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Start-up strategy and process performance of semi-continuous anaerobic digestion of raw sugarcane vinasse

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Abstract

The sugarcane distillery waste water (vinasse) is generated throughout the sugarcane molasses fermentation and distillation. In Reunion Island, a part of the vinasse production is treated by anaerobic digestion process. However, the remaining part is diluted then discharged into the sea. The aim of this study is to propose an alternative solution in order to treat the vinasse while producing energy through anaerobic digestion. Vinasse pollutant load (chemical oxygen demand COD) is difficult to treat.

Regarding the experimentations, the biochemical potential (BMP) test is used for the determination of the methanogen potential. The BMP is then modelled with the modified Gompertz model, and first order regression. Furthermore, a pilot study (16 L) is carried out for studying the methane production of raw vinasse in semi-industrial scale over a period of 130 days. The sludge from the sugarcane distillery is used for the launch of the digester. The start-up strategy of the pilot for the anaerobic digestion of vinasse is proposed, in particular the gradual increase of organic loading rate. The physico-chemical analysis of the medium is needed to prevent and explain the failure of the process. Indeed, the methane production, the pH, the total and volatile solids, the COD, the total volatile fatty acids (VFA), the alkalinity and the ammonium concentration during the digestion are presented in this paper. The digestion occurs at 37°C and with minimal mixing: 15 min before sample collection at 20 rpm. The maximum methane yield of the BMP is 185.59 NL_{CH₄}.kg_{COD}⁻¹, obtained with I / S ratio in terms of volatile solids of 0.7. The outcomes showed that the first-order regression and modified Gompertz model fit well with the BMP test curves. Concerning the pilot test, the launching period lasted 45 days the maximum specific production was 151.00 NL_{CH₄}.kg_{COD}⁻¹ (232.31 NL_{biogas}.kg_{COD}⁻¹). In further studies, others mixing strategies and pre-treatment of vinasse will be studied.

Keywords

Anaerobic digestion
Sugar cane vinasse
Pilot scale
BMP
Process performance

1. INTRODUCTION

Anaerobic digestion is a widely used process for waste treatment and biogas production. Anaerobic digestion consists in the degradation of fermentable waste by microorganisms in absence of oxygen, unlike aerobic digestion. The biogas produced through anaerobic digestion is composed mainly of methane and carbon dioxide, with traces of hydrogen sulphide and water vapour. Anaerobic digestion respects the natural cycle of carbon. The five modes of valorisation of the biogas are (Bastide, 2015):

- Heat production, energy efficiency is interesting if the need for heat markets is important enough to maximise the value of available energy. It also requires nearby outlets to limit the costly transportation of heat or biogas.
- Electricity production, energy efficiency is lower (-37%) because of the energy yield of electricity being limited, for engines, to about 33%.
- The combined production of electricity and heat, also called cogeneration, is the most common way of biogas valorisation. In addition to the electricity generated by a generator, heat is recovered, mainly at the level of the cooling system. The valorisation of this heat requires an outlet nearby.
- Fuel for vehicles, to be used as a vehicle fuel, biogas follows a series of purification / compression steps. This valuation was mainly developed in Sweden and Switzerland.
- The injection of clean biogas into the natural gas network, in some European countries, the injection of biomethane into dedicated or non-dedicated networks is more common, for example in Sweden, Germany, Switzerland, and the Netherlands. The injection of purified biogas into the natural gas network is the most efficient method of upgrading. In France, many projects have been identified in 2012, particularly on the farm.



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Anaerobic digestion is very interesting for an insular territory such as Reunion Island, which remains today dependent on imported fossil energies. The ambition to achieve energy self-sufficiency by 2025-2030 was initiated by the Region in 2000 through its Regional Plan for the Development of Renewable Energies and Rational Use of Energy (PRERURE) (Farinet, 2010). Following the environment Grenelle, this ambition was relayed by the State with the GIP Project GERRI and it also materialised in 2009 with the program STARTER (Strategy of Energy Autonomy for the Recovery and Transition of the Reunionese economy) (Farinet, 2010). The PETREL report, prepared by the ARER (the regional energy agency of Reunion Island), presents an initial assessment of the Reunion energy mix in the horizons of 2020 and 2030 (Farinet, 2010). The demand and the electricity production are evaluated according to two scenarios, one of them following STARTER (Farinet, 2010). The valuation of biomass is preponderant in the latter scenario, especially as it provides a so-called "base" energy because it is permanently available (Farinet, 2010). According to a study conducted by ADEME in 2010, the methanisation of waste in Reunion Island corresponds to the production of 34.3 million m³ of biogas per year from 853 thousand tons of waste, of which: 44% of effluents from farming, 21% of agro-industrial effluents, 21% of sewage sludge, 11% of bio-waste and 3% of wet green waste (Farinet, 2010). The assumptions made are that 25% of the livestock effluents produced to date on the island will be valorised by methanisation by 2020 and 50% by 2030 (Farinet, 2010). The sewage sludge would be 91% mobilised, 44% wet green waste and 100% agro-industrial and biowaste effluents (Farinet, 2010).

In addition, the waste in Reunion is currently buried, however, this solution is not sustainable because the landfills are saturated. Concerning the vinasse, which is a sugarcane distillery waste water generated throughout the sugarcane molasses fermentation and distillation, they are first treated and then discarded on the high seas via an emissary at 80 m depth. Anaerobic digestion is the method widely used in the world to reduce the organic load of the waste, both liquid and solid. In Reunion Island, this process is used for the sewage sludge treatment and to the treatment of an agro-industrial effluent: the sugarcane vinasse. The sugarcane vinasse is treated with this process in many countries on an industrial scale especially in Brazil, India and South Africa with adapted processes and a simple acclimation of the microbial flora to the conditions of the vinasse. In Reunion Island, the first major methanisation unit was built at the Rivière du Mât distillery in 2011. Its implementation was directly linked to the drastic increase in energy costs over the last 5 years (Farinet, 2010), and an important need of wastewater treatment. The distillery produces 8,000 m³ of pure alcohol per year and the production of vinasse is around 600 m³.day⁻¹ during the sugarcane crop season (Farinet, 2010). Experimental results showed particular difficulties for methanisation, given high salinity and high organic matter content (80-120 kg_{COD}.m⁻³) (Farinet, 2010). The first phase of the project of anaerobic digestion of the vinasse (2011) concerned only half of the vinasse flow treated in a 5800 m³ digester. The organic load is thus reduced by 80% and the biogas produced is used in a steam boiler thus ensuring the energy autonomy of the process distillation (Farinet, 2010). In a second phase (2018), according to the outcomes obtained by the first anaerobic digester, an additional digester is being built to treat all the vinasse. The additional production of biogas will then be intended to produce electricity that will be sold to the electricity producer (Farinet, 2010). Vinasse is characterised as an highly polluting effluent, containing high levels of organic compounds and nutrients (mainly potassium but also nitrogen and phosphorous) (Cruz-Salomón et al., 2017; Ramos-Vaquerizo et al., 2018). Furthermore, vinasse are very aggressive and recalcitrant effluents, whose their direct discharge to water bodies and soil may cause severe environmental impact like salinity, sodicity, phytotoxicity, anoxia, eutrophication, death of aquatic life, and many severe health problems (Cruz-Salomón et al., 2017; Ramos-Vaquerizo et al., 2018). Due to the recalcitrant nature of the vinasse, the Rivière du Mât distillery in Reunion Island is constrained to treat a diluted vinasse to guarantee its anaerobic digestion while avoiding inhibitions of the process. The drawback is therefore the massive use of water for the anaerobic digestion of the vinasse. This



is why this study focuses on the anaerobic digestion of raw vinasse on a laboratory scale. The objective is to create a database on the anaerobic digestion of vinasse to study the impact of pre-treatments on the latter as well as industrial parameters (such as the configuration of the tank, agitation, rate of hydraulic profit, the organic load ...), in order to optimise the methane production of vinasse with the minimum addition of water.

Before the industrial treatment of a specific waste, the process must be studied on a laboratory and pilot scale. Indeed, biochemical potential test (BMP) are broadly used for evaluating the ultimate methane production from organic materials. The protocol of this test have been recently standardised because the outcome can vary significantly between laboratories (Holliger et al., 2016). Nevertheless, a key parameter of this test, the ratio of volatile solid (VS) from inoculum to VS from the substrate (I / S ratio) depends on the substrate (Holliger et al., 2016). The ratio should be between two and four for most applications (Holliger et al., 2016). However, for less degradable substrates, a ratio less than or equal to one can be applied, and only if two ISRs lead to the same BMP, one can assume that there was no overload or inhibition (Holliger et al., 2016). Concerning unknown substrates, the authors recommend to test several ratios (Holliger et al., 2016). Thereby, in this study, we test various ratios in order to evaluate the methane yield of the sugarcane vinasse.

There is no standardised method for the pilot experiments. Studies have recently been carried out on pilot tests on sugarcane vinasse, mainly in co-digestion. Among these studies, we find the work led in 2015 on start-up strategies of anaerobic co-digestion of sugarcane filter cake and bagasse (Janke et al., 2016). When launching their pilot digester, the load increase is done gradually and the steady conditions were obtained after 70 days (Janke et al., 2016). The effect of total solid was studied with the addition of water (Budiyono et al., 2014). The result showed that vinasse / water ratio of 1 / 3 (TS 7.015%) produced the maximum total biogas (37.409 mL.g_{COD}⁻¹) however vinasse / water ratio of 1 / 2 (TS 9.310%) had the biggest COD removal (23.580%) than others (Budiyono et al., 2014). Moreover, in a study published in 2015, the authors said that biogas production failed when sugar beet vinasse alone was fed to the reactor (Moraes et al., 2015). For this reason, they studied the added cow manure during digestion, which has the consequence of increasing the C / N ratio, which is low in the case of vinasse substrate (Moraes et al., 2015). Anaerobic digestion was the most stable when cow manure was supplied to digestion of vinasse (Moraes et al., 2015). The steady conditions were obtained after 50 days (Moraes et al., 2015). Another study has been carried out on vinasse in 2016 in order to evaluate the anaerobic conversion of vinasse into biomethane with gradual increase in organic loading rate (OLR) in two up flow anaerobic sludge blanket (UASB) reactors of 21.5 L (R2) and 40.5 L (R1), in mesophilic conditions (Barros et al., 2016). The OLR values applied in the reactors were 0.2–7.5 g_{COD}.L⁻¹.d⁻¹ in R1 and 0.2–11.5 g_{COD}.L⁻¹.d⁻¹ in R2 (Barros et al., 2016). The average COD removal efficiencies ranged from 49% to 82% (Barros et al., 2016). In 2017, co-digestion of sugarcane press mud with vinasse was studied in order to improve the digestion of press mud (López González et al., 2017). The methane yield was 64% higher in case of co-digestion compared to mono-digestion of press mud and the process was more stable (López González et al., 2017). All these studies show that co-digestion of vinasse improves yields and stabilises the process. Nevertheless, in this study, we will not carry out experiments in co-digestion. We present the outcomes for the case of vinasse in mono-digestion and slowly increase the OLR to avoid destabilisation of the process as (Moraes et al., 2015).

Furthermore, these studies previously mentioned presented examples of pilot launching. We retain from these articles that the pilot digester must be launched with inoculum (such as manure or sludge), followed by the micro-organisms acclimation and then a gradual increase in load. In this paper, we present the methodology and outcomes for the vinasse and sludge characterisation especially the BMP test of raw vinasse, the pilot launching and the monitoring of experimentation over a period of 130 days. The aim of this study is firstly to propose a protocol for launching a pilot with raw vinasse as substrate. Secondly, we study the increase of OLR of the pilot while following the physico chemical properties of the medium to avoid dysfunctions of the process in case of an



increase of OLR too fast. Finally, we study the pilot in steady-state conditions while following the physico chemical properties. In this work, we choose to not adding chemicals to adjust the physico-chemical parameters are not optimal, and to not dilute the vinasse. Indeed, we want to obtain data without interfering with the process and let the process stabilise alone. This case has not been studied yet. The data produced will allow us to create an experimental database to study the impact of mechanical agitation on the anaerobic digestion of raw vinasse in further studies.

2. METHODOLOGY

2.1 Substrate and inoculum

The vinasse and the sludge come from the active mesophilic biogas plant of the sugarcane distillery Rivière du Mât (Saint-Benoit, Reunion Island). The sludge is used as the inoculum in the biochemical potential (BMP) tests and the launching of the pilot digester. It is then stored at ambient temperature and incubated at 37°C before the BMP tests, which is the process temperature (mesophilic conditions). Regarding the vinasse, it is stored in cold storage at 4°C before the tests in order to avoid the degradation of the substrate before the digestion in the pilot. The vinasse is stored in the cold storage for a maximum of two months before being used. In this study, the vinasse is not frozen because the freezing has the effect of breaking up the cells, which improves the digestion of the latter.

2.2 Physicochemical analysis

Table 1 Physico-chemical characteristics of vinasse and sludge

Characteristics	Sludge	Vinasse
TS %	1.99	6.64
VS %	0.72	4.04
MES g.L ⁻¹	-	10.0
pH	4.84	7.57
COD gO ₂ .L ⁻¹	11.60	86.70
TOC mg.L ⁻¹	-	29 875
VFA g.L ⁻¹	16.34	19.36
Am mg.L ⁻¹	-	37.40
Alk mg _{CaCO₃} .L ⁻¹	2,361.9	1,080.6
N mg.L ⁻¹	1070	1120
Phosphorus mg.L ⁻¹	-	190
Alk/COD	0.204	0.013
VFA/alk	6.92	17.91
C / N ratio	-	26.67

The substrate and inoculum are homogenised with the Ultra turrax IKA T25 digital at 12,000 rpm for 10 min before the characterisation tests. We carried out total solid (TS), volatile solid (VS), pH, chemical oxygen demand (COD), total organic carbon (TOC), volatile fatty acids (VFA), ammonium (Am), alkalinity (Alk) and Kjeldahl nitrogen (Ni) measurements. The TS content is obtained after drying 20 g of the samples for 24 h at 105°C and the VS content after burning the dried samples for 4 h at 550°C. The chemical tests were conducted on the Hach Lange DR5000 Spectrophotometer, using the Hach Lange tests LCK 914 (COD), LCK 381 (TOC), LCK 365 (VFA), LCK 303 (Am), LCK 362 (Alk) and LCK 338 (Ni). The physico-chemical characteristics of the vinasse and the sludge are given in the Table 1.

The BMP tests are carried out using the Automatic Methane Potential Test System II (AMPTS II - Bioprocess Control). We refer to the last recommendations for the BMP test organisation (Holliger et al., 2016). The tests are carried out in mesophilic conditions in 50 days. As the substrate is



unknown, we must test different inoculum to substrate ratios. The ratios of COD from the substrate to VS from the inoculum tested are 1, 2, 2.5 and 3, which corresponds to a ratio of VS from the inoculum to VS from the substrate of 1.8, 0.9, 0.7 and 0.6. The total volume of the digesters is 650 mL. The operating volume is 400 mL. The digesters volume are adjusted with distilled water in order to have the same test working volumes. The experiment includes substrate tests, the positive tests and the blank tests. All the tests are carried out in triplicates. The BMP value is expressed in the volume of methane produced per gram of organic matter which is expressed in COD as the vinasse is liquid.

2.3 The biodegradability and the COD removal

The biodegradability of the substrate in the BMP test is estimated by the following equation:

$$B = \frac{Y_{\max}}{350} \quad (1)$$

Where 350 represents the theoretical maximum biodegradability of methane expressed in liters of methane per kilogram of removal COD at normal temperature and pressure.

The COD removal is calculated by the following equation:

$$R = \frac{M_{COD,digested}}{M_{COD,added}} * 100 = \frac{M_{COD,added} - M_{COD,pilot}}{M_{COD,added}} * 100 = 100 - \frac{M_{COD,pilot}}{M_{COD,added}} * 100 \quad (2)$$

Where, $M_{COD,added}$ is the cumulated mass added in terms of COD, $M_{COD,digested}$ is the cumulated digested mass in terms of COD and the $M_{COD,pilot}$ is the COD measured on the sample collected from the pilot.

2.4 Kinetic models and statistical analysis

According to Kim and al. (2003) anaerobic degradation after initial lag-phase time is limited by the terms associated with substrate and kinetics, which generally could be represented by a first order kinetic law with some assumptions (Kim et al., 2003). According to the approach reported by Llabres-Luengo and Mata-Alvarez (1987), the first order linear regression is (Llabres-Luengo and Mata-Alvarez, 1987):

$$Y(t) = -Y_{\max} (e^{-kt} - 1) \quad (3)$$

Where Y_{\max} is the maximum methane production ($NL_{CH_4}.kg_{COD}^{-1}$) and k the kinetic constant (day^{-1}).

It has been shown that the BMP fits with the modified Gompertz equation in case of mono-digestion is (Kim et al., 2003; Lay et al., 1997):

$$Y(t) = Y_{\max} * \exp \left[-\exp \left(R * \frac{\exp(1)}{Y_{\max}} * (\lambda - t) \right) + 1 \right] \quad (4)$$

Where λ is the lag-phase time (day).

The root mean square error (RMSE) and determination coefficient R^2 are used to evaluate the model results. The RMSE is expressed as follows:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (Y_{m,i} - Y_{c,i})^2} \quad (5)$$

Where n is the number of measurements during the experiment, $Y_{m,i}$ is the measured cumulative methane production ($NL_{CH_4}.kg_{COD}^{-1}$) and $Y_{c,i}$ is the calculated cumulative methane production potential ($NL_{CH_4}.kg_{COD}^{-1}$).

As mentioned in the last recommendations for the BMP tests, test results must be rejected if the standard deviation is upper than 10% as vinasse is a heterogeneous substrate (Holliger et al., 2016). The standard deviation is calculated with the following equation:

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^n (x_i - \bar{x})^2} \quad (6)$$

2.5 Pilot tests

2.5.1 Degradation index

The degradation index is calculated according to the following equation (Janke et al., 2016):

$$D_{index} = \frac{SMP}{TMP} \quad (1.7)$$

Where, SMP is the specific methane production and TMP the theoretical methane production.

2.5.2 The pilot set-up

The set-up of the pilot is shown in Fig. 1. The total volume of the pilot is 16 L. The operating volume is 14.5 L and the gaseous sky is 1.5 L. The experiment is carried out in mesophilic conditions at 37°C in order to limit energy consumption. The temperature is controlled with water recirculation in the double membrane. The water is maintained at a constant temperature with a thermostatically controlled water bath. The stirring is mechanical whose intensity varies from 20 rpm to 100 rpm. The biogas volume is measured with a bucket counter. The biogas is then temporally stored in a gas storage pocket and then analysed in terms of proportions of methane, carbon dioxide and oxygen.

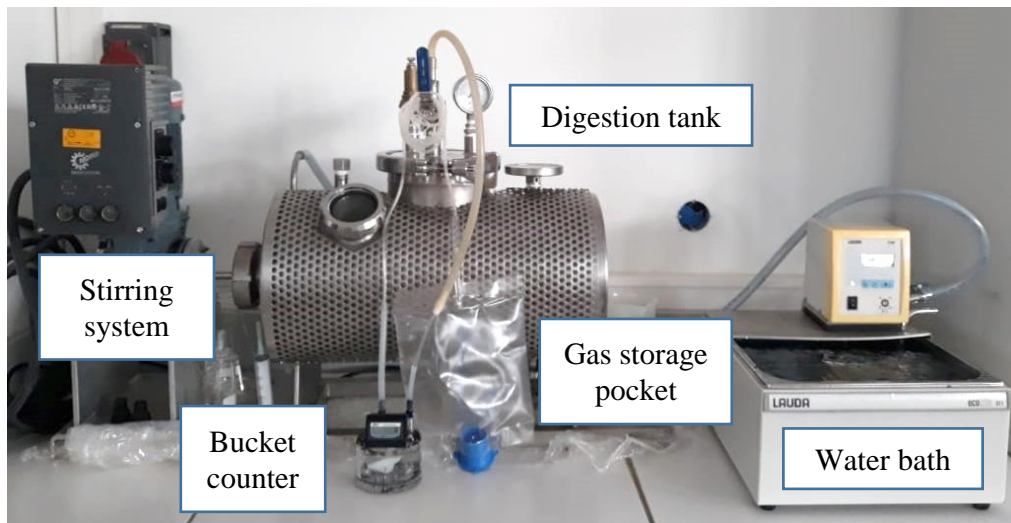


Fig. 1 Pilot 16-l set-up

2.5.3 Pilot launching and monitoring

For the launching of the digester, the digester is filled with 13.5 L of sludge from the sugarcane distillery (which corresponds to 97.20 g_{Vs} and 156.60 g_{COD}) for the micro-organisms input and 500 mL of vinasse (which corresponds to 24.40 g_{Vs} and 43.35 g_{COD}). The physico-chemical properties of the sludge are presented in Table 1. As the sludge comes from the same distillery of the vinasse, the sludge is already acclimatised to the vinasse and therefore, acclimatisation period is not needed. Next, the digester is fed with 500 mL of vinasse and a digestate sample of 500 mL is taken once a week during one month. Experimentally, for the digester feeding, we have to open it to recover the digestate and add the substrate. The objective of the launch of the pilot phase, is to gradually replace the sludge by the vinasse. We slowly feed the digester with vinasse in order to avoid inhibitions and failure of the process. The major drawback of the feeding of the digester is the fact of allowing oxygen to enter the medium, which must stay anaerobic.



Physico-chemical tests are carried out on the digestate samples: the pH, the COD, the ammonium, the VFA concentrations, alkalinity and the TS and VS percentages. The biogas volume is measured with a bucket counter and then stocked in a 1500 mL gas storage pocket and daily analysed in terms of percentage of methane, carbon dioxide and oxygen.

As previously said, if the physico-chemical parameters are not optimal, we do not adjust them with addition of chemical, but change the organic loading rate.

2.5.4 Mixing conditions

During the launching of the pilot, the mixing is minimal: 15 min at 20 rpm before the taking of sample in order to homogenise the medium. This choice is made in the aim to homogenise the medium before taking a sample without destabilising the process or the bacterial centers. Indeed, opening the pilot and allowing oxygen to enter necessarily disrupts the process that can cause the death of methanogenic bacteria, and so the reduction of the population of micro-organisms. Moreover, as the growth of methanogenic populations is slow, we must preserve them.

Then the minimal mixing was maintained during two weeks before modification. Indeed we then tested intermittent agitation: 10 hours per day at 20 rpm. As it revealed an absence of biogas production, the mixing was stopped and returned to minimal agitation for the rest of the experiment. We supposed that the continuous stirring prevented the micro-organisms from digesting the substrate. Consequently, the OLR was changed, in order to recover initial physicochemical parameters and biogas production. Indeed, according to Vavilin et Angelidaki (2005), during the launching of the digester, the methanogenesis is the limiting-step, consequently, vigorous agitation must be avoided to prevent the dissipation of methanogenic centers (Vavilin and Angelidaki, 2005).

2.5.5 Organic loading rate (OLR)

The Table 2 shows the OLR used in literature for vinasse in case of mono and co-digestion. The maximum OLR in terms of volatile solids is 3.0 and 11.5 in terms of COD. During the digestion of the sugar beet vinasse and press mud, the authors make the choice to dilute the vinasse with water. In addition, recirculation makes it possible to reduce the dilution of the vinasse (Barros et al., 2016). Moreover, press mud is used as co-substrate for the digestion of vinasse (López González et al., 2017), or cellulose and straw for additional carbon source (Moraes et al., 2015). Vinasse having a pH lower than the optimal pH of the anaerobic digestion, the authors alkalise the vinasse by adding NaOH solution (López González et al., 2017).

Table 2 Organic load in literature

Source	Substrate	Remark	OLR range	
			$\text{g}_{\text{VS}} \cdot \text{L}^{-1} \cdot \text{d}^{-1}$	$\text{g}_{\text{COD}} \cdot \text{L}^{-1} \cdot \text{d}^{-1}$
(Jiménez et al., 2003)	Molasses	Mono-digestion	-	1.5-7.5
(Moraes et al., 2015)	Sugar beet vinasse	Dilution of vinasse Addition of cellulose and straw	2.0-3.0	-
(Janke et al., 2016)	Sugarcane filter cake and bagasse	Co-digestion Addition of water	2.0-3.0	-
(Barros et al., 2016)	Vinasse	Dilution with water, then recirculation Addition of NaOH	-	0.2-11.5
(López González et al., 2017)	Press mud and water Vinasse and press mud	Mono-digestion with addition of water co-digestion	0.5-2.2	-



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With this pilot test, we chose to study the vinasse in mono-digestion, in that respect, no addition of carbon source was made. Moreover, we also chose to not dilute the vinasse as we want to study the anaerobic digestion without consuming water. As these actions would help to stabilise the process, we have increase the OLR very gradually to avoid inhibitions of the process, which could occur under this conditions.

The organic load and the feeding frequency used in this study are recapitulated in the Table 3 for the whole study. The initial feeding is 13.5 L of sludge and 0.5 L of vinasse, which corresponds to $14.28 \text{ gCOD.L}^{-1}$. During the first study phase, the digester is fed with 500 mL of vinasse every two days. The biogas is produced in two days when adding 500 mL, which corresponds to an OLR of $0.85 \text{ gVS.L}^{-1}.\text{day}^{-1}$ and $1.51 \text{ gDCO.L}^{-1}.\text{day}^{-1}$. A low initial OLR is chosen because inhibitions due to an accumulation of VFA occur during an excessive OLR during the anaerobic digestion of the vinasse. The latter having a low C / N ratio, the inhibitions are frequent in the case of mono-digestion of vinasse.

The feeding frequency is then changed in order to open the digester less often, to reduce the oxygen input into the digester. Thus 750 mL of vinasse are added every three days, then 1000 mL every 4 days. During the next phase, the OLR is increased from 0.25 L.d^{-1} to 0.38 L.d^{-1} .

In case of a drop in biogas production, 250 mL of vinasse and 250 mL of sludge are added instead of 500 mL of vinasse. Sludge is introduced to input micro-organisms.

Table 3 Mixing strategies and organic load

Description	Period (day)	Mixing strategy	Feeding frequency	Average feeding rate		Average OLR	
				Sludge (L.d^{-1})	Vinasse (L.d^{-1})	($\text{gVS.L}^{-1}.\text{d}^{-1}$)	($\text{gCOD.L}^{-1}.\text{d}^{-1}$)
Initial feeding	0	No mixing	Initial	13.5	0.5	8.69	14.28
Launching of the pilot	1-28	Minimal mixing*	Once a week	-	0.07	0.25	0.45
	29-42	Minimal mixing	Every 2 days	-	0.25	0.85	1.51
Continuous mixing test	43	10h at 20 rpm	Every 2 days	-	0.25	0.85	1.51
Resumption of minimal agitation	44-53	Minimal mixing	Every 2 days	-	0.25	0.85	1.51
Addition of sludge	54-63	Minimal mixing	Every 2 days	0.125	0.125	0.49	0.85
Modification of feeding frequency	64-68	Minimal mixing	Every 3 days	-	0.25	0.85	1.51
	69-72		Every 4 days				
Increase of OLR	73-112	Minimal mixing	Every 4 days	-	0.31	1.06	1.88
	113-130			-	0.38	1.27	2.26

*Minimal mixing: 15 min at 20 rpm before feeding.

3. RESULTS AND DISCUSSIONS

3.1 Biochemical potential test performance

The methane production of the vinasse and the blank are represented in Fig. 2. The maximum production is reached in 12 days for the vinasse and in 43 days for the inoculum. The biochemical potential of vinasse measured with the ratios in terms of VS 0.9, 0.7 and 0.6 are almost the same (181.72 to 185.59 $\text{NL}_{\text{CH}_4} \cdot \text{kgCOD}^{-1}$). The maximum value is obtained with the ratio 0.7. The potential obtained with the ratio 1.8 is well below with a value of 152.95 $\text{NL}_{\text{CH}_4} \cdot \text{kgCOD}^{-1}$. As we obtained similar methane yields for different ratios, we can retain the BMP value. The biodegradability (B) for each ratio is given in Table 4. The biodegradability is 0.44 for the S / I ratio 1, 0.52 for the ratios 2 and 2.5, and 0.53 for the ratio 3. Thus, we recommend to use an I / S ratio inferior to 1 for the vinasse BMP and we retain the BMP value of 185.59 $\text{NL}_{\text{CH}_4} \cdot \text{kgCOD}^{-1}$.

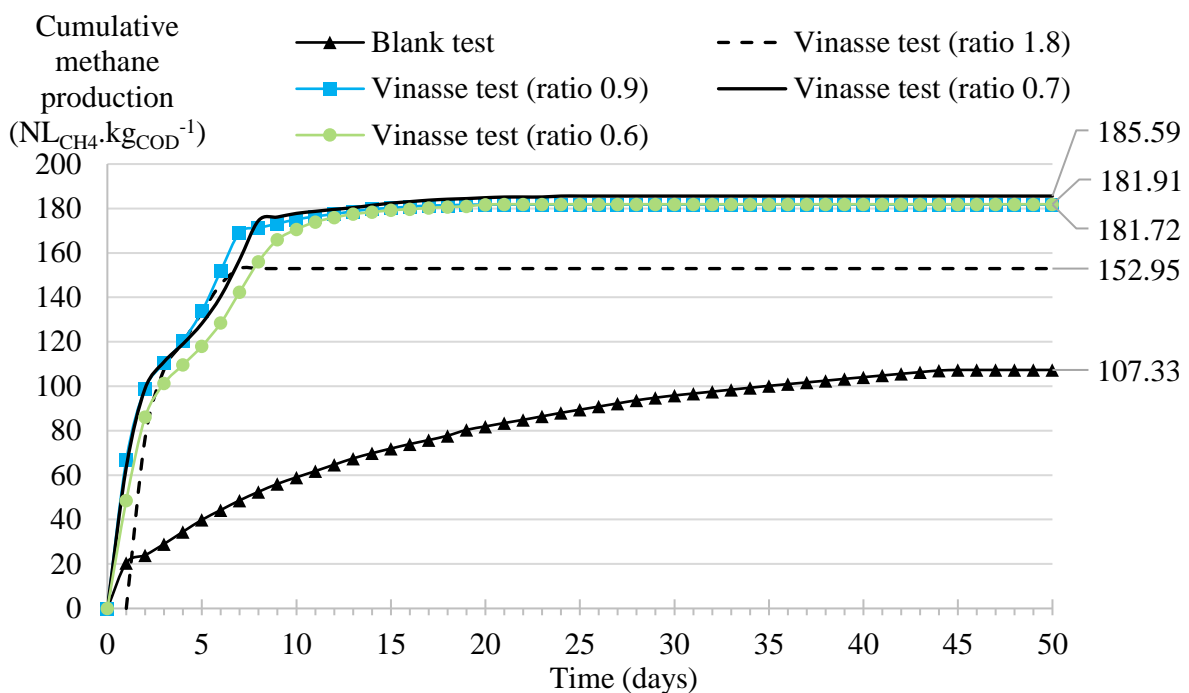


Fig. 2 Biochemical potential test results

Table 4 Methane yield

Ratio S / I	B	Methane yield		
		$\text{NL}_{\text{CH}_4} \cdot \text{kgVS}^{-1}$	$\text{NL}_{\text{CH}_4} \cdot \text{kgCOD}^{-1}$	$\text{NL}_{\text{CH}_4} \cdot \text{L}_{\text{sample}}^{-1}$
1	0.44	180.53	152.95	8.81
2	0.52	219.93	181.72	16.14
2.5	0.53	251.86	181.59	12.35
3	0.52	322.95	181.91	15.72

Table 5 Standard deviation

Ratio S / I	Standard deviation			Standard deviation		
	$\text{NL}_{\text{CH}_4} \cdot \text{kgCOD}^{-1}$			%		
$\text{gCOD} \cdot \text{gVS}^{-1}$	Min	Max	Average	Min	Max	Average
1	19.51	53.49	42.51	15	38	28
2	3.80	9.17	5.33	2	13	3
2.5	7.36	11.10	10.11	5	12	6
3	0.61	9.19	4.61	1	6	3



The methane yield in terms of COD, VS, sample and the standard deviation are given in Tables 4 and 5. We clearly see that the methane yield is becoming more important with increasing the ratio S / I. Moreover, we notice that the standard deviation is at least five times more important for ratio 1 than for the other ratios. The maximum standard deviation for the ratio 1 is 53.49 $\text{NL}_{\text{CH}_4} \cdot \text{kg}_{\text{COD}}^{-1}$ (38 %), which is upper than 10%, thus this test result must be rejected. Since the standard deviation for the ratio 1 is important, this means that the dispersion of the BMP results for this ratio is important, the average BMP results for this ratio is therefore not representative. We interpret this result as follows, for this ratio we put a sample mass too small to be representative of the substrate. Indeed, vinasse being heterogeneous, it requires a sufficiently large sample to be representative of the substrate in terms of methanogenic potential. We free ourselves from the heterogeneity of the vinasse by increasing the ratio S / I, allowing to obtain representative results with standard deviation less than 10 %. A second explanation is that inhibitions occur at this ratio, which would explain that the production of some BMP is lower. Concerning the other tested ratios, the average standard deviation is lower than 6 %, thus the BMP results are acceptable.

3.2 Regression analysis of BMP tests

The coefficients for the first-order regression and the modified Gompertz model for each ratio are given in the Table 6. The first-order regression provides the kinetic constant of hydrolysis, the highest value of 0.61 day^{-1} is obtained with the S / I ratio 1, the kinetic constant for the ratio 1 is rejected because this BMP was rejected. Then the kinetic constant decreases with the S / I ratio increasing. The kinetic constant is 0.32 day^{-1} for S / I ratio 2. The lowest value is therefore obtained with the S / I ratio 3 with a value of 0.25 day^{-1} . Thereby, despite the fact that the kinetic constant is higher for the ratio S / I 1 (I / S of 1.8), the maximum methane production is the lowest. Thus, lower kinetic coefficients lead to higher methane yields. Moreover, the average kinetic constant, rejecting the value of the ratio 1, is 0.29 day^{-1} . The kinetic constant values obtained are very closed, with a standard deviation of 0.04 day^{-1} (12 %). The kinetic constant will be used in biochemical model as the hydrolysis constant. As the hydrolysis phase is considered as the rate-limiting step, this coefficient is crucial in the anaerobic digestion modelling. The correlation factor is between 0.97 and 0.99 and the RMSE between 3.98 and $4.77 \text{ NL}_{\text{CH}_4} \cdot \text{kg}_{\text{COD}}^{-1}$. The modified Gompertz model provides the methane production rate and the lag-phase time. The methane production rate decreases with the increasing of S / I ratio from 56.16 to $27.43 \text{ NL}_{\text{CH}_4} \cdot \text{kg}_{\text{COD}}^{-1} \cdot \text{day}^{-1}$. The correlation factor is between 0.97 and 0.98 and the RMSE between 4.06 and $6.29 \text{ NL}_{\text{CH}_4} \cdot \text{kg}_{\text{COD}}^{-1}$.

Table 6 First-order regression and modified Gompertz model coefficients

Parameters		Units	Coefficients				
Ratio	S / I	$\text{g}_{\text{COD}} \cdot \text{g}_{\text{VS}}^{-1}$	1	2	2.5	3	A*
	I / S	$\text{g}_{\text{VS}} \cdot \text{g}_{\text{VS}}^{-1}$	1.8	0.9	0.7	0.6	
First-order regression	Kinetic constant k	Day^{-1}	0.61	0.32	0.29	0.25	0.29
	Maximum methane production Y_{max}	$\text{NL}_{\text{CH}_4} \cdot \text{kg}_{\text{COD}}^{-1}$	152.9	181.7	185.6	182.5	183.3
	Correlation factor R^2	-	0.97	0.99	0.98	0.99	0.99
	RMSE	$\text{NL}_{\text{CH}_4} \cdot \text{kg}_{\text{COD}}^{-1}$	4.60	4.01	4.77	3.98	4.25
Modified Gompertz model	Methane production rate R_m	$\text{NL}_{\text{CH}_4} \cdot \text{kg}_{\text{COD}}^{-1} \cdot \text{day}^{-1}$	50.39	28.54	25.44	22.01	25.33
	Lag-phase time λ	Day	0.866	1.483	1.598	1.967	1.683
	Maximum methane production Y_{max}	$\text{NL}_{\text{CH}_4} \cdot \text{kg}_{\text{COD}}^{-1}$	150.4	181.2	184.8	181.0	182.3
	Correlation factor R^2	-	0.97	0.97	0.97	0.98	0.97
	RMSE	$\text{NL}_{\text{CH}_4} \cdot \text{kg}_{\text{COD}}^{-1}$	4.06	5.65	6.29	5.53	5.83

*Average of BMP (ratio 2, 2.5 and 3)

The Fig. 3 shows the comparison between measured data, calculated data with the first order regression and the calculated data with modified Gompertz model for cumulative methane production at different S / I ratios. The correlation factor of the first-order regression is between 0.97 and 0.99. It is similar to the correlation factor of the modified Gompertz model, which is between 0.97 and 0.98. Concerning the RMSE, it is between 3.98 and 4.77 for the first-order regression, and between 4.06 and 6.29 for the modified Gompertz model. The first-order regression and the modified Gompertz model fit well with the measured data.

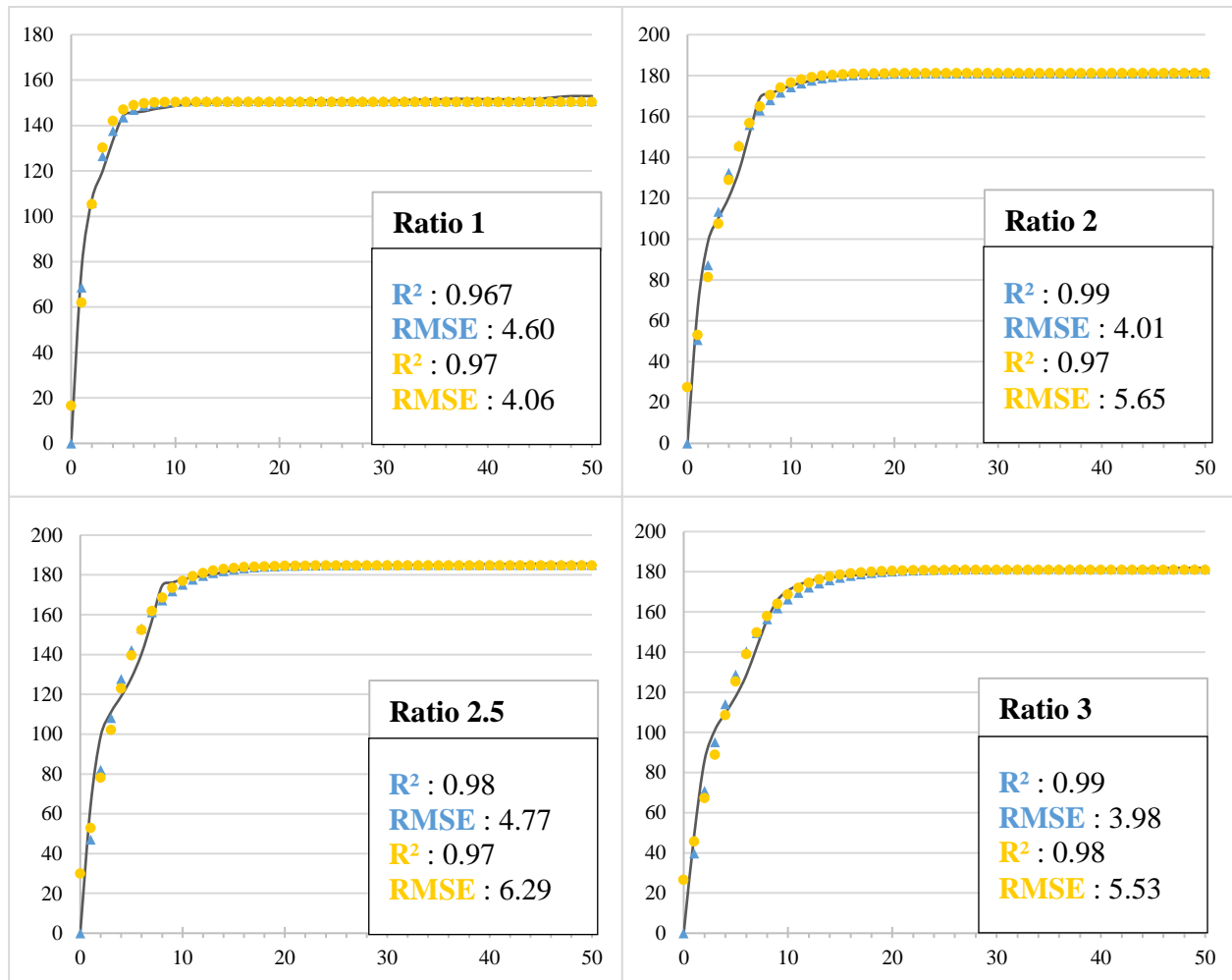


Fig. 3 Comparison between measured data (full line), calculated data with the first order regression (triangles) and calculated data with modified Gompertz model (points) for cumulative methane production at different S / I ratios (cumulative methane production in $NL_{CH_4}.kg_{COD}^{-1}$ in function of time in days)

In Table 7, we present the comparison of kinetic constant (first-order regression) with literature. In this paper, we retain the range 0.25-0.32 d^{-1} , we exclude the value 0.61 d^{-1} because the methane production of this BMP has a standard deviation upper to 10%. The average value is therefore 0.29 d^{-1} . Compared to literature, the kinetic constant found in this study is similar to the kinetic constant of vinasse with water with a value of 0.30 d^{-1} (López González et al., 2017) and vinasse with press mud with a range of 0.23-0.33 d^{-1} (López González et al., 2017).

Table 7 Comparison of kinetic constant (first-order regression) with literature

Source	Substrate	Kinetic constant range d^{-1}
This paper	Vinasse	0.25 - 0.32
	Vinasse + water	0.30
(López González et al., 2017)	Press mud	0.16
	Vinasse + press mud	0.23 - 0.33
(Iqbal Syaichurrozi and Sumardiono, 2014)	Vinasse + rumen	0.073 - 0.210
	Vinasse + rumen + urea	0.087 - 0.206

3.3 Pilot tests performance and physico-chemical analysis

3.3.1 The specific biogas production and COD removal

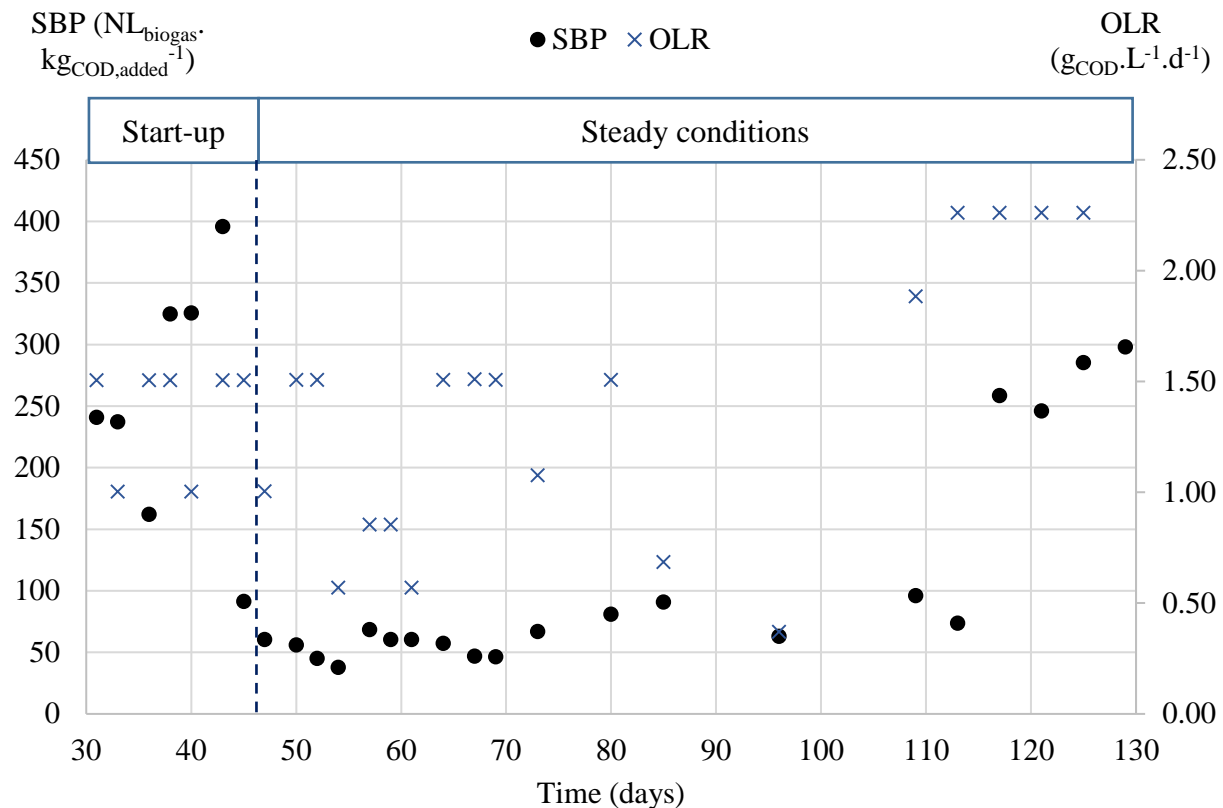


Fig. 4 Specific biogas production in $NL.kg_{COD,added}^{-1}$ and organic loading rate (OLR)

The Fig 4. shows the specific biogas production in liters per kilogram of COD added in the digester and the OLR. The graph illustrates two phases, the start-up phase from day 0 to day 45 and the steady conditions phase from day 46 to day 130. The steady conditions phase begins when the production of biogas stabilises. The duration of the start-up phase is in the same order of magnitude as the duration that the study (Moraes et al., 2015) which is 50 days. During the continuous agitation test (day 43), the production of biogas stopped, so we only tested this stirring for a period of 10 hours and then return to minimal agitation that we maintained until the end of the experiment. Thus, this agitation was tested just before the end of the pilot start-up period. However, as the production of biogas stabilises during the recovery of minimum agitation, we still consider that the steady-conditions phase starts on day 46. We conclude from this test that continuous agitation stops the production of biogas, this may be due to the fact that there is no longer sufficient contact between the microorganisms and the substrate. Stirring the medium only during the filling of the pilot is



enough in the case of the treatment of a liquid waste for the studied volume (16 L). However, it would be interesting to study other intensities of agitation.

During the period 113-130 days, the production of biogas per kilogram of COD is three times higher than in the previous period. It seems that the micro-organisms concentration is larger and the micro-organisms are better acclimated, which would explain this consequent increase in production. In fact, the TS and the VS of the sludge and the liquid phase increase over this period, which means that the amount of biomass increases within the digester. Thus, the physico-chemical conditions at this time are conducive to the anaerobic digestion of the raw vinasse.

Table 8 COD removal, specific methane production, specific biogas production and degradation index

Period (day)	COD removal	SMP*	SMP	SBP	D _{index}
	%	NL _{CH₄} .kg _{COD,r} ⁻¹	NL _{CH₄} .kg _{COD} ⁻¹	NL _{biogas} .kg _{COD} ⁻¹	
1-28	51	-	-	-	-
29-42	49	-	182.69	281.07	0.98
43-53	64	59.64	37.79	58.13	0.20
54-63	68	58.59	40.10	61.68	0.22
64-68	75	40.65	30.32	46.65	0.16
69-72	74	58.50	43.48	66.89	0.23
73-112	79	69.06	52.60	82.74	0.28
113-130	84.3	179.40	151.00	232.31	0.81
Steady conditions	73	87.54	68.21	104.93	0.37
46-130					

*COD_r: removal COD

The Table 8 shows the COD removal, the specific methane production (SMP), the specific biogas production (SBP) and degradation index. The biogas production during the start-up phase is more important than the production during the steady conditions phase. It goes from an average of 182.69 NL_{CH₄}.kg_{COD}⁻¹ during the period 29-42 days (start-up phase) to an average of 37.79 NL_{CH₄}.kg_{COD}⁻¹ during the period 43-53 days (beginning of the steady-conditions phase). Indeed, during the start-up phase, the production of methane is due to the digestion of the vinasse but also to the digestion of the sludge initially inserted into the digester. This is consistent with the BMP blanks assays where only vinasse sludge is inserted into the digesters, we note that the maximum production of methane is reached after days around 45 days, the same duration as the start-up phase.

The average production of biogas during the start-up phase is 281.17 NL_{biogas}.kg_{COD}⁻¹ and during the steady conditions phase is 104.93 NL_{biogas}.kg_{COD}⁻¹. During the steady conditions phase, the minimum and maximum biogas production are respectively 37.90 NL_{biogas}.kg_{COD}⁻¹ at day 54 (OLR is 0.85 g_{COD}.L⁻¹.d⁻¹) and 298.10 NL_{biogas}.kg_{COD}⁻¹ at day 130 (OLR is 2.26 g_{COD}.L⁻¹.d⁻¹). We observe that the production of biogas per kilogram of COD added tends to increase: with an average of 58.13 NL_{biogas}.kg_{COD}⁻¹ over the period 43-53 days, 61.68 NL_{biogas}.kg_{COD}⁻¹ over the period 54-63 days, 66.89 NL_{biogas}.kg_{COD}⁻¹ over the period 69-72 days, 82.74 NL_{biogas}.kg_{COD}⁻¹ over the period 73-112 days, and 232.31 NL_{biogas}.kg_{COD}⁻¹ over the period 113-130 days. In Table 8, for the calculation of the production of methane, we assume that the percentage of methane in the biogas is 65% in the results following the analysis of biogas on some samples, all samples must be analysed by chromatography to obtain the proportion of gases for the entire study. Thereby, the specific methane production has an average of 37.79 NL_{CH₄}.kg_{COD}⁻¹ over the period 43-53 days and 151.00 NL_{CH₄}.kg_{COD}⁻¹ over the



period 113-130 days (Table 8). The maximum biogas production is obtained with the maximum OLR tested of $2.26 \text{ g}_{\text{COD}} \cdot \text{L}^{-1} \cdot \text{d}^{-1}$.

The Table 8 shows also the percentage of COD removal and the degradation index for each period delimited by a change in OLR. During the start-up phase (the first two periods of the Table 8), the COD removal has an average of 50%, and during the steady conditions phase, the COD removal gradually increases from 64% to 85% with an average of 73%. Concerning the degradability index, it is 0.98 over the period 29-42 and varies from 0.16 to 0.81 during the steady conditions phase with an average value of 0.37. This difference in degradation index between the two periods is explained by the fact that the vinasse is a recalcitrant waste.

3.3.2 The follow-up of the physico-chemical properties of the pilot medium and the sludge analysis

The Fig 5. regroups the graphics of the physico-chemical analysis of the effluent: the ammonium, the VFA, the alkalinity, the VFA / Alk ratio, the pH, the COD and COD removal, the TS, the VS and the VS / TS ratio. The Table 9 shows the maximum, minimum and average values of physico-chemical analysis of the effluent during the start-up period, and the Table 10 shows the values during the rest of the study. These values must be taken cautiously since the pilot is very slightly agitated before taking a sample: 15 min at 20 rpm. Therefore, a layer of sedimentation formed as the time at the bottom of the digester. Thus, the results correspond to the liquid phase of the pilot. As the test progresses, the solid particles sediment and accumulate at the bottom of the pilot, forming a mud. The mud is also present on the side walls as well as on the agitator. The physico-chemical measurements on this mud were carried out. The measurements are given in the Table 9. The COD, the VFA and the alkalinity of the sludge are higher than the medium. The pH and the ammonium concentration of the sludge are in the same range as the medium. Thus the recalcitrant COD and VFA accumulate in the bottom of the pilot, but the pH is barely affected thanks to the increasing of the alkalinity. Moreover, as the COD include the biological oxygen demand (BOD), the biomass also accumulates in this sludge. Furthermore, the VFA concentration is two to three times that of the liquid medium, this means that the products of the acidogenesis accumulate in the mud, and that organic loading is too important compared to the kinetics of acetogenesis reactions. Indeed, under ideal digestion conditions, AGV production rates are compensated for by the rates of consumption and thus there is no accumulation of AGV. Nevertheless, certain conditions can cause imbalances: an organic overload, the presence of organic or inorganic toxins, or temperature fluctuations (Bollon, 2012).

Table 9 Physico-chemical properties of the pilot sludge

Day	pH	TS %	VS %	COD $\text{g}_{\text{O}_2} \cdot \text{L}^{-1}$	VFA $\text{mg} \cdot \text{L}^{-1}$	Am $\text{mg} \cdot \text{L}^{-1}$	Alk $\text{mg}_{\text{CaCO}_3} \cdot \text{L}^{-1}$	VFA/alk
109	7.469	5.48	2.85	53.1	10760	312	10685	1.01
117	7.813	5.81	3.92	47.7	18500	226	14868	1.24
129	7.428	-	-	41.3	14900	224	13507	1.10

The Table 10 shows the maximum, minimum and average values of physico-chemical analysis of the effluent during the start-up period. The Table 11 shows the maximum, minimum and average values of physico-chemical analysis of the effluent at different OLR.

The ammonium concentration (A) decreases during the start-up phase from 511 to $314 \text{ mg} \cdot \text{L}^{-1}$, and stabilises during the steady-conditions phase with an average value of $310.45 \text{ mg} \cdot \text{L}^{-1}$. The VFA (A) increases during the start-up phase from 1980 to $5270 \text{ mg} \cdot \text{L}^{-1}$, and stabilises during the following phase with an average value of $4279.00 \text{ mg} \cdot \text{L}^{-1}$. Sludge was added in the digester between days 55 and 65, we note that the VFA decreases from 4310 to $3230 \text{ mg} \cdot \text{L}^{-1}$. Thus, the addition of sludge has the effect of reducing the VFA concentration. The VFA and ammonium concentrations stabilised over the period 46-112 days. However, when we increase the OLR from 1.88 to $2.26 \text{ g}_{\text{COD}} \cdot \text{L}^{-1} \cdot \text{d}^{-1}$



(113-25 days), we note an increase in VFA concentration from 4570 to 7260 mg.L⁻¹ and a decrease in ammonium concentration from 298 to 217 mg.L⁻¹. This may lead to inhibitions of digestion, we stop the increase of the OLR until these concentrations stabilise. Despite the increase in the VFA concentration and the decrease in the ammonium concentration, the biogas production increases significantly over this period, from 73.67 to 285.29 NL_{biogas}.kgCOD⁻¹. We conclude that these concentration variations do not lead to inhibitions of the process, but on the contrary, favour the production of biogas. However, inhibitions may occur if the VFA concentration continues to increase and ammonium to decrease. Indeed the acclimation of the microorganisms and the selection of the populations makes it possible to have a better resistance to the high contents of AGV for a stability of the processes (Bollon, 2012). Compared to literature, the VFA was between 3570 and 7850 mg.L⁻¹ in the case of the digestion of vinasse (Moraes et al., 2015).

The alkalinity (B) globally increase over the test period. It varies between 5594 to 7691 mg_{CaCO₃}.L⁻¹. The VFA / Alk ratio (B) varies from 0.49 to 0.87 with an average value of 0.65 over the period 46-72 days. Then, it varies from 0.56 to 0.65 with an average value of 0.59 over the period 73-112 days. Next, the ratio increases over the period 113-130 with the augmentation of the OLR, the ratio varies from 0.65 to 0.87 with an average value of 0.73. The minimum value follows the addition of sludge from day 54 to 63. The VFA / Alk ratio above 0.8 may inhibit methanogenic archaea, of 0.3-0.4 indicates an unstable system, and a ratio of 0.1-0.2 is appropriate (Barros et al., 2016; Zhao, 2004). Compared to these ranges, we have an unstable system. However, the digester is only started for 130 days and the ratio decreases so we could be in appropriate conditions.

The anaerobic digestion process occurs in the pH range of 6.0 to 8.3 (Angelidaki and Ahring, 1994). Most methanogens have an optimal pH between 7 and 8 while acid-forming bacteria often have a lower optimum (Angelidaki and Ahring, 1994). The pH (C) of the influents were 4.84 for the sludge and 4.57 for the vinasse. Then, the pH of the medium varies between 7.10 and 7.50 during the start-up phase with an average of 7.31. It varies between 7.35 and 7.60 during the next phase with an average of 7.49. According to the graph, we see that the pH is stabilising during the steady conditions phase. The pH remains stable over the period 113-130 days despite the increase in VFA concentration during this period. Thus, the alkalinity of the digestion medium is sufficiently important to guarantee the stability of the pH. In most digesters, a neutral condition, as indicated by an average pH of 6.8-7.2, is considered normal (Zhao, 2004).

Concerning the COD concentration (C), the initial concentration of COD is 14.28 g.L⁻¹. During the start-up phase, small amount of vinasse was added, thus, the concentration of COD in the pilot is mainly brought by the sludge. As in the BMP tests, the maximum methane production of the blanks assays (only the sludge) is reached in 43 days, we make the assumption that the COD of the sludge is fully consumed after 45 days (steady conditions phase). It slowly decreases between days 1 to 17 from 14.28 to 8.95 g.L⁻¹. Then, the COD concentration globally increases during the rest of the test from 8.95 to 19.5 g.L⁻¹ with a maximum value of 21.20 g.L⁻¹ at day 73. We deduce from this outcomes that the vinasse has a recalcitrant COD which will accumulate in the digestion medium, unlike the sludge. However, this accumulation of organic matter does not seem to affect the production of biogas since it increases over the test period.

In terms of the variation of TS and VS (D), both increase during the assay period. The TS of the samples varies from 1.69% (day 5) to 3.01% (day 125) and the VS from 0.52% to 1.18% (day 125). The averages of TS and VS during start-up phase are respectively 1.96% and 0.64%, and during the steady conditions phase are 2.45% and 0.92%. The ratio VS / TS (E) ranges from 0.25 to 0.42 with an average of 0.32 for the start-up period and ranges from 0.31 to 0.43 with an average of 0.38 for the steady conditions period. The TS and the VS increase on the period 113-130 days, respectively from 2.51 to 3.01% and 0.82 to 1.19%, and the VS / TS ratio remains constant. As previously said, it is the period with the maximum biogas production, which means that this augmentation of TS is due to the micro-organisms growth. Measures of biological oxygen demand could confirm this hypothesis.



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As we see on the graph, the VFA and ammonium concentrations are not stabilised on the last period, during the increase of the OLR. Therefore, we need to continue the test until these parameters are stabilised. Indeed, as we want to test another mixing intensity, we need to have constant data in order to evaluate the impact of the change of mixing intensity. If the data are not constant, we will not be sure that the changes will be due to the change of agitation.

Table 10 Maximum, minimum and average values of physico-chemical analysis of the effluent during the start-up period

Parameters	Units	Start-up 0-45 days		
		Min	Max	Average
Ammonium	mg.L ⁻¹	314	511	425.4
VFA	mg.L ⁻¹	1980	5270	3751.8
Alkalinity	mg _{CaCO₃} .L ⁻¹	5594.4	5947.2	5770.8
VFA / Alk	-	-	-	-
pH	-	7.10	7.50	7.32
COD	g.L ⁻¹	7.66	17.90	14.38
COD removal	%	36.25	62.65	50.96
TS	%	1.69	2.18	1.96
VS	%	0.48	0.80	0.64
VS / TS	-	0.25	0.37	0.32

Table 11 Maximum, minimum and average values of physico-chemical analysis of the effluent at different OLR

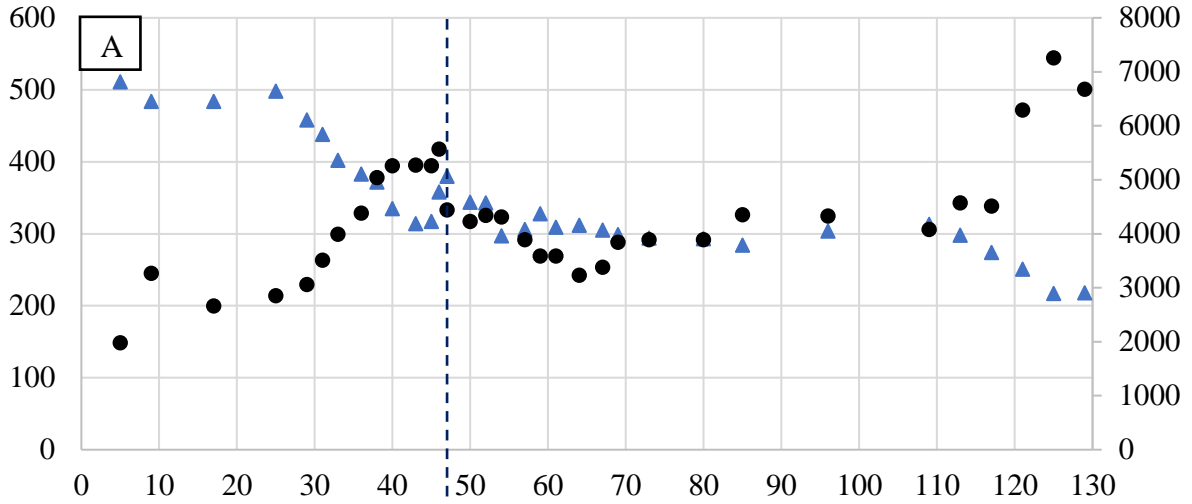
Parameters	Units	46-72 days			73-112 days			113-130 days		
		1.51 g _{COD} .L ⁻¹ .d ⁻¹			1.88 g _{COD} .L ⁻¹ .d ⁻¹			2.26 g _{COD} .L ⁻¹ .d ⁻¹		
		Min	Max	A*	Min	Max	A*	Min	Max	A*
Ammonium	mg.L ⁻¹	297	380	325.6	284	313	297.6	217.0	298	260.0
VFA	mg.L ⁻¹	3230	5570	4037	3890	4350	4108	4510	6290	5123
Alkalinity	mg _{CaCO₃} .L ⁻¹	5645	6653	6300	6602	7691	6931	6854	7268	6996
VFA / Alk	-	0.49	0.87	0.65	0.56	0.65	0.59	0.65	0.87	0.73
pH	-	7.35	7.51	7.46	7.40	7.59	7.54	7.46	7.60	7.53
COD	g.L ⁻¹	14.9	18.7	16.9	16.0	21.2	17.8	16.8	19.5	17.9
COD removal	%	62.5	76.5	68.5	71.3	82.3	78.8	82.7	85.0	84.3
TS	%	2.25	2.34	2.29	2.42	2.53	2.47	2.51	3.01	2.79
VS	%	0.75	0.98	0.88	0.89	0.96	0.93	0.82	1.19	1.05
VS / TS	-	0.33	0.42	0.38	0.37	0.38	0.38	0.33	0.43	0.38

*Average value

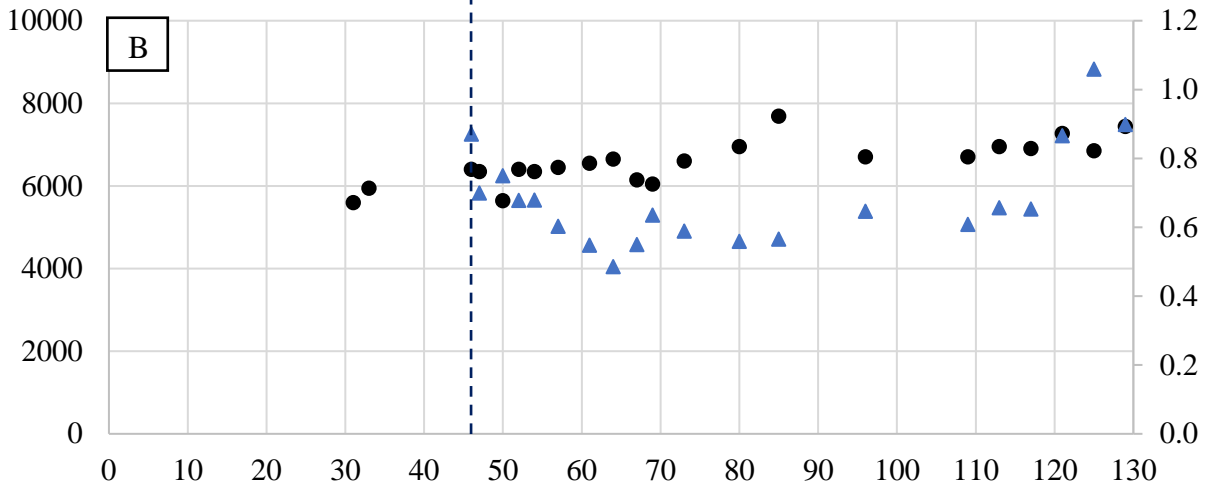


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Ammonium (mg.L⁻¹) ▲ Ammonium ● VFA VFA (mg.L⁻¹)



Alkalinity (mg_{CaCO₃}.L⁻¹) ● Alkalinity ▲ VFA / Alk VFA / Alk



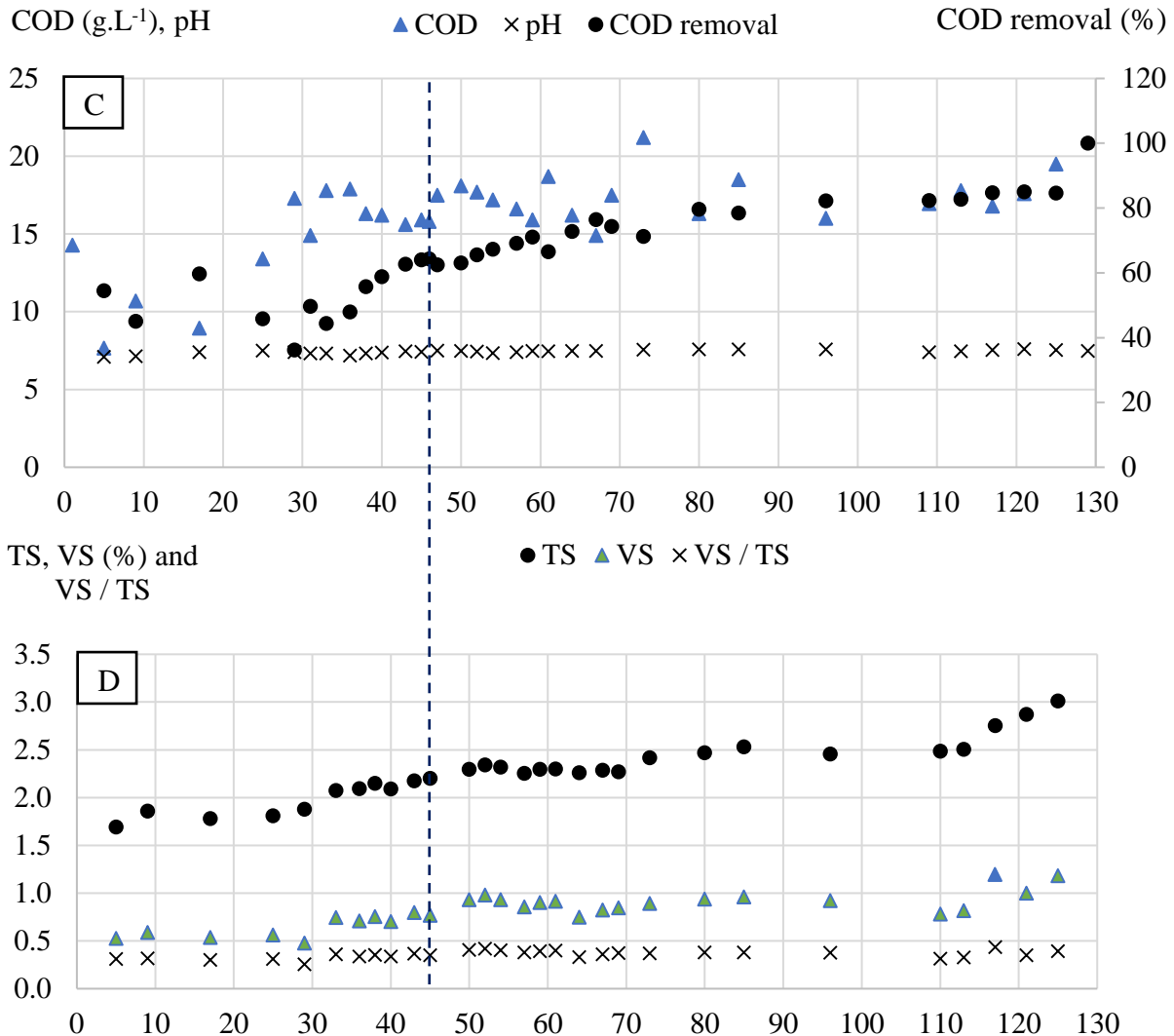


Fig. 5 Physico-chemical analysis in function of time (days) of the effluent: (A) Ammonium and VFA, (B) Alkalinity and VFA / Alk ratio, (C) pH, COD and COD removal, (D) TS, VS and VS / TS

3.4 Perspectives

In this work we obtained the results (biogas production and physicochemical analyses) in the case of mono-digestion of vinasse without any pre-treatment and with constant stirring. Thereafter, we wish to continue the increase of the OLR up to a value of 3 g_{VS}.L⁻¹.d⁻¹ as did the authors cited in this article during their pilot studies. The broader perspectives will be to study a pre-treatment of vinasse to improve the biogas yields obtained without diluting the vinasse. The major interest is to limit water consumption in anaerobic digestion plants. In addition, a study will also be performed on different modes of agitation including intermittent agitation.

4. CONCLUSION

The study showed that the first-order regression and the modified Gompertz model fit well with the BMP test curves with a correlation coefficients respectively upper to 0.98 and 0.97. Concerning the I / S ratio, the outcomes demonstrated that a ratio in terms of volatile solids lower than 1 (0.9, 0.7 and 0.6 ratios lower than 1 were tested) gives the maximum methane yield with a value of 185.59



$\text{NL}_{\text{CH}_4} \cdot \text{kgCOD}^{-1}$ (I / S ratio of 0.7). Moreover, we retain a value of 0.29 days^{-1} for the kinetic constant of the sugarcane vinasse.

In the present study, the biogas production and physico-chemical analysis are given for the pilot test over a period of 130 days. The results showed that the start-up period with vinasse sludge from the same distillery as the vinasse, lasted 45 days. Then the physico-chemical parameters and the biogas production were stabilised for each OLR. The BMP of the vinasse was $185.59 \text{ NL}_{\text{CH}_4} \cdot \text{kgCOD}^{-1}$ and the average specific biogas production of the last period (OLR of $2.26 \text{ gCOD} \cdot \text{L}^{-1} \cdot \text{d}^{-1}$) of the test was $151.00 \text{ NL}_{\text{CH}_4} \cdot \text{kgCOD}^{-1}$ ($232.31 \text{ NL}_{\text{biogas}} \cdot \text{kgCOD}^{-1}$), which gave a degradability index of 0.81. The maximum COD removal is 84.3%, it was obtained during the steady-conditions phase (OLR of $2.26 \text{ gCOD} \cdot \text{L}^{-1} \cdot \text{d}^{-1}$).

As the biogas yield gradually increased in pilot test, the OLR will be further increased progressively in future studies; in order to avoid inhibitions. We will not add a source of carbon neither water. Indeed we want to create a database for mesophilic mono-digestion of raw vinasse. The next step will be to test different mixing conditions and pre-treatment on vinasse.

5. Acknowledgements

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