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Co-digestion of Waste Coffee and Cocoa Hulls: Modeling of Biogas Production by the Particle Swarm Method

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Abstract: Energy is a crucial material for the development of our economy. Access to sufficient energy remains a major concern for developing countries, particularly those in sub-Saharan Africa. The major challenge lies in access to clean, environmentally friendly, quality and low-cost energy in different households in our municipalities. To cope with this vast energy gap, many households are dependent on fossil fuels. In Cameroon, the consumption of wood for the supply of energy is increasing by 4% per year. Overall, approximately 80% of households in Cameroon depend on woody biomass as the sole main source of energy supply in Cameroon and demand is growing over time. In view of the climatic variations that our countries, particularly Cameroon, undergo through deforestation, the use of wood as a source of energy is expensive and harmful to the environment, hence the urgency of replacing wood with renewable energy. Biogas is one of the most versatile sources of renewable energy. On an industrial scale, it is important to automate the process control. The main objective of the present work is to model the anaerobic digestion of coffee and cocoa hulls using the particle swarm optimisation method. Pretreatment using the organosolv process was done. This resulted in 48% lignin removal and 22% cellulose increase. For the pretreated biomass, the maximum production rate was 21 $NmLCH_4$ per day with a biomethane yield of 90 $NmLCH_4/gVS$. This represents an enhancement of 117% in biomethane yield. A positive flammability test was recorded after the 10th day of retention time. Moreover, the data collected during anaerobic digestion allowed implementation of a two-phase mathematical model. The thirteen parameters of the model were estimated with particle swarm optimisation method in Matlab. The model was able to simulate the biomethane production kinetics and variation of volatile fatty acid concentration.

Key words: Lignocellulosic biomass, organosolv process, anaerobic digestion, mathematical model, particle swarm optimisation.

1. Introduction

Energy, produced in its various forms, plays a major role in our society and is indispensable in the production of goods and services. With growing demographics, urbanization and the development of towns and communities, electrical energy is no longer able to meet social needs. This dependence on electrical energy has increased over the last 20 years [1]. The use of biomass for energy purposes has stimulated the agricultural economy and promoted local development. Biomass refers to any organic substance from which a certain

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type of energy can be extracted, whether mechanical, electrical or thermal, using agricultural, industrial, forestry or even urban waste. Cameroon, whose economy is essentially based on agriculture, has tones of woody and organic waste that is dumped in our landfill sites and rots in the fields. This could be a good precursor for producing energy as an alternative to fossil fuels, which release tones of greenhouse gases and have a considerable impact on our ecosystem. In view of all these factors, there is an urgent need to develop alternative energies to satisfy the local market and ensure people's livelihoods. Biomass, because of its wide availability and its ability to degrade in a short time under well-controlled conditions, can be transformed into various bioenergy such as biogas, bioethanol, bio hydrogen and biodiesel. One of the most common and widely applied technologies is methanisation to produce biogas. In view of the environmental constraints linked to the use of fossil fuels, it is becoming more urgent than ever to develop clean technologies that respect our universe. Biomethane is a hydrocarbon gas consisting mainly of methane (CH_4), carbon dioxide (CO_2) and other trace compounds. Previous work has shown that biomethane can be used to produce heat or electricity. Its composition makes it less polluting than other biofuels [2, 3]. Biogas is generated during the controlled decomposition of biodegradable organic matter by micro-organisms in the absence of oxygen: this is known as anaerobic digestion [4]. Anaerobic digestion is a relatively inexpensive and efficient technology which, in addition to generating biogas, enables organic waste to be managed, greenhouse gas emissions to be reduced and biofertilisers to be produced [5, 6]. Various types of biomass are currently used as substrates for methanisation, including food industry waste, wood residues and cocoa shell waste. Coffee and cocoa hulls production is well developed in most tropical regions of the world and this exploitation generates a significant volume of cocoa cortex waste. Cameroon is the world's fifth-largest cocoa producer [7], and is taking a keen interest in the recovery of this waste. Cocoa cortex cocoa pods, represent 68% by mass of the total fruit and are one of the largest sources of agricultural waste left in the fields after harvest. It is estimated that 600,670 t/year of fresh cocoa cortex are obtained in Cameroon, with a dry matter content of around 16%, i.e. 93,704 tonnes of dry cocoa cortex; these cocoa cortex carry a fungus responsible for brown rot on cocoa plants [8], hence the need to dispose of them in the fields after harvesting. Recycling residues remains a challenge for the cocoa industry in Cameroon and elsewhere. At IRAD, potassium fertiliser, potash and local soap are used in production. Cocoa cortex is also used in broiler diets [9], and at the Cocoa Downstrem Research Center in Malaysia, a study has been carried out on the production of volatile perfume compounds by impregnating nitrogen sources into cocoa cortex [9]. To the best of our knowledge, there has been almost no work on cocoa and coffee husks.

As is the case with most agricultural waste, cocoa and coffee hulls are lignocellulosic in nature consisting mainly of cellulose, hemicellulose and lignin [10, 11]. Pre-treatment is a key stage in the production of biomethane. One method of lignocellulosic pre-treatment is the use of the organosolv process. Successful research into organosolv pretreatment has been carried out on the enzymatic hydrolysis of biomass and on the enzymatic hydrolysis of biomass. The organosolv process carried out on the enzymatic hydrolysis of biomass including coffee peel. The feasibility of organosolv processes using aspen software plus where the results of the optimization of the organosolv process have been very favourable. The choice of the type of organic solvent used in the organosolv process depends largely on the economic value of the material. According to Xie et al. [12], organosolv pretreatment is more advantageous in terms of ease of processing, low pretreatment costs and energy savings. easy process, not too high pre-treatment costs, easy conversion to solvent, hemicellulose partially hydrolysed hemicellulose and high xylose yield, as almost all of the lignin is colonised and breaks the internal bonds of the lignin and xylose.

The main aim of the pretreatment is: the elimination of lignin, reduction of cellulose crystallinity and the increase in specific surface [13, 14]. There exist several lignocellulosic biomass pretreatment techniques and the three main classes are: physical, physico-chemical and biological [3].

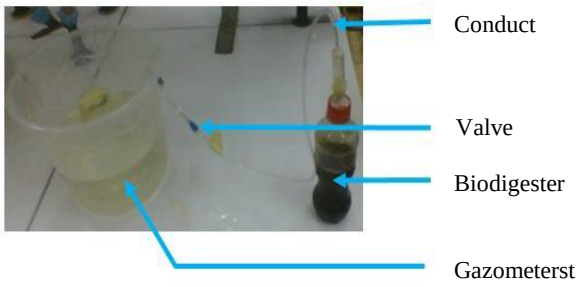
A model is a mathematical representation of a concrete phenomenon. Dynamic models are the most used in process engineering due to the fact that they facilitate process optimization and control but the use of a dynamic model implies that all the model parameters are known [15]. This is not always obvious given the non-linear nature of phenomena such as anaerobic digestion. In order to overcome this difficulty, several algorithms such as the particle swarm method have been developed and they are being widely used both in research and in industries. The latter has the advantage of robustness and simplicity [16, 17]. The general objective of this study is to model the anaerobic digestion of association of coffee and cocoa hulls using the particle swarm method. More specifically:

- Test the methanogenic potential of the coffee and cocoa hulls;
- Describe the anaerobic digestion of coffee and cocoa hulls using a mathematical model.
- The hypothesis are as follows:
- The composition of coffee and cocoa hulls is favorable to anaerobic digestion
- Anaerobic digestion can be modelled using the particle swarm method.

2. Material and Methods

2.1 Experimental Device for Anaerobic Digestion: Biodigester + Gasometer

The biodigester is made up of a plastic bottle. The total capacity of each biodigester is 350 mL though the useful volume is 200 mL. The biodigester bathes in a water bath whose temperature 39 °C. A discharge pipe that channels the biogas produced to the gasometer is fitted into it. This system enables the measurement of the volume of biogas produced by the liquid displacement method. During anaerobic digestion, the biogas produced is stored between the liquid front and the bottom of an inverted test tube. This results in a drop in the liquid barrier due to an increase in pressure. In this case, the liquid barrier layer used is a potassium hydroxide solution extracted from the alkalis extracted from banana stalk. Valves are used to reduce the flow rate of gas through the pipes.



Picture 1 Experimental anaerobic digestion device.

2.2 Methods

2.2.1 Procedure for Obtaining Coffee and Cocoa Hulls Powder

The coffee and cocoa hulls powder used is obtained through the process described. The raw materials are washed and dried in an oven at 45 ℃ until a constant mass is obtained. The dried coffee and cocoa hulls are then crushed and sieved with a 1 mm mesh sieve. The powder obtained is packaged in polyethylene bags and stored at room temperature.

2.2.2 Physicochemical Characterization of Coffee and Cocoa Hulls Powder

The analyses consisted in determining of water and dry matter content, crude fiber, content, lignin content, cellulose content, reducing sugars content and determination of mass loss.

2.2.3 Pretreatment of Hulls by the Organosolv Process

The pretreatment was carried out using batch reactor with a total volume of 100 mL with the useful volume being 80 mL. The experimental protocol was inspired from that described by Kabir et al. [6] and Matsakas et al. [18]. A mass of 4 g of coffee and cocoa hulls powder

is mixed with 80 ml of the pretreatment solvent (ethanol-water mixture 61:39 *v*/*v*) and loaded into the reactor. The latter is tightly sealed using silicone glue to ensure it is watertight. It is then put in an oven preheated to 200 ℃. The treatment is stopped by cooling under running water to room temperature. After cooling, the two solid and liquid phases are separated by filtration. The coffee and cocoa hulls powder thus treated is dried and stored in a glass jar for later use.

2.2.4 Organosolv Pretreatment of Coffee and Cocoa Hulls Powder

(1) Organosolv pretreatment parameters

The latter's work involves optimizing the organosolv pretreatment of cocoa shell powder using the experimental design method. The resulting optimal preprocessing parameters include:

- Liquid /solid ratio 15:5 volume/mass (40 mL of solution/g of raw mixture materials);
- Temperature 200 ℃; Processing time 25 minutes; Solvent used: ethanol-water mixture 61:39 (*v*/*v*).

(2) Collection and characterization of the inoculum

The inoculum used in this study was harvested at the municipal beef slaughterhouse in the town of Maroua. The collected inoculum was stored at room temperature before inoculation into the digester. The physicochemical characteristics of the inoculum were determined by the same methods used for the pretreated cocoa shell powder. These are the dry matter content and the organic matter content. In addition, other analysis was performed on the inoculum. These include the measurement of pH, volatile fatty acid content, and total alkalinity.

2.2.5 Measurement of pH, volatile fatty acid concentration and alkalinity

(1) Principle

The method used is that described by Bachmann et al. [19]. It consists of a gradual titration using sulfuric acid.

(2) Biomethane potential test

The biomethane potential test was carried out following the recommendations made by Bachmann et al. [19]. In the experiment, three series of biodigesters are used:

- Biodigesters which contain coffee and cocoa hulls powder pretreated with the inoculum: PCCP biodigesters;
- Biodigesters that contain coffee and cocoa hulls powder with inoculum: PCC biodigesters;
- Control biodigesters which contain only inoculum.

(3) Preparation of the inoculum

The inoculum is well mixed to ensure homogeneity. The inoculum is then put in each biodigester. These are then sealed and incubated at 39 ℃ until the production of biogas is zero.

(4) Substrate introduction

All the biodigesters are opened including the controls which do not contain any substrate. The pretreated cocoa shell powder (PCCP biodigesters) as well as the previously moistened cocoa shell powder (PCC biodigesters) are introduced while respecting a S/I (Substrate/Inoculum) ratio of 2/1 (organic matter base). This value of the S/I ratio guarantees the absence of an acidification phase detrimental to the proper progress of digestion. An S/I ratio also makes it possible to avoid too much biogas production by the inoculum, which can give a faulty yield [19, 20].

Sodium bicarbonate is added at a concentration of 5 g/L to buffer the reaction medium. This is to prevent possible fluctuations in pH due to the production of acid during acidogenesis. Adjusting the pH between 7.2 and 7.8 is done using a decimolar solution of hydrochloric acid, as recommended by Akobi et al. [21]. The final load volume in each biodigester is adjusted to 200 mL with water while maintaining a total concentration of 40 gOM/L. The biodigesters are closed using Teflon to ensure tightness. The overhead gas of each biodigester is purged with nitrogen in order to ensure anaerobiosis. The biodigesters are then incubated at 39 ℃.

(5) Test monitoring and calculation of results

The biodigesters are continuously stirred throughout the operation with 2 hours stops. The production of

biogas evaluated by the difference in the volume of the barrier liquid is measured every day throughout the experiment. The production of the controls is subtracted from that of the PCCP and PCC biodigesters. At each measuring point, the procedure is as follows:

- The production of each biodigester with substrate is subtracted from the possible average production of the controls and the average production of the PCC and PCCP biodigesters is then calculated;
- The volume thus found includes that of the water vapor contained in the biomethane.

The correction of the volume in order to express it in the Normal Conditions of Temperature and Pressure (CNTP) (273.15 K and 1013 mbar) is done according to the following relation:

$$P_{H2O} = 6{,}1121 \times \exp\left[\left(18{,}678 - \frac{T_{\exp}}{234{,}5}\right) \times \frac{T_{\exp}}{257{,}14 + T_{\exp}}\right]$$

$$V_{cntp} = V_{312} \times \frac{T_{cntp}}{T_{\exp}} \times \frac{P_{atm} - P_{H_2O}}{P_{cntp}}$$

With V_{312}: volume of gas measured experimentally;

T_{Cntp}, P_{Cntp}: normal temperature and pressure (273.15 K and 1013 mbar);

T_{exp}: experimental temperature (39 ℃); $P_{Atm:}$ atmospheric pressure;

P_{H2O}: partial pressure of water vapor.

The partial pressure of water vapor denoted P_{H2O} can be calculated using the modified Arden Buck equation reported by Parajuli [22].

Monitoring of the test was continued until the production of PCCP biodigesters (blank control) was negligible. Additional PCCP biodigesters were intended to be sacrificed at five-day intervals. The analysis and tests performed during the biodigester sacrifice are: (1) the organic matter content, (2) the volatile fatty acid content and (3) the flammability test.

2.2.6 Characterization of Biogas: Flammability Test

The flammability test is a qualitative test which assesses the ability of the biogas produced to ignite. From an experimental point of view, this test is carried out by spraying the biogas produced in the direction of the flame of a lighted candle in order to visually assess its combustion quality [23].

(1) Modeling of anaerobic digestion

Modeling the kinetics of anaerobic digestion provides a dynamic model describing the behavior of the reaction medium over time. The anaerobic digestion biodigester is the site of several highly complex phenomena. Thus the modeled kinetics are: the degradation kinetics of biodegradable organic matter; the degradation kinetics of volatile fatty acids; the growth kinetics of microorganisms and the kinetics of cumulative biogas production.

(2) Modeling assumptions

Assumptions were made to model the progress of digestion within the biodigester. These assumptions are as follows: the biodigester is a perfectly stirred batch reactor. So there are no concentration gradients and diffusive phenomena are not taken into account; the volume of the reactor is constant; the volume of the gaseous phase in the biodigester is empty. So all the gas collected at the level of the gasometer comes from anaerobic digestion.

Biogas consists of methane which is insoluble in the liquid phase. The barrier solution dissolves the impurities in the biogas; Anaerobic digestion takes place in two stages (acidogenesis and methanogenesis); Two families of microorganisms (acidogenic and methanogenic bacteria) are each responsible for one of the steps in anaerobic digestion; these two microbial families are susceptible to bacterial decay; the pH and temperature within the biodigester are constant throughout the retention time.

(3) Parameter estimation and model simulation

The model is solved numerically using MatLab. To be able to do this, the MatLab integrated function ode45 which applies the Runge-Kutta method is used. For that, it is imperative to provide the initial conditions as well as the experimental parameters. Table 1 contains the initial conditions as well as the fixed simulation parameters used.

Table 1 Initial conditions and fixed parameters of the proposed model.

Initial condition	Value	Reference
S_1 organic matter concentration	40 g/L	Experimental
S_2 volatile fatty acid concentration	2.1 g/L	Experimental
X_1, X_2 bacteria concentration	0.01 g/L	Ref. [4]
Minimum temperature	11 ℃	Ref. [24]
Experimental temperature	39 ℃	Experimental
Optimum temperature	37 ℃	Ref. [24]
Maximum temperature	60 ℃	Ref. [25]
Minimum PH	6	Ref. [25]
Experimental pH	7.2	Experimental
Optimum pH	7	Ref. [24]
Maximum pH	8.3	Ref. [25]
Retention time	30 days	Experimental
Useful reactor volume	0.2 L	Experimental

The model also comprises thirteen parameters whose values are unknown and which are to be estimated. The estimation of the parameters is formulated in the form of a minimisation problem of an objective function [16].

$$J = \sum_{j=1}^{k}\left(\frac{\left|\vec{y}\left(t_j;\vec{x}_i\right)-\vec{y}_j\right|}{\left|\vec{y}_j\right|}\right)^2$$

$$\vec{y}\left(t_j;\vec{x}_i\right)=\left\{a_{mn};m=1,2,...30;n=1,2,3\right\}$$

$$\vec{y}_j=\left\{a_{mn};m=1,2,...30;n=1,2,3\right\}$$

$$t_j\in[1;30]$$

$$\vec{x}_i=\left[\mu_{\max\_a}\quad \mu_{\max\_m}\quad K_1\quad K_2\quad K_3\quad K_4\right.$$
$$\left.K_{s\_a}\quad K_{i\_a}\quad K_{s\_m}\quad K_{i1\_m}\quad K_{i2\_m}\quad K_{d\_a}\quad K_{d\_m}\right]^T;$$

In this expression of the objective function, x_i is a vector whose terms are the parameters to be estimated. t_j is the retention time. y_j is the vector of the experimental data. y ρ(t j; x ρ_i) is the vector of the simulated data. The data are: The cumulative volume of biomethane; the concentration of volatile fatty acids in the biodigester; the concentration of organic matter in the biodigester. The smaller the value taken by this objective function, the smaller the difference between the simulated data and the experimental data. The objective function J thus defined is minimized by the method of particle swarms [26]. The algorithm of this method according to Dutot et al. [27] is as follows (Figs. 1 and 2):

Tant Que *crière d'arrêt pasvérifié*
  Pour i de 1 de N faire
    Si $\left(f(\vec{x}_i)>Pbest_i\right)$
      $Pbest_i \leftarrow f(\vec{x}_i)$
      $\vec{x}_{Pbest_i} \leftarrow \vec{x}_i$
    Fin Si
    Si$\left(f(\vec{x}_i(t))>Gbest\right)$
      $Gbest \leftarrow f(\vec{x}_i)$
      $\vec{x}_{Gbest} \leftarrow \vec{x}_i$
    Fin Si
  Fin Pour
  Pour i de 1 à N faire
    $\vec{v}_i \leftarrow \omega\times\vec{v}_i + r_1c_1\times\left(\vec{x}_{Pbest_i}-\vec{x}_i\right)+r_2c_2\times\left(\vec{x}_{Gbest}-\vec{x}_i\right)$
    $\vec{x}_i \leftarrow \vec{x}_i+\vec{v}_i$
  Fin Pour
Fin Tant Que

Fig. 1 Algorithm of the particle swarm method.

Tant Que *crière d'arrêt pasvérifié*
  Pour i de 1 de N faire
    Si $\left(f(\vec{x}_i)>Pbest_i\right)$
      $Pbest_i \leftarrow f(\vec{x}_i)$
      $\vec{x}_{Pbest_i} \leftarrow \vec{x}_i$
    Fin Si
    Si$\left(f(\vec{x}_i(t))>Gbest\right)$
      $Gbest \leftarrow f(\vec{x}_i)$
      $\vec{x}_{Gbest} \leftarrow \vec{x}_i$
    Fin Si
  Fin Pour
  Pour i de 1 à N faire
    $\vec{v}_i \leftarrow \omega\times\vec{v}_i + r_1c_1\times\left(\vec{x}_{Pbest_i}-\vec{x}_i\right)+r_2c_2\times\left(\vec{x}_{Gbest}-\vec{x}_i\right)$
    $\vec{x}_i \leftarrow \vec{x}_i+\vec{v}_i$
  Fin Pour
Fin Tant Que

Fig. 2 Algorithm of the particle swarm method [27].

2.2.7 Initialization

Randomly generated position (x_i) and velocity (v_i) particles

Evaluate the objective function for each particle (Pbesti) and pose (Gbest) the best solution

In this algorithm, N represents the number of particles in the swarm. X_i corresponds to the vector of the parameters to be estimated and represents the position of a P_i particle. P_{besti} is the best-known value of the objective function of a Pi particle. xPbesti is the position of the particle Pi for its best value of the objective function. XGbest ρ is the position of the

particle among all the particles in the swarm with the best value of the objective function. As for v_i, it represents the speed of a particle P_i. It is calculated from the following expression:

$$\vec{v}_i = \omega \times \vec{v}_i + r_1 \times c_1 \times \left(\vec{x}_{Pbest_i} - \vec{x}_i\right) + r_2 \times c_2 \times \left(\vec{x}_{Gbest} - \vec{x}_i\right)$$

This expression, which is the basis of the particle swarm method, has three components, each of which is responsible for the behavior of particles in the search space.

The first right-hand term of Eq. (23) enables the conservative behavior governed by the inertia factorω. A high value of ω allows fast travel and therefore global exploration as long as a low value allows local exploration. The second right-hand term of Eq. (23) allows for cognitive behavior governed by the personal experience of the particle through xPbesti. Finally, the third right-hand term of Eq. (23) integrates the social behavior component governed by the best known global position of the particle swarm through xGbest [28]. The variables c_1 and c_2 are positive constants determined empirically so that the following condition is met: $c_1 + c_2 \leq 4$. The variables r_1 and r_2 are random constants between 0 and 1 [17, 28].

2.2.8 Model Validation Criteria

The model was validated according to: (1) the cumulative volume of biomethane produced, (2) the concentration of volatile fatty acids and (3) the concentration of organic matter. Table 2 shows the acceptability thresholds for the various model validation criteria.

Table 2 Acceptability thresholds for the various model validation criteria.

Validation indicator	Standards	acceptable	references
R^2	1	≥ 0.8	Ref. [29]
Adjusted R^2	1	≥ 0.8	Ref. [29]
Bias factor	1	[0.75-1.25]	Ref. [30]
Exactitude factor	1	[0.75-1.25]	Ref. [30]
AADM	0	[0-0.03]	Ref. [31]
RMSE	0	[0-0.05]	Ref. [32]

3. Results and Discussion

3.1 Physicochemical Characteristics of Cocoa Shell Powder

The physicochemical characteristics of the mixture coffee and cocoa shell powder are given in Table 3.

Table 3 Physico-chemical characteristics of cocoa shell powder.

Constituents	Before pretreatment	After pretreatment
Dry matter content (g/100*g)	88.1 ±0.1	18.2 ±1.3
Water content (g/100*g)	11.9 ±0.1	81.9 ±1.3
organic matter content (g/100$^+$g)	92.1 ±0.2	91.8 ±1.6
Ash content (g/100$^+$g)	7.9 ±0.2	8.2 ±1.6
Reducing sugar content (g/100*g)	0.020 ±0.003	0.11 ±0.002
Crude fiber content (g/100$^+$g)	40.1 ±1.2	25.8 ±1.1
Lignin content (g/100$^+$g)	35.3 ±1.8	18.2 ±1.7
Cellulose content (g/100$^+$g)	41.4 ±0.3	53.1 ±0.2

+ Dry base, * wet base.

The mixture coffee and cocoa shell powder has a dry matter content of 88.1% and an organic matter content of 92.1%. This high organic matter content shows that mixture of coffee and cocoa hulls can be an important source of nutrients for microorganisms in anaerobic digestion. On the other hand, these values are slightly higher than those of Daud et al. [11] who obtained 85.9% for dry matter and 87.7% for organic matter.

All these results demonstrate the variability in the composition of the mixture coffee and cocoa shells. This can be explained by the differences in the soil composition of the place of origin, the difference in the degree of maturity as well as the harvest period. But the fact remains that cocoa hulls constitute a promising biomass for the production of biofuels as already mentioned by Marsiglia et al. [33].

Looking at these results, it is observed that the powder after pretreatment has a dry matter content of 18.2% and an organic matter content of 91.8%. In addition, there is a slight increase in the content of reducing sugars. This can be explained by the breakdown of cellulose into reducing sugars. These results are consistent with those of Kabir et al. [6]. Furthermore,

the low dry matter content is due to the fact that at the end of the pretreatment, a pasty solid phase is obtained which still contains water. The lignin and cellulose contents are the main criteria for comparing the effect of the organosolv pretreatment.

3.2 Organosolv Pretreatment of Mixture Coffee and Cocoa Shell Powder

The pretreatment efficiency is the ratio of the actual mass loss to the theoretical mass loss. An efficiency of 89.6% means that only 10.4% of the theoretically expected cellulose was not extracted during the pretreatment (Table 4). Furthermore, the relative mass loss following the organosolv pretreatment of the cocoa shell powder is 52.5%. This percentage represents the fraction of the biomass which has passed into the liquid phase during the pretreatment. This relatively high rate reflects a great solubilization of the biomass, mostly consisting of lignin and hemicellulose in the liquid phase. This rate also invites reflection on strategies for recovering and upgrading the liquid phase. The equivalent recovery percentage is 47.8%. These results are different from those obtained by Hesami et al. [34]. The latter had a relative mass loss oscillating around 40% following the organosolv pretreatment of sunflower stems.

Table 4 Dry matter balance of the organosolv pretreatment.

Parameters	Values
Initial dry weight (g)	4.00 ±0.03
Dry mass final residue (g)	1.9 ±0.02
Relative loss mass (%)	52.5
Pretreatment efficiency (%)	89.6

3.3 Physico-chemical Characteristics of the Inoculum

The characteristics presented in Table 5 were also used in calculating the load of the biodigesters.

Table 5 Physico-chemical characteristics of the inoculum.

Constituents	Value
Dry matter content (g/100 g)	16.0 ±0.8
Organic matter content (g/100 g)	75.0 ±0.5
pH	8.1 ±0.1
Volatile fatty acid (g/L Ac eq)	2.9 ±0.1
Alcalinity (g/L $CaCO_3$eq)	9.3 ±0.1

The analysis carried out on the inoculum show that it has a pH of 8.1. This pH value is not within the optimal range of methanogenesis which is between 6.6 and 7.4 [35]. However, there are several authors who have successfully used inocula whose pH was outside this range. This is the case of Liew et al. [36] whose inoculum had a pH of 8.5. As for the concentration of volatile fatty acids, it is 2.9 g/L. Volatile fatty acids are important metabolic intermediates in anaerobic digestion. In fact, they are mostly the products of acidogenesis, but also the reagents of acetogenesis and acetoclast methanogenesis [4]. This is why their presence indicates that anaerobic digestion is in progress.

3.4 Daily Production Kinetics

Fig. 3 shows the curves describing the change in daily volumes of biomethane produced as a function of time.

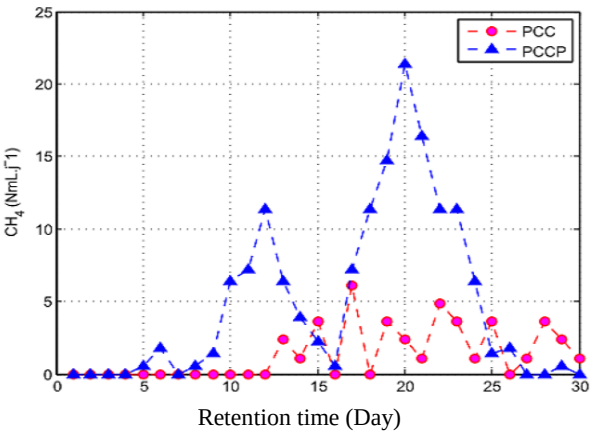


Fig. 3 Kinetics of daily biomethane production.

The production of biomethane in the case of the PCCP biodigester begins after 5 days. This time represents the time required for the microorganisms to adapt. This time is comparable to that of Tou et al. [37] who also observed a start of production after 5 days of anaerobic digestion. This relatively short duration is inherent to a weak inhibition within the PCCP biodigester. The inhibition phenomena can be of several types. Following the pretreatment, traces of the solvent used may constitute a source of inhibition of

even some of the inhibitory compounds formed [38]. The production period which runs from the 5th to the 29th day has two production phases. The first phase is the medium production phase which begins on the 5th day and ends on the 16th day. A production peak of 11 NmL/day occurs on the 12th day. This phase would correspond to the conversion of easily biodegradable compounds such as simple sugars, as well as traces of ethanol into methane. It is the depletion of these compounds that justifies the brief drop in production on day 16. The second production phase is the high production phase due to a better synergy between the microorganisms within the biodigester. More than 50% of the biomethane is produced during this phase. It corresponds to the degradation of more complex compounds such as cellulose as well as hemicellulose released during pretreatment. A production peak of 21 mL/day is reached on the 20th day, followed by a gradual drop until the 29th day when the daily production tends towards zero. The drop which occurs at this level corresponds to the depletion of biodegradable organic matter within the biodigester. In the case of the PCC biodigester, production begins on the 13th day. Such a long adaptation period compared to the PCCP biodigester is mainly a sign of inhibition phenomena of various kinds within the PCC biodigester. This is explained by a low availability of biodegradable biomass within the biodigester leading to low productivity. In fact, the cocoa shell powder has a reinforced lignocellulosic structure. The cellulose present there is highly crystalline and protected by lignin which at the same time limits its hydrolysis as reported by Wertz et al. [39]. Additionally, lignin can inhibit enzyme activity by forming hydrophobic bonds with enzymes produced by microorganisms involved in anaerobic digestion [40].

3.5 Material Balance and Yield of Anaerobic Digestion

The data relating to the cumulative production of biomethane as well as the variation of the organic matter content within the PCCP and PCC biodigesters enable us to calculate the biomethane yield. This yield is 41 NmL/g OM for the PCC biodigester. This low yield once again reflects the incomplete degradation of organic matter. This can be explained by the strong presence of lignin at a content well beyond the 15% DM inhibition limit according to the work of Yeqing et al. [20]. In addition, cellulose would be found essentially in a crystalline form. Conversely, this yield is 90 NmL/g OM for the PCCP biodigester, which represents an increase of approximately 117%. This increase in yield can be explained by the fact that the organosolv pretreatment enabled a greater digestibility of the cocoa shell powder. This rate of increase is higher than that of Mirmohamadsadeghi et al. [5], who had an 84% increase after organosolv pretreatment of pine wood residues. On the other hand, our results are well below those of Ostovareh et al. [41] who had growth rates of around 270% after organosolv pretreatment of sorghum stems. These differences can be explained by the difference in the composition of the biomass considered as well as the pretreatment conditions.

3.6 Flammability Test

The flammability test was successful from the 10th day. Fig. 4 illustrates the performance of a flammability test.

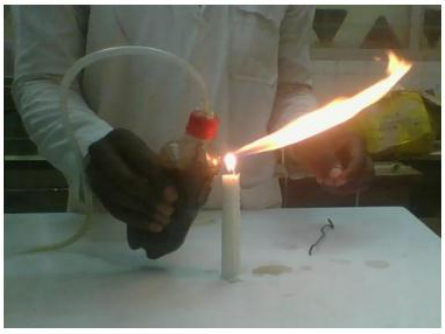


Fig. 4 Flammability test of biomethane.

The yellow color of the flame is explained by the fact that the biogas comes directly from the biodigester and therefore still contains impurities consisting mainly of carbon dioxide. But the ability of biogas to ignite from

the 10th day can be explained by the fact that the biomethane has reached the minimum threshold of 45% as reported by Deublein and Steinhauser [24]. Thus, the negative test on the 5th day justifies a low content of biomethane produced.

3.7 Model Simulation and Validation

3.7.1 Simulation of the Cumulative Production of Biomethane

Fig. 5 shows the experimental curve and the simulated curve of the cumulative production of biomethane as a function of time.

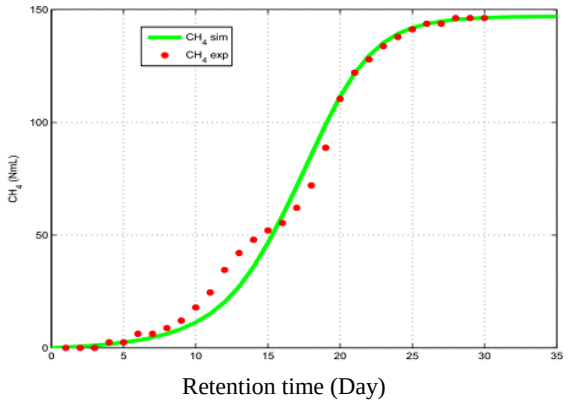


Fig. 5 Experimental and simulated curves of biomethane production as a function of time.

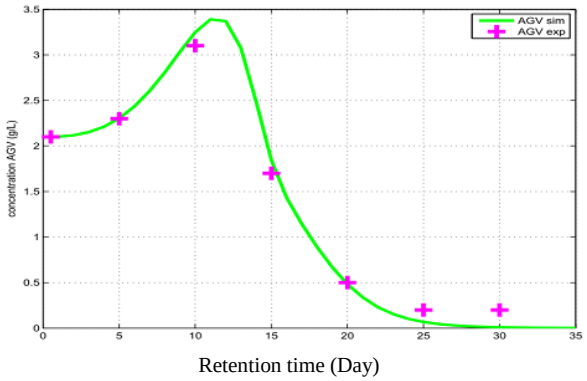


Fig. 6 Experimental curve and simulated curve of the concentration of volatile fatty acids as a function of time.

The cumulative biomethane production curve in the PCCP biodigester has three phases. The first phase where production is zero or very low which begins on day 1 and continues up to day 5. The second is the exponential production phase which is characterized by a very rapid increase in production. It goes from the 6th to the 25th day. In addition, nearly 80% of the biomethane is produced during this phase. The last phase is the stationary phase during which production is low. This phase begins on day 25 and continues up to day 30. This drop in biomethane production would mark the depletion of biodegradable organic material in the biodigester. This duration therefore represents the time necessary to exhaust the biodegradable material. This duration is comparable to 30 days of Liew et al. [36] who made an anaerobic digestion of various lignocellulosic biomasses (corn stalk and wheat straw). On the other hand, Hesami et al. [34] observed the depletion of the substrate consisting of sunflower stems pretreated by the organosolv process after 45 days, as did Zhai et al. [42]. In the case of Ostovareh et al. [41], 50 days were required for the anaerobic digestion of pretreated sorghum straw. Table 6 gives the validation criteria for the cumulative production of the biomethane model. Table 6 shows that the cumulative production of biomethane model is statistically valid.

3.7.2 Simulation of the Concentration of Volatile Fatty Acids

Fig. 7 shows the experimental and simulated curves of the variation in the concentration of volatile fatty acids during anaerobic digestion.

It can be seen in Fig. 7 that the concentration of volatile fatty acids evolves in three phases during anaerobic digestion. At the start of anaerobic digestion, there is an increase in biodegradables followed by acidogenesis (production of volatile fatty acids) as reported by Augusto [25]. In addition, a peak of 3.5 g AGV/L occurs around the 12th day. There is also a rapid decline after this peak. This is explained by the consumption of volatile fatty acids and the production of biomethane by methanogenic bacteria. This drop continues up to the 25th day when the concentration of volatile fatty acids tends to zero at the same time as the production of biomethane ceases. Similar observations were also made by Zhai et al. [42] with a mixture of cow dung and household waste. Table 6 presents the

model validation criteria relative to the variation in the concentration of volatile fatty acids. This increase in the concentration of volatile fatty acids is thought to be due to the hydrolysis of the materials. It appears that the model is statistically valid

3.7.3 Simulation of Organic Matter Concentration

Fig. 8 shows the experimental curve and the simulated curve of the variation in the concentration of organic matter in the reaction medium as a function of time during anaerobic digestion.

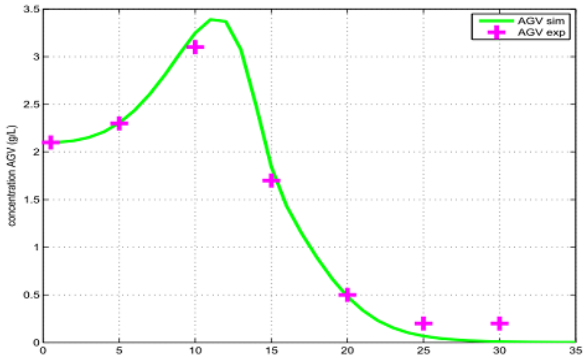


Fig. 7 Experimental and simulated curves of the variation in the concentration of volatile fatty acids as a function of time.

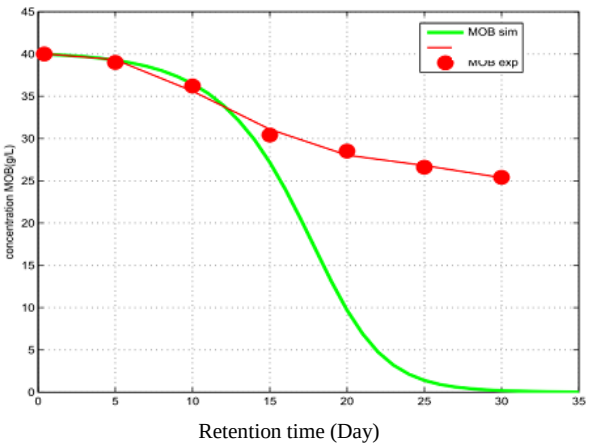


Fig. 8 Experimental curve and simulated curve of the variation in organic matter concentration.

It can be seen that there is an overall decrease in the concentration of organic matter over time. These results are in agreement with those of Madani-Hosseini et al. [43]. This drop in the concentration of organic matter could be explained by the consumption of organic matter by acidogenic bacteria with the production of volatile fatty acids. In addition, it should be noted that the rate of fall is not constant throughout the retention time. This rate of fall in concentration makes it possible to segment this organic matter kinetics into three phases. Indeed, the rate of fall is low during the first five days of anaerobic digestion, on the other hand during the second phase which goes from the sixth to the 25th day, this rate of fall increases; with a consequent rapid drop in the concentration of organic matter due to the strong activity of acidogenic bacteria. Finally, in the third phase which runs from day 26 until the end, the fall speed becomes low again. These results are in agreement with those of Derbal et al. [44]. Furthermore, there is a certain adequacy between the experimental and simulated results at the start of anaerobic digestion between the 1st and the 15th day. This could be explained by the fact that majority of the readily biodegradable biomass is consumed during this period. These are mainly reducing sugars such as glucose or glucose oligomers from the hydrolysis of polymers such as cellulose during the organosolv pretreatment. Because these reducing sugars are relatively simple molecules such as glucose, they are consumed quickly. According to the work of Ohimain et al. [45], a simple sugar such as glucose can directly undergo acidogenesis with the production of volatile fatty acids such as acetate, propionate and butyrate. A disaccharide can undergo rapid hydrolysis followed by acidogenesis. This is in perfect agreement with our modeling hypotheses which do not take into account hydrolysis, hence the proximity of the experimental and simulated results. Conversely, there is a clear difference between the experimental results and the simulated results from the 16th to the 30th day. Indeed, during this period, the organic matter consumed would essentially consist of macro-polymer such as cellulose. Due to their size, such molecules will first undergo complete hydrolysis into single molecules. These in turn would undergo acidogenesis. We can therefore think that it is the absence of the hydrolysis step in the proposed model that justifies this difference between

experimental and simulated results. The model validation criteria for the variation in organic matter concentration are listed in Table 6. The variation model of the simulated matter concentrations describing the variation in concentrations of acidogenic and methanogenic bacteria is represented in Table 6.

Table 6 Model validation criteria for the cumulative production of biomethane.

Validation Indicator	Production of Biomethane	Concentration of Volatile Fatty Acids	Organic Matter Concentration
R^2	0.99	0.96	-
Adjusted R^2	0.98	0.95	-
Bias factor	0.29	0.12	0.08
Exactitude factor	0.03	0.06	5.84
AADM	0.78	1.09	0.89
RMSE	1.09	1.07	1.11

3.7.4 Simulation of Bacteria Growth

Fig. 9 illustrates that the growth of bacteria within the biodigester has three distinct phases. The first phase lasts up to the 5th day. During this phase, the two bacterial families are weakly present and have the same concentration. This period corresponds to the latency period necessary for the adaptation of microorganisms and during which their growth is very low. The second phase which goes from the 6th to the 23rd day is characterized by an exponential growth of both bacterial families. Peak concentrations of 1.35 and 1.1 g/L are reached on day 23 for acidogenic and methanogenic bacteria, respectively. But we also observe that throughout this phase, the concentration of acidogenic bacteria is always higher than that of methanogenic bacteria. This could be explained by the difference in the maximum growth rates of these two bacterial families. It is respectively 0.97 and 0.70 day-1 for acidogenic and methanogenic bacteria. These results are in agreement with those of Sharma et al. [46]. The third phase begins from the 23rd day till the end. It is marked by a gradual drop in the concentration of each of the bacterial families. This decrease in bacterial populations is explained by the depletion of their respective substrates. In such a circumstance, bacterial

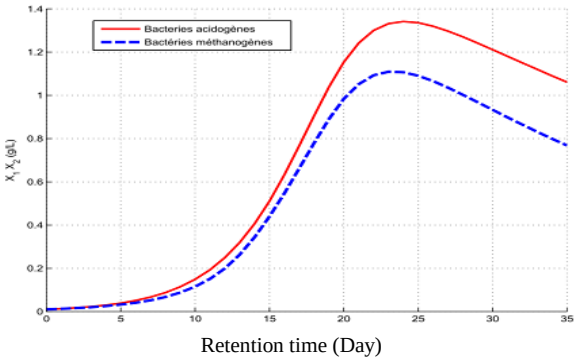


Fig. 9 Simulated curves of the concentration of microorganisms.

growth is inhibited while bacterial decay takes over. It should also be noted that the fall in the bacterial population is more rapid for methanogenic bacteria than for acidogenic bacteria. This could be explained by the rate of decrease which is 0.02 and 0.04 day^{-1} for the acidogenic and methanogenic bacteria respectively. These results can be used to predict the evolution of a biodigester after depletion of the biodegradable material and interruption of the charge [47-51].

4. Conclusion

The objective of this work was to model the anaerobic digestion of cocoa hulls using the particle swarm method. Analysis has made it possible to highlight the physicochemical and lignocellulosic characteristics of the cocoa shell powder before and after an organosolv pretreatment under optimal conditions.

The solid fraction obtained after pretreatment underwent anaerobic digestion with an inoculum from a pig manure biodigester at a temperature of 39 ℃ for 30 days. In addition, a mathematical model of the biological process of anaerobic digestion with two phases, namely acidogenesis and methanogen, was implemented in order to simulate the functioning of the biodigester. It is observed that the cocoa shell is a biomass with a high energy potential given its high organic matter content of 92.1%. In addition, the organosolv pretreatment as a delignification process simultaneously allowed a 48% drop in the lignin

content and a 22% increase in the cellulose content of the cocoa shell powder. On one hand, the maximum production speed of biomethane was 11 NmL per day with a production yield of 41 NmL/ g OM before the pretreatment of the cocoa shell powder. On the other hand, the maximum speed increased to 21 NmL per day and the production efficiency to 90 NmL/g MO after the pretreatment. This represents a 117% increase in the production efficiency. In addition, the flammability test was positive from the 10th day of the retention time. Also, the model used enabled the appropriate analysis of the anaerobic digestion of the cumulative production of biomethane. These estimated parameters also made it possible to describe the variation in the concentration of volatile fatty acids. The model only partially described the experimental data of the variation in organic matter concentration. Finally, the model made it possible to simulate the evolution of the concentrations of acidogenic and methanogenic bacteria during anaerobic digestion. Based on the above, we can say that the hypotheses have been verified. Since this work did not cover all aspects, it would be very interesting and beneficial to carry out further studies. These include: carrying out an economic study; use further complex anaerobic digestion model; carrying out a comparative study in terms of pretreatment with other solvents.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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