Hydrogen prod n by dark fermentation process from pig manure, cocoa mucilage and coffee mucilage

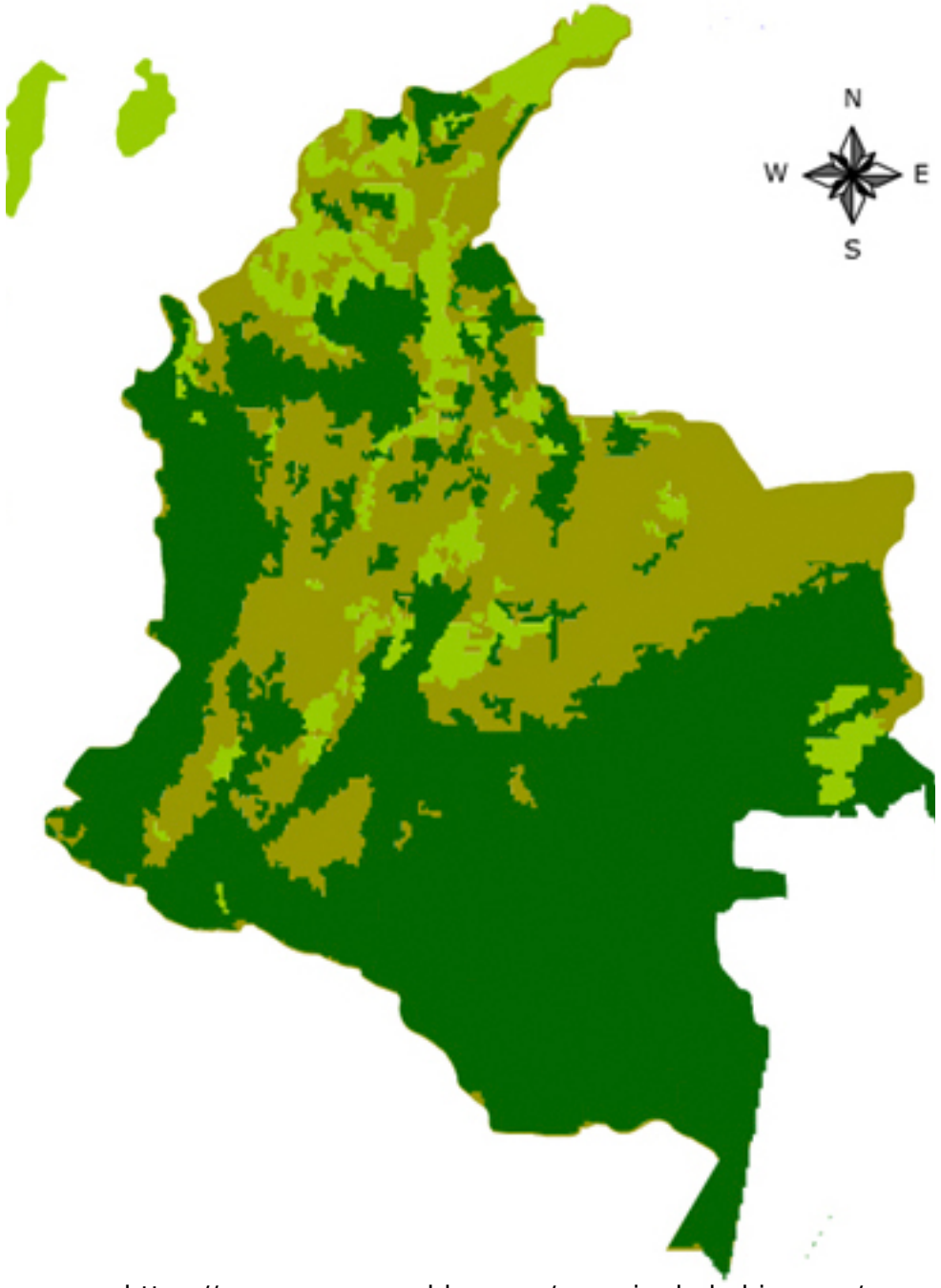
C.J. Rangel 1 , M.A. Hernández 1 , J.D. Mosquera 2 , Y. Castro 3 , I. O. Cabeza 2 , P. A. Acevedo 3 .

1 Department of Engineering Process, EAN University, Bogotá, Colombia
2 Department of Environmental Engineering, Universidad Santo Tomás, Bogotá, Colombia
3 Department of Industrial Engineering, Universidad Cooperativa de Colombia, Bogotá, Colombia

COLCIENCIAS
Ciencia, Tecnología e Innovación

Introduction

- Fossil fuels world demand and reserves depletion.
- Bio-hydrogen production lies in the consumption of residual biomass [1].
- Global warming due to the emissions of CO_2, CH_4, and N_xO.



https://www.asorenovables.com/energia-de-la-biomasa/

Introduction

- Colombia has a high potential for the generation of biomass to energy pathways.
- Agricultural sector generates approximately 7,5 million tons of organic residues [2].
- Cocoa and coffee are the primary crops in the country and the ones with higher export incomes.

Materials and Methods

Residual biomass from Santander and Cundinamarca regions were used

Pig manure

Cocoa mucilage

Coffee mucilage

Inoculum pre-tratement
thermal shock of anaerobic sludge.

Experimental design

Conditions: thermophilic environment of 55°C and pH 5.5

- A respond surface experimental design Box-Behnken was constructed to evaluate the effect of independent variables affecting the H production.
- Three independent variables were established, each with three own levels, as shown in **Table 1**.
- The initial organic load and the C/N ratio were adjusted according to the

The test was allowed to run until the hydrogen production rate decreased.

Information collected was analyzed to determine the experimental point with the highest BHP, using the Box-Behnken model and the mathematical model of MARS.

Table 1 Experimental design

Combination	RS CFM:CCM (gCOD CFM:gCOD CCM)	Organic load (g COD/L)	C/N
1	3:1	2	35
2	1:3	2	35
3	3:1	8	35
4	1:3	8	35
5	3:1	5	25
6	1:3	5	25
7	3:1	5	45
8	1:3	5	45
9	2:2	2	25
10	2:2	8	25
11	2:2	2	45
12	2:2	8	45
13	2:2	5	35

The physicochemical characterization of the effluent mixtures: TS (2540B APHA SM); VS (ASTM D3174); Kjeldhal total nitrogen (ASTM D1426); VFA (5560D APHA SM); alkalinity (2320B APHA SM) and CODs (ASTM D1252-0).

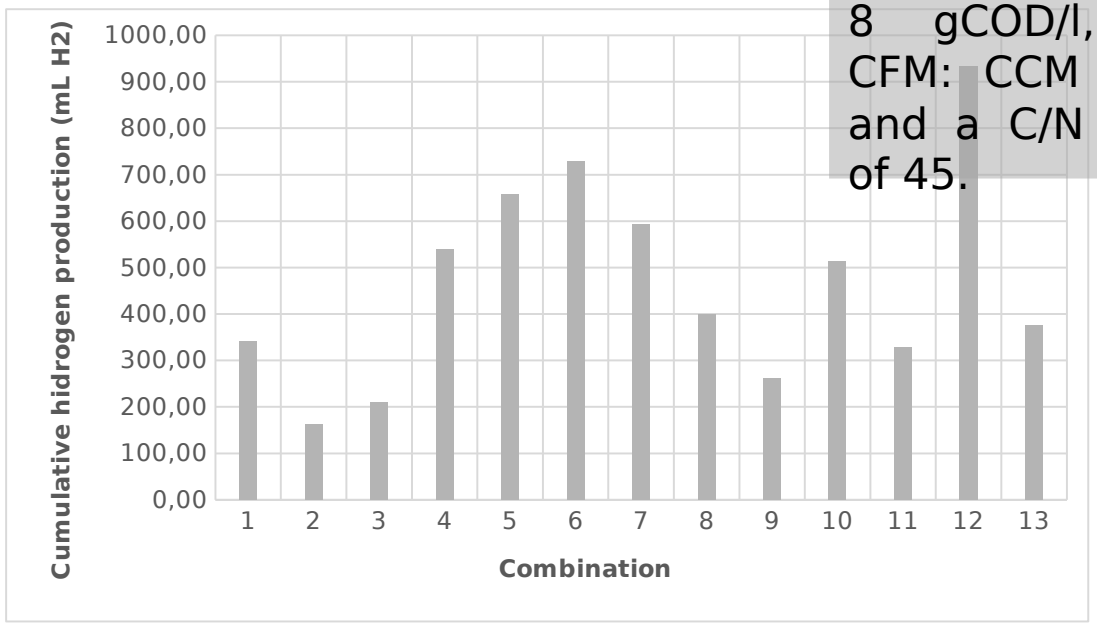
Results and discussion

Table 2 Characterization of the residual biomass used in the study

		Substrates			
		PM	**CCM**	**CFM**	**Inoculum**
Moisture	%	77,08±0,7	80,72±0,8	97,2±0,4	94,4
NTK	%	2,10	0,58	0,31	
Organic matter	%	71	79,6	97	96,6
N	%	2,07	0,21	0,06	
COD	g/l	23,87	10,50	21,75	
Proteins	%	22	4	6,5	
Carbohydrates	%	2,9	60,37	85,95	

* The analyses were performed on a wet basis

Results and discussion



Organic load of 8 gCOD/l, RS CFM: CCM of 2 and a C/N ratio of 45.

Fig. 1 Cumulative production of each of the combinations given in ml of H_2

Box-Behnken combinations

Combination 12 reported the highest production with 155,3 ml H_2/d, showing a direct relationship between the production and the substrates concentrations [3].

Effluent characterization

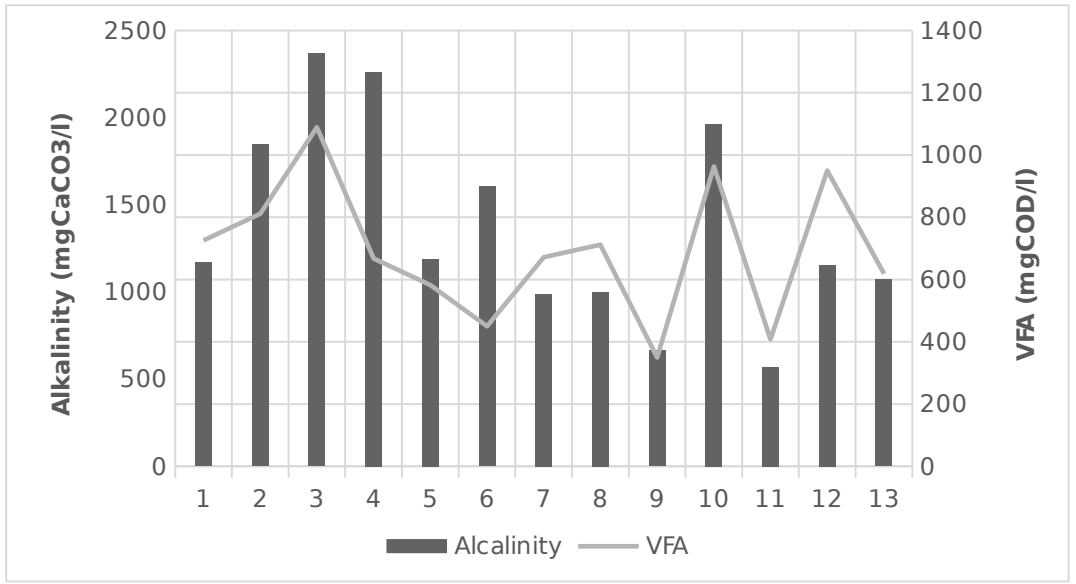


Fig. 2 Relationship between alkalinity and VFA production for each of the 13 mixtures

The alkalinity is a desired effect between the reactors since it is an indicator of the buffer effect that the mixture possesses.

Effluent characterization

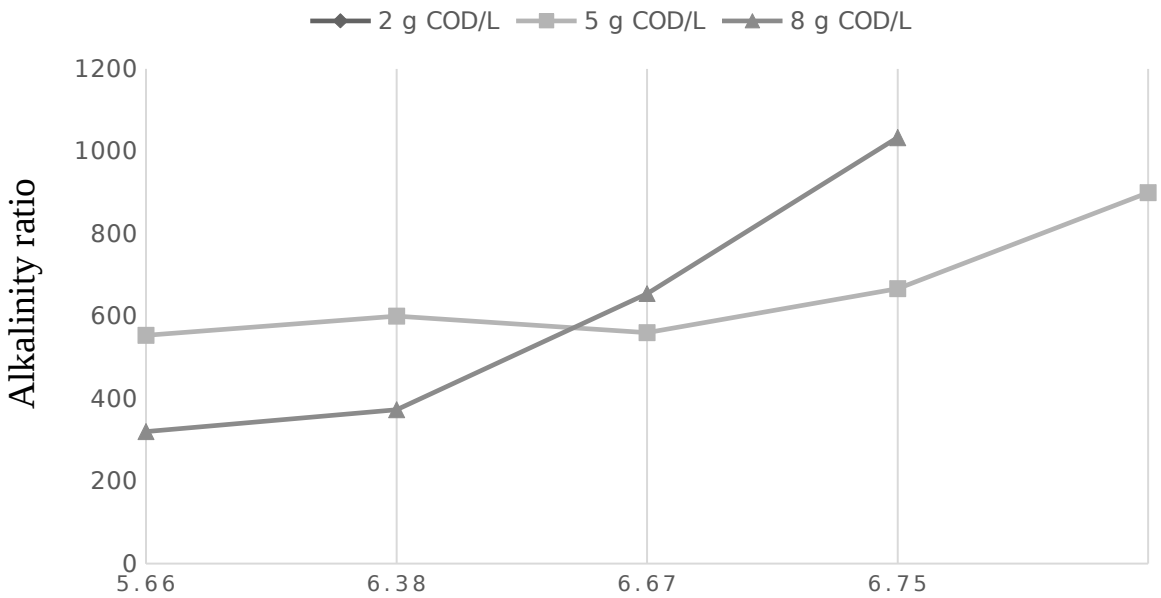


Fig. 3 pH vs. alkalinity ratio

- The relationship between pH and alkalinity is directly proportional. They affect the production of VFA and the consumption of hydrogen [4].

- In **Fig. 3** where it is observed how pH and alkalinity have similar behavior.

Statistical analysis

Pareto analysis:

- A negative influence was estimated for the RS CFM: CCM; the decrease in the production is because CFM has a lower presence of carbohydrates per gram of COD comparing with CCM.

- Coffee and cocoa are seasonal crops in Colombia, so the availability of these two residues will change during the different months of the year.

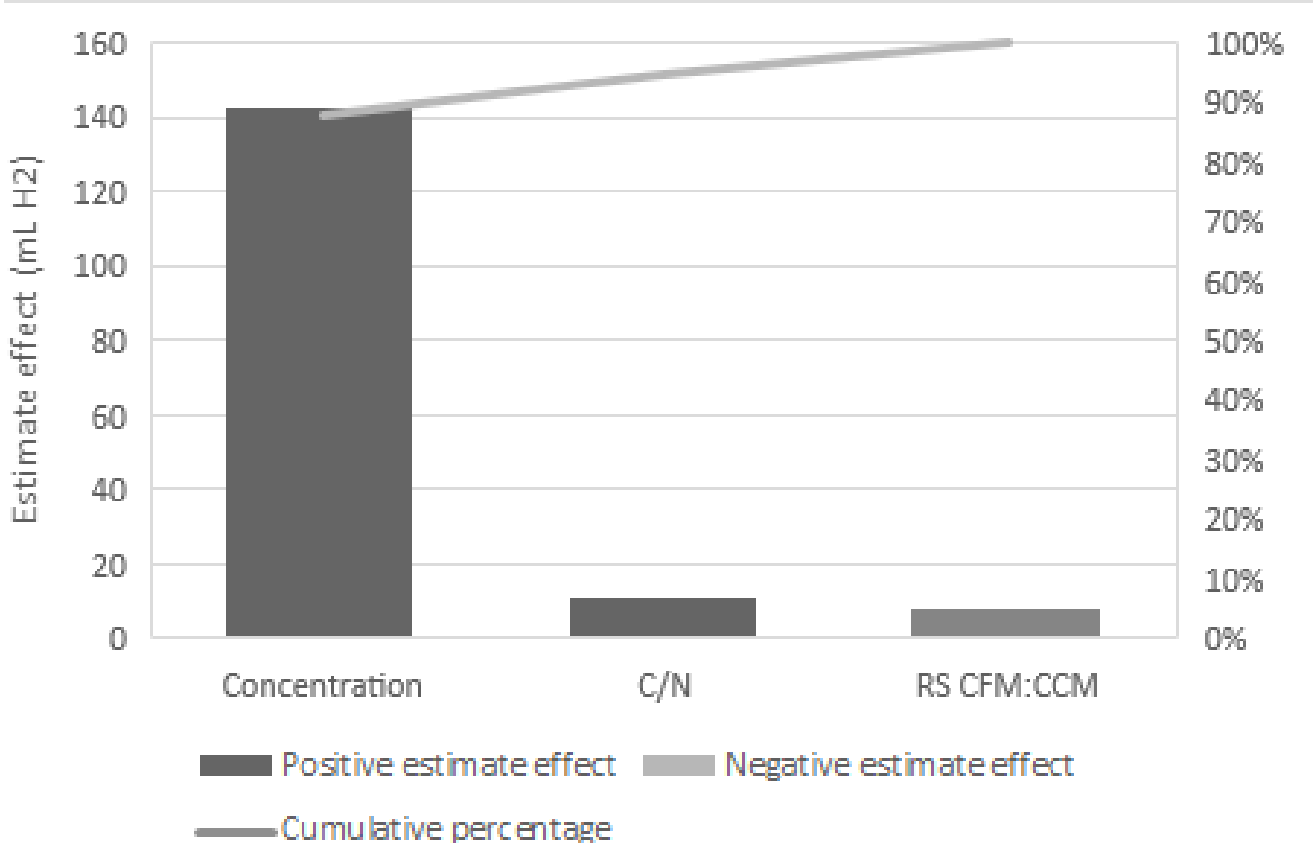


Fig. 4 Effects of the independent variables on the BHP

Box-Behnken

The equation was the result of a simulation performed through the software STATGRAPHICS

$$ml\ H_2 = 374{,}5 - 8{,}48229 * RS\ CFM{:}\ CCM + 143{,}185 * [\ ] + 11{,}5052 * C/N + 17{,}6281 * RS\ CFM{:}\ CCM^2 - 137{,}371 * RS\ CFM{:}\ CCM * [\ ] + 66{,}4063 * RS\ CFM{:}\ CCM * C/N - 68{,}5073 * [\ ]^2 + 88{,}2917 * [\ ] * C/N + 202{,}716 * C/N^2$$

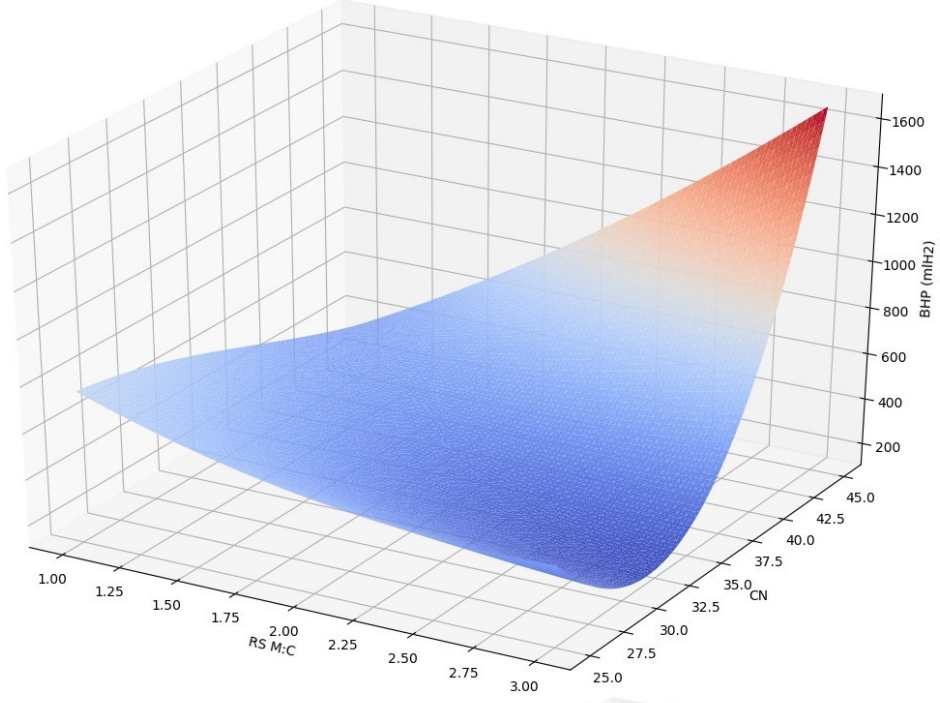
The equation that was obtained presents a correlation coefficient capable of explaining 75%

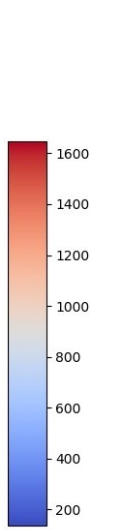
MARS

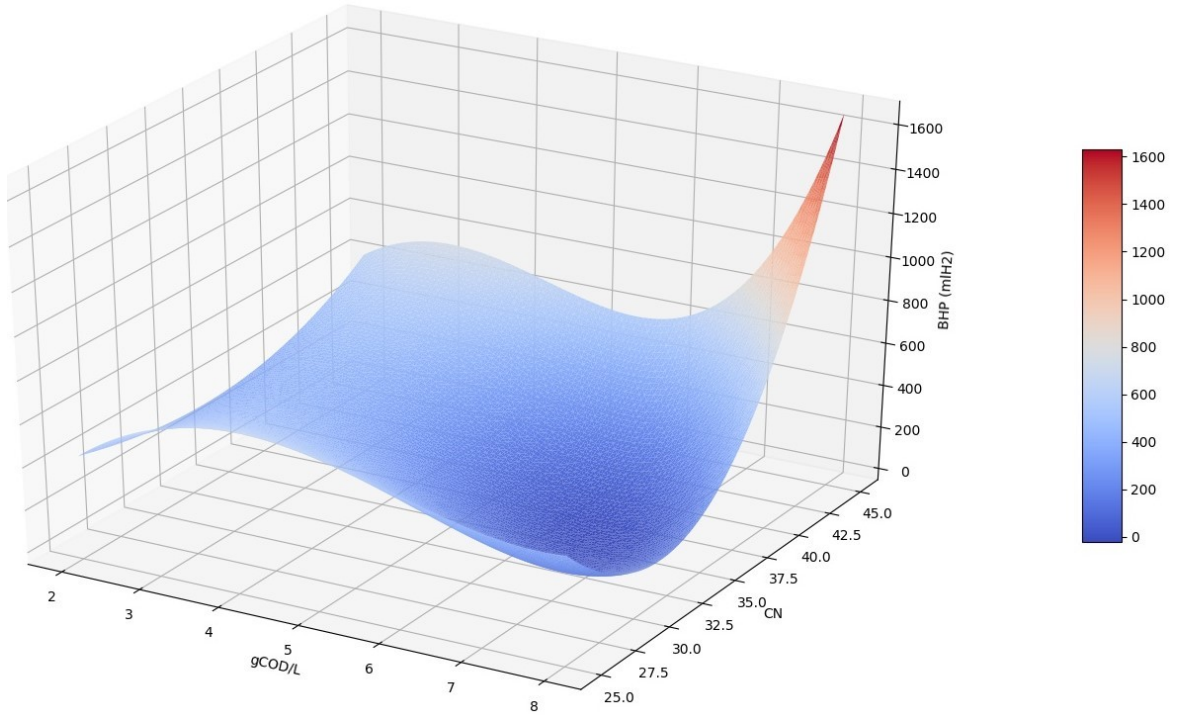
Using the MARS lines regression:

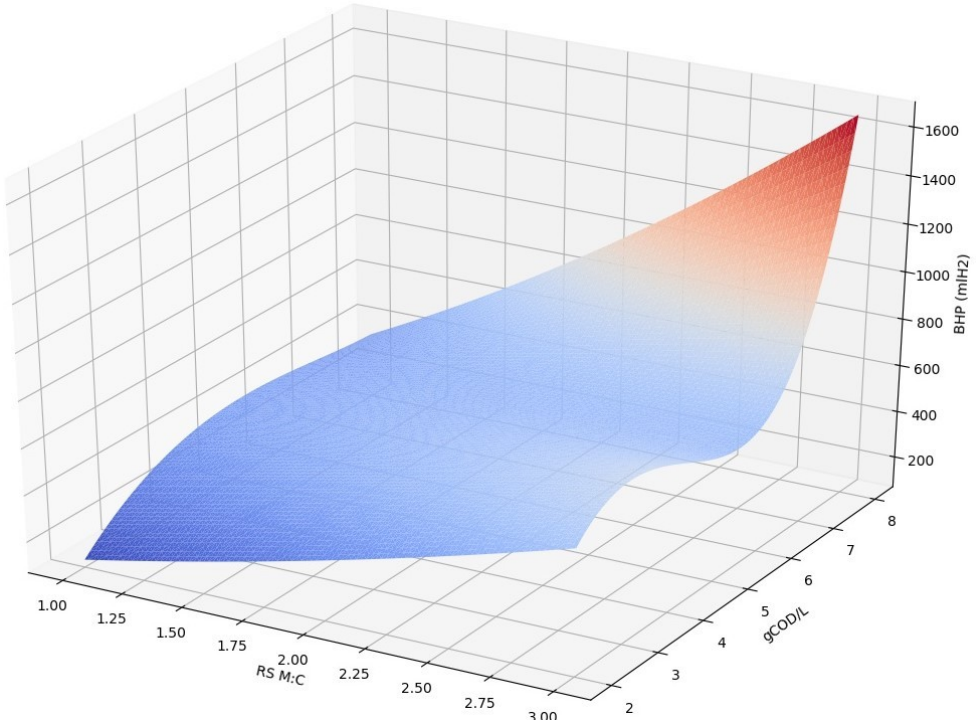
$$ml\ H_2 = -483{,}059 - 25{,}9812x_1x_1 - 170{,}278x_0x_1 - 1{,}42628x_0x_0x_1x_1 + 40{,}1349x_0x_0x_1 - 0{,}0523742x_2x_0x_1x_1 + 30{,}5188x_2x_1 - 0{,}551239x_2x_2x_1 - 0{,}0523742x_2x_0x_1x_1 - 11{,}6596x_2x_0x_1 - 0{,}12025x_2x_0x_0x_1x_1 - 0{,}00351634x_0x_2x_2x_0x_1x_1 + 0{,}00479633x_0x_2x_2x_2x_1 + 7{,}80912^{-5}x_1x_1x_0x_2x_2x_0x_1x_1$$

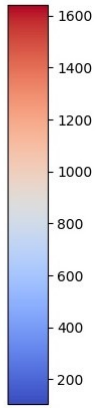
The model equation has a correlation coefficient of 76%











Optimal point:

- Organic load 8gCOD/L
- C/N 45
- RS CFM: CCM of 3:1

Conclusions

- The maximum hydrogen production achieved was 155.33 ml H_2/d when the organic loading rate was 8 gCOD/l, the RS CFM:CCM of 2:2 and C/N ratio was 45 in the combination 12.
- In general, the mixtures with organic loads between 5 - 8 gCOD/l reported higher production.
- Regarding the C/N ratio, it was found that the best hydrogen productions are achieved with the lower and higher value (25 and 45).
- On behalf of RS CFM:CCM, the conclusion is that mixtures with more content of CCM produce more quantity of hydrogen thanks to the higher content of carbohydrates of this substrate.

Conclusions

- The lower influence of the RS CFM: CCM variable that was presented in the Pareto chart helps the scale up of the process, because the hydrogen production will be similar despite the mucilage used.
- The removal of COD of 37% allows suggesting secondary processes associated with biorefinery schemes, which allows higher removals of COD and the obtention of other value-added sub-products such as VFA.

References

- 1. Posso, F., Narváez C., R.A., Siguencia, J., Sánchez, J.: Use of Municipal Solid Waste (MSW)-Derived Hydrogen in Ecuador: Potential Applications for Urban Transportation. Waste Biomass Valorization. (2017). doi:10.1007/s12649-017-0161-1
- 2.Bolétin Técnico- Residuos Sólidos, https://www.dane.gov.co/files/investigaciones/pib/ambientales/cuentas_ambientales/cuentas-residuos/Bt-Cuenta-residuos-2016p.pdf
- 3. Argun, H., Dao, S.: Hydrogen gas production from waste peach pulp by dark fermentation and electrohydrolysis. Int. J. Hydrog. Energy. (2015). doi:10.1016/j.ijhydene.2015.11.170
- 4. Mu, Y., Yu, H.-Q., Wang, Y.: The role of pH in the fermentative H2 production from an acidogenic granule-based reactor. Chemosphere. 64, 350-358 (2006). doi:10.1016/j.chemosphere.2005.12.048

Acknowledgments

The authors acknowledge financial support from Colciencias (Administrative Department of Science, Technology, and Innovation of Colombia):

- Call 745 for CTeI projects, and its contribution to country challenges 2016

- Call 771 for Santander 2017.