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Article

Spent Coffee Grounds for Energy Generation

Klusener, A.K. [1]; Cunha, E.S.L. [1]; Silva, J.F.[2]; Morais, J.R.[2]; Souza, V.L.[2]; Tres, M.V.[2]; and Zabot, G.L.[2,*]

[1] Department of Mechanical Engineering, Federal University of Santa Maria, Campus Cachoeira do Sul
[2] Laboratory of Agroindustrial Processing Engineering (LAPE), Federal University of Santa Maria (UFSM), 1040, Sete de Setembro St., Center DC, Cachoeira do Sul – RS, 96508-010, Brazil
***** e-mail for correspondence: giovani.zabot@ufsm.br

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Abstract: Novel purposes have been emerged aiming to adopt alternative biomasses for energy generation. In this work, the utilization of spent coffee grounds (SCG) wastes, a domestic urban reject, is proposed for biofuels production and energy generation. A methodological route was designed and conducted. The moisture content in the coffee grounds varied from 69.02% to 74.68% (± 0.42%). Four different methods were compared for oil content extraction: supercritical CO_2, Soxhlet, centrifugation with ethyl ether, and centrifugation with n-hexane. These methods permitted to obtain oil content (mass basis) from 6.67% (± 0.38%) to 23.85% (± 1.85%). The average proportion biodiesel/glycerine from the transesterification of spent coffee grounds oil was 73.2% / 26.8%. The by-product dry mass was submitted to a subcritical hydrolysis process, with different parameters, resulting in fermentable sugars, in concentration within 17 and 64 (grams of sugar / kilograms of spent coffee grounds). A thermoelectrical plant was designed based on bibliography data, resulting in the possibility of generation of 8.26 MW by a 2 kg/s dried coffee grounds mass flow in a boiler. Simultaneously, the energy balance of the main processes was made. The results confirm the possibility of energy generation from spent coffee grounds, introducing this biomass as a future alternative in the Brazilian energetic matrix.

Keywords: Biofuels; Coffee Grounds; Energy; Environment; Waste utilization

Resumo: Em face da necessidade do desenvolvimento de novas tecnologias para geração de energia, têm surgido propostas que visam a adoção de biomassas alternativas para tal finalidade. No presente trabalho, é proposta a utilização da borra de café, um rejeito urbano doméstico geralmente descartado, para produção de biocombustíveis e geração de energia. Uma rota metodológica foi criada e conduziu o andamento do trabalho. Os teores de umidade encontrados na borra de café variaram entre 69,02% a 74,68% (± 0,42%). Na extração de óleo, quatro diferentes métodos foram comparados: CO_2 supercrítico, Soxhlet, centrifugação com éter etílico e centrifugação com hexano. Tais métodos permitiram obter teores mássicos de óleo entre 6,67% (± 0,38%) a 23,85% (± 1,85%). A proporção biodiesel/glicerina média resultante da transesterificação de óleo da borra foi de 73,2% / 26,8%. A massa seca residual foi submetida à hidrólise subcrítica, visando a obtenção de açúcares fermentescíveis, utilizando-se diferentes parâmetros, e obtendo-se valores de teor de açúcar entre 17 e 64 (g açúcar / kg borra). Uma usina termelétrica foi dimensionada, observando-se a possibilidade de geração de 8,26 MW a partir da queima de 2 kg/s de borra de café seca. Simultaneamente, foram feitos os balanços energéticos dos principais processos deste trabalho. Os resultados encontrados permitem confirmar a possibilidade de geração de energia a partir da borra de café, introduzindo esta biomassa como uma alternativa futura de implantação na matriz energética brasileira.

Palavras-chave: Biocombustíveis; Borra de café; Energia; Meio Ambiente; Resíduos

1. Introduction

The exponential worldwide population growth is a problem that implicates in higher number of people living in cities, which is responsible for the highest energy levels consumed. Specifically, the transport sector corresponds to one third of that consumption. This segment uses mainly fossil fuels, which generates greenhouse gases, partially responsible for the global warming. As a direct purpose of substitution of fossil fuels, the use of biofuels has been engaged notorious attention all over the world. It includes a high number of raw materials, conversion technologies, and final uses. The biofuels can be used isolated or in a mixture with common fuels.

Biodiesel, for example, is resultant from a transesterification reaction, in which an oil (triglyceride) reacts with an alcohol, resulting in a mixture of alkyl esters (biodiesel) and glycerin. On the other hand, second-generation bioethanol is resultant of a 3-step process: hydrolysis, fermentation, and distillation. The first step allows obtaining fermentable sugars, and consists in a depolymerization of the polysaccharides cell walls (Cortez et al, 2014). A promissory alternative is subcritical hydrolysis, due to its low cost, small level of inhibitors, and short reaction time (Abaide et al, 2019). Environmentally, biodiesel and bioethanol are more viable, respectively, than fossil diesel and pure gasoline. Compared to diesel, the combustion of biodiesel reduces sulfur dioxide, carbon monoxide and carbon dioxide emissions. Similarly, the second-generation bioethanol is produced by the lignin-cellulosic vegetable by-products, which implies in economic and environmental benefits. The combustion of bioethanol reduces in almost 90% the greenhouse gases emission. In Brazil, the National Agency of Petroleum and Natural Gas (ANP) specifies the regulation about the obligatory mixture of the commercial fuels, currently stablished in 13% of biodiesel added to diesel and 27% of ethanol added to gasoline.

Among all renewable energy resources, biomass have the largest potential of improvement on the next years due to its economic and environmental benefits. Specifically, in the Brazilian context, biomass corresponds to 32% of its energetic matrix, as against 13% in worldwide. However, the assurance of food and energetic security is one of the challenges faced in this context (Goldemberg, 2009). Therefore, lignocellulosic biomasses, like spent coffee grounds, can become promissory due to its potential to minimize these conflicts. Brazil is the largest producer of coffee, figuring out as the second highest consumer all over the world (USA figures out as the first). According to CONAB (2021), in 2021 Brazil harvested 47.7 million of 60 kilograms bags, that corresponds to almost 28% of the worldwide production (170 million of bags in 2021). Brazil exported 38.4 million bags, 2.2% lower than 2020, because of the negative biennial. Some features of the country are responsible for these great numbers, such as: climate conditions, high insolation, favorable soil, and territorial extension. Domestic spent coffee grounds result after the preparation of the drink and are usually discarded. According to ABIC (Brazilian Association of Coffee Industry), around 2.000 tons of coffee grounds are discarded every year in Brazil. These wastes could show improved commercial values if established in a circular economy, contributing to the sustainable development (Stroub, 2021). Cardoso (2021) cited different initiatives of use of spent coffee grounds, including: as abrasives for skin treatment, soot cleaning, as a constitute in paint and dyes, as activated carbon to store anthropogenic gases from industrial processes, compound in charcoal briquettes, as a basis to get lactic acid, as filler or reinforcement in polymer matrices, as a compound in bio composites, among other applications.

Alternative biomasses can be used for electrical power generation, in a steam power cycle, substituting coal, from which combustion produces toxic effluents. Particularly, spent coffee grounds shows energetic advantage, when compared to other biomasses, usually adopted in thermoelectrical plants. According to Caldeira (2015), the Higher Calorific Value is between 19.5 to 19.9 MJ/kg, what is straightly higher than rice husks, bean pods, wood, sugarcane bagasse, and corn straws. The technological route usually consists in a direct biomass combustion, heating the fluid to saturated steam condition and flowing the resultant steam in a steam turbine. The movement of its blades rotates the shaft, producing work. The turbine has its shaft coupled to an electrical generator, which produces electrical power. According to Paiva et al. (2015), molding briquettes with waste coffee grounds and wood is a viable propose. Similar research was performed by Magnago et al. (2019), comparing different combinations of briquettes molded with wood, spent coffee grounds, rice husks, and potato peels. Based on this context, this work aims to analyze the potentiality of spent coffee grounds for energy production, showing a purpose of reutilization of this biomass for biofuels production (biodiesel and second-generation bioethanol) and electrical power generation.

2. Materials and Methods

2.1 Spent coffee grounds preparation

Approximately two kilograms of spent coffee grounds were collected (Cachoeira do Sul, RS, Brazil) and transferred to the laboratory. Moisture content was reduced at approximately 70% by a drying process at 60°C in a non-vacuum stove (LUCA 80/150, Lucadema, Brazil). After that, oil was extracted in four different methods, for further biodiesel production. Resultant dry mass was measured and evaluated to verify its viability for second-generation bioethanol production and electrical power generation. Figure 1 shows the technological route used in the study, indicating the main steps of the whole work.

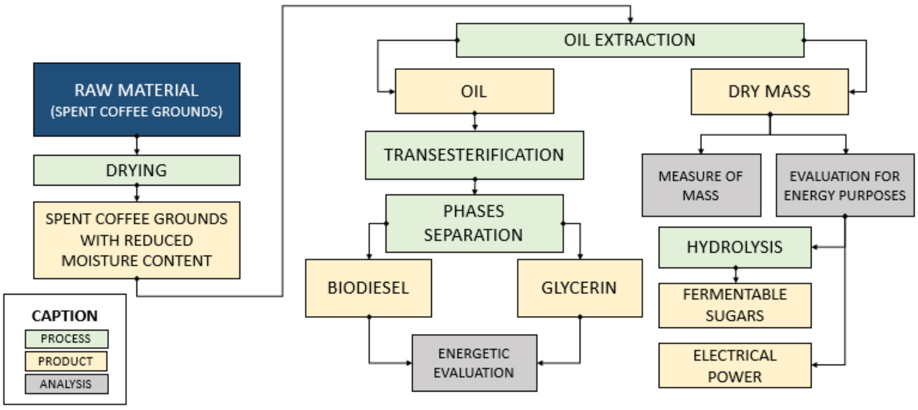

Figure 1. Technological route used in the study.

From now and then, mass and energy balances of the main steps of the work are designed. Considering the oven at drying process as control volume and steady-state process, mass and energy balances are specified in equations 1 and 2. Indices 1 to 3 indicate, respectively, inlet of high-moisture content samples, dried samples, and water steam outlet. Temperatures in these points are indicated by T_i. M_{CG}, M_{dried}, and M_{steam} represent, respectively, the masses of spent coffee grounds, dried mass (low moisture content), and the steam removed from the samples. The specific heats at constant pressure of the coffee grounds and the steam are indicated by $C_{P_{CG}}$ and $C_{P_{steam}}$. Q_{drying} represents the heat inserted in the samples at drying process.

$$M_1 = M_2 + M_3 \rightarrow M_{CG} = M_{dried} + M_{steam} \quad (1)$$

$$(M_{CG} \cdot C_{P_{CG}} \cdot T_1) + Q_{drying} = (M_{dried} \cdot C_{P_{CG}} \cdot T_2) + (M_{steam} \cdot C_{P_{steam}} \cdot T_3) \quad (2)$$

2.2 Oil extraction

The oil extraction was performed in four different methods: supercritical carbon dioxide extraction, Soxhlet extraction, centrifugation with n-hexane, and centrifugation with ethyl ether.

Supercritical fluid extraction with carbon dioxide (SFE-CO_2) was developed similarly to performed by Araujo (2019) and Confortin et al. (2019). The procedure consists of: i) absorption of the supercritical solvent by the substrate; ii) dissolution of the soluble compounds by the solvent; iii) transference of the solubilized compounds to the solid surface; iv) and transport of the compounds by the solvents and removal by extractor vessel (Araujo, 2019). In Figure 2a, the indices indicate the following conditions: (1) CO_2 exits the cylinder in gas condition; (2) heat exchanger (Solab®, model SL 512, Brazil) transforms CO_2 into saturated liquid; (3) fluid exits the 2-step high-pressure pump (Jasco®, model PU-4387, Japan); (4) another heat exchanger (Solab®, model SL 150/6, Brazil) heats the fluid to its supercritical condition; (5) and mixture of fluid and biomass exits the extraction vessel, which has a band heater to assure the project temperature. After exiting, carbon dioxide evaporates to surroundings. In each run, approximately 18 g of sample was charged into the extraction vessel. The temperature, pressure, and flow rate were defined as 40℃, 35 MPa, and 4.3 mL/min, respectively, for a total extraction time of 180 min. The oil was collected in collection tubes every 15 min. This procedure was repeated 6 times to evaluate the oil content and elaborate kinetics curves.

Soxhlet extraction was performed using n-Hexane for 6 h. The method consists of evaporating and condensing intermittently the solvent, respectively with a heating mantle (Fisatom®, model 52E, Brazil) and a condenser, fed with an ultra-thermostatic water bath (Solab®, model SL-152, Brazil). After being condensed, the solvent drips on the sample, extracting its oil content. Then, a siphon directs the alcohol-oil mixture to the bottom. In each run, 2 g of spent coffee grounds was charged into a filter paper inside the extraction vessel and the procedure was repeated thrice. After extraction, the oil was separated from the alcohol with a rotary vacuum-evaporator (Even®, model SKL-25A, Brazil), coupled with a heat exchanger at 45℃.

Oil extraction by centrifugation method was done with n-Hexane and ethyl ether. For each solvent, 1 g of spent coffee grounds was charged in a Falcon tube with 8 mL of each solvent. Firstly, a double manual agitation was performed interspersed by a 30 min rest. Thereafter, a centrifugation was performed (NovaTécnica, model NT 815, Brazil), at 3500 rpm for 5 min (Zabot et al, 2014). After this procedure, the supernatant fluid was collected and the separation oil-alcohol was performed by a rotary evaporator procedure (similarly to Soxhlet process).

2.3 Biodiesel production

A preliminary test was performed for biodiesel production, using soy oil. After this, the best molar ratio alcohol:oil of 9:1 was identified, following which has been already reported by Caldeira (2015). After that, the oil from spent coffee grounds was submitted to a transesterification reaction. In each run, 10 mL of oil was charged in an Erlenmeyer flask, with 3.6 mL of methanol and 0.15 g of potassium hydroxide (1%, w/v). The mixture was done by an incubator with orbital agitation (Tecnal, model TE-424, Brazil) for 1 h at 60℃ and 150 rpm, similarly to which has been already performed by Caldeira (2015). The whole process was performed in quintuplicate. After this time, transesterification reaction was completed. Chemically, triglycerides were substituted for the alcohol, resulting in a product with better fuel properties. In addition to methyl ether (biodiesel), another fraction of the final product corresponds to glycerin. Due to the difference of density of the compounds, glycerin and biodiesel were separated by a separatory funnel, and collected in measuring cylinders, in order to verify the volumetric proportion of biodiesel/glycerin.

2.4 Rankine cycle simulation

A simplified simulation of a Rankine cycle was performed to evaluate the potentiality of spent coffee grounds for electrical power generation in a small thermoelectrical central. Combustion of the biomass heats the work fluid to saturated steam condition, feeding a steam turbine coupled to an electric generator. Design was performed adopting bibliography data.

Isentropic efficiency of turbine (η_t) and pump (η_p) are considered, respectively, of 90% and 80%, based on Çengel and Boles (2013). Boiler efficiency is represented as η_{boiler}, and is considered of 85%, for convenience. The software EES® was used to determine specific entropies ($\widehat{H}_i$) and specific entropy ($\hat{S}_i$) at each point, considering water as work fluid. Indices (1) to (4) are the boundary conditions for the control volumes.

In the inlet of the pump (1), saturated liquid (quality of 0%) flows into the control volume at 100 kPa and approximately 100℃, exiting at 4000 kPa. Through EES simulation, point (1) is determined as $\widehat{H}_1 = 417.4\,\frac{kJ}{kg}$ and $\hat{S}_1 = 1.302\,\frac{kJ}{kgK}$.

For an isentropic process, an ideal condition (2s) has a value of entropy equal to (1), and the enthalpy at this point is calculated from the values of entropy and pressure in the outlet of the pump. This way, enthalpy in point (2s) is $\widehat{H}_{2s} = 421.3\,\frac{kJ}{kg}$. The real condition (2) differs from (2s) by the isentropic efficiency, calculated by equation (3) as the ratio of isentropic work / real work. With the parameters of enthalpy in points (1) and (2s), and considering the isentropic efficiency of the pump, enthalpy in the real point (2) is calculated from equation (4).

$$\eta_p = \frac{\widehat{H}_{2s}-\widehat{H}_1}{\widehat{H}_2-\widehat{H}_1} \tag{3}$$

$$\widehat{H}_2 = \frac{\widehat{H}_{2s}-\widehat{H}_1}{\eta_p} + \widehat{H}_1 = 422.3\,\frac{kJ}{kg} \tag{4}$$

After exiting the pump, work fluid flows in the pipes, and considering energy losses negligible, enters the boiler with the same pressure of 4000 kPa. The boiler is fed with a spent coffee grounds mass flow rate of 2 kg/s, which is continuously fully burned, heating the work fluid to supersaturated steam condition at 600℃ at (3). From the values of temperature and pressure, parameters at point (3) are determined from EES: $\widehat{H}_3 = 3674.3\,\frac{kJ}{kg}$ and $\hat{S}_3 = 7.369\,\frac{kJ}{kgK}$. Not all the heat produced in the boiler is completely absorbed by the work fluid, due to many issues (among others, flow rate, pipe geometry, thermal conduciveness of the pipe walls, rate of excess of air, and heat losses for convection and radiation). Efficiency of the boiler is adopted at this point, in order to mathematically express these energy losses. Heat transferred to the fluid is calculated considering the boiler efficiency, fuel flow rate, and the higher calorific value (HCV) of the fuel, as showed in section 3. This is an important parameter to evaluate the thermal efficiency of the system. The use of the HCV on the contrary of LCV (lower calorific value) aims to include the energy spent on vaporizing the residual water in the biomass. Once again, energy losses in the pipes from the outlet of the boiler to the inlet of the turbine are negligible.

Analogously to the procedure performed in the pump, evaluation in the inlet and outlet of the turbine requests an entropy efficiency inclusion. Steam enters the turbine (3) at 4000 kPa and 600°C, exiting at 100 kPa. For an isentropic process, condition (3) has the very same entropy of (4s), and the enthalpy at this point is determined from the values of entropy and pressure in the outlet of the turbine. From EES: $\widehat{H}_{4s} = 2678.9 \frac{kJ}{kg}$. The real condition (4) differs from (4s) by the isentropic efficiency, calculated with the ratio of real work / isentropic work in equation (5). With the parameters of enthalpy in points (3) and (4s), and considering the isentropic efficiency, enthalpy in the real point (4) is calculated from equation (6).

$$\eta_t = \frac{\widehat{H}_4 - \widehat{H}_3}{\widehat{H}_{4s} - \widehat{H}_3} \tag{5}$$

$$\widehat{H}_4 = \eta_t \cdot (\widehat{H}_{4s} - \widehat{H}_3) + \widehat{H}_3 = 2778.4 \frac{kJ}{kg} \tag{6}$$

After exiting the turbine, steam with high quality percentage requests to enter a condenser to turn back to saturated liquid condition, in order to conclude the cycle. In this control volume, cooling coils fed with cooling water increase the area for energy transference, removing heat from the work fluid. Once more, energy losses in the pipes from the condenser to the pump are negligible. The heat removed from the work fluid is calculated from its flow rate, and the enthalpies in the inlet (4) and the outlet (1), following the data which was previously calculated.

2.5 Subcritical water hydrolysis

Dry mass resultant from oil extraction process was submitted to a subcritical water hydrolysis, based on Abaide et al. (2019). Distillated water was pumped (JASCO®, model PU-4087, Japan) and flowed by a pre-heating water bath (Solab®, model SL-150, Brazil). Then, water passed through a reaction vessel, heated by a band heater. Hydrolyzed samples were collected by a collector tube. Five different parameters for flow rate and temperature were compared: (i) 10 mL/min at 180°C; (ii) 10 mL/min at 220°C; (iii) 10 mL/min at 260°C; (iv) 20 mL/min at 180°C; and (v) 20 mL/min at 220°C. In each run, 10 g of dried spent coffee grounds was loaded in the reaction vessel. Water was pumped for 7.5 minutes at 25 MPa. In Figure 2b, the indices indicate: (1) distillated water feeding; (2) pressurized water as saturated liquid; (3) subcritical condition stablished at work pressure e previously heated; and (4) sugar-rich solution obtained.

Fermentable sugars in the samples were analyzed by a visible ultraviolet light beam absorption spectrophotometry (Shimadzu, model UV-1900, Japan), following the method described in Vedovatto et al. (2021). The samples obtained from the conditions (i) to (iii) were diluted 10 times (100 µL of sample with 900 µL of water). Otherwise, the samples obtained in the conditions (iv) and (v) were diluted 5 times (200 µL of sample with 800 µL of water). Light absorption is supported with dinitrosalicylic acid.

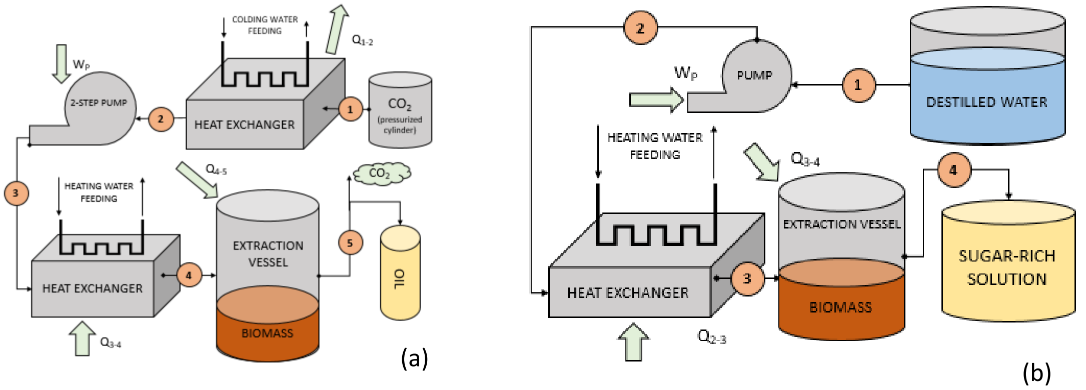

Figure 2. Flowcharts of the main processes. **(a)** Supercritical fluid extraction with CO_2; W_p: Pump work; Q_{1-2}: Heat removed from the fluid by the cooling heat exchanger; Q_{3-4}: Heat transferred to the fluid by the heating heat exchanger; Q_{4-5}: Heat transferred to the mixture of fluid and biomass by the band heater; **(b)** Subcritical water hydrolysis; W_p: Pump work; Q_{2-3}: Heat transferred to the fluid by the heating heat exchanger; Q_{3-4}: Heat transferred to the mixture of fluid and biomass by the band heater.

3. Results and discussion

3.1. Drying

Moisture content in the 40 samples varied between 66.47% and 75.59%, with average of 71.97% and 2.65% of uncertainty. These high values are justified by the inexistence of previous drying processes, like air rest or natural drying at sun. In fact, the samples were collected after the drink preparation and submitted to the drying process for experimental purposes. If this biomass can be used directly for hydrolysis processes, the complete drying pretreatment is not mandatory.

Aiming an industrial application, other approaches can be performed to reduce moisture content. One of these possibilities is sun exposure, in which high amounts of the raw material are exposed to the sunlight on the ground, on a plastic groundsheet, dried newspaper, or paper sheets. The mass transference is more efficient as much as the samples are scattered. This process requires no equipments, providing an easy and flexible drying, with no risk of burning. Future studies can perform a comparison between the results obtained from these methods.

3.2 Oil extraction

Regarding SFE-CO2, the oil content varied from 7.32% to 9.88%, with average of 8.79% and 0.36% of uncertainty. Figure 3 shows the kinetic curves of extraction, adopting average values of all samples. Both accumulated and time-specific analyses, respectively presented in Figure 3a and 3b, demonstrated that the best interval for the extraction was the first 60 minutes. SFE-CO2 mass and energy balances are summarized in Table 1.

Table 1. Mass and energy balance of supercritical fluid extraction

CONTROL VOLUME	MASS BALANCE	ENERGY BALANCE
Heat exchanger (colding)	$\dot{m}_1 = \dot{m}_2 = \dot{m}_{CO_2}$ (7)	$\dot{Q}_{1\text{-}2} = \dot{m}_{CO_2}(\hat{H}_1 - \hat{H}_2)$ (8)
2-step pump	$\dot{m}_2 = \dot{m}_3 = \dot{m}_{CO_2}$ (9)	$\dot{W}_P = \dot{m}_{CO_2}(\hat{H}_3 - \hat{H}_2)$ (10)
Heat exchanger (heating)	$\dot{m}_3 = \dot{m}_4 = \dot{m}_{CO_2}$ (11)	$\dot{Q}_{3\text{-}4} = \dot{m}_{CO_2}(\hat{H}_4 - \hat{H}_3)$ (12)
Extraction vessel	$\dot{m}_4 = \dot{m}_5 = \dot{m}_{CO_2}$ (13) $M_{CG} = M_{oil} + M_{residue}$ (14)	$\dot{Q}_{4\text{-}5} = \dot{m}_{CO_2}(\hat{H}_4 - \hat{H}_5)$ (15)

Source: authors.

Andrade et al. (2012) observed a yield increasement with the pressure enhancement in SFE-CO_2 extraction, identifying the best condition with 300 bar and 40℃, in which 10.5 ± 0.2% of oil content was obtained and straightly similar to the condition applied in this work. Melo et al. (2014) noticed that temperature in this process impacts the diffusivity of the CO_2, corroborating that 40℃ is a temperature that does not affect this property. Authors also performed an economic analysis, reaching promising results for spent coffee grounds oil extraction with SFE-CO_2. Coelho et al. (2020) verified that the supercritical fluid extraction with CO_2 and a co-solvent decrease in half the time necessary to obtain the maximum oil content, what can be better visualized is the work of Couto et al. (2009), in which 19.4% of oil content was obtained using ethanol as a co-solvent (mass ratio of 6.5:93.5, w/w). Authors also emphasized that the adoption of mathematical models, not performed in this work, are useful for commercial purposes, in order to optimize the operating conditions and minimize costs.

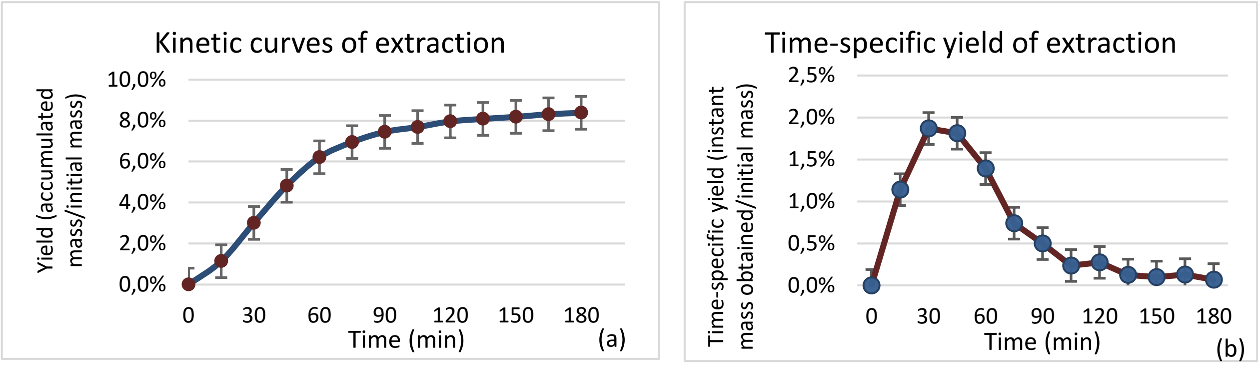

Figure 3. Kinetic curves of SFE-CO_2; **(a)** Accumulated yield; **(b)** Time-specific yield.

Soxhlet extraction resulted in 16.25% - 23.85% of oil content, with average of 20.62% and 1.85% of uncertainty. This process permitted to recognize those values as the maximum oil content in the samples. Kamil et al. (2019) observed a maximum value of 14.12%, obtained from a 45 min Soxhlet extraction. Heile (2014) conducted Soxhlet extraction with different settings, identifying oil content percentages of 15.6% (n-hexane), 17.5% (ethyl ether), and 20.6% (mixture of n-hexane and isopropanol, 50:50 %vol). Melo et al. (2014) determined a yield average value of 15.0%, normalizing following results from this value. Couto et al. (2009) obtained a yield of 18.3% with this process. At this point, following what was observed by Heile (2014), it is important to notify that the variation in oil content between results and bibliography data can be attributed to many parameters, such as variety of coffee, solvent type used in the extraction, extraction time-spent, and cultivation conditions. Notwithstanding, the recognizing of the maximum oil content foresees other viable applications for spent coffee grounds, such as bioactive compounds additives for food, cosmetic and pharmaceutical applications (López-Linares et al., 2021).

Centrifugation extraction methods with ethyl ether and n-hexane allowed to obtain, respectively, oil content averages of 11.12% and 7.63%. Short time spent is a potential reason to indicate those processes as fair purposes for spent coffee grounds oil extraction.

3.3 Biodiesel production

The average proportion of biodiesel compared to glycerin resultant of the transesterification reaction was 73.2%, with maximum value of 84.2%. These values show that the molar fraction adopted (9:1) was ideal, in terms of volumetric efficiency. The glycerin resultant presented a small fraction of sedimentary materials, probably from centrifugation extraction methods. Despite of these aspects, it is important to emphasize that the approach performed in this work for biodiesel production is not the only one. Catalyzed conventional approach with potassium hydroxide is used because allows a faster reaction, and is usually adopted in industry (Cortez et al., 2014). Karmakar and Halder (2019) performed an overview about the best-known techniques, citing: uncatalyzed conventional approach (pyrolysis and microemulsions), catalyzed conventional approach (acid-catalyzed esterification, base-catalyzed transesterification, and enzyme-catalyzed transesterification), and uncatalyzed modern approaches (supercritical transesterification and superheated transesterification). Future studies are required, such as gravimetric analysis, biodiesel yield, the lipid content conversion into biodiesel, and the implementation of different approaches for biodiesel production.

Kamil et al. (2019) analyzed the feasibility and profitability of biodiesel produced from spent coffee grounds, concluding that the production becomes feasible and profitable when at least 10,000 tonnes/y of biodiesel are produced. In the same work, authors verified the reduction of emissions from SCG biodiesel (B10), detecting reductions of until 19.14% (HC), 29.85% (CO), and 3.12% (CO_2). Also, authors emphasized that SCG biodiesel contains a lower energy content, what implies in less combustion efficiency.

Comparing many preliminary works, Atabani et al. (2019) observed that coffee produces more oil per unit of area (386 kg/ha) than soybean (375 kg/ha), usually adopted in biodiesel production. The authors also supported that the blending of SCG and cooking oils can improve economics of this industry. These data can guide future more-developed researches.

Regarding about the glycerin resultant from the process, Haile (2014) observed that the addition of glycerin in combustible pellets increases the combustion heating value from 19.3 to 21.6 MJ/kg. Karmee (2018) also cited that this by-product can be valorized for bio-oil and biohydrogen production. For instance, no potential uses for glycerin were tested or verified in this work.

Quality parameters of biodiesel are specified by resolution n. 07/2008, from ANP (*Agência Nacional de Petróleo, Gás Natural e Biocombustíveis*). Specific mass, ignition point, iodine content, acidity, and ash content are some of these parameters. These features are important to improve the environmental benefits and quality control among the production route of the biodiesel for commercial purposes. Thus, in order to prove de viability of biodiesel production from used coffee grounds, this resolution needs to be verified in future studies.

3.4 Subcritical water hydrolysis

Subcritical water hydrolysis mass and energy balances are summarized in Table 2. The different light beams lengths indicated different values of absorbance, which were plotted in a standard calibration curve, in order to correlate linearly the values of absorbance and concentration in a graphic. Specific characterization of the hydrolysates samples was not performed (e. g. inhibitors, organic acids, sugar conversion).

Table 2. Mass and energy balance of subcritical water hydrolysis.

CONTROL VOLUME	MASS BALANCE		ENERGY BALANCE	
Pump	$\dot{m}_1 = \dot{m}_2 = \dot{m}_{water}$	(16)	$\dot{W}_P = \dot{m}_{water}(\hat{H}_2 - \hat{H}_1)$	(17)
Heating exchanger	$\dot{m}_2 = \dot{m}_3 = \dot{m}_{water}$	(18)	$\dot{Q}_{2\text{-}3} = \dot{m}_{water}(\hat{H}_3 - \hat{H}_2)$	(19)
Reaction vessel	$\dot{m}_3 = \dot{m}_4 = \dot{m}_{water}$ $M_{residual} = M_{sugars} + M_{rest}$	(20) (21)	$\dot{Q}_{3\text{-}4} = \dot{m}_{water}(\hat{H}_4 - \hat{H}_3)$	(22)

Source: authors.

The spectrophotometry resulted in different values of concentration (g/L). A rule of three was performed to identify the mass concentration (grams of sugar / grams of spent coffee grounds). Comparing the results of total sugar content among the 5 different conditions, the best one was number iii (260℃ and 10 mL/min), which resulted 64 g sugar / kg of spent coffee grounds. Compliance of results are shown in Table 3.

Table 3. Results of subcritical water hydrolysis.

CONDITION	i	ii	iii	iv	v
Temperature (℃)	180	220	260	180	220
Flow rate (mL/min)	10	10	10	20	20
Sugar rate (g sugar / kg used coffee grounds)	22	40	64	17	45
Residual mass (g)	5,587	4,928	2,970	7,267	6,139
Reuse percentage	55,87%	49,13%	29,69%	72,63%	61,38%

Source: authors.

Besides this biochemical process, other conversion routes can be applied to SCG, aiming to convert this solid residue into energy. Some of these are referred by Mendoza Martinez et al. (2021), including biomechanical treatments (composting), thermochemical processes (pyrolysis for charcoal, bio-oil and syngas production, hydrothermal carbonization, and direct combustion), and physical processes (densification for pellets production).

As evidenced by Kwon et al. (2013), the previous extraction of oil content from spent coffee grounds allows to produce hydrolysate samples containing 50 g/L of total sugar (approximately 50 g sugar / kg of spent coffee grounds), from which 0.46 g of bioethanol / g of sugar can be produced. This fact corroborates this technique as a better option for bioethanol feedstock. In another point of view, A. W. Go et al. (2020) demonstrated that oil content from SCG can be enhanced up to 50% when the hydrolysis process is performed right before extraction, what implies in a great advantage for biodiesel production.

3.5 Rankine cycle

The Rankine cycle simulated is shown in Figure 4. Fuel and work fluid flow rates are indicated by $\dot{m}_{fuel}$ and $\dot{m}_{fluid}$; heat offered by the boiler and rejected by the condenser are represented, respectively, as $\dot{Q}_{boiler}$ and $\dot{Q}_{cond}$; terms $\dot{W}_p$ and $\dot{W}_t$ indicate the shaft works of the pump and the turbine, respectively.

The energy balances at each control volume are performed from the values already calculated as followed.

$$\dot{W}_p = \dot{m}_{fluid}(\widehat{H}_2 - \widehat{H}_1) \tag{23}$$

$$\dot{Q}_{boiler} = \dot{m}_{fluid}(\widehat{H}_3 - \widehat{H}_2) \tag{24}$$

$$\dot{Q}_{boiler} = \dot{m}_{fuel} \cdot HCV_{fuel} \cdot \eta_{boiler} \tag{25}$$

$$\dot{W}_t = \dot{m}_{fluid}(\widehat{H}_3 - \widehat{H}_4) \tag{26}$$

$$\dot{Q}_{cond} = \dot{m}_{fluid}(\widehat{H}_4 - \widehat{H}_1) \tag{27}$$

Combining equations (24) and (25) and assuming the Higher Calorific Value of dried spent coffee grounds as 19.9 MJ/kg (Caldeira, 2015), the flow rate required for the work fluid is:

$$\dot{m}_{fluid}(\widehat{H}_3 - \widehat{H}_2) = \dot{m}_{fuel} \cdot HCV_{fuel} \cdot \eta_{boiler} \tag{28}$$

$$\dot{m}_{fluid} = \frac{\dot{m}_{fuel} \cdot HCV_{fuel} \cdot \eta_{boiler}}{(\widehat{H}_3 - \widehat{H}_2)} = \frac{2\ \text{kg/s} \cdot 19900\ \text{kJ/kg} \cdot 0.85}{3674.3\ \text{kJ/kg}} = 9.21\frac{\text{kg}}{\text{s}} \tag{29}$$

Substituting equation (29) at (26), turbine work results in:

$$\dot{W}_t = \dot{m}_{fluid}(\widehat{H}_3 - \widehat{H}_4) = 9.21\frac{\text{kg}}{\text{s}}\ (3674.3 - 2778.4)\frac{\text{kJ}}{\text{kg}} \rightarrow \dot{W}_t = 8251.24\ \text{kW} \tag{30}$$

The thermal yield is:

$$\eta_{thermal} = \frac{\dot{W}_t - \dot{W}_p}{\dot{Q}_{boiler}} = \frac{(\widehat{H}_3 - \widehat{H}_4) - (\widehat{H}_2 - \widehat{H}_1)}{\widehat{H}_3 - \widehat{H}_2} = \frac{(3674.3 - 2778.4) - (422.3 - 417.4)}{3674.3 - 422.3} \rightarrow \eta_{thermal} = 27.4\% \tag{31}$$

According to Allesina et al. (2017), the pelletization with spent coffee grounds and wood (1:1, m/m) leads to an overall efficiency of 41.2%, from which 8.86 kW of thermal power were generated (5.26 kWh/kg). Kang et al. (2017) showed that a 6.5 kW boiler can generate heat with 1.7 kg/hr spent coffee grounds consumption rate. From this, the development of a small boiler (for example, an one-cilinder ignition compression engine) designed in short scale, can guide future projects and enhance this possibility.

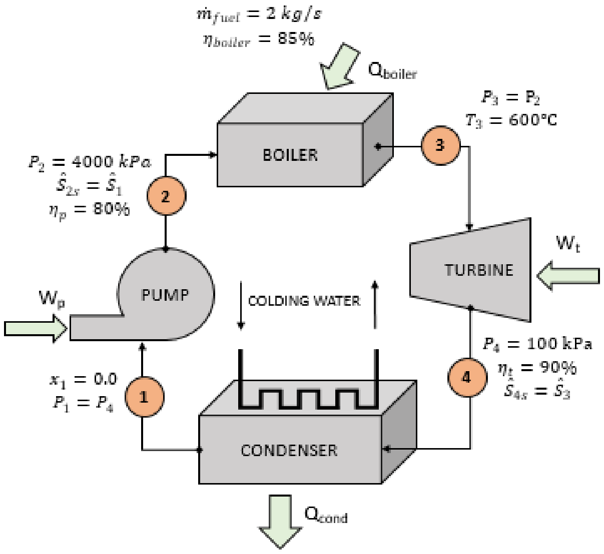

Figure 4. Rankine cycle simulated in the study. P_1: Pressure in the inlet of the pump; P_2: Pressure in the inlet of the boiler; P_3: Pressure in the outlet of the boiler; P_4: Pressure in the inlet of the condenser; x_1: Quality in the inlet of the pump; $\hat{S}_1$: Entropy in the inlet of the pump; $\hat{S}_{2s}$: Ideal entropy in the outlet of the pump; $\hat{S}_3$: Entropy in the inlet of the turbine; $\hat{S}_{4s}$: Ideal entropy in the outlet of the pump; η_p: Isentropic efficiency of the pump; η_t: Isentropic efficiency of the turbine; η_{boiler}: Isentropic efficiency of the boiler; W_t: Turbine work; W_p: Pump work; Q_{boiler}: Heat transferred to

the fluid in the boiler; Q_{cond}: Heat removed from the fluid in the condenser; $\dot{m}_{fuel}$: Flow rate of the fuel; T_3: Temperature in the outlet of the boiler

3.6 Overview of the procedures performed in the work

To better visualize all the procedures, Figure 5 shows a flowchart involving main yields of the processes and possible quantities of production of the main products, considering the average results. From 1000 kg of moist spent coffee grounds, 278.1 kg of dried spent coffee grounds (by-product) can be obtained. From this amount, 23.50 to 63.50 L of oil can be extracted, from which a maximum of 63.50 L of biodiesel can be produced. Extraction methods would result in until 256.88 kg of reusable biomass, with average of 244.37 kg. This reusable mass could produce until 15.64 kg of fermentable sugars (64 g sugar / kg spent coffee grounds), still generating 177.48 kg of reusable mass. Summing fractions of the by-product's masses, thermoelectrical plant could generate 8.26 MW of electrical power, during 3.5 min of operation.

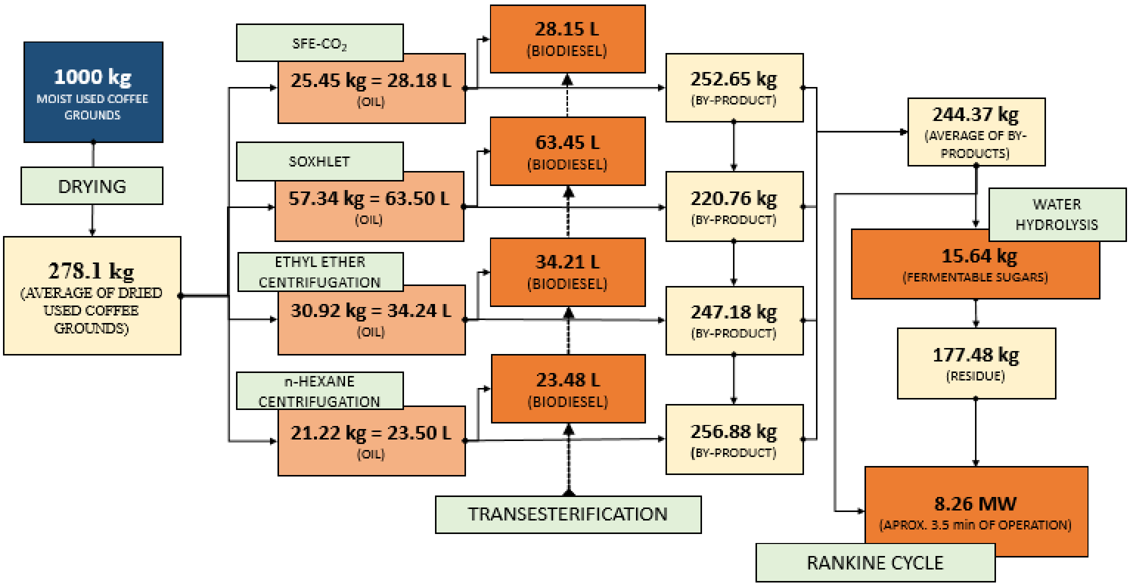

Figure 5. Flowchart with main processes performed in this work.

3.7 Processing remarks

Soy oil is used in Brazil, like mentioned before, as a traditional biomass for biodiesel production, and is easier extracted by mechanical compression methods than others. Otherwise, oil extracted from used coffee grounds is impracticable to be obtained this way, because of the necessity of biomass chemical fragmentation. Future studies, the establishment of a concrete technological route, and a cost reduction at a production cell are some perspectives to improve economic viability at oil extraction from spent coffee grounds.

According to Ignacio (2017), the average oil content in soybeans is 18.38 ± 0.28% (m/m), a value straightly competitive to the oil contents observed in spent coffee grounds. To improve this competitiveness, some challenges are requested, according to César et al. (2019). Among these, institutional environment, management and inputs technology, infrastructure, market structure, and governance can be cited. On the other hand, spent coffee grounds are highly favored due to its food and energy security offered, since there is no request of improving agricultural areas for production.

Regarding about the possibility of bioethanol production, important remarks are requested, such as yeast features, glucose conversion into ethanol, and distillation process. The energy balances of the main steps of the work showed only a full summary about thermodynamic processes. In practical terms, to accomplish all the variables involved in the procedures, an exergetic analysis is requested.

4. Conclusions

The maximum lipid content, from Soxhlet extraction, indicates the biomass as a potential option for a future energetic implementation in Brazil, due to its close similarity with soy oil yields. This work permitted to analyze, with an original scientific point-of-view, different methods of extraction, from which average values of 20.62%, 8.79%, 11.12% and 7.63% were obtained, respectively from Soxhlet extraction, SFE-CO_2, centrifugation with ethyl ether, and centrifugation with n-Hexane. The work focused in analyzing these procedures, performing mass and energy balances. Furthermore, the data acquired reinforced the importance of the use of wasted products, which are a great source of energy. The values permitted to indicate spent coffee grounds as a strong resource for biodiesel production, since the conventional biomass used in Brazil is soybean, with an average of 18.38% of oil content. Besides that, the foreseeing of implementation of alternative biomasses for energy generation is corroborated through this work. An overview of the work was performed, and allowed to demonstrate the possibility of energy generation from spent coffee grounds, through production of biodiesel and fermentable sugars used in bioethanol production, in addition to electrical power generation. If established into a circular economy model, there are many steps along the coffee production that could be explored, as showed in the work of Stroub (2021), from the harvest to the coffee cup. Considering the overview previously exposed and the amount of SCF in Brazil (around 2.000 tons/year), the final amount of co-products would be certainly insignificant compared to other sources (approximately 128,000 liters of biodiesel, 31,280 kg of fermentable sugars, and 16,000 MW of electrical power could be obtained), but it can be surely guaranteed as a possible alternative biomass in the processes referred. Since this co-product becomes strongly established in circular economy for other applications (such as pharmaceutical industry), the possibilities exposed here can be deeply analyzed. Oil content, yield of the processes, cost, time spent, and resources are some features that implicate directly on viability of the purposes. Future assessments will indicate the insertion of this biomass in the Brazilian energetic matrix. Caption of resources, production logistic, distribution and financial stimulations are some of those.

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