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Studies on the influence of organic waste biodegradability in the composting process

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Dissertação apresentada à Faculdade de Ciências e Tecnologia da Universidade de Coimbra, com vista à obtenção do grau de Mestre em Engenharia Química.

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“Continuous effort,

not strength or intelligence,

is the key to unlocking our potential.”

Winston Churchill

“The important thing is not to stop questioning.”

Albert Einstein

“O Homem é do tamanho do seu sonho.”

Fernando Pessoa

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ABSTRACT

Amongst the waste management strategies composting is gaining interest as a suitable method with economic and environmental profits. The mixture of wastes used in composting must be potentially biodegradable to favor biologically catalyzed breakdown of organic matter in aerobic conditions and drive the composting process into thermophilic temperatures required for pathogen reduction. Thus, this work aimed firstly to predict the biodegradability of an initial waste mixture and to investigate how this property determines the changes in organic matter characteristics during the composting process. A second objective for this work was to develop a dynamic mathematical model for aerobic composting process and its validation by fitting the experimental data.

The initial mixtures tested were made from potato-peel industrial waste, grass clippings and sawdust in four different proportions. These blends were composted in self heating reactors (SHR) with 120 L of internal volume and well isolated. During composting, a data acquisition system for on-line monitoring of temperature and oxygen concentration was used, and feed air flow rate was measured with rotameters. The waste mixtures were sampled in pre-determined times along the period of composting. Biodegradability of each sample was assessed by measuring lignin content, by using the Klason method, which involves the gravimetric measurements after extracting the sample with sulphuric acid.

Regarding the biodegradability of the mixtures the results indicated that independently of the initial mixture composition, there is an increase in lignin content that can be related to the decrease of the potential for biodegradation of the mixtures. The initial samples with the lower and higher lignin content showed a greater and smaller mass reduction, at the end of composting period, respectively. Therefore, higher lignin content of an initial mixture led to lower biodegradation. The mathematical model developed showed good fitting to experimental data, namely for temperature of substrate, organic matter conversion and water loss in the composting system. Thus, the proposed pseudohomogeneous model can be used for future prediction purpose.

RESUMO

De entre as estratégias de gestão de resíduos, a compostagem tem vindo a ganhar interesse e com benefícios económicos e ambientais. Os resíduos submetidos a compostagem devem ser potencialmente biodegradáveis para favorecer a degradação biológica da matéria orgânica em condições aeróbias que conduzam a manutenção de temperaturas termofílicas no sistema de compostagem, necessárias para a higienização do composto.

Este trabalho teve como objectivos principais prever a biodegradabilidade de uma mistura inicial de resíduos e desenvolver e avaliar um modelo matemático em regime dinâmico para o processo de compostagem.

As misturas testadas foram obtidas a partir de casca de batata, aparas de relva e serradura, em quatro proporções diferentes. Estas misturas foram submetidas a compostagem em reactores de auto-aquecimento com 120 L de volume e adequadamente isolados. Durante a compostagem, a temperatura e o oxigénio foram medidos a partir de um sistema de aquisição de dados com monitorização on-line e a taxa de alimentação de ar foi medida com rotâmetros. Diversas amostras foram recolhidas em tempos pré-determinados durante todo o processo de compostagem. A avaliação da biodegradabilidade de cada amostra foi realizada a partir da determinação do teor de lenhina, utilizando o método de Klason, que envolve medições gravimétricas após a extracção da amostra com ácido sulfúrico.

Em relação a biodegradabilidade, os resultados obtidos indicaram que, independentemente da composição da mistura inicial, durante o processo de compostagem há um aumento no teor de lenhina que pode ser relacionado com a diminuição do potencial de biodegradação das misturas testadas. As amostras iniciais com os teores de lenhina inferior e superior mostraram uma redução de massa maior e menor, respectivamente, no final do período de compostagem. Os resultados permitem concluir que o alto teor de lenhina de uma mistura inicial leva a um baixo potencial de biodegradação da mesma.

A comparação entre os resultados da simulação numérica e os resultados experimentais mostraram que o modelo desenvolvido prevê com sucesso o comportamento das principais variáveis de compostagem. Nomeadamente, o perfil de temperatura no substrato, a conversão da matéria orgânica e a perda de água no sistema de compostagem são razoavelmente previstos com a proposta de abordagem pseudohomogênea.

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ACRONYMS

AT - Respiration Activity
BMP- Bio Methane Potential
BMW - Biodegradable Municipal Waste
BOD - Biochemical oxygen demand
DOC- Dissolved Organic Carbon
DRI- Dynamic Respiration Index
EC- Electrical Conductivity
EHT- Enzymatic Hydrolysis
FAS- Free Air Space
FTIR- Fourier Transform Infrared
GC- Grass Clippings
IS – Inorganic Solids
LC- Lignin Content
MBT- Mechanical–Biological Treatment
MC- Moisture Content
MSW- Municipal Solid Waste
OUR - Oxygen Uptake Rate
PP- Potato-Peel
SD- Sawdust
SHR- Self Heating Reactors
SM- Safety Margins
SRI – Static Respiration Index
SW- Solid Wastes
TS-Total Solids

NOMENCLATURE

A - Area of heat transfer, m^2

AD- Average percentage deviation, %

BD- Bulk density, kg m^{-3}

C -Bulk weight coefficient for the substrate

c_{pa} - Specific heat capacities of air, J kg^{-1} K^{-1}

c_{pw} - Specific heat capacities of water, J kg^{-1} K^{-1}

c_{pOM}- Specific heat capacities of organic matter, J kg^{-1} K^{-1}

c_{PIM}- Specific heat capacities of inorganic matter, J kg^{-1} K^{-1}

Ed - time for total die-off at temperature above 55 ºC during the time interval t, h

k- Reaction rate constant, kg^{1-n} h^{-1}

k_{O2}- Oxygen saturation constant, kg_{O2} m^{-3}

LC- Lignin content (% of Volatile Solids)

m_{OM}- Mass of organic matter in the substrate, kg

M_{rw}- Water molecular weight, mol kg^{-1}

M_a- Air flow, kg h^{-1}

MC- Moisture content, %

m_a - Mass of air, kg

m_0 – Mass of composting feed mixture, kg

m – Mass of finished compost, kg

n- Reaction order

Ps_0- Saturation water vapor pressure at initial temperature of inlet air, Pa

Ps- Saturation water vapor pressure at temperature of the composting mixture, Pa

Q- Volumetric air flow, m^3 h^{-1}

R- Universal gas constant, J $kmol^{-1}$ K^{-1}

S_m - Fractional solids content of the mixture solids

SD -Stability degree of the organic matter, %

t- Time, h

T- Temperature, K

T_0- Initial temperature of inlet air, K

T_{a}- Air Temperature, K

T_{amb} - Ambient temperature, K

U - Overall heat transfer coefficient, J h^{-1} m^{-2} K^{-1}

VS - Volatile fraction of substrate solids

V_r -Volume of the reactor, m^3

W_m – Percentage of composting mass, %

x_{max}- Maximum conversion of organic matter,%

x_{lignin}- Conversion of biodegradable organic matter by measuring of lignin content, %

x_{Vs}- Organic matter conversion, %

Yw- Stoichiometric coefficient of water

YO_2 - Stoichiometric coefficient of oxygen

$[O_2]$- Oxygen concentration, kg_{O2} m^{-3}

ρ_s - Specific gravity of substrate solids, kg m^{-3}

ρ_V - Specific gravity of the volatile fraction of the substrate solids, kg m^{-3}

ρ_f - Specific gravity of the fixed fraction of the substrate (inorganic fraction), kg m^{-3}

ρm - Bulk weight of the mixed material to be composted, kg m^{-3}

ρw - Density of water , kg m^{-3}

ρ_a - Density of air, kg m^{-3}

ΔH - Reaction enthalpy, $J\ {kg_{OM}}^{-1}$

βVS - Biodegradable volatile solid, kg

(1-β)VS - Non-biodegradable volatile solids, kg

β - Biodegradable volatile solid fraction

ρ_p- Density of substrate solids, kg m^{-3}

1. INTRODUCTION

The decomposition of organic materials in fertilizers is considered a practice as old as the emergence of agriculture. In this scope, the process of composting, which refers to the controlled decomposition of organic materials, has been used by humans since prehistoric times to recycle wastes and make them useful for plant growth. In the nature, composting process occurs when leaves pile up and begin to decay with some of them returning to the soil, where living roots reclaim their nutrients. Since prehistoric times, composting has been used for the benefit of agriculture. However, research studies, as well as the development of this technology has just begun in the early 20th century with the first attempt to give a scientific basis occurring in 1924-1926 by Howard and Wad [1,2].

Since the Second World War, as the growing fields have become larger and the work became mechanized, the use of fertilizers and other traditional means of improving soil productivity decreased. Recently, a renewed attention in the composting process has been observed. Restrictive legislation in many environmental areas have been responsible for encouraging this interest, which led to the development of a new generation of composting facilities throughout Europe [3].

The amount and diversity of solid wastes (SW) produced around the world has been increased in recent decades, mainly due to the growth of the population, industrialization and use of disposables. These residues must be then managed under appropriate disposal practices to avoid negative impacts on the environment becoming difficult for governmental agencies to face the challenge of handling such enormous quantities produced worldwide. Composting cannot be considered a new technology, but amongst the waste management strategies it is gaining interest as a suitable method with economic and environmental profits. The finished composts are mainly used in agriculture as soil improvers to increase organic matter that is important for plant growth and decrease of the risk of erosion. Nowadays, there is an intensive research in order to obtain scientific information for building more efficient composting systems [4-6].

This work has two main objectives. The first one is to predict the biodegradability of an initial waste mixture and to investigate how this property progresses during the composting process in a pilot-scale reactor. The biodegradability assessment in the starting materials seems to be an important parameter in order to determine the self heating capabilities of a blend, enabling thus to foresee if a specific mixture is adequate to be further composted. The second objective is to develop a dynamic mathematical model for the aerobic composting process under analysis and its validation by using experimentally measured dynamic state variables.

The initial mixtures that were tested were made from potato-peel industrial waste (PP), grass clippings (GC) and sawdust (SD) in four different proportions. These blends were composted in isolated self heating reactors (SHR) with 120 L of internal volume. During composting, a data acquisition system was used for on-line monitoring of temperature and oxygen concentration, and feed air flow rate was measured with rotameters. The waste mixtures were sampled in pre-determined times along the period of composting and biodegradability of each sample was assessed by measuring lignin content, through the Klason lignin method.

This work is organized into seven chapters. Chapter 1 is the introductory part. In chapter 2 an overview of the composting process is made and the substrates usually used are characterized. The existing composting systems were also described in this chapter.

In Chapter 3 a full description of the mathematical model developed is provided, and all variables and parameters are defined. Chapter 4 focus the state of the art with reference to studies that have been made in assessing the biodegradability of solid wastes, as well as those related with the development of models that describe the composting process. The experimental methodology used, monitoring strategies and quantification of various parameters are described in Chapter 5.

Finally, Chapter 6 presents the analysis and discussion of the results obtained during the work and Chapter 7 summarizes the main conclusions and prospects for future work.

2. THEORETICAL FOUNDATIONS OF COMPOSTING

An approach to the composting technology is given in this section, including the analysis of important process factors and microbiological aspects.

2.1. Composting process

Composting can be defined as the aerobic microbial decomposition of organic matter of vegetable and animal origin, under conditions that allow the development of thermophilic temperatures as a result of the heat produced by biological reactions. Involving the mineralization and partial humification of the organic matter, this process will lead to a stabilized and hygienized final product (i.e. free of pathogens and seeds) commonly known as compost. Thus, this technique permits waste stabilization under special conditions of mixing and aeration in order to reach the required thermophilic temperatures responsible for microbial growth, weed seeds elimination, pathogen inactivation and helminthes kill, avoiding generation of noxious gases as well [7,8].

Composting is thus a microbiological process based on the activity of various bacteria, actinomycetes and fungi. The main product is rich in humus and plant nutrients such as nitrogen and phosphorous, and the foremost reaction by-products are carbon dioxide, water, ammonium and heat (equation (2.1)). The CO_2 and water losses can amount to half the weight of the initial materials, thereby reducing the volume and mass of the final product. In this procedure, aerobic microorganisms use organic matter as energy source by decomposing substrates, turning them into simpler compounds. This transformation is conditioned by the nature of the initial substances and its degradability character, an important property that affects decomposition rates, gas emissions, process duration and oxygen requirements. The labile organic compounds such as simple carbohydrates, fats and amino acids are quickly transformed (oxidized) through successive activities of different microbes. Meanwhile, the residual organic matter as cellulose, hemicellulose and lignin become more and more resistant to microbial biodegradation and are partially converted into stable organic matter, which chemically and biologically resembles humic substances. The extent of these changes depends on the available substrates and the process variables used to control the composting [1,4,9].

$$Fresh\ organic\ materials + O_2 \rightarrow stabilized\ organic\ materia(compost) + CO_2 + H_2O + NH_3 + \ other\ gases + \ heat \qquad (2.1)$$

During composting, mineralization and humification occur simultaneously and are the main processes causing the degradation of the fresh organic matter. The humified fraction (humus) is the principal responsible for the organic fertility functions in the soil as it is the most resistant to microbial degradation, being considered a major reservoir of organic carbon in soil. Humus is then the final product of the humification process, in which natural materials are partially transformed into humic substances nearly inert mainly formed of lignin, polysaccharides and nitrogenous species. Thus, these compounds are not totally mineralized during composting. In fact, the humification of the organic matter during composting is revealed by the formation of humic acids with increasing molecular weight, aromatic characteristics, oxygen and nitrogen concentrations and functional groups, in agreement with the generally accepted humification theories of soil organic matter. During composting, humic substances are produced and humic acid-like organic increases, while fulvic acid-like organic and water-extractable organic decrease due to microbial degradation [4].

The chemical steps of organic matter to form humus are very complex and involve a number of degradative and condensation reactions. Lignin is degraded by extracellular enzymes to smaller units, which are then absorbed into microbial cells partially converted further into phenols and quenones. When placed into soil, these substances along with the oxidative enzymes polymerize by a free radical mechanism. The structure of humic compounds is not yet well known, being usually divided into three groups based on chemical fractionation: humin (insoluble in water at any pH), humic acids (insoluble in water under acidic conditions) and fulvic acids (soluble in water under all pH conditions) [10].

The objective of composting has traditionally been to convert biologically degradable organic materials to a stable and hygienized form also characterized by reduced odor because of the low rate of decomposition of such resistant compounds. This compost may finally serve as a source of organic matter with beneficial effects when applied to land either as fertilizer (source of nitrogen or phosphorus), soil corrector (transfer of specific physical properties), or as crop substrate to agricultural lands, green areas, forests and home gardening. When used as soil corrector, it improves the drainage of water, increases water and nutrients retention capacity and acts as pH regulator. It also allows adjust temperature, control erosion, improve aeration, slowly release nutrients to the soil, increase the cation exchange capacity of sandy soils, and prevent desertification and floods [11].

In general, composts may contain important nutrients including nitrogen, phosphorus, potassium, and a variety of small quantities of other essential elements. This nutrient content is mainly related to the quality of the original substrates and operating process conditions. However, most of the composts are poor in nutrients to be classified as fertilizers so, their main applications are as soil conditioners and landfill cover [7]. Compost may also help to increase the effectiveness of chemical fertilizers and consequently, emissions of CO_2 and other green houses gases related to fertilizers production may be indirectly decreased. Finally, it is important to note that organic material in soil may have a key role in the global warming control. Indeed, there is a good interaction between land use, optimization of waste management and carbon sequestration. The organic matter stability, along with other characteristics, may be essential to achieve this positive interaction and for the maximization of soil carbon fixation, and thus, for the reduction of the emission of CO_2 to the atmosphere [6].

2.2. Composting substrates

Composting is usually applied to any biodegradable organic solid and semi-solid material, and thus, the amount of substrates potentially suitable for composting is really huge. However, it is important to stress that the optimum feedstock for it should be mainly from source separated organic materials. The main categories of composting substrates include municipal solid waste (MSW), industrial and agricultural waste [11].

2.2.1. Waste management

The Decreto-Lei n. ° 73/2011 established the general regime of waste management in Portugal, by repealing the previous diploma, the Decreto-Lei n. ° 178/2006 of September 9th. This legislation defines waste as “any substance or object which the holder discards or intends to or is obliged to discard, particularly those indentified in the European Waste List.” It also defines the general principles of waste management, the hierarchy of waste management operations, which state that the landfill should be the last management option, only justified when others are technically and financially inviable. In fact, it is well known that the waste disposal in landfill has negative impacts on the environment. The legislation issued during the past few years has a key role in addressing this situation by imposing targets on the elimination of organic waste and simultaneously encouraging waste management based on a hierarchy in which are privileged solutions to waste reduction, recycling, recovery energy instead of disposal in landfill. Requiring a progressive reduction of the quantities deposition of biodegradable waste in landfills, Decreto-Lei n. °152/2002 of May 23th concerning the disposal of waste into landfills, presents an important challenge. This law aims to improve the general conditions of landfill operation, preventing or reducing as far as possible the adverse environmental effects of disposing waste in landfills. In this context, all types of depositions, including water monitoring and leachate management, protection of soil and groundwater and gas monitoring were regulated. It also requires the implementation of strategies in order to gradually reduce the amount of organic waste going to landfill. Thus, the total amount (by weight) of biodegradable municipal land filled in 1995 was expected to decrease to 75% in 2006, 50% in 2009 and 35% in 2016. Decreto-Lei n. ° 152/2002 of May 23th was recently repealed by Decreto-Lei n. ° 183/2009 of August10th, which delays in four years the time limits specified in the previous draft, imposing tough new targets to reduce landfill disposal of biodegradable municipal waste, also in relation to 1995 data is expected to decrease to 50% in 2013 and 35% in 2020. Limiting the amount of biodegradable waste going to landfill implies the diversion of this waste towards appropriate treatment options such as composting. This waste treatment technology will clearly have an important role in processing much of the biodegradable waste, which in future will have to be diverted from landfill [2].

2.2.2. Municipal solid waste

The quantity and diversity of MSW produced around the world has increased in recent decades. There are several factors that have contributed to this growing production of waste, such as the population explosion and economic growth. In mainland Portugal, the production of municipal waste was approximately 5.184 million tons in 2009. With regard to the amount of MSW generated per capita, 511 kg/(hab.year) were produced in 2009, which corresponds to a daily production of 1.4 kg of MSW per capita. Figure 2.1 shows the amount of MSW produced between 2005 and 2009[12].

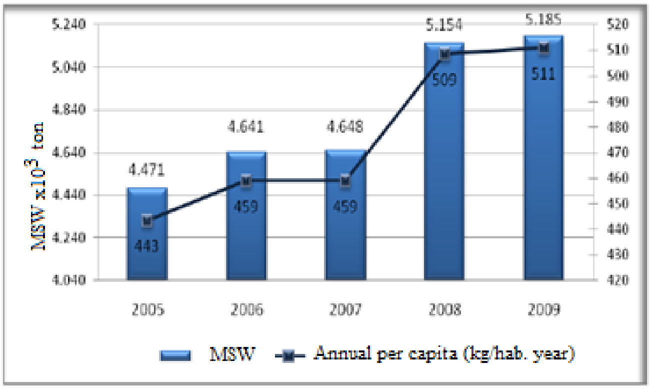


Figure 2.1- Evolution of the total production and annual per capita MSW between 2005 and 2009 (redrawn from [12]).

Besides the waste production, is also important to know their composition, which often varies depending on a number of factors: geographical location, seasons, urban or rural area, cultural and dietary habits, standards of living, characteristics of collection services offered and the level of promotion of home composting. According to its composition MSW may be grouped by type and the quantity is expressed as percentages. Figure 2.2 shows the composition of MSW in Portugal, where the major fractions correspond to fermentable materials often referred to as “kitchen waste” and paper and paperboard. Kitchen waste is usually rich in organic that may have more than 90% of biodegradability. The paper is also part of the biodegradable fraction. Although, it is often assumed that paper recycling is a better option than the use of biological treatment, depending on local conditions and availability of infrastructure and outlets for the paper recycling, waste paper and paperboard can sometimes serve as a valuable source of carbon, allowing the composting of food waste [13,11].

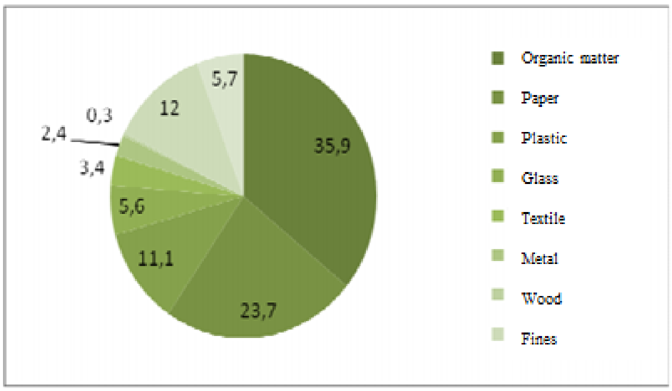


Figure 2.2 - Composition of the municipal solid waste in Portugal in 2008 (redrawn from [13]).

Figure 2.2 confirms that the organic matter often represents the most significant fraction of the waste stream.

The main options for the treatment of biodegradable MSW are composting, anaerobic digestion, incineration, gasification and pyrolysis. In the last decades composting has gained an important role on MSW management, and it can be applied both to mixed MSW and to separately collected biodegradable fraction. When the substrate is mixed MSW, the infrastructure for its treatment is called a mechanical–biological treatment (MBT) plant. This includes a combination of mechanical, other physical and biological processes that are mainly used to reduce the volume and weight and stabilize the fermentable fraction of MSW [14].

In Europe the concept of large-scale municipal composting was originated in Holland in 1929, and the facility was used to dispose of the refuse from several cities to produce compost. However, the first serious attempts to use large-scale composting to treat mixed MSW in Europe began in the 1970s and extended into the 1980s, at which time it was expected that these plants could treat approximately 35% of the total MSW [2].

2.3. Composting systems

Today, different composting technologies are used depending on the location, the substrate, the scale of operation, time required to reach compost stability and maturity, the availability of land, and the skills and the machinery available. Among the composting technology, the most basic distinction is between reactor and non reactor systems, Figure 2.3. Reactor technology is often termed “in-vessel”, whereas non reactors are open systems. The “non reactors” includes the ones used from prehistoric times to the windrows, static pile, and household systems used in the present days.

“Non reactor” systems may be categorized on the basis of the aeration method. Thus, these systems are divided in agitated solids bed and static bed. An agitated solid bed means that the composting mixture is disturbed or broken up in some manner to introduce oxygen as well as to (and accordingly) control the temperature, and effect mixing of the material during the composting cycle. The agitation may be by periodic turning, tumbling, or other methods of agitation. The windrow and the static pile processes are examples of the agitated and the static bed aeration systems, respectively [1,7].

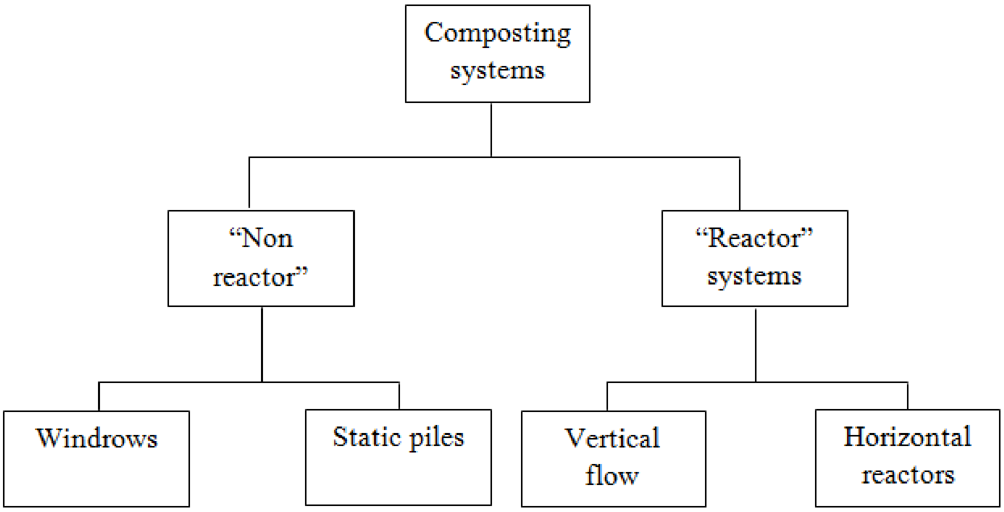


Figure 2.3 - Classification of composting systems.

In the windrow composting, mixed feeds stocks are placed in parallel rows and turned periodically, usually by mechanical equipment, which aerates and homogenizes the materials, leading to a more uniform breakdown as new surfaces are exposed to the degradation process. Oxygen is supplied primarily by natural ventilation resulting from the buoyancy of hot gases in the windrow system, and to a lesser extent, by gas exchange during turning. Therefore, the size of a windrow that can be effectively aerated is determined by its porosity, and the oxygen transfer into the windrow is aided by forced or induced aeration from blowers.

Windrows require large areas of land and can cause odor problems especially during the turning operations. If the windrow is too large, mechanical turning cannot control compost temperatures precisely, and unless the material is turned frequently, anaerobic conditions are unavoidable, interfering with the composting. On the other hand, small windrows lose heat quickly and may not attain temperatures high enough to kill pathogens and weed seeds [1,7].

In the static pile composting, like windrows, the material is in parallel rows, but as its name suggests, no agitation or turning of the static bed during compost cycle. The substrate is mixed with a bulking agent such as wood chips, and formed into a large pile. Bulking agent is a material, organic or inorganic, of sufficient size to provide structural support and maintain air spaces within the composition matrix. So it provides structural stability to the material and maintains air voids without the need of periodic agitation. Although "non-reactors" composting systems are easy to manage, they require large areas of land and can cause odor because anaerobic zones may occur during the process.

“Reactor” systems are design according to engineering principles and may be categorized according to the manner of solids flow as either vertical flow reactors (towers) or horizontal flow reactors. In these systems the waste is made to undergo decomposition within an enclosed space, which makes possible to be rigorously controlled. Various forced aeration and mechanical turning devices are used to optimize aeration in these systems.

Vertical flow reactors systems are further defined according to bed conditions in the reactor and are divided into those that allow agitation of solids during transit down the reactor, which are termed moving agitated bed reactors and those that where the composting mixture occupies the entire bed volume and is not agitated. These systems are termed moving packed bed.

Horizontal flow includes a number of reactors types in which the reactor is inclined slightly from the horizontal to promote solids flow. This horizontal flow reactors fall into three categories: tumbling solids bed reactors, which employ a rotating or rotary drum; agitated solids bed reactors, which use a bin structure with agitation; and static solids bed reactor, which also use a bin structure but with a static solid bed.

The “reactor” systems enable composted larger masses of waste within much shorter land spaces than conventional composting methods. But the use of machinery and power places significant cost burden on in-vessel systems, making them more expensive than the conventional systems [1,2,7].

2.4. Stages of composting process

Although the technologies described above may utilize different configurations, there are three basic components to the composting process: Pre-processing, composting and post-processing (Figure 2.4). Pre-processing of the waste usually is implemented prior to the composting stage, and may include particle size reduction, screening, and the addition of amendments and bulking agents. The goal of this phase is to create a more homogeneous input into the system, to exclude undesirable material (such as metals, plastics and glass) and to control several factors in the composting operation to avoid nuisance problems such as odors and dust, and also for obtaining a quality agricultural product [15]. Amendment is a material added to other substrates to condition the feed mixture and is divided into two types: structural or drying amendment, which is an organic material added to reduce bulk weight and increase air voids allowing for proper aeration and energy or fuel amendment, which is an organic material added to increase the quantity of biodegradable organics in the mixture and, thereby, increase the energy content of the mixture.

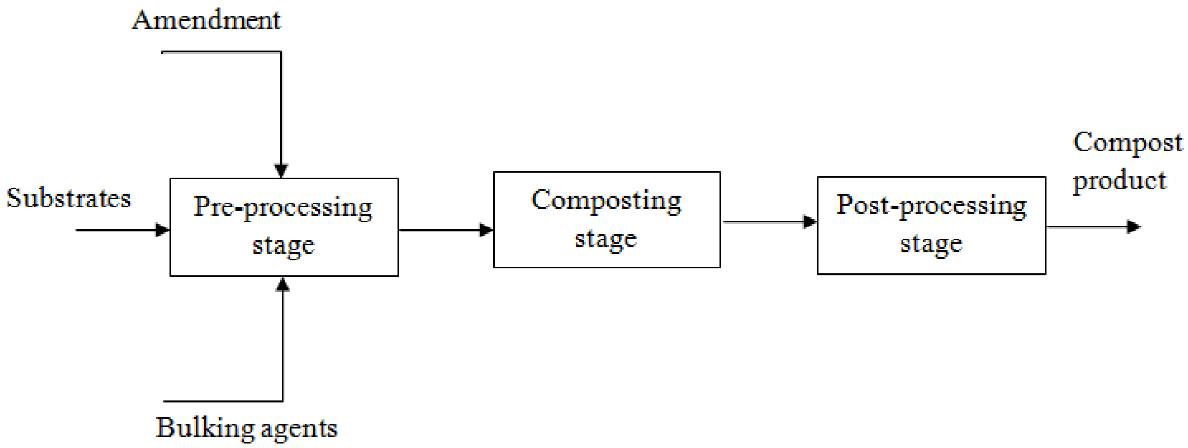


Figure 2.4 - Generalized diagram for composting process stages.

Once the pre-processing is complete, the organic waste is loaded into the composting system, and the process may begin as soon as the raw materials are mixed together. Composting stage can be divided into three phases, based on the temperature of the system: (1) a mesophilic, or moderate-temperature phase (up to 40 °C), which typically lasts for a couple of days; (2) a thermophilic, or high temperature phase (over 40 °C), which can last from a few days to several months; and (3) a several-month mesophilic curing or maturation phase (Figure 2.5). The length of the composting phases depends on the composition of the organic matter being composted and the efficiency of the process, which is determined for example by the degree of aeration, agitation, and the size of the system [3].

At the start, the raw materials are at ambient temperature and usually slightly acidic. During the initial stages of the process, oxygen and soluble, easily degradable components of the materials are rapidly consumed by the microorganisms. Firstly, mesophilic bacteria actinomycetes, fungi, and protozoa colonize the biodegradable solid waste. These microorganisms grow between 10 and 45˚C and break down easily degradable components such as monosaccharides, starch and lipids. Due to the oxidative action of microorganisms, the temperature increases and there is a drop in pH at the very beginning of composting, caused by the formation of fatty acids from the biodegradable compounds during degradation.

Once temperatures exceed 40°C, the mesophilic microorganisms become less competitive and are replaced by thermophilic ones. At this thermophilic phase, high temperatures accelerate the breakdown of proteins and fatty acids formed at the mesophilic phase, resulting in the liberation of ammonium and an increase in the pH. After the easily degradable carbon sources have been consumed, more resistant compounds such as cellulose, hemicellulose and lignin are partly degraded. The optimum temperature for thermophilic micro-fungi and actinomycetes which mainly degrade lignin is 40–50˚C. Above 60˚C, these microorganisms cannot grow and lignin degradation is slowed down. After the thermophilic phase the microbial activity decreases, and mesophilic microorganisms once again take over for the final phase of “curing” or maturation. Although the compost temperature is close to the ambient, this last phase is important because, chemical reactions continue to occur that make the remaining organic matter become more stable and additional humus-like substances are produced to form mature compost [1,3,9,10]. Once the compost is finished in the curing or maturation phase, it may be post- processed according to the feedstock characteristics and desired product quality.

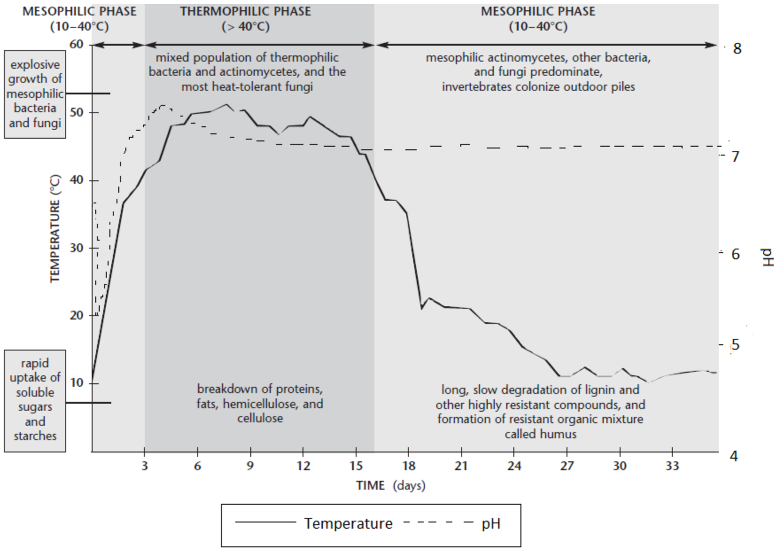


Figure 2.5 - Temperature and pH variation during composting process [redrawn from [3]].

2.5. Factors affecting the composting process

While composting occurs naturally, for guarantee that efficient thermophilic composting is attained optimal microbial growth conditions are required for organic matter degradation and thus good quality compost. The control of some variables and parameters may significantly affect the composting efficiency. Recently, research has been focused on the study of the interaction between physical, chemical and biological factors. Some of the more important factors in the composting operation are: aeration, temperature, nutrient balance, pH of materials, moisture content, surface area and particle size, size of compost system, porosity, bulk density, free air space (FAS), electrical conductivity (EC) and the microorganisms itself. Nutritional balance is mainly defined by the Carbon: Nitrogen ratio (C: N) [4,16].

Aeration

Aeration is a key variable for composting as oxygen is essential for the metabolism and respiration of aerobic microorganisms and thus for oxidizing the various organic molecules present in the waste material. Indeed, composting consumes large amounts of oxygen, particularly during the initial stages of most vigorous activity. Proper aeration controls the growth of adequate aerobic microbe populations, the development of stabilizing temperature and removes excess moisture and CO_2 as well. If oxygen supply is limited, the composting process may turn anaerobic, which is a much slower and odorous process. The aeration flow rate must supply the depleted oxygen to the composting mixture and carries away excess heat from the system with fresh air. A minimum oxygen concentration of 5% within the pore spaces of the compost is necessary for aerobic composting. However, the optimum O_2 concentration is between 15% and 20% and the air flow rate should maintain temperatures below 60–65 ˚C. Therefore, compost systems need to be designed to provide adequate air flow using either passive or forced aeration systems [3,4,9] .

Temperature

The temperature at any point during composting depends on the balance between the heat produced by microorganisms as they decompose organic material and the lost through conduction, convection, and radiation (Figure 2.6).

Conduction refers to energy that is transferred from atom to atom by direct contact. If the “reactor” or “non reactor” system of composting is smaller, the surface area-to-volume ratio is greater, and therefore, the degree of heat loss due to conduction is larger. Insulation helps to reduce this loss in small compost “reactors” systems.

Convection is the movement of molecules within fluids. When compost gets hot, occur the buoyancy of hot gases within the system, and the resulting convective currents cause a slow but steady movement of heated air upward through the compost and out the top. In addition to this natural convection, some composting systems use “forced convection” driven by blowers or fans.

Radiation refers to a process in which energetic particles or energy or waves travel through a medium or space. Radiation is a negligible loss of heat from compost because of the relatively small difference in temperature between the outer edges of the compost and the surrounding air [3,9,16].

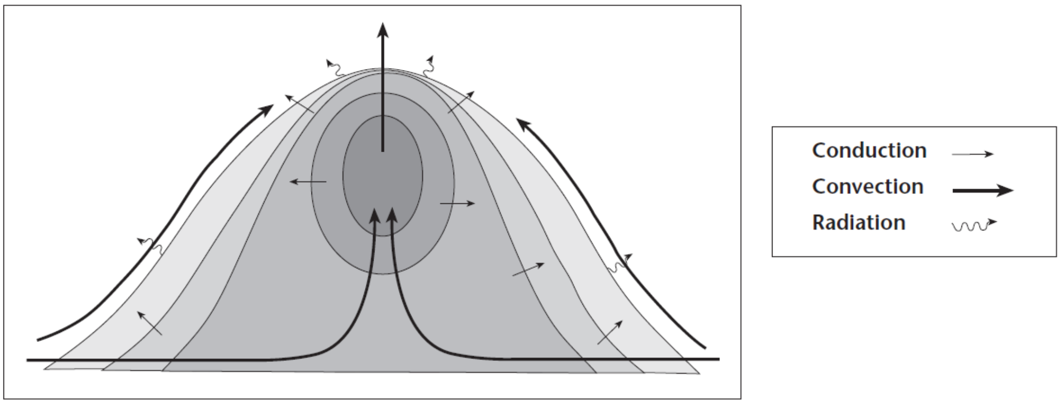


Figure 2.6 - Three mechanisms of heat loss from a composting pile [3].

Composting will essentially take place within two temperature ranges known as mesophilic (10-40 °C) and thermophilic (over 40 °C). The temperature of the compost is a good indicator of the microbial activity. Temperatures greater than 60 °C reduce the activity of many of the active organisms. Therefore, the optimum temperature range is between 32 °C and 60 °C. There is a direct relation between temperature and rate of oxygen consumption. Higher temperature led to greater oxygen uptake and faster rate of decomposition. Temperatures of composting materials characteristically follow a pattern of rapid increase to 55 – 60 °C and remain near this thermophilic level for several days or weeks. Temperatures gradually drop to 38°C and finally drop to ambient air temperature.

It is important to note that for destroying pathogenic microorganism the temperature should reach at last 55 °C for some hours to a few days.

Carbon: Nitrogen ratio (C:N)

Carbon, nitrogen, phosphorous, and potassium are the primary nutrients required by the microorganisms involved in composting. The optimum value of the carbon-to-nitrogen ratio (C:N ratio) is also an essential factor for microorganisms decompose of organic wastes during composting processes, as it usually ensures that the other required nutrients are present in adequate amounts. Carbon serves primarily as energy source for the microorganisms, while a small fraction of the carbon is incorporated into the microbial cells. Nitrogen is essential for microbial population growth, as it is a constituent of protein that forms over 50% of dry bacterial cell mass.

Raw materials blended to provide a C:N ratio of 25:1 to 30:1 are ideal for active composting, but initial C:N ratios from 15:1 up to 40:1 consistently give good composting results. High C:N ratios make the process very slow as there is not enough N available for the growth of microorganisms which results in a longer time for composting process. But with a low C:N ratio there is an excess of N per degradable C which can mineralize into ammonia it can be lost through ammonia volatilization, leaching from the composting mass and denitrification producing unpleasant odors. Denitrification can occur as a result of the development of anaerobic micro sites within the material. Thus, the aerobic conditions of the compost should be ensured throughout the process.

Most materials available for composting do not fit the ideal C:N ratio, so different materials must be blended to meet the required ratio. The carbon sources for microorganisms usually come from bulking agents such as sawdust and wood chip. Green wastes, such as foliage and manure, contain relatively high proportions of nitrogen and thus can be used as nitrogen sources [1,4,8,9,17].

pH of materials

Another parameter that greatly affects the composting process is the pH of the blend. During the course of composting, the pH in general varies between 5.5 and 8.5. The range of pH values suitable for bacterial development is 6.0–7.5, while fungi prefer an environment in the range of pH 5.5–8.0.

Composting itself leads to major changes in materials and in pH as well. In the early stages of composting, organic acids accumulate as a by-product of the organic matter degradation by bacteria and fungi and may, temporarily or locally, lower the pH (increase acidity). Usually, the organic acids break down further during the composting process, and the production of ammonia from nitrogenous compounds may raise the pH (increase alkalinity). Thus, the pH is very relevant factor for controlling N-losses by ammonia volatilization, which can be particularly high at pH >7.5. Later in the composting process, the pH tends to become neutral as a result of humus formation with its pH buffering capacity at the end of composting activity. Finished compost should have pH within the range of 5.0 to 8.0 to be compatible with plant growth and to avoid odors [1,3,4,16].

Moisture

Moisture plays an essential role in the metabolism of microorganisms and indirectly in the supply of oxygen, as it provides a medium for the transport of dissolved nutrients required for the metabolic and physiological activities of microorganisms. The optimum water content for composting varies with the waste to be composted, but an initial moisture content of 40–75% by weight is generally considered optimum because it provides sufficient water to maintain microbial growth but not so much that air flow is blocked. When the moisture content is too high (over 75%) nutrients may be leached, air volume is reduced and will close the air pores, reduce the oxygen content and consequently turns composting into an anaerobic process. Experience has shown that the bacterial activity will slow down when the moisture content is below 40%, and will cease entirely below 15 % [1,3,16,17].

Particle size and surface area

Microbial activity occurs at the interface of particle surfaces and air. Therefore, the rate of aerobic decomposition increases with smaller particle size, because high surface areas allows microorganisms to digest more material, and generate more heat, and so improve the biological activity and rate of composting. Smaller particles, however, may reduce the effectiveness of oxygen movement within the composting system, and thus the oxygen available to microorganisms decreases. Optimum composting conditions are usually obtained with particle sizes ranging from 5 to 12.5 cm of average diameter [3,9,16].

Size of compost system

The system volume can have great influence on the degradation rate of the material. The system must be large enough to prevent rapid dissipation of heat and moisture, yet small enough to allow good air circulation for the microbial activity [3].

Porosity and free air space

Substrate porosity carries a great influence on composting performance since appropriate conditions of the physical environment for air distribution must be maintained during the process. Porosity refers to the spaces between particles in the compost system. If the material is not saturated with water, these spaces are partially filled with air that can supply oxygen to decomposers and provide a path for air circulation. As the material becomes water saturated, the space available for air decreases [4,16].

Free air space (FAS) is a representation of the available air filled voids in a composting matrix. This parameter is very important as it is intrinsically related to the availability of water and oxygen, which are determinant factors for the biological activity of the microorganisms. The maintenance of optimum oxygen concentration is important to remove carbon dioxide and excess moisture, as well as to avoid or prevent an excessive heat accumulation, which depends on the air content and its movement trough composting material. Thus, maintaining adequate FAS levels satisfies the oxygen concentration required to achieve desired composting conditions. Minimum FAS requirements were established at 35% while maximum FAS levels recommended in order to avoid heat losses varies according to the wastes composition [19].

Bulk density

Bulk density is a property of particulate materials, and corresponds to the mass of many particles of the material per unit of bed volume, including the pore space. It is a useful indicator of materials compaction and so must be controlled [18].

Electrical conductivity (EC)

Electrical conductivity (EC) is expression of the ability of an aqueous solution to carry an electrical current. It is generally related to the total solute concentration and can be used as a quantitative measure of dissolved salt concentration, even though it is also affected by the mobility, charge and relative concentration of each individual ion present in the solution. Generally, EC increases during composting as volatile solids(VS) are degraded and the amount of water-soluble salts increases on a total solids (TS) basis[1,20].

Microorganisms

Organic matter decomposition is carried out by many different groups of microbial populations. The microorganisms involved in composting develop according to the temperature of the mass, which defines the different steps of the process. Naturally occurring microorganisms and invertebrates are the primary decomposers that accomplish composting. These microorganisms include bacteria, fungi, actinomycetes and protozoa. Different decomposers prefer different organic materials and temperatures and therefore, the microbial populations should be diverse. Changing operating conditions during the composting process lead to an ever-changing ecosystem of decomposition organisms. Among all microorganisms, aerobic bacteria are the most important initiators of decomposition and temperature increase within the compost system. Fungi are present during all the process but predominate at water levels below 35% and are not active at temperatures over 60 °C. Actinomycetes predominate during stabilization and curing, and together with fungi are able to degrade resistant polymers.

The ability of microorganisms to assimilate the organic matter depends on its capacity to produce enzymes necessary for degradation of specific substrate. The more complex the substrate, more varied enzymes system is needed. Through the synergic action of microorganisms, complex organic compounds are degraded to smaller molecules that can be used by microbial cells [4,10,16].

2.6. Finished compost Properties

The aim of composting should be to yield consistent product quality. However, the effectiveness of compost with regard to beneficial effects on soil depends on its quality, whose properties vary widely, as a function of the initial ingredients, the process used, and the age of the compost. Physical characteristics such as color, odor and temperature give a general idea of the decomposition stage reached, but give little information about the quality of the compost. In fact, the quality criteria for compost are usually established in terms of: nutrient content humified and stabilized organic matter, the maturity degree, the hygienization and the presence of certain toxic compounds such as heavy metals and soluble salts. The principal requirement for it safe use in soil is a high degree of stability and maturity, which implies stable organic matter content and the absence of phytotoxic compounds and pathogens. Phytotoxicity is mainly attributed to the presence of fatty acids but may also be caused by salinity, heavy metal, NH_3 and some toxic trace elements..

The terms stability and maturity are both commonly used to define the degree of decomposition of organic matter during the composting process even if they are conceptually different. Compost stability refers to a specific stage of decomposition during composting, which is related to the types of organic compounds remaining and the resultant biological activity that can be measured, for example, by respiration rates. When compost is unstable, microbial activity is high and the substrates pass through rapid changes. Maturity is the degree or level of completeness of composting and implies improved qualities resulting from ‘ageing’ or ‘curing’ of a product. Therefore, it is related to suitability in final use and crop growing. The use of immature compost is adverse to soil as anaerobic conditions develop as the microorganisms in soil use oxygen to decompose the compost, letting plant roots without oxygen and potentially generating toxic intermediates. Stability and maturity usually go hand in hand, since phytotoxic compounds are produced by the microorganisms in unstable composts.

Several variables have been proposed for monitoring the composting process and evaluating the stability of the compost. These variables may include physical, chemical, and biological parameters of the organic material, such as temperature, degree of self-heating capacity, oxygen consumption, biochemical parameters of microbial activities, analysis of biodegradable constituents, phytotoxicity assays, organic matter nutrient content, C/N ratio, and humus content and quality [1,4,6,10].

2.7. Biodegradability of organic matter

The definition of the criteria by which a material can be considered as compostable is a topical issue for the use of composting as a feasible waste management treatment. Among other criteria mentioned above, the biodegradability of materials in composting conditions is a key property. However, the practice to determine the biodegradability of waste is not very common, and the composting systems are usually designed based on assumed biodegradability of the waste reported on previous studies.

Biodegradability is defined as the biologically catalyzed breakdown of organic matter carried out by microorganisms. As in the natural environment or in technical facilities, there are a number of parameters which affect the level of biodegradation. The biodegradability of substances depends primarily but not only on their molecular structure. In general, biodegradable substances can be decomposed into carbon dioxide or water methane as the final products. In practice, only biodegradable organic material can be converted in products by its reaction with oxygen (aerobic processes), or without oxygen (anaerobic reactions). The main constituents of a composting feed mixture (m_0) and product (m) is shown in Figure 2.7, where it is defined a biodegradability index (β) as the fraction of the volatile solids (VS) (organic matter) that is susceptible of being decomposed during typical composting conditions. Thus, from the total mass of composting exist an inorganic solid fraction (IS), biodegradable volatile solid fraction (βVS) and non-biodegradable volatile solid fraction (1-β) VS.

The inorganic and non-biodegradable volatile solid fractions should behave as conservative substances through the process. Therefore, the mass of inorganic and non-biodegradable volatile solids entering the process should be equal to the mass of these leaving the process at steady state.

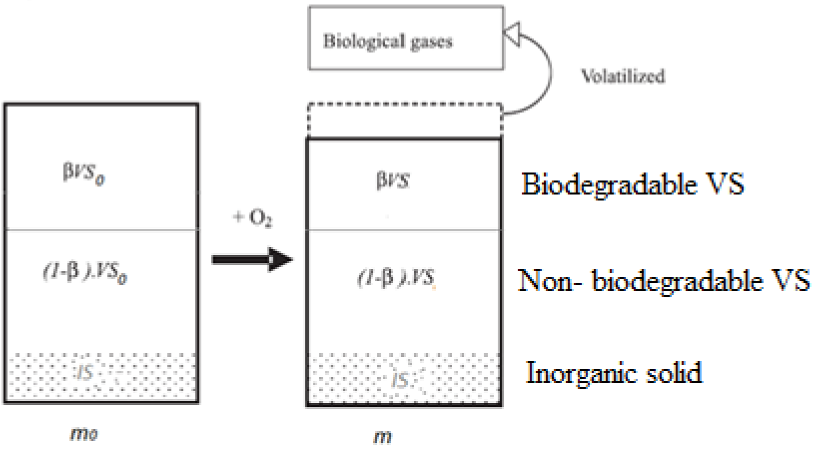


Figure 2.7 - Generalized bar diagram showing the components for substrate mixture and compost product (redrawn from [21]).

Aerobic and anaerobic biodegradation

Aerobic biodegradation is the breakdown of an organic compound by microorganisms in the presence of oxygen into carbon dioxide, water and mineral salts of any other elements present (mineralization) plus new biomass. Therefore, the chemistry of the system, environment, or organism is characterized by oxidative conditions. Aerobic bacteria use oxygen as an electron acceptor, and breakdown organic chemicals into smaller organic compounds, often producing carbon dioxide and water as the final product. Aerobic biodegradation is also known as aerobic respiration.

Anaerobic digestion occurs when microorganisms breakdown biodegradable material in the absence of oxygen. Generally the breakdown in anaerobic conditions proceeds sequentially from the complex to the simple molecules. The process begins with bacterial hydrolysis of complex particulate materials in order to break down insoluble organic polymers such as proteins, carbohydrates and lipids to yield monomers like amino acids, sugars, and high molecular fatty acids and make them available for other bacteria. Amino acids and sugars are converted into acids, carbon dioxide, hydrogen, ammonia, and organic acid. The resulting organic acids are converted into acetic acid, along with additional ammonia, hydrogen, and carbon dioxide. Finally these products may be converted to methane and carbon dioxide [22-25].

2.7.1. Methods to assess the biodegradability of organic matter

Test methods used to estimate biodegradability are an important part of organic waste characterization as they can be used to predict the biodegradation behavior of a test material and to assess the effectiveness of a certain treatment process, including composting. The degradation processes can occur in very different environmental situations. Thus, there are several biological and non-biological testing methods available for assessing this propertiy. Biodegradability tests typically involve incubation of the organic waste in the presence of live microorganisms that decompose the organic matter (biological test methods). The basic principle of these tests is to assess how much of the carbon can be mineralized and how quickly it will be degraded. Therefore, the degree to which the rate of biodegradability of the waste is reduced, and the extent of decomposition achieved, can both be used as an indication of the performance and efficiency of the treatment process. The biodegradability tests may be carried out under anaerobic or aerobic conditions and are monitored by measuring biogas production (CH_4 and CO_2) in anaerobic tests and either O_2 consumption or CO_2 production in aerobic tests [6,26].

Anaerobic methods

Anaerobic test methods measure the biodegradability of a material in the absence of oxygen by measuring the amount of biogas released (CO_2 and CH_4) resulting from the decomposition of organic materials carried out by methanogenic bacteria. An example of this decomposition for cellulose and hemicellulose is shown in Eqs. (2.2a) and (2.2b), respectively.

$$\mathrm{n(C_6H_{10}O_5) + n(H_2O) \rightarrow 3nCH_4 + 3nCO_2} \tag{2.2a}$$

$$\mathrm{2n(C_5H_8O_4) + 2n(H_2O) \rightarrow 5nCH_4 + 5nCO_2} \tag{2.2b}$$

The Bio Methane Potential (BMP) test is one method that can be used to estimate the amount of methane that could be produced from anaerobically digesting organic matter in a temperature controlled system [26].

Aerobic methods

Aerobic test methods measure the biodegradability of a material in the presence of oxygen by measuring the O_2 consumption or CO_2 production of a test material. The aerobic biodegradation of cellulose and hemicelluloses are shown as example in equations (2.3a) e (2.3b), respectively.

$$\mathrm{n(C_6H_{10}O_5) + 6nO_2 \rightarrow 5nH_2O + 6nCO_2} \tag{2.3a}$$

$$\mathrm{n(C_5H_8O_4) + 5nO_2 \rightarrow 4nH_2O + 5nCO_2} \tag{2.3b}$$

There are several aerobic waste biodegradability test methods as well as different monitoring techniques and ways of expressing results. They can be classified as ‘dynamic’ or ‘static’ depending on whether or not the sample is aerated, respectively. Oxygen uptake rate (OUR) and dynamic respiration index (DRI) are examples of static and dynamic test method, respectively, and both were developed and designed to assess the degree of biological stability of waste derived materials.

Biological methods are referred in literature as the most suitable stability determination and are also proposed as a biodegradability measure. Although, the BMP method has been reported to show good reproducibility it has the disadvantage of require long periods to be complete, thereby not providing rapid feedback on routine monitoring. Aerobic methods including the DRI test have other disadvantages such as preferentially decomposing the readily biodegradable components of the material and therefore may not indicate potential long-term biodegradability. Therefore most of current microbial based biodegradability test methods have limitations and none of them is suitable for the whole range of biodegradability testing requirements [26].

Since biological tests are time consuming and costly it is desirable to have simpler, rapid and cheaper methods that may be a useful surrogate for biological tests.

Alternative method

A large proportion of MSW consists of biopolymers (proteins, fats, polysaccharides and lignin). Lignin-containing materials are often referred as poorly biodegradable, so as a general rule, the higher the lignin content, the lower biodegradable is the substrate. On other hand, lignin is also the main precursor for humic substances and it is mainly humified (not mineralized) during degradation in compost or soil. Therefore, the assessment of the material lignin content may provide a non-biological test method of assessing biodegradability [7].

Lignin is a natural composite material in all vascular plants, which provides plant strength and resistance to microbial degradation by decreasing water permeation across the cell wall. It is an amorphous, aromatic, water insoluble, heterogeneous, three-dimensional, and cross-linked polymer (Figure 2.8).

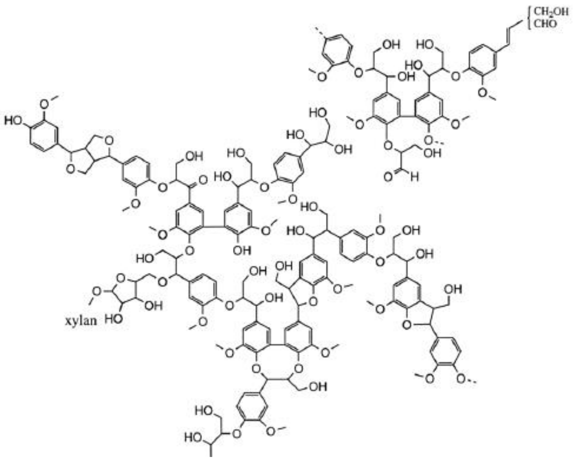


Figure 2.8 - Lignin polymer of softwood. The figure is a part of lignin macromolecule, a schematic example which is qualitative, not quantitative [27].

The macromolecular properties and structural characteristics of lignin make biodegradation studies difficult. The best isolation method of lignin would allow the collection of chemically unmodified lignin with quantitative recovery and free of non-lignin contaminants. A suitable method to isolate lignin would allow predicting substrate biodegradability by using, for example, the empirical formula shown in Eq. (2.4), which is a correlation between volatile solids biodegradation and lignin content. This empirical formula was developed by Chandler that used procedures developed by Van Soest to partition certain substrates such as wheat straw, corn stalks, corn leaves, and so on, into detergent soluble fractions, including cell soluble constituents, hemicelluloses, cellulose and lignin. The degradability of the selected substrates tested was assessed during anaerobic digestion at 35 °C [7].

$$\beta = 0.830 - (0.028) \times \mathrm{LC} \qquad (2.4)$$

where β is the biodegradable fraction of the volatile solids and LC is lignin content (% of VS). The Eq. (2.4) suggests that materials without lignin only achieve a maximum degradability of 83%.

The methods used for isolating lignin can be classified into two main categories: gravimetric and non-gravimetric methods. The first group can be further classified into methods where lignin is selectively removed and recovered from the final solution, and methods in which lignin is left as an insoluble residue. Determination of Kappa number and Klason lignin are the most common methods used to analyze lignin quantitatively and both are gravimetric. The non-gravimetric methods include spectroscopy such as Fourier transform infrared (FTIR) and those based on optical properties of lignin.

Klason lignin is determined gravimetrically after extracting the sample with sulphuric acid 72% to dissolve out the other components. Kappa number is usually used in the pulp and paper industry and it is determined by oxidizing lignin selectively from pulp using a solution of potassium permanganate. So Kappa number represents the amount of permanganate consumed by the pulp sample [10, 28].

3. MATHEMATICAL MODELING OF COMPOSTING PROCESS

Composting is a process that involves many coupled physical, chemical and biological mechanisms that are challenging to analyze both empirical and theoretically. Kinetics behavior is an example of a major issue in the study of composting facilities, as well as, to know how operating factors affect process rate. Mathematical modelling has been widely used in science and engineering in order to allow an integration of knowledge on the considered phenomena, resulting on an improved understanding of the behavior of systems, to orientate experimental design, explore new theoretical concepts, predict system performance and test hypothesis. Mathematical modelling may be particularly important to reduce, or even replace, the need for physical experimentation when exploring new material and/or process options [29].

3.1. Description of model

The system under analyses is heterogeneous and involves solid, liquid and gaseous phases. However, in this study the modelling approach is pseudo-homogeneous. Thus, the basic approach used to model composting processes is to couple derived substrate degradation kinetics with mass and energy balances for the physical state variable such as temperature (T), water content (m_W) and oxygen concentration (C_{O_2}). These state variables are the most important ones for representing the compost process dynamics. In this work, the mathematical model involves three parts based on basic principle of chemical reaction engineering: organic matter biodegradation kinetics, energy balance equation and mass balance equation.

Through mass and energy balances, transport processes and thermodynamics, a set of equations describing a composting process were derived. The general form adopted for analysis is as shown in Eq. (3.1).

$$\text{accumulation} = \text{input} \pm \text{transformation} \pm \text{exchanging} - \text{output} \tag{3.1}$$

At the beginning of the process, the material of composting consists of inorganic part, organic part and water. The Organic part is degraded by biochemical exothermic reactions with consumption of oxygen and generation of carbon dioxide, water and ammonia as shown in Eq. (3.2)

$$C_vH_yO_zN_w + \left(\frac{4v + y - 2z - 3w}{4}\right) O_2 \rightarrow vCO_2 + \frac{y - 3w}{2} H_2O + wNH_3 \tag{3.2}$$

where v, y, z and w are indexes which describe the molar fraction of carbon, hydrogen, oxygen and nitrogen, respectively, in the organic part of substrate. These indexes are useful to calculate the stoichiometric coefficients of the consumed and produced gases.

The system is supplied with a constant composition air to ensure adequate levels of oxygen concentration to maintain aerobic condition for organic matter oxidation and to remove the excess of moisture from the substrate. The mass and heat transfer phenomena included in the model are shown in Figure 3.1.

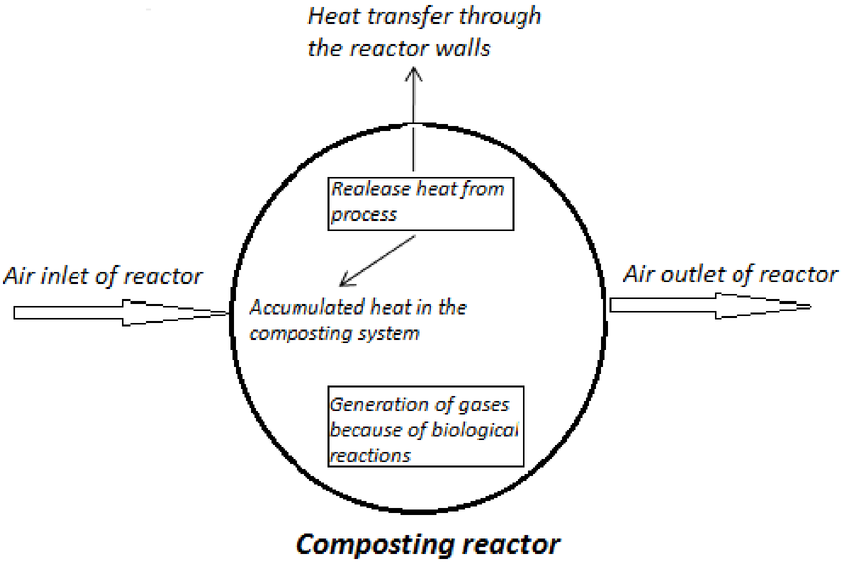


Figure 3.1- Mass and heat transfer phenomena included in the model.

Model assumptions and simplifications

To simplify the equations and numerical calculation, several assumptions and simplifications were taken into account while developing the model:

- Complete mixing of material in terms of O_2 concentration is achieved by efficient aeration;
- The system maintains a constant pressure;
- Gas mixture is saturated with water vapor;
- The system has a uniform temperature;

- The temperature of compost, water and air is equal in each point of the reactor;
- The temperature of the outlet air is equal to the composting material temperature;
- The mass of air flow rate remains constant;
- The composting material is a homogeneous mixture of uniform composition;
- All heat specific capacities are constant;
- The gaseous phase behaves as ideal gas.

3.1.1. Process kinetic

The composting reaction is described by the organic matter degradation rate, through the kinetic Eq. (3.3) [29]

$$\frac{dm_{OM}}{dt} = -km_{OM}^{n} \tag{3.3}$$

where m_{OM} is the mass of organic matter in the substrate (kg), t the time (h), k the rate constant ($kg^{1-n}h^{-1}$) and n the reaction order.

Reaction rate constant is dependent on the system design, the type of material under treatment, and other factors that may affect the overall system performance. In our work , this constant is defined as a function of temperature, oxygen concentration, moisture and free air space as shown in Eq. (3.4) [7]

$$k = F(T) \times F(O_2) \times F(W) \times F(FAS) \tag{3.4}$$

where F(T), $F(O_2)$, F(W), and F(FAS) are the correction factors for temperature, oxygen concentration, moisture content and free air space, respectively.

There is an extensive set of equations in literature to describe the dependence of the reaction rate on temperature. In our study, the Eq. (3.5) was used [29].

$$F(T) = a\left[b^{(T-20)} - c^{(T-60)}\right] \tag{3.5}$$

where a, b and c are constants determined empirically through an optimization method.

The dependence of reaction rate constant on oxygen concentration is estimated using the Eq. (3.6)

$$\mathrm{F}(\mathrm{O}_2) = \frac{\mathrm{C}_{\mathrm{O}_2}}{\mathrm{k}_{\mathrm{O}_2} + \mathrm{C}_{\mathrm{O}_2}} \quad (3.6)$$

where $C_{O_2}$is oxygen concentration (kgO$_2$ m^{-3}) and $k_{O_2}$is oxygen saturation constant (kgO$_2$ m^{-3})

For modelling the effect of moisture content on the reaction rate the correction factor developed by Haug (Eq. 3.7) was used [7].

$$\mathrm{F}(\mathrm{W}) = \frac{1}{e^{(-17.684[1-\mathrm{S_m}]+7.0622)} + 1} \quad (3.7)$$

where S_m is fractional solids content of the mixture solids. The model equation used for FAS correction is shown in Eq. (3.8)

$$\mathrm{F}(\mathrm{FAS}) = \frac{1}{e^{(-23.675\mathrm{FAS}+3.4945)} + 1} \quad (3.8)$$

Fractional free air space of the composting material was calculated using the Eq. (3.9) [7]

$$\mathrm{FAS} = 1 - \frac{\rho_m \mathrm{S_m}}{\rho_s \rho_m} - \frac{\rho_m (1 - \mathrm{S_m})}{\rho_w} \quad (3.9)$$

$$\rho_m = \frac{\mathrm{C}}{\mathrm{S_m}} \quad (3.10)$$

$$\frac{1}{\rho_s} = \frac{\mathrm{V_s}}{\rho_V} + \frac{(1 - \mathrm{V_s})}{\rho_f} \quad (3.11)$$

where V_s is volatile fraction of substrate solids, ρ_s is specific gravity of substrate solids (kg/m^3), ρ_V is specific gravity of the volatile fraction of the substrate solids, ρ_f is specific gravity of the fixed fraction of the substrate (inorganic fraction), ρ_m is unit bulk weight of the mixed material to be composted, (kg/m^3), ρ_w is density of water (kg/m^3), C is bulk weight coefficient for the substrate, range from 0.15 to 0.4. The specific gravity of the volatile solids normally is about 1.0 and that of fixed solids about 2.5.

3.1.2. Mass balance

The mass changes of oxygen and moisture in the substrate were estimated based on the principle of mass conservation.

Water mass balance

The water mass balance in composting material is shown in Eq. (3.12) and it relates water transport by the air flow throughout the reactor and the water formed in the composting reaction.

$$\frac{\mathrm{dm_W}}{\mathrm{dt}} = \frac{\mathrm{P_{s0}QMr_W}}{\mathrm{RT_0}} - \mathrm{Y_w}\frac{\mathrm{dm_{OM}}}{\mathrm{dt}} - \frac{\mathrm{P_sQMr_W}}{\mathrm{RT}} \tag{3.12}$$

where P_{s0} and P_s are saturation water vapor pressure (Pa) at initial temperature of inlet air and at temperature of the composting mixture, respectively; T_0 is the initial temperature of inlet air (K); Q the volumetric air flow (m^3 h^{-1}); Y_w the stoichiometric coefficient of water; R the universal gas constant (J $kmol^{-1}$ K^{-1}) and Mr_w is water molecular weight (mol kg^{-1}).

Oxygen mass balance

The oxygen concentration in the compost was estimated by Eq.(3.13)

$$\frac{\mathrm{dC_{O_2}}}{\mathrm{dt}} = \frac{\mathrm{M_a}}{\rho_\mathrm{a}\mathrm{V_r}}\left(\mathrm{C_{O_{2,in}}} - \mathrm{C_{O_{2,out}}}\right) + \mathrm{Y_{O_2}}\frac{\mathrm{dm_{OM}}}{\mathrm{dt}}\frac{1}{\mathrm{V_r}} \tag{3.13}$$

where C_{O_2} is the concentration of oxygen in the reactor (kgO_2 m^{-3}), M_a the air flow (kg h^{-1}); V_r is the working volume of the reactor (m^3); Y_{O_2} the stoichiometric coefficient of oxygen; and ρ_a the density of air (kg m^{-3}), which was calculated based on psychometric relationships from the temperature and humidity ratio [30] .

3.1.3. Energy balance

As aforementioned the heterogeneous nature of the system under analysis was modeled assuming pseudo-homogeneous approach. Thus, the temperature of solid, liquid and gaseous phase is the same inside the reactor. The overall heat capacity was calculated from the heat content of the organic matter, inorganic matter, water and dissolved gas in interstitial water. The temperature variation in the system along time was calculated by Eq. (3.14)

$$\frac{\mathrm{dT}}{\mathrm{dt}} = \frac{\mathrm{M_a c_{pa}(T_a - T) + (-\Delta H_{rx})\frac{dm_{OM}}{dt} - UA(T - T_{amb})}}{\mathrm{m_w c_{pw} + m_{OM} c_{pOM} + \ m_{IM} c_{pIM} + \ m_a c_{pa}}} \tag{3.14}$$

where c_{pa}, c_{pw},c_{pOM},c_{PIM} are specific heat capacities of air, water, organic matter and inorganic matter, respectively, (J kg^{-1} K^{-1}); T_a the air Temperature (K), ΔH_{rx} is the reaction enthalpy (J kg_{OM}^{-1}); U the overall heat transfer coefficient (J $h^{-1}m^{-2}$ K^{-1}); A the area of heat transfer (m^2), m_a the mass of air and T_{amb} is ambient temperature (K).

The specific heat capacities and overall heat transfer coefficient used in the model are from the literature. The reaction enthalpy is calculated by Eq. (3.15) [7]

$$\Delta H_{rx} = \left[145C + 610\ \left(H - \frac{O}{8}\right) + 40S + 10N\ \right] \times 2326 \tag{3.15}$$

where C, H, O, S and N are the weight percentages of carbon, hydrogen, oxygen, sulfur and nitrogen, respectively, on an ash-free basis. The Eq. (3.15) is known as the modified Dulong formula and is useful in estimating gross heating values from the composting feed composition. This equation requires an ultimate analysis of composting mixture to determine the percentages of C, H, O, S and N.

3.1.4. Initial conditions

For solving the differential equations of the model, Eqs.(3.3), (3.12), (3.13) and (3.14) it is necessary to establish the initial conditions (IC). In our simulations, the IC used are the ones indicated in Eq. (3.16) to (3.19).

$$\mathrm{m_{OM}(t = 0) = m_{OM,0}} \tag{3.16}$$

$$\mathrm{m_W(t = 0) = m_{W,0}} \tag{3.17}$$

$$\mathrm{C_{O_2}(t = 0) = C_{O_2,0}} \tag{3.18}$$

$$\mathrm{T(t = 0) = T_0} \tag{3.19}$$

The initial mass values of water and organic matter were calculated using the experimental data. The initial oxygen concentration was calculated using the equations of ideal gases at ambient temperature. The initial temperature in the composting system was considered as equal to ambient temperature.

3.1.5. Inputs of mathematical model

The data required in the model are categorized in three groups: constants (physical, thermodynamic and stoichiometric), kinetic parameters and operational conditions. Table 3.1 and Table 3.2 show some constants values used in other works and in the present model, respectively. The operational conditions such as air flow rate were given in the experimental procedure. The molecular formula, $C_{20}H_{35}O_{10}N$, of the compost mixture is obtained using the elemental composition of initial mixture shown in Appendix B.

Table 3.1 - Constants values used in composting mathematical models.

Ref.	Substrate	*Parameters*						
		U ($J\ h^{-1}K^{-1}\ m^2$)	ΔH_{rx} ($J\ kg^{-1}$)	C_{pw} ($J\ kg^{-1}K^{-1}$)	C_{pa} ($J\ kg^{-1}K^{-1}$)	$C_{Pdrymatter}$ ($J\ kg^{-1}K^{-1}$)	Cp_{OM} ($J\ kg^{-1}K^{-1}$)	C_{PIM} ($J\ kg^{-1}K^{-1}$)
[32]	Sewage sludge and wheat straw	4.4×10^3	2.2×10^3	4.2×10^3	1.0×10^3	1.1×10^3	ni	ni
[29]	Poultry manure and wheat straw	4.2×10^3	1.57×10^7	4.2×10^3	ni	ni	1.3×10^3	848
[35]	Synthetic food waste	ni	1.6×10^7	4.2×10^3	1.0×10^3	1.8×10^3	ni	ni
[33]	Domestic solid waste	ni	1.76×10^7	4.2×10^3	ni	2.1×10^3	ni	ni
[36]	Manure and wheat straw	ni	ni	4.2×10^3	1.0×10^3	ni	1.5×10^3	840
[7]	Sludge solids	ni	2.2×10^4	4.2×10^3	1.0×10^3	1.1×10^3	ni	ni
[34]	ni	ni	$1.78 - 24.7 \times 10^3$	ni	ni	ni	ni	ni

ni – not indicated

Table 3.2 - Physical, thermodynamic and stoichometric constants used in the model.

Description of the constant	Symbol	Value	Unit	References
Specific heat capacity for water in composting mixture	c_{pw}	4200	$J\ kg^{-1}K^{-1}$	[7]
Specific heat capacity for air	c_{pa}	1013	$J\ kg^{-1}K^{-1}$	[7]
Specific heat capacity for organic matter	c_{pOM}	1320	$J\ kg^{-1}K^{-1}$	[29]
Specific heat capacity for inorganic matter	c_{pIM}	848	$J\ kg^{-1}K^{-1}$	[29]
Overall heat transfer coefficient	U	11580	$J\ h^{-1}m^{-2}\ K^{-1}$	Assumed
Reaction enthalpy $C_{20}\ H_{35}O_{10}N$	ΔH_{rx}	$2.27x10^7$	$J\ kg_{OM}^{-1}$	Calculated using Dulong formula
Oxygen saturation constant	k_{O_2}	0.07	$kg_{O_2}kg_{OM}^{-1}$	[29]
Stoichiometric coefficient for oxygen	Y_{O_2}	0.705	$kg_{O_2}kg_{OM}^{-1}$	[29]
Stoichiometric coefficient for water	Y_w	0.360	$kg_w kg_{OM}^{-1}$	[29]

4. STATE OF THE ART

The increasing amount of organic solid wastes generated has become a worldwide problem, and thus, the number of treatment facilities based on biological processes has been increasing the last years. These installations are receiving municipal and industrial organic wastes with the common main goal of reducing their biodegradable organic matter content. Among the available biological technologies to treat and recycle organic wastes, composting is referred as one of the most useful options to recycle organic materials to obtain a valuable organic fertilizer or amendment known as compost. The proper knowledge of the characteristics of the wastes to be composted is essential to carry out the process in a favorable way to obtain the desirable compost quality. The measurement of biodegradable organic matter content is of most importance for the proper analysis and design of the composting treatment facilities. However, consensus has not been reached about which shall be the most suitable method measuring biodegradability organic matter content in a solid organic waste. In fact, a wide range of biological and non biological test methods are now available. Table 4.1 provides a summary of the key aspects of number studies of biodegradability test methods which can be correlated with the stability assessment.

Suitability factors of the test methods include the timescale, applicability to a wide range of materials and ability to indicate the long-term biodegradability of organic materials samples. Among the methodologies suggested, aerobic respiration indices have been highlighted as the most suitable tool for biodegradability assessment. However, these test methods are time consuming and costly. Thus, it is desirable to have efficient, simpler, rapid and cheaper methods, as the assessment of lignin content, which may be a useful surrogate for aerobic method. The evaluation of lignin content to assess the substrate biodegradability can be useful when long term biodegradability studies cannot be performed, which is the approach used in our work.

Table 4.1- Studies of biodegradability test methods

Reference	Objectives	Methods	Conclusions
Wagland et al., (2009)	Evaluation of test methods for assessing waste treatment process performance and monitoring the diversion of biodegradable municipal waste (BMW) from landfill	Respirometric; Anaerobic tests (BMP), Temperature increase; Spectrographic; Enzymatic hydrolysis	The anaerobic methods produce reliable results but take long time to complete; Aerobic methods offer a significantly improved timescale compared with anaerobic test methods, however, do not measuring the full extent of sample biodegradability; Temperature increase methods are not suitable. For the purpose of monitoring BMW diversion from landfill, FT-IR is not suitable; For the enzymatic method there is a necessity to perform several measurements which is a disadvantage of this approach.
Ponsá et al., (2010)	Evaluation of different indices to express biodegradability in organic solid wastes	Dynamic respiration indices expressed as average oxygen uptake at 1 and 24 h of maximum activity (DRI1h, DRI24h); Cumulative oxygen consumption in 24 h of maximum activity and 4 days (AT24h, AT4)	The combined analysis of DRI 24h and AT4 is presented as the best tool for biodegradable organic matter content characterization and process requirements estimation
Godley et al., (2004)	Evaluation of methods for biodegradability determination of municipal waste	Gravimetric; Elemental composition; Anaerobic biochemical methane potential (BMP); Respirometric DRI, SOUR, SRI); Water extractable dissolved organic carbon (DOC), BOD and COD; Cellulose and lignin content; Cellulase hydrolysis	The gravimetric and elemental tests do not characterize the relative biodegradability of the waste. The DRI and BMP are promising tests methods and cellulase enzymatic hydrolysis method may provide a rapid surrogate measure of relative biodegradability.
Wagland et al., (2008)	Comparison of enzymatic; biodegradability test method with microbial degradation methods	Dynamic respiration over 4 days (DR4); Biochemical methane potential over 100 days (BM100); Enzymatic hydrolysis (EHT)	The EHT is a suitable alternative routine biodegradability test method, offering a reduction on the timescales and cost of the DR4 and BM100 test methods. However, further research is needed to improve the versatility and validity of the EHT method.
Ylijoki et al., (2004)	Biodegradability testing of the municipal solid waste	Gas formation (GB21), Respiration activity (AT4),ASTM D 5210-92, DOC at neutral pH, Selective dissolution method	No single test method was found to be completely sufficient for routine biodegradability analysis suitable for monitoring the municipal solid waste.
López et al., (2010)	Approaching compost stability from Klason lignin modified method	Chemical stability degree (SD); Klason method for lignin determination	SD is an useful method to determine the stability because it is not affected by certain sample conditions such as temperature, water content and particle size, as observed in respirometric techniques or self-heating test.
Haug (1993)	Evaluation of composting substrates biodegradability	Lignin content	Good predictive model for substrate biodegradability.

Mass and energy balances have been developed for the composting process and translated into a number of mathematical models since 1976 [29] and from that time a number of models have been further investigated. Recently, the model developed by Haug has been used as the basis for subsequent studies of mathematical model for composting process. The models developed so far showed more or less success in predicting the profiles of temperature, water content, substrate degradation and oxygen concentration. Table 4.2 provides a summary of the key aspects of number of mathematical models developed, namely the kinetic model considered.

As shown in Table 4.2, the authors of several mathematical models have used first-order substrate degradation kinetics, Monod-type expressions or empirical substrate degradation equations in modelling biological energy production. The first-order kinetic relationships have been based mostly on the volatile solids (VS) degradation and with correction of the rate constant for some state variables. The major differences in the model developed so far are the assumptions regarding heat and mass transport mechanisms. In the review of mathematical modelling of composting process, Mason (2006) concluded that models incorporating either empirical expressions or first order kinetic were generally more successful in predicting the evolution of dynamic state variables than models incorporating Monod-type kinetic expressions. Thus, in this work the new process kinetic developed by Petric *et al*. (2007), was combined with the mass and energy balance developed here.

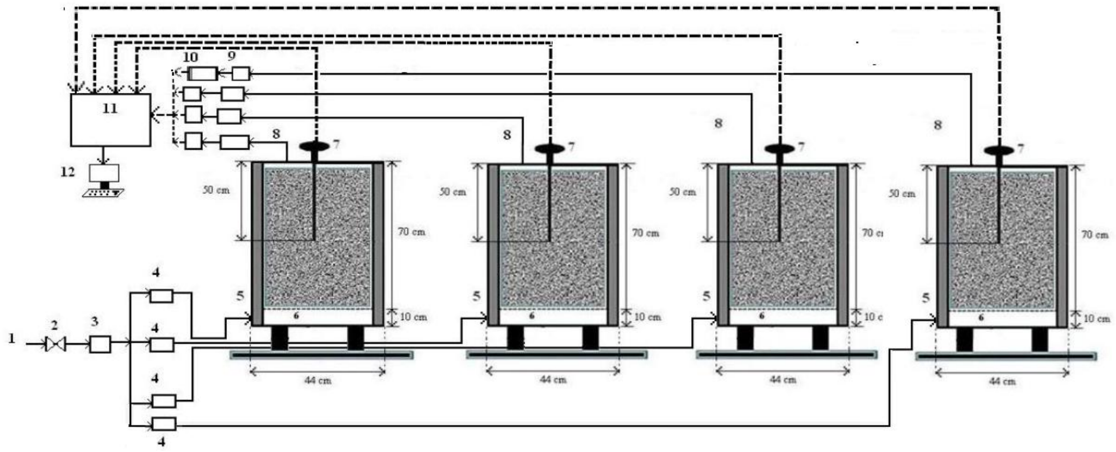
Table 4.2 - General overview of composting kinetic models.

Reference	Objectives	Kinetics	Conclusions
Petric et al., (2007)	Development and validation of mathematical model for aerobic composting process	$\frac{dm_{OM}}{dt} = -km_{OM}^{n}$	Comparisons of experimental and simulation results for temperature, organic matter conversion, carbon dioxide concentration and oxygen concentration, showed good agreement during the whole process.
Baptista et al., (2010)	Test a kinetic model based on VS content change for describing the composting process in MBT plants, and to identify the model parameters that affected the estimation of the reaction rate constant.	$VS_{consumed_t} = [\beta VS_0] \times (1 - e^{-k' \times t})$	The kinetic model satisfactorily described the experimental data for the plants. Sensitivity analysis showed that the model parameters that most affected the estimation of k were the initial βVS, the maximum temperature for biodegradation and the MC
Zhang et al., (2010)	Simulation of substrate degradation in composting of sewage sludge.	$\frac{d(\beta VS)}{dt} = -k(\beta VS)$	Simulation was a good fit compared with experimental values.
Xi et al (2010)	Dynamic simulation for domestic Solid waste composting processes	$\frac{dX}{dt} = \mu = \mu_{max}\left(\frac{SX}{KcX + S}\right)$	The simulation results were well consistent with the experimental results. Tthe model showed that the efficiency of composting processes could be raised and aeration requirements could be reduced by controlling the oxygen concentration in the exhaust air within a proper range.
Mason (2006)	Evaluation of the mathematical models of composting process		The most successful models in predicting temperature profiles were those which incorporated either empirical kinetic expressions for VS degradation or CO_2 production, or which utilized a 1st order model for VS degradation, with empirical corrections for temperature and moisture variations. Models incorporating Monod-type kinetic expressions were less successful.
Higgins et al., (2001)	Validation of a new model for aerobic organic solids decomposition	$\mathrm{R_{CO_2}} = \mathrm{R_{CO_2\,opt}}(\mathrm{f_T})(\mathrm{f_{O_2}})\left[\frac{\mathrm{CO_2}}{\mathrm{kgVS\ per\ day}}\right]$	In all the observations the model tended to over predict values of the state variables.
Yu et al., (2009)	Influence of free air space on microbial kinetics in passively aerated compost	$\frac{dX}{dt} = k_{d,i}X_i$	The result from this study demonstrates a new method for describing the relationship between microbial kinetics and substrate FAS, which could be used to improve the design, optimization, and management of passively aerated composting facilities.
Haug (1993)	Development of simulation model of composting process	$\frac{d(\beta VS)}{dt} = -k(\beta VS)$	Simulation may be a good fit compared with experimental values.

5. EXPERIMENTAL METHODS

5.1. Experimental apparatus

Experiments were performed in a system of four self-heating reactors (SHR) with 120 L of internal volume and isolated with a rubber based elastomeric material (Aeroflex MSR) arranged in parallel. The experimental reactors system is shown schematically in Figure 5.1.



where

1- Compressed air inlet
2- On/off valve
3- Air moisture regulator
4- Rotameter
5- Insulation layer (Aeroflex MSR)
6- Perforated plate
7- Temperature sensor
8 - Gases outlet
9 - Condensate retention system
10- Oxygen sensor
11- Data acquisition system
12- Computer

Figure 5.1 - Schem of the pilot-scale experimental apparatus.

The reactors have a side hole that allowed the entry of compressed air that is uniformly distributed across a perforated Perspex plate. On the top of the reactors there are two openings for the introduction of a temperature sensor and another to allow the release of gases generated in the biological reactions along the process, as well as the release of the excess air.

5.2. Materials

The components used to experiments were from different sources and included potato-peel industrial waste (PP) from a Portuguese industry of potato chips, grass clippings (GC) from a garden centre and a football stadium, and sawdust (SD). Potato-peel is classified as waste and its identification according to the European Waste List is 020399. These individual raw materials were blended in four different formulations. The initial mixtures tested were formulated in order to ensure proper conditions, such as nutrient balance (C:N ratio), moisture content (MC) and FAS, for optimal microbial growth and organic matter degradation. For achieve the specification concerning to C: N ratio (15:1 to 40:1) and MC (40-75%) for the composting mixture is only necessary to know the nitrogen, carbon and moisture content of the individual ingredients as it is shown in the mass balance Eqs. (5.1) and (5.2) for C:N ratio and moisture content, respectively. These equations were solved exactly for the considered mixture of three materials.

$$C{:}N_m = \frac{m_1[C_1 \times (1 - MC_1)] + m_2[C_2 \times (1 - MC_2)] + m_3[C_3 \times (1 - MC_3)]}{m_1[N_1 \times (1 - MC_1)] + m_2[N_2 \times (1 - MC_2)] + m_3[N_3 \times (1 - MC_3)]} \tag{5.1}$$

$$MC_m = \frac{m_1 \times MC_1 + m_2 \times MC_2 + m_3 \times MC_3}{m_1 + m_2 + m_3} \tag{5.2}$$

where $C{:}N_m$ is the C:N ratio of compost mixture, MC_m the moisture content of composting mixture (%), m_i the mass fraction of material *i* (*i*=1,2,3), C_i is carbon fraction of material *i*, N_i the nitrogen fraction of material *i* and MC_i is moisture content of material *i* (a fraction in equation (5.1) and a percentage in Eqs.(5.2)).

The approach described above for C:N ratio and MC is not applicable for FAS because this parameter depends on the structural characteristics of the material and not on its elemental composition. Therefore, appropriated method for this purpose such as Mixture Design was used.

5.2.1. Mixture design

Mixture design is statistical methodology that allows varying the proportions of two or more ingredients of a mixture to study the influence of individual proportions of the components tested in a measured response, which is dependent on the ingredient composition.

Then, the method use response surface approach to identify the area (mixture region) where all specifications can be achieved. The effect of composition in a response variable, Y, can be described by the polynomial shown in Eq. (5.3) [31]

$$Y = \sum_{i=1}^{q} \gamma_i x_i + \sum_{i<j}^{q-1} \sum_{j}^{q} \gamma_{ij} x_i x_j + \varepsilon \tag{5.3}$$

where x_i represent the independent variable i , γ_j correspond to the polynomial coefficients j, q is number of the mixture components and ε is the variable response estimative error.

The experimental design was obtained by using Design-Expert® version 8.0.4 software using the simplex-centroid mixture design augmented. The working strategy for mixture design applied to the present work materials (potato peel, grass clippings and sawdust) was according to Eriksson (1998)[31]. After defining the factors and bounds for the mixture design map and also the experimental objective and mixture model (quadratic), a simple-centroid design was generated. The design points correspond to all permutations of the pure blends (e.g., 1 0 0; 0 1 0; 0 0 1), the permutations of the binary blends (½ ½ 0; ½ 0 ½; 0 ½ ½), the permutations of the blends involving three components, and so on, given a total of thirteen experiments. Each blend was characterized experimentally including the determination of the desired parameter (FAS). Then, the software analyzed these data and evaluated the best model that described the composition effects of the individual materials fractions in the FAS.

5.3. Monitoring of composting process

The reactors are equipped with a data acquisition system for on-line monitoring of temperature and oxygen concentration, and feed air flow rate was measured with rotameters. The air flow rate was controlled in order to firstly maintain the oxygen concentration of the outlet gas in the range of 5 to 15% (v/v) and at the same time control the temperature of the composting material in the reactor. The mixtures were sampled in pre-determined times (once a week) along the period of composting after revolving the reactors to ensure the representativeness of the samples. The samples were obtained from a set of sub-samples randomly collected at several different points for each of the reactors. The mass of each sample was on average 500 g. To quantify some parameters, the samples were pre-dried and milled. Characterization of the samples at each time included the determination of moisture content, organic matter content, pH, elemental composition, bulk density, FAS and biodegradability. Biodegradability of each sample was assessed by measuring lignin content using the Klason lignin method .All the determinations were performed in triplicates except the lignin content that was in duplicate due to the method time scale.

5.3.1. Temperature and air flow rate

Temperature monitoring was performed by inserting a probe into the geometric center of each of the reactors, and the data acquisition was made by an online system.

Aeration of the reactors was made through a compressed air line linked on the bases of the reactors. Measurement of air flows rates for each reactor was made using rotameters (Figure 5.2).

Figure 5.2 - Feed air flow measuring.

5.3.2. Moisture content

1. Weigh a small container;
2. Weigh about 20 g of compost into the container;
3. Dry the sample for 24 h in a 105 °C oven;
4. After drying, cool the sample in a desiccator and reweigh.

The percentage of moisture is calculated using Eq. (5.4).

$$MC(\%) = \frac{wet\ weight\ of\ the\ sample - weight\ of\ the\ sample\ after\ drying}{wet\ weight\ of\ the\ sample} \tag{5.4}$$

5.3.3. Organic matter content

1. Weigh a porcelain crucible;
2. Weigh about 2.5 g of compost into the porcelain crucible;
3. Calcinate the sample in a muffle furnace for 4 h at 550 °C;
4. After calcination, cool the sample in a desiccator and weigh.

The percentage of organic matter is calculated by Eq. (5.5)

$$OM(\%) = \frac{dry\ weight\ of\ the\ sample - calcinated\ weight\ of\ the\ sample}{dry\ weight\ of\ the\ sample} \tag{5.5}$$

5.3.4. Bulk density

The bulk density was determined according to the method described in TMECC (Test methods of the examination of composting and compost).

1. Weigh the tare of a graduated beaker;
2. Transfer a 600 cm^3 aliquot of compost into the graduated beaker through a funnel;
3. To ensure uniform packing of compost throughout the graduated beaker, allow beaker to fall freely onto an adequate support from height of 15 cm;
4. Repeat the filling with 600 mL and free falling operation, two more times (three times total). After the third free-fall drop, fill the graduated beaker to volume with sample material, 1800 mL;
5. Weigh and record gross weight of the filled graduated beaker containing 1800 mL of compost.

The bulk density is calculated by Eq. (5.6)

$$BD = \frac{weight\ of\ 1800\ mL\ sample}{final\ volume\ of\ compost\ in\ graduated\ beaker\ (1800\ mL)} \tag{5.6}$$

5.3.5. pH

1. Weigh an amount of sample equivalent to 20 mL, estimated from the bulk density of the mixture, into a flask;
2. Add 100 mL of distilled water to the flask;
3. Agitate the suspension for 2 h;
4. Measure the pH using the specific equipment.

5.3.6. Elemental composition

The elemental composition of the samples was determined by using the EA1108 CHNS-O – Fisons equipment that measured the total amount of C, H, N, S and O.

5.3.7. Free air space

The free air space depends on the bulk density (BD) and the density of substrate solids (ρ_p) and was determined using Eq. (5.7)

The determination of the density of substrate solids, ρ_p, was as follow:

1. Using a clean and dry graduate beaker of known mass, measure the density of kerosene by adding a specific volume and weighing the beaker;
2. Using another clean and dry graduate beaker of known mass, add some particulate matter of compost and weigh its mass in the graduate beaker;
3. Add kerosene until all the particles are covered and read the total volume as well as weigh the graduate beaker and its content;
4. From the kerosene mass added, compute the volume from the density in step 1; the difference in volume is that of the particles;
5. Calculate the particles density using the mass and volume calculated in the steps above.

$$FAS = 1 - \frac{BD}{\rho_P} \tag{5.7}$$

5.3.8. Biodegradability

The biodegradable fraction of the volatile solids, β, is defined as the biodegradable amount of VS (βVS) divided by the total VS input to the process. The biodegradable amount of VS is determined by measuring lignin content (LC) in percentage of VS, which means it is considered that the lignin content represent the non biodegradable fraction. The biodegradable amount of VS is calculated by Eq. (5.8) and the biodegradable fraction by Eq. (5.9)

$$\beta VS = VS - L \times VS \tag{5.8}$$

$$\beta = \frac{\beta VS}{VS} \tag{5.9}$$

The lignin content (L) is determined using the Klason method.

1. Weigh 0.5 g of dry compost into a beaker;
2. Add gradually to the beaker containing the compost 7.5 mL of 72% sulfuric acid in small increments while stirring the suspension;
3. Keep the beaker in a bath at 20 °C during dispersion of the material. After the material is dispersed keep the beaker in the bath for 2 h and stir the material frequently during this time to ensure complete dissolution;
4. Add about 150 mL of water to a flask and transfer the material from the beaker to the flask. Rinse and dilute with water to 3% concentration of sulfuric acid, to total volume of 287.5 mL;
5. Boil the solution for 4 h, maintaining constant volume by addition of hot water;
6. Allow the insoluble material (lignin) to settle “overnight”;
7. Without stirring up the precipitate, filtering the supernatant solution. Then transfer the lignin quantitatively to the filter and wash it with hot water;
8. Transfer the filter with lignin and dry in an oven at 105 °C during 4 h. Cool in a desiccator and weigh;
9. Take the sample to a muffle furnace for 4 hours at 550 °C;
10. After the 4 h in the muffle, cool the sample in desiccators and weigh.

The lignin content is determined by Eq. (5.10).

$$LC(\%) = \frac{lignin\ weighted\ in\ step\ 8 - ash\ weighted\ in\ step\ 10}{VS} \times 100 \tag{5.10}$$

6. ANALYSIS AND DISCUSSION OF RESULTS

This work has two main objectives: assess biodegradability during the composting process in pilot-scale reactors and develop a new dynamic mathematical model for predicting the behavior of aerobic composting. In this chapter, it is shown how the initial mixtures were formulated, the monitoring strategies during operation and the validation of the proposed model with experimental data.

6.1. Formulation of mixtures for composting

The raw materials used in our experiments included potato-peel industrial waste (PP), grass clippings (GC) and sawdust (SD), and Table 6.1 shows some of their most important properties for composting operation.

Table 6.1 - Characterization parameters of the raw materials used in this work.

Parameter	potato-peel (PP)	grass clippings (GC)	sawdust (SW)
Moisture content (MC) (%)	80.9	73.3	12.2
Organic matter content (OM) (%)	85.8	75.8	76.8
Bulk density (BD)(kg m^{-3})	749	154	238
pH	4.7	8.4	5.5
C (%)	48.5	52.4	54.2
N (%)	1.9	5.8	0.8
C:N ratio	26	9.0	68
Free air space (FAS) (%)	26.2	85.7	72.3

The individual materials were blended in four different formulations. The initial mixtures tested were prepared in order to ensure proper conditions, such as carbon-nitrogen (C:N) ratio, moisture content (MC) and free air space (FAS), for optimal microbial growth and organic matter degradation. The models which describe the effects of the components mixture on the C:N ratio, MC and FAS are shown in equations (6.1), (6.2) and (6.3), respectively.

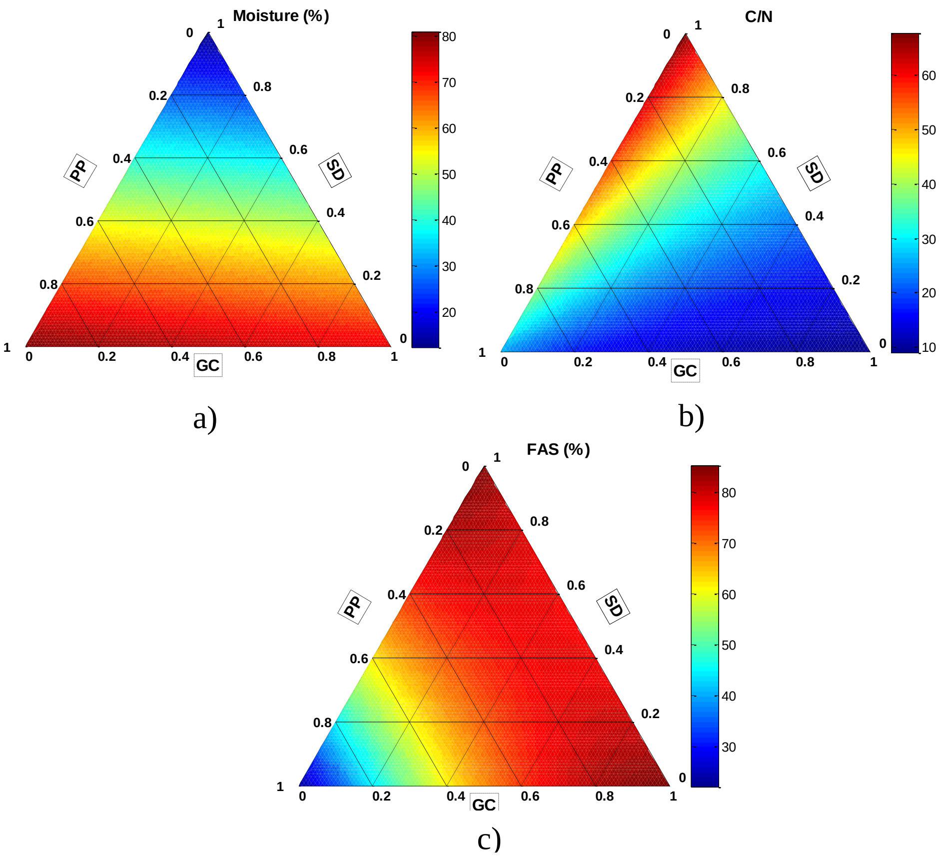
$$C{:}N_m = \frac{m_{PP}[0.48 \times (1-0.809)] + m_{GC}[0.524 \times (1-0.733)]}{m_{PP}[0.019 \times (1-0.809)] + m_{GC}[0.058 \times (1-0.733)]}$$

$$\frac{+\, m_{SD}[0.542 \times (1-0.122)]}{+\, m_{SD}[0.542 \times (1-0.122)]} \tag{6.1}$$

$$MC_m = m_{PP} \times 80.9 + m_{GC} \times 73.3 + m_{SD} \times 12.2 \qquad (6.2)$$

$$FAS = 21.64 \times PP + 84.49 \times GC + 82.34 \times SD + 66.55 \times PP \times GC + 102.43 \times PP \times SD - 69.65 \times GC \times SD \qquad (6.3)$$

The best models that described the composition effects of the individual materials fractions in the C:N ratio and moisture content were obtained from the mass balance equations (5.1) and (5.2), respectively, and the FAS model was gathered up through the mixture design method described in Chapter 5. The correlation coefficient (R^2) for FAS was 0.9975. After determining these models, simple-centroid mixture designs were drawn showing the effects of the individual materials fractions on each parameter, as shown in Fig. 6.1.



a)

b)

c)

Figure 6.1- Effects of the individual materials fractions on a) moisture content, b) C:N ratio c) FAS.

As observed, PP (potato peel) is the material that presents the highest moisture content and the lowest FAS. The SD (sawdust) has the highest C:N ratio which makes this substrate a carbon source for the composting process and also a good corrector for the excess moisture of

PP since its moisture content is low. Sawdust allows a well aerated process because of its high free air space character. Due to the low C:N ratio of GC (grass clippings this material is a good nitrogen source. According to this evaluation it is possible to conclude that the three substrates selected for making the composting mixture are adequate, since their properties are complementary.

The contour plot representing the models obtained for each of the three desired responses was overlaid to identify the area (mixture region) where all specifications can be achieved to easily choose suitable compositions for composting (Figure 6.2).

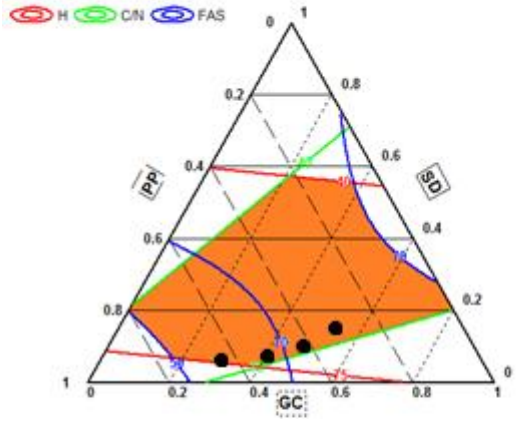


Figure 6.2 - Overlaid contour plots for blend with PP, GC and SD imposing 40%≤MC≤75%, 15≤C:N≤40 and 55%≤FAS≤70% (the upper limit for FAS is determined by the SD).

The four formulations were then selected according the points represented in the painted area and the initial compositions for each reactor are shown in Table 6.2.

Table 6.2 - Initial composition mixtures of composting.

	Mixture proportions			Weight				Predicted responses		
Reactor	PP (%w/w)	GC (%w/w)	SD (%w/w)	Total (kg)	PP (kg)	GC (kg)	SD (kg)	C: N	H (%)	FAS (%)
1	53.0	39.8	7.2	34.8	18.4	13.9	2.51	16.2	72.9	66.9
2	66.0	28.0	6.0	34.9	23.0	9.80	2.09	17.9	74.7	58.1
3	38.7	53.0	8.3	35.3	13.7	18.7	2.93	14.6	71.2	73.7
4	34.3	51.6	14.1	33.4	11.5	17.2	4.71	16.7	67.3	74.3

Firstly, an experimental characterization of the initial blends was done and some of the most important properties are shown in Table 6.3.

The error values indicated in this table were obtained by comparing C:N ratio, FAS and MC contents with their predictions shown in table 6.2. The FAS and moisture content calculated for the formulation blends are a good approximation of the real values measured analytically. The difference between the actual and the predicted C:N ratios is mainly due to the variability of the individual materials and the uncertainty associated to the analytical measurements of the elemental composition of the materials.

Table 6.3 – Characterization of initial composting mixtures.

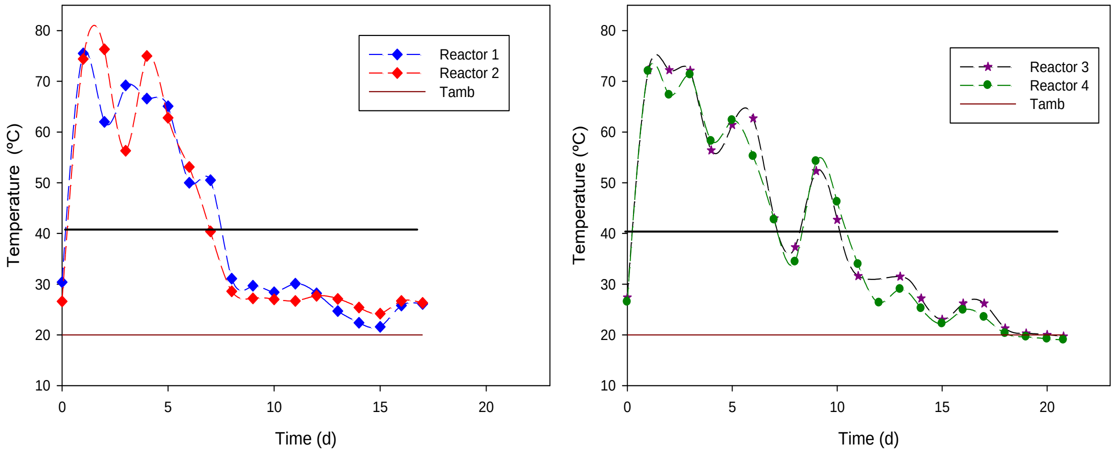
Parameter		Reactor 1	Reactor 2	Reactor 3	Reactor 4
C:N ratio	Real	20.2	17.6	18.7	19.6
	Error (%)	24.8	2	27.9	17.5
Free air space (%)	Real	70.3	63.1	73.1	71.1
	Error (%)	5.08	9.0	1.0	4
Moisture content (%)	Real	73.9	74.2	71.6	71.4
	Error (%)	1.35	0.05	0.62	6.2
Organic matter (%)		90.8	92.3	91.0	88.6
Biodegradable matter (%)		76	78.7	73.5	73.4
Bulk density (BD)(kg m^{-3})		318	388	269	268
pH		6.17	6.02	6.01	5.53
Total mass (kg)		34.8	34.9	35.3	33.4
Total volatile solids (VS) (kg)		8.2	8.2	9.1	8.5
Biodegradable volatile solids (βVS) (kg)		6.3	6.4	6.71	6.2
Non- biodegradable volatile solids ((1-β)VS) (kg)		1.9	1.7	2.4	2.2

6.2. Monitoring the composting process

During the composting process several parameters were monitorized and the results are discussed in the following sections.

6.2.1. Temperature profiles

The temperature profiles observed during the composting process are illustrated in Figure 6.3a) - b) for the Reactors 1 to 4.



a)

b)

Figure 6.3 - Temporal profile of temperature in the a) Reactor 1 and 2, b) Reactor 3 and 4.

Analyzing the temperature profiles illustrated in Figure 6.3, it can be seen that the composting process in the four reactors essentially take place within two temperature ranges known as mesophilic (20-40˚C) and thermophilic (over 40˚C) as expected. At the start of composting, the mass in the four reactors is near ambient temperature. Due to the oxidative action of microorganisms, the temperatures of the composting mixtures follow a pattern of rapid increase to about 75˚C, and remain in thermophilic level for 7 days in reactor 1 and reactor 2, and 10 days in reactor 3 and reactor 4. Thus, it can be concluded that the hygienization of the mixtures was achieved, since there was the maintenance of thermophilic temperatures for several days in the four reactors. After the thermophilic phase the microbial activity decreases, and so the temperatures gradually drop to ambient air temperature. At this last phase, although the compost temperature is close to ambient, chemical reactions continue to occur that make the remaining organic matter more stable.

The "oscillations" observed of the temperature are related with the fact that it is difficult to maintain homogeneity of the mixture throughout the composting process, despite the aeration and the homogenization of mixtures at least once a week. As shown in Figure 6.3, the times when the temperature rises (except for the first phase of rapid increase in temperature corresponding to intense microbial activity) are the moments after revolving the reactors.

6.2.2. Composting material profile

During composting there is a significant reduction of weigh due to the microbial decomposition of the biodegradable organic matter (according to Eq. 2.1) as shown in Figure 6.4.

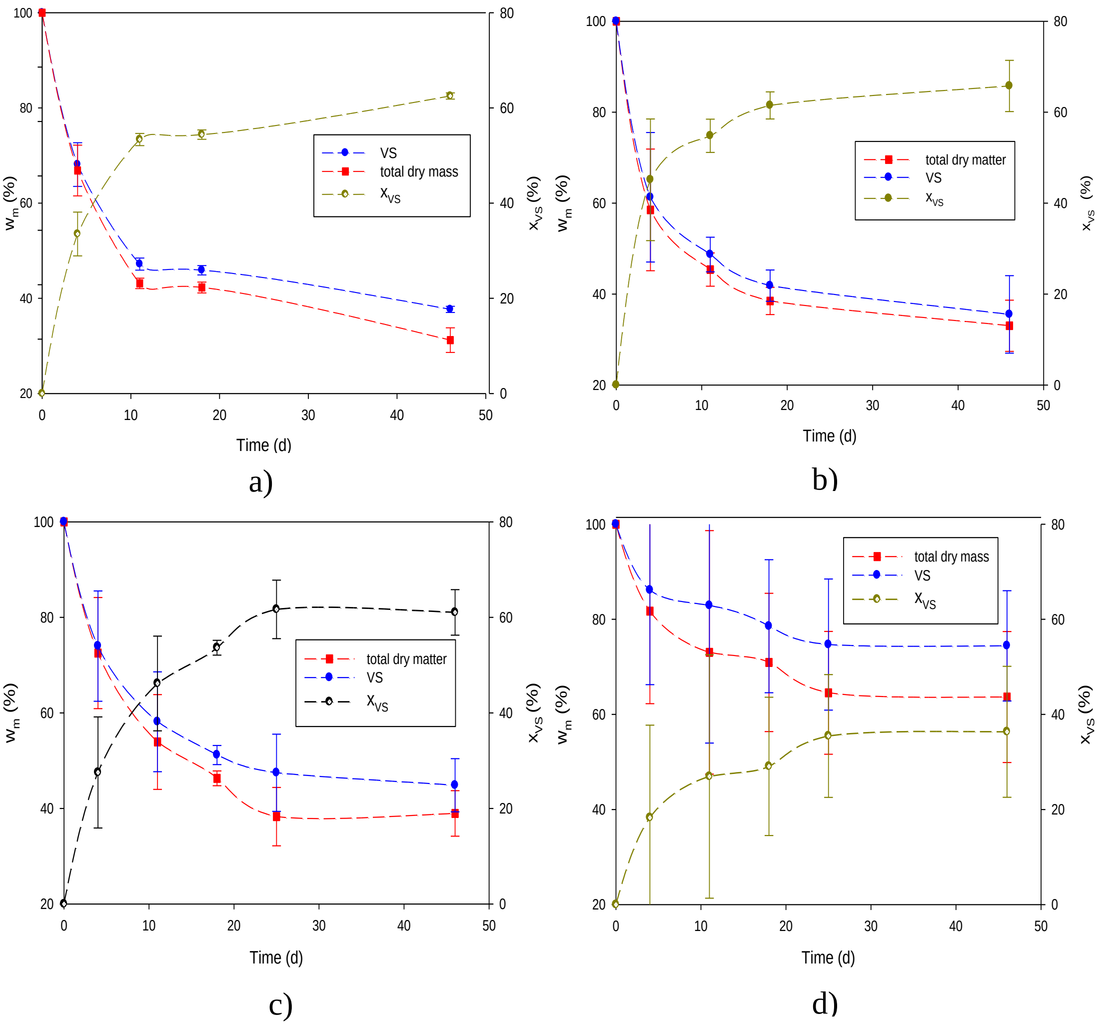
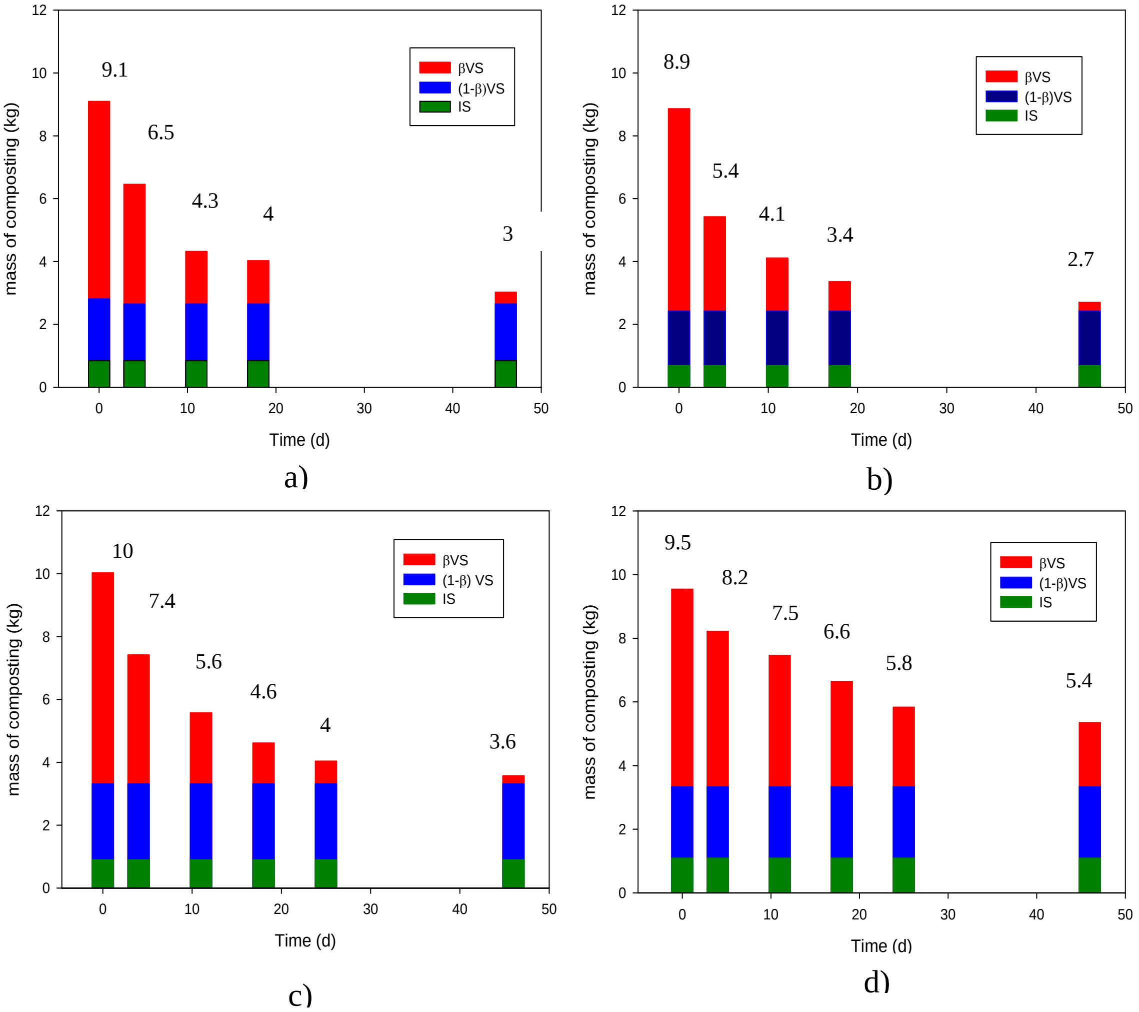


Figure 6.4 Temporal evolution of the percentage of dry matter, volatile solids and the conversion of volatile solids in the a) Reactor 1, b) Reactor 2, c) Reactor 3, d) Reactor 4.

The percentage mass in each reactor (W_m) is computed over the composting process as the ratio between the mass of mixture at the sampling time and the mass at the beginning of the composting process. As shown in Figure 6.4 this parameter is calculated for both the total dray mass and the volatile solids (VS) in each reactor. There is, as expected, a significant reduction of the composting mass in the four reactors due to microbial degradation of organic matter present in compost mixtures. However, the conversion of organic matter in the reactor 4 was lower, about 36%, compared to the conversions observed in the other reactors, which exceed 60%. This can be justified by the unpredictable nature of the microorganisms activity and the availability of biodegradable organic matter due to non-homogeneity of the mixture. The dry mass loss during the composting process, in quantitative terms, is shown in Figure 6.5 for each reactor.



a) b) c) d)

Figure 6.5 - Composting mass during the process in the a) Reactor 1, b) Reactor 2, c) Reactor 3, d) Reactor 4.

As shown in Figure 6.5 the mass loss in the reactor 4 is much smaller compared to other reactors. The reactor 4 begins with a mass of 9.5 kg and at the end of composting remaining 5.4 kg, while in reactor 3, for example, despite starting with a relatively greater mass (10 kg), at the end of composting the amount of material mixture is lower (3.6 kg) compared to the reactor 4. Figure 6.5 also shows that the mass loss in the composting process is due only to the degradation of biodegradable volatile solids (βVS), which is calculated using equation (5.11). In Table 6.4 it is shown the mass that is biodegradable at the beginning and the end of composting and the fraction that it represents in relation to the total dry mass.

Table 6.4 - Biodegradable material in the initial and final blends.

		Reactor 1	Reactor 2	Reactor 3	Reactor 4
Biodegradable mass (kg]	At the beginning of composting	6.3	6.4	6.7	6.2
	At the end of composting	1.6	1.4	1.6	2.5
Biodegradable fraction (%)	At the beginning of composting	76	78.7	73.5	73.4
	At the end of composting	19.8	17.4	17.2	29.5

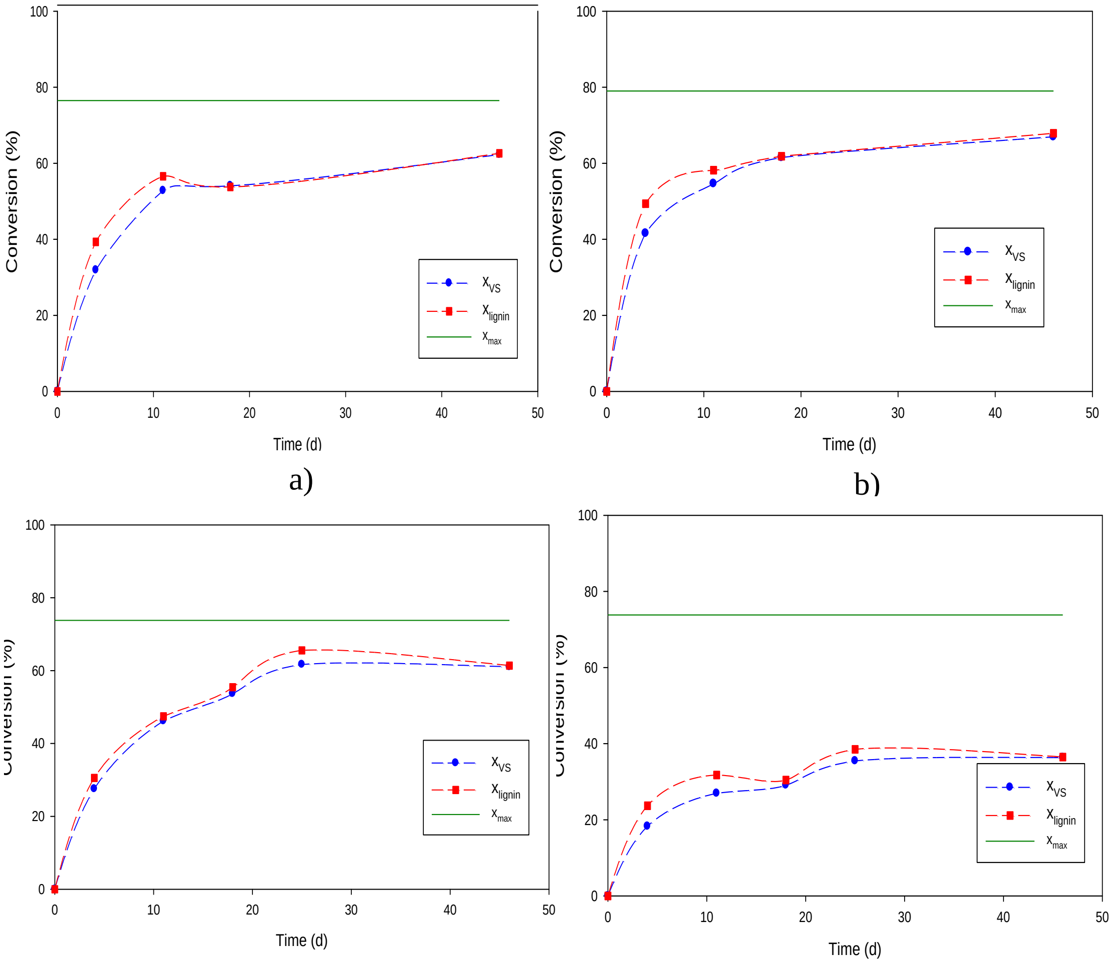
It is important to note, from Table 6.4 and Figure 6.5, that not all biodegradable mass was degraded by the end of the composting period analyzed. The remaining biodegradable mass could still be degraded (mainly in the reactor 4 which still has a high proportion of material capable of be degraded) if the compost period was extended.

6.2.3. Organic matter biodegradation by lignin assessment

From the measurement of lignin content of the initial composting mixtures for each reactor, it was possible to predict the conversion of organic matter that would be obtained if all biodegradable organic matter was degraded, resulting in the maximum conversion of organic matter (x_{max}). The conversion of organic matter for each instant t is calculated by Eq. (6.4).

$$x_t = \frac{VS_{t-1} - VS_{t+1}}{VS_{t-1}} \tag{6.4}$$

The lignin content was also monitored throughout the composting process and consequently the conversion of organic matter in the process was also estimated from this determination. Figure 6.6 shows the comparison of the conversion of organic matter obtained experimentally with the conversion measured from the quantification of lignin in each sampling periods prescribed. It also shows the maximum conversion of organic matter predicted for each reactor.



a)

b)

c)

d)

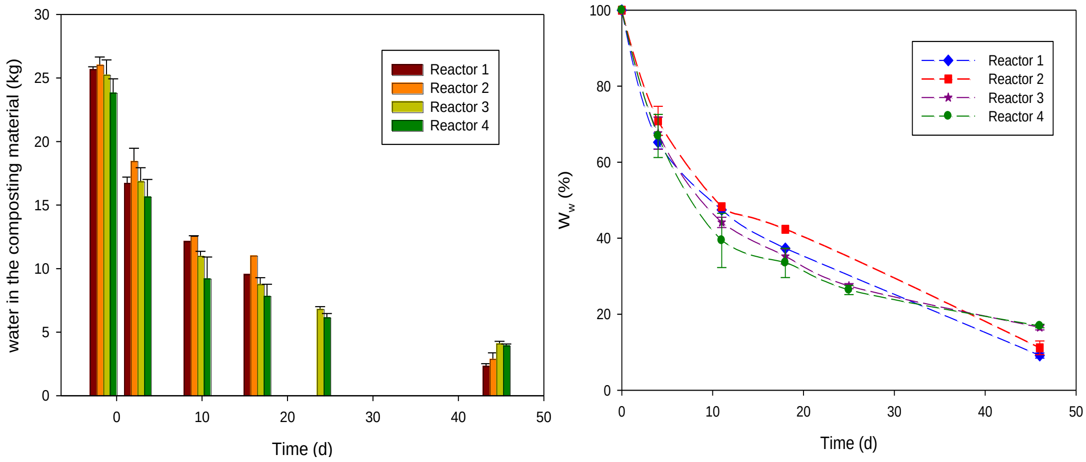
Figure 6.6- Conversion of organic matter obtained experimentally and by measured from the quantification of lignin in a) Reactor 1, b) Reactor 2, c) Reactor 3, d) Reactor 4.

Figure 6.6 shows that the evolution of the conversion of biodegradable organic matter assessed by measurement of lignin content, x_{lignin}, is very close to one observed experimentally by assessing organic matter conversion (x_{VS}). In the four reactors, it is verified that the conversion of organic matter stays below the maximum conversion predicted by lignin content measurement.

In summary, the results indicated that independently of the initial mixture composition, there is an increase in lignin content that can be related to the decrease of the potential for biodegradation of the tested mixtures. The initial samples with the lower and higher lignin content (Reactor 2 and Reactor 4) showed a greater and smaller mass reduction, respectively, at the end of composting period. These results showed that higher lignin content of an initial mixture led to lower biodegradation of the mixture.

6.2.4. Water content profile

Water content is very important factor to be controlled during composting as it influences the structural and thermal properties of the material, as well as the rate of biodegradation and metabolic process of the microorganisms. In Figure 6.7 it is shown the water content profile in the composting mixture during the process.



a) b)

Figure 6.7- Water content profile in the composting material during the process a) mass content, b) percentage content.

The water in compost comes from either the initial feedstock or the metabolic water produced by microbial activity. However, during aerobic composting, some heat energy is released, which vaporize water in composting material. This water loss is further coupled with losses due to aeration. As shown in the Figure 6.7, the loss of water in the four reactors during the composting process follows the same profile. In the Figure 6.7 b) it is clear that, in percentage terms, reactors 1 and 2 lost the same amount of water as well as Reactors 3 and 4 when compared with each other. Reactors 1 and 2 lost more water at the end of composting because they were opened before the end of the period prescribed for compost analysis.

6.2.5. C:N ratio

The C:N ratio is an important factor to take into account at the beginning and throughout the composting process and Figure 6.8 shows the evolution of this parameter during the process.

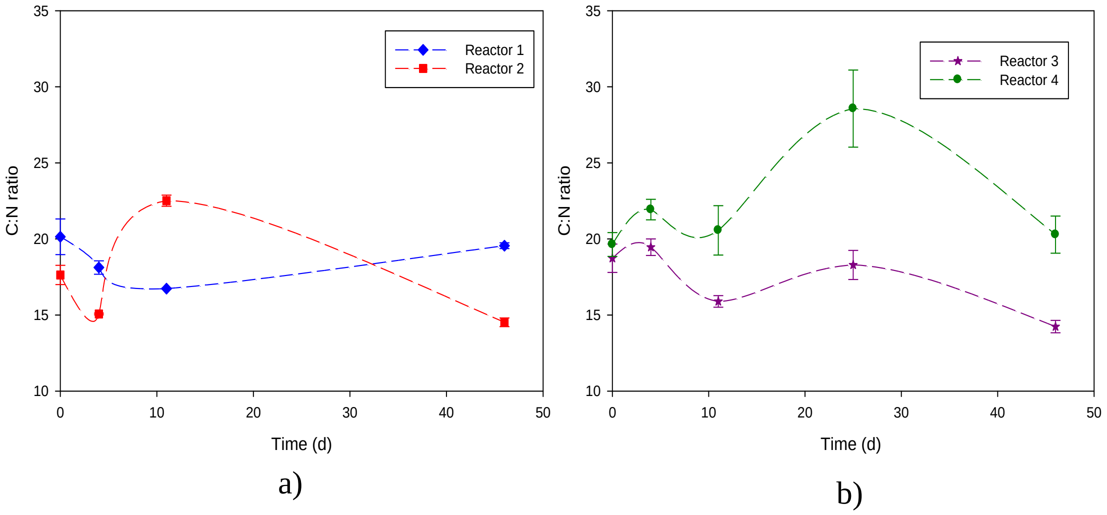


Figure 6.8 - Evolution of the C:N ratio in the a) Reactors 1 and 2, b) Reactors 3 and 4.

Usually the C:N ratio gradually decreases during composting, because of the loss of CO_2 from the starting materials. The amount of carbon lost during composting usually exceeds the nitrogen loss. However, in this experiments the starting C:N ratios are relatively low in the four reactors, less than 21:1 , thus the nitrogen losses may have been large to cause little change in the C:N ratio in the four reactors. On the other hand, the uncertainty in the quantification of N (see Appendix B) also enhances the differences of the results of the C:N ratio obtained since this is quantified in total basis and is N present in various forms. In addition, the homogeneity of the sample is a relevant aspect of these measurements, which are made with very low amounts (a few milligrams). It is worth to emphasize that the measurement of N is done after the sample is dry which potentiates the loss of N as ammonia. Thus, the uncertainties in the measurement of N strongly influence the profile of the C: N ratio.

6.2.6. Monitoring of other parameters

During the composting, other parameters were also evaluated to obtain a better understanding of the process evolution. Figure 6.9 shows the evolution of bulk density (BD) and free air space (FAS) in the four reactors.

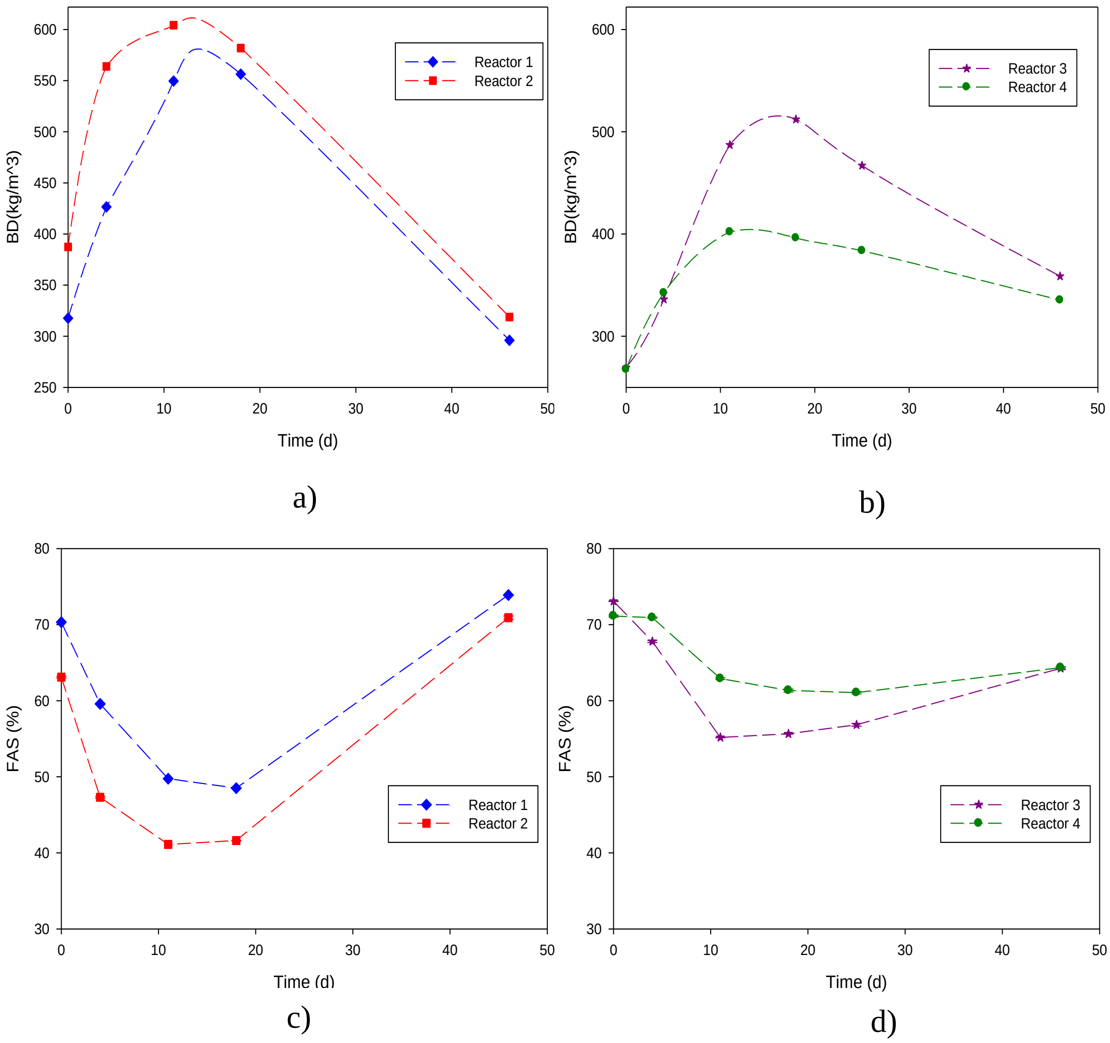
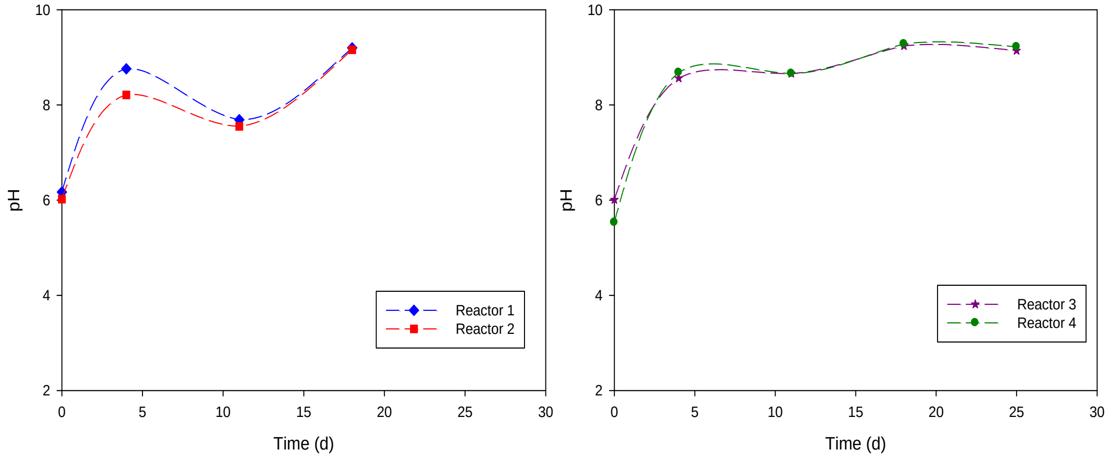


Figure 6.9 - Evolution of bulk density, a) and b), and the free air space, c) and d), during the composting process in Reactor 1 to 4.

Substrate FAS and BD carry a great influence on composting performance since appropriate conditions of the physical environment for air distribution must be maintained during the process. Usually during composting, the material tends to be more compacted, as the particulate material become more homogeneous. Thus, The evolution of the BD and FAS in the Reactors 3 e 4 (Figure 6.9 b) and Figure 6.9d)) follow the expected pattern. On the other hand, in Reactors 1 and 2, the bulk density (Figure 6.9 c)) increases dramatically, which indicate the increase of the materials compaction and so the decrease of the space available for air (Figure 6.9 a)). As high bulk density does not allow the air movement through the mixtures these reactors (Reactor 1 and Reactor 2) may had some areas of the reaction mixture under anaerobic conditions, which generated unpleasant odors.

Although not essential, periodic pH measurements are useful in monitoring the conditions in the reactors, and Figure 6.10 shows the evolution of this parameter along time.



a) b)

Figure 6.10 - Evolution of the pH during the process in a) Reactor 1 and 2, b) Reactors 3 and 4.

As can be seen in Figure 6.10, the composting mixtures start slightly acid. As composting process proceeds, the high temperatures accelerate the breakdown of proteins and fatty acids formed at the beginning of composting, resulting in the release of ammonium and an increase in the pH, which reach values exceeding 9.0 in the four reactors. Then the pH is expected to stabilize or drop slightly again to near neutral as a result of humus formation with its pH buffering capacity at the end of composting activity.

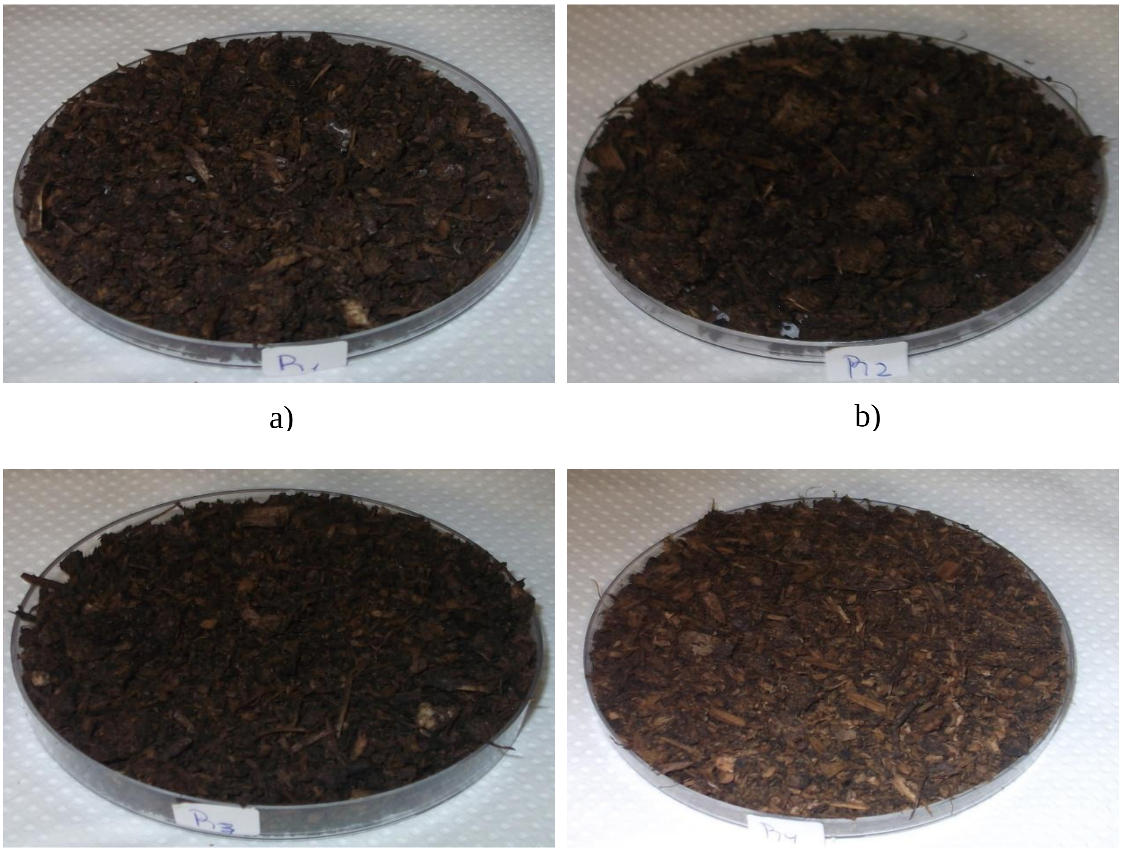
6.3. Stability analysis of the finished compost

The finished compost aims to have beneficial effects on soil, but this depends on its quality. In this work, the quality criteria for composts are established based on the assessment of the stabilized organic matter. Physical characteristics such as color and odor were also taken in account.

The establishment of a generally accepted stability index suitable to be used as a routine test at a large-scale composting facility is still a major area of research in waste management. According to Haug (1993), compost is sufficiently stabilized when the rate of oxygen consumption is reduced to the point in which anaerobic or malodorous conditions are not created such that they interfere with the storage, marketing and use of the end product.

Several indicator variables have been proposed for monitoring the process and evaluating the stability of the compost In our study it was made the analysis of biodegradable constituents and organic matter nutrient content, C:N ratio.

In terms of nutrient content, Reactor 3 presents the best results as the C:N ratio during compost tends to decrease as expected. The composted raw mixture C:N ratio was reduced from 19 to 14 (on average basis), which is a good indicator of the stable humified organic matter in the finished compost product (Figure 6.8 b)). The dark color observed in composted material of the Reactor 3, (Figure 6.11c)), further supported this premise. The C:N ratio of finished compost is reported to be in range of 10 to 17, depending on the initial compost mixture[1]. Although the C:N ratio in the Reactor 2 increases at the start of composting, this parameter returns to decrease and reaches a low value (C:N=14) in the established range for stable compost, which is not verified in the Reactors 1 and 4.



a) b)

c) d)

Figure 6.11 - Products at 46 days of the composting process a) Reactor 1, b) Reactor 2, c) Reactor 3),d) Reactor 4.

The analysis of biodegradable constituents of the end products for each reactor is made by the calculation of the stability degree of the organic matter (SD). Stability degree is related to Klason method of lignin content determination, which was enhanced and applied by López (2010). This method allows determination of the stability of organic matter through resistant organic matter (equation (6.4))

$$\mathrm{SD}\ (\%) = (1 - \beta_{\mathrm{end}}) \times 100 \tag{6.5}$$

where β_{end} is the fraction of biodegradable organic matter at the end of compost. The SD of the four reactors were calculated using the Eq. (6.1) and the results are shown in Table 6.5.

Table 6.5 - Stability degree of the finished composts.

	Reactor 1	Reactor 2	Reactor 3	Reactor 4
Stability degree SD (%)	80.2	82.6	82.8	70.5

As shown in Table 6.5, the Reactors 2 and 3 achieved the highest stability degree of the organic matter at end of composting. Reactor 4, on the other hand, reached the lowest degree of stability since the percentage biodegradable organic matter available at end was high. The determination of lignin content was based on two replicates in each sample; therefore, the values indicated in Table 6.5 are mean values between the two determinations.

6.4. Model evaluation

The model presented in Chapter 3 was used simulate profiles of temperature, VS and water for each reactor along time. A simple sensitivity analysis was also performed to evaluate the relative importance of selected model parameters. All the calculations and simulations were made in Matlab R2009b.

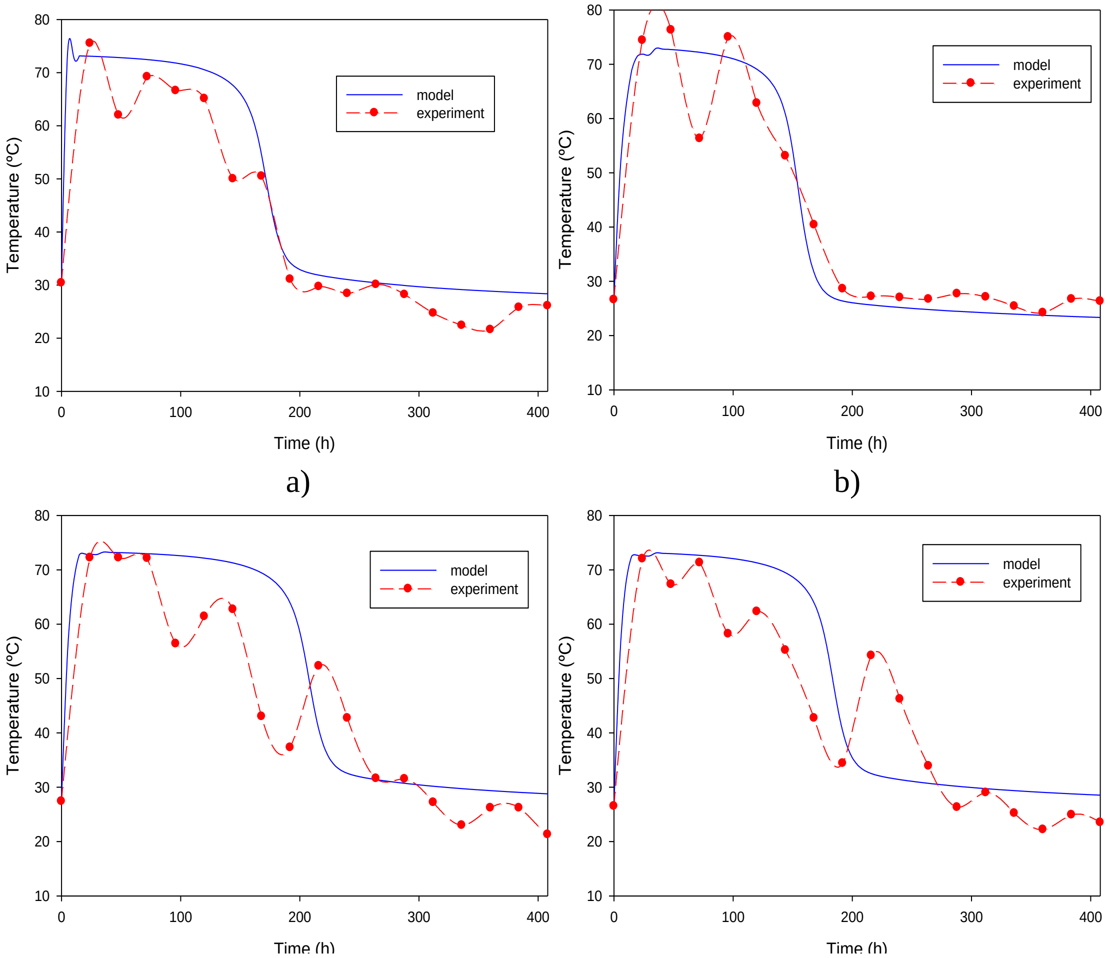
6.4.1. Model Simulations

By comparing model prediction with experimental data, the mathematical model may be validated and a quantitative measure of performance was calculated. The quality of the model fitting to the experimental data was evaluated by the average percentage deviation of the estimates (AD), which was calculated using Eq. (6.6).

$$AD = \frac{1}{\mathrm{N}}\sum_{\mathrm{i}=1}^{\mathrm{N}}\left|\frac{\mathrm{R}_{\mathrm{exp,i}} - \mathrm{R}_{\mathrm{model,i}}}{\mathrm{R}_{\mathrm{exp,i}}}\right| \times 100 \tag{6.6}$$

where $R_{exp,i}$ and $R_{model,i}$ are the individual values obtained experimentally and by simulation, respectively, at each process time analyzed. N is the number of individual values considered.

Comparisons of temperature between simulations and experimental results were performed for the first 408 h for each reactor as shown in Figure 6.12.



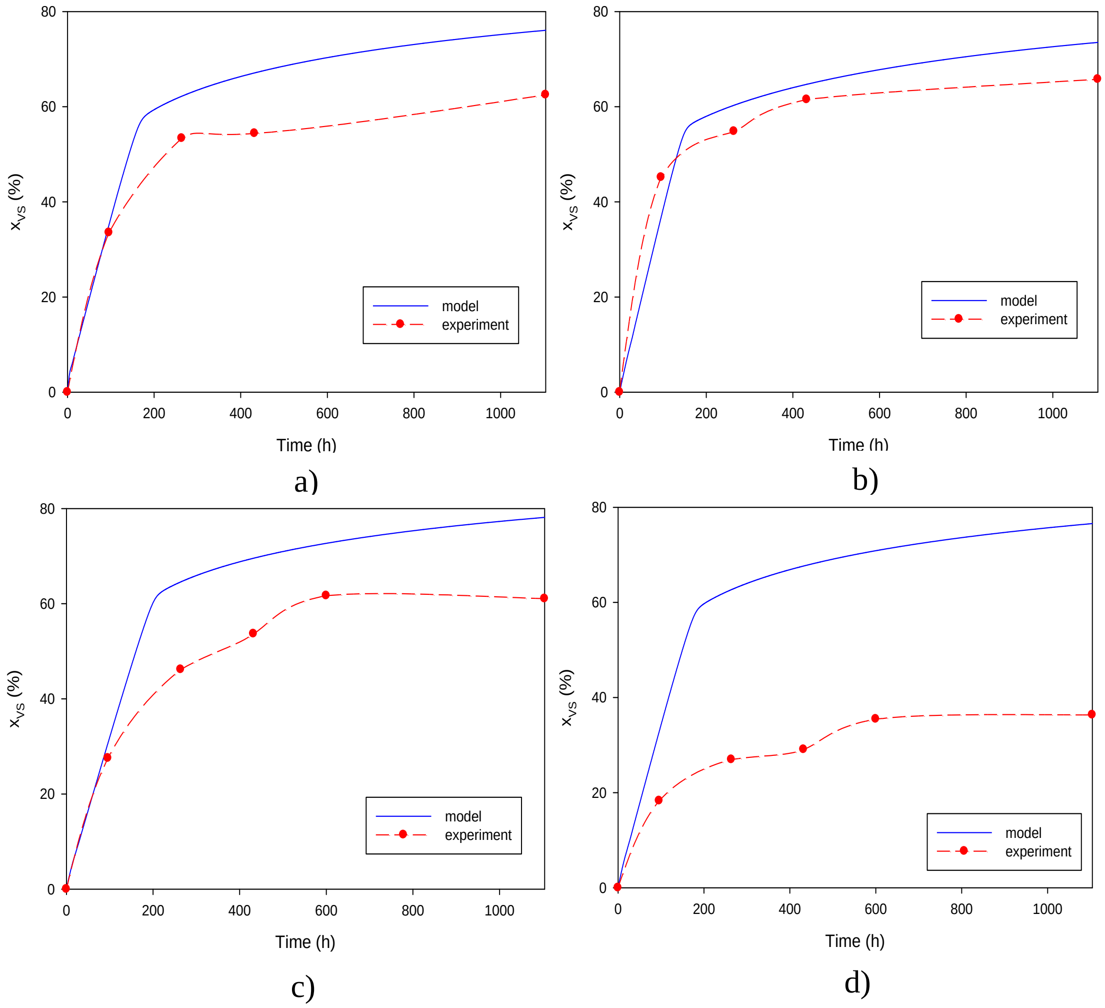
a) b)

c) d)

Figure 6.12 - Comparison of experimental data and model predictions for temperature in a) Reactor 1 b) Reactor 2, c) Reactor 3, d) Reactor 4.

By comparing simulated and experimental results of the temperature profile in the reactors showed that the best fitting results were observed for Reactor 2 as the calculated average percentage deviation for this reactor was the lowest comparing with other reactors. In fact, the average percentage deviations (AD) between simulation and experimental results are 12%, 9%, 19% and 18 % for Reactor 1, Reactor 2, Reactor 3 and Reactor 4, respectively. It is important to note that maximum differences between modeled and experimental temperature profiles occurred in the times after revolving the reactors in the experiments. This difference in the temperature profiles can be explained by the fact that the model has been constructed assumed perfect mixing conditions, which was not observed in the experiments, hence the need for periodic revolving of the reactors.

Regarding volatile solids conversion, the simulations and experimental results were performed for 1104 h for each reactor as shown in Figure 6.13.



a)

b)

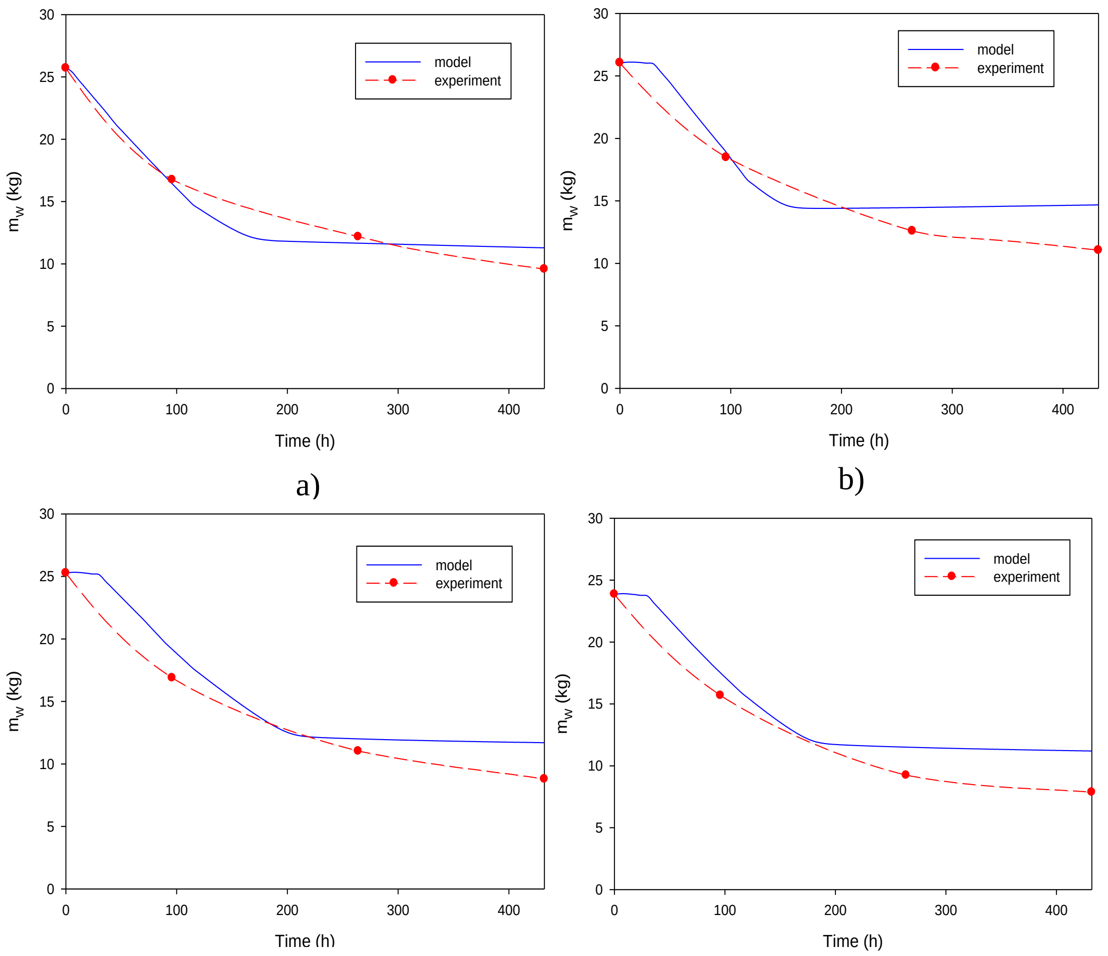
c)

d)

Figure 6.13 - Comparison of experimental data and model predictions for volatile solids conversion in a) Reactor 1 b) Reactor 2, c) Reactor 3, d) Reactor 4.

During the 1104 h of composting process, the predicted values of volatile solid conversion in the Reactor 1 to 4 were 76%, 73%, 78% and 77% respectively. Experimentally the results for x_{VS} were 62 %, 66%, 61% and 36% for Reactor 1 to 4, respectively, and the corresponding average percentage deviation, AD, were 13%, 9%, 21% and 92%. Taking the AD values into consideration, the simulation of mathematical model for volatile solids conversion gives a reasonable prediction for Reactor 1 to 3, but not for Reactor 4. This high deviation in Reactor 4 is due to the weak substrate degradation observed experimentally.

Comparisons of water profile between the simulations and experimental results were performed for the first 432 h as shown in Figure 6.14.



a) b) c) d)

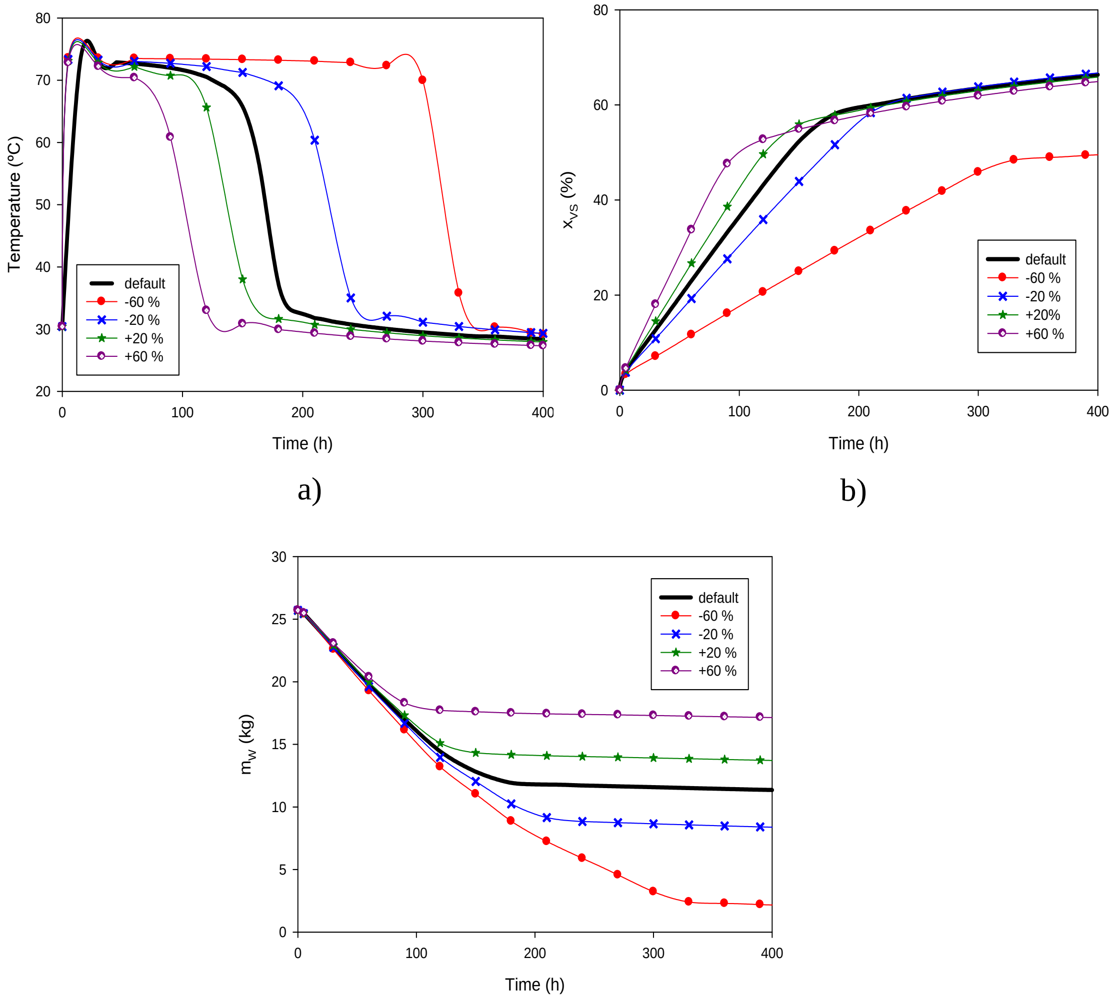
Figure 6.14 - Comparison of experimental data and model predictions for water loss in a) Reactor 1 b) Reactor 2, c) Reactor 3 and d) Reactor 4.

These periods of comparison between the simulations and experimental data was because at this moment the reactors were maintained opened and significant water losses occurred. The average percentage deviation, AD, between the predicted and experimental water profile values for Reactor 1 to 4 are 6%, 13%, 14% and 20%, respectively.

6.4.2. Analysis of sensitivity

Sensitivity analysis of state variables to some key parameters that were held constant during simulation was performed to assess the robustness of the model. The parameters examined were the overall heat transfer coefficient (U) and the reaction enthalpy (ΔH_{rx}), and in these simulations all other parameters were set at their default values (Table 3.2). Both parameters were varied to ± 60% and ± 20% of its default values, and simulations were done over a 400 h simulation period. All parameter values used are shown in Table 6.6. As an example, temperature, conversion of organic matter and water profiles in Reactor 1 were the output values examined during a simulation period of 400 h. Results from this analysis are shown graphically in Figures 6.15 and Figures 6.16

In this work, the sensitivity of the model is evaluated by calculating the average percentage deviation between the profile obtained by using the default values and the profile obtained with variations of the parameters analyzed based on Eq. (6.6).

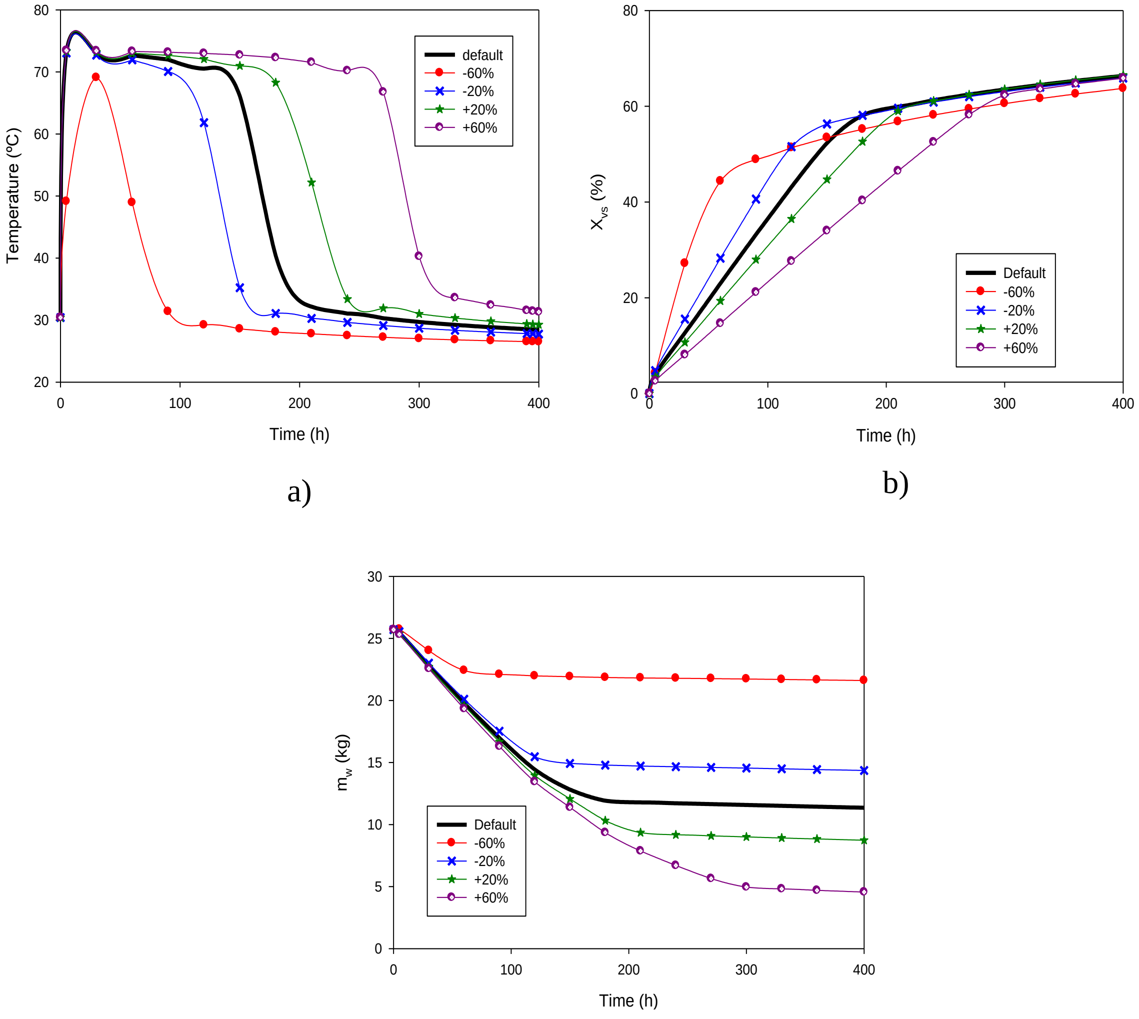


a)

b)

c)

Figure 6.15 - Effect of overall heat transfer coefficient, U, variation on the a) temperature, b) organic matter conversion and c) water.



a)

b)

c)

Figure 6.16 - Effect of reaction enthalpy, ΔH_{rx}, variation on the a) temperature, b) organic matter conversion and c) water.

Table 6.6 - Parameter values in sensitivity analysis.

Parameter	Unit	Percentage change in parameter analysis (%)	Value	Average percentage deviation (%)		
				T	X_{VS}	M_w
U	$J\ h^{-1} m^{-2}\ K^{-1}$	-60	4.63×10^3	39	34	45
		-20	9.26×10^3	12	6	16
		Default	1.16×10^4	na	na	na
		+20	1.39×10^4	6	4	14
		+60	1.85×10^4	12	11	35
ΔH_{rx}	$J\ kg_{OM}^{-1}$	-60	9.08×10^6	21	23	58
		-20	1.82×10^7	7	8	16
		Default	2.27×10^7	na	na	na
		+20	2.72×10^7	10	7	12
		+60	3.63×10^7	33	21	27

*na- not applicable

The effect of U and ΔH_{rx} on state variables are significant, and thus, their real values should be assessed carefully while developing a mathematical compost model. According average percentage deviations indicated in Table 6.6, the most sensitive state variable seems to be the water content while the organic matter conversion, x_{VS}, showed in general the smallest influence.

As expected, the increase or decrease of U and ΔH_{rx} has opposite consequences on the objective functions, since U is related with the lost of heat in the system and the ΔH_{rx} with the generation heat on the system. The deviations observed on T, x_{VS} and M_w when U and ΔH_{rx} change by $\pm$ 60 % functions are very high (Table 6.6). Therefore, it should be concluded that the values of U and ΔH_{rx} are far away from the real one

Still for the sensitivity analysis, the importance of each of the correction factors (F(T), F(W), $F(O_2)$ and F(FAS)) on the reaction rate constant (Eq. (3.4)) was assessed. Figure 6.17 shows the profile of reaction rate constant, k, along time, for Reactor 1.

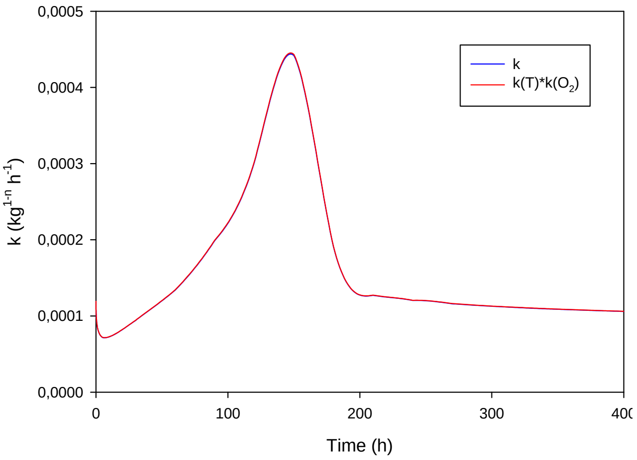
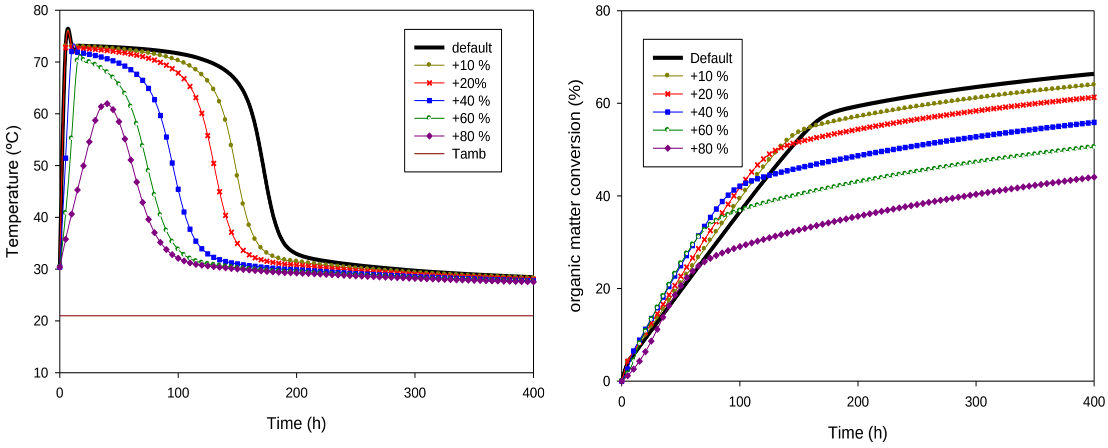


Figure 6.17 - Sensitivity analysis with the effect of the correction factors (F(T), F(W), F(O2) and F(FAS)) on the reaction rate constant.

These results show that the reaction rate constant was only affected by temperature and oxygen concentration. During first 30 h, k first decreased from 1.19×10^{-4} to 9.41×10^{-5} $kg^{1-n} h^{-1}$ (n=2.89), and then increased sharply to 4.42×10^{-4} $kg^{1-n} h^{-1}$. From 150 to 200 h k decrease rapidly to 1.27×10^{-4} $kg^{1-n} h^{-1}$.

The effect of the variation of inorganic initial content on the temperature and organic matter conversion was also assessed and thus, the mass of organic matter in the initial mixture was examined. The inorganic material is incorporated in 10%, 20%, 40%, 60% and 80% (w/w). Results of this analysis are shown graphically in Figure 6.18, for Reactor 1.



a) b)

Figure 6.18 - Analysis of the effect of initial inorganic matter content variation on the a) temperature and b) organic matter conversion.

The results obtained from the composting simulation indicate that the process temperature and organic matter conversion are sensitive to the organic matter content as expected. As shown in Fig. 6.18 a) the decrease of organic matter content leads to a decrease on the maximum temperature achieved and on the time of maintenance of thermophilic temperature which is not suitable in terms of hygienization because it narrows the safety margin for deactivation. This premise is supported by the calculation of safety margins (SM) for total die-off of pathogens that represents the number of times limit (*t*) of no viable pathogens is achieved, supposing a 12 $\log_{10}$ inactivation at temperature (T) above 55 º C [41] (Eq. (6.7))

$$\mathrm{SM} = \frac{\mathrm{t}}{\mathrm{Ed(T)}} \tag{6.7}$$

where Ed is the time for total die-off at temperature above 55 ºC during the time interval t. Calculated from Eq.(6.8) for Salmonella inactivation.

$$\mathrm{Ed} = 75.4 \times 10^{-0.1466(\mathrm{T}-45)} \tag{6.8}$$

In our experiments safety margins achieved for Salmonella inactivation were 108, 97, 66, 46 and 23 for 10%, 20%, 40%, 60% and 80% of incorporated inorganic matter, respectively. Independently of the % of inorganic matter incorporated in the mixture, composting process can be driven successfully until thermophilic temperatures superior to 55 ºC. Only incorporation up to 80% (w/w) does not fulfill the criteria of maintaining temperatures superior to 55 ºC during 3 consecutive days for pathogen reduction, achieving 55 ºC during 2.5 days [42].

7. CONCLUSIONS AND PROSPECTS FOR FUTURE WORK

This work had two main objectives. The first one was to predict the biodegradability of initial waste mixtures and to investigate how this property progresses during the composting process in pilot-scale reactors. The second objective was to develop a dynamic mathematical model for aerobic composting process and its validation by fitting experimental data.

The experimental apparatus consisted in four self heating reactors with 120 L of internal volume and isolated where four different blends made from potato-peel industrial waste, grass clippings and sawdust were composted.

The process monitoring included temperature, mass content, moisture content, pH, bulk density, free air space, biodegradability of organic matter and other parameters. Concerning to the temperature monitoring, it was found that the four reactors quickly reached thermophilic temperatures and remained in this range for several days, which allowed the compost hygienization. The organic matter conversion was above 60% except for Reactor 4, which only reached the maximum organic matter conversion of 36%.

The assessment of biodegradability of organic matter by determining of lignin content proved to be an appropriate methodology for this purpose since the predictions for the biodegradation of organic matter were consistent with those obtained experimentally. The estimation of the maximum biodegradation of organic matter was made considering that all biodegradable organic matter present in the initial mixture will be degraded. In practice, the degradation of organic matter is not complete, which explains the difference between the maximum biodegradation estimated from the determination of lignin and the one observed experimentally. The great disadvantage of this methodology is related to the time scale to determine the lignin content in each sample (approximately 2 days). Reducing the time required for lignin determination is a challenge to be evaluated in future work because it would allow the suitability of this method in cases of full-scale composting. In terms of compost characterization, Reactors 2 and 3 present the best results as the finished compost had good level of stabilized humified and organic matter.

By comparing simulation and experimental results it was concluded that the developed model could be used for simulating solid waste composting processes. Namely, temperature of substrate, organic matter conversion and water profile in the composting system fitting well the experimental data. The model was described by a set of 4 differential equations state variables (3 corresponding to mass balances and 1 related with energy balance. Since the model showed good results, it could be used for explaining and demonstrating the complex interactions which occur in the composting process and also to simulate the efficiency and cost of compost processes under different operation conditions. Adjusting operation conditions by changing key factors (eg. Overall heat transfer coefficient), optimal operation condition could be determined. For future work in this area, the overall heat transfer coefficient and reaction enthalpy should be determined specifically for the system analyzed, since both have significant effect on the model predictions. Other important aspect to be improved in future is the fact that the model could take in account the heterogeneous nature of the system.

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APPENDIX

A- Characteristics of the equipment used
B- Elemental composition of the samples
C- Mathematical model program in Matlab

A- Characteristics of the equipment used

Characteristics of the reactors isolation:

- Product Brand: MSR Manta Aeroflex;
- Type of material: foam rubber;
- Thickness: 19 mm;
- Number of layers to be applied in each reactor: two layers, a total of 38mm thick;
- Electrical conductivity: 0.035 W / m.K.

Characteristics of the temperature sensors

- Product reference : Bresimar.T.K.1.8.500.S5
- Thermocouple, Type: K;
- conductors combination: Nickel-Chromium-Nickel;
- Sheath diameter: 8 mm;
- Length of sheath: 500 mm;
- sheath coating : stainless steel AlSl316;
- Thermocouple cable length: 5 m;
- Thermocouple temperature range: 0 to 1100 ° C;
- Coating connecting cable: silicone (supports up to 200 ºC)

Characteristics of the oxygen sensors

- Product reference: *Oxygen gas sensor* XLS1047;
- Percentage concentration range: 0 to 100% oxygen;
- Resolution: 0.03% (12bit);
- Response time: 90% - 30 seconds;
- Relative humidity: 0-95%;
- Temperature range: 0 to 50 ° C

B- Elemental composition of the samples

The elemental composition of the each sample collected in Reactor 1 to 4 was determined during the composting time and analyzed in a EA1108- Fisons

The operating principle for determining C, H, N and S is based on the instantaneous oxidation of all organic and inorganic substances and their conversion to combustion products (N_2, N_xO_y, CO_2, H_2O, SO_2, SO_3, etc.) using high purity oxygen. The combustion gases are then reduced or oxidized to N_2, CO_2, H_2O and SO_2 and these compounds are introduced into a chromatography column, where they are separated and subsequently detected in a conductivity detector, which produces a signal proportional to the concentration of components in the mixture. In the analysis of oxygen, the sample undergoes flash combustion in an atmosphere of He, and O2 is released as CO that reaches the chromatographic column and is detected in a specific conductivity detector. The Concentration of S is lower than the detection limit (DL) for all samples, which is 100 ppm.

Table B1. Elemental composition

Sample	Sampling time	% C (w/w)	% N (w/w)	% H (w/w)	% O (w/w)
Reactor 1	15.04.2011	42.538	1.995	6.173	28.451
		42.646	2.444	6.238	28.036
		41.836	1.931	5.995	28.131
	19.04.2011	44.303	2.592	5.486	
		45.988	2.522	6.019	
		45.868	2.409	6.400	
	03.05.2011	44.738	2.690	4.956	
		45.175	2.690	5.251	
		44.172	2.631	5.841	
	31.05.2011	47.127	2.455	6.086	
		47.040	2.411	5.655	
		46.051	2.306	5.356	
Reactor 2	15.04.2011	43.503	2.606	6.720	29.053
		43.217	2.239	6.425	29.562
		43.184	2.554	6.558	29.043
	19.04.2011	47.702	3.142	6.802	
		48.669	3.266	6.752	
		49.171	3.250	6.656	
	03.05.2011	49.757	2.232	5.736	
		49.756	2.262	5.695	
		49.874	2.145	5.867	
	31.05.2011	41.854	2.986	5.727	
		41.721	2.704	5.791	
		41.475	2.937	6.047	

Sample	Sampling time	% C (w/w)	% N (w/w)	% H (w/w)	% O (w/w)
Reactor 3	15.04.2011	46.214	2.210	6.825	28.085
		45.313	2.669	6.771	27.158
		45.249	2.471	6.672	27.060
	19.04.2011	48.197	2.352	6.738	
		47.873	2.439	6.863	
		47.850	2.620	6.524	
	03.05.2011	47.919	2.832	6.207	
		46.508	3.099	6.539	
		47.777	3.033	6.290	
	10.05.2011	53.549	3.061	6.457	
		53.503	2.587	4.787	
		53.822	3.223	5.855	
	31.05.2011	41.734	2.696	5.608	
		42.045	2.997	5.728	
		42.423	3.211	4.947	
Reactor 4	15.04.2011	44.246	2.358	6.639	26.077
		44.930	2.091	6.592	26.093
		44.976	2.412	6.280	26.198
	19.04.2011	47.478	2.173	6.403	
		47.755	2.058	6.371	
		47.076	2.270	6.119	
	03.05.2011	39.860	2.200	5.222	
		41.213	1.706	5.652	
		41.289	2.125	5.472	
	10.05.2011	55.610	1.884	6.295	
		55.024	1.743	6.459	
		55.470	2.253	6.135	
	31.05.2011	36.045	1.576	5.396	
		36.686	2.029	4.574	
		37.877	1.903	5.413	

C- Mathematical model program in Matlab

The mathematical model established for the system under analysis was solved by using some Matlab functions, as indicated in the following script.

```
function dx = mathematicalmodel(t, x)

global par
global u

 % state variables

 T = x(1);    % temperature
 mMO = x(2);  % organic matter mass
 CO =x(3);    % oxygen concentration
 mW=x(4);     % water mass
 C=x(5);      % bulk weight coefficient for the substrate, range from 0.15 to 0.4

% input variables
F0 = u(1);    % volumetric air flow rate
Ta0= u(2);    % initial air temperature
m0= u(3);     % total subtrate mass
ms0=u(4);     % dry substrate mass
fMO=u(5);     % organic matter fraction
mMO0 = u(6);  % inial organic matter mass
mMI= u(7);    % inorganic matter mass
T0=u(8);      % initial substrate temperature
CO0=u(9);     % initial oxygen concentration

% model parameters

a = par(1);   % constant
b = par(2);   % constant
c = par(3);   % constant
k_o = par(4); % oxygen saturation constant
FAS= par (5); % Free air space
mDHR= par(6); % reaction entalpy
n= par(7);    % reaction order
UA= par(8);   % overall heat coefficient * area of heat exchange
Tamb=par (9); % ambient temperature
```

```
YW= par(10);  % Stoichiometric coefficient for water
Vr= par (11); % reactor volume
MrW=par(12);  % water molar mass
R= par(13);   % universal gases constant
Patm=par(14);
Mra= par(15); % air molar mass;
MrMO = par(16);% organic matter molar mass
MrMI= par(17); % massa molar da matéria inorgânica
C1=par(18);   % contsant
C2=par(19);   % constant
C3=par(20);   % constant
C4=par(21);   % constant
C5=par(22);   % constant

% ------------------------------------------------
% Mathematical model
% ------------------------------------------------

%% mass balance

m = mW+mMO+mMI;
ms=m-mW;
Sm = ms./m; % fractional solids content of the mixture solids
rho = C/Sm; % unit bulk weight of the mixed material to be composted
Vm = m/rho;
Vg= Vr-Vm;  % gas volume
rhoW=1;     % density of water
Vs=mMO/ms;  % voltalite solids fraction
Gv=1;       % specific gravity of the volatile fraction of the substrate solids
Gf=2.5;     % specific gravity of the fixed fraction of the substrate (inorganic fraction)
Gs= 1/((Vs/Gv)+(1-Vs)/Gf); % specific gravity of substrate solids
FAS1= 1-((rho/1000)*Sm/(Gs*rhoW))- ((rho/1000)*(1-Sm)/rhoW);

% cinética da degradação do substrato

kT = a*(b^(T-273.15-20)-c^(T-273.15-60));  % temperature correction function
kO = CO/(k_o + CO);                         % oxygen correction function
kW = 1/(exp(-17.684*(1-Sm)+7.0622)+1);     % moisture correction function
kF = 1/(exp(-23.67*FAS1+3.4945)+1);        % free air space correction function
 k= kT*kO*kW*kF;                            % reaction rate constant
 rMO= -k*mMO^n;
```

```
dmMO = rMO;

% water balance
Pvs = exp(C1 + (C2/T) + C3*log(T)+ C4*T^C5); water % saturation pressure at temperature T
Pvs0 = exp(C1 + (C2/Ta0) + C3*log(Ta0)+ C4*Ta0^C5);% saturation pressure at temperature T0

Mar0=(Patm-Pvs0)*F0*Mra/(R*Ta0); % mass air flow rate at temperature
Mar=(Patm-Pvs)*F0*Mra/(R*T);

rW=Pvs0*F0*MrW/(R*Ta0)-YW*rMO-Pvs*F0*MrW/(R*T);
dmW= rW;

% Oxygen balance
rhoa0=1.18;   % air specif gravity
rhoa =Mra*(Patm-Pvs)/(R*T);

dCO =CO0*Mar0/(Vr*rhoa0) -(CO*Mar0/(Vr*rhoa))+0.705*rMO/Vr;

dC=0.01;
%% enthalpy balance

cpai= 1009;      % air specific heat
cpW= 4200;       % water specific heat
cpMO= 1320;      % organic matter specific heat
cpMI=  848;      % inorganic matter specific heat

Var= FAS1*Vm;    % air volume
mar= rhoa*Var;   % mass volume

dT = (F0*cpai*rhoa0*(Ta0-T)+ mDHR*rMO-UA*(T-Tamb)) /
(cpW*mW+cpMO*mMO+cpMI*mMI+cpai*mar);

dx = [dT;dmMO;dCO;dmW;dC];

end




clc
clear
global par % parameters vector
```

```
global u   % input variables vector

%   Reactor 1
%% inputs variables
F0  =  0.56 ;              % m^3/h
Ta0 = 20+273.15;       % K
 m0  = 34.8;               % kg
 ms0= 9.0954;            % kg
 fMO= 0.908;
 mMO0 =fMO*ms0 ;           % kg
 mMI= (1-fMO)*ms0;          % kg
 T0= 20+273.15;                 % K
 CO0 =0.2609 ;                 % kg_O2*m^-3
 u   =  [F0;Ta0;m0;ms0;fMO;mMO0;mMI;T0;CO0]; % input variable inputs

 % state variables on steady state

T   = 30.4 +273.15;        % K
mMO= mMO0;             % kg
CO =  0.2609;              % kg_O2*m^-3
mW= 25.7046;             % kg_O2*m^-3
C=83;
  x=[T;mMO;CO;mW;C]; % state variables vectors

  % model parameters
a = 0.0000883;                 % kg^(1-n)*h^-1
b = 1.0533;
c= 1.2247;
k_o = 0.07;                      % kg_O2*m^-3
FAS= 0.5322;
mDHR= -2.27*10^7;          % J*kg_MO^-1
n= 2.8944;
UA= 12800;                      % J*h^-1*K^-1
Tamb=25+273.15;            % K
 mMI= mMI ;                    % kg
 YW= 0.360 ;                    % kg_H2O*kg^-1
 kLW= 1*10^-4;               % kg*h^-1*Pa^-1
 Vr= 0.12;                       % m^3
 MrW=18*10^-3;             % kg/mol
R= 8.314;                        % J*mol^-1*K
Patm= 101325;                 % Pa
```

```
Mra= 28.96*10^-3;           % kg/mol
MrMO = 449*10^-3;          % kg/mol usando a fórmula C20H35105N
MrMI= 60.07*10^-3;         % kg/mol usando a fórmula SiO2
C1=73.649;
C2=-7258.2;
C3=-7.3037;
C4=4.1653*10^-6;
C5=2;

% vector parameters
par =
[a;b;c;k_o;FAS;mDHR;n;UA;Tamb;mMI;YW;kLW;Vr;MrW;R;Patm;Mra;MrMO;MrMI;C1;C2;C3;C4;C5];

%outros parâmetros do modelo
cpai= 1009;      % J mol^-1 K^-1
cpW= 4200;     % J mol^-1 K^-1
cpMO= 1320;   % J mol^-1 K^-1
cpMI=  848;    % J mol^-1 K^-1
m = mW+mMO+mMI; % kg
ms=m-mW;        %kg
Sm = ms./m;
rho = C/Sm;      % kg/m^3
Vm = m/rho;      % m^3
Vg= Vr-Vm;      % m^3
rhoW=1;           % kg/m^3
Vs=mMO/ms;
Gv=1;
Gf=2.5;
Gs= 1/((Vs/Gv)+(1-Vs)/Gf); % kg/m^3
FAS1= 1-((rho/1000)*Sm/(Gs*rhoW))- ((rho/1000)*(1-Sm)/rhoW);
kT = a*(b^(T-273.15-20)-c^(T-273.15-60));
kO = CO/(k_o + CO);
kW = 1/(exp(-17.684*(1-Sm)+7.0622)+1);
kW0=1/(exp(-17.684*(1-(ms0/m))+7.0622)+1);
kF = 1/(exp(-23.67*FAS1+3.4945)+1);
k= kT*kO*kW*kF;
rMO= -k*mMO^n;
Pvs = exp(C1 + (C2/T) + C3*log(T)+ C4*T^C5);        % Pa
Pvs0 = exp(C1 + (C2/Ta0) + C3*log(Ta0)+ C4*Ta0^C5); % Pa

Mar0=(Patm-Pvs0)*F0*Mra/(R*Ta0);                  % kg h^-1
```

```
Mar=(Patm-Pvs)*F0*Mra/(R*T);                         % kg h^-1
rhoa=Mra*(Patm-Pvs)/(R*T);                          % kg/m^3
rW=Pvs0*F0*MrW/(R*Ta0)-YW*rMO-Pvs*F0*MrW/(R*T);
Var= FAS1*Vm;  % m^3
mar= rhoa*Var; % m^3

%------------------------------------------------------------------------
      sampling time
%------------------------------------------------------------------------
dt =5; % h
% initial time
t = 0; % h
imax =250;

tres = zeros (1, imax);
xres = zeros (length (x), imax);
ures = zeros (length (u), imax);
Cres= zeros (1, imax);

 for i=1:imax
 % F0 perturbance
 if ( i == 7)
 F0 = 0.56;
 u( 1 ) = F0;
 elseif (i==8)
 F0=0.59;
  u( 1 ) = F0;
  elseif (i==10)
 F0=0.52;
  u( 1 ) = F0;
  elseif (i==20)
 F0=0.52;
  u( 1 ) = F0;
 elseif (i==24)
 F0=0.37;
  u( 1 ) = F0;
  elseif (i==39)
 F0=0.24;
  u( 1 ) = F0;
  elseif (i==58)
 F0=0.27;
```

```
 u( 1 ) = F0;
  elseif (i==75)
 F0=0.27;
  u( 1 ) = F0;
end

tres(:,i) = t;
xres(:,i) = x;
ures(:,i) = u;
tnew = t + dt;

[tsol,xsol] = ode45('mathematicalmodel',[t tnew],x);
x = xsol(end,:)';
t = tsol(end);
 end

% organic matter conversion
 y= ((xres(2,1)-xres(2,:))/xres(2,1))*100;

%% Figures
figure (1)
subplot(2,1,1)
plot(tres,xres(1,:)-273.15);
title ('Temperature profile')
ylabel('T / ºC')
xlabel('t / h')
axis([0 415 20 80]);
hold off

subplot(2,1,2)
plot(tres,xres(2,:));
title ('organic matter mass')
ylabel('mMO / kg')
xlabel('t / h')
hold off;

figure  (2)
subplot(2,1,1)
plot(tres,xres(3,:));
title('oxygen concentration ')
ylabel('CO /kg_O2*m^-3 ')
```

```
xlabel('t / h')
hold off;

subplot(2,1,2)
plot(tres,O);
title ('oxygen percentage')
ylabel('O/ %')
xlabel('t / h')
hold off;

figure  (3)
subplot(2,1,1)
plot(tres,y);
title('organic matter conversion ')
ylabel('x_V_S / %')
xlabel('t / h')
axis([0 1120 0 80])
hold off;

subplot(2,1,2)
plot(tres,xres(4,:));
title ('water mass')
ylabel('mW / kg')
xlabel('t / h')
axis([0 440 0 30])
hold off;

figure (4)
subplot(2,1,1)
plot(tres,k);
title('reaction rate constant ')
ylabel('k / ')
xlabel('t / h')
hold off;

subplot(2,1,2)
plot(tres,kT);
title(' kT ')
ylabel('kT / ')
xlabel('t / h')
hold off;
```

```
figure (5)
subplot(2,1,1)
plot(tres,kW);
title(' kW ')
ylabel('kW / ')
xlabel('t / h')
hold off;

subplot(2,1,2)
plot(tres,kO);
title(' kO ')
ylabel('kO / ')
xlabel('t / h')
hold off;

figure (6)
subplot(2,1,1)
plot(tres,YFAS1);
title (' FAS')
ylabel('FAS/ % ')
xlabel('t / h')
axis([0 440 0 100])
hold off;

subplot(2,1,2)
plot(tres,kF);
title('kF ')
ylabel('kF / ')
xlabel('t / h')
hold off;

figure (7)
subplot(3,1,1)
plot(tres,ures(1,:));
title('evolução do caudal de entrada no reactor ')
ylabel('F0 / m3/h')
xlabel('t / h')
hold off;
```