Solvent Selection for the Extraction of Sugars from Spent Coffee Grounds using Three Different Ionic Liquids.

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***Abstract*—** Various countries, including South Africa, are experiencing a high accumulation of spent coffee grounds (SCGs) due to the high consumption of coffee daily as a popular morning hot beverage. Biomass has been seen as a potential energy source since it is the most abundant resource on earth. This makes cellulose the most prominent and abundant material in nature. Coffee grounds are a low-value waste product with great potential to be valorised into useful bio-products. In this investigation, sugars were extracted from spent coffee grounds (SCG) without pre-treatment using an environmentally friendly solvent, namely 1-ally-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride and 1-ethyl-3-methylimidazolium acetate. These sugars are used as building blocks to produce hydrocarbons and bioethanol and as feedstock using microorganisms or chemicals. To obtain optimal conditions to produce the highest possible percentage yield of sugars. Response surface methodology (RSM) was used to optimize the valorisation of SCGs into sugars. A maximum sugar yield was obtained using the following conditions: temperature of 180 °C, a reaction time of 80 min, and solid/liquid ratio of 15 mL, with reference to mannose a yield of 2.484 g/g SCGs (1-ally-3-methylimidazolium chloride),0.669 g/g SCGs (1-butyl-3-methylimidazolium chloride),1.988 g/g SCGs (1-ethyl-3-methylimidazolium acetate).1-ally-3-methylimiidazolium chloride was the most performing. Confirmatory runs were conducted. Mannose was the most prevalent sugar in all experimental runs. Findings suggest the prospect of extracting mannose from SCGs is viable for commercialisation and must be given attention.

***Keywords*—** Coffee, Ionic liquids, SCG-Spent coffee grounds, Lignocellulosic structure.

I. INTRODUCTION

With this ever- increasing demand on energy, due to population growth and economic growth. The absolute reliability on non-renewable energy has had a huge negative effect on the environment and has increased the ecological footprint that's imposed on the environment [1]. The global human population growth increases by an estimated 83 million annually; it is predicted to increase from 8.6 billion in 2030 to 9.8 billion in 2050 [2]. An increase in population has a domino effect on energy demand and economic growth. The more the population, the higher the energy demand. The higher the consumption of fossil fuels, the more greenhouse gas emissions will be, thus increasing the global warming rate, ozone layer depletion and the consequence of climate change [3]. Climate change is a serious global crisis. Since it threatens various elements of life, such as access to clean, drinkable water, food harvesting, use of land, physical capital, and health. Globally, CO_2 emission was said to have increased by an average of 1.1% per annum, which has accelerated to a 3% annual growth rate over the next 7 years [4]. This not only has a negative effect on the environment but has also led to the possible depletion of fossil fuels in the future. According to [5], oil reserves will dry, and coal reserves will be depleted by 2090. The application of fossil fuels in transport and industries generated about 23 billion metric tons of CO_2 gas emitted. By 2019, the CO_2 emissions were discovered to have increased to 36.44 billion metric tons [6]. This has led to various researchers investigating green methods and renewable energy as an alternative to fossil fuels.

Spent coffee grounds are commonly known as coffee waste. Coffee waste consists of not only consist of spent coffee grounds (SCGs) as a by-product of the roasting process but also silver skin (CS). After the processing of coffee with hot water, the solid residue left is known as spent coffee grounds. They are lignocellulosic, meaning they consist of 3 polymers, namely, lignin, cellulose and hemicellulose [7]. South Africa and Nigeria are not cold climate countries like the United Kingdom. Yet more than 3 billion cups are consumed in South Africa, and about 275 million cups are consumed in a year in Nigeria [8]. This shows how popular this drink is. Globally, on a daily basis, 2.25 billion cups of coffee are consumed. According to World Bank records, the world generates over 2 billion tonnes of solid waste annually. It is predicted to accumulate tremendously to 3.4 billion tonnes of waste by the year 2050. With the solid waste generated in the world being at 2 billion of that amount, an estimated 18 million tonnes is said to be wet, waste coffee grounds [9].

In most countries, spent grounds are discarded in landfills, where they emit methane gas, which in turn contributes to an increase in global warming and global warming effects. Not only does discarding coffee waste have a negative impact on the atmosphere, but it has an impact on the soil it falls on when discarded. It has been discovered that SCGs have antimicrobial properties. The addition of SCGs in soil reduces microbial activity in soil by altering the bacterial community structure in soil while increasing microbial activity of the soil. Coffee grounds are a low-value waste product with great potential for valorisation into useful bio-products such as bioethanol, biodiesel, etc. This waste has been found to contain a large percentage of useful organic compounds such as fatty acids, cellulose, galactomannans, lignin, and other polysaccharides. The valorisation of coffee waste to produce high-value substances/products has drawn much attention. With its high antioxidant character, it has been viewed as a viable option to be utilised as feedstock for biofuels. The sugars are used as building blocks to produce hydrocarbons and bioethanol as feedstock for microbial growth due to active substances such as caffeine (0.35 %) and chlorogenic acid (0.16%). SCGs can be used in the pharmaceutical [10]. Biomass is the most abundant material on earth, composed of carbon compounds which consist of atoms containing hydrogen, oxygen, and nitrogen elements, including various particles like salt and antacid earth metals in small quantities [7]. SCGs are composed of more than 1000 chemical compounds, mainly containing the following elements: carbon (52.10- 53 wt%), hydrogen (6.80-7.03 wt%), oxygen (34.70 – 38.10 wt%) and nitrogen (1.71 – 3.47 wt%). Coffee beans are lignocellulosic material composed of 3 polymers, namely, lignin, hemicellulose, and cellulose. According to Kourmentza et al., [11] SCGs contain numerous organic chemical compounds such as cellulose (59.20 – 62.94 wt%), hemicellulose (5 - 10 wt%), lipids (6.70 -24 wt%), oil (10 -20 wt%), phenolics (24 wt%), lignin (19.80 -26.50 wt%), proteins (4.30 -17 wt%) and other polysaccharides [11]. Polysaccharides are polymers of sugars that are potentially a source of fermentable sugars.

Due to the structure of lignocellulosic material, it is often challenging to get access to the cellulose and hemicellulose components without harsh treatment, whether it be chemical or physical treatment prior extraction. Pre-treatment is often required to break-down the lignin structure to give access to cellulose which is present in the form of microfibrils enfolded by hemicellulose and lignin fractions. While hemicellulose is composed of different monosaccharides, unlike cellulose which is built up of one structure [12]. There is emphasis placed on how crucial pre-treatment is due the lignocellulosic structure of biomass which has placed difficulty in the extraction of useful components. The hydrolysis of biomass further breaks down and releases the other components. With proposed effective methods known to decrease cell wall barriers being physiochemical, chemical, physical and biological treatment methods [13]. Conventional pre-treatment methods have pros and cons, which result in different products and product yields. However, these methods have been rendered effective. There is a challenge when it comes to waste disposal and the environmental damage it poses to nature [14].

With the idea of sustainability becoming more attractive over the years. There has been an unending need for innovation and green technology ideas that utilize raw materials more efficiently yet eliminate or minimise waste while avoiding the use of material that could be toxic to the environment and all life forms on earth. The major challenges with the use of green methods have been high production costs, poor efficiency, and lack of equipment availability for industrial-scale processing. However, through further investigations, these issues can be overcome, and new implementations would be put in place [15].

In this study, fermentable sugars were to be extracted from SCGs using 1-butyl-3-methylimidazolium chloride, an ionic liquid without any pre-treatment method. In recent years, for the past two decades, research has been done on ionic as they showed potential in being used as solvents, catalysts, lubricants, additives and so forth. They provide a large range of solvation properties as solvents due to their limitless combinations of cations and anions [16]. Ionic liquids have been deemed "green solvents of the future" because they are environmentally friendly in comparison to volatile organic compounds, non-flammable solvents that are designed for a specific purpose with unique solubility potential.

Recent studies have done a comparison study between protic and organic aprotic solvents; it was discovered that the majority of sugars were soluble in protic solvents as opposed to organic aprotic solvents, which inhibited their dissolution [17]. ILs containing an ether pendant substitute are called "sugar-phililic" since they establish a hydrogen bonds with the hydroxyl of the carbohydrate. Dicyanamide was one of the recognised anions that could dissolve carbohydrates based on its hydrogen acceptor properties [18, 19]. Imidazolium ionic liquids have been the most used for the treatment of wood, lignocellulose and cellulose. The above-mentioned are said to be all cationic and based on 1-alkyl-3-alkylimidazolium. Egorov et al., [20] discovered that BMIMCL could dissolve 56% fructose at a temperature of 110 °C. There is a growing interest in ILs, the widely used form of ILs are the water stable imidazolium cation-based which are said to be toxic. Whereas cholinium or amino acid cation-based IL have gained popularity due to their less toxic nature.

II. MATERIAL AND METHODS

The wet SCGs were collected from a local coffee shop (located in Berea, Durban, South Africa), the wet SCGs were dried in an oven for 24 h. Hydrous ethanol (96%) was used as an antisolvent, nitrogen gas to purge the reactor, 1-butyl-3-methylimidazolium chloride (99%), 1-ethyl-3-methylimidazolium acetate, 1-ally-3-methlimidazoluim chloride and high purity standards: D-cellobiose, D(+)

glucose, D(+)xylose, D (+)galactose, L(+)arabinose and D(+)mannose.

A. Characterisation of SCGs

SCGs were characterised according to the Technical Association of Pulp and Paper (TAPPI) method. SCGs (500g) were dried using an oven to a moisture content below 10 wt% on a wet basis. To attain the moisture content mentioned above, the wet SCGs were dried for 4 h at a temperature of 105 °C. Particle size distribution was done to the SCGs; they were subjected to screening using a series of screens mounted on a shaker for 5 min. SCGs with particle sizes less than 500 μm were used. Chemical characterisation was done to attain the SCGs composition in terms of ash, lignin, and carbohydrates. For the determination of ash content, 10g of dry SCGs were heated in a table top muffled kiln at 525 °C for 35 min. The white ash attained after heating was weighed using an analytical balance (TM-EXA5003H). Equation (1) was used to estimate the ash content of SCGs, where A is the weight of ash in (g), and B is the weight of dry SCGs (g).

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

Lignin fraction was determined with the use of acid hydrolysis. 2 wt% sulphuric acid solutions were used to dissolve 10 g of SCGs at a temperature of 200 °C for 20 min. The acid during hydrolysis solubilises the carbohydrates, while the lignin remains in its solid state, making it possible to filter out, dry and weigh. Equation (2) was used for lignin determination.

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

Where, m (g) is the mass of the dry filtrate and M (g) is the mass of dry SCGs used. This was done as per TAPPI standard, T 222 om-98 "Acid –Insoluble Lignin in Wood and Pulp". Carbohydrate fraction determination was attained using 17 wt% and 9.45 wt% sodium hydroxide solutions. 10 g of SCGS was used. The alpha cellulose in SCGS was determined using Equation (3).

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

Where V_1 is the titration of pulp filtrate (mL), V_2 is the blank titration (mL), N is the exact normality of the ferrous ammonium sulphate solution, A is the pulp filtrate volume used in oxidation (mL) and W is the oven-dry weight of the pulp specimen (g). The hemicellulose quantity was determined using equation (4). Where V_3 is the titrate volume of the solution after precipitation of beta-cellulose (mL), $V_4$is the blank titration volume (mL), N is the normality of ferrous ammonium sulphate solution, and W is the oven–dry weight of the pulp specimen (g).

B. Extraction of Sugars using the three different ionic liquids

The dried SCGs underwent hydrolysis reactions at various solvent ratios ranging from 5-15 mL IL/ g dry SCG. The reactor operated at temperature settings ranging from 55 to 205 °C with a reaction time ranging between 20-80 min. Fig.1 (a) below depicts the Parr reactor and experimental setup used to extract sugars from SCGs. The required reactor pressure for the duration of the reaction. When the reaction is done, the reactor is cooled by placing it in an ice bath.

The solution obtained from the reactor is viscous and dark, as depicted by Fig. 1 (b). Prior to filtration, hydrous ethanol (96 %) was utilised as an anti-solvent. The addition of the anti-solvent made solid-liquid separation via vacuum filtration possible.
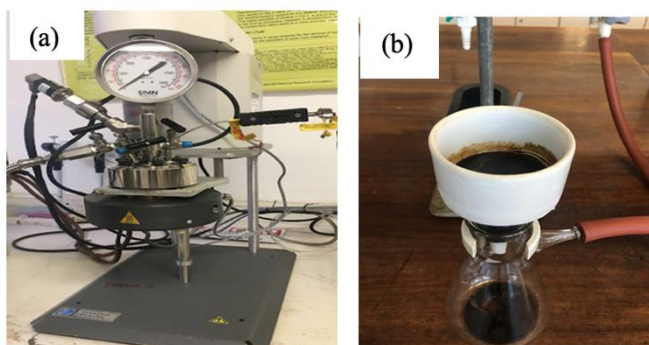

Fig. 1 (a) 200 mL Parr reactor with IL and SCGs reacting inside, (b) Vacuum filtration apparatus with SCG residue and the sugar containing filtrate at the bottom of the flask.

After vacuum filtration, the filtrate was a mixture of sugars, IL, and ethanol. The removal of ethanol from the mixture was achieved via vacuum distillation at a temperature of 83 °C. Fig. 2, depicts the vacuum distillation used to separate ethanol and IL from the mixture. The solution left after distillation contains mostly sugars with miniature traces of ethanol and 1-butyl-3-methylimidazolium chloride. The distillate was further analysed for sugars (arabinose, galactose, mannose, xylose, cellobiose and glucose) with the use of a High Performance LiquidChromatography (HPLC).

Fig. 2 Rotary evaporator with a sample being separated in terms of their relative boiling points.

The ethanol anti-solvent was the solution that was evaporated to confirm this. A drop test was done using 2 % chromate and acidified potassium dichromate. Fig.3 depicts the test conducted to check whether the solvent evaporated was ethanol or not.

Fig.3 Six test tubes were used to confirm that the solvent extracted via distillation is ethanol.

The first three test tubes on the left contain 96 % hydrous ethanol and the next three to the right contain the solvent evaporated from the rotary evaporator. The tubes on the far left and far right (the first and last tube from the left side of the rack /stand) were oxidised with two drops of 2% dichromate, and the colour changed from a colourless solution to a dark green colour. The second test tube on both ends was tested with two drops of acidic potassium dichromate. The solvent in both tubes turned from colourless to a light orange colour. Looking at the colour similarity in the tubes, this proved that the liquid/solvent extracted during distillation was indeed ethanol.

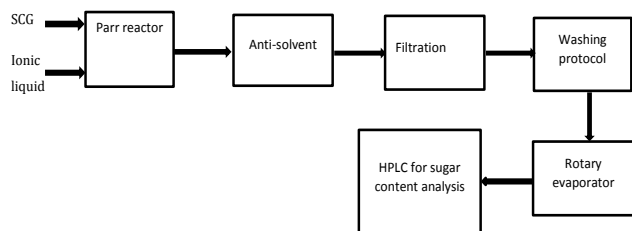### C. Sugar extraction procedure outline

Fig. 4 Process flow diagram for the extraction of sugars

III. SUGAR EXTRACTION OPTIMISATION FROM SCGs

In the 200ml Stainless steel 1.0011 g SCGs and 15 ml of 1-butyl-3-methylimidazolium chloride were heated/ reacted at a temperature of 165.6°C for a duration of 80 min. The Parr reactor (Parr, USA) equipped with a J thermocouple (iron-constantan), with a stirrer at 80 rpm, reactor pressure of 7 bar were set on the reactor panel. The Grant Instruments (Cambridge) Ltd water bath was turned on to cool the reactor transducer was turned on. Nitrogen gas cylinder was open to allow gas flow into the reactor, in-order to purge and maintain pressure within the Parr reactor.

Once the reaction duration was done, the reactor was placed in an ice bath to cool the outer and inner temperature of the cylindrical vessel. The solution in the reactor consisted of ionic liquids, sugars, SCG particles and other impurities; this was poured into a vial and temporally stored in the fridge prior to further processing and analysis.

The mixture in the vial was dark, viscous, and oily, and this posed a challenge when it came to filtration. Fig.5 displays the

dark colour and viscosity of the mixture from the Parr reactor prior vacuum filtration. 20 ml of hydrous ethanol (96% ethanol, 4% water) was added to the mixture to reduce the viscosity and enable vacuum filtration to take place. After the solid-liquid separation, the filtrate consisted of sugars, ionic liquid and ethanol. The ethanol and ionic liquid were separated from the mixture with the use of a rotary evaporator. Due to boiling point elevation, evaporation took place at a temperature setting of 83 °C. The distillate contained sugars, with miniature amounts of ethanol, ionic liquid, and other impurities. The distillate was then analysed with the use of a High Perf

Fig.5 Mixture from Parr reactor prior filtration, depicting the dark colour and viscosity of the mixture.

IV. EXPERIMENTAL DESIGN

In this investigation a Box-Behnken design (response surface methodology) was used to design the experiments. The experiments evaluated three variables namely, temperature, liquid–solid ratio and reaction time on the extraction of sugars from SCGs using three different ionic liquids namely,1-ethyl-3-methylimidazolium, 1-ally-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium chloride. The factors, parameter ranges and the upper value and lower values used to run the experiment using design expert software displayed by table I.

TABLE I displays the factors, parameter ranges, upper and lower values used to run the experiment on the design expert software.

Factor	Parameter	Range	Upper value	Lower value
Factor 1	Temperature (°C)	80 -180	180	80
Factor 2	Time (minutes)	20-80	80	20
Factor 3	Liquid-solid ratio (ml)	5-15	15	5

The SCGs and IL ratio ranged from 5-15 ml per gram SCG, reactor pressure was kept consistent for each run at 7 bar with stirring speed of 80 rpm set on the reactor panel. Grants Instruments (Cambridge) Ltd water bath was run to cool the transducer. Nitrogen gas from the gas cylinder was opened to purge and maintain pressure within the Parr reactor. The

statistical analysis was carried out using design expert software version 13.

V. PRODUCT ANALYSIS

Qualitative and quantitative analysis was performed with the use of High-Performance Liquid Chromatography (HPLC). The separation technique of this equipment involves the separation, identification and quantification of the components that are dissolved in the mixture. The equipment used was the SHIMADZU high-performance liquid chromatography (SHIMADZU, Japan), Bio-Rad Aminex HPX-87P with guard column with the following conditions: column refractive index detector- RID-20A, column temperature- 80 °C, mobile phase of water at a flow rate of 0.6ml/min, Injection volume 20 µL, column pump code Lc-20AB, column heater CTO-20A. Fig.6 displays the high-performance liquid chromatography apparatus in the laboratory located at Durban University of Technology (DUT), S10 level 5. The retention time for all the sugars to be eluted was 50 minutes per run. Sugars were eluted within 10 minutes of the run. Sucrose was eluted first in 10 min, 62 s, followed by glucose with a retention time of 12 min,5 s, xylose with a retention of 13 min, 5 s, galactose within 14 min, 36 s, an arabinose retention time of 15 min, 53 sc and lastly mannose which was eluted within 16 min and 25 s.

Fig.6 High Performance Liquid Chromatography apparatus in the laboratory located at DUT, S10 level5.

A. Response Surface Methodology (RSM) modelling procedure

The study's foundation is a three-level Box Behnken design (BBD) in response surface methodology, which determines the ideal circumstances for employing three distinct ionic liquids to extract sugars from SCGs. Version 13.0 of the Design Expert software was used to create experimental runs and optimize the procedure using the fewest possible experiments. Three factors influence the amount of sugar extracted: temperature (80-180°C), reaction time (20-80 min), and solid-to-liquid ratio (5-15 ml).

Optimization was done with reference to mannose since it was extracted in all runs using the various ionic liquids and it was more noticeable than the other sugars (sucrose, glucose, xylose, and arabinose). The three ionic liquids' performances

were tracked using the sugar that produced significant models as a guide. Given that all the sugars were present in the mixture solution, this extraction was successful.

B. Optimisation of extraction process variables

One of the objectives of this study was to optimize the operating conditions of the extraction process to improve the performance of solvents and maximize sugar yield. The software's numerical and graphical optimization was used to find the specific points that maximize the response desirability function. To optimise the three operating conditions, the numerical optimisation approach was used. This technique searches the entire design space using the designed models to find the best solution.

The objective functions are the model equations 7-9, with the three independent variables (response variables) serving as constraints. Table II shows the predicted model solutions at various operating conditions within the design space which were achieved using BBD. All input variables were within range, and the first option was selected as the optimum condition because it reflects a high efficiency for sugar yield. 1-ally-3-methylimidazolium chloride produced 2.484 g/g SCGs, 1-butyl-3-methylimidazolium chloride produced 0.669 g/g SCGs, and 1-ethyl-3-methylimidazolium acetate produced 1.988 g/g SCGs at 165.6 °C, 80 minutes, and a liquid-solid ratio of 15 mL, respectively, for each ionic liquid. The computer generated 66 solutions. In-order to verify the outcomes predicted by the software, a confirmatory run of experiments was carried out under ideal circumstances.

TABLE II *depicts the first ten predicted model solutions from a total of 66 solutions generated at different operating conditions* which were achieved using BBD.

No.	Temp.	Time	Liquid-Solid Ratio	Ally [AMIM Cl] (g/g SCGs)	Butyl [BMIM Cl] (g/g SCGs)	Ethyl [EMIMO Ac] (g/g SCGs)	Desirability	
1	165.643	80.000	15.000	2.484	0.669	1.988	0.276	Selected
2	166.035	80.000	15.000	2.495	0.669	1.977	0.276	
3	165.125	80.000	15.000	2.470	0.668	2.003	0.276	
0	166.802	80.000	15.000	2.517	0.671	1.955	0.276	
5	163.625	80.000	15.000	2.427	0.665	2.043	0.276	
6	168.287	80.000	15.000	2.558	0.673	1.909	0.275	
7	162.776	79.999	15.000	2.404	0.664	2.065	0.275	
8	169.982	80.000	15.000	2.606	0.676	1.855	0.275	
9	165.261	80.000	14.961	2.471	0.667	1.984	0.275	
10	170.791	80.000	15.000	2.629	0.678	1.827	0.275	

VI. RESULTS AND DISCUSSION

A. Compositional Analysis of Spent Coffee Grounds

The SCGs contained ash (13.12 %), carbohydrates (33-73 %) and lignin (23.12%) which are in agreement with results reported by [21].

B. Analysis of variance (ANOVA) for models validation

The response models were assessed using ANOVA in -order to determine the important factors that were fitted to the models. After setting the conditions within the range and aiming to maximize the output at a 95% confidence level, 66 solutions with a desirability of 0.276—roughly 28%—were found.

The models had four degrees of freedom, a 5% significance level, and a 95% confidence level. It was discovered that the values given below—sum of squares (regression sum), AP (adequate precision), F-values (Fisher variation), P-values (probability), and LOF (lack of fit)—were all within the ranges that were established to determine the significance of the models.

Model terms are considered strongly significant when the P-value is less than 0.05, and the models are considered slightly significant when the value falls between 0.05 and 0.1. They produce a good prediction, are hierarchy terms, and make the model significant. P-values less than 0.0001 indicate a good fit between the experimental data and the regression model equations.

When one or more terms in the model are present but do not significantly affect the model because of noise or pure error, the LOF values greater than 0.05 indicate this. Quadratic terms of models that were found to be partially significant arise when P-values exceed 0.1 (Design Expert, 2017). The adjusted determination (R^2) and predicted determination (R^2) of the regression coefficient were used to evaluate the model's performance. The R^2 measure, which went from 0 to 1, indicated how well the experimental data fit the models. A value of 0 meant no fit. A correlation exists among the data. The straight line depicted in fig.7 (A, B and C) fits the data quite well, and all the R^2 values were found to be near 1.

For 1-ally-3methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride, and 1-ethyl-3-methylimdazolium acetate, the corresponding R^2 values were found to be 0.5836, 0.9189, and 0.8770. It is better to have a large value greater than 0.05 for Prob > F for LOF. A reasonable relationship with adjusted R^2 is essential, as is a high R^2 value. Since the acceptable precision, also referred to as the signal-to-noise ratio, was greater than 4, the model would perform reasonably well in predictions. These were the ratios. The values of 1-ally-3methylimidazolium chloride are 7.2297, 1-butyl-3methylimidazolium chloride is 12.7913, and 1-ethyl-3methylimidazolium acetate is 10.0423. The P-values for 1-ally-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride and 1-ethyl-3-methylimidazolium acetate are 0.0235 ,0.0003 and 0.0172 respectively.
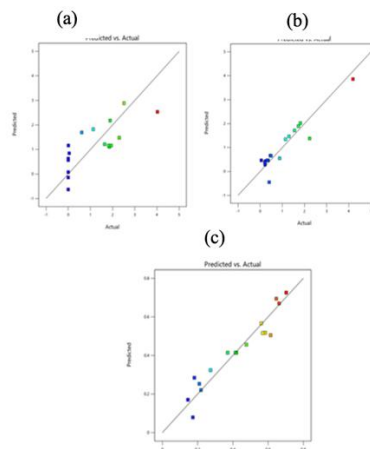

Fig .7 Diagnostic plots displaying the predicted versus actual values, to assist in evaluating whether the model is satisfactory or not for when using (a) AMIMCl , (b) BMIMCl and (c) EMIMAc as a solvent to extract sugars from spent coffee grounds.

C. Sugar yield attained during confirmatory run.

(a)

Fig. 8 represents the confirmatory run conducted using optimum extraction conditions, a temperature of 165.6 °C, a reaction time 80 minutes and a liquid-solid ratio 15mL. Sugar yield done using mannose as the reference sugar since it's the most prominent sugar and its present in all runs.

Fig.8 represents the actual and predicted yield acquired using the three different ionic liquids under optimised conditions according to the RSM. The sugar yield from the confirmatory run and the sugar yield from the predicted runs that were optimized using the Box-Behnken design (BBD) are shown in the graph above. The actual run produced a value of 0.5759 (g/1g SCGs), which was less than the predicted yield of 2.485 (g/1g SCGs) for sugar using AMIMCl as a solvent. which is 1.9091 (g/1g SCGs), less than the run that was anticipated.

The predicted yield value of 0.669 (g/g SCGs) when using BMIMCl as the extraction solvent is significantly higher than the confirmatory run yield of 0.5402 (g/g SCGs), with a difference of 0.1288 (g/g SCGs). The real yield value of 0.1072 (g/1g SCGs) when reacting with EMIMOAc is lower than the software-predicted value of 1.988 (g/1g SCGs). With a difference of 1.8808 (g/ 1g SCGs), the two values are highly gapped apart.

The gap between the actual and predicted values is due to the analysis of variance (ANOVA), for 1-ally-3-methylimidazoluim the lack of fit was not significant in relation to the pure error, according to the lack of fit F-value of 0.63. A large lack-of-fit F-value had a 74.98% probability of being caused by noise. The absence of significant misfit was favourable since a model's fit is what matters most. Compared to the adjusted R^2 value of 0.4448, which was expected, the predicted R^2 value of 0.1389 was not as close. They diverge by more than 0.2. This might be a sign of a significant block effect or a potential issue with the data or model. Confirmation runs were used to test each empirical model.

When working with 1-butyl-3-methylimidazolium chloride, given the pure error, the lack-of-fit, with an F-value of 9.18, suggests that the lack-of-fit is not significant. A large lack-of-fit F-value has a 10.17% probability of being caused by noise. A non-significant lack-of-fit was good. It is pivotal to ensure the model fit. There was a reasonable degree of agreement between the adjusted R^2 of 0.8558 and the predicted R^2 of 0.6646. They differed from one another by less than 0.2. The experimental signal to noise ratio is measured by the term Adequate Precision (AP) [22]. For 1-ethyl-3-methylimidazolium acetate, the large lack of fit, as indicated by the F-value of 15.43, suggests that there was a 6.20% possibility that noise was the cause of the misfit. This was a poor fit, and the low probability (<10%) raised some red flags. An adverse figure, the predicted R^2, suggested that rather than the current model, the overall mean might be a more accurate predictor of the response. In certain situations, a higher order could also provide a better prediction.

D. Solvent selection

The performance and effectiveness of the ionic liquid in terms of sugar extraction and yield quantity are as follows: 1-ally-3-methylimidazolium chloride is the most performing solvent, followed by 1-ethyl-3-methylimdazolium acetate, and 1-butyl-3-methylimidazolium chloride. The micrographs obtained using the Tescan MIRA3 RISE Scanning Electron Microscope (SEM) show the morphology of SCGs before and after extraction using the three ionic liquids at a 10 X magnification.
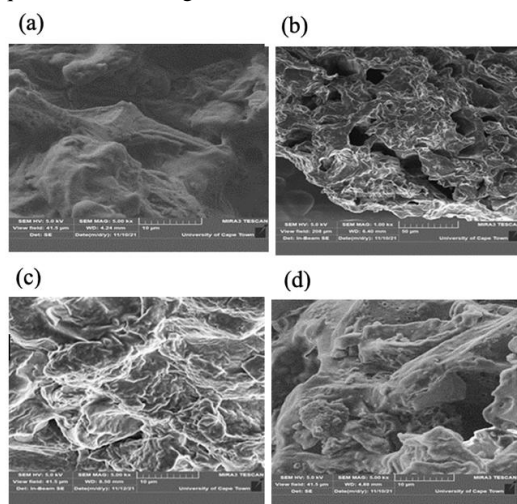

(a)   (b)

(c)   (d)

Fig.9 Micrograph of SCGs before extraction or exposure to IL (a); micrograph of SCGs after sugar extraction using 1-ally-3-methylmdazolium chloride (b); micrograph of SCGs after sugar extraction using 1-butyl-3-methylimidazolium chloride (c); and micrograph of SCGs after sugar extraction using 1-ethyl-3-methylimidazolium acetate (d).

Fig.9 micrograph (a), the SCGs morphology is lumpy, with a smooth surface, this prior exposure to the IL solvents. The morphology in Fig.9 (b), (c) and (d) has a rough surface, indicating that there has been an aggressive interaction between the IL and the SCG. The surface has holes/ it's perforated, indicating that the IL did penetrate and break the cell wall (lignocellulosic structure) to it, and sugar was extracted. The white surface in Fig. 9 (b) and (c) depicts the oil in the sample. The above images emphasized the deduction of 1-ally-3-methylimidazolium chloride being the most performing IL; looking at micrograph B, the surface of the SCG has been aggressively interacted with, and the holes on the surface are bigger compared to fig.9 (c) and (d) which have smaller perforations on the exterior.

VII. CONCLUSION

Solvent performance due to sugar extraction quantity of the IL ascended in the following order, AMIMCl > EMIMOAc > BMIMCl. AMIMCl extracted the highest quantity of sugar, all five sugars were eluted but lacked variety per run. EMIMOAc extracted mostly mannose the other sugars were very minute to be quantified. There was a lack of variety per run, but looking at quantity, it had a higher sugar quantity as compared to BMIMCl. BMIMCL had a lower sugar yield compared to the other solvents but had the best performance in terms of sugar variety per run, as all five sugars were extracted, including xylose (according to literature, xylose is hardly detectable or extracted), which was not extracted by the other two solvents.

All three parameters influence the quantity of sugars extracted. When temperature increases with increasing reaction time in the presence of sufficient/increasing liquid-solid ratio, this causes an increase on sugar extraction. Extract increases due to sufficient solvent coating each granule of SCGs, thus maximising extraction with increasing temperature and reaction time. Keep in mind that temperature must be closely monitored to prevent it from increasing to a point that causes the sugar monomers to denature.

Optimum extraction conditions were as follows: Temperature at 165,6°C, reaction time at 80 minutes, and liquid-solid ratio of 15 mL. All play a pivotal role in the extraction of sugars, especially temperature and reaction time. I recommend that further studies be done on the extraction of fermentable sugars from SCGs without any form of pretreatment. Limitations in the study were the application of the extracted sugar, and further studies should utilise the extracted sugars (mannose) to produce lactic acid and hydrocarbons. The recycling and reuse of ionic liquids is encouraged for the reduction of cost and waste minimization.

The commercialisation of sugar extraction, specifically mannose for lactic acid production, is possible based on the amount of mannose extracted. Feasibility studies and waste management strategies should be conducted and explored prior to commercialisation.

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