Energy potential of vinasse derived from rum manufacturing

To cite this article: Carmen Luisa Vásquez Stanescu *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **872** 012032

IOP Conf. Series: Materials Science and Engineering **872** (2020) 012200 doi:10.1088/1757-899X/872/1/012200

Publisher's Note on: Energy potential of vinasse derived from rum manufacturing (*IOP Conf. Series: Materials Science and Engineering* **872** 012032)

This article was retracted in error on 15 September 2020. The retraction notice was removed on 25 September 2020. IOP Publishing apologises for this error.

IOP Conf. Series: Materials Science and Engineering **872** (2020) 012032 doi:10.1088/1757-899X/872/1/012032

Energy potential of vinasse derived from rum manufacturing

Carmen Luisa Vásquez Stanescu[1], Kevin Carrillo[1], Betzabeth Espinoza[1], Aniello Rizzo[1], Carla Fajardo[1] , Rodrigo Ramírez-Pisco[2] and Amelec Viloria[3]

[1] Universidad Nacional Experimental Politécnica Antonio José de Sucre, Av. Corpahuaico, Barquisimeto, Venezuela
[2] Universidad de Barcelona y Universidad Politécnica de Cataluña, Barcelona, España.
[3]Universidad de la Costa, Barranquilla, Colombia.

[1]**Email**: cvasquez@unexpo.edu.ve

Abstract. The purpose of this study is to analyse the energetic potential of the vinasse coming from the distillation of rum. 10 to 15 l of vinasse are obtained for each unit of alcohol. This is being used as fertilizer for the cultivation of sugar cane. Three samples are analysed for physical, chemical and fuel properties: raw vinasse, its distillate and residue. The results demonstrated that raw vinasse can be used as an additive to liquid fuels with a calorific value of approximately 792 kJ/kg and a boiling point above that of flammability, which flavours the non-formation of vapours. The amount of solid waste present could be detrimental to atomization inside furnaces or its flow through combustion chambers, so it must be pre-treated.

Introduction
The decarbonisation of the electricity production sector [1] and the energy transition [2] in the search for achieving the millennium goals [3], have encouraged to explore new renewable energy sources and the use of biofuels that produce less environmental impact. Among these, bioethanol from plant foods stands out, whose use has been widely discussed [4]. One of the options for its production is from industrial organic waste [5], among these, the vinasse from the manufacture of rum [6].
The juice or molasses of the sugar cane is used in the manufacture of rum. After fermentation and distillation, the raw alcohol is obtained, as well as other by-products, such as vinasse. The Vinasse is considered as a waste, and is discarded as it is not useful for the distilleries. This material contains a large organic load that can become a contaminant if not properly treated, and is used for irrigation or fertilization of some crops [7].
The present study shows the results of the physical, chemical and energy potential analysis of vinasse as a by-product of rum manufacturing. The samples were taken directly from the distillation tank.

1.1. Vinasse as a by-product of rum
The vinasse is an organic residue generated in the liquor industries during the process of distillation of the fermented must to obtain alcohol, such as brandy, rum and cachaça, among others. It is characterized by a substance with a suspended solid content, brown or dark brown in color, honey aroma and malt flavour. On average, 10 to 15 litters of vinasse are generated for every litter of alcohol produced, depending on the technology in the distillery [8]. It has a higher pollution potential than wastewater,

mainly because it has a pH between 3,5 and 5. Additionally, it has a high biochemical oxygen demand (BOD), between 10 and 65 g/l. In addition to possessing high concentrations of potassium and sulphates. The vinasse is used as a fertilizer, mainly in sugarcane crops, due to its high content of organic matter and micronutrients. However, their prolonged use or in large quantities can saturate the soil and contaminate water sources [9].

1.2. Materials and methods

A sample of about eight (8) litters of vinasse is taken once the distillation process has been completed. In order to understand the intrinsic properties, present in the vinasse, qualitative and quantitative measurements were made. Initially, in order to obtain information on the volatile material present, distillations were carried out at atmospheric pressure and in a vacuum. As far as atmospheric distillation is concerned, a distillation assembly is carried out at a temperature of 98° C, working with a volume of vinasse of 200 ml. On the other hand, vacuum distillation is carried out at a temperature of 70°C and working with a volume of 250 ml of vinasse, in order to obtain more volatile fractions of low molecular weight.

For the different determinations mentioned above to the samples of vinasse, distillation residue and distillate, the following is analysed: total quotient of dry matter dissolved in a liquid (Degrees Brix), density, dynamic viscosity, refraction index, conductivity, solid residue, suspended solid, pH, functional degrees (alcohols, ketones, aldehydes and phenols) and elemental analysis. For fuel analysis, properties such as ash content, moisture content, calorific value, boiling point and flash point are analysed according to [11] [12] [13]. The materials, reagents and laboratory equipment used are shown in Table 1.

Table 1. Materials, reactive and laboratory equipment used

Materials	Reactive	Equipment
– 25mL graduated cylinder – Test tube – Capillary – Tape – Thiele Tube – Glycerin (or paraffin) – Watch glass – Cresol – Capillary – Burner – Thermometer – Centrifuge tube	– $KMnO_4$ 0,5% – 2,4-dinitrophenylhydrazine – Distilled water – Ethanol – H_2SO_4 Conc. – $AgNO_3$ 5% – NaOH 5% – NH_3 2M – $(NH_4)_2C_2O_4$ a 0,2M – $K_4[Fe(CN)_6]$ – NH_4OH 6M – Na_2HPO_4 0,5 M – Na_2S 0,5 M	– Handheld Refractometer Model REF – 107. – Analytical balance – GENESYS 10uv Spectrophotometer – Pycnometer – DYNAC Centrifuge – Thermo Scientific Orion Versa Star Pro Desktop meter – HANNA Instruments Microprocessor pH Meter – Oxygen heat pump – Drying oven – Heating blanket

Table 2 shows the results of elemental analysis by atomic absorption for the distillate and qualitative analysis. The distillation residue was discarded from this analysis because it has a high concentration of organic matter and solid residues that do not make it suitable for qualitative analysis, nor for analysis by atomic absorption.

Table 2. Chemical composition of vinasse

Sample	Fe	Mg	Ca	Zn	Cu
Raw vinasse	Negative	Positive	Positive	Negative	Negative
Distillate (ppm)	9	5	6	171	1
Residue of the distillate	N/A	N/A	N/A	N/A	N/A

The vinasse was studied by qualitative analysis due to the presence of particles suspended in the solution that do not allow analysis by atomic absorption. By analysing the presence of magnesium and calcium in the vinasse, a precipitate is obtained, indicating the presence of both elements. It should be noted that, as this is an analysis with limited sensitivity, it is possible that the presence of iron, zinc and copper is not zero, but that these elements are found in a much lower proportion to calcium and magnesium and, for this reason, have not been detected. In the case of the distillate, a moderate concentration of zinc and traces of iron, magnesium, calcium and copper is observed. On the other hand, results from studies of vinasse carried out by [11] indicate that in terms of metals, a higher proportion of iron (85 ppm), zinc (9,2 ppm), manganese (7,8 ppm) and copper (7,7 pm) were present, thus showing that not all vinasse have the same chemical composition.
Table 3 shows the results of the physical and chemical characteristics of vinasse and its derivatives. The three (3) samples have a medium acidic pH, due to the presence of already degraded organic compounds. According to [11], the acid pH is a common characteristic in stillages, with an average pH of 4,99. This is a limiting factor in the strategy of using raw vinasse in an oven or other equipment. It should be noted that this pH value defines the sample as a possible biofuel input, that is, it can be used in smaller proportions and complement a standard liquid fuel, once treated with some pH buffer chemical that allows its use in larger proportions. Finally, it is evident that as brix degrees increase, so does density, which is consistent with the reported results [12].

Table 3. Physical and chemical characteristics of vinasse

Sample	pH	Degrees Brix (°Bx)	Density (g/cm^3)
Raw vinasse	4 ± 0,01 to 24,5°C	1,5 ± 0,2	1,0126 to 23°C
Distillate	3,50 ± 0,01 to 24,5°C	-----	0,9904 to 24,5°C
Residue of the distillate	4,08 ± 0,01 to 24,5°C	23,5 ± 0,2	1,1206 to 24,5°C

It is possible to obtain an estimate of the presence of minerals by measuring conductivity. Table 4 shows the conductivity and refractive index of the analysed samples.

Table 4. Conductivity and refractive index of vinasse samples

Sample	Conductivity (ms⁄cm)	Refraction Index
Raw vinasse	8,40 ± 0,01	1,3351 ± 0,0001
Distillate	0,220 ± 0,01	1,3313 ± 0,0001
Residue of the distillate	28,95 ± 0,01	1,3912 ± 0,0001

The vinasse and residue have relatively high conductivity, due to the presence of minerals. On the other hand, the distillate has very low conductivity due to its absence. The results in Table 4 show a value similar to the one reported in [13], where he explains that "vinasse is very conductive (28,4 mS/cm) compared to other solutions, this is due to its high content of inorganic salts, especially potassium salts". Likewise, analysing the refraction index, no trend is observed in relation to the density of the solutions. There is no testable or measurable reference for the refractive index.
The results of solid and suspended waste are reported in Table 5. As each of the species leads to dryness, it is evident that no solids are present in the distillate compared to the high concentration present in the residue. On the other hand, it is observed that the vinasse and the residue of the distillate present a certain number of solid residues that could damage the atomization inside the furnaces or the flow of the same through the combustion chambers, therefore it must be pre-treated.

Table 5. Solid waste and suspended solids from the vinasse

Sample	Solid waste (g)	Suspended solids (g of sediment/g of vinasse)
Raw vinasse	0,0149	0,0705
Distillate	0,0001	N/A
Distillate waste	0,2075	N/A

In order to identify oxygenated organic compounds, qualitative tests were performed on vinasse and its derivatives to determine functional groups such as alcohols, carbonyl groups and phenols as shown in Table 6. Both vinasse and distillation residue were discarded from this analysis because the sensitivity of the test applied to this type of samples is limited.
Table 6 shows the unique presence of alcohols; however, the low pH values can be explained by the possible presence of acids resulting from the degradation of the carbonyl groups. On the other hand, as viscosity allows to understand the behaviour of the samples, tests were carried out with the NDJ-5S viscometer, where the results obtained indicate that they are non-Newtonian fluids whose viscosities are 0,2467 poise (with a torque of 24,65%) in the case of stillage, and 0,2628 poise (with a torque of 26,28%) in the case of distillate.

Table 6. Vinasse functional groups

Sample	Alcohols	Aldehydes	Ketones	Phenols
Raw vinasse	N/A	N/A	N/A	N/A
Distillate	Positive	Negative	Negative	Negative
Distillate waste	N/A	N/A	N/A	N/A

For the purpose of analysing combustible characteristics, Table 7 reports the results obtained from the ash content, moisture content and calorific value of the analysed samples.

Table 7. Vinasse functional groups

Property	Raw vinasse	Distillate	Distillate waste
Ash content (%)	0,74	N/A	4,7
Moisture content (± 0,001%)	N/A	0,085	N/A
Calorific value (kJ/kg)	792,086	107,337	327,511

It can be noted that the waste presents 4,70% of ashes, a value much higher than that reported by the vinasse, which is 0,74%, which is evidenced by the high concentrations of solids and organic matter present in the waste. The distillate was discarded from this test due to the absence of solid residues.
One advantage of vinasse ash over other fuels is that it is rich in minerals and materials that can be collected from boiler ashes and used in other economically important industrial sub-processes. Most of these ashes are carbon that can be burned with oxygen and provide heat in the CO2 and CO formation reaction [11]. According to the latter, "13,2% is ash which is made up of metals and minerals, the latter in greater proportion. The rest of the vinasse is made up of water, volatile acids, and alcohols".
On the other hand, the samples were analysed to determine the available calorific value, the results of which are reflected in Table 8. As can be seen, the magnitude of the calorific value is relatively low for the samples, which defines them as possible low-calorific fuels. However, vinasse has the highest calorific value of the samples.

Table 8. Combustion characteristics of stillage

Properties	Raw vinasse	Distillate	Distillate waste
Boiling point (°C)	98	102	112
Flash point (°C)	90 - 92	70 – 72	92 – 94

The difference between the different values of ΔH is due to the fact that the highest calorific value is provided by the carbon from the organic matter present in the vinasse [1], although the alcohols could also increase this calorific value. Finally, Table 8 shows that the boiling point is higher than the flash point, which is an important issue to consider. Otherwise, there is a risk that water vapor will form inside the pipes when the temperature rises. According to [11], "because the boiling point is higher than the flash point, it is ensured that the volatiles will not be affected by water vapors inside the vinasse burner pipes". On the other hand, the flash point determines the heating range to be given before entering the furnace for combustion.

Conclusions

The physical, chemical and combustible properties of the vinasse from the rum distillate become an important contribution to the use of this material, not only for irrigation or fertilization of sugar cane. There are indications that vinasse can be used as a biofuel, however, there is an important variance with other similar studies, as shown in Table 9**.**

Table 9. Comparison of the combustible properties of vinasse

Country	**Guatemala [11]**	**Venezuela**		
Sample	Liquid vinasse	Distillate	Raw vinasse	Distillate waste
Calorific value (kJ/kg)	13.920	107,337	792,086	327,511
Boiling point (°C)	95	98	102	112
Flash point (°C)	41,33	90 - 92	70 – 72	92 – 94

Acknowledgments
The authors would like to acknowledge the Destilerías Unidas SA (DUSA) from Venezuela and the Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo (CYTED), as this was developed within the framework of the Red Iberoamericana de Transporte y Movilidad Urbana Sostenible (RITMUS, 718RT0566).

References
[1] Albarracín, L. R. *El cambio climático y el desarrollo energético sostenible en América Latian y el Caribe al amparo del Acuerdo de París y de la Agenda 2030.* s.l. : Docuemntos de Trabajo (Fundación Carolina). Segunda época, 2019.
[2] Sánchez, Leadina, Vásquez, carmen, Viloria, Amelec. *Greenhouse gases emissions and electric power generation in Latin American countries in the period 2006–2013.*. 2017, International Conference on Data Mining and Big Data, págs. 777-785.
[3] Torres, R.C. *Transición energética: Obstáculo o estímulo al desarrollo.*. 49, 2020, EconomíaUNAM, Vol. 17, págs. 46-65.

[4] Gutiérrez, R.M., Pérez, L.O. y Hernández, J.J.*Biocombustibles, ambiente y sociedad. Una mirada desde la perspectiva bioética.* 2019, InfoCiencia, pág. 12.
[5]. —.Guitiérrez, R.M., Pérez, L.C. y Hernández, J.J. 4, 2019, InfoCiencia, Vol. 19, pág. 12.
[6] Solano, J.A. y Barriga, J.E.C. *El valor agregado de un sistema de gestión ambiental más allá de la certificación* . 1, 2019, BISTUA REVISTA DE LA FACULTAD DE CIENCIAS BÁSICAS, Vol. 16, págs. 86-91.
[7] Diez, O.A., y otros. *Producción simultánea de azúcar y alcohol: optimización energética incluyendo concentración de vinaza.* 1, 2020, Revista Industrial y Agrícola de Tucumán, Vol. 96, págs. 35-41.
[8] Torres, E.G., y otros . *Evaluación de abono órganico de vinaza y bagazo de la caña de azúcar para la producción ecológica de rabanito (raphanus sativus L.).*, 2019, Aposte Santiaguino, Vol. 12, págs. 236-249.
[9]Aristizábal Alzate, Carlos Esteban.*Caracterización físico-química de una vinaza resultante de la producción de alcohol de una industria licorera, a partir del aprovechamiento de la caña de azúcar.* 2, 2015, Ing. USBMed, Vol. 6, págs. 36-41.
[10] Armengol, J.E., Lorenzo, R. y Fernández, N. *Utilización de la vinaza como enmienda orgánica y su influencia en las proiedades químicas de vertisoles y en los rendimientos de la caña de azúcar.* 3, 2003, Cultivos Tropicales, Vol. 24, págs. 67-71.
[11] Muñoz, M. *Potencial energético de la vinaza para su utilización como biocombustible.* 2015.
[12] Dávila Rincon, J, Marriaga Cabrales, N y Machuca Matínez, F. *Remoción de sólidos totales de la vinaza por electrocoagulación-electroflotación.* 158, 2009, Dyna, Vol. 76, págs. 41-47.
[13] Zamora Rueda, G.D.H, y otros. *Caracterización energética de vinaza de caña de azúcar como posible biocombustible para calderas de vapor bagaceras.* La Plata : s.n., 2016. XXXIX Reunión de Trabajo de la Asociación Argentina de Energías Renovables y Medio Ambiente (ASADES).