, potassium, calcium, sulfur, magnesium, manganese, iron, molybdenum, cobalt, zinc, nickel and selenium as well as carbon and hydrogen. All of the organic matters contain carbon, hydrogen and nitrogen. Many trace elements are effective in biohydrogen production, but the most effective elements are determined as nitrogen, zinc, iron, sodium and magnesium (İlkilic and Deviren, 2011 ; Azbar et al., 2009).

Toxicity: Detergents like soap, disinfectants, antibiotics and heavy metals prevent the growth of bacteria in gas biofuel (biogas and biohydrogen) production and cause a toxic effect (Gulen and Cesmeli, 2012).

Temperature and pH: Temperature is an important parameter in biogas systems for metabolic rate and solubility of nutrients. Biogas, for reproduction and efficient production of bacteria, is generally employed between two temperature ranges, thermophilic and mesophilic. Since 50-60 ^{0}C thermophilic temperature ranges require more use of energy, operation is mostly made between 30-40 ^{0}C mesophilic temperature ranges. However, the process is operated between 15-20 ^{0}C psychrophilic temperature ranges in regions with high temperature drop during winter. Anaerobic digestion process temperature ranges are presented in Figure 3. Optimum pH range is 7.0-7.5 for biogas and 4.5-6.5 for biohydrogen (İlkilic and Deviren, 2011 ; Gulen and Cesmeli, 2012). In the studies conducted, minimum pH values that will affect bacteria negatively in gas biofuel processes have been determined. In biogas systems pH value falling by 6.7 causes a toxic effect on bacteria. This increases the number of bacteria forming acid, and thus reduces pH and stops methane formation. In biohydrogen systems, however, synthesis of organic acids causes pH value to fall. Drop by 4.5 in pH value reduces hydrogen production efficiency.

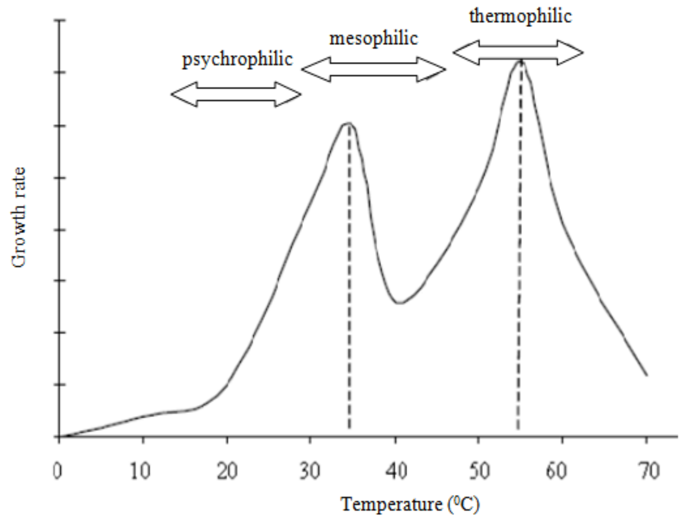

Figure 3. Anaerobic digestion process temperature ranges (Azbar et al., 2013)

Reactor Configuration: The high rate of methane production is also dependent on the reactor configuration as well as optimum operating conditions. In two-stage anaerobic digestion, while the first stage is comprised of hydrolysis and acetogenesis and the second stage is comprised of acetogenesis and methanogenesis. In these processes, the step of hydrolysis and acetogenesis in a separate reactor ensures that this step is more controlled and the acidification efficiency is increased. The higher the acid production, the more efficient the second stage becomes. When two-stage and single-stage anaerobic digestion processes arecompared, methane production yield is higher in two-stage processes (Demirer and Chen, 2004 ; Hawkes et al., 2007 ; Guwy et al., 2011).

2.3. Areas of Use

Methane and hydrogen are used in various fields. In addition, by-products resulting from gas production can also be used for different purposes.

2.3.1. Biogas (Methane) Application Areas

Biogas is a gas mixture resulting from decomposition of organic substances in an anaerobic environment. The areas of use are presented below in general. The composition of the biogas is given in Table 1.

Table 1. Biogas composition (Öztürk, 2008 ; Acaroglu, 2003 ; Çallı, 2012)

Gas	Volumetric composition (%)
CH_4	40-75
CO_2	30-40
N_2	0-7
O_2	0-0.5
H_2	0-1
H_2S	0-1

Use of heating: Biogas has burning characterization due to methane gas in its composition. Full combustion occurs when biogas is mixed with air at certain ratios (1/7). Cookers, ovens, water heaters and instant water heaters can be operated using biogas. Biogas can also be used in stoves. However, it requires the use of a chimney to prevent the "hydrogen sulphide" gas in its composition from diffusing into the atmosphere. For this reason, radiator heating systems should be preferred for better heating (Öztürk, 2008 ; Akinbami et al., 2001).

For use in engines: Biogas can be used in engines powered by gasoline by refining the methane in its composition. It can also be used directly without the need for any additives. In order to be used in diesel engines, it is necessary to be pre-mixed with diesel fuel at a rate of 18-20% (Öztürk, 2008 ; Porpatham et al., 2007 ; Weiland, 2003).

Use as an energy source: Biogas can be converted to electricity and used for lighting purposes. For direct lighting purposes, lamps working with liquefied petroleum gases are used. In these systems, amianthus shirt and bell glass are used to increase the lighting flame. The bell glass can support the flame to be bigger by returning the heat to the system, just as it fixes the light (Öztürk, 2008 ; Akinbami et al., 2001 ; Weiland, 2003).

Possibilities of use of the by-products: The waste or sludge from anaerobic reactor contains many trace elements such as phosphorus, nitrogen, potassium. For this reason, the sludge from the reactor can be used as soil remediation agent in terms of organic matter. Organic fertilizer obtained in liquid form as a result of biogas production can be applied in liquid form to agricultural areas. The most important advantage of organic fertilizer obtained as a result of anaerobic fermentation is that most of the pathogenic microorganisms are destroyed. This advantage ensures that organic fertilizer is about 10% more efficient (Öztürk, 2008).

2.3.2. Areas of Usage for Hydrogen

Hydrogen, which has flaming combustion feature, can be used as fuel in burners, internal combustion engines and gas turbines.

Use in internal combustion engines: Hydrogen burns 50% more efficiently than gasoline, resulting in less environmental pollution. It can be mixed with gasoline, methanol, ethanol and natural gas to reduce pollution. By adding hydrogen to the gasoline/air mixture of 5%, the nitrogen oxide emission can be reduced by 30-40%. In engines where pure hydrogen is used as fuel, only water and little nitrogen oxide is produced. Hydrogen is an ideal fuel. Problems such as condensation on cold surfaces, insufficient evaporation, poor mixing, etc., which are seen in fuel engines, are not present in hydrogen engines (Öztürk, 2008 ; Das and Veziroglu, 2001).

Use of hydrogen in other areas: Hydrogen is used in ovens, kitchen stoves and stoves due to its flameless (catalytic) burning feature. Several uses of hydrogen in the industry are given in Table 2 (Öztürk, 2008).

Table 2. Several uses of hydrogen in the industry (Öztürk, 2008)

As fuel	Welding flame In the metal heat composition In electricity generation In rockets
Catalytic hydrogenation	Vegetable oil hardening Alcohol production from fatty acids Artificial yarn production Medicine production Methyl alcohol synthesis
In metallurgy	As a reduction material Tungsten and molybdenum production

3. DISCUSSION AND CONCLUSION

Biofuels (bioethanol, biodiesel, biohydrogen and biomethane), sustainable and environmental negative effects compared to fossil fuels are the advantages of these types of fuel. In addition, the use of hydrogen gas, a gas biofuel, as a single fuel in space vehicles makes this fuel privileged. In our country, it is necessary to recycle the waste/wastewater with anaerobic processes in order to solve the energy problem and meet energy need. For this purpose, it is necessary to determine waste/wastewater energy production potentials, anaerobic degradation conditions and suitable production parameters and to develop gas biofuel technologies. As mentioned in our review study, there are many factors affecting the biogas and biohydrogen production with anaerobic fermentation. Optimization of the study parameters will increase the biogas and biohydrogen production efficiency in the works to be done. Therefore, in the future gas biofuel production works, in order to obtain better results than the previous works, the necessity to give extra importance to optimization of the factors determined in our paper is quite obvious. Biofuel production processes;

- They are cheap, sustainable and environmentally friendly processes.
- With waste recovery, energy is obtained by using biomass waste types such as urban wastes, wastewater, animal wastes, agricultural industrial wastes.
- Methane resulting from animal feces, which affect global warming, has a greenhouse effect twenty times higher than CO_2. Methane produced from biofuel processes can be converted to CO_2 by burning and the environmental adverse effects can be minimized.

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NOMENCLATURE

HRT: Hydraulic retention time
OLR: Organic loading rate

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