MAKALAH ILMIAH

SLOW RELEASE FERTILIZER PRODUCTION FROM COFFEE SPENT GROUND: A PRELIMINARY STUDY

OLEH:

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Makalah ilmiah yang dimuat dalam AIP Conference Proceedings Volume 2278 (020022) Tahun 2020, yang terindeks Scopus dan Schimagojr.

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Cite as: AIP Conference Proceedings **2278**, 020022 (2020); https://doi.org/10.1063/5.0015332
Published Online: 26 October 2020

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Slow Release Fertilizer Production from Coffee Spent Ground: A Preliminary Study

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Abstract. Jember is an area in East Java that has potential in the agricultural and plantation sectors. Coffee as one of the commodities of Jember Regency is very well known throughout the world proven by the existence of the coffee and cocoa research center in Jember Regency. Spent Coffee Ground (SCG), the by-product of coffee beverages, is a natural carbon source which can be utilized as an adsorbent matrix in the production of Slow Release Fertilizer (SRF). Jember is an area that relies on economic resources from the agricultural and plantation sectors. It is better to use SCG in advance for a matrix in making Slow Release Fertilizer. The focus of the research was to study the possibility of SCG to be used as a matrix by analyze the yield and surface area after activation. The results show that the total yield of SCG become matrix of SRF is vary 10 – 16% regarding the parameters implemented. The optimum surface area was produced from active carbon using KOH as activator at 400 °C as much as 1047.75 mg iodine/g carbon followed by ZnCl2 as activator at 400 °C as much as 1028.7 mg iodine/g carbon. The bigger the temperature produces the lower surface area of activated carbon. The surface area differences had been checked by LSD method to describe the significance. Hence, the optimum activator is KOH to produce SRF because of the yield and surface area obtained.

INTRODUCTION

As one of the promising agriculture regions in East Java, Jember has several superior commodities such as coffee, cocoa, sugar cane, corn, cassava, and rice. With shifting trend recently, agriculture wastes become fruitful resources to substitute fossil fuel as energy resources and intermediate chemicals. Furthermore, Jember produced 10,542 ton coffee in 2015 as shown in Table 1 [1]. Even though it only contributes around 21% of province and 2% of country production which has higher yield compared to the average of province and country yield. It means that the production rate of coffee in Jember is relative high. To maintain this production rate, the sustainable utilization of coffee waste should compromise with the condition. At this moment, the utilization of coffee waste as a promising material to support the agriculture is mandatory.

One of byproducts from coffee industry is Spent Coffee Ground (SCG) which is rich of carbon content as reported by many researches [2-5]. Spent Coffee Ground (SCG) can be utilized for many applications such as solid fuel [6-8], biodiesel and bioethanol [9-11], and carbon active [11-14]. Last mentioned utilized product has broad applications in many sector such as an adsorbent and a catalyst. Due to the activation of SCG, the specific surface of SCG becomes larger and has a specific active ions regarding on the conducted activation. In addition, the carbon active can also be applied as a nitrogen absorbing medium contained in urea fertilizer. Due to ineffective fertilization process occurred in agriculture sector, the utilization of carbon active would be a solution to compromise this issue to control the release of urea within fertilization process. These ineffective fertilization process could disrupt the nature by impair the ecosystem because excess urea would drive off into irrigation system and trigger the rapid growth of algae, plankton, and hyacinth [15]. Doberman and Fairhurst (2000) was reported that only 30% of urea is absorbed by plants during the fertilization process [16].

Climate Change and Sustainability Engineering in ASEAN 2019
AIP Conf. Proc. 2278, 020022-1–020022-7; https://doi.org/10.1063/5.0015332
Published by AIP Publishing. 978-0-7354-4008-1/$30.00

TABLE 1. Area and coffee production comparison [1]

Region	Area, Ha				Production, Ton	Yield, Kg/Ha	Farmers, Person
	Immature	Mature	Damaged	Total			
Jember	2,737	13,338	1,780	17,855	10,542	790	47,202
East Java	20,223	68,711	10,820	46,930	51,357	747	242,847
Indonesia	183,602	905,003	141,395	863,626	639,412	707	1,849,094

Many researches have been conducted to improve the efficiency of urea fertilizer use in various ways, such as by increasing the size of urea, add fertilizer violence, and create a layer (coating) on urea. The release of the nutrient content in fertilizer could be controlled and slowed as known as Controlled Release Fertilizer (CRF) and Slow Release Fertilizer (SRF) respectively. Both types of fertilizer have the same purpose, which is increasing its efficiency by release a sufficient amount of nutrient to be absorbed by plants. In the case of slow release fertilizer, a matrix is needed as a medium to protect the nutrients contained in fertilizer to reduce its release to the environment. Lehman et al. (2009) had been used zeolites and active carbon as an adsorbent agent for producing SRF to increase the effectiveness of the fertilization process [17]. Meanwhile, A. Manikandan (2013) had successfully implemented *Prosopis juliflora* bio-char as a media of SRF [18]. Azeem et al., 2014 had been made a review of the several products that have been sold in the market as Controlled Released Coated Urea resulted that Controlled Released Coated Urea can slow down the process of nutrient release so as to improve the process of adsorption of nutrients by plants and reduce the loss of nutrients from fertilizers due to the process of leaching, evaporation and denitrification [19].

In the other hand carbon active remains relatively expensive caused by the precursors from petroleum residues, coal, and hard wood. Active carbon production must balance its economic viability and performance. In order to overcome these issue, this study would propose SCG to be converted into carbon active and utilized for the agricultural sector to maintain its sustainability which becomes an interesting environmental and sustainable concept. In this study, the carbon will be activated using chemical-physical methods for preparing SCG. Furthermore, a study by CerveraMata, 2017 reported that the application on SCG as a soil amendment has three major function such as a reuse of this bio-residue, increase in soil organic carbon, and a decrease in CO_2 emissions into the atmosphere [20]. These study would briefly propose an addition function of SCG utilization as a prospective SRF medium to control nutrient release and maintain the pollution occurred during ineffective fertilization process.

MATERIALS AND METHODS

Materials

Coffee powder was bought from local store in Jember, East Java to obtain uniform SCG samples. The activator used were all in the reagent grade of Merck such as HCl, KOH, and $ZnCl_2$. Potassium iodide and sodium thiosulfate as iodine number reagent was purchase from Merck.

Methods

Sample preparation

The coffee grounds obtained were washed by using distilled water as many as 3 times which were then filtered using filter paper. The coffee grounds are then dried at 80□C for 5 hours. The dried coffee grounds are then sieved using a 100 mesh sieve to produce a uniform particle size. The activation process were used HCl, $ZnCl_2$, and KOH as the chemical activator by varying the drying temperature at 400, 500, and 600 °C. The concentration of activator in this study was 30% w/v and impregnation time was 1 hour.

Analysis of several parameters

Gravimetric method was implemented on the carbon measurement for SCG. Analysis of the constituent elements of coffee grounds was carried out with Energy Dispersive X-ray Spectroscopy (EDX) analysis in the Laboratory of Instrumental Analysis, Department of Chemical Engineering, Faculty of Engineering, Universitas

Gadjah Mada. Yield was calculated based on final product mass of active carbon compared with initial coffee powder mass, as follow:

$$Yield = \frac{m_{coffee\,powder} - m_{active\,carbon}}{m_{coffee\,powder}} \quad (1)$$

The analysis of surface area was carried out by titration method in the Laboratory of Research, Department of Chemical Engineering, Faculty of Industrial Engineering, Universitas Islam Indonesia. The sample was prepared by weighting 0.05 – 0.1 g of active carbon and diluted into 10 mL of 0.1 N iodine solution. The solution was stirred for 15 min and filtered to separate the solid phase and filtrate. Five mL of filtrate was titrated by 0.1 N sodium thiosulfate. The titration method was carried out three times for each sample. The iodine number was calculated using following equation:

$$Iodine\ number = \frac{(V_1 - V_2) \times N \times MW}{w} \quad (2)$$

where iodine number in mg/g; V_1 and V_2 describes initial and final sodium thiosulfate volume respectively (mL); N is thiosulfate normality, N; MW is Iodine molecular weight, 126.9 g/mole; and w describes active carbon weight, g. To distinguish the effectiveness of activation reagent, a comparative calculation of iodine number and yield was conducted with following equation:

$$\overline{Iodine\ number} = Iodine\ number \times yield \quad (3)$$

Iodine number which represents surface area of active carbon from Equation (3) was analyzed using Least Significant difference (LSD) method to investigate the significance of the data.

RESULTS AND DISCUSSIONS

SCG compounds and analysis

The elemental analysis of SCG and chemical components had been conducted to identify the constituents. The carbon content of SCG in this study is lower compared to another studies [2-5]. The minerals component on SCG could be beneficially to improve the soil quality. Cruz-Lopes et al. (2017) reported that many minerals such as Potassium, Calcium, Magnesium, Sulfur, and Phosporus contained in the SCG in considerable amount. This study also revealed some minerals from the analysis as seen in Table 2. Although the cellulose is still high enough in this study seen in Table 2, the valorization of SCG as SRF is still promising to control the carbon cycle in the atmosphere. Otherwise, a preliminary process with the extraction of cellulose with several solvents could be conducted to utilize as bio-refinery as reported by many researcher.

TABLE 2. SCG analysis for chemical components

Chemicals	References		
	This study	**[21]**	**[22]**
Hemicellulose	24.57	39.1	28.36
Cellulose	17.22	12.4	10.78
Lignin	9.50	23.9	10.72
C	47.97	47.18	-
O	35.59	-	-
Si	6.66	-	-
Al	4.31	<<	-
Ca	3.04	0.12	-
Fe	1.67	0.52	-

Table 3 shows the comparison of SCG and active carbon from SCG. It clearly seen that the fixed carbon of active carbon is higher than SCG because of pyrolysis process. The water and ash content of active carbon would be beneficially for SRF media. From this data, it revealed that the preparation of active carbon was successfully conducted in the laboratory.

TABLE 3. Proximate analysis of SCG and pyrolysis product of SCG

Material	Water content, %	Volatile matter, %	Ash content, %	Fixed Carbon, %
SCG	3.66	76.76	1.94	17.64
Pyrolysis of SCG	8.69	6.93	8.98	75.41

Yield from SCG processes

High production of coffee beverages has substantially increase the waste generation of SCG. Reported by Tsai et al. 2012, the approximately 50% of the input mass of coffee feedstock would be a waste as SCG during soluble coffee beverages production [8]. Furthermore, the hot dripping method produces ratio of between 66.67% and 80% [11]. This study conducted the yield of coffee powder to produce SCG as shown in Table 4. The process was occurred with dripping coffee powder with hot water as much as 3 times and continued with heated the coffee at 80 – 100 °C for 5 hours. This study resulted that the yield of SCG from coffee beverages production with dripping process is 87.2%.

TABLE 4. The yield of SCG from coffee beverages production

Initial coffee powder, Kg	SCG produced, Kg			Yield
1	0.8948	0.8948	0.8358	89.5%
2	1.7	1.7		85.0%
Total Yield				**87.3% ± 3.2%**

SCG previously was performed pyrolysis at 500°C for 3 hours before chemical activation was occurred. This process would significantly decrease the amount of SCG processes as shown in Table 5. The chemical activation thus carried out after the pyrolysis process. Moreover, the activation was continued with thermal activation in various temperature. The activation was carried out in physically and chemically to obtain optimum surface area of active carbon. The larger surface area is the ideal variable to be used as SRF media.

TABLE 5. Yield on pyrolysis process of SCG

Initial SCG weight, gram	Final SCG weight, gram	Yield
100.1	24.0	24.0%
126.4	27.7	21.9%
136.0	29.2	21.5%
136.0	29.4	21.6%
100.0	22.1	22.1%
22.0	5.6	25.2%
95.0	21.7	22.8%
95.0	20.8	21.9%
95.0	18.2	19.2%
Average yield		**22.2% ± 1.6%**

The carbon active production from SCG had less yield compared to SCG generation from coffee powder. It is mainly caused by many processes imposed to SCG for producing carbon active such as chemical and physical activation. The yield for carbon active production varied from 50% until 81.9% depend on the activation process as seen in Table 6. The lower yield of carbon active production does not directly make the activation process less attractive compared to others. The properties of its material should be reviewed such as provided surface area and the capability to release fertilizer into the nature. From Table 4 and 5 yield, the overall yield was calculated by multiply the yield accordingly which is presented in Table 6.

TABLE 6. The yield of carbon active from SCG with various activator

Activator	Temperature, °C	Initial weight, gram	Carbon active, gram	Yield, %	Overall yield, %
KOH	400	40.0	31.2	78.0%	15.1%
	500	40.0	27.3	68.3%	13.2%
	600	40.0	25.6	64.0%	12.4%
$ZnCl_2$	400	40.0	23.2	58.0%	11.2%
	500	40.0	20.0	50.0%	9.7%
	600	40.0	20.3	50.8%	9.8%
HCl	400	16.6	13.1	81.9%	15.9%
	500	16.6	11.7	73.1%	14.2%
	600	21.6	15.5	71.9%	14.0%

Adsorption Capability

The adsorption capability was analyzed using titration method. Iodine number is presented at Table 7. The phenomena were occurred in this study. The higher the temperature, the lower iodine number was occurred. This result was believed caused by bigger pore occurred by higher temperature which resulted in lower surface area. In his study Saka (2012) presented that the average pore diameter was increasing from 2.626 nm into 2.822 with increasing of temperature from 400°C into 500°C [23].

TABLE 7. Surface area of active carbon from SCG as iodine number in mg/g

Activator	Temperature, °C		
	400	500	600
KOH	1048±135	718±135	781±368
$ZnCl_2$	1029±36	902±180	527±278
HCl	806±296	787±144	591±260

To analyze overall process, the evaluation of SCG was presented in Table 9 which was calculated by Equation (3). The LSD method was also conducted to give clear perspective of the effectiveness of the process which can be seen in Table 8. The result showed that all activators have the same tendency, but KOH gives the best result among the others even though the number is still in the same group. Furthermore, the average of KOH iodine number gave the best result and different group of significance.

TABLE 8. The LSD calculation

MS	t-table	alpha	dfe	r	LSD difference
837	2	0.05	15	2	62

Further analysis of pore diameter and surface morphology is required to support the findings. The BET analysis also can be conducted to compare the titration method. Basically, the titration method and BET analysis have the same tendency and do not vary substantially. Further research would be conducted to implement this findings as the media of SRF production.

TABLE 9. $\overline{Iodine\ number}$ on several process of activation in mg

Activator	Temperature, °C			Average
	400	500	600	
KOH	158±20[a]	95±18[b]	97±46[b]	117[a]
$ZnCl_2$	115±4[a]	87±17[b]	52±27[b]	85[b]
HCl	128±47[a]	112±20[a]	83±36[b]	108[b]

a and b indicate the group significance

CONCLUSIONS

This study was successfully prepared the active carbon from SCG with several activator. The active carbon will be used as SRF media to intensify the fertilizer process. The optimum activator was obtained by using KOH as the activator. It has the highest surface area which is presented by iodine number as much 1048 mg/g. If the yield is being considered, KOH is still being the most effective activator. As a perquisite, the suitable media of SRF is high surface area which could bind Nitrogen effectively from urea fertilizer. Hereby the further analysis of pore diameter and surface morphology is required to support the findings.

ACKNOWLEDGEMENTS

The authors send the gratitude to the Universitas Jember for the awarding grant with 8854/UN25/LT/2018 contract number. The authors also be thankful for the facilities provided by Universitas Islam Indonesia and Universitas Gadjah Mada.

REFERENCES

1. D.G.o.E.C.M.o. Agriculture, Tree Crop Estate Statistics of Indonesia 2015-2017, in: D.G.o.E.C.M.o. Agriculture (Ed.) Coffee, Directorate General of Estate Crops Ministry of Agriculture, Jakarta, 2016.
2. W. Bizzo, Generation, Distribution and Use of Steam, Apostila de Curso, UNICAMP, Brasil, Google Scholar (2003).
3. N.S. Caetano, V.F. Silva, A.C. Melo, A.A. Martins, T.M. Mata, Spent coffee grounds for biodiesel production and other applications, Clean Technologies and Environmental Policy 16(7) (2014) 1423-1430.
4. G. Melo, V. Melo, W. Melo, Composting, Faculdade de CiêncasAgrárias e Veterinarinárias Jaboticabal (2007) 10.
5. D. Pujol, C. Liu, J. Gominho, M. Olivella, N. Fiol, I. Villaescusa, H. Pereira, The chemical composition of exhausted coffee waste, Industrial Crops and Products 50 (2013) 423-429.
6. N. Kondamudi, S.K. Mohapatra, M. Misra, Spent coffee grounds as a versatile source of green energy, Journal of agricultural and food chemistry 56(24) (2008) 11757-11760.
7. M. Silva, S. Nebra, M.M. Silva, C. Sanchez, The use of biomass residues in the Brazilian soluble coffee industry, Biomass and Bioenergy 14(5-6) (1998) 457-467.
8. W.-T. Tsai, S.-C. Liu, C.-H. Hsieh, Preparation and fuel properties of biochars from the pyrolysis of exhausted coffee residue, Journal of Analytical and Applied Pyrolysis 93 (2012) 63-67.
9. E.E. Kwon, H. Yi, Y.J. Jeon, Sequential co-production of biodiesel and bioethanol with spent coffee grounds, Bioresource technology 136 (2013) 475-480.
10. M.V.P. Rocha, L.J.B.L. de Matos, L.P. de Lima, P.M. da Silva Figueiredo, I.L. Lucena, F.A.N. Fernandes, L.R.B. Gonçalves, Ultrasound-assisted production of biodiesel and ethanol from spent coffee grounds, Bioresource technology 167 (2014) 343-348.
11. N.F. Tehrani, J.S. Aznar, Y. Kiros, Coffee extract residue for production of ethanol and activated carbons, J Clean Prod 91 (2015) 64-70.

12. G.Z. Kyzas, Commercial coffee wastes as materials for adsorption of heavy metals from aqueous solutions, Materials 5(10) (2012) 1826-1840.
13. C. Liu, D. Pujol, M. Olivella, F. De La Torre, N. Fiol, J. Poch, I. Villaescusa, The role of exhausted coffee compounds on metal ions sorption, Water, Air, and Soil Pollution 226(9) (2015) 289.
14. M.-S. Kim, H.-G. Min, N. Koo, J. Park, S.-H. Lee, G.-I. Bak, J.-G. Kim, The effectiveness of spent coffee grounds and its biochar on the amelioration of heavy metals-contaminated water and soil using chemical and biological assessments, Journal of environmental management 146 (2014) 124-130.
15. S. Hardjowigeno, Ilmu Tanah Ultisol, Akademika Pressindo, Jakarta, 2003.
16. A. Dobermann, Rice: Nutrient disorders & nutrient management, Int. Rice Res. Inst.2000.
17. J. Lehmann, J. Gaunt, M. Rondon, Bio-char sequestration in terrestrial ecosystems–a review, Mitigation and adaptation strategies for global change 11(2) (2006) 403-427.
18. A. Manikandan, K. Subramanian, Urea intercalated biochar–a slow release fertilizer production and characterisation, Indian Journal of Science and Technology 6(12) (2013) 5579–5584.
19. B. Azeem, K. KuShaari, Z.B. Man, A. Basit, T.H. Thanh, Review on materials & methods to produce controlled release coated urea fertilizer, Journal of controlled release 181 (2014) 11-21.
20. A. Cervera-Mata, S. Pastoriza, J.Á. Rufián-Henares, J. Párraga, J.M. Martín-García, G. Delgado, Impact of spent coffee grounds as organic amendment on soil fertility and lettuce growth in two Mediterranean agricultural soils, Archives of Agronomy and Soil Science 64(6) (2018) 790-804.
21. L.F. Ballesteros, J.A. Teixeira, S.I. Mussatto, Chemical, functional, and structural properties of spent coffee grounds and coffee silverskin, Food and Bioprocess Technology 7(12) (2014) 3493-3503.
22. L. Cruz-Lopes, I. Domingos, J. Ferreira, B. Esteves, A new way of using spent coffee ground, Journal of International Scientific Publications: Agriculture and Food 5(1000023) (2017) 85-93.
23. C. Saka, BET, TG–DTG, FT-IR, SEM, iodine number analysis and preparation of activated carbon from acorn shell by chemical activation with ZnCl2, Journal of Analytical and Applied Pyrolysis 95 (2012) 21-24.