2022

Techno – Economic analysis of activated carbon production from spent coffee grounds: Comparative evaluation of different production routes

Mukherjee, Alivia

Elsevier

Mukherjee, A., Okolie, J.A., Niu, C., Dalai, A.K., Techno – Economic analysis of activated carbon production from spent coffee grounds: Comparative evaluation of different production routes, Energy Conversion and Management: X, Volume 14, 2022, 100218,ISSN 2590-1745, https://doi.org/10.1016/j.ec

https://hdl.handle.net/10388/15113

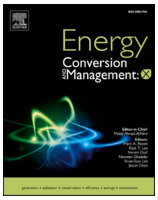
10.1016/j.ecmx.2022.100218

Energy Conversion and Management: X 14 (2022) 100218

Contents lists available at ScienceDirect

Energy Conversion and Management: X

journal homepage: www.sciencedirect.com/journal/energy-conversion-and-management-x



Techno – Economic analysis of activated carbon production from spent coffee grounds: Comparative evaluation of different production routes

Alivia Mukherjee, Jude A. Okolie, Catherine Niu, Ajay K. Dalai *

Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada

ARTICLE INFO

Keyword:
Activated carbon
Spent coffee grounds
Techno – economic analysis
Biochar
Pyrolysis

ABSTRACT

Activated carbon (AC) has gained immense popularity owing to its excellent physicochemical properties and its ability to remove carbon dioxide (CO_2) from flue gas stream. This study examines the potential of spent coffee grounds (SCG) as a precursor for activated carbon (AC) production via prominent thermochemical conversion technologies. Different production routes, such as slow pyrolysis, activation, and deep eutectic solvent (DES) functionalization were compared in terms of their economic viability. Three scenarios (Scenario 1–3) involving combinations of the technologies and production routes were evaluated. Scenario 1 comprises of slow pyrolysis, CO_2 activation and flue gas recycling for activation. Scenario 2 includes flue gas combustion while the third scenario comprise of flue gas combustion and DES impregnation. All processes were simulated with Aspen plus, while a detailed cash flow analysis was used to estimate the profitability parameters. The price of AC was found to be the most crucial determinant of an AC production plant's viability and feasibility. The minimum selling price (MSP) of AC samples produced from scenarios 1,2 and 3 are U.S $0.15/kg, $0.21/kg, $0.28/kg respectively. The price of pristine AC and DES treated AC were lower than the commercially available activated carbon (U.S $0.45/kg).

Introduction

Coffee is a promising agricultural product as well as a widely consumed beverage worldwide. It is often regarded as the second largest traded commodity after petroleum, with nearly 2 billion cups of coffee consumed each day globally [1]. Moreover, the processing of coffee beans involves a series of steps, including milling, roasting, grinding and brewing. Coffee processing is accompanied by production of significant amount of waste known as spent coffee grounds (SCG) [2]. For every kg of soluble coffee bean processed, about 2 kg of SCG is generated [2]. SCG is often dumped in landfills or incinerated, thereby creating several environmental pollutions due to its composition. About 9 million tons of SCG are dumped in landfills annually [3].

SCG is a non – edible by-product from the coffee industry rich in carbohydrates, oil, carbon, nitrogen, proteins, and bioactive compounds. With the elevating coffee demand and consumption, it is imperative to balance the production with the proper valorization of the byproducts, including SCG. The conversion of SCG to biofuels and green chemicals has been gaining momentum to foster sustainable waste management. As a result, several researchers have studied the production of biofuels and bioactive compounds from SCG [4,5].

SCG could also be used to produce biochar and activated carbon (AC) for subsequent CO_2 capture under post-combustion scenario [6]. Biochar production from SCG has the potential to alleviate the challenges of climate change, greenhouse gas emissions and environmental pollution. Biochar can also be produced from other lignocellulosic biomasses such as sugarcane bagasse [7], almond shells [8], and food waste [9]. A recent study demonstrated that the biochar produced from SCG showed superior CO_2 adsorption capacity compared to biochar from other lignocellulosic materials [6]. In another study, it has been demonstrated that the physical and chemical activation of biochar to AC could improve the surface properties and CO_2 adsorption capacity [8,10,11].

Abbreviations: AC, Activated carbon; SCG, Spent coffee grounds; DES, Deep eutectic solvent; CAPEX, Capital expenditure; CEPCI, Chemical engineering plant cost index; DCFA, Detailed discounted flow analysis; DCFR, Discounted cash flow rate of return; COE, Equipment purchase cost; FCI, Fixed capital investment; FOC, Fixed operating cost; IRR, Internal rate of return; MPa, Mega Pascal; MSP, Minimum selling price; MW, Mega Watt; NPV, Net present value; OPEX, Operating expenditure; OCB, Oracle Crystal Ball; PBP, Payback period; PR-BM, Peng-Robinson-Boston-Mathias; RM, Raw material; TEA, Techno-economic analysis; WC, Working capital.

* Corresponding author at: Department of Chemical and Biological Engineering, University of Saskatchewan, 57 Campus Drive, Saskatoon, Saskatchewan S7N 5A9, Canada.

E-mail address: ajay.dalai@usask.ca (A.K. Dalai).

https://doi.org/10.1016/j.ecmx.2022.100218
Received 18 February 2022; Received in revised form 26 March 2022; Accepted 28 March 2022

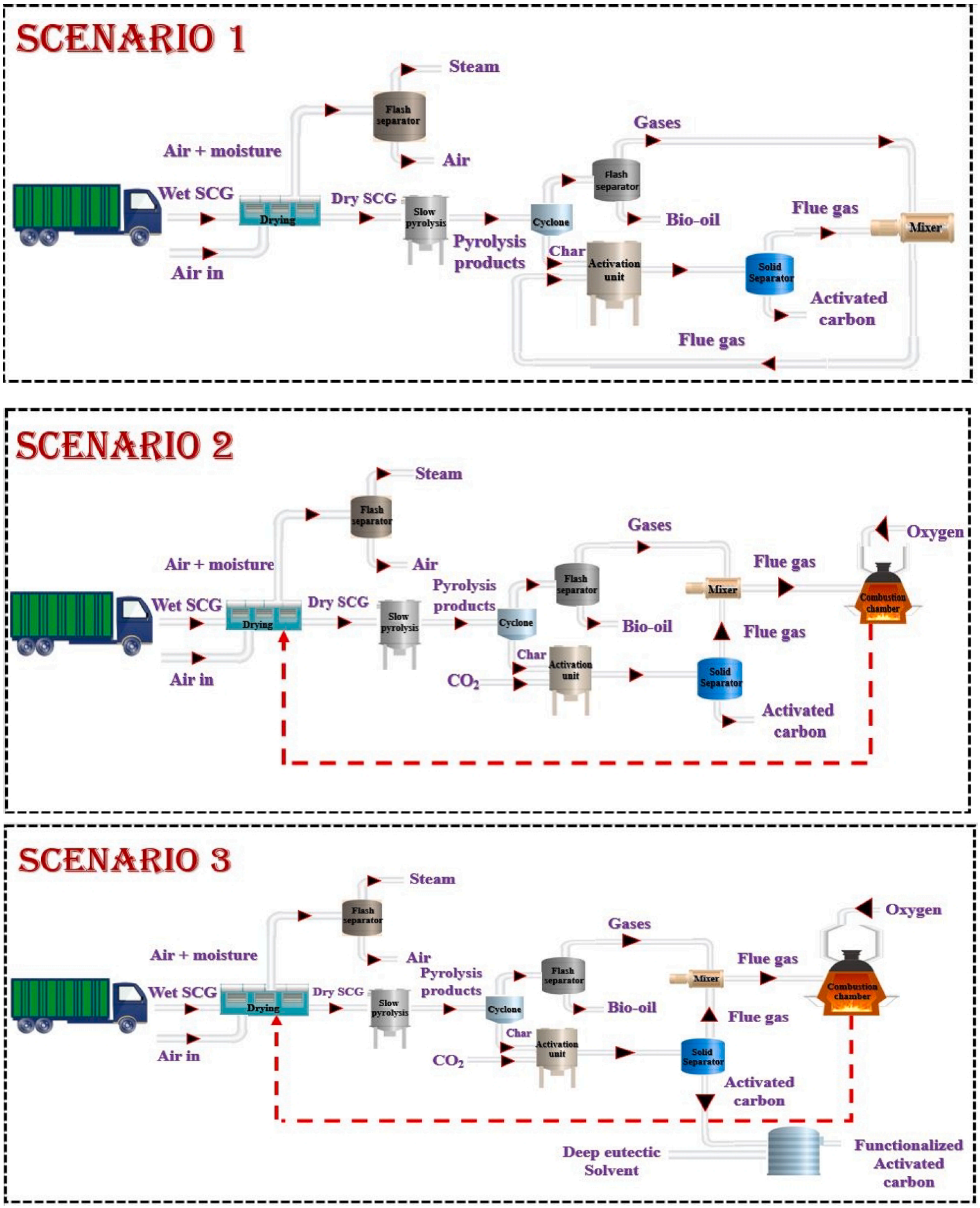


Fig. 1. Flowsheet of the proposed design, (scenario 1), slow pyrolysis and physical activation; (scenario 2), slow pyrolysis, physical activation, and flue gas combustion; (scenario 3), slow pyrolysis, physical activation, DES functionalization and flue gas combustion.

Moreover, the use of environmentally friendly deep eutectic solvents (DES) comprising of a mixture of choline hydroxide and urea to functionalize the activated carbon has been shown to improve its CO$_2$ adsorption capacity [12]. In another study, the functionalization of AC with ionic liquids also increases the CO$_2$ adsorption capacity [13]. However, the preparation of DES is relatively simple compared to that of ionic liquids. In addition, DES exhibits some unique properties such as non – toxicity, high ionic conductivity, low cost, thermal stability and biodegradable which could favor the CO$_2$ capture [12].

Recently, Qian et al. (2021) performed the techno-economic analysis (TEA) of AC production from spent mushroom substrate [14]. However, a cash flow analysis and the MSP of AC were not determined. In another study, the TEA of an integrated process for producing biodiesel, glycerol and AC from SCG was estimated [15]. However, the process is applicable to China. In addition, a detailed cash flow analysis was not performed. Furthermore, a comprehensive evaluation of the effects of process parameters on the MSP is missing from the study. Although extensive research has been carried out on the techno – economic analysis (TEA) of different biomass conversion processes, to the best of the author’s knowledge, there is no available study on detailed TEA and sensitivity analysis of AC production from SCG.

Although the preparation and functionalization of AC from SCG for CO$_2$ capture is a promising strategy to minimize greenhouse emissions, the economic feasibility of the entire process is scarcely reported. More importantly, a comparative evaluation of the process economics of AC production with and without functionalization is missing in the literature. The present study presents a novel approach to assess the economic viability of different activated carbon production routes from SCG. The study also compares the minimum selling price (MSP) of the pristine and DES functionalized AC.

Research methodology

Process design and simulation

Three different scenarios for the production of AC routes were assessed in the study, as shown in Fig. 1. Scenario 1 is a straightforward route and provides a foundation for further assessments. It consists of SCG drying, slow pyrolysis and CO_2 activation. Furthermore, the flue gas from pyrolysis process consists mostly of CO_2 and used for activation process. In scenario 2, the product gas from the pyrolysis and activation process was sent to the combustion chamber. Combustion of the product gas produces heat used for biomass drying, thereby minimizing the energy requirement of the process. Scenario 3 comprises of slow pyrolysis, CO_2 activation, combustion unit and DES functionalization unit. Overall, the process aims to compare different activated carbon production routes in terms of their economic viability.

The overall process for the three scenarios was simulated and implemented with Aspen Plus v12.1 (AspenTech, Bedford, USA), licensed by the University of Saskatchewan. The process was designed to process approximately 50,000 tons/y of SCG. However, the developed model could also be applied to other biomass materials. Aspen plus was used for the simulation because of the array of inbuilt physical properties databases that are useful for thermodynamics calculations and the mass and energy balance. Aspen plus does not contain an inbuilt model for biomass pyrolysis; therefore, the entire process was simulated into different unit operations, as shown in Fig. 1. Moreover, SCG was defined as a non-conventional component whose components were determined based on the proximate and ultimate analysis.

The moisture (3.3 wt%), volatile (81.2 wt%), fixed carbon (14.6 wt %), and ash content (0.9 wt%) of SCG were reported in our previous study [6]. Additionally, the C, H, N, S and O are 50.0 wt%. 6.7 wt%, 2.5 wt%, 0.9 wt%, and 39.0 wt%, respectively. The RYield block was employed to decompose SCG into its components (C, H_2, N_2, O_2, H_2O, ash, and S), while a calculator block was used to perform the decomposition through a FORTRAN subroutine statement. Details of the subroutine statement and the calculator block methodology have been reported elsewhere [16].

As described in Fig. 1 (scenario 1), wet SCG is sent to the air dryer operating at 100 °C and 0.1 MPa. The dryer reduces the moisture content of SCG to less than 5 wt%. A biomass dryer in Aspen plus was represented with a stoichiometric block. In contrast, a calculator block was used to determine the moisture content of SCG at the exit of the reactor.

The dried SCG enters the RYield reactor at 600 °C and 0.1 MPa. According to the ultimate and proximate analysis, the reactors decompose SCG into C, H_2, N_2, O_2, H_2O, ash, and S. The biochar derived from SCG is sent to the pyrolysis reactor. RGibbs block was used to simulate slow pyrolysis at 600 °C and atmospheric pressure. Moreover, a cyclone separator was used to remove the solid char while the liquid, gases and volatiles were cooled before entering the flash separator for the removal of gases. It should be noted that the temperature and pressure of slow pyrolysis were selected based on our previous experimental report [6].

The produced char was physically activated with CO_2 at 800 °C and atmospheric pressure. The activation process was simulated with the RGibbs block, while the amount of CO_2 required to ensure that 57.4 wt% yield of AC is produced was specified with design specs The yield of 57.4 wt% was chosen based on the optimized experimental yield of AC derived using the Box- Behnken design of experiments. It should be mentioned that the ratio of DES and the activating agent used in this regard is 1:2.

The product gases from the activation process and the gases from pyrolysis were sent to the combustion chamber according to scenarios 2 and 3. A stoichiometric reactor (Rstoic) operating at 1000 °C under 1.1 MPa pressure was used to represent the combustion unit. Rstoic reactor was modeled based on Eqs. (1)–(5) [14].

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O \tag{1}$$

$$C_2H_4 + 3O_2 \leftrightarrow 2CO_2 + 2H_2O \tag{2}$$

$$C_2H_6 + 3.5O_2 \leftrightarrow 2CO_2 + 3H_2O \tag{3}$$

$$H_2 + 0.5O_2 \leftrightarrow H_2O \tag{4}$$

$$CO + 0.5O_2 \leftrightarrow CO_2 \tag{5}$$

The entire process simulation uses the Peng-Robinson-Boston-Mathias (PR – BM) equation of state which is suitable for low pressure streams [14]. Moreover, the operating conditions for the unit operations are obtained from experimental studies. That way the model could be validated against lab studies. All the assumptions used in the Aspen plus model as well as the economic model is presented in Table 1.

Table 1

Assumptions used in the Aspen plus simulation and economic model.

Parameters	Assumptions
Assumptions in process simulation	
Biomass decomposition products	Biochar, CO, CO_2, N_2, H_2, O_2 and H_2O
Ash	Does not participate in the reactions
Biochar decomposition products	Carbon and Ash
Equation of state	PR – BM equation
Assumptions in the economic model	
Currency used in economic model	U.S$
Base year	2021
Cost of land	2% of fixed capital investment
Plant construction duration	1 year
Plant lifetime	20 years
Plant annual operation	8000 h/y
SCG capacity	50,000 tons/y
Depreciation	Straight line method

Table 2

CAPEX and OPEX Estimation methodology.

CAPEX Estimation	
Cost estimation	Fraction of the purchase cost of all equipment
Purchase cost of all equipment (COE) (a)	COE
Cost of equipment installation (b)	0.4COE
Controls and instrumentation cost (c)	0.26COE
Piping and electrical systems (d)	0.41COE
Building and services (e)	0.1COE
Direct cost (DC)	DC = (a) + (b) + (c) + (d) + (e)
Indirect cost (IC)	IC = 0.22DC
Fixed capital investment (FCI)	FCI = DC + IC
Startup cost (SUC)	0.05FCI
Working capital (WC)	0.15FCI
CAPEX	CAPEX = FCI + SUC + WC
OPEX Estimation	
Cost of labor	COL
supervision and overhead cost (f)	1.25COL
Maintenance and miscellaneous expenses (g)	0.04FCI
Fixed operating cost (h)	(h) = COL + (F) +(G)
Spent coffee grounds cost (i)	USD $ 0.1/ dry ton
Deep eutectic solvent (Choline chloride + Urea) (j)	USD $ 144 for Choline chloride [32] USD $ 96.30 for Urea [33]
Total raw material cost (k)	(k) = (i) + (j)
Electricity cost (m)	USD $0.069/KWh per unit [18]
Cooling water cost (l)	USD $14.8/1000 m^3 [18]
Variable operating cost (p)	(p) = (k) + (m) + (l)
OPEX	OPEX = (h) + (p)

Economic analysis

The economic analysis of AC production from SCG was estimated using the bottom-up approach. The method calculates the cost components as a part of the purchase cost of all equipment (COE) also known as the bare module cost [17]. The capital expenditure (CAPEX) and operating expenditure (OPEX) were estimated based on Table 2. The CAPEX

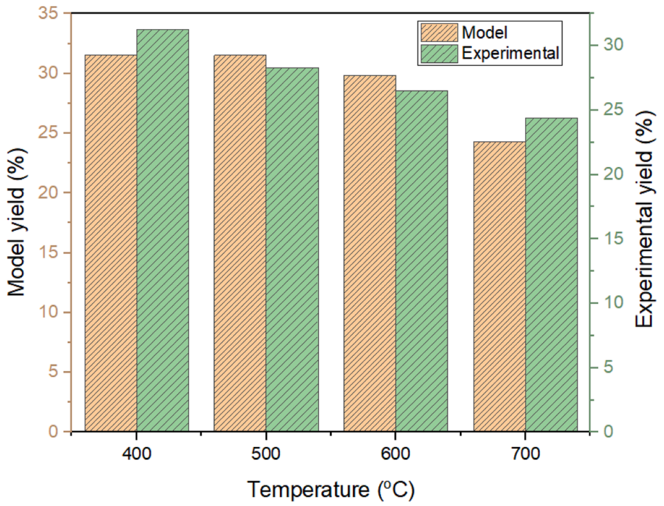


Fig. 2. Comparison of biochar yield from experimental and model results. Experimental yields were obtained from previous study (Mukherjee et al., 2021).

includes the direct and indirect cost while the OPEX comprises of the fixed and variable operating cost [18]. The labor cost was estimated as part of the fixed operating cost from equation (6). Where P and N_{NP} indicate the number of solid handing steps and on-particulate processing steps. The average annual salary of each workers was set at U.S $35,000 [18]. Based on the expression in equation (6), the overall number of operators required for scenarios 1, 2 and 3 are 6, 7 and 12, respectively [17–18].

$$N_{OL} = \sqrt{31.7P^2 + 0.23N_{NP} + 6.29} \tag{6}$$

Discounted cash flow analysis (DCFA) was performed and used to determine the MSP of AC as well as the economic feasibility of different AC production routes. The process is economically viable if the MSP of AC is above the breakeven point. The economic viability of the process was also assessed with major parameters such as the net present value (NPV), payback period (PBP), net rate of return (NRR) and DCFA of the project. Detailed description of each economic indicators as well as their advantages and limitations has been reported by Ulrich and Vasudevan. [19].

The proposed plant is set up in Saskatchewan, Canada. However, a location factor (0.91) could be used to show the disparities in cost between Canada and Europe [20]. The economic model was developed with currency in U.S $. The cost of SCG was estimated to be U.S $ 0.1/

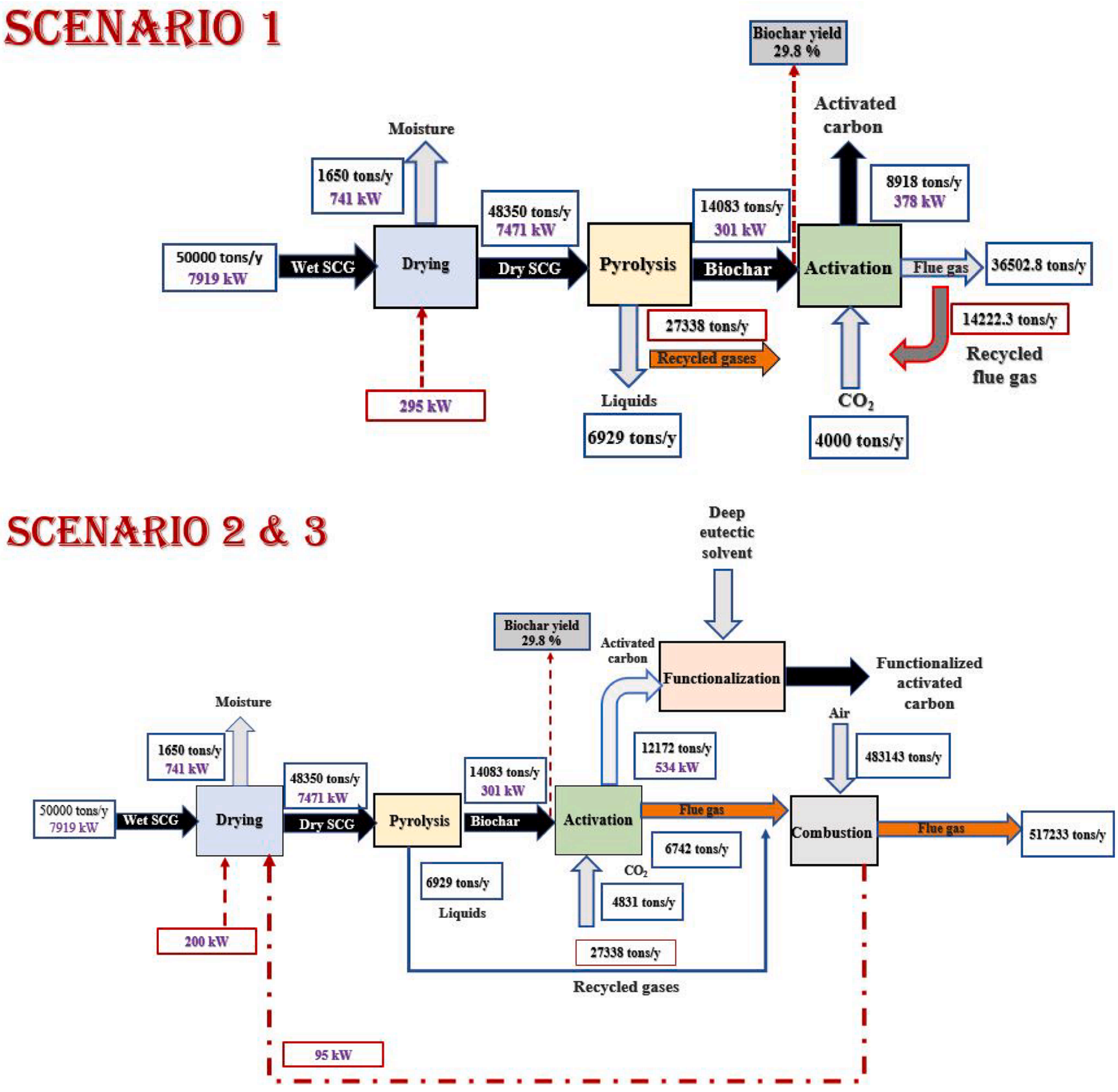


Fig. 3. Mass and energy balance for scenarios 1–3.

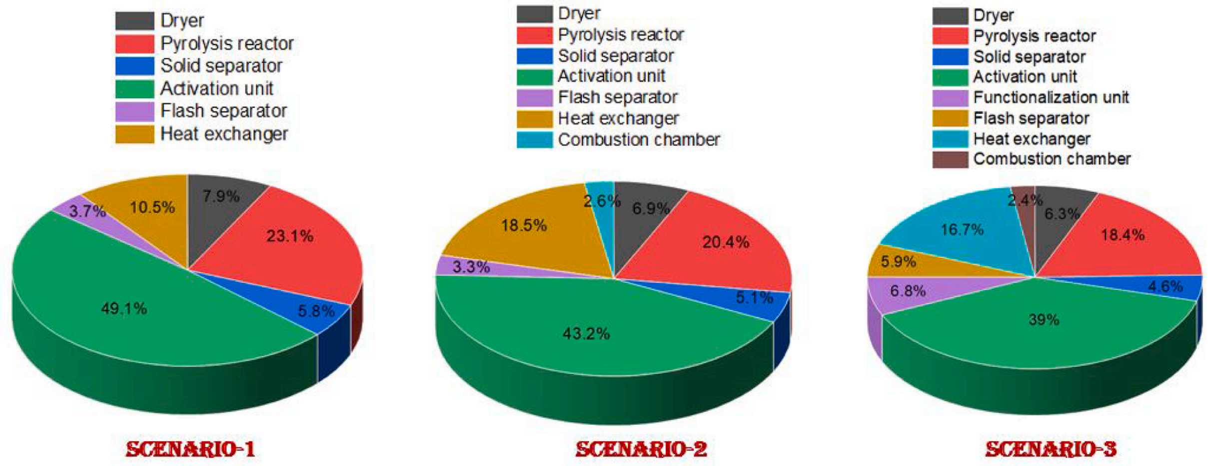


Fig. 4. Breakdown of the equipment purchase costs for all the three scenarios.

dry ton based on the present market price of transportation and logistics [14]. Moreover, the reference year was 2021 with the Chemical Engineering Plant Cost Index (CEPCI) used to adjust the cost of equipment to the base year. All the assumptions used in the economic model and Aspen plus simulation are summarized in Table 1. The COE was determined with the scaling method [21]. The approach calculates the cost of equipment with the base cost of similar equipment whose size is known (Equation (7)).

$$C = C_o\left(\frac{S}{S_o}\right)^f \tag{7}$$

S is the equipment capacity obtained from Aspen Plus simulation, while S_0 is the base capacity. C and Co are the actual and base equipment cost respectively. In contrast, f represents the scaling factor.

Monte Carlo simulation was used to quantify the uncertainty and associated risk in the developed economic model. The Monte Carlo simulation was performed with Oracle Crystal Ball (OCB) software. OCB is a stochastic tool designed as a spreadsheet based application suitable for uncertainty and risk analysis [22]. The present study applies normal distribution with 30,000 trials for the estimation of the associated uncertainty in the economic model.

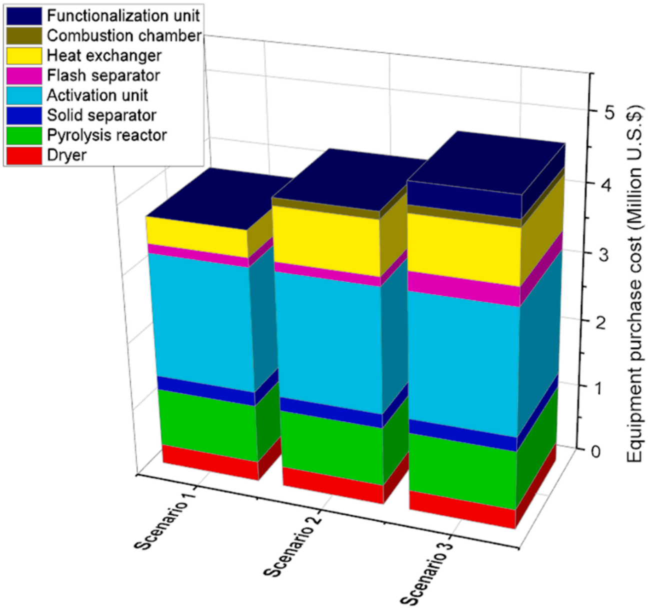


Fig. 5. Overall cost of equipment for all the three scenarios.

Results and discussions

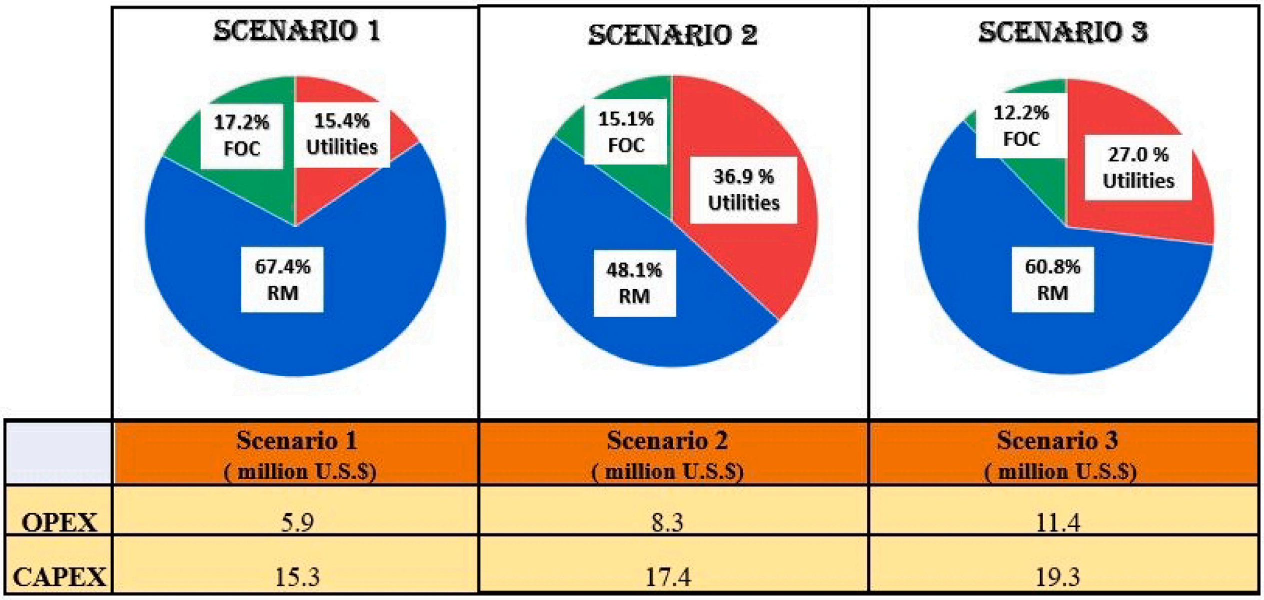
Model validation, mass, and energy analysis.

The experimental biochar yields from slow pyrolysis of SCG was compared with model results at temperatures range of 400 – 700 °C (Fig. 2). The model predictions were obtained from the sensitivity analysis of RGibbs block in Aspen plus. The comparison of model and experimental results is useful in the validation of the model. It also helps to assess the proximity of the model predictions to reality. As shown in Fig. 2 all the model results are close to the experimental values with minimum deviations (less than 10%). This shows that the developed model is effective in the prediction of biochar yields even at high temperatures.

Fig. 3 shows the mass and energy balance for scenarios 1 – 3. The use of heat recycled from the combustion of flue gas in scenarios 2 and 3 saves 95 kW energy in the drying process. Moreover, 295 kW of energy was required for scenario 1. In scenario 1, 4000 tons/y of CO_2 was required for activation compared to 4831 tons/y as in case of scenarios 2 and 3. For every 50, 000 tons/y of SCG, 8918 tons/y and 12,172 tons/y of AC were produced for scenarios 1 and scenarios 2 and 3 respectively. Overall, biochar yield from slow pyrolysis for the three scenarios is 29.8 %, which is close to experimental yield (25.4 %). Scenarios 1 and 2 comprises of two sequential steps for the AC production (slow pyrolysis of spent coffee grounds for biochar production followed by physical activation). However, scenario 3 comprises of three sequential steps for the production of AC production (slow pyrolysis for biochar production, physical activation followed by functionalization with deep eutectic solvent (DES)). The physicochemical properties of biochar derived from slow pyrolysis of spent coffee grounds for all the three scenarios (1–3) have been documented in our previous study [6]. However, scenario 1 is a new concept which we modelled conceptually with Aspen plus. Our future studies would focus on the determination of physicochemical characteristics of AC produced from the scenario 1.

Economic analysis

Detailed analysis of the COE for the three scenarios are presented in Fig. 4. Activation unit and pyrolysis reactor are the most expensive equipment for all three scenarios. Activation unit accounts for 49.1 %, 43.2 % and 39% of the overall equipment costs for scenario 1, 2 and 3 respectively. In contrast, the cost of pyrolysis reactor accounts for 23.1%, 20.4% and 18.4% of the overall COE for scenario 1, 2 and 3



	Scenario 1 (million U.S.$)	Scenario 2 (million U.S.$)	Scenario 3 (million U.S.$)
OPEX	5.9	8.3	11.4
CAPEX	15.3	17.4	19.3

Fig. 6. Total CAPEX and OPEX for the three scenarios and the OPEX break down.

respectively. The high costs of activation unit could be attributed to the increased temperature requirement compared to the pyrolysis unit. Activation is performed at higher temperature range of 800 – 1000 °C which requires specialized reactor materials to withstand such temperatures. The total COE is illustrated in Fig. 5. The cost declines in the following order: scenario 3 (4.7 million U.S $) > Scenario 2 (4.2 million U.S $) > Scenario 1 (3.7 U.S $). The high cost of scenario 3 could be as a result of the extra functionalization and combustion units. Although, the functionalization unit helps to improve the activated carbon properties, it contributes towards an increase in the COE.

The breakdown of the CAPEX and OPEX estimation is shown in Fig. 6. The OPEX for the three scenarios increases as follows: scenario 1 (5.9 million U.S $) < scenario 2 (8.3 million U.S $) < scenario 3 (11.4 million U.S $). The greater OPEX for scenario 3 could be because of the higher variable and fixed operating cost. The variable operating cost includes the cost of SCG, DES chemicals (urea and choline chloride), Industrial grade CO_2 cost and utility cost [23]. Additionally, the fixed operating cost (FOC) comprises of overhead cost, maintenance cost, insurance and labor and they remain constant regardless of the production level. The addition of combustion and functionalization unit in

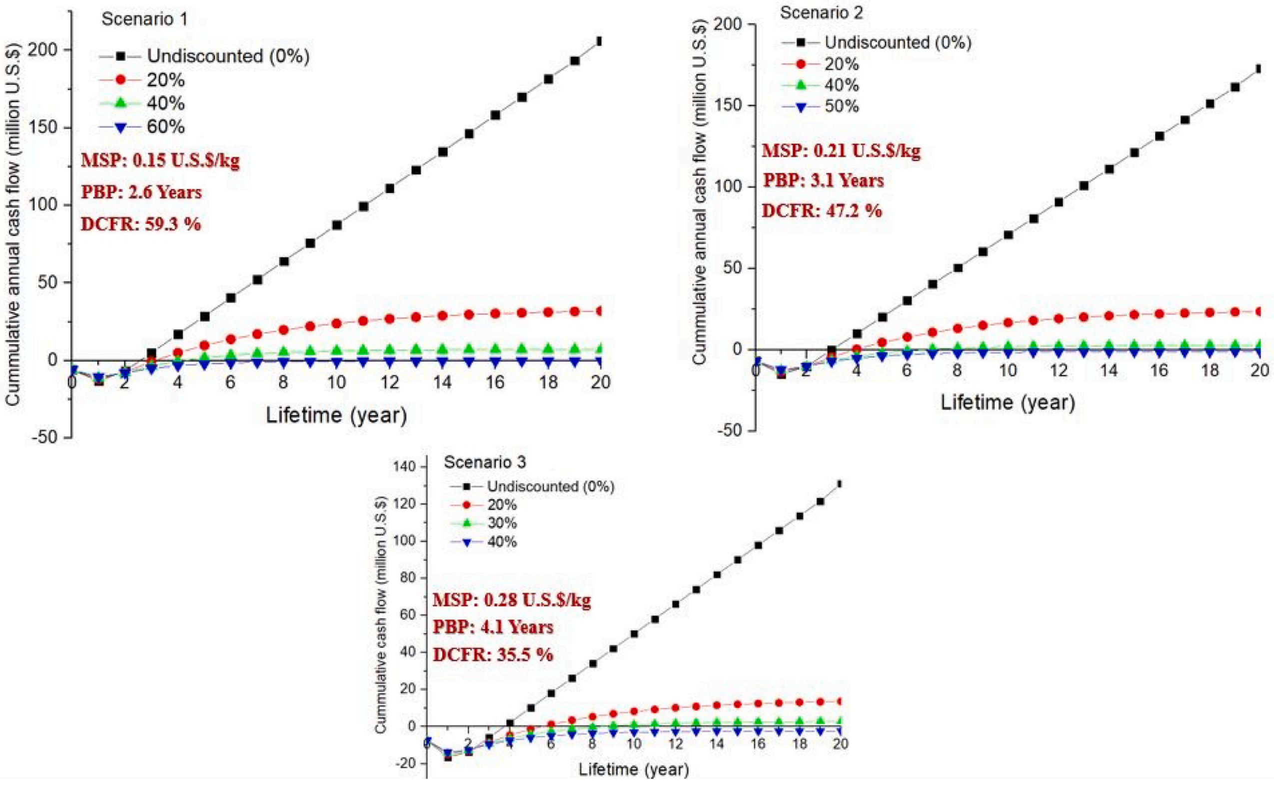


Fig. 7. Discounted and undiscounted cash flow analysis for the three scenarios for AC production.

Table 3
Comparison of the minimum selling price of biochar and activated carbon from different studies.

Feedstock	Processing technology	Main product	MSP (U.S $/kg)	Ref.
Palm oil empty fruit bunches	Slow Pyrolysis	Biochar	0.53	(Harsono et al., 2013)
Woodchips briquettes (WCB)	Slow pyrolysis	Biochar	1.044	(Sahoo et al., 2019)
Poplar	Fast and Slow pyrolysis	Biochar	0.067 for fast pyrolysis derived biochar and 0.074 for slow pyrolysis derived biochar	(Kung et al., 2013)
Coffee husks (COF)	Microwave slow pyrolysis	Biochar	0.49 (€ 0.43)	(Haeldermans et al., 2020)
Medium-density fiberboard (MDF)			0.64 (€ 0.57)	
Palm date fronts (PDF)			0.88 (€ 0.78)	
Wood mix (AB)			0.63 (€ 0.56)	
Tree bark (TB)			0.55 (€ 0.49)	
Olives Stone kernels (OS)			0.96 (€ 0.86)	
Cattle manure	Mobile slow pyrolysis unit	Biochar	0.27	(Struhs et al., 2020)
Poultry litter	Slow pyrolysis	Biochar	0.076–0.091	(Bora et al., 2020)
Honeydew peels	Slow pyrolysis and H_2SO_4 impregnation	Activated carbon	0.26	(Yunus et al., 2020)
Commercial activated carbon	Not available	Activated carbon	0.45	(“Charcoal, Activated, Norit®, Alkaline, Decolourizing | Canadawide,” 2021)
Spent coffee grounds	Slow pyrolysis, CO_2 activation, flue gas combustion and DES impregnation	Activated carbon	0.28	This study
Spent coffee grounds	Slow pyrolysis, CO_2 activation and flue gas combustion	Activated carbon	0.21	This study
Spent coffee grounds	Slow pyrolysis and CO_2 activation.	Activated carbon	0.15	This study

scenarios 2 and 3 increases the number and cost of labour as well as the raw materials cost. This could ultimately increase the OPEX of scenarios 2 and 3 compared to scenario 1. Breakdown of OPEX cost indicates that the utility and raw material cost accounts for most of the OPEX in all the three scenarios (Fig. 6). Raw material cost accounts for 60.8 % of the OPEX in scenario 3 due to the use of DES. Moreover, the electricity cost is higher for scenarios 2 and 3 compared to scenario 1 due to the addition of the combustion chamber. The contribution of the FOC was not substantial for all the three scenarios. FOC contributed 17.2%, 15.1% and 12.2 % for scenarios 1, 2 and 3 respectively.

The CAPEX for the three scenarios declines in the following order: scenario 3 (19.3 million U.S $) > scenario 2 (17.4 million U.S $) > scenario 1 (15.3 million U.S $). The CAPEX includes the fixed capital investment (FCI), startup cost and the working capital (WC) all of which are dependent on the COE. Therefore, the superior CAPEX of scenario 3 could be attributed to the increased COE.

CAPEX and OPEX estimation provided the information needed for the discounted flow analysis (DCFA). The analysis was used to evaluate the MSP of AC and to calculated different profitability index [23,24]. The profitability of AC production from different routes were determined by comparing parameters such as payback period (PBP), net present value (NPV), discounted cash flow rate of return (DCFR). Detailed explanation of the profitability index and their significance can be found elsewhere [25].

Fig. 7 shows the cash flow analysis for three different scenarios for AC production. As shown in Fig. 7, negative cash flow was obtained for year zero due to the money use for land purchase and the total capital investment. Moreover, funds are recovered from sales and investments after complete construction and project initiation. These funds ensures that the cash flow becomes positive over the years. The PBP estimated for the three scenario decreases as follow: Scenario 3 (4.1 years) > scenario 2 (3.1 years) > scenario 1 (2.6 years). The PBP indicates the time it takes for the investment cash flow to equal the initial cost. The PBP should be less than the entire project life for an investment to be economically feasible. Based on the PBP all the three scenarios are profitable. Although promising, the PBP does not explain the performance of the project once the investment recovers its initial outlay. Therefore, the NPV and DCFR are also used as complimentary profitability index.

The NPV of all the three scenarios are positive indicating that they are all profitable. However, scenario 1 had the most superior undiscounted NPV of 206.4 million U.S $. On the other hand, scenario 3 had the lowest undiscounted NPV of 131.1 million U.S $. Based on the NPV values the DCFR was obtained at the discount rate that yields NPV of zero. The DCFR increases in the following order: scenario 3 (35.5%) < scenario 2 (47.2%) < scenario 1 (59.3 %). The results of DCFA, PBP and NPV of the three scenarios indicates that scenario 1 is more profitable from economic perspective. However, scenario 3 produces high quality AC compared to the other scenarios. It should be mentioned that the third scenario costs more in terms of the CAPEX, OPEX and COE due to the additional combustion and DES unit. These extra processing units influenced the NPV, PBP and DCFR compared to other scenarios.

The MSP of the three production routes (the cost of AC that produces zero NPV) was assessed and compared with literature values and the price of commercial AC (Table 3). The AC produced from scenario 1 had the lowest MSP (0.15 U.S $/kg). In contrast, scenarios 2 and 3 had MSP of AC as 0.21 U.S $/kg and 0.28 U.S $/kg respectively. The minimum selling price of AC for the three scenarios are comparable to that of commercial biochar and AC (Table 3). Struhs et al. [26] developed a mobile pyrolysis unit and assessed the MSP of biochar produced from slow pyrolysis of the unit using cattle manure as feedstock. They obtained a MSP of 0.27 U.S $/kg. In another study, Palm oil empty fruit bunches were used as feedstock to estimate the MSP of a slow pyrolysis plant in Selangor [27]. The produced biochar had an MSP of 0.53 U.S $/kg. It should be mentioned that the cost estimation methods, and MSP reported in the studies in Table 3 are different. Moreover, the price documented for different studies is relevant to the date of publication.

Combining technologies such as slow pyrolysis and acid impregnation have the potential to improve the activated carbon properties for several industrial applications. Honeydew peels was used as feedstock for slow pyrolysis and acid impregnation (sulfuric and phosphoric acid) to produce activated carbon [28]. MSP value of 0.26 was obtained by the integrated AC production process. Moreover, the AC showed promising results in the removal of heavy metals from mining effluents. Advanced pyrolysis technologies such as microwave pyrolysis have also been used to produce biochar from different feedstocks including tree bark, palm

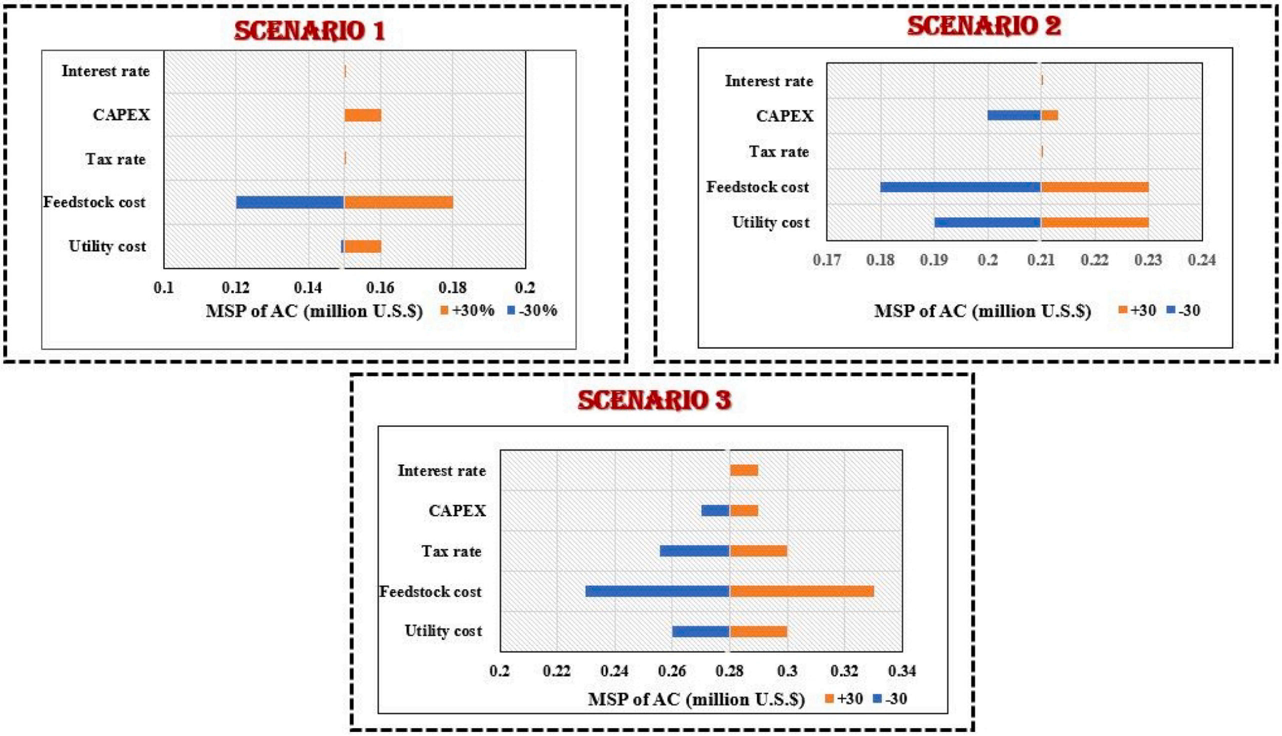


Fig. 8. Sensitivity analysis showing the influence of several independent parameters on the MSP of AC for the three scenarios.

date fronts and wood mix [29]. MSP value ranging from 0.49 to 0.88 U.S $/kg were obtained using different feedstocks.

It is noteworthy to mention that although the MSP of AC reported in the present study are promising, several government policies schemes and study limitations should be considered. For instance, the carbon pricing for specific countries is not applied in this study. If applied, the MSP could decrease. However, the carbon pricing varies for different countries. Also, the produced activated carbon is intended to be used for several applications including wastewater treatment, catalysts support, and for energy applications all of which requires specific properties. These properties could be tailed to a pyrolysis process conditions and activation routes. All of which has an impact on the MSP.

Sensitivity analysis

A local sensitivity analysis was carried out to determine the effect of different parameters including the CAPEX, interest rate, feedstock cost, and utility cost on the MSP. Sensitivity studies is performed by varying one input variable while maintaining the nominal values for the other variables [30]. Fig. 8 shows the sensitivity analysis results for the three scenarios. Feedstock and utility cost had the greatest influence on the MSP for all scenarios. A 30% rise in the feedstock cost led to an increase in MSP from 0.15 to 0.18 U.S $/kg for scenario 1. In contrast, the feedstock cost rose from 0.21 to 0.23 U.S $/kg for scenario 2 and 0.28 – 0.33 U.S $/kg for scenario 3. It should be mentioned that feedstock cost is dependent on the plant location and logistics. Therefore, these should be considered in future studies. Some studies have also proposed a mobile biorefinery to minimize the cost of feedstock transportation and logistics [26,31]. The feedstock cost also includes the cost of chemicals used in the DES, and the CO_2 cost. Although, the CO_2 cost could be reduced by recycling the effluent CO_2 after activation (scenario 2 and 3).

The utility cost comprises of electricity cost and cooling water and contributes significantly towards the OPEX. A 30% increase in utility cost led to a rise in the MSP to 0.16 U.S $/kg for scenario 1, 0. 23 U.S $/kg for scenario 2, and 0.3 U.S $/kg for scenario 3. Moreover, a 30% decline in utility cost influenced the MSP positively. The MSP declined to 0.149 U.S.$/kg for scenario 1, 0.19 U.S $/kg for scenario 2 and 0.26 U.S $/kg for scenario 3. The utility cost had greater influence for scenarios 2 and 3 due to the additional combustion unit. Moreover, effective heat integration and peach analysis can be used to reduce the utility cost.

Changing other factors such as CAPEX, tax rate and interest rate had very little influence on the MSP. The CAPEX has medium effect on the MSP for all the scenarios. The accuracy of CAPEX is dependent on obtaining detailed cost data from a commercial plant, which is often challenging.

Uncertainty analysis using Monte Carlo simulation

The main limitation for excel for sensitivity analysis is that it provides a single outcome. However, probabilistic models can include the worst case and best-case outcomes. A Monte Carlo simulation generates thousands of outcomes instead of one. Moreover, the local sensitivity analysis evaluates one variable at a time while other parameters are kept constant. Thus, the interactions among different variables and the influence on MSP is not considered [23]. The probabilistic approach assigns distribution functions to several independent variables. These distributions are varied repetitively with the Monte Carlo simulation to produce a distribution function showing the probability of a specific outcome. Therefore, the same approach was used to study the effect of uncertainty or variability of the independent parameters on the MSP of AC.

Oracle crystal ball used in the study is an excellent and straightforward tool to create probabilistic models in Microsoft excel. A total of 30, 000 outcomes trials were performed. In addition, the shape of the probability distribution for all the parameters were selected based on the understanding of different independent variables. For instance, the uniform distribution was selected for the CAPEX. This kind of distribution requires that the user specify the minimum and maximum values and suggest that all the parameters have equal chance of occurrence. The uniform distribution was selected for CAPEX because the capital costs were estimated based on information from academic literature not

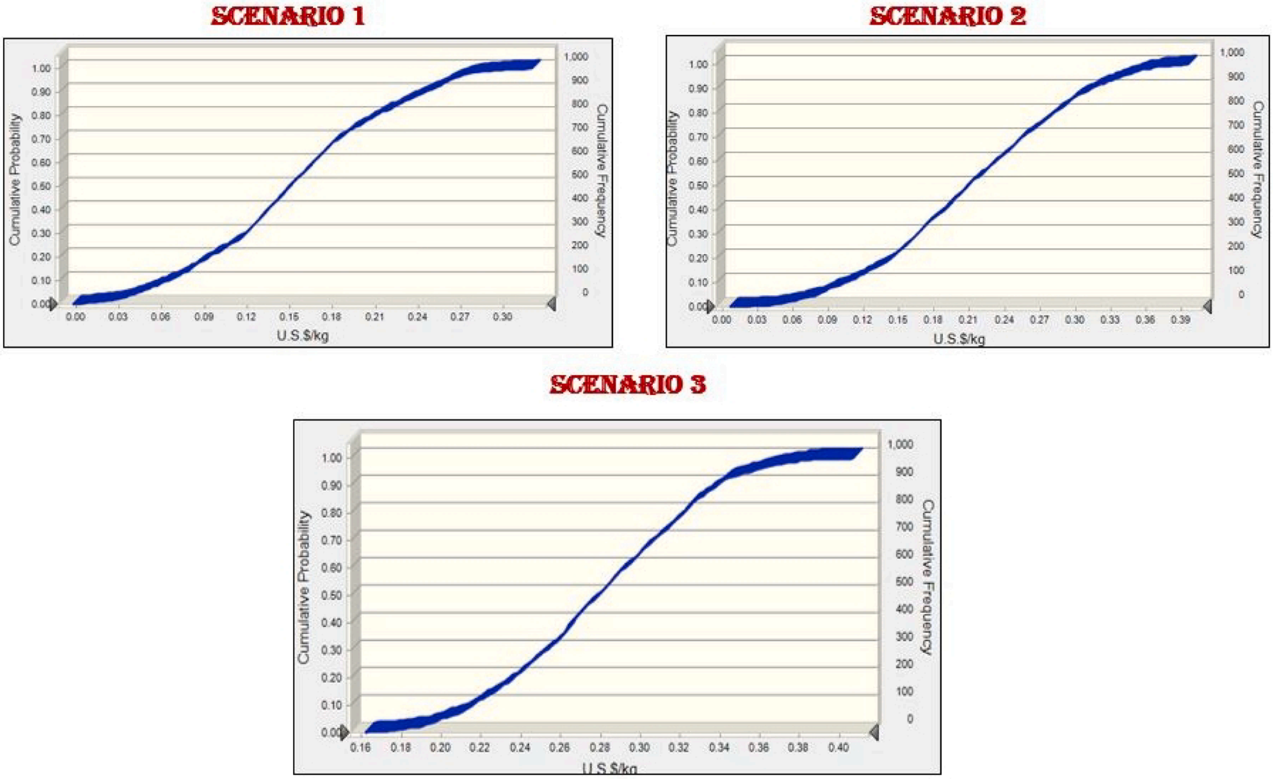


Fig. 9. Monte Carlo simulation results on the MSP of AC for the three scenarios.

industrial data. Other parameters such as the utility cost, interest rate, tax rate and feedstock cost were assigned the triangular distribution. In this kind of distribution, the minimum, maximum and most likely values are specified.

Fig. 9 shows the cumulative probability function and cumulative frequency curve for 1000 trials. The mean MSP values (50 % probability) for scenarios 1, 2, 3 are 0.151 U.S $/kg, 0.23 U.S $/kg and 0.282 U.S $/kg respectively. Moreover, scenario 1 has 95% confidence interval for the MSP to be within the range of 0.04 – 0.27 U.S $/kg. In contrast, scenario 2 showed 95 % confidence interval for the MSP of AC to be within the value of 0.03 – 0.36 U.S $/kg. Scenario 3 has MSP range of 0.18 – 0.39 U.S $/kg at 95% confidence interval. For all the three scenarios, there is a 70% probability for the MSP to be lower than the one computed. Based on the sensitivity and uncertainty results the project remains economically viable for all three scenarios considering future uncertainties including tax rate, interest rate, feedstock, and utility cost. Although, a rigorous lifecycle assessment (LCA) should be performed, and the results combined with TEA before commercialization decision can be made.

Conclusions

The present study assessed the economic viability of three scenarios for the production of activated carbon. Scenario 1 includes the slow pyrolysis and CO_2 activation unit. In addition, a flue gas recycling unit was implemented. Scenario 2 comprises of flue gas combustion while the third scenario comprise of flue gas combustion and deep eutectic solvent impregnation. All the scenarios are economically viable based on the NPV, PBP and MSP determined. The NPV of all the three scenarios are positive indicating that they are all profitable. However, scenario 1 had the most superior undiscounted NPV of 206.4 million U.S.$. On the other hand, scenario 3 had the lowest undiscounted NPV of 131.1 million U.S.$. The AC produced from scenario 1 had the lowest MSP (0.15 U.S $/kg). In contrast, scenarios 2 and 3 had MSP of AC as 0.21 U.S $/kg and 0.28 U.S $/kg respectively. Sensitivity analysis shows that different factors such as feedstock cost, utility cost, tax rate and interest rate influenced the MSP.

CRediT authorship contribution statement

Alivia Mukherjee: Conceptualization, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Jude A. Okolie:** Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Catherine Niu:** Investigation, Resources, Writing – review & editing. **Ajay K. Dalai:** Investigation, Resources, Writing – review & editing, 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.

Acknowledgements

The authors would like to acknowledge Natural Sciences and Engineering Research Council of Canada (NSERC), BioFuel Net, and Canada Research Chair (CRC) for the financial aid provided.

References

[1] Du Y, Lv Y, Zha W, Hong X, Luo Q. Effect of coffee consumption on dyslipidemia: A meta-analysis of randomized controlled trials. Nutr Metab Cardiovasc Dis 2020;30 (12):2159–70. https://doi.org/10.1016/j.numecd.2020.08.017.

[2] Karmee SK. A spent coffee grounds based biorefinery for the production of biofuels, biopolymers, antioxidants and biocomposites. Waste Manag 2018;72:240–54. https://doi.org/10.1016/j.wasman.2017.10.042.

[3] Murthy PS, Madhava NM. Sustainable management of coffee industry by-products and value addition - A review. Resour Conserv Recycl 2012;66:45–58. https://doi.org/10.1016/j.resconrec.2012.06.005.

[4] Al-Hamamre Z, Foerster S, Hartmann F, Kröger M, Kaltschmitt M. Oil extracted from spent coffee grounds as a renewable source for fatty acid methyl ester manufacturing. Fuel 2012;96:70–6. https://doi.org/10.1016/j.fuel.2012.01.023.

[5] Jenkins RW, Stageman NE, Fortune CM, Chuck CJ. Effect of the type of bean, processing, and geographical location on the biodiesel produced from waste coffee grounds. Energy Fuels 2014;28(2):1166–74. https://doi.org/10.1021/ef4022976.

[6] Mukherjee A, Borugadda VB, Dynes JJ, Niu C, Dalai AK. Carbon dioxide capture from flue gas in biochar produced from spent coffee grounds: Effect of surface chemistry and porous structure. J Environ Chem Eng 2021;9(5):106049.

[7] Creamer AE, Gao B, Zhang M. Carbon dioxide capture using biochar produced from sugarcane bagasse and hickory wood. Chem Eng J 2014;249:174–9. https://doi.org/10.1016/j.cej.2014.03.105.

[8] Tiwari D, Goel C, Bhunia H, Bajpai PK. Dynamic CO2 capture by carbon adsorbents: Kinetics, isotherm and thermodynamic studies. Sep Purif Technol 2017;181:107–22. https://doi.org/10.1016/j.seppur.2017.03.014.

[9] Patra BR, Nanda S, Dalai AK, Meda V. Slow pyrolysis of agro-food wastes and physicochemical characterization of biofuel products. Chemosphere 2021;285:131431. https://doi.org/10.1016/j.chemosphere.2021.131431.

[10] Shahkarami S, Azargohar R, Dalai AK, Soltan J. Breakthrough CO2 adsorption in bio-based activated carbons. J Environ Sci (China) 2015;34:68–76. https://doi.org/10.1016/j.jes.2015.03.008.

[11] Shahkarami S, Dalai AK, Soltan J, Hu Y, Wang D. Selective CO2 capture by activated carbons: evaluation of the effects of precursors and pyrolysis process. Energy Fuels 2015;29(11):7433–40. https://doi.org/10.1021/acs.energyfuels.5b00470.

[12] Hussin F, Aroua MK, Yusoff R. Adsorption of CO2on palm shell based activated carbon modified by deep eutectic solvent: breakthrough adsorption study. J Environ Chem Eng 2021;9(4):105333.

[13] Garip M, Gizli N. Ionic liquid containing amine-based silica aerogels for CO2 capture by fixed bed adsorption. J Mol Liq 2020;310:113227. https://doi.org/10.1016/j.molliq.2020.113227.

[14] Liu Li, Qian H, Mu L, Wu J, Feng X, Lu X, et al. Techno-economic analysis of biomass processing with dual outputs of energy and activated carbon. Bioresour Technol 2021;319:124108. https://doi.org/10.1016/j.biortech.2020.124108.

[15] Tian H, Zhou T, Huang Z, Wang J, Cheng H, Yang Y. Integration of spent coffee grounds valorization for co-production of biodiesel and activated carbon: An energy and techno-economic case assessment in China. J Clean Prod 2021;324:129187. https://doi.org/10.1016/j.jclepro.2021.129187.

[16] Okolie JA, Nanda S, Dalai AK, Kozinski JA. Hydrothermal gasification of soybean straw and flax straw for hydrogen-rich syngas production: experimental and thermodynamic modeling. Energy Convers Manag 2020;208:112545. https://doi.org/10.1016/j.enconman.2020.112545.

[17] Brown TR. Capital cost estimating. Hydrocarb Process 2000;79. doi:10.1016/b978-0-12-821179-3.00007-8.

[18] Okolie JA, Tabat ME, Gunes B, Epelle EI, Mukherjee A, Nanda S, et al. A techno-economic assessment of biomethane and bioethanol production from crude glycerol through integrated hydrothermal gasification, syngas fermentation and biomethanation. Energy Convers Manag X 2021;12:100131. https://doi.org/10.1016/j.ecmx.2021.100131.

[19] Ulrich GD, Vasudevan PT. Chemical Engineering Process Design and Economics: A Practical Guide, second ed. 2018.

[20] Pahrump N. Richardson International construction factors manual 2008. https://scholar.google.com/scholar?q=Cost Data On Line Inc., 2008. Richardson International Construction Factors Manual Internet. Pahrump, NV; Available from: http:www.icoste.orgBook_ReviewsCFM-Info.pdf. (accessed July 21, 2021).

[21] Michailos S, Walker M, Moody A, Poggio D, Pourkashanian M. Biomethane production using an integrated anaerobic digestion, gasification and CO2 biomethanation process in a real waste water treatment plant: A techno-economic assessment. Energy Convers Manag 2020;209:112663.

[22] Oke EO, Okolo BI, Adeyi O, Adeyi JA, Ude CJ, Osoh K, et al. Process Design, Techno-Economic Modelling, and Uncertainty Analysis of Biodiesel Production from Palm Kernel Oil. *Bioenergy Res* 2021;1:1–15. doi:10.1007/s12155-021-10315-y.

[23] Michailos S, McCord S, Sick V, Stokes G, Styring P. Dimethyl ether synthesis via captured CO2 hydrogenation within the power to liquids concept: A techno-economic assessment. Energy Convers Manag 2019;184:262–76. https://doi.org/10.1016/j.enconman.2019.01.046.

[24] León M, Silva J, Carrasco S, Barrientos N. Design, cost estimation and sensitivity analysis for a production process of activated carbon fromwaste nutshells by physical activation. Processes 2020;8:945. https://doi.org/10.3390/PR8080945.

[25] Gutiérrez Ortiz FJ. Techno-economic assessment of supercritical processes for biofuel production. J Supercrit Fluids 2020;160:104788. https://doi.org/10.1016/j.supflu.2020.104788.

[26] Struhs E, Mirkouei A, You Y, Mohajeri A. Techno-economic and environmental assessments for nutrient-rich biochar production from cattle manure: A case study in Idaho, USA. Appl Energy 2020;279:115782. https://doi.org/10.1016/j.apenergy.2020.115782.

[27] Harsono SS, Grundman P, Lau LH, Hansen A, Salleh MAM, Meyer-Aurich A, et al. Energy balances, greenhouse gas emissions and economics of biochar production from palm oil empty fruit bunches. Resour Conserv Recycl 2013;77:108–15. https://doi.org/10.1016/j.resconrec.2013.04.005.

[28] Yunus ZM, Al-Gheethi A, Othman N, Hamdan R, Ruslan NN. Removal of heavy metals from mining effluents in tile and electroplating industries using honeydew peel activated carbon: A microstructure and techno-economic analysis. J Clean Prod 2020;251:119738. https://doi.org/10.1016/j.jclepro.2019.119738.

[29] Haeldermans T, Campion L, Kuppens T, Vanreppelen K, Cuypers A, Schreurs S. A comparative techno-economic assessment of biochar production from different residue streams using conventional and microwave pyrolysis. Bioresour Technol 2020;318:124083. https://doi.org/10.1016/j.biortech.2020.124083.

[30] Michailos S, Parker D, Webb C. Design, sustainability analysis and multiobjective optimisation of ethanol production via syngas fermentation. Waste Biomass Valoriz 2019;10(4):865–76. https://doi.org/10.1007/s12649-017-0151-3.

[31] Badger PC, Fransham P. Use of mobile fast pyrolysis plants to densify biomass and reduce biomass handling costs - A preliminary assessment. Biomass Bioenergy 2006;30(4):321–5. https://doi.org/10.1016/j.biombioe.2005.07.011.

[32] Sigmaaldrich. Choline Chloride - ZENNOH.pdf 2021. https://www.sigmaaldrich.com/CA/en/product/sigma/c1879 (accessed November 23, 2021).

[33] SIgmaadlrich. Urea ACS reagent, 99.0-100.5% | 57-13-6 2021. https://www.sigmaaldrich.com/BR/pt/product/sial/u5128?gclid=Cj0KCQjwkbuKBhDRARIsAALysV49W1NV1L68Vz26SMTCuv28SpIxaxUX99kfNtL4HDoItgG55XUs6lYaAh0BEALw_wcB (accessed November 23, 2021).