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Extraction of Fermentable Sugars from Spent Coffee Grounds using 1-Butyl-3-Methylimidazolium-Chloride for Bioethanol Production

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Spent coffee grounds (SCGs) are a renewable source that can be converted into different types of biofuels or chemicals. Recent research has focused on the examination of a two-step bioconversion process that involves;1) extraction of fermentable sugars from SCGs, and 2) conversion of sugars into fuels and/or chemicals by microbial fermentation. The capability of SCGs as a source of fermentable sugars has not been fully realised, due to their complex structure. Which makes the depolymerisation of the SCGs into its component monomeric sugars relativity difficult. The use of ionic liquids (ILs) as green solvents is an attractive alternative for the pre-treatment of lignocellulosic biomass such as SCGs. It has been shown that pre-treatment with imidazolium-based ILs containing anions such as chloride, acetate, and alkyl phosphate can greatly speed up the subsequent enzymatic hydrolysis of lignocellulosic biomass. The present investigated the use of 1-Butyl-3-methylimidazolium chloride as a green solvent for the extraction of sugars from SCGs for the production of bioethanol. The maximum concentration of sugars extracted was 22.55 wt% of mannose in 100 g of SCGs, galactose, 15 wt% of galactose in 100 g of used, 9.81 wt% glucose in 100 g of SCGs, 6.36 wt% arabinose and 10.46 wt% of, sucrose in 100 g of dry SCGs used. Mannose yield was prominent in all runs, the high content of this sugar causes difficulty in bioethanol production but is advantageous in the production of itaconic acid.

1. Introduction

With gradual depletion of fossil fuels coupled with the environmental issues associated with their use, it has become necessary to synthesis green and sustainable liquid fuels. The world population is projected to increase from 7.8 billion, (2020) to 9.7 billion by 2050 (Vollset et al., 2020). The increase in global population is unfortunately accompanied by an increase in energy demand, which was about 2.30 % in 2018 (Kuo et al., 2019). It is estimated that by 2052 oil reserves will be dry and coal reserves will be depleted by 2090 (Kuo, 2019). Moreover, the use of fossil fuels for transport and by industries generates about 23 $\times 10^9$ t of CO_2 but by 2019 it had reached a record high of 36.44 $\times$ 10^9 t of CO_2 (Tiseo, 2021). In the attempt to mitigate the issues associated with the use of fossil-based fuels, biofuels have been long introduced. Biofuels are synthesised from renewable organic materials and have the potential to diminish some of the unwanted aspects of production and use of fossil fuels such as greenhouse gasses (GHG) defilement emissions, reliance on unstable foreign supplies and depletion (Huang et al., 2013). The production and use of biofuels comes with it's own hindrances which need to be overcome before they can efficiently compete with or replace fossil fuels. Feedstock's used in the production of biofuels require, water, land and fertilizers, research have shown that synthesis of biofuels may result in a number of undesirable effects. These include pressure on water resources, increase in land use which can increase GHG emissions and could also increase air and water pollution. The type of feedstock and the process used for the production of the biofuel higher volumes of GHG can be produced relative to those produced by fossil fuels on an energy-equivalent basis. The major concern is the direct competition between the food industry and production of biofuels, which creates problems like high food (Ajanovic, 2011). Production of biofuels may result in an unwanted impact on food security but can also prompt positive development in terms of agricultural development (Koizumi, 2015). To eliminate the competition between the fuel and food industry, non-edible renewable feedstock must be use for biofuel production.

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In the modern-day coffee has become a popular morning drink and it has been deemed the second favourite drink after water for most people (Cerino-Córdova et al., 2020). At the beginning of 2022, the International Coffee Organization (ICO) reported a total export of all forms of coffee over the first 10 months of the coffee year 2020/21 (October 2020 – July 2021) amounted to 108.96 M bags, an increase of 2.2 % compared with 106.63 million bags during the same period in the coffee year 2019/20 (International-Organization-Coffee, 2021), which is approximately 9 billion tons of coffee beans. It has been estimated that for every 1 kg of soluble coffee 2 kg of solid waste (wet spent coffee grounds) is generated and for 1000 kg of green coffee beans used to make coffee beverages 650 kg of spent coffee grounds (SCGs) are generated (Kookos, 2018). The general mass ratio of produced SCGs to processed coffee beans is 0.65, and the mass ratio of SCGs to roasted coffee beans is approximately 0.91 (PERTA-CRISAN, URSACHI and MUNTEANU 2019). As a result, an enormous amount as high as 6 billion tons of water-free SCGs are generated annually worldwide (Hardgrove and Livesley, 2016). SCGs are lignocellulosic biomass with more than 1000 individual chemical compounds, mainly composed of carbon (52.10 – 53 wt%), hydrogen (6.80 – 7.03 wt%), oxygen (34.70 – 38.10 wt%), and nitrogen (1.71 – 3.47 wt%). Which primary form a variety of valuable organic chemical compounds such as cellulose (59.20 – 62.94 wt%), lignin (19.80 – 26.50 wt%), phenolics (24 wt%), hemicellulose (5 – 10 wt%), lipids (6.70 –24 wt%), oil (10 – 20 wt%), proteins (4.30 –17 wt%) and other polysaccharides. This makes SCGs the most valuable biomass amongst other types of biomasses since numerous important chemical compounds can be derived from them (Kourmentza et al., 2018).

The challenge with lignocellulosic materials such as SCGs is that they always required pre-treatment before they can be converted to biofuel. The pre-treatment is required to weaken the rigid structure of the lignocellulosic material. Four pre-treatment techniques are commonly adopted, namely physical (grinding for particle size reduction), biological (use of enzymes), chemical (used of basis and acids), and combinatorial (physicochemical and biochemical) (Awogbemi et al., 2021). The pre-treated lignocellulosic biomass undergoes a hydrolysis process, fermentation, finally distillation (Aditiya et al., 2016). The pre-treatment step is energy intensive, requiring high investments. This has hindered industrial scale production of biofuels from lignocellulosic biomass in developing countries. It has become apparent than cost effective and environmentally friendly techniques for extracting fermentable sugars from lignocellulose biomass needs be investigated. The present investigation aimed to extract fermentable sugars from SCGs using ionic liquids and as green solvents. The objectives of the present study were to investigate the capability of 1-Butyl-3- methylimidazolium chloride to extract fermentable sugars from SCGs without the pre-treatment process. The present study also investigated the effect of solvent to SCGs mass ratio and the effect of extraction duration on the quantities of sugars extracted.

2. Materials and methods

Wet SCGs as source sugars, were collected from a local coffee street vendor, the wet SCGs were dried in oven of 8 h. 72 % sulphuric acid, hydrous ethanol (96%), nitrogen gas, 1-butyl-3- methylimidazolium chloride (99 %), 17 % and 9.45 % sodium hydroxide solutions, phenanthroline-ferrous sulphate, H_2SO_4 (98 wt%), H_2SO_4 3N and high purity standards: D-cellobiose, D(+)glucose, D(+)xylose, D(+)galactose, L(+)arabinose, and D(+)mannose.

2.1 Characterisation of SCGs

SCGs were characterised in in terms of ash, lignin, and carbohydrates. SCGs (500 g) were dried to moistures below 10 wt% on wet basis, using an oven for 8 h. The dry SCGs were subjected to screening via a series of screens mounted on a shaker for 5 min. SCGs with the particle size less than 500 µm were used.

To determine the ash content of the SCGs,10 g of dry SCGs were weighed and heated in a muffle kiln (Tabletop) at 550 °C for 5 h. The mass of the resulting white ash was weighed using an analytical balance (TM-EXA5003H). Eq (1) was used to estimate the ash content of the SCGs, where B is the weight of ash (g) and is the mass of dry SCGs (g).

$$\%\,\mathrm{Ash} = \frac{\mathrm{A}}{\mathrm{B}} \times 100 \tag{1}$$

To determine the lignin fraction of the SCGs (as presented in Eq(2)), acid hydrolysis was used. 2 wt% sulphuric acid solutions were to dissolve 10 g of SCGs, at 200 °C for 20 min. Sulphuric acid during acid hydrolysis of SCGs solubilizes the carbohydrates, while the insoluble lignin remains in its solids state making it easy to filter out and dry.

$$\%\,\mathrm{Lignin} = \frac{\mathrm{m}}{\mathrm{M}} \times 100 \tag{2}$$

Where, m (g) is the mass of the dried filtrate and M (g) is the mass of the dried SCGs used. The procedure used as accorded by the TAPPI standard, T 222 om-98 “Acid-Insoluble Lignin in Wood and Pulp”.

To determine the carbohydrates fraction of the SCGs (see Eq(3)), 17 wt% and 9.45 wt% sodium hydroxide solutions were used.10 g of SCGs were added in.

$$\%\,\text{Alpha} - \text{cellulose} = \; 100 - \frac{6.85((V_2 - V_1)\times N\times 20}{A\times W} \tag{3}$$

Where V_1 is the titration of the pulp filtrate (mL), V_2 is the blank titration (mL), N is the exact normality of the ferrous ammonium sulfate solution, A is the volume of the pulp filtrate used in the oxidation (mL), and W is the oven-dry weight of pulp specimen (g).

$$\%\,\text{hemicellulose} = \frac{6.85(V_4 - V_3)\times N\times 20}{25\times W} \tag{4}$$

Above is Eq(4), where V_3 is the titrate of the solution after precipitation of beta-cellulose (mL), V_4 is the blank titration (mL).

2.2 Extraction of the sugars using 1-butyl-3-methylimidazolium chloride ([C4mim] Cl

The dried SCG's will undergo hydrolysis reactions, [C4mim] Cl solution, at different solids to solvent ratios, ranging between 10 to 30 mL ILs/g dry SCGs. The reactor was operated at temperatures between 55 to 205 °C and the reaction time will range between 20-80 min. Figure 1a depicts the SCG's and IL in the 200 mL stainless steel batch cylindrical Parr reactor, which was used for the sugars extraction. The reactor is fitted with a pressure sensor, reactor heating chamber, stirrer, temperature sensor and pressure regulator.

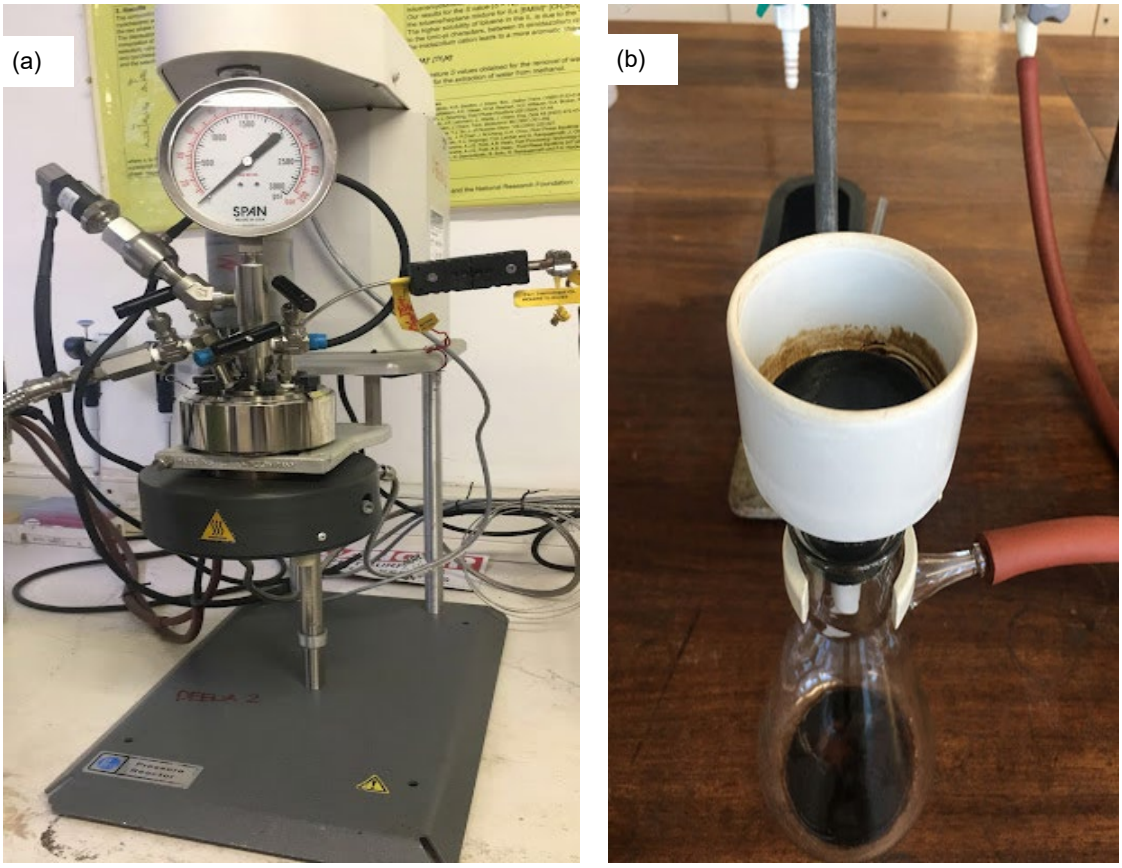

Figure 1: (a) Parr reactor with SCGs and IL reacting inside (b) Vacuum filtration apparatus with SGCs residues

The temperature of the reactor was maintained by submerging the reactor on a cooling bath. The reactor content was discharged into the vacuum filtration system as depicted by Figure 1b. The filtrate will be analysed for sugars using a high-performance liquid chromatography (HPLC).

3. Results and discussion

SCGs were found to contain, ash (1.40 wt%), lignin (23.12 wt%), cellulose (12.20 wt%), hemicellulose (39.15 wt%). These results were in agreement with those reported by (Karmee 2018).

Figure 2a depicts the SCGs, 1-butyl-3-methylimidazolium chloride ([C_4mim] Cl), and ethanol (anti-solvent) mixture. Prior filtration and vacuum distillation. The samples were dark and viscous, with solid spent coffee ground present. The samples were subjected to vacuum filtration to separate the liquid mixture and the solids. Figure 2b depicts the filtered liquid mixture. The filtrate appeared dark and viscous and free of solids. The filtrate underwent vacuum distillation to enable liquid to liquid separation through the manipulation of the liquids boiling points. Due to the dark colour and the high viscosity of the sugar solution, the solution was diluted with distilled water, using a 1mL: 1mL ratio. The colour of the solution appeared light brown and less viscous. The samples were analysed using a high-performance liquid chromatography (HPLC). Five types of sugars were dominantly present in all the solutions tested, namely; Sucrose, Mannose, Arabinose, Galactose and Glucose.

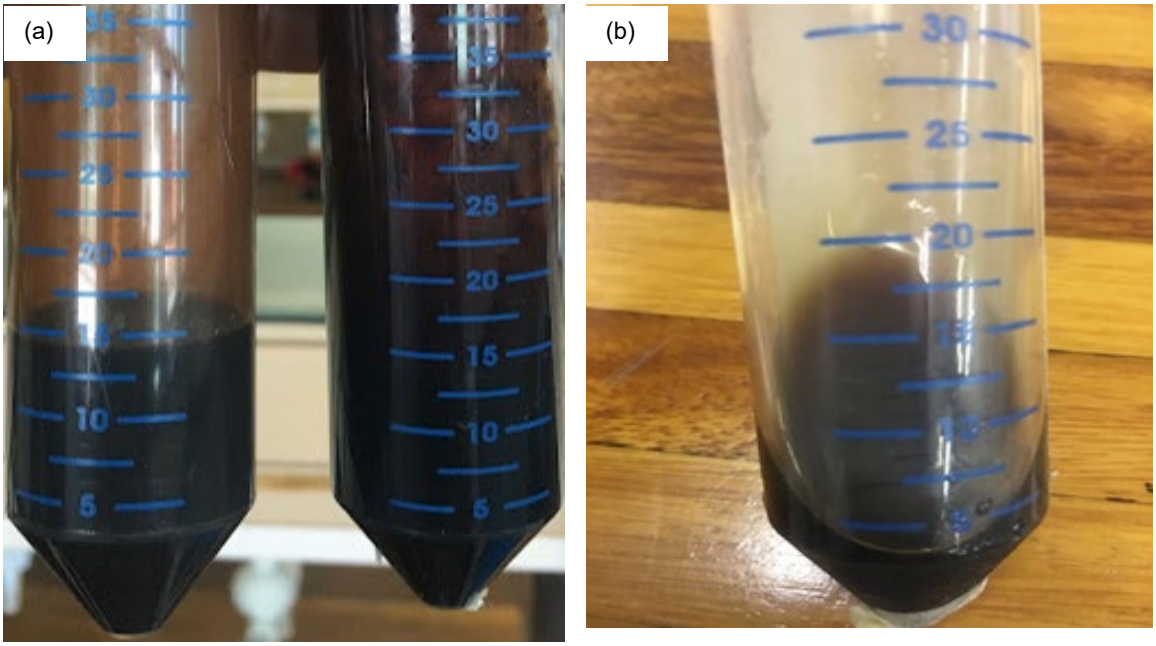

Figure 2: (a) Depicts liquid mixture of IL, ethanol and SCG solids prior vacuum filtration and distillation and (b) is the filtrate which consists of sugars with miniature traces of IL and ethanol

3.1 Effect of temperature

Figure 3a depicts the effect of extraction temperature on the quantity of sugars extracted from dried SCGs by using [C_4mim] Cl –water, ethanol (96 wt%) mixture (water content of 4 wt%) for 0.5 h at 7 bar reactor pressure. Up on analysis of the water sugars mixture in the HPLC, six types of sugars were present, mostly being Sucrose, Mannose, Arabinose, Galactose, Glucose and very small quantities of xylose. At 80 ℃, mannose and galactose were the most extracted sugars. With mannose reaching a maximum 451 mg/2 g of SCGs used, which corresponds to 22.55 wt% of mannose in 100 g of SCGs. This was slightly higher than those reported by (Ballesteros, Teixeira and Mussatto 2014). i.e.,19.92 wt%. Galactose was the second most extracted sugar, with a value of 300 mg/ 2 g of SCGs used, which corresponds to 15 wt% of galactose in 100 g of used. This value was lower than those reported by (Ballesteros, Teixeira and Mussatto 2014). i.e.,18.09 wt%.
Increasing the extraction temperatures had a negative impact on the quantities of mannose and galactose extracted. The quantity of mannose remained fairly high than the other sugars, after decreasing from the peak extraction. Glucose was the third most extracted sugar, which was achieved at 180 °C. Reaching a maximum extraction of 196.27 mg / 2 g of dry SCGs used. This value corresponds to 9.81 wt% of glucose in 100 g of SCGs, this value was lower than those reported by (Ballesteros, Teixeira and Mussatto 2014). i.e.,12.40 wt%. Arabinose and sucrose were the other sugars extracted optimally at 180 ℃, achieving 6.36 wt% arabinose of 100 g of SCGs used and 10.46 wt% sucrose in 100 g of dry SCGs used. These observations were in contrast to those reported by (Ballesteros et al, 2014). i.e.,3.6 wt% arabinose and 0 wt% glucose. The archived contrasted the results obtained by Scully et al. (2016), who extracted sugars from SCGs using 4.97 g of SCGs for 120 h via hydrolysis. They reported a value of 0.087 mg/ mL of mannose, 0.108 mg/ mL of arabinose. From these results, it is evident that [C_4mim] Cl, favors the extraction of mannose from SCGs.

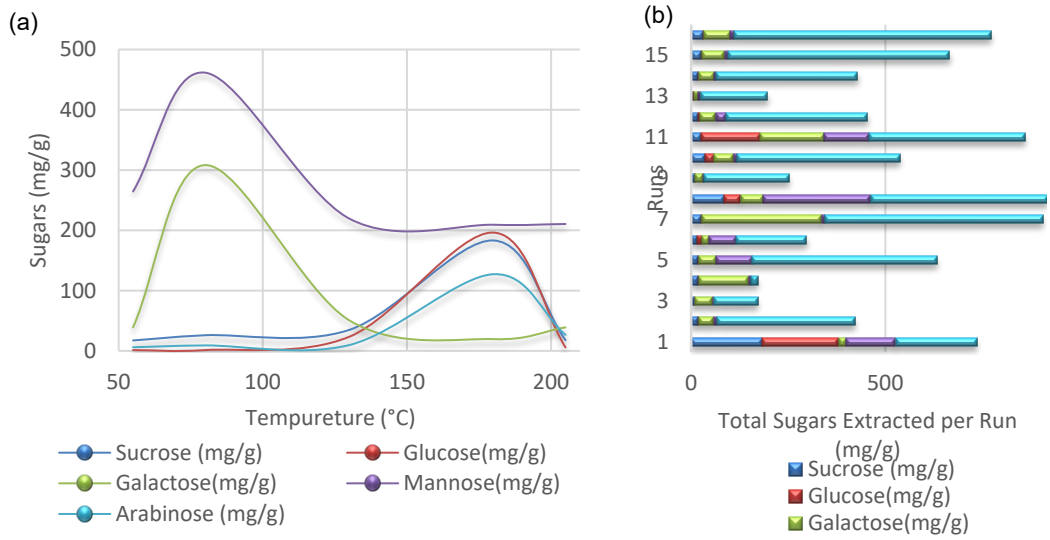

Figure 3: Illustration the effects (a) of extraction temperature on sugar yield and (b) total sugars extracted per run in 1 g SCG's

3.2 Effects of different extraction parameters on sugar yield

There are a number of extraction parameters which affect the efficiency of sugar extraction, these parameters include, solvent to solids ratio, extraction time and extraction temperature. A combination of these parameters was investigated to determine the optimum extraction set. Figure 3b depicts the results obtained from 16 different combinations of the selected parameters.

Table 1: Combination of process parameters for sugar extraction from SCGs using [C_4mim] Cl

Runs	Temperature (°C)	Time (min)	Liquid to solvent ratio (ml/g)
1	180	80	5
2	130	6	10
3	80	80	5
4	130	50	10
5	130	95	10
6	180	20	5
7	80	20	15
8	180	80	15
9	80	20	5
10	130	50	10
11	180	20	15
12	205	50	10
13	130	50	10
14	55	50	5
15	80	50	10
16	130	80	15

All the combination of the process parameters displayed in Table 1, favoured the extraction of mannose from SCGs, this may be attributed to the high content of mannose in SCGs as the result of high hemicellulose. Run 8 provided the highest sugar extraction, all the sugars were present, with mannose being the highest sugar extracted at 228.20 mg/g of the dry SCGs used.as depicted in Figure 3b. Lack of literature on extraction of sugars from SCGs made it difficult to extensively compare the results obtained in this study. Each It is worth noting that the mixture of sugars produced in this study can-not be used for bioethanol production. The high quantities of mannose the sugar mixture makes it difficult be fermented by lactic acid-producing bacteria requiring specialized strains. The mixture of sugars extracted in the present study is suitable for the production of itaconic acid (Saha et al., 2017).

4. Conclusion

The results obtained in the present study were in agreement literature, from the SCGs composition's point of view. [C4mim] Cl was capable of extracting all sugars present in the SCGs. Out of the five types of sugars extracted, mannose was the most prevalent sugar in the extracted mixture. lower extraction temperatures appeared to favour the extraction of mannose and galactose. The interaction of [C4mim] Cl and sugars in the SCGs needs to be further investigated. High mannose content in the extracted sugar mixture makes it difficult to produce bioethanol from the sugars using conversional strains.

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