FORSCHUNGSBERICHT AGRARTECHNIK
des Fachausschusses Forschung und Lehre der
Max-Eyth-Gesellschaft Agrartechnik im VDI (VDI-MEG) **498**

Sandra Patricia Cuervo-Andrade

Quality oriented drying of Lemon Balm (*Melissa officinalis* L.)

Dissertation Witzenhausen 2011

ISSN 0931-6264

Universität Kassel
Fachbereich Ökologische Agrarwissenschaften
Fachgebiet Agrartechnik
Prof. Dr. Oliver Hensel

Quality oriented drying of Lemon Balm (*Melissa officinalis* L.)

Dissertation zur Erlangung des akademischen Grades einer
Doktorin der Agrarwissenschaften (Dr. agr.)

von
Dipl.-Ing. Sandra Patricia Cuervo-Andrade
aus Bogotá, Kolumbien

2011

Die vorliegende Arbeit wurde vom Fachbereich Ökologische Agrarwissenschaften der Universität Kassel als Dissertation zur Erlangung des akademischen Grades „Doktorin der Agrarwissenschaften“ angenommen.

Tag der mündlichen Prüfung: 21.03.2011

Erster Gutachter: Prof. Dr. Oliver Hensel
Zweiter Gutachter: Prof. Dr. Werner Hofacker

Mündliche Prüfer: PD Dr. Jens Gebauer
PD Dr. Johannes Kahl

Im Selbstverlag: Sandra Patricia Cuervo Andrade
Bezugsquelle: Universität Kassel, FB Ökologische Agrarwissenschaften
Fachgebiet Agrartechnik
Nordbahnhofstr. 1a
37213 Witzenhausen

Acknowledgements

This work was developed in the department of agricultural engineering at the University of Kassel in Witzenhausen led by Prof.Dr.Oliver Hensel.

I particularly want to thank to Prof.Dr. Oliver Hensel for his continued support in carrying out the work. His technical suggestions were crucial to the successful conclusion of the work. His good sense of humor always kept me motivated to continue and overcome the difficulties inherent in the research.

I also want to thank to Prof.Dr. Werner Hofacker , to PD Dr. Jens Gebauer and to PD Dr. Johannes Kahl for their participation in the supervisory committee.

A special gratefulness to the STIBET scholarship program for their financial support for the latest stage of my doctoral work.

Special thanks to the members of the department of agricultural engineering in Witzenhausen, for their contributions and help during my stay in Germany, mainly to Christian, Heiko, Petra, Uwe and Franz.

I appreciate the support of my friend Mr. Christian Schellert, who helped me both in technical and personal aspects during my stay in Witzenhausen.

I thank to my friends for the support and to share cheerful times during my stay and that of my family in Germany. Especially to Sonia, Alexander, Javier, Esteban, Achim, Beatriz, Hernando, Victor and Yolanda.

I thank my parents Socorro and Dionisio who have always offered me their support to achieve my formation goals. Also I want to thank to my husband Carlos Julio whose support was fundamental for the development and culmination of this project. Thanks to my children Juliana Patricia and Sebastian Camilo for their patience, great support and motivation also for the whole time that they have given me of their company to finish this work.

Sandra Patricia Cuervo Andrade
Witzenhausen, March 2011

Contents

Nomenclature

Symbol	Unit	Meaning
a_w	-	Water activity
A	m^2	Area
A_o		Empirical coefficient
C_i	kj/kgh	specific heat
C_o	-	Covering
D	-	Overall desirability
d	-	Individual desirability
D_m	m^2/s	Diffusion coefficient
$d.m.$		Dry matter
$d(y)$		Desirability function
DR	-	Dimensionless drying rate
K_o		coefficient
L_d	g/m^2	Drying Load
M	g	Mass
m_a	kg_{air}/h	Mass flow rate
$MC_{w.b.}$	%	Moisture content (wet base)
MR		Moisture ratio
m_w	g	Mass of water
O_c	%	Essential oil content
Q	W	Heat transferred
q_r	kJ	Required energy
R^2		Determination coefficient
R_d	$g_{water}/g_{d.m}$h	Drying rate

Symbol	Unit	Meaning
t	h	Time
t_d	h	Drying time
T	K	Temperature
V_a	m/s	Air velocity
x	m	Distance
X	$g_{water}/g_{d.m}$	Moisture content (dry base)
X_e		Equilibrium moisture content
X_o		Initial moisture
X_p	m	Position in solar tunnel
L^*	-	Brightness
b^*, a^*	-	Chromatic coordinates
ΔE	-	Color difference
φ	%	Relative humidity
υ	°C	Drying temperature

Acronyms	Meaning
EMC	Equilibrium moisture content
MSI	Moisture sorption isotherm
RSM	Response surface methodology
CCD	Central composite design

1 Introduction

The first objective of drying is to remove water and hence to stabilize the biological products. However, during drying of medicinal plants, many changes occur simultaneously resulting in a modified overall quality. In general, drying leads to reduction of visual, organoleptic and functional characteristics that affect significatively the final quality. Reactions lead to well-known changes in the fresh biological products during drying: change of color, loss of aroma, textural changes, reduction of essential oil content, cracking and altering of shape. These reactions are caused by both the increase in product temperature and the removal of moisture. For these reasons, it is necessary to purpose adequate drying strategies and to known the optimal values of the process parameters in order to obtain the required quality characteristics and the decrease of the energy consumption.

This research work is related to the quality oriented drying of Lemon Balm (*Melissa officinalis* L.). Different strategies and aspects have been considered and treated experimentally and mathematically in order to obtain the best conditions to reach an adequate productivity and the required quality characteristics in terms of color change and essential oil content.

In Chapter 2 relevant aspects of problem outline are presented. The chapter is focused on background of the problematic and the problem definition which describes the consequences on quality due to an inadequate selection of drying parameters in processing medicinal plants by using dryers based on forced convection with hot air and solar tunnels. Starting from this problem definition, the research objectives and the methodology are purposed. The methodology considers the obtaining of sorption isotherms and drying kinetics of lemon Balm and the corresponding fitting to mathematical models. Likewise a stepwise drying strategy was analyzed as alternative to obtain better results in terms of quality and energy consumption. Additionally an experimental design by using response surface methodology was purposed for multi objective optimization of quality characteristics and required energy. Finally, in order to observe the influence of drying parameters on product quality by using a solar tunnel, design of experiments techniques were considered.

In Chapter 3 presents the state of the art, contempled as main aspect the research on drying of medicinal plants focused on Lemon Balm; sorption models, techniques for the determination of quality characteristics, analysis of drying process and effects of drying on quality and strategies for quality drying and energy saving. Chapter 4 the fundamentals and concepts required to understand the aspects considered in the problem definition and the research strategies and results are evaluated.

Chapter 5 is focused on the experimental methods to measure the considered quality characteristics and moisture product conditions. The methodologies for determining moisture content, essential oil content and measuring of color are described. In Chapter 6, the experimental determination of sorption isotherms for Lemon Balm and the corresponding mathematical evaluation for the best fitting to different models are presented.

In Chapter 7 the characterization and analysis of drying kinetics for Lemon Balm are presented. The influence of air drying temperature and relative humidity on drying time, drying rate and were studied in order to characterize the behavior of the drying process for Lemon Balm. Moreover, the behavior of drying for different conditions of the product was observed. The comparison of drying kinetics for processing leaves, stalks and complete branches were observed and the differences in final quality were evaluated to define the adequate drying parameters to minimize effects on quality and difficulty for posterior processing in terms of separation and storage. Furthermore according to the obtained experimental data, mathematical models of drying were fitted to describe the process.

In Chapter 8 different strategies of stepwise drying control for Lemon Balm were considered. The purposed stepwise drying strategies are based on processing with two temperatures which were compared with conventional drying using constant temperature. The change points for stepwise processing were defined at four moisture content (50,40,30 and 20%). Comparison of stepwise strategies in order to find the optimal change point was focused on reaching quality requirements (color change and essential oil content) and energy consumption.

In Chapter 9, a research on multi objective optimization of drying of Lemon balm is presented. Experimental design based on response surface methodology (RSM) was considered. A central composite design (CCD) with drying temperature and relative humidity as experimental factors was defined. For this CCD, drying time, essential oil content, color difference and required energy were considered as responses. With the obtained experimental data, regression models were generated for each response and the behavior of the drying process was described. For the multi objective optimization of the previously considered responses, the desirability function approach was considered. Multi objective optimization was developed for different combinations of priorities of the objective responses (drying time as priority, essential oil content as priority, etc...) or same priority for all responses.

In Chapter 10 the effect of solar drying parameters on quality characteristics was observed. By drying Lemon Balm in a solar tunnel and applying methods of design of experiments (DoE), the effect of type of covering, position in the solar tunnel, drying load and air velocity on drying time, color difference and essential oil content was analyzed. Additionally, regression models for the different responses considering the significant factors as independent variables were developed.

2 Problem outline

2.1 Background

Drying is an important process in the production chain in order to add value to the medicinal plants. Fresh medicinal plants normally contain a high level of moisture, due to that there is the big risk of microbiological activity. The moisture in the plants has similar properties as pure water. It can serve as medium for chemical, enzymatic and microbial reactions, many of which lead to ultimate loss of quality and nutritional value. So, in the fresh state of plants, deterioration and spoilage occur under ambient conditions. At lower moisture values, the water is more bound to the material, and cannot take part in the deteriorative reactions. Consequently, it is not so much the water content, but its state, nature or availability in the plants, expressed by the moisture that plays a role in the deteriorative processes. Changing the availability of water, by reducing the moisture, can result in an effective prevention of plants from spoilage (Quirijins, 2006). Therefore, the immediate and adequate drying is the most important operation in post harvest processing to avoid quality losses. Medicinal plants are widely used in pharmaceutical industry due to their active ingredients which contain essentials oil, bitter substances, glycosides, saponins, alkaloids, and flavonoids. Likewise medicinal plants are used for cosmetics, dyes, perfumes, flavouring, pesticides, herbicides, foods and beverages. The growing demand in industrialized countries for natural products in place of synthetic compounds has created a niche market for medicinal and aromatic plants. The entry into market depends not only on the demand but also on the competitive price of production, quality and the ability to provide the quantities required by the purchaser. These requirements involve having to make a systematic management of the variables of the drying process. The objective of drying is to improve the conditions of use and preservation of the product. Drying is defined as the decreasing of crop moisture content, aimed at preventing enzymatic and microbial activity, and consequently preserving the product for extended shelf life (Martinov, 2007). As consequence of drying, there is a reduction of the weight and volume that has a positive effect for transport and storage as well as for the preparation for other industrial processes (distillation, extraction, etc). For proper and efficient application, drying process must meet the following requirements:

- Moisture content must be reduced to equilibrium level that is defined for certain temperature and relative air humidity, and which is defined as storage condition by international standard or user.

- Reduction of quality must be minimal, in terms of active ingredients, color, flavor, and aroma.

- Microbial content should be below the limits prescribed. The use of chemical additives is not recommended.

2.2 Problem definition

At present, for the case of Lemon Balm, there are various problems in the drying process that do not allow the achievement of complete requirements for the market. There is not enough information of the drying parameters to select the initial set of parameters to adjust, reports of drying parameters for similar plants are considered. Another alternative is trial and error to adjust the parameters of drying to obtain the quality requirements.

Likewise the inadequate selection of drying parameters generates the following problems:

- Overdrying that causes mechanical damage to the structure of the product, such as excessive fragility, collapse of the support structure and pulverizing, with consequent loss of quality and difficulties in post handling.
- Inadequate drying, which means that the final moisture content obtained after the process is above the minimum required, for example 12% of moisture content in accordance with Deutsche Arzneibuch 1996 (Heindl & Müller, 1997) and 6-8 % according to literature. The result of this condition is enzyme activity, browning and lipid oxidation.
- Failure to obtain the quality required, expressed as appreciable change in color and excessive loss of essential oil. This is associated with the difficulty to obtain reproducible quality characteristics. In other words a high variability of the quality characteristics is generated and the required tolerance is not achieved due to poor process control.
- Non-uniformity in the drying of leaves and stems due to differences in structural and geometrical configuration and different thermo mechanical properties. Additionally there is no uniformity due to differences in the thickness of dried layer. **Figure** 2.1 shows that Leaves of *Melissa officinalis* typically contain a volatile oil, located in peltate glandular hairs, responsible for some of the medical and aromatic properties of the plant. The vegetative organs of *Mellisa officinalis* (leaves) are covered by an indumentums containing glandular needle-shaped tichomes (Figure 2.1a), Glandular trichomes remained plump and the change are minimum for the optimal drying conditions (Figure 2.1b). However, when an over drying process occur, a few of the glandular tichomes appeared slightly deflated, suggesting oil loss, while most of them appeared to be damaged (Figure 2.1c). The reduction in oil yield is associated with the observed loss of glandular contents, is attributed to the evaporation of volatile components due to over drying processes and the effect of this extended post-harvest drying damage the integrity of the trichomes and causes a complete evacuation of the oil glands, corresponding with desiccation of the material.

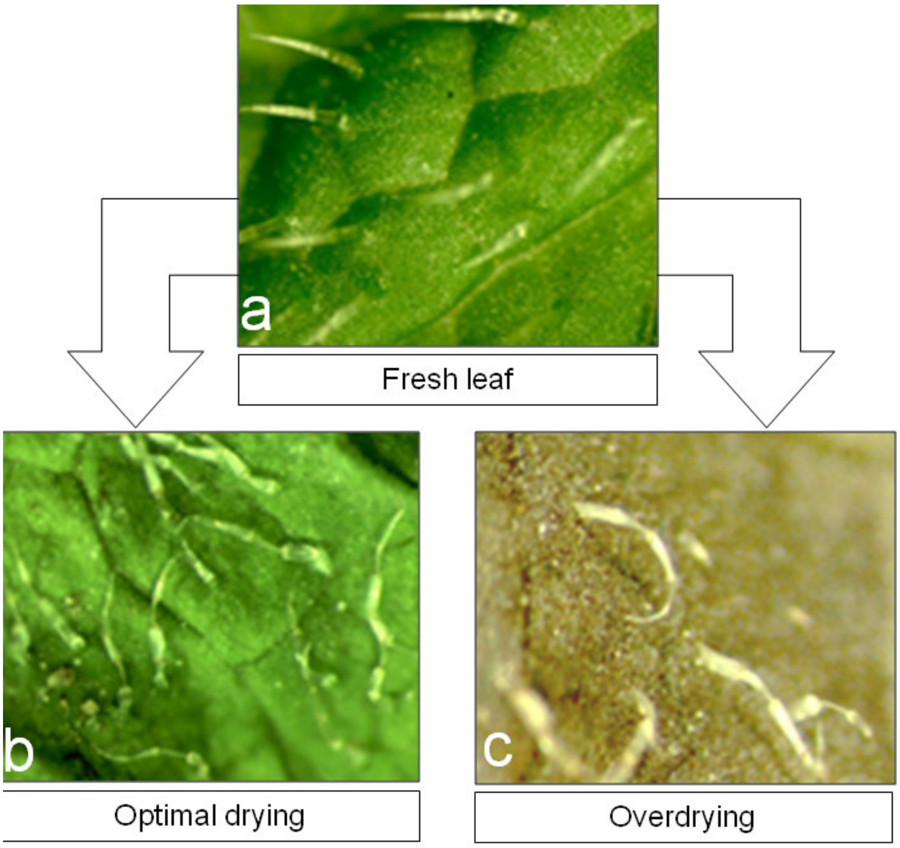


Figure 2.1: Different drying of leaves

- Inefficient use of energy due to inappropriate selection of parameters that cause additional energy consumption by processing out of the optimal point of parameter combination associated with optimum of quality and drying time. Additionally there may be additional energy consumption by excessive drying (drying up more down to the point of minimum moisture). On the other hand, may consume extra energy by maintaining the operation of the drying process even having reached the equilibrium moisture content. This may be not due by considering the precise information of the equilibrium moisture of the product with the surrounding environment.

- Excessive drying times due to inadequate selection of drying parameters, which generates low production rate and the consequent decrease in production capacity and increase of the costs of processing.

Often solar energy is employed for drying purposes in agriculture. For drying in solar tunnel additionally the following problems are considered

- Because of the randomness in the radiation, the control of the drying temperature is complex.

- The radiation affects the color of the product by photo-decomposition.

- The high variation of radiation, temperature and humidity generates drying conditions not constant over time, causing high variability in quality characteristics.

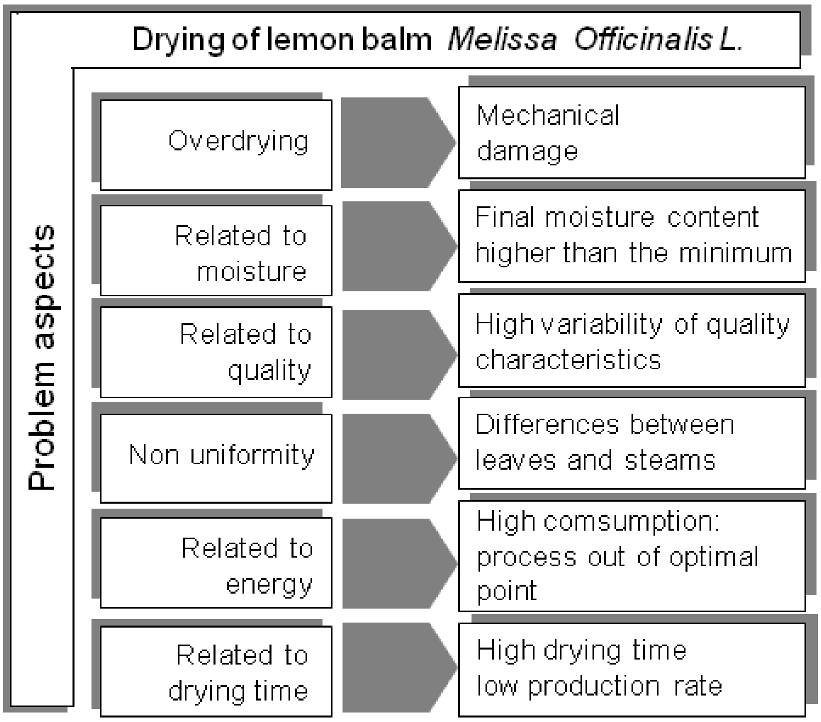


Figure 2.2: General aspects considered in the problem definition

In order to solve the different aspects of the problem, the following considerations are required:

- To characterize the behavior of the drying process of Lemon Balm, in terms of temperature range in which it is possible to dry without drastic losses in quality.
- To know the equilibrium moisture content for different combinations of temperature and relative humidity in order to determine the conditions for completing the process in terms of temperature and humidity.
- To know the behavior of the drying process of Lemon Balm in terms of drying time and the influence of temperature and humidity.
- To know the optimal drying parameters required to achieve the minimum moisture content considering the requirements for quality, drying time and energy required in order to avoid problems of inadequate drying.
- For drying in solar tunnel, knowing the behavior of drying through the effect of drying variables on the quality and the drying time.

2.3 Research objectives

Considering the aspects required to solve the problems associated with drying Lemon Balm, the following research objectives are proposed:

- To determine the sorption isotherms for Lemon Balm.

- To describe the drying kinetics of Lemon Balm.
- To propose alternatives and new concepts in stepwise drying as an alternative to improve the obtained results of conventional drying process in terms of quality, drying time and energy consumption.
- To propose a methodology for finding the optimal parameters for drying considering as variables the drying temperature and relative humidity of drying air and as responses: drying time, essential oil content, color difference and required energy.
- To analyze the effect of the parameters of drying with solar tunnel dryers (covering, position, drying load and air velocity) on the quality characteristics (content of essential oil and color difference), and the drying time.

2.4 Methodology

Below a description of the strategies for achieving the objectives are presented:

- To obtain sorption isotherms the methodology recommended by the project COST 90 (Spiess & Wolf, 1983) was considered. Additionally mathematical fitting using nonlinear regression for different models proposed in the literature was performed. The most adequate model is selected according to the appropriate statistical criteria.
- The drying kinetics were described by the experimental determination of the drying curves made at different temperatures and humidities, this trials were made in the Drying Laboratory of the Department of Agricultural Engineering University of Kassel. Additionally, mathematical fitting to models proposed in the literature was performed by using nonlinear regression. The most adequate model was selected according to statistical criteria.
- For the analysis of stepwise drying, curves using two drying temperatures and different points of change of moisture were experimentally determined. The optimal point of change in terms of quality characteristics, drying time and energy was observed. This analysis is performed for different combinations of temperature of stepwise drying.
- For the multi objective optimization analysis of the drying process the response surface methodology (RSM) was considered. Using a central composite design (CCD), second order polynomial models for drying time, essential oil content, color difference and required energy were proposed. Drying temperature and relative humidity of drying air were considered as experimental factors.To solve the problem of multiple response optimization the desirability function method is proposed. Various prioritization options for each response were studied by using the desirability function in order to obtain different optimal combinations.
- To observe the effect of the drying parameters of the solar tunnel on drying time, color difference and essential oil content, design of experiments (DOE) techniques were applied. By using factorial design the significance of the experimental factor is

observed and by applying regression analysis an experimental model that describes the process was proposed.

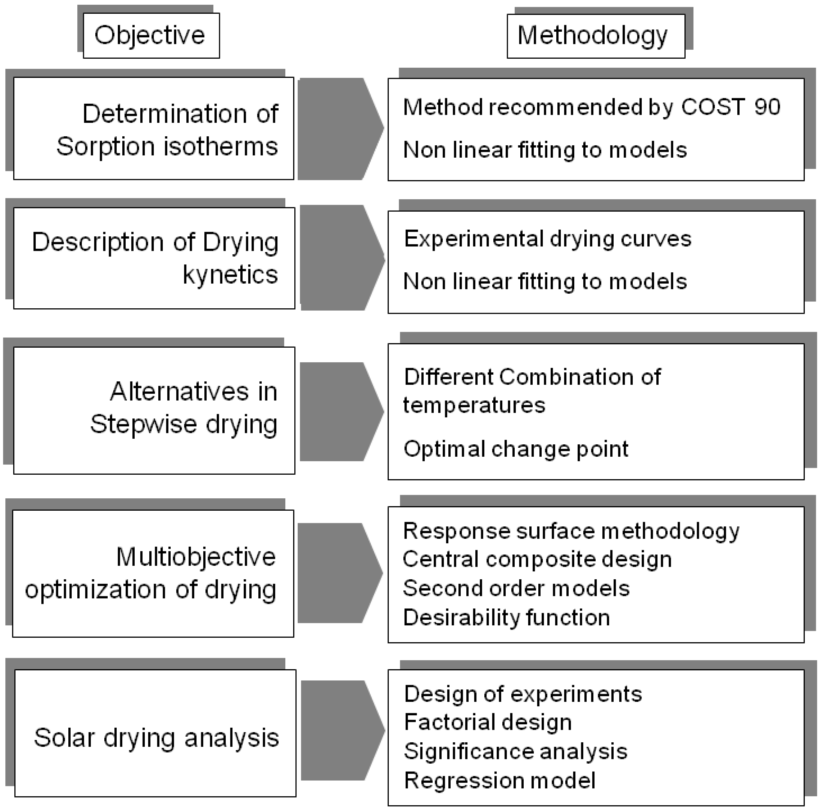


Figure 2.3: Activities corresponding to the research objectives and proposed methodology

3 State of the Art

Plants have provided man with all his needs in terms of shelter, clothing, food, flavours and fragrances as not the least, medicines. Plants have formed the basis of sophisticated traditional medicine systems among which are Ayurvedic, Unani, Chinese amongst others. These systems of medicine have given rise to some important drugs still in use today. Among the lesser known systems of medicines are the African and Australian, Central and South American amongst others (Ameenah, 2006).

Currently, the worldwide interest in herbal or medicinal plant products has increased significantly. According to World Health Organization (WHO) survey, about 70-80% of the world population relies on non-conventional medicines for their primary health-care. This strategy is mostly based on the medicinal plants products known as botanical, herbal, medicines or phetomedicines (Akerele, 1993; Calixto, 2000; Chan, 2003). Herbal medicines are composed of plant parts or plant materials in either the crude or processed state as active ingredients and may contain inert excipients (Busse, 2000). Herbal products are traded as fresh or dry products or as essential oils. These are in general used as raw materials for the extraction of active substances or chemical precursors and mainly for the production of teas, homemade-remedies, fluid extracts and also powders resulting from dried and comminuted plants or from the drying an extract(Runha et al., 2001).

Chemical constituents with antioxidant activity found high concentrations in herbs plants (Velioglu et al., 1998) determine their considerable role in the prevention of various degenerative diseases (Challa et al., 1997; Hu, 2002). Besides the fruits and vegetables that are recommended at present as optimal source of such components, the supplementation of human diet with herbs, containing especially high amounts of compounds capable of deactivating free radicals may have beneficial effects (Madsen & Bertelsen, 1995). The benefits resulting from the use of natural products rich in bioactive substances has promoted the growing interest of pharmaceutical, food and cosmetic industries as well as of individual consumers in quality of herbal products (Kapecka et al., 2005).

The herb industry can be separated into three main categories, essential oils, medicinal crops and culinary herbs. The establishment of herb production venture involves relatively high capital investment, particularly for plant material, irrigation, machinery and distillation or drying equipment. In addition, there is only limited information available. Therefore, there is high level risk involves in setting up a venture based herbal production. The level of risk declines as the industry develops, production technology increases, markets are defined and an industry infrastructure is established (Bruce, 2001).

Drying of medicinal herbs should take place as soon as possible after harvesting; otherwise insects and fungi, which thrive in most conditions, render them unusable. Conventional drying methods such as open sun drying and conventional-fuel dryers are not suitable; since they may yield a less quality product and may increase the drying cost or time. Moreover, they may not be reliable and environmentally safe. In most countries, enormous quantities of food losses have resulted from spoilage, contamination, attack by insects/rodents/birds and deterioration during the storage period. There are number of factors, which are responsible for the post harvest losses, such as system of harvesting, processing, storage, handling, and marketing. Drying of product is one of the important post harvest processes and it has enough potential to reduce the post harvest losses, and to prevent spoilage of the product in storage drastically. Moreover, good drying technique can enhance the quality of the product significantly (Garg, 2001). Therefore, the drying of medicinal herbs must be accomplished as soon as possible after harvesting, to increase the quality of the herb and to prevent the expected contamination and losses caused by the infestation of rodents, birds, insects, and fungi which thrive in moist conditions (Garg, 2001; Yahya et al., 2001).

Drying is one of the most important processes in the food industry, as well as one of the most frequently studied topics in food engineering. Optimizing this process will result in lower production costs and increased product quality. Moisture transfer in heterogeneous materials, such as foods, is a complex process where more than one mechanism may occur. After over eighty years of applying Fick's Second Law diffusion equation to drying of foods, there are still wide variability in reported diffusion coefficients. This article reviews moisture transfer mechanisms, models developed to predict moisture transfer, measurement of effective moisture diffusivity, which is the most common parameter used in predicting moisture transfer, and advanced measurements of moisture profiles to quantify and validate predictive models (Srikiatden & Roberts, 2007).

The technical drying process necessitates an enormous amount of thermal and electrical energy. An improvement in the quality of the product to be dried and at the same time a decrease in the drying cost and time are achieved through the utilization of a controlled conventional drying method, which is based on a good utilization of the renewable energy sources. A complete dynamic modeling of the solar thermal subsystem, using the energy balance principle, is developed and the system results are indicated. The results illustrate that the designed control technique enables the developed herb dryer system to be in correct and continuous operation during the sunny/cloudy day and night hours (Fargali et al., 2008).

Generally, high temperature influence essential oil quality and quantity in medicinal and aromatic plants not only during drying; reduction in active ingredients continues during the storage period as well. Similar results are confirmed by different references (Koller, 1987; Shilcher, 2008). According to Jud (citepd in (Müller, 1992), the maximum drying temperature of *Salvia officinalis* is declared as 30°C. By increasing the drying temperature from 30°C to 55°C, essential oil losses increase by 15% and the drug color changes from green to gray. Drying temperature usually has an influence on the temperature sensible components of essential oil.

Color is an important component of quality throughout agriculture and food industry, because color is closely associated with factors such as freshness, ripeness, desirability, and food safety. It is often the primary consideration of consumers when making purchasing decisions (Ahmet & Orhon, 2009; Arabhosseini et al., 2009). The color change kinetics of food is a complex phenomenon and there are not much reliable models to predict color change, which can be used in engineering calculations (Arabhosseini et al., 2009). Thermal processing is one of the most widely used and important method of food preservation, and it affects the food quality as measured by sensory evaluation or instrumental methods (Guine et al., 2009). The effect of thermal processing on the color of food material has been studied by various researchers, and different color systems have been used for describing color changes of food material (Arabhosseini et al., 2009). Color can be used to define adequate thermal processing conditions for maximizing final product quality if its degradation kinetics are determined. It was shown that Graphical determination of drying process and moisture transfer parameters for solids drying (Sahin & Dincer, 2002).

For colour measurement, the CIELAB system is frequently applied using lightness L*, chroma C* and hue h as parameters (Müller & Heindl, 2006). In a comparison study of these parameters involving ranking by a panel of specialists, h proved best to represent quality in terms of colour of dried *A. dracunculus* (Hosseini, 2005a). The effect of the temperature of the drying air on the colour of *Salvia officinalis* from 50 to 55°C causes discontinuity in the colour parameters, most apparent for h, which decreased from 112 to 87 degrees. This means that h was changing from the green to the red region, which indicates the browning that was also visually apparent. Browning occurred early during the drying process, but when the leaves were pre-dried for a certain time at 50°C, a subsequent increase to 60°C did not affect colour. Based on this knowledge, a conveyor dryer can be controlled following a staged temperature regime to achieve high drying capacity via high temperatures without affecting quality in terms of colour (Müller & Heindl, 2006).

Colour calculations followed the same methodology as (Shaw et al., 2005), and thus color measurements were reported based on Hunter L, a, and b values. The relative colour of the dried samples is compared using the index value ΔE. The base values of Hunter L, a, and b represent that of the fresh (un-dried) sample. The Hunter L value represents the lightness or darkness of a sample on a scale of 0 to 100 (100 being white and 0 being black). Hunter a value represents the greenness or redness of the sample (-50 being green and $+50$ being red). Hunter b value is also rated on a scale of -50 to $+50$, with -50 representing blue and $+50$ representing yellow (Shaw et al., 2005). Drying temperature has important effects on the color of medicinal and aromatic plants. The changes in color parameters of fresh and dried peppermint (*Mentha piperita L.*) as affected by drying air temperature were given in (Soysal, 2000). Statistical tests show that the color parameters of the fresh peppermint differed significantly from the dried products exposed at different drying air temperatures. Higher temperature could raise dramatic color deteriorations and burning of the product.

To withdraw the high amount of moisture from fresh crops, a large amount of energy is needed. The specific drying energy for drying depends on the material dried, material initial and final moisture content, drying process and the type of the dryer. According to the experiments conducted by (Müller, 1992) in a laboratory dryer, the results show a high influence of drying temperature on specific drying energy of *S. officinalis*. It was 13 MJ/kg at drying temperature 30°C and increases to 42 MJ/kg at 40°C. In the light of above discussion, the drying process is not only an energy intensive process but it deteriorates the quality of essential oil contents in the plant material. So, it is always preferable to process the fresh plant materials for good quantity and quality of the essential oils (Arabhosseini et al., 2009).

Essential oils are the aromatic portions of the plant located within distinctive oil cells, glands, or internal sector canals. In some exceptional cases, essential oils are formed during the extraction of the source plant material. However, some essential oils are formed only as a result of enzymatic reaction. They originate from a single botanical source and can be described as highly concentrated, volatile, and aromatic essence of the plant. Each essential oil contains hundreds of organic constituents that are responsible for their therapeutic actions and characteristic odor of the source plant material. These components are classified as monoterpenes, sesquiterpernes, aldehydes, esters, alcohols, phynols, ketones, oxides, and coumarins. Essential oils are extracted from various parts of the plant like leaves, roots, wood, bark, seeds/fruits, flowers, buds, branches, twigs, or whole plants (Öztekin & Martinov, 2007). About 65% of the essential oils produced in the world are obtained from the woody plants that are trees and bushes (Baser, 1999). Essential oil is a mixture of fragrant, volatile components, named after the aromatic plant material of a single type and identify from which it has been derived by a physical process and whose odor it has. The definition indicates that a given essential oil is derived from a single specie or variety. The definition given above states that an essential oil is derived by a physical process, i.e., it has not purposely changed chemically. The physical process by which the essential oils are obtained may also influence the chemical composition of an essential oil.

Essential oils and other flavoring products are isolated from plant material by various extraction techniques such as cold pressing or expression, distillation, solvent extraction, vacuum microwave distillation, maceration, and effleurage. The products of extraction are usually termed as concretes, absolutes, pomades, and resinoid, which are not regarded as essential oils. Although the extraction and distillation refer to different isolating techniques, in this text, we use the extractable compounds like essential oils and other flavoring products from the plant materials (medicinal and aromatic plants), mixtures and compounds by chemical, physical, or mechanical ways. Essential oils are generally obtained by various distillation techniques such as water distillation, water and steam distillation, steam distillation, and expression or cold pressing. Among them steam distillation or hydro distillation is the most widely accepted method for the production of essential oils on a commercial scale. Approximately 90% of the essential oils are produced in this way (Öztekin & Martinov, 2007).

4 Fundamentals

4.1 Importance and purposes of drying

The objective of drying medicinal plants is to extend the shelf life and conserving the fresh characteristics. This is achieved by reducing the water activity (a_w) of the product to a value which will inhibit the growth and development of pathogenic and spoilage microorganisms, significantly reducing enzyme activity and the rate at which undesirable chemical reactions occur. By this adjustment of a_w, and the use of appropriate packing, the shelf life of the product can be extended without the need for refrigerated storage. The removal of most of the water from the product reduces the weight to be carried per unit product value. This can lead to substantial savings in the cost of handling and transporting the dried product as compared with the fresh material. A reduction in volume of the dried material, as compared with the fresh, can lead to savings in the cost of storage and transport.

Drying can also bring about undesirable changes in medicinal plants. Physical and structural changes such as the size and shape of solid product pieces change during drying, due to the shrinkage discussed above. Color changes may also occur due to the removal of water or as a result of exposure to high temperatures during drying. Changes in flavor may also occur as a result of drying. These may be due to the loss of volatile flavor compounds during drying and/or to development of an undesirable cooked flavor because of exposure to high temperatures. The extent of these changes depends on the drying method. Exposure of the product to a high temperature at a moisture content intermediate between that of the fresh material and the dried product is likely to lead to high losses. Such conditions should be minimized by careful selection of the drying method and conditions and good control of the drying operation.

4.2 Drying process

Biological materials have a decreasing drying rate at low moisture contents. In most drying models this behavior is captured by making the diffusion coefficient dependent on moisture content. During drying, the effective diffusion coefficient is constant with moisture down to a critical moisture content. Below this critical value, the diffusion coefficient shows a sharp decrease with decreasing water concentration (Van, 1981). It can be assumed that the observed decrease of the drying rate is mainly caused by the decreasing availability of free water molecules (Srikiatden & Roberts, 2007). This assumption is based on the existence of two classes of water: the bound and free water. The bound moisture corresponds to water molecules connected strongly to the material molecules. The free moisture corresponds to the water molecules connected loosely to the material molecules. The portion of free moisture content is initially very large. As drying reaches its last stages, the bound moisture molecules form the majority of the water molecules, and then the conversion between the bound and free water controls the overall mass transfer phenomenon. This forms the basis of the newly developed diffusion-sorption drying model, the moisture transfer during the drying process is described by three basic transfer phenomena: free water diffusion, conversion between bound and free water inside the material and external convection at the boundary of the material. The model for the conversion between bound and free water makes the diffusion-sorption model original. The conversion is physically described as a sorption process. The interaction between water and the material is then modeled through the adsorption of free water to become bound water and, in reverse, the desorption of bound water to become free water. The thermodynamic variables for sorption required in the model are derived from the sorption isotherm (Quirijins, 2006).

The heat transfer occurs inside the plant and is related to the temperature gradient between the surface and the surface of water inside of it. If enough energy for evaporation is provided, the vapor produced is transported from the surface of the wet layer on the inside of the product to its surface. The water vapor pressure gradient between the inside and outside the plant, causes the water vapor diffusion to the surface.

Effects of drying on chemical and physical characteristics

Drying increases the duration of product storage, but generates changes in: appearance, texture, taste and nutritional composition. The degradation of the product is linked mainly to the drying time and temperature. For each product, a maximum allowable temperature can be defined. Many physical-chemical reactions are activated by temperature and consequently the drying causes an acceleration of these reactions. These changes are inevitable, but according to product composition and drying parameters some (Normal)reactions are limited. It is important therefore to know what are going to be the predominant factor of the disturbance in order to match the better conditions of the conservation treatment.

The major side effect of drying is the loss of quality of the material. It is caused by several irreversible modifications in the material (biological, chemical, physical) as a consequence of the removal of water and the increase of temperature during the drying process (Quirijins, 2006). In drying processes it is well established that the most important variables are time, temperature and moisture content. Due to differences between the inner and outer part of the material in resistance towards mass and heat transfer, profiles of moisture and or temperature arise.

The color of plants varies with drying. The color depends on the circumstances under which the plant is seen and the ability of its surface to reflect, scatter, absorb or transmit visible light. Since the drying changes the physical and chemical properties, it is expected that this affects its ability to disperse, absorb and transmit light, and therefore, to change their color. Moreover, the drying alters the natural plant dyes. Carotenoids are fatsoluble pigments present in green leafy vegetables and red and yellow. Unsaturated chemical structure makes them susceptible to degradation factors such as oxidation. These alterations of the carotenoids are greater the higher the temperature and the longer the drying treatment. The anthocyanins are also altered in this process. Chlorophyll,under damp heat conditions, is transformed into pheophytin, losing a magnesium (Rodriguez-Amaya, 2003).

Physical changes
Changes of structure in vivo cellular tissue, animal or plant, has a typical Turgor. Cell walls are under tension and cellular content under compression. The cell wall has a strength and elasticity, making it capable of supporting specific efforts and then return to its original state, but beyond a certain limit, changing the structure becomes irreversible. Upon cessation of the force causing the deformation, the cell does not return to its original state free of tension. This type of plastic deformation occurs to a greater or lesser degree, when dried plant or animal tissues, with the exception of freeze-drying, in which the original dimensions of quick frozen tissues are kept unchanged after drying (Srikiatden & Roberts, 2007).

As drying continues, the cells of the superficial layers flatten increasingly loses its eight cube vertices that become rounded. Following drying, the shrinkage or contraction begins to manifest itself throughout the piece, the eight vertices of the cube will have dried and hardened, while the center remains moist and plastic. The later phases of the contraction occurring mainly in central and parts of shapes, although it is normal to present distorted forms irregularly. If drying conditions are soft enough so that the surfaces are not much drier than the center, the piece will shrink with minimal distortion in shape. However, if the initial conditions are rigorous drying, the surface layers will dry up to a rigidity and mechanical strength, while the interior of the piece still remains wet and with little resistance. Under these circumstances, the final volume of the piece is now almost fixed when its average humidity is still high. The result is that the tissue breaks cracks or internally by one or more sites and wrinkles. The internal cracks open more and more. One consequence of this effect is that the overall density of a dried product is influenced significantly by the drying conditions. Quickly dehydrated products have a lower bulk density than dried slowly. If the drying air temperature is high and low relative humidity, there is danger of moisture from the surface of the product is removed faster than it can make the diffusion of water inside the product, which then produced called "case hardening". This phenomenon is avoided by controlling the relative humidity of air circulation and temperature. Obviously, these structural changes affect product texture, heat addition protoplasm coagulates proteins and destroys the properties of cell walls, missing the turgidity of the tissues. It is also concerned with the drying power of the starch thickener. These changes are irreversible so that the texture is changed, even after rehydration.

4.3 Water activity and sorption isotherms

The sorption isotherm relates the water activity to the water content of the mixture of water and material at a certain temperature and pressure. The water activity is defined as the ratio of the partial vapor pressure in equilibrium with the water in the product material and the vapor pressure in equilibrium with pure water at the same temperature (Van, 1981). Therefore, it characterizes the state of the water in products. This means that the sorption isotherm gives an impression how strong and in which way water is bound by the material constituents. The diffusion sorption drying model uses this information for three purposes. First, it describes the existence of two different classes of moisture in the material: bound and free moisture Second. The thermodynamics corresponding to this boundary are derived from the sorption isotherm. Both the boundary and the corresponding thermodynamics are used to model the conversion between bound and free water.

The water activity or equilibrium moisture content are determined by the type of material to be treated, its temperature and humidity. Likewise, depending on humidity and temperature the material has a characteristic vapor pressure that determines whether the material ar deliver adsorbs moisture on their exposure to the environment (Barbosa-Canovas & Fontana, 2007).

Moisture Sorption Isotherms

When a product is placed in an environment at a constant temperature and relative humidity, it will eventually come to equilibrium with that environment. If the product was originally fresh, it will probably lose water to the atmosphere (e.g. wilting); if the product is dehydrated it may well gain moisture becoming soft or soggy- it may also reach a point where bacteria may start to grow. This allows the definition of the equilibrium moisture content which is the moisture content of the material after it has been exposed to a particular environment for an infinite period of time, i.e. it has reached a state of equilibrium with the surrounding air.

The relationship between total moisture content and the corresponding a_w of a product over a range of values at a constant temperature yields a moisture sorption isotherm (MSI) when graphically expressed. These can be classified in to five general types. Type I is the Langmuir, and type II is the sigmoid or S-shaped adsorption isotherm. No special names have been attached to the other three types (Srikiatden & Roberts, 2007). MSI's of most products are non-linear, generally sigmoidal in shape, and have been classified as type II isotherms. Products rich in soluble components, such as sugars, have been found to show type III behaviour. Another behaviour commonly observed is that different paths are followed during adsorption and desorption processes, resulting in a hysteresis. The desorption isotherm lies above the adsorption isotherm, and therefore more moisture is retained in the desorption process compared to adsorption at a given equilibrium relative humidity (Lamharrar et al., 2007).Sorption isotherms are typically sigmoid in nature. For convenience they can be divided into three regions: R.H. 0-20%, water is tightly bound and unavailable for reactions; R.H. 20-80%, water is loosely bound; R.H. > 80%, water in the capillaries is free for reaction. This is an oversimplification.

4.4 Kinetics of the drying

Drying kinetics is generally evaluated experimentally by measuring the weight of a drying sample as a function of time. Drying curves may be represented in different ways; averaged moisture content versus time, drying rate versus time, or drying rate versus averaged moisture content. Several theories on the mechanism of moisture migration have been reviewed by, however, only capillary and liquid diffusion theories are, generally, applicable to the drying of food materials. Drying process can be described completely using an appropriate drying model, which is made up by differential equations of heat and mass transfer in the interior of the product and at its inter phase with the drying agent. Thus, knowledge of transport and material properties is necessary to apply any transport equation. Such properties are the moisture diffusivity, thermal conductivity, density, and specific heat and inter phase heat and mass transfer coefficients. Sometimes, in the literature instead of these properties, the drying constant, is used. This is a lumped parameter of the properties (Saeed et al., 2008).

Assuming that the resistance to moisture flow is uniformly distributed throughout the interior of the homogeneous isotropic material, the diffusion coefficient D_c is independent of the local moisture content and if the volume shrinkage is negligible, Fick's second law can be derived as follows (Panchariya et al., 2002; Barbosa-Canovas & Fontana, 2007):

$$\frac{\partial X}{\partial t} = D_c \frac{\partial X^2}{\partial x^2} \tag{4.1}$$

Where X is the moisture content, t is the time in seconds and $x$is the distance in meters. According to Fick's law, D_c is assumed as constant and diffusion as unidirectional where the external mass transfer resistance and volume change on moisture loss or gain are assumed negligible.

Crank in 1975 gave the analytical solutions of equation 4.1 for various regularly shaped bodies such as rectangular, cylindrical and spherical. Using Fick's second law with Arrhenius-type temperature dependent diffusivity these have been successfully predicted (Panchariya et al., 2002; Barbosa-Canovas & Fontana, 2007)

$$MR = \frac{X_i - X_e}{X_o - X_e} = \frac{8}{\pi^2} \sum \frac{1}{(2n+1)^2} \exp\left[\frac{-(2n+1)^2 \pi^2 Dt}{4L^2}\right] \tag{4.2}$$

Where, MR are the moisture ratio, X_i are the moisture content at any time, X_e are the equilibrium moisture content, X_o are the initial moisture content, D_t is the effective diffusivity coefficient (m^2/s), L is the thickness of the slab (m) and n is the positive integer. For sufficiently long drying times, only the 1^{st} term of the n=1 in equation 4.2 can be used with small error.

Effective moisture diffusivity was calculated by equation 4.2, using slopes derived from the linear regression of $[(\pi^2/8) * MR]$ versus time. It is noticed that the drying curves have a concave from when the curves. The semi-theoretical models are generally derived by simplifying general series solutions of Fick's second law or modification of simplified models and valid within the temperature, relative humidity, air flow velocity and moisture content range for which they were developed. These models required small time compared to theoretical thin-layer models and do not need assumptions of geometry of a typical biological product, its mass diffusivity and conductivity. Among semi-theoretical thin-layer drying models, the two-term model equation 4.3, the Henderson and Pabis model equation 4.4, the Lewis model equation 4.6, the Page model equation 4.7 and the modified Page model equation 4.8 are used widely. A two-term model to predict the drying rate of shelled corn fully exposed to air is suggested (Panchariya et al., 2002). This model presented is the first two terms of general series solution to the analytical of equation 4.1. However, it requires constant product temperature and assumes constant diffusivity. The two-term exponential model has the form

$$MR = \frac{X - X_e}{X_o - X_e} = A_0 \exp(-k_0 t) + A_1 \exp(-k_1 t) \tag{4.3}$$

where MR is a dimensionless number based on moisture content and referred to as the unaccomplished moisture ratio, X is the moisture at time t, X_0 and X_e are the material, initial, and equilibrium moisture contents in dry basis, respectively, and A_0; k_0; A_1 and k_1 are empirical coefficients. The Henderson and Pabis model is the first term of a general series solution of Fick's second law (Kröll, 1989; Kneule, 1975; Panchariya et al., 2002; Srikiatden & Roberts, 2007)

$$MR = \frac{X - X_e}{X_o - X_e} = A_0 \exp(-k_0 t) \tag{4.4}$$

This model was used successfully to model drying of corn, wheat and peanut. The slope of this model, the coefficient k_0; is related to effective diffusivity when drying process takes place only in the falling rate period and liquid diffusion controls the process. The Lewis model is a special case of the Henderson and Pabis model where intercept is unity. It described that the moisture transfer from the product products and agricultural material can be seen as analogous to the flow of heat from a body immersed in cool fluid. By comparing this phenomenon with Newton's law of cooling, the drying rate is proportional to the difference in moisture content between the material being dried and the equilibrium moisture content at the drying air condition as this model was used to study the drying behavior(Srikiatden & Roberts, 2007):

$$\frac{dX}{dt} = -k_0(X - X_e) \tag{4.5}$$

Or after integrating yields

$$MR = \frac{X - X_e}{X_o - X_e} = \exp(-k_0 t) \tag{4.6}$$

The Page model is a modification of the Lewis model to overcome its short comings. This model has produced good fits in predicting drying of grain and rough rice, white bean, and shelled corn (Panchariya et al., 2002).

$$MR = \frac{X - X_e q}{X_o - X_e} = \exp(-k_0 t^n) \tag{4.7}$$

White also modified the Page model to describe the drying of soybean

$$MR = \frac{X - X_e q}{X_o - X_e} = \exp(-k_0 t)^n \tag{4.8}$$

The empirical models derive a direct relationship between average moisture content and drying time. They neglect the fundamentals of the drying process and their parameters have no physical meaning. Therefore, they cannot give a clear accurate view of the important processes occurring during drying although they may describe the drying curve for the conditions of the experiment. Among them, the Thompson model presented in (equation

4.9) was used to describe the shelled corn drying and the Wang and Singh model (equation 4.10) was applied to study the intermittent drying of rough rice.

$$t = a\ln(MR) + b(\ln(MR))^2 \tag{4.9}$$

where:

$$MR = 1 + at + bt^2 \tag{4.10}$$

The influence of the experimental drying variables is determined by the values of the model parameters, A_0 from the initial conditions and k_0 in the form of Arrhenius- and Power-type equations in the following way:

In the Arrhenius type:

$$k_0 = (\alpha_0 V^{\alpha_1} \exp\left(\frac{\alpha_2}{T}\right)) \tag{4.11}$$

In the Power type:

$$k_0 = \beta_0 T^{\beta_1} V^{\beta_2} \tag{4.12}$$

Here T is the absolute temperature of the air (K), V is the air velocity (m/s), α_0; α_1; α_2; β_0, β_1, and β_2 are constants.

The dry-basis moisture content X_t of the product at time t is defined as the ratio between the amount of water in the product and the amount of dry solid ($g_{water}/g_{drymatter}$). In order to express a characteristic drying curve, the biological product must be evaluated with respect to the equilibrium moisture content in a given drying system:

$$X = X_t - X_{eq} R_d = -\frac{MdX}{Adt} \tag{4.13}$$

When R_d is the rate of evaporation of water (g/m^2h), A is the evaporation area and M is the mass of dry solid. If A is not know, then the drying rate may be expressed in g water evaporated per hour (Baker, 1997).

It has been accepted that drying phenomenon of biological products during the falling rate period is controlled by the mechanism of liquid and/or vapour diffusion. Thin-layer drying models that describe the drying phenomenon of these materials mainly fall into three categories namely, theoretical, semi-theoretical and empirical. The first takes into account only internal resistance to moisture transfer while the other two consider only external resistance to moisture transfer resistance between product and air (Panchariya et al., 2002).

A typical curve for convective drying of capillary-porous materials is presented in **Figure** 4.1. The preheating period, characterized by non-linear curve, appears at the very beginning of drying. After preheating begins the constant drying rate period, called also the first period of drying. The period is characterized by a straight section if the drying conditions are stable. At point K_1 the straight section ends, and the curve tends asymptotically to the equilibrium moisture content at given drying condition (Kowalski, 2003; Molnár, 2007; Kneule, 1975).

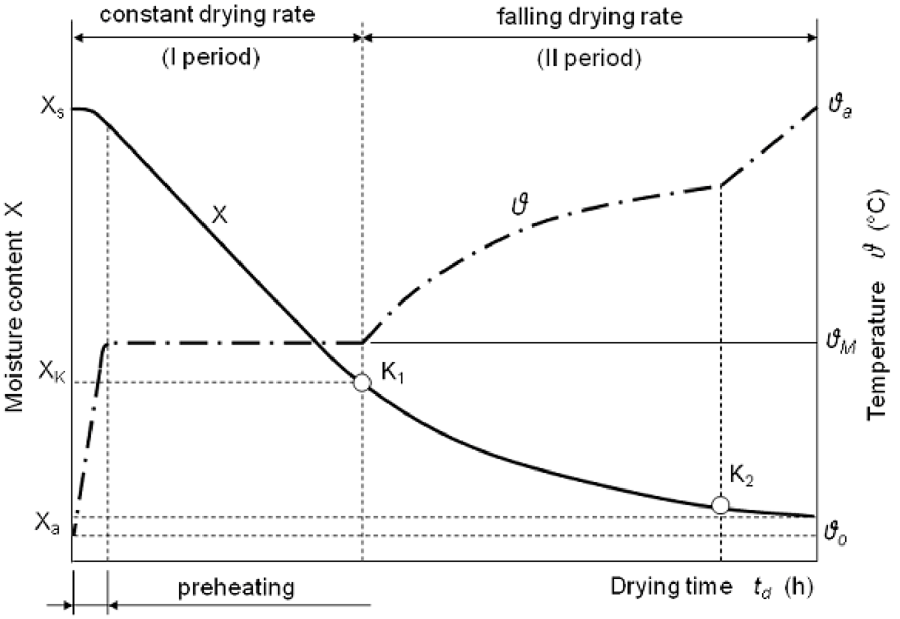


Figure 4.1: A typical drying curve for a colloidal capillary- porous body. Adapted from (Kowalski, 2003)

From point K_1 begins the falling rate period, called also the second period of drying. The falling rate period may be divided in some cases into determined and undetermined falling rate periods. Point K_1, which separates the first and second period of drying, has been called the critical point of drying, and the moister content corresponding to this point the critical moisture content. During the first period of drying,free water is removed from the surface and macro capillaries. The temperature of the dried body becomes constant and equal to the wet bulb temperature. The surface of the material remains wet until the critical point of drying as water is supplied from the interior of the material mainly due to capillary forces.

When the free water is removed, the second period of drying begins. A characteristic feature of this period is a continuous increase of the dried body temperature, beginning from the wet bulb temperature up to the temperature of the drying medium. The moisture inside the capillary-pore space is in funicular (continuous liquid on the pore walls) or pendular (isolated pockets of liquid) states. The retreating of liquid/air meniscuses into the body may occur in this stage of drying in materials with relatively large pores. Initially it involves the meniscuses in capillaries of greater dimensions and gradually also the capillaries of smaller dimensions. It causes an elongation of the diffusion path for the vapor molecules.Thus, the drying rate decreases constantly until the end of drying (Maltry et al., 1962; Mujumdar, 1997; Masters, 1997; Baker, 1997)

4.5 Characteristics of Lemon Balm

Botanical name: *Melissa officinalis* L. This medicinal and aromatic plant owes its name to the lemony scent of its leaves. The will of the family Lamiaceae belonging balm grown for centuries in Europe. The first cultivation of drug stocks yielding balm was laid in 1650 near Nuremberg. Originally this plant comes from the eastern Mediterranean and was introduced around 800 years after Christ by Benedictine monks in Germany. 1938 amounted to approximately 10 hectares of cultivated area in Germany (Heeger, 1989; Bundessortenamt, 2002). The yield of essential oil is approximately an oil yield 3 to 5 $liters/ha$ in two sections (Bayerischen, 2001; Bomme, 2001).

The essential oil content depending on provenances, variety, harvesting stages, harvesting hours and the drying method. Dry leaves of Lemon balm contain 0.002-0.30 essential oil. As a result of low essential oil has a very high price level. The chemical composition of its essential oil has been extensively studied. The main compounds of the essential oil of Lemon Balm leaves are citral (geranial and neral), citronellal, geraniol, linalool, $\beta - caryophyllene$, $\beta - caryophylleneoxide$, germacrene D and ocimene (Karasova & Lehotay, 2005; Ayanoglu et al., 2005; Özgüven et al., 1999; Dastmalachi et al., 2008).

Botany
Depending on the variety, the Lemon Balm reached a height of 100-120cm. Their stem is square and has heart-shaped, 2-6cm long, 1.5-5 wide, regularly notched- and sawed up becoming small leaves. The essential oil-containing leaves smell when rubbed strongly lemon zest and spicy taste. The oil is located in oil reservoirs, such as glands and glandular hairs shed (see **Figure** 4.2).

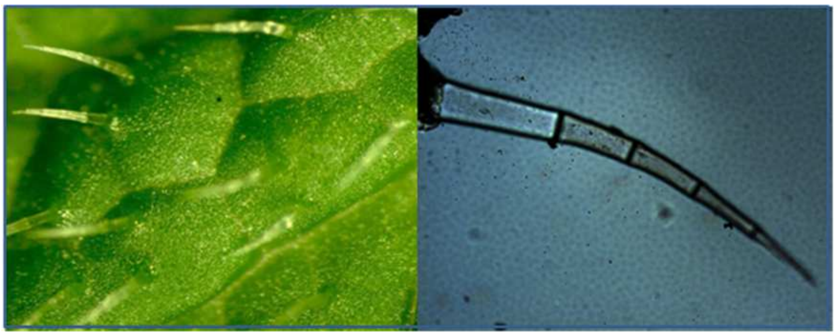


Figure 4.2: Ethereal oil of *Melissa officinalis* L. location. a) glandular hairs on fresh leaf of *Melissa officinalis* L. (40X magnification). b) glandular hair by light microscopic view (magnification 100X)

Their flowering period begins in late June and can take place by the end of August-September. The color of the flowers is bluish white, or yellowish white (Heeger, 1989; Bayerischen, 2001). The balm can be considered in the beekeepers' bees-herb known. The plant is rubbed into the hives, because the smell reminds swarm of the scent of Lemon Balm herb (Heeger, 1989).

4.5.1 Uses of Lemon Balm

Harvest and Use: Lemon balm has many uses. As a cosmetic, it makes a good skin cleanser. Steamy facials are recommended for acne. Dry leaves are used in potpourri. It is reputed to repel insects and can be blended with other insect repelling herbs such as lavender, lemongrass, and rue. Rub down the kitchen table with the herbs to keep bugs from product and throw some in the campfire or barbecue pit to keep bugs away. Beekeepers have rubbed it on the inside of the hives to encourage a new swarm to stay.

Lemon balm makes both delicious beverage and medicinal teas. It is also nice added to black tea. Fresh leaves can be chopped and added to green salads, fruits salads, marinated vegetables, poultry stuffing, and fish marinades and sauces. Medicinally Lemon Balm is used in tea for fevers, to help digestion, and for tension headache. The essential oil is used in aromatherapy for depression, melancholy, and nervous tension. Externally in salve, it has been effective in relieving symptoms of herpes simplex, sores, and painful swellings. A compress is good for gout. A most exciting development is that this very common plant is being investigated along with common sage as herbs with memory-improving properties (Bomme, 2001; Chung et al., 1967; Halsey, 1985). The volatile oil contains citral, citronellal, eugenol acetate and geraniol. Both oil and hot water extracts of the leaves have been shown to possess strong antibacterial and antiviral qualities. The extract of Lemon balm was also found to have exceptionally high antioxidant activity. Lemon balm is mentioned in the scientific journal Endocrinology where it is explained that *Melissa officinalis* L. exhibits antithyrotropic activity, inhibiting TSH from attaching to TSH receptors, hence making it of possible use in the treatment of Graves' disease or hyperthyroidism.

4.5.2 Loss of essential oil

To achieve increased dryer capacity, drying temperature should be chosen as high as possible without reducing the quality of the product. Maximum allowable temperatures depend mainly on the chemical composition of the active ingredients of the medicinal plant species under consideration. For glycoside species, a maximum temperature of 100°C is recommended, for mucilage species 65°C and for essential-oil species 35 to 45°C (Maltry et al., 1962). Due to the high heterogeneity among medicinal plant species, these global recommendations can only serve a rough indication (Müller & Heindl, 2005).

Monoterpenes are the major components of essential oils, and particularly of the essential oil of Lemon Balm (*Melissa officinalis* L.). There are several factors that influence its emission: environmental variables, own physiological processes of the plant and environmental stress (water-physical). In the first factor, the variables of temperature, humidity and light are considered. It was found that when leaves are exposed to high levels of radiation and temperature, increases the capacity for isoprene and monoterpenes emission and in the presence of high humidity there is a slight but positive influence on the emission, as has been observed for sage, mint (Sabillon, 2002). Although the boiling points of the main compounds of essential oil are larger than for the water, these compounds can evaporate at lower temperatures by hydro-distillation following the principle of heterogeneous substances, under which each exerts its own vapor pressure as the other component is absent and when the combined vapor pressure reaches the pressure of compound (atmospheric pressure for example), the mixture is evaporated, which in essence is similar to what happens in drying as these compounds are in contact with water that is removed and they are transported by the hot air.

4.5.3 Color change of leaves by drying

As many medicinal plant species are used as tea, colour is an essential quality criterion because it is directly apparent to consumers. For colour measurement, the CIELAB system is frequently applied using lightness L*, chroma C* and hue h as parameters (Müller & Heindl, 2005). Regarding the effects on the color, the elements of hue, saturation and Lightness change significantly with drying. The change in color of the leaves of Lemon Balm can be explained chemically. The bright yellow-green color of the leaves of Lemon Balm is due to chlorophyll a (blue-green) and chlorophyll b (yellow green) that are in chloroplasts in 3:1 ratio and in the carotenoid especially β-carotene (Maiocchi & Avanza, 2004). Chlorophyll can present different types of alterations, the most frequent and more damaging to the color of the leaves containing it, is the loss of the magnesium atom, forming the so-called feofitina that is olive green with brown tones, instead of brilliant green of chlorophyll. The loss of magnesium is produced by being replaced by two H+ ions and consequently this situation is favored by acidic conditions and the conditions of temperature and pressure. Plants are always acid, and the heat treatment generally liberates acids present in the vacuoles of the cells by decreasing the pH of the medium (Calvo, 2003). Moreover carotenoids have many double bonds, which make them very susceptible to oxidation, particularly in photooxidation reactions. Such oxidation reactions lead to loss of color of the leaves. These alterations are greater as the temperature is higher and longer the drying treatment (Vanaclocha, 2008). This is in agreement with previously reported investigations (Capecka et al., 2004) related to the antioxidant activity of fresh and dried herbs. Particularly for Lemon Balm is reported more than 50% loss of carotenoids after drying.

4.5.4 Quality attributes of Lemon Balm

Quality is the extent to which a product meets the needs of the consumer. It includes sensory properties, psychological factors as well as other factors such as contributions to health and compatibility with life-style conditions. In general, the quality experience of the consumer can be linked to product properties, so-called quality attributes.

Quality attributes can be divided into three major categories: sensory, hidden and quantitative (Salunkhe et al., 1991). The sensory characteristics of quality include colour, gloss, size, shape, texture, consistency, flavour and aroma, which the consumer can evaluate with his senses. One of the most important sensory quality attributes is colour, because it measures the first impact of the product on the consumerï¿½s perception. Other important attributes in the initial acceptance of a product are appearance, flavour and texture.

Quality attributes that the consumer cannot evaluate with his senses are the hidden characteristics, such as nutritive value, presence of harmful or toxic substances. Quantity is also considered an attribute of quality, since it forms a part of the total quality evaluation of a product, e.g. the finished product yield of medicinal plants (Salunkhe et al., 1991).

Lemon balm is known by its pharmaceutical applications. Since 2001, considering for standards in the European Pharmacopoeia that this drug at least 4.0% rosemary acid, more than 2% foreign matter and not more than 10% moisture content to include. 10% of the stem portion may be larger than $1mm$ in diameter (Bundessortenamt, 2002; Bayerischen, 2001). A minimum content of essential oil, there is no official requirement. Frequently requested by client companies have a minimum oil content, which, depending on the origin of between 0.015 to 0.17 $ml/100g_{d.m.}$ Main components of the essential oil: citral (mixture of neral and geranial are), citronellal, linalool and β-caryophyllene. By gas chromatographic a total of 70 components in the essential oil are known (Salzer & Gerhardt, 2007). The real oil is a rare commercial product. It is often offered to trade the less valuable melissa oil from lemon, lemon grass or citronella. The balm oil is mainly used in the pharmacological field.

5 Measurement of quality characteristics

5.1 Moisture Content Determination

To determine the moisture content of Lemon Balm before and after drying, the oven method was used. In this method the sample is placed inside an oven at 103°C (±2 °C) for 24 hours and the loss of weight is registered in order to determine the moisture content of the sample (Association of official analytical chemists, 1990)

The moisture content MC of a product is determine by using two references: dry or wet basis. The moisture content by using wet basis can be calculated by using equation 5.1 and is expressed in percent (Kneule, 1975; Martinov et al., 2007).

$$MC_{w.b.} = \frac{m_w}{m_w + m_{d.m.}} \times 100 \tag{5.1}$$

Where $MC_{w.b.}$ is the moisture content in wet basis, m_w is the mass of water and $m_{d.m.}$ is the mass of dry matter.

The moisture content by using dry basis (X) is defined as mass of water per dry mass and is calculated using equation 5.2. The results of the expression are frequently expressed as a percentage, but is preferred to refer them as a ratio (Müller & Heindl, 2005).

$$X = \frac{m_w}{m_{d.m}} \tag{5.2}$$

Where X is the moisture content in dry basis, m_w is the mass of water and $m_{d.m.}$ is the mass of dry matter.

The relationship between $MC_{w.b.}$ and X is represented by equation 5.3.

$$X = \frac{MC_{w.b.}}{1 - MC_{w.b.}} \tag{5.3}$$

5.2 Essential oils content

The determination of essential oil content for each experiment (before and after drying) was performed considering freshly harvested material and dry drug by using steam distillation according to the method recommended by the DAB 10 (Deutsches Arzneibuch, 1986). The size of the samples used for the determination of essential oil content from the leaves of Lemon Balm were: 100g of leaves for fresh material, taken the same day of harvest, and 20 g for dry material, which were taken randomly from the dried material.

The distillation-extraction process was carried out for 3 hours considering three replicates.

The total amount of essential oil recovery was calculated in $ml/100g$ based on the dry matter (d.m). Losses of essential oil were calculated in percentage based on the difference of the essential oil content between the fresh leaves and samples taken from the dried material. **Figure** 5.1, shows the device recommended by the DAB 10 (Deutsches Arzneibuch, 1986) for the distillation process.

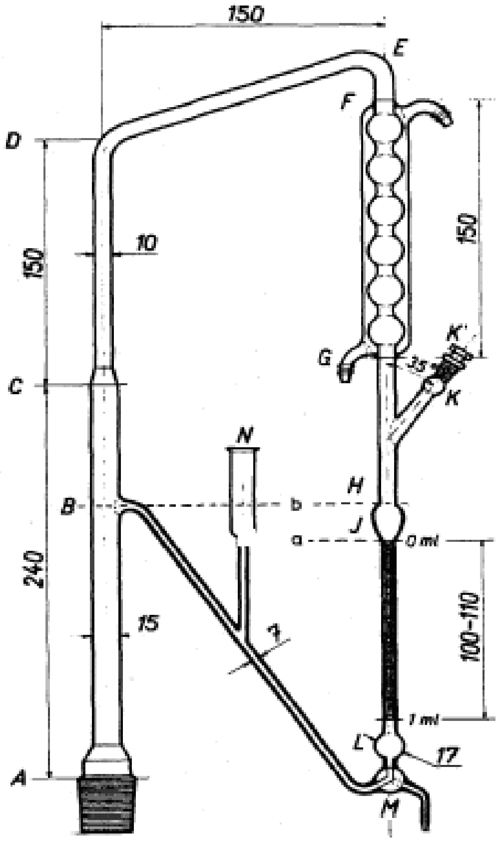


Figure 5.1: Apparatus for the determination of the essential oil content in drugs from DAB10

5.3 Measurement of Color

The method used for measuring the color of leaves of Lemon Balm, before and after reached a 10% moisture content value with the drying process, was the same for all the experiments. For the measurements, a chromameter Minolta CR-400© was used. The chromameter was calibrated before the measurements by using a white ceramic plate as reference. Additionally a sample size of five leaves selected randomly was considered. Furthermore for measuring the color of fresh product the samples were taken the same day of the experiment.

The evaluation of color was based on chromaticity values in the CIELAB color space system as shown in **Figure** 5.2. In the CIELAB system (see **Figure** 5.3) the L-axis is defined in a range between (0) and (100) which represents darkness (0) to lightness (100). The a-axis describes the green to red intensity on a negative to positive scale, while the b-axis is used in the same manner to describe the blue to yellow intensity.

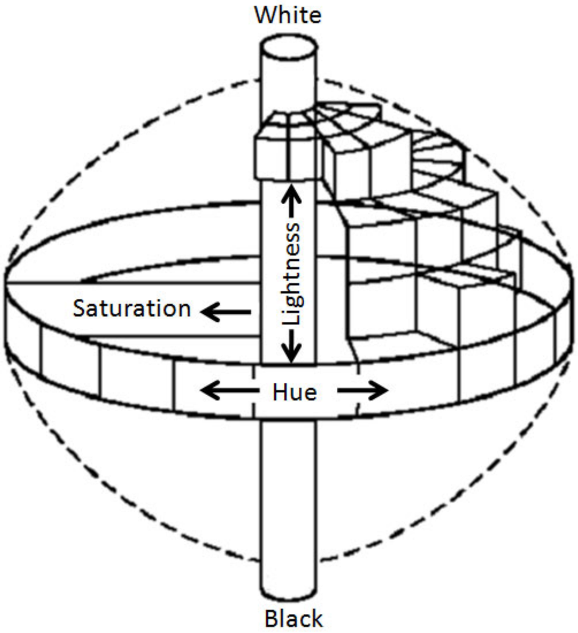


Figure 5.2: Three-dimensional representation of the elements of color

Colorimeters make quantitative and repeatable measurements of the color and their difference. For this several spaces have been developed for defining the coordinates of color. For the experiments the coordinates $L^*a^*b^*$ were considered (see **Figure** 5.3). In this space L^* indicates the brightness, a^* and $b*$ are the chromatic coordinates or address of the colors: $+a^*$ indicates the address to red, $-a*$ indicates the address toward green, $+b^*$ the address to yellow and $-b^*$ the address to blue; the center is achromatic.

For determination of color difference the norm DIN 6174 (DIN, 1979) was applied. For all the experiments, the measurement of the color of the fresh product was considered as reference. For this procedure, five leaves, harvested the same day of the experiment, were selected randomly to obtain the reference sample. Then five leaves of dried product were selected randomly and the color was measured with the same protocol as the fresh product.

For the determination of color difference the values of the reference sample were compared with each of the measurements of the samples of dried product. Later on the average of the color differences was calculated.

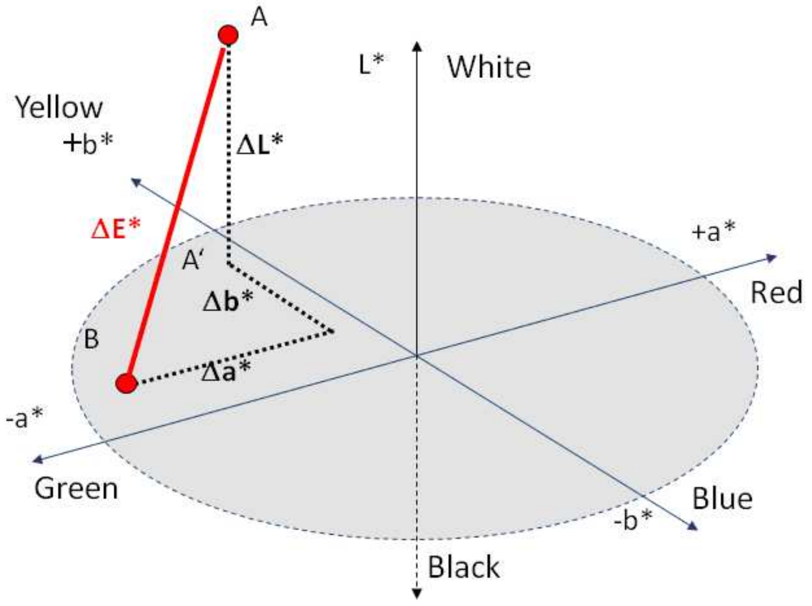


Figure 5.3: Chromacity diagram: L*, a* and b*

The colorimeter is used to measure the color difference with respect to a reference. The values of L^*, a^* and b^* of the reference are compared with the respective values of the sample under analysis in order to determine ΔL^*, Δa^* and $\Delta b*$. From this values the color difference ΔE is calculated by using the following expression:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{5.4}$$

To obtain the difference in saturation and hue, using the same color space, the following equations are considered:

$$C = \sqrt{(a^*)^2 + (b^*)^2} \tag{5.5}$$

$$\Delta H = \sqrt{(\Delta E^*_{ab})^2 + (\Delta L^*)^2 + (\Delta C^*)^2} \tag{5.6}$$

$$\Delta H = \sqrt{(a^*)^2 + (b^*)^2 + (\Delta C^*)^2} \tag{5.7}$$

Where C is the saturation and ΔH is the difference of tonality. A positive value of C indicates that the color of the sample is more alive and if not the color is more opaque. The hue angle h^* is the color value which is defined as starting from the positive a^* axis and it is expressed in degrees: 0° (red), 90° (yellow), 180° (green) and 270° (blue). The hue angle h^* is the color value which is defined starting from the positive a^* axis. It is expressed in degrees: 0° (red), 90° (yellow), 180° (green) and 270° (blue).

$$h^* = arctang(b^*/a^*) \tag{5.8}$$

6 Experimental determination and mathematical fitting of sorption isotherms

Experimental evaluation of sorption characteristics can aid in the improvement of the processing quality of medicinal and aromatic plants. In the literature, numerous equations have been suggested to represent the relationship between equilibrium moisture content and relative humidity (Van, 1981). Knowledge of the equilibrium moisture content (EMC) is important for modeling and planning the drying process and to select the conditions for storage of the product. Knowledge of the sorption properties of medicinal plants has great importance in the analysis of dehydration, especially in the quantitative approach to the prediction of the useful life of dried products. Equations for modeling water sorption isotherms are of special interest for many aspects of product preservation by dehydration, including evaluation of the thermodynamic functions of the sorption water in medicinal plants. Knowledge of the thermodynamic properties associated with sorption behavior of water is important to dehydration in several aspects, especially in design and optimization of drying units and equipment.

6.1 Materials and methods

Lemon Balm (*Melissa officinalis* L.) was used for the determination of sorption isotherms. The Lemon Balm was planted in Witzenhausen- Germany (51°20'45.76" N, 9°51'52.08"E) and the samples were harvested little before the flowering and only the leaves were taken randomly to complete the selected size of the sample. For the measurement of the weight of the samples a precision analytic balance with resolution of 0.0001g was used. To obtain the required temperature conditions for each test a forced ventilation oven was considered. The required humidity conditions were obtained by using saline solutions that generate different humidity conditions depending on the temperature (DIN, 1982). During the test, the samples were placed inside glass bottles that contain the solutions, in order to maintain the product at constant conditions of humidity and temperature. The bottles are transparent and have one liter of capacity with hermetic seal. The samples were placed inside the bottles by using a perforated stainless steel container that allows gas exchange.

To determine the isotherms, the methodology recommended by the European project COST 90 was applied (Spiess & Wolf, 1983). This methodology is based on the gravimetric method that uses saline solutions. The saline solutions were prepared according to the norm DIN 50008 (DIN, 1982), considering humidity ranges between 10 and 80% as shown in **Table 6.1**. In this study, isotherms of desorption at 25, 40, 50 and 60°C and isotherms of adsorption at 40, 60°C were obtained. **Figure 6.1** shows the considered methodology to determine the sorption isotherms.

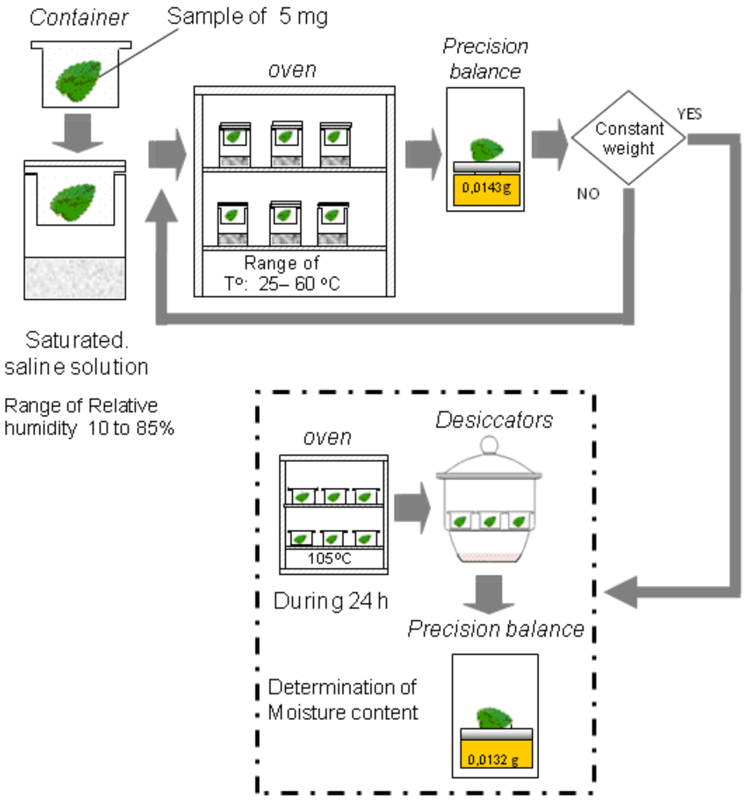


Figure 6.1: Steps for determining the sorption isotherm.

The samples at constant relative humidity and temperature conditions were weighed every 3 days until there is no weight difference (it was assumed no more than 0.0001 g). At this point the equilibrium between the product and surroundings is reached. After that, the moisture content of the sample was determined by using the oven method, in which the temperature was maintained at 105°C during 24 hours (Association of official analytical chemists, 1990). At last, the sample was maintained inside a desiccator during 30 minutes before weighing it. The amount of equilibrium moisture content EMC in a product is determined considering dry or wet basis. On wet basis it can be calculated as follows using the following equation:

$$EMC(w.b) = \frac{m_w}{(m_w + m_{d.m})}100 \tag{6.1}$$

The moisture content on dry basis (X) which is defined as mass of water per dry mass was also calculated using the following mathematical equation:

$$X = \frac{m_w}{m_{d.m}} \tag{6.2}$$

Where, m_w: is weight of water contained in the product $m_{d.m}$: dry matter weight of the product

Table 6.1: Relative humidity (%) obtained by the salt solution in a closed vessel at different temperatures (DIN 50008-part1)

Salt	25°C	40°C	50°C	60°C
LiCl	12	11	11	11
CH_3COOK	22	20	-	-
$MgCl_2$	33	32	31	30
K_2CO_3	43	40	38	36
$Mg(NO_3)_2$	53	48	46	43
$NaNO_2$	64	61	60	58
NaCl	75	75	75	75
KCl	85	83	81	80

The values obtained in the experiment are fitting using the models of BET, GAB, Halsey, Oswin, Peleg, Henderson and Chung & Pfost. The non-linear regression and the method Marquart were used. To evaluate the level of fitting, statistical analysis with the Chi-square test and the determination coefficient R^2 were considered (see Appendix A). The models used in this study for the fitting of isotherms obtained experimentally are presented in the **Table 6.2**.

Table 6.2: Mathematical models used to describe the sorption isotherms of Lemon Balm

Modell	Formel
BET lineal (Bell & Labuza, 1984)	$X_e = \frac{a_w\ X_m\ C}{(1-a_w)\ 1+(C-1)\ a_w}$
GAB (Timmerman et al., 2001)	$X_e = \frac{X_m K a_w}{(1-ka_w)(1-ka_w+Cka_w)}$
Halsey (Halsey, 1985; Silva et al., 2007)	$X_e = X_m \left[\frac{-A}{\log(a_w)}\right]^{\frac{1}{n}}$
Henderson (Bell & Labuza, 1984)	$X_e = \left[\frac{-\log(1-a_w)}{k \times (T+C)}\right]$
Langmuir (Soysal, 1999)	$X_e = \frac{X_m C a_w}{1+C a_w}$
Oswin (Barbosa-Canovas & Fontana, 2007)	$X_e = A\left[\frac{a_w}{1-a_w}\right]$
Peleg (Timmerman et al., 2001)	$X_e = k_1 A_w^{n_1} + k_2 A_w^{n_2}$
Chung & Pfost (Spiess & Wolf, 1983)	$X_e = E - D\ln((C-T)\ln(a_w))$

A, B, C, k, k_1, k_2, n, n_1, n_2, E and D are constants of models

6.2 Results

Figure 6.2 and 6.3. show the experimental data obtained after desorption performed on *Melissa officinalis L.* at 25, 40, 50, and 60 °C and adsorption at 40°C and 60°C for eight relative humidities. It can be observed that sorption isotherms are temperature dependent. A higher temperature will decrease the binding energy between molecules, because of an increased state of excitation of the molecules, their mutual distances increase and the attractive forces between them decrease. They become less stable and break away from the water binding site of the food materials. Consequently, the results reveal the temperature dependence of the sorptive behavior, with an increase in temperature decreasing the sorption capacity. This is consistent with the thermodynamics of sorption (Hossain et al., 2001). The EMC increases with decreasing temperature at the constant relative humidity. The sorption isotherms present the characteristic S-shaped curve (Type II), typical of many hygroscopic products.

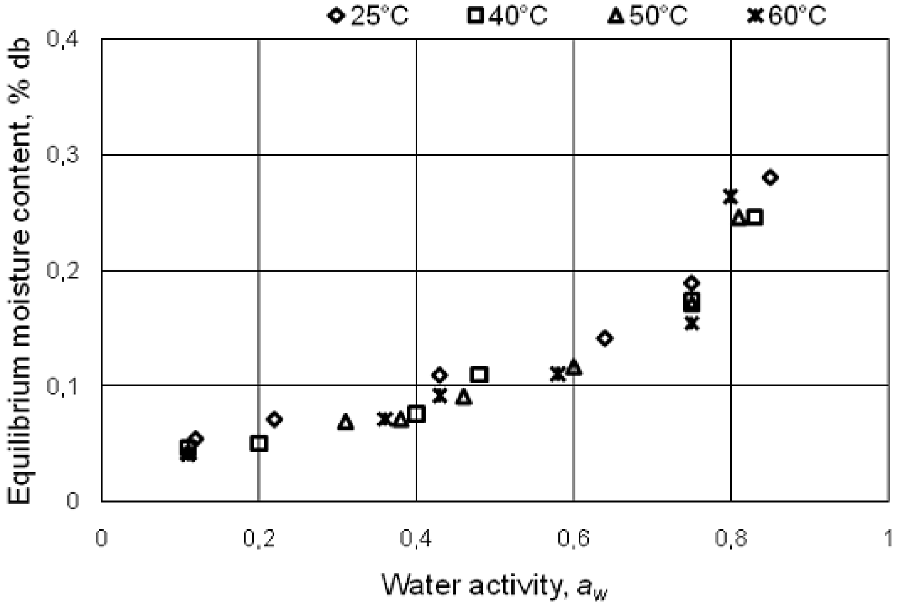


Figure 6.2: Experimental data for four temperatures corresponding to desorption isotherms of Lemon Balm with relative humidity between 10 and 80%.

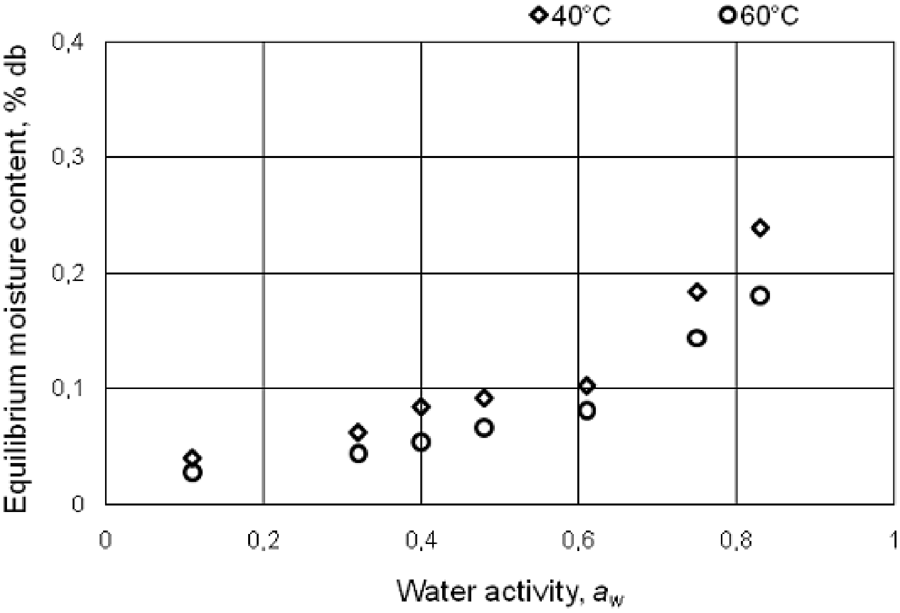


Figure 6.3: Experimental data for two temperatures corresponding to adsorption isotherms of Lemon Balm considering relative humidity between 10 and 80%.

6.3 Mathematical models evaluation

By using non-linear regression analysis (Ross, 2005), the models in **Table 6.2** were fitted to the experimental data proposed. For the evaluation of the non-linear regression two approaches were considered: Chi-square test X^2 and the coefficient of determination R^2 (see appendix A). From these approaches, the values of the lowest X^2,or those that tend to zero and the highest R^2 or those that tend to 1, are considered optimal, and are used as criteria to determine the best model (Ross, 2005).

The results of nonlinear regression analysis for fitting desorption and adsorption models to experimental data and the estimated constants for all models analyzed in this research, the coefficient determination R^2 and Chi-square test (see appendix A) for all models data are presented in **Table 6.3**. In **Table 6.4** and **Table 6.5** are the values of desorption equilibrium moisture content for different values of temperature and relative humidity, obtained with the models that best fitted the experimental values.

Table 6.3: Estimated parameter values and criteria for comparing the models in desorption for Lemon Balm.

	Adsorption			Desorption				
Model	Constant	40°C	60°C	Constant	25°C	40°C	50°C	60°C
BET	X_m	0.0428	0.0355	X_m	0.0444	0.0434	0.046	0.048
	C	142.68	23.15	C	3.12	3.35	79.54	30.79
	Chi^2	0.0007	0.0001	Chi^2	0.0019	0.0015	0.0003	0.0021
	R^2	0.989	0.9975	R^2	0.9646	0.9561	0.9913	0.9337
GAB	X_m	0.0318	0.0041	X_m	0.0711	-	-	0.0752
	C	-38.356	0.0206	C	26.742	-	-	14.932
	k	10.444	-37.205	k	0.9062	-	-	0.9042
	Chi^2	0.0079	0.0041	Chi^2	0.0039	-	-	0.0054
	R^2	0.8697	0.9014	R^2	0.9547	-	-	0.9061
Halsey	X_m	0.1558	0.1371	X_m	0.1692	0.1618	0.1601	0.1608
	A	0.1471	0.1306	A	0.1561	0.1496	0.1524	0.1553
	n	13.719	12.697	n	11.663	1.517	13.184	12.113
	Chi^2	0.0004	0.0001	Chi^2	0.0002	0.0007	0.0004	0.0024
	R^2	0.9932	0.9984	R^2	0.9947	0.9774	0.9867	0.9237
- Henderson	k	0.5034	0.5967	k	0.4547	-0.372	0.9182	-
	n	19.551	18.193	n	13.841	14.157	24.609	-
	C	12.071	11.716	C	-13.18	-55.24	-3.17	-
	Chi^2	0.0055	0.0027	Chi^2	0.0018	0.0018	0.0088	-
	R^2	0.9067	0.9277	R^2	0.9498	0.9546	0.7664	-
Langmuir	X_m	0.393	0.3113	X_m	13.778	15.627	126.211	-
	C	0.9456	0.919	C	0.2266	0.1787	0.0182	-
	Chi^2	0.0089	0.0049	Chi^2	0.0051	0.0031	0.005	-
	R^2	0.8435	0.866	R^2	0.858	0.8985	0.8378	-
Oswin	A	0.0955	0.0742	A	0.1184	0.1083	0.0994	0.0971
	B	0.5709	0.6045	B	0.474	0.4965	0.5809	0.6295
	Chi^2	0.0007	0.0001	Chi^2	0.0006	0.0007	0.0009	0.003
	R^2	0.9892	0.9964	R^2	0.984	0.976	0.9719	0.9047
Peleg	k_1	0.1451	-0.218	k_1	0.1437	0.1376	0.1449	0.1532
	n_1	14.654	11.812	n_1	12.009	1.157	14.335	15.458
	k_2	0.1451	0.4561	k_2	0.1437	0.1376	0.1449	0.1532
	n_2	15.518	13.857	n_2	0.9854	11.646	14.041	15.194
	Chi^2	0.0028	0.0012	Chi^2	0.0042	0.0022	0.0032	0.0056
	R^2	0.9551	0.9719	R^2	0.8827	0.9287	0.8974	0.8259
Chung & Pfost	E	0.5105	-	E	0.4993	0.5153	0.5347	0.5585
	D	0.0808	-	D	0.0821	0.0792	0.082	0.0846
	C	-168.62	-	C	-102.05	-170.41	-197.01	-212.85
	Chi^2	0.0025	-	Chi^2	0.0021	0.0016	0.0029	0.0054
	R^2	0.9572	-	R^2	0.9414	0.9483	0.904	0.8266

Table 6.4: Desorption equilibrium moisture contents of Lemon Balm leaves obtained at different water activities and temperatures and estimated by different models

	BET				Halsey				Oswin			
a$_w$	25°C	40°C	50°C	60°C	25°C	40°C	50°C	60°C	25°C	40°C	50°C	60°C
0.1	0.049	0.048	0.046	0.041	0.054	0.046	0.038	0.035	0.042	0.036	0.028	0.024
0.2	0.055	0.054	0.055	0.053	0.067	0.059	0.05	0.046	0.061	0.054	0.044	0.041
0.3	0.063	0.062	0.064	0.064	0.08	0.071	0.063	0.059	0.079	0.071	0.061	0.057
0.4	0.074	0.072	0.075	0.076	0.095	0.085	0.077	0.074	0.098	0.089	0.079	0.075
0.5	0.089	0.087	0.091	0.093	0.113	0.102	0.096	0.093	0.118	0.108	0.099	0.097
0.6	0.111	0.108	0.114	0.117	0.136	0.125	0.12	0.12	0.144	0.132	0.126	0.125
0.7	0.148	0.145	0.153	0.158	0.17	0.158	0.158	0.161	0.177	0.165	0.163	0.166
0.8	0.222	0.217	0.229	0.238	0.227	0.215	0.226	0.237	0.228	0.215	0.222	0.233
0.9	0.444	0.434	0.46	0.478	0.362	0.353	0.399	0.441	0.336	0.322	0.356	0.387

Table 6.5: Adsorption equilibrium moisture contents of Lemon Balm leaves obtained at different water activities and temperatures and estimated by different models

	BET		Halsey		Oswin	
a_w	40°C	60°C	40°C	60°C	40°C	60°C
0	0	0	0	0	0	0
0.1	0.045	0.028	0.039	0.028	0.027	0.020
0.2	0.052	0.038	0.050	0.037	0.043	0.032
0.3	0.060	0.046	0.062	0.046	0.059	0.044
0.4	0.071	0.056	0.075	0.057	0.076	0.058
0.5	0.085	0.068	0.092	0.071	0.096	0.074
0.6	0.106	0.086	0.115	0.090	0.120	0.095
0.7	0.142	0.116	0.150	0.120	0.155	0.124
0.8	0.213	0.176	0.211	0.173	0.211	0.171
0.9	0.427	0.354	0.365	0.313	0.335	0.280

6.4 Analysis of results

Figure 6.4 though 6.8, shows the best values fitted desorption isotherm models for different considered temperatures. In **Table 6.3** can be observed that the BET, Oswin and Halsey are those with the lowest Chi-square values and R^2 values near to 1.

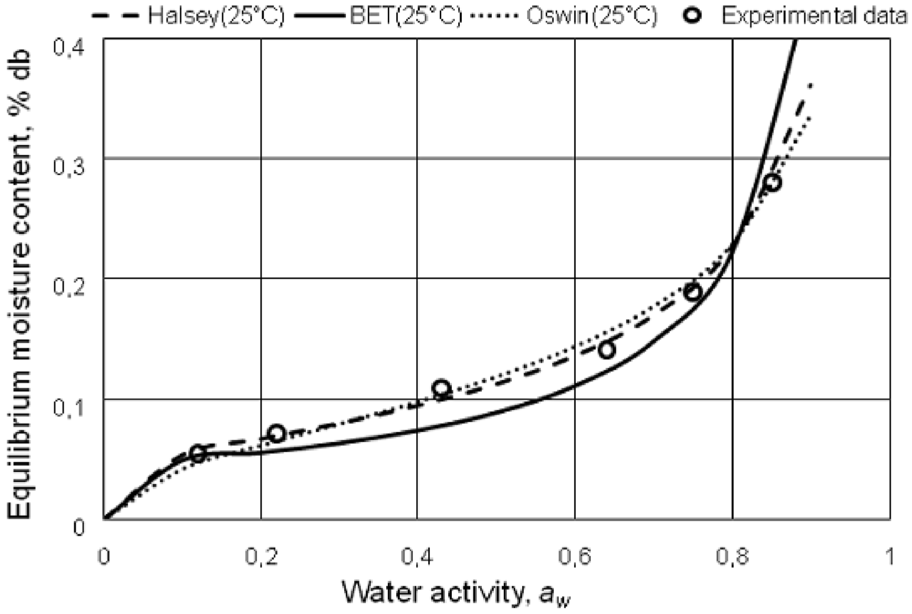


Figure 6.4: The best fitting for desorption isotherm models at 25°C

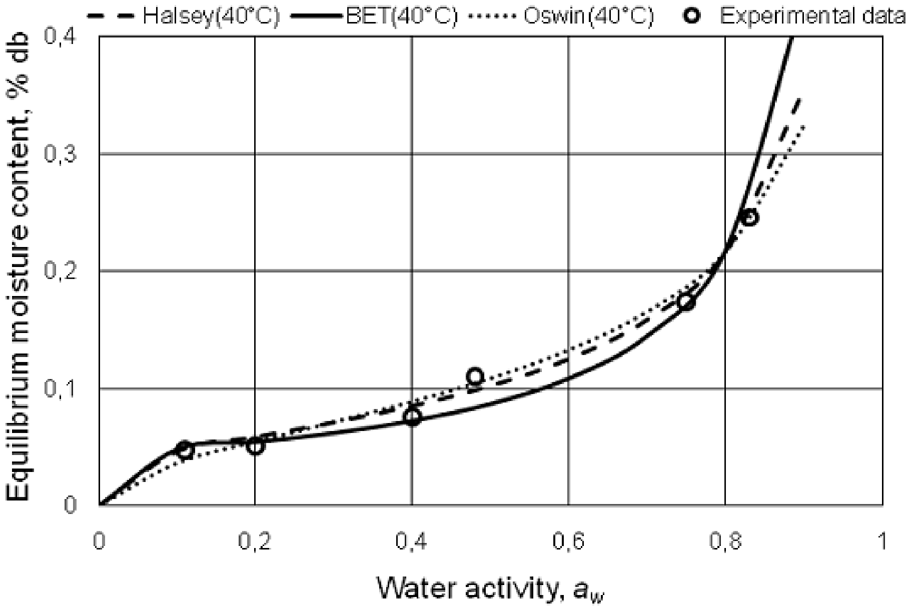


Figure 6.5: The best fittings for desorption isotherm models at 40°C

The best fit was obtained by the model for Halsey that is suitable for temperatures of 25 °C and 40 °C with X^2 values of 0.0002 and 0.0007 respectively and R^2 from 0.9947 and 0.9774. For temperatures of 50 °C and 60 °C is the BET model the best fitting with X^2 of 0.0003 and 0.0021 and R^2 y 0.9337 from 0.9913 respectively.

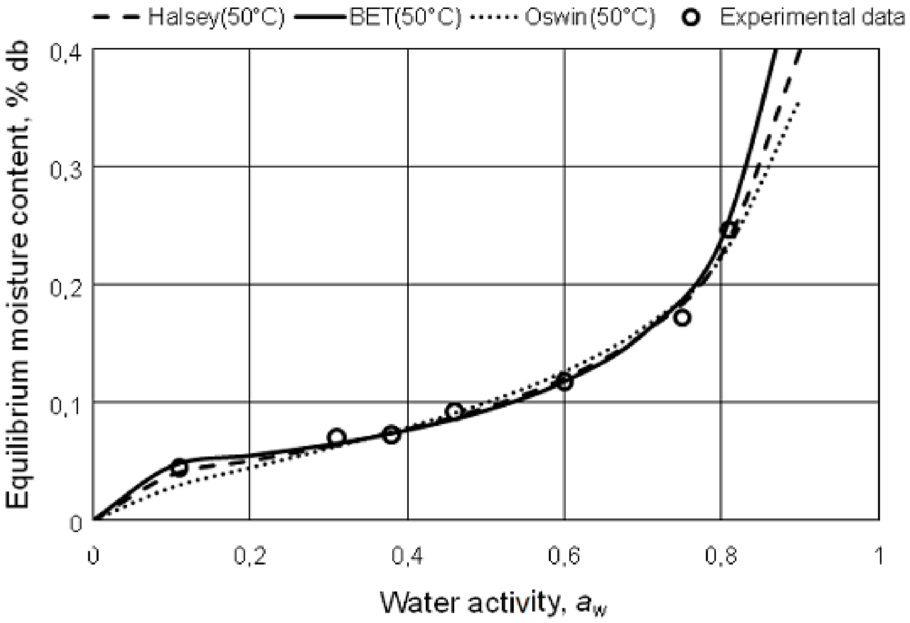


Figure 6.6: The best fitting for desorption isotherm models at 50°C

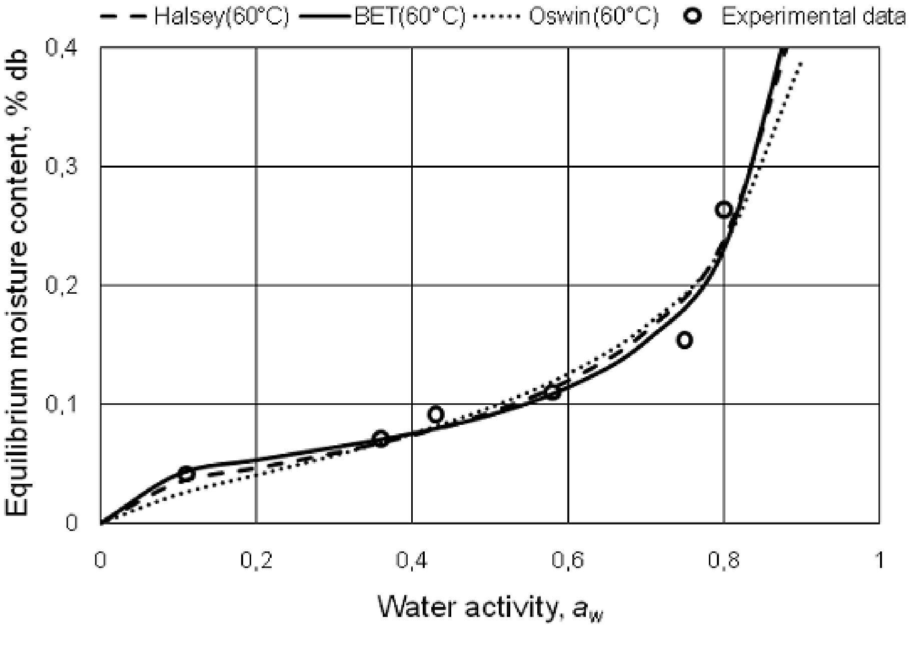


Figure 6.7: The best fitting desorption isotherm models at 60°C

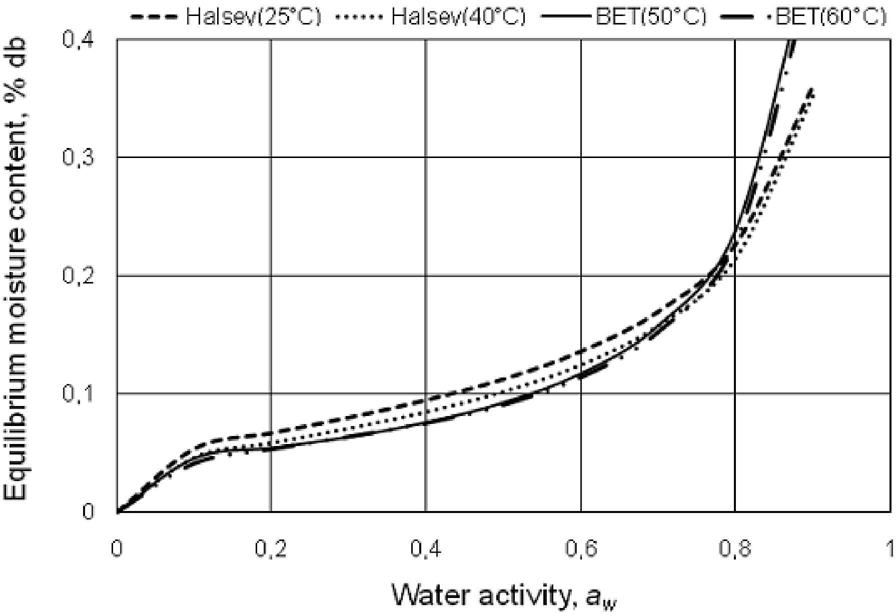


Figure 6.8: The best fitting desorption isotherm models

Figure 6.9 and 6.10 shows the best fitted adsorption isotherm models at 40°C and 60°C. In **Table** 6.3, the parameters Chi-square and coefficient determination R^2 of the considered models can be observed. The BET, Oswin and Halsey models presented the lowest Chi-square values and values R^2 near to 1.

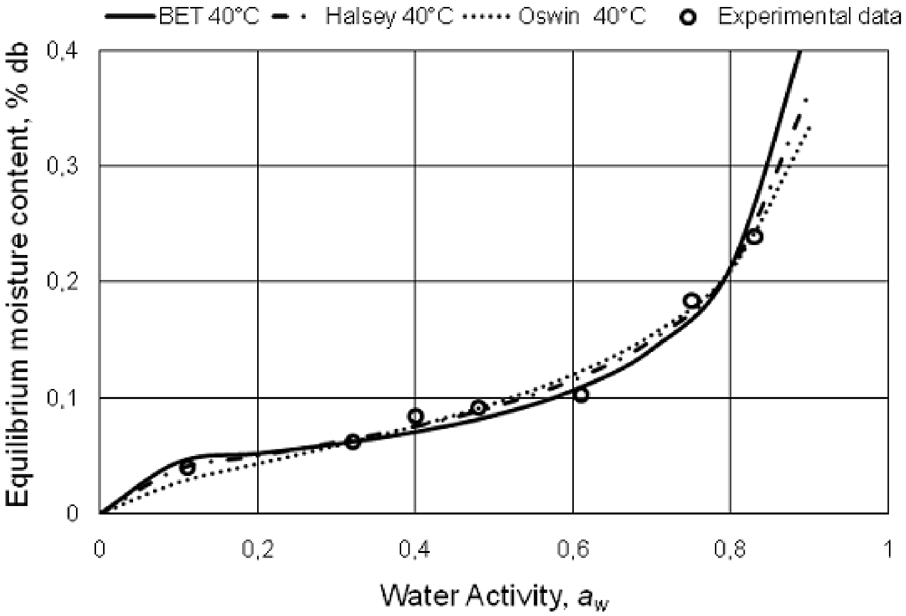


Figure 6.9: The best fitting for adsorption isotherm models at 40°C

The best fit was obtained by the model of Halsey that is suitable for temperatures of 40°C and 60°C with X^2 values of 0.0004, 0.0001 and R^2 from 0.9932, 0.9984 respectively.

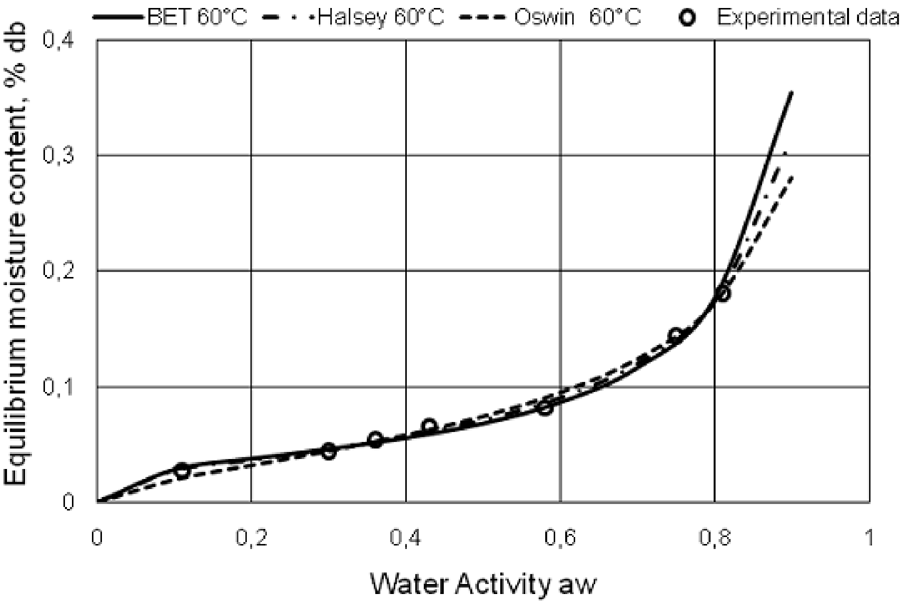


Figure 6.10: Best fitting for adsorption isotherm models at 60°C

The hysteresis effect was observed in **Figure** 6.11 and 6.12. At constant water activity, the equilibrium moisture contents of desorption is higher than the adsorption one. Several hypotheses have been put forward to explain this phenomenon. Considering a rigid pore structure connected to its surrounding by a small capillary. During adsorption, the capillary begins to fill as a result of the rising in water activity, while the pore is still empty. For desorption, the pore is initially full of liquid at saturation. This liquid can escape only when the pressure of the surrounding air becomes lower than the vapor pressure of liquid inside the capillary. As the system of pores has generally a large range of capillary diameters, differences between adsorption and desorption are observed (Rockland & Beuchat, 1987; Barbosa-Canovas & Fontana, 2007).

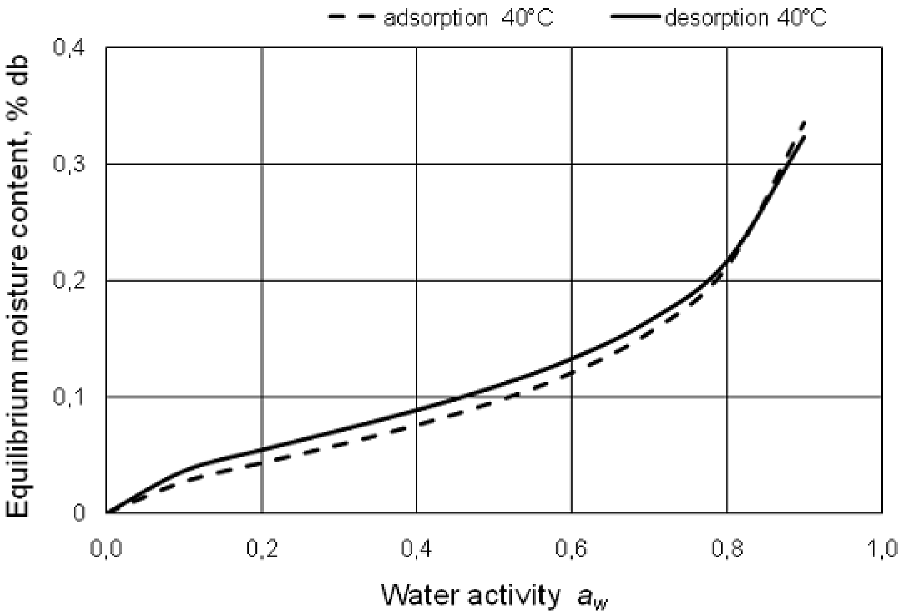


Figure 6.11: Curve sorption hysteresis at 40°C

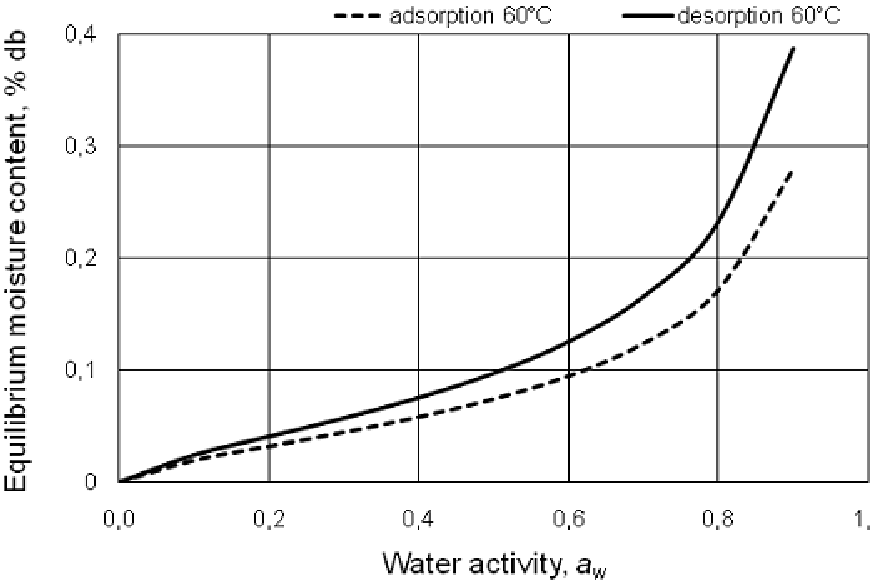


Figure 6.12: Curve sorption hysteresis at 60ºC

The behavior of the sorption hysteresis curve at 60°C is similar to the presented by Lamharrar in the studies to carried out of *Artemisia herba-alba* at 30°C (Lamharrar et al., 2007)

7 Drying kinetics

Drying by hot air is a process of mass transfer by contact gas-solid, where the humidity contained in the solid is transferred by evaporation to the gas phase depending on the difference between the vapor pressure exercised by the humid solid and the partial pressure of vapor of the gassy current. When these two pressures are equal, it is said that the solid and the gas are in equilibrium and the drying process ceases (Treybal, 1989; Maltry et al., 1962; Keey, 1972). In the drying process of medicinal plants by hot air, heat transfer takes place inside the plant and it is related to the temperature gradient between its surface and the surface of the water inside of it. If enough energy is given for its evaporation, the produced vapor will be transported from the surface of the humid layer inside the product toward the surface of this.

7.1 Materials and methods

The drying experiments were conducted using a cabinet dryer developed by the company INNOTECH in close cooperation with the Hohenheim University. Due to the construction of the dryer and application of the over current principle a low airflow resistance is reached within the equipment. This results in a low energy requirement of the fan as well as the possibility to use cross flow fans. The application of this type of fans leads to a uniform air distribution in the drying chamber. In combination with the registered profiled layout of the trays there is no need to shift single trays during the drying process to reach the desired uniform drying rate. **Figure** 7.1 shows the general characteristics of the experimental set up including the cabinet dryer and the air conditioning unit connected for obtaining the conditions of the drying air and the corresponding air flow.

Plants of Lemon Balm (*Melissa officinalis* L.) variety citronella were used for the drying experiments. Fresh plants were collected from May until September before flowering. Harvesting was carried out manually the day of the experiment between 10:00 and 13:00. The branches were cut to $15cm$ long pieces to be dried at different air temperatures the mass of product used in drying experiments was $300g$. Each test was carried out for triplicate.

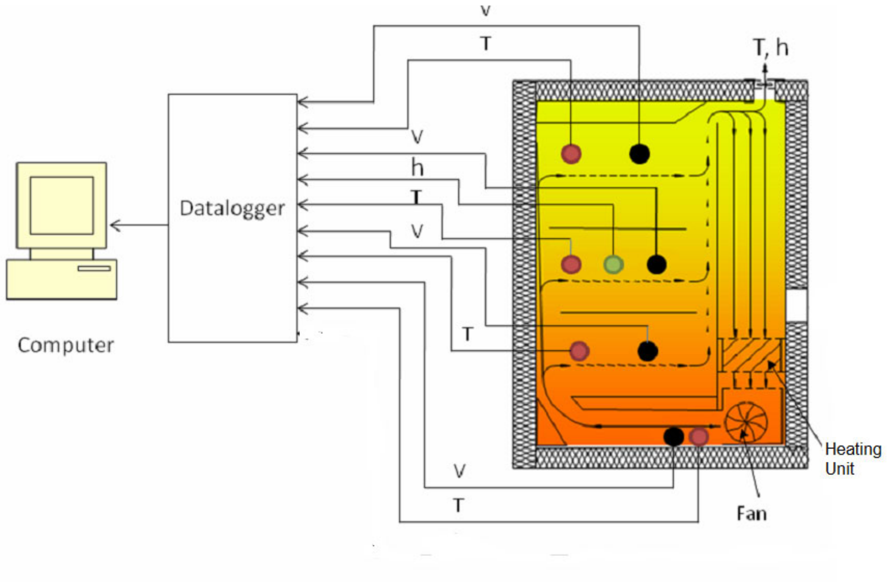


Figure 7.1: Experimental set up including the cabinet dryer the air conditioning unit instrumentation and data acquisition system. (T:thermoelement, h:hygrometers, V:anemometer).

The measured variables, and the used measuring methods are summarized in **Table** 7.1

Table 7.1: Compilation of the measured variables, measurement methods and accuracy used during the experimental work.

Measure	Measurement Methods	Measurement Accuracy
Energy consumption	Energy Checker	± 2W
Wind speed, V	Anemometer	± 3% full scale
Relative humidity,h	Hygrometer	± 5% RH
Weight, M	Weighing scale	± 0.001g
Temperature sensor, T	Thermocouple	Type $K\pm$ 0.5 ; Type $T\pm$ 1.5
Color, ΔE	Chromameter	± 2% ± 1 digit of displayed value

A digital weighing apparatus (with resolution of ±0.001g) measures the mass loss of the product during the drying process. During each drying experiment, the weight of the products on the tray was measured. These measurements were undertaken every 10 min the first hour of the experiment and at every hour at terwards during until finishing the process.

The initial and final moisture contents of each sample were determined by a drying oven method as presented in section 5.1. The difference of mass before and after drying in the oven gives the moisture content. In this study, the cut branches of *Melissa officinalis* L. were dried by using the set up showed in **Figure** 7.1. The considered variables were air temperature and relative humidity. The drying experiments were carried out at different drying air temperatures: 30, 40, 50 and 60 °C and with different relative humidity levels: 20, 40 and 60% and considering constant air velocity of 0.45 m/s. The objective of the study was to analyze the behavior of drying Lemon Balm considering moisture content vs. drying time, drying rate vs. drying time, drying rate vs. moisture content, drying time vs. relative humidity. Subsequently mathematical models of thin layer drying were fitted for moisture ratio vs. drying time. Additionally the difference among the drying of leaves, stalks and branches (leaves and stalks jointly) was observed. Finally the relationship between the temperature of leaves and drying time was analyzed. Moisture ratios (MR) and drying rate of *Melissa officinalis* L. samples considering thin layer drying were calculated by using the following equation:

$$MR = \frac{X_t - X_e}{X_i - X_e} \tag{7.1}$$

$$R_d = \frac{X_{t+dt} - X_t}{dt} \tag{7.2}$$

Where, MR is moisture ratio, X_e is equilibrium moisture content, X_i is initial moisture, R_d is the drying rate, X_{t+dt} and X_t are the moister content at $t + dt$ and moister content at t ($kg_{water}/kg_{dry\ matter}$) respectively, t is drying time.

For mathematical modeling, the thin layer drying equations in were tested to select the best model for describing the drying curve equation of Lemon Balm samples during drying process.

7.2 Results and discussion

7.2.1 Influence of air drying temperature

Effect on drying time

The study considered the thin layer drying of Lemon balm (*Melissa officinalis* L.) branches at average initial moisture content of 76% w.b..

Figure 7.2 shows different drying rate curves at different temperatures. The drying period at constant ratio is not presented, which indicates that drying process is determined primarily by a diffusive process. Likewise it is observed that the drying rate decreases throughout the process for each of the considered temperatures, which shows that the removal of moisture is proportional to the concentration of product water. This suggests that the moisture content depends on the effective diffusion and can be modeled by the Fick's second law.

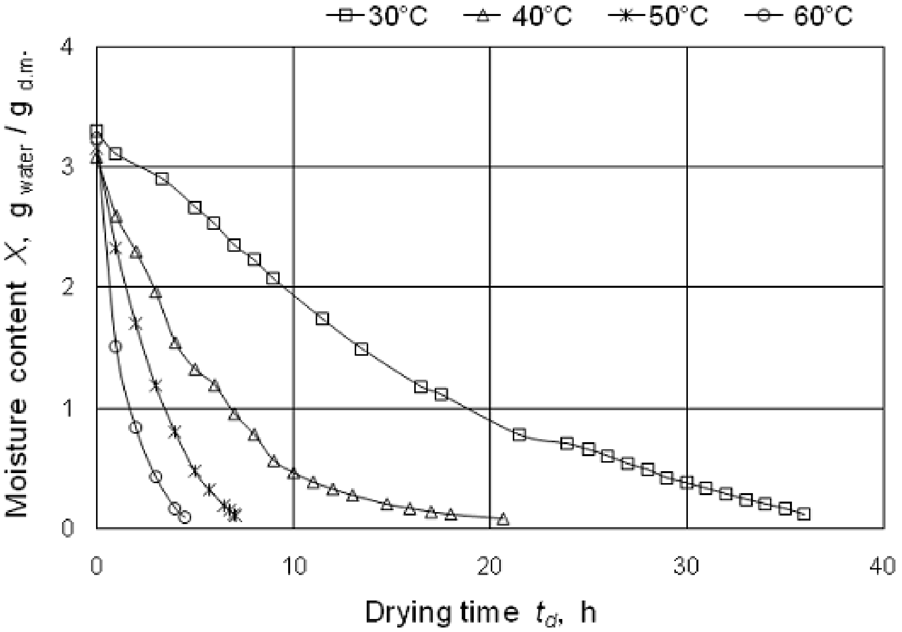


Figure 7.2: Drying process von Lemon Balm at different drying temperatures

Similar studies carried out with mint and nettle reveal that there is an important influence on the curve drying when the conditions of the drying air are modified (Kaya & Aydinv, 2008; Hosseini, 2005b). The relative humidity of the drying air has a significant impact on the final moisture content of the material, because it controls the rate of water vapor transport from its surface to the air and influences the value of the equilibrium moisture content.

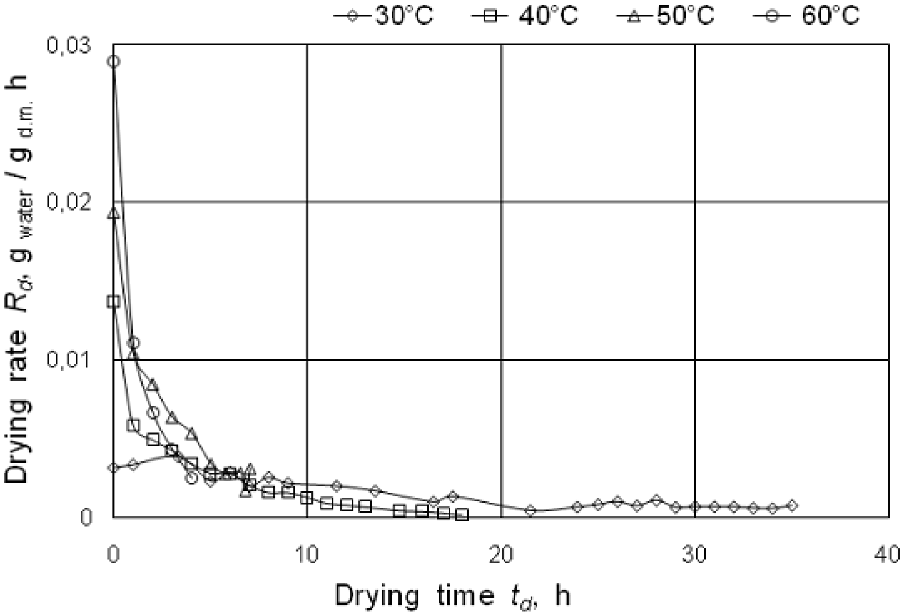


Figure 7.3: Drying rate of Lemon Balm as function of drying time at different drying temperatures

Drying rate describes the amount of water removed per time unit. **Figures** 7.3 and

7.4 present the values of drying rate as function of drying time and moisture content d.b. The variation of drying rate with moisture content during thin layer drying considering drying air temperature of 30, 40, 50 and 60°C can be observed. At a specific temperature the drying rate increases as the temperature increases.

Considering that the mass transfer mechanism that controls the process is the molecular diffusion, this can be considered as a system property that depends on the temperature, pressure and the nature of the components (water inside the leaves and drying air). In gassy state the temperature is the most influential factor. The diffusivity increases as the temperature increases in consequence the transference of water vapour to hot air. Therefore, it can be inferred that the diffusion is the physical mechanism governing moisture movement in the Lemon Balm samples. The drying air temperature has a significant effect on the evolution of the moisture content.

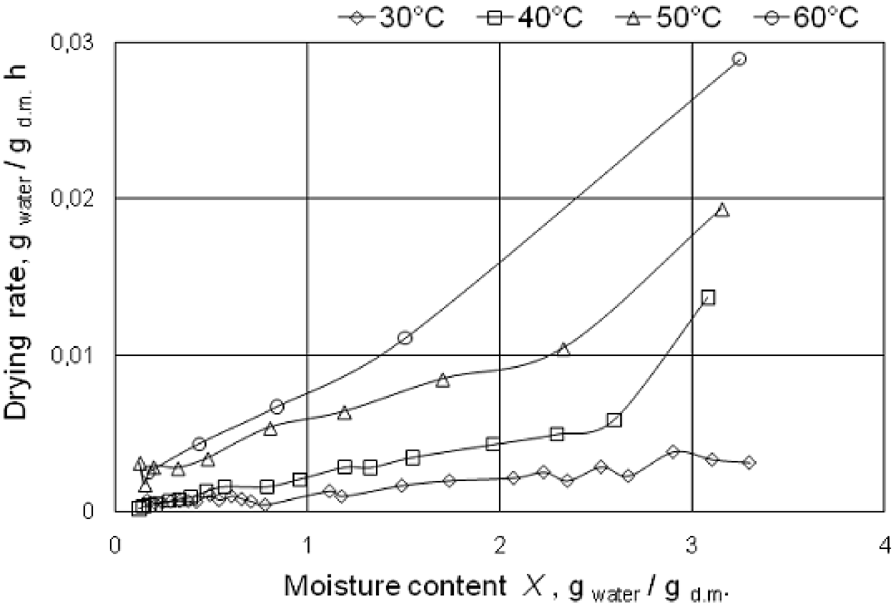


Figure 7.4: Drying rate of Lemon Balm a function of moisture content X at different drying air temperatures

In **Figure** 7.5 can be observed the behavior of drying time depending on drying air temperature. For air drying temperature of 30°C, a final drying time of 36h was obtained to reach moisture of 10% w.b. The obtained time is considerable high compared with 4.05h that was the drying time at 60°C, that corresponds to a reduction in time of 88.75%. In contrast, the difference in drying time between drying at 50°C and 60°C is moderate. At 50°C the drying time was 7h and at 60°C was 4.5h, which represents a reduction of 36%.

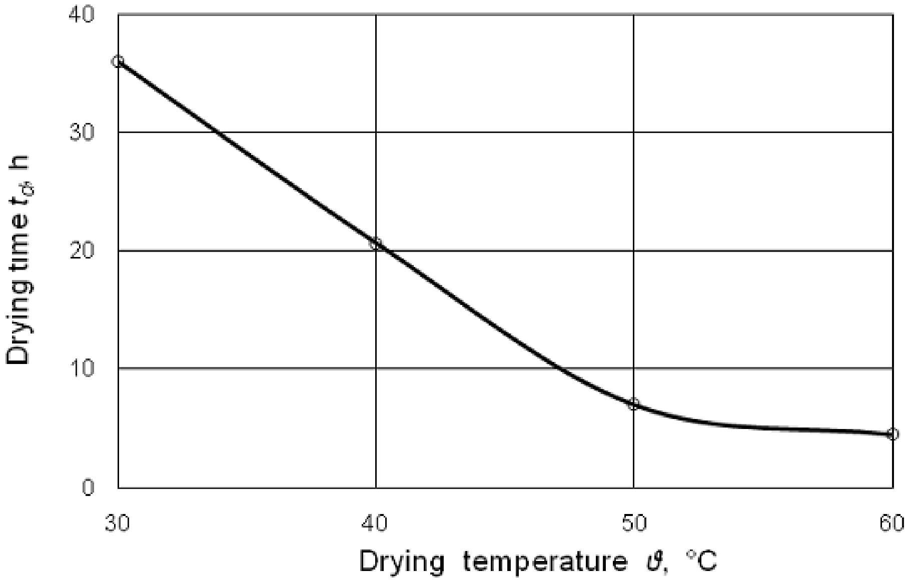


Figure 7.5: Drying time for different air drying temperatures

Effect on color difference
Table 7.2 presents the statistical results of color measurement (CIELAB color parameters) at different temperatures.

Table 7.2: Parameter value color dried Lemon Balm leaves at different drying air temperatures

Temperature	L*	a*	b*	h*	Δ L	Δ a*	Δ b*	Δ E
30°C	33.455	-11.804	17.848	123.480	-5.752	8.022	-10.522	14.484
40°C	36.738	-12.915	22.426	119.940	-3.918	7.440	-8.275	11.919
50°C	26.274	-5.377	11.700	114.680	29.110	14.875	-20.469	29.110
60°C	24.185	-1.254	8.616	98.050	-16.017	18.996	-23.550	34.319

The drying air temperature has a significant effect on the color of the dried leaves as is suggested by the value of h in **Table 7.2**. The samples dried at 30, 40 and 50°C, presented the highest values of h , which are 123, 119.9 and 114.6 respectively. This indicates that the final color of these leaves is green and therefore more similar to the color of the fresh leaves considered as reference. For the leaves dried at 60°C the h value was 98 and that indicates a considerable degradation from the initial color. The leaves dried at 60C turned yellow as can be observed in **Figure 7.6**. In addition the highest values of color difference were 34, 29 and 14 presented at 60, 50 and 30C respectively. The observed lower hue value at 30°C for *Melissa officinalis* L. was attributed to the long drying time resulting in chlorophyll degradation.

The **Figure 7.6** shows the obtained color difference between fresh and after drying the product at different temperatures. It can be seen that the the best color was obtained after drying at 40 to 45°C. The color at 30°C was attributed to the long drying time resulting in chlorophyll degradation.

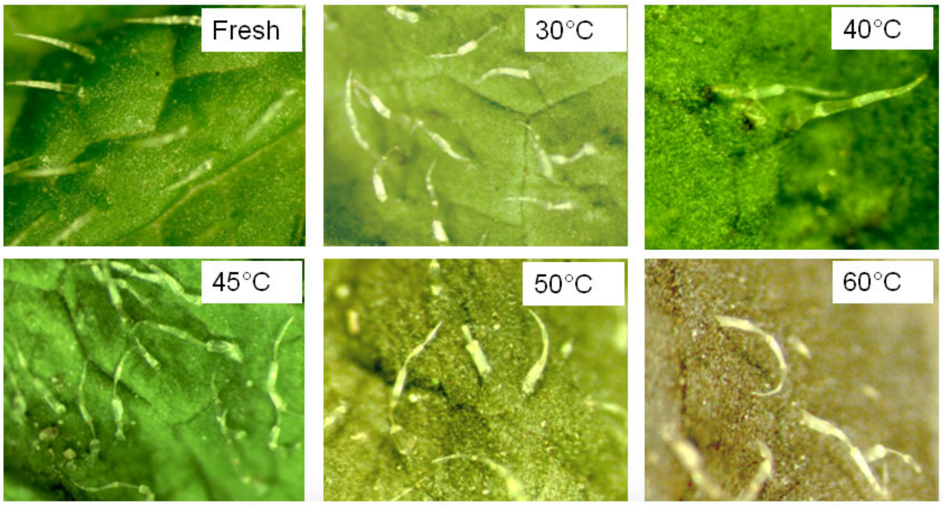


Figure 7.6: Effect of different drying temperatures on color changes

7.2.2 Influence of relative humidity

Figure 7.7 summarizes the influence of the relative humidity of drying air on drying time at 30°C considering humidities of 20, 30, 40, 50 y 60%. The greatest drying time was 55.76h corresponding to 60% of humidity. For humidities of 20, 30 and 40% there was no significant difference in drying time. For 20, 30 and 40% the drying time were 25.6h, 27.9h, and 28.8h respectively. The difference between drying time corresponding to 20 and 30% of humidity was only 2.3h and between 30 and 40% was less than 1h.

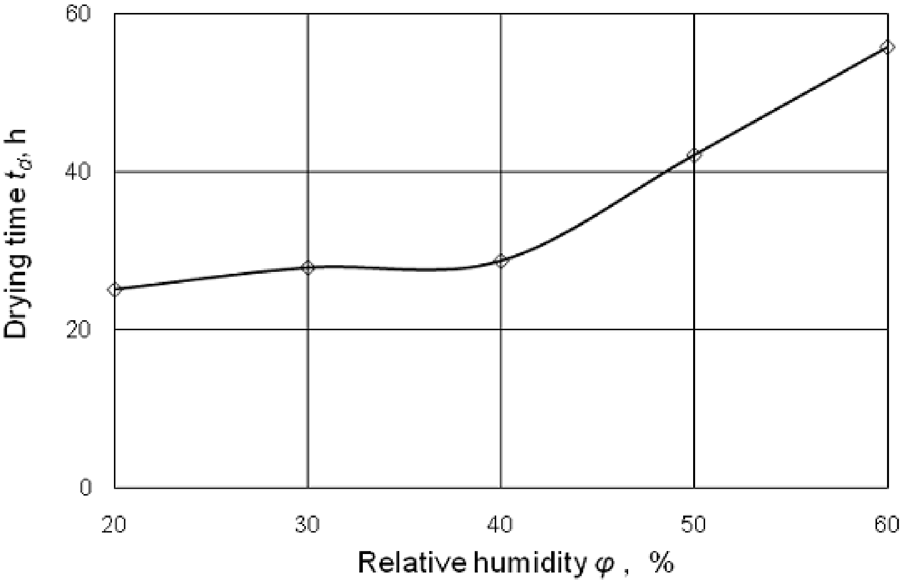


Figure 7.7: Drying time of Lemon Balm a function of relative humidity at 30C

Figure 7.8 shows the effect of the relative humidity of drying air on drying time considering air drying temperature of 40°C. For relative humidities of 12, 20 and 40% the differences in drying time were not significant. On the contrary, the drying time for 50% was 18h and for 68% was 29h, that represents an increase of 37.9% in drying time.

Comparing the drying time at 12% and 68%, relative humidity at 40°C, a difference of 16.8h is obtained, considering that the drying time for 12% was 12.2h and for 60% was 29h, this represents an increase of more than twice. These results are in accordance with the fact that an increase in relative humidity of drying air decreases the saturation deficit of drying air and consequently this diminishes the capacity for absorbing the humidity from the surroundings and as a result the drying time increases.

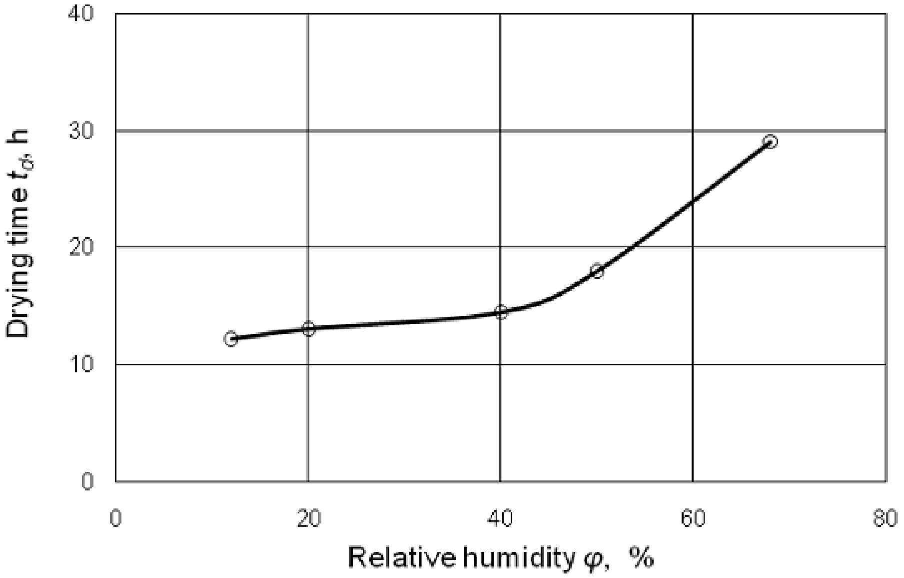


Figure 7.8: Drying time of Lemon Balm a function of relative humidity at 40C

7.2.3 Drying behavior for different conditions of the product

Figure 7.9 presents the drying behavior of Lemon Balm considering different conditions of the product; drying of leaves and stalks separately and drying of branches (complete: leaves and stalks jointly). Drying was performed at 40°C and for comparison of results a fixed drying period of 11h was considered. In this period the recommended final moisture of leaves is reached (10% w.b). As result of the drying tests, severe differences in moisture content (wet basis w.b.) after 11h were observed. When performing drying at 40°C of single leaves, with initial moisture content of 80% w.b. the moisture content of the leaves was 10% w.b, and considering the drying of branches at 40°C, with the same initial moisture, and observing the leaves in this condition their moisture content was 7.98% w.b. Moreover, in the same tests, the moisture of the branches was observed. When the branches reach the recommended final moisture of 10% w.b, after 25h, the leaves from these branches have final moisture of 7.41% w.b. showing over-drying, that affects severely the quality characteristics. Likewise, appreciable differences in color change and loss of essential oils were observed, comparing among the drying strategies and conditions proposed. From these results, it is possible to define the adequate drying parameters to minimize the effects on quality characteristics and the difficulty for post-processing, for example separation of leaves and stalks.

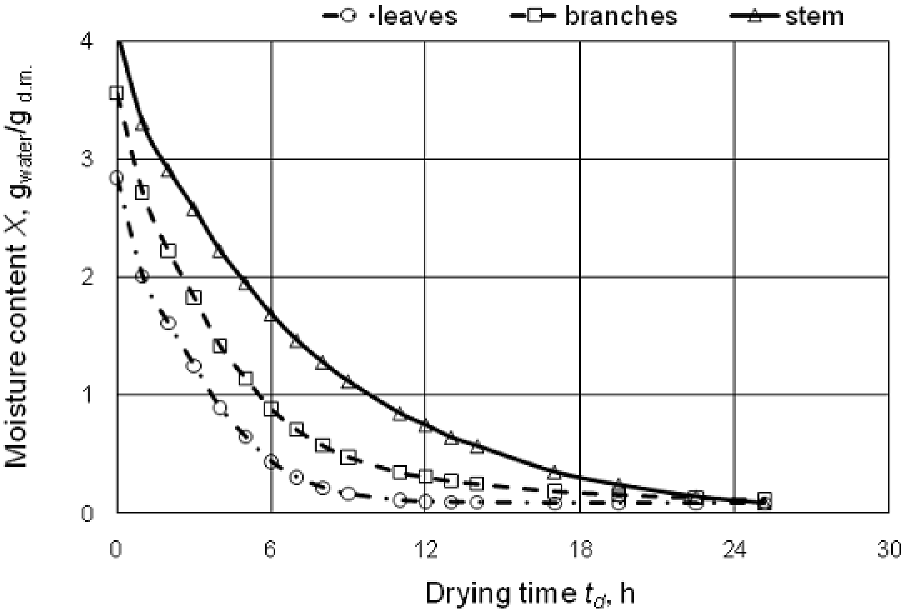


Figure 7.9: Drying process for different parts of Lemon Balm . Drying performed at 40°C

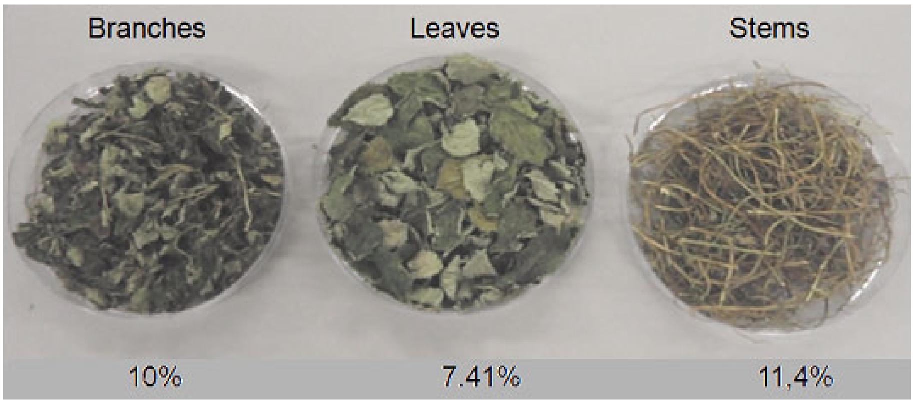


Figure 7.10: Comparison of drying process for different parts of Lemon Balm

7.3 Fitting to mathematical models

Many researchers have developed mathematical models to describe drying processes in product stuffs. There are generally three types of approaches for developing drying models: 1) models based on the concept of characteristic drying curves in different drying stages; 2) distributed-parameter models, using coupled heat and mass diffusion equations; and 3) empirical models obtained entirely by simple or multivariable regression methods. Several types of models are commonly used to describe the falling rate period of drying. These include the diffusion model which is based on the diffusion transport of water, the receding front model which is based mostly on capillary transport, and the model based on the complete conservation equations, which give mathematically complex formulations. The levels of model complexity depend on consideration of shrinkage or no shrinkage, assuming isothermal conditions or non-isothermal conditions, and assuming moisture concentration dependence of the diffusion coefficient. Two major boundary conditions distinguishing these models are moving boundary condition, which takes shrinkage into account, and equilibrium at the surface, which is associated with no external resistance. Most models are usually based on the assumptions that the external surface of the material is at equilibrium and the geometry (shape) is unchanged (no shrinkage) (Srikiatden & Roberts, 2007). **Table** 7.3 shows the results of nonlinear regression analysis for fitting thin layer models to experimental data. Additionally the estimated constants for all models analyzed in this research are considered with the coefficient of determination R^2 and the Chi-square test for all models.

Table 7.3: Estimated parameter values and criteria for comparing the mathematical models applied to drying curves for Lemon Balm

Model	Costant	30°C	40°C	50°C	60°C
Wang and Singh	a	-0.0008	-0.0021	-0.0044	-0.0086
(Doymaz, March 2005; Kröll, 1978)	b	1.5727	1,0965	4.9281	1.8763
$MR = l + at + bt^2$	Chi^2	0.0063	0.024	0.0011	0.0142
	R^2	0.9988	0.9932	0.9995	0.99
	a	1.0026	1	2.644	1
Diffusion approach	k	0.011	0.003	0.0028	0.0123
(Murthy, 2009)	b	1.0025	1	1	1
$MR = a\exp(-kt) + (l - a)\exp(-kbt)$	Chi^2	0.0675	0.0107	0.0002	0.0002
	R^2	0.987	0.9969	0.999	0.9989
Henderson and Pabis	a	1.0844	1.0299	1.0382	0.996
(Mustafa et al., 2009)	b	0.0012	0.0031	0.0064	0.0123
$MR = a\exp(-bt)$	Chi^2	0.0452	0.009	0.0147	0.0015
	R^2	0.9917	0.9975	0.9939	0.999
Lewis	a	0.0011	0.003	0.0062	0.0123
(Fatouh et al., 2006)	Chi^2	0.0675	0.0107	0.0167	0.0015
$MR = \exp(-at)$	R^2	0.987	0.9969	0.9926	0.9989
Page	a	0.0002	0.0013	0.002	0.0146
(Arabhosseini et al., 2009)	b	1.2408	1.1355	1.2035	0.9643
$MR = \exp(-at^b)$	Chi^2	0.0089	0.0035	0.004	0.0015
	R^2	0.9984	0.999	0.9984	0.9991
Exponencial decay	a	-0.2515	-0.0417	-0.1634	-0.0098
(Cuervo & Hensel, 2008)	b	339.243	19.878	35.112	0.3416
$MR = a + \exp(-c(t - b))$	c	0.0007	0,0028	0.0044	0.0119
	Chi^2	0.0071	0.0051	0.0002	0.0014
	R^2	0.9986	0.9985	0.9999	0.9999

Figure 7.11 summarizes the values of moisture ratio obtained experimentally by drying Lemon Balm at 30, 40, 50 and 60°C. These data were used to fit the mathematical models of thin layer drying.

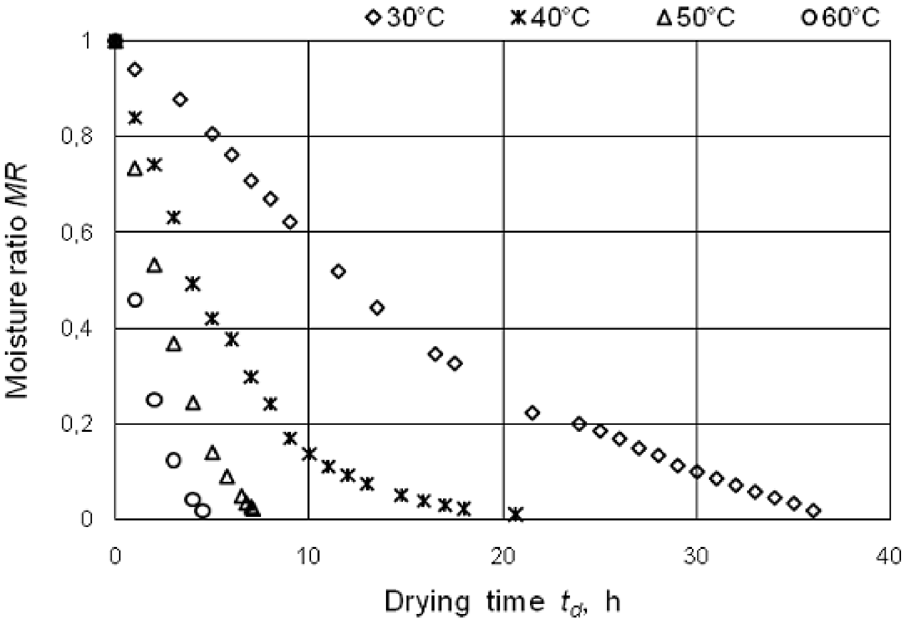


Figure 7.11: Experimental data for drying rate for Lemon Balm a function of drying time at different drying air temperatures.

Figure 7.12 shows the best fitted models of thin layer drying for the considered temperatures. It can be observed from **Table** 7.3 that the model of Wang and Singh is suitable for temperature of 30°C with the lowest Chi-square value of 0.0063 and value R^2 of 0.9988. For 40°C the model of Page is the best fitted with Chi-square of 0.0035 and R^2 of 0.9990. For 50°C the model of exponential decay is the best fitted with Chi-square value of 0.0002 and R^2 of 0.9999. For 60°C the model of diffusion is the best fitted with Chi-square of 0.0002 and R^2 of 0.9989.

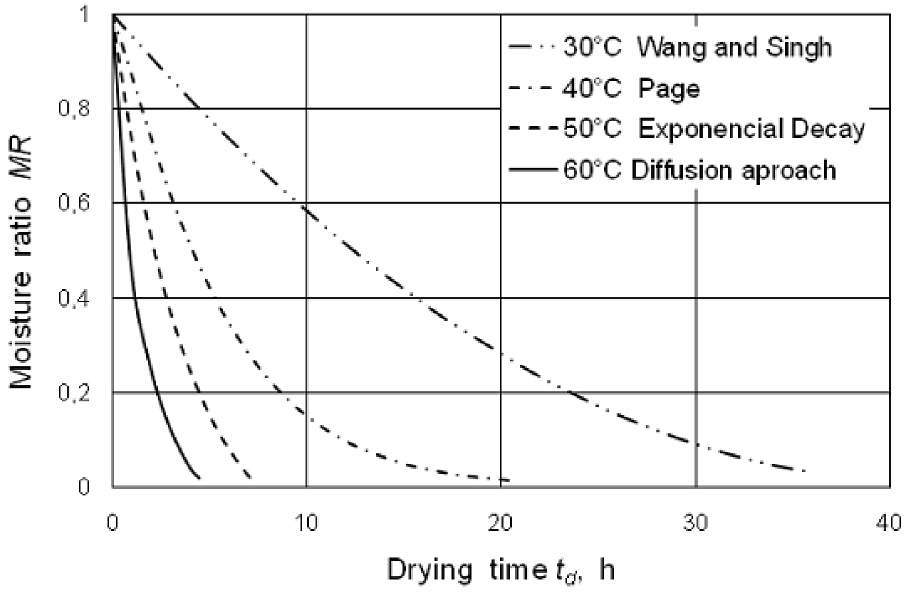


Figure 7.12: Best fitted mathematical models of thin layer drying

7.4 Behavior of the leaves temperature

The temperature of leaves during the drying process of Lemon Balm has great influence in quality characteristics. For this reason a study of the behavior of the leaves temperature was carried out. **Figure** 7.13 shows the leaves and air drying temperatures depending on drying time for drying at 30°C. It can be observed that the temperature of leaves is under the temperature of air drying due to evaporative cooling. At the beginning of the process, the temperature difference is higher and diminishes as the drying time increases. This is related with the decrease of the moisture content of the product and consequently the decrease of free water on the surface of leaf that produces a decrease in the process of evaporative cooling.

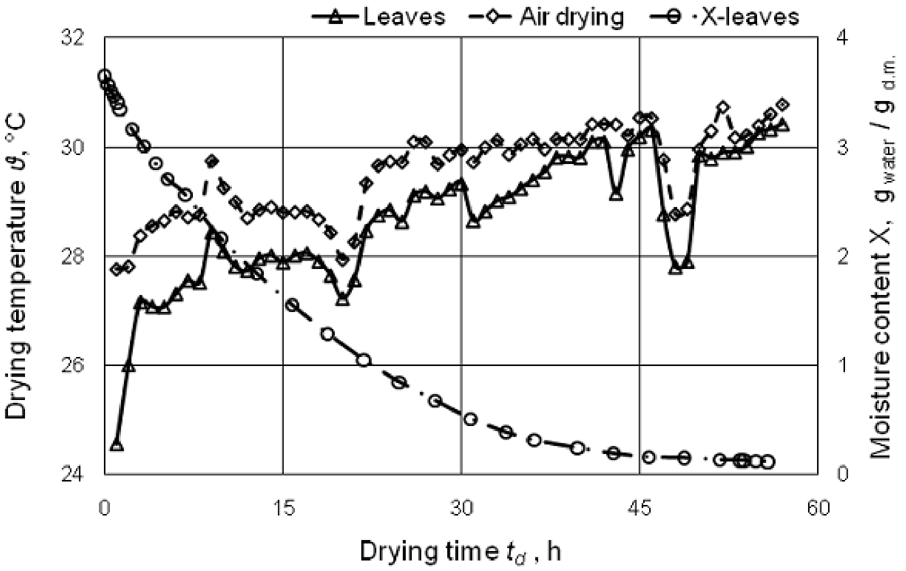


Figure 7.13: Temperature behavior of Lemon Balm leaves during the drying process at drying temperature of 30°C

8 Drying by using stepwise process control

8.1 Description of the process

In this work the method of stepwise drying of medicinal plants is presented as an alternative to the conventional drying that uses a constant temperature during the whole process. The objective of stepwise drying is the decrease of drying time and energy saving. In this process, apart from observing the effects on process time and energy, the influence of the different combinations of drying phases on several characteristics of the product is observed.

Drying curves were obtained to observe the dynamics of the process for different combinations of temperature and points of change, corresponding to different conditions of moisture content of the product. Finally it was found that combinations of temperatures beginning with high temperature are not advisable since they produce severe changes in the color that affect negatively the final quality of the product, diminishing their commercial value.

The standard drying, was conducted at only one temperature (ϑ_1) and stepwise drying using two temperatures. The experimental data for drying of Lemon Balm in a convective tray dryer was obtained at first step at low temperature (ϑ_1) and final step with high temperature (ϑ_2) and having different change points corresponding to different moisture content of the product as shown in **Figure** 8.1.

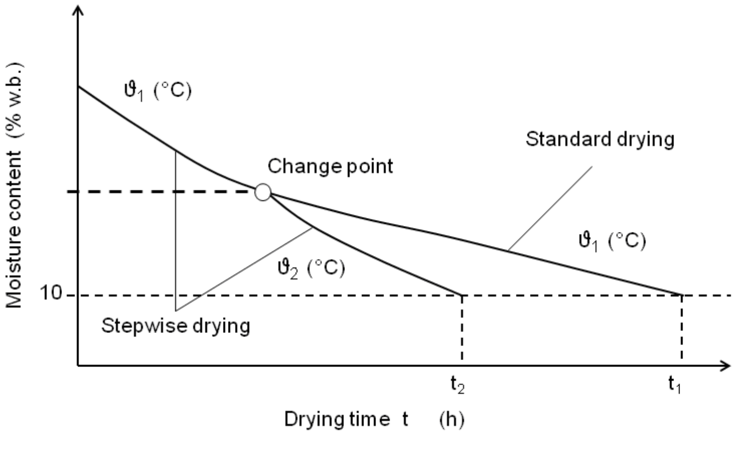


Figure 8.1: Drying methods considered: standard drying and stepwise drying

8.2 Materials and methods

The material used for the research was Lemon Balm (*Melissa officinalis* L.), variety citronella sown at the University of Kassel in Witzenhausen (51°20´45.76” N, 9°51´52.08” E). The material was harvested manually at 10cm of soil and then cut into pieces of 15cm. The samples were harvested randomly and little before the flowering and after that the leaves were transported quickly to the laboratory in order to avoid mechanic damage that causes loss of essential oil (Heeger, 1989).

During drying, the amount of water removed during the process was determined by periodic weighing.The energy consumption was measured by a Voltcraft Energy-check 3000 electrical monitor which was connected to the drying during each trial. Solids content was determined after each experiment by the oven drying method. For the stepwise drying process at different combinations of initial and final temperature were considered, with different transition points associated with different moisture contents of the product during the process. To determine the color difference a Chroma-meter device is used that carries out the colorimetric evaluation of color coordinates and color differences by means of the CIELAB color space, in accordance with the norm DIN 6174 (DIN, 1979) as presented in section 5.3. After the drying process, the essential oil content and color change were determined by using the methodology proposed in section 5.2. **Figure** 8.2 show the methodology used to obtain the data for comparing different strategies of stepwise and standard drying.

The measured variables, and the used measuring methods are summarized in **Table** 8.1

Table 8.1: Compilation of the measured variables, measurement methods and accuracy used during the experimental work.

Measure	Measurement Methods	Measurement Accuracy
Energy consumption	Energy Checker	± 2W
Wind speed, V	Anemometer	± 3% full scale
Relative humidity,h	Hygrometer	± 5% RH
Weight, M	Weighing scale	± 0.001g
Temperature sensor, T	Thermocouple	Type K± 0.5 ; Type T± 1.5
Color, ΔE	Chromameter	± 2% ± 1 digit of displayed value

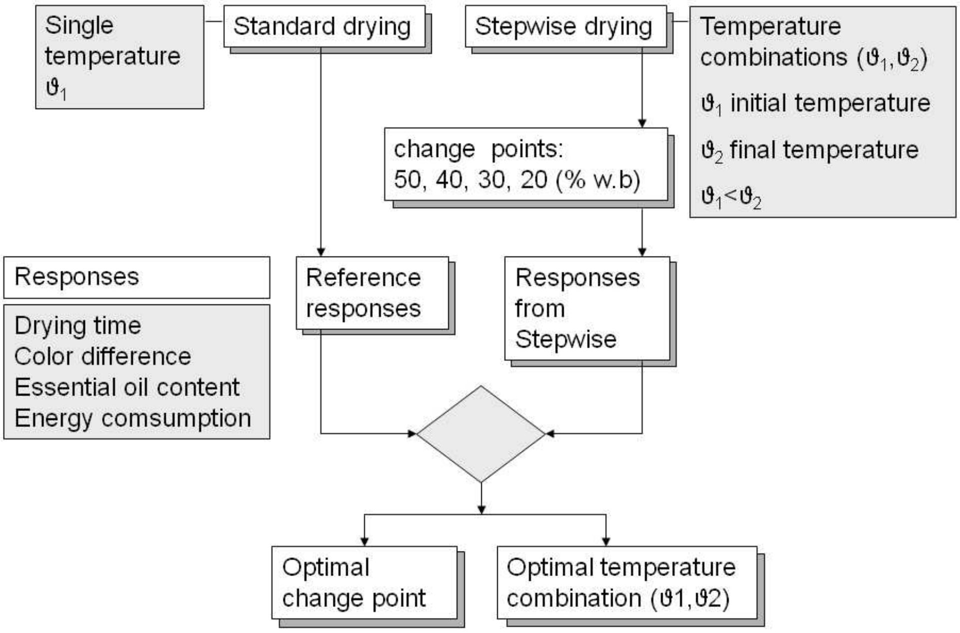


Figure 8.2: Methodology

In **Figure** 8.3 can be observed the different temperature combinations considered for stepwise drying at different change points.

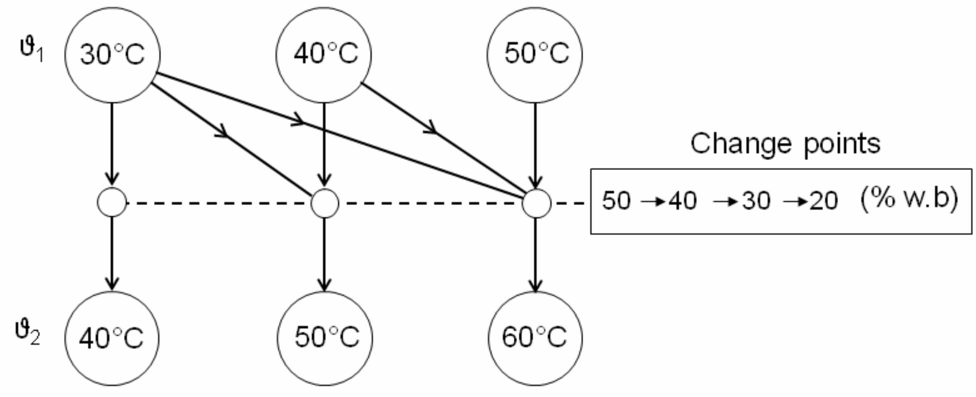


Figure 8.3: Different temperature combinations considered for stepwise drying

Figure 8.4 shows as example the combination 40°C/50°C and the different change points considered in the research. During the drying process the moisture content loss of the product was measured by monitoring the weight until a moisture content of 10% is reached. Parallel to this observation, the consumed energy during the drying process was measured.

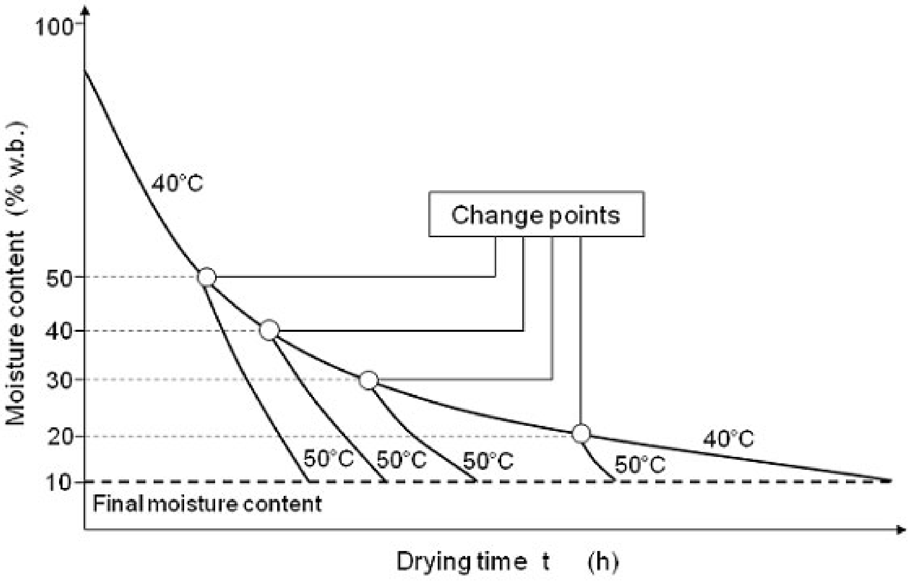


Figure 8.4: Different change points for stepwise drying

8.3 Results and discussion

8.3.1 Drying curves

In **Figures** 8.5 to 8.10, the drying curves corresponding to standard drying, for different drying air temperatures, and stepwise drying combination, considering different change points are presented. A considerable decrease on drying time by using stepwise drying compared to standard drying is observed.

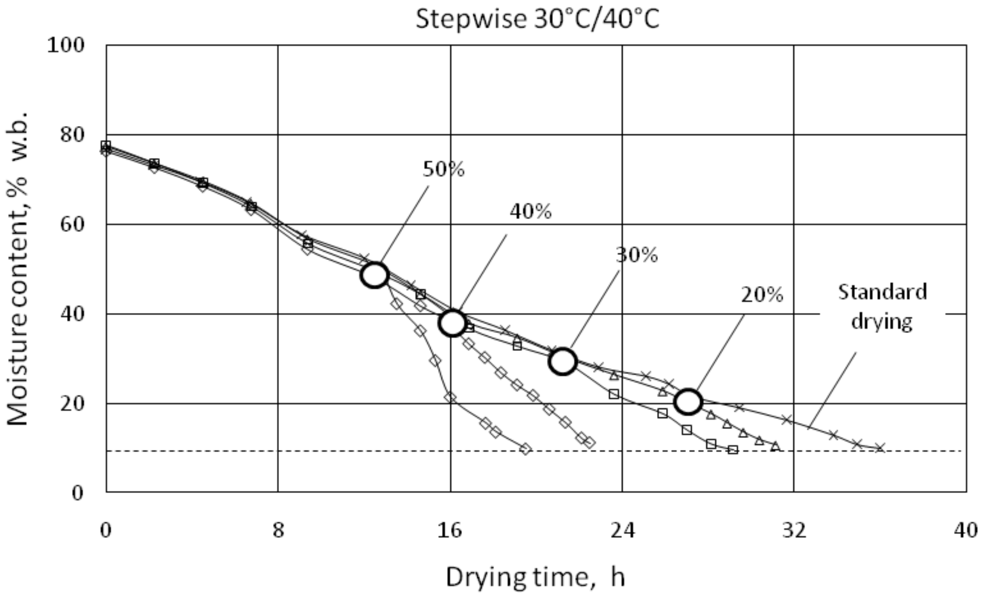


Figure 8.5: Comparison of drying: standard 30°C and stepwise 30°C/40°C

In **Figure** 8.5 the behavior of the drying process is observed, at the standard to 30°C and the stepwise for the combination 30°C/40°C, in which a clear decrease in the time can be appreciable from 36h to 30.3h for a change point of 20%, and of 16.5 for the changes point of 50%.

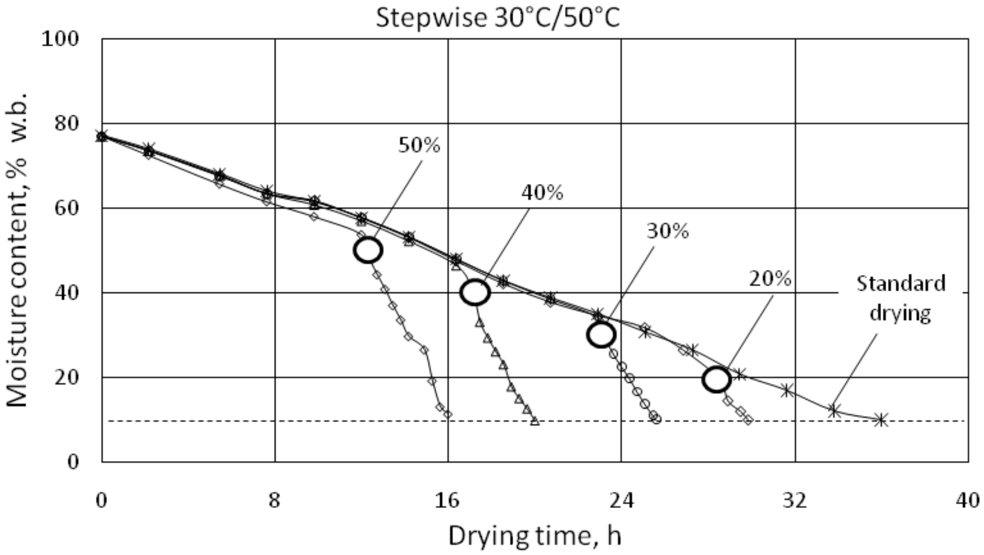


Figure 8.6: Comparison of drying: standard 30°C and stepwise 30°C/50°C

Figure 8.6 For the stepwise 30°C/50°C, the decrease in the drying time for change point of 20% went from 36h to 29.9h and for the change point of 50% it was of 16 hours.

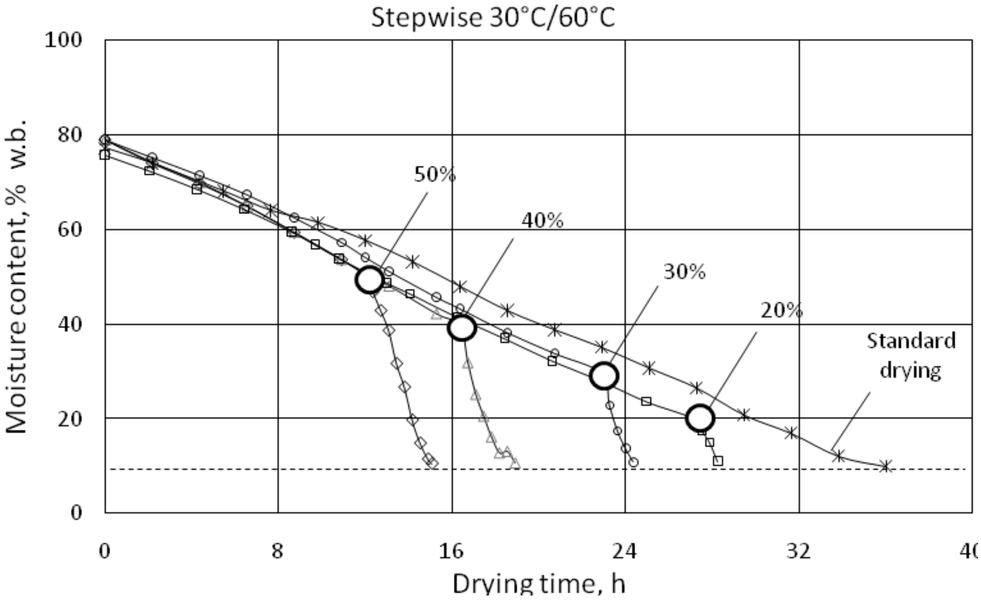


Figure 8.7: Comparison of drying: standard 30°C and stepwise 30°C/60°C

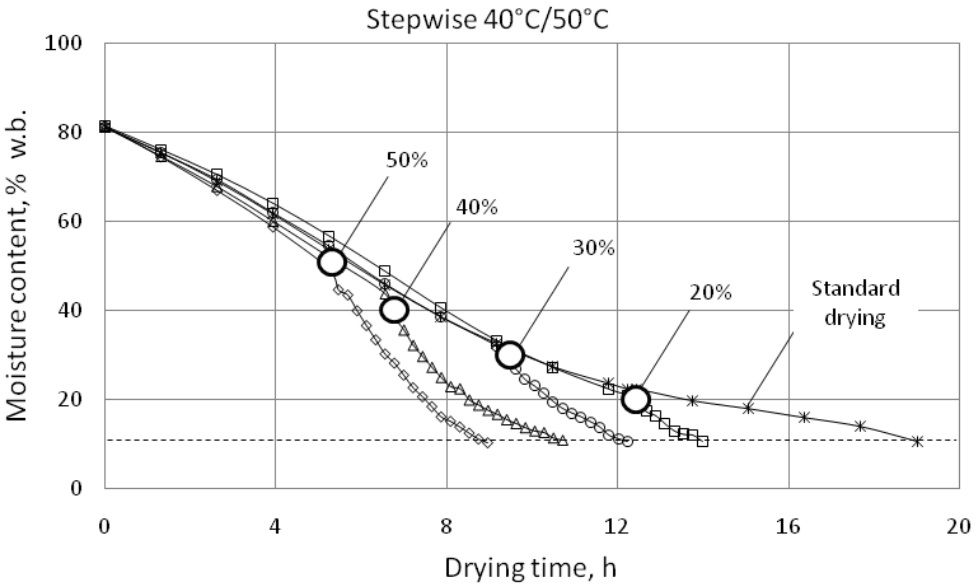


Figure 8.8: Comparison of drying: standard 40°C and stepwise 40°C/50°C

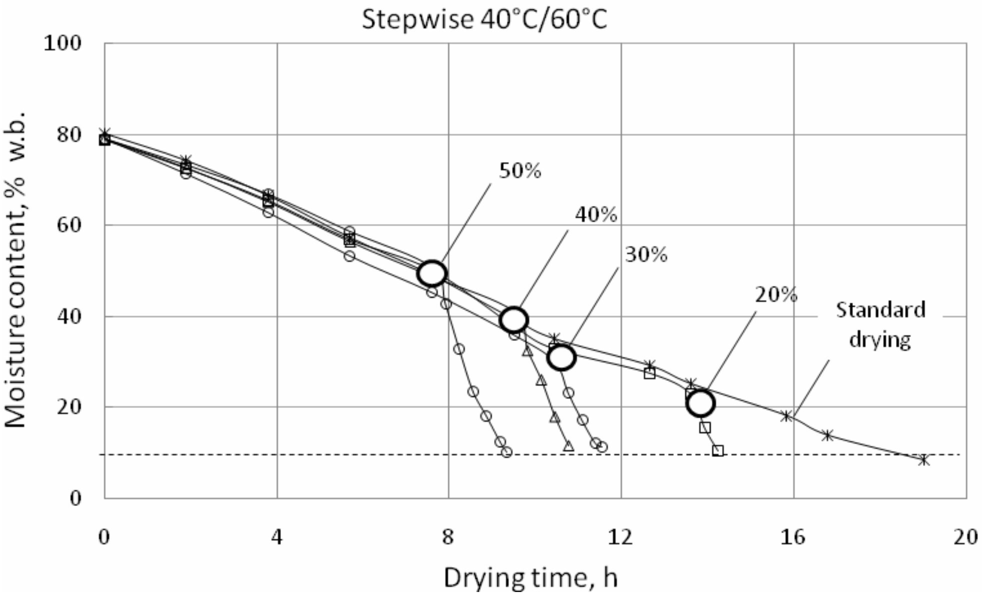


Figure 8.9: Comparison of drying: standard 40°C and stepwise 40°C/60°C

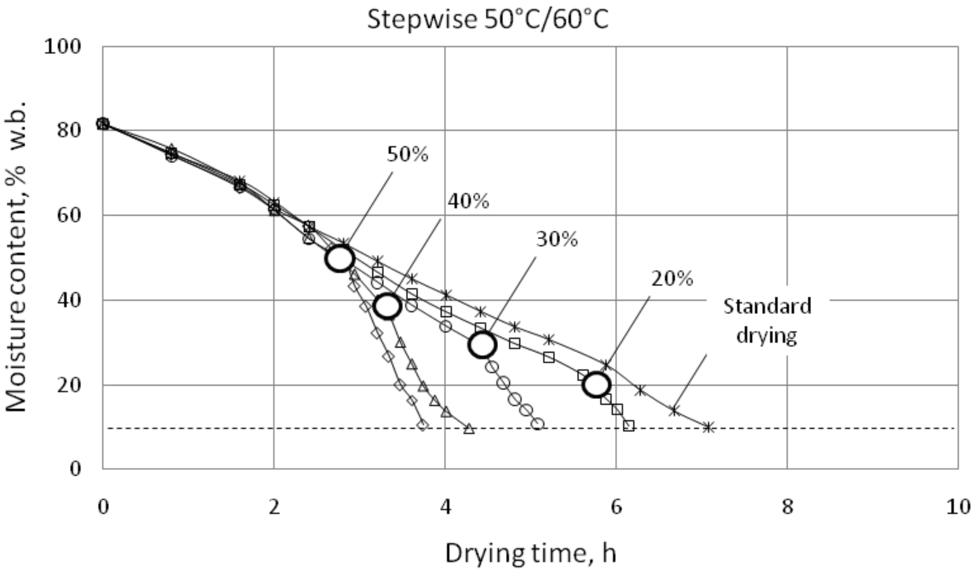


Figure 8.10: Comparison of drying: standard 50°C and stepwise 50°C/60°C

In general, considering the behavior of drying for different temperature combinations, it can be observed that the earlier the change of point is (the greater the residual moisture is) the shorter drying time.

8.3.2 Influence of temperature on drying time

Table 8.2 and show a summary of the obtained values of drying time for each stepwise drying experiment with their respective change points. It can be observed that for standard drying at 30°C the drying time was 36h, at 40°C 19h and at 50°C it was 7.08*h*. Additionally, the drying times for the different stepwise combinations were shorter than for standard drying at different temperatures and change points.

Table 8.2: Mean values of drying time obtained for several stepwise combinations considering different change points

	Drying time, h					
change point	30°C/40°C	30°C/50°C	30°C/60°C	40°C/50°C	40°C/60°C	50°C/60°C
Standard	36.00	36.00	36.00	19.00	19.00	7.08
20%	30.38	29.87	28.23	13.98	13.58	6.15
30%	26.63	25.63	24.37	12.23	11.72	5.08
40%	22.50	20.02	18.90	10.70	10.07	4.28
50%	19.52	16.02	15.12	9.37	8.59	3.73

Figure 8.11 shows the behavior of drying time considering the different stepwise combinations and change points regarding the standard condition. For the combination 30°C/40°C with change point 50% of moisture content, the drying time diminishes from 36*h* (standard drying as reference) to 19.5*h*, corresponding to a decrement of 46%. For the combination 30°C/50°C the drying time diminishes from 36h to 16h corresponding to a decrement of 55.6% and for the combination 30°C/60°C the drying time diminishes from 36h to 15h corresponding to a decrement of 58%. For the combinations 40°C/50°C and 40°C/60°C with the same change point (50% moisture content) the drying time reducierte was from 19h to 9.37h and 8.95h, corresponding to a decrement of 51% and 53% respectively. Finally for the combination 50°C/60°C the shorter drying time was obtained and the drying time diminished from 7.08h (standard) to 3.73h corresponding to a decrement of 47%. In summary: by using the stepwise strategy, shortest drying times are reached in order to obtain the same final moisture of 10% w.b.

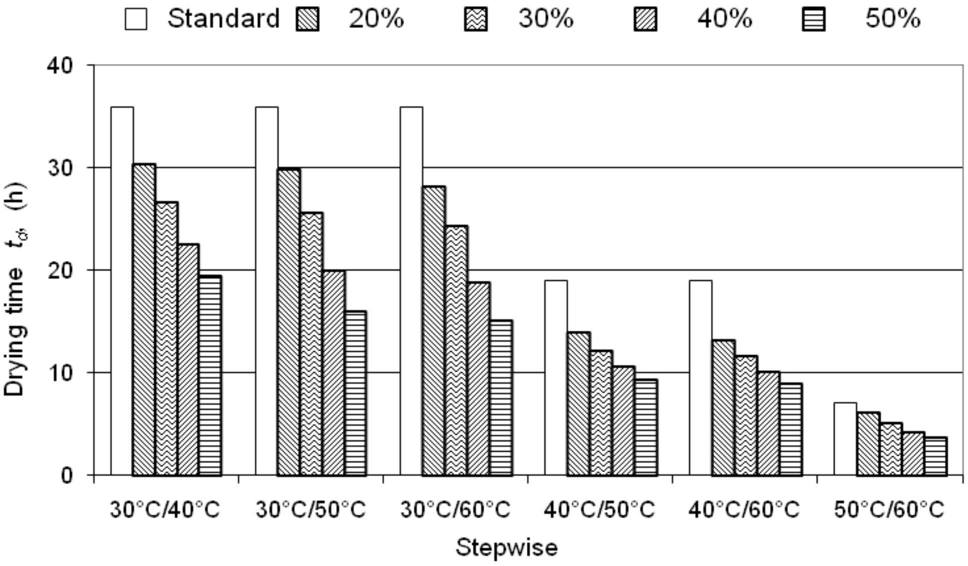


Figure 8.11: Drying time for several stepwise combinations considering different changes points

8.3.3 Effects of drying on essential oil content

Table 8.2 presents the values of essential oil content for standard drying and the different stepwise combinations and change points considered in this study. Considering only the standard drying, it is observed that the greatest content of essential oil was obtained for the standard method at 30°C with $0.24ml/100g_d.m.$, and the smallest content was obtained for the standard method at 50°C with 0.06 $ml/100g_{d.m.}$

Table 8.3: Mean values of essential oil content obtained for several stepwise combinations considering different change points

	Essential oil content, $ml/100g_{d.m.}$					
change point	30°C/40°C	30°C/50°C	30°C/60°C	40°C/50°C	40°C/60°C	50°C/60°C
Standard	0.24	0.22	0.22	0.20	0.18	0.06
20%	0.22	0.19	0.18	0.17	0.17	0.06
30%	0.22	0.11	0.09	0.11	0.15	0.06
40%	0.20	0.06	0.09	0.06	0.11	0.06
50%	0.17	0.06	0.06	0.06	0.11	0.06

Figure 8.12 summarizes the values of the essential oil content for standard drying and different stepwise combinations and change points. Considering the results for stepwise drying , the combination that obtained the greatest essential oil content and with small variations among the different change point was the 30°C/40°C. For this combination the change points with greater essential oil content were 30% and 20% of moisture content with 0.22 $ml/100g_{d.m}$, corresponding to a decrease of 8% regarding the standard value at 30°C. The lowest value of essential oil content was obtained for the change point 50% with 0.17 $ml/100g_d.m$.

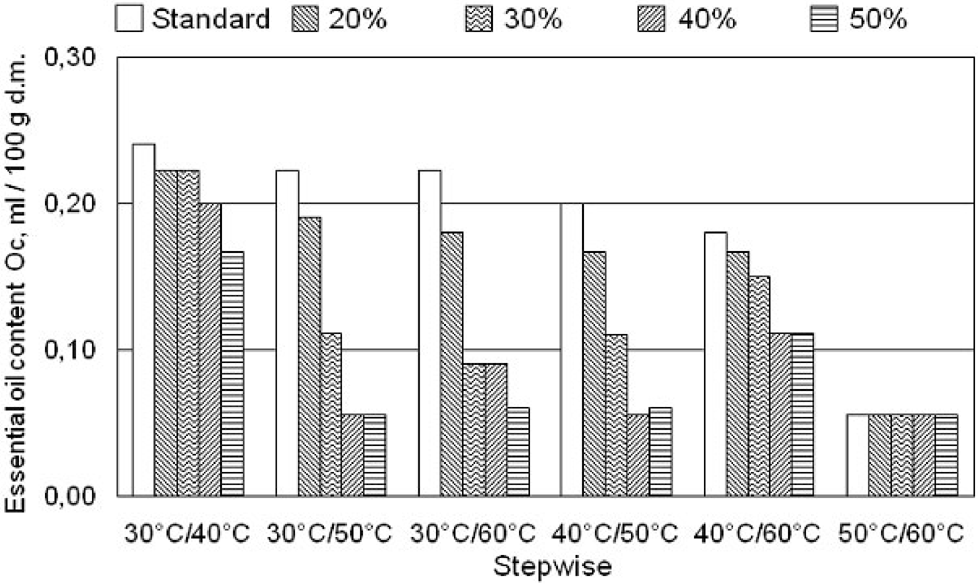


Figure 8.12: Essential oil content for several stepwise combinations considering different change points

Likewise Figure 8.12 shows that the combination 50°C/60°C obtained the smallest content of essential oil, implying that this combination is not recommendable for drying Lemon Balm.

8.3.4 Effects of drying on color difference

Table 8.3 presents the results of color difference, expressed as ΔE, obtained by standard drying and different stepwise combinations and change points. For standard drying at 30°C and 40°C the color change is between 10.8 and 15.4, but for standard drying at 50°C the color change is 29.1, which is quite severe compared with those previously mentioned. This evidences that temperature of drying in the order of 50°C for Lemon Balm causes strong effects on the color of the leaves. Therefore, it is not recommendable drying Lemon Balm at temperatures above 50°C when the color conservation is required.

Table 8.4: Mean values of color changes obtained for several stepwise combinations considering different change points

	Color difference					
change point	30°C/40°C	30°C/50°C	30°C/60°C	40°C/50°C	40°C/60°C	50°C/60°C
Standard	15.37	13.42	14.47	11.91	10.79	29.11
20%	14.98	14.48	17.05	13.59	13.26	30.97
30%	14.64	16.82	18.35	16.73	16.89	30.65
40%	13.62	20.36	21.73	18.87	24.99	35.24
50%	13.21	21.19	23.69	22.07	28.90	34.32

Figure 8.13 summarizes the values obtained for color difference ΔE considering standard and different combinations of stepwise drying. It can be observed that for all the combinations, except 30°C/40°C, the greatest values of color difference correspond to change points of 40% and 50% moisture w.b. Therefore, in order to diminish the effect of drying temperature on color change, a change point of 30% or lower is recommended. For standard drying at 30°C the obtained color difference was $\Delta E = 15.4$ and for the stepwise combination 30°C/40°C was $\Delta E = 13.2$, that represents a diminishing of 24% regarding the standard. This behavior is contrary to the rest of relationships between stepwise combinations and the corresponding standard drying. This can be explained due to the lengthy times of drying that allow the enzymatic activity affecting the color of Lemon Balm leaves.

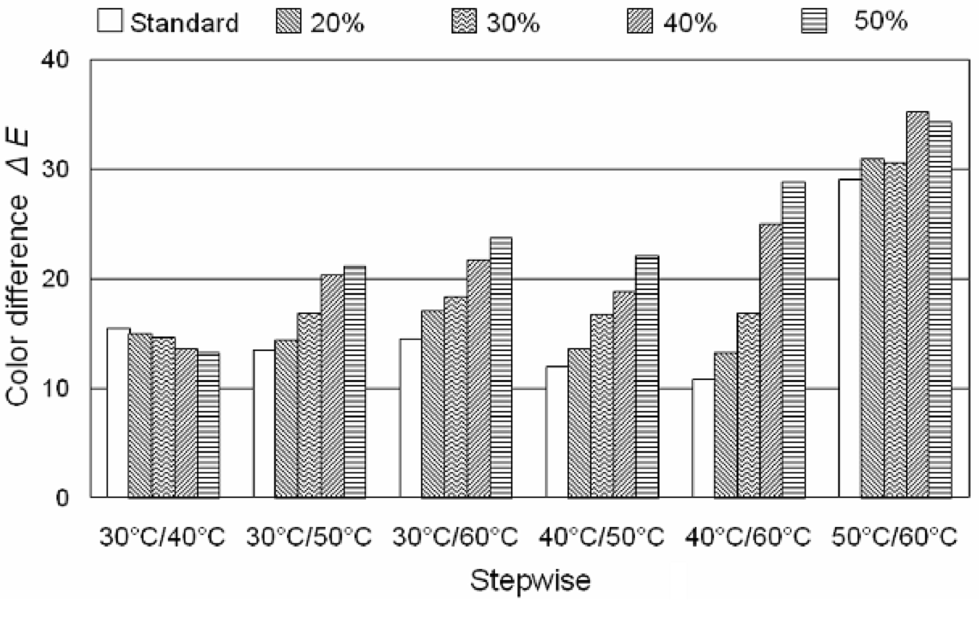


Figure 8.13: Color difference for several stepwise combinations considering different change points

8.3.5 Energy consumption

Table 8.5 and **Figure** 8.14 show the results for energy consumption considering standard and stepwise drying combinations with different change points. To measure the energy consumption a Energy-check was connected to the dryer during each one of the trials and then the average consumption value was calculated. For standard drying at 30°C, 40°C and 50°C the energy consumption was $2.6kWh$, $4.29kWh$ and 2.8 kWh respectively. These values are compared with the values obtained by the corresponding stepwise combinations. For the combination 30°C/40°C and change point 50% moisture w.b. the value of energy consumption was $4.09kWh$, corresponding to an increase of 57% regarding the value for standard drying at 30°C. This was the greatest increment in energy consumption from the different combinations and change points.

Table 8.5: Mean values of energy consumption obtained for several stepwise combinations considering different change points

	Energy consumption, kWh					
change point	30°C/40°C	30°C/50°C	30°C/60°C	40°C/50°C	40°C/60°C	50°C/60°C
Standard	2.60	2.60	2.60	4.29	4.29	2.80
20%	3.24	2.80	2.76	3.85	3.81	2.76
30%	3.45	2.86	2.90	3.70	3.74	2.84
40%	3.77	2.88	2.83	3.40	3.35	2.75
50%	4.09	2.87	2.85	3.07	3.05	2.78

Considering the information presented in **Figure** 8.14, it can be observed that for the stepwise combinations 30°C/40°C, 30°C/50°C and 30°C/60°C, the energy consumption increases as the change point increases. On the contrary for the stepwise combinations 40°C/50°C, 40°C/60°C and 50°C/60°C, the energy consumption diminishes as the change point increases. The smallest energy consumption was 2.75 kWh and was obtained by stepwise combination drying 50°C/60°C and change point 40% moisture w.b.

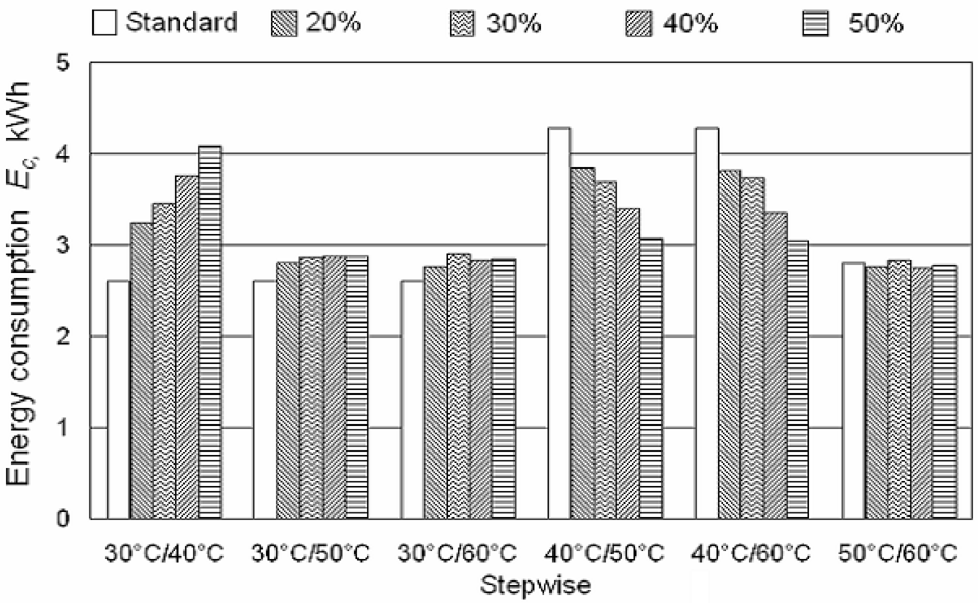


Figure 8.14: Energy consumption for several stepwise combinations considering different change points

8.3.6 Process recommendation

Considering the selection of the drying conditions for satisfying the criteria for lower color difference ΔE, the best stepwise combination was 30°C/40°C with change point 50% moisture w.b. With this combination ΔE=13.214 and the corresponding energy consumption was 4.09 kWh, which is the highest from the different combinations. In addition, the essential oil content obtained for this combination was $0.17 ml/100 g_{d.m.}$ that is 29% lower than the content for standard drying at 30°C. Finally the drying time for the selected combination was $19.52h$ that is 46% lower than the drying time for the corresponding standard drying at 30°C. For satisfying the criteria of lower loss of essential oil, the best combinations were 30°C/40°C with change point 20% and 40°C/60°C with change point 20%. With the first combination the essential oil diminished 8% regarding the oil content obtained by standard drying at 30°C. Considering the second combination, the essential oil diminished 6% regarding the obtained by standard drying at 40°C. For the combinations considered; 30°C/40°C with change point 20% and 40°C/60°C with change point 20%, the energy consumption was 3.24 kWh and $3.82kWh$ respectively. The first case corresponds to an increase of 25% regarding the corresponding standard drying and in the second case a decrease of 11% regarding the standard. Regarding the drying time, in the first combination was 30h (16% less than the standard) and in the second combination was 13.6h (29% less than the standard). For the combination 30°C/40°C with change point 20%, the color difference was 3% less than the standard at 30%, and finally for 40°C/60°C with change point 20% the color difference was 23% more than the standard at 40%.

9 Multiobjective optimization of drying process

Quality can be defined as a measure of adequacy of a product for specific uses. Different situations require different quality criteria. Actually, quality is more associated to the consumer, who gives a quality judgement to a product. The quality experience a consumer is linked to product properties, which can be described to as quality attributes. A quality attribute for example is colour. Colour may be affected by many factors. Therefore, quality attributes are discerned into quality indicators, which are measurable. In the present research the quality indicator is a function of the characteristics of the drying process and of the product properties (Quirijins, 2006). The quality indicator is determined by gradients of moisture content and temperature inside the material. Crack formation is a good example. In quality control or optimization average values are generally used. So for the definition of quality, a quality indicator should be determined (Martinov et al., 2006). The quality indicator considered in this study are color difference and essential oil content.

9.1 Materials and methods

The material considered for the experimentation was Lemon Balm variety Citronella. The amount used for each test was 1000g, which was divided and placed in three trays containing equal amounts in each one. The observed initial moisture of the material was 76%. The tests were performed at temperatures between 30°C and 50 °C and with relative humidity between 20 and 60%.

The drying experiments were conducted using a same dryer as explaining in secction 7.1. Due to the construction of the dryer and application of the over current principle a low air-flow resistance is reached within the equipment. This results in a low energy requirement of the fan as well as the possibility to use cross flow fans. The application of this type of fans leads to a uniform air distribution in the drying chamber. In combination with the registered profiled layout of the trays there is no need to shift single trays during the drying process to reach the desired uniform drying rate. **Figure 7.1** shows the general characteristics of the experimental set up including the cabinet dryer and the air conditioning unit connected for obtaining the conditions of the drying air and the corresponding air flow.

This set up was used to obtain constant and stable humidity conditions needed for developing the drying tests. The drying air velocity during the experimentation was 0.45 m/s and it was maintained constant for all of the tests. During the tests, the temperatures as well as the relative humidity were measured every 15m, at the entrance and at the exit of the dryer by using thermocouples and digital hygrometers. To observe the loss of moisture, the product was weighted every hour until that the final moisture of 10% was reached. Quality measurements (of color difference and essential oil content) before and after drying were performed according to the methodology described in chapter 5. The values of the required energy for the moisture evaporation were determined by using the following equation:

$$q_r = \dot{m}_a(C_i T_i - C_o T_o) d_t \tag{9.1}$$

Where, m_a is the mass flow rate in kg_{aire}/h, C_i, C_o are the specific heat of inlet and outlet air in kJ/kg°C and T_i and T_o are the temperature of the inlet and outlet air drying in °C and d_t is the drying time in h.

9.2 Experimental design and response surface methodology (RSM)

To model the drying process, design of experiments and statistical analysis were used. Developing an empirical model requires fewer restrictive assumptions than a physical model when representing complex, dynamic systems, and is fairly simple and of relatively low dimensionality. The performance of a model depends on a large number of factors that act and interact in a complex manner. In **Figure 9.1** the methodology for the analysis of multi-response optimization is presented.

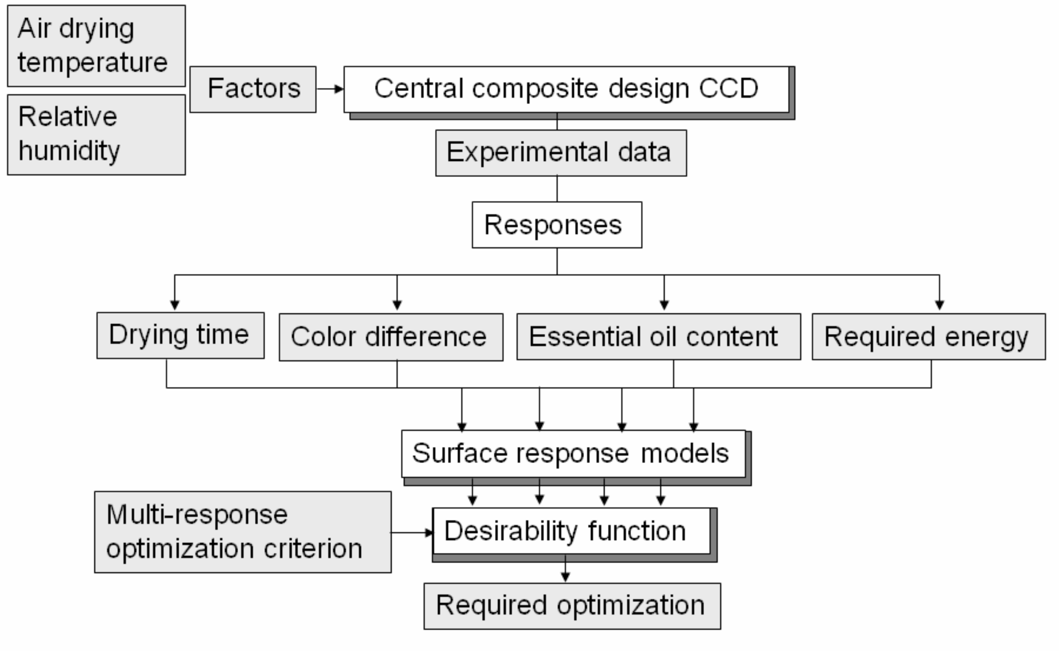


Figure 9.1: Proposed methodology for multi-response optimization of drying

To model the drying process in order to optimize, the response surface methodology RSM was considered. RSM is a collection of mathematical and statistical techniques that are useful for modeling and analysis in applications where a response of interest is influenced by several variables and the objective is to optimize this response (Myers & Montgomery, 2002).

In most RSM problems, the form of the relationship between the response and the independent variables is unknown. Thus, the first step in RSM is to find a suitable approximation for the true relationship between Y and independent variables. Usually, a low-order polynomial in some region of the independent variables is employed. A polynomial type of a model is chosen and the correlation between the process factors and responses is identified using experimental data. In the context of polynomial regression, we mean that for the particular regressors, x_1, $x_2 \ldots$ x_k an experiment is performed whose measured outcome y has the form (Myers & Montgomery, 2002):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum \sum_{i<j=2}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{9.2}$$

Where the random errors ε are uncorrelated, normally distributed with zero mean and variance σ^2. Central composite design (CCD) is used to fit a second-order model (Myers & Montgomery, 2002). The design is a two-level full factorial with n_f factorial points, augmented with additional n_0 center and 2^k axial points. Axial points are located at a specific distance α from the design center in each direction in each axis. The factorial points represent a first-order model, while center points, set to the midpoint of each factor range, provide information about curvature existence. In addition, axial points allow estimation of the pure quadratic properties of the model.

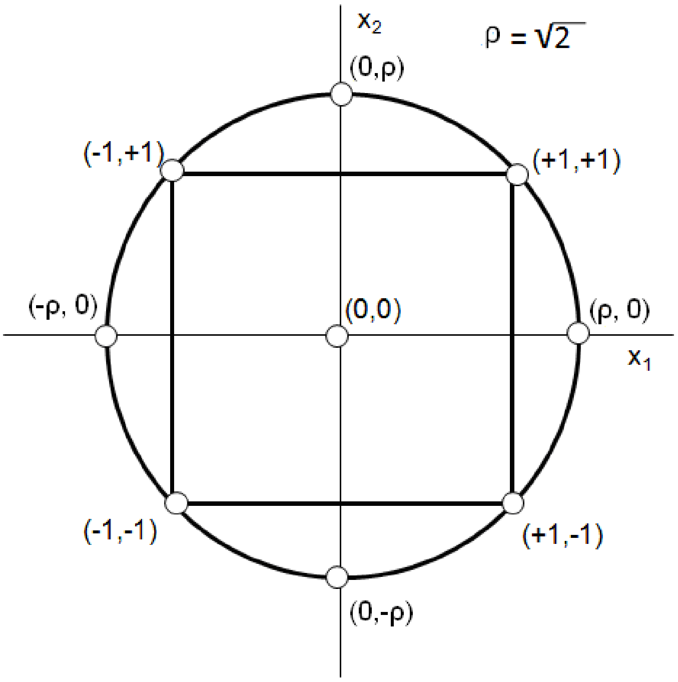


Figure 9.2: Central composite design for $k = 2$ and $\rho = \sqrt{2}$

This design involves $n_f = 4$ factorial points, $2k = 4$ axial points (axial distance is $\rho =$

$\sqrt{2}$) and, n_c center runs (in this case $n_c = 5$). For the surface response two experimental factors are considered; temperature ϑ and relative humidity φ of drying air, with working ranges between 26°C and 54°C and 12 % and 68% respectively. The considered responses are drying time (t_d), color difference (ΔE), essential oil content (O_c), and required energy (q_r) (see **Table** 9.1).

Table 9.1: Experimental factors and responses

Experimental factors	symbol	Unit
Drying temperature	ϑ	°C
Relative humidity	φ	%
Responses		
Drying time	t_d	h
Essential oil content	O_c	%
Color difference	ΔE	-
Required energy	q_r	kJ

The developed response surface model is able to predict drying time, color difference, essential oil content and required energy. In **Table** 9.2 the constant conditions for experimenting are presented. In **Table** 9.3 the considered experimental factors and responses are shown.

Table 9.2: Constant conditions for experimenting

Experimental constant conditions	
Product	*Melissa officinalis* L
Variety	citronella
Weight of sample	$1000g$
Environment temperature	$\bar{\vartheta}_e$= 25° C
Environment relative humidity	$\bar{\varphi}_e = 51\%$
Air velocity	0.45 m/s

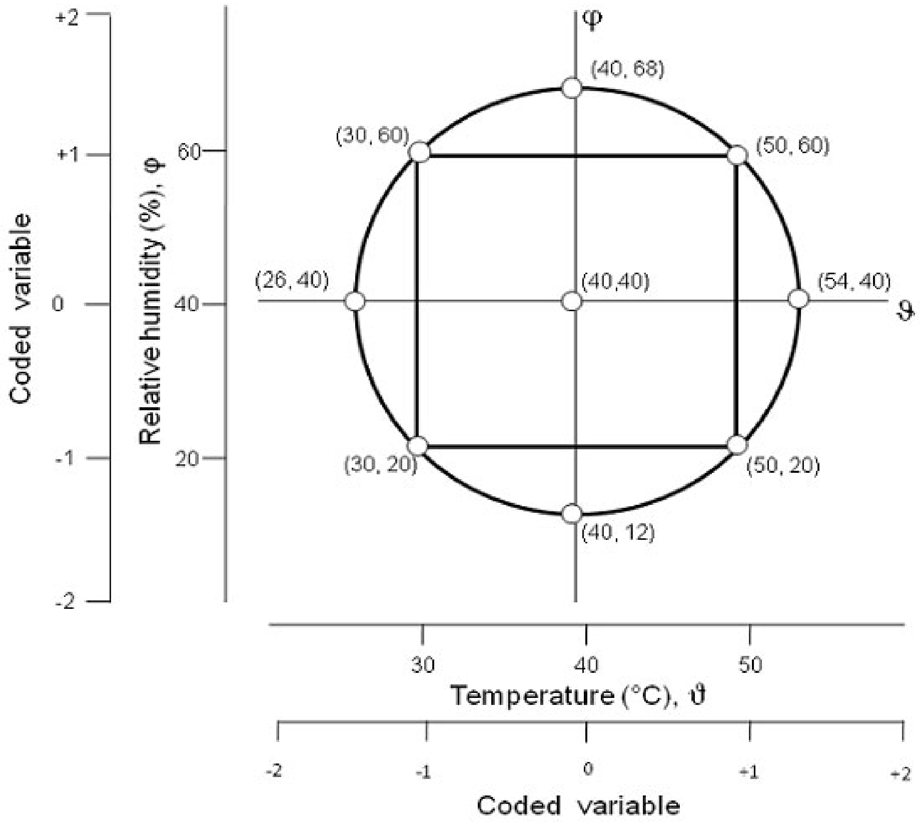


Figure 9.3: Central composite design (CCD) for the considered variables

Table 9.3: Experimental factors and responses

	Experimental factors		Responses			
Nr.	Air Temperature ϑ (°C)	Relative Humidity φ (%)	Drying Time t_d (h)	Essential oil content O_c (% of fresh)	Color difference ΔE	Required energy q_r (kJ)
1	30	20	25.16	87.54	10.237	13449.51
2	50	20	6.25	35.15	14.316	5073.36
3	30	60	55.75	87.50	14.487	13245.19
4	50	60	19.00	44.00	16.028	6018.74
5	26	40	41.00	84.62	10.324	14286.59
6	54	40	8.75	68.35	25.624	6929.47
7	40	12	11.00	78.14	10.872	9758.28
8	40	68	29.00	83.93	10.799	6315.72
9	40	40	16.00	90.25	6.977	7475.91
10	40	40	15.25	85.81	10.382	7125.48
11	40	40	14.00	97.05	6.947	6541.42
12	40	40	15.00	87.95	6.073	7008.67
13	40	40	14.50	98.20	8.995	6775.05

9.3 Regression models

In the practical application of response surface methodology it is necessary to develop an approximating model for the true response surface. The approximating model is based on observed data from the process. Multiple regression is a collection of statistical techniques useful for building the type of experimental models required in response surface methodology (RSM) (Montgomery, 2005).

Models that are complex in appearance as presented in equation B.1, may be analyzed by multiple linear regression techniques. Regression analysis is used to investigate and model the relationship between the response variable Y and one or more predictors X. In most real-world problems, the values of the parameters (the regression coefficients β_j) and the error variance σ^2 will not be known, and they must be estimated from sample data. The fitted regression equation or model is typically used in prediction of future observations of the response Y or for estimating the mean response at a particular level of the predictors X (Myers & Montgomery, 2002; Fahrmeir et al., 2007). The set of regression coefficients $\beta\text{`}s$ of equation B.1 are unknown and estimated by least squares.

By using regression analysis considering air drying temperature and relative humidity as factors, experimental models for drying time, required energy, color difference and essential oils content were obtained. Below the results of regression analysis for the mentioned models are presented.

9.3.1 Drying time

Considering the experimental data from **Table 9.3**, and the reference model presented in equation B.1, a regression model for drying time, was proposed. The model is described by means of equation 9.3. **Figure 9.4** shows the experimental data for drying time as function of air drying temperature and relative humidity obtained following the CCD experimental design.

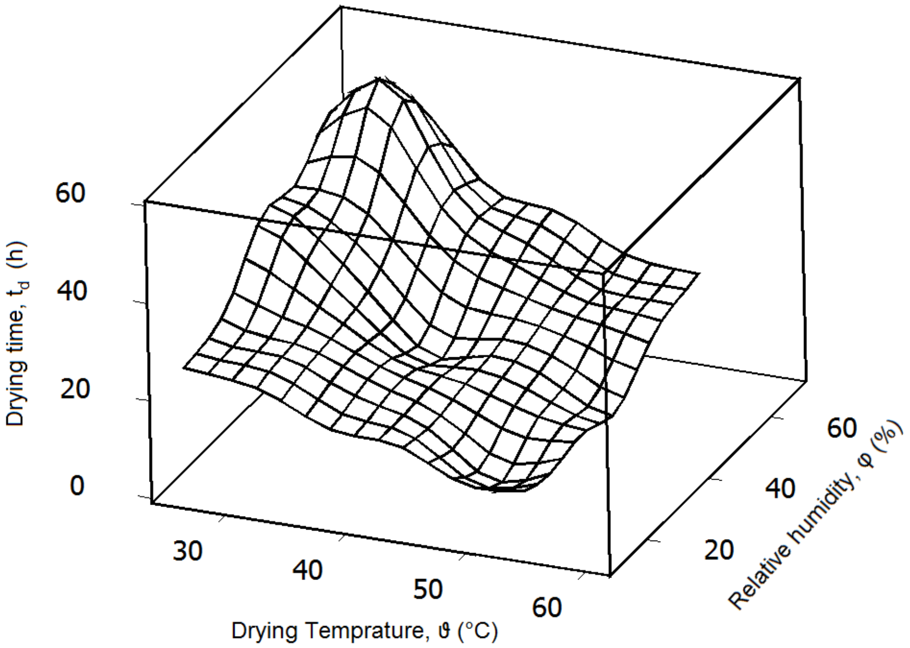


Figure 9.4: Experimental data for drying time

$$t_d = 122.718 - 5.164\,\vartheta + 0.612\,\varphi + 0.06\,\vartheta^2 - 0.022\,\vartheta \cdot \varphi \tag{9.3}$$

In this equation, the coefficient of the square of relative humidity is not relevant showing that the curvature is small and the relationship regarding the relative humidity tends to be linear.

In Appendix B, the results of the regression analysis and the corresponding analysis of variance for the model of equation 9.3 are presented.

By using the model presented in equation 9.3, surface and contour plots can be generated in order to observe the behavior of the drying time t_d for different combinations of air drying temperature and relative humidity (see **Figures** 9.5 and 9.6).

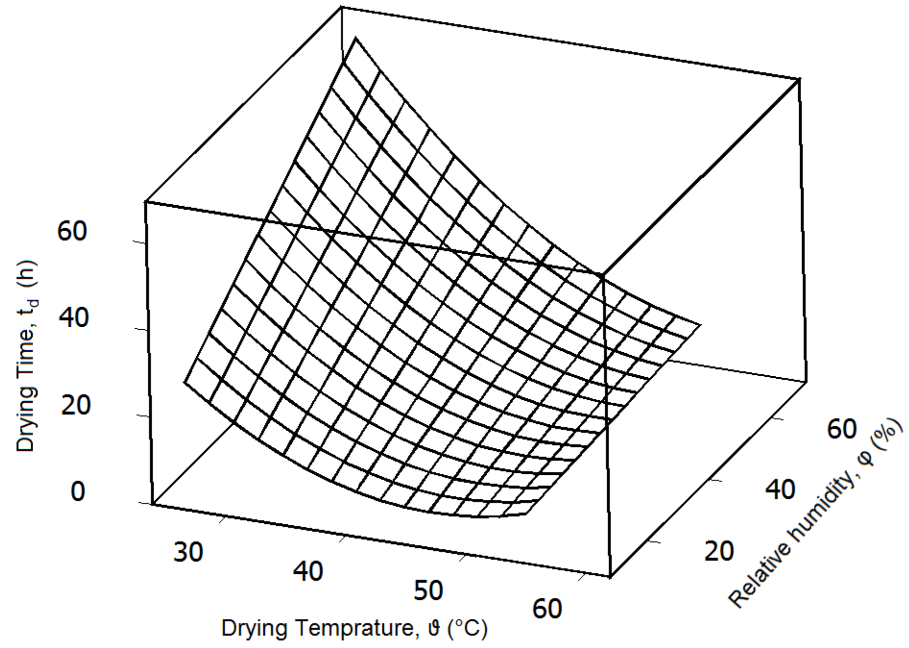


Figure 9.5: Surface plot for drying time t considering air drying temperature and relative humidity

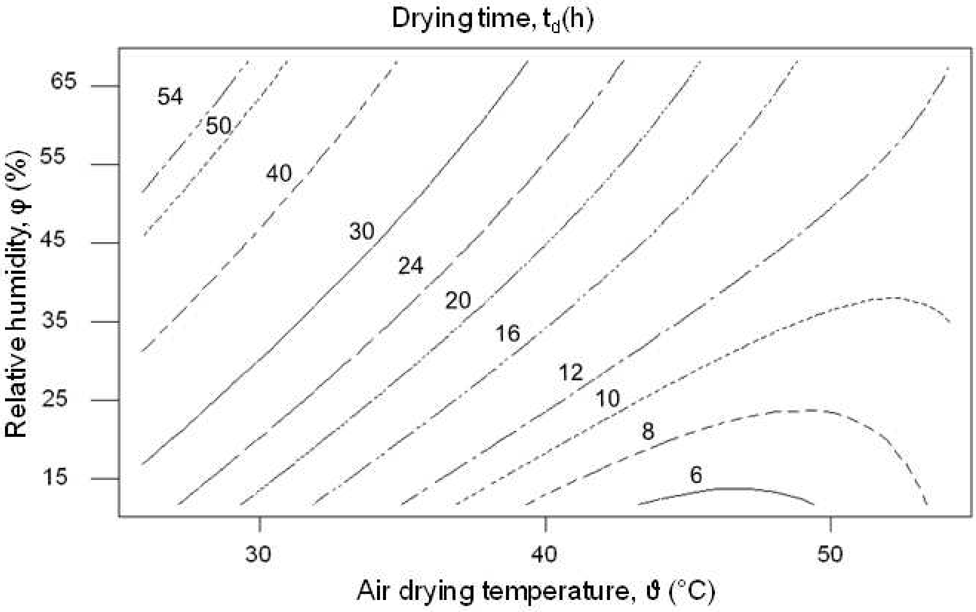


Figure 9.6: Contour plot for drying time t_d (h) considering air drying temperature and relative humidity

Figure 9.6 shows a contour plot obtained from equation 9.3. For the ranges considered in the plot for air drying temperature and relative humidity, a tendency for the minimum of drying time can be observed. A local minimum of drying time can be found at temperatures between 42 to 43°C with relative humidity below 15%. This optimum takes in account only the optimization for drying time in the studied range of the variables and does not consider the complementary optimization of the rest of the responses (essential oil content, color difference and required energy). Such aspect is analyzed by the multiobjective optimization process presented in section 9.4.

9.3.2 Color difference

By using the experimental data from **Table** 9.3, and the reference model presented in equation B.1, a regression model for color difference was proposed. The model is described by means of equation 9.4. **Figure 9.7** shows the experimental data for color difference as function of air drying temperature and relative humidity obtained following the CCD experimental design.

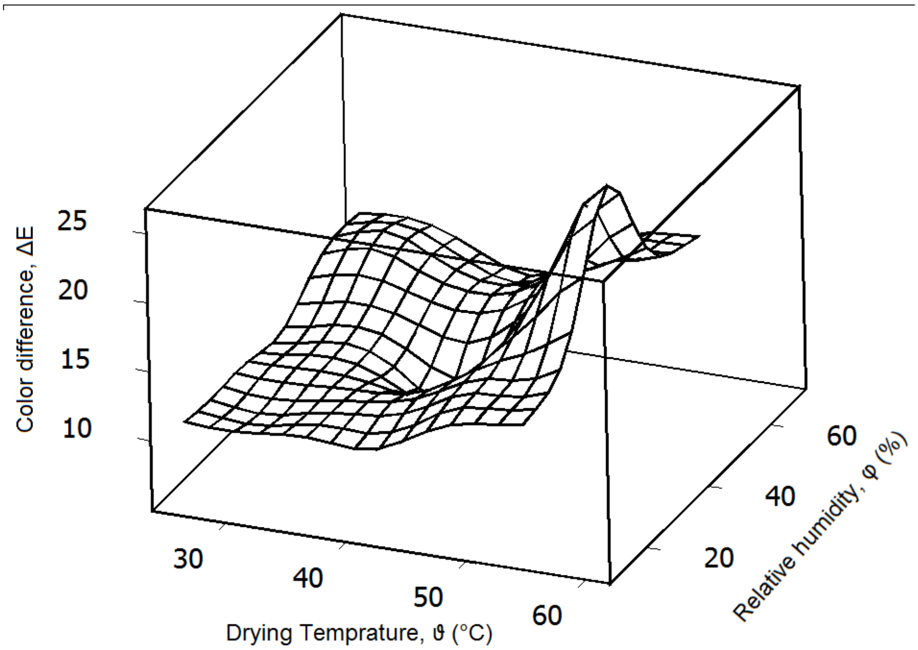


Figure 9.7: Experimental data for color difference

$$\Delta E = 71.230 - 3.444\,\vartheta - 0.101\,\varphi + 0.049\,\vartheta^2 + 0.003\,\varphi^2 - 0.003\,\vartheta \cdot \varphi \qquad (9.4)$$

In Appendix B, the results of the regression analysis and the corresponding analysis of variance for the model of equation 9.4 are presented.

By using the model presented in equation 9.4, surface and contour plots can be generated in order to observe the behavior of the color difference for different combinations of temperature and relative humidity (see **Figures** 9.8 and 9.9).

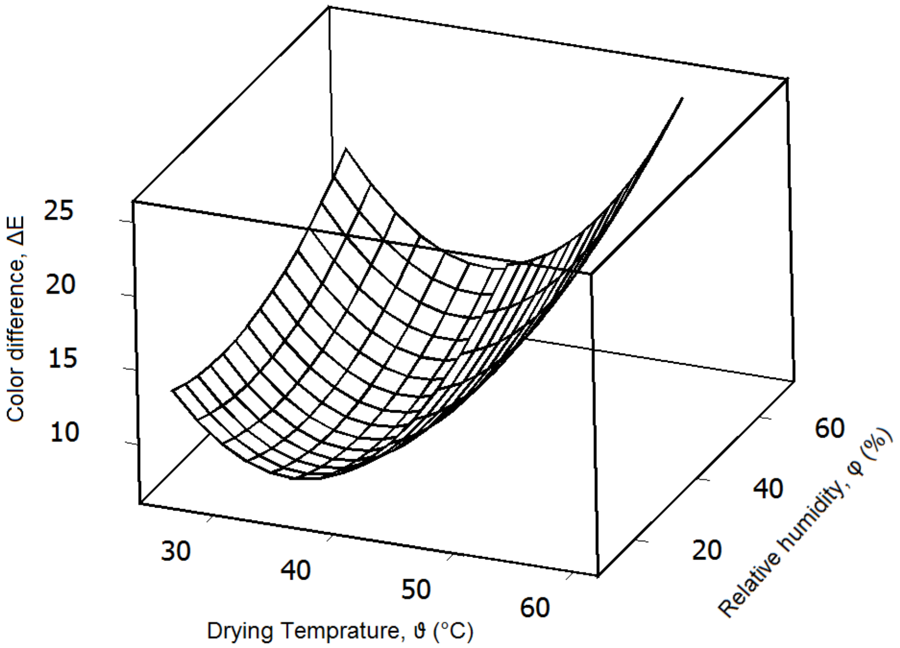


Figure 9.8: Surface plot for Color difference ΔE considering air drying temperature and relative humidity

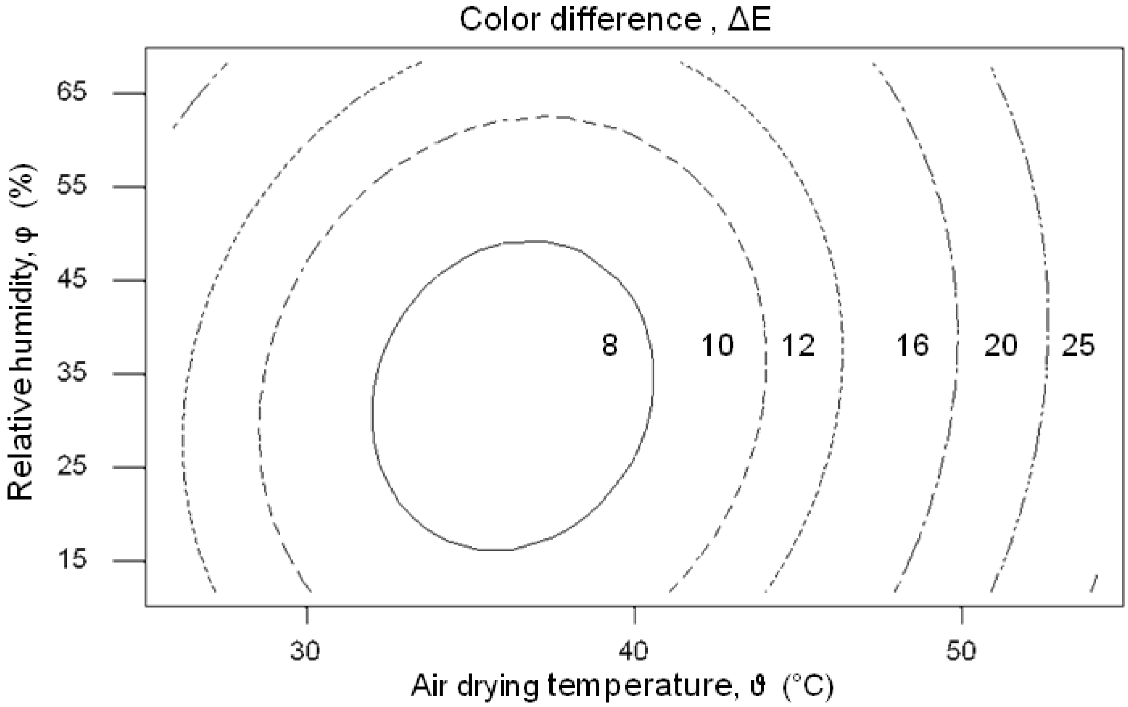


Figure 9.9: Contour plot for color difference ΔE considering air drying temperature and relative humidity

From the contour plot presented in **Figure 9.9** can be observed that the minimum of the color difference is inside the contour with value 8 for color difference. The optimum of color difference corresponds to a drying air temperature around 36°C and relative humidity of 33%. With the information obtained from the model and the generated plots, the value of the color difference corresponding to a selected combination of air drying temperature and relative humidity can be found.

9.3.3 Essential oil content

Considering the experimental data from **Table** 9.3, and the reference model presented in equation B.1, a regression model for essential oil was proposed. The model is described by means of equation 9.5. **Figure 9.10** shows the experimental data for essential oil content as function of air drying temperature and relative humidity obtained following the CCD experimental design. In **Figure 9.11** the response surface corresponding to the proposed model is presented and **Figure 9.12** shows a contour plot obtained from the model.

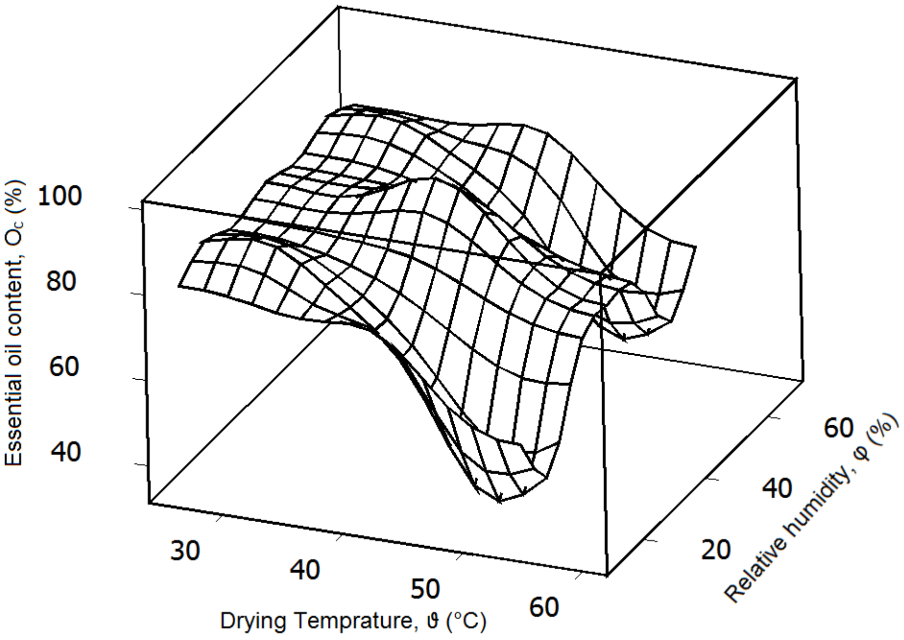
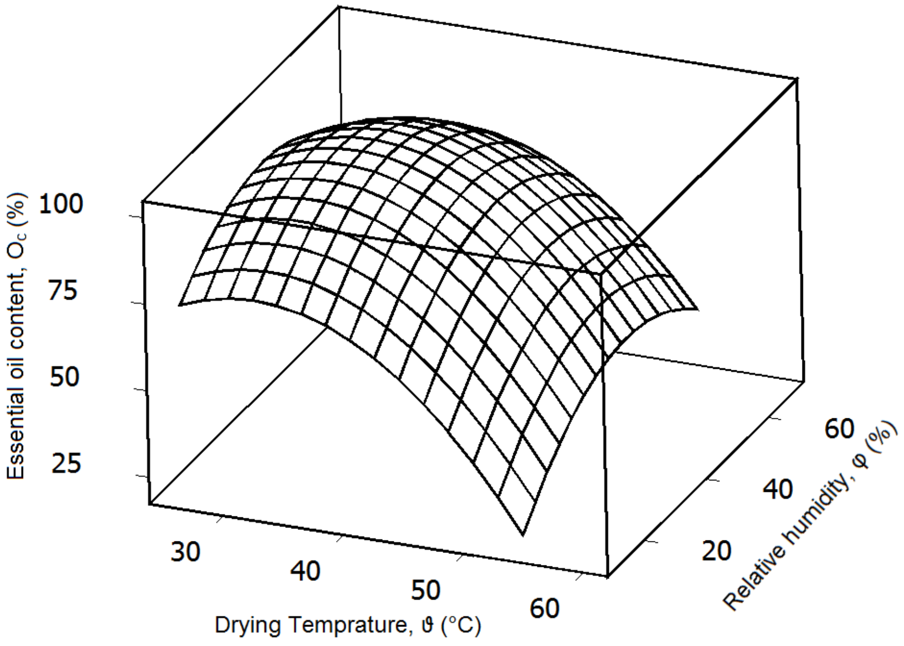


Figure 9.10: Experimental data for essential oil content

$$O_c = -55.80 + 7.26\,\vartheta + 1.50\,\varphi - 0.11\,\vartheta^2 - 0.02\,\varphi^2 + 0.01\,\vartheta \cdot \varphi \tag{9.5}$$

In Appendix B, the results of the regression analysis and the corresponding analysis of variance for the model of equation 9.5 are presented.



|

Figure 9.11: Surface plot for essential oil content O_c considering air drying temperature and relative humidity

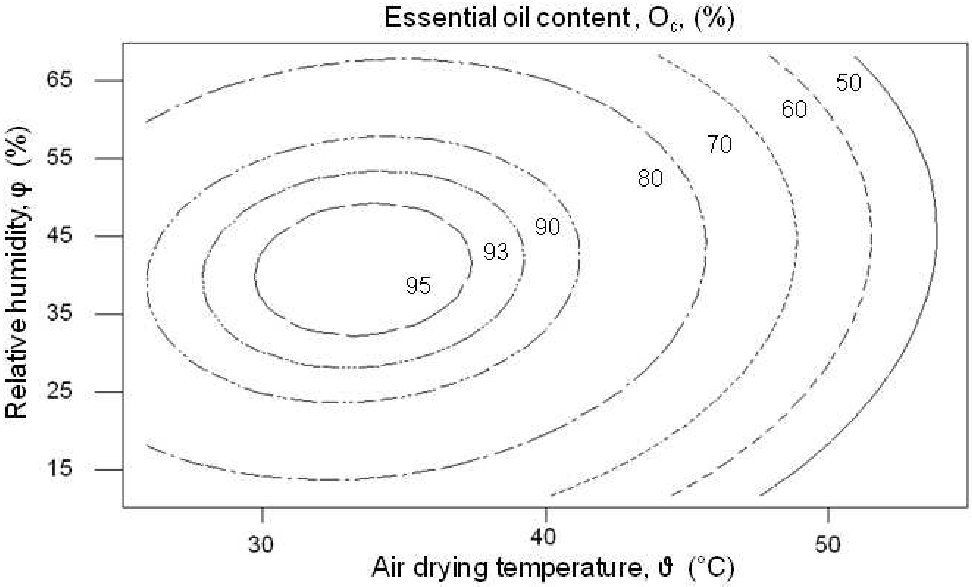


Figure 9.12: Contour plot for essential oil content O_c considering air drying temperature and relative humidity

Observing the contour plot presented in **Figure 9.12** that was generated from the model presented in equation 9.5, it is possible to estimate the optimum for essential oil content. The maximum of essential oil content is located inside the contour line for 95% of essential oil content, and corresponds to a combination of air drying temperature around 33°C and relative humidity of 42%.

9.3.4 Required energy

Considering the experimental data from **Table** 9.3, and the reference model presented in equation B.1, a regression model for the required energy was proposed. The model is described by means of equation 9.6. **Figure 9.13** shows the experimental data for essential oil content as function of air drying temperature and relative humidity obtained following the CCD experimental design. In **Figure 9.14** and 9.15 the response surface and a contour plot corresponding to the proposed model are presented.

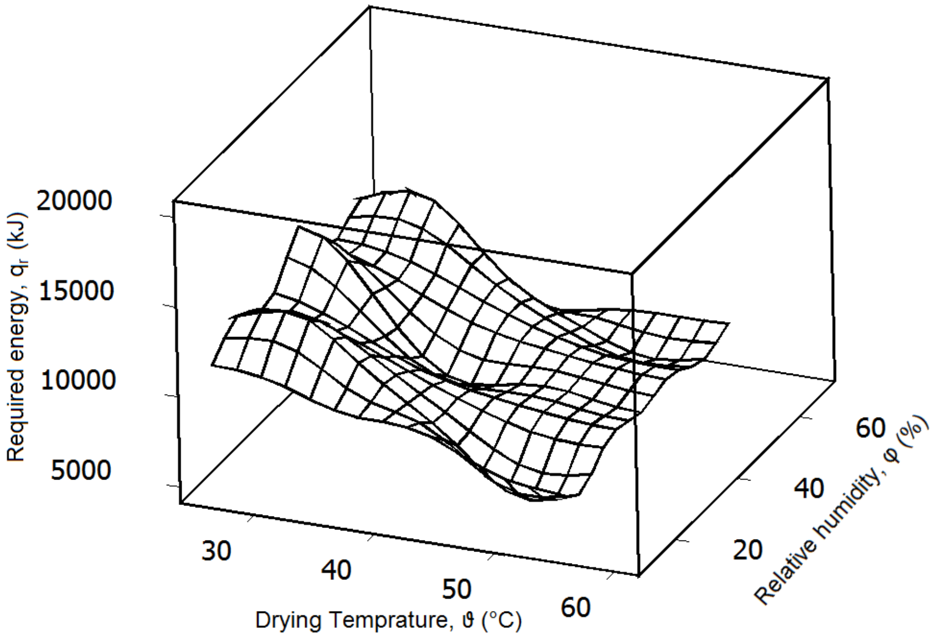


Figure 9.13: Experimental data required energy

$$q_r = 45588 + 1854\,\vartheta + 716\,\varphi - 18.4\,\vartheta^2 - 4\,\varphi^2 - 8\,\vartheta \cdot \varphi \qquad (9.6)$$

In Appendix B, the results of the regression analysis and the corresponding analysis of variance for the model of equation 9.6 are presented.

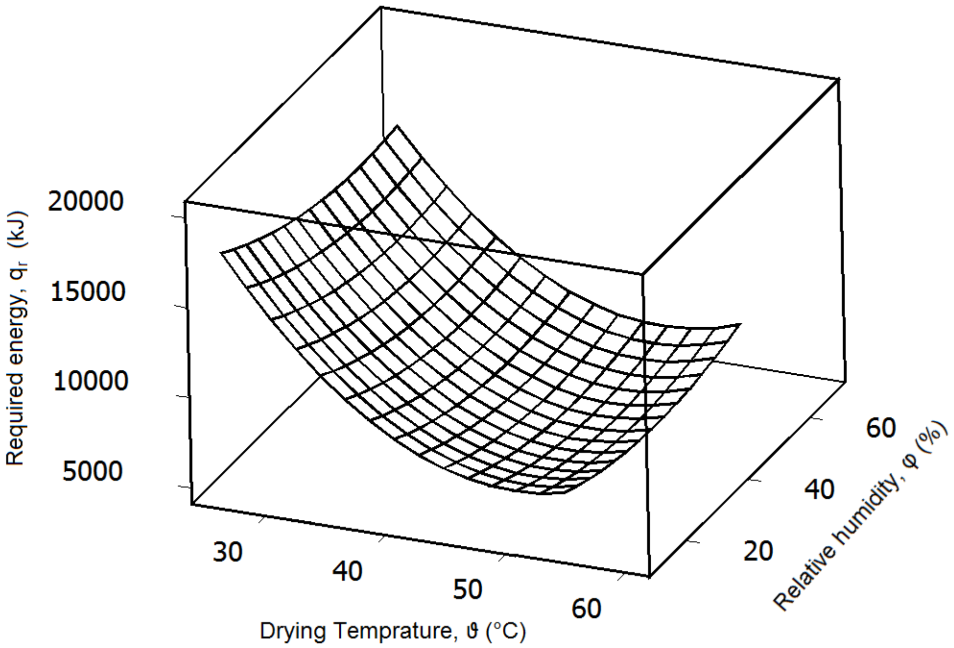


Figure 9.14: Surface plot for required energy q_r considering air drying temperature and relative humidity

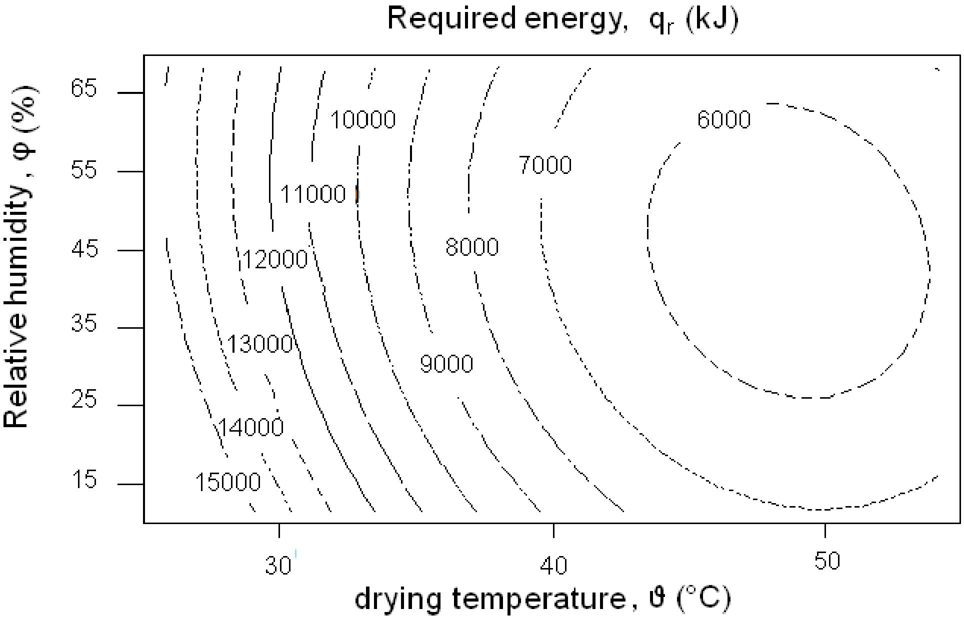


Figure 9.15: Contour plot for required energy q_r considering air drying temperature and relative humidity

Figure 9.15 presented a contour plot obtained from equation 9.6, which describes the behavior of the required energy as function of air drying temperature and relative humidity. From this contour plot can be observed that the minimum of the required energy corresponds to a combination of air drying temperature around 48°C and 44% of relative humidity.

9.4 Multiobjective process optimization

For quality oriented drying it is necessary to determine the input variable settings that result in a product with desirable properties (responses). Since each property or response is important in determining the quality of the product, it is necessary to consider these properties simultaneously. Optimal settings of the input factors for one response may be far from optimal or even physically impossible for another response. Response optimization is a method that allows the optimization for compromise among the various responses.

For optimization purposes it is necessary to characterize how the factors affect the investigated response,i.e. to develop the appropriate model, and to define an objective for improving the response of interest. The study of drying process was formulated as a constrained optimization problem. This problem can be solved by various methods, which offer a direct search procedure that suggests a combination of factor levels that simultaneously satisfy the requirements placed on the response and factors. The goal is to minimize drying time, color difference and required energy and to maximize essential oil content within the region of interest. In order to attain independent and reliable optimization, the desirability function, as nonlinear programming approach was considered (Myers & Montgomery, 2002).

The desirability function approach is used for the optimization of multiple response process. The overall (or composite) desirability (D) is a measure of how well are satisfied the combined goals for all responses. Overall desirability has a range of zero to one. One represents the ideal case; zero indicates that one o more responses are outside their acceptable limits. As general approach, simultaneous experimental numerical optimization technique is based on a single-objective desirability function $d(y)$, which is to first convert each response y_i into an individual desirability function d_i that varies over the range
$0 \leq d \leq 1$

Where if the response y_i is at its goal or target, then $d_i = 1$, and if the response is outside an acceptable region, $d_i = 0$. Then the design variables are chosen to maximize the overall desirability

$$\Delta D = (d_1 d_2 ... d_m)^{1/m} \tag{9.7}$$

Where there are m responses. The individual desirability functions are structured as shown in **Figure 9.16**. If the objective or target T for the response y is a maximum value (Myers & Montgomery, 2002).

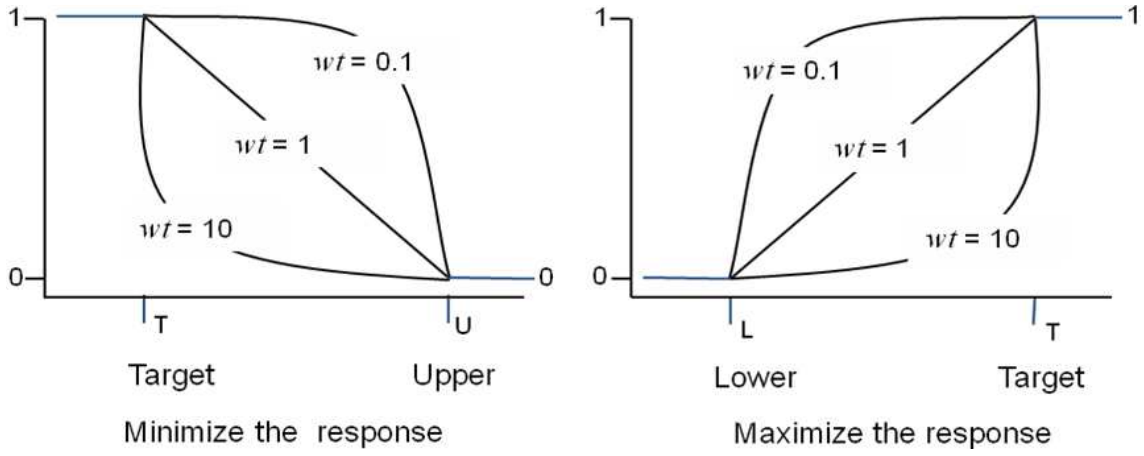


Figure 9.16: Desirability functions for a response to be minimized and maximized

$$d(y) = \begin{Bmatrix} 0, \quad y < L \\ \left[\dfrac{y-L}{T-L}\right]^{wt}, \quad L \leq y \leq T \\ 1, \quad y > T \end{Bmatrix} \tag{9.8}$$

The objective is to maximize the desirability function. The weight, wt, can be assigned to goal to adjust the shape of desirability function, shown in **Figure 9.8**. Increased weight moves the result towards the goal or its decrease creates the opposite effect.

When the weight $wt = 1$, the desirability function is linear. Choosing $wt > 1$ places more emphasis on being close to the target value, and choosing $0 < wt < 1$ makes this less important. If the target for the response is a minimum value (Myers & Montgomery, 2002),

$$d(y) = \begin{Bmatrix} 1, \quad y < L \\ \left[\dfrac{U-y}{U-T}\right]^{wt}, \quad T \leq y \leq U \\ 1, \quad y > U \end{Bmatrix} \tag{9.9}$$

Where y, L, U and T are denominate response, lower value, upper value, and target respectively.

Considering the algorithm and computer implementation (Minitab-Inc, 2009), after calculating an individual desirability for each response, they are combined to provide a measure of the composite, or overall, desirability of the multi-response system. This measure of composite desirability (D) is the weighted geometric mean of the individual desirabilities for the responses. The individual desirabilities are weighted according to the importance assigned to each response.The method considers the following steps (Minitab-Inc, 2009):

a) Obtaining individual desirability: the algorithm obtains an individual desirability (d) for each response using the provided goals and boundaries. There are three goals to consider: to minimize the response (smaller is better), to target the response (target is best) and to maximize the response (larger is better).

b) Obtaining the composite desirability: after calculating an individual desirability for each response, they are combined to provide a measure of the composite, or overall, desirability of the multi-response system. This measure of composite desirability (D) is the weighted geometric mean of the individual desirabilities for the responses. The individual desirabilities are weighted according to the importance that was assigned each response.

c) Maximizing the composite desirability: by using a reduced gradient algorithm with multiple starting points that maximizes the composite desirability to determine the numerical optimal solution (optimal input variable settings).

It is necessary to asses the importance of each response in order to assign appropriate values. Importance values must be between 0.1 and 10. If all responses are equally important, use the value 1.0 for each response. The composite desirability is then the geometric mean of the individual desirabilities.

However, if some responses are more important than others, you can incorporate this information into the optimal solution by setting unequal importance values. Larger values correspond to more important responses, smaller values to less important responses.
Table 9.4 to 9.9 and **Figures** 9.17 to 9.21, show the results for different optimization analysis. The individual desirability, composite desirability and the optimal values of the factors (temperature and relative humidity) considering different importance for the responses are presented.

9.4.1 Drying time as priority

In order to minimize the drying time, a value of 10 for the importance of drying time and low importance (0.1) for the rest of responses were assigned. A minimal drying time of 10.84 hours was obtained for an optimal combination of drying temperature of 40°C and relativity humidity of 21%. The desirability for drying time is 0.857, which has a satisfactory value for the optimization required.

Table 9.4: Multiobjective optimization considering drying time as priority

Parameters	Goal	Lower	Target	Upper	Weight	Import
Drying Time	Minimum	6	6	40	1	10
Essential oil content	Maximum	80	98	98	1	0.1
Color difference	Minimum	6.07	6.07	10	1	0.1
Required energy	Minimum	5000	5000	14000	1	0.1

Global Solution	
Temperature	40.4095
Rel.Humidity	21.3784

Predicted Responses			
Drying Time	10.84	desirability	0.85755
Essential oil content	81.18	desirability	0.06529
Color difference	8.51	desirability	0.37912
Required energy	7807.45	desirability	0.68806

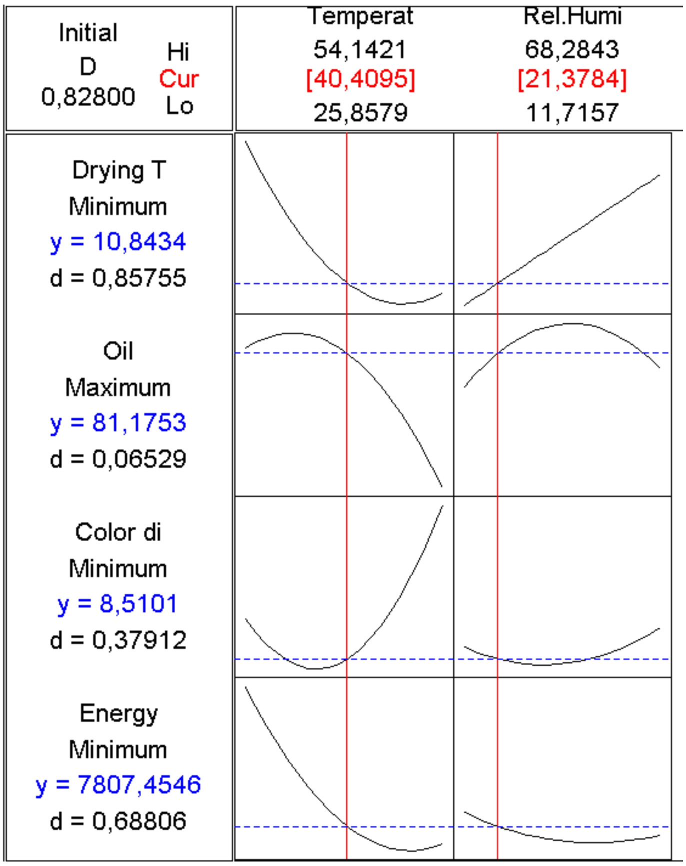


Figure 9.17: Plots of multi objective optimization considering drying time as priority

Figure 9.17 shows that for the optimization considering drying time as priority, the value of drying time obtained is not exactly coincident with the absolute minimum of the function that depends on the air drying temperature. For this condition an individual desirability for drying time of 0.85 is obtained. In addition the optimum values of essential oil content, color difference and required energy are not coincident with the absolute optimal points for these functions that depend on air drying time and relative humidity. Accordingly the individual desirability for these functions is relatively low.

9.4.2 Essential oil content as priority

In order to maximize the essential oil content, a value of 10 for the importance of essential oil content and low importance (0.1) for the rest of responses were assigned. A maximal essential oil content of 96.7% was obtained for an optimal combination of drying temperature of 33°C and relativity humidity of 41%. The desirability for essential oil 0.93, which has a satisfactory value for the optimization required.

Table 9.5: Multiobjective optimization considering essential oil contents as priority

Parameters	Goal	Lower	Target	Upper	Weight	Import
Drying Time	Minimum	6	6	40	1	0.1
Essential oil content	Maximum	80	98	98	1	10
Color difference	Minimum	6.07	6.07	10	1	0.1
Required energy	Minimum	5000	5000	14000	1	0.1

Global Solution	
Temperature	33.6865
Rel.Humidity	41.0033

Predicted Responses			
Drying Time	28.71	desirability	0.33211
Essential oil content	96.67	desirability	0.9261
Color difference	7.73	desirability	0.5768
Required energy	9738.57	desirability	0.47349

Composite Desirability = 0.90679

Figure 9.18 shows that the optimum temperature point is nearly enough to the absolute maximum value of the essential oil content and the minimum value of difference in color. The Figure shows as well that the drying time and the required energy are far away from their minimum values, which indicates that to obtain maximum quality in the final product, the values of drying time and required energy are higher than the minimum.

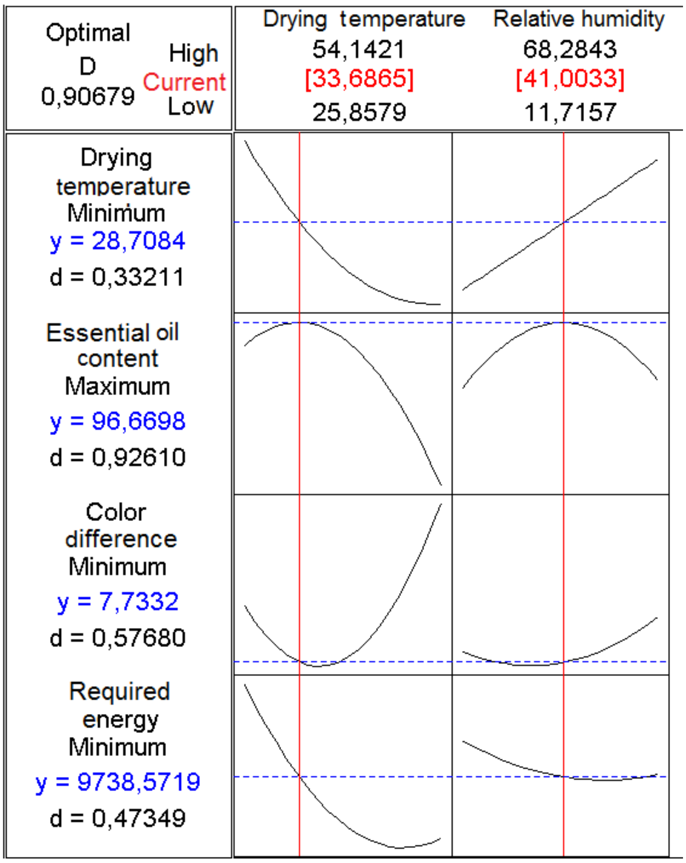


Figure 9.18: Plots of multi objective optimization considering essential oil content time as priority

9.4.3 Color difference as priority

In order to minimize the color difference, a value of 10 for the importance of color difference and low importance (0.1) for the rest of responses were assigned. A minimal color difference of 7.1 was obtained for an optimal combination of drying temperature of 36°C and relativity humidity of 32%. The desirability for color difference is 0.74, which has a satisfactory value for the optimization required.

Table 9.6: Multiobjective optimization considering color difference as priority

Parameters	Goal	Lower	Target	Upper	Weight	Import
Drying Time	Minimum	6	6	40	1	0.1
Essential oil content	Maximum	80	98	98	1	0.1
Color difference	Minimum	6.07	6.07	10	1	10
Required energy	Minimum	5000	5000	14000	1	0.1

Global Solution	
Temperature	36.3224
Rel.Humidity	32.7009

Predicted Responses			
Drying Time	20.18	desirability	0.5828
Essential oil content	94.06	desirability	0.78112
Color difference	7.11	desirability	0.73619
Required energy	8731.08	desirability	0.58544

Composite Desirability = 0.73331

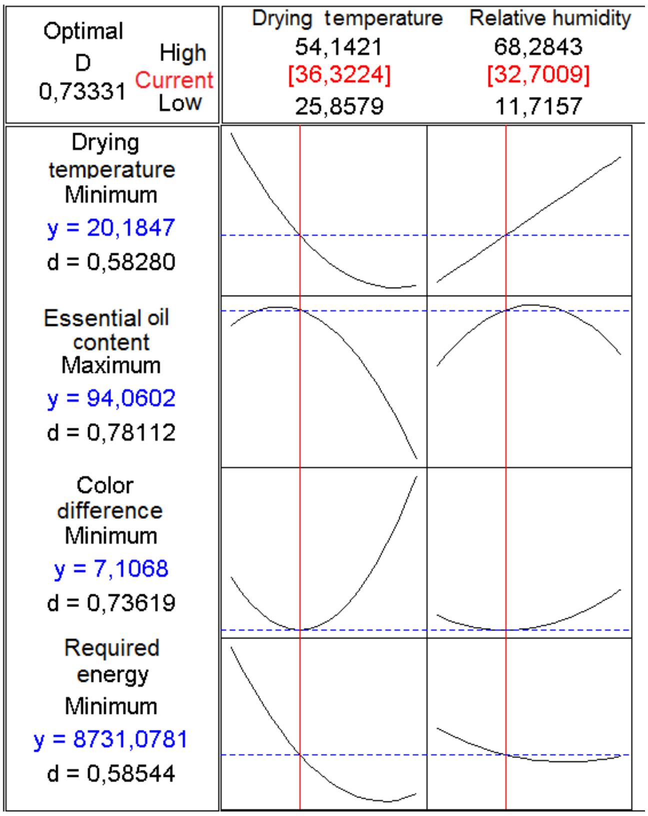


Figure 9.19: Plots of multi objective optimization considering color difference as priority

Figure 9.19 shows that the optimum temperature point is nearly enough to the absolute minimum value of difference in color and the maximum value of the essential oil content. The Figure shows as well that the drying time and the required energy are far away from their minimum values, which indicates that to obtain maximum quality in the final product, the values of drying time and required energy are higher than the minimum.

9.4.4 Required energy as priority

In order to minimize the required energy, a value of 10 for the required energy and low importance (0.1) for the rest of responses were assigned. A minimal required energy of 6049.4 kJ was obtained for an optimal combination of drying temperature of 43°C and relativity humidity of 43%. The desirability for required energy is 0.883, which has a satisfactory value for the optimization required.

Table 9.7: Multiobjective optimization considering required energy as priority

Parameters	Goal	Lower	Target	Upper	Weight	Import
Drying Time	Minimum	6	6	40	1	0,1
Essential oil content	Maximum	80	98	98	1	0.1
Color difference	Minimum	6.07	6.07	10	1	0.1
Required energy	Minimum	5000	5000	14000	1	10

Global Solution	
Temperature	43.358
Rel.Humidity	43.1278

Predicted Responses			
Drying Time	15.46;	desirability	0.72174
Essential oil content	85.79;	desirability	0.32165
Color difference	9.68;	desirability	0.08041
Required energy	6049.44;	desirability	0.8834

Composite Desirability = 0.85298

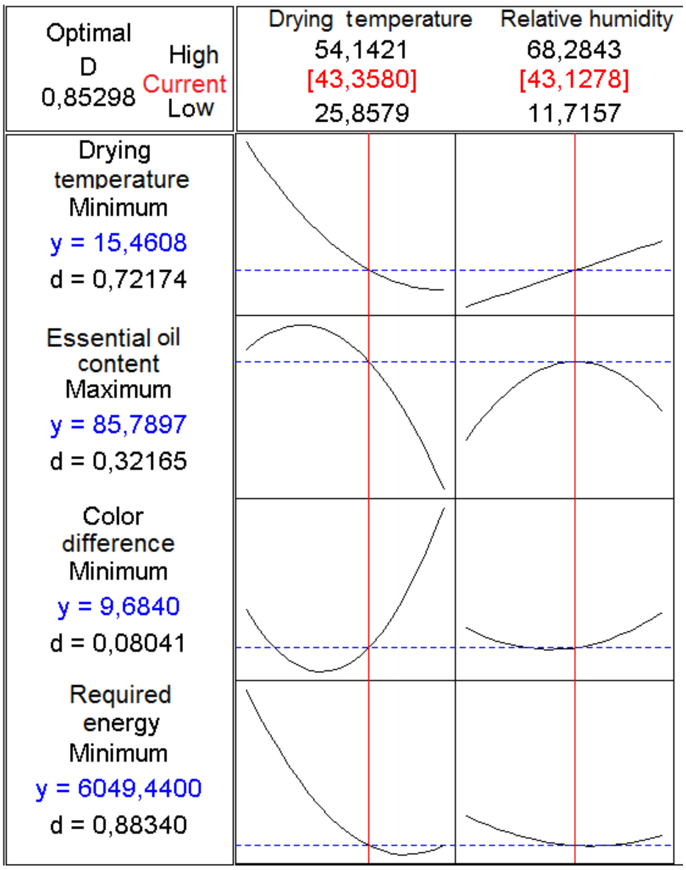


Figure 9.20: Plots of multi objective optimization considering required energy as priority

Figure 9.20 shows that the optimum temperature point is close to the absolute minimum value of the required energy and distant than the maximum value of the essential oil content and the minimum value the color difference, which indicates that to obtain optimal energy required compromises the quality of the product.

9.4.5 Same priority for all responses

In order to optimize all responses simultaneously, a value of 1 for the importance of each response was assigned see . An optimal combination of drying temperature of 34°C and relativity humidity of 39% was found. The composite desirability is relatively low which means that it is difficult to obtain a combination of factors that produce an overall optimum value for all responses close to the absolute optimum values considering the individual optimization for each response.

Table 9.8: Multiobjective optimization considering same priority for all parameters

Parameters	Goal	Lower	Target	Upper	Weight	Import
Drying Time	Minimum	6	6	40	1	1
Essential oil content	Maximum	80	98	98	1	1
Color difference	Minimum	6.07	6.07	10	1	1
Required energy	Minimum	5000	5000	14000	1	1

Global Solution	
Temperature	37.6694
Rel.Humidity	36.5284

Predicted Responses			
Drying Time	19.94	desirability	0.59013
Essential oil content	94.14	desirability	0.78531
Color difference	7.23	desirability	0.70395
Required energy	7961.01	desirability	0.671

Composite Desirability = 0.68401

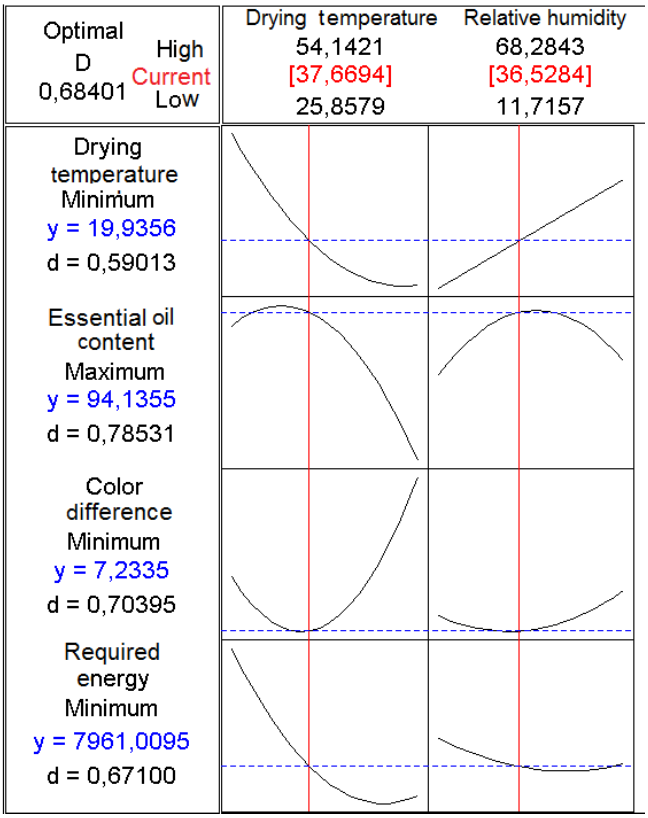


Figure 9.21: Plots of multi objective optimization considering the same priority

Figure 9.21 shows that the optimum temperature point is nearly enough to the absolute minimum value of the difference in color and not far from the maximum value of the essential oil content . The Figure shows as well that the drying time and the required energy are far away from their minimum values, which indicates that to obtain maximum quality in the final product, the values of drying time and required energy are higher than the minimum.

9.4.6 Quality characteristics as priorities

In order to optimize the quality characteristics (minimize the color difference and maximize the essential oil content) a value of 10 for the importance of color difference and essential oil content was considered and low importance (0.1) for the rest of responses were assigned. A minimal color difference of 7.23 and a maximal essential oil of 94.1% were obtained for an optimal combination of drying temperature of 38°C and relativity humidity of 37%. The desirability for color difference is 0.703 and the desirability for essential oil content is 0.785, which are satisfactory values for the composite optimization required.

Table 9.9: Multiobjective optimization considering quality characteristics as priority

Parameters	Goal	Lower	Target	Upper	Weight	Import
Drying Time	Minimum	6	6	40	1	0.1
Essential oil content	Maximum	80	98	98	1	10
Color difference	Minimum	6.07	6.07	10	1	10
Required energy	Minimum	5000	5000	14000	1	0.1

Global Solution	
Temperature	34.4628
Rel.Humidity	38.6535

Predicted Responses			
Drying Time	26.07	desirability	0.40965
Essential oil content	96.46	desirability	0.91432
Color difference	7.42	desirability	0.65632
Required energy	9398.24	desirability	0.51131

Composite Desirability = 0.77063

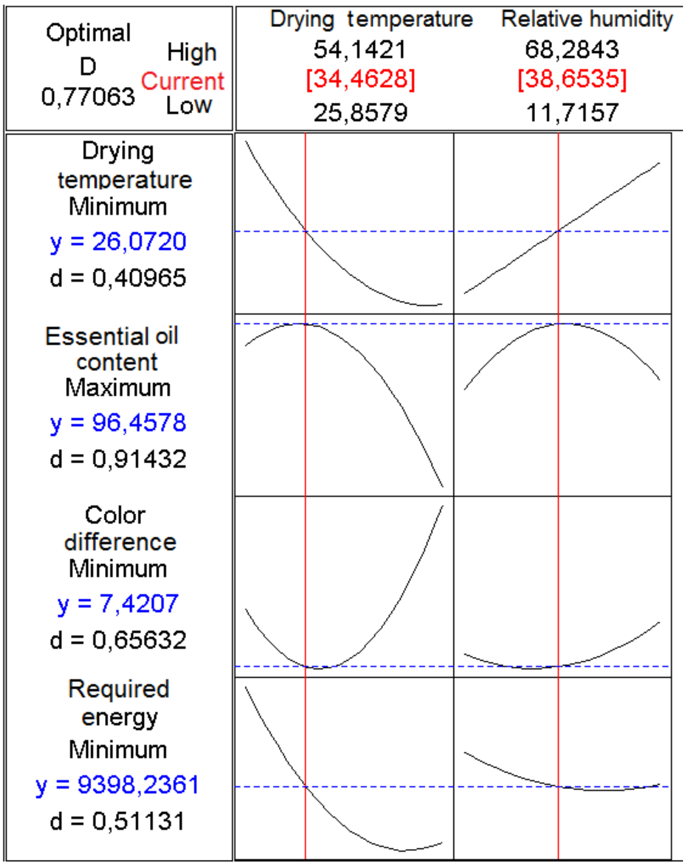


Figure 9.22: Plots of multi objective optimization considering quality characteristics as priority

Figure 9.22 shows that the optimum temperature point is nearly enough to the absolute maximum value of the essential oil content and to the minimum value of difference in color. The Figure shows as well that the drying time and the required energy are far away from their minimum values, which indicates that to obtain maximum quality in the final product, the values of drying time and required energy are higher than the minimum.

Lastly **Table 9.10** presents a summary of the values of overall desirability and the individual desirabilities for each of the responses to optimize considering different approaches of optimization.

If the essential oil content is considered as priority in the optimization process, a high value of required energy is obtained ($9739kJ$). For this condition the overall desirability was 0.91. The desirability corresponding to the essential oil content was 0.92 and for the required energy was 0.47. Likewise for this condition the drying time is high ($28.7h$) and the corresponding desirability was 0.33.

Table 9.10: Comparison of results considering different approaches of optimization

Priority	D	υ(°C)	φ (%)	d_t (h)	d	O_c (%)	d	ΔE	d	q_r (kJ)	d
Drying time	0.83	40	21	11	0.86	81	0.07	8.5	0.38	7807	0.69
Essential oil	0.91	34	41	29	0.33	97	0.92	7.7	0.58	9739	0.47
Color difference	0.73	36	33	20	0.58	94	0.78	7.1	0.74	8731	0.59
Required energy	0.85	43	43	16	0.72	86	0.32	9.7	0.08	6049	0.88
All parameter	0.68	38	37	20	0.59	94	0.79	7.2	0.70	7961	0.67
Quality	0.77	34	39	26	0.41	96	0.91	7.4	0.66	9398	0.51

Similarly considering the color difference as priority for the optimization process, a required energy of 8731 kJ is obtained. For this condition the overall desirability was 0.73. The desirability for color difference was 0.74 and for required energy was 0.59. Moreover for this condition the drying time was 20h and the corresponding desirability was 0.58.

Considering jointly the essential oil content and the color difference as quality characteristics and defining these as priority in the optimization process, high values of required energy ($9398kJ$) and drying time ($26h$) were obtained. For this condition the overall desirability was 0.77, the desirability for essential content was 0.91 and for color difference was 0.66. Moreover the desirability for required energy and drying time were 0.51 and 0.41 respectively.

10 Effect of solar drying parameters on quality characteristics

Despite its reliance on climatic conditions, solar drying is increasingly becoming a popular method of drying medicinal plants. Solar drying is cheap compared to other advanced methods of drying since it mainly relies on energy from the sun and the dryers are relatively cheap and easy to construct. This makes it suitable for use in rural areas with limited electrification and frequent load shedding. The use of such a low cost processing technology can help plants and fruit growers to increase their income by encouraging full utilization of locally available produce as raw material.

The purpose of this chapter is to analyze the effects of the considered drying parameters on the quality characteristics and drying time for processing with solar tunnel type solar dryer. The considered process parameters or experimental factors are; air velocity, thickness of the product or drying load, position of the product along the solar tunnel and covering conditions (shade or light). As quality characteristics, essential oil content and color change (as color difference) were observed.

For the mentioned analysis, techniques of design of experiments (DoE) were applied. Full factorial designs to analyze the effects of the factors were selected and additionally regression models for the responses were proposed.

10.1 Description of process and equipment

The solar drying using solar tunnel type dryer uses solar radiation as energy source for heating the air used to remove the water from the product. **Figure 10.1** shows the equipment used for the experimentation of solar drying of Lemon Balm.

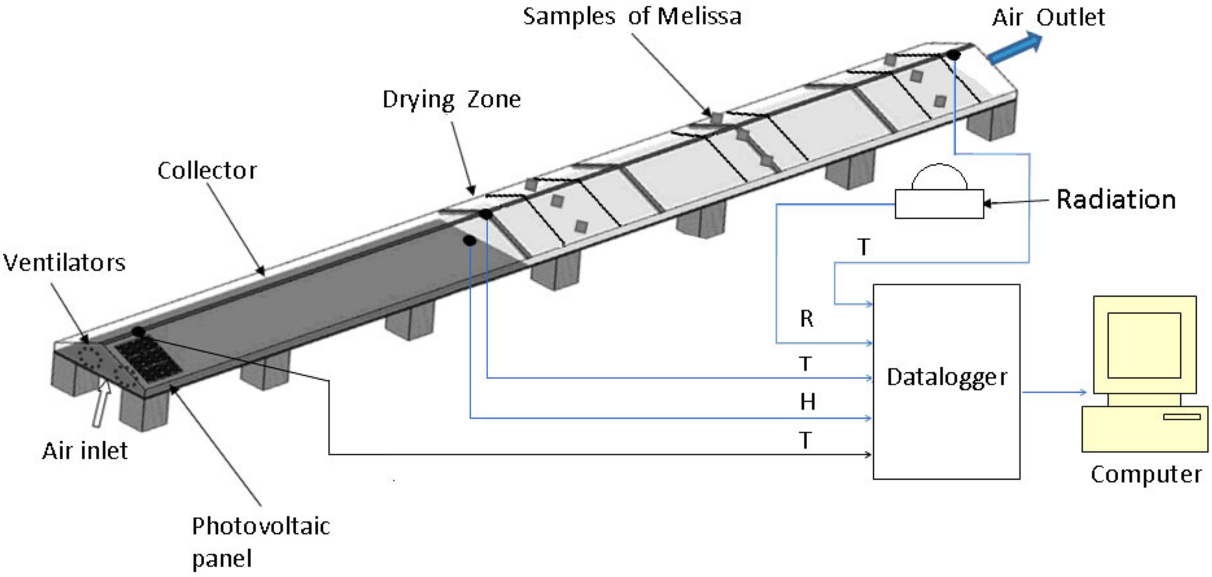


Figure 10.1: Solar Tunnel dryer. T:thermocouples (T_d:dry bulb and T_w:wet bulb), H:humidity sensor and R:radiation measurement device

For experimenting, a solar tunnel dryer type Hohenheim was used. Tunnel solar dryers consist of a long solar collector, a drying tunnel and, in some cases, incorporate forced air flow using two small fans. The solar flat-plate collector is connected directly to the drying tunnel without any additional air ducts. Air flows, by means of the fans, along the collector (8 meters in length) where the air is heated before entering the drying area where is placed the product. The surface of the collector is painted black to absorb solar radiation. The collector is covered with a transparent U.V stabilized PE plastic sheet which is fixed to the collector frame using reinforced plastic clamps. The drying tunnel is covered with a U.V-stabilized plastic sheet. For the analysis of solar drying of Lemon Balm (*Melissa officinalis* L.) two covering conditions, shade (using black film) and light (using transparent film) were considered. The solar tunnel uses solar energy both in the thermal form for the drying process and the electrical form (photovoltaic) for driving the fans. The solar tunnel has two small axial flow fans as shown in **Figure 10.1**. Fans operate normally by energy supplied by a photovoltaic panel. For experimentation, in order to control the speed of the drying air, the rotational speed of the fans was adjusted by using a potentiometer and the electricity was supplied from the conventional network. Both the collector and the drying tunnel are installed on concrete block substructures. The solar energy absorption area of the collector is $2 \times 8\ m^2$ and the drying area of the drying tunnel has $2 \times 10\ m^2$. The drying area of the solar tunnel consists of a metal mesh that allows air flow under the material to dry and a plastic mesh where is placed the product.

10.2 Materials and methods

The material used for the research was Lemon Balm (*Melissa officinalis* L.), variety citronella sown at the University of Kassel in Witzenhausen (51° 20´ 45, 76” N, 9°51´ 52, 08” E). The material was harvested manually at 10cm of soil and then cut into pieces of 15cm. In general the initial Lemon Balm had a moisture content of 76% w.b.

For all drying tests, moister content, color difference and essential oil content for fresh product and processed material were determined according to the methods presented in chapter 5. Sensors and measurement devices for measurement of process parameters were installed in the solar tunnel in order to monitor the behavior of the process. Thermocouples for monitoring the dry and wet-bulb temperature were installed along the tunnel and hygrometers were placed at the beginning and end of the tunnel to monitor the conditions of the drying air inlet and outlet. A pyranometer to measure the global solar radiation was employed. All the signals from these sensors and measurement devices were registered by a data acquisition unit (Hydra) controlled by computer in order to collect the data every 5 minutes. Additionally to determine the loss of moisture, the weight of the product placed in metal wire baskets ($21 \times 34 \times 3\ cm$) with approximately 60g or 120g of product (for thin or thick layer respectively) was monitored. For the determination of humidity loss in each point along the tunnel, three samples (three baskets) per point were weighed by using a Sartorious precision balance (± 0.01g). A schematic diagram showing the position of the sensors and measuring devices is presented in **Figure 10.2**.

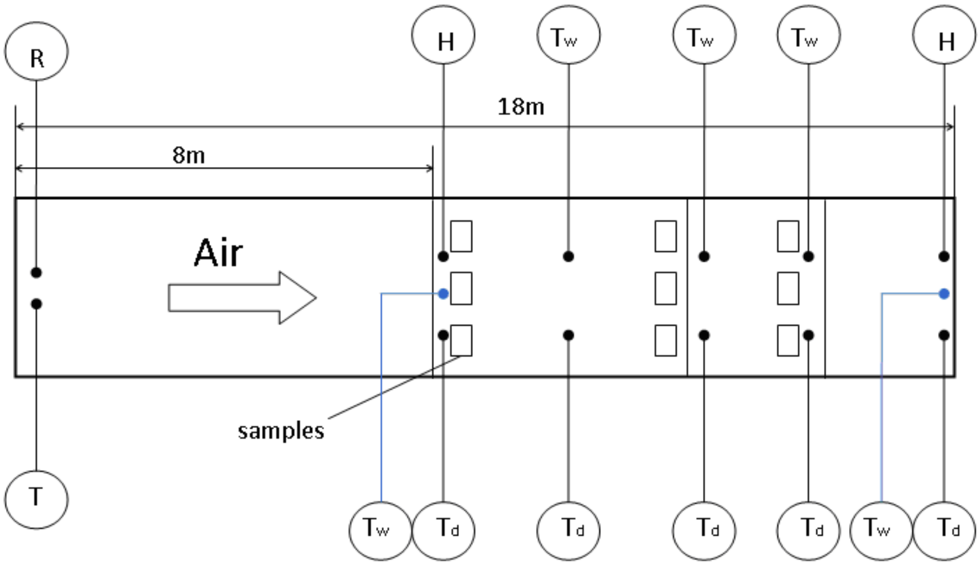


Figure 10.2: Position of the measurement devices and sensors to monitor the drying process. T:thermocouples (T_d:dry bulb and T_w:wet bulb), H:humidity sensor and R:radiation measurement device

The measured variables, and the used measuring methods are summarized in **Table** 10.1

Table 10.1: Compilation of the measured variables, measurement methods and accuracy used during the experimental work.

Measure	Measurement Methods	Measurement Accuracy
Solar irradiance, R	Pyranometer SP lite	± 5% of incoming radiation
Wind speed, V	Anemometer	± 3% full scale
Relative humidity	Hygrometer	± 5% RH
Weight, M	Weighing scale	± 0.001g
Temperature sensor, T	Thermocouple	Type $K\pm$ 0.5 ; Type $T\pm$ 1.5
Color, ΔE	Chromameter	± 2% ± 1 digit of displayed value

10.3 Experimental design

In order to analyze the effects of the solar drying parameters on the quality characteristics (color difference and essential oil content) and the drying time and to in order to obtain a regression model for describing the relationship between the process parameters and responses, methods of design of experiments (DoE) were applied. Specifically for the analysis of significance for the drying parameters (factors) a full factorial design was considered (Montgomery, 2005, 2007; Klein, 2007; Kleppmann, 2006; Scheffler, 1997).

Factorial designs are widely used in experiments involving several factors where it is necessary to investigate the joint effects of the factors on a response variable. By joint factor effects, typically mean main effects and interactions. A very important special case of the factorial design is that where each of the k factors of interest has only two levels. Because each replicate of such a design has exactly $2k$ experimental trials or runs, these designs are usually called $2k$ factorial designs (Montgomery, 2005; Klein, 2007).

The effect of a factor is defined as the change of response produced by a change in the level of the factor. The average effect of a factor is defined as the change in response produced by a change in the level on that factor averaged over the levels of the other factor (Myers & Montgomery, 2002). The proposed full factorial design allows obtaining the main effect of the factors, the effect of the two-factor interactions and the effect of the three-factor interactions. For the selected full factorial design four experimental factors were considered:

Covering C_o:corresponds to the type of plastic cover selected. There are two alternatives or conditions for: light or shadow. Position in solar tunnel X_p:corresponds to the distance since the beginning of the drying area of the solar tunnel to the position of the considered sample. Drying load L_d:corresponds to thickness of the drying layer the expressed as grams of product per square meter of the drying area. Air velocity V_a:is related to the air velocity of the drying air along the tunnel.

To analyze the effects of the covering C_o, position in solar tunnel X_p, drying load L_d and air velocity V_a on the drying time t_d, color difference ΔE and essential oil content O_c, a 24 full factorial design was considered. In **Table** 10.2 the different combinations of experimental factors and the obtained responses according to the proposed factorial design are presented.

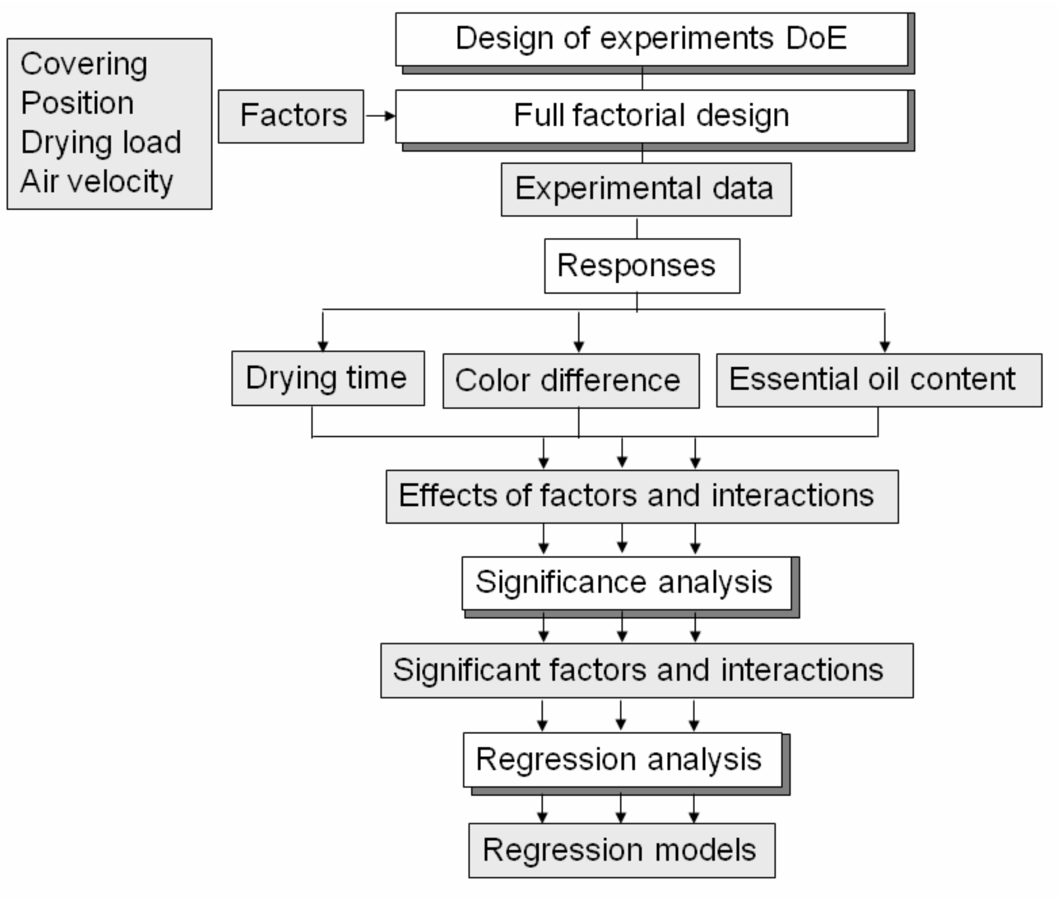


Figure 10.3: Proposed methodology for analysis of solar tunnel drying

Table 10.2: Experimental factors

	Factor			
	Covering	Position (m)	Drying load (g/m^2)	Air velocity (m/s)
Level	C_o	X_p	L_d	V_a
Low	Light	0.8	900	0.4
High	Shade	7	1800	0.8

Following the analysis of the factorial experiment for each considered response is presented. The statistical study considers the analysis significance, the results are reported by means of a Pareto´s chart and diagrams that show the main effects and effects of interactions.

For each factor and each interaction the effects are determined. After that, it is important to know the statistical significance. The significance describes statistically if the effect of a given factor or interaction is sufficiently representative to be taken into account. Each effect is the difference of two means and the determination of the significance is performed using a test for the difference of means (Montgomery, 2005). For this test a confidence interval is selected and the corresponding significance level α is defined.

10.4 Results and discussion

Table 10.3 shows the mean of the responses as result of the experimentation for drying Lemon Balm with solar tunnel. The responses considered were drying time, essential oil content and color change. Three replicates were carried out for each combination of parameters.

Table 10.3: Experimental factors and response for solar drying process

Experimental factors				Measured responses		
Covering	Position (m)	Drying load (g/m^2)	Air velocity (m/s)	Time (h)	Color difference ΔE	Essential oil (% fresh)
Light	0.8	900	0.4	9	22.96	61.7
Shade	0.8	900	0.4	16	12.98	64.4
Light	7	900	0.4	10.5	19.44	46.5
Shade	7	900	0.4	16	11.75	69.2
Light	0.8	1800	0.4	13	17.38	70.0
Shade	0.8	1800	0.4	18	12.11	90.5
Light	7	1800	0.4	13.0	21.31	70.0
Shade	7	1800	0.4	18.0	13.18	75.7
Light	0.8	900	0.8	8.2	16.69	61.5
Shade	0.8	900	0.8	9.5	9.74	83.7
Light	7	900	0,8	8.2	9.63	45.6
Shade	7	900	0.8	12.5	8.47	82.6
Light	0.8	1800	0.8	11.0	14.75	87,5
Shade	0.8	1800	0.8	11.35	10.03	96.3
Light	7	1800	0.8	11.0	17.75	77.05
Shade	7	1800	0.8	13.3	7.52	88.9

10.4.1 Drying time

Table 10.2 shows the combinations of factors corresponding to the selected full factorial design in order to analyze the effects on the drying time. Additionally **Figure** 10.4 shows a cube plot that describes the experimental design used to determine the effects of the process parameters on drying time.

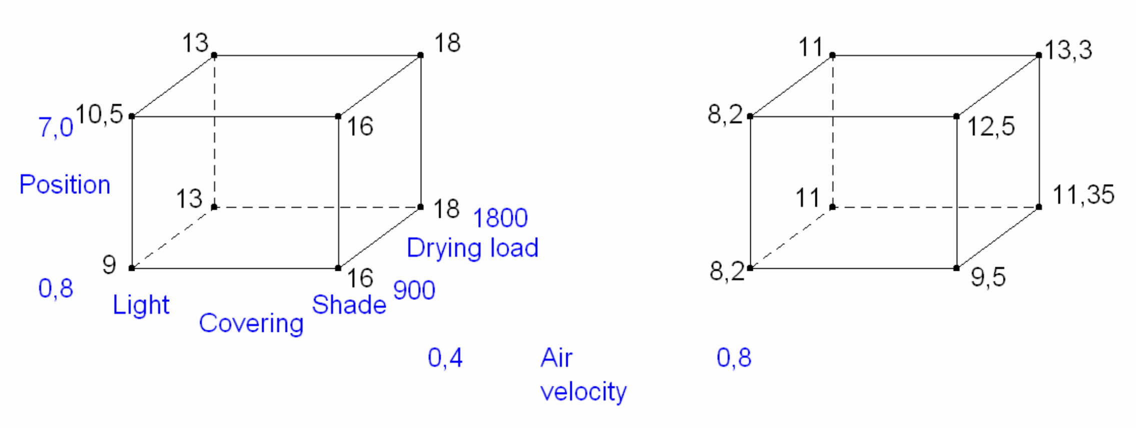


Figure 10.4: Cube plot (data means) for drying time

Figure 10.5 shows a Pareto´s chart that presents the absolute value of the effects for the main factors and interactions between two, three and four factors. For the significance analysis, a significance level $\alpha = 0.10$ was selected. The vertical dashed-line defines the boundary of the main factors and interactions that are significant considering the selected level α. In this case, only covering, air velocity, drying load and the interaction between covering and air drying result significant. The covering and air velocity are found to be the most significant.

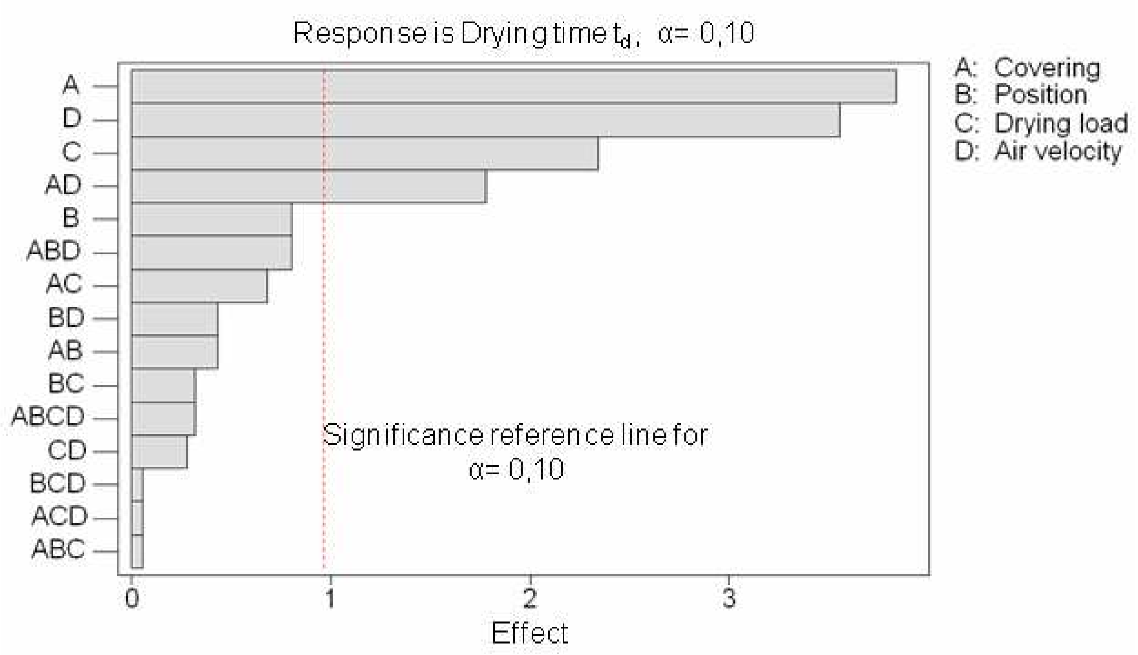


Figure 10.5: Pareto’s chart of effect on drying time

In **Figure 10.6** the effects and influence of the main factors covering, position, drying load and air velocity, on drying time are presented. It is possible to appreciate graphically the magnitude of the effect for each factor. The magnitudes of the effects of covering and air velocity on drying time are substantially higher than for other factors. Additionally it is observed that changing the covering type from light to shade produces a substantial increase in drying time. Similarly an increase in air velocity causes a significant decrease of drying time. Likewise an increase in drying load causes a moderate increase on drying time. Finally an increase in position generates a non representative effect on drying time.

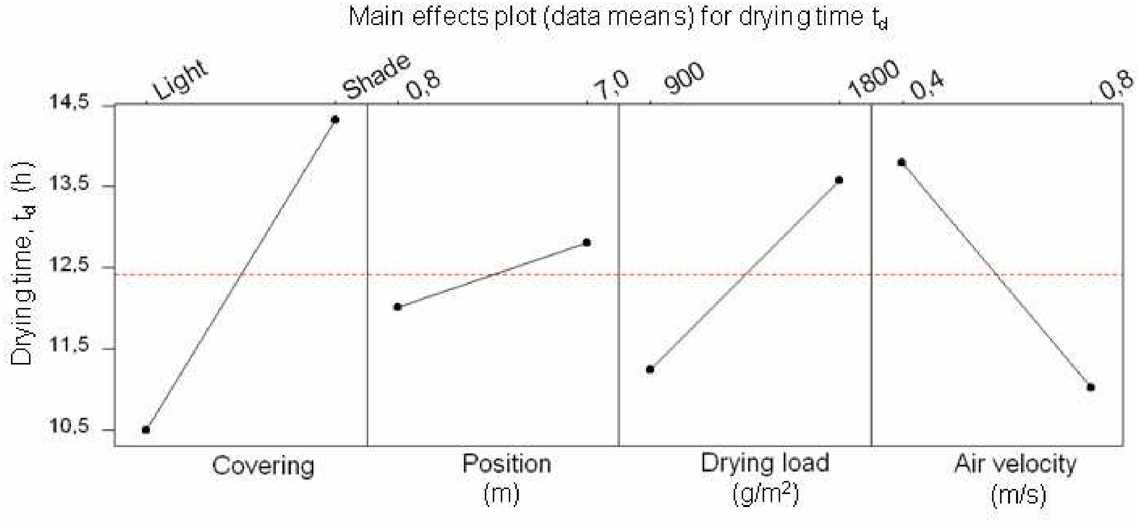


Figure 10.6: Main effects plot for drying time

Figure 10.7 shows an interaction plot used to observe the impact that causes the setting of one factor on another factor. An interaction can magnify or diminish main effects; this aspect can be appreciated by means of the difference between the slopes for each two lines that represent the effects in each section of the interactions diagram. It is observed that there is an appreciable interaction between air velocity and covering and that the other two-factor interactions are moderate. The interaction between drying load and air velocity is insignificant.

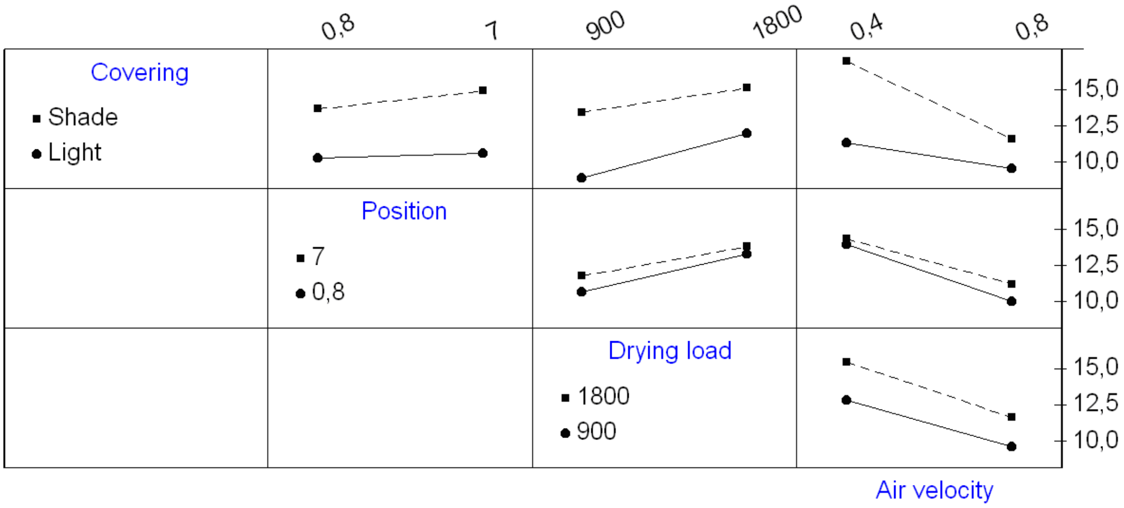


Figure 10.7: Interaction plot for drying time

10.4.2 Color difference

Table 10.2 shows the combinations of factors corresponding to the selected full factorial design in order to analyze the effects on the color difference ΔE. Additionally **Figure 10.8** shows a cube plot that describes the experimental design used to determine the effects of the process parameters on color difference.

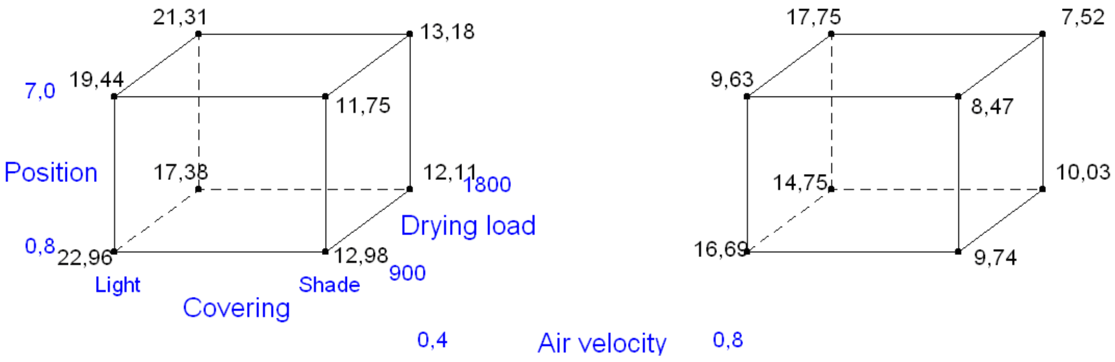


Figure 10.8: Cube plot (data means) for color difference ΔE

For the significance analysis, a significance level $\alpha = 0.10$ was selected. **Figure 10.9** shows a Pareto´s chart that presents the absolute value of the effects for the main factors and interactions between two, three and four variables, on color difference ΔE. The vertical dashed-line defines the boundary of the main factors and interactions that are significant considering the selected level α. In this case, only covering and air velocity significant.

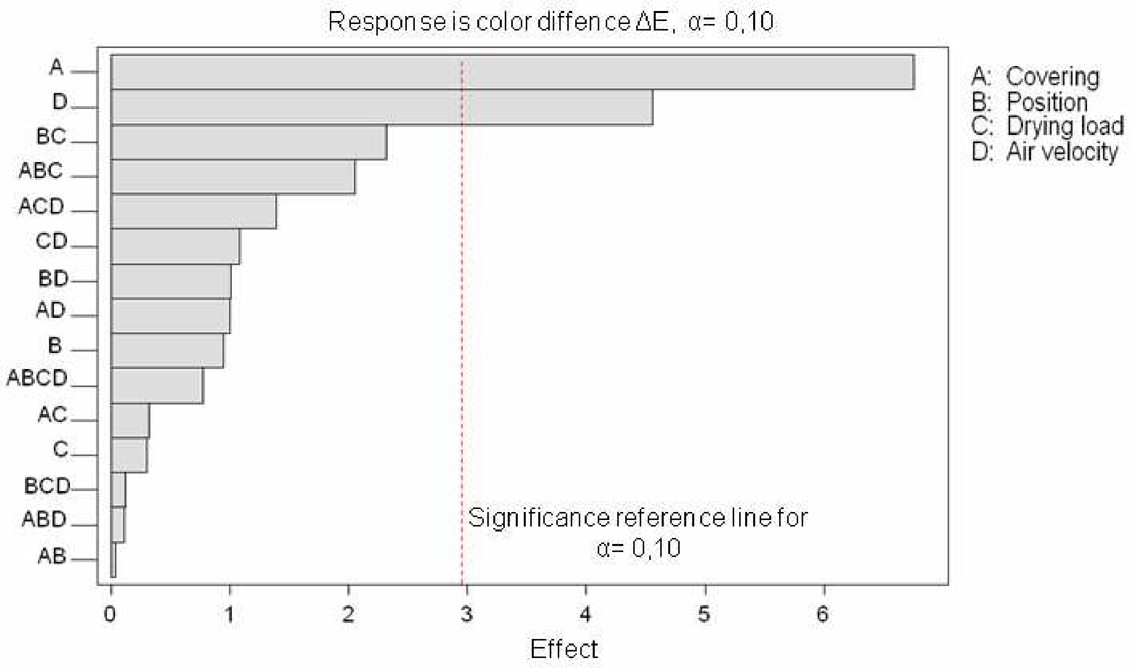


Figure 10.9: Pareto´s chart of effects on color difference ΔE

In **Figure 10.10** the effects and influence of the main factors covering, position, drying load and air velocity, on color difference ΔE.

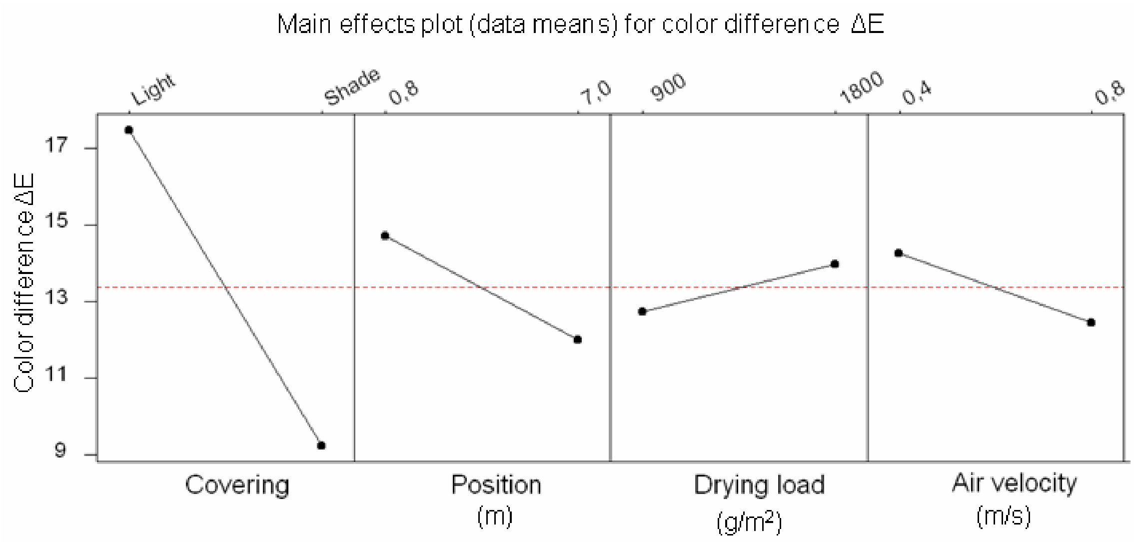


Figure 10.10: main effects plot on color difference ΔE

Figure 10.11 shows an interaction plot in order to observe the impact that changing the setting of one factor has on another factor. An interaction can magnify or diminish main effects; this aspect can be appreciated for the differing slopes for each two lines that represent the effects in each section of the interactions diagram. The diagram shows several interactions; drying load with position, air velocity with drying load and position with air velocity but these interactions are not representative.

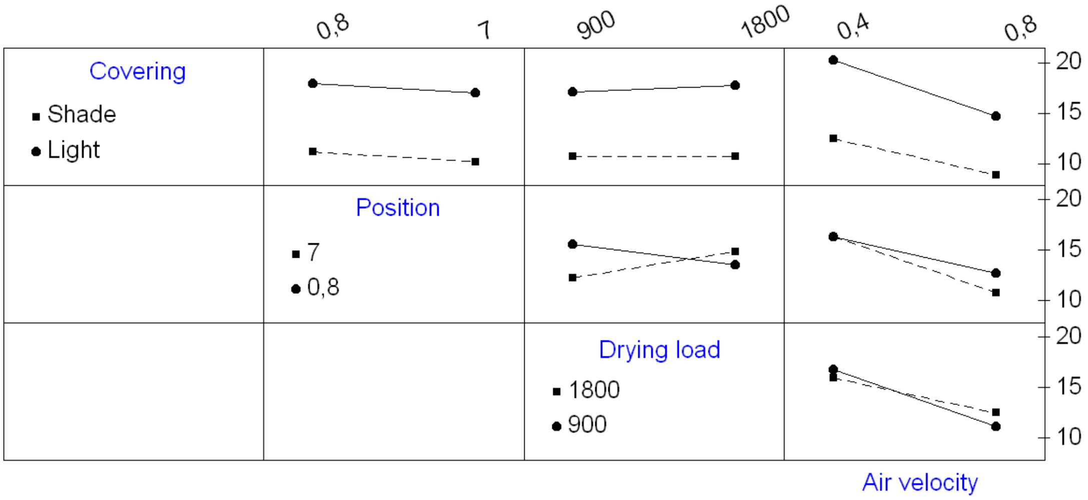


Figure 10.11: Interaction plot for color difference ΔE

10.4.3 Essential oil content

Table 10.2 shows the combinations of factors corresponding to the selected full factorial design in order to analyze the effects on the essential oil content O_c. Additionally **Figure**

10.12 shows a cube plot that describes the experimental design used to determine the effects of the process parameters on essential oil content O_c.

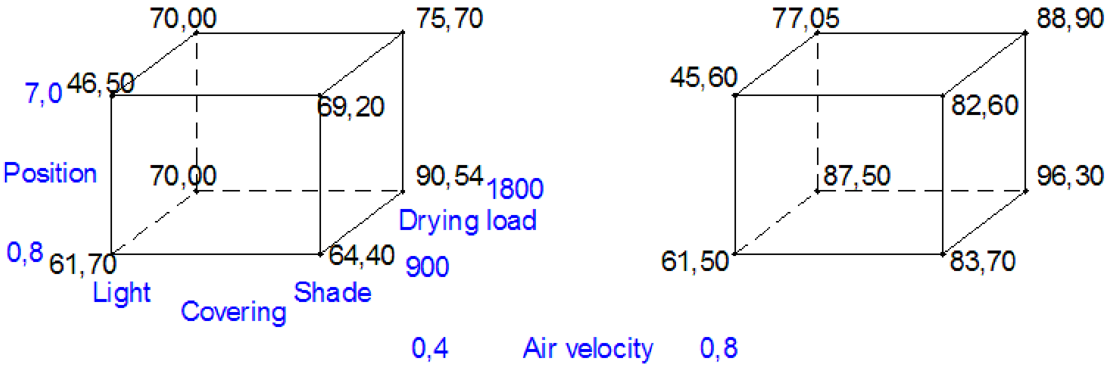


Figure 10.12: Cube plot (data means) for essential oil content

Figure 10.13 shows a Pareto´s chart that presents the absolute value of the effects of the main factors and interactions between two, three and four factors on essential oil content O_c. For the significance analysis, a significance level $\alpha = 0.10$ was selected. The vertical dashed-line defines the boundary of the main factors and interactions that are significant considering the selected level α. In this case, the effect of covering C_o, drying load L_d and air velocity V_d result significant but the effect of position and the interactions are not significant.

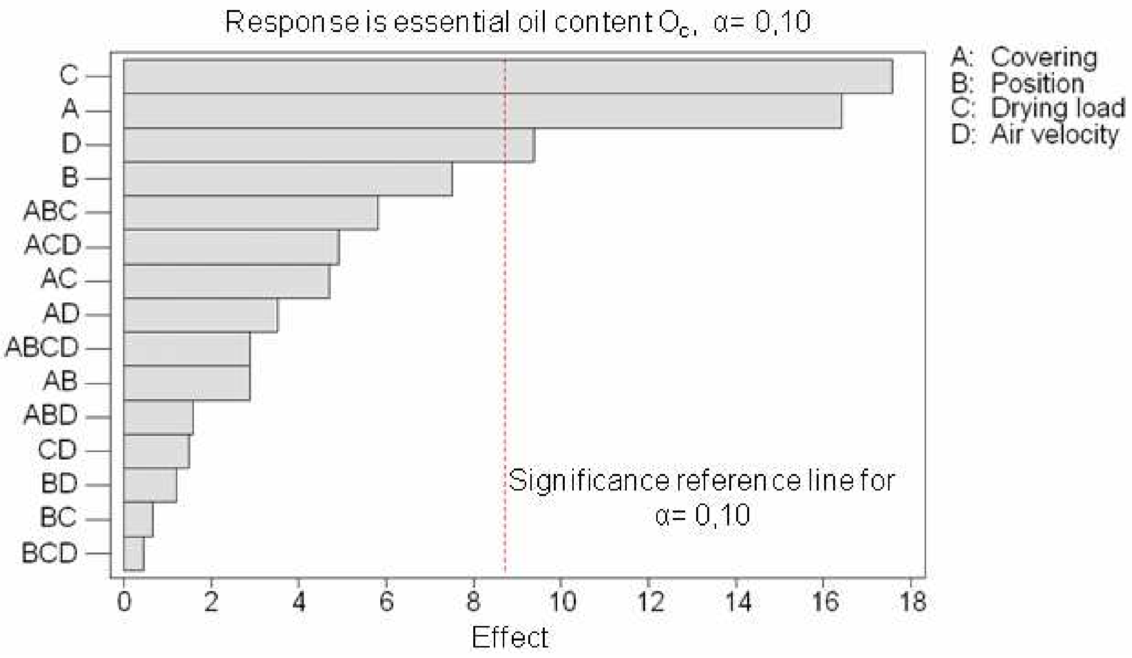


Figure 10.13: Pareto´s chart of effects on essential oil content O_c

In **Figure 10.14** the effects of the main factors covering, position, drying load and air velocity, on essential oil content are presented. The magnitudes of the effects of covering and drying load are substantially higher than for other factors. Additionally it is observed that changing the covering type from light to shade causes a substantial increase in essential oil content. Similarly an increase in drying load causes an appreciable increase of essential oil content. Additionally it is observed that variations of position or air velocity cause a moderate effect on essential oil content.

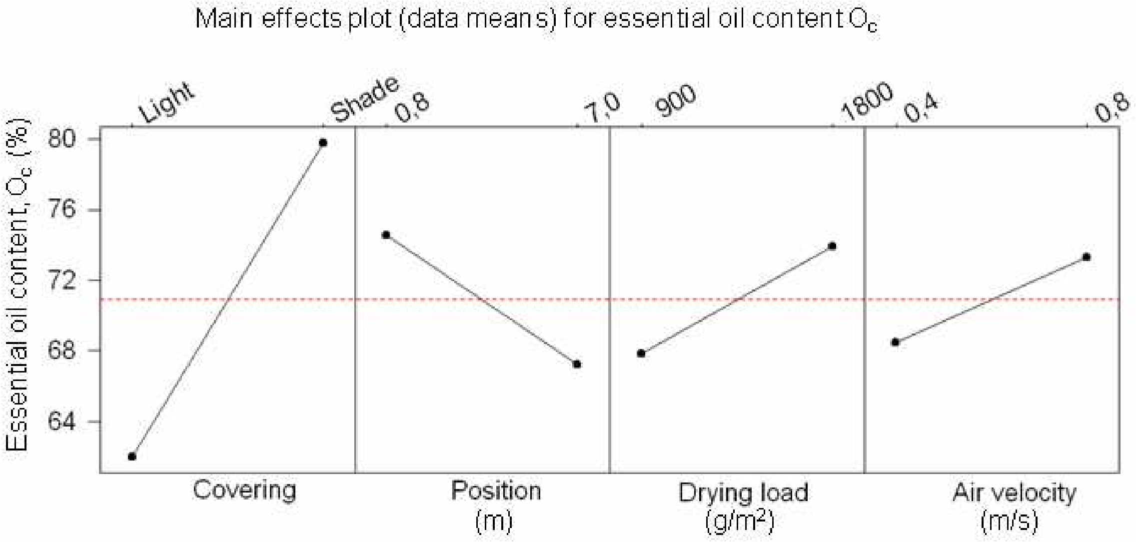


Figure 10.14: Main effects plot for essential oil content

Figure 10.15 shows an interaction plot used to observe the impact that causes the setting of one factor on another factor. An interaction can magnify or diminish main effects; this aspect can be appreciated by means of the difference between the slopes for each two lines that represent the effects in each section of the interactions diagram. The diagram shows that there are not representative interactions between the main factors considered for the response essential oil content.

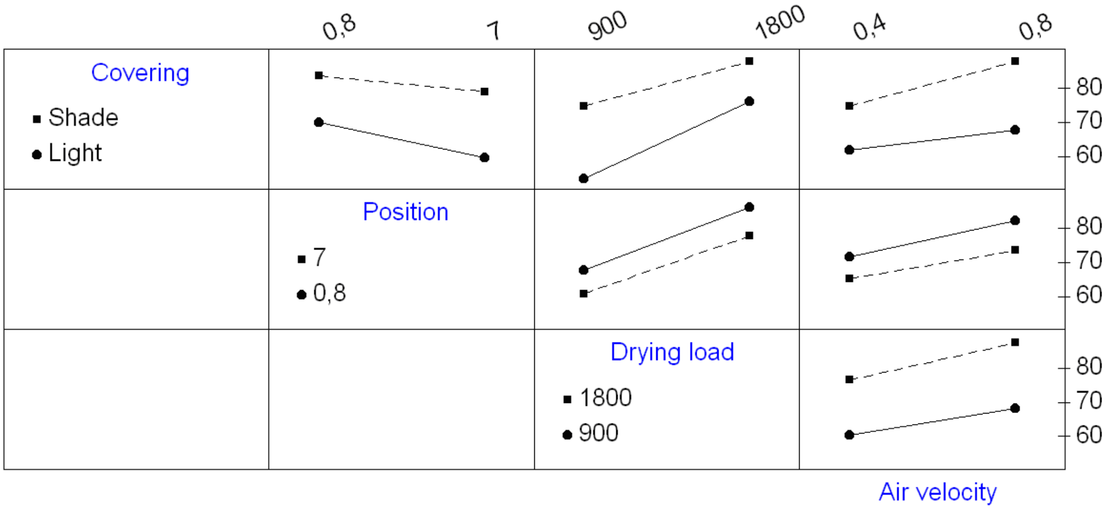


Figure 10.15: Interaction plot for essential oil content

10.5 Regression models

Regression models (Myers & Montgomery, 2002; Kleinbaum et al., 1988; Montgomery, 2005; Fahrmeir et al., 2007) for each of the responses (drying time, color difference and essential oil content) are proposed considering only the factors and interactions that are significant and that are shown in the corresponding Pareto´s diagram for each response.

In any designed experiment it is important to examine a model for predicting responses. Furthermore, there is a close relationship between the analysis of a designed experiment and the regression model that can be used easily to obtain predictions from a 2^k experiment. A potential concern in the use of two-level factorial design is the assumption of linearity is unnecessary, and the 2^k system will work quite well even when the linearity assumption holds only very approximately. A general model that considers the principal effects or first-order and the interaction terms, can be expressed as (Montgomery, 2005):

$$y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum \sum_{i<j} \beta_{ij} x_i x_j + \varepsilon \tag{10.1}$$

Where:
β_0, β_j, β_{ij}: Regression coefficient S
x_1, x_2,..., x_p: Regressors
ε: Experimental error

The presented model has the capacity to represent some curvature in the response function. The curvature, of course, is the result of bending of the plane induced by the interaction terms $\beta_{ij} x_i x_j$ (Montgomery, 2005, 2007; Scheffler, 1997).

By considering the proposed regression model for drying time as function of the significant factors, it is possible to observe the influence of the combinated effects of drying load, air velocity and covering condition on the behavior of drying time (see **Figure 10.17**). High drying time is obtained by having shade condition of covering, low air velocity and high drying load. Moreover the curvature in the surface plot is originated by the interaction $C_o V_a$ (covering condition- velocity of air drying), expressing the influence of the covering on the effect of the velocity (see Figure 10.16).

10.5.1 Drying time

By using regression analysis (Myers & Montgomery, 2002; Fahrmeir et al., 2007) and considering the significant factors covering C_o, air velocity V_a, drying load L_d and interactions covering- air velocity observed in **Figure 10.5**, a regression model for the drying time is proposed. The obtained regression model for drying time t_d can be written as:

$$t_d = 18.8 - 9.19\, C_o - 13.3\, V_a + 8.91\, C_o\, V_a + 0.00260\, L_d \tag{10.2}$$

In appendix C section C.1 the corresponding regression analysis for drying time oil content is presented.

By using the model presented in equation 10.2, plots to observe the behaviour of the drying time for different combinations of main factors can be generated. For each pair of factor combinations, the hold values considered for other factors are presented. **Figure** 10.16 and 10.17 show a surface plot and a contour plot that illustrate the response the drying time t_d as function of air velocity and drying load considering different two covering conditions C_o (shade and light) and position X_p=7m.

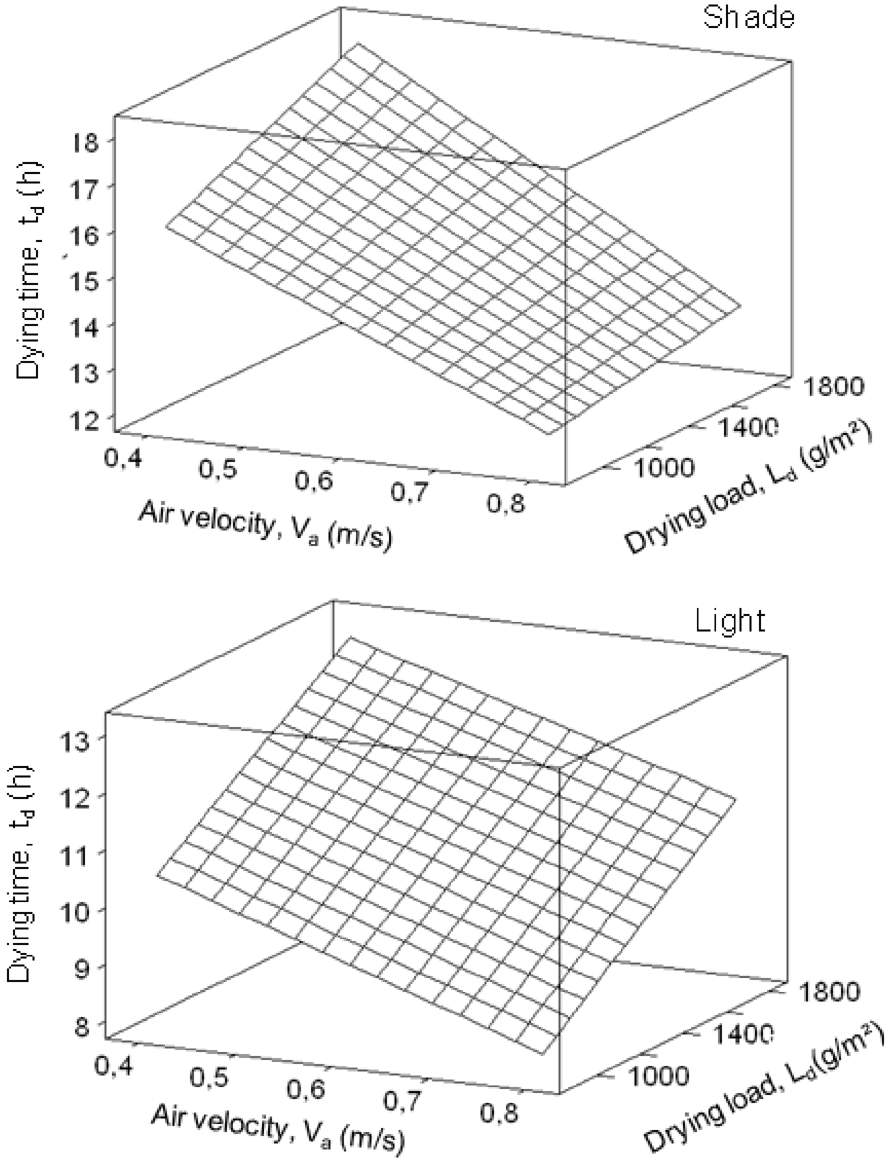


Figure 10.16: Surface plot for drying time considering air velocity and drying load for the two covering conditions: shade and light and position X_p=7m

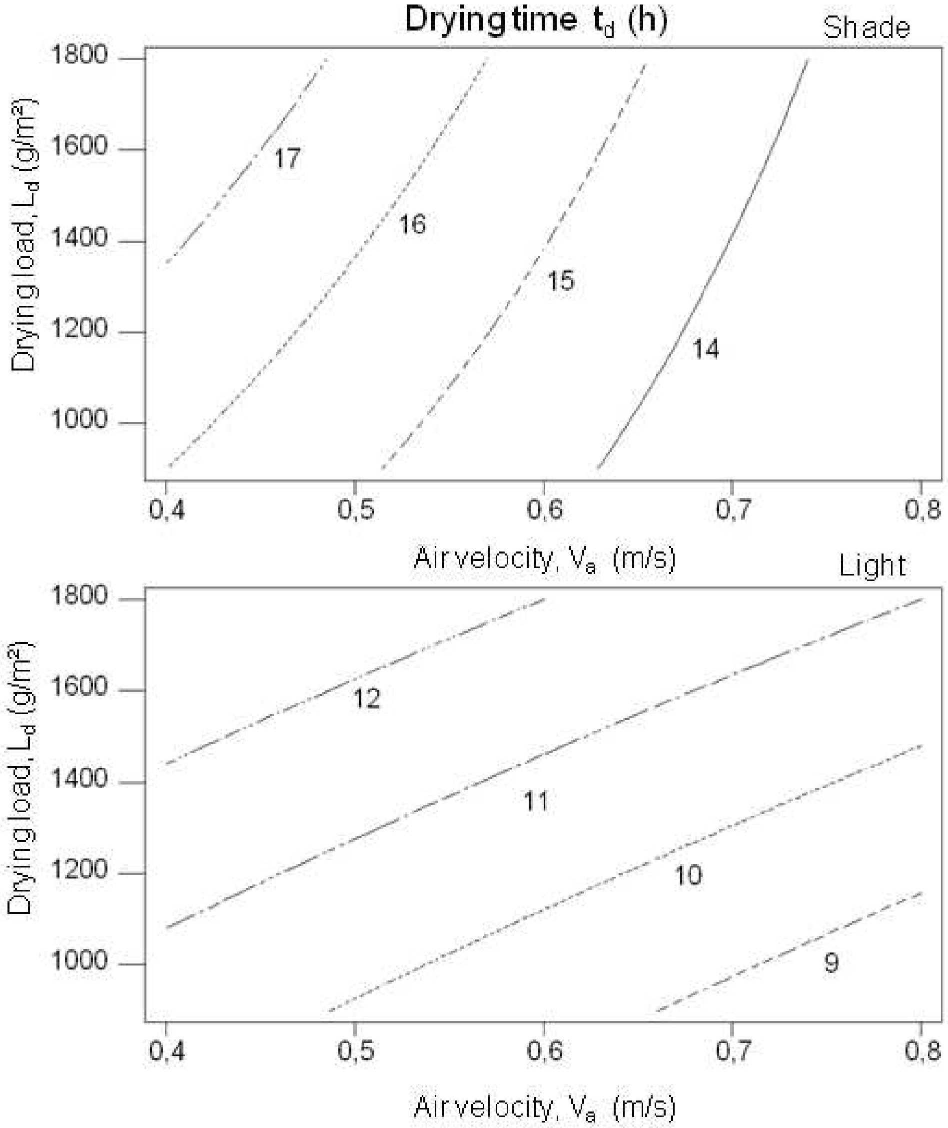


Figure 10.17: Contour plot for drying time considering air velocity and drying load for the two covering conditions: shade and light and position X_p=$7m$

Observing the graphics presented in **Figures** 10.16 and 10.17, the behavior of the drying time for the conditions light and shadow can be compared. For a certain point X_p=$7m$ inside the tunnel and considering a drying air velocity value of $0.6m/s$ and a drying load of $1400g/m^2$, the drying time is around 11h and $15h$ for light and shadow conditions respectively.

The significant factors on the drying time were covering condition C_o, air velocity V_a, drying load L_d and the interaction C_oV_a. The analysis of the effects allows to observe that the change of covering condition, from light to shade causes an appreciable increment of drying time, due to that the heat transfer by radiation is less by shade condition and therefore there is a lower temperature of the drying air. Likewise the increase of drying load produces an increase of drying time, this is because it is requires to remove more water from the product with the same drying air conditions (carrying capacity of water) therefore requires more process time. Additionally the increase of air velocity causes a substantial decrease in the drying time. It is because, having even laminar flow, there is more flux of drying air with the same capacity for carrying water therefore requires less processing

10.5.2 Color difference

By using regression analysis (Myers & Montgomery, 2002; Fahrmeir et al., 2007) and considering the significant factors; covering C_o and air velocity V_a observed in **Figure 10.9**, a regression model for the color difference is proposed. The obtained regression model for color difference ΔE can be written as:

$$\Delta E = 17.6 + 6.77\, C_o - 11.4\, V_a \tag{10.3}$$

In appendix C section C.2 the corresponding regression analysis for color difference is presented.

By using the model presented in equation 10.3, plots to observe the behavior of the color difference for different combinations of main factors can be generated. For each pair of factor combinations, the hold values considered for other factors are presented. **Figures** 10.18 and 10.19 show a surface plot and a contour plot that illustrate the response the color difference ΔE as function of air velocity and drying load considering two different covering conditions C_o and position X_p=7m.

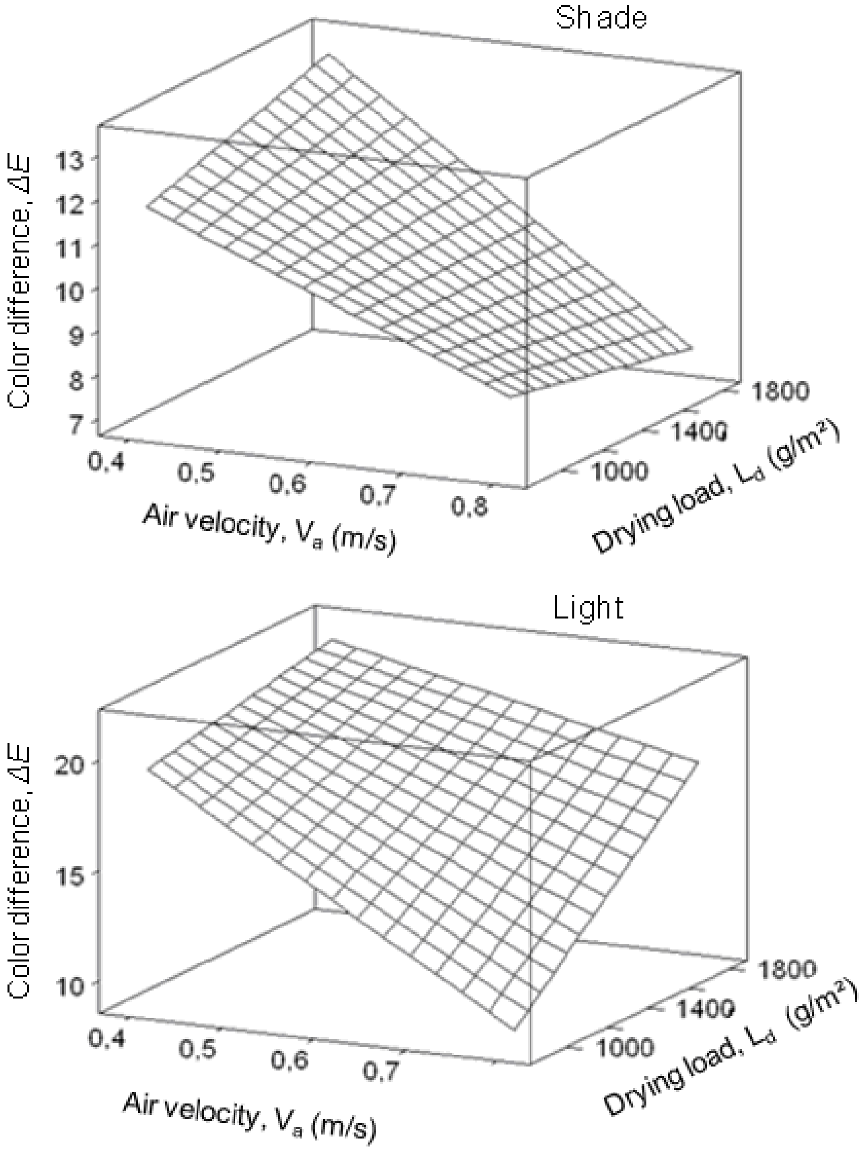


Figure 10.18: Surface plot for color difference considering air velocity and drying load for the two covering conditions: shade and light and position $X_p = 7m$

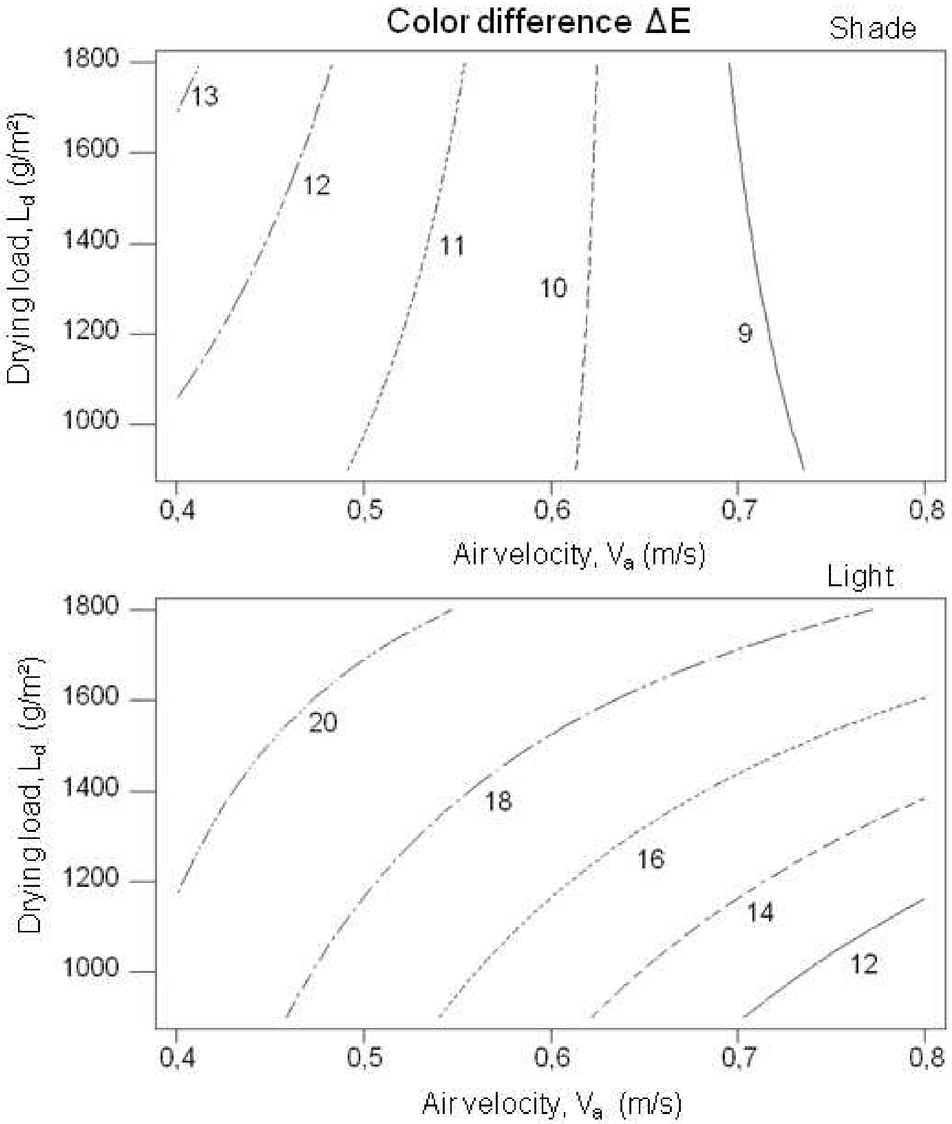


Figure 10.19: Contour plot for color difference considering air velocity and drying load for the two covering conditions: shade and light and position $X_p = 7m$

Observing the graphics presented in **Figures** 10.18 and 10.19, the behavior of the color difference for the conditions light and shadow can be compared. For a certain point X_p=$7m$ inside the tunnel and considering a drying air velocity value of $0.6m/s$ and a drying load of $1400g/m^2$, the color difference is around ΔE=17.5 and ΔE=10 for light and shadow conditions respectively.

The significant factors on the color change expressed as color difference ΔE were covering condition C_o and air velocity V_a. The analysis of the effects allows observing that the change of covering condition, from light to shade causes an appreciable decrement in ΔE, originated by the high photo-decomposition in light condition of covering comparing with virtually no photo-decomposition in shade condition. Likewise the increase of air velocity produces a decrease of ΔE (less color change). For light condition this may be due to less drying time and therefore less exposure to solar radiation and for shade condition of covering the shortest processing time means less chance of thermal damage.

The regression model for color difference as function of the experimental factors allows to observe the influence of the combinated effects of drying load, air velocity and covering condition on the behavior of color difference (see **Figures 10.18** and 10.19).

10.5.3 Essential oil content

By using regression analysis (Myers & Montgomery, 2002; Fahrmeir et al., 2007) and considering the significant factors covering C_o, drying load L_d and air velocity V_a observed in **Figure 10.12**, a regression model for the essential oil content is proposed. The obtained regression model for essential oil content O_c can be written as:

$$O_c = 40.9 - 16.4\, C_o + 0.0196\, L_d + 23.5\, V_a \tag{10.4}$$

In appendix C section C.3 the corresponding regression analysis for essential oil content is presented.

By using the model presented in equation 10.4, plots to observe the behavior of the essential oil content for different combinations of main factors can be generated. For each pair of factor combinations, the hold values considered for other factors are presented. **Figures** 10.20 and 10.21 show a surface plot and a contour plot that illustrate the response the essential oil content O_c as function of air velocity and drying load considering two different covering conditions (shade and light) C_o and position X_p=$7m$.

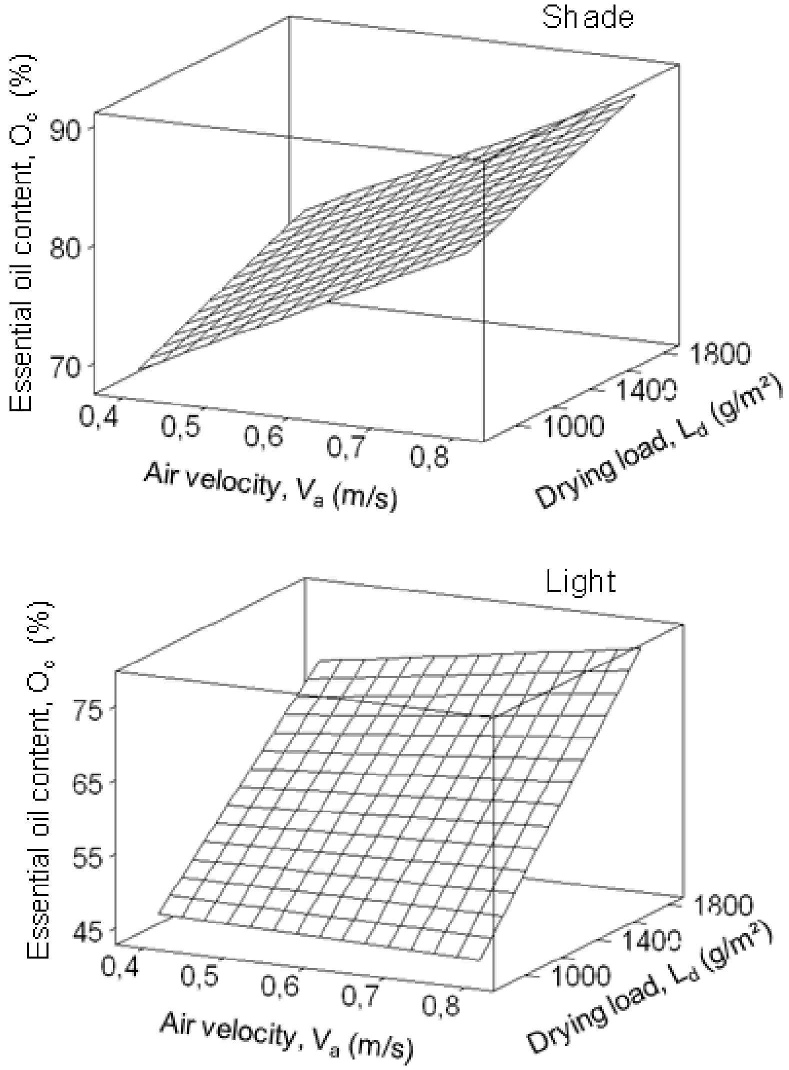


Figure 10.20: Surface plot for essential oil content considering air velocity and drying load for the two covering conditions: shade and light and position X_p=7m

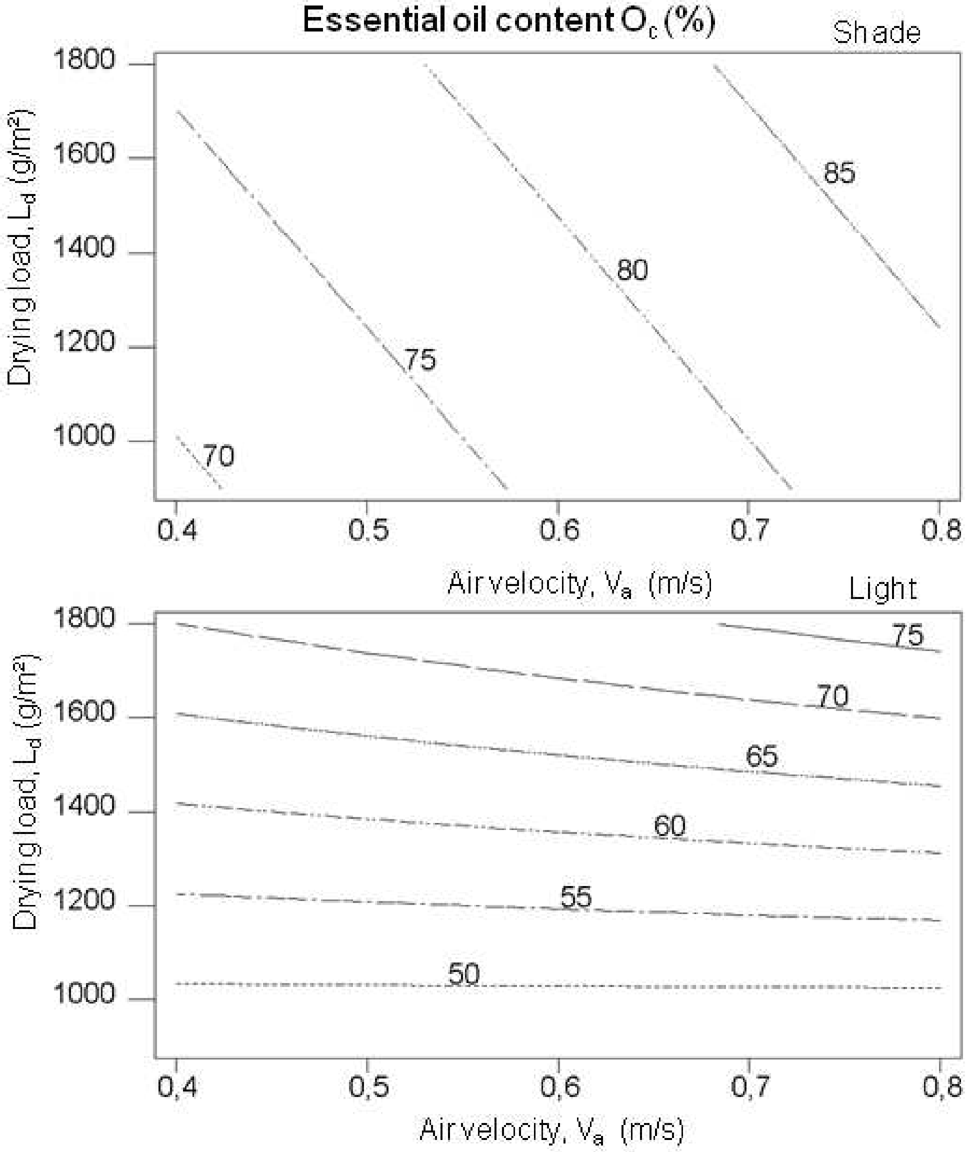


Figure 10.21: Contour plots for essential oil content considering air velocity and drying load for the two covering conditions: shade and light and position $X_p = 7m$

Observing the graphics presented in **Figures** 10.20 and 10.21, the behavior of the essential oil content for the conditions light and shadow can be compared. For a certain point X_p=$7m$ inside the tunnel and considering a drying air velocity value of $0.6 m/s$ and a drying load of $1400 g/m^2$, the essential oil content is 61% and around 80% for light and shadow conditions respectively.

The significant factors on the essential oil content were the drying load L_d, condition of covering C_o and air velocity V_a. The analysis of the effects allows to observe that the change of covering condition, from light to shade causes an appreciable increment of obtained essential oil, due to less temperature with shade condition that avoids volatilization of the active ingredients. Likewise the increase of drying load produces an increase of the obtained essential oil, originated by change in the conditions of heat transfer due to the thickness of the product. Additionally the increase of air velocity causes an increase in the obtained essential oil, this is caused by less process time therefore less thermal effect on the volatilization of essential oil components.

By considering the proposed regression model for essential oil content as function of the significant factors, it is possible to observe the influence of the combinated effects of drying load, air velocity and condition of covering on the behavior of essential oil content (see **Figures 10.20** and **10.21**). High essential oil content is obtained by having shade condition of covering, high air velocity and high drying load.

11 Overall discussion

The following is a summary of the findings and conclusions as a result of achieving the research objectives proposed to solve the problems in drying of Lemon Balm.

11.1 Sorptions isotherms

Regarding the sorption isotherms, the desorption curves of Lemon Balm leaves (*Melissa officinalis* L.) were determined at four temperatures (25°C, 40°C, 50°C and 60°C). The experimental data of sorption isotherms were fitted for eight mathematical models. For the considered conditions, the best fittings were obtained for the models of Halsey, BET and Oswin that represent the behavior of the sorption data.

Considering the coefficient of determination R^2 and the Chi-square test as decision criteria for selecting the best fittings, it was concluded that the model of Halsey is the best in order to describe the hygroscopic behavior of Lemon Balm leaves for temperatures of 25°C and 40°C. Likewise, for temperatures of 50°C and 60°C the BET model was the best for fitting the experimental data.

The hysteresis effect was observed at 40°C and 60°C being most notorious for 60°C. At constant water activity, the equilibrium moisture content for desorption is higher than the adsorption. That could be caused by the rigidity of pores obtained during the drying process. During adsorption, the capillary or pore is empty and begins to fill as a result of increased water activity, while during desorption the pores is filled with water and the liquid can escape only when the surrounding air pressure becomes less than the vapor pressure of liquid inside the capillary.

11.2 Drying kinetics

Additionally, for the description of drying kinetics of Lemon Balm, the drying behavior at 30°C, 40°C, 50°C and 60°C were analyzed. The drying kinetics of branches of Lemon Balm for the four temperatures studied can be described by the Fick's second law. That is observed according to the obtained experimental data and the fitted mathematical models.

The proposed models for fitting the experimental data of the drying kinetics were evaluated by using the coefficient of determination R^2 and the Chi-square test. The best model to describe the drying behavior of lemon Balm at 30°C and 40°C was the model of Wang and Singh. For 50°C the best model was the model of Page and for 60°C the best model was the exponential decay.

The mechanism governing the transfer of moisture during dehydration is complex and depends largely on the structure of the product. For this reason there are significant differences in the results of the quality characteristics and moisture content when branches or only leaves are considered in the analysis of the drying process. In consequence the determination of moisture content must be done separately for leaves and stalks. That is necessary in order to control overdrying and loss of essential oil in leaves and to observe the adequate moisture content of stalks for subsequent handling and separation processes. To observe these aspects several experiments of drying Lemon Balm at 40°C considering only leaves, only stalks and branches were carried out. The results show for example that for 11h of drying time,the moisture content for leaves was 10%, for stalks was 46% and for branches was 26%.

Considering the large differences in drying of each of the parts of the Lemon Balm plant (leaf, branch and stem) observed in chapter 7, it is required to conduct research on efficient and reliable methods of separation of leaves and stems that allow to dry only leaves in order to increase energy efficiency and to achieve optimal quality characteristics.

11.3 Drying by stepwise

New strategies for quality oriented drying of Lemon Balm were proposed by considering the analysis of different possibilities of stepwise drying. Comparing stepwise drying method with standard drying (at a single temperature) it was observed that there is a significant difference on the total drying time for each of the combinations studied. The difference was also reflected in the change point of temperature because the sooner the change in drying air temperature, the greatest the decrease in the total drying time became of over 50% compared to the standard drying. Analyzing the effect on each of the quality characteristics analyzed in this study, the best combination in order to obtain the highest content of essential oil was 40°C/60°C and the change point of humidity was 20%. The obtained essential oil content was 94% of that obtained with the standard drying method.

For color change can be concluded that for the combination of temperature 30°C /40°C the color change diminished with increasing the humidity change point. This was caused possibly by the decrease in drying time which produces a decreasing in the oxidation processes that affects color change. The combination 30°C/40°C with 50% of change point had the lowest color difference of all combinations studied. The color difference obtained for this case was 13. Another important factor to consider the selection of drying parameters is the energy consumption. Taking as criteria for selection of drying parameters, the obtaining of the slightest change of color combined with the lowest power consumption, the best combination is 30°C/50°C with change point of 20% with the respective power consumption of $2.8kWh$. Considering as criteria the loss of essential oil and the lowest power consumption, the best combination was 30°C/40°C with 20% of change point. For this combination the loss of essential oil was 8% and the power consumption was $3.24kWh$.

The effectiveness of drying is improved by the application of the stepwise method this tends to benefit the process by decreasing the duration of the drying process and hence the amount of energy required. The product quality is also better, employing this method the necessary drying time can be substantially reduced, and therefore the quality of the products should be higher when is compared with the standard drying process.

11.4 Optimization of drying

By using surface response methodology combined with the concept of desirability function, a strategy for finding the values of drying temperature and relative humidity of drying air that optimize the required responses of the process (drying time, essential oil content, color difference and required energy) was proposed. Additionally regression models (polynomial models of second order with interactions) were proposed for drying time, color difference, essential oil content and required energy as responses, considering air drying temperature and relative humidity as factors.

Regarding the optimization process by using desirability functions, the optimal combination for a minimum drying time (as relevant criterion) was 40°C for air drying temperature and 21% for relative humidity. The corresponding drying time for this combination was 11 hours and the obtained value of the desirability function was 0.86.

The optimal combination to maximize the content of essential oil from dried leaves of Lemon Balm was: drying air temperature of 34°C and a relative humidity of 41%. The content of essential oil obtained for this combination was 97% relative to the content for fresh leaves. For this optimal combination, the corresponding value of function of desirability was 0.91.

To minimize the difference in color of the leaves of Lemon Balm after the drying process, the obtained optimal combination was: drying air temperature of 36°C and humidity of 33%. The obtained smallest color difference was 7, and the corresponding value of the desirability function for this case was 0.74.

To minimize energy requirements, which would be reflected in a decrease in production costs, the optimal combination was: drying air temperature of 43°C and relative humidity of 43%. The corresponding required energy was $6049 kJ$ and the obtained value of the desirability function was 0.85.

Considering the same relevance for all responses (drying time, color difference, loss of essential oil and energy consumption) the optimal combination was: drying air temperature of 38 °C and relative humidity of 37%. The obtained optimum drying time was 20 hours and the corresponding value of the desirability function was 0.59. The optimum essential oil content was 94% with a value of 0.785 for the desirability function. The optimum color difference was 7.23 and the corresponding value of desirability function was 0.70. The required energy was $7961 kJ$ with a value of 0.67 for the desirability function.

Considering in the optimization process only the relevance of the two quality characteristics (color difference and essential oil content) the optimal combination was: air drying temperature of 34°C and relative humidity of 39%. For this combination, the obtained essential oil content was 96.5% relative to the content for fresh material and the color difference was 7. The values of the desirability functions were 0.91 and 0.66 respectively.

From the optimization analysis that considered essential oil content, color difference, required energy and drying time as targets, depending on the values of drying temperature and relative humidity, it is observed that the optimization of quality characteristics (represented by essential oil content and color difference) implies at the same time high values of required energy and drying time.

11.5 Solar drying

For the analysis of the effects of the parameters of drying Lemon Balm by using a solar tunnel (covering, position, drying load and air velocity) on quality characteristics (essential oil content and color difference), drying time and consumed energy, statistical design of experiments (DoE) was considered by applying factorial design. In this research conducted for solar tunnel drying was found that the significant factors that influence the drying time are in order of relevance: type of covering, drying air velocity, drying load and the interaction between type of covering and air drying velocity. For color difference, the most significant factors are type of covering and air drying velocity. Equally, the results of the research show that the factors with most significance for the essential oil content are in order of relevance: drying load, type of covering and air drying velocity. Considering the most significant factors for each response, regression models (based on principal factors and significant interactions) to describe the behavior were proposed.

In general the use of the solar tunnel is not very convenient for drying of Lemon Balm because the conditions of temperature and humidity that can be reached by this method are very far from the optimal recommended for obtain acceptable quality characteristics. The optimal conditions recommended were obtained as a result of the multiobjective optimization study presented in chapter 9. These optimal conditions are difficult to reach in the solar tunnel because the process parameters cannot be controlled economically.

The research questions were completelly considered and answered and different strategies for quality oriented drying of Lemon Balm were proposed in order to contribute to the solution of the problems related with drying of Lemon Balm. Likewise the general contribution of the present research work, represented in the proposed methodologies and strategies, can be applied to other products having similar difficulties and characteristics of drying by using the same considered technology.

12 Summary

During drying of medicinal plants, many changes occur simultaneously resulting in a modified overall quality. This research work is related to the quality oriented drying of Lemon Balm (*Melissa officinalis* L.). As main result, different strategies that consider experimental and mathematical aspects have been suggested to obtain the best conditions to reach high adequate productivity and the required quality characteristics in terms of color change and essential oil content. At present, for drying of Lemon Balm, there are various problems that do not allow the achievement of the quality requirements for the market. There is not enough information of drying parameters and in order to select the initial set of conditions for processing. Due to this data from similar plants are considered and trial and error are applied to adjust the process and obtain the quality requirements. As consequence, an inadequate selection of drying parameters can be obtained and as a result different problems are generated, among others; over-drying that causes damage to the structure. Deficient drying which means that the moisture obtained is above the minimum required. Likewise unacceptable change in color and excessive loss of essential oil are produced. Furthermore non-uniformity in the drying of leaves and stems due to differences in structure and thermal and mechanical properties. Equally excessive drying times and inefficient use of energy is observed. Additionally for drying in solar tunnels the following problems are evaluated: difficulty to control the drying temperature due to randomness in the radiation. Likewise the radiation affects the color of the product by photo-decomposition. Additionally, the high variation of radiation, temperature and humidity generates unstable drying conditions causing high variability in quality characteristics. Considering the presented problems, the following research objectives were considered: To propose new strategies of drying as an alternative to improve the obtained results for conventional drying in terms of quality, drying time and energy consumption. To find the optimal parameters for drying time, essential oil content, color difference and required energy, considering as variables the temperature and relative humidity. For solar tunnel; to analyze the effect of drying parameters on the quality characteristics and drying time. To achieve the objectives different research activities were carried out. The sorption isotherms and drying kinetics of Lemon Balm and the corresponding fittings to mathematical models were obtained. Likewise stepwise drying strategies were applied and analyzed as alternative to obtain better results in terms of quality and energy consumption. Additionally a central composite design (CCD), response surface methodology (RSM) and desirability functions were used for multi objective optimization of quality characteristics and required energy considering temperature and relative humidity as variables. With the obtained experimental data, regression models were generated and the behavior of the drying process was described. Finally, methods of design of experiments (DOE) were applied to observe the influence of drying parameters on product quality by using a solar tunnel. The effects of type of covering, position in the tunnel, drying load and air velocity on drying time, color difference and essential oil content were analyzed. Equally, for solar tunnel, regression models for the different responses were developed. As principal results, the optimal parameters and drying conditions to obtain the required quality and energy consumption were determined. Likewise the main contribution of the present research work is represented by the proposed methodologies and strategies that can be applied to other products having similar characteristics and difficulties of drying.

13 Zussamenfasung

Heilkräuter sind während des Trocknungsprozesses zahlreichen Einflüssen ausgesetzt, welche die Qualität des Endproduktes entscheidend beeinflussen. Diese Forschungsarbeit beschäftigt sich mit der Trocknung von Zitronenmelisse (*Melissa officinalis* L.) zu einem qualitativ hochwertigen Endprodukt. Es werden Strategien zur Trocknung vorgeschlagen, die experimentelle und mathematische Aspekte mit einbeziehen, um bei einer adäquaten Produktivität die erforderlichen Qualitätsmerkmale im Hinblick auf Farbänderung und Gehalt an ätherischen Ölen zu erzielen. Getrocknete Zitronenmelisse kann zurzeit auf Grund verschiedener Probleme beim Trocknungsvorgang den hohen Qualitätsanforderungen des Marktes nicht immer genügen. Es gibt keine standardisierten Informationen zu den einzelnen und komplexen Trocknungsparametern. In der Praxis beruht die Trocknung auf Erfahrungswerten, bzw. werden Vorgehensweisen bei der Trocknung anderer Pflanzen kopiert, und oftmals ist die Trocknung nicht reproduzierbar, oder beruht auf subjektiven Annäherungen. Als Folge dieser nicht angepassten Wahl der Trocknungsparameter entstehen oftmals Probleme wie eine Übertrocknung, was zu erhöhten Bruchverlusten der Blattmasse, einer nicht vertretbaren Farbänderung und einem übermäßigen Verlust an ätherischen Ölen führt. Eine zu geringe Trocknung hat wiederum einen zu hohen Endfeuchtegehalt im Produkt zur Folge, was die Gefahr eines mikrobiologischen Verderbs birgt. Auf Grund der unterschiedlichen thermischen und mechanischen Eigenschaften von Blättern und Stängel ist eine ungleichmäßige Trocknung die Regel. Es wird außerdem eine unnötig lange Trocknungsdauer beobachtet, die zu einem erhöhten Energieverbrauch führt. Das Trocknen in solaren Tunneltrocknern bringt folgendes Problem mit sich: wegen des unkontrollierbaren Strahlungseinfalles ist es schwierig, die Trocknungstemperatur zu regulieren. Ebenso beeinflusst die Strahlung die Farbe des Produktes auf Grund von photochemischen Reaktionen. Zusätzlich erzeugen die hohen Schwankungen der Strahlung, der Temperatur und der Luftfeuchtigkeit instabile Bedingungen für eine gleichmäßige und kontrollierbare Trocknung. In Anbetracht der erwähnten Probleme werden folgende Forschungsschwerpunkte in dieser Arbeit gesetzt: neue Strategien zur Verbesserung der Qualität werden entwickelt, mit dem Ziel die Trocknungszeit und den Energieverbrauch zu verringern. Um eine Methodik vorzuschlagen, die auf optimalen Trocknungsparameter beruht, wurden Temperatur und Luftfeuchtigkeit als Variable in Abhängigkeit der Trocknungszeit, des Ätherischen Ölgehaltes, der Farbänderung und der erforderliche Energie betrachtet. Außerdem wurden die genannten Parametern und deren Auswirkungen auf die Qualitätsmerkmale in solaren Tunneltrocknern analysiert. Um diese Ziele zu erreichen, wurden unterschiedliche Ansätze verfolgt. Es galt die Sorption-Isothermen und die Trocknungskinetik von Zitronenmelisse an verschiedene mathematische Modelle anzupassen. Eine alternativ gestaffelte Trocknung in gestuften Schritte erhöht die Qualität des Endproduktes senkt gleichzeitig den Gesamtenergieverbrauch. Zusätzlich wurde ein statistischer Versuchsplan nach der CCD-Methode (Central Composite Design) und der RSM-Methode (Response Surface Methodology) vorgeschlagen, um die gewünschten Qualitätsmerkmalen und den notwendigen Energieeinsatz in Abhängigkeit von Lufttemperatur und Luftfeuchtigkeit zu erzielen. Anhand der gewonnenen Daten wurden Regressionsmodelle erzeugt und das Verhalten des Trocknungsverfahrens beschrieben. Schließlich wurde eine statistische DoE-Versuchsplanung (design of experiments) angewandt, um den Einfluss der Parameter auf die zu erzielende Produktqualität in einem solaren Tunneltrockner zu bewerten. Die Wirkungen der Beschattung, der Lage im Tunnel, des Befüllungsgrades und der Luftgeschwindigkeit auf Trocknungszeit, Farbänderung und dem Gehalt an ätherischem Öl, wurden analysiert. Ebenso wurden entsprechende Regressionsmodelle bei der Anwendung in solaren Tunneltrocknern erarbeitet. Die wesentlichen Ergebnisse werden in Bezug auf optimale Trocknungsparameter in Bezug auf Qualität und Energieverbrauch analysiert.

Bibliography

Abreu, K., & Mazzafera, P. (2005). Effect of water and temperature stress on the content of active constituents of itypericum brasiliense choiry. *Plant Physiology and Biochemistry*, (pp. 241–284).

Abuhamdah, S., & Chazot, P. (2008). Lemon balm and lavender herbal essential oils: Old and new ways to treat emotional disorders. *Anesthesia and Critical Care: Neuropharmacology*, *V.19*, 221–226.

Afolayan, A., Ashafa, O., & Grierson, D. (2008). Effects of drying methods on the chemical composition of essential oil from felicia muricata leaves. *Asian Journal of plant Science*, *V.7,6*.

Aghbashlo, M., Kianmehr, M., & Akhijahani, H. (2008). Influence of drying conditions on the effective moisture diffusivity, energy of activation and energy consumption during the thin-layer drying of berberis fruit berberidaceae. *Energy Conversion and Management*, .

Ahmet, K., & Orhon, A. (2009). An experimental study on drying kinetics of some herbal leaves. *Energy Conversion and Management*, *50*, 118–124.

Akerele, O. (1993). Nature's medicinal bounty: don't throw it away. In *World health forum*.

Akpinar, E. (2006). Mathematical modelling of thin layer drying process under open sun of some aromatic plants. *Journal of Food Engineering. Turkai: Elsevier*, *77,4*, 864–870.

Ameenah, G. (2006). Medicinal plants: Traditions of yesterday and drugs of tomorrow. *Molecular Aspects of Medicine*, *27*, 1–93.

Arabhosseini, A., Padhye, S., Huisman, W., Boxtel, V., & Müller, J. (2009). Effect of drying on the color of tarragon (*Artemisia dracunculus* l.) leaves. *Food and Bioprocess Technology*, .

Asekun, O., Grierson, D., & Afolayan, A. (2007). Effects of drying methods on the quality and quantity of the essential oil of mentha longifolia l. subsp. capensis. *Food and Bioprocess Technology. s.l.: Elsevier*, *101,3*, 995–998.

Ayanoglu, F., Arslan, J., & Hatay, A. (2005). Effects of harvesting hours and drying methods of essential oil content of lemon grow in eastern mediterranean. *In: International Journal of Botany*, (pp. 138–142).

Baker, C. (1997). *Industrial Drying of Foods*. London: Blackie Academic Profesional.

Bakkali, F., Averbecks, D., & Idaomar, M. (2008). Biological effects on essential oils- a review. *Food and chemical Toxicology*, (pp. 446–475).

Balladin, D., & Headley, O. (1999). Evaluation of solar dried thyme (*Thymos Vulgaris Linné*) herbs. *Renewable Energy*, *17*, 523–531.

Barbosa-Canovas, G., & Fontana, J. L. T., J.and Shelly (2007). *Water activity in foods: Fundamentals and applications Fundamentals and applications desorption phenomena in food dehydratation processes*. Ames, Iowa: Blackwell Publishing and the Institute of Food Technologists.

Barrie, A. (2002). *Drying food for profit: A Guide for small businesses*. London: ITDG Publishing.

Baser, K. (1999). Industrial utilization of medicinal and aromatic plants. In B. A. B. G. C. N. Martinov, M. (Ed.), *Proceedings of Second World Congress on Medicinal and Aromatic Plants for Human Welfare* (pp. 21–29). Mendoza, Argentina.

Bayerischen, L., Landesanstalt (2001). *Kulturanleitung für Zitronenmelisse. Bd.4 Auflage*. Freising.

Bell, L., & Labuza, T. (1984). *Moisture sorption: Practical aspects of isotherm measurement and use*. St.Paul, Minnesota: Department of Foods Sience and Nutrition-University of Minnesota.

Blum, H., & Lorenz, J. (2005). Ergebnisse (*Melissa officinalis* l.). *In: Zeitschrift von Arznei und Gewürzpflanzen*, (pp. 133–139).

Bomme, U. (2001). Kulturanleitung für zitronenmelisse. *Bayerische Landesanstalt für Landwirtschaft.*, .

Bomme, U., Hillenmeyer, G., Reiter, H., & Rinder, R. (2000). Optimiertes verfahren zur praxisnahen wasserdampf-destillation ätherischer Öle aus frischen pflanzenteilen. *Zeitschrift für Arznei und Gewürzpflanzen*, (pp. 132–144).

Brennan, J. (1994). *Food dehydratation*. Butterworth-Heinemann: Oxford.

Brink, H. (1975). *Trocknung von Körnigen und Pulverförmigen Gütern in Förderlofttrocknern*. Dresden: Verlag Theudor Stein Kopff.

Bruce, S. (2001). *Introduction to growing herbs, for essential oils, Medicinal and Culinary purposes*. Technical Report New Zealand Institute for Crop & Food Research Ltd A Crown Research Institute.

Bundessortenamt, B. (2002). *Beschreibende Sortenliste-und Gewürzpflanzen*. Hannover: Deutcher Landwirtschaftverlag GmbH.

Busse, W. (2000). The significancy of quality for efficacy and safety of herbal medicinal products. *Drug Information Journal.*, *34*, 15–23.

Calixto, J. (2000). Efficacy, safety, quality control, marketing and regulatory guidelines for herbal medicines (phytotherapeutic agents). *Brazilian Journal of Medical Biological Research*, *33*, 179–189.

Calvo, M. (2003). *Bioquímica de los alimentos.* http://milksci.unizar.es /bioquimica/temas/pigmentos/carotenoides.html: Publicaciones Universidad de Zaragoza.

Capecka, E., Mareczek, A., & Leja, M. (2004). Antioxidant activity of fresh and dry herbs of some lamiaceae species. *Food chemistry*, *93*, 223–226.

Carle, R. (1992). *Atherische Öle Anspruch und Wirklichkeit. Band 34*. Stuttgart: Wissenschaftliche Verlagsgesellschaft mbtt.

Challa, A., Ahmad, N., & Mukhtar, H. (1997). Cancer prevention through sensible nutrition. *International Journal of Oncology*, *11*, 1387–1392.

Chan, K. (2003). Some aspects of toxic contaminants in herbal medicines. *Journal Chemosphere*, *52*, 1361–1371.

Association of official analytical chemists, A. (1990). *Official methods of analysis: Moisture content plants.*

Chung, D., H., P., & St.Joseph. (1967). Adsorption and desorption of water vapour by cereal grains and their products. *Transactions of ASAE, St. Joseph*, *10(4)*, 149–157.

Cordeiro, D., & Oliveira, W. (2005). Technical aspects of the production of dried extract of maytenus ilicifolio leaves by jet spouted bed drying. *In International Journal of Pharmaceutics.*, (p. 299).

Cuervo, P., & Hensel, O. (2007). Experimental determination of desorption isotherm for lemon balm (*Melissa officinalis*l.). *Proceeding of Tropentag 2007:International Research on Food Security: Natural Resource Management and Rural Development*, .

Cuervo, S., & Hensel, O. (2008). Drying of lemon balm (*Melissa Officinalis* l.) using stepwise process control. In *Proceedings of Tropentag 2008: Conference on International Research on food security, natural resource Management and Rural Development*. Stuttgart.

Dastmalachi, K., Dorman, D., Oinonen, P., Darwis, Y., Laakso, I., & Hiltunen, R. (2008). Chemical composition and invitro antioxidative activity of lemon balm (*Melissa officinalis* l.) extract. *LWT-Food Science and Technology*, (pp. 391–400).

Díaz-Maroto, C., Pérez-Coello, S., & Cabezudo, D. (2002). Effect of drying method on the volatiles in bay leaf (*Laurus nobilis L.*). *Journal of Agricultural and food chemistry*, (pp. 4520–4524).

Díaz-Maroto, C., Pérez-Coello, S., & Cabezudo, D. (Septiembre 2002). Effect of different drying methods on the volatile components of parsley (*Petroselinum crispum* l.). *European Food Research Technology*, *215,3*, 227–230.

Deutsches Arzneibuch, D. K. (1986). *Wissenschaftliche Verlagsgesellschaft mbh*. Stuttgart.

DIN (1979). *DIN 6174: Farbmetrische Bestimmung von Farbabständen bei körperfarben nach der CIELAB-Formel.*

DIN (1982). *DIN 50008 Teil 1: Konstantzklimate über wäßringen Lösungen.*

Diplock, T., Charleux, L., Crozier-Willi, G., Kok, J., Rice-avans, C., Roberfroid, S. W., M., & Vina-Ribes, J. (1998). Functional food science and defence against reactive oxidative species. *British Journal of Nutrition*, *80*, 77–112.

Dostmalchi, e. a., K. (2008). Chemical composition and invitro antioxidative activity of a lemon balm (*Melissa officinalis* l.) extract. *Science Direct*, *41*, 391–400.

Doymaz, I. (March 2005). Thin-layer drying behaviour of mint leaves. *Elsevier*, (pp. 370–375).

Doymaz, I., Tugrul, N., & Pala, M. (2006). Drying characteristics of dill and parsley leaves. *Journal of Food Engineering*, *77*, 559–565.

Dudai, N., Weintein, Y., Kup, M., & Polanski, T. (2005). *Citral is a new inducer of caspase-3 in tumor cell lines*. Stuttgart, New York: Planta medicinal Georg thieme verlag KG.

Duffiee, A., & Beckman, W. (1980). *Solar engineering of thermal processes*. John Wiley & Sons.

Ebert, K. (1982). Arznei- und gewürzpflanzen: ein leitfaden für anbau und sammlung. *wissenschaftliche Verlagsgesellschaft mbH*, .

Ekechukwu, O., & Norton, B. (1999). Review of solar-energy drying systems iii: low temperature air-heating solar collectors for crop drying applications. *Energy Conversion & Management*, *40*, 657–667.

Fahrmeir, L., Kneib, T., & Long, S. (2007). *Regression, Modell, Methoden und Anwendungen, 1 Auflage*. Berlin, Heildelberg: Springer Verlag.

Fargali, M., Nafeh, A., Fahmy, H., & Hassan, A. (2008). Medicinal herb drying using a pholovoltaic array and a solar thermal system. *Journal Solar Energy*, *82*, 1154–1160.

Fatouh, M., Metwally, N., Helali, A., & Shedid, M. (2006). Herbs drying using a heat pump dryer. *Energy Coversion and Management*, (pp. 2629–2643).

Figiel, A., Szumny, A., Gutiérrez-Ortíz, A., & Carbonell-Barrachina, A. (2010). Composition of oregano essential oil (origanum vulgare) as affected. *Journal of Food Engineering. s.l.:Elsevier*, (pp. 240–247).

Garcia, A. (2007). Isotermas de adsorción y cinética de secado de ciertas hortalizas y aromáticas cultivadas en misiones. *Revista de Investigaciones Agropecuarias- Argentina*, *36*, 115–129.

Garg, R., P.and Kumar (2001). Developments in solar drying. In *In: Proceedings of the Second Asian-Oceania Drying Conference (ADC 2001)* (pp. 297–319). Batu Feringhi, Pulau Pinang, Malaysia.

Gauvin, A., Ravaomanarivo, H., & Smadja, J. (2004). Comparative analist by gas chromotography - mass spectrometry of the essential oils from bark and leaves of cedrelopsis grevei baill and aromatic medicinal plant from madagascar. *Journal of Cromatography*, *A. 1029*, 279–282.

Gbaha, e. a., P. (2007). Experimental investigation of a solar dryer with natural convective heat flow. *In: Renewable energy*, *32*, 1817–1829.

Gomis, A. (1999). *Introducción a las operaciones de separación contacto continuo*. Alicante: Publicaciones de la Universidad de Alicante.

Groot, J., & Van der Rest, J. (2006). *Quality Controlin the Production Chain of Herbal Products.*. Berlin, Heidelberg : Springer, Verlag: Medicinal and Aromatics Plants Agricultural Commercial.

Guine, F., Henrriques, F., & Barroca, J. (2009). Mass transfer coefficients for the drying of pumpkin (*cucurbita moschata*) and dried product quality. *Food and Bioprocess Technology Journal*, .

Gunhan, e. a., T. (2005). Mathematical modelling of drying of by leaves. *Energy Conversion and Monagement Polomer*, *46*, 1667–1679.

Halsey, G. (1985). Physical adsorption on uniform surfaces. *Chemical Physics*, *16 (10)*, 931–937.

Heeger, F. (1989). *Handbuch des Arznei- und Gewürzpflanzenbaues, 2 Auflage*. Berlin: Deutscher Landwirtschaftsverlag.

Heindl, A. (1999). Trockner für arznei- und gewürzpflanzen - Überblick und mögliche entwicklungen in der zukunft. *Drogenreport Information about Medicinal and Spice Plants*, *21*, 45–53.

Heindl, A., & Müller, J. (1997). Trocknung von arznei- und gewürzpflanzen. *Zeitschrift von Arznei Gewürzpflanzen*, *2*, 90–97.

Hossain, D., Bala, A., Hossain, M., & Mondol, R. (2001). Sorption isotherms and heat of sorption of pineapple. *Journal of Food Engineering*, *48*, 103–107.

Hossain, M., Woods, J., & Bala, B. (2004). Optimization of solar tunnel drier for drying of chilli without color loss. *Journal Renewable Energy*, (pp. 729–742).

Hosseini, A. (2005a). Long term effects of drying conditions on the essential oil and color of tarragon leaves during storage. *Journal of Food Engineering*, *79*, 561–566.

Hosseini, A. (2005b). *Quality, energy requirement and cost of drying tarragon (Artemisia dracunculus L.)*. Van Wageningen Universität.

Hu, C., F.B.and Willet (2002). Optimal diets for prevention of coronary heart diseases. *Journal of American Medical Association*, (pp. 2569–2578).

Iglesias, H., & Chirife, J. (1982). *Handbook of food isotherms water sorption parameters for food components*. New York: Academic Press.

Inchuen, S., & Narkrugsa, W. (2010). Effect of drying methods on chemical composition, color. *Journal Natural Science*, *Bd.44*, 142–151.

Janjai, S., Srisittipokakun, N., & Bala, K. (2007). Experimental and modelling performances of a roof- integrated solar drying system for drying herbs and spices. *Journal Energy*, .

Janjai, S., & Tong, P. (2005). Performance of a solar dryer using hot air from roof-integrated solar collectors for drying herbs and spices. *Renewable Energy*, (pp. 2085–2095).

Jowitt, R. e. a. (1983). *Physical properties of foods*. London: Applied Science Publishiers.

Kabganian, R., Carrier, J., & Sokhansanj, S. (2002). Physical characteristics and drying rate of echinacea root. *In Drying Technology*, *20*, 637–649.

Kaleemullah, S., & Karlappan, R. (2006). Modelling of thin- layer drying kinetics of red chillies. *In:Journal of Food engineering*, *72*, 531–537.

Kapecka, E., Mareczek, A., & Leja, M. (2005). Antioxidant activity of fresh and dry herbs of some lamiaceae species. *Food chemistry*, *93*, 223–226.

Karasova, G., & Lehotay, J. (2005). Chromotography determination of derivatives of p-hydroxybenzoic aerd in *Melissa officinalis* l. by hplc. *In Journal of Liquid Chromotography & Related Technologies*, (pp. 2421–2431).

Kavak Akpinor, E. (2006). Mathematical modelling of thin layer drying process under open sun of same aromatic plants. *In Journal of Food Engineering*, *77*, 864–870.

Kaya, A., & Aydinv, O. (2008). *An experimental study on drying kinetics of some herbal leaves*. Trabzon, Turkey: Technical University Karadeniz.

Keey, R. (1972). *Drying principles and practice*. Oxford: Pergamon Press.

Klein, B. (2007). *Vesuchsplanung DoE. 2*. München, Wien: Verlag.

Kleinbaum, D., Kupper, L., & Muller, K. (1988). *Applied regression analysis and other multivariable methods*. Duxbury Press: Belmont.

Kleppmann, W. (2006). *Taschenbuch Versuchsplanung.3*. München, Hanser.

Kneule, F. (1975). *Das Trockner, 3. Auflage*. Frankfurt am Main: Verlag Sauerländer.

Kokkini, S., Karousou, R., & Lanaras, T. (1995). Essential oils of pepermint (carvone-rich) plants from the island of crete (greece). *Biochemical Systematics and Ecology*, *Bd.23, 4*, 425–430.

Koller, D. (1987). Problems with the flavour of herbs and spices. In *Proceeding of the fifth International Flavour conference* (pp. 123–132). Porto Karras, Chalkidiki, Greece.

Ökoplant, H., Stiftung Ökologie und Landbau (1999). Praxis des ökologischen kräuteranbaus. *Biolandverlags GmbH, Mainz*, .

Kowalski, S. (2003). *Thermomechanics of drying processes*. Berlin: Springer-Verlag.

Krischer, O. (1992). *Trocknungstechnik. Erster Band. Die Wissenschaftlichen Grundlagen der Trocknungstechnik*. Berlin: Springer Verlag.

Kröll, K. (1978). *Trockner und Trocknungsverfahren. Zweiter Band*. Berlin: Springer Verlag.

Kröll, K. (1989). *Trocknen und Trockner in Produktion. Trocknungstechnik: Dritter Band*. Berlin: Springen Verlag.

Kudra, T., & Mujumdar, A. (2002). *Advanced drying technologies*. New York: Marcel Dekker, Inc.

Lamharrar, A., Idlimam, A., & Kouhilal, M. (2007). Thermodynamic properties and moisture sorption isotherms of *Artemisia herba-alba*, .

Lebert, e. a., A. (1992). The drying kinetics of mint (*Mentha spicata huds*). *In Journal of Food Engineering*, (pp. 15–28).

Lesmes, L., Rodríguez, A., & Acosta de la Luz, L. (2001). Estudios agrícolas en *Melissa officinalis* l. (toronjil) fecha de propagación y plantación. *Revista Cubana Plant Meol*, (pp. 93–97).

Loncin, M., & Weisser, H. (1977). Die wasseraktivität und ihre bedeutung in der lebensmittelverfahrestechnik. *Chemie-Ingenieur-Technnik*, (pp. 312–319).

Madsen, L., & Bertelsen, G. (1995). Species as antioxidants. *Trends in food Science and Technology*, *6*, 271–276.

Maiocchi, G., & Avanza, R. (2004). *Degradación de clorifilas y feofitinas a diferentes temperaturas en Ilex dumosa e Ilex paraguariensis*. Universidad Nacional del Nordeste, Facultad de Ciencias Exactas y Naturales y Agrimesura-Comunicaciones Científicas.

Maltry, W., Pötke, E., & Schneider, B. (1962). *Landwirtschaftliche Trocknungstechnik*. Berlin: Verlag Technik.

Maroulis, B., Kiranoudis, T., & Marinos-Kouris, D. (1995). Heat and mass transfer modeling in air drying of foods. *Journal of Food Engineering*, *26*, 113–130.

Martinov, I. M. J., M.;Mujic (2007). Impact of drying air temperature on course of drying and quality of *hypericum perforatum. In: Zeitschrift von Arznei und Gewürzpflanzen*, (pp. 136– 140).

Martinov, M., Adamovic, D., Ruzic, D., & Abrel, D. (2006). *Investigation of medicinal plants drying in batch dryers - quality and energy characteristics*. Bulgaria: In: Proceedings of EE & AE'International Scientific Conference. Rousse.

Martinov, M., Öztekin, S., & Müller, J. (2007). *Drying in medicinal and aromatic crops; harvesting, drying and processing*. Haworth food and Agricultural Product Press.

Martins, e. a., M. (2001). Evaluation of microbiological quality of medicinal plants used in natural infusions. *International Journal of Food Microbiology*, *68*, 149–153.

Martins, M. (2000). *Influencia da temperatura e da velocidade do ar de secagem no teor e na composicao quimica do óleo essencial de capim-limao (Cymbopongo citratus)*. Universidad de Vicosa: Tesis de maestria.

Masters, K. (1997). *Spray dryers. Industrial drying of foods*. London: Blackie academic & professional.

Mellmann, J., & Fürll, C. (2008). *Trocknungsanlagen für Arznei- und Gewürzpflanzen - spezifischer Energieverbrauch und Optimierungspotenzial. Forum. Potsdam*. Leibniz-Institut für Agrartechnik Potsdam-Borninm e.V. (ATB), 06.

Melo, C., & Radünz, L. (2007). Influencia do processo de secagem na qualidade de pantas medicinais. *Engenharia na Agricultura, Universidade Vicosa*, (pp. 307–315).

Miceli, A., Negro, C., & Tommasi, L. (2006). Essential oil of melissa romana (miller) grow in southern apulio (italy). *In Journal of Essential Oil Research*, .

Midilli, A., Kucuck, H., & Yapar, Z. (2002). A new model for single layer drying. *Drying Technology*, *Bd.20*, 1503–1513.

Minitab-Inc (2009). *Minitab 15 User´s Guide*. www.minitab.com.

Minolta, K. (1998). *Precise color communication*. Japan.

Müller, J. (1992). *Trocknung von Arzneipflanzen mit Solarenergie*. Stuttgart: Ulmer.

Müller, J., & Heindl, A. (2005). Drying of medicinal plant. *Proceedings of the Frontis Workshop on Medicinal and Aromatic plants. Wageningen-Netherlands : Springer Science*, *17*, 237–252.

Müller, J., & Heindl, A. (2006). Medicinal and aromatic plants -agricultural, commercial, ecological, legal, pharmacological and social aspects. chapter Drying of medicinal plants. (pp. 237–252). Berlin, Heidelberg, Germany: Springer-Verlag.

Molnár, K. (2007). *Experimental techniques in drying. Aruns Mujumdar. Handbook of industrial drying*. Boca raton: Taylor & Francis.

Montgomery, D. (2005). *Design and analysis of experiments.*. New Jersey: John Wiley and Sons.

Montgomery, e. a., D. (2007). *Engineering Statistics*. New York: John Wiley & Sons.

Mujumdar, A. (1997). *Drying Fundamentals.*. London: Blackie academic & professional.

Murthy, V. (2009). A reviw of new technologies, models and experimental investigations of solar driers. *Renewable and Sustainable Energy Reviews. s.l.: Elsevier*, *Bd. 13*, 835–844.

Murugesan, K., Suresh, H., Seetharamu, N., Aswatha, P., & Sundararajan, T. (2001). A theorical model of brick drying as conjugate problem. *International Journal of Heat and Mass Transfer*, *44*, 4075–4086.

Mustafa, I., Sopian, K., & Daud, R. (2009). Study of the drying kinetics of lemon grass. *In American Journal of Applied Science*, (pp. 1070–1075).

Myers, R., & Montgomery, D. (2002). *Response surface methodology*. New york: John wiley & Sons.

Natru, D. e. a. (2005). *Citral is a new inducer of caspace 3 in tumor cell lines*. Stuttgart, New York: Planta medicinal Georg Thieme Verlag KG.

Norton, B. (2001). *Solar Energy: The state of the art ises position papers*. London: James & James (Science Publishers) Ltd.

Panchariya, C., Popovic, D., & Sharma, L. (2002). Thin- layer modelling of black tea drying process. *In Journal of Food Engineering*, *52*, 349–357.

Pande, K., Sonune, U., & Philip, K. (2000). Solar drying of coriander and methi leaves. *In Journal Food Sciene Technology*, *Bd.37*, 592–595.

Park, K., Vohnikoua, Z., & Reis, F. (2002). Evaluation of drying parameters and desorption isotherms of garden mint leaves (*Mentha Crispa* l.). *Journal of Food Engineering*, *51*, 193–199.

Pino, J., Rosado, A., & Fuentes, V. (Junio 1999). Composition of the essential oil of *Melissa oficinalis*l. from cuba. *Journal of essential oil research*, (pp. 363–364).

Quirijins, E. (2006). *Modelling and dynamic optimization of quality indicator profiles during dryin*. Wageningen, The Netherlands: PhD. Thesis Wageningen University.

Reynolds, L. (1998). Effects of drying on chemical and physical characteristics of american ginseng (panax quinquefolius l.). *Journal of Herbs, Spices & Medicinal Plants. s.l*, *Bd.6,2*, 9–21.

Rockland, L., & Beuchat, L. (1987). *Water Activity: Theory and Applications to Foods*. New York and Basel: Marcel Dekker, Inc.

Rodriguez-Amaya, D. (2003). *Enhancing the carotenoid levels of foods through agriculture and food technology*. Technical Report Departamento de Ciência de Alimentos, Faculdade de Engenharia de Alimentos, Universidade Estadual de Campinas. Brasil.

Ross, M., Sheldom (2005). *Introductory Statistics*. Amsterdam: Elservier.

Roth, H. (1982). *Trocknungsprozesse*. Berlin: Akademie-Verlag.

Roth, L., & Kormann, W. (1997). Duftpflanzen, pflanzendüfte,. *Ecomed Verlagsgesellschaft AG & Co*, .

Runha, P., Cordeiro, S., Pereira, M., Vilegas, J., & Olivera.P. (2001). Production of dry extracts of medicinal brazilian plants by spouted bed process: Development ofprocess and evaluation of thermal degradation during the drying operations. *International group of Chemical and Process Engineers and Materials*, *79*, 160–168.

Sabillon, D. (2002). *Determinación de los factores de emisión de monoterpenos en tres especies tipicas de la vegetación terrestre mediterranea.Tesis doctoral*. Cataluna.

Saeed, E., Sopian, K., & Zainol, A. (2008). Thin-layer drying of roselle (i): Mathematical modeling and drying experiments. *Agricultural Engineering International: the CIGR Journal. Manuscript*, *X*, 1–25.

Sahin, A., & Dincer, I. (2002). Graphical determination of drying process and moisture transfer parameters for solids drying. *International Journal of Heat and Mass Transfer*, *45*, 3267–3273.

Salunkhe, D., Bolin, H., & Reddy, N. (1991). *Storage, processing and nutritional quality of fruits and vegetables. Volume II. Processed fruits and vegetables.*. Boca Raton: CRC Press, Inc.

Salzer, U., & Gerhardt, U. (2007). *Handbuch der Aroma und Gewürze*. Herausgeber: Behrs Verlag. Balue.

Scheffler, E. (1997). *Statische Versuchplanung und-auswertung*. Stuttgart: Deutscher Verlag für Grundstoffindustrie.

Senedeera, W., Wijesinghe, B., Young, G., & Bhandari, B. (2006). Fluidization characteristics of moist food particles. *International Journal of Food Engineering*, *Bd.2,1*.

Shaw, M., Meda, V., & Tabil, L. (2005). *Development and Trends in Drying of Herbs and Specialty Crops in Western Canada*. Technical Report Department of Agricultural and Bioresource EngineeringUniversity of Saskatchewan Winnipeg, Manitoba, Cacada.

Shilcher, H. (2008). Chamamile. In W. V. mbH (Ed.), *In German:Internationaler verband zum schutz von pflanzenzüchtungen*. Stuttgard, Germany.

Silva, F., Park, J., & Magalnäes, M. (2007). Isotermas de dessorcao de *calendula officinalis* l. determinacao experimental e modelagan matemática. *Revista Brasilera Plant Medicinal, Botucatu*, *v9, n1*, 21–28.

Singh, S., Singh, P., & Dhaliwal, S. (2004). Multi-shelf portable solar dryer. *Renewable Energy*, *29*, 753–765.

Soysal, S., Y. und Öztekin (1999). Equilibrium moisture content equations for some medicinal and aromatic plants. *In Journal of agricultural engineering research*, (pp. 317–324).

Soysal, Y. (2000). *Research on Fundamental of MAF Drying and developing a Field Scale Cabinet Dryer*. Phd. thesis Cukurova University Adana, Turkey.

Soysal, Y. (2005). Matematical modeling and evaluation of microwaye drying kinetics of mint (mentha spicota l). *In Journal of Applied Sciences*, (pp. 1266–1274).

Soysal, Y., & Öztekin, S. (2001). Technical and economic performance of a tray for medicinal and aromatic plants. *Journal Agricultural Engng*, (pp. 73–79).

Spiess, L., & Wolf, W. (1983). *The result of the COST 90 project on water activity*. London: Applied science publishers.

Srikiatden, J., & Roberts, S. (2007). Moisture transfer in solid food materials: a review of mechanisms, models, and measurements. *International Journal of Food Properties*, (pp. 739–777).

Tankoa, H., Carriera, D., Duana, L., & Clausena (2005). Pre- and post-harvest processing of medicinal plants. *Plant Genetic Resources: Characterization and Utilization. s.l.: Cambridge University Press*, *Bd.3*, 304–313.

Temple, S., & Boxtel, V. (1999). Thin layer drying of black tea. *Journal Agrucultural Engineering*, *Bd.74*, 167–176.

Timmerman, E. (2001). Water sorption isotherms of foods and foodstuffs: Bet or gab parameters. *Journal of Food Engineering*, *4*.

Timmerman, E., Chirife, J., & Iglesias, A. (2001). Termodinámica de isotermas de sorción. *Journal of Food Engineering*, *48*, 19–31.

Timoumi, S., & Zagrouba, F. (2005). Water sorption and dehydration kinetics of tunisian leaves. *In Desaliniation*, *185*.

Treybal, R. (1989). *Operaciones de transferencia de masa*. (2nd ed.). Mexico: MacGraw Hill.

Van, C., den-Berg (1981). *Vapor sorption equilibrium and other water-starch interactions: a physico-chemical approach*. Ph.D. thesis Wageningen Agricultural University, section Process Engineering Department of Food Science.

Vanaclocha, A. (2008). *Procesos de conservación de alimentos*. http://cite.ebrary.com /lib/unalbogsp/Doc?id=1024663.

VDMA (1973). *Wasserdampf- Sorptions Thermen von Lebensmitteln*. Frankfurt: Maschinenbau-Verlag Gmbh.

Velioglu, S., †Mazza, G., Gao, L., & Omah, D. (1998). Antioxidant activity and total phenolics in selected fruits, vegetables, and grain products. *Journal Agricultural Food Chemische.*, *46*, 4113–4117.

Walters, C., Hill, M., & Wheeler, J. (2005). *Drying While Dry: Kinetics and mechanisms of deterioration in desiccated organisms*.

Wisniewski, G. (1997). Drying of medicinal plants with solar energy utilisation. *Drying Technology*, (pp. 2015–2024).

Wolf, W., Spiess, W., Jung, G., & Weisser, B. (1984). The water-vapour sorption isotherms of microcrystalline cellulose and purified potato starch. results of collaborative study. *Journal of Food Engineering*, *Bd.3,1,*, 51–73.

Wongpornachi, S., Dumri, K., Jongkaewattana, S., & Siri, B. (2004). Effects of drying methods and storage time on the aroma and milling quality of rice. *Food Chemistry. s.l.: Elsevier*, *Bd.87, 3*, 407–414.

Yahya, M., Sopian, K., Daud, W., Othman, Y., & Yatim, B. (2001). Design of solar assisted dehumidification of air drying system for medicinal herbs: pegaga leaf. In *In: Proceedings of the Second Asian-Oceania Drying Conference (ADC 2001)* (pp. 383–392). Feringhi, Pulau Pinang, Malaysia.

Yamaguchi, S., Kawamura, T., Noro, Y., & Kawamura, K. (2001). Drying method of medicinal plant for the quality control of crude drugs: Numerical evaluation of surface color and comercial value. nat-med. s.l. *Scince links Japan*, *Bd.55, 3*, 139–142.

Zechini, e. a., A. (1995). Micro morphological and chemical investigation into the effects of fungal diseases on *Melissa officinalis* l, *Menta piperita L* and *salvia officinalis L. In: Journal Phytopathology*, *143*, 179–183.

Özgüven, M., Koller, D., & Range, P. (1999). Ertrags- and qualitätseigenchaften von melissa- wildsammlungen aus der südost- turkei. *Zeitschrift von Arznei und Gewürzpflanzen*, *4*, 39–43.

Öztekin, S., & Martinov, M. (2007). *Medicinal and Aromatic Crops. Harvesting, Drying and Processing*. New York: Haworth Food & Agricultural Products Press.

A Chi-square test and determination coefficient

Next the approaches used to evaluate the non-linear regressions are presented. The non-linear regressions were used for fitting the experimental data to different proposed models.

Chi-square X^2 approach:

$$X^2 = \frac{\sum_{i=1}^{n}(O_i - E_i)^2}{E_i} \tag{A.1}$$

Were O_i is observed frequency, E_i expected frequency and n number of observations.Of the lowest X^2 or those that tend to zero are considered optimal.

The criterium for a good fitting consider that values Coefficient of determination R^2 approach:

$$R^2 = \frac{SS_R}{SS_T} = 1 - \frac{SS_E}{SS_T} \tag{A.2}$$

Where SS_R is the regression sum of squares, SS_T is the total sum of squares and SS_E is he sum of squared errors.

The criterium for a good fitting consider that values of the highest R^2 or those that tend to 1, are considered optimal, and are used to determine the best model Ross (2005).

B Polynomial regression in multiobjective optimization of drying process

In the context of polynomial regression, we mean that for the particular regressors, $x_1, x_2 \ldots \; x_k$ an experiment is performed whose measured outcome Y has the form (Myers & Montgomery, 2002):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum \sum_{i<j=2}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{B.1}$$

Where the random errors ε are uncorrelated, normally distributed with zero mean and variance σ^2

In compact vector-matrix notation, the equation for a polynomial least square fit is given by:

$$y = X\beta + \epsilon \tag{B.2}$$

The least square estimator $\hat{\beta}$ of $q = k + 1$ regression coefficient β is solved by pre-multiplying by the non-singular regression matrix transpose $X‘$

$$\hat{\beta} = (X‘X)^{-1} X‘y \tag{B.3}$$

With X, $N \; x \; q$ regression matrix and y, vector of responses in N experimental runs. Finally, we are able to formulate a fitted second-order response surface model as

$$\hat{Y} = X\hat{\beta} \tag{B.4}$$

Required data analysis is rather straightforward with the applications of analysis software packages that include regression analysis computational algorithms. In multiple linear regression problems, certain tests of hypotheses about the model parameters are helpful in measuring the usefulness of the model (Myers & Montgomery, 2002). In special two tests are considered: test for individual regression coefficients and test for significance of regression. The hypotheses for testing the significance of any individual regression coefficient, say β_j , are:

$H_0 : \beta_j = 0$

$$H_1 : \beta_j \neq 0 \tag{B.5}$$

If H_0 is not rejected, then this indicates that x_j can be deleted from the model. The test statistic for this hypothesis is t_0 (T) from t-test (Myers & Montgomery, 2002). The corresponding p-value (P) can be used for hypothesis testing and, thus, reject H_0 if the p-value for the statistic t_0(or T) is less than $\alpha = 0.05$. In this case $\alpha = 0.05$. The test for significance of regression is a test to determine if there is a linear relationship between the response variable y and a subset of the regressors variables $x_1, x_2, \ldots, x_k$. The appropriate hypothesis is:

$$H_0 : \beta_1 = \beta_2 = ... = \beta_k = 0$$

$$H_1 : \beta_j \neq 0 \text{ for at least one } j \tag{B.6}$$

Rejection of H_0 implies that at least one of the regressor variables $x_1, x_2, \ldots, x_k$ contributes significantly to the model. The test procedure for H_0 is to compute the statistic F_0 (or F). The p-value (P) can be used to hypothesis testing and, thus, reject H_0 if the p-value for the statistic F_0 (or F) is less than α. In this case $\alpha = 0.05$.

Following the regression analysis for each of the responses considered in Chapter 9 are presented.

Table B.1: Regression analysis for drying time

Estimated regression coefficient for Drying time				
Term	Coef	SE-Coef	T	P
Constant	122.718	26.6664	4.602	0.002
Air drying temperat	-5.164	1,143	-4.518	0.003
Rel.Humidity	0.612	0,4508	1.357	0.217
Temperat*Temperat	0.06	0.0135	4.44	0.003
Rel.Humi*Rel.Humi	0.009	0.0034	2.633	0.034
Temperat*Rel.Humi	-0.022	0.0089	-2.508	0.041
S = 3.557	R-Sq = 96.20 %		R-Sq(adj) = 93.50 %	

Analysis of variance for Drying time						
Source	DF	Seq-SS	Adj-SS	Adj-MS	F	P
Regression	5	2256.81	2256.81	451.363	35.67	0
Linear	2	1873.52	368.73	184.364	14.57	0.003
Square	2	303.73	303.728	151.864	12	0.005
Interaction	1	79.57	79.56	79.566	6.29	0.041
Residual Error	7	88.57	88.57	12.653		
Lack-of-Fit	3	86.27	86.27	28.757	50.01	0.001
Pure Error	4	2.3	2.3	0.575		
Total	12	2345.38				

Considering the analysis of variance, the p-value (P) for the regression is lower than the significance level α (see Appendix B. That means that at least one of the regressor variables contributes significantly to the model. Additionally the p-value of the test of lack-of-fit is lower than α that means that the regression model adequately fits the experimental data.

Table B.2: Regression analysis for color difference

Estimated Regression Coefficients for Color difference				
Term	Coef	SE-Coef	T	P
Constant	71.23	20.0226	3.557	0.009
Air drying temperatur	-3,444	0.8582	-4,014	0.005
Rel.Humidity	-0.101	0.3385	-0.297	0.775
Air dryi*Air dryi	0.049	0.0101	4.829	0.002
Rel.Humi*Rel.Humi	0.003	0.0025	1.304	0.233
Air dryi*Rel.Humidity	-0.003	0.0067	-0.475	0.649
S = 2.671	R-Sq = 84.30 %		R-Sq(adj) = 73.10%	

Analysis of Variance for Color difference						
Source	DF	Seq-SS	Adj-SS	Adj-MS	F	P
Regression	5	268.42	268.42	53.68	7.53	0.01
Linear	2	97.16	122.59	61.29	8.59	0.013
Square	2	169.65	169.65	84.82	11.89	0.006
Interaction	1	1.61	1.61	1.61	0.23	0.649
Residual Error	7	49.93	49.935	7.13		
Lack-of-Fit	3	37.48	37.482	12.49	4.01	0.106
Pure Error	4	12.45	12.453	3.11		
Total	12	318.36				

Regarding the analysis of variance, the p-value (P) for the regression is lower than the significance level α. That means that at least one of the regressor variables contributes significantly to the model. Additionally the p-value of the test of lack-of-fit is close to α (see Appendix Bthat means that the regression model is acceptable to adjust the experimental data considering the value of alpha suggested.

Table B.3: Regression analysis for essential oil content

Estimated regression coefficients for essential oil content				
Term	Coef	SE-Coef	T	P
Constant	-55.8	100.11	-0.557	0.595
Air dryi*Air drying	7.26	4.29	1.69	0.135
Rel.Humi	1.5	1.693	0,889	0.404
Air dryi*Air drying	-0.11	0.051	-2.26	0.058
Rel.Humi*Rel.Humi	-0.02	0.013	-1.81	0.112
Air dryi*Rel.Hum	0.01	0.033	0.333	0.749
S = 13,35	R-Sq = 71.70 %		R-Sq(adj) = 51.50 %	

Analysis of variance for essential oil content

Source	DF	Seq-SS	Adj-SS	Adj-MS	F	P
Regression	5	3161.92	3161.92	632.38	3.55	0.065
Linear	2	1803.25	534.43	267.21	1.5	0.287
Square	2	1338.91	1338.91	669.46	3.75	0.078
Interaction	1	19.76	19.76	19.76	0.11	0.749
Residual Error	7	1248.45	1248.45	178.35		
Lack-of-Fit	3	1126.84	1126.84	375.61	12.35	0.017
Pure error	4	121.61	121.61	30.4		
Total	12	4410.37				

Regarding the analysis of variance, the p-value (P) for the regression is lower to the significance level α. That means that at least one of the regressor variables contributes significantly to the model. Additionally the p-value of the test of lack-of-fit is lower than α that means that the regression model adequately fits the experimental data.

Table B.4: Regression analysis for required energy

Estimated regression coefficients for energy

Term	Coef	SE Coef	T	P
Constant	55026.3	7935.69	6.93	0
Temperature	-1856.5	340.14	-5.45	0.001
Rel.Humidity	-194.7	134.16	-1.45	0.19
Temperature*Temperature	18.4	4.01	4.59	0.003
Rel.Humidity*Rel.Humidity	1.4	1	1.38	0.208
Temperature*Rel.Humidity	1,4	2.65	0.54	0.604
S = 1058.56	R-Sq = 93.42%		R-Sq(adj)	88.72%

Analysis of variance for energy

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	5	111329443	111329443	22265889	19,87	0,001
Linear	2	86675951	33487071	16743536	14,94	0,003
Square	2	24323040	24323040	12161520	10,85	0,007
Interaction	1	330452	330452	330452	0,29	0,604
Residual Error	7	7843875	7843875	1120554		
Lack-of-Fit	3	7341744	7341744	2447248	19,49	0,008
Pure Error	4	502130	502130	125533		
Total	12	119173317				

Regarding the analysis of variance, the p-value (P) for the regression is lower to the significance level α. That means that at least one of the regressor variables contributes significantly to the model. Additionally the p-value of the test of lack-of-fit is lower than α that means that the regression model adequately fits the experimental data.

C Regression models for quality characteristics in solar drying

Tables C.1, C.2 and C.3 present the regression analysis corresponding to drying time, color difference and essential oil content respectively. These tables give the estimated coefficients, β_0, β_j, β_{ij} along with their standard errors. In addition, a t-value that tests whether the null hypothesis of the coefficient is equal to zero and the corresponding p-values is given (Minitab-Inc, 2009)

The p-values are used to test whether the constant and slopes are equal to zero. These p-values indicate that there is sufficient evidence that the coefficients are not zero for likely Type I error rates (α levels) (Minitab-Inc, 2009). Equally **Tables** C.1, C.2 and C.3 provide the following information:

S = 0.9396. This is an estimate of σ, the estimated standard deviation about the regression line.

R-Sq = 93.7 %. This is R^2, also called the coefficient of determination.

Note that R^2 = Correlation $(Y, \widehat{Y})^2$. Also

$$R^2 = \frac{SS\ Regression}{SS\ Total} \tag{C.1}$$

The R^2 value is the proportion of variability in the Y variable

R-Sq (adj) = 91.4%. This is R^2 adjusted for degrees of freedom. If a variable is added to an equation, R^2 will get lager even if the added variable is of no real value.

$$R^2(adj) = 1 - \frac{SS\ Error/(n-p)}{SS\ Total/(n-1)} \tag{C.2}$$

Converted to a percent, where p is the number of coefficient fit in the regression equation. In the same notation, the usual R^2 is

$$R^2(adj) = 1 - \frac{SS\ Error}{SS\ Total} \tag{C.3}$$

Additionally, **Tables** C.1, C.2 and C.3 show the corresponding analysis of variance, that contains sum of squares (abbreviated SS). SS Regression is sometimes written SS (Regression β_0) and sometimes called SS Model. SS Residual error is sometimes written as SS Residual, SSE, or RSS. MS Residual error is often written as MSE. SS Total is the total sum of squares corrected for the mean. Use the analysis of variance table to assess the overall fit. The F-test is a test of the hypothesis H_0: All regression coefficients, excepting β_0, are zero (Minitab-Inc, 2009).

C.1 Drying time

In **Table** C.1 the regression analysis for drying time presented. The p-values for the constant and the coefficients of C_o, V_a, and L_d are less than 0,0005 (in the table the values are rounded to three decimal places) this indicates that there is sufficient evidence that the coefficient are not zero. For the coefficient of the interaction C_oV_a the p-value is 0.003, that is sufficiently small to evidence that the coefficient is not zero. Additionally the value of the coefficient of determination R-Sq is close to 100%, that means that there is no lack of fit. As complement, in the analysis of variance of the regression, the p-value for the F-test indicates that not all the coefficients are zero.

Table C.1: Regressions analysis for drying time

Predictor	Coef	SE Coef	T	P
Constant	18.822	1.265	14.88	0.000
C_o	-9.187	1.486	-6.18	0.000
V_a	-13.344	1.661	-8.03	0.000
$C_o \times V_a$	8.906	2.349	3.79	0.003
L_d	0.003	0.001	4.99	0
S = 0.9396	R-Sq = 93.7%		R-Sq(adj)=91.4%	

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	4	144.349	36.087	40.87	0.000
Residual Error	11	9.712	0.883		
Total	15	154.061			

C.2 Color difference

In **Table** C.2 the regression analysis for color difference presented. The p-values for the constant and the coefficient of C_o is less than 0.0005 (in the table the values are rounded to three decimal places) this indicates that there is sufficient evidence that the coefficient are not zero. For the coefficient of air velocity the p-value is 0.001 that is sufficiently small to evidence that the coefficient is not zero. Additionally the value of the coefficient of determination R-Sq is 80.2%, that means that the fit can be considered acceptable. As complement, in the analysis of variance of the regression, the p-value for the F-test (less than 0.0005) indicates that not all the coefficients are zero.

Table C.2: Regression analysis for color difference

Predictor	Coef	SE Coef	T	P
Constant	17.572	1.866	9.42	0.000
Co	6.766	1.125	6.01	0.000
Va	-11.416	2.812	-4.06	0.001

S = 2.250 R-Sq = 80.2% R-Sq(adj) = 77.20%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	2	266.53	133.27	26.32	0.000
Residual Error	13	65.81	5.06		
Total	15	332.34			

C.3 Essential oil content

In **Table** C.3 the regression analysis for essential oil content are presented. The p-value for the constant is less than 0.0005, for the coefficients of C_o and L_d are 0.001 this indicates that there is sufficient evidence that these coefficients are not zero. For the coefficient of air velocity the p-value is 0.039 that is sufficiently acceptable to evidence that the coefficient is not zero. Additionally the value of the coefficient of determination R-Sq is 79.50%, that means that the fit can be considered acceptable. As complement, in the analysis of variance of the regression, the p-value for the F-test (less than 0.0005) indicates that not all the coefficients are zero.

Table C.3: Regression analysis for essential oil content

Predictor	Coef	SE Coef	T	P
Constant	40.936	8.482	4.83	0.000
Co	-16.436	3.793	-4.33	0.001
Ld	0.019	0.004	4.64	0.001
Va	23.472	9.483	2.48	0.029

S = 7.586 R-Sq = 79.50% R-Sq(adj) = 74.30%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	3	2672.06	890.69	15.48	0.000
Residual Error	12	690.6	57.55		
Total	15	3362.66			