

An integrated biorefinery approach based on spent coffee grounds valorization

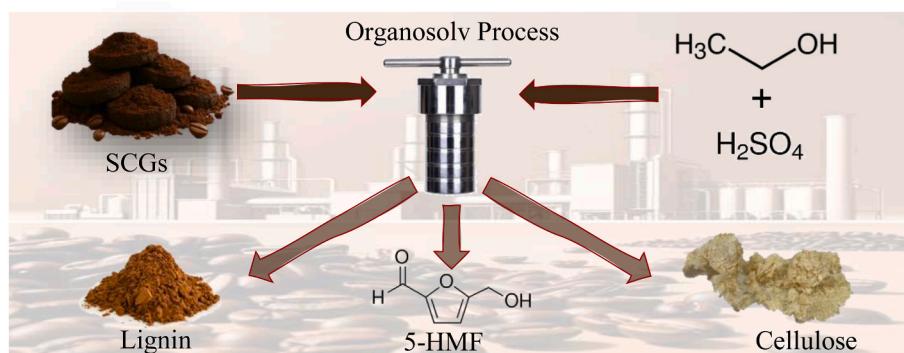
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GRAPHICAL ABSTRACT



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ABSTRACT

Spent coffee grounds (SCGs) are an abundant lignocellulosic biomass with significant potential for industrial valorization, with great social and environmental benefits, due to their rich composition in cellulose, hemicellulose and lignin. In this study, the organosolv process, a method widely used in the paper industry, was employed to efficiently fractionate SCGs into their primary components. Hemicellulosic liquors containing up to 25 wt% sugars, predominantly galactose and mannose, were successfully extracted and subsequently dehydrated to produce 5-hydroxymethylfurfural (5-HMF), reaching a maximum yield of 90 % within 15 min of reaction time. The residual cellulose and lignin fractions were characterized by X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR), confirming their effective separation. These findings highlight the viability of SCGs as a sustainable feedstock for biorefinery applications, contributing to waste valorization and the development of a circular economy.

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1. Introduction

Over the past few decades, the global demand for energy has increased sharply, primarily driven by rapid industrialization, technological advancement, and population growth. This surge in development has led to a heavy reliance on fossil fuels as the dominant energy source, resulting in significant environmental concerns such as greenhouse gas emissions, climate change, and resource depletion. As awareness of these challenges grows, there is a pressing need to transition toward more sustainable and renewable alternatives (Achakulwisut et al., 2023; Yi et al., 2023). Among various strategies, the valorization of lignocellulosic biomass, especially agricultural and food industry residues, has emerged as a promising pathway for the production of bio-based chemicals and fuels. In this context, spent coffee grounds (SCGs), a widely available and underutilized waste material, present a valuable feedstock for biorefinery applications due to their rich chemical composition and high annual generation worldwide.

Coffee is among the most widely consumed beverages globally, and its production generates vast quantities of waste biomass. One of the most significant by-products of this industry is SCGs, with an estimated global annual output of approximately 60 million tons. This substantial volume not only poses environmental challenges due to improper disposal but also represents an underexploited resource with considerable valorization potential (Forcina et al., 2023; Luo et al., 2023). SCGs generally contain approximately 15–24 wt% cellulose, 25–37 wt% hemicellulose and the 14–30 wt% lignin (Atabani et al., 2018, 2022; Ballesteros et al., 2014; Luo et al., 2023; Mussatto et al., 2011). Therefore, SCGs offer a unique opportunity for integration into biorefinery models aimed at producing a broad spectrum of high value-added chemicals and materials. Leveraging SCGs as a feedstock could contribute to the development of sustainable technologies for the production of biofuels, platform chemicals like 5-hydroxymethylfurfural (5-HMF), and other bio-based products. As such, SCGs stand out as a viable and promising candidate for establishing efficient, low-cost, and environmentally friendly biorefinery systems that align with circular economy principles and waste reduction goals.

Cellulose is a polymer of glucose units linked by β -1,4-glucosidic bonds, forming natural crystalline structures. Its physicochemical properties allow its use in adsorbent materials, activated carbons, and for producing platform molecules like 5-HMF through glucose dehydration. 5-HMF can be further converted into compounds such as 2,5-furandicarboxylic acid, levulinic acid, and 1,6-hexanediol. Additionally, cellulose's chemical inertness and biocompatibility make it a common excipient in pharmaceuticals, serving as a filler or binder in tablets and formulations (Aziz et al., 2022; Du et al., 2023; Etale et al., 2023; Ganje et al., 2024; Jeong, 2022; Jin Cho et al., 2022; Park et al., 2022; W. Liu et al., 2022).

In addition, cellulose is chemically inert and biocompatible structure makes it a widely utilized excipient in the pharmaceutical industry, where it serves as a filler or binder in various tablets and medicinal formulations and nanocellulose formulations (Chandel et al., 2023; Pradeep et al., 2022; Shokri et al., 2013; Phanthong et al., 2018; Zhang et al., 2021; Zhu et al., 2022).

The hemicellulosic fraction of SCGs is mainly composed of galacto-gluco-mannan and gluco-mannan, with glucose, galactose and mannose as the main carbohydrates. It also contains small amounts of C₅ sugars, such as arabinose and, in some cases, xylose (Jin Cho et al., 2022; Kondamudi et al., 2008; Kovalcik et al., 2018). The abundance of C₅ sugars underscores their suitability for the production of 5-HMF, with well-established applications in the synthesis of bio-based fuels and value-added chemicals (Chen et al., 2025).

The lignin present in SCGs is composed of polyphenol-derived monomeric units, characterized by structural modifications involving functional groups such as methoxyl and carbonyl groups. Due to its complex aromatic structure and functional versatility, lignin holds significant potential for a wide array of applications, including the

production of biofuels, advanced carbon materials, and filaments for 3D printing technologies (Ballesteros et al., 2014; Kovalcik et al., 2018; Lage-Rivera et al., 2024; Leynaud Kieffer Curran et al., 2022).

SCGs can be also used for the preparation of different inorganic materials, such as heterogeneous catalysts based on metal particles, bioactive products with microbial activity and even biodiesel from the lipid fraction of SCGs (Andrade et al., 2022; Battista et al., 2020; Cho et al., 2016; Nguyen et al., 2019). Lipid extraction is a crucial preliminary step prior to the separation of lignocellulosic components, commonly carried out using conventional methods, such as Soxhlet extraction, air-carried evaporating separation (ACES), hydrothermal treatment, or even cell disruption techniques. These approaches facilitate the breakdown of cell wall structures, thereby improving the efficiency and yield of lipid extraction (Ramluckan et al., 2014; Vera et al., 2022; Yu et al., 2024). Implementing mechanochemical extraction with solvents could further enhance yields by partially or completely breaking down cell walls, increasing the surface area for extraction. This system is considered a green technology and can thus contribute to the circular economy and green chemistry (Rincón et al., 2019; K. Wu et al., 2017).

An alternative for biomass valorization is the organosolv process, introduced in the 1970s as a solution to the environmental issues faced by the paper industry in the pulp purification using conventional Kraft and sulfite method. This process takes advantage of the different chemical properties of cellulose and lignin to separate and purify them (Duff and Murray, 1996; Kurt Wagemann - Nils Tippkötter, 2019; Vera et al., 2022). The organosolv process has unique advantages. The use of organic solvents such as ethanol, methanol, acetone or tetrahydrofuran (THF), together with an acidic aqueous phase, changes the polarity of the medium, promoting the dissociation of structures formed between lignin and carbohydrates, resulting in their separation. A significant advantage of the organosolv process lies in its capacity to selectively solubilize lignin in the organic fraction, while preserving cellulose and hemicellulose as solid residues. Upon the addition of water, dissolved lignin precipitates, allowing for its straightforward physical recovery from holocellulose. Compared to conventional methods, organosolv processing generates fewer toxic by-products and yields high-purity lignin, which can be utilized in diverse high-value applications, including the production of bio-based chemicals, advanced materials, and polymers. Furthermore, the process conditions and choice of solvent can be tailored to optimize the extraction and quality of cellulose and hemicellulose, making this approach highly versatile. (Bozell et al., 2011; Hamzah et al., 2020; Thoresen et al., 2020).

Cellulose obtained by organosolv process is easier to purify, which is important in the paper industry, as a solution to the environmental problems associated with pulp bleaching, and, in the chemical industry, as high-purity starting materials are often required. In addition, cellulose produced this way exhibits better bleaching properties and viscosity retention capacity compared to cellulose obtained by conventional Kraft or soda processes (Cronlund and Powers, 1992; Shatalov and Pereira, 2007).

To develop more sustainable and efficient biomass fractionation methodologies, particularly for SCGs, the present research is focused on the application of the organosolv process in combination with green solvents, such as bioethanol and water. This integrated approach aims to enhance the selective recovery of primary components, including cellulose and hemicellulose, while also facilitating the production of valuable chemicals, such as 5-hydroxymethylfurfural (5-HMF) and furfural.

The objective of this work is the valorization of SCGs by exploring a pathway not previously studied for this type of biomass, namely the organosolv process. This study focuses on the separation of the different fractions that compose SCGs, as well as on their valorization and characterization.

2. Materials and methods

2.1. Reactants

γ -Al₂O₃ and CaCl₂ were supplied by Alfa Aesar and VWR respectively. Cellulose Sigma-Aldrich (Quality Level: 200, fibers and particle size medium). Glucose, galactose, mannose, arabinose, 5-HMF and furfural were also obtained from Sigma-Aldrich (>99 %). Absolute ethanol (99 %), isopropanol (99 %) and H₂SO₄ (98 %) were supplied by VWR Chemicals.

2.2. SCGs fractionation

2.2.1. Preparation of spent coffee grounds without extractables (SCGs_E)

SCGs was obtained using an Italian coffee machine in the laboratory, using a mix of Arabica and Robusta coffee, then being dried at 70 °C h for 24 h.

The extraction process was carried out using a semi-continuous flow mechanochemical reactor, DYNOMILL RESEARCH LAB (RL), equipped with yttrium-doped ZrO₂ microbeads. Isopropanol was chosen as the extraction solvent, and the experimental parameters were as follows: 55 °C, 1 h, 10 ml isopropanol/g SCGs, and micro-beads size of 1 mm. After the mechanochemical treatment, the resulting emulsion was centrifuged to separate the liquid with the extractables from the solid, which was washed with isopropanol and dried for 24 h at 70 °C. This SCGs without extractables, obtained by mechanochemical extraction, is referred to as SCGs_E (Pérez-Merchán et al., 2025).

2.2.2. Organosolv process

The organosolv process was performed by mixing 5 g of SCGs_E with 50 ml of an ethanol/H₂O mixture (ranging from 20 to 60 vol% ethanol), in the presence of 1 wt% H₂SO₄. The mixture was placed in a 100 ml hydrothermal reactor (Parr instrument), which was heated in an aluminium block at different temperatures, from 140 to 210 °C and different times, from 1 to 3 h, at 1000 rpm, following the Box-Behnken design generated using the Statgraphics programme (see Table 1). After the different treatments, the mixtures were vacuum filtered. The resulting solid, SCGs_CEL (mainly composed of cellulose), was washed with approximately 50 ml of the ethanol/H₂O in the same proportion used in the organosolv treatment and dried for 24 h at 70 °C. The cellulose fraction was determined gravimetrically, taking into account the proportion of SCGs used in the process. The liquor, containing hemicellulose and lignin, was labelled as Liquor_HEMLIG. Subsequently, water was added to the Liquor_HEMLIG in a 5:45 liquor:water volume ratio, causing the lignin to precipitate after 10 min, while the remaining

liquid, called Liquor_HEM, contained mainly hemicellulose. The precipitated lignin (SCGs_LIG) was vacuum filtered, washed with about 10 ml of water and dried for 24 h at 70 °C. The lignin fraction was determined gravimetrically, taking into account the proportion of SCGs used in the process. Fig. 1 shows a simple scheme of the SCGs fractionation process previously described.

To determine the total amount of carbohydrates in the hemicellulosic liquor, this was subjected to acid hydrolysis, by concentrating the solution to 4 wt% H₂SO₄ and heated to 100 °C for 1 h at 450 rpm in a round-bottom flask equipped with a condenser. These liquors were denoted as Liquor_HEM_AH.

2.3. Catalytic dehydration of hemicellulosic liquors

The Liquor_HEM obtained under optimal conditions was used for the production of 5-HMF and furfural by dehydration of C₆ and C₅ monomers, respectively. Various CaCl₂ concentrations, ranging from 0.22 to 0.05 g CaCl₂/ml liquor, were tested, along with 0.05 g γ -Al₂O₃ as acid catalyst, 5 ml Liquor_HEM, at 180 °C, 450 rpm, with reaction times from 5 to 60 min. In addition, under similar experimental conditions, the reaction was carried out without catalyst and without CaCl₂. These reactions were conducted in different batch reactors (15 ml, Ace), placed inside aluminium blocks at the desired temperature. Samples were analyzed by high-performance liquid chromatography (HPLC), using a JASCO equipment, by injecting 6 μ L samples with an auto-injector (AS-2055) from a vial. For the aqueous mobile phase, 0.0025 M H₂SO₄ in deionized water was microfiltered, degassed and delivered by a quaternary gradient pump (PU-2089) at a flow rate of 0.35 ml/min through a Phenomenex Rezex ROA Organic Acid (8 %) column (300 mm × 7.8 mm, 5 μ m). This column, housed in an oven (co-2065) at 40 °C, separated the analytes, which were detected by a UV-visible detector (MD-2015) for analysing the aromatic compounds, and a universal refractive index detector (RI-2031 PLUS) for identifying and quantifying the rest of analytes.

Conversion, selectivity and yield were calculated as follows:

$$\text{Conversion}_Y = ((\text{mol}_{\text{initial}Y} - \text{mol}_{\text{final}Y}) / \text{mol}_{\text{initial}Y}) \cdot 100 \quad (1)$$

$$\text{Selectivity}_X = (\text{mol}_{\text{final}X} / (\text{mol}_{\text{initial}Y} - \text{mol}_{\text{final}Y})) \cdot 100 \quad (2)$$

$$\text{Yield}_X = (\text{Selectivity}_X \cdot \text{Conversion}_Y) / 100 \quad (3)$$

where Y refers to the initial feedstock (5-HMF or glucose as indicated in each experiment) and X refers to the products and intermediates resulting from the feedstock transformation.

2.4. Characterization techniques

Cellulose and lignin were characterized by FTIR spectroscopy and X-ray diffraction (XRD). FTIR spectra of SCGs_LIG and SCGs_CEL were recorded using a Bruker Vortex70 spectrophotometer with a Golden Gate Single Reflection Diamond ATR system, taking air samples without the need to scatter or treat them. For the acquisition of the spectra, a standard spectral resolution of 4 cm⁻¹ across the 4000–500 cm⁻¹ spectral range, using 64 accumulations.

Powder XRD patterns were enregistered on a Philips EMPYREAN automated diffractometer using Cu K_{α1,2} (1,5406 Å) and a PIX cel detector. Divergence and anti-divergence slits were fixed at 1/4° and 1/2° Soller slits, respectively, for incident and refracted rays were employed at 0.04 rad. Measures were taken from 5 to 80° (2θ) for approximately 30 min with a step size of 0.0167°. The X-ray tube voltage employed was 45 kV with a current of 40 mA. The sample was continuously rotated to improve particle statistics.

Table 1
Experimental conditions studied for the organosolv process Box-Behnken DOE.

| Experiment | Temperature (°C) | Time (min) | Vol. % Ethanol |
|------------|------------------|------------|----------------|
| OS1 | 185 | 120 | 40 |
| OS2 | 185 | 180 | 60 |
| OS3 | 160 | 120 | 20 |
| OS4 | 210 | 180 | 40 |
| OS5 | 210 | 120 | 60 |
| OS6 | 160 | 120 | 60 |
| OS7 | 210 | 120 | 20 |
| OS8 | 185 | 120 | 40 |
| OS9 | 210 | 60 | 40 |
| OS10 | 160 | 60 | 40 |
| OS11 | 185 | 60 | 60 |
| OS12 | 185 | 180 | 20 |
| OS13 | 185 | 60 | 20 |
| OS14 | 160 | 180 | 40 |
| OS15 | 185 | 120 | 40 |
| OS16 | 140 | 120 | 20 |
| OS17 | 140 | 180 | 40 |
| OS18 | 140 | 120 | 60 |
| OS19 | 140 | 60 | 40 |

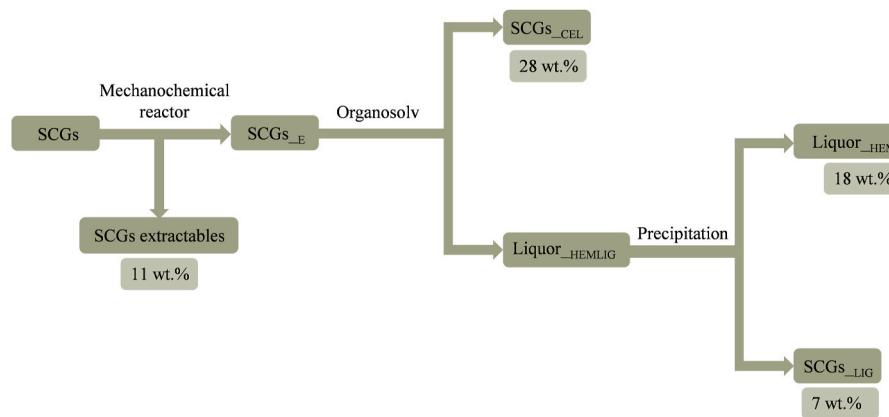


Fig. 1. Simple scheme of SCGs fractionation.

3. Results and discussion

3.1. Preparation of spent coffee grounds without extractables (SCGs_E)

Mechanochemical extraction of soluble components from SCGs resulted in a $11 \pm 1\%$ yield, close to the 15 % extractable content of SCGs, as determined by conventional Soxhlet method. This corresponds to an extraction efficiency of 73 %, highlighting the effectiveness of the mechanochemical process. Moreover, in most experiments, up to 75 % of the solvent used was successfully recovered, contributing to the sustainability and cost-effectiveness of this mechanochemical method.

Compared with conventional Soxhlet extraction method following TAPPI standards, which typically requires 6 h (amounting to roughly 20 siphon cycles depending on the solvent used) at the solvent's reflux

temperature, the mechanochemical process used in this study, previously optimized by Pérez Merchan et al. substantially reduces the extraction conditions to only 1 h at 55 °C. This represents a significant decrease not only in temperature but, more notably, a 5-h reduction in extraction time. Both processes require a similar drying stage, which is carried out in an oven at 70 °C. These improvements highlight the advantages of mechanochemical extraction for industrial application, including greater efficiency, lower energy demands, and shorter processing times (Luque de Castro and Priego-Capote, 2010; Pedras et al., 2019; Pérez-Merchán et al., 2025; TAPPI Standards: Regulations and Style Guidelines, 2018; K. Wu et al., 2017).

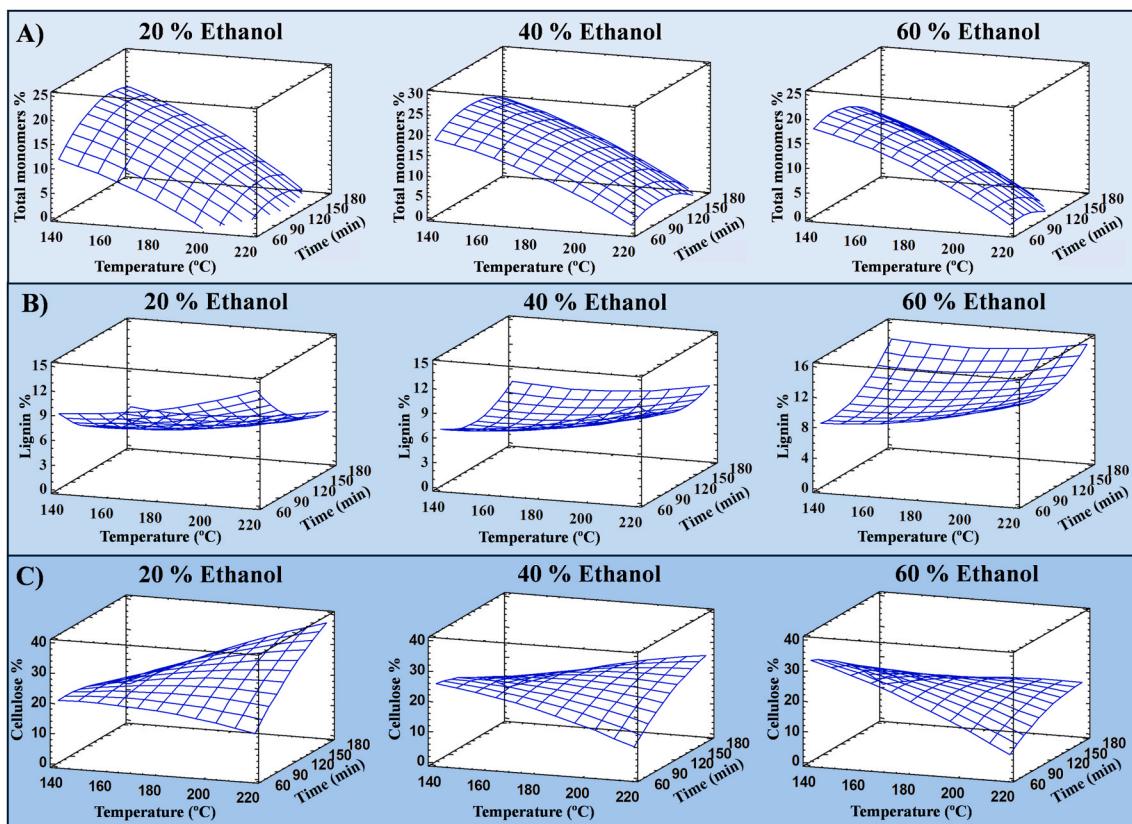


Fig. 2. Surface response curves as a function of ethanol percentage, temperature and reaction time: A) Total monomers in solution (%), B) Lignin recovered (%), and C) Cellulose recovered (%).

3.2. Hemicellulosic liquors from organosolv process

To optimize organosolv process for maximizing monosaccharide content in the hemicellulosic liquor, a series of experiments was designed using the Statgraphics program. Table 1 outlines the conditions (temperature, reaction time and ethanol percentage), and the monosaccharide contents in the hemicellulosic liquors are shown in Fig. 2A. In addition, the composition in s monosaccharide, cellulose (SCGs_CEL) and lignin (SCGs_LIG) obtained after fractionating SCGs_E through the organosolv process, under different experimental conditions, are shown in Fig. 2B and C, respectively.

To contextualize the selected temperature ranges, reaction times, and ethanol concentrations, these parameters were established based on a comprehensive review of methodologies applied to SCGs. Initially, a broad temperature range was systematically examined to evaluate its impact on hemicellulose hydrolysis efficiency and lignin solubility dynamics. Concurrently, ethanol concentration gradients were analyzed to monitor lignin dissolution in the reaction medium, a critical factor for its subsequent precipitation. Finally, time intervals were optimized using empirical data from prior studies to balance reaction kinetics with product yield (Bartolucci et al., 2024; Ravindran et al., 2018; Schulze et al., 2016; Sun et al., 2023).

The main monosaccharides present in Liquor_HEM are C₆ sugars, mainly galactose and mannose. Minor quantities of glucose and arabinose, C₅ and C₆ sugars respectively, are present, but with very low concentrations (see Table 1 in supplementary material). The content of monosaccharides of these liquors is high, reaching a maximum of approximately 17 %. However, oligomeric carbohydrates are not detected by HPLC, being necessary an acid hydrolysis treatment to convert them into detectable monomers (Fúnez-Núñez et al., 2020).

As shown in the response surface plots in Fig. 2A, treatment temperature is a critical parameter influencing monosaccharide yield. The surface curves clearly indicate that as the temperature increases, the content of monosaccharides in solution decreases significantly, reaching values as low as approximately 2 %. This reduction is attributable to the thermal degradation of sugars, which leads to the formation of by-products such as acetic, lactic, and formic acids. Notably, galactose exhibits a higher susceptibility to degradation, as evidenced by a pronounced decline in its concentration at higher temperatures (D. Liu et al., 2021; Y. Liu et al., 2020; Y. Shi et al., 2012).

However, temperature is not the only factor influencing the hydrolysis of hemicellulose from SCGs to produce dissolved monomers; there is also a clear synergy among the experimental variables, as demonstrated by the response surface curves (Fig. 2A). This behavior is directly related to the ethanol concentration and reaction time, with the optimal temperature identified as 140 °C. Increasing the ethanol percentage in the solution enables the maximum monosaccharide yield to be achieved in a shorter reaction time. This is evidenced by the response surface slopes approaching zero, indicating the point of maximum yield for this specific temperature.

Increasing reaction time does not significantly improve the sugar yield but does increase lignin content (SCGs_LIG) (Arauzo et al., 2020; D. Liu et al., 2021). The lignin recovery percentages reveal noteworthy trends regarding the interplay among the three variables studied (Fig. 2B). At low ethanol concentrations, the response surface curves indicate a tendency for lignin to undergo degradation over time, with temperature playing a relatively minor role in this process. This suggests that the use of organic solvents helps protect lignin from degradation or hydrolysis. However, as the ethanol concentration increases, a clear effect on reaction time is observed, resulting in higher lignin recovery percentages. This implies that a higher ethanol content facilitates lignin solubilization over time, whereas at low ethanol concentrations, not all lignin is protected and it is progressively degraded as the reaction proceeds (Dionísio et al., 2021; Hamzah et al., 2020; Yuan et al., 2021).

Finally, cellulose exhibits the opposite behavior to lignin (Fig. 2C). An increase in ethanol concentration has a pronounced negative impact

on cellulose recovery, as the amount of cellulose obtained decreases with higher ethanol percentages and over time when more ethanol is present. Moreover, all three variables, ethanol concentration, temperature, and reaction time, are important. In addition to the previously mentioned effects, ethanol appears to exert a contrary effect on cellulose compared to lignin: rather than protecting it, ethanol facilitates its degradation, especially at elevated temperatures.

The selected experimental conditions (OS19) for the organosolv process were 140 °C, 60 min and 40 vol % ethanol, were determined through the optimization of the response surface equation in relation to the monosaccharide yields, as simultaneous optimization of all three parameters was not feasible. These conditions were selected due to the high yield of sugars achieved at relatively low temperatures and short reaction times, which subsequently facilitates their valorization into 5-HMF. Although the recovery percentages of lignin and cellulose are not at their maximum under these conditions, they remain sufficiently high to allow for their further valorization into other products of significant industrial interest.

The resulting Liquor_HEM contains 18 ± 1 and 22 ± 1 g monosaccharides/100 g SCGs_E, before and after acid hydrolysis, respectively, corresponding to 0.01 g galactose-mannose and 0.0025 g arabinose per ml of Liquor_HEM. Fig. 3 shows the chromatogram of liquor OS19, where the peaks corresponding to H₂SO₄, galactose, arabinose, degradation products and the solvent are clearly identified.

3.3. Catalytic tests: 5-HMF and furfural production

To valorize the sugars, present in the selected hemicellulosic liquor, their dehydration to produce furan compounds was carried out using experimental conditions similar to those reported by Funez Nuñez et al. (Fúnez-Núñez et al., 2020). Figs. 4 and 5 exhibit the furfural and 5-HMF yields as a function of reaction time, after adding different amounts of CaCl₂, whose presence has been demonstrated to improve the yields of furfural and 5-HMF from C₅ and C₆ carbohydrates, respectively (Fúnez-Núñez et al., 2019).

Furfural yields attained a maximum value of 50 %. These results are promising, as they allow to valorize at least 50 % of the arabinose content. It must be considered that furfural tends to degrade in an aqueous medium, which in most cases requires the use of a biphasic water:organic solvent medium to continuously extract it in the organic phase where it is stabilized (Lin et al., 2021; Morais et al., 2021; Xia et al., 2023).

Conversely, the predominant sugars in the liquor, galactose and mannose, both C₆ monosaccharides, are susceptible to dehydration,

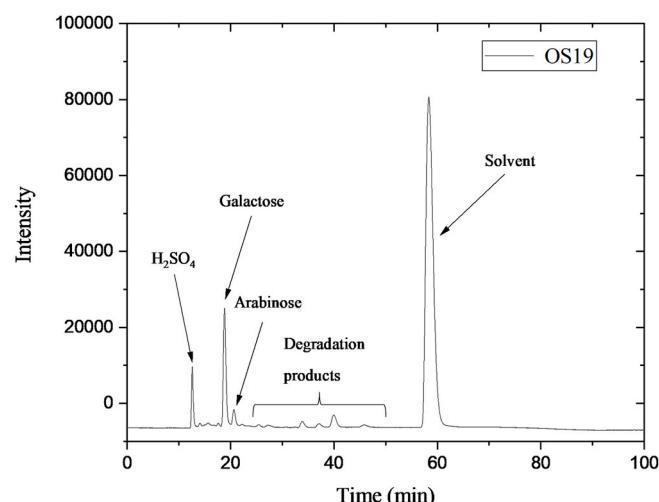


Fig. 3. Chromatogram (Index refraction) of the Liquor_HEM obtained organosolv process under at 140 °C, 60 min and 40 % ethanol (OS19).

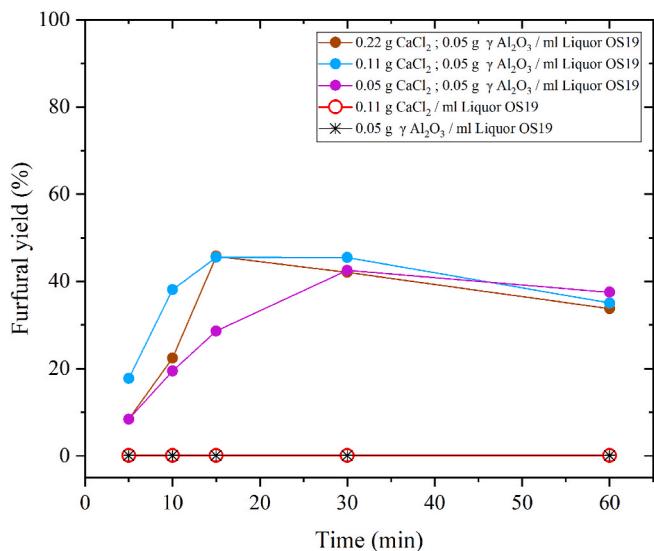


Fig. 4. Furfural yield vs reaction time with varying amounts of CaCl_2 in the dehydration of Liquor_HEM obtained under OS19 conditions. Dehydration conditions: batch reactor, 5 ml liquor, 180 °C, 0,05 g $\gamma\text{-Al}_2\text{O}_3$, 450 rpm.

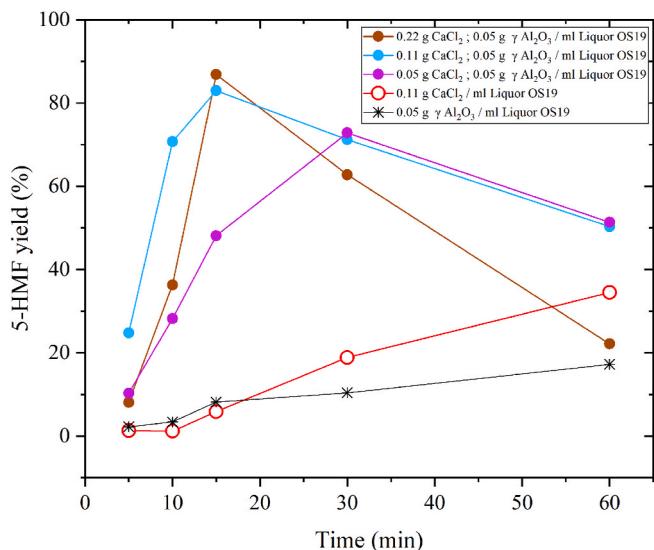


Fig. 5. 5-HMF yield vs reaction time with varying amounts of CaCl_2 in the dehydration of Liquor_HEM obtained under OS19 conditions. Dehydration conditions: batch reactor, 5 ml liquor, 180 °C, 0,05 g $\gamma\text{-Al}_2\text{O}_3$, 450 rpm.

leading to the formation of 5-HMF. The data presented in Fig. 5 indicate a favorable trend, as the presence of CaCl_2 markedly promotes the conversion of these C₆ sugars into 5-HMF. Initially, increasing CaCl_2 concentrations leads to higher 5-HMF yields; however, beyond 0.11 g of CaCl_2 per mL of liquor, the product yields reached plateaus. At higher concentrations, an increase in degradation products is observed, suggesting that excessive salts levels may catalyze side reactions detrimental to 5-HMF stability (Fúnez-Núñez et al., 2020; Pyo et al., 2020; Román-Leshkov and Dumesic, 2009).

Dehydration of C₆ sugars is observed in the presence of either $\gamma\text{-Al}_2\text{O}_3$ and CaCl_2 individually. However, the resulting 5-HMF yields remain lower than 25 %, with maximum formation after 60 min of reaction. Notably, a substantial increase in 5-HMF yield is observed within the initial 15 min in the presence of both $\gamma\text{-Al}_2\text{O}_3$ and CaCl_2 , indicating a synergistic effect between them that significantly enhances the rate of product formation. Furthermore, after just 15 min of reaction, a

complete (100 %) conversion of the monosaccharides present in the Liquor_HEM is achieved, which further supports the strong synergistic effect of the salt in accelerating the reaction. Under these experimental conditions, both the selectivity and yield to 5-HMF reach up to 90 %. That means that 280 kg 5-HMF/(L·kg_{cat}·h) can be produced from the Liquor_HEM. Qiong Wu et al. obtained yields of 85 % in 5-HMF using only water together with 1 g cellulose, 0.2 g Ni_{2,0}/CS at 200 °C and H₂ pressure of 6 MPa (Q. Wu et al., 2019). These experimental conditions are harder than those used in the present work, where autogenous pressure and 180 °C were employed to obtain a 90 % 5-HMF yield. The papers dealing with the dehydration of galactose in water are scarce, whereas the use of hemicellulosic liquors obtained from SCGs has not been reported yet.

A very important aspect of this reaction, utilizing a hemicellulosic liquor derived from SCGs is that it does not require the use of an organic phase during the dehydration process. This greatly simplifies the overall procedure, as it eliminates the need for complex phase separation steps and reduces the amount of chemicals involved. As a result, process operability is significantly facilitated, industrial risks associated with handling flammable or toxic organic solvents are minimized, and overall production costs are reduced.

After approximately 30 min of reaction, a decline in the yields of furfural and 5-HMF is observed, particularly pronounced for furfural. This behavior can be attributed to the enhanced degradation of these compounds under the studied aqueous conditions, as previously noted. In the absence of an organic extraction phase, both furfural and 5-HMF are less stable in aqueous media, making them more susceptible to degradation pathways such as rehydration, condensation, or further conversion into organic acids and other by-products. Notably, the implementation of a subsequent extraction step using an organic phase could facilitate more efficient recovery of these compounds, preventing their prolonged exposure to conditions promoting degradation. Additionally, it is well-established in the literature that furfural exhibits lower stability than 5-HMF in aqueous environments (Karimi and Shekaari, 2022; Xin et al., 2016). The presence of an additional hydroxyl group on 5-HMF confers a modest increase in stability through enhanced hydrogen bonding with water, which partly explains its relatively higher persistence compared to furfural. However, even 5-HMF undergoes substantial degradation over time, particularly when not rapidly extracted from the reaction medium.

A key aspect to highlight is the high reproducibility of these reactions using these liquors. As demonstrated in previous studies, the standard deviation of the yields obtained is less than 1 %, attesting to the robustness and reliability of the process (Pérez-Merchán et al., 2025).

Moreover, the absence of an organic phase during the main reaction means that the process is inherently safer and more environmentally friendly, aligning well with green chemistry principles. Alternatively, 5-HMF can be efficiently separated by N₂ stripping, further enhancing the sustainability and scalability of the process. This streamlined approach not only improves the economic viability of 5-HMF production from SCG-derived hemicellulosic liquors but also makes it more attractive for industrial applications.

These results suggest that this salt-catalyzed approach, along with liquors obtained from SCGs_E, could be scaled up to industrial level due to the relevance of the product and the remarkable results achieved.

3.4. Cellulose and lignin from SCGs

Cellulose and lignin can also be isolated from SCGs through the organosolv process. The solid recovered from SCGs_E after the organosolv treatment (SCGsCEL) is expected to consist mainly of cellulose. Lignin remains in solution along with hemicellulosic sugars (Liquor_HEMLIG), and precipitates upon the addition of water (SCGsLIG). The recovery percentage of SCGsCEL and SCGsLIG in each experiment are shown in Fig. 1 varying significantly upon the experimental conditions. SCGsCEL ranges approximately from 14 to 32 % while SCGsLIG does

from 1 to 14 %.

X-ray diffraction (XRD) is a suitable characterization technique for the structural analysis of these two fractions of SCGs. Fig. 6 A) and B) shows the XRD patterns of cellulose and lignin obtained after organosolv process under the OS19 conditions (140 °C, 60 min and 40 vol% ethanol), respectively. Compared to commercial cellulose, the cellulose obtained from the SCGs is less crystalline, as inferred from the reduced intensity of the three main peaks of type I cellulose, at 20 (°): 16.5, 22.5 and a weaker peak at 34.6, corresponding to the crystallographic planes (110), (200) and (004), respectively (Besbes et al., 2011; Chadel et al., 2023; Kim et al., 2013). The low crystallinity of the cellulose obtained could be due to the severity of the organosolv process.

The diffractogram of SCGs_LIG shows a unique broad band at 15°, revealing its amorphous structure, with no peaks associated with cellulose. This is due to its solubilization in the organosolv process and subsequent precipitation, which promotes amorphization rather than crystallization (Gomide et al., 2020).

On the other hand, FTIR spectroscopy was also used for the physicochemical characterization of both fractions. These data are displayed in Fig. 7 and Table 2. Fig. 7A shows the FT-IR spectrum of cellulose, with a broad band at 3350 cm⁻¹ representing the stretching vibration of hydrogen-bonded hydroxyl groups. The symmetric and asymmetric C-H vibrations of methyl and methylene groups are observed at 2917 and

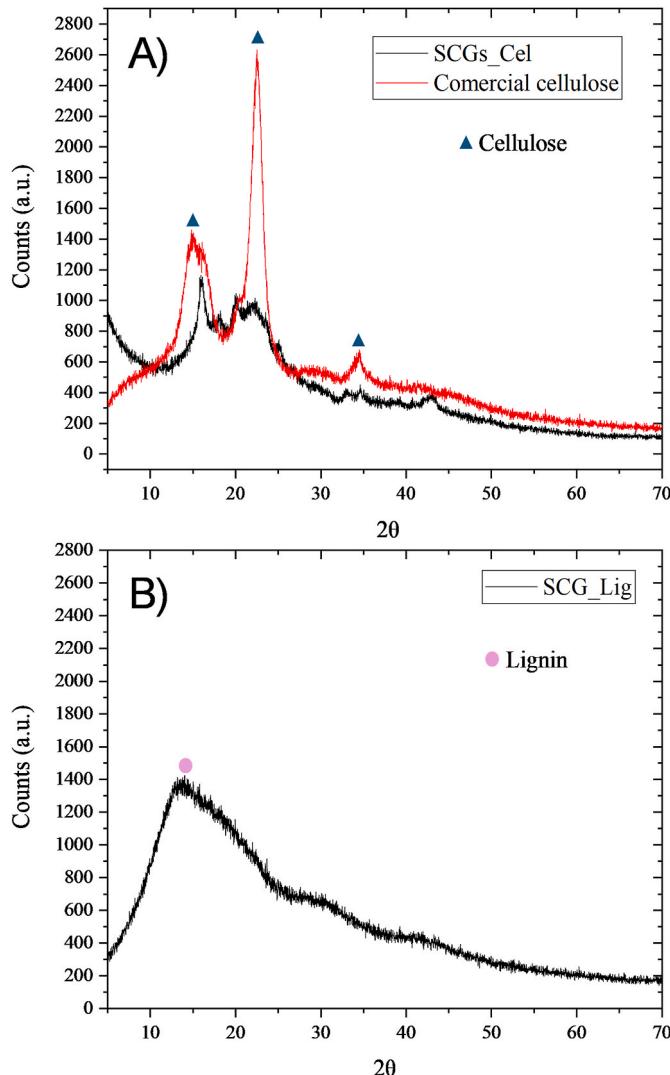


Fig. 6. XRD patterns for cellulosic and lignin fractions recovered from SCGs: A) commercial cellulose and SCGs_CEL and, B) SCGs_LIG.

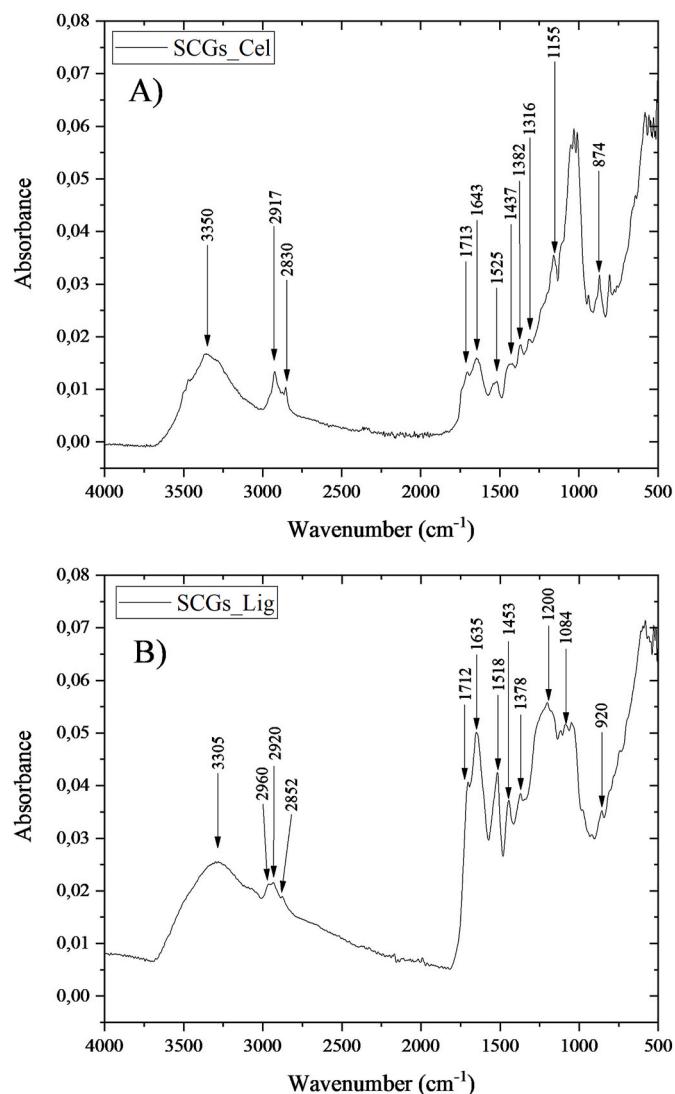


Fig. 7. FTIR analysis of cellulosic and lignin fractions recovered from SCGs: A) SCGs_CEL and, B) SCGs_LIG.

2830 cm⁻¹, respectively. In the region from 1800 to 1500 cm⁻¹, there are differences with respect to the expected FTIR bands. C=O stretching at 1713 cm⁻¹ indicates partial cellulose oxidation, while the amino group deformation at 1525 cm⁻¹ would reveal the presence of proteins. SCGs contain small amounts of proteins that do not undergo complete hydrolysis and thus remain in the cellulose fraction (Abidi et al., 2014; Olsson and Salmén, 2004). Further cellulose-specific bands include O-H in plane deformation, C-H bending and CH₂ rocking at 1437, 1382 and 1316 cm⁻¹, respectively. The vibration bands at 1155 and 874 cm⁻¹ can be associated with the cellulose structure, and would correspond to the anti-symmetrical bridge C-O-C stretching mode, movement associated with the bonds of glucose monomers and the linkage of cellulose, respectively (Abidi et al., 2014; Del Río et al., 2012; Astete et al., 2021; Oh et al., 2005; Olsson and Salmén, 2004).

Fig. 7B shows the FTIR spectrum of lignin. Although similar in appearance to cellulose, specific differences are evident. The 3000-2800 cm⁻¹ region reveals, as for cellulose, the large presence of hydroxyl groups, consistent with lignin's polyphenol derivates. At 1712 cm⁻¹, aldehyde and carbonyl groups appear, indicating lignin oxidation. However, the main distinction features appear at 1635 and 1518 cm⁻¹, associated with C=C -(Ar)C-C stretching vibration modes. Comparing both spectra, these double bonds, in phenolic groups, differentiate lignin and cellulose. Finally, aromatic groups linked by ether/ester bonds

Table 2

Assignment of the most important bands of the SCGs_CEL and SCGs_LIG samples in FTIR.

| SCGs_CEL | | | |
|--------------------------------|---|--------------------------------|---|
| Vibrations (cm ⁻¹) | Assignments | Vibrations (cm ⁻¹) | Assignments |
| 3350 | Intra-molecular hydrogen bonding | 3305 | Intra-molecular hydrogen bonding |
| 3288 | Inter-molecular hydrogen bonding | 2920 | Inter-molecular hydrogen bonding |
| 2930, 2857 | CH ₂ asymmetrical and symmetrical stretching | 2960, 2852 | CH ₂ asymmetrical and symmetrical stretching |
| 1713 | C=O stretching | 1712 | C=O stretching |
| 1650 | O-H bending of adsorbed water | 1635 | C=C -(Ar)-C—C stretching/ |
| 1525 | NH ₂ deformation or C=C -(Ar) | 1518 | C=C -(Ar)-C—C stretching |
| 1437 | O-H in plane deformation | 1453 | O-H in plane deformation |
| 1382 | C-H bending | 1378 | C-H bending |
| 1316 | CH ₂ rocking | | |
| 1155 | C-O-C stretching Anti-symmetrical bridge | 1200 | (Ar)-C—O—C Anti-symmetrical bridge |
| 874 | B-Linkage of cellulose | 1084 | (Ar)-C—O—C Anti-symmetrical bridge |
| | | 857 | (Ar)-C-H Out of plane bending vibration |

appear at 1084 cm⁻¹, with out-of-plane bending vibration of - C-H (Ar) observed at 857 cm⁻¹ (Biswas et al., 2022; Del Río et al., 2012; Derkacheva and Sukhov, 2008; Astete et al., 2021; Z. Shi et al., 2019).

4. Conclusion

This study demonstrates the potential of spent coffee grounds (SCGs) as a promising feedstock for the extraction and synthesis of valuable chemicals through innovative processing methodologies.

Mechanochemical extraction yielded 11 ± 1 % of extractives, with an extraction efficiency of 73 %, substantially reducing processing time compared to conventional methods while achieving a high solvent recovery rate of up to 75 %, thereby ensuring both sustainability and industrial feasibility.

Under optimized organosolv conditions, hemicellulosic liquors were obtained with a maximum monosaccharide concentration of 22 ± 1 g/100 g of extracted SCGs (SCGs_E), underscoring the potential for sugar recovery. Process parameters, particularly temperature and ethanol concentration, were found to significantly influence the balance between lignin solubilization and sugar yields. Elevated temperatures led to sugar degradation, whereas an ethanol concentration of 40 vol% provided optimal lignin solubilization without compromising sugar yields.

Catalytic dehydration of sugars present in the hemicellulosic liquor yielded up to 50 % furfural and 90 % 5-HMF, demonstrating the effectiveness of the salt-catalyzed approach in water, which simplifies the process and enhances scalability. Thus, the addition of CaCl₂ markedly enhanced C₆ sugar conversion of, particularly during the initial 15 min of reaction, attributed to the synergistic interaction between γ-Al₂O₃ and CaCl₂. This approach simplifies the reaction system by removing the necessity for an organic phase, thus reducing process costs, minimizing industrial hazards and improving scalability.

Cellulose (SCGs_CEL) and lignin (SCGs_LIG) fractions recovered through the organosolv process exhibited yields ranging from 14 to 32 % and 0.8–13.6 %, respectively. Structural characterization via XRD and FTIR revealed that the cellulose fraction displayed reduced crystallinity due to the severity of processing conditions, while the lignin fraction

showed an amorphous nature. These properties enhance the suitability of both fractions for applications in material science and biochemical production.

In conclusion, the findings would confirm the viability of SCGs as a renewable feedstock in sustainable biorefinery platforms, offering economically viable and environmentally friendly solutions for agro-industrial waste valorization.

5. Limitations and future directions

While this study demonstrates the potential of SCGs as a renewable feedstock for sustainable biorefinery platforms, several limitations should be acknowledged. Although key fractionation and conversion steps were successfully performed at the laboratory scale, further experiments are required to validate the scalability of these processes. Parameters such as long-term process stability, continuous operation and scale-up effects need to be addressed.

A qualitative life cycle perspective highlights the environmental benefits of valorizing spent coffee grounds (SCGs) through the proposed biorefinery route. Compared with conventional disposal pathways such as landfill or incineration, which contribute to greenhouse gas emissions and resource losses, the organosolv-based fractionation enables the recovery of cellulose, hemicellulose, and lignin as valuable feedstocks. The mechanochemical extraction step further reduces energy demand relative to traditional Soxhlet extraction, while the use of bioethanol as solvent improves alignment with circular economy and green chemistry principles. By generating bio-based products such as 5-HMF, furfural, biodiesel, and activated carbon, the integrated approach displaces fossil-derived alternatives and thus avoids associated emissions. In addition, the efficient separation and recovery of multiple SCG fractions minimizes waste generation and supports closed-loop resource utilization. Although a complete life cycle assessment is beyond the scope of this work, these results qualitatively indicate that the integrated valorization of SCGs could achieve significant environmental gains compared with current end-of-life practices (S. Wu et al., 2025; Yu et al., 2024; Zha et al., 2025).

Further work is needed to optimize reaction conditions, minimize energy and solvent consumption and ensure compatibility with existing industrial infrastructure. Moreover, the current work focuses on experimental valorization, future studies should combine Life Cycle Assessment, techno-economic analysis and exergy evaluation to comprehensively quantify environmental and economic sustainability.

CRedit authorship contribution statement

Antonio M. Pérez-Merchán: Writing – original draft, Methodology.
Ramón Moreno-Tost: Supervision, Project administration, Funding acquisition.
Irene Malpartida-García: Writing – review & editing, Supervision.
Cristina García-Sancho: Supervision. **Josefa M. Mérida-Robles:** Writing – review & editing, Supervision. **Pedro Maireles-Torres:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2025.146716>.

Data availability

Data will be made available on request.

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