Preparation and gasification of brewers' spent grains

V. Pérez[1], J.M. Murillo[1], R. Bados[1], L.S. Esteban[1], R. Ramos[1] and J.M. Sánchez[2]

[1]CEDER-CIEMAT, Energy Department. Autovía A15, salida 56, Lubia, Soria, 42290, Spain
[2]CIEMAT, Energy Department. Avenida Complutense, 40 , Madrid, 28040, Spain
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Presenting author email: virginia.perez@ciemat.es

Abstract

Preparation and gasification of brewers' spent grains (BSG) were studied to evaluate the potential of this waste to obtain gas by means of gasification. The fuel preparation included drying and pelletizing. A prototype hybrid-solar biomass dryer was used to reduce the moisture contents. The densification process was studied, using a pelletizing plant of 300 kg/h capacity. Air gasification tests of the dried and pelletized brewers spent grains were carried out focusing on the influence of the equivalence ratio and the throughput used. The tests were performed in a bubbling fluidized bed gasifier at atmospheric pressure and autothermal operation, without the use of any external heating. Gasification tests were conducted at 130-220 MW_{th} and temperatures around 800 ºC, using silica sand as bed material. The moisture content of the BSG was reduced from more than 80 % to less than 20 % in order to obtain high quality pellets, regarding some physical parameters such as durability and bulk density. The produced gas is made up of 2.1-3.6 % H_2, 7.4-13.1 % CO, 2.0-12.8 % CH_4 and 1.0-2.4 % C_2H_4, as the main components which contribute to its heating value of 2.7-8.1 MJ/Nm^3. Its tar contents are 13-20 g/Nm^3. An appropriate fuel was obtained to be used in the air gasification process where the gas produced can be used to obtain energy.

Keywords

Brewers' spent grain (BSG), drying, gasification, tar, biomass.

1. Introduction

The beer sector is prominent in the Spanish industry, being the fourth producer in the European Union. Brewers' spent grains (BSG) account around 20% of produced beer, and represent approximately 85 % of total by-products generated by the brewer industry [1].
BSG is mainly composed of the barley malt grain husks in mixture with part of the pericarp and seed coat layers of these grains. Since it is rich in sugar, protein and mineral contents, the main and quickest alternative for its elimination has been as animal feeding. However, BSG is an interesting raw material for application in different areas because of its low cost and large availability throughout the year, and valuable chemical composition. Many methods for application BSG in foods as an ingredient for animal or human nutrition, in energy production and in chemical and biochemical processes have been reported [2].
Due to its high humidity and fermentable sugar content, BSG deteriorates very easily. In this sense, the use and marketability of BSG for gasification and most of the uses is significantly improved when the material is dried. Several methods have been proposed to prolong BSG storage time as a result of their high moisture content. Drying is a possible alternative for BSG preservation with the advantage that it also reduces the product volume, and therefore, decreases transport and storage costs [3]. The traditional process for drying BSG is based on the use of direct rotary-drum dryers, a procedure considered to be very energy-intensive. Nevertheless, hybrid-solar biomass dryers can be a quite interesting alternative for BSG deep drying in areas of high solar radiation and low ambient humidity [4].
The production of energy from BSG is motivated by the search for new sources of renewable energy and raw materials. Numerous alternatives have been proposed for BSG use in this area, including thermochemical conversion (combustion, gasification and pyrolysis), biogas production and ethanol production. BSG presents important net and gross calorific values and therefore can be an interesting raw material to produce energy by thermochemical processes. An example of this effort is the "Green Brewery" concept which aims to an energy efficiency increase and use of 100 % renewable energy sources in breweries [5]. BSG can cover 20% of breweries energy demand [6].
Gasification appears a better alternative than combustion, avoiding particle emissions and toxic gases that can contain nitrogen and sulphur dioxide [7]. Gasification is a thermochemical process by which the BSG is converted to a combustible gas The process takes place at high temperatures, around 800 ºC, using a gasifying agent, i.e. air, in sub-

stoichiometric conditions. The produced gas is composed by a mixture of carbon dioxide, carbon monoxide, hydrogen, methane, other hydrocarbons, water, and, when air is used as a gasifying agent, nitrogen. This gas can be used not only to obtain thermal energy but also electric power, chemicals and biofuels, as in a biorefinery.
For most applications, the gas must be cleaned to reduce the contents of inorganic and organic contaminants, such as tar, and dust. Indeed, one of the major issues in biomass gasification is dealing with the tar formed. Tar is a mixture of compounds that are easily condensable at temperatures below 400 ºC, which causes clogging problems in pipes, filters and internal deposits and limit the end use of the gas produced [8]. Tar removal technologies can be classified as primary or secondary methods. Primary methods occur throughout the gasification process, while secondary methods transpire after this process. Both procedures are required to achieve a total elimination of tar [9].
The correct selection of the operating conditions is one of the primary methods to reduce tar content in biomass gasification. The operating conditions are a set of variables that affect the quality of the final product. Operating temperature and equivalence ratio are some of the most influential parameters in the gasification process. In autothermal reactors, the equivalence ratio determines the temperature. Throughput or feed rate is another significant factor that affects both the gas composition and the tar content, as the above variables.
The current paper deals with the preparation of brewers' spent grains for thermochemical process, making a special focus in reducing its moisture content and increasing its density. On the other hand, air gasification of brewers' spent grains has been done to determine the influence of equivalence ratio and throughput on gas quality, tar production, low heating value, gas yield, carbon conversion and efficiency.

2. Materials and methods

This research requires some materials such as brewers' spent grains and silica sand. Preparation and gasification of BSG were performed at some experimental facilities located at the Centre of Development of Renewable Energy Sources (CEDER), belonging to the Research Centre for Energy, Environment and Technology (CIEMAT), in Spain.

2.1. Raw Materials

BSG supplied by a Spanish beer industry was used. Its characterization and the standard methods used for it in the laboratory are shown in Table 1.
Table 1. Characterization of the BSG and the standard methods used.

Parameter	Unit	Value	Standard method
Moisture	% w.b.	81.3	ISO 18134-1:2015
Proximate analysis			
Ash	% d.b.	4.0	ISO 18122:2015
Volatile	% d.b.	77.1	ISO 18123:2015
Fixed carbon	% d.b.	18.9	Calculated
Ultimate analysis			
C	% d.b.	50.4	ISO 16948:2015
H	% d.b.	6.5	ISO 16948:2015
N	% d.b.	4.44	ISO 16948:2015
S	% d.b.	0.32	ISO 16994:2016
Cl	% d.b.	0.01	ISO 16994:2016
O	% d.b.	34.33	Calculated
Heating value			
HHV	MJ/kg d.b.	21.35	EN 14918:2009
LHV	MJ/kg d.b.	19.94	Calculated

2.2. Fuel preparation

BSG preparation can be divided into two steps. The first one was focused on reducing its moisture content and the second one on increasing its density.

2.2.1. Drying
A prototype hybrid-solar biomass dryer was used. The dryer is a hybrid concept based on the heating for the biomass using solar radiation within a greenhouse enclosure and other sources of low-temperature heat, such as hot water from

engine cooling systems or from heat exchangers of combustion gases. The dryer was designed for drying chipped or ground lignocellulosic biomass to values of 10-15% wet basis (w.b.), which are usually required by pelletizing industry [4].

There are four heat sources that enable to achieve the maximum water evaporation target:

1. Solar radiant heat directly focused on the biomass bed and the subsequent heating of the indoor air, as a consequence of the collection of the solar radiation inside the greenhouse tunnel.
2. Hot air contribution from solar collector panels (thermosolar).
3. Radiant floor in the drying tunnel.
4. Hot air introduced into the drying tunnel using biomass as a fuel support.

The operating capacity of the facility was tested using BSG. Before the drying process, the materials were weighted. Afterwards, they were downloaded in the biomass inlet silo of the facility, having previously taken a representative sample of the biomass to measure its moisture content in the laboratory. Some control parameters and the electric consumption were registered in the test. The dry biomass of the outlet silo is weighted and its moisture content measured, in order to calculate the corresponding energy values.

2.2.2. Densification

The facility used in the experiments was a pellet plant with a capacity of 300 kg/h. The pellet press had a flat type Amandus Kahl 33-500 Kahl 33-500: die diameter 500 mm, roller width 75 mm, drive power 30 kW. Besides, the press was equipped with a hydraulic pressure system that enables to generate a pressure up to 110 bar. The pellet plant has also a blending system, a pellet mill and a cooling and bagging equipment.

The pelletizing process was optimized to ensure acceptable quality properties of fuels. The quality properties of pellets were evaluated in terms of moisture content, bulk density and durability.

2.3. Gasification

Air gasification of BSG pellets was evaluated. The set-up of the plant is shown in Figure 1..

A bubbling fluidised bed gasifier (BFB) was operated in autothermal mode and at atmospheric pressure. It is 3.0 m high, with an inner diameter of 0.3 m. It is internally coated with a layer of refractory concrete of an outer diameter of 0.720 m. There is also an overflow pipe that is used to ensure a constant fluidized bed height. Under the distributor plate, a plenum reduces the velocity of the incoming air to make sure a uniform distribution when entering the nozzles.

The air for gasification is supplied by a roots blower. A propane preheater is used to perform the start-up. During the gasification process, autothermal conditions at around 800ºC were kept, without the necessity of external heating sources, often applied in allothermal gasifiers.

The feeding system consists of two hoppers and two helical screws, one between the two hoppers and the other to feed the BSG pellets into the reactor. During the tests carried out for this work, a thermal power of 130-220 kW_{th} was tested.

Downstream of the freeboard, a high-efficiency cyclone is placed to collect most of the particles. A gas pipeline connects the cyclone to the flare, where the gas produced is burnt.

A Supervisory Control and Data Acquisition (SCADA) system is employed to operate the plant.

The system includes two gas sampling points located in the pipeline after the cyclone, with the aim of evaluating the gas composition and the tar content. The gas is analysed using a FTIR analyser to measure CO, CO_2, CH_4, C_2H_2, C_2H_4 and C_2H_6, a thermal conductivity analyser to quantify H_2 and a paramagnetic analyser for O_2. Tars are determined following the Technical Specification CEN/TS 15439:2006 [10].

Tar compounds can be classified in 5 different classes according to the solubility and condensation criteria recommended by the Energy Research Centre of the Netherlands (ECN) [11]:

- Class-1: GC undetectable tars. This class includes the heaviest tars condensing at high temperatures even at very low concentrations. In this work, GC undetectable tars were not quantified.
- Class-2: Heterocyclic components. These are components that generally exhibit high water solubility, due to their polarity. In this study, pyridine, phenol and benzonitrile are evaluated.
- Class-3: Aromatic components. Light hydrocarbons that do not present problems regarding their condensation and water solubility issues. In this research, benzene, toluene, o-xylene, m-xylene and p-xylene are taken into account. Benzene is not often considered as a tar.
- Class-4: Light poly-aromatic hydrocarbons (2-3 rings PAH's). These components condense at relatively high concentrations and intermediate temperatures. In this investigation, naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene and anthracene are estimated.
- Class-5: Heavy poly-aromatic hydrocarbons (4-5 rings PAH's). These components condense at relatively high temperature and low concentrations. In this work, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene are assessed.

The tar dew point or condensation temperature of the produced gas is calculated using the complete model developed and validated by the ECN [11].
Air gasification of BSG pellets was conducted using silica sand as bed material. Silica sand was used as bed material. The employed sand has an average particle size of 450 µm and a particle density of 2600 kg/m^3. Silica sand is considered an inert material in gasification processes [12].
Gasification tests were carried out in auto-thermal conditions and at atmospheric pressure. The study was performed at around 800 ºC. A set of experiments were undertaken to determine the influence of equivalence ratio (ER), using values of 0.16-0.25. The equivalence ratio is defined as the ratio between the airflow rate divided by the fuel flow rate in real conditions and the stoichiometric conditions. Additionally, tests at different throughput (THR), 424, 567 and 706 kg/(h·m^2), were performed. The throughput is the fuel flow divided by the gasifier crossover section.
Gas quality has been determined after the gasifier, using for the main gas species the on-line gas analyzing system describe above and following the Technical Specification for sampling and analysis of tar and particles in Biomass gasification [10]. Gas yield, carbon conversion and cold gas efficiency of the gasification process was also determined.

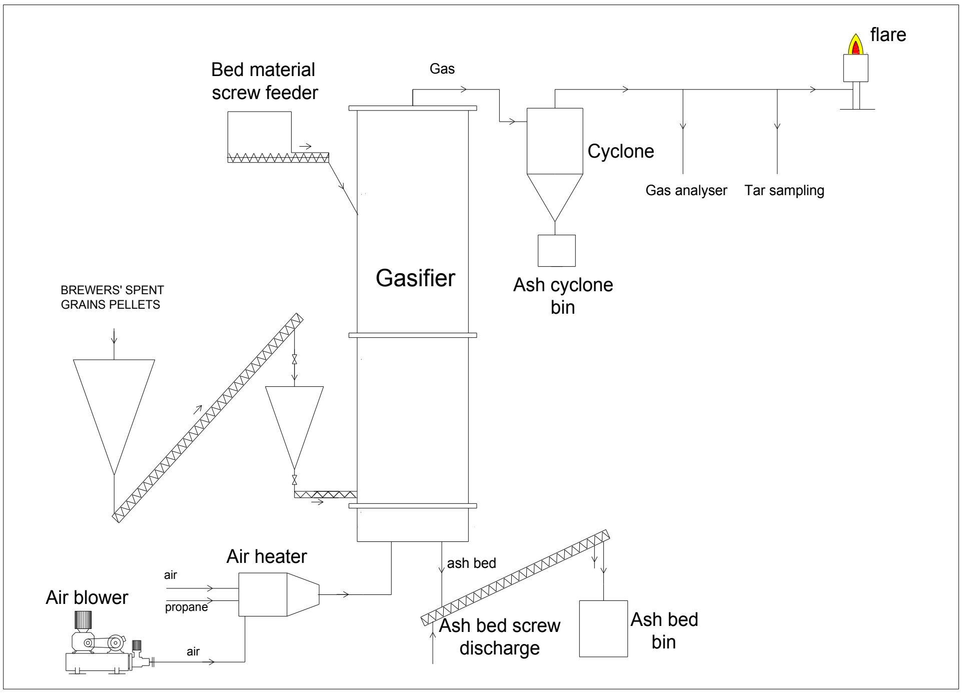

Figure 1. Experimental gasifier set-up.

3. Results and discussion

3.1. Fuel preparation

3.1.1. Drying
The drying test was carried out during 217 hours using the hybrid solar biomass dryer. Table 2 shows the dryer variables, including the mean values of ambient relative humidity inside and outside, ambient temperature inside and outside, temperature of the radiant floor and solar radiation.

Table 2. Dryer variables.

Variable	Unit	Inside	Outside
Mean ambient relative humidity	%	52.7	39.03
Mean ambient temperature	ºC	31.87	23.93
Mean temperature of the radiant floor	ºC	51.20	-
Average solar radiation	W/m^2	-	516.97

The variables of the drying process of BSG can be seen in Table 3. Initial and final values of the amount of BSG, moisture and dry matter are shown. The total amount of evaporated water (e.w.) is 9960.2 kg, corresponding to the difference between the balance of the amount of BSG and the balance of the dry matter.

Table 3. Drying process of BSG.

Variable	Unit	Initial	Final	Balance
Amount of BSG	kg w.b.	12970	2997	9973
Moisture	%	81.3	19.5	-
Dry matter	kg d.b.	2425.39	2412.58	12.80

The energy balance of the drying process of BSG is shown in Table 4. It includes heat energy in the radiant floor, raw solar energy received, thermosolar energy, fuel support and total electric power. As can be seen only the 6.1 % of the energy used in the drying test is not renewable energy.

Table 4. Energy balance in the drying process.

Variable	Energy (kWh)	Contribution (%)
Heat energy in the radiant floor	2864.0	30.3
Raw solar energy received	5298.1	56.1
Thermosolar energy	478.1	5.1
Fuel support: biomass	229.6	2.4
Total electric power	578.5	6.1
Total	9448.3	100

Table 5 presents the overall results of the drying test. The wet inlet flow per hour was 59.8 kg/h of BSG wet basis (w.b.), and the dry outlet flow per hour was 11.1 kg of BSG on dry basis (d.b.). The specific consumption was 3415 kJ/kg e.w., and 93.9 % of renewable energy was used.

Table 5. Results of the drying test.

Variable	Unit	Value
Biomass yield	kg w.b./h	59.8
Evaporating yield	kg e.w./h	45.9
Specific consumption	kJ/kg e.w.	3415
Renewable energy contribution	%	91.5

3.1.2. Densification

A dry (19.5 %) and low density (148 kg/m^3) BSG was produced in the drying process. In order to increase BSG's density, pelletization was used. 354 kg/h of BSG pellets were produced in the pelletization plant. Its characterization and the standard methods used can be seen in Table 6.

Table 6. Characterization of the BSG pellets and the standard method used

Parameter	Unit	Sample number			Standard method
		1	2	3	
Moisture	% w.b.	12.58	9.79	12.36	ISO 18134-1:2015
Bulk density	kg/m^3 d.b.	523.2	515.4	511.6	ISO 17828:2015
Durability	%	81.0	82.5	n.a.	ISO 17831-1:2015

3.2. Gasification

Air gasification of BSG pellets was featured smooth operation. In Figure 2, pressure and temperature of bed and freeboard evolution over time is presented. Gas quality and tar composition was evaluated during stable operation. Good fluidization and neither sintering nor agglomeration were found for bed temperatures up to 900 ºC.

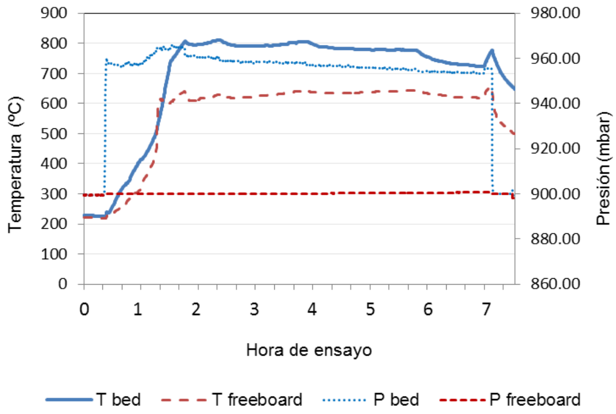

Figure 2. Bed and freeboard temperatures and pressure evolution

Table 7 summarises the operating conditions and the experimental results from the eight gasification tests conducted. The parameters analysed as operating conditions include bed temperature, fluidization velocity (u_f), throughput (THR) and equivalence ratio (ER). Additionally, gas composition, tar content and efficiency are presented.

Table 7. Operating conditions and experimental results of the gasification tests

Parameter	Unit	Test number							
		1	2	3	4	5	6	7	8
Operating conditions									
Bed Temperature	ºC	724	776	791	802	816	827	826	862
u_f / u_{mf}	-	16.5	17.7	17.9	18.7	26.0	18.9	22.3	18.9
THR	Kg/(h·m^2)	567	567	567	567	706	567	567	424
ER	-	0.157	0.172	0.174	0.190	0.192	0.193	0.208	0.246
Gas composition									
H_2	% d.b.	3.43	3.71	3.62	3.17	2.45	3.30	2.87	2.10
CO	% d.b.	13.10	11.40	11.22	10.28	9.90	10.14	8.45	7.44
CO_2	% d.b.	11.93	12.38	12.53	12.64	13.12	13.01	12.07	12.28
CH_4	% d.b.	12.76	8.29	7.58	5.91	4.01	3.81	2.56	1.96
C_2H_2	% d.b.	0.18	0.22	0.22	0.22	0.22	0.24	0.17	0.42
C_2H_4	% d.b.	1.94	2.10	2.40	2.03	2.00	2.00	1.02	1.00
C_2H_6	% d.b.	0.40	0.29	0.27	0.23	0.13	0.12	0.10	0.04
LHV_{gas}	MJ/Nm^3	8.07	6.34	6.21	5.21	4.32	4.38	3.05	2.72
Tar content									
Total tar	g/kg fuel d.a.f.	31.56	34.45	38.31	32.20	34.27	33.53	28.58	30.82
Total tar	g/Nm^3	17.08	17.84	19.70	15.81	16.76	16.34	13.38	13.08
Class-2 tar	g/Nm^3	2.64	3.19	3.12	3.00	4.28	3.15	3.03	2.47
Class-3 tar	g/Nm^3	13.05	12.36	14.28	10.39	9.21	10.32	7.92	7.52
Class-4 tar	g/Nm^3	1.34	2.18	2.17	2.28	2.99	2.62	2.23	2.76
Class-5 tar	g/Nm^3	0.05	0.11	0.13	0.14	0.28	0.24	0.21	0.33
Tar dew point	ºC	146.2	162.8	158.5	163.5	167.9	165.5	152.5	159.7
Efficiency									
Y_{gas}	Nm^3/kg fuel d.a.f.	1.85	1.93	1.94	2.04	2.04	2.05	2.14	2.36
CGE	%	84.8	69.5	68.7	60.4	50.2	51.1	37.0	36.4
X_c	%	80.8	73.4	73.6	70.2	66.2	66.3	55.9	59.2

The effect of ER on temperature is given in Figure 3. Three throughput (424, 567 and 706 kg/(h·m^2) has been studied As expected, in an autothermal gasifier, the temperature increases with ER, because, when more oxygen is fed to the gasifier, oxidation reactions prevail. The influence of THR is not clear from the results.

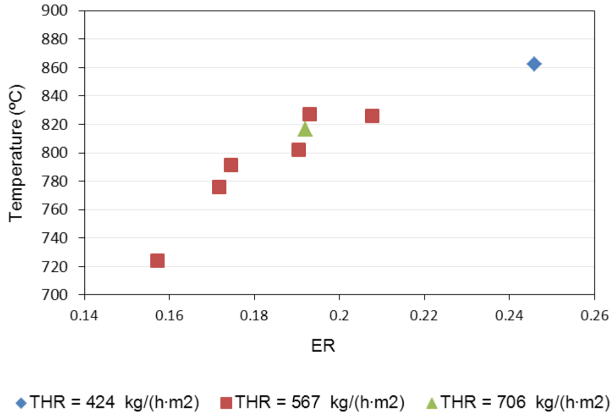

Figure 3. Temperature vs ER.

The effect of ER on gas composition is shown in Figure 4. H_2, CO, CH_4, C_2H_4 and C_2H_6 contents decreases with ER. The trend of CO_2 with ER is to increase, due to the effect of oxidation reactions. The tendency of C_2H_2 with ER is not clear. Regarding the influence of THR on gas composition should be said that H_2, CO, CO_2, CH_4, C_2H_4 and C_2H_6 contents increase with THR and only C_2H_2 contents decrease with THR. Nevertheless, this influence is not so clear, because ER is also different in these tests.

Additionally, Figure 4 presents the lower heating value (LHV) of the gas produced as a function of ER, calculated accounting for the measured fuel species: H_2, CO, CH_4, C_2H_2, C_2H_4 and C_2H_6. The LHV is seen to decrease with ER, due to the increase in the main compounds responsible for the heating value of the gas. On the other hand, the LHV of the gas produced increases with THR.

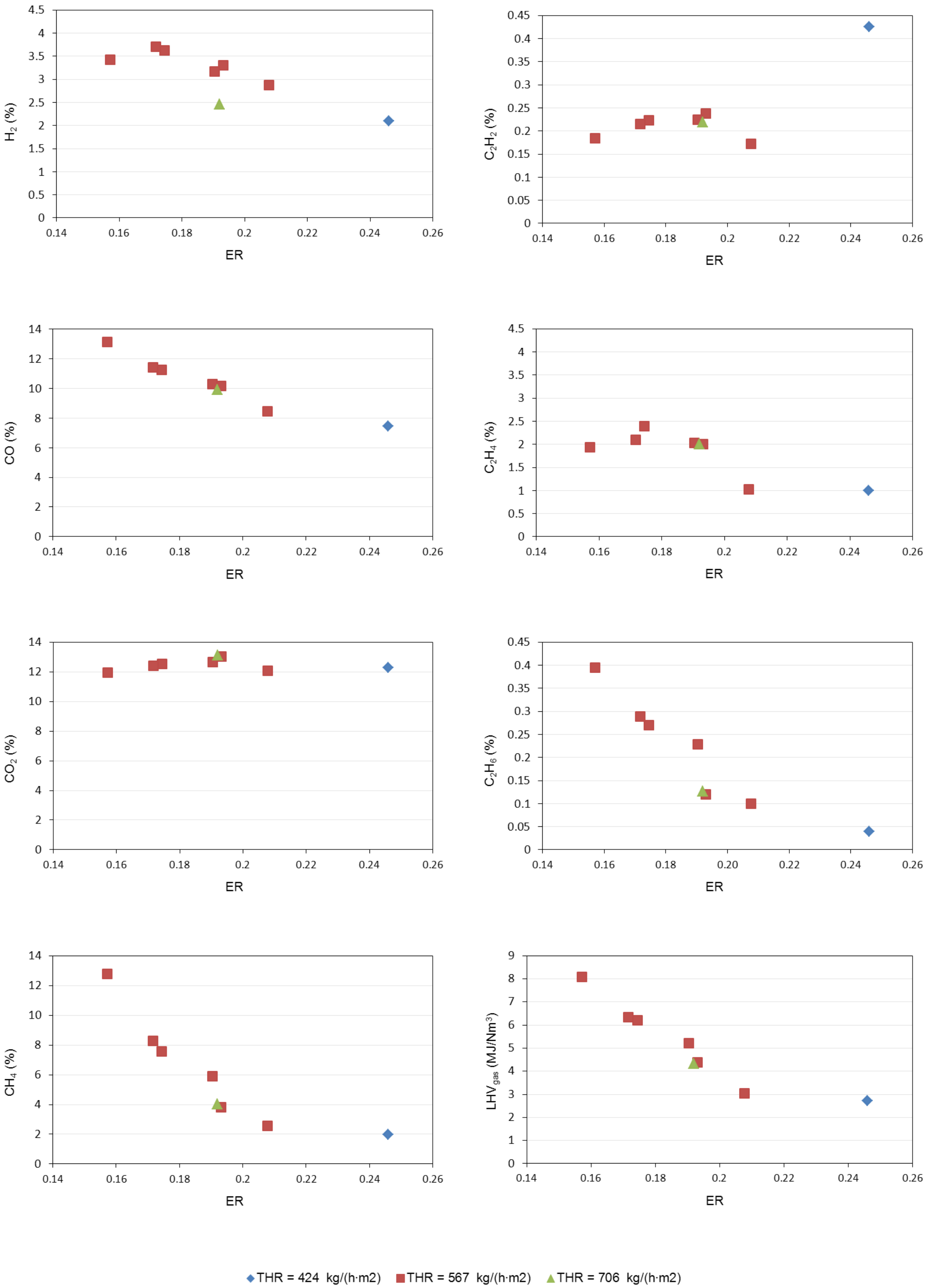

Figure 4. Gas composition and low heating value of the gas produced.

Figure 5 shows the variations in tar contents. Total tar contents are the sum of tar class 2, tar class 3, tar class 4 and tar class 5, and present values between 13-20 g/Nm3 and 28.6-38.3 g/kg fuel d.a.f. Its values decrease with ER and increase with THR.
As it can be seen in Figure 6, the tar dew point of the gas produced is between 146-168 ºC and does not present clear trend neither with ER nor with THR.

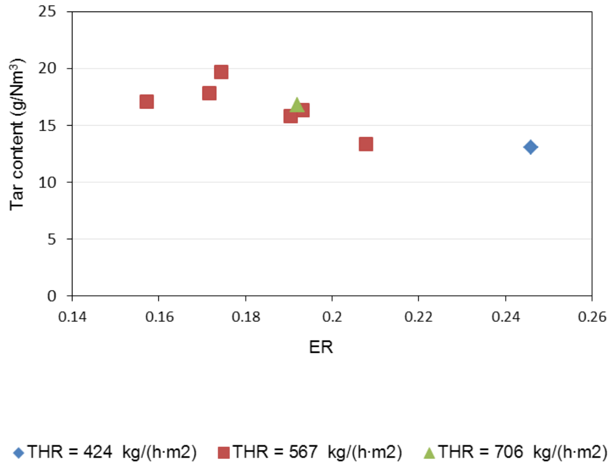

Figure 5. Tar content of the gas produced as a function of ER.

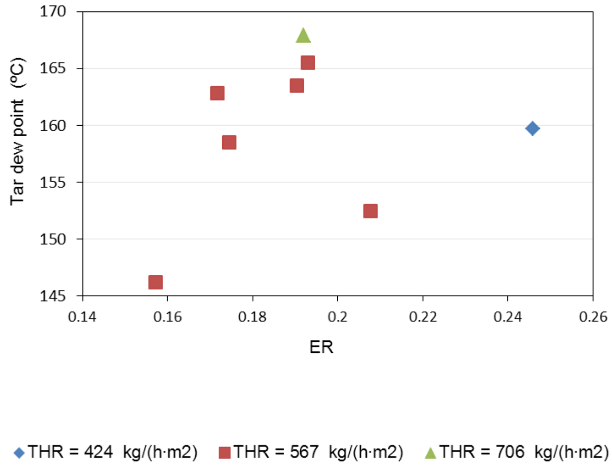

Figure 6. Tar dew point of the gas produced as a function of ER.

As can be seen in Figure 7, tar components are composed by tar class 3, tar class 2, tar class 4 and tar class 5, in order of quantity. Tar class 3 contents mean up to 60 % of the total tar amount, due mainly to the high values of benzene. In spite of tar class 5 contents only stand for 1.5-2.5 % of total tar composition, their influence in the tar dew point is higher. Tar class 2 and tar class 3 contents decrease with ER and increase with THR. Tar class 4 and tar class 5 contents increase with ER and decrease with THR. This is an interesting point, due to the fact that the tar class 4 and tar class 5 are the most important components increasing the tar dew point.

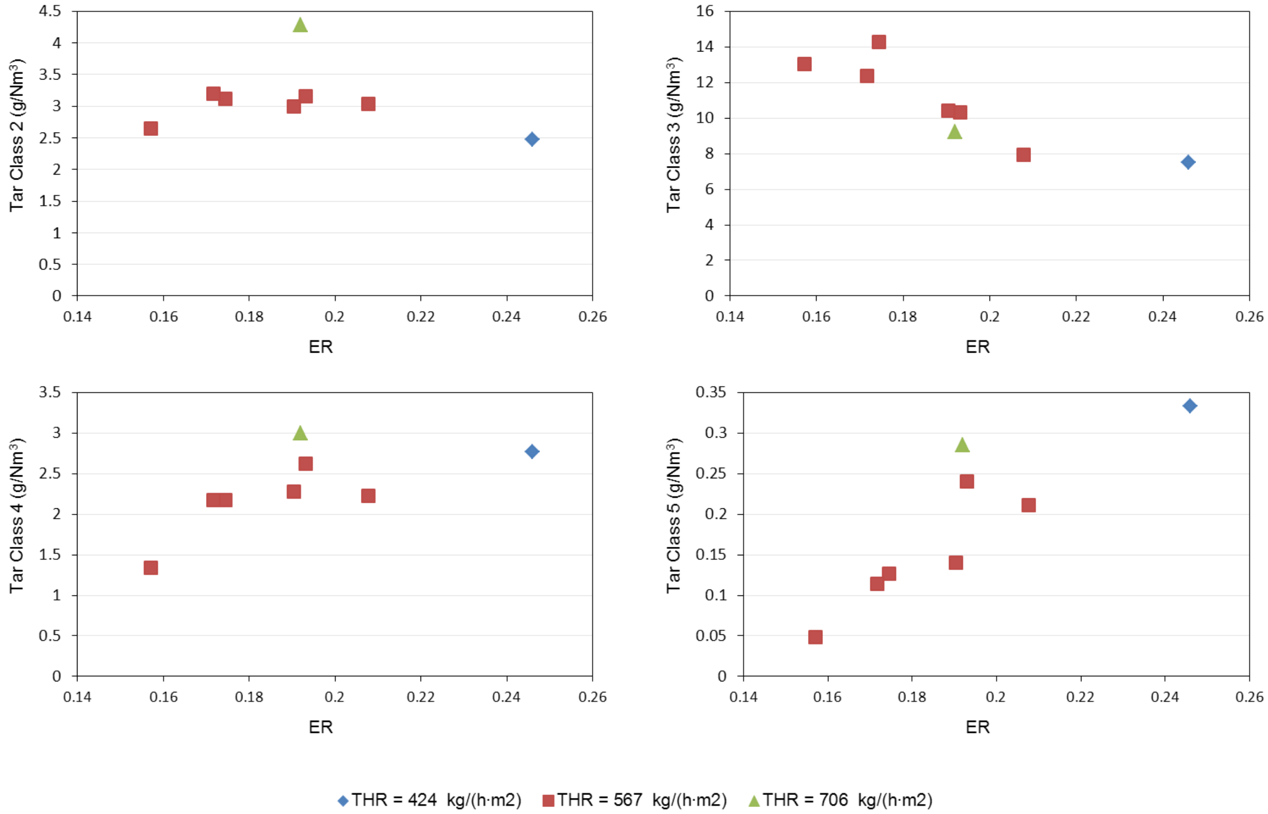

Figure 7. Tar Class 2, 3, 4 and 5 contents.

Cold gas efficiency (CGE) is defined as the ratio of the LHV of the produced gas to the LHV of the fuel. The gasification efficiency as a function of ER is shown in Figure 8. It is shown that the increase in ER, decreases the CGE, due to the reduction in the LHV of the gas produced. On the other hand, an increase in THR, increases the CGE of the process.
Carbon conversion is defined as ratio between the mass flow rate of carbon in the produced gas and the mass flow rate of carbon fed with the fuel. Figure 9 presents the carbon conversion of the tests as a function of ER. The carbon conversion decreases with ER and increases with THR.

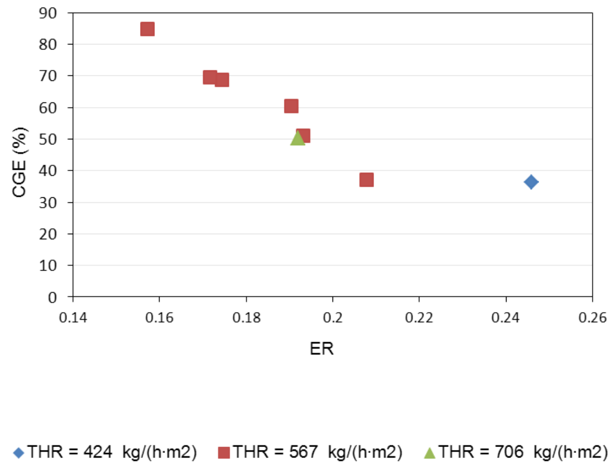

Figure 8. Cold gas efficiency of the gas produced as a function of ER.

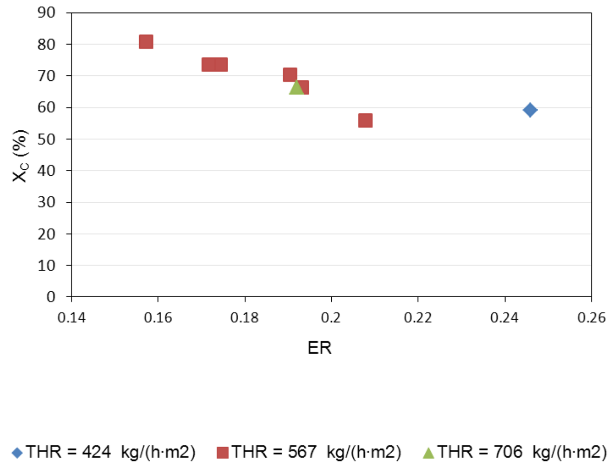

Figure 9. Carbon conversion gas produced as a function of ER.

5. Conclusions

The current paper deals with the preparation of brewers' spent grains for thermochemical process, making a special focus in reducing its moisture content and increasing its density. On the other hand, air gasification of brewers' spent grains has been done to determine the influence of equivalence ratio and throughput on gas quality, tar production, low heating value, gas yield, carbon conversion and efficiency.
This study sets out the results obtained when brewers' spent grains are prepared for thermochemical process and their gasification. BSG preparation was composed of two stages: drying and densification.
The drying was performed in a hybrid solar biomass drying facility and was an interesting alternative to reduce moisture content from 81.3 % to 19.5 %. Concerning energy consumption, the specific consumption was 3415 kJ/kg e.w. using 93.9 % of renewable energy.
The densification process was carried out in a pelletization plant. The density of the feedstock material was increased from 148 kg/m^3 to 517 kg/m^3 and pellets with enough quality to feed the gasifier were produced.
Air gasification of BSG pellets showed smooth operation. The produced gas has a LHV between 2.7-8.1 MJ/Nm^3 and between 13-20 g/Nm^3 of tar contents.
The influence of the equivalence ratio on the process was studied. The operating temperature increases with ER. Relating to gas composition, it can be assumed that H_2, CO, CH_4, C_2H_4 and C_2H_6 contents decrease with ER, while CO_2 increases. The LHV of the heating gas decreases with ER. Moreover, total tar, tar class 4 and tar class 5 contents decrease with ER, while tar class 2 and tar class 3 contents reduce. The increase in ER decreases the CGE and carbon conversion.
Regarding the influence of THR, it can be said that H_2, CO, CO_2, CH_4, C_2H_4 and C_2H_6 contents increase with THR and only C_2H_2 contents decrease with THR. The LHV of the gas produced increases with THR. Tar content, tar class 4 and tar class 5 contents increase with THR. The increase in THR increases CGE and carbon conversion. Further work should be done in order to determine the influence of THR in air gasification of BSG pellets.
The optimal operating conditions of the gasification process depend on the final application of the gas produced. It could be more important its LHV, its composition or its tar contents.

6. Acknowledgements

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7. Abbreviations

BFB	Bubbling Fluidised Bed
BSG	Brewers' spent grains
CEDER	Centre of Development of Renewable Energy Sources
CEN	European Committee of Standardization
CGE	Cold Gas Efficiency
CIEMAT	Research Centre for Energy, Environment and Technology
d.a.f.	dry and ash free basis
d.b.	dry basis
ECN	Energy and Research Centre of the Netherlands
e.w.	evaporated water
ER	Equivalence ratio
FTIR	Fourier Transform Infrared Spectroscopy
HHV	High Heating Value
LHV	Low Heating Value
PAH	Poly-aromatic Hydrocarbon
SCADA	Supervisory Control and Data Acquisition
THR	throughput
TS	Technical Specification
u_f	fluidisation velocity
u_{mf}	minimum fluidisation velocity
w.b.	wet basis
X_c	carbon conversion

Y_{gas} gas yield

8. References

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