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Energy recovery from brewers' spent grain combustion/co-combustion with lignite

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Abstract

A global interest can be observed in alternative management of agro-industrial wastes in the context of the accomplishment of the 2030 sustainable development goals. Reducing these wastes by turning them into solid biofuels for energy production is a viable solution for global environmental issues. In this work, brewers' spent grain (BSG) and its blends with lignite, in several proportions, were in depth assessed as sustainable solid biofuels through energy content analysis, proximate analysis, ultimate analysis, ion chromatography, thermogravimetric/derivative thermogravimetric analysis, and scanning electron microscope/energy-dispersive spectrometer. Arrhenius kinetic modeling and thermodynamic analysis were performed. The potential maximum emission factor for CO_2, SO_2, and NO was calculated using the results of the ultimate analysis and expressed per produced energy. The environmental footprint regarding secondary solid wastes was expressed per produced energy. Furthermore, empirical chemical formulas of BSG and its blends with lignite were determined, and several case studies for sustainable management of BSG were developed for the first time in the literature. The experimental results fulfill the scientific gap regarding an alternative utilization of solid waste produced from brewery industry. The results indicate that BSG could be used as an alternative solid biofuel, and BSG blends with lignite could enhance the fuel quality. Moreover, the results of case studies showed that BSG could cover a small amount of energy demand in Greece and Europe; thus, consequently, this waste could be used for local energy needs, e.g., district heating in industrial regions or beer industry energy needs.

Keywords Brewers' spent grain (BSG) · Biomass residues to energy (B/WtE) · Co-combustion · Energy cover · Sustainable management · Synergistic effect

Introduction

Energy security has become one of the major issues that European countries have to deal with. Regional energy security can be improved through energy efficiency. By enhancing national accounts and lowering the need for expensive supply and storage facilities, cutting energy imports can be cost-effective advantageous for a nation. Enhanced effectiveness of energy efficiency can play a significant role in accomplishing both long-term and short-term energy securities that are both affordable and practical because it can reduce the dependence on imported coal, oil, and gas as well as the need for additional infrastructure for power transmission and distribution. Europe, under current management (re-opening or postponing to close coal power plants), will not be able to achieve the goal of reducing greenhouse gas emissions by 80% by the year 2050 compared to the year 1990 (European Commission 2011). Therefore, it is essential to find new policies in order to achieve sustainable development and energy independence (e.g., biomass/waste fuels and co-combustion of mixed/composite fuels). Nowadays, in Greece, finding alternative fuels for energy production is a crucial issue in order to reduce the use of fossil fuels and be prepared for the post-lignite era. The utilization of biomass residues (such as BSG) via combustion or/and co-combustion with lignite could help in energy production in an economical way, as existing lignite power plants could be used (with various modifications) without requiring the

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construction of an expensive power plant from scratch. In addition, by combustion or co-combustion of biomass residues with lignite, the following can be achieved: A step-by-step transition to the post-lignite era as part of the fuel comes from residual biomass, reduction in the utilization of fossil fuels, a better management of waste biomass, etc.

Biomass as a fuel is one of the largest clean energy sources worldwide, has a zero-carbon footprint, and is one of the most important sustainable energy resources that can contribute to sustainable development. Biomass fuels are widely used in power plants due to their multiple advantages: (1) reduced pollution, (2) energy security (independence), (3) low cost, (4) wide variety of sources, (5) easy storage and transportation, (6) high combustion efficiency, (7) job opportunities, (8) reduce the dependence on fossil fuels, (9) effective management of biomass residues/wastes, etc. (Jazinaninejad et al. 2022).

Biomass residues should not be treated as waste but as sustainable resources to be reused for bioenergy. In recent years, research on the reuse of organic solid waste has been a constantly growing area of study, not only due to the new options that are constantly being explored (Thomas and Rahman 2006; Vasileiadou et al. 2023), but also due to the stricter regulations for environmental protection. Biomass residues have many benefits, but several parameters must be considered as the quality characteristics of these biofuels vary depending on geographical, social–economic, plants factors, etc. For these reasons, several fuel, environmental, and ash quality tools have been introduced (Cherney and Verma 2013; Vasileiadou et al. 2021b, 2022). Knowledge of the fuel characteristics is essential in order to avoid the formation of slag from ash deposits and to ensure complete combustion of the fuel (Loo and Koppejan 2008; Zhai et al. 2022).

Biomass combustion and co-combustion with coal could be part of the solution to environmental issues. If China replaced about 27% of fossil fuels with biofuels, then greenhouse emissions (GHG) could be reduced by 49% by the year 2050 (Kang et al. 2020). The utilization of agriculture residue for energy production could reduce in Alberta (Canada) about 13 percent of GHG emissions by substituting about 15% of total energy demand in 2030 (Weldemichael and Assefa 2016). A case study in Uttar Pradesh (India) presented biomass power and GHG emissions inventories in comparison with coal, resulting in significantly lower GHG emissions than coal (Hiloidhari et al. 2019). In Portugal, several biomass combustion power plants have been built in recent years as a result of the National Energy Strategy contributing to the reduction of GHG emissions (Briones-Hidrovo et al. 2021). In Columbia, a bioenergy potential of 61,000–119,400 GWh of the bioenergy potential from agricultural residues and livestock wastes can be technically exploited (Sagastume Gutiérrez et al. 2020). Important changes due to the synergistic effect of other types of biomass (microalgae, forest residues, and cotton residues) co-combustion with coal are found on kinetic devitalization graphs (peak temperature and burnout times), on COx, SOx, NOx, and Cl emissions, and on physical desulfurization (capture of S in the ash, mainly due to Ca and Mg contained in the fuel ash) by ash produced from fuel (Kastanaki et al. 2002; Wischnewski et al. 2006; Peng et al. 2015).

Beer production in Greece, Europe, and worldwide in 2017 was about 3,800,000 hl, 397,000,000 hl, and 1,950,000,000 hl, respectively (Brewers of Europe 2018). Brewers' spent grain (BSG) represents 85% of beer industry waste (Mussatto et al. 2006). BSG waste from the brewing industry is an interesting waste as it is cheap, available in all seasons of the year, and has a valuable nutritional chemical composition (Gupta et al. 2013).

The greatest research interest in brewing industry wastes (brewer's spent grain) concerns their use as animal feed due to their nutritional value (Cooray and Chen 2018; Mukasa-fari et al. 2018; Sajib et al. 2018). Due to the high humidity and the content of fermentable sugars, BSG can cause an environmental problem after a short period of time (~ 8 days), and for that reason, BSG should be immediately consumed as animal feed (El-Shafey et al. 2004). About 70% of BSG is used as animal feed; however, it has been reported that due to microbial activity (< 48 h of life), it should not be used as animal feed (Russ et al. 2005). Moreover, approximately, 20% of BSG is landfilled, but according to a recent EU directive, the disposal of untreated BSG should be avoided, as 1 ton of landfill BSG releases 513 kg CO_{2eq} (European Commission 2021). Other authors studied BSG for biogas production (Čater et al. 2015; Bachmann et al. 2022), biohydrogen (Zhang and Zang 2016), biodiesel (Mallen and Najdanovic-Visak 2018), biobutanol (Plaza et al. 2017), and ethanol (Rojas-Chamorro et al. 2018), but few studied BSG as a solid biofuel, and zero studied it as a composite solid fuel (BSG blends with lignite, in different wt.%). Zanker and Kepplinger (2002) evaluated the combustion of BSG to cover the energy needs of the beer industry (Zanker and Kepplinger 2002). A recent study of thermogravimetric analysis of brewing wastes was performed (Arranz et al. 2021), but the thermogravimetric analysis of BSG blends with lignite and the synergistic effects of BSG co-combustion with lignite have never been reported. The key concept of this research is to find alternative solid fuels that can be used in the existing power stations in Greece, making minimal modifications, with the ultimate goal of increasing the country's energy security and independence from other countries in the most economical way, as part of the fuel (mixtures with lignite) or all of it will consist of biomass waste, and the need for the construction of a new factory will not arise. Moreover, a gradual transition to the post-lignite era can be performed, by gradually reducing the lignite percentage contained in the fuel mixture. The significance of the current work is that it proposes an alternative way of utilizing brewing

industry wastes. As mentioned just above, many authors have studied BSG for the production of (liquid and gas) biofuels, but limited authors have studied the direct utilization via combustion, and not via pyrolysis of BSG as a solid alternative biofuel, and no research has been carried out on the co-firing of BSG with lignite, sustainable utilization of their ash, or their potential energy cover. In this work, a detailed experimental evaluation of the agro-industrial wastes of the beer industry (brewers' spent grain) and their blends with lignite, in several proportions, was performed in order to access their potential as fuels. Thus, this work aims to fulfill the scientific gap regarding BSG combustion and BSG co-combustion characteristics (with lignite) in order to be used as an alternative solid biofuel for energy production. The environmental footprint of the secondary solid wastes produced from BSG combustion and BSG co-combustion with lignite, expressed per produced energy was evaluated. Maximum potential CO_2, SO_2, and NO emission factors were expressed per produced energy. Empirical chemical formulas for these alternative biofuels were also calculated. Arrhenius kinetic and thermodynamic analyses were performed. Ash composition analysis of the secondary wastes produced from combustion was performed. For the first time in the literature, several case studies for sustainable management of brewery industry wastes were performed in order to examine the potential energy cover in Greece and Europe.

Materials and methods

Materials and sample preparation

Brewers' spent grain (BSG) dry sample was taken from the brewery industry located in Thessaloniki, Greece. A lignite (LIGA) sample was taken from the Agios Dimitrios Thermal Power Plant in Greece. The samples were air-dried and then dried in an oven (80 °C for 24 h). The grounding of the samples (1-mm size) was performed using a SM100 Retsh cutting mill. Three BSG blends with lignite (30 wt.%, 50 wt.%, and 70 wt.%) were prepared.

Methods

The gross calorific value (GCV) was obtained after the combustion of the samples under oxygen atmospere (at 420 psi) in an isoperibol bomb calorimeter AC-500 (Leco) according to the ASTM D5865-13 standard (ASTM International 2013). The determination of volatiles, moisture, ash, and fixed carbon (proximate analysis) was performed using the TGA 701 instrument (Leco) according to the ASTM D 7582 standard (ASTM International 2015). The environmental footprint index (EFI_{sw}) was developed by expressing secondary solid wastes (ash) produced from the combustion of the samples per produced energy (produced

Megajoule, MJ), and the percentage deviation compared to lignite. More specifically, the amount of ash produced from 100,000 tons of fuel was calculated, as well as the amount of ash per produced energy (MJ) by dividing the ash quantity (in kg) produced from 100 kg of fuel with the MJ produced from 100 kg of fuel. The mathematical tool that was used to establish correlations in statistical analysis was simply linear regression, where R^2 is the coefficient of determination. Thermogravimetry (TG) and derivative thermogravimetry (DTG) were carried out by using a TGA 701 instrument (Leco) according to the literature (Vasileiadou et al. 2021b). A FlashEA (ThermoFinnigan instrument) was used for elemental analysis as described in the literature (Vasileiadou et al. 2021a). The maximum emission factor expresses the amount of CO_2 (or SO_2 or NO, etc.) that is produced from the combustion of 1 kg of fuel or from the quantity of fuel that produces 1 MJ of energy. It is calculated from the stoichiometry of the reaction by assuming 100% reaction (combustion) yield. Empirical chemical formulas were calculated using elemental analysis. The determination of chlorides and sulfate sulfur was determined by ion chromatography (Metrohm ion chromatographer, model 881, compact IC Pro) based on the ISO 10304-1 standard according to Tex-620-J 2005. The kinetic parameters (activation energy, E and pro-exponential factor, A) were determined using the Arrhenius kinetic model according to the literature (Vasileiadou et al. 2021a). The thermodynamic parameters (enthalpy change, ΔH_α, Gibbs free energy change ΔG_α, and entropy change, ΔS_α) determined according to the literature (Vasileiadou et al. 2023). Electron microscope analysis was performed via a scanning electron microscope (SEM) JEOL JSM-6390LV equipped with an energy-dispersive spectrometer (EDS) INCA 300 as described in the literature (Vasileiadou et al. 2022).

Case studies for sustainable management of beer industry solid wastes (BSG)

Several case studies regarding waste-to-energy production of BSG were performed in this study for Greece and Europe. Three different scenarios were performed: scenario I: 100% of solid wastes in the brewing industry (BSG) used for WtE, scenario II: 70% of solid wastes in the brewing industry (BSG) used for WtE, and 50% of solid wastes in the brewing industry (BSG) are used for WtE in the case that brewing wastes are used for other applications (e.g., biogas production). Nine different cases for every scenario were developed by taking into account data on beer production from the previous years (2017) for Greece and Europe. These case studies were developed by taking into account multiple variables:

Table 1 Gross calorific value of BSG samples, lignite, and BSG blends with lignite in different proportions (30 wt.%, 50 wt.%, and 70 wt.%)

Sample ID	GCV (MJ/kg)	s.d. GCV (MJ/kg)	GCV$_{theor.\ blends}$	%dev. GCV$_{exp.}$ versus GCV$_{theor.\ blends}$	ΔGCV (%)	ΔGCV group category
BSG	19.05	± 5.88			50.26	[45.1–60%]
BSG70 LIG30	18.38	± 1.44	17.14	7.25	44.98	[30.1–45%]
BSG50 LIG50	15.82	± 0.04	15.87	− 0.29	24.77	[15.1–30%]
BSG30 LIG70	14.23	± 0.00	14.59	− 2.47	12.23	[< 15%]
LIGA[a]	12.68	± 0.11				

[a]The results of LIGA sample were taken from a previous study of authors (Vasileiadou et al. 2020)

- Annual data of beer production,[1] in 2017 for Greece and Europe were 3.80E + 06 and 3.97E + 08 hl (Brewers of Europe 2018), respectively.
- The moisture content of exhausted brewers' spent grain (BSG) is 70% on a wet basis (w.b.) (Arranz et al. 2021).
- From 100-l beer production, 20-kg BSG are produced (Arranz et al. 2021) whereas other studies have reported that it is possible to produce up to 45 kg of BSG during 100-l beer production (Thomas and Rahman 2006). In the present study, the worst-case scenario was used: 20 kg of BSG, w.b., resulted from 100-l beer production.
- From the two above-mentioned assumptions (moisture content 70% and 20-kg BSG/100-l beer production) and from the results of the proximate analysis of the sample BSG (moisture content: 2 wt.% in dry basis, d.b.), it follows that: from 1-hl beer production results in the production of 6-kg BSG, d.b. (from 100-kg BSG, w.b.: 70 kg are water and 30 kg are BSG, d.b., so, from 20-kg BSG, w.b.: 14 kg are water and 6 kg are BSG, d.b.).
- By taking into account the above-mentioned assumptions, it follows that BSG, in d.b., in Greece and in Europe (in the year 2017) was 2.28E + 07 kg/year and 2.38E + 09 kg/year, respectively.
- The average value of the gross calorific value (GCV) of BSG samples, which was found to be equal to 19.05 MJ/kg (results of the present study), was used for the calculations.

Results and discussion

Energy content of brewers' spent grain, lignite, and blends

The gross calorific value is one of the major characteristics of a fuel. The gross calorific value of the analyzed samples is illustrated in Table 1. The percentage difference in GCV of every sample in comparison with the GCV of the LIGA

sample is calculated by Eq. 1. The regression analysis of the GCV of the analyzed samples is presented in Fig. S1 (Supplementary Material).

$$\Delta GCV_{sample}(\%) = \frac{GCV_{sample} - GCV_{LIGA}}{GCV_{LIGA}} \cdot 100 \qquad (1)$$

where ΔGCV_{sample} is the difference between the GCV of each sample and the GCV of lignite sample, GCV_{sample} is the GCV of each sample, and GCV_{LIGA} is the GCV of lignite sample.
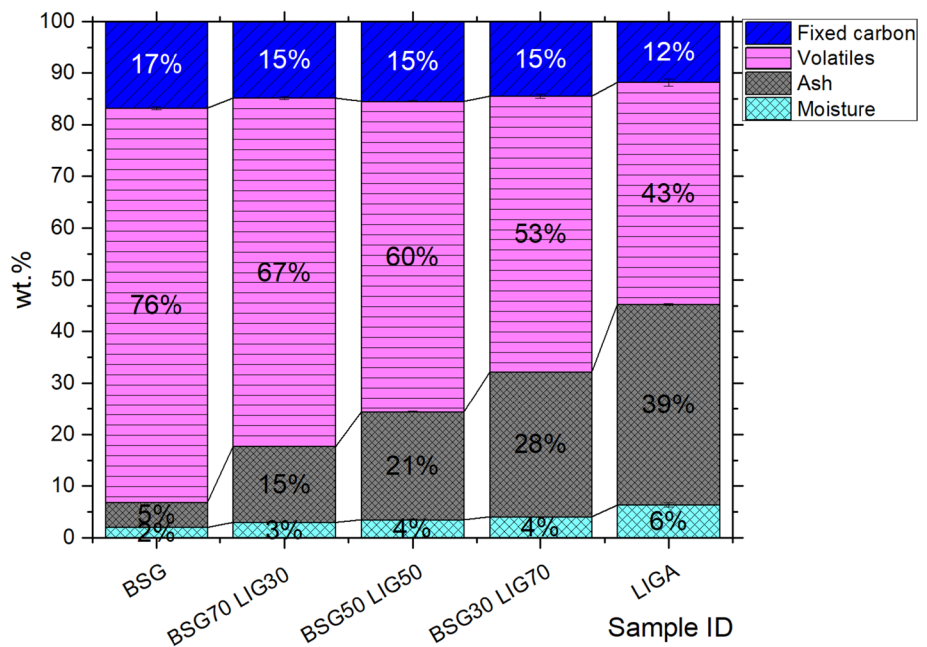
Brewers' spent grain sample revealed an almost double gross calorific value compared to the lignite sample (reference sample). The calorific value of the BSG sample is in agreement with that of a recent study (Arranz et al. 2021). By blending brewing residues with lignite, the energy content was increased. In BSG blends with lignite, as the BSG percentage increased, the GCV also increased.

There are zero studies about the use of BSG in solid composite fuels with lignite.

Simple linear regression of the dependent variable (*y*: GCV, in MJ/kg) and the independent variable (*x*, %waste in blends with lignite) can be expressed by the regression equation presented in Fig. S1a ($R^2 = 0.9535$). The relationship between independent and dependent variables is expressed by a linear regression equation. Additionally, it can forecast new values for the dependent variable given the independent variables you provide. According to Evans (1996) and the results ($R > 0.8$), GCV showed a very high positive correlation with the biomass waste percentage in the blend with lignite. The regression model is considered significant as long as the *p*-value is less than 0.05. The *R*-Sq value indicates that 95.3% of the total variability in the *y* data has been explained by fitting the standard (Fig. S1c). As the percentage of waste increases in the blend with lignite, the gross calorific value also increases. Moreover, the GCV of several blends could be predicted using the regression equation. For instance, the GCV of a blend fuel with 90% BSG and 10% lignite could be predicted as follows: GCV (MJ/kg) = 12.57 + 6.922 × 0.9 = 18.8 MJ.

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[1] hl = 100 L.

Fig. 1 Proximate analysis of brewers' spent grain, lignite, and blends (where *V*: volatiles, *M*: moisture, *A*: ash, and F.C.: fixed carbon, in wt.%)

Proximate analysis

The results of the proximate analysis are presented in Fig. 1. The results of lignite were taken from the literature (Vasileiadou et al. 2021a). The raw brewers' spent grain sample revealed almost double the content of volatile matter (~76 wt.%) than the lignite sample (~43 wt.%). The high percentage of volatiles is in agreement with the high calorific value of the fuel. Combustion efficiency increases as fuel's volatile matter content rise. Combustion efficiency is known as the ratio of heat output by the fuel to heat input by the fuel. The bed temperature, the kind of fuel, the quantities of excess air, and the gas velocity affect the combustion efficiency. Generally, in fluidized bed combustion (FBC) systems, combustion efficiency is high. Because of the use of finer particles, a more turbulent environment, and high solids recycle rate, it is often higher in a circulating fluidized bed (CFB) boiler than in a bubbling fluidized bed (BFB) boiler. Similar to this, pressurized circulating fluidized bed combustor (PCFBC) boilers operate more efficiently due to smaller, more frequent bubbles that improve gas–solid interaction (Miller 2011). The BSG sample revealed an ash content less than 5 wt.% while the lignite sample revealed a large amount of solid waste (almost 40 wt.% ash). Low ash content and high volatile matter in various biomass fuels have also been reported in related studies (Werther et al. 2000; Sarker et al.

Furthermore, the regression among the experimental gross calorific values versus the theoretical (calculated) GCV of blends is presented in Fig. S1b ($R^2 = 0.9815$). BSG blends showed a very high correlation between experimental and theoretical GCV.

2021). The ash content resulting from the combustion of a fuel is a critical factor in choosing the appropriate type of combustion technology. For example, moving grate technology could be used for the combustion of biomass fuels with an ash content less than 10 wt.% (d.b.) in a large-scale plant. Although spent brewer's grains in their raw form exhibit a high moisture content, drying costs do not seem to be a major problem, as there are several studies that used wastes with a high moisture content, e.g., tomato waste with a moisture content of 60% w.b. (Kraiem et al. 2016) and microalgae with a moisture content of 80% w.b. (Miranda et al. 2018), as fuel. In general, the moisture content of the fuel affects the combustion behavior, the adiabatic combustion temperature, and the volume of exhaust gases produced during combustion. Loo and Koppejan (2008) reported that the quality of a fuel can be improved by using appropriate pre-treatment technologies before combustion. Biomass fuels with a high moisture content require a longer residence time for drying, and as a result, they require a larger combustion chamber.

Figure S2 (Supplementary Material) illustrates scatterplots and regression models of the samples. As the percentage of biomass in blend with lignite increases, volatile matter increases ($R^2 = 0.9987$), and ash content decreases ($R^2 = 0.999$), see Fig. S2 a and b. Very strong positive correlation was revealed between calorific value and volatile content ($R^2 = 0.9642$), see Fig. S2c. Samples revealed increased volatile matter and also revealed increased calorific value. This fact is confirmed by the results of the GCV of the samples. The low ash content is in agreement with the high total weight loss of the samples. Blending lignite with BSG could increase the effectiveness of combustion. Fuel ratio (= fixed carbon/volatiles) of samples revealed a very strong negative correlation ($R^2 = 0.9537$) with

Table 2 Gross calorific value of BSG sample, lignite, and BSG blends with lignite, in different proportions (30 wt.%, 50 wt.%, and 70 wt.%)

Sample ID	Ash production from combustion 100,000 t fuel (t)	%Deviation of ash production from the corresponding quantity produced from lignite (LIGA) combustion (%)	$EFI_{sw,}$ Ash per MJ (kg/MJ)	%Deviation of ash production per MJ from the corresponding amount produced from lignite (LIGA) combustion (%)
BSG	4810	− 87.63	0.0025	− 91.77
BSG70 LIG30	14,650	− 62.34	0.0080	− 74.02
BSG50 LIG50	20,880	− 46.32	0.0132	− 56.98
BSG30 LIG70	28,070	− 27.84	0.0197	− 35.70
LIGA	38,900	0.00	0.0307	0.00

the calorific value of the samples, which means that samples with a lower fuel ratio showed a higher gross calorific value than others with higher values of fuel ratio (see Fig. S2d). This is consistent with the results reported by Prabhakaran (Prabhakaran 2020), who concluded that there is an inverse relationship between fuel ratio and combustion efficiency.

Environmental impact regarding solid secondary wastes produced from beer industry solid wastes and their blends with lignite

Table 2 presents the results of the environmental footprint index (EFI_{sw}) of the BSG samples and blends with lignite, expressed either as the amount of produced ash per kilogram (kg) of the fuel or as the amount of produced ash per produced megajoule (MJ) and their percentage deviation in relation to the corresponding values of lignite combustion.

The results showed that the BSG sample revealed a significantly lower (about 92% lower) value of the environmental footprint index (0.0025 kg/MJ) than the lignite sample (0.0307 kg/MJ). The EFI_{sw} expresses ash production in a more objective manner compared to ash production per kg of fuel, as the EFI_{sw} is expressed per unit of produced energy, that is, it takes into account the gross calorific value of the fuels. In blends, as the amount of BSG increases, the environmental footprint of the composite fuels becomes better.
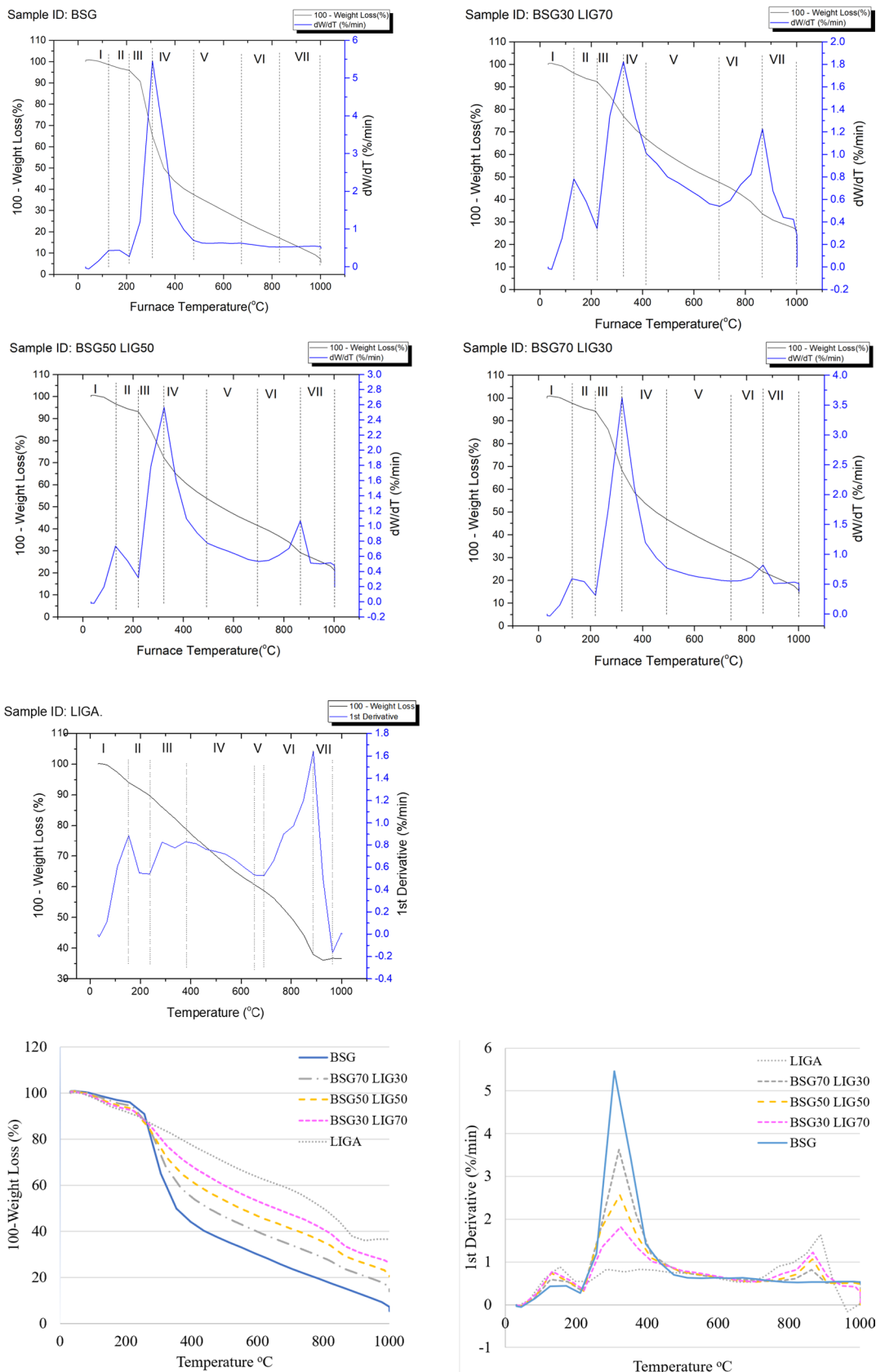
Thermogravimetric and derivative thermogravimetric analysis, TG/DTG profiles, combustion characteristics, and synergistic effect

The combustion characteristics and the corresponding temperatures of BSG, lignite, and their blends are presented in Table S1 (Supplementary Material). The results of LIGA sample were taken from the literature (Vasileiadou et al. 2023). The thermochemical characteristics depicted via thermogravimetric and derivative thermogravimetric analysis provide important information about the combustion characteristics (ignition temperature, T_i, burnout temperature, T_b, burnout time, t_b, maximum temperature, T_{max}, at which there is the maximum rate of weight loss, R_{max}) and the combustibility

of fuels. The ignition performance of a biomass fuel is different from that of lignite due to different fuel combustion characteristics, fuel properties, and particle sizes, which influence the combustion characteristics of solid composite fuels (biomass blends with lignite). More specifically, the brewers' spent grain sample revealed a higher maximum rate of weight loss at smaller maximum temperature (5.46%/min, 307 °C) than the lignite sample which means that the fuel ignites easier. The total weight loss of the BSG sample revealed higher (~95%) than that of the lignite sample (~64%), which means that the unburned content is less than 5% for the BSG sample and more than 36% for the lignite sample. The high total weight loss of BSG is in agreement with the low ash content of the sample. Similar tendencies (high R_{max} and low T_{max}) have been reported for BSG pellets originated in Spain (Arranz et al. 2021). The total weight loss content of blends increases with the increase in biomass content in blends with lignite, while the maximum temperature decreased. A similar tendency has been observed in other (not BSG) cases of biomass co-combustion with lignite (Iordanidis et al. 2018).

Figure 2a illustrates the TG/DTG profiles of the BSG sample, lignite sample (reference sample), and their blends. All samples revealed three characteristic peaks of degradation (DTG curves). The first peak (drying to remove moisture content) takes place between room temperature and 200 °C. Volatile degradation occurs at temperatures ranging from approximately 250 to 400 °C. The third peak occurs at temperatures of about 800–900 °C. The last stages include char oxidation. On the TG graph of the BSG sample, a sharp slope alteration before 400 °C was found. After 400 °C, the TG graph of the BSG sample showed a reduced slope. The TG curve of the lignite sample does not follow this trend and showed a stable (high) slope at all furnace temperatures. The trend of the BSG TG graph affected the TG graph of the analyzed blends, as it seems that the TG curve of the blends, before 400 °C, revealed a similar (very sharp) slope alteration as the one of BSG, and after 400 °C, the slope of the TG line of blends reduced (as it happens in the BSG TG curve). At the same temperature (e.g., 400 °C), the BSG sample had exhibited the highest weight mass loss, while the lignite sample exhibited the lowest mass loss. In the blends, the higher the biomass content, the greater the weight loss.

a.

Fig. 2 **a** Thermogravimetric analysis: TG/DTG graphs of BSG, LIGA, and their blends in different proportions, under air atmosphere with flow rate of 3.5 l/min and heating rate 10 °C/min, **b** DTG theoretical profiles versus DTG experimental of blends synergy effect
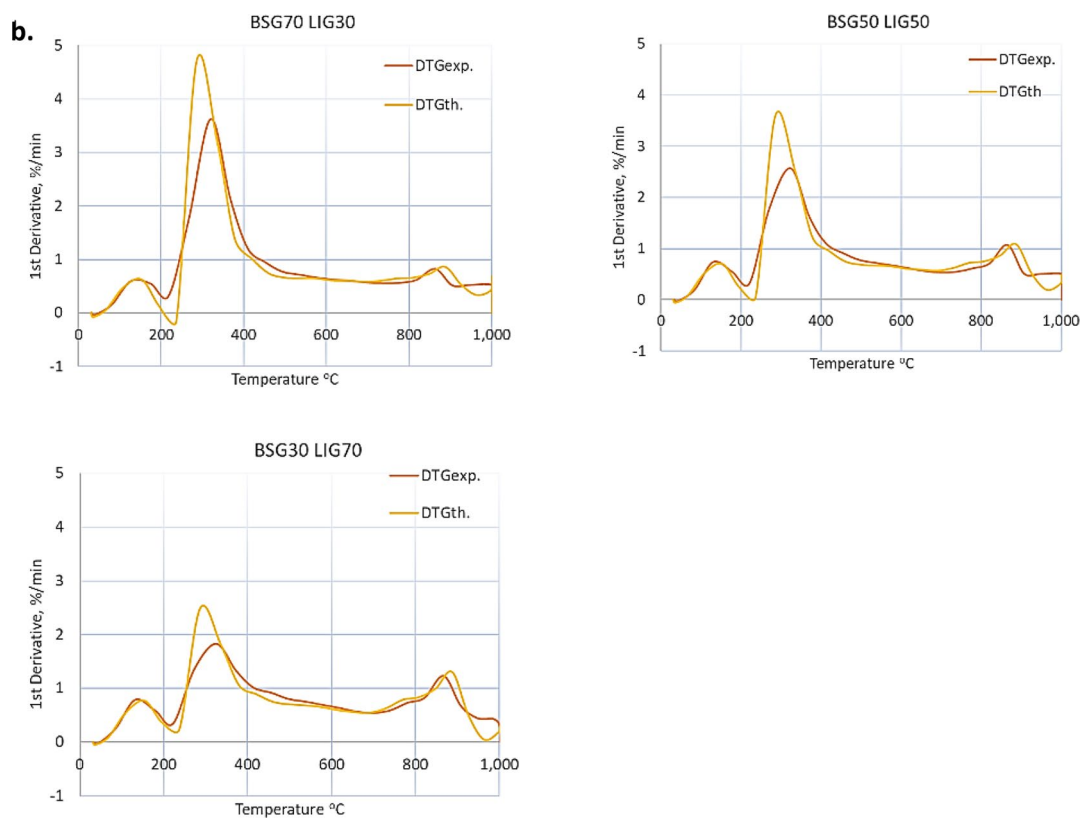
b.

Fig. 2 (continued)

Figure 2b compares the experimental DTG profiles of the fuels to the theoretical DTG profiles. From the comparison of the experimental DTG curves with the corresponding theoretical ones, it can be observed that the experimental curve of BSG mixtures, in the temperature range of 200–400 ℃, is shifted to the right (at a higher temperatures), indicating synergistic effects between the samples that take part in the mixture. This means that stage III of the combustion process, after dehydration (first peak), occurred at a higher temperature than expected compared to the theoretical curves. Also, in the area just before the end of the combustion (> 800 ℃), synergy effects also occurred, as in the experimental DTG curves, the distinct peak of this stage was found shifted to the left, at a lower temperature compared to the corresponding peak of the theoretical DTG profile, which means that the last stages of combustion process (the third peak) finished earlier at a lower temperature.

Ultimate analysis and determination of chlorides and sulfate sulfur

The results of the ultimate analysis are presented in Table 3. Carbon, hydrogen, oxygen, nitrogen, and sulfur affect the energy content of a fuel, combustion efficiency, and emissions. More specifically, high oxygen content enhances combustion efficiency, high H/C ratio translates to high volatile matter, but high N and S content does not always translate to high NOx and SOx emissions, as several parameters affect emissions (combustion technology, exceed air, combustion temperature, synergy effect, ash elements of the fuel, etc.). All analyzed fuels revealed higher carbon content than the lignite sample (35.58 wt.%), with a range from about 38 wt.% (BSG30 LIG70) to 48 wt.% (raw brewing industry waste sample). The carbon content of BSG blends with lignite increased as the percentage of brewing solid industry waste increased. Hydrogen content of the BSG raw sample revealed a value significantly higher (more than 4 wt.%) than the value of the lignite sample (lower than 1 wt.%). The hydrogen content of blends follows the same tend as the carbon content. The BSG sample revealed high N content, while S and Cl content revealed low acceptable values. The results of the BSG sample are in agreement with Arranz et al. (2021). High Cl contents are not necessarily translated to high respective emissions as due to their synergistic effects, they may be captured in the ash of the fuel (more details in Par. "Ash analysis, ternary diagrams and sustainable use of secondary wastes").

Table 3 Ultimate analysis (determination of C, H, N, S, and O), sulfate sulfur (S–SO_4^{2-}), and chloride anions (Cl^-) content of brewers' spent grain sample and their blends with lignite, in different proportions (30 wt.%, 50 wt.%, and 70 wt.%). All values are expressed in wt.%

Sample ID	C (wt.%)		H (wt.%)		N (wt.%)		S (wt.%)		O^b (wt.%)	Cl^- (wt.%)	S as SO_4^{2-} (wt.%)	Empirical chemical formulas
BSG	47.77	±0.14	6.25	±0.08	4.24	±0.03	<1.00[c]		35.93	0.03	0.05	$C_{255}N_{19}SH_{398}O_{146}$
BSG70 LIG30	44.30	±0.10	5.56	±0.05	3.32	±0.03	<1.00[c]		31.17	0.03	0.05	$C_{237}N_{15}SH_{354}O_{127}$
BSG50 LIG50	42.73	±0.03	5.47	±0.10	3.01	±0.01	0.58	±0.07	27.33	0.02	0.05	$C_{197}N_{12}SH_{305}O_{94}$
BSG30 LIG70	38.08	±0.41	3.97	±0.07	1.88	±0.01	0.58	±0.05	27.42	0.02	0.05	$C_{175}N_7SH_{218}O_{95}$
LIGA[a]	35.58	±0.05	3.73	±0.06	0.90	±0.09	<1.00[c]		58.79	0.02[c]	0.05	$C_{95}N_2SH_{119}O_{40}$

[a]Result from lignite (LIGA) sample was taken from the literature (Vasileiadou et al. 2021b); [b]oxygen was calculated by difference (O = 100–C–H–N–S–Ash); [c]oxygen was calculated with maximum value of S content; and [d]Cl^- content of lignite sample was taken from the literature (Vasileiadou et al. 2022)

Table 4 Maximum potential CO_2, NO, and SO_2 emission factors per produced energy of the samples and the % deviation compared to lignite

Sample ID	gCO_2/MJ	%deviation gCO_2/MJ compared to lignite	gSO_2/MJ	%deviation gSO_2/MJ compared to lignite	gNO/MJ	%deviation gNO/MJ compared to lignite
BSG	91.9	− 10.7	1	− 37.5	4.8	213.7
BSG70 LIG30	88.4	− 14.1	0.6	− 62.5	3.9	154.9
BSG50 LIG50	99.0	− 3.8	0.7	− 56.3	4.1	168.0
BSG30 LIG70	98.1	− 4.7	0.8	− 50.0	2.8	83.0
LIGA	102.9	0.0	1.6	0.0	1.53	0.0

Empirical chemical formulas

Empirical chemical formulas of the brewers' spent grain sample, lignite, and their blends, in different percentages, are illustrated in Table 4. An empirical chemical formula is the simplest way to express the compositional analysis of a compound. The empirical chemical formula of the brewers' spent grain sample and BSG blends with lignite has never been reported. The empirical chemical formula of the raw brewers' spent grain sample was found to be $C_{255}N_{19}SH_{398}O_{146}$ while lignite sample revealed $C_{95}N_2SH_{119}O_{40}$. Empirical chemical formula of composite fuel with 30% BSG was found to be $C_{175}N_7SH_{218}O_{95}$ while composite fuel with 70% BSG was found to be $C_{237}N_{15}SH_{354}O_{127}$.

Maximum potential CO_2, SO_2, and NO emission factors

The calculated maximum potential emission factors of the analyzed samples are illustrated in Table 4. BSG sample revealed lower CO_2 and SO_2 emissions per produced energy (91 gCO_2/MJ, 1.0 gSO_2/MJ) than lignite sample (103 gCO_2/MJ, 1.6 gSO_2/MJ) and higher NO maximum emissions (4.8 gNO/MJ) than lignite (1.5 gNO/MJ). As the BSG concentration increases in the blend with lignite, the CO_2 emissions per produced energy decreased (except from BSG50 LIG50). NO and SO_2 emissions of BSG blends with lignite do not follow a trend related to the amount of BSG in the blend, maybe due to the synergistic effect of co-combustion.

Compared to lignite, there is a reduction in maximum CO_2 emissions per unit of energy from 4.7 (for blend with 30% BSG) to 10.7% (for blend with 70% BSG). Biomass is renewable and carbon neutral; so, the CO_2 emissions resulting from biomass co-combustion with lignite contain a part that is renewable (from the biomass that takes part in the blend) and a part that is not renewable (from the lignite that takes part in the blend). So, the non-renewable CO_2 emissions are much lower than the maximum potential emissions per unit of energy produced. Furthermore, there is a high reduction of SO_2 emissions per produced megajoule that ranges from about 38% (BSG sample) to about 63% (BSG70 LIG30). The NO emissions per unit of energy produced were revealed to be higher than lignite, but this could be reduced by using a combustion technology with a low combustion temperature (e.g., fluidized bed combustion, FBC), adjusting the air ratio and residence time, and/or using a deNOx system. In other words, biomass residue combustion and/or co-combustion could contribute to achieving the sustainable development goals (sustainable energy, sustainable consumption and production, sustainable economic growth, climate action, etc.).

Arrhenius kinetics and thermodynamic analysis

The results of applying the Arrhenius kinetic model and the results of the thermodynamic analysis of BSG sample,

Table 5 Kinetic and thermodynamic parameters of the analyzed fuels (raw samples and solid composite fuels)

Sample ID	T range (°C)		R^2	E (kJ mol^{-1})	A (s^{-1})	T_m (K)	ΔH_α (kJ mol^{-1})	ΔG_α (kJ mol^{-1})	ΔS_α (kJ mol^{-1} K^{-1})
	From	To							
BSG	211	307	0.9915	81.97	3.4395E+04	580	77.15	195.59	−0.20
BSG70 LIG30	218	320	0.9699	59.96	1.9356E+02	594	55.02	174.75	−0.20
BSG50 LIG50	221	323	0.9133	49.15	1.5057E+01	596	44.19	162.93	−0.20
BSG30 LIG70	223	325	0.9221	40.51	1.6358E+00	598	35.53	152.48	−0.20
LIGA	695	889	0.9686	70.79	9.26E−01	924	63.11	125.95	−0.07

Fig. 3 Arrhenius plots (logK versus 1/T) of the analyzed solid biofuels
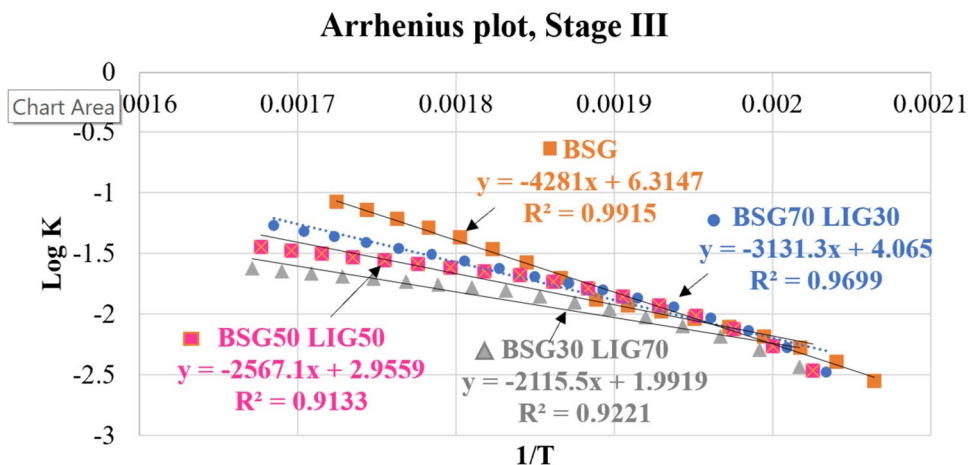
lignite, and their blends with lignite are presented in Table 5. The corresponding Arrhenius plots (logarithm of the rate constant, K, versus the inverse temperature, $1/T$) are illustrated in Fig. 3. The resulting negatively-sloped line of Arrhenius plots of BSG sample and BSG blends with lignite is presented in Arrhenius plots. Kinetic and thermodynamic analyses are performed for stage III of the samples where the beginning of this stage coincides with T_i, and the end of the stage coincides with T_{max} (DTG curves). The BSG sample revealed a little higher activation energy (E) than the lignite sample. Although the value of activation energy increased, as the BSG percentage increased in blends with lignite, solid composite fuels showed lower activation energy than the activation energy of raw lignite sample. A fuel with lower activation energy translates to more economically produced energy because combustion requires less energy to start the chemical reactions of the process (Rathore et al. 2021). The value of pro-exponential factor (A) increased significantly, as the BSG content in the blend increased. The pre-exponential factor of the analyzed samples and blends was found to be greater than the lignite sample. The pre-exponential factor is related to the reaction rate of the fuel. This is in accordance with the maximum reaction rate of the analyzed fuels (thermogravimetric analysis results). The Arrhenius plot of the brewers' solid waste sample and of the solid composite

fuels revealed 'very strong' negative correlation between the logarithm of the weight loss rate (log K) and the $1/T$ ratio according to Evans' classification (1996). BSG Arrhenius plot ($Y = \log K$ versus $X = 1/T$) showed the highest slope of the line ($Y = aX + b$, where the constants a and b were found from the regression slope and intercept of stage III Arrhenius plot), followed by BSG70 LIG30, BSG50 LIG50, and BSG30 LIG70. In other words, fuels with low activation energy deal with fewer difficulties (in stage III) regarding starting the combustion reactions than fuels with high activation energy. This trend is in accordance with activation energy. The BSG sample revealed the highest activation energy, in stage III of the TG/DTG profile of the fuel (from ignition temperature to maximum temperature), and as the percentage of BSG in fuel decreases, activation energy also decreases. This is in accordance with the results of the ignition temperature (T_i, see Table S1). This trend has been revealed in the compost-like output from municipal solid waste blends with lignite (Vasileiadou et al. 2021a). In addition to the determination of kinetic parameters, the determination of thermodynamic parameters is essential in order to define the feasibility of the process (Dhyani et al. 2017) and in order to perform a complete characterization of a fuel. The spent brewer's grain sample, BSG, showed higher value of enthalpy change (~77 kJ mol^{-1}) than the corresponding

value of lignite sample (~ 63 kJ mol^{-1}), while composite fuels revealed lower ΔH_α values. In other words, raw BSG sample requires a little more energy, from the system to overcome the 'barriers' and start the chemical combustion reactions of stage III, while BSG blends with lignite require less energy from the system to overcome the 'barriers' and start the chemical combustion reactions of stage III.

The BSG sample showed a much higher Gibbs free energy value (~ 196 kJ mol^{-1}) than the corresponding value of the lignite sample (~ 126 kJ mol^{-1}). As the content of BSG grows in the mixture, the ΔG_α is increasing. A fuel with a high ΔG_α change means a high-energy content of the fuel, since the ΔG_α change determines the total energy of the system. ΔS_α of the BSG raw and composite fuels was found to be negative, low, and similar to each other, while lignite sample showed a value of almost zero, indicating that at the end of this stage, the material is almost in equilibrium. As ΔS_α is negative, and ΔH_α is positive (endothermic at stage III), the process is nonspontaneous at any temperature.

Ash analysis, ternary diagrams, and sustainable use of secondary wastes

The chemical (elemental) composition and their morphology are crucial characteristics of a fuel, as many oxides affect slagging tendency in the heat exchangers, and in the combustion plant, corrosion, heat transfer, and the possibility of using the ash in cement production, or other value-added products in the context of the circular economy.

Table S2 (Supplementary Material) illustrates the results of the ash elemental analysis of the fuels. Calcium was found to be the main element of the analyzed BSG ash sample and of the ashes of the solid composite fuels (BSG blends with lignite in different proportions, 30 wt.%, 50 wt.%, and 70 wt.%). The calcareous in minerals of biomass fuels contributes to the high content of calcium oxides in the ash. The high content of calcium oxides leads to alkaline ash leading to self-desulfurization in circulating fluidized bed (CFB) power plants (Li et al. 2012). CaO and MgO could contribute to eliminate SOx emissions at reaction temperatures lower than 800 °C (Xie and Ma 2014; Yang et al. 2018). Brewer's spent grain ash sample showed no K_2O and P_2O_5 oxides. Arranz et al. (2021) studied brewing spent grains pellets reporting different ash chemical compositions (very high percentages in SiO_2 and P_2O_5 oxides) maybe due to different qualities, possible soil-improvers, climate, and pre-treatment of the sample. Various inconsistencies can be observed in the ash composition of the blends. There are two possible explanations for this: (1) Although the ash composition was measured with SEM/EDS in at least four different regions, this may be not representative for inhomogeneous samples, such as the blends, since in SEM analysis, only a very small area

is observed, and (2) the ash composition of the blends is influenced by synergistic effects that occurred during co-combustion.

In general, the elements of the ash elemental analysis should not be discussed individually, but in various combinations with each other, due to the occurrence of synergistic effects, in order to study slagging tendency, fouling, agglomerations, and deposits of ash resulting from fuel combustion. For that reason, various indicators—ash quality index (Vasileiadou et al. 2022), ternary diagrams, B/A index, Fu index, etc. (Pronobis 2005)—have been developed.

Figure 4a–e illustrates the backscattered electron images of the analyzed fuels. For all analyzed ashes, more than five different surfaces (spectrum pink areas) and at least three points were examined. SEM images of the analyzed fuel ashes show the morphology and microstructure of the ashes. BSG ash sample (Fig. 4a) presents larger particles than lignite ash sample (Fig. 4e). The composition of lignite ash is in agreement with other Greek lignite studies (Iordanidis et al. 2020a, 2020b). In BSG ash, blends with lignite revealed lower particles and some heterogeneity in the structure. It seems that the BSG percentage influences the morphology of the ash. Small pores are also observed. More specifically, blends with a high BSG percentage revealed high particle sizes. This particle size most likely arises from coagulation. Spherical particles may contain high amounts of CaO and SiO_2 (Strzałkowska 2021).

Figure 4e illustrates the ternary (triangular) diagram with peaks the oxides $SiO_2 + Al_2O_3 + Fe_2O_3 + Na_2O + TiO_2$, $CaO + MgO + MnO$, and $K_2O + P_2O_5 + SO_3$ of the elemental analysis of the analyzed ashes.

According to the ternary diagram, there are four types of ashes: types C, S, K, and CK. Type S ('silicon angle' type) and type K ('potassium' type) present high risks of deposits due to the formation of silicates and the presence of potassium. Type C ('calcium angle' type) is expected to have high melting temperature, which is translated to low deposits due to high Ca concentrations (García et al. 2015). Type CK is an intermediate type between type C and type K and has a medium tendency for slagging (Wang et al. 2017). According to the results, all ashes of the analyzed fuels are characterized as 'Type C' ashes which are translated to high melting temperature resulting in low deposits and limited slagging and fouling problems during combustion.

Moreover, the ternary diagram categorizes the ash fuels according to their acidity into 'high,' 'medium,' and 'low,' which affects the corrosion phenomena and the melting point of the ash. BSG ash sample is characterized as 'low acidity' ash, while BSG blends with lignite as 'Medium acidity' ashes.

All analyzed ashes revealed CaO greater than 20% (C-Type). Ashes with more than 20% CaO have pozzolanic properties, self-cementing properties, resistance to
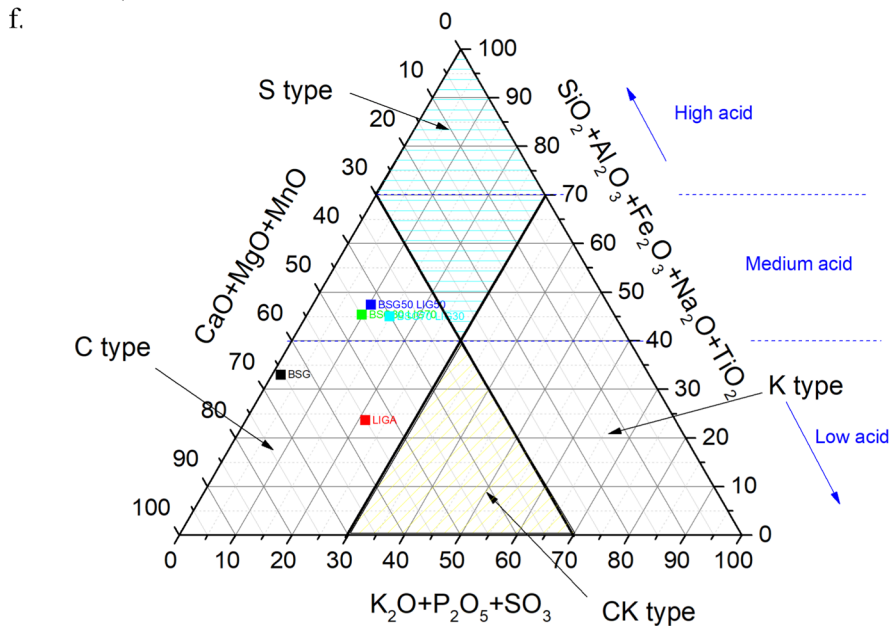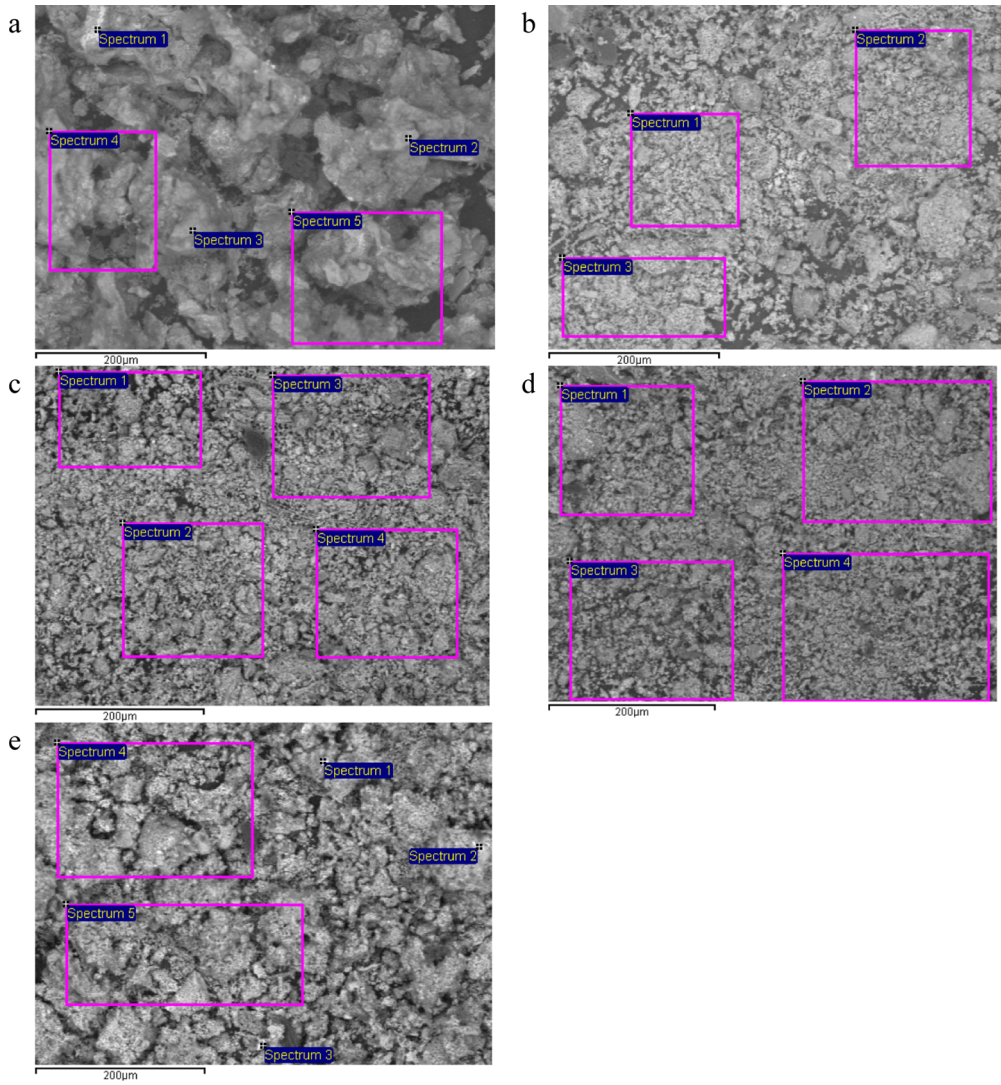
◄**Fig. 4** Backscattered electron images of the fuels. **a** BSG, **b** BSG70 LIG30, **c** BSG50 LIG50, **d** BSG30 LIG70, **e** LIGA, and **f** ternary diagram $SiO_2 + Al_2O_3 + Fe_2O_3 + Na_2O + TiO_2 – CaO + MgO + MnO – K_2O + P_2O_5 + SO_3$

expansion from chemical attack, and do not require an activator. Class C ash is used at 15–40% by mass of cementitious material (Kim and Prezzi 2008). By using biomass residue ash in concrete production could lessen the environmental impact of waste disposal. Sustainable utilization of the analyzed secondary wastes (ashes resulting from biomass residue combustion) could be performed by using these ashes instead of cement in concrete production.

Case studies for sustainable management of beer industry solid wastes (BSG)

The results of the several case studies for sustainable energy production using BSG as solid biofuel, based on the results of the current study (GCV), data on beer and BSG production from the year 2017 (case study 4), for Greece, Europe, and worldwide, are presented in Table 6. Case studies 1, 2, 3, 4, 5, 6, 7, 8, and 9 refer to energy production in case of increased/or degreased beer production (BSG quantity) −15%, −10, −5, and 0% (same quantity BSG with the BSG quantity of the year 2017), +5, +10, +20%, +49%, and +100%, respectively. Three different scenarios were developed: scenarios I, II, and III in the case of using 100% BSG waste from the beer industry, 70% BSG, and 50% BSG.

The results of *scenario I* (100% of produced BSG could be used for energy production) showed that burning 2.28E+07 kg BSG in Greece could produce 1.04E−02 Mtoe (case study 4) covering only 0.14% of 7.5 Mtoe (primary energy production in Greece, in year 2017, as a reference), and burning 2.38E+09 kg BSG in Europe could produce 1.08E+00 Mtoe (case study 4) covering only 0.14% of 758.2 Mtoe (primary energy production in Europe, in year 2017, as a reference).

The results of energy cover using BSG as a fuel, based on scenarios II and III, are reduced compared to the results of scenario I, as it is assumed that 70% (scenario II) and 50% (scenario III) of the amount of BSG, produced from the beer industry, used for energy production, making the assumption that the rest percent is used for other purposes, e.g., as animal feed, in chemical processes (Serrano-Pérez et al. 2017), as biocarbon for wastewater treatment (Yinxin et al. 2015), in industrial applications (Mussatto 2014), etc.

In order to eliminate the transportation cost of BSG (~ $16 US/tn wet BSG/8 km), breweries could use BSG as a fuel themselves. By installing special equipment for combustion BSG could cover more than 50% of energy costs (Mussatto 2014).

Conclusion

This study examined the potential of alternative utilization of brewers' spent grain (BSG) as solid biofuel for energy production via multiple thermo-analytical methods and approaches. The main contribution of this study is a comprehensive assessment of the BSG and their blends in several proportions as alternative sustainable fuels and the assessment of their secondary waste production resulting from combustion. In addition, several case studies were performed in order to study the possible coverage of energy demand by these alternative solid biofuels. The case studies are based on real data from brewery industries in Europe and Greece.

The results of this study showed that:

- BSG revealed high fuel quality characteristics (high calorific value, low ash content, low maximum temperature with a high rate of weight loss, higher Gibbs free energy value, etc.).
- The BSG sample revealed a considerably lower value of the environmental footprint index (0.0025 kg/MJ) than the lignite sample (0.0307 kg/MJ), which means that the production of secondary solid waste (ash) is significantly decreased if the same amount of energy is produced by combusting BSG instead of lignite.
- BSG blends with lignite revealed better characteristics as the BSG in the blend increased.
- Synergistic effect in BSG co-combustion with lignite occurs, regarding DTG profiles of fuels, emissions, and ash composition.
- The Cl and S contents of BSG were found to be similar to the ones of lignite (0.03 and < 1.00 wt.%, respectively).
- BSG sample revealed lower CO_2 and SO_2 emissions per produced energy (91 gCO_2/MJ, 1.0 gSO_2/MJ) than lignite (103 gCO_2/MJ, 1.6 gSO_2/MJ) but higher NO maximum emissions (4.8 gNO/MJ) than lignite (1.5 gNO/MJ).
- BSG ash and BSG blends with lignite ashes are characterized as 'Type C' ashes which is translated to high melting temperature, which is translated to low slagging/fouling problems during combustion and could be used sustainably in concrete production.
- Energy production from utilization of brewers' spent grain as a fuel could cover a small percentage of primary energy demand of a single country; nevertheless, it would be beneficial if these wastes were utilized in order to cover local energy demand, e.g., of beer industries or in district heating of villages.

In overall conclusion, BSG could be used as a sustainable energy source, either individually or in blend with lignite. However, a pre-treatment method to reduce the high moisture content should be adopted. The only drawback

Table 6 Various case studies for sustainable energy production using brewing wastes (BSG) as a solid biofuel (in Greece and in Europe). Case study 4: uses real data on beer production in 2017

Scenario I (using 100% BSG wastes of beer industries, db)			Case studies, in Mtoe								
			c.s. 1:	c.s. 2:	c.s. 3:	c.s. 4:	c.s. 5:	c.s. 6:	c.s. 7:	c.s. 8:	c.s. 9:
Solid waste from beer production (BSG, db)	Region	Units	BSG, db (100% BSG, in 2017):	−15%	−10%	−5%	0%	5%	10%	20%	49%	100%
	In Greece	kg	2.28E+07	8.82E−03	9.34E−03	9.86E−03	1.04E−02	1.09E−02	1.14E−02	1.24E−02	1.55E−02	2.07E−02
	In Europe	kg	2.38E+09	9.20E−01	9.74E−01	1.03E+00	1.08E+00	1.14E+00	1.19E+00	1.30E+00	1.61E+00	2.17E+00
Scenario II (using 70% BSG wastes of beer industries, db)			Case studies, in Mtoe									
			c.s. 1:	c.s. 2:	c.s. 3:	c.s. 4:	c.s. 5:	c.s. 6:	c.s. 7:	c.s. 8:	c.s. 9:
Solid waste from beer production (BSG, db)	Region	Units	BSG, db (70% BSG, in 2017):	−15%	−10%	−5%	0%	5%	10%	20%	49%	100%
	In Greece	kg	1.60E+07	6.17E−03	6.54E−03	6.90E−03	7.26E−03	7.62E−03	7.99E−03	8.71E−03	1.05E−02	1.45E−02
	In Europe	kg	1.67E+09	6.44E−01	6.82E−01	7.20E−01	7.58E−01	7.96E−01	8.34E−01	9.10E−01	1.10E+00	1.52E+00
Scenario III (using 50% BSG wastes of beer industries, db)			Case studies, in Mtoe									
			c.s. 1:	c.s. 2:	c.s. 3:	c.s. 4:	c.s. 5:	c.s. 6:	c.s. 7:	c.s. 8:	c.s. 9:
Solid waste from beer production (BSG, db)	Region	Units	BSG, db (50% BSG, in 2017):	−15%	−10%	−5%	0%	5%	10%	20%	49%	100%
	In Greece	kg	1.14E+07	4.41E−03	4.67E−03	4.93E−03	5.19E−03	5.45E−03	5.71E−03	6.22E−03	7.52E−03	1.04E−02
	In Europe	kg	1.19E+09	4.60E−01	4.87E−01	5.14E−01	5.41E−01	5.69E−01	5.96E−01	6.50E−01	7.85E−01	1.08E+00

1 MJ = $2.38458966275 \cdot 10^{-11}$ Mtoe (millions of tonnes oil equivalent) and db: dry basis

of BSG seems to be the high nitrogen content that could lead to high NOx emissions so an appropriate method for the reduction of NO_x emissions (e.g., selective catalytic reduction, deNOx system) should be adopted in order to avoid photochemical smog.

Declarations

Conflict of interest The author declares no conflict of interest.

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