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Abstract: Brewers Spent Grain (BSG) is a widely available feedstock representing approximately 85% of the total by-products generated in the brewing industry. This is currently either disposed of to landfill or used as cattle feed due to its high protein content. BSG has received little or no attention as a potential energy resource, but increasing disposal costs and environmental constraints are now prompting the consideration of this. One possibility for the utilisation of BSG for energy is via intermediate pyrolysis to produce gases, vapours and chars. Intermediate pyrolysis is characterised by indirect heating in the absence of oxygen for short solids residence times of a few minutes, at temperatures of 350-450°C. In the present work BSG has been characterised by chemical, proximate, ultimate and thermo-gravimetric analysis. Intermediate Pyrolysis of BSG at 450°C was carried out using a twin coaxial screw reactor known as Pyroformer to give yields of char 29%, 51% of bio-oil and 19% of permanent gases. The bio-oil liquid was found to separate in to an aqueous phase and organic phase. The organic phase contained viscous compounds that could age over time leading to solid tars that can present problems in CHP application. The quality of the pyrolysis vapour products before quenching can be upgraded to achieve much improved suitability as a fuel by downstream catalytic reforming. A bench scale batch pyrolysis reactor has then been used to pyrolyse small samples of BSG under a range of conditions of heating rate and temperature simulating the Pyroformer. A small catalytic reformer has been added downstream of the reactor in which the pyrolysis vapours can be further cracked and reformed. A commercial reforming nickel catalyst was used at 500, 750 and 850 °C at a space velocity about 10000 l/h with and without the addition of steam. Results are presented for the properties of BSG, and the products of the pyrolysis process both with and without catalytic post-processing. Results indicate that catalytic

reforming produced a significant increase in permanent gases mainly (H2 and CO) with H2 content exceeding 50 vol % at higher reforming temperatures. Bio-oil yield decreased significantly as reforming temperature increased with char remaining the same as pyrolysis condition remained unchanged. The process shows an increase in heating value for the product gas ranging between 10.8-25.2 MJ/m3 as reforming temperature increased.

1. Introduction

Recently there has been growing concern for the need to reduce emissions of greenhouse gases, principally CO_2, and a drive to produce energy from alternative and renewable sources including biomass. Biomass has stored solar energy from the sun and carbon dioxide from the atmosphere through photosynthesis. There are various types of biomass falling into four main categories: woody plants, herbaceous plants, grasses and wastes. [1] By-products from the food processing industry are an abundant source of biomass which can be made available for energy recovery.

Brewers spent grain (BSG) is the widely available non-fermentable main by-product of the brewing process. It is the solid residue that remains from the barley after separation and filtration of the wort.[2] Breweries generate more than 250 million tons of wet BSG every year in the UK. BSG is either sent to landfill, or used as animal feed, primarily for cattle, but also for pigs, goats, fish and other livestock. It is used as animal feed due to its large content of fibre (60%) and protein (20%).[3] Wet BSG contains a large amount of moisture, typically 67-81% (w/w). Due to its high moisture content as well as its fermentable sugar content, BSG is difficult to store and transport as it deteriorates rapidly due to microbial activity.[4] Therefore to be considered as a potential energy feedstock, methods must be adopted to reduce its moisture content significantly.

BSG has received little or no attention as a marketable commodity, but as it is now becoming increasingly expensive to dispose of as well as presenting an increasing environmental problem, options for its uses are starting to be considered. The chemical composition of BSG indicates that it can be of value as a raw material for energy production.[5]

Thermo chemical conversion technologies such as pyrolysis, gasification and combustion can convert biomass to energy. Pyrolysis is considered to be an attractive technology as reactions are under controlled conditions with a wide range of products suitable for different applications. [6 & 7] There are several processes in which the pyrolysis of biomass has been applied for heat and power applications, or combined with gasification as a pre-conditioning step for hydrogen production or sequential catalysis to produce methanol or synthetic fuels.[8] Bridgwater, A.V, (2007) described pyrolysis as the thermal decomposition of biomass in the absence of oxygen.[9] It occurs as the first step in combustion and gasification where it is then followed by total or partial oxidation of the primary products. Relatively low temperatures of 300-800˚C are employed in pyrolysis compared with 800-1200˚C in gasification. The three main products obtained during pyrolysis are non-condensable gases, liquids (in the form of vapours) and solid chars. The proportions of gas, liquid and solid products obtained from the pyrolysis process are dependent on the residence time, rate of heating and the reaction temperature.

Pyrolysis primarily for liquids production from biomass is a relatively new technology and has made significant advances in the past 15-20 years. It offers the advantage of a liquid product ("bio-oil") that can be stored and/or transported. Fast pyrolysis, with residence times of a few seconds, is used to maximise the liquid product yield (to 75% wt on a dry feed

basis). The bio-oil, formed by cooling and condensation of the pyrolysis vapours, is a dark brown liquid which has a heating value somewhat less than half that of conventional fuel oil. Slow pyrolysis on the other hand, also known as carbonisation, is used to maximise solid charcoal production. This method of pyrolysis has been practiced for centuries and requires long residence times of hours or days at low temperatures to maximise solid char yield.

A new type of pyrolysis, called intermediate pyrolysis, can utilise a diverse range of feedstocks such as waste wood to food wastes and sewage sludge, grass and algae. The temperature range of intermediate pyrolysis is 350-450°C with a product distribution of typically 50% liquids, 25% char and 25% gas. The brittle dry char is suitable for co-combustion in thermal plants or for use as a soil conditioner and carbon sequestration medium. The product streams are easily separated without contamination.

The most significant difference between fast pyrolysis and intermediate pyrolysis is the residence time of the solids within the reactor, typically a few minutes, although the gas phase residence times are similar. Whereas fast pyrolysis has proved to be successful with woody biomass, [10] fast pyrolysis of non-woody feedstocks can lead to the production of highly reactive liquids and can be rich in high tars with some products bituminous in character and solid at room temperature leading to storage and processing issues.[11] The liquids produced from intermediate pyrolysis of non-woody biomass show much lower tar content and could be suitable for direct application in boilers and engines. Their suitability could however be further enhanced by catalytic steam reforming of the pyrolysis vapours prior to condensation, leading to an increased combustible gas content (notably H_2) and a lowering of the viscosity of the final liquid. This could be particularly attractive for close-coupled heat/power systems and for further upgrading. Previous work in this area has mainly aimed to upgrade the bio-oil by reducing the oxygen content so as to improve properties such as viscosity, thermal stability and corrosiveness. Other studies have investigated steam reforming of bio-oil (in particular the water fraction) to produce hydrogen by the use of catalytic hydro-treatment and catalytic cracking.[12, 13 & 14]

The aim of this work is to investigate the intermediate pyrolysis of BSG followed by catalytic steam reforming of the pyrolysis vapours to produce an upgraded fuel for IC engines in heat and power applications. This paper will describe the pre-treatment and characterisation of BSG determining the chemical, proximate, ultimate analysis and energy content of the potential biomass feedstock, followed by experimental pyrolysis and catalysis at both pilot scale using a patented intermediate pyrolysis reactor, and at bench scale using a batch fixed bed pyrolysis reactor with downstream catalytic steam reformer.

2.   Experimental Methods

2.1.   BSG Feedstock and Characterisation

Fresh wet BSG was obtained from Molson Coors brewery in Burton on Trent approximately 35 miles from Aston University, Birmingham. The BSG was initially stored in double black bin lining bags at 0°C in a cold store room at the brewery to prevent microbial degradation. When collected it was immediately stored in a freezer box. It was then oven dried the night before experimental work was carried out. A Retsch SM 200 cutting mill was used to reduce the BSG size once it was dried.

The moisture content for BSG was determined using British Standard BS EN 14774-3:2009, the sample prepared is dried at a temperature of 105 ±2°C in an air atmosphere until constant mass is achieved and the percentage moisture is calculated from the loss in mass of the sample. The ash content was determined using British Standard BS EN 14775-2:2009, in which the ash content is determined by calculation from the mass of the residue remaining after the sample is heated in air under rigidly controlled conditions of time, sample weight and equipment specifications to a controlled temperature of 550 ± 10°C. Volatiles and Fixed Carbon were determined using the British Standard (BS EN 15148:2009). Chemical compositional analysis of BSG was determined using the FiberCap 2021/2023 Fibre analysis system to obtain cellulose, hemicelluloses, and lignin and extractive properties.

Prepared samples of dried, ground and sieved BSG was sent to an external company MEDAC Ltd for CHN analysis (with oxygen determined by difference) using a Carlo-Erba EA1108 CHNS-O analyser. Poisonous elemental analysis was also conducted. Samples were also sent to ESG Bretby to determine the major elemental oxides in the ash using ICP OES. The ash moisture content and ash fusion temperatures were also determined in a reducing atmosphere.

Thermo gravimetric analysis was conducted using a Perkin Elmer Pyris 1 TGA apparatus with auto sampler. Approximately 5mg of dried sample was loaded into a crucible.

Calorific value was determined using a Parr 6100 Compensated Jacket Oxygen Parr Bomb calorimeter.

2.2.   Pilot Scale Experiments (Pyroformer)

The Pyroformer is the intermediate pyrolysis reactor recently patented by A. Hornung at Aston University - see Figure 2. It is constructed of carbon-steel and measures approximately 1.8m in length and has a diameter of 0.2m, and consists of twin horizontal rotary coaxial screws. The twin coaxial screw system offers the advantage of defined residence times which can be varied between about 1 and 4 minutes by adjusting the speed of the internal screw. The outer screw transports a fraction of the char produced during pyrolysis back, so that there is an internal recycling. This not only ensures better heat transfer but also promotes catalytic reforming within the process.[15] The operating temperature range of the Pyroformer is 300- 450°C depending on the feedstock material to be pyrolysed.

The bio-oil liquid was sent to an external company MEDAC Ltd for CHN analysis (with

oxygen determined by difference) using a Carlo-Erba EA1108 CHNS-O analyser. Poisonous elemental analysis was also conducted.

GC-MS was performed to identify the most abundant compounds present within the pyrolysis oil. Samples of the oil were diluted in ethanol in a 1:10 ratio. GC-MS analysis was conducted using a Hewlett Packard HP 5890 Series II Gas Chromatograph with an automatic injector and auto sampler with a DB 1706 non-polar capillary column of 60m x 0.25 mm x 0.25 μm. Helium was used as the carrier gas at a constant flow rate of 1.5ml/min The initial oven temperature was 40°C and ramped up to 290°C. Identification of the GC-MS peaks was based on the comparison between the Mass finder library and Wiley library.

Kinematic viscosity, which is the resistance to flow of a fluid under gravity, was measured in accordance with ASTM D445 with a Cannon-Fenske Routine glass capillary viscometer. During the test, fixed volume of oil samples are passed through the capillary of the viscometer under gravity at 40°C. The sample travelling time is recorded. The kinematic viscosity is then the product of the viscometer calibration constant and the measured flow time.

Flash point was determined in accordance with ASTM D7236 by a Seta Flash Series3 plus Closed Cup (Auto Ramp) Tester. A test flame is directed to the pre-set location where the vaporised oil may be released at specified temperature intervals until the flash is detected.

Total acid number (TAN) of the oils was measured with A Mettler Toledo V20 Compact titrator using the potentiometric titration method in accordance with ASTM D664. The oil sample is dissolved in 50/50 toluene and isopropanol solution and titrated potentiometriclly with 0.1N alcoholic potassium hydroxide using a combination electrode. Readings are automatically plotted against the volume of titrating KOH solution used until the titration end-point is achieved.

The oil corrosiveness test was carried using a Stanhope-SETA cooper corrosion test station in accordance with ASTM D130. Polished copper strips were immersed into the tested oil samples which were placed in a 40°C oil heating bath. The copper strips were compared to the ASTM corrosion standard board after periods between 6 and 24 hours.

The water content of the bio-oils was determined using a Mettler Toledo V30 Compact Volumetric Karl Fischer (KF) titrator in accordance with ASTM E203. The pH was obtained using the Sartorius basic meter PB-11.

The Conradson Carbon Residue test was performed in accordance with ASTM D189 by a manual method. A weighed sample is placed in a crucible and undergoes strong heating by a Meeker burner. The carbonaceous residue remaining after the cracking and coking reactions is cooled to room temperature and weighed. The Conradson Carbon Residue is then the carbonaceous residue expressed as a mass percentage of the original oil sample

Ash content of the oil was determined in accordance with ASTM D482. The carbonaceous solid samples produced from the Carbon Residue test were combusted in a muffle furnace at 775°C. The remaining ash was cooled at room temperature and weighed, and then expressed

as a mass percentage of the original oil sample.

Analysis of permanent gases produced from Pyroformer experiments was analysed using a Hewlett Packard HP-5890 series 2 device Gas Chromatograph Thermal Conductivity Detector (GC-TCD) with a 60/80 Carboxen-1000, 15' x 1/8" SS (2.1mm ID) column. Helium is used as the carrier gas with a flow rate of 30ml/min. The oven temperature is programmed with an initial temperature of 35°C and is heated at a ramping rate of 20°C/min to 225°C.

The calorific value of the oil and char was determined using a Parr 6100 Compensated Jacket Oxygen Parr Bomb calorimeter. Elemental and chemical composition of the char was also carried out by sending out a sample to MEDAC Ltd.

2.3. Bench Scale Experiments

2.3.1. Catalysts

Commercial reforming catalyst pellets ($Ni/Al2O3$) with high nickel content were used in these experiments as supplied by Johnson Matthey. The pellets were fully reduced at 900°C in 40% H_2/N_2 gas and then passivated.

2.3.2 Batch Fixed Bed Pyrolysis and Catalytic Reactors

A bench scale batch fixed bed pyrolysis reactor was used to pyrolyse small samples of BSG under a range of conditions of heating rate and temperature chosen to simulate continuous intermediate pyrolysis. A small catalytic steam reformer was added downstream of the reactor in which the pyrolysis vapours can be further cracked and reformed. The arrangement is shown in Figure 3.

The pyrolysis reactor is a cylindrical quartz tube measuring 400mm length x 215mm diameter and is immersed in an externally heated electrical furnace. The outlet of the pyrolysis reactor is connected to a catalytic reactor via a series of transition tubes. The hot pyrolysis vapours leaving the pyrolysis reactor are subjected to additional cracking reactions and afterwards flow into a condenser. Two condensers are used to quench the hot vapours; the condensed liquid is collected in an oil pot. Following Condenser 2 is a cylindrical tube containing a scrubbing agent with glass beads to capture any solids or tars that may still have been present after quench. The clean product gas may be sampled with a gas tight syringe and injected into a GC for gas analysis. The final product gas passes through a meter that records flow rate, temperature and pressure simultaneously and this data is sent to a computer.

The connecting tubes before and after the catalytic reactor were all made of high temperature resistant material (1000°C), whilst the rest were made of mid temperature material (525°C). Nitrogen was the carrier gas serving as the purge and was passed through a flow meter at flow rate of 50cm³/min. The pyrolysis reactor temperature is measured by thermocouple which is inserted through the top of the pyrolysis reactor. The reactor heater operates on a temperature controlled program via a heater controller, on which the heating rate and final

temperature set point can be configured. A thermocouple inserted on the inner wall is used to measure the catalytic reactor furnace temperature.

The bio-oil liquid was sent to was sent to an external company MEDAC Ltd for CHN analysis (with oxygen determined by difference) using a Carlo-Erba EA1108 CHNS-O analyser. Poisonous elemental analysis was also conducted.

Permanent gases from the bench scale experiments were analysed using a Hewlett Packard HP-5890 series 2 device Gas Chromatograph Thermal Conductivity Detector (GC-TCD) with a 60/80 Carboxen-1000, 15' x 1/8" SS (2.1mm ID) column. Helium is used as the carrier gas with a flow rate of 30ml/min. The oven temperature is programmed with an initial temperature of 35°C and is heated at a ramping rate of 20°C/min to 225°C.

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The water content of the bio-oils was determined using a Mettler Toledo V30 Compact Volumetric Karl Fischer (KF) titrator in accordance with ASTM E203.

Total acid number (TAN) of the oils was measured with A Mettler Toledo V20 Compact titrator using the potentiometric titration method in accordance with ASTM D664. The oil sample is dissolved in 50/50 toluene and isopropanol solution and titrated potentiometriclly with 0.1N alcoholic potassium hydroxide using a combination electrode. Readings are automatically plotted against the volume of titrating KOH solution used until the titration end-point is achieved. The pH was obtained using the Sartorius basic meter PB-11.

Bench scale bio-oils were unable to be analysed for viscosity, corrosiveness, and flash point due to small quantities. The calorific value of the bio-oils and residual char was determined using a Parr 6100 Compensated Jacket Oxygen Parr Bomb calorimeter.

3. Results and Discussion

3.1. Biomass Characterisation

The elemental analysis of BSG is presented in Table 1. Table 2 presents the proximate and chemical analysis for brewers spent grain.

Thermo gravimetric analysis results are shown in Figure 4. Much of the weight loss occurs in the range 200-450°C, with significant weight loss peaks at 302°C and 367°C. This indicates that a suitable maximum temperature for pyrolysis of BSG would be 450°C. The ash content was determined to be 4.55%, consistent with the result in Table 2.

3.2   Pilot Scale Experiments (Pyroformer)

The Pyroformer experiments were carried out under atmospheric pressure with nitrogen gas used as purge, with a pyrolysis temperature of 450°C. Table 3 shows the distribution of yields produced. The condensate was found to separate into two phases, an aqueous phase and an organic phase. The organic phase of the bio-oil, the permanent gases and the char were analysed.

3.2.1   Bio-oil Analysis

The condensate bio-oil produced was found to have an organic and an aqueous phase that could be separated using a gravimetric settler. The organic phase was of more interest and was analysed to see its suitability as a fuel. The aqueous phase was approximately 20% higher than what was reported in literature for liquids produced with intermediate pyrolysis. The water contents for the organic and aqueous phase were 6.5 % and 62% respectively. The water comes from moisture in the feed and dehydration reactions during pyrolysis. Some water can be dissolved in bio-oil in water-soluble compounds and this can offer both advantages and disadvantages to the properties of the bio-oils. The water content lowers NOx emissions which contribute to acid rain, and improves the bio-oil's flow characteristics; however it also lowers the heating value and flame temperature of the fuel, which increases the ignition delay and decreases the combustion rate compared to petroleum fuels. It also means that the bio-oil is immiscible with petroleum fuels.

Table 4 indicates the elemental analysis of the organic phase which shows an increase in C, H and S content by 1, 3% and 0.56% respectively and notably a reduction in N and O content by 0.1% and 12% in comparison to the original feedstock. Oxygen content is still however high, although bio-oil from fast pyrolysis processes generally have oxygen contents of about 40-50%.[16]

Table 5 gives physical properties of the bio-oil of relevance for use as an engine fuel. The calorific value of the bio-oil obtained was 20 MJ/kg, which is about half the energy content of fossil diesel. The low energy content is associated with the high oxygen content present in the oil. Bio-oils are quite acidic with pH values ranging between 2-3, this is due to the presence of organic acids such as acetic and formic acid, however BSG oil has a pH of 6. However the acidity number of the oil was found to be 49 mgKOH/g which is relatively high in comparison to bio-diesel (0.8) indicating potential corrosion problems if considered as fuel for engine applications.[18] This may be because of the high water content and some unidentified components present. The carbon residue and ash were 1.93% and 0.44% respectively which in contrast to diesel and biodiesel are relatively high and could indicate potential blockage problems in engine applications. Viscosity was very high; this may be due to the amount of solids present in the oil. The bio- oil upon visual inspection contained many solids which gave the bio-oil a very dark appearance, however was not measured in this study. The solids content must remain low to be suitable for engine applications.

Figure 5 shows the GC/MS mass spectrum. The major chemical components present are illustrated in Table 6. The bio-oil consists of a number of complex organic oxygenated compounds. Much of the abundant components are aromatic hydrocarbons and alkanes, followed by phenols.

The area% in the table represents the peak areas of each identified component as a fraction of the whole integrated mass spectrum, thus giving an approximate mass fraction of that component.

It was found that the bio-oil contains a complex mixture of low to intermediate molecular hydrocarbon chains ranging from C_5-C_{19}. Alkenes such as, Benzene, Cyclooctatetraene, Hexene, Toluene and Xylene were present with the latter two presenting significant quantity of 11.29% ,7.39% and Cyclooctatetraene of 5%. Phenolic derived aromatic compounds were the other major components present comprising of approximately 24% of the bio-oil fraction. Undecanoic acid, methyl esters, was the only acidic and fatty acid component identified. The acidity however could be due to the large quantity of phenolic components detected and some unidentified components. Higher aromatic components were detected such as Tridecane which comprises of approximately 6% of the mass fraction, higher aromatics have poorer combustibility compared with paraffins and naphthenes.[18]

Phenylacetonitrile and Undecanenitrile are the alkyl nitriles identified peaks with a maximum of 6.85% which corresponds to the low Nitrogen content in the bio-oil see table 6. Alkylnitriles compounds are highly toxic, and the oil should be handled with care to avoid direct skin contact. Decane-1-Chloro represents approximately 2-3% in the bio-oil and is a surprise finding as it contains chlorine and would have been expected to be present in the char.

3.2.2 Permanent Gas Analysis

The permanent gases were analysed post quench using an offline GCMS and the results are given in Table 7. The permanent gases detected were hydrogen, nitrogen, carbon monoxide, methane and carbon dioxide). Hydrogen of about 1-2vol% was produced; this is not normally present during pyrolysis processes and may be due to small cracking reforming reactions taking place between hot char and pyrolysis vapours contacting each other. The calorific value of the gas produced was 1-2MJ/m^3.

The gas chromatogram of the pyrolysis gases illustrated in figure above shows some of the species that were formed which led to the increased heating value of the pyrolysis gas. Components such as methane and carbon monoxide are formed.

3.2.3 Char Analysis

The char (shown in Figure 7) was analysed for its heating value and its composition. Table 8 gives the elemental analysis of the char, showing that it is rich in carbon (approximately 15% higher than represented in the original feedstock). The heating value by bomb calorimeter was 26-28 MJ/kg. Table 9 gives the elemental analysis of the char ash.

Table 8 illustrates the elemental analysis of the char produced from Pyroformer. The char is rich in carbon content and has a useful energy content that can be of use for combustion in boilers and furnaces or as a medium to be combusted to provide heat for the pyrolysis process. Other applications such as uses for activated carbon and for fertiliser could be explored for BSG char uses.

The use of char as a soil improver or fertiliser is attracting widespread attention as industrial agriculture has a high demand. Such a use also sequesters atmospheric carbon into the soil. By applying char to agricultural land could improve soil fertility promoting plant growth as well as store carbon.[19] Nutrients such as nitrogen, phosphorous, potassium and carbon are important for plant growth and was found to be 5.2%, 1.68%, 0.1% and 61.8%

3.3   Bench Scale Experiments

3.3.1   Pyrolysis Without Catalysts at Different Heating Rates

Approximately 100g of BSG dried feedstock was placed into the batch fixed bed reactor. The nitrogen purge was set at $50cm^3$/min then introduced into the reactor, afterwards the reactor heater was switched on to heat the pyrolysis reactor to the desired temperature of 450°C at two different heating rates 25 and 100°C/min. The BSG particles are heated by the radiation of the heated furnace and finally reach the desired temperature. At the desired temperature the biomass is kept for approximately 20 minutes until no further pyrolysis volatiles form. In these initial experiments no catalysts were used, however the catalytic reforming reactor was set at 500°C to prevent condensing of vapours from occurring. For each experiment the reactors transition tubes and condensers are weighed before and after each experiment, this allows determination of the product yields, and the overall mass balance.

At the lower heating rate the product yield was 35% bio-oil, 31% char and 34% gas, and at the higher heating rate 48% bio-oil, 31% char and 21% permanent gases. Figure 8 shows these data comparatively. The yield of char remains the same and therefore appears unaffected by heating rate; however the yield of condensable liquids increased by 13% and the amount of permanent gases reduced correspondingly. The products yielded at 100°C/min are comparable to the yields produced by the Pyroformer at the same temperature. Therefore in order to carry out reforming experiments simulating the Pyroformer the higher heating rate of 100°C/min was selected.

Figure 9 shows that there was no real difference in the composition of permanent gases produced as heating rate increased. No H_2 or O_2 was produced which is normal for pyrolysis. CO concentrations were about 17 vol%, CH_4 concentration about 10% and CO_2 concentrations about 45%. The condensable liquids produced were analysed using liquid gas chromatography and showed no significant difference in the peak range and oil composition between the two heating rates, and also when compared with the oil produced by the Pyroformer.

3.3.2 Pyrolysis and Catalytic Reforming Without Steam

During the catalytic experiments 10g of commercial reforming catalyst was used with three different reforming temperatures: 500°C, 750°C and 850°C. The catalyst was placed into the catalytic reforming reactor with quartz wool. Initial studies were conducted to see the effect of reforming pyrolysis vapours without steam at the selected temperatures, as the presence of significant water content in the pyrolysis vapours may be sufficient for the catalytic reforming reactions to proceed.

The steam reforming reaction of any oxygenated organic compound can be represented as follows: [20]

$$C_nH_{2n+2} + 2H_2O \leftrightarrow C_{n-1}H_{2n} + CO_2 + 3H_2 \qquad (1)$$

Other reactions that may take place are as follows:

$$C_nH_m + {}_nH_2O \leftrightarrow {}_nCO_2 + (n + m/2)H_2 \qquad (2)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad (3)$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad (4)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (5)$$
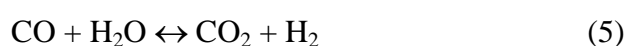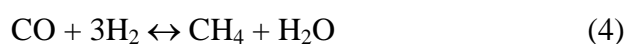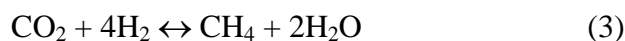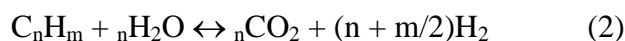
These reactions are only a guide, as pyrolysis vapours contain complicated hydrocarbon chains, but also oxygenated compounds.

Figure 10 shows the yield of products from pyrolysis and catalytic reforming at 500°C, 750°C and 850°C without the addition of steam. The results indicate that as the reforming temperature increases permanent gases also increase, reducing the yield of condensable liquids (7%, 22% and 26% at 500, 750 and 850°C respectively). Char remained the same as pyrolysis conditions remained constant.

Figure 11 illustrates the comparison of permanent gas composition produced at the three different reforming temperatures. As much as 43 vol% of hydrogen was produced at 850°C,

24 vol% at 750°C and 10% at 500°C, much higher values than without catalytic reforming. CO_2 concentrations was 35-53 vol%, CO concentrations 15-17 vol% and CH_4 9-14vol%.

3.3.3 Pyrolysis and Catalytic Reforming With Steam

The runs without steam were then replicated using fresh catalyst samples with the addition of steam.

Pyrolysis combined with steam reforming at low and high reforming temperatures showed a significant increase in the product gas yield of between 78 and 108% on a mass basis and a significant reduction in liquid yield. The amount of additional steam added for each run ranged between 90-100ml.Char again remains the same see Figure 12.

Figure 13 illustrates the composition of permanent gases at the three different reforming temperatures with the addition of steam. As much as 57vol% of hydrogen was produced at reforming temperatures of 750°C and 850°C which is an increase of about 14% in comparison to reforming at the same temperatures without steam. The increase was 22% at 500°C. CO concentration also increased by 9%. CH_4 concentration reduced by 6-8% at 500°C and 750°C, however increased by 7% at 850°C. CO_2 concentration decreased by 13% at 500°C and by 31% at 750°C and was not found at 850°C. The reduction of CO_2 with catalyst shows evidence of decarboxylation reactions occurring. The addition of water (steam) had increased H_2 in the product gas and this can be due to the promotion of water-gas shift reaction (reaction 5) carried out in the presence of Nickel catalysts.

3.3.4 Permanent Gas Calorific Value

The increase of reforming temperature and the addition of steam gives an increase in the heating value of the gases see Figure 14. Pyrolysis without catalytic reforming produced a gas with a typical heating value of 1 MJ/m^3. Best results were with steam added: at 500°C the heating value was 10.8MJ/m^3, at 750°C heating value was 15.7 MJ/m^3 and at 850°C heating value was 25.2 MJ/m^3. For reforming without steam at 500°C, the heating value was about 2MJ/m^3, and at 750°C and 850°C the heating value was about 5 MJ/m^3.

3.4. Bio-oil analysis

The bio-oils all separated into an aqueous and an organic phase except oils produced at higher reforming temperatures with the addition of steam; this can be seen in Figures 15 and 16. The organic fraction contains the heavy condensable phase are mainly tars, and the aqueous fraction is the light condensable phase mainly comprising of water.

Table 10 shows the compositional analysis of the bio-oils. Compared with the oil produced in the Pyroformer, the bench scale oil without catalysis showed an increase in C by

approximately 15%, and a reduction in H, N, and O (1.78%, 1.99%, and 4.91%) respectively. Increases in S and Cl were seen of 0.7% and 0.1% respectively.

The C content in the oils for all experiments decreased as the reforming temperature increased, indicating catalytic activity and decarboxylation reactions. The high C content with catalytic reforming at 850°C may be due to experimental error.

All the oil samples contained S and Cl between 0.1-2.01% and 0.1-0.31% respectively. Visual inspection of the catalysts showed very little carbon precipitation, but the declining activity of the catalysts with time associated with S and Cl poisoning could not be assessed. The pH value of all samples for both organic and aqueous phases were found to be between 5.1 and 8.9. The HHVs obtained for all oils were clearly related to the O content - the lower the O content, the higher the HHV.

The acid number of the oils without catalysts was found to be 60.2 mg/g, and at LT reforming with and without steam 50.34mg/g and 48.81mg/g respectively, which indicates potential corrosion problems. However at HT reforming with and without the addition of steam the acid number could not be determined. This may be due to acidic components being reformed.

3.4.1. GCMS Bio-oil without catalyst at 100°C/min heating rate

The tar samples or bio-oil produced and collected from biomass comprised of low molecular hydrocarbons, phenols and oxygenated compounds. Figure 17 illustrates peaks obtained for the organic phase of bio-oil produced without catalysis by GC/MS analysis with Table 11 identifying those peaks. The results show that there was no significant difference from the Pyroformer oils (see Figure 5 and Table 6).

3.4.2. GCMS Bio-oil at 500°C with catalysts and steam

Oil produced at a catalytic reforming temperature of 500°C without steam was found to contain 12.05% toluene, and a high acetic acid content of 24.26%. Much of the complex mixture contained alkenes from C3-C8 groups such as benzene, ethylbenzene, and styrene. The presence of chlorine was detected with octane-1-chloro identified in the peak range, see Table 12.

The peaks for LT reforming with and without the addition of steam (see Figures 16) are similar, however with the addition of steam the composition of the oils had altered. With the addition of steam at LT reforming (500°C) a increase of benzene, toluene, pyridine, cycloctateraene and naphthalene (25.44%, 15.63%, 6.55%, 8.55% and 17.76% respectively). This may have been due to the further cracking of phenolic components with the addition of steam. Thiophene and propanenitrile, 3,3'-thiobis- are components that contain S which can poison catalysts. Cl was not identified in the peaks, see Table 13. Formation of polycyclic aromatic hydrocarbons (PAH's) were formed such as anthracene, acenapthylene, fluorene, napthalene, phenanthrene and pyrene. These are cause for concern due to their carcinogenic characteristics.

3.4.3. GCMS Bio-oil at 750°C with catalysts and steam

Oils produced at HT (750°C) reforming with the addition of steam was found to have an increase in C5-C8 alkene components. The peaks when reforming at 750°C with and without the addition of the steam are similar, however with the addition of steam the peaks are smaller indicating catalytic activity (see Figure 17). The identified components are given in Table 13. The peaks indicate cracking of phenolic components to lighter hydrocarbons, with an increase in naphthalene.

3.4.4. GCMS Bio-oil at 850°C with catalysts and steam

Bio-oil produced at (850°C) HT reforming with the addition of steam showed significant cracking of most PAH's and alkene groups in particular benzene and toluene, and the formation of a significant quantity of pyridine as seen in Table 14. Figure 18 illustrates the main peak of pyridine and the significant cracking and reduction of other components such as phenols, furans and some oxygenated compounds that may have been present in oils at LT reforming.

The presence of 2-propanol, 1-chloro and propanenitrile, 3,3'-thiobis- indicate potential Cl and S poisoning of catalysts.

In comparing the GC/MS chromatograms obtained at different reforming temperatures there was a large decrease in the number of compounds at 850°C, in comparison to those reforming temperatures 500°C and 750°C during the analysis of bio-oils. This was also observed similarly by Gilbert et al.[21]

It can be seen that at all reforming temperatures much of the oxygenated components in the bio-oils were not identified in the GC/MS peaks indicating these components were reformed completely. At reforming temperatures 500°C and 750°C the (tar) organic composition contain some polycyclic aromatic hydrocarbons (PAH). At LT reforming 500°C the PAH compounds identified were anthracene, fluorene, naphthalene and pyrene, while at HT reforming 750°C the quantity of PAH had decreased with some naphthalene identified. However at HT reforming 850°C PAH compounds in the bio-oil were not identified but showed some presence of benzene, toluene, pyrrol and a large fraction of pyridine.

The PAH's presented and mentioned represent concern due to their carcinogenic and mutagenic characteristics and have been classified by the Environmental Protection Agency (EPA) as priority pollutants. By using a Ni catalysts bed and steam reforming at high temperature close coupled to a pyrolysis unit , (PAH) 3 and 4 ring compounds such as phenanthrene, pyrene and other PAH compounds are reformed into single and two ring aromatic compounds of lower molecular weights such as benzene, toluene and styrene. This reduction could be due to higher molecular weight hydrocarbons being thermally degraded into lighter hydrocarbons. [22] This confirms the effect of the catalyst and the cracking of higher compounds and the increase of hydrogen in the syngas.

4. Conclusions

Catalytic reforming of pyrolysis vapours of brewers spent grain (BSG) was investigated using a commercial reforming catalyst in a catalytic reforming reactor directly coupled to a batch fixed bed pyrolysis reactor. Initial pyrolysis experiments without a catalyst were carried out at 450°C at low and high heating rates to see the effects of product yield and composition changes. Catalytic reforming experiments were performed at three different reforming temperatures 500°C, 750°C and 850°C with and without the addition of steam.

- Intermediate pyrolysis products bio-oil, char and gas of BSG have been successfully produced in an intermediate pyrolysis reactor (the Pyroformer). Product streams have been analysed for their potential to produce heat and power
- Bench scale pyrolysis of BSG conducted at different heating rates resulted in an increase in liquid yield and reduced gas yield at higher rates, char remained unchanged with no differences noted in product composition.
- Catalytic reforming of the pyrolysis vapours before quenching produced a significant increase in permanent gases mainly (H_2 and CO) with H_2 content exceeding 50 vol % at higher reforming temperatures.
- Bio-oil yield decreased significantly as reforming temperature increased with char remaining the same as pyrolysis condition remained unchanged.
- Pyrolysis of biomass with post catalytic reforming shows an increase in heating value for the product gas, ranging between 10.8 to 25.2 MJ/m^3 as the reforming temperature increased.
- Polycyclic aromatic hydrocarbons (PAH) such as phenanthrene, pyrene, naphthalene and fluorene components were present in bio-oils at LT reforming 500°C and some naphthalene at HT reforming 750°C were formed. However at HT 850°C reforming PAH were converted to lighter single ring hydrocarbons such as benzene, toluene and a large fraction being pyridine.
- Further experiments with the bench scale pyrolysis unit coupled to a catalytic reformer would be recommended to replicate studies with the use of other steam reforming and PGM catalysts.

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Table(s)

Table 1. Elemental Composition of Brewers Spent Grain (Mass %)

feedstock	mass % dry ash free basis				
	C	H	N	S	O [a]
BSG	46.6	6.85	3.54	0.74	42.26

[a] By difference

Table 2. Proximate and Chemical Analysis of Brewers Spent Grain (Mass %)

Feedstock	Moisture	ash	Fixed carbon	Volatiles	extractives (fats)	cellulose	hemicelluloses	lignin
BSG	8	4.5	9.5	78	34.82	18.98	33.59	12.61

Table 3. Yield of Products (Mass %) Pyrolysis Final Temperature = 450 °C

Products	Pyroformer Yield (Mass %)
Char	29
Total liquid	52
Water	79.15
Organics	20.85
Gases (by difference)	19

Table 4: Elemental Analysis of Bio-oil

feedstock	mass % dry ash free basis				
	C	H	N	S	O [a]
Bio-oil	47.6	9.9	3.4	1.3	30.7

[a] By difference

Table 5: Physical properties of Bio-oil produced from Pyroformer

Carbon Residue (%)	Copper Corrosion	Density (g/cm³)	Gross Calorific Value (MJ/kg)	Viscosity @ 40°C cSt	pH	Total Acid Number (mgKOH/g)
1.93	1A	1.02	20.39	222	6.43	49.16

Table 6: GC/MS Tests of the (Organic Phase) Bio-oil Produced (Pyroformer)

Retention Time	Chemical Name	Molecular Formula	Area %
5.271	**4,6-Heptadiyn-3-one**	**C7H6O**	**2.29**
6.133	**Furan, 2-methyl-**	**C5H6O**	**1.69**
8.466	2,5-Dimethylfuran	C6H8O	1.21
10.375	2,4-Dimethyl-1-heptene	C9H18	1.07
10.938	**Toluene**	**C7H8**	**11.29**
14.582	Cyclopentanone	C5H8O	0.89
14.835	Pentane,2,2,3,4-tetramethyl-	C9H20	1.26
15.249	**p-Xylene**	**C8H10**	**6.24**
17.49	**Cyclooctatetraene**	**C8H8**	**5.4**
20.031	**Decane, 1-chloro-**	**C10H21Cl**	**2.63**
20.916	2-Cyclopenten-1-one, 2-methyl-	C6H8O	1.39
22.146	Azetidine, 3-methyl-3-phenyl-	C10H13N	1.12
25.376	Heptane, 2,4-dimethyl-	C9H20	1.61
25.618	Benzene, (2-methylpropyl)-	C10H14	1.15
29.066	5-Octen-1-ol, (z)-	C8H16O	1.01
30.63	**Phenol**	C6H6O	**6.95**
30.951	Benzene, pentyl-	C11H16	1.43
31.676	Guaiacol	C7H8O2	2.47
33.17	**2-Methylphenol**	**C7H8O**	**1.37**
34.894	**Phenol, 4-methyl-**	**C7H8O**	**8.2**
35.584	**Phenol, 4-methyl-**	**C7H8O**	**2.44**
36.895	2-Methoxy-4-methylphenol	C8H10O2	0.96
37.308	2,4-Dimethylphenol	C8H10O	1
39.24	4-Ethylphenol	C8H10O	2.55
40.964	4-Ethylguaiacol	C9H12O2	3.61
44.746	**Tridecane**	**C13H28**	**5.96**
46.033	Phenylacetonitrile	C8H7N	1.57
55.586	Benzene,1,1'-(1,3-propanediyl)bis-	C15H16	2.57
63.483	Undecanoic acid, methyl ester	C12H24O2	1.77
63.736	**1-Propene, 3-propoxy-**	**C19H18N2O2**	**0.99**
65.472	Undecanenitrile	C11H21N	3.71

Table 7: Yield of permanent gases produced from Pyroformer

	vol% permanent gases					
Gases	H	O	N	CO	CH$_4$	CO$_2$
	1.6	0.45	4.6	19.74	9.43	64.18

Table 8: Elemental analysis of Char produced from Pyroformer

Feedstock	mass % dry ash free basis				
	C	H	N	S	O [a]
BSG (This Study)	61.8	4	5.2	1.9	1.9

[a] By difference

Table 9: Elemental Analysis of char ash produced from Pyroformer

	mass %,					
	Al	Ca	Fe	K	Mg	P
BSG char	0.2	0.9	0.3	0.1	0.4	1.68

Table 10: Compositional analysis of Bio-oils from Bench scale experiments

Bio-oil Fraction	BSG	Catalytic reforming at 500°C	Catalytic reforming at 750°C	Catalytic reforming at 850°C	Catalytic reforming at 500°C + steam	Catalytic reforming at 750°C + steam	Catalytic reforming at 850°C + steam
C	62.57	58.4	47.6	70.4	70.8	68.2	48.1
H	8.12	9.3	8.6	7.5	8.9	9.7	8.1
N	1.41	3.7	4.1	3.5	5.5	4.8	3.5
S	2.01	1.7	0.8	1.3	1.3	0.1	0.1
O	25.79	26.7	38.6	17.2	13.5	17.0	40.1
Cl	0.1	0.12	0.31	0.17	0.1	0.18	0.1
Water Content:							
Organic (wt%)	3.8	3.2	3.6	66.6	67.0	68.1	45.4
Aqueous (wt%)	65	63.9	72	85.2	76.3	80	40.4
pH:							
organic	5.3	5.6	8.3	8.8	8.3		
aqueous	5.1	5.3	8.28	8.9	8.3	8	8.6
Acid Number mg/g	60.2	50.34			48.81		
HHV	28.9	28.7	22.7	31.7	33.9	33.4	22.2

Table 11: Composition of BSG Intermediate Pyrolysis oil without catalysts at 100°C/min heating rate

Time	Chemical Name	Molecular formula	Area %
8.493	2,5-Dimethylfuran	C6H8O	1.51
9.654	trans,trans-1,3,5-Heptatriene	C7H10	1.88
10.413	1-Octene, 3,7-dimethyl-	C10H20	1.2
10.965	Toluene	C7H8	11.48
11.678	Pyridine	C5H5N	0.62
14.564	Cyclopentanone	C5H8O	1
15.265	Ethylbenzene	C8H10	3.6
15.668	p-Xylene	C8H10	1.28
17.139	m-Xylene	C8H10	1.32
17.496	Cyclooctatetraene	C8H8	2.05
20.048	Decane, 1-chloro-	C10H21Cl	3.53
21.715	3-Ethyltoluol	C9H12	1.28
25.394	Undecane	C11H24	2.27
25.613	Benzene, Butyl-	C10H14	1.54
29.016	Spiro[2.4]heptan-4-one	C7H10O	1.23
30.591	Carbamic acid, methyl-, phenyl ester	C8H9NO2	6.69
30.948	Benzene, (3-methylbutyl)-	C11H16	1.86
31.638	Ethanone,	C14H18O7	2.14
33.132	2-Methylphenol	C7H8O	2.38
34.857	Phenol, 4-methyl-	C7H8O	7.13
35.581	Tridecane	C13H28	3.07
36.087	Benzene, Hexyl-	C12H18	1.52
37.248	2,4-Dimethylphenol	C8H10O	1.88
39.18	4-Ethylphenol	C8H10O	2.42
40.939	4-Ethylguaiacol	C9H12O2	1.53
44.722	Tetradecane	C14H30	6.76
63.428	Pentadecanoic acid, 14-methyl-, methyl ester		2.01
65.394	Pentadecanenitrile	C15H29N	2.64
71.568	6-Nonenal, (E)-		1.5
76.489	Palmitic Acid	C16H32O2	2.07
101.519	Cholest-5-en-3-ol(3B)-,9-octadecenoate, (z)-		1.42

Table 12: Composition of BSG Intermediate Pyrolysis oil after catalytic reforming at 500°C with steam

Time	Chemical Name	Molecular formula	Area %
7.412	Benzene	C6H6	25.44
7.825	Thiophene	C4H4S	0.32
10.815	Toluene	C7H8	15.63
11.413	Pyridine	C5H5N	6.55
14.804	Pyrrol	C4H5N	1.29
15.494	m-Xylene	C8H10	1.11
17.023	Phenylethyne	C8H6	1.15
17.311	Cyclooctatetraene	C8H8	8.55
19.254	Unknown		1
26.244	Indene	C9H8	7.05
30.418	Phenol	C6H6O	0.44
34.603	Naphthalene		17.76
38.731	Quinoline	C9H7N	1.03
45.733	Phenylacetonitrile	C8H7N	0.96
46.825	Napthalene, 2-ethenyl-		0.26
48.4	Acenaphthylene	C12H8	2.37
52.597	Naphthalene, 1-isocyano-		0.29
53.781	Fluorene	C13H10	0.59
59.357	Propanenitrile, 3,3'-thiobis-	C6H8N2S	1.25
62.404	Phenanthrene	C14H10	1.86
62.772	Anthracene	C14H10	0.43
72.89	Pyrene	C16H10	0.4
74.683	Pyrene	C16H1O	0.52

Table 13: Composition of BSG Intermediate Pyrolysis oil after catalytic reforming at 750°C with steam

Time	Chemical Name	Molecular formula	Area %
5.124	Benzene, 1,3-bis(3-phenoxyphenoxy)-	C30H22O4	5.16
5.986	2-Propenitrile		1.11
9.274	Acetic Acid (60, 60, RI 0)	C4H7ClO4S	34.56
11.516	Pyridine (79, 79, RI 0)	C5H5N	7.48
13.413	Hydroxyacetone	C3H6O2	6.89
14.828	Pyrrol	C4H5N	2.72
17.84	Butanoic Acid	C4H8O2	1.99
20.53	Methanimine, N-Methoxy-N-nitriso-	C8H9N	1.71
20.783	2-Cyclopenten-1-one, 2-methyl-	C6H8O	1.01
25.842	2-Cyclopenten-1-one, 3-methyl-	C6H8O	1.24
26.314	Benzene, 1-ethynyl-4-methyl-	C9H8	1.51
30.476	Phenol	C6H6O	3.16
34.684	Napthelene (128, 128, RI 1294)		3.94
35.04	Piperidine-2,5-dione	C5H7NO2	4.49
40.145	2,5-Pyrrolidinedione	C4H5NO2	3.69
40.364	4(1H)-Pyridinone	C5H5NO	4.19
41.582	2-Propanol, 1-chloro-	C3H7ClO	0.47
41.95	1,4,3,6-Dianhydro-d-glucopyranose		2.02
50.55	2,5-Imidazolidinedione, 1-(hydroxymethyl)-5,5-dimethyl-		4.29
69.59	N-Morpholinomethyl-isopropyl-sulfide		2.08
86.4	Arsenous acid, tris(trimethylsilyl) ester		0.46

Table 14: Composition of BSG Intermediate Pyrolysis oil after catalytic reforming at 850C with steam

Time	Chemical Name	Molecular formula	Area %
5.413	Unknown		1.7
6.01	2-Propenenitrile	C3H3N	1.49
7.413	Benzene	C6H6	1.17
10.839	Toluene	C7H8	1.11
11.426	Pyridine (79, 79, RI 0)	C5H5N	84.52
14.829	Pyrrol	C4H5N	2.76
50.46	2-Propanol, 1-chloro-	C3H7ClO	0.91
59.416	Propanenitrile, 3,3'-thiobis-	C6H8N2S	6.32

Figure 1: (left) Wet BSG with signs of degradation, (right) dried and grinded BSG material
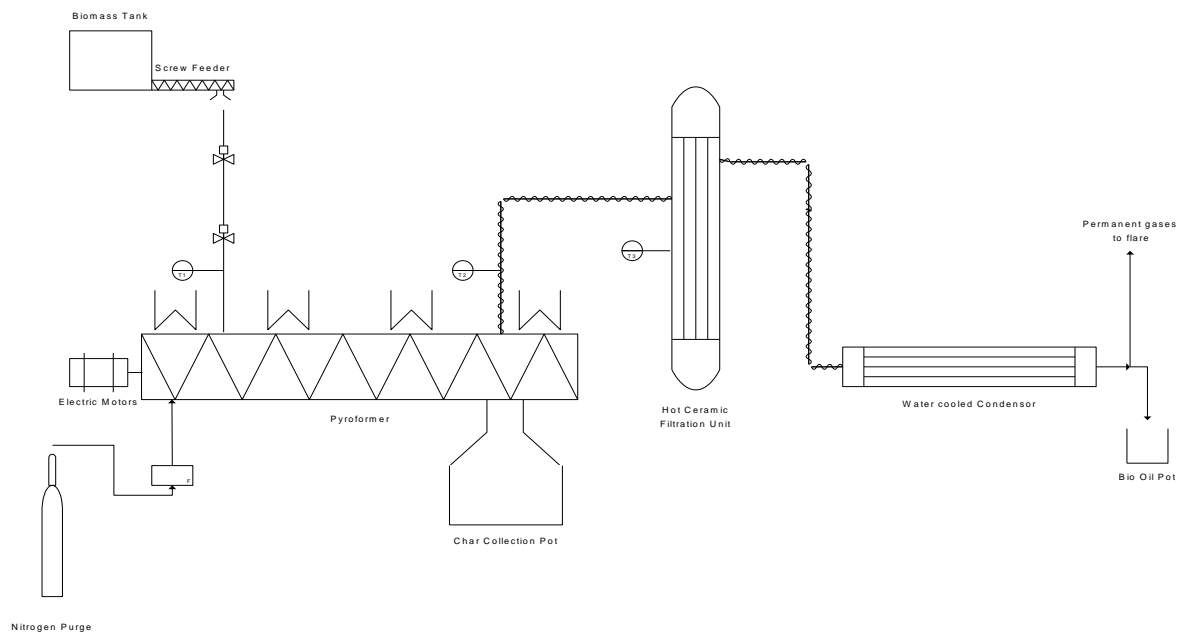
Figure 2: Pyroformer (Intermediate Pyrolysis) schematic diagram

Pyroformer Intermediate pyrolysis reactor used in the conversion of BSG; (1) Biomass Tank, (2) Biomass screw feeder, (3) Feed entry pipe, (4) Actuator Valves, (5) Electric Motors, (6) Heaters, (7) Twin coaxial screw reactor (Pyroformer), (8) N_2 bottle, (9) Char collection pot, (10) Heated vapour exit line 1, (11) Hot ceramic filtration, (12) Heated vapour exit line 2, (13) Water-cooled condenser, (14) Bio-oil collection pot, (15) Permanent gases vent line
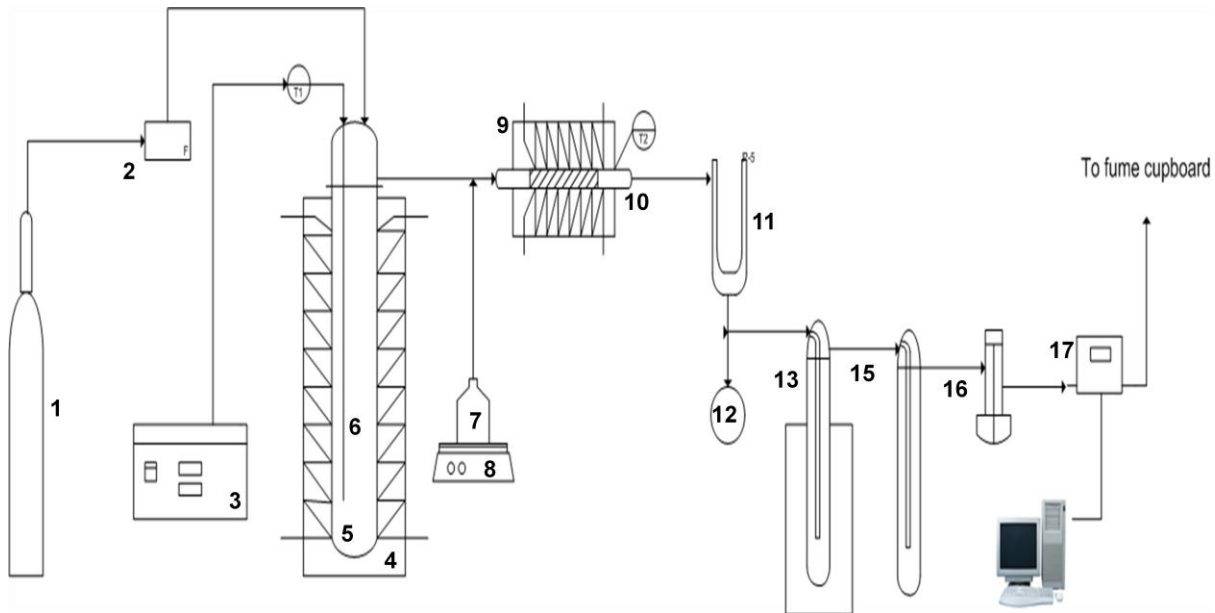
Figure 3: Bench Scale Pyrolysis and Catalytic reactor

Batch fixed bed pyrolysis and catalytic reforming reactor used in the conversion of BSG. (1) Nitrogen gas bottle, (2) N_2 flow meter, (3) Pyrolysis heater controller, (4) Pyrolysis heater, (5) Pyrolysis reactor, (6) Thermocouple, (7) Kettle, (8) Kettle heater, (9) Reformer heater, (10) Catalytic reformer, (11) Condenser 1, (12) Bio-oil pot, (13) Condenser 2, (14) Ice bath (15) Scrubber, (16) Gas sampling port, (17) Flow/Temp/Press meter
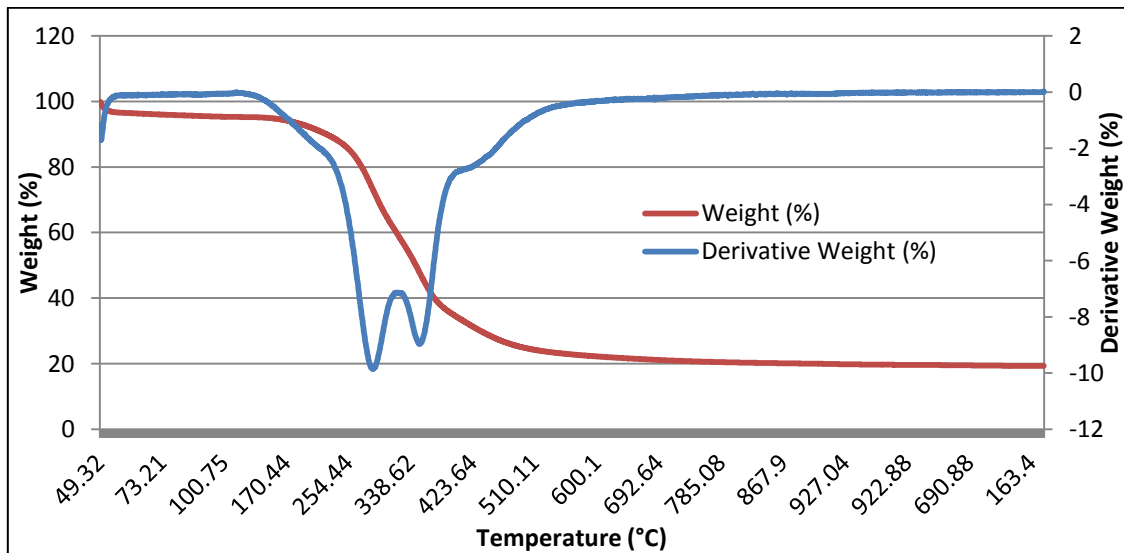
Figure 4. Brewers Spent Grain TGA Derivative Weight Loss Profile at 900°C
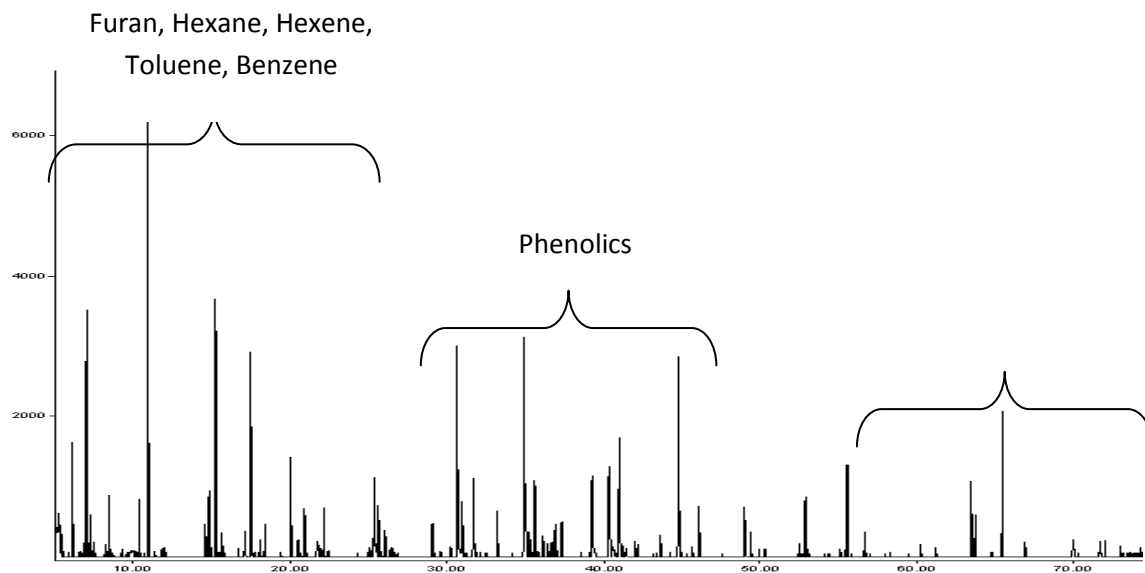
Figure 5: GC/MS Analysis of Bio-oil (Organic phase) produced from Pyroformer
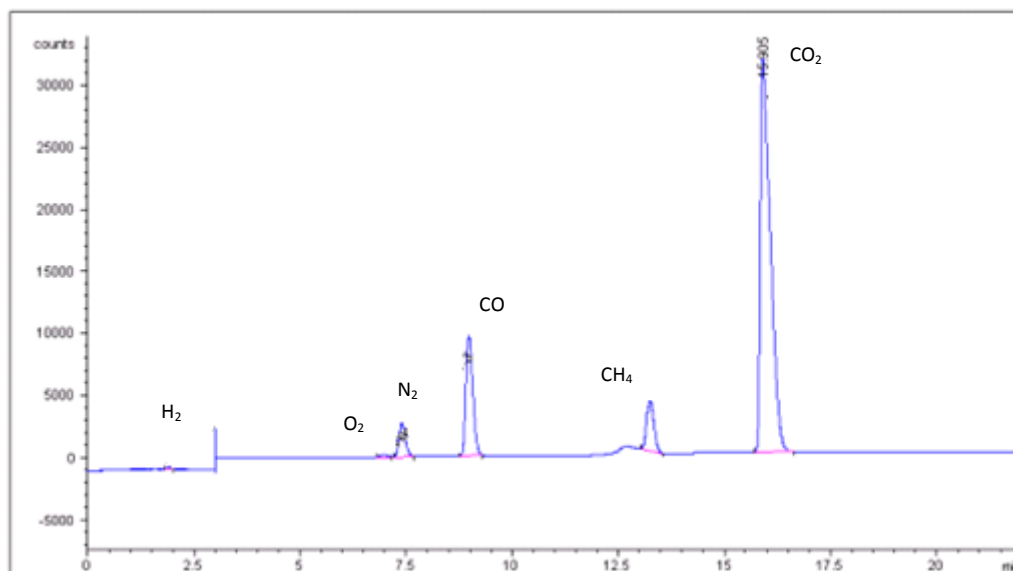
Figure 6: GC/MS mass spectra peaks of permanent gases obtained

Figure 7: Char produced from Pyroformer
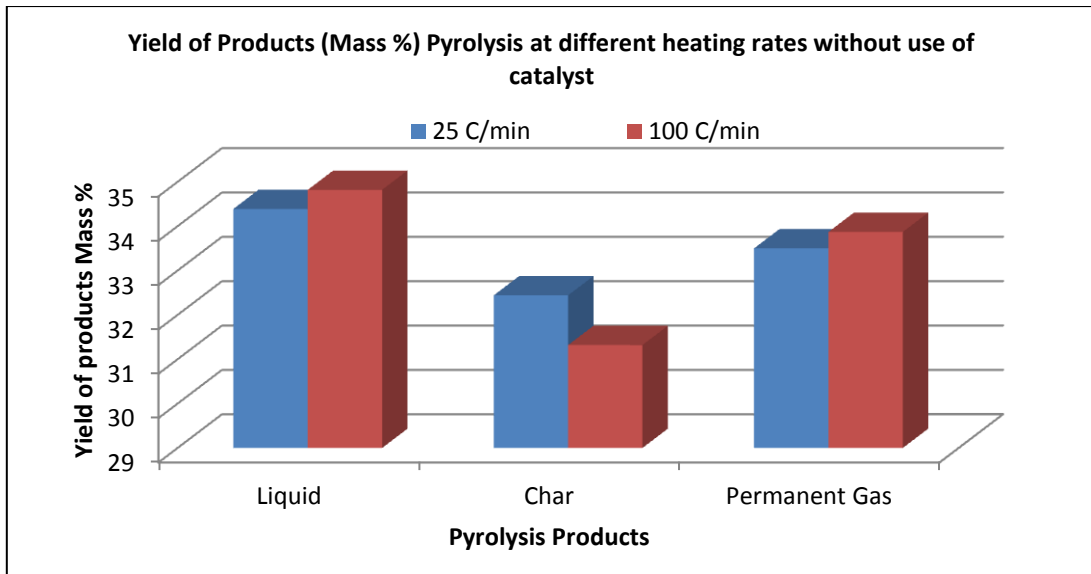
Figure 8: Yield of Products (Mass %) Pyrolysis at different heating rates
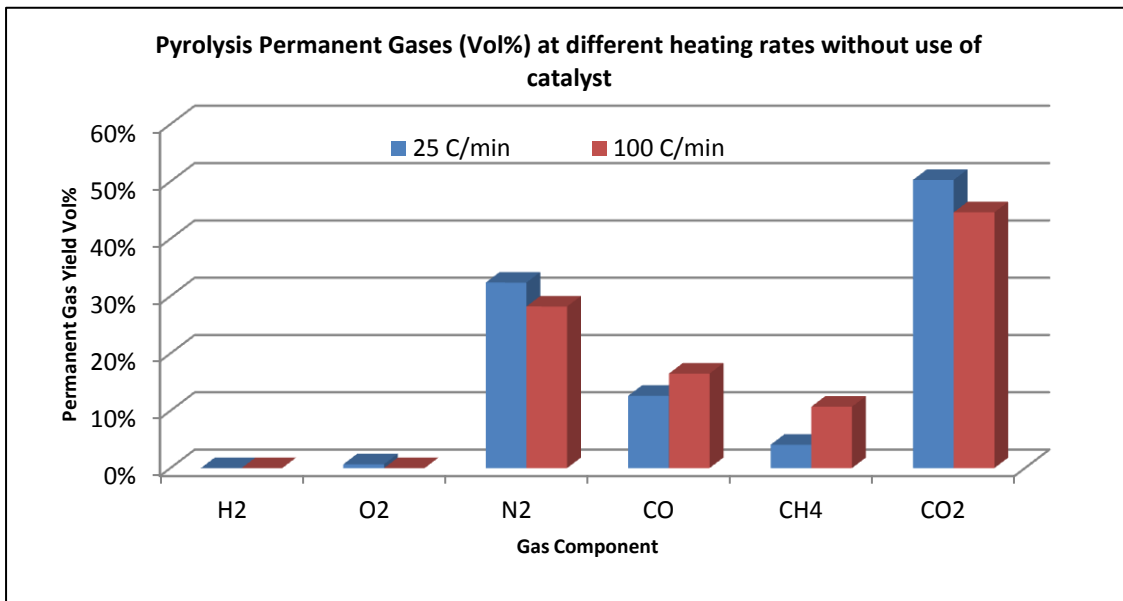

Figure 9: Yield of Pyrolysis Permanent Gases Vol%
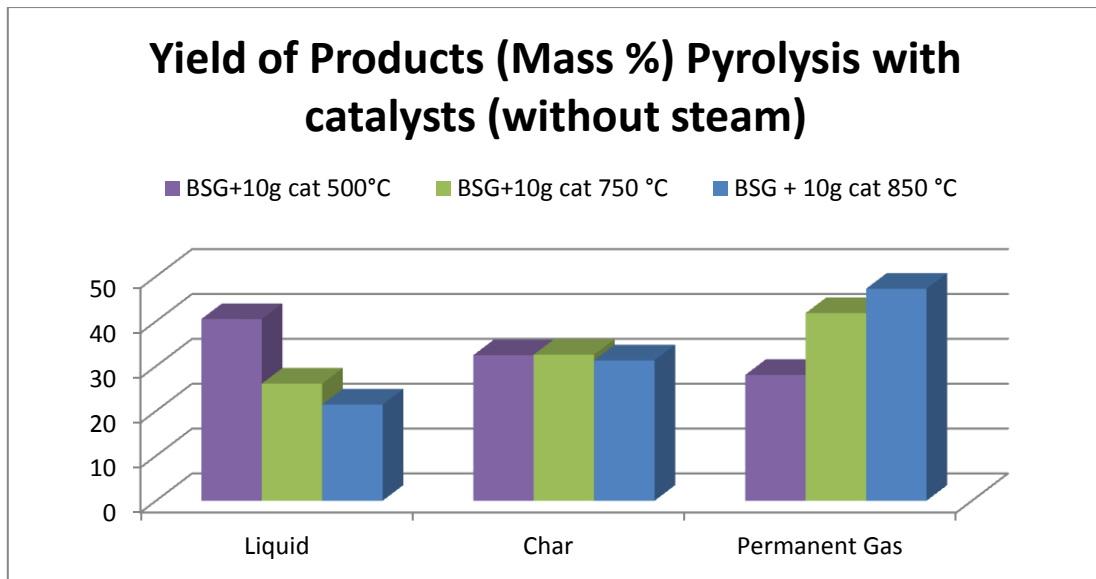
Figure 10: Comparison of the yields of products from measurements with catalysts and without steam
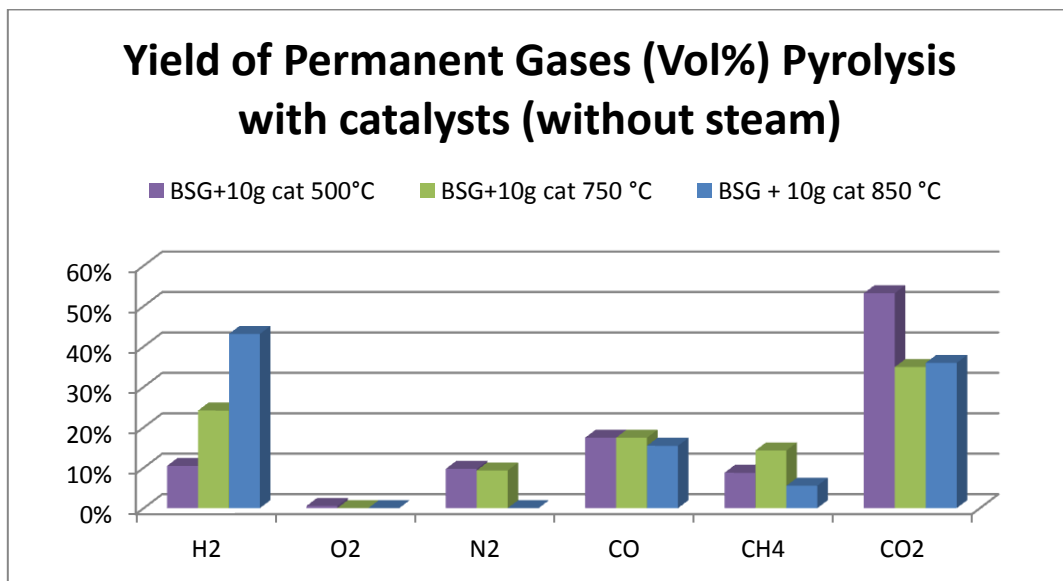
Figure 11: Comparison of the yields of permanent gases produced from measurements with catalyst and without steam
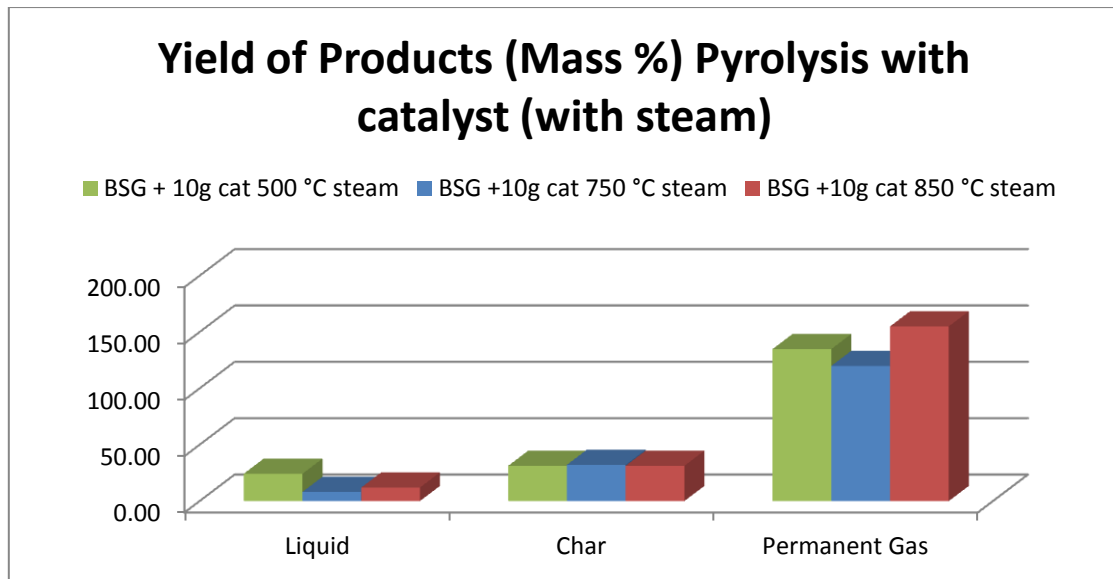
Figure 12: Comparison of the yields of products from measurements with catalysts and with steam added
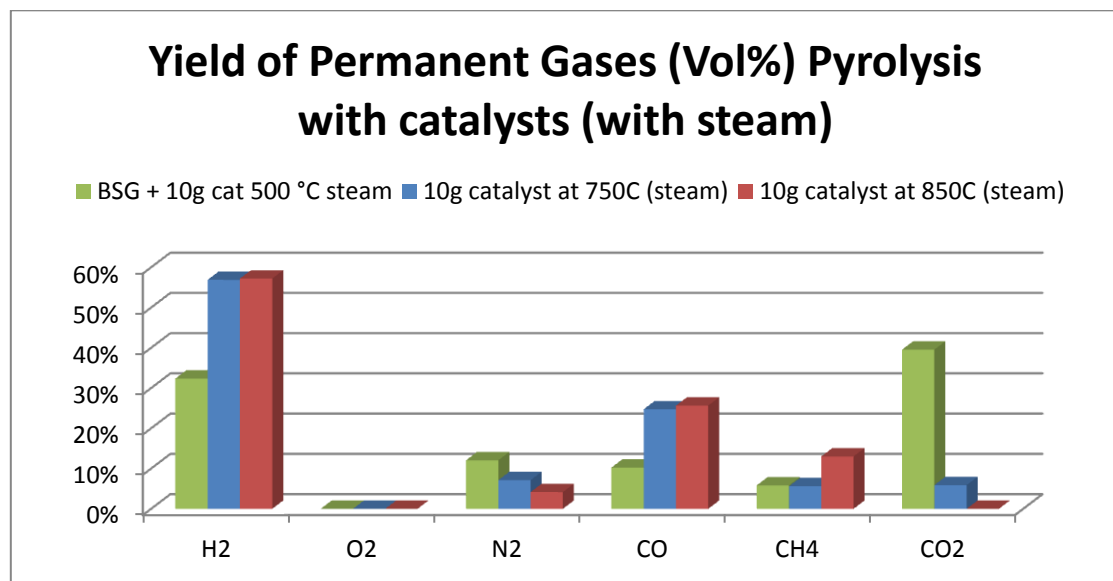
Figure 13: Comparison of the yields of permanent gases produced from measurements with catalyst and with steam added
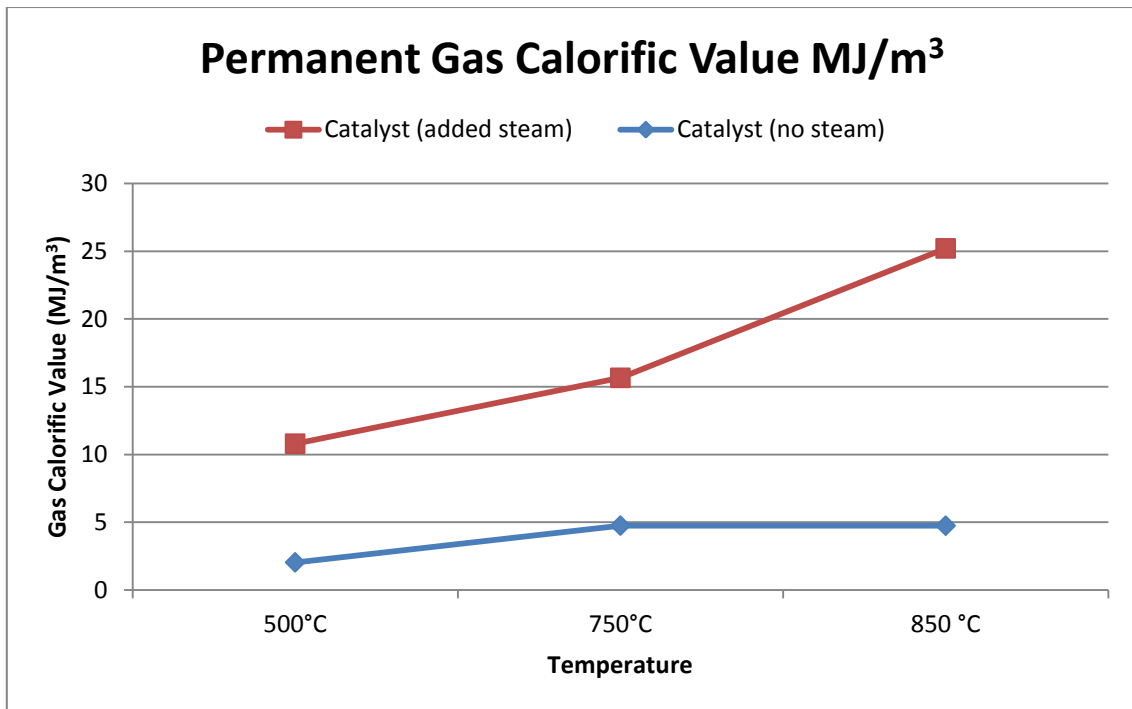
Figure 14: Comparison of heating value of product gases at different reforming temperatures and condition

Figure 15: Bio-oil samples recieved different heating rates (left) 25°C/min (right) 100°C/min
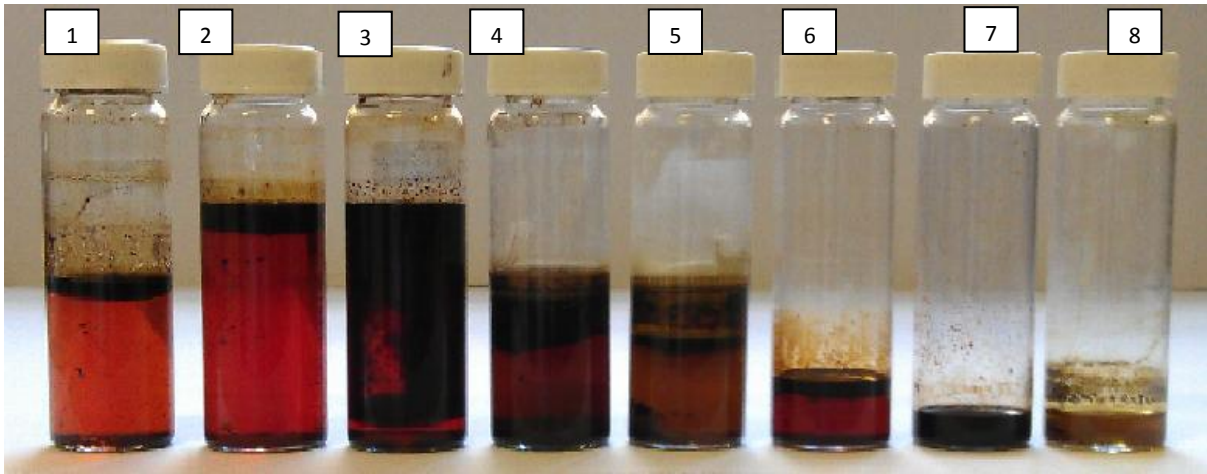
Figure 16:Comparison of Bio-oil samples, (1) at 25°C/min; (2) at 100°C/min; (3) catalytic reforming at 500°C; (4) catalytic reforming at 500°C with steam; (5) catalytic reforming at 750°C; (6) catalytic reforming at 750°C with steam; (7) catalytic reforming at 850°C; (8) catalytic reforming at 850°C with steam
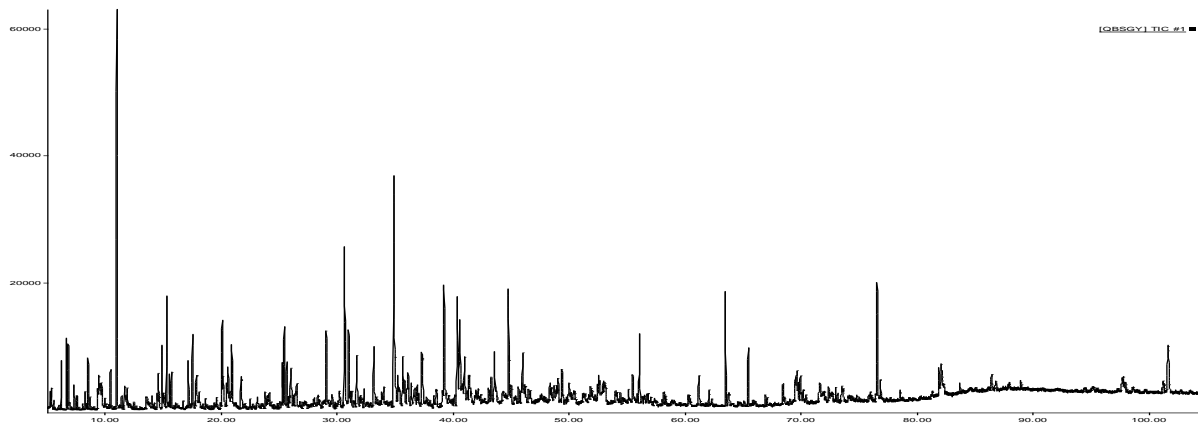

Figure 17: GC/MS analysis of BSG bench scale bio-oil Intermediate Pyrolysis Oil (chemical abundant vs. Retention time)
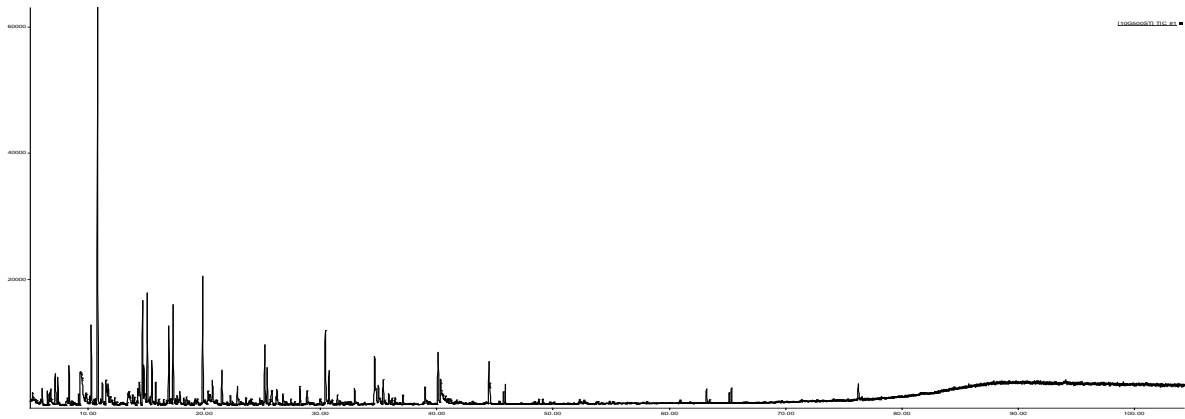
Figure 18: GC/MS analysis of BSG Intermediate pyrolysis oil after catalytic reforming at 500°C with steam (chemical abundant vs. Retention time)
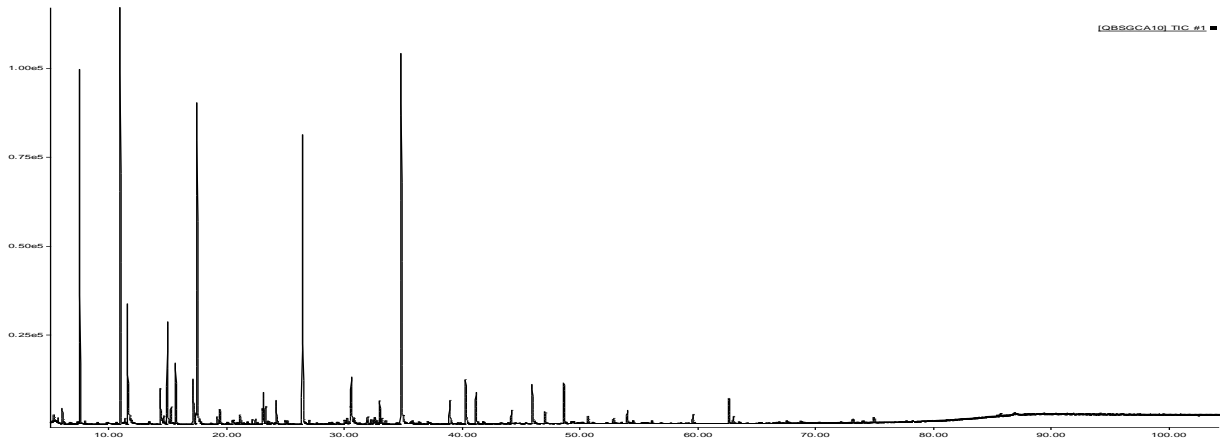

Figure 19: GC/MS analysis of BSG Intermediate pyrolysis oil after catalytic reforming at 750°C (chemical abundant vs. Retention time)
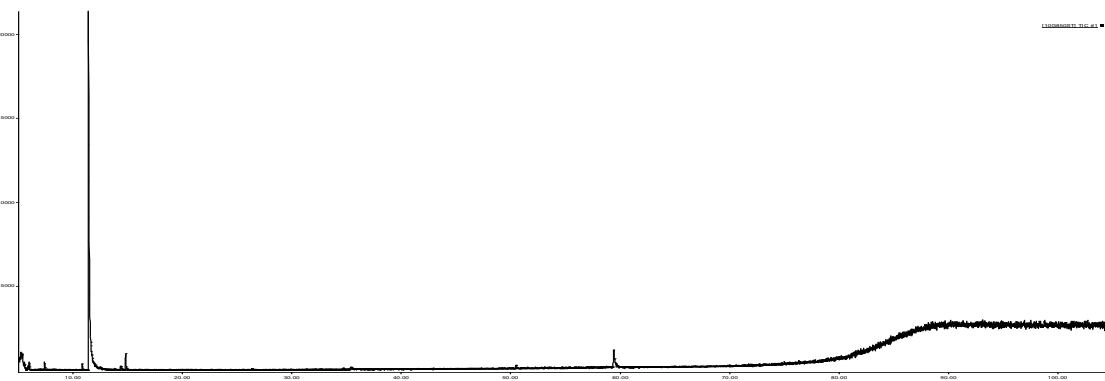

Figure 20: GC/MS analysis of BSG Intermediate pyrolysis oil after catalytic reforming at 850C with steam (chemical abundant vs. Retention time)