Impact of hydrogen potential on anaerobic digestion of organic waste

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Abstract: The world's waste deposit has become more important due to the growth of the world economy and demography. Biomethanation is method of choice for the treatment of fermentable fractions of municipal waste. However, low methane yield due to operational issues and process instability prevent this technology from being widely applied. It shows that biogas is made up of approximately 50-70% CH_4; 30-50% CO_2 from traces of other gases. Solutions for improving CH_4 production include controlling anaerobic digestion factors. These factors are essentially: the methanogenic potential, the carbon/nitrogen ratio (C/N), temperature, Hydrogen potential (pH) and tightness of the reactor. Among these factors, one of the most important, the pH, is analysed in this article in order to ensure production's optimization. 02 substrates are studied potato peel and cow's stomach waste: As results, the production of biogas varies constantly with the variation of pH. With a pH lower than 5 the production decreases. The best productions were obtained pH value between 6.9 and 7.4. That said, it is important to find a way to stabilize the pH variation in the production of biogas for better sustainability. Eggshell has been studied in order to maintain the balance and good results have been obtained.

1. Introduction

The management of municipal solid waste is a major concern, due to its negative effects on the environment and on sustainable development. Indeed, according to World Bank estimates, global waste production in 2018 represented 2.01 billion tonnes. The ineffective management of these is the source of many environmental problems and health risks. Thus, for several years, the need to reduce dependence on fossil resources and to ensure optimal waste management has accentuated the reflection on the production processes of bioresources, especially in certain African countries. Also the problems caused by fossil fuels lead to a quest for clean energy sources. To this end, several ways of recovering energy from waste have been developed, among which we have the methanation or production of biogas (gaseous mixture consisting essentially of CH_4 and CO_2) from waste by way of anaerobic digestion. This technique turns out to be a very interesting solution insofar as it can be extended to power plants for the production of electricity, in the production of heat, in cogeneration and in transport; moreover, the digestate can be evaluated in the processes of soil amendment and composting [1]. The use of biogas for energy production could thus replace fossil fuels, reduce greenhouse gas emissions and reduce dependence on imported energy. However, the process of transforming waste into an energy carrier (biogas) by way of anaerobic digestion has so far led to fairly low proportions of biomethane production. Several studies have demonstrated this, in particular Halil Şenol, Erika Winquist et al. which show that biogas consists of approximately 50 to 70% CH_4; 30 to 50% CO_2; 0.1 to 1% N_2, 0.01 to 0.2% O_2; 10-4000 ppm H_2S[2], [3]. This leads us to find out why this problem of non-optimization and how to achieve better energy yields because the more the biogas consists of CH_4, the better the quality of the biogas is.

Indeed, several authors in their work have evoked the important nature of pH whose mastery has a role in the optimization of anaerobic digestion. Usually, a pH between 6.2 and 8.2 is beneficial for anaerobic digestion. The methanogenic microbial community is also very sensitive to pH variations. This is why for the proper functioning of a digester the PH must be controlled, it affects the performance and stability of an anaerobic digester. **Essam Almansour** in his work "Energy and environmental balances of biogas sectors: Approach by type sector" highlights this consideration, it appears that the accumulation of volatile fatty

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acids or hydrogen can produce acidification in the methanizer and thus inhibit methanization. Therefore, it emphasizes to track the pH value and adjust it if necessary. This stabilization consists in the injection of soda detergent (Sodium Hydroxide) NaOH in liquid form to lower the acidity of the medium in the digester[1]. As for **LAURA ANDRE** in her work "Study of scientific and technological locks for the understanding and optimization of the process of discontinuous dry methanization of by-products of agricultural origin" explains that products such as sodium bicarbonate NaHCO3 are used to maintain the balance of anaerobic digestion[2]. The work of **Cun-fang Liu et al**., also goes in the same direction[3]. Others, however, use potassium hydroxide KOH for pH stabilization. The difference in pH variation in anaerobic digestion can vary from 0.8 or even 4.5 according to several authors depending on the conditions of anaerobic digestion and the types of substrates. It should be noted that this difference in variation can be seen in our work. The limit of this work is at three levels: first of all, most of these products used to maintain the balance of anaerobic digestion are chemical and therefore toxic substances, secondly all these substances are expensive and therefore do not allow a sustainability of the biogas sector and finally despite their use we always witness a fluctuation in pH during the reaction which makes it possible to say that the stabilization is temporary.

2. Materials et Methods

2.1. Substrates

The substrates used are organic residues from the city of Niamey (Niger). These are essentially: Potato peel as well as rumen waste.
A survey conducted in the city of Niamey shows a habit and a great consumption of potatoes in families, in restaurants, hotels and in all the crossroads of the city. It is eaten in the form of fries, stews, stir-fries, mashed potatoes, appetizers, vegetable sauces and even crisps.
On average, the capital of Niger consumes 100 tons of potatoes per day, or 3,000 tons per month. Indeed 1.3 billion FCFA are spent to meet the monthly need of the city of Niamey in potatoes, that is nearly 16 billion FCFA over the year. Most of it comes from outside the country, so Niger loses this financial windfall according to Agri Challenge journal of Niger.
It should be noted that the potato peels almost thrown in the trash represent 14% of the potato.
The city of Niamey also has a refrigerated slaughterhouse and according to the National Institute of Statistics of Niger, the cattle slaughter rate in 2019 represents 64,088 heads, i.e., an average of 175 heads per day.

2.2. Characterization of substrates

The rate of dry matter DM and volatile dry matter VDM were determined according to AFNOR NF U44-160 using a universal UN110 Memmert heating oven and a NABERTHERM L 9/12/B410 muffle furnace. Total carbon (TC) and total nitrogen (TN) were measured by a TOC meter. The pH was measured using a HANNA HI 98150 GLP pH/ORP METER equipped with an electrode and an integrated temperature sensor.

2.3. Anaerobic digestion

The production of biogas from treated organic waste was studied using the laboratory scale anaerobic digestion process with a 1 L reactor filled to 70%. To start the experiment, the raw material flow was a mixture of 50% substrate and 50% distilled water. The quantity of raw material introduced into the digester is therefore 350g against 350ml of water. The substrates were prepared and then loaded into the digester. The banana and potato peels were mixed into a paste of about less than 1mm using an electric blender.
The homogenization of the mixture was carried out using a magnetic stirrer at the speed of 300 rpm during anaerobic digestion. For the experiment, the production of the biogas of the substrates according to the variation of the pH was studied. The experiment was conducted in this work under mesophilic temperature conditions of 35°C using a JBL PROTEMP S 300 thermal regulator, over a hydraulic retention time of 21 days. The initial pH of some substrates was adjusted before the start of the reaction and during the process from a solution of potassium hydroxide (KOH) in the range of 7-8.2 considered as optimal pH. The pH variation was monitored during production. The daily biogas production was measured by the water displacement method. it is presented in the following figure 1:

Fig.1: Biodigester and anerobic digestion

2.4. Co-digestion

Always with the aim of balancing the pH and thus improving the production of biogas, co-digestion was carried out according to the following plan:

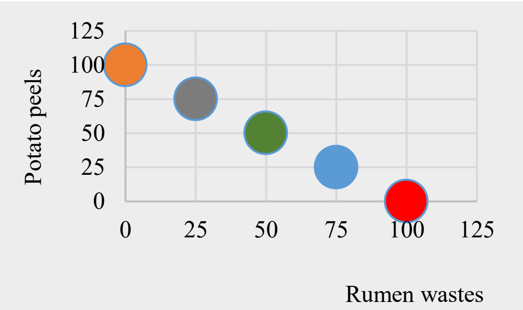

Fig 2: Mixing plan

2.5. Difference between the effect of KOH and eggshell in anaerobic digestion

The effect of eggshell on anaerobic digestion was also investigated to analyze a possibility of replacing chemicals such as KOH used to maintain buffer balance. The eggshell is dried in the oven and then ground into powder and dissolved. It should be noted that according to the literature the eggshell consists of 94% calcium carbonate and a small amount of organic matter estimated at 2.3%. It contains 37.5% calcium and 58% carbonate but also portions of magnesium and phosphorus.

3. Results and Discussions

3.1. substrates characterization

Table 1 presents substrates characterization. the interpretation of the results will be presented in the discussion.

Table 1: Substrates characterization

Substrates characterization	**Potato peels**	**Rumen wastes**
Dry matter (DM)%	22,13	14,97
Volatil dry matter (VDM) %	85,79	83,4
Initial pH	4,25	8,41
Ratio Carbon/Nitrogen (C/N)	35,11	17,1

3.2. Variation of biogas production in function of pH.

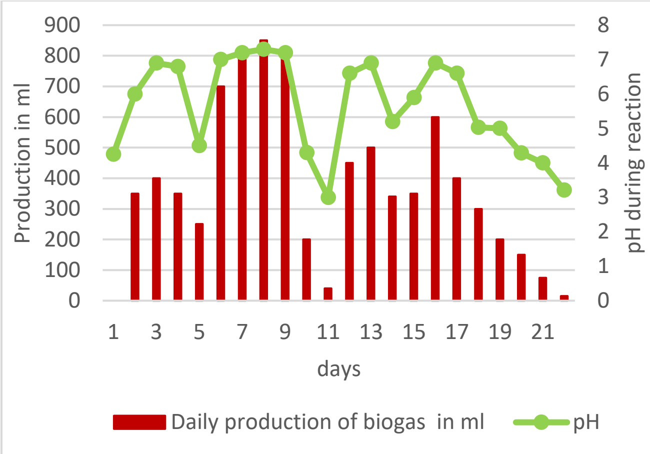

Fig. 3: Variation of biogas production from de potato peels in function of pH.

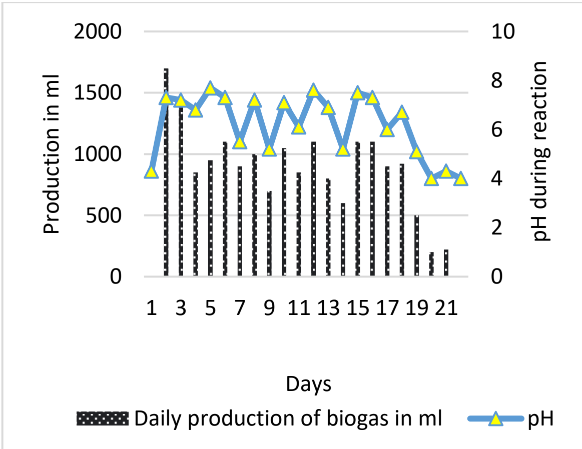

Fig. 4: Variation of biogas production rumen wastes in function of pH

Table 1 above presents the results of substrates characterization:

- The three 02 substrates have a dry matter rate greater than 10%. In the literature, according to several authors such as Weiland et al., we speak of wet digestion when the rate of dry matter in a substrate is less than 10% [4]. However, authors such as Laura et al., in these works set this value below 15% and beyond that we speak of dry digestion [2]. According to the advantages of wet digestion; to opt for this method in our case study, it will be necessary to go through a dilution in aiming to have a dry matter content of less than 15%.
- pH is a key parameter in anaerobic digestion. Having good anaerobic digestion amounts, according to several authors, to stabilizing the pH around 7. A pH favorable to the survival and activity of microbial species can therefore be between 6.2 and 8.2 according to the literature[4], [5]. In the case of this characterization, we note that.

- To grow, bacteria use nitrogen and carbon. The nutrient content, respectively the C/N ratio should be well balanced to avoid process failure by ammonia accumulation. The C/N ratio should be between 15 and 30[4].

Fig. 3 et 4 show the variation of biogas production as a function of pH. Each of the three materials behaves differently. But the general observation is as follows: each time the pH of the substrate drops, the production of biogas drops. This implies that the drop in pH during the reaction negatively affects the biogas yield. This drop in pH results in an increase in the production rate of the volatile fatty acid. Note that in this case during the reaction the pH is gradually stabilized by the addition of a KOH solution in order to maintain the buffering capacity of the reaction.

The initial pH of fermentable waste is very often lower than 6.5, however there are others whose pH is much higher than 7. The acid nature of the substrates would certainly be due to the presence of organic acid in these different wastes. . A pH lower than 6.5 causes an inhibition of the activity of microorganisms involved in the process of anaerobic digestion, in particular methanogenic bacteria. This is why many authors like ***Kouadio Marc Cyril; Pooria Latif; Wachiranon Chuenchart; Visva Bharati Barua and Hamdi Muratçobanoğlu*** [6]–[9] beyond the addition of KOH in their work proceeded to a co-digestion, that is to say a mixture of two or more substrates of different pH in order to bring the pH back to the optimal range. As part of this work, the maximum production was obtained at pH 7.4; 7.3 and 7.1 respectively for banana peel, potato peel and rumen rumen waste.

Table 2 opposite presents the codigestion work carried out by these authors as well as the values of the different pH.

Table 2. Mixture of substrates of different pH

Substrates	Cow manure	Food waste	Inoculum
pH	7,2	4,6	7,45
Authors	[6]		
Substrates	Water hyacinth	Banana peels	
pH	5,8	5,2	
Authors	[7]		
Substrates	Food waste	Chicken manure	Inoculum
pH	4,67	_	8
Authors	[8]		
Substrates	Poultry slaughterhouse wastes	Sewage sludge	
pH	6,2	7,1	
Authors	[9]		

As a result, these mixtures perform better than the substrates taken with their pH individually.

it should also be noted that co-digestion does not only improve the pH, the work carried out shows that it also improves the low carbon to nitrogen ratio of certain substrates. Hence it could be a good alternative to anaerobic digestion

3.3. Co-digestion

The results of co-digestion are as follows in Figure 5 below. It allows us to see the impact of a mixture on methanization.

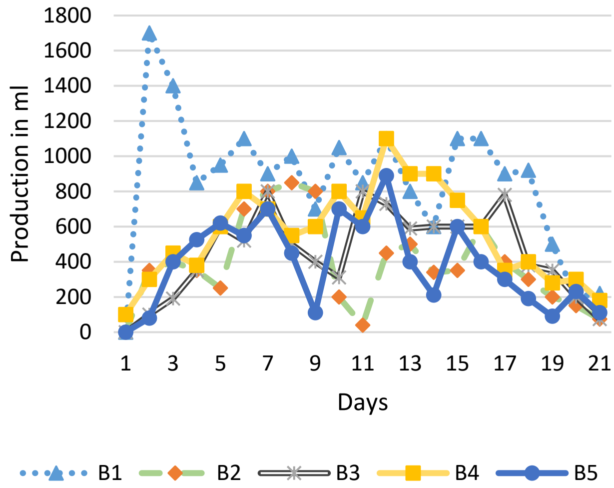

Fig 5: Co-digestion with Rumen waste (DPR)/Potato peels (EPT).

The legend of the figure of this co digestion is as follows:

Mixture	DPR%	EPT %
B1	100	
B2		100
B3	50	50
B4	75	25
B5	25	75

Figure 6 shows the cumulative production of biogas in 21 days to clearly see if the mixture has improved the anaerobic digestion of a substrate.

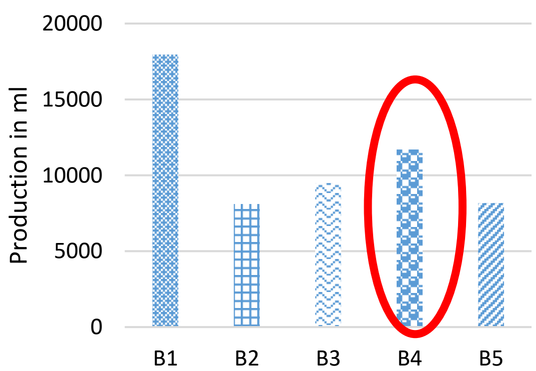

Fig 6: Cumulative production of biogas in 21 days

It is found that co-digestion had a positive effect on the monodigestion of potato peel.

Similarly, the B3 and B4 curves are much more stable than in monodigestion B1 and B2. This may be due to the fact that during a co-digestion the rate of nutrient it is at the rate of carbon and nitrogen is also very often improved.

Indeed, B3 and B4 have seen their cumulative production increased by 1370 and 3585 ml respectively compared to B2.

3.4. Difference between the effect of KOH and eggshell in anaerobic digestion

The best results of co-digestion, i.e., B3 and B4, have been chosen. then anaerobic digestion was followed. initially the balance was maintained with KOH and second stabilized with the eggshell. The results are as follows:

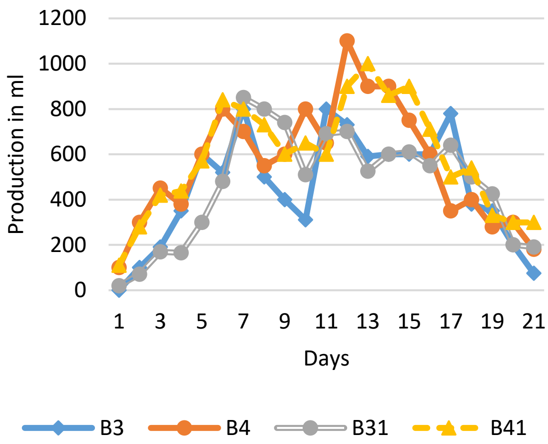

Fig 7: effect of KOH and eggshell in anaerobic digestion

The legend of the figure of this co digestion is as follows

Mixture	DPR%	EPT %	
B3	50	50	KOH
B4	75	25	KOH
B31	50	50	CO
B41	75	25	CO

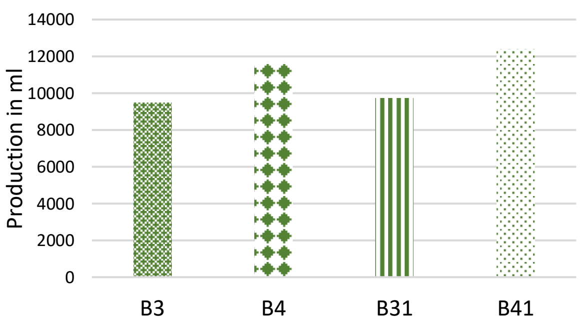

Fig 8: Cumulative production of biogas in 21 days

The chemical and expensive nature of sodium hydroxide has led to the use of the eggshell as a pH stabilizer and improve anaerobic digestion. It is then seen through the graphs that the variation of the curves B31 and B41 balancing with the eggshell are more stable than the curves B3 and B4 stabilized with the KOH. In addition, the cumulative production for 21 days shows that biogas production is better at B31 and B41 compared to B3 and B4. The eggshell could therefore be a means of exploration for the maintenance of pH balance.

4. Conclusion

The evaluation of the physical and chemical properties of these 03 substrates as well as the follow-up of the production of biogas according to the pH were carried out in order to analyze the behavior of the pH during the production in order to take initiatives for an optimum production. The production of biogas varies with the fluctuation of the pH. In fact, it drops each time the pH value tends towards acidity. The best productions were obtained at a pH between 6.9 and 7.4.

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