



Bio-Chemicals Derived from Waste: Building on the Concept of a Bio-Refinery

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Abstract

The work presented here has looked into the thermal-conversion of wheat and barley spent grains (SG). Wheat fermentation was carried in the laboratory to get a mashed product while barley grain residues were sourced from a local brewing company. Pyrolysis carried at 460, 520 and 540 °C at ambient conditions of pressure in a bench scale fluidized bed reactor resulted in producing bio-oil, charcoal and non-condensable gases. These products were characterized by using the Gas Chromatography Mass Spectrometry (GC-MS), Differential Thermo-gravimetric Analysis (DTG), Elemental Analyzer (E.A) and a Bomb Calorimeter. The final pyrolysis product analysis revealed that the bio-oil production yields and Higher Heating Value (HHV) largely depended on the pyrolysis temperature and the sample type. In comparison with original raw grain samples, the analysis of thermally treated (pyrolysis) spent grains revealed the presence of high carbon and low oxygen contents. Results gathered in this work have shown that high bio-crude-oil production yields can be obtained at 520 °C (53 and 37wt% bio-oil from wheat and barley SG). Pyrolysis of wheat and barley SG resulted in giving a Higher Heating Value (HHV) of 21.80 and 21.86 MJ/kg at 540 and 460°C, which is considerably more in comparison to their virgin counterparts. This suggested route thus has a potential for further up-gradation of waste bio-mass for use as an intermediate fuel or as a raw material source for producing other bio-chemicals.

Keywords: wheat spent grains; barley spent grains; bio-oil; pyrolysis; bio-refinery; bio-ethanol residues.

Introduction

High carbon dioxide contents in air are blamed for the current global climate change [1-4]. This has resulted in compelling the industrialized nations to develop sustainable ways to tackle this issue [5]. As a result the European Union (EU) has planned to improve the production and consumption of renewable energy resources [6] such as biomass [7, 8]. The use of biomass as an energy source is projected to increase in future [9-11] and as a result the biomass waste will also increase as recorded in countries such as U.S.A [12].

In wake of the anticipated increase in the use of biomass resources for energy production,

this study has looked into the use of biomass waste and/or by-products from a bio-ethanol plant to be used as a source of energy which will lead to the maximization of profit and will help decrease the environmental load by minimizing the waste generation. Figure-1 highlights the bio-refinery concept and entails the route for the production of bio-fuels and other chemicals from wheat Spent Grains (SG). A complete bio-refinery can integrate different conversion processes (biological, chemical, and thermal) to produce different fuels, power and chemicals [13, 14] from biomass as shown in (Fig. 1).

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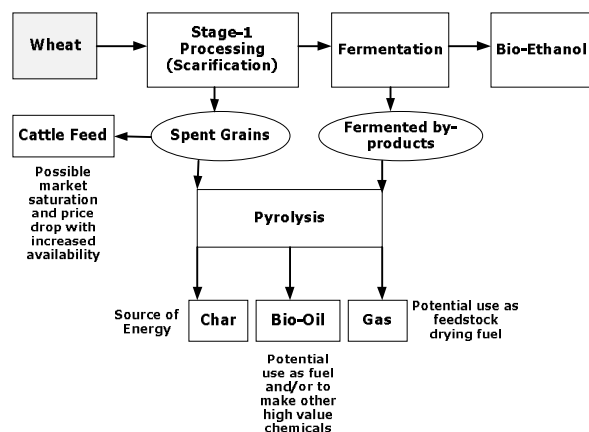


Figure 1. Proposed bio-fuel production from spent wheat grains

The concept of a bio-refinery is still young [5], however, if considered in an integrated form then the produced bio-oil can be used as a feed stock in the already well developed infrastructures of crude oil refining to get a range of valuable products [14-16]. This will help eliminate the present economic disadvantage of producing bio-oil and will help integrate the two processes by utilizing the waste from one industry as a valuable new raw material for another. The integration of two production and refining systems can potentially decrease the waste generation and green house effects simultaneously increasing process competitiveness. One profitable possibility is to integrate a wheat based bio-refinery with a parallel process such as the rapeseed bio-refinery.

The use of ethanol as an additive replacement to hydrocarbon fuel is on the rise especially in the industrially developed countries [17, 18]. This will lead to an increased quantity of ethanol production by-products such as Dried Distillers Grains (DDG) resulting from wet and dry milling [12]. It has been estimated that each tonne of grain used for ethanol production leave behind almost 30wt% of Dry Distillers Grains with Soluble (DDGS) [12, 19]. This is a huge percentage considering the fact that UK alone produces nearly 15 million tonnes of wheat each year [20] with 1.8 million hectares of cultivated area (nearly 70% of total UK area) dedicated to wheat production [21].

In addition to economic advantages other factors such as Renewable Transport Fuels Obligation in UK [22] has necessitated the

consumption of renewable fuels by 5% in 2010 and a possible increase to 10% by 2015. If 50% of renewable fuel is assumed to come from bio-ethanol route, the amount of dedicated non-food wheat comes to around 4 million tons generating 1.2 million tons spent wheat by-products based on annual wheat harvesting in UK of around 12-15 million tons. In addition to harvested land some 500000 hectares of set-aside land is also available for possible growth of non-food wheat in UK alone. In 2006 about 3-4 million ton of wheat was exported [20]. Together these can fulfill the feedstock requirements to produce bio-energy without creating any competition with the staple food requirements. Capitalizing on the opportunity, three companies are already producing nearly 3 million tons of wheat sourced ethanol since 2008 [22]. In UK, the production of barley is around 6.5 million tons [20] of which 1.5 million tons is exported, 2 million tons are used for brewing while 3 million ton ends up as an animal feed [20].

At present, ethanol production by-products are profitably marketed as animal feed [23]; however, their projected increased availability with time will affect the current profitability, necessitating exploring other uses. One such potential is to transform these by-products into high calorific value and less volume bio-fuels [24, 25] by thermal conversion methods.

In light of the discussion presented above, this work is planned to look into the thermal conversion processes for spent wheat and barley grains to produce valuable fuels. The literature review in this area has indicated a very limited amount of work on bio-oil production from barley spent grains via pyrolysis [26]. Limited reported literature exists for the production of bio-fuels from spent wheat grains via the selected pyrolysis route reported in this work [18, 27].

Pyrolysis is a well-established thermal degradation technique and has a long history for the production of bio-oil [28, 29]. In this process the thermal decomposition of organic substances is encouraged in the absence of atmospheric oxygen [30]. The process involves complex and variant typology reactions to decompose the organic material. Temperature has been identified as one of

the most influential variable to affect the pyrolysis yields of char, oil and synthesis gas by controlling the reactions. The intrinsic low quality of bio-oil due to its high viscosity, high oxygen content and an un-stable nature has restricted its use, however, several up-gradation technologies exists which can promote its use as a valuable new raw material for producing high value chemicals [29].

Several biomass sources have been characterized under thermo-chemical conversion processes such as hulled barley [31], rice hulls and husks [32], Barley [33], seed residues, brewer's spent grains [25], potato pulp [34], wheat and corn straw [35], sewage sludge [36], straw and stalk of rapeseed plant [37]. The emphasis in this work is on exploring the bio-fuel potential of bio-ethanol based processes which produce spent grains as their main by-product.

Experimental Methods

Experimental material

Wheat samples used in this work were sourced from a local animal feed shop while the barley samples were sourced from a local (Derby, UK) industrial brewing process for beer production. The initial processing of spent wheat grains involved washing to eliminate any foreign particle adhesion after which they were dried in an air-induced oven at 105°C for 24 hours. Next, the particle size of the wheat sample was reduced to pass through a sieve size of 512µm by using a rotating cutting mill. Next the wheat grains were cooked at different temperatures for a known amount of time to promote scarification (a process which converts starch into sugar). Filtration was used to separate the sugar solution. The sugar free spent grains were then characterised for moisture content, proximate and ultimate analysis, high calorific value and thermo-gravimetric profiles by using ASTM standard procedures (ASTM E790, E711, E777, E778, E775).

An IKA 5000 series bomb calorimeter was used for finding the Higher Heating Value (HHV) while the bio-oil product analysis was performed by a Varian 1200 Triple Quadru-pole Gas-Chromatography/Mass Spectrometry (GC-MS) technique with enhanced selectivity that was capable of identifying anything up to a

concentration level of 10^{-15} g. The ultimate analysis was performed by the Flash EA-1112 Series elemental analyzer. The elemental oxygen content was determined by difference. The weight loss experiments were done by using a Perkin Elmer TA Q600 STD thermogravimetric analyzer. In this analysis, crucibles were first tarred and then a 10 mg sample was carefully spread. High purity nitrogen was used at 100 ml/min. Each sample was heated in absence of oxygen to evaluate the moisture content and volatile matter. The process was repeated again in the presence of oxygen to determine the fixed carbon and ash contents.

Experimental rig

The experimental device used in this work is shown in (Fig. 2).

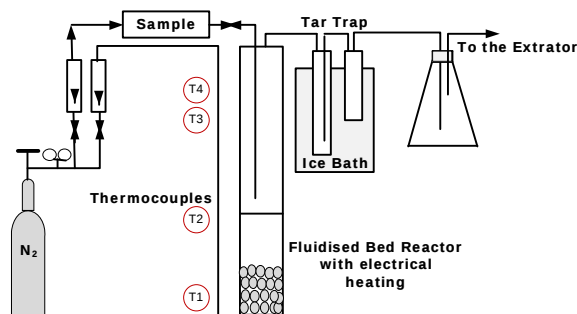


Figure 2. Schematic description of the experimental rig: 1 sample chamber, 2 fluidised bed reactor, 3 silica sand bed, 4 pre-heater chamber, T thermocouples

The experimental rig principally consisted of an inert nitrogen pressure injection system, a pipe sample chamber, a fluidised bed reactor, an electrical heater, a tar trap and 4 thermocouples to check the temperature. The pressure injection system uses nitrogen to push sample into the reactor. The fluidised bed reactor (Fig. 2) mainly comprised a pre-heating chamber that heated nitrogen before its entry into the main reaction chamber. The pyrolysis of biomass was performed in the main chamber with silica sand as a fluidisation medium. The fluidised bed reactor was made with SS-316 stainless steel cylinder having a width of 4.8 cm and a height of 64 cm. The tar trap was composed of two cylindrical glass bottles of 500 and 250 ml capacity which were placed in a dry ice trap to facilitate gas condensation into bio-

oil and tar, followed by a weak basic solution immersion to neutralize acidic fumes. Thermocouples were in-placed at desired locations in the main fluidised bed reactor chamber to record temperature changes during the pyrolysis experiments.

Experimental procedure

The experimental time of approximately 4 hours was allowed for the conduction of each experimental run which included the stabilization of required temperature. Nearly 115 g of silica sand was in-placed in the fluidised bed column and 15 g test sample was charged in the sample chamber. The temperature of the furnaces was set according to the desired requirements. As soon as the required temperature was attained, nitrogen gas flow rate set at 9.5 L/min was initiated. Once system stabilization was attained, the sample was injected using a constant nitrogen flow rate of 5L/min in the reactor. The observed time for the thermo-chemical conversion of feed sample was in minutes and each experiment was stopped after 10 minutes. Time was then allowed for slow cooling in the absence of air during which the reaction gases continued to release from the main fluidised bed reaction chamber, subsequently condensing in the ice bath before neutralisation release from the extractor. Three repeat experiments were done for each experimental run.

Each experimental run produced three main products, i.e. bio-oil/tar, charcoal and un-condensable gases. A mass balance was performed by considering the weight difference of ice bath bottles for bio-oil/tar contents. The weight difference of char plus sand minus initial sand sample resulted in giving the un-condensable gas yields by difference. The pyrolysis products were stored in an air tight container for further analysis.

Results and Discussion

Fig. 3 shows that the carbon content of wheat and barley spent grains was less while the oxygen content was high, in comparison with conventional hydrocarbon fuel sources such as coal and crude oil (carbon content >70 wt%), that could have been the main reason that resulted in giving low calorific values.

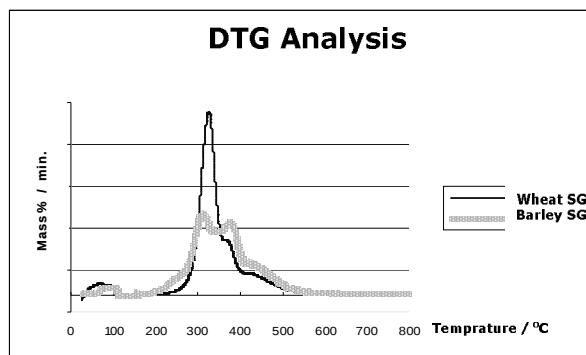


Figure 3. Derivate thermo-gravimetric (DTG) curves of barley and wheat spent grains

The proximate and ultimate analysis of raw materials (barley and wheat SG) used in this study are tabulated in (Table-1).

Table 1. Proximate and Ultimate Analysis of wheat and Barley spent grains.

Proximate Analysis (%wt wet basis)		
	Wheat SG	Barley SG
Moisture	6.60	4.6
Ash	2.20	6.50
VM	75.2	61.4
Fixed Carbon	16.00	17
Ultimate Analysis (%wt Dry Ash Free (DAF))		
H	6.50	6.67
C	43.20	47.83
N	4.50	3.68
O	43.60	38.52
S	< 0.1	< 0.1
HHV (MJ/Kg)	18.35	18.55

A comparison among the two shows that barley SG had comparatively high ash content (6.5 wt%) and carbon content (47.83 wt%), whereas a lower volatile matter (61.4 wt%) and oxygen content (38.52 wt%). This resulted in giving a slightly Higher Heating Values for Barley SG at different processing temperatures. In the next stage thermogravimetric analysis (DTG) was performed which measured the mass change as a function of temperature and time. The DTG results are presented in (Fig. 4) in the form of curves for wheat and barley spent gains.

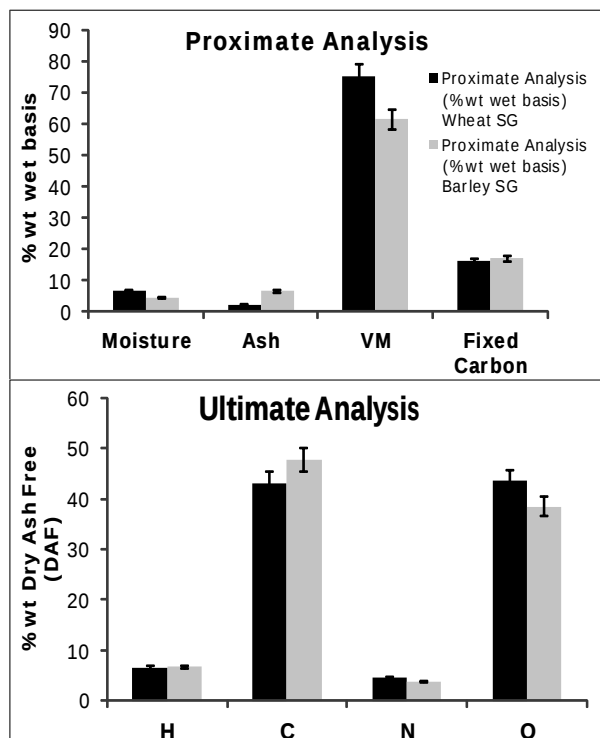


Figure 4. Proximate and Ultimate analysis of barley and wheat spent grains (SG). (H=hydrogen, C=Carbon, N=Nitrogen and O=Oxygen)

An analysis of the curves reveals that at around 100 °C dehydration occurred for both type of raw materials. As the temperature was further increased the decomposition of hemicellulose was observed to start at around 200 °C for barley SG and just over 250 °C for the wheat SG sample. These hemicellulose and cellulose peaks for wheat SG sample were observed to be not well distinct, however, the curve was well developed and separate in case of barley SGs. The hemicellulose decomposition was observed to be of maximum magnitude at 316 °C for barley and 328 °C for wheat SGs. Furthermore, (Fig. 4) shows that the decomposition of cellulose started at 205 °C and ended just before 500 °C for the barley SG. The decomposition of wheat SGs was observed to start at 30 °C but ended around the same temperature as barley SGs. The lignin decomposition did not present a clear sharp peak and was observed to be widely distributed in a temperature range above 500 °C. The DTG data was then used to decide on the operating temperatures in the fluidised bed reactor for carrying the pyrolysis of wheat and barley SGs.

In choosing the operating temperatures, consideration was also given to the possible quality of resulting bio-oil. Since complete sample decomposition was observed at around 500 °C, operating temperatures of 460, 520 and 540 °C were chosen to look for the effects of temperature on the quality and quantity of resulting bio-oil. (Table-2) enlist the proximate and ultimate analysis of resulting bio-oil from experiments carried at chosen operating temperatures.

Table 2. Proximate and Ultimate Analysis of bio-oil obtained from: wheat and Barley spent grain at 460, 520 and 540 °C.

	Bio-oil Wheat SG at 460°C	Bio-oil Wheat SG at 520 °C	Bio-oil Wheat SG at 540 °C	Bio-oil Barley SG at 460°C	Bio-oil Barley SG at 520°C	Bio-oil Barley SG at 540°C
Proximate Analysis (% wt wet basis)						
Moisture	11.1	17.38	15.72	20.88	10.38	18.6
Ash	0	0	0.1	0	0.1	0
VM	69.85	65.57	68.63	63.62	65.83	65.97
Fixed C	19.09	17.05	15.55	15.50	23.09	14.76
Ultimate Analysis (% wt DAF)						
C	46.42	46.42	43.95	44.44	47.34	-
H	3.11	33.33	3.00	44.44	3.31	-
N	6.12	-	-	5.24	5.96	-
O	44.35	-	47.72	-	-	47.34
S	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
HHV (MJ/Kg-DAF)	21.8	21.25	19.23	19.02	20.86	18

In case of wheat SGs it is observed that negligible ash content was produced in both samples while the moisture content varied considerably at different temperatures with considerably more moisture content present in the barley SG in comparison with wheat SG sample. Nearly negligible volatile matter (VM) magnitudes were recorded at studied temperature ranges. Considerable difference in fixed carbon content was found with barley SG sample containing a maximum of 23.09 wt% at 520 °C. The readings obtained in proximate analysis were also confirmed by the ultimate analysis where high elemental carbon presence was found in the barley SG sample at 520 °C and thus this sample gave Higher Heating Value (HHV) of 21.86 MJ/Kg on Dry Ash Free (DAF) basis.

Consideration of product yields (Fig. 5) and (Table-3) revealed that bio-oil production was more from wheat SG samples at all the investigated temperatures. In comparison, the barley SG sample gave high non-condensable gas contents.

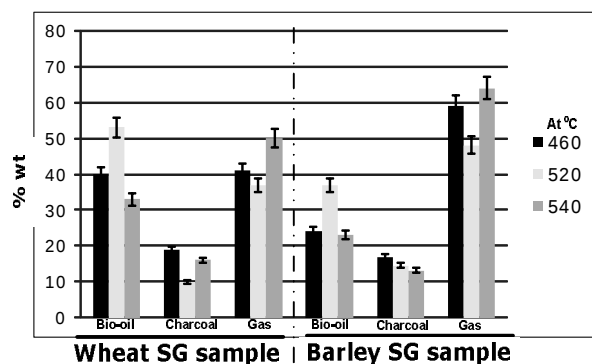


Figure 5. Bio-oil, Charcoal and Gas yields from Wheat and Barley spent grains

Table 3. Relationship between temperature and the products yields from wheat and Barley Spent Grain (SG).

Temperature (°C)	Wheat SG %wt			Barley SG %wt		
	Bio-oil	Charcoal	Gas	Bio-oil	Charcoal	Gas
460	40	19	41	24	17	59
520	53	10	37	37	14.6	48
540	33	16	50	23	13.1	64

Conclusions

The waste raw material characteristics for a proposed bio-refinery are explored in this work. The experiments were performed on a bench scale fluidized bed reactor by using waste wheat and barley spent gains as pyrolysis raw materials to explore the thermal conversion characteristics of resulting products (bio-oil, charcoal, and non-condensable gases). The bio-oil product was analyzed by using the Bomb Calorimeter, thermogravimetric analyzer (TGA, DTG), pyrolysis product, Gas Chromatography Mass Spectrometer (GC-MS) and Elemental Analyzer (E.A) to understand the coalification behavior and to evaluate the chemical composition of different kinds of products. The reported results show nearly

the same HHV values for both raw materials however when proximate and ultimate analysis was performed on pyrolysis products barley spent grains had comparatively high percentage of fixed carbon and HHVs (21.86Mj/kg) at 520°C as reported in (Table-2). On the other hand, the bio-oil production yields were lower (24, 37 and 23 wt% at 460, 520 and 540 °C, respectively) for barley spent grains at all the investigated temperatures.

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