에너지공학, 제27권 제1호(2018)
Journal of Energy Engineering, Vol. 27, No. 1, pp.51~58(2018)
https://doi.org/10.5855/ENERGY.2018.27.1.051

Extraction of Precipitated Calcium Carbonate from Oyster Shell waste and Its Applications

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(Received 23 January 2018, Revised 23 February 2018, Accepted 26 February 2018)

Abstract

In this paper, we reported that the influence of advanced functional mineral filler calcium carbonate ($CaCO_3$) extracted from oyster shell waste, which are rich mineral sources of $CaCO_3$. Oyster Shells, available in abundance, have no eminent use and are commonly regarded as waste. Their improper disposal causes a significant level of environmental concern and also results in a waste of natural resources. Recycling shell waste could potentially eliminate the disposal problem, and also turn an otherwise useless waste into high value added products. Oyster shell waste calcination process to produce pure lime (CaO) which have good anti-microbial property for waste water treatment and then focuses on its current applications to treat the coffee waste and its effluents for biological treatment and utilization as a fertilizers.

Key words : Oyster Shell Waste, Calcium Carbonate, Coffee Waste, Mineral Filler.

1. Introduction

Shellfish cultivation is an expanding economic activity worldwide. It represented more than 40% of all marine aquaculture production in 2008 [1]. Global shellfish production has exceeded 20 million tons since 2006 [2], and China accounts for about 54%, remaining by far the largest shellfish producer. In China, shellfish production during the decade of 2001-2010 has stabilized at over 10 million tons and marine shellfish production accounts for about 95% of this amount [3].

In the southern coast of Korea, a lot of oyster shells are dumped as a by-product of marine aquaculture industry. A large amount of oyster shells is a general waste fishermen should take care of but it seems difficult to handle it effectively due to the problems of securing of landfill sites and collection/transportation of oyster shells [4, 5]. This waste piles up at coastal areas and causes many environmental problems including pollution of coastal fisheries, management problem of public water surface, damage of natural landscape, and health/sanitation problem. Table-I, shows as oyster culture production (with shell, tons) by country [6].

Environmental problems caused by waste oyster shells were as follows, i) increase of waste, ii) pollution of marine eco-system due to illegal landfill, iii) increase of bad smell due to negligence, iv) a huge amount of treatment expense, and v) weak demand on recycled materials (Filler and fertilizer etc.) from oyster shells. Oyster shell waste has become a serious problem, in most cases, the shell is disposed of in fields, dumped into public waters or onto reclaimed lands. The dumping sites, if the waste is left untreated for a long time, can cause noxious odors as a consequence of the decay of remaining attached

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flesh or of the microbial decomposition of salts into gases, such as H_2S, NH_3, and amines.

The research on application of oyster shells to a sorbent for incineration and desulfurization is judged to be very helpful in preserving marine eco-system, preventing the damage of natural landscape and solving health/sanitation problem. Therefore, new applications utilizing these wasted oyster shells are expected to contribute towards recycling consciousness within the society [7]. The application of many kinds of waste shells, which have been dried, crushed and calcined, to sorption of acidic gases and nitrogen oxides is not only economically valuable but also very significant in the aspect of waste recycling. In

Table (I). Oyster culture production (with shell, tons) by country [6], FAO yearbook, Fishery statistics, Aquaculture production, Vol.100/2 (2005)

Species	Country	Production of Shell (Tons)	
		Year-2000	Year-2005
Pacific cupped oyster *(Crassostrea gigas)*	China	3,291,929	3,826,363
	Japan	221,252	218,896
	Korea Rep	177,079	251,706
	France	133,500	118,120
	USA	38,418	21,323
	Taiwan	19,972	28,430
	Australia	4,693	7,295
	Canada	5,500	7,638
	Chile	5,641	2,226
	Ireland	5,031	5,811
	New Zealand	3,500	2,800
	Other	3,722	6,477
Thai oyster *(Crassostrea spp.)*	Thailand	13,556	27,680
American oyster *(Crassostrea virginica)*	USA	38,255	55,188
	Canada	4,124	4,946
Slipper oyster *(Crassostrea iredalei)*	Philippines	14,222	16,495
European flat oyster *(Ostrea edulis)*	Spain	3,383	2,980
	France	2,000	1,280
	Other	656	909
Sydney oyster *(Saccostrea commercialis)*	Australia	4,961	4,456
	Other	6,836	4,144
Grand Total		3,998,513	4,615,400

addition, considering that chlorine which has been found to be a precursor of such toxic organic substances as dioxin and furan lately creating social concerns is an acidic gas, the use of waste shells as mixed sorbents is judged to be feasible.

Calcium carbonate ($CaCO_3$) is one of the most widely used inorganic fillers for polymers [8]. Since shell waste consists predominantly of $CaCO_3$ (~95%) with a small amount of bio-macromolecules, such as polysaccharides, glycoproteins and proteins [9-11], making it a possible substitute for commercial fillers yielding a polymer with unique mechanical properties [12]. Oyster shells have been utilized effectively as fertilizers, soil conditioners, natural medicines rich in calcium, waterworks filter mediums, etc. dried oyster shells had an effective bacteriostasis. In addition, the fact that burned and finely powdered oyster shells, as compared with oysters shells dried at room temperature, showed a stronger bacteriostasis. In various kinds of tests by using limestone powder or pure calcium carbonate ($CaCO_3$) to determine if the bacteriostasis of oyster shells was caused by $CaCO_3$ [13]. Oyster shells are not fishery waste material but valuable source material for a new industry. It shows such a strong bactericidal activity that it kills one of the most virulent pathogens, *Escherichia coli* O-157:H7 effectively [14], and the oyster shell can neutralize acidic waste water from mines very fast and remove 99% of heavy metals, and so it is judged to be a useful material to replace natural limestone.

The main objective of this work is the oyster shell are major composition $CaCO_3$ and it utilizing for the synthesis of aragonite needles for industrial applications and also utilizing as a anti-microbial agent in waste water treatment and used as a fertilizer. Therefore, oyster shell waste new applications are expected to contribute towards recycling consciousness within the society.

2. EXPERIMENTAL PROCEDURE:

The starting materials were $MgCl_2$ of 95% purity (Junsei Company, Japan), oyster shell waste (Namhae, South Korea), and pure CO2 gas (Jeil Gas Company, South Korea).

Oyster shell waste collected from waterfront areas in Namhae, South Korea, and cleaned with alcohol and water to remove impurities attached to the surfaces. This cleaned oyster shells was calcined in an electric furnace at 1000 ^oC for 2 h, which was increased to this point at a rate of 10 ^oC/min. The calcined raw materials were mechanically grinded for 1 h until the particle size was less than 100μm. This fine powder characterized by XRD analysis and to used for the synthesis of aragonite needles by carbonation process.

In carbonation process for the synthesis of aragonite calcium carbonate, we used oyster Shell waste as the raw material; powder was calcined at 1000 ^0C for 2 h in electrical furnace to produce CaO as follows:

$$CaCO_3 \rightarrow CaO + CO_2 \quad (1)$$

The calcined raw materials were mechanically grinded for 1 hour until the particle size was less than 100μm. This calcinated fine powder is processed to hydration with distilled water at 80^{0}C for 1 hour and filtered with 200mesh then the solution was washed three times with distilled water again filtered with 325mesh and collects filtrate and dried at 80^{0}C for 12 hours.

$$CaO + H_{2O} \rightarrow Ca(OH)2 \quad (2)$$

After hydration and filtering process, calcium carbonate is synthesized by a carbonation method in which gaseous CO_2 is injected (50ml/min) into a Ca^{2+} ion solution to precipitate calcium carbonate.

$$Ca(OH)_2+MgCl_2 \rightarrow Mg(OH)_2+ CaCl_2 \quad (3)$$

$$CaCl_2+ H_2CO_3+Mg(OH)_2 \rightarrow CaCO_3 + MgCl_2+ 2H_2O \quad (4)$$

3. RESULTS AND DISCUSSION:

3.1. Oyster shells chemical composition.

Oyster shells major composition is $CaCO_3$ are present, remaining other impurities, X-ray Fluorescence spectroscopic (XRF) results shows in Table 2, presents the chemical composition analysis, it was found that oyster shells consists of mostly CaO (53.66 %) and the Ignition loss (44.56 %) from the decomposition of $CaCO_3$ to release CO_2 gas, which is comparable to that of commercial Jungsun limestone and was in good agreement with the results of Yoon & Jung et al. [15, 16], reporting the CaO content of oyster-shells was about 53.7 wt.% and also some of other impurities such as SiO_2 (0.45%), Al_2O_3 (0.12%), Fe_2O_3 (0.06%) MgO (0.26%), K_2O (0.06%), Na_2O (0.55%), P_2O_5 (0.16%) are present.

X-ray diffraction (XRD) patterns of waste oyster shells raw material and calcined waste oyster shells are shown in Fig. 2. The results of XRD analyses of the waste oyster shells with and without calcination. The patterns for waste oyster shells raw material diffraction peaks of $CaCO_3$ as major phases (95.37 %) are identified and the patterns for calcinated at 1000 ^{o}C/2h, the oyster shells waste were exhibited peaks characteristics of lime (CaO) (98.13%) of CaO. These results indicated that after calcination process oyster shell are producing pure lime (CaO).

3.2. Aragonite needles synthesis by carbonation process.

In these carbonation process, temperature, reaction time and carbon dioxide flow rates play a key role

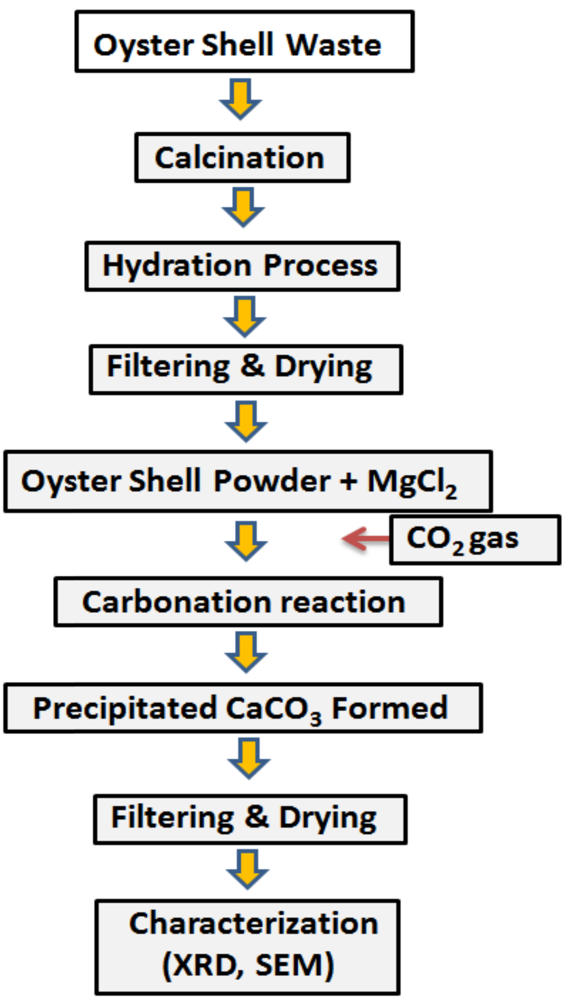

Fig. 1. Calcium carbonate synthesized by carbonation process.

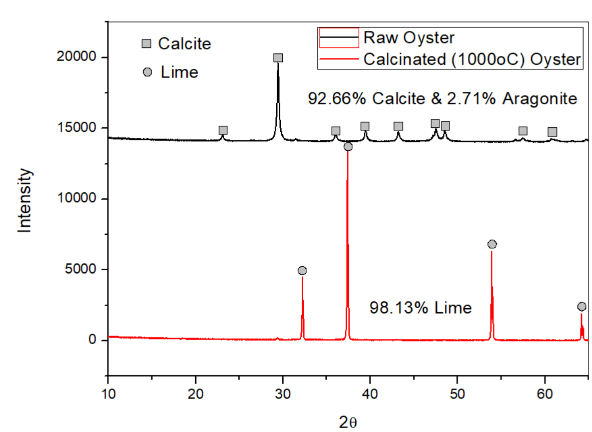

Fig. 2. XRD analysis of Raw oyster shells waste and calcinated oyster at 1000oC/2h.

Table. 3. Chemical composition of oyster shells.

Oxides	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	P_2O_5	Ig Loss
Oyster (%)	**53.66**	**0.45**	**0.12**	**0.06**	**0.26**	**0.06**	**0.55**	**0.16**	**44.56**

for the synthesis of aragonite precipitated calcium carbonate. In this process, 30gr/lit calcium-rich oyster shell hydrated dried powder was added to 0.6M magnesium chloride solution and gaseous CO_2 is injected (50ml/min) into a suspension of $MgCl_2$ - Ca^{2+} rich oyster powder at pH-11, for 3 hours carbonation reaction to form a calcium carbonate precipitation.

In the carbonation process, the needle-like aragonite yield increased gradually with an increase in the temperature from 60 to 80 ^oC, at 50ml/min carbon dioxide flow rate for a 3 h reaction. Similarly, the reaction time also affects the pure aragonite yield; hence, the carbonation reaction time duration was increased gradually (2, 2.5 and 3 h) at 80 ^oC, and carbon dioxide (CO_2) also plays a key role in the formation of aragonite; thus, the CO_2 flow rate was increased up to 50mL/min. Needle like aragonite precipitated calcium carbonate was synthesized at the optimized condition at 80^{o}C with 50cc carbon dioxide flow rates for 3 hours reaction time is clearly observed in the morphology of aragonite needles from XRD and scanning electron microscopy (SEM) analysis as shown in Fig. 3.

The synthetic pure aragonite precipitated calcium carbonate from oyster shell waste by carbonation process was used as a filler for improving mechanical properties in plastics and paper industries. Li et al.[17, 18] reported higher yield strain, yield strength, tensile strength and elongation at break point, of polypropylene (PP) composites filled with bio-aragonite, as compared with commercial $CaCO_3$. de Melo et al. [19] found that the incorporation of mollusc shell waste could increase the degree of crystallinity and stiffness of high-density polyethylene.

3.3. Utilization of Oyster Shell wastes and its applications:

Recycling shell waste offers many advantages and has potential application in various fields. However, oyster shell waste to utilize in water treatment specifically in coffee wastes. The coffee industry uses large quantities of water during the various stages of the production process. Consequently, the amount of waste water comes out from the industry is high. Nowadays Coffee produced a large number of countries throughout the world. However, the ten largest coffee producing countries are responsible for approximately 80% of the world production. Of this percentage, South America participates with around 43%, Asia with 24%, Central America 18%, and Africa with 16%. Brazil, Vietnam, Colombia, and Indonesia are respectively the first, second, and third largest world producers, responsible for more than half of the world supply of coffee, according to the International Coffee Organization [20].

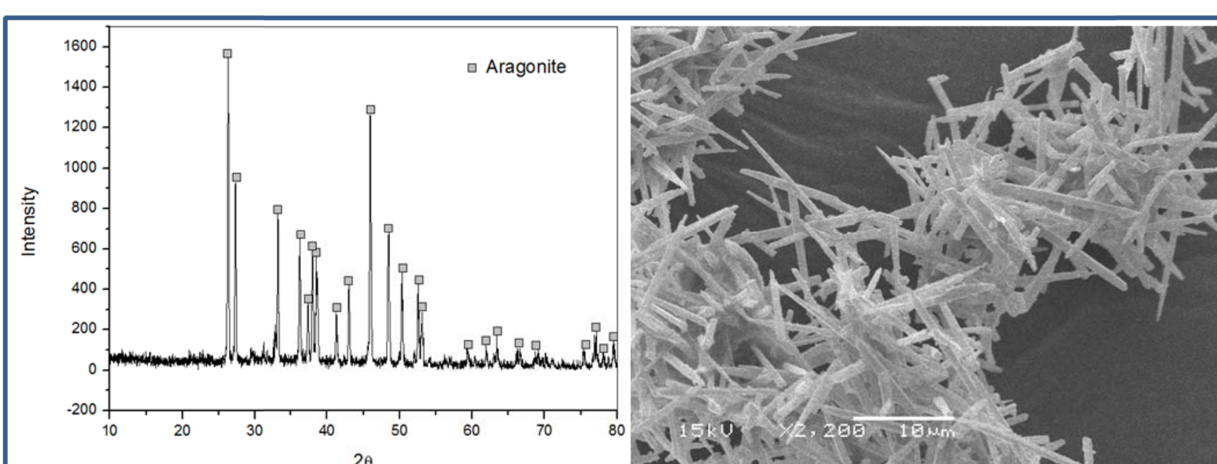

Fig. 3. XRD and scanning electron microscopy (SEM) analysis for aragonite synthesis from oyster shell waste by carbonation process.

3.3.1. Coffee waste treated with Oyster shell powder and utilizes as a safety fertilizer.

Coffee waste is produced at high temperatures (70^0C), the pH is near 4 and, due to the roasting process, a number of phenol heterocyclic compounds may appear. The anaerobic digestion of coffee waste has been reported at mesophilic temperatures [21, 22]. Fresh coffee pulp contains a vast microbial population of bacteria, fungi and yeast. During composting of pulp, an increase of mesophile and actinomycete populations has been observed [23]. Fungi play an important role in the initial steps of composting because of their saprophytic activity and the attack of lignin and cellulose transforming them into simple carbohydrates [24], by the adding oyster shell waste to neutralize the pH and reduced the toxic effluents and micro organisms and utilized as a fertilizer has gained attention due to the great potential in both the availability of used coffee grounds and its beneficial properties in compost. In Fig.4, shows diagram can show the extracted calcium carbonate from oyster shell waste and utilization as a fertilizer with coffee waste water effluents.

While there have been few studies conducted on used coffee grounds, multiple studies have discovered the benefits of coffee waste, or pulp. The pulp, the fruit part of the coffee berry, is attributed to greater soil and compost quality. When the pulp is placed in the soil, its rich nutrient levels, along with the relatively high alkalinity of soil humus, contributes to reductions in soil acidity with oyster shell waste and increased retention of water, and increased levels and retention of nutrients. The organic matter of coffee waste also provides more nitrogen and potassium than common fertilizers, making it a valuable organic fertilizer [25]. Nutrient value enhancement with the presence of coffee pulp provides soil fertility richness along with nutrients for both plants and the soil microorganisms [26]. Based off of these known positive effects of coffee pulp on soil nutrients and organisms, we look to extrapolate from these known benefits to investigate the effect of coffee wastes adding with oyster shell powder.

Fig. 4. Oyster shell waste and coffee waste treatment and utilized as a fertilizer.

In North America, almost two million metric tons of spent coffee grounds are generated annually and are either put into landfills or processed at waste facilities with other organic wastes [27]. If coffee drinkers began to compost their used grounds instead of throwing them away, they could create a significant reduction in their environmental impact. Because of the widespread availability of coffee grounds, along with its known ability to improve soil composition, coffee grounds were chosen as the experimental compost with oyster shell waste to be further investigated.

4. Conclusions:

Recycling shell waste offers many advantages and has potential application in various fields. However, Oyster shell wastes are reused as substitute materials, the effect must be evaluated since they containing a high content of $CaCO_3$ and less organic matrices; hence it is better to use them directly as substitutes lime stone for the synthesis of needle shape pure aragonite by carbonation process, has the great potential to be used as a filler in plastic and paper industries.

This research study demonstrated that calcinated oyster shell waste can be used for coffee wastewater, significantly improve the pH and nutrient balance. Oyster shell waste treatment with coffee waste water was beneficial as a fertilizer for improving soil organic matter, soil nutrients, chemical and biological properties as well as crop productivity. This treatment process is simple, economic ecofriendly a novel method for recycling waste oyster material to provide a beneficial product and promises to greatly reduce landfill problems.

Further research is needed to optimize the conditions to extract the calcium carbonate from oyster shell matrix. This extracted calcium carbonate used as an advanced functional filler to waste water treatment, fertilizer, pathogens removal and coffee waste treatment.

Acknowledgements

This research was supported by the National Strategic Project-Carbon Upcycling of the National Research Foundation of Korea(NRF) funded by the Ministry of Science and ICT(MSIT), the Ministry of Environment(ME) and the Ministry of Trade, Industry and Energy (MOTIE). (2017M3D8A2084752, 2017 M3D8A2086037)

References:

1. Food and Agricultural Organization (FAO). "Global aquaculture production 1950-2009," Rome: Italy, 2011.
2. Food and Agricultural Organization (FAO), "Yearbook of fishery and aquaculture statistics 2008," Rome: Italy, 2010.
3. Bureau of Fisheries, Ministry of Agriculture. *China Fisheries Yearbook 2011*. Beijing: China Agriculture Press, 2011.
4. J.H. Jung, "Reactivity of Bio-sorbent Prepared by Waste Shells of Shellfish in Acid Gas Cleaning Reaction," *The Korean Jour.of Chem.Eng.,* **22**[4] 566-68 (2005).
5. J.H. Jung, "Reuse of waste oyster-shells as a SO2/NOx removal absorbent," *Jour. of Indus.and Eng. Chem.,* **13**[4] 512-17 (2007).
6. FAO, FAO yearbook, Fishery statistics, Vol. 100/2 (2005), Food and Agriculture Organization of the United Nations, Rome. 2007.
7. S. Asaoka, "Removal of hydrogen sulfide using crushed oyster shell from pore water to remediate organically enriched coastal marine sediments," *Bioresource Tech.,* **100** 4127-32 (2009).
8. L. Xiang, Y. Xiang, Y. Wen and F. Wei, "Formation of CaCO3nanoparticles in the presence of terpineol," *Mater. Lett.,* **58** 959-65 (2004).
9. Z. T. Yao, T. Chen, H. Y. Li, M. S. Xia, Y. Ye and H. Zheng, "Mechanical and thermal properties of polypropylene (PP) composites filled with modified shell waste," *J. Hazard. Mater.,* **262** 212-7 (2013).
10. M. Suzuki, S. Sakuda and H. Nagasawa, "Identification of chitin in the prismatic layer of the shell and a chitin synthase gene from the Japanese pearl oyster, Pinctada fucata," *Biosci. Biotechnol. Biochem.,* **71** 1735-44 (2007).
11. S. Sudo, T. Fujikawa, T. Nagakura, T. Ohkubo, K. Sakaguchi, M. Tanaka, K. Nakashima, and T. Takahashi, "Structures of mollusc shell framework proteins," *Nature.,* **387** 563-64 (1997).
12. Z. T. Yao, M. S. Xia, H. Y. Li, T. Chen, Y. Ye and H. Zheng, "Bivalve shell: not an abundant useless waste but a functional and versatile biomaterial," *Crit. Rev. Environ. Sci. Technol.,* **44** 2502-30 (2014).
13. Tsuyoshi Mori, " Recycling of waste oyster shells: Production of clean and Bactericidal drinking water," The Foundation of Oyster Research Institute 31-5 Sanezawa-Nakayamaminami, *Izumi*, *Sendai*, Japan, **981** 3217 (1994).
14. K. Mori and K. Takahashi, "Bactericidal effects on *Escherichia coli* of the water treated with new ceramics manufactured by a combination of burned oyster shells and natural zeolite," *Mizushorigijutu* (*Water Purification and Liquid Waters Treatment).,* **39** 1-7(1998).

15. G.L. Yoon, "Chemical-mechanical characteristics of crushed oyster-shell," *Waste Management.*, **23** 825-34 (2003).
16. J.H. Jung, "Reuse of waste oyster-shells as a SO2/NOx removal absorbent," *Jour. of Indus.and Eng. Chem.*, **13**[4] 512-17 (2007).
17. H. Y. Li, Y. Q. Tan, L. Zhang, T. Chen, Y. H. Song, Y. Ye and M. S. Xia, "Bio-filler from mussel shell: preparation and its effects on polypropylene composites properties," *J. Inorg. Mater.*, **27** 1-7 (2012).
18. H. Y. Li, Y. Q. Tan, L. Zhang, Y. X. Zhang, Y. H. Song, Y. Ye and M. S. Xia, "Bio-filler from waste shellfish shell: preparation, characterization, and its effect on the mechanical properties on polypropylene composites," *J. Hazard. Mater.*, **217** 256-62 (2012).
19. P. M. A. de Melo, L. B. Silva, A. S. F. Santos, T. A. Passos, S. J. G. Lima and M. M. Ueki, "Evaluation of thermal and mechanical behavior of HDPE/mollusk shell composites prepared in single screw extruder," *Proceedings of 22nd International Congress of Mechanical Engineering (COBEM 2013)*, **3**[7] 3757-62 (2013).
20. ICO, International Coffee Organization. Available at: http://www.ico.org/. Accessed (05 March 2010), 2010.
21. A.G. Lane, "Anaerobic digestion of spent coffee grounds," *Biomass.*, 3 247-68 (1983).
22. E. Raetz, "Anaerobic Digestion of wastes; spent coffee grounds," Nestle´ Research Centre no. 42 1990.
23. C.G. Blandon, V.N. Rodriguez and A.M.T. Davila, "Characterization microbiological fisino-quimica de los subproductos del beneficio del cafe en procesode compostaje. Cenicafe," *Colombia.*, 49 169-185 (1998).
24. M. Mustin, "Le compost - gestion de la matière organique," *Editions François Dubusc* - Paris. 954, 1987.
25. R.K Kasongo and A. Verdoodt, "Coffee waste as an alternative fertilizer with soil improving properties for sandy soils in humid tropical environment," *Soil Use and Management*. 27 94-102 (2011).
26. Raphael. Kurian, and K. Velmourougane, "Chemical and microbiological changes during vermicomposting of coffee pulp using exotic (Eudrilus eugeniae) and native earthworm (Perionyx ceylanesis) species." *Biodegradation.*, 22 497-507 (2011).
27. K. Liu and G.W. Price, "Evaluation of three composting systems for the management of spent coffee grounds," *Bioresource Technology*. 100[2] 7966-74 (2011)