Pogaku Ravindra *Editor*

Advances in Bioprocess Technology

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To all the noble souls who are relentlessly striving to integrate technology with human touch for sustainable society.

It has become appallingly obvious that our technology has exceeded our humanity.

ALBERT EINSTEIN

Preface

Fuelled by rapid economic growth, bioprocessing of a variety of feedstocks has increased drastically, making bioprocess technology the larger revenue generator in the world within a short span of few decades. There is continuously ever-increasing gap between traditional and bioprocess technology, which is a positive sign for the welfare of a sustainable society. Taking into account the trend of bio economic growth, every nation's strong dependence on traditional process technology cannot be mitigated in the future without developing self-dependent bio-based alternatives, which not only secure the sustainability of its own economy, but also impact the rest of the world for a healthy society. On an average, every country has leading grain production in the world, producing more than 300 MT of grain per year on an average, and correspondingly generating 600–700 MT agricultural residues. Due to the lack of economically viable technologies for their utilization, most agricultural residues are burnt in the field by farmers, which pollutes environments and even presents public hazards such as the disruption of air transportation by smoke clouds in the sky. The abundant of cellulosic waste can be used for bio-based products. Therefore, producing biofuels, bioenergy, and bio-based chemicals through the refinery of lignocellulose biomass has been acknowledged worldwide as an alternative to the oil refinery, since the oil crisis occurred in the 1970s. It has also recently been highlighted again because of global climate change caused by the over-consumption of petroleum-based products, particularly vehicle emissions. Without doubt, the successful development of biomass refineries will help it to sustain its own economy, and in the meantime contribute to the whole world. Driven by these imperatives, governmental funding for R&D of biomass refineries has increased significantly in many nations. This momentum is expected to be maintained for a long term to make such a pathway economically competitive.

I am honored to be invited by the Springer to edit the book entitled "Advances in Bioprocess technology," with a focus on bioprocess technology, biofuels, and bioenergy to present major progress achieved by eminent scientists and challenges to be addressed collectively by international communities.

The bio-based platform is the prerequisite for the bioconversion of lignocellulose biomass, and highly efficient and low-cost cellulose enzymes are the bottleneck. Therefore, all the authors have emphasized and reviewed the bioprocess technology scope for the sustainable world. The book is divided into five parts. The first part is with a theme of advances in biochemical engineering. It comprises five chapters. Chap. 1 is authored by Abu Zahrim et al. It has focused on life cycle review on biomass combustion. Chap. 2 deals with bioleaching of nickel written by Pogaku Ravindra et al. Hari Vuthaluru reviews on ash formation from pulverized fuel combustion in Chap. 3. Waste management methods are reviewed by Faheem in Chap. 4 and Chap. 5 makes a comprehensive study of free fatty acid modelling in palm oil refinery by Ravindra et al. In Part II, with the title of Biomass and Bionergy, there are ten chapters. Ravindra et al. authored Chap. 6 entitled Production of Biogas from Palm Oil Mill Effluent. Danquah authored Chap. 7, a very relevant topic, on the process analysis of microalgae biomass. Chapter 8 is reviewed by Gangagni Rao on biogas from poultry. Chapter 9, on biogas production, is reviewed by Chan et al. The detailed review on bioenergy is well reviewed by See Ram et al. in Chap. 10. Optimization of catalytic coal gasification for hydrogen is highlighted by Suzana Yusup in Chap. 11. Further Suzana Yusup et al. wrote Chap. 12 on the effect of process parameters on bio oil yield. Anantha Raman et al. narrated agro residue as fuel in Chap. 13. A novel method for biogas as clean fuel is described by Vijay Kumar et al. in Chap. 14. Sarma et al. have described the thermochemical processing of biomass in Chap. 15. Part III under the title Bioprocess Technology has three chapters. Chapter 16 is written by Azlina Kamruddin et al., with a focus on dynamic enzymatic kinetic resolution of NSAID. This is followed by catgut waste utilization for protease production in Chap. 17 by Jegan et al., and Chap. 18 discusses about membrane processes for microalgae by Rosalam et al. Part IV emphasizes on food biotechnology. It has three chapters. Chapter 20, authored by Inge Russell et al., narrates innovation in alcohol beverage production. Chapter 21 is written on starter cultures technology for fermented foods by Ravindra et al., and Chap. 22 highlights specialized studies on liquid core capsules for lactobacilli fermentation. This chapter is authored by Boon Beng Lee et al. The final Part V contains policy and regulations in Chap. 23. The framework of policy regulations for bioprocess is well explained by Sripathi Kulkarni Rao et al.

We expect this special volume to be a window for international colleagues to learn the current R&D progress in bioprocess technology, biofuels, and bioenergy in many nations. On behalf of Springer and Co, I express my sincere thanks to all authors and reviewers for their dedication, contributions, and valuable comments.

Professor Devinder Mahajan, Chemical & Molecular Engineering Materials Science Engineering Dept. Stony Brook University, NY, USA for his encouragement.

Gregory Baer and **Merry Stuber** of Springer Science+Business Media for their delicate coordination.

Also, I greatly appreciate the generosity of my University Malaysia Sabah (UMS), my colleagues and graduates at Faculty of Engineering and my family for all their support.

Kotakinabalu, Malaysia Dr. Pogaku Ravindra

About the Editor

Pogaku Ravindra has diverse and intense, yet rewarding experiences in teaching, research, industry, executive and administrative fields spanning over 35 years.

Professor Ravindra was visiting scientist at Cornell University and visiting professor at Pennsylvania State University. He has an expertise in the area of bioprocess technology for high value products and bioenergy. At present, his research group is focused on bioprocessing of palm oil waste and bio-derived energy for sustainable development. Over the course of his 35 years, he has published more than 200 articles in journals and proceedings. He has edited 4 books, authored 8 books and 12 book chapters. He has reviewed more than 1000 journal manuscripts for reputed international journals. He has a patent and four copyrights.

Professor Ravindra is bestowed with the national and international prestigious awards. He has received gold and silver medals for his research contributions in the Oil and Gas, Chemical and Bioprocessing fields. Professor Ravindra's LCP model was given an award from International Invention and Innovation Exhibition (ITEX), Malaysia. Professor Ravindra was recipient of distinguished chemical engineer award from the Indian institute of Chemical engineers. He has received the best researcher award from the *International Journal of Science and Technology*.

Professor Ravindra was also a UNESCO consultant on Sustainable energy projects. He has also carried out at least 25 major industry studies. He serves as the editor-in-chief, editorial board member, guest editor and reviewer for multiple referred journals.

Professor Ravindra has delivered invited lectures, plenary talks and keynote address at various National and International institutions, symposia, conferences etc. He is also advisory committee member for international conferences. Professor Ravindra has organized short-term refresher courses, workshops, conferences and seminars.

Professor Pogaku Ravindra's primary research interest is to develop the sustainable process for bioconversion of lignocellulose into renewable energy and bio-chemicals, by bridging the gap between research laboratories and industries. Professor Ravindra's focus is on the Green engineering and technology for sustainable development of the society.

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Part I
Advances in Biochemical Engineering

Chapter 1
A Review on the Empty Fruit Bunch Composting: Life Cycle Analysis and the Effect of Amendment(s)

A.Y. Zahrim, T. Asis, M.A. Hashim, T.M.T.M.A. Al-Mizi, and P. Ravindra

Introduction

Palm oil industry significantly contributes to the national economy in Malaysia and currently accounts for RM53 billion (Kabbashi et al. 2014). The empty fruit bunches (EFB) of oil palm is one of the major wastes from oil palm industry. It is reported that about 3.0 million tons of oil palm empty fruit bunch (EFB) fibers are produced every year (Sajab et al. 2013). The typical physicochemical analysis for EFB is shows in Table 1.1. Due to the fact that EFB are generated daily and every year its disposal becoming a great concern, thus sustainable technology for EFB disposal is vital to be developed. Composting is regarded as a proven technology for processing EFB from the palm oil mill (Zahrim and Asis 2010). Composting is an accelerated bioconversion of organic matter to humic substances known as compost. Furthermore, composting could reduce the volume and initial weight of the fresh EFB by 85 % and 50 % respectively (Saletes et al. 2004).

The compost can be applied as a soil amendment (Yaser et al. 2007) or mulching as well other non-agricultural usage such as biofilter. Recently, indigenous microorganisms from EFB compost were developed into advanced or multifunctional biofertilizer products (Phua et al. 2012). Among others, the quality of compost depends on the raw material itself (Zahrim and Asis 2010) as well as turning frequency (Tiquia et al. 2002).

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Table 1.1 Typical physicochemical analysis of EFB

Parameters	Value	Ref.
Moisture, %	58–65	Zahrim and Asis (2010)
Cellulose, %	46	Saletes et al. (2004)
Lignin, %	16.5	Saletes et al. (2004)
C/N	45–70	Saletes et al. (2004)
N, % on dry	1.1–1.2	Zahrim and Asis (2010)
P_2O_5, % on dry	0.05–2.6	Zahrim and Asis (2010)
K_2O, % on dry	2.4–2.7	Zahrim and Asis (2010)
MgO, % on dry	0.4–0.5	Zahrim and Asis (2010)

Life Cycle Assessment (LCA)

Life cycle assessment (LCA) has been used to evaluate and compare the impacts of different waste disposal scenarios, including composting. By using a common metric, LCA methodology allows for the quantification and comparison of environmental impacts between stages of a product or service throughout its life cycle, including raw material acquisition, processing, distribution, use, and end of life. Several LCA studies have reported that composting is more advantageous, i.e. less environmental impacts, than other organic waste disposal scenarios, such as landfill and incineration (Saer et al. 2013).

Stichnothe and Schuchardt (2010) studied a detailed life cycle model has been used to calculate the environmental impacts of POME and EFB treatment. The authors investigated several options, i.e. (1) dumping EFB and storing POME and ponds, (2) returning EFB to the plantation and POME as before, (3) using EFB and POME for co-composting and returning the produced compost to the plantation, (4) generating biogas from POME and thereafter as in (3). The sensitivity analysis has been carried out in order to estimate the influence of good and poor management practice on the environmental performance. From this study, Stichnothe and Schuchardt (2010) stated that the main contributor to the Global Warming Potential (GWP) is methane from POME and EFB dumping. The GWP of palm oil mill waste treatment can be reduced from 245 kg CO_{2eq} per ton FFB to up to 5 kg CO_{2eq} per ton FFB due to the reduction of methane emissions and nutrient recycling. Co-composting of POME and EFB leads to considerable nutrient recovery, in addition to GWP reduction (Stichnothe and Schuchardt 2010). Recently, Chiew and Shimada (2013) analysed seven technologies for EFB management: ethanol production, methane recovery, briquette production, biofuel for combined heat and power (CHP) plants, composting, medium density fiberboard (MDF) production, and pulp and paper production. The authors reported that the methane recovery and composting are more environmentally friendly than other technologies, as measured by reduction of greenhouse gas emissions (Chiew and Shimada 2013). In another study, Norhasmillah et al. (2013) compared the life cycle inventory (LCI) obtained from three commercial oil palm biomass composting projects in Malaysia which use the open windrow composting system. Interestingly, the authors found that composting saved 65 % of time required for a complete degradation of POME when compared to ponding system, and 89 % of time required for a complete degradation of EFB compared to mulching (Norhasmillah et al. 2013).

The advantages of EFB composting not only reduces environmental burdens; it also leads to net environmental benefit regarding most environmental impact categories, e.g., acidification potential, eutrophication potential, ozone layer depletion potential, etc. due to the avoided emissions from inorganic fertilizer production (Stichnothe and Schuchardt 2010). Yoshizaki et al. (2013) reported that the compost production using shredded empty fruit bunch (EFB) and POME anaerobic sludge obtained from the anaerobic digester is equivalent of 579 tonnes, 151 tonnes and 761 tonnes per year of nitrogen, phosphorus and potassium respectively (Yoshizaki et al. 2013).

A Review on the Effect of Different Amendment(s)

Rapid decomposition of empty fruit bunch (EFB) can be obtained by adding suitable material(s) such as animal waste and palm oil mill effluent (Table 1.2). The effects of composting EFB alone, EFB-poultry layer deep-litter-urea, and EFB-poultry broiler floor-litter-urea were studied by Thambirajah and Kuthubutheen (1989). The initial C: N ratios of the three mixtures were 40:1, 33:1 and 26:1, respectively. After 8 weeks of composting the C: N ratios of the mixtures were 26:1, 17:1 and 16:1, respectively (Thambirajah and Kuthubutheen 1989). The composting of EFB alone, EFB-goat dung, EFB-cow dung and EFB-chicken manure were studied by Thambirajah et al. (1995). The initial C:N ratios (52:1, 35:1, 48:1, 47:1) for the four compost heaps were significantly reduced to 24:1, 14:1, 18:1 and 12:1, respectively, after 60 days of composting (Thambirajah et al. 1995). In this study, the maximum heap temperature of 70 °C was maintained for 3 days during composting phase. Both mesophilic and thermophilic bacteria showed consistent activity throughout the process, whereas fungal activity was completely suppressed during the peak heating phase (Thambirajah et al. 1995). Saletes et al. (2004) have added urea and/or ripe compost to amend the initial C/N of EFB. They reported that after 70 days, the compost could be considered matured. However, almost 50 % of the phosphorus, 70 % of the potassium, 45 % of the magnesium and between 10 % and 20 % of the calcium theoretically applied were lost during composting period. The authors suggested that the better distribution of the effluent applications, combined with a system to

Table 1.2 Mass of each raw material in the compost heap

	Banana skin, kg	EFB, kg	Total initial compost, kg	% Banana skin
H0	0	100.0	100	0.0
H5	5.3	100.0	105.3	5.0
H10	11.1	100.0	111.1	10.0

recover the leachings, should substantially reduce these losses, while maintaining suitable humidity for microbial degradation (Saletes et al. 2004).

Schuchardt et al. (2005) reported that the conventional ponding system of palm oil mill effluent (POME) treatment is not only contribute highest pollution of the environment also the system with the lowest profit. The authors recommended utilisation of nutrients from POME and EFB for composting process (Schuchardt et al. 2005). The investigation of co-composting EFB with partially treated palm oil mill effluent (POME) was carried out by Baharuddin et al. (2009). The temperature was increased up to 58.5 °C at day three of treatment, after that fluctuated between 50 and 62 °C and then decreased in the latter stage of the process. The pH of the system (7.75–8.10) did not vary significantly during the treatment period while moisture content was reduced horn 65–75 % to about 60 % at the end of the treatment. The initial C/N ratio of 45 was significantly reduced to 12 after 60 days of composting. The final cured compost contained a considerable amount of nutrients (carbon, nitrogen, phosphorus, potassium, calcium, magnesium, sulfur and iron) and trace amounts of manganese, zinc, copper. In addition, very low levels of heavy metals were detected in the compost. The number of bacteria involved in the composting process was decreased at the end of the composting period. The compost product may useful in palm oil plantation as fertilizer and soil amendment (Baharuddin et al. 2009).

The co-composting of pressed-shredded EFB and palm oil mill effluent (POME) anaerobic sludge from 500 m^3 closed anaerobic methane digested tank was investigated by Baharuddin et al. (2010). High nitrogen and nutrients content were observed in the POME anaerobic sludge. The sludge was subjected to the pressed-shredded EFB to accelerate the co-composting treatment. The co-composting treatment was completed in a short time within 40 days with a final C/N ratio of 12.4. The co-composting process exhibited a higher temperature (60–67 °C) in the thermophilic phase followed by curing phase after 4 weeks of treatment. Meanwhile, pH of the composting pile (8.1–8.6) was almost constant during the process and moisture content was reduced from 64.5 % (initial treatment) to 52.0 % (final matured compost). The use of pressed-shredded EFB as a main carbon source and bulking agent contributed to the optimum oxygen level in the composting piles (10–15 %). The biodegradation of composting materials is shown by the reduction of cellulose (34.0 %) and hemicellulose (27.0 %) content towards the end of treatment. In addition, considerable amount of nutrients and low level of heavy metals were detected in the final matured compost (Baharuddin et al. 2010). Baharuddin et al. (2011) reported that shredding-pressing treatment on EFB gave better results in removing the debris and silica bodies as compared to only shredding treatment. With the aspiration of reducing the composting yard area and energy consumption, the production of non-shredded EFB-POME compost in industrial scale windrow was reported by Zahrim and Asis (2010). The authors reported that the total composting time including preparation of the windrow was about 40–45 days and the windrow was turned every 10 days. Compost quality i.e. moisture content, pH, nitrogen and other nutrients, was evaluated during 6 months operations, and it was found that the nutrient in compost is acceptable for soil conditioner (Zahrim and Asis 2010). A study on EFB-POME- non-food cassava starch was carried out by Mohammad et al. (2015). The authors reported that the total period of composting was 35–40 days and found that the 2-mm particle size of EFB was most suitable to grow microbes, gave the highest protein of 85 g kg^{-1} and degraded fastest (lowest C/N ratio of 16). In addition, substrate ratio 1:3 (EFB and POME) and pH 5.0 were found to be favorable for mature compost (Mohammad et al. 2015).

Decanter cake (DC) is generated by palm oil milling plant from three-phase CPO purification. The production rate of DC is about 4–5 wt% of fresh fruit bunch processed and consuming a lot of space. Moreover when dried, the DC could becoming fire hazard and contribute toward increasing the amount of suspended particles in the vicinities of mills (Dewayanto et al. 2014). Composting EFB-decanter cake (DC)-palm oil mill effluent (POME) was reported by Yahya et al. (2010). The addition of decanter cake slurry has accelerated the composting process of the EFB. The C/N ratio after 51 days for the mature compost with the decanter cake slurry was 18.65 while that of the matured compost without the decanter cake slurry remained high at 28.96. The compost formed from the addition of decanter cake (DC) to EFB and POME had 46.4 % nitrogen, 17.9 % phosphorus, 17.7 % potassium and 23.1 % calcium more than that without decanter cake (Yahya et al. 2010). Nutongkaew et al. (2014a) investigated the composting of EFB-palm oil mill sludge (POMS)-DC. The compost appeared dark brown in color, crumbly, attained an ambient temperature and had the C/N ratio of 11:1 after 40 days fermentation, indicating the maturity of the compost. The authors also reported that the compost quality complied with the national compost standard set by the Ministry of Agriculture, Thailand (Nutongkaew et al. 2014a). In another study, Nutongkaew et al. (2014b) investigated a composting study on EFB-DC-palm oil mill biogas sludge (POMS)-palm oil fuel ash (POFA). The authors found that the compost piles turned dark brown and attained an ambient temperature after 40 days incubation. The pH values were stable in the range of 6.9–7.8 throughout the process whereas the moisture content tended to decrease till the end with the final value around 30 %. After 60 day's incubation, the mixture ratio of POMS:PEFB: DC at 2:1:1 with the addition of biogas effluent gave the highest quality of the compost. Its nitrogen content was 31.75 % higher than the other treatments that may be a result of growth of ink cap mushroom (*Coprinus* sp.). This is the first report on the occurrence of this mushroom during composting. In addition, its nutrients (3.26 % N, 0.84 % P and 2.03 % K) were higher than the level of the Organic Fertilizer Standard (Nutongkaew et al. 2014b). However, in another study Kananam et al. (2011) reported that the use of decanter sludge did not have an effect on any biochemical conditions of either aerobic or anaerobic EFB composting. Moreover, the oil palm EFB compost with decanter sludge in an aerobic condition completed within 30 days whereas compost in the anaerobic condition failed to complete composting within 90 days. By adding red soil to the compost pile, it does not affected the composting time, but it reduced the odour generated from the pile (Kananam et al. 2011). In another study, Kabbashi et al. (2014) studied composting of EFB-POME-DC-sawdust. The maturity of the composting could be reflected by the best C/N ratio obtained was run 6 which are 16.51, pH, and germination index result of 154 %. This simple technology urge to enhance the productivity and sustainability of the Malaysian palm oil milling industry by improving the local isolated fungal strains and increasing composting utilization (Kabbashi et al. 2014).

Addition of recycled paper mill sludge (RPMS) to EFB for the production of compost was investigated by Rosazlin et al. (2011). Then, the EFB-RPMS compost mixtures were evaluated for physical, chemical, phytotoxicity and short term plant growth effects. These composts mixtures had no toxicity effects on plants, had 100 % seed germination, high in nutrient contents, low in C/N ratio and had fine particle size of <18 mm. The concentrations of heavy metals were also within the recommended level of the Council of European Communities (CEC) for compost (Rosazlin et al. 2011). Composting oil palm wastes (EFB-frond-trunk) with sewage sludge was carried out by Kala et al. (2009). Shredded oil palm wastes were mixed with sewage sludge in three different ratios (1:0, 3:1 and 4:1 ratio). Oil palm wastes with sewage sludge at 4:1 ratio was found to be the most optimum compost as potting media for ornamental plants because of its texture suitable for potting media, not stringent or stiff, had high nutrient contents (2.05 % N, 0.640 % P, 1.39 % K, 0.705 % Ca, 0.229 % Mg), pH 6.2 and low C/N ratio, 19 (Kala et al. 2009). The efficiency of EFB-frond- poultry litter composting was investigated by Vakili et al. (2012). From the study, the 1:3 ratio of EFB-frond and poultry litter had the lowest C/N ratio, TOC and the highest value of TKN, 18, 27 % and 1.48 %), respectively (Vakili et al. 2012).

An investigation of several organic materials in Malaysia as additives/amendments for composting EFB was carried out by Chai et al. (2013). The authors found that the organic waste materials with a C/N ratio of <30 can be applied as a nitrogen source in EFB co-composting. The outcome of this study suggested that the percentage of EFB ranged between 50 % and 60 %, which is considered as the ideal mixing ratio in EFB co-composting (Chai et al. 2013). Talib et al. (2014) the composting of EFB-rabbit manure using forced-aeration system and reported that aeration rate of 0.26 L min^{-1} dry matter^{-1} provided enough oxygen level (10 %) for the rest of composting period, showing 40.5 % of OM reduction that is better than other aeration rates (Talib et al. 2014). From the above review, selection and dosage of amendments are critical for the enhancement of EFB composting. In the next section, a new amendment for EFB composting i.e. banana skins is discussed.

Case Study: Addition of Banana Skin as Amendment

As one of the most consumed fruits in the world, banana is a very common fruit. The main banana residue is the fruit skin, which accounts for 30–40 % of the total fruit weight. It was reported that several tons of banana peels are produced daily in small-medium food processing industry, marketplaces, household garbage and restaurants (Mohammed and Chong 2013). In Malaysia, banana skins have not been fully utilized for production of useful by-products.

Co-composting of banana skins with empty fruit bunch could reduce waste management problems and conserve plant nutrients. Nasreen and Qazi (2012) investigated composting of banana skins in glass jars. The authors found that the seed germination indices for the compost is 63 %, indicated the conversion of the wastes into value added phytotoxin free fertilizer, which can escalate the agricultural output (Nasreen and Qazi 2012). In another study, Kalemelawa et al. (2012) evaluated the efficacy of aerobic and anaerobic composting of inoculated banana peels, and assess the agronomic value of banana peel-based compost. The study suggested that the final composts contained high K (>100 g kg^{-1}) and TN (>2 %), indicating high potential as a source of K and N fertilizer (Kalemelawa et al. 2012). Recently, a co-composting banana stem-swine manure-eucalyptus bark was carried out by Deng et al. (2014). The authors reported that when C/N ratio of the composting material was 25–27, the heaps of compost were the highest in temperature, reaching up to 56 °C or higher and maintained the high temperature for 10–11 days, respectively, and they were also higher in content of nutrients, and the pot experiment also shows that composts had a certain growth-promoting effect on banana seedlings (Deng et al. 2014).

The aim of this study was to evaluate the effect of amount of banana skin on the heap temperature and final nutrient of EFB-POME compost. Results from this study could give valuable insight on the effect of banana skin as an amendment for enhancing composting performance.

Methodology

The palm oil mill effluent (POME) from an anaerobic digestion pond No. 1 and empty fruit bunch were collected from Merotai Palm Oil Mill, Tawau, Sabah. Banana skin was collected from various small food stall around Tawau, Sabah. One hundred kilograms of EFB was mixed with different percentage of banana skins (BS) as indicated in Table 1.2. The 28 m^3/h POME (from day 0 to day 35) was sprayed carefully so that the banana peel does leached from the compost heap. The composting process was performed over the course of 45 days. Turning of the compost was carried out at day 5, 10, 15, 20, 25, 30 and 35. This study was carried out at Merotai Composting Plant, Tawau, Sabah. All experiments were carried out in duplicate.

Physicochemical Analysis

During the whole co-composting process, the temperatures at three points along the length of the middle of composting mixtures (5 cm, 10 cm deep and at the core of the compost heap) were measured almost daily. The three readings per composting mixture were averaged. Ambient temperature was also recorded. Sampling for nutrients analysis was made on ten randomly selected points on each compost heap. The chemical analysis was carried out by Sime Darby Research Sdn. Bhd. Method used for moisture content burn at 103 °C. The nitrogen content was analyzed using distillation method (MS 677: Part 1–VIII:1980). The organic matter (OM) content (volatile solids) was determined with a furnace at 550 °C (MS 417: Part 8:1997). The total P was estimated using spectrophotometric molybdovanadophosphate (MS417: Part 4:1994). The potassium and magnesium were determined using atomic absorption spectroscopy (AAS) (MS417: Part 5 and Part 6:1994).

Result and Discussion

Temperature Profile

The temperature monitoring is a very simple way to follow the progress of composting (Yaser et al. 2007). In this study, the oxygen content for all heaps i.e. H0, H5 and H10, is maintained around 19–20 %, which is necessary for maximum biodegradation (Baharuddin et al. 2009). The trends of the temperatures in the H0, H5 and H10 were not similar indicating different effect of percentage of BS addition. Stentiford (1996) suggested that temperatures higher than 55 °C maximized sanitation, those between 45 and 55 °C maximized the biodegradation rates, and between 35 and 40 °C maximized microbial diversity in the composting process. Throughout the experimental period, the ambient temperature ranged from 24 to 29 °C. During the composting period, at day 3, the H10 achieved the maximum temperature of 47.5 °C while the H0 and H5 only achieved temperature of 36.0 and 40.5 °C (Fig. 1.1). The sharp increase in temperature to greater than 45 °C for H10 in

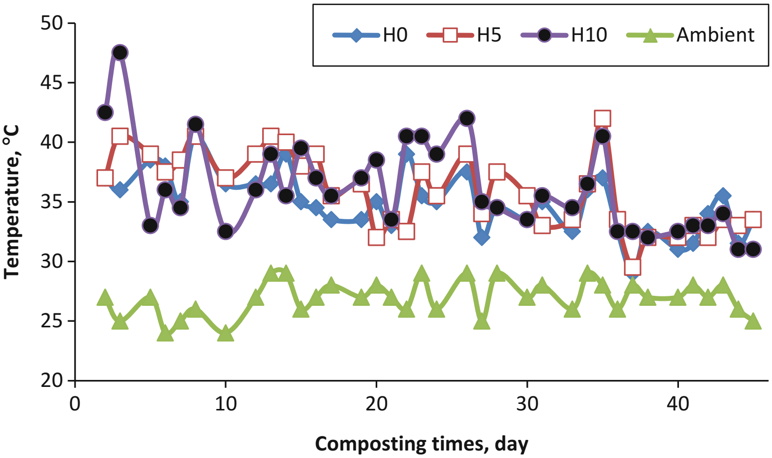

Fig. 1.1 Temperature during the composting EFB-POME-BS as affected by different percentage of BS. Ambient air temperature is also indicated and was the same for all treatments

the first 3 days of composting reflects the rapid initiation of the composting process (Placha et al. 2013; Stentiford 1996). Both H0 and H5 did not achieve temperature for maximum biodegradation rates. The maximum temperature for the H0 is 40.5 °C and was achieved at day 8 while the H5's maximum temperature is 42 °C (day 35). However, it can be seen also that the large drop in temperature also experienced by the H10 might be due to the limited ability of BS to adsorb heat.

From Fig. 1.1, the temperature in H10 can be raised again by turning the heap. After biodegradation process, the structure of compost e.g. porosity, may change. The turning operation improves the aeration of the compost materials by increasing its porosity. Therefore, the availability of more air within the composting materials favors the renewal of microbial activities which indirectly increase the decomposition process of the composting materials (Yahya et al. 2010). In this study, the effect of turning was very significant especially for H10. It can be seen that at day 5, the temperature drop to 33 °C, but after turning process, the temperature is rise again to 41.5 °C. Similar trend also found after each turning process until after day 35 (i.e. last turning was carried out), the temperature for the H10 is around 34 °C due to lack of carbon that has been fully utilized by the microorganisms and consequently, minimize the metabolism and the heat production (Zahrim and Asis 2010).

Moisture Content, pH and Nutrients

The final physicochemical compositions of the final compost are shown in Table 1.3. From the table, it could be seen that the value for moisture content, pH, phosphorus, and potassium of the compost material with banana skin slurry are greater than un-amended compost (control). In comparison with others studies (Table 1.3), the potassium in this study is greater than others, indicating positive improvement by adding banana skin as amendments.

Increasing of the final moisture content due to addition of banana skin might be due to the ability of banana skin to adsorb water. Due to the fact that the protein content in banana is around 8–11 % (Happi Emaga et al. 2007) while only 2–3 % for EFB (Abdullah et al. 2009), as expected, the final pH (protein degradation) for both H5 and H10 were higher than the control.

The addition of banana skin contributes little effect on the final N content based on R^2 value in Eq. (1.1). The best equation to describe the correlation for mass of banana skin (x) and nitrogen content is as follows:

$$\begin{aligned}\text{Nitrogen content, }\% &= 0.066\,(\%\text{ banana skin}) + 1.5463,\\ &\quad\text{Coefficient correlation, } R^2 = 0.60\end{aligned} \tag{1.1}$$

From Table 1.3, it is suggested the addition of sludge from anaerobic digestion system to improve the N content (Yaser et al. 2007; Baharuddin et al. 2010;

Table 1.3 Nutrients content in EFB compost for several studies

Amendment(s) material	Composting time, days	Moisture content, %	pH	C/N	N, %	P, %	K, %	Ref.
Partially treated POME	45	75	6.8	27	1.6	0.2	2.7	This study
Partially treated POME + 5 % banana skin	45	79	8.3	29	1.5	1.4	3.4	This study
Partially treated POME + 10 % banana skin	45	79	8.5	27	1.6	1.7	3.0	This study
Anaerobic digestion sludge + decanter cake	60	60	7.8	13	3.3	0.9	2.0	Nutongkaew et al. (2014b)
Fresh POME + decanter cake	52	58	8.8	19	1.7	1.0	2.5	Yahya et al. (2010)
Anaerobic digestion sludge	40	52	8.1	12	2.3	1.4	2.8	Baharuddin et al. (2010)
Fresh POME	45	55	7.9	20	1.9	0.6	2.0	Zahrim and Asis (2010)
Partially treated POME	60	61	8.1	13	2.2	1.3	2.8	Baharuddin et al. (2009)
POME + Wheat flour	60	ND	5.6	20	ND	ND	ND	Kabbashi et al. (2007)
Without any amendment material	60	65	8.5	24	1.7	ND	ND	Thambirajah et al. (1995)
Goat dung	60	65	8.5	14	2.5	ND	ND	Thambirajah et al. (1995)
Cow dung	60	65	8.5	18	1.9	ND	ND	Thambirajah et al. (1995)
Chicken manure	60	65	8.5	12	2.0	ND	ND	Thambirajah et al. (1995)
Sewage sludge + oil palm trunk, frond	90	60	6.2	19	2.1	0.6	1.4	Kala et al. (2009)

ND = not determined

Nutongkaew et al. 2014b). While the best equation to describe the correlation for mass of banana skin (x) and K_2O is given as:

$$\begin{aligned} \%K_2O &= 0.0277(\%\text{banana skin}) + 2.9018, \\ \text{Coefficient correlation, } R^2 &= 0.13 \end{aligned} \tag{1.2}$$

The banana skin increases the potassium content from 2.7 % to around 3.0 %, however the addition of more than 5 % BS did not increases the K content might be due to the solubilisation of K in compost leachate as shown in Eq. (1.2). However, the addition of banana skin highly affected the final P_2O_5 and MgO (data not shown) as shown in Eqs. (1.3) and (1.4).

$$\begin{aligned} \%\,P_2O_5 &= 0.1401\ (\%\ \text{banana skin}) + 0.3962, \\ \text{Coefficient correlation, } R^2 &= 0.88 \end{aligned} \tag{1.3}$$

$$\begin{aligned} \%\,\text{MgO} &= 0.1599\ (\%\ \text{banana skin}) + 0.2802, \\ \text{Coefficient correlation, } R^2 &= 0.99 \end{aligned} \tag{1.4}$$

Conclusion

(1) LCA study by various investigators confirmed that composting is more really environmentally friendly based on the greenhouse gas reduction measurement.
(2) The EFB composting with suitable amendments give acceptable quality of compost and accelerate the process to less than 60 days.
(3) In the case study, the addition of banana skin could enhance rapid EFB decomposition and increase nutrients such as P and K.

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Chapter 2
Effect of Adaptation of *Acidothiobacillus ferrooxidans* on Ferrous Oxidation and Nickel Leaching Efficiency

Pogaku Ravindra, Bharathi Kodli, and V. Prasarnth Raaj Veera Rao

Introduction

It is known that microorganisms possess ability to tolerate the presence of particular element in growth medium through development of adaptation of cells over a prolonged period (Elzeky and Attia 1995). In natural environment, the metal ions are accumulated in to solutions and confer metal resistance due to acclimatization of the bacteria to that environment. This property was utilized to enhance the metal tolerance as well as the leaching ability of microorganisms (Garcia and da'Silva 1991; Ballester et al. 1990; Bharathi et al. 2004).

Bacterial adaptation to ores and floatation concentrates prior to bioleaching was found to play an important role in enhancing the leaching rates (Li and Ke 2001; Das et al. 1997). Adaptation to leaching environment enables the bacteria to function more efficiently in high concentrations of metals and low pH thereby enhancing the leaching efficacy of the bacterium. Sulfide mineral leaching involves the role of lixiviant Fe^{3+} ion produced from the oxidation of pyrite, which acts as the typical energy source of chemolithotrophs such as *Acidothiobacillus ferrooxidans* (*Tf*).

Tf is the preferred organism for leaching of sulfide concentrates within mesophilic temperatures (Mason and Rice 2002; Adamov et al. 1997; Torma 1997) with an unique character to derive energy from oxidation of Fe^{2+}, generating heat energy that is required for chemical reactions of sulfides. The barophilic nature of *Tf* renders the organism to get adapted to versatile mining conditions leading to enhanced leaching efficacy (Natarajan and Iwasaki 1983). Mineralogy of ores and

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flotation concentrates plays a role in selective leaching of metals (Valix et al. 2001). Oxidation of pentlandite mineral phase is essential to selectively leach nickel (Giaveno and Donati 2001; Mehta et al. 1997, 1999).

UCIL (Uranium Corporation of India Limited), India, produces tons of copper flotation concentrate which is dumped out as waste since this concentrate is unworthy for efficient copper metallurgy due to high nickel content in it. Processing of this concentrate by conventional technologies has emerged as uneconomical and environmentally unfriendly (Bandhyopadhyay 2003). Recently, mineral biotechnology shot in to prominence in mineral engineering for the utilization of wastes and low-grade ores (Kar et al. 2003; Bosecker 2001).

Bacterial oxidation process has been established in gold and copper industries. But, application in nickel extraction from ore wastes and lower grade nickel sulfide resources is sparse (Bharathi et al. 2000, 2002; Acevado 2002). Hence, the need to improve the bacterial growth rates and enhance the efficiency of *Tf* strains to achieve better yields of nickel during leaching process should be focused (Bharathi et al. 2004).

Though the technique of adaptation of *Tf* prior to leaching is attractive, much attention has not been paid by researchers regarding ferrous oxidation ability and selective leaching of nickel by adapted cells of *Tf*. Hence, comparative studies were conducted to leach nickel by unadapted strains and strains adapted to synthetic salts of copper, nickel and copper flotation concentrate.

Materials and Method

Copper Flotation Concentrate

The representative samples of copper flotation concentrate were obtained from UCIL, Jaduguda, Chhattisgarh, India. The finely ground concentrate samples were subjected to elemental analysis using AAS. The chemical composition of the concentrate sample and different mineral phases were analyzed by X-ray diffraction spectroscopy (X-RD) (Tables 2.1 and 2.2).

Microorganism

Tf-44 and *Tf*-231 were obtained from Agharkar Research Institute, Pune, India. *Tf* strains were activated and regularly subcultured on modified 9K medium.

Table 2.1 Chemical composition of copper flotation concentrate obtained by X-RD analysis

Sample	Elements	% Composition
Copper flotation concentrate	S	31.5
	Fe	29.5
	Cu	21.4
	Ni	2.73
	Mo	1.38

Table 2.2 Presence of different mineral phases of the copper concentrate sample. Prior to and after leaching as analyzed by X-RD analysis

Sample	Major phases	Minor phases
Copper flotation concentrate (prior to leaching)	Chalcopyrite ($CuFeS_2$) Pentlandite [$(Fe,Ni)_9S_8$]	Pyrite (FeS_2), Pyrrhotite (FeS), Violarite [$(NiFe)_3S_4$]
Copper flotation concentrate (leach residue)	Chalcopyrite ($CuFeS_2$)	Pentlandite [$(FeNi)_9S_8$] Hydronium jarosite [$H_3OFe_2(SO_4)_3(OH)_6$]

The composition of the medium in g L^{-1}; ammonium sulfate-2.0, magnesium sulfate-0.5, dipotassium hydrogen orthophosphate-0.025, ferrous sulfate-40 was adjusted to pH value of 2.5 (Paknikar and Agate 1995).

Bacterial Activation and Growth

Tf cultures were maintained in 250 ml standard Erlenmeyer shake flasks on a biological incubator shaker (model: Remi-RIS-24) at 120 rpm (revolutions per minute), pH-2.5 and temperature 30 °C. For inoculation 10 % v/v cells were harvested from late exponential phase of growth. The cells were harvested by centrifugation by refrigerated centrifuge at 4 °C (Hitachi make, model-Mikro 22R) followed by resuspension in mineral salts solution. The growth studies were conducted in terms of substrate utilization (ferrous oxidation) of *Tf* strains by dichromate titration using sodium diphenylamino sulfonate as indicator (Jeffery et al. 1989; Vogel 1978).

Preadaptation Studies

For 0.3 g of powdered concentrate sample, 0 ml of 105 tartaric acid solution and 6 ml of concentrated nitric acid (HNO_3) were added and allowed to stand at room temperature over night for digestion. The solution prepared was then heated on a sand bath for 2–3 h to reduce al sulphur compounds to elemental sulphur. The undissolved residue was washed with deionized water and filtered. The concentration of the elements of interest against standard and blank containing similar acid concentrations was analyzed by Atomic Absorption Spectroscopy (Ravindra and Bharathi 2009).

Adaptation to Metals

Tf cultures were serially subcultured in M9K$^-$ medium (without ferrous sulphate) in the presence of copper and nickel salts by gradually increasing their concentration up to 20 g L^{-1}.

Adaptation to Copper Flotation Concentrate

Tf strains were preadapted to copper concentrate by continuously growing in M9K$^-$ medium (flotation concentrate in the absence of chemical supplementation of ferrous). The concentration of flotation concentrate was gradually increased from 1 g L^{-1} to 10 g L^{-1}.

Efficacy of Adaptation

The ferrous oxidizing ability was determined after every subculture. The efficacy of adaptation was tested by the oxidizing ability of adapted *Tf* strains in fresh M9K medium (Selvi et al. 1998).

Bacterial Leaching Technique

Bacterial leaching in batch operation at lab scale level was carried in 250 ml and 500 ml Erlenmeyer flasks. Aeration of the pulp in the flasks was achieved by agitation on a rotatory incubator shaker at a frequency of 140–150 rpm in order to prevent the sedimentation of solids from pulp. The ratio of the volume of the reactor to the pulp was 1:2.5. The pH, E_h of the pulp and concentration of Fe^{2+}, Ni^{2+} and Cu^{2+} in the liquid phase of the pulp was checked intermittently at fixed interval of 24 h. The temperature of shaker was kept at 30–32 °C and the pH was set to 2.3. The pH of leaching suspensions was monitored periodically and adjusted, till the pH stabilized to 2.3 using 1 N H_2SO_4. Once the pH was stabilized at set pH, medium was inoculated with the bacterial culture of exponential phase. The loss of medium due to evaporation was compensated by adding distilled water. Total contents of each flask were filtered through Whatman no. 1 filter paper. Sterile controls were kept in parallel using 1 % thymol as bactericide. The liquid filtrate was used for the analysis of Fe^{2+}, Ni^{2+} and Cu^{2+}.

Leachability Studies

Leaching experiments were conducted under optimal conditions (Bharathi and Ravindra 2006). Bacterial leaching abilities of unadapted and adapted strains of *Tf* were compared by conducting separate bioleaching tests. Uninoculated control experiments were also carried out in order to determine the contributions from chemical leaching due to aerial oxidation.

Analytical Methodology

Various metals present in the leach liquor and leach residue were analyzed by Atomic absorption spectroscopy. Different mineral phases of the concentrate were analyzed by X-ray diffraction spectroscopy.

Results and Discussion

Adaptation of Tf *Strains to Copper and Nickel*

The development of membrane-associated enzyme protecting system, which enables the cells to secure energy provision through ferrous iron oxidation, is metal specific and hence the lag phase depends on specific metal cation (Gehrke et al. 1998, 2001). Therefore, the bacterial strains tolerant to a particular metal are preferred. Figure 2.1a, b show the effect of *Tf* strains adapted to Ni^{2+}, Cu^{2+} and mixture of Ni^{2+} and Cu^{2+} at a concentration of 20 g L^{-1} each on iron utilization ability. Ni^{2+} adapted strains could sustain the ferrous oxidizing ability. But, strains adapted to copper and mixture of Ni and Cu ions lost their ability to oxidize iron when grown in modified 9K medium due to their acclimatization to the adapted environment.

Adaptation of Tf *Strains to Copper Flotation Concentrate*

Figure 2.2a, b show the ferrous oxidizing ability of concentrate adapted cells of *Tf* strains in fresh M9K growth medium. Time taken for total oxidation of ferrous (T_{ox}) was 6 days initially in the case of unadapted strain and it was increased to 9 days after subculturing three times. At the end of sixth subculture, T_{ox} could not be achieved even after 11 days of incubation. The efficiency of oxidation decreased with increased time period of adaptation. After nine subcultures, *Tf* strains failed to utilize synthetic ferrous sulfate. The loss of ferrous oxidizing ability of adapted strains indicates the efficacy of adaptation of bacterial cells to the new environment as observed by Selvi et al. (1998).

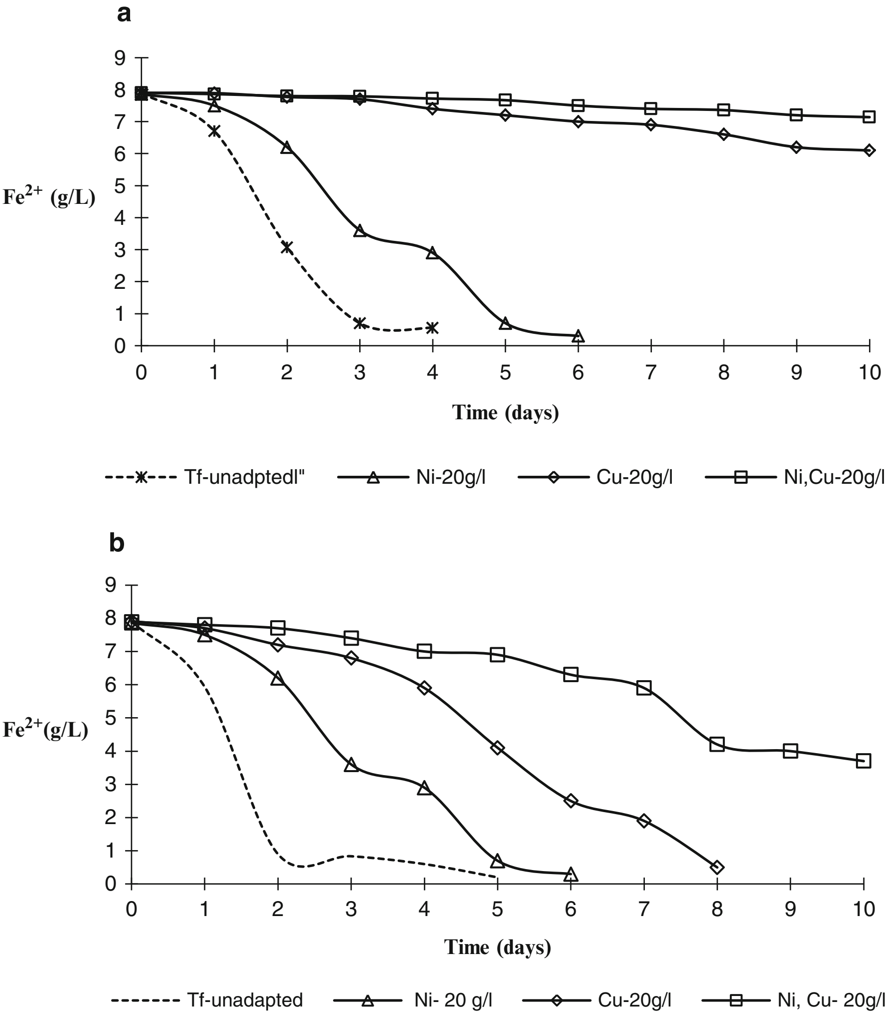
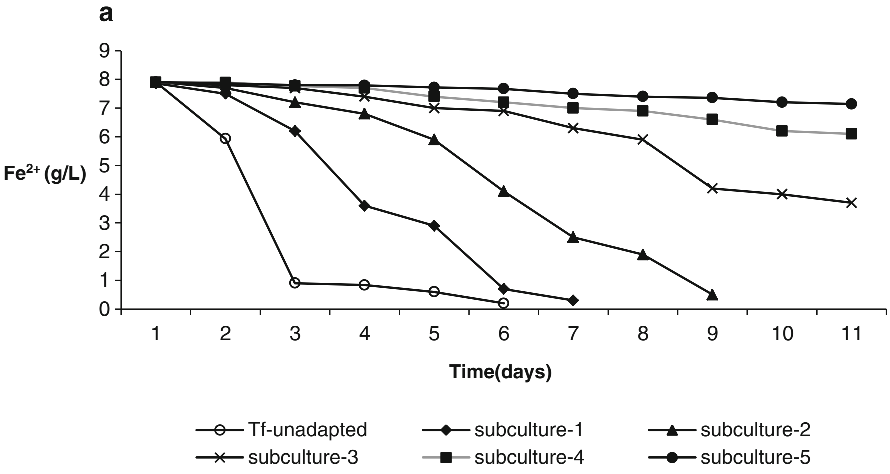


Fig. 2.1 Effect of adaptation of *Tf* onto Cu^{2+} and Ni^{2+} in M9K medium. Cultures used: (**a**) *Tf*-44, (**b**) *Tf*-234

Nickel Leaching by Metal/Concentrate Adapted Strains

Metal adapted strains have shown variable results on efficacy of Ni leaching. Table 2.3 shows the percent leachabilities of Ni obtained by Cu^{2+} tolerant, Ni^{2+} tolerant and strains tolerant to Cu^{2+} and Ni^{2+}. The % recoveries of Ni by strains adapted to copper and mixture of Cu^{2+} and Ni^{2+} were less compared to Ni^{2+} adapted strains. The percent recovery of nickel by Ni^{2+} adapted strains was improved by 10 % over that achieved by unadapted strains. Nickel recovery was significantly increased by *Tf* strains adapted to concentrate.



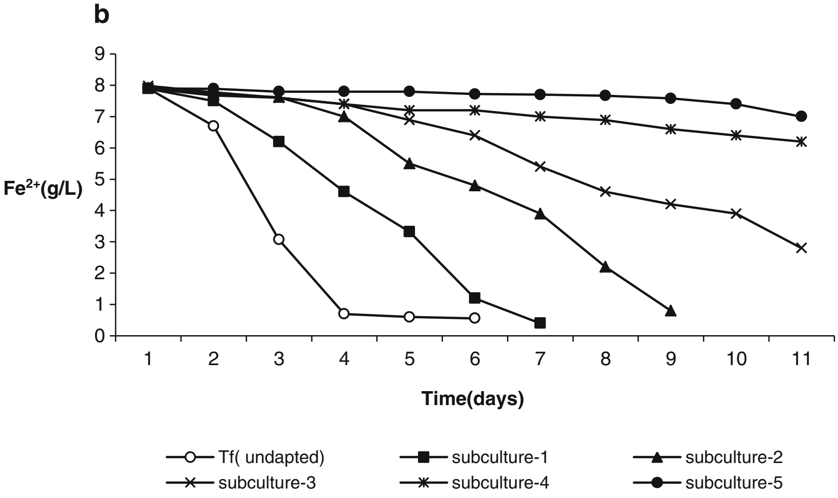


Fig. 2.2 Loss of ferrous oxidizing ability of *Tf* strains with preadaptation to copper flotation concentrate in M9K medium. Cultures used: (**a**) *Tf*-44, (**b**) *Tf*-231

Table 2.3 Percent recoveries of nickel by metal adapted and concentrate adapted strains

	% Ni leachability	
Type of *Tf* strains	*Tf*-44	*Tf*-231
Cu^{2+} adapted strains	12	10
Cu^{2+} + Ni^{2+}adapted strains	25	20
Ni^{2+} adapted strains	65	57
Concentrate adapted strains	83.4	80

Comparison of Nickel Leachabilities by Different Strains

Figure 2.3 shows the percent recovery of nickel by different strains of *Tf*. The recovery of nickel from concentrate was 85 % by strains adapted to concentrate. The percent recovery by sterile control was only 5 % showing that 80 % of the nickel was leached by bacterial action (Table 2.3). The percent leachability of controls containing bactericide 1 % thymol/Hg_2Cl_2 was lower than any bacterial system. Both the *Tf* strains adapted to high concentrations of nickel have shown improved Ni leachabilities compared to unadapted as well as strains adapted to copper. Better leachabilities were obtained by concentrate adapted strains of *Tf*. This is due to the increased tolerance of bacterial cells to high concentration of metals which affected the physiology of *Tf* cells leading to enhanced leachabilities as studied by Natarajan et al. (1994) and Puskas et al. (1980). These results coincide with the fact that the efficiency of microbiological metal recovery depends on the ability of the microorganisms to tolerate or become adapted to high concentrations of soluble compounds in the leach liquor as observed by Leduce et al. (1997) and Kai et al. (1995).

An improvement of nickel leachability by 40 % was achieved by *Tf* strains adapted to the copper flotation concentrate under optimized conditions within in a period of 15 days of residence time of leaching. Bacterial adaptation has successfully eliminated lag period of cells or initial pH rise during bioleaching process owing to increase in the secretion of iron and sulfur enzymes by the bacterial cells during adaptation as observed by Li and Ke (2001). The improvement in Ni leachabilities that were obtained by adapted strains could also be attributed to the rapid development of membrane-associated enzyme protecting system as reported by Mason and Rice (2002). Selective leaching of nickel was possible due to the development of galvanic couple between the mineral phases present in the concentrate. Upon

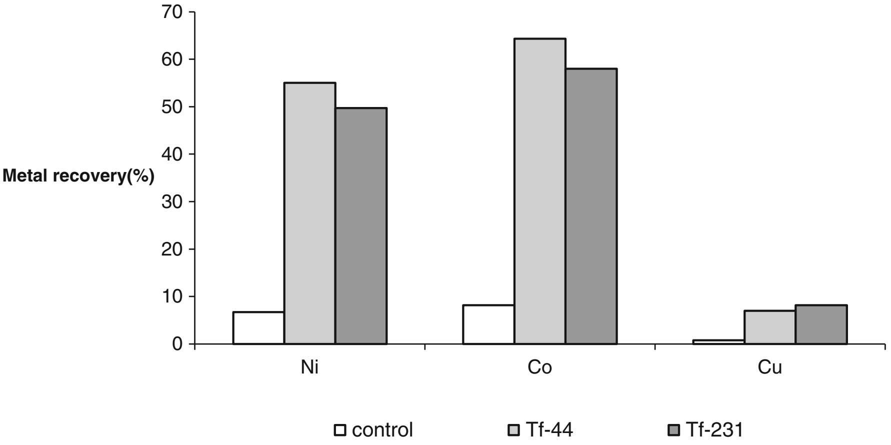


Fig. 2.3 Comparison of leachability of nickel by different strains of *Tf*. Cultures used: (**a**) *Tf*-44, (**b**) *Tf*-231

adaptation through sub culturing, Ni leaching performance of the organisms increased significantly due to preferential leaching of pentlandite from a predominantly chalcopyrite concentrate (Bharathi et al. 2008) (Table 2.2).

Conclusions

Adaptation of *Tf* cells to high concentration of nickel and flotation concentrate has resulted in increased metal tolerance levels and selective leachability of nickel. The efficacy of *Tf* strains to utilize ferrous from concentrate was enhanced with adaptation of cells to nickel, copper and copper flotation concentrate. Better nickel leachabilities were obtained by nickel adapted strains, in comparison to unadapted strains. Therefore, it can be concluded that the acclimatization of cells to the leaching environment played key role in enhancing ferrous recovery and nickel leaching performance of *Tf* strains. The order of efficiency of strains could be termed as concentrate adapted strains $>$ Ni^{2+} adapted strains $>$ mixture of Cu^{2+} and Ni^{2+} adapted strains.

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Chapter 3
A Review on Ash Formation During Pulverized Fuel Combustion: State of Art and Future Research Needs

Kalpit V. Shah, Mariusz K. Cieplik, and Hari B. Vuthaluru

Introduction

Pulverized coal and a variety of biomass fuels are used as a feed in the power station boilers, where a large amount of thermal energy is generated because of the exothermic reaction taking place during the combustion of fed hydrocarbon which is later converted to electrical energy by several other means. The mineral matter present in quite significant proportions alongside with the hydrocarbons usually fragments, devolatilize (evaporates) and subsequently partly condenses during combustion. This inorganic, mineral residue after combustion, commonly called ash, travels towards the smokestacks carried by the flue gas, may lead to various operational problems such as slagging, fouling, corrosion and erosion of heat exchanging, internal boiler and flu gas duct surfaces etc.

Extensive studies on ash formation during combustion have been conducted World-wide. As a result, theories on ash formation mechanisms have been formulated and described in detail by several researchers (Livingston 2007; Sarofim and Helbe 1994; Baxter 1993; Sarofim et al. 1977; Van Lith 2005). It is evident from several experimental investigations that solid fuel particles undergo various physical transformations during combustion, as shown in Fig. 3.1. The important physical

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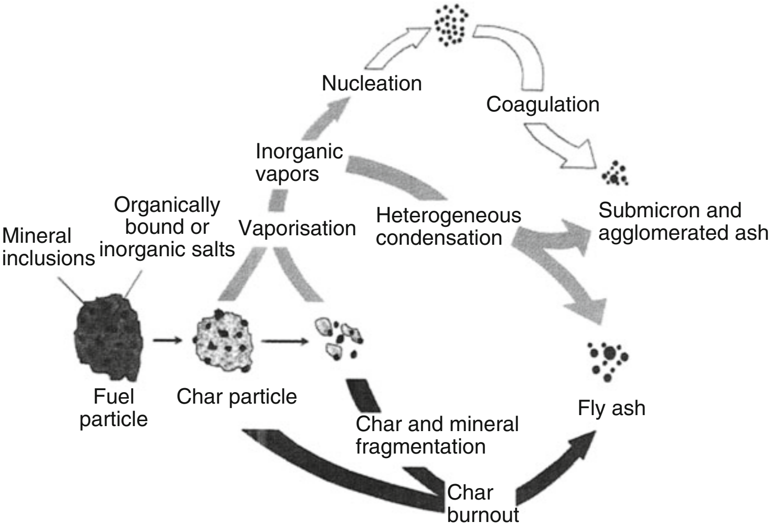


Fig. 3.1 Physical transformations involved for ash formation during coal/biomass combustion (Sarofim and Helbe 1994)

transformations are fragmentation and/or coalescence and vaporization. It is postulated that the fragmentation/coalescence of the ash/char particles along with chemical oxidation and physical devolatilization, will lead to coarse ash formation. The vaporized minerals chemically react with other gas-borne matter, and may condense homogeneously or heterogeneously to form submicron aerosols and fine ash particles. The physical and chemical transformations during thermal conversion of solid fuel are time-dependent and very difficult to understand as a continuous process.

These physical and chemical transformations of minerals depend on several fuel characteristics i.e. fuel, fixed carbon, volatile matter, total ash content and mineral matter elemental composition, mineralogy (either included or excluded especially for coal), char reactivity, char morphology, density, particle size etc. The fuel characteristics will be different for different fuels according to their age, formation history and handling. This paper highlights the effects of all the above fuel characteristics on ash transformations during combustion.

The mineral transformations can also be significantly influenced by several operating conditions i.e. mode of combustion, temperature, pressure, heating rate, residence time, reaction kinetics of various mineral gaseous, slag and solid species etc. Currently, a broad range of technologies is available for the combustion and co-firing of coal and biomass. These include: Atmospheric Fluidized Bed (AFBC), Pressurized Fluidized Bed (PFBC), Pulverized Fuel (PF) and Grate Fired (GF) combustors. All the technologies have their own advantages and limitations (European Biomass Industry Association). The route of mineral transformations will be similar in nearly all the mentioned options, but the extent and criticality will be different for each technology due to differences in operating conditions. The present paper reviews mainly the efforts made to identify the effect of the mentioned operating parameters on ash transformations during pulverized fuel (PF) combustion.

Experiments ranging from lab-scale-combustion simulators to pilot- and plant-scale furnaces under laminar- through turbulent flow conditions, are usually designed and analyzed to understand the ash formation processes during combustion. To date, several methods/sub models/models have been employed to study and identify the effect of different fuel characteristics and operating parameters on ash formation. The present work also briefly reviews some of the basic analytical methods used to measure various parameters responsible for ash formation. It also highlights the modeling efforts undertaken to date, ranging from the simple calculations to advanced numerical simulations for predicting the ash transformations during PF combustion. As there appears to be a lack of a comprehensive literature review to date covering all of this basic information related to ash transformations, such synthesized information may give an overview on the updates in the concerned field. Furthermore it also gives some insight on the future research needs in this area.

Parameters Responsible for Mineral Transformations During PF Combustion

Fuel Mineral Matter Composition and Their Association

Coal and Biomass (or their blend) can be subjected to different ash formation mechanisms during pulverized fuel (PF) combustion, as the fuel mineral matter composition and their association varies greatly in different fuels. The mineral matter in the fuel may be present in the form of free ions, salts, organically bound or as excluded minerals. The lignite and woody biomass contain a major fraction of volatile compounds (and less excluded minerals) compared to Bituminous or anthracite coals. Alkalis in low rank coals and woody biomass, remain primarily in included minerals as free ions, salts and organically associated inorganic elements and start vaporizing at lower temperatures. Even before reaching the char burnout, these vaporized species will chemically react and will condense, nucleate and coagulate on each other or onto the furnace surfaces, to produce submicron ash. Other elements such as calcium and magnesium partly devolatilize, fragment or coalesce (Baxter 1993; Schurmann et al. 2007). Thy (2000) found that if alkali metals occur as network-modifying and charge balancing cations in highly depolymerized melts, such as typical for wood ash, they are easily evaporated during prolonged heating and subsequently deposit onto the heat exchanger surfaces. However, if the melt is highly polymerized such as in the case for rice straw, where alkali metals occur as network modifying cations, they are strongly retained in the polymerized network. During diffusion-limited char combustion, the interior of the particle becomes hot and fuel rich. The non-volatile oxides (e.g. Al_2O_3, SiO_2, MgO, CaO, and Fe_2O_3) can be reduced to more volatile suboxides or even down to elements, and partly vaporized. These reduced species re-oxidize while passing through the boundary layer surrounding the char particle, becomes instantaneously highly supersaturated which make them nucleate homogeneously (Kramlich et al. 1995).

Ash melting behavior is affected by the elemental composition of ash (alkali metals, phosphorous, chlorine, silicon and calcium species), as well as the chemical concentration of the compounds which can alter reaction kinetics of the fuel combustion. Commonly analyzed ash-forming elements are silicon (Si), aluminum (Al), iron (Fe), calcium (Ca), magnesium (Mg), manganese (Mn), sodium (Na), potassium (K), phosphorus (P), sulfur (S) and chlorine (Cl).

Baxter (1992) studied three different ranks of coal (high-volatile bituminous, sub-bituminous, and lignite) and observed that for high-volatile bituminous coals more than 100 fly ash particles were formed from a single 80 μm (initial diameter) char particle, whereas only ten fly ash particles are produced from single 20 μm (initial diameter) char particle. However, regardless of its initial size, fragmentation of lignite particles was far less extensive, with less than five fragments from a single char particle.

The volatile inorganic matter content is one of the most important parameter in coal and biomass as far as submicron particulate formation is concerned. Buhre et al. (2005) observed that formation of submicron aerosol ash particles during coal combustion is mainly due to condensation of evaporated species and not due to the fragmentation.

Mineralogy

Mineralogy of coal and biomass can also play a critical role in various physical and chemical transformations. Physically, the inorganics can be present as included and excluded minerals in the fuel especially for coal. Excluded minerals present in biomass are mainly a result of the contamination with soil during the harvest or handling while presence in coal is due to mining or handling. It is quite obvious that the amount of excluded minerals in most of the biomass fuels will be significantly lower than the in coals, of which deposits are inherently in close contact with rocks and soil. Included minerals in the biomass are the inorganics required for plant growth; and as such they are still present in coals even after millennia of peatification and coalification (Terttalisia 1999), however their physical and chemical form may be altered by the said geological processes.

Included minerals have a higher tendency to remain in the char during combustion. Due to exothermic reactions occurring in the char during combustion, the included mineral matter can reach very high temperatures (above the temperature of the surrounding flue gas). As included minerals are situated close to each other, reactions between them can easily take place. Included minerals may contain more volatile inorganic matter than excluded minerals. The volatile minerals from the included and excluded minerals will be vaporized in the early stage of combustion. The vaporized minerals will condense later on to produce sub-micron ash. During char burnout, the included minerals may either appear as molten particle on a reducing char surface or as a lattice network in char particle. As char burnout proceeds, the minerals may coalesce within a single particle or fragment into several smaller entities. The extent of fragmentation or coalescence depends on several operating parameters and fuel characteristics. This subject has been studied in detail by many research groups, combining both experimental as well as modeling work. Wilemski et al. (1992) and Kang (1991) tried to validate experimental results with no and a full coalescence limit. Morone (1989) in her Ph.D. thesis reported that a partial coalescence is likely to occur in real life systems. Helble and Sarofim (1989) observed very small number of fragments being created during devolatilization. Wilemski and Srinivasachar (1993) later on validated his shrinking core model with partial coalescence limit. Wigley et al. (1997) stated that coal particles containing included mineral matter will have a greater specific heat capacity than particles consisting of organic material alone, hence included particles would be expected to heat up and combust more slowly. Included minerals may fuse and coat the surface of burning char particles, reducing the rate of char combustion. On the other hand, the included mineral matter may catalyze char combustion. The difference in thermal expansion between included minerals and their organic matrix may cause localized thermal stress, thus, leading to an increased char fragmentation. Agglomeration may occur when particles collide or when they meet on a deposit surface on a boiler wall or tube. Mitchell (1997) observed attrition, breakage and percolative-type fragmentation of included minerals during the devolatilization stage. Excluded minerals (especially in the case of coal) on the other hand will reach lower temperatures than included minerals, and they will not be influenced by locally reducing environment. The transformations occurring in excluded minerals and the behavior with respect to the ash deposition may therefore be significantly different from included minerals. Excluded minerals can either be carried through the combustion system with their original structure intact or they can melt and fragment. Decombe et al. (1999), Yan et al. (2001a) and many others concluded that excluded minerals always fragment randomly, due to thermal stress. ten Brink et al. (1996) and Yan et al. (2001b) observed that calcite and pyrite as excluded minerals fragment at high temperature and high heating rate conditions while siderite and ankerite grains did not fragment at the same conditions.

Particle Shape, Size and Density

Experimental and theoretical investigations indicate that particle shape, size and density influence particle dynamics, including drying, heating rate and oxidation reaction rate (Baxter et al. 2008). It is generally observed that spherical particles devolatilize quickly compared to other shape particles. Badzioch and Hawksley (1970) found that particle size had no significant effect on the weight loss because the heating rate of the particle was controlled mainly by the heating rate of the carrier gas, so that the large particles heated only at slightly lower rates than the fine particles. Mathews et al. (1997) observed that mineral matter and macerals composition of the char will be different for different particle sizes, which can affect the devolatilization rate. No and Syred (1990) and Decombe et al. (1999) observed that large particles form more fragments than small particles, likely due to larger

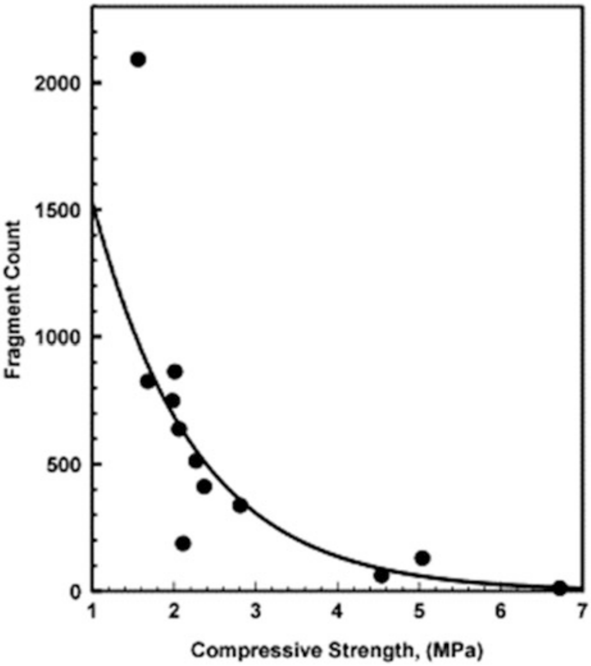
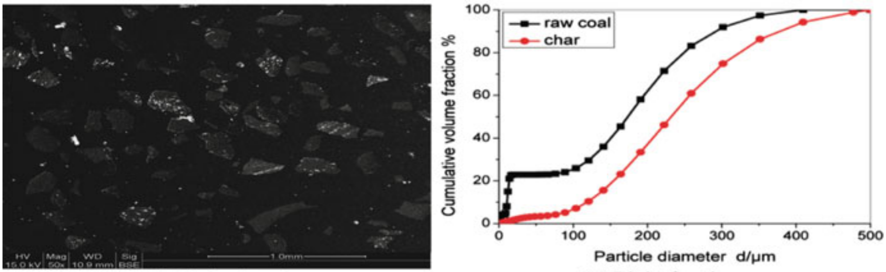


Fig. 3.2 Variation in the extent of the fragmentation of a coal against compressive strength (Dacombe et al. 1999)

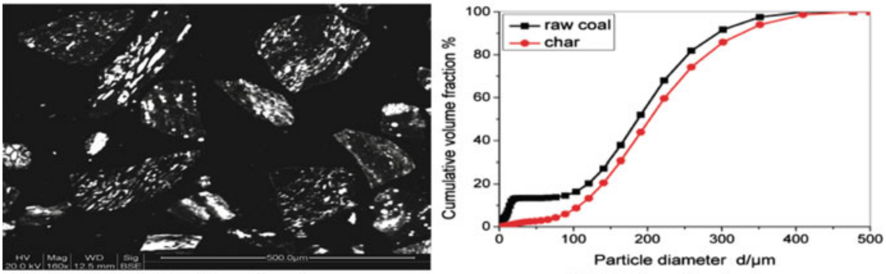
internal temperature gradient. Wigley et al. (1997) confirmed that a decrease in char particle size may lead to more complete combustion. Decombe et al. (1999) suggested the relationship of fragmentation extent with compressive strength as shown in Fig. 3.2. However, compressive strength of the coal particle is inversely proportional to the particle size.

The ash transport behavior is affected to a large extent by the size of the particle after combustion. Large ash particles tend to impact onto boiler heat transfer surfaces by inertia, whereas fine ash particles tend to reach wall surfaces by thermophoresis or Brownian motion. For example, a 60 μm ash particle was estimated to reach the deposit surface almost three times faster compared to 30 μm particle primarily due to inertial effect (Yan et al. 2001a).

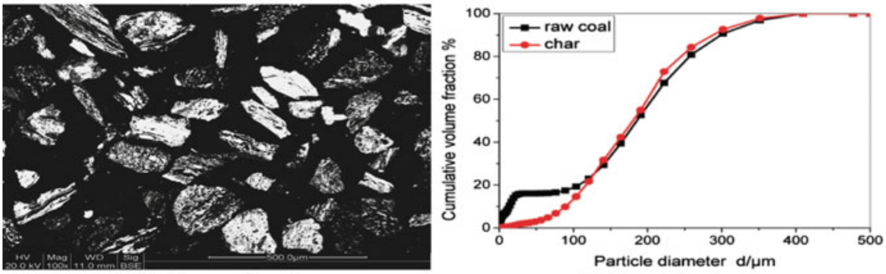
Liu et al. (2008) studied Chinese bituminous coal with three density fractions. The fragmentation was severe with light density fractions as shown in Fig. 3.3. The median size of each coal fraction was almost the same. The reasons for the above were particle size, mineralogy and swelling ratio. The light fraction and the medium fraction of the coal contained mostly included minerals, and the heavy fraction contained largely excluded minerals.



(C1) Light fraction (a) Light fraction



(C2) Medium fraction (b) Medium fraction



(C3) Heavy fraction (c) Heavy fraction

Fig. 3.3 BSE images with comparison of PSD (by volume) of char and coal (Liu et al. 2008). (**a**) Light fraction. (**b**) Medium fraction. (**c**) Heavy fraction

Fuel Characteristics After Milling

Milling of raw coals or biomass fuels, i.e. fineness of the material after grinding as well as the applied mill technology, has a profound effect on ash formation. It has been observed by several researchers that mineralogy, ash percentage, volatile matter, density and char reactivity will be different for different particle size ranges (PSD)**.** Bridgeman et al. (2007) studied two energy crops (switchgrass and reed canary grass) in terms of their physical and chemical properties in different size fractions after grinding with ball mills at lab scale. The results summarized in Table 3.1 indicate that smaller particles of the two grasses have a significantly higher concentration of inorganic matter as well as the moisture content than larger particles. In contrast the larger-sized fractions had higher carbon content and lower