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Energetic Valorization of Solid Wastes from the Alcoholic Beverage Production Industry: Distilled Gin Spent Botanicals and Brewers' Spent Grains

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Featured Application: Valorization of wastes from agri-food industries by their use as fuels and sources of power.

Abstract: In this paper, the authors assess the possibilities of energetic valorization for two solid wastes from alcoholic beverage production. Distilled gin spent botanicals (DGSB) and brewers' spent grains (BSG) are tested, both by themselves and as co-substrates, for their possibilities as substrates for anaerobic digestion in a system of box-type digesters, suited for the process. While BSGs show a good performance for anaerobic digestion, DGSBs, despite showing an acceptable biomethanogenic potential result as not suitable for the process. Experiments using DGSBs as substrate in the reactors result in failure. And, as a co-substrate, the biomethanogenic digestion process appears to be hampered and lagged. Possible explanations for this behavior are explored, as well as other possibilities for the use of the material as a power source given its high heating value.

Keywords: biochemical methane potential (BMP); biogas; by-products; higher heating value; alcoholic beverage production

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1. Introduction

Alcoholic beverage production is, globally, one of the most important industries in the agri-food sector. Both fermented and distillate beverage productions have several things in common, among which we can cite a high usage of resources, both in terms of raw materials and energy. On the other hand, the alcohol-making process produces a flow of waste and by-products that have to be dealt with due to their high pollution potential [1]. A number of countries have established regulations and guidelines for this specific sector. However, the problem is that the differences in the raw materials and processes used for the specific production of the different beverages demand specific analyses and studies for each particular case [2,3], making it difficult to establish unified ways to tackle the particular problems for the differenttypes of waste.

The current socio-economical situation worldwide, with an increased global concern about the environment and the effects of climate change, together with awareness about the scarcity of resources and energy, has resulted in a demand for new solutions to the problems caused by human activities in generaland processing industries in particular.Following the principles of circular economy and using the tools of life cycle analyses and the carbon footprint of the products is a way to ensure the welfare of the planet and its inhabitants, increasing the resilience of society and global economy.

The case of the alcoholic beverage production among other industrial fields is significant. Breweries have been among the first industries which have raised concerns about their pollution creation [4], which has led to the adoption of different domestic regulations (we can cite as examples the Australian Effluent management guidelines for Australian

wineries and distilleries [5,6] or the U.K. Guidance for Pollution Prevention GPP29 for Wales, Scotland, and Northern Ireland [7]) and, in other cases, rules of good practice. On the other hand, it is a demanding industrial field, not only in terms of raw materials and water consumption [8] but also in energy power, mainly used for heating in several operations of the alcoholic beverage production process (alcoholic fermentation, boiling of the worts, distillation, etc.). It is noteworthy to say that the sector combines a mixture of tradition (for example, the use of century-old copper pot stills or yeast strains fully developed in the particular industrial premises) with an open mind for development and improvement of those processes; aiming to optimize results both in terms of economy and product quality as well as image improvement towards society [9,10]. Thus, the industrial sector is eager to adopt measures to reduce both their inputs of raw matters, water and power, as well as to improve their production processes and reduce their waste [11]. This leads in a reasonable way to the interest of industries in the reduction and/or valorization of their waste. And an obvious way of dealing with such waste is as a powersource [12], achieving the double benefit of their reduction or elimination, as well as the reduction of power obtained through external sources.

Wastes in alcoholic beverage production can vary in form and nature, depending on the particular beverage produced. However, they usually havea series of things in common, as their origin is from natural matters (almost always from plant material) which usually makes them biodegradable and thus susceptible to biologic treatments. Their aforementioned diversity creates the necessity for the research of characterization and treatment options suited for each kind. And among the different possibilities available to deal with these wastes, anaerobic digestion with biomethane production has been a subject of study for a long time. Currently, there is literature available about anaerobic treatment and valorization in general for waste of almost any kind of alcoholic beverage, from beer or wine production [13–15], whisky and other grain distillates [16,17], to even tequila and other agave-based beverages [18,19]. However, there's a void in studies dealing with the wasteof gin production.

The making process of distilled gin as defined in the European legislation involves the mixing of botanicals and aromatics with ethyl alcohol of agricultural origin and water [20] and the distillation of that mixture. The botanicals used may be a mixture ofdifferent components in different proportions according to the producer's recipe (which is almost always a company secret) but the use of juniper berries (*Juniperus communis* L.) is mandatory, as its taste must be predominant by definition [21]. Other common flavoring agents that may be used or not are angelica (*Angelica archangelica* L.) roots, cinnamon (*Cinnamomum verum P.*) bark, caraway (*Carum carvi* L.) and coriander (*Coriandrum sativum* L.) seeds, and orris root (the rhizomes of *Iris germanica L.* and/or *Iris pallida Lam.*). The distillation product is mixed with water to achieve the desired alcoholic strength by volume, which has to be a 37.5% minimum.

A minimum of two flows of wastes can be identified in the making process. One of solid matter, consisting of the spent botanicals and aromatics, which will be wet and impregnated with a certain amount of alcohols, and another of liquids. At first sight, it appears as a mass of mixed items, which can be distinguished under close inspection, showing their nature. The liquid waste can consist of the heads and tails of the distillation process as well as the filtered remains in the pot still and spent wash. Process and cleaning waters can be added to this flow, increasing its volume.

Through the course of their research career, the authors have had previous experience with distilled gin waste, having dealt with the liquid waste of distilled gin production [22]. However, and knowing the working system of a gin distillery, there's no knowledge available on the treatment of the solid waste flow of distilled gin spent botanicals (DGSBs). Thus, it can be considered necessary to add research for the possible treatment and energetic valorization of these wastes to achieve a total overview of the ways to deal with them.

Experience with distilled gin liquid waste showed the possible need for a co-substrate for anaerobic digestion treatment, as the biological process can be hampered by the nature

and characteristics of the substrate. The use of brewer's spent grains (BSGs) resulted in an obvious choice for several reasons. The gin distillery was planning to expand their business, creating their own grain alcohols from malts (and thus, reducing their dependence from external sources of ethyl alcohol of agricultural origin), and the characteristics and composition of distiller's spent grains (DSGs) are very similar to those of BSGs, if not identical.

As the authors had previously proven the feasibility of anaerobic digestion treatment for distilled gin liquid waste, it was decided to try anaerobic digestion for solid wastein box-type reactors for both substrates, alone and in co-digestion. Some other research lines showed the influence of the use of a conductive material in the biochemical methane potential for some substrates from alcoholic beverage production [23], so it was decided to use granulated activated charcoal in some experiments.

2. Materials and Methods

2.1. Substrates

Solid waste from dry gin production was obtained from the distillery of Destilería Siderit S.L. in Puente Arce (Cantabria, Spain). Some of the different kinds of botanicals could be distinguished under the naked eye, as is the case for juniper berries, cinnamon bark or citric peel. Others were not easily distinguishable in the waste mass. The company is reluctant to provide the full recipe of the used flavours and their origin though, if possible, they preferentially acquire them from sources taking in account geographic proximity criteria.

Spent brewer's grains were collected at the facilities of Cervezas Artesanales de Cantabria S.L. (which operates under the brand "Dougall's") located in the municipality of Liérganes (Cantabria, Spain). Those were a Maris Otter barley malt (the usual malt type to brew "british style pale ale" beers; provider not detailed, but the characteristics of these malts are well established, being a product with known and predictable attributes for its use and for the produced beer qualities) with whole or coarsely ground grains.The characteristics of these substrates are shown in Table 1.

Table 1. Characteristics of wastes and by-products analyzed in the study (TS and VS are expressed as a percentage of the total mass).

Wastes and By-Products	TS (%)	VS (%)	TKN (g/kg TS)	P (g/kg TS)
Gin spent botanicals	35.6	34.3	1.56	0.17
Brewers' spent grains	25.2	24.2	3.59	0.56

2.2. Inoculum and Conductive Material

The inoculum used was, originally, the anaerobic effluent from a lab-scale digester treating liquid dairy manure and food waste (manure inoculum-MI). Afterward, it was used in the experimental setup for the box-type assays using food waste as a substrate described in Rico et al., 2020 [24]. Thus, it was assumed that the inoculum was well adapted to the experimental conditions in the laboratory and to substrates with a high degree of heterogeneity, as the ones for this study. This inoculum was used for both BMP tests and box-type reactor assays. Characteristics of the inoculum are shown in Table 2.

Table 2. Characteristics of the inoculum used in the study (TS and VS are expressed as a percentage of the total mass).

	Inoculum
TS (%)	2.23
VS (%)	1.16
pH	7.9
Alkalinity (g $CaCO_3$ L^{-1})	12.1
TAN (g NH_4^+-N L^{-1})	2.7

As commented in the introduction, the use of a conductive material in addition to the inoculums has been shown as a significant factor maximizing the biomethanogenic performance of the processes for some substrates as shown in Valero et al. (2019) [23]. Thus, Granular Activated Charcoal (GAC, 20 × 40) was used as a conductive material in some experiments.

2.3. Experimental Set-Up

The research part focused in the feasibility of waste treatment and their energetic valorization through anaerobic digestion follows the methodology of obtaining the maximum possible methane production for the tested substrates in optimum conditions and for as much time as the necessary for the depletion of the nutrients in the substrate by means of BMP tests. Biogas and biomethane production in similar conditions to real scale functioning digesters are attained through experimentation with lab-scale box digesters. The closest the attained values are to the ones reached in the BMP tests for the substrate, the more suited the substrate is for anaerobic digestion. A biogas production above 75% of the attained BMP values can be considered as very good.

2.3.1. BMP Experiments

All batch experiments were conducted in triplicate in anaerobic 250 mL serum bottles capped with rubber septum sleeve stoppers. Bottles were filled with the amount of substrate containing 0.5 g VS and the amount of inoculum to provide an inoculum to substrate ratio of 2 (based on volatile solids). Blanks were also tested. After filling the bottles, nitrogen was flushed to remove the oxygen in the headspace of the bottles and thereafter placed in an incubator at 38 °C. All the reactors were manually stirred once a day. The test was stopped for each substrate when methane production was negligible in all the samples. Results are expressed as means subtracting methane production from the blanks. Once the experiment was stopped, the reactors were opened to measure the pH, redox potential and VFA in the effluents.

2.3.2. Box Digesters

Two sets of box digesters, laboratory scale, were used. They were made of 304 stainless steel and consisted of two separate airtight-sealed compartments, one of them containing the feedstock (box tank) and the other for the liquid inoculums (percolate tank). Both tanks were provided with thermostat-controlled electric heating blankets that covered the externalwalls and floor of the box tank and the externalwalls of the percolate tank in order to keep stable operation temperatures in the optimum range for the selected biomethanogenic processes (in this case and as the experiments were performed at the mesophilic range, 36–38 °C).

The box tank compartment works as a solid substrate digester. It is 25 cm wide, 50 cm long, and 25 cm high, with a volume of 31.2 L (21.0 L of useful volume). The bottom has a 1.5% slope to facilitate percolate drainage and the compartment is provided with a physical barrier to contain the solid feedstock. The physical barrier has several openings at the bottom to allow the flow of the percolate, which is gathered at an opening in the bottom that is the opening of the percolation line.

The percolate tank is 25 cm wide, 25 cm long, and 23.5 cm high, provided with a conical bottom, having a volume of 16 L (12 L of useful volume). It works as an inoculum storage tank as well as a liquid digester for the nutrients and chemical compounds washed from the feedstock in recirculation operations.

The box and the percolate tanks were constructed with the indicated size in such a way that in the case of needing a higher or lower liquid inoculum to feedstock ratio, both the tanks could be filled with variable amounts of both materials. Both the compartments are equipped with temperature sensors (bimetallic thermometer, 15 cm stem length, 0–80 °C).

Both tanks in each set were connected by two different lines: a percolation line, through which the liquid in excess in the box tank could percolate by gravity to the percolate

tank and which could be closed allowing the box tank and feedstock to be flooded; and a recirculation and distribution line, through which the liquid inoculum stored in the percolate tank could be pumped (by a time controlled peristaltic pumpwhich was set to pump an instant flow of 2 L min^{-1})and distributed at will over the feedstock in the box tank through a sprinkler system(which consists in three perforated pipes in parallel). Both lines were set in a way that allowed only liquids to go from one compartment to the other while making impossible a transmission of the biogas produced in each tank. The compartments were provided with independent openings through which created biogas could be collected in gas bags in order to assess thegas composition and production amount in each chamber.

A detailed explanation and sketch of the system, as well as its mode of operation, can be found in Rico et al., 2020 [24].

2.4. Analytical Techniques

The biogas and methane production in the BMP tests was measured by the manometric method as described in Valero et al. (2016) [25]. Headspace pressure was measured in the headspace of the reactors through the septum with a syringe connected to a digital pressure transducer with silicon measuring cell (ifm, Germany-type PN78, up to 2000 mbar). Biogas production in each box digester set was measured connecting the different gas bags to a liquid displacement system device. Biogas samples from the BMP testsand box digesters were analyzed on a 2m Poropak T column in an HP 6890 gas chromatograph (GC) system (Agilent Technologies, Inc. 2850 Centerville Road Wilmington, DE 19808-1610 USA) with helium as the carrier gas and a TCD detector. The methane volumes are expressed at 0 °C and 1 atm in dry conditions. VFA's were determined using an HP6890 GC (fitted with a 2 m 1/8-in glass column, liquid phase 10% AT 1000, packed with solid-support Chromosorb W-AW 80/100 mesh. Nitrogen was used as the carrier gas at a flow rate of 14 mL/min, and a FID detector was installed. The Higher Calorific Value (HCV) of both substrates was evaluated using a Parr calorimeter model 1341EE (Parr Instrument Company211 Fifty-Third StreetMoline, IL 61265-1770 USA) provided with a 1108 Oxygen bomb and a 2901 Ignition unit, both from the same manufacturer. Total Solids (TS), Volatile Solids (VS), chemical oxygen demand (COD), total ammonia nitrogen (TAN) and bicarbonate alkalinity were analyzed according to Standard Methods (APHA, 1998).

2.5. Data Analysis

Statistical significance was tested by ANOVA analysis, complemented with mean value comparison using Tukey's HSD tests. Statistical significant difference was analyzed for data related to the relationship between methane production and substrate composition (proportion in weight of each co-substrate in the sample) was determined at a threshold *p*-value of less than 5%.

3. Results and Discussion

3.1. BMP Tests

A series of biomethanogenic potential tests (BMP) was performed, following the procedures and parameters proposed in Holliger et al. (2016) [26]. Keeping an inoculum to substrate ratio of 2 based on volatile solids, both substrates were tested, as well as a number of mixtures of the substrates.

Due to the heterogeneous nature of DGSBs, a significant sample of the matter (1000 g, making sure by visual inspection that the different components were present, in the same apparent proportion as shown in the bulk sample) was ground and blended until its particles were small and uniform enough to the naked eye. BSGs were also ground coarsely. Milling of the samples was performed taking into account the need of not overheating the samples, with the consequent loss of volatile compounds and water and alcohol contents in the original substrates.

The different mixes of substrates used in this series of tests were performed keeping in mind that both substrates (but mainly DGSBs) have a complex chemical composition, and

so interactions and reactions could be expected throughout the biological process, not only because of the original composition but also because of the different nature of by-products created through the process in the decomposition of the original ones. Thus, the series was planned from samples 100% DGSBs (which we named M1) to 100% BSGs (which we named M6), with intermediate steps changing the mixture proportions in 20% (by original weight) each. This way, the tests performed with a mixture of 80% DGSBs and 20% BSGs were the M2 samples, the ones with 60% DGSBs and 40% BSGs were the M2, and so on. The results of the different series of BMP tests can be seen in Figure 1.

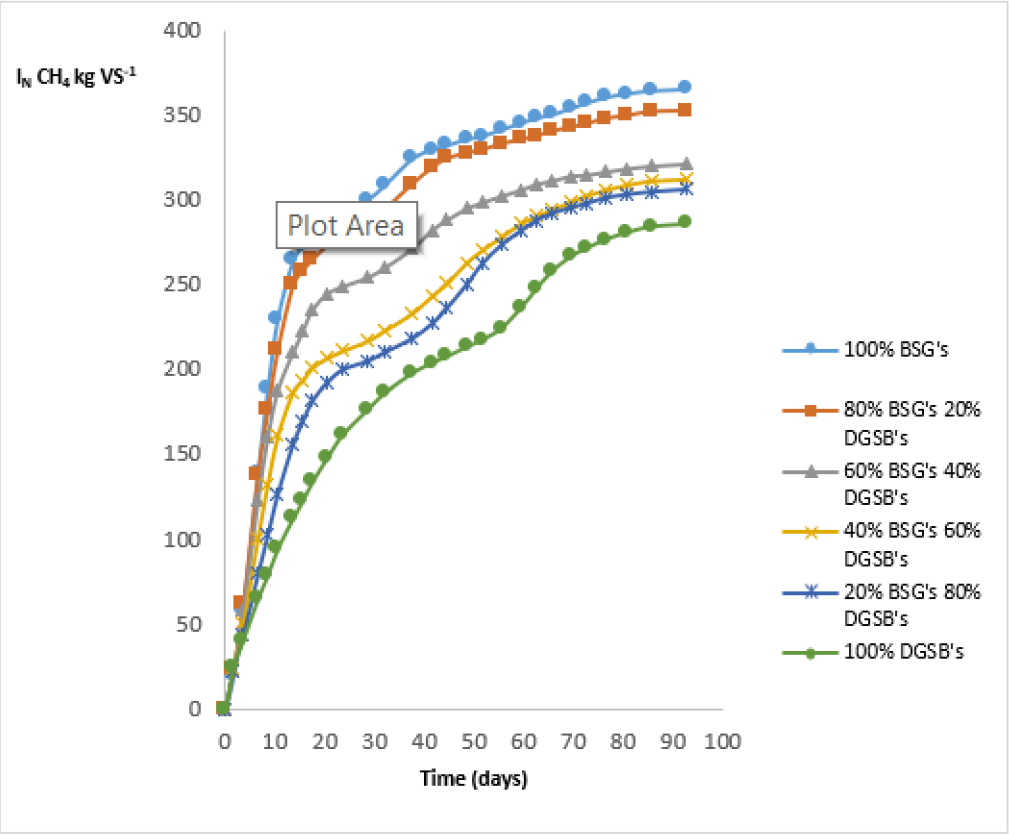


Figure 1. Total specific methane production in l_N CH_4kgVS^{-1} from the BMP tests (SD for each sample: M1 (100% DGSBs), 12; M2 (80% DGSBs, 20% BSGs), 15; M3 (60% DGSBs, 40% BSGs), 19; M4 (40% DGSBs, 60% BSGs), 23; M5 (20% DGSBs, 80% BSGs), 15; M6 (100% BSGs), 22.

Two things become apparent from the evolution of the accumulated biogas yield. Firstly, the time needed for the total exhaustion of the biological process is very high. This might be the result of the usage of substrates with a complex nature, a high content in cellulose and lignin as well as other substances, and with a complex degradation through which intermediate compounds (which can pose difficulties for the process) are created. There is a correlation ($p < 0.05$) between the speed of the process and the final biogas yield with the content of DGSBs. In effect, the higher the proportion of DGSBs in the sample, the lower the slope of the yield curve on the first stages of the process (on the first two weeks) and the lesser the final biogas production (it should be reminded that the total content in VS in each sample was the same, regardless of the proportions of the co-substrates used). It was expected a high degree of variability in samples with a high DGSBs content due to the heterogeneous nature of the substrate and the small size of the sample, which implies differences in the presence and proportion of some components in each sample.

Secondly, in relation to the shape of the curves throughout their evolution with time, there is a first phase in which biogas is created normally, with a daily yield that reduces with time as the available substances for anaerobic digestion are reduced in the batch

process. However, in all cases and after a lag in the process appears, there is a second relative increase in biogas production, appearing as an inflection point. This second relative increase appears in all cases regardless of the composition of the sample and proportions in the mixture of DGSBs and BSGs. However, it is to be noted that, the higher the content of DGSBs, the later this inflection point appears throughout the experiment. It is also noteworthy that this phenomenon is more remarkablewith the higher content in DGSBs of the sample, at least apparently. Following the inflection point, the biogas yield follows a similar path to the previous state, with its slope decreasing with time and the depletion of available feed substances for the methanogenic biomass.

Several hypotheses can be used to explain this behavior. One of them could be the aforementioned one of the production of intermediate by-products throughout the process, which could lag it with their accumulation. Eventually, specialized biomass that could deal with those by-products could develop and start decomposing them. For BSGs it is known that inhibition can appear due to the creation of p-cresol and other phenolic by-products throughout the process [27]. Due to the complex nature of DGSBs, a similar behavior could be also expected. Another hypothesis is that, due to the nature of the substrates, the hydrolysis phase in the anaerobic digestion process could take longer for substrates high in lignin and other complex matter as DGSBs but, once the mechanism is finally accomplished and activated, it translates in a sudden increase in available feed for biogas production. Finally, it can't be discarded that the inoculum, nevertheless it is supposed to be well adapted and able to cope with almost any feedstock, while starting the process with good efficiency dealing with the easiest to digest substances, at a certain point needs some time and biomass adjustment to cope with other more complex substrates (especially with DGSBs). Once the adaptation is adequate and the biomass and microbial communities are adjusted, there's an increase in biogas production due to the increase in the ability to use the feedstock by the rearranged biomass community.

In the end, it is far beyond the possibilities of the researchers and the scope of this paper to determine which is the correct hypothesis (or combination of them) to explain the attained results. From a practical point of view, the BMP results give a hint that it can be expected that the biological process, applied to laboratory conditions and standard digestion systems, could be difficult and take a longer time than what could be desirable.

The specific methane production values attained of 3659 l_N $CH_4 kgVS^{-1}$ for BSGs and 2863 $l_N CH_4$ $kgVS^{-1}$ for DGSBs are in line with those attained in Montes and Rico [28].

3.2. Box-Type Digester Assays

Two sets of two experiments in parallel were performed. In the first roll of experiments, which we'll call E1 and E2, only DGSBs were used as substrate. In experiment E1, the box tank for solid substrate was filled with 9.97 kg of feedstock, while 10 L of inoculum were put in the percolate tank. The amounts of feedstock and inoculum for experiment E2 were 10.006 kg and 10 L, respectively. In this experiment, GAC (20 × 40) was added to the percolate tank with the purpose to assess the possible influence of the presence of a conductive material. To avoid the possible interference with the pumping recirculation system and the clogging of pipes and distribution devices, the charcoal was put in a cage-like container, which allowed the flow of inoculum and percolate to pass through and get in contact with the conductive material.

On the first day, the substrates were inoculated by sprinkling 3 L of inoculum (in one run) in each digester and letting them rest, allowing them to reach mesophilic conditions. The same operation was performed on the following two days. On the third day, recirculation was increased to a total of 4.5 L in three runs (of 1.5 L each). And on the fourth day, it was observed that biogas production, which had been increasing both in the box digesters and in the percolate tanks in the previous days, had plummeted. It was detected that Volatile Fatty Acids (VFA's) COD in the percolate tank had experienced a sudden increase (reaching 13.1 and 12.77 g/L respectively in E1 and E2) so inoculum recirculation was stopped.

On the following days, the efforts were focused on the recovery of the inoculums from the failure by acidification. All actions performed (addition of a total of 15% fresh inoculums by volumeand of calcium bicarbonate on several occasions) proved worthless. VFA's COD kept increasing reaching 40.98 and 34.11 g/L in each experiment. Biogas production disappeared in percolate tanks and was residual in box digesters, being observed (but not measured) the presence of H_2 in the latter. Finally, after 15 days from the beginning of the experiments, it was decided to stop and reevaluate decisions and the course of actions.

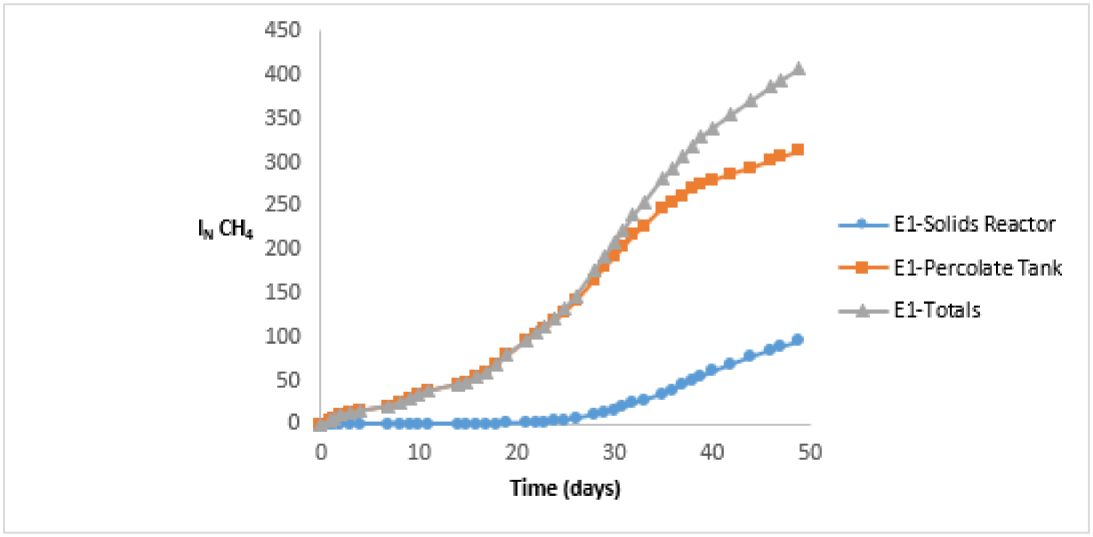
On the following days, two new batches of inoculum were acclimatized by progressively adding 2 L of inactivated inoculum from the previous run of experiment E1 and with a VFA's COD of around 41 g/L to 9 L of fresh inoculum each. Biogas production in the new batches was observed and after 21 days the adaptation seemed satisfactory, so these new batches of 11 L of inoculums each were used in a new run to end the experiments with the partially digested substrate.

The digesters were again inoculated by sprinkling another 3 L of the new inoculums and allowed to rest and reach the mesophilic range of temperatures for the rest of the day. After that, a 1 L recirculation was performed. Biogas production started, but on the following day it was highly reduced, so recirculation was stopped for 10 days while biogas production and VFA's COD in the percolate tanks were controlled. After that and since VFA's COD had been highly reduced, recirculations started again, starting with 0.5 L in two runs (of 0.25 L each) per day. After a week and as the process stabilized, the volume of percolate recirculation was progressively increased, first with another run of 0.25 L (totalling 0.75 L) at which point, the box digesters (which had been inactive) started showing activity and biogas production. Percolate recirculation was increased in the following days as VFA's COD was kept under control and its amount was below 7 g/L. Thus, after 12 days the recirculation volume was 12 L spared into 4 runs along the day. After that, and as the reactor setting allowed the closing of the return line and the accumulation of percolate in the box reactor (acting as a percolating reactor system), recirculation was substituted by daily "substrate floodings". The inundation time was also increased along time, starting from 20 min per day, until reaching 2 h by the end of the experiment and with the feedstock showing depletion.

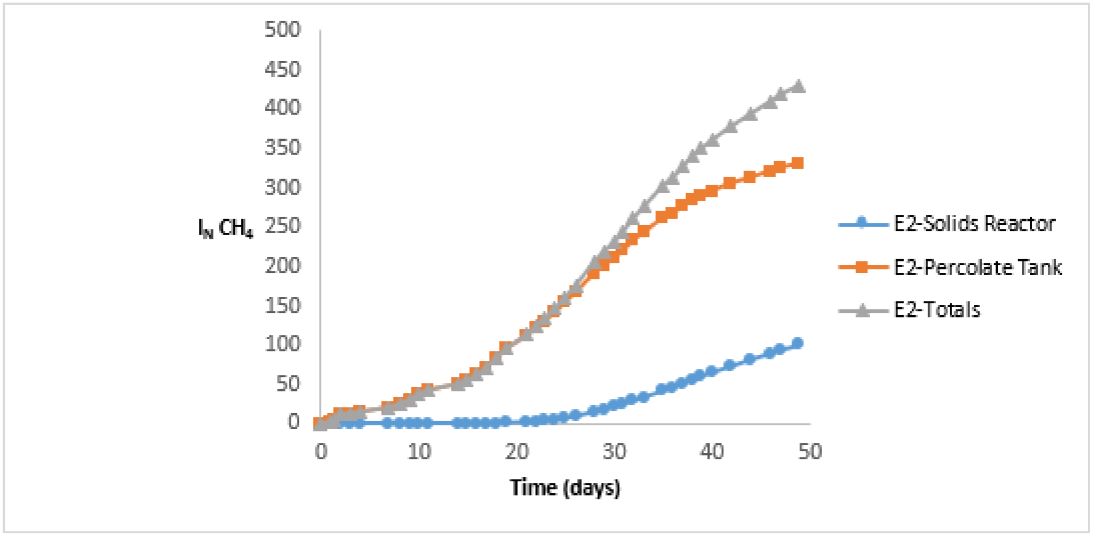
The experiment was called to an end after 49 days of this second run. The substrate was showing signs of exhaustion and, while still producing biogas, daily yield decreased no matter how aggressive the reinoculation system adopted was. Accumulated methane production along time in this recovery run in both experiments can be seen in Figure 2.

The final specific methane productions in E1 and E2 were 119.14 and 125.50 l_N $CH_4 kgVS^{-1}$, respectively. That amounts to 41.6% and 43.8% of the results attained in the BMP tests. It has to be said that, as the experiments went, a lot of the biomethanogenic feed substances in the substrate might have been lost in the first runs wasted percolate and dissipated or aerobically decomposed during the time the second batch of inoculums was in the adaptation process. Both experiments running in parallel showed very similar behavior, which allowed us to perform the same actions throughout the experimentation process. While the experiment with the conductive material had slightly better results in terms of VFA's COD reduction on the first stages and in final biogas production, the differences in performance in both experiments were negligible.

Two more experiments were performed. In this second run, it was decided to go on the cautious side. Thus, the box reactors were filled with just 8 kg of substrate to keep a lesser substrate/inoculum ratio. The substrates assayed were BSGs in E3 and a mixture consisting of 6.4 kg of BSGs and 1.6 kg of DGSBs (thus, 80% BSGs and 20% DGSBs) in E4. The percolate tanks were filled with 10 L each of the percolate used in the previous experiment and which was now supposed to be perfectly adapted to the substrates after the previous runs.



(**a**)



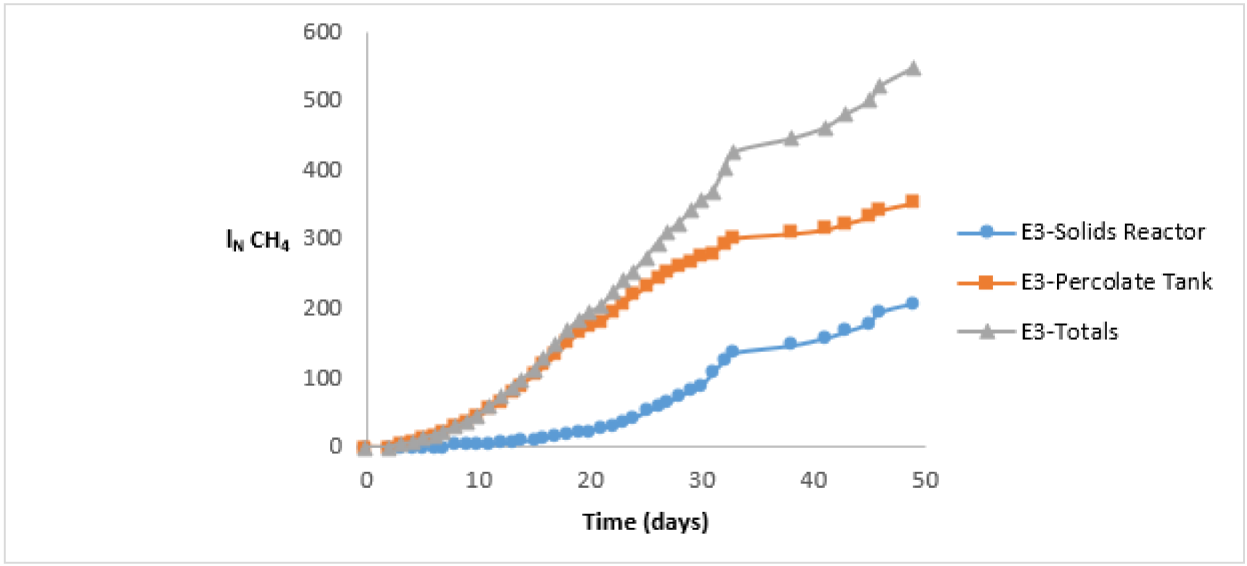
(**b**)

Figure 2. Methane production through time in l_N CH_4 in experiments E1 (DGSBs as substrate, subfigure (**a**) and E2 (DGSBs as substrate with GAC used in the percolate tank, subfigure (**b**)) and the second phase of the experiment.

After the first inoculation of the feedstocks with a 3 L sprinkling of inoculum from the percolate tank and leaving the experiments to rest and reach mesophilic conditions for the first day, the adopted recirculation rate was of a total of 0.75 L distributed in 3 runs throughout the day. From then on, recirculation was adjusted according to biogas production and the evolution of VFA's COD in the percolate, which was carefully controlled throughout the experiments. In fact, after the 7th experimentation day, while recirculation was increased in E3 to 1 L distributed in 4 runs, it had to be temporarily stopped in E4 for 2 days and, after that, reduced to a single 0.25 L run per day as VFA's COD showed a steady increasing trend reaching levels around 16 g/L, which we deemed as dangerous. On the 13th day, when conditions were apparently stabilized in E4 and recirculation was increased to 0.5 L distributed in 2 runs, the sudden increase in VFA's COD (which reached 17.64 g/L) forced to stop temporarily recirculations in the experiment and let it rest again for two days and start again with a single recirculation of 0.25 L. At the same time, conditions in E3 had allowed to gradually increase the recirculation rate up to 2.4 L distributed in 6 runs.

After those first two weeks, conditions got permanently stabilized in E4, which allowed a gradual increase in the recirculation rate, performing the same operational way as in E3 but only with a 14-day lag. Thus, at the beginning of the 4th week, while inundation cycles were starting to be performed in E3, the recirculation rate in E4 was of 9 L spared in 6 daily runs.

The experiments were called to an end after 49 days. Accumulated methane production along time in both experiments are shown in Figure 3.



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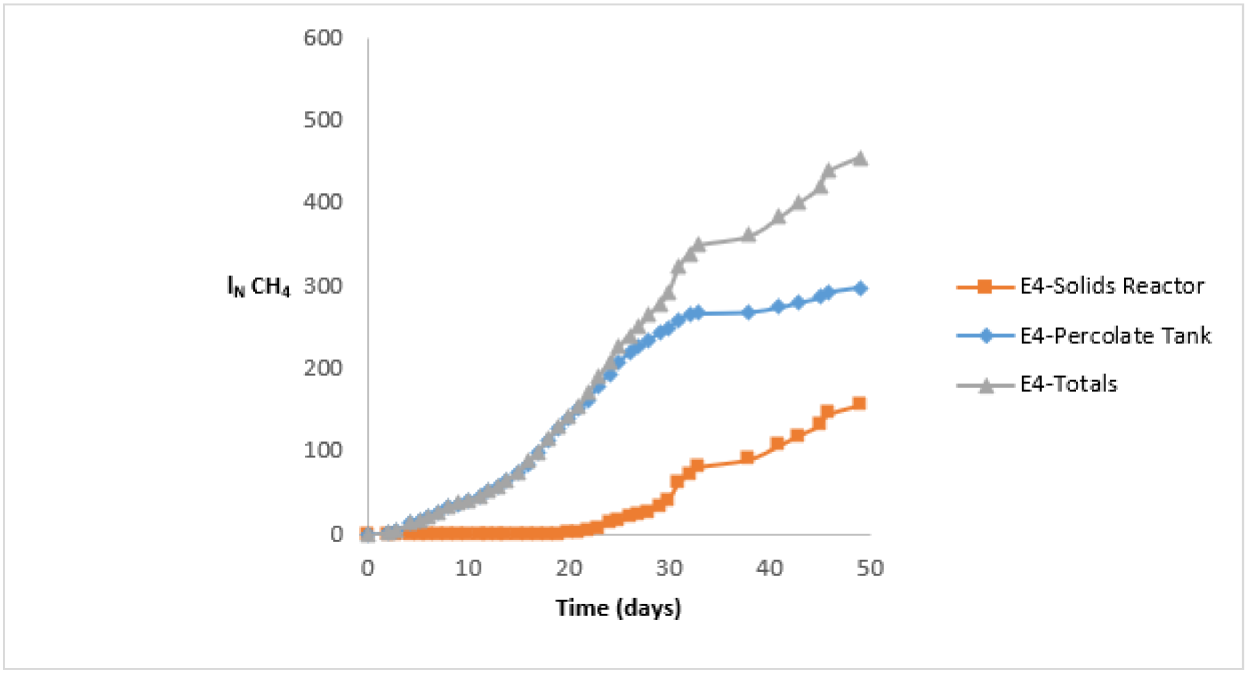

(**b**)

Figure 3. Methane production through time in l_N CH_4 in experiments E3 (BSGs as substrate, subfigure (**a**)) and E4 (a mixture of 80% BSGs and 20% DGSBs by weight, subfigure (**b**)).

The final specific methane productions in E3 and E4 were 295.06 and 217.57l_N CH_4kgVS^{-1} respectively. That amounts to 80.6% and 61.6% of the results attained in the BMP tests and can be considered quite satisfactory in terms of the translation of biomethanogenic potential

to work conditions in E3, not so much in E4. As a comment, while biogas production in the percolate tank was the main methane source in all experiments, only in E3 (using 100% BSGs as feedstock) was there a steady production in the box-type solids reactor from the start of the experiment. In all cases, biogas production in the solids reactor increased when the inoculation system was changed from sprinkling to substrate inundation.

When the experiments were finished and the solid digestatecould be observed, it was noticeable that, while BSGs appeared fairly decomposed and its volume had experienced a very noticeable reduction, where DGSBs had been used, some individual distinguishable items could be seen quite unaltered. This was the case with juniper berries, for example.

3.3. Calorific Value

Complementary to the previously described tests and assays, it was estimated useful to assess the calorific value of the substrates to complement the studies about their potential value as energy sources. Thus, both substrates were tested for their higher heating value (HHV) using a Parr oxygen bomb calorimeter.

The attained results were of an HHV of 19.95 MJ/kg for DGSBs and 18.51 MJ/kg for BSGs, respectively. These values are typical of materials with a composition high in lignin and cellulose as will be discussed in the discussion section.

3.4. Discussion

Several conclusions can be extracted after the experimentation process. First, the importance of having a well-adapted and strong inoculum can never be underestimated.

BSGs have resulted in a good feedstock for anaerobic digestion processes. While the usual way to dispose of both brewers' and distillers' spent grains is to use them as feed for livestock [29,30] (with the limitations for DSGs of copper toxicity, especially for ovine and caprine livestock) or even for human consumption [31], a lot of interest has arisen lately for their use in biogas production [32,33], with a good final biomethane production and, as a by-product, a digestate with a good volumetric reduction and which could still be useful in agriculture as a fertilizer or as an organic amendment for soils [34]. This fact has lead to the appearance of several studies and works focused on its use. In this experimental process, the results attained were fairly good. The only objection could be the long time needed throughout the experiment to attain good results with a good amount of final biogas production. In that sense, it should be commented that, after the first experiences and failures with the other substrate, the experimentation was performed on a very cautious side. The values of VFA's COD accumulated in the percolate tank never reached levels which, after the experience, could be considered dangerous for the process. Thus, the general process could be accelerated using a more intense recirculation in terms of volume and frequency (always bearing in mind it should be a progressive process). Further studies would be needed to adjust and optimize the operational actions in order to speed up the process while keeping it on the safe side to avoid process failure.

On the other side, DGSBs have resulted in a problematic feedstock. This could be the product of the substrate nature in itself. As commented in the introduction, juniper berries are a mandatory ingredient for distilled gin by definition, according to the EU regulations for alcoholic beverages [21]. Juniper galbuli (berries) essential oils have a complex composition with a large number of chemical compounds [35] and have shown anti-microbial and anti-fungal effects [35,36]. While it could be objected that other distilled gin producers could use different recipes and mixes of botanicals, affecting the repeatability of similar experiments, the obligatory nature of the use of a high proportion of juniper berries in the botanicals mixture allows one to think that results similar to ours would be attained, unless an unusually high inoculum-to-substrate ratio (normally not feasible in real-scale dry batch anaerobic digestion reactors) were used. Other frequent distilled gin ingredients, suchas angelica roots and seeds or cinnamon bark, have also shown anti-microbial effects [37,38]. As a first measure to deal with the treatment of these products, procedural changes in the distillation process could be adopted. The use of "infusers"

(mesh containers made of an inert material which don't transmit unexpected flavors to the distillate while allowing free contact between botanicals and the liquid phase of water and ethanol) for each ingredient, for example, could make easier to separatethe different species and fractions of botanicals after distillation is completed. This way, the different types of waste could be treated accordingly to their own characteristics, enabling the extraction of valuable chemicals from the separate fractions and using the less problematic products to be used in anaerobic digestion.

After these experiments, it could be supported that DGSBs are not suited for dry batch anaerobic digestion, as it is usually performed in current standard appliances; and its addition as a co-substrate, whileitshould be analyzed on a case-to-case basis, could result in process problems, especially in the initial phases. Some experiences can be found in literature about the problems of dealing with a recalcitrant substrate associated with the alcoholic beverage production industry [39]. In that sense, UASB systems have proven robust and adequate to deal with liquid compounds that could be deleterious in other types of anaerobic processes. That suggests that it could be possible to use hybrid UASB-Dry batch box-type systems like the ones described in Panjičko et al. [40] as the systems of choice which could enable the anaerobic digestion of DGSBs.

On the other hand, both products have shown a good performance as biomass fuels, with a good HHV, very similar to that of wood in the case of DGBs (with net calorific values of 12.5, 14.7, 17 and 19 MJ/kg for wood chips, stacked log wood, wood pellets, and oven dried log wood respectively) [41] and, in general, in line with that of other materials from agri-food production rich in lignin and cellulose (among which we can cite HHV's of 17.1 MJ/kg for wheat straw and for banana waste, 18.17 MJ/kg for sugarcane bagasse, or 19.3 and 20.2 MJ/kg for hazelnut and almond shells respectively) [42]. While extraction of their water content should be necessary for their use as fuels, their nature and appearance would only make necessary a minimum grinding in the case of DGSBs, not even so for BSGs, previously to a pelletization to attain commercial characteristics as a biomass fuel that could be commercialized as it is, or used for heat production in the industrial premises. Though these heating values might appear as modest compared to those of traditional fuels (with HHV's of 46.03 and 45.56 MJ/kg for diesel and gasoline) or those of products originated in the valorization of plastic waste (with HHV's of 44.5, 44.22, 44.63 and 40.17 MJ/kg for pyrolysis generated oils and 99.83, 99.46, 105.04 and 121.18 MJ/kg for pyrolysis generated gas for high-density polyethylene, low-density polyethylene, polypropylene, and polystyrene, respectively) [43,44], it should be taken in account the renewable origin of the biomass fuels and their significantly lower carbon footprint under an environmental point of view.

4. Conclusions

This work has dealt with two types of waste from alcoholic beverage production, focusing on their energetic valorization. BSGs have proven to be a good material for this purpose, either as feedstock for anaerobic digestion processes using technologies commonly used in dry batch digestion or by itself as a pelletisable biomass fuel, attaining good heating values similar to those from other natural feedstock rich in lignin and cellulose. This fact opens new ways of dealing with them, other than their traditional use as feed for livestock.

The other material, however, has shown to have less potential. While technically feasible, dry batch anaerobic digestion of DGSBs seems to be a very delicate process, especially in the first phases, where there might be a strong presence of antimicrobial chemical compounds and high accumulations in VFA's COD. Either an effective previous treatment might be required or the adoption of hybrid systems. In any case, it seems to be a difficult to digest substrate which, when used in co-digestion, might hamper and delay the general process. It has good potential as a pelletisable biomass fuel with good calorific power, however. And it is worth noting that those chemical compounds in the substance could be extracted and used, transforming waste into a valuable raw material.

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Author Contributions: While I. S. units have been used in this work, some others (as the standard atmosphere atm, liters L, grams per liter g/L and so on) have been kept due to figure representativity and normal use in works dealing with similar matters. The unit $l_N CH_4 kg\ VS^{-1}$, liters of methane in standard conditions per kilogram of volatile solids in the feedstock, has been defined as the unit of choice to express methane yield since Holliger et al. (2016). To translate into SI units ($m^3{}_N CH_4 kg\ VS^{-1}$), the values should be multiplied by 10^{-3}.

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