

International Program in Agricultural Development Studies

Master Thesis

**Study on the Roasting Kinetics and Colour
Change of Coffee Bean under Pre-roasting,
Roasting, and Over-roasting Conditions**

Daniel Pramudita

Supervisor:

Tetsuya Araki, Ph.D.

Associate Professor

International Agro-Informatics Laboratory
Department of Global Agricultural Sciences
Graduate School of Agricultural and Life Sciences
The University of Tokyo

This research is conducted in collaboration with
Ajinomoto General Foods, Inc. and
Food Kansei Communications, Corp.

and with great assistances from **Dr. Tomoaki Söma**
and **Dr. Shigeaki Ueno**

Acknowledgements

Thank you to my supervisor **Araki-sensei** for every support in all possible way, even before I came to this university. Thank you for the chance you gave to me. Thank you for the discussions, great talks, and drinking times. From you I learnt a lot, especially on how to be more cautious and try to see everything in a wider perspective. Thank you for becoming a really good friend.

Thank you to **Okada-sensei**, the man in charge of the IPADS. Thank you for all your supports and efforts to make the IPADS office our home. I still remember the very first question you asked us in the IPADS Seminar. I guess I will be asking the same question to myself in my whole life time. Thanks for your advices and choice of books for the seminar. They really made me start to think in different way. Thank you also for becoming one of my examiners together with **Nabetani-sensei**.

Next is **Sagara-sensei**. You really made me learnt a lot. It is something everyone can expect from someone with great career and experiences. I love it every time you talked about your experiences. Thank you for your offer and for involving me in the project, and also for the discussions and explanations of your idea. I learnt a lot from your philosophy of being a teacher, and I still remember your words.

Special thanks to all the researchers of the **Ajinomoto General Foods, Inc.** who are involved in the project, especially **Hashimoto-san, Imura-san, Fujii-san, and Nonaka-san**. Thank you for the chance given to me to experience and learn from the experts. I am impressed with your hospitality and support. Thank you for the discussions and assistances. Without your help I would not be able to finish conference paper. Thank you for the coffees as well. Thanks are also given to **Sōma-sensei** and **Ueno-sensei** for helping me with the experiments. Thank you for being so kind.

I also want to thank all the staffs of the International Agro-informatics Laboratory. For **Mizoguchi-sensei**, thank you for the talks, karaoke, and drinking times. I always feel happy when you invite me to drink. You made me laugh, but learn at the same time. To **Doi-sensei**, thank you for the talks and the 空芯菜 (morning glory, kangkung)! Big thanks also to **Hayashi-sensei, Niwa-san, and especially Furukane-san** who was in charge of all administrative matters. I bet I have caused you so many troubles. Thank you also to all the lectures of this department who have taught me some good lessons, especially to **Taro Takahashi-sensei** and **Kobayashi-sensei**. Thanks for the talks.

Thank you also to all member of the IAI Lab-plus: **Shinya, Yoshinori, Ryo, Yuka, Matsuyama, Sasaki-san, Yoshida-kun, Ishiwata-kun, Oscar, Sasao, Matsuki, Malika, Mito-san, Yukari, Hana-dono, Kei-chan, Kawana-chan, Keren, Ebi-chan,**

and every girl in between. Thank you for Yōjimbō, jokes, meal times, gossips, softballs, and parties! Special thanks to **Airi-san** for being a good senpai and friend who listens to me and gives advices for my worries.

Thank you to all citizens of the IPADS office: **Yinn Mar, Xie, Satoru, Mitchy, Nuwan, Chen, Nga, Ria, Sonali, Shanta, and Ogawa-senpai**. You really made my days! Thank you for the senpais for the advices and encouragement. Good luck for the kouhais! You have only one year left...

Thank you to all members of the Indonesian Student Community (**PPI-Todai**), especially those who hung out a lot with me. I cannot imagine my life in Tokyo without having you all here. Thank you for the foods, angklung, Go-gatsu-sai, and fun gatherings. Special thanks to **Rizka** for the proofreading of my thesis, **Bujed** for the sharings and encouragements during my time writing this thesis, and **Mas Andang** for being a very nice room-mate. Good luck with your new life and study. Thanks also to friends of ARC Academy and Toshima Church.

All my achievements would not be possible if there were no assistances from the INPEX Scholarship Foundation and Raya Finance. Thank you for this chance and trust. Thank you for **Sasa-san** and **Ito-san** who always support me in many ways. Thank you for the understanding and all Japanese lessons you gave me. I really enjoyed them.

Of course there have been so great supports from all my dearests in Indonesia. It is going to be so long if I mention all of you, and I have mentioned your names in my bachelor thesis, so you can refer to it. You all know better than anyone how much I feel grateful for your loves and supports.

Finally, thank you to **Jesus Christ** for being my best friend that never leaves me despite the fact that I left You so many times. You know everything better than I do.

I cannot express all my gratitude here. It really took longer to write this than the summary. I feel so grateful for everything I have learnt during my master study in this university. It was actually far from what I imagined and expected, but I got a lot of things I never thought I would. If a university is the 'universe' where people learn, then I learnt everything I could. I tried some things I never tried, and learnt many new ways of doing things. Not all of them were the best, but maybe they have become the biggest lessons in my life. In the end I just realised how stupid we are all, but the humility of everyone here has really impressed me and helped me to improve myself more and more.

I hope this research can be a good contribution to the study.

Regards,
Daniel Pramudita

Contents

Acknowledgements	ii
Contents.....	iv
List of Figures	vii
List of Tables.....	ix
Nomenclature	x
Summary	xiii
Chapter I: Introduction	1
1.1. Coffee roasting.....	2
1.1.1. Phenomena occurring during the process	3
1.1.1.1. Maillard reactions	4
1.1.1.2. Strecker degradation	5
1.1.1.3. Degradation of trigonelline.....	6
1.1.1.4. Reactions of other acids.....	6
1.1.1.5. Decreases in solid mass and moisture content.....	6
1.1.1.6. Bean swelling	6
1.1.2. Cooling	7
1.1.3. Roast degree based on colour	7
1.1.4. Types of coffee roaster	9
1.1.5. Attempts to control the process and product's quality	10
1.2. Studies on effects of roasting condition.....	11
1.3. Objectives of the study	14
1.4. Outline of this thesis	14
Chapter II: Overview of Coffee	16
2.1. About coffee plant	16
2.1.1. Early history of coffee	16
2.1.2. Species and varieties.....	16
2.1.2.1. Arabica coffee.....	16
2.1.2.2. Robusta coffee	17
2.1.2.3. Liberian coffee.....	17

2.1.2.4. Other species	18
2.1.2.5. Some hybrids and mutants	19
2.1.3. Bean.....	19
2.1.4. Cultivation.....	20
2.1.4.1. Soil and climatic requirements.....	20
2.1.4.2. Propagation	21
2.1.4.3. Post-planting treatments.....	21
2.1.5. Harvesting	22
2.1.6. Postharvest handling	22
2.1.6.1. Drying and peeling.....	22
2.1.6.2. Hulling (and polishing)	23
2.1.6.3. Bean sortation.....	25
2.2. Production of coffee beverages.....	25
2.2.1. Blending	25
2.2.2. Roasting.....	25
2.2.3. Grinding	26
2.2.4. Brewing	26
2.2.4.1. Decoction methods.....	27
2.2.4.2. Infusion	27
2.2.4.3. Pressure methods.....	27
2.2.5. Soluble coffee making.....	27
2.3. World coffee trade.....	28
2.4. Effects of coffee on health	31
Chapter III: Study of Coffee Roasting under Various Temperature Conditions	33
3.1. Background and objectives	33
3.2. Material and methods	34
3.2.1. The coffee bean	34
3.2.2. Experimental oven.....	34
3.2.3. Measurement of initial moisture content.....	37
3.2.4. Measurement of bean dimension and density	38
3.2.5. Investigation on dehydration process of roasting.....	39
3.2.6. Roasting experiments at different temperatures.....	41

3.3. Results and Discussion	41
3.3.1. Measurement of initial moisture content	41
3.3.2. Measurement of bean dimension and density	42
3.3.3. Investigation on dehydration process of roasting	43
3.3.4. Roasting experiments at different temperatures	44
3.4. Conclusions.....	52
Chapter IV: Colour Change during Roasting	53
4.1. Background and objectives.....	53
4.2. Materials and methods	54
4.3. Results and discussion	55
4.4. Conclusions.....	62
Chapter V: Measurement of Specific Heat Capacity Using Differential Scanning Calorimetry	63
5.1. Background and objectives.....	63
5.2. Theory of Differential Scanning Calorimetry.....	63
5.3. Materials and methods	66
5.4. Results and discussion	68
5.5. Conclusions.....	75
Chapter VI: Towards Modelling of Heat and Mass Transfer in Roasting	76
6.1. Background and objectives	76
6.2. Review on previous works.....	76
6.3. Development of the heat and mass transfer model of current study.....	79
6.3.1. Heat balance.....	79
6.3.2. Mass transfer: moisture diffusion from the bean.....	81
6.3.3. Determination of coefficients and dimensionless numbers	82
6.3.4. Results and discussion	85
6.4. Possible measures to improve modelling of coffee roasting	89
Chapter VII: Conclusions and Future Perspectives	90
References	92
Appendix 1. VBA Codes of Bezier Spline.....	107

List of Figures

Fig. 1-1.	Popular roasts of coffee	8
Fig. 1-2.	Outline of this thesis	15
Fig. 2-1.	Structure of coffee berry and beans	19
Fig. 2-2.	Illustration of some terms used for coffee fruit and bean	24
Fig. 2-3.	Flowchart of production of coffee beverages	26
Fig. 2-4.	Share of world coffee production in 2011	29
Fig. 2-5.	Coffee productions of Indonesia and Vietnam from 1991 to 2011	29
Fig. 2-6.	Coffee supplies of Indonesia and Vietnam from 2000 to 2009	30
Fig. 2-7.	Share of world coffee consumption in 2011	30
Fig. 3-1.	Appearance of the experimental oven.....	35
Fig. 3-2.	Schematic diagram of the experimental oven and measurement system..	36
Fig. 3-3.	Thermometric points by using thermocouples during drying and roasting experiments	36
Fig. 3-4.	Periods of drying illustrated in a characteristic drying curve	38
Fig. 3-5.	Illustration of an ellipsoid	39
Fig. 3-6.	Change in bean components during roasting	40
Fig. 3-7.	Characteristic drying curve of coffee beans dried at 105 °C for 24 h.....	42
Fig. 3-8.	Characteristic dehydration and roasting curves of coffee.....	43
Fig. 3-9.	Change in bean volume at different roasting temperature	45
Fig. 3-10.	Kinetics of coffee bean mass during 24 h of roasting.....	46
Fig. 3-11.	The roast loss for the first hour of roasting at different temperatures	48
Fig. 3-12.	Gradient, of linear regression line of roasting time-loss relationship as function of roasting temperature	48
Fig. 3-13.	Characteristic dehydration and roasting curves of coffee at 140°C.....	49
Fig. 3-14.	Characteristic dehydration and roasting curves of coffee at 180°C.....	50
Fig. 3-15.	Characteristic dehydration and roasting curves of coffee at 220°C.....	50
Fig. 3-16.	Characteristic dehydration and roasting curves of coffee at 260°C.....	51
Fig. 3-17.	Characteristic dehydration and roasting curves of coffee at 300°C	51
Fig. 4-1.	Beans were ground using the electric grinder of a coffee maker.....	54
Fig. 4-2.	Handy spectrophotometer NF-333 (Nippon Denshoku, Ind. Co. Ltd.)	55

Fig. 4-3.	The CIE Lab colour space	55
Fig. 4-4.	Bean colour change during roasting	56
Fig. 4-5.	Change in bean lightness (L^*) as a function of roasting time	57
Fig. 4-6.	Colour data of coffee beans of all roasting temperatures plotted into 3D diagram	58
Fig. 4-7.	Characteristic colouring curve in a L^* , a^* , b^* coordinate system	58
Fig. 4-8.	Parabolic relationships found between L^* and a^* & b^*	59
Fig. 4-9.	Relationship between a^* and b^* in coffee roasting	60
Fig. 4-10.	Relationship between lightness value and hue angle	60
Fig. 4-11.	Relationship between L^* and roast loss at various roasting temperatures	62
Fig. 5-1.	Schematic illustration of the DSC	64
Fig. 5-2.	Specific heat determination by measurements of heat differences	66
Fig. 5-3.	Differential scanning calorimeter (Shimadzu DSC-50)	67
Fig. 5-4.	Specific heat capacity of α -alumina	67
Fig. 5-5.	Two types of data of the DSC measurement on green coffee bean	68
Fig. 5-6.	Change in bean mass during the DSC measurement.....	69
Fig. 5-7.	TGA spectra of sets of coffee samples.....	69
Fig. 5-8.	a. Change in apparent specific heat capacity; and b. Heat difference during the DSC measurement.....	71
Fig. 5-9.	Modulated Differential Scanning Calorimetry (MDSC) spectra of coffee samples, with scanning rate of 5 °C/min.....	72
Fig. 5-10.	Estimated bean temperature at roasting temperature 240 °C and 300 °C .	73
Fig. 6-1.	Changes in temperature and moisture of bean roasted at 140 °C.....	86
Fig. 6-2.	Changes in temperature and moisture of bean roasted at 180 °C.....	86
Fig. 6-3.	Changes in temperature and moisture of bean roasted at 220 °C.....	87
Fig. 6-4.	Changes in temperature and moisture of bean roasted at 260 °C.....	87
Fig. 6-5.	Changes in temperature and moisture of bean roasted at 300 °C.....	88

List of Tables

Table 1-1. SCAA Colour Classification.....	9
Table 2-1. Botanical characteristics of <i>C. arabica</i> (Arabica) and <i>C. canephora</i> (Robusta).....	18
Table 2-2. Chemical composition of green bean.....	20
Table 2-3. Defect count for sun-dried (natural) coffee	24
Table 3-1. Data of coffee bean used for experiment	34
Table 3-2. Sampling time for each roasting temperature	41
Table 3-3. Physical properties of Arabica coffee beans (Colombia excelso)	43

Nomenclature

Chapter 3

X = dry basis moisture content

m_w = mass of wet bean (kg)

m_d = mass of dried bean (kg)

R_w = drying rate ($\text{kg}^{-1} \text{s}^{-1}$)

m_n = mass of bean at time $t = t_n$ (kg)

t_n = time (s)

V_b = bean volume (m^3)

A_b = bean surface area (m^2)

L_1 = bean longest length (m)

L_2 = bean second longest length (m)

L_3 = bean shortest length (m)

C_t = concentration of material C at time t

m_{Ct} = mass of material C at time t (kg)

m_{s0} = initial mass of bean total solid (kg)

RL = roast loss

m_{gb} = mass of green bean (kg)

m_{rb} = mass of roasted bean (kg)

T_r = roasting temperature ($^{\circ}\text{C}$)

t = time (s)

Chapter 4

L^* = CIELab lightness value (0–100)

a^* = CIELab green-red value (-50–50)

b^* = CIELab blue-yellow value (-50–50)

h_{ab} = hue ($^{\circ}$)

RL = roast loss

Chapter 5

dq/dt = heat flux ($J s^{-1}$)

C_{p_a} = specific heat capacity of the reference material a ($J kg^{-1} K^{-1}$)

C_{p_b} = specific heat capacity of the investigated sample b ($J kg^{-1} K^{-1}$)

m_a = mass of the reference material a (kg)

m_b = mass of the investigated sample b (kg)

h_a = heat flow difference between the reference material a and the empty cell ($J s^{-1} kg^{-1}$)

h_b = heat flow difference between the investigated sample b and the empty cell ($J s^{-1} kg^{-1}$)

T_a = temperature of α -alumina ($^{\circ}C$)

T_b = bean temperature ($^{\circ}C$)

X = dry basis moisture content

C_{p_s} = specific heat capacity of bean solid ($J kg^{-1} K^{-1}$)

Chapter 6

Q_{conv} = heat received through convection ($J s^{-1}$)

Q_{rad} = heat received through radiation ($J s^{-1}$)

Q_{react} = heat resulted from chemical reactions ($J s^{-1}$)

\dot{Q}_r = heat resulted from reactions per kg dry ($J s^{-1} kg^{-1}$)

r_b = bean radius (m)

T_b = average temperature of bean (K)

T_a = temperature of roasting air (K)

h_{conv} = effective heat transfer coefficient of convection ($J s^{-1} m^{-2} K^{-1}$)

T_w = temperature of heating oven wall (K)

σ = Stefan-Boltzmann constant ($5.670373 \times 10^{-8} W m^{-2} K^{-4}$)

ε = bean emissivity

m_s = mass of bean solid (kg)

f_A = Arrhenius equation prefactor times the amount of heat generated per unit amount of reaction ($J s^{-1} kg^{-1}$)

H_a = activation energy ($J mol^{-1}$)

R = the perfect-gas-law constant ($8.341 J mol^{-1} K^{-1}$)

H_e = accumulated heat produced per kg dry at the current time ($J kg^{-1}$)

H_{et} = the total amount of reaction heat produced per kg dry ($J\ kg^{-1}$)
 C_{pb} = specific heat capacity of bean ($J\ kg^{-1}\ K^{-1}$)
 L_{vap} = latent heat of water evaporation ($J\ kg^{-1}$),
 X = dry basis moisture content of bean
 t = time (s)
 r_1 = distance of position 1, which is the sphere radius (m)
 N_{A1} = flux of diffusing gas A at surface of sphere ($kg\ m^{-2}\ s^{-1}$)
 D_{AB} = diffusivity of gas A inside gas B ($m^2\ s^{-1}$)
 c_{A1} = concentration of gas A at position 1, r_1 ($kg\ m^{-3}$)
 c_{A2} = concentration of gas A at position 2 ($kg\ m^{-3}$)
 P = total pressure ($N\ m^{-2}$)
 P_{BM} = log mean inert partial pressure of B ($N\ m^{-2}$)
 N_{wb} = flux of diffusing moisture ($kg\ m^{-2}\ s^{-1}$)
 D_{wb} = diffusivity of moisture inside the bean ($m^2\ s^{-1}$)
 c_w = moisture concentration ($kg\ m^{-3}$)
 c_{we} = equilibrium moisture concentration, equal to zero ($kg\ m^{-3}$)
 X = dry basis moisture content
 h_a = convective heat transfer coefficient of the roasting air ($J\ s^{-1}\ m^{-2}\ K^{-1}$)
 k_a = heat conductivity of the roasting air ($J\ s^{-1}\ m^{-1}\ K^{-1}$)
 k_b = heat conductivity of the bean ($J\ s^{-1}\ m^{-1}\ K^{-1}$)
 ρ_b = bean density ($kg\ m^{-3}$)
 Bi = Biot number
 T_s = temperature of bean surface (K)
 Nu = Nusselt number
 Gr = Grashof number
 Pr = Prandtl number
 V_b = bean volume (m^3)
 r_b = bean radius (m)
 d_b = bean diameter (m)

Study on Roasting Kinetics and Colour Change of Coffee Bean under Pre-roasting, Roasting, and Over-roasting Conditions

Laboratory of International Agro-informatics : Daniel Pramudita

Supervisor : Tetsuya Araki

The flavour and aroma of coffee created during roasting are determined by the paths of chemical reactions. Roasting can be divided into three stages: pre-roasting stage (including drying) at less than 150-160 °C, roasting at more than 150-160 °C, and over-roasting. Mostly constant roasting temperature is employed, but the use of stepwise temperature settings in industry and studies is also found. Since each setting uses different combinations of temperature and retention time, the effects of retaining coffee beans at certain temperature for a certain time must be deeply understood to design an optimum design of roasting condition. A matrix of time and temperature can be used in designing the research experiments. The objectives of this study are: (1) to measure changes in mass fractions and colour during roasting at different temperatures covering pre-roasting and over-roasting condition for elucidating the effects of roasting temperature and time on the coffee beans, (2) to investigate the relationships among roasting parameters for predicting their changes during the process, and (3) to look toward the possibility of modelling the heat and mass transfer during coffee roasting.

Materials and methods

Colombia coffee beans (Arabica) were used in experiments. Initial properties of bean were measured and used as the basis for analyses. The experiments were carried out using an oven developed to continuously measure the changes in mass and temperatures. The temperature near the bean layer was used as the roasting temperature. Several constant temperatures ranging from 140 to 300 °C were employed to investigate pre-roasting and over-roasting conditions. To obtain the samples for measurement of bean dimension, moisture content and colour, the roasting experiments were repeated from the beginning up to certain time periods for each temperature.

Results and discussion

The reduction in solid mass that indicates the start of roasting reactions was found to start before the water evaporation completely finishes. A large gap in mass fraction during roasting between the samples roasted at 220 °C and those roasted at 260 °C indicates more intense reactions of chemical compounds and oil migrations at higher roasting temperatures. The fact that the fractions of solid that could transform to

volatiles are smaller at lower temperatures than at the higher ones proved that roasting reactions require certain ranges of temperature to start, not only the activation energy.

Kinetics of coffee roasting has been shown to have a two-stage phenomenon (see Fig. 1). The changes in rate were found to happen at different conditions of roast loss for different roasting temperatures. The relationship between roast loss and roasting time at the first stage could be assumed linear and the slope was determined by the roasting temperature.

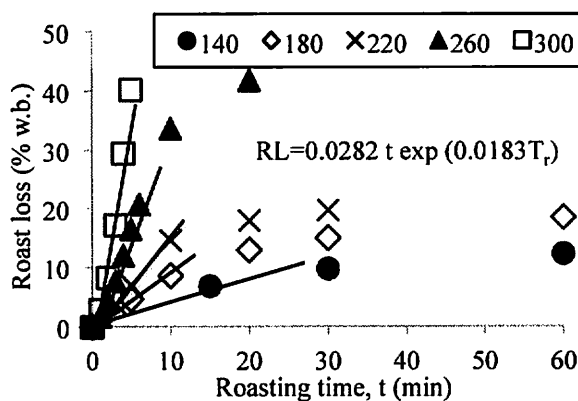


Fig. 1. Roasting kinetics at various temperatures

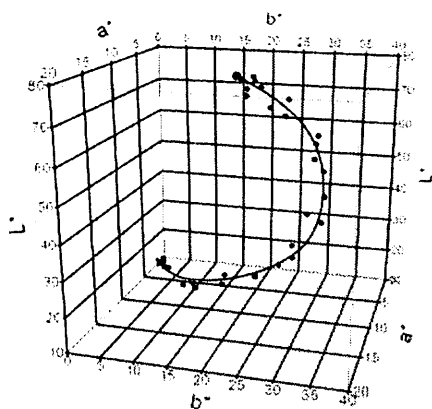


Fig. 2. Characteristic colouring curve

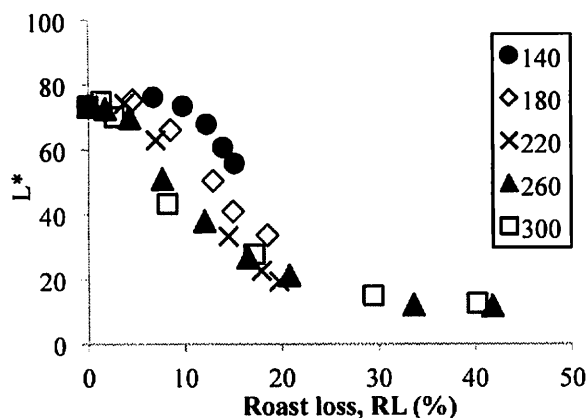


Fig. 3. Relationship between L* and RL

Changes in bean colour were found to follow a certain path (Fig. 2) called the characteristic colouring curve, regardless of roasting temperature. The curve might be used for determining the relationship among colour parameters. By relating the colour and roast loss data (Fig. 3) it was confirmed that compound profiles of roasted coffee beans cannot be determined only from the colour-based roasting degree, as the roasting temperature affects how fast bean colour changes relatively to the change in mass.

In modelling of heat and mass transfer of coffee roasting, the coefficients of heat and mass transfer really affect the performance of a model, and thus should be measured accurately. Assumptions used to make modelling easier can actually limit the predicting ability and the accuracy of the model. Even seemingly right assumptions may cause some underestimations and overestimations that may have counterbalanced each other in a seemingly accurate model. A segmentation of the whole process is suggested rather than the use of an all-round estimation in measurement and modelling.

Chapter I

Introduction

Coffee is known as one of the most popular beverages in the world. It is popular for its unique flavour and aroma. For some people, drinking one or more cups of coffee every day is a must, as if it is a ritual. The reasons vary among people; some drink coffee mostly because of the flavour and aroma, some do because of the stimulant effect it has thanks to the caffeine, and some do because of health-related benefits. Personal preferences of coffee are often associated with the thickness of flavour, variety (Robusta or Arabica), origins, or its servings (espresso, latte, sugary, etc.).

A common knowledge is a good cup of coffee needs an excellent touch of the hand of a coffee barista. Not many of coffee drinkers really understand how the beans are processed and why the processing is important. To understand such things, enough knowledge of what is happening inside coffee beans during processing or coffee making is required. With a good understanding of the process, obviously one can improve how the coffee should be prepared and get the best coffee with desired flavour and aroma. In fact, most practice are based only on experiences: 'This coffee was made of beans of a variety, roasted by them at a certain roaster temperature for some time, and brewed using this machine. The taste and aroma is good, then that's the best way to make a coffee'.

Roasting is the first process in coffee bean processing. Arguably only few people know that unroasted green coffee beans have totally different aroma compared to the coffee beverages consumed widely. The aroma of green coffee bean is mild, green, more bean-like (Naidu, *et al.*, 2008). Roasting is the process where the flavour and aroma of coffee beverages are developed (Eggers & Pietsch, 2001). Typical flavour and aroma of coffee beverages are first created inside the bean through series of chemical reactions. Compounds arising from the reactions also bring out many positive biological activities of the coffee brew (Daglia, *et al.*, 2008). Antioxidant capacity of coffee product is determined by roasting more than by the brewing methods or even the bean varieties (Sacchetti, *et al.*, 2009).

Roasting is therefore a very crucial step, if not the most, in the chain of coffee production. Thus, understanding more deeply about roasting is very important for getting the best out of the beans. So far the practises of coffee roasting have been so experiment and experience-based. As aforementioned, good flavour and aroma are often associated with certain coffee cultivars. Some coffees are popular while some are not, and this in fact has brought some disparity among production areas. That kind of assumption is not totally wrong, but actually misleading because it is how the beans are roasted that will determine the final quality. Improvement on the process may help bring out the potential inside a coffee bean, and so even the coffees that have been regarded as low quality may have a better value.

1.1. Coffee roasting

Roasting can be divided into three stages, which are pre-roasting stage (including drying) at less than 150-160 °C, roasting at higher than 150-160 °C, and over-roasting. The shifting temperature to roasting stage and the starting point of formation of volatile organic compounds (VOCs) differ for different varieties of coffee, despite the same temperature roasting profile applied (Gloess, *et al.*, 2014). Over-roasting is defined as a state where the exothermic reactions responsible of flavour and aroma generation are reduced and the beans begin to burn (Hernández, *et al.*, 2007).

Flavour, weight loss, and other quality parameters of roasted coffee are roasting path-dependent (Yeretzian, *et al.*, 2002), as evidenced by variation in weight loss behaviour (Franca, *et al.*, 2009). Roasting temperature, time, and air speed affect the organoleptic properties of coffee (Summa, *et al.*, 2007), as well as the intensity and relative composition of components of different coffee varieties (Gloess, *et al.*, 2014). For example, slow roasting forms more pyridines, while medium and fast roasting forms more ketones (Petisca, *et al.*, 2013). Intensified roasting has been found to decrease caffeine content and antioxidant potential of coffee (Hečimović, *et al.*, 2011).

It is difficult, if not impossible, to judge which one is better: to roast at relatively lower temperature but for longer time (LTLT), or to roast at high temperature for shorter time (HTST). Headspace intensity in HTST roasting is found higher, which

means stronger aroma, than that of LTLT (Gloess, *et al.*, 2014). However, it does not guarantee better quality because the aroma is determined by the composition of volatiles. Zhou, *et al.* (2013) argued that, from nutritional point of view, roasting at lower temperature for longer time has been said better compared to that of higher temperature and shorter time as more phospholipids are preserved. However, the temperatures used in the study ranged only from 200 to 235 °C.

The most popular coffees: Arabica and Robusta coffees have different flavour characteristics upon roasting. Arabica coffee is characterised by its mild and acid flavour, whereas Robusta has full and bitter flavour (Leino, *et al.*, 1991; Charrier & Eskes, 2004). Originally Arabica has less caffeine contained in green bean than Robusta. However, some reports have found Arabica as roasted or instant coffee to have greater amount of caffeine than Robusta (Wasserman, 1992; Oestreich-Janzen, 2010). Arabica coffee has some aroma similar to cocoa and brown sugar, whereas Robusta coffee aroma is more papery, earthy, and burnt (Leino, *et al.*, 1991). Robusta coffee has been found to have higher overall content of total phenols and individual classes of polyphenols than Arabica coffee does (Hečimović, *et al.*, 2011).

From the above illustration, it is clear that the most suitable roasting condition depends on the desired product types, properties and quality. Moreover, the production of coffee beverages does not stop at roasting and the following steps will affect the quality parameters (Bhumiratana, *et al.*, 2011). The desired product characteristics then depend on the target market of the products. In designing product quality, a deep understanding of the phenomena occurring during roasting is necessary.

1.1.1. Phenomena occurring during the process

Change in flavour and aroma come from a series of chemical reactions and physical phenomena take place. They are Maillard reactions, Stecker degradation, breakdown of amino acids, degradations of trigonelline, phenolic acids, quinic acid, carotenoid, pigments and lipids, and reactions of intermediate products (Holscher & Steinhart, 1992; Reineccius, 1995; Buffo & Cardelli-Freire, 2004; Ribeiro, *et al.*, 2009). Physical structure and properties of the bean also change due to the reactions

(Schenker, *et al.*, 2000; Pittia, *et al.*, 2001; Eggers & Pietsch, 2002). Some of the phenomena are explained briefly here.

1.1.1.1. Maillard reactions

Maillard reactions or non-enzymatic browning are the reactions of free amino acids with reducing sugar (Oestreich-Janzen, 2010). Sugars and amino groups react and the reaction leads to the so-called Amadori product that then degrades into breakdown products (Martins, *et al.*, 2001). The reactions produced several pyrazines (Gloess, *et al.*, 2014). The reactions can be divided into three stages (reviewed in de Oliveira, *et al.*, 2014). The early stage is marked by initial glycosylation reaction. The advanced stage begins when the Amadori product degrades. The final stage leads to the formation of nitrogenous polymers and melanoidins. Attempts have been made to clearly understand the mechanisms and reaction pathways of Maillard reactions. Multi-response modelling, a tool to model complicated, consecutive and parallel reactions, has been found powerful in dealing with Maillard reactions (Martins, *et al.*, 2001).

Change in bean colour during roasting is governed by the advanced and final stages (de Oliveira, *et al.*, 2014). Flavour chemicals are dominated by the Maillard reaction products (MRPs) that are heterocyclic compounds containing nitrogen (Moon & Shibamoto, 2009), thus the MRPs can be used as flavour enhancer (Eric, *et al.*, 2013). They also influence the antioxidant activity of the product (Liu & Kitts, 2011). However, the antioxidant activity may reach its peak while the browning is still continuing (Morales & Jiménez-Pérez, 2001). Furthermore, since Maillard reactions also help the formation of acrylamide, attempting to increase the antioxidant capacity of coffee can result in higher acrylamide content (Summa, *et al.*, 2006). Fortunately, acrylamide content inside the bean itself has been found to decrease with the roasting time (Bagdonaitė, *et al.*, 2008).

Melanoidins, the end-product of Maillard reactions, are brown nitrogenous chromophores responsible for colour change (Martins & van

Boekel, 2005). They contribute to the acidity found in roasted coffee (Bekedam, 2008) and contain roasting induced-antioxidants that are formed upon roasting (Bekedam, *et al.*, 2008a). Proteins and chlorogenic acids are the main substances primarily involved in melanoidin formation (Bekedam, *et al.*, 2008b). The exact formation and structure of melanoidins are still not understood (Bekedam, 2008). It has been shown that some reactions other than the Maillard reactions are involved in the formation of melanoidins (Bekedam, 2008; Bekedam, *et al.*, 2008b). The structures of melanoidin vary depends on the composition of polysaccharides, amino acids, proteins, and phenolic compounds found in coffee (Moreira, *et al.*, 2012; Langner & Rzeski, 2014). Thus, it is possible that no melanoidin molecule is alike (Bekedam, 2008).

Just like other compounds, melanoidins in coffee can be classified based on their molecular weight: low, intermediate, and high molecular weight. Bekedam, *et al.* (2008b) pointed out that intermediate molecular weight (IMw) material might contain more protein-based melanoidin structures whereas the high molecular weight (HMw) material might contain more carbohydrate-based melanoidin structures. They found that roasting coffee bean to light roast results in more IMw melanoidins than HMw melanoidins. However, continuous increase in the density of brown-coloured structures upon roasting was found only in HMw material, and the melanoidins in HMw material of coffee accumulate when roasting is intensified. Level of low molecular weight (LMw) melanoidins seems to remain unchanged during the roasting process.

1.1.1.2. Strecker degradation

Strecker degradation is a process in which α -amino acids reacts with carbonyl compound and degrades to aldehydes and ketones (Schönberg & Moubacher, 1951). In coffee roasting it leads to formations of pyrazines and oxazoles (Oestreich-Janzen, 2010). Its products also play some role in formation of melanoidins (Martins & van Boekel, 2005).

1.1.1.3. Degradation of trigonelline

Trigonelline and its derivatives contribute to the aroma perception of roasted beans and brewed coffee beverages (Oestreich-Janzen, 2010). They are found higher in *C. arabica* than in other coffee species (Wasserman, 2002). Pyridines found in roasted coffee are mainly resulted from the degradation trigonelline (Gloess, *et al.*, 2014).

1.1.1.4. Reactions of other acids

Chlorogenic acids and quinic acids form chlorogenic lactones that increase the bitter taste of coffee (Ginz & Engelhardt, 2001; Farah, *et al.*, 2005). Total soluble solids and chlorogenic acids have been found higher at higher roasting temperature (Nagaraju, *et al.*, 1999). Chlorogenic acids also transform into gas, thus the real consumption of chlorogenic acids should be evaluated more carefully (Dutra, *et al.*, 2001). Four aliphatic acids resulted from carbohydrate degradation (mainly degradation of sucrose) during roasting: formic, acetic, glycolic and lactic acids contribute greatly to the acidity of coffee. However, their secondary reactions with other components do not contribute at all to acid formation (Ginz, *et al.*, 2000).

1.1.1.5. Decreases in solid mass and moisture content

Bean mass decreases due to the release of moisture and some gaseous compounds as result of reactions of solid compounds (Schenker, *et al.*, 2000), mainly the carbohydrates in form of polysaccharides. During roasting the structure of insoluble polysaccharides changes and they become more easily extractable (Oosterveld, *et al.*, 2003). In most of practices, the final moisture content of bean is about 2% when the roasting is ended (Eggers & Pietsch, 2001). Changes in moisture content and density during coffee roasting have been found to mainly contribute to changes in mechanical properties of the beans (Jokanovic, *et al.*, 2012; Pittia, *et al.*, 2011).

1.1.1.6. Bean swelling

Size of beans gets bigger during roasting process. The gases and

evaporated moisture entrapped in cells build up internal pressure and cause bean to swell and pop (crack), and thus making bean pores bigger. Moisture and the compounds leave the bean through the pores. The bean expansion has been found uniform in all directions (Hernández, *et al.*, 2008a). At higher temperature, the volume of bean, pores and micropores in cell walls are higher (Schenker, *et al.*, 2000). Bean porosity may increase up to about 8 times after roasting. Cracks during roasting occur more in outer regions of the bean and in area between mucilage and parenchyma (Pittia, *et al.*, 2011).

1.1.2. Cooling

Beans are unloaded and cooled after the desired roasting degree has been reached. The roasted bean can be cooled by blowing cool air onto them and agitating them or by water quenching. Quenching gives higher cooling speed, but it may potentially quicken the loss of freshness attributes of coffee, due to higher thiol oxidation rates caused by different evolution of dimethyl trisulfide in roasted beans with higher moisture content (Baggenstoss, *et al.*, 2007).

1.1.3. Roast degree based on colour

In common industrial practise, roast degrees ('roast type' or just 'roast') are usually determined based on the surface colour. In most studies on coffee, term "roasting degree" is more commonly used. The National Coffee Association of the United States of America (NCAUSA, <http://www.ncausa.org/>) gives a classification of roasting type based on colour. They are (from the less coloured to the dark coloured):

a. Light roasts: *Light City, Half City, Cinnamon, New England*

The coffee has light brown colour and acid but mild taste. Original taste of the coffee regional (variety) can be recognised more easily. At this roast level, migration of oil to bean surface has yet to happen.

b. Medium roasts: *City, American, Breakfast*

The term American roast is often generalised to all medium roasts. The characteristics of medium roasts are similar to that of light roasts, except the stronger roasted flavour and bigger bean size. At medium roast, newly formed

volatiles are found the most. Their intensities decrease as the roasting continues (Yeretzian, *et al.*, 2002).

c. Medium-dark roasts: *Full City*

The beans are dark coloured. They have rich taste and a bittersweet aftertaste. Some oil is found on the surface.

d. Dark roasts: *High, Continental, New Orleans, European, Vienna, Espresso, French, Italian, Spanish*

The colour is shiny black due to much oil on the surface. The taste is bitterer but less acid compared to medium-dark roast. The regional flavours are far less expressed here compared to medium roasting (Bhumiratana, *et al.*, 2011).

Other classifications are also used by companies in the determination of roast degree. Agron roast colour classification (Agron Inc., <http://www.agtron.net/>) created in collaboration with the Specialty Coffee Association of America (SCAA, <https://www.scaa.org/>), for example, has been used in some studies (Ferraz, *et al.*, 2010; Petisca, *et al.*, 2013). Combined with the ColorTrack Coffee Color Selector (Coffee Laboratory, <http://www.coffeelabequipment.com/>), the classifications are compiled in Table 1-1.



Fig. 1-1. Popular roasts of coffee (Winston, *et al.*, 2005)

Table 1-1. SCAA Colour Classification

SCAA description	ColorTrack	Agtron	L*
Very light	30	95	58<
Light	15–19	85	51–57
Moderately Light	20–25	75	45–50
Light medium	26–40	65	41–45
Medium	41–50	55	36–40
Moderately dark	51–60	45	26–35
Dark	61–70	35	18–25
Very dark	71–80	25	<18

1.1.4. Types of coffee roaster

Types of roasting can be divided based on the bean flow to batch process and continuous process. However, mostly found roasters are continuous roaster. In most practices, roaster is heated up until the temperatures of air and drum walls reach the desired, then after that beans are loaded into the roaster (Bottazzi, *et al.*, 2012). If the heat source is hot air, relative mass of coffee beans and roasting air determine the temperature and time required for roasting process. However, since volume of air is critical for oxidation, the free radical content of the final product is also affected (Goodman, *et al.*, 2011). Energy use in roasting can be made more efficient by employing a recirculation scheme, where the air coming out from the roaster (which is still hot) is reheated and recirculated (Bottazzi, *et al.*, 2012).

There have been many technologies developed for roasting. Conventional roasting uses a rotating drum where bean and hot gases mix. Another variation is rotating-bowl roaster where a bowl rotating in vertical axis is used instead of drum (Schwartzberg, 2002; Schenker, 2000). The temperature of inlet gas must be very high (compared to the modern processes) so that the required time will not be long (Eggers & Pietsch, 2001). The uniformity of roast is often low, and mechanical agitation is needed to minimise this disadvantage.

Better heat transfer can be achieved by using fluidised bed roaster (Eggers &

Pietsch, 2001). In this roaster, beans are fluidised and kept floating simultaneously by high velocity hot gas. The better heat transfer that can be achieved allows lower roasting temperature and shorter roasting time (Eggers & Pietsch, 2001; Basile & Kikic, 2009; Fabbri, *et al.*, 2011). Since effect of thermal treatment during roasting has been found positive in reducing ochratoxin A concentration, a dangerous toxin produced by *Aspergillus ochraceus* that often contaminates foods (Oliveira, *et al.*, 2013), roasting with high external heat transfer has been found very effective in reducing ochratoxin A (Ferraz, *et al.*, 2010). Other advantages are high uniformity of roasting and no mechanical agitation needed (Eggers & Pietsch, 2001). The roaster requires a minimum flow velocity to make sure the beans are fluidised. The theoretical minimum velocity is influenced by roasting temperature and bed height.

The mechanism of fluidised bed roasting is improved in spouted bed roaster and packed bed roaster. In the spouted bed roaster the beans are not fluidised equally, but punched through the bed by spouted gas and transported to the top of the bed. This roaster increases heat transfer but reduces uniformity compared to fluidised bed roaster. Air velocity must be kept not only above the minimum one needed to punch the bed, but also below a maximum one to avoid full fluidisation. The spouted bed roaster is suitable for medium or small batch roasting (Eggers & Pietsch, 2001; Nagaraju, *et al.*, 1997). Packed bed roaster combines the advantages of both common fluidised bed roaster and spouted bed roaster. It uses conical chamber that allow very high fluidisation speed thus removing the limitation of spouted bed roaster. Roasting gas enters the roaster tangentially and the bed rotates in vertical axis due to centrifugal force (Eggers & Pietsch, 2001).

1.1.5. Attempts to control the process and product's quality

The main requirements of a promising control system are accuracy, possibility of on-line measurement and control, and reproducibility. On-line measurement of temperature is not an easy task in the real roasting situation, as too many factors may affect the measurement.

A classic attempt to control coffee roasting is by monitoring the temperatures.

Temperature sensors are commonly found in industrial and home roasters, and how the temperatures change can be controlled as desired using thermostats. However, the term 'bean temperature' and 'roasting temperature' have not been well defined as different definitions were used in studies. Furthermore, different sizes and types of roaster will give different results.

A prediction model of caffeine content and roasting colour using near infrared spectroscopy that is combined with powerful wavelength selection method has been reported (Pizarro, *et al.*, 2007). Near infrared spectroscopy has also been utilised for predicting roasting degree based on weight loss, moisture content and density (Alessandrini, *et al.*, 2008), and the result showed good accuracy when compared to the conventional analyses. Variance of free radical dynamics in different types of coffee bean has been confirmed by a real time monitoring system that utilises electron paramagnetic resonance spectroscopy (Goodman, *et al.*, 2011). The SAFES (systematic approach to food engineering systems) technique has been applied to coffee roasting and claimed useful to predict all changes in the product (Fito, *et al.*, 2007). Dutra, *et al.* (2001) confirmed that degree of roast can be determined by monitoring the composition and pH of exhaust gas.

1.2. Studies on effects of roasting condition

As aforementioned, roasting plays an important role in coffee production because it creates the flavour and aroma of coffee via chemical reactions. Several studies have been conducted on changes in chemical composition during roasting. For example, Oosterveld, *et al.* (2003) studied the effect of roasting on carbohydrate composition of Arabica coffee, comparing light, medium and dark roasting. Contents of various volatiles affected by roasting condition have been measured by Moon & Shibamoto (2009). Kinetics of ochratoxin A during roasting at several temperatures ranging from 180 to 240 °C and different roast levels have been measured by Ferraz, *et al.* (2010) and Oliveira, *et al.* (2013). Hečimović, *et al.* (2011) measured the polyphenols and caffeine content in different coffee varieties of different roasting degree, while Mills, *et al.* (2013) compared chlorogenic acid content of differently processed commercial

coffees. Zhou, *et al.* (2013) investigated changes in individual phospholipids in coffee beans roasted at 220, 225 and 235 °C. Effects of roasting time on sensory profile and formation of furans and other volatiles in ground roasted and espresso coffees have also been studied (Petisca, *et al.*, 2013; Bicho, *et al.*, 2014).

Beside the chemical compounds, the physical properties and structure changes of coffee beans undergoing roasting have also been studied. Pittia, *et al.* (2001) conducted a study on textural changes in beans roasted at 170 and 200 °C, and in beans roasted in a so called 'high yield cycle' (at 240 °C for 4 min followed by 190 °C for 16 min). Drying temperatures (90 and 105 °C) were also employed to observe the effects of only moisture reduction. Similar study was conducted on two Brazilian coffee samples roasted at 170 °C for 40 min (Jokanovic, *et al.*, 2012). Mendonça, *et al.* (2009) investigated the effect of bean defects on physical characterisation of Arabica and Robusta coffees before and upon roasting at 200 °C. Defective beans have been found smaller and the colour is different compared to non-defective ones. Type of defects also affects the chemical and physical attributes of beans roasted at 200 °C (Franca, *et al.*, 2005). Schenker, *et al.* (2000) investigated the structure of bean pores resulted from two roasting conditions used to produce relatively same products. The first one is called low-temperature long-time process (LTLT) as the beans were roasted at 220 °C of hot air temperature for 540–720 s, whereas the second one is called high-temperature short-time process (HTST), at 260 °C for 155–180 s.

Use of stepwise temperature setting in roasting as seen in the 'high yield cycle' in Pitia, *et al.* (2001) is actually something that is commonly found in coffee industry. Some studies also employed such inconstant roasting temperatures. For example, Schenker (2000) used four combinations of temperature setting in his Ph.D. dissertation. Companies usually have their own temperature settings that are employed for different coffee products. Mostly, determination of the temperature settings is experimental, trial and error-based, even though the effects of each trial were carefully noted. So far there is no clear and disclosed scientific basis of the settings. Since each setting uses different combinations of temperature and retention time, the effects (and their magnitudes) of retaining coffee beans at certain temperature for a certain time

must be deeply understood to design an optimum design of roasting condition.

From the given examples, one can notice that most of the studies used narrow ranges of roasting time and temperature variations. It is difficult to refer to or compare among results of the studies, despite the fact that the variables studied may relate one to another and thus bring a deeper insight to coffee roasting. The variables of observation in a study are usually few, as researchers tend to focus on few process phenomena. Therefore, in conducting a study on roasting a broader range of roasting condition is preferable not only for the elucidation of the process but also for supporting the whole learning process.

The standards used for defining the roasting levels and conditions were different. Oosterveld, *et al.* (2003), for example, determined the degree of roasting by the weight loss: 11% for light, 15% for medium, and 22% for dark roast. Yeretjian, *et al.* (2002) determined the roasting degrees based on the time needed to roast beans with the input air temperature set at 185 °C. Use of colour as a basis of roast degree determination is also common in some studies (see also section 1.1.3). However, the conditions used to define the degrees of roast (light, medium, dark, etc.) differed one to another, even when the same colorimeters were used. Rather than using the 'not commonly accepted' names of roasting degree, using physical parameters is obviously more reliable in conducting a study.

A comprehensive investigation that can clearly help understand the effects of roasting time and temperature variations is therefore expected. How fast bean temperature increase, or the time spent by the beans at certain temperature range, has been shown to affect the flavour of beans of same roast level (Lyman, *et al.*, 2003). However, the mechanism and influences of temperature and time condition are not clear yet. If the effects of roasting temperature and speed on the bean quality can be elucidated, roasting condition can be designed optimally based on the desired product quality. Nguyen, *et al.* (2013) used a matrix of time and temperature in designing experiment to find the optimum roasting temperature for Vietnamese Robusta. The same approach can be used to investigate more comprehensively the effects of roasting temperature and time to the bean quality. In current study, the investigations are first

focused on the influences of roasting time and temperature on roasting kinetics and change in colour. Considering the time limitation of the master course, other analyses such as chemical compound analysis and sensory analysis were not included in this study.

As aforementioned, the final goal of the investigations on coffee roasting is obviously a better control of the process so that it may result in the product with expected quality. A model that takes into account the phenomena in coffee roasting as many as possible can be a great tool for process control. However, it takes time to really understand the whole phenomena, while the need of process control cannot wait. Since roasting is a thermal process, thus the basic model that can be developed is the model of heat and mass transfer, which is so far has been delivered in some studies. It will be great if one can combine the phenomena of heat and mass transfer and the phenomena of chemical process. Due to the absence of other chemical analyses, in this study we could only discuss the development of heat and mass transfer model in coffee roasting.

1.3. Objectives of the study

The objectives of this study are:

- a. To measure changes in mass fractions and colour during roasting at different temperatures covering pre-roasting and over-roasting condition and elucidate the effects of roasting temperature and time on the coffee beans.
- b. To investigate the relationships among roasting parameters for predicting their changes during the process.
- c. To look toward the possibility of modelling the heat and mass transfer during coffee roasting.

1.4. Outline of this thesis

This thesis consists of seven chapters. Chapter I introduces the main topic of the research. A brief review of the background and the objectives of this research are presented. Chapter II gives an overview of coffee production. It covers the history of coffee, the basic knowledge on the agronomy of coffee beans, and the common

production methods of the beverages. Some information of coffee production and consumptions are also given. The main part of the research is divided into two sections, which are the effects of roasting conditions (time and temperature) in Chapter III and IV, and the efforts to model the heat and mass transfer in coffee roasting process (Chapter V and VI). Chapter III covers the design of the experiments, preliminary experiments, and the basic investigations of effects of various roasting temperature on coffee beans. Chapter IV discusses the effects of roasting temperature on change in bean colour, which is an important parameter of coffee roasting. The relationships among the colour parameters and some other roasting related parameters are also discussed. Chapter V presents the use of differential scanning calorimetry to measure specific heats and to elucidate the phenomena that occur inside the bean due to thermal process. In Chapter VI, the efforts to model heat and mass transfer coffee roasting are discussed, along with the drawbacks and possibilities. Chapter VII summarises all the findings of the research and brings out the conclusions. It also gives future challenges and prospective research continuations.

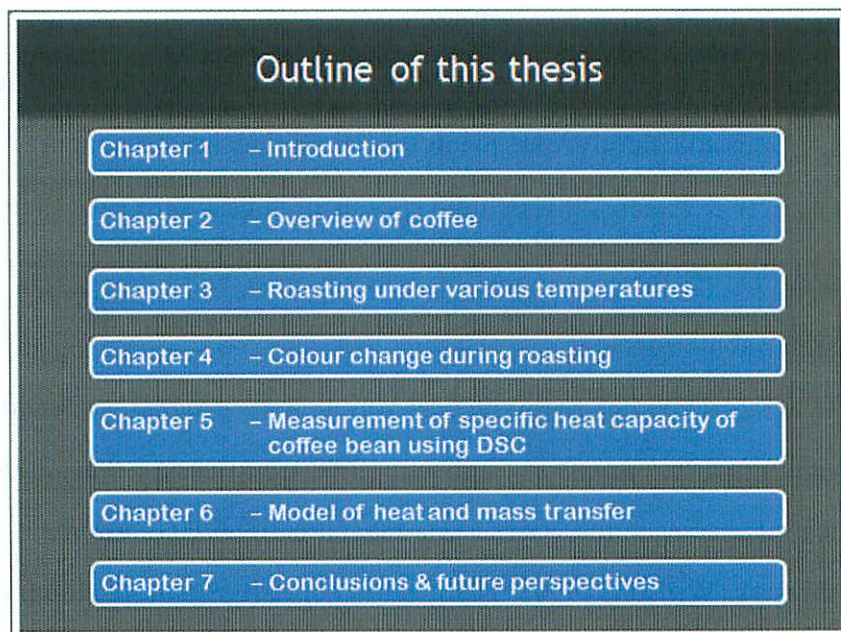


Fig. 1-2. Outline of this thesis

Chapter II

Overview of Coffee

2.1. About coffee plant

2.1.1. Early history of coffee

Coffee plant most likely originated in Africa and Madagascar, with the history of coffee is believed to start from coffee growing in Ethiopia and Yemen. The Arab people became the first consumers of roasted coffee; giving it the name Arabica (*Coffea arabica*). The beverage spread throughout the world since beginning of the 17th century (Oestreich-Janzen, 2010; <http://www.ico.org/>, 2014). Robusta coffee (*Coffea robusta*) was discovered later in the 18th century. Its name came from its robustness against diseases and adaptive traits (Oestreich-Janzen, 2010), compared to the previous species (Arabica). Right now, of the genus *Coffea* only, more than a hundred coffee species have been discovered (Davis, *et al.*, 2006).

2.1.2. Species and varieties

The term coffee tree refers to every plant of the Rubiaceae family that produces coffee beans. Under the family, the plants are classified into 2 genera: *Coffea* and *Psilanthus* (Charrier & Eskes, 2004). Some species of coffee trees (and their varieties) are described in this section.

2.1.2.1. Arabica coffee

C. arabica has two botanical varieties: *C. arabica* var. *arabica* (a.k.a. var *typica*) and var. *bourbon* (Willson, 1999; Charrier & Eskes, 2004). Unlike the most of species in the genus *Coffea* that are diploid, *C. arabica* is tetraploid, with $2n = 44$ (Willson, 1999). The plant is normally small, attaining a height of 15 to 18 feet (Keable, 1923). It can actually grow to about 15 m height, but usually it is pruned for commercial purpose. The leaves are fresh green colour and glossy with well-marked veins, and borne in pairs at each node. The main stem is orthotropic, thus branching is induced by cutting the stem. Branches

grow at 90° in var. *arabica* and 55° in var. *bourbon* (Willson, 1999). Up to 20 flowers can grow in each axil, and the flower initiation is not affected by day length (Cannell, 1985). The fruits are dark crimson when ripening, and each fruit contain two seeds (Keable, 1923), with length of 8-13 mm (Willson, 1999).

2.1.2.2. Robusta coffee

The Robusta coffee plant (*C. canephora*) is diploid ($2n = 22$), just like most of coffee species are. In many ways it is similar to *C. arabica*, although its sizes are larger (Willson, 1999; Keable, 1923). Up to 80 flowers per node can be borne on first year lateral branches (van der Vossen, 1985). The Robusta coffee plants can be classified into two main groups: Guinean and Congolese based on their isozyme profiles (Charrier & Estes, 2004). As mentioned earlier, most cultivars of *C. canephora* has great resistances to coffee rust and coffee berry disease, compared to *C. arabica*. Table 2-1 concludes a botanical comparison between *C. arabica* and *C. canephora*.

2.1.2.3. Liberian coffee

Liberian coffee (*C. liberica*) originated from Liberia and other parts of the west coast of Africa, from Sierra Leone to Angola. The species was discovered before the *C. robusta*, and gained importance in West Africa and South East Asia during the early years (Eskes & Leroy, 2004). However, since the taste is considered to be poor compared to Arabica and Robusta, it lost its popularity and its market share is now really small, with the production is mainly for local use (Willson, 1999). Its taste is closer to Robusta than Arabica (Keable, 1923; <http://ecocrop.fao.org/ecocrop/srv/en/cropView?id=751>).

Liberian coffee is now largely found Southeast Asia countries like Philippines, Malaysia, and Indonesia. Its plant is bigger than those of Arabica and Robusta coffees, as it can grow up to 17–20 m. The berries are also comparatively large. The pulp is tougher than *C. arabica*, thus it requires the use of special machines in its postharvest handling (Keable, 1923).

Table 2-1. Botanical characteristics of *C. arabica* (Arabica) and *C. canephora* (Robusta) (<http://www.ico.org/>, 2014)

	Arabica	Robusta
Date species described	1753	1895
Chromosomes (2n)	44	22
Time from flower to ripe cherry	9 months	10-11 months
Flowering	after rain	irregular
Ripe cherries	fall	stay
Yield (kg beans/ha)	1500–3000	2300–4000
Root system	deep	shallow
Optimum temperature (yearly average)	15–24° C	24–30° C
Optimal rainfall	1500–2000 mm	2000–3000 mm
Optimum altitude	1000–2000 m	0–700 m
Resistance to diseases		
Hemileia vastatrix	susceptible	resistant
Koleroga	susceptible	tolerant
Nematodes	susceptible	resistant
Tracheomycosis	resistant	susceptible
Coffee berry disease	susceptible	resistant
Shape of bean	flat	oval
Body	average 1.2%	average 2.0%

2.1.2.4. Other species

Some other species are *C. excelsa*, which originated from Africa but was also introduced in Trinidad & Tobago, the Sierra Leone coffee (*C. stenophylla*) (Keable, 1923), *C. congensis*, *C. humilis*, *C. eugenioides* (Charrier & Eskes, 2004), *C. zanguebariae*, *Mascarocoffea* (Charrier & Berthaud, 1985), and many more.

2.1.2.5. Some hybrids and mutants

Hybridisation has been practiced to improve the quality of coffee plant. For examples, hybridisation of *C. canephora* with *C. congensis* produced the Congusta or Conuga, *C. canephora* and *C. arabica* gave Arla, whereas that of *C. liberica* and *C. arabica* resulted in Kalimas and Kawisari in Indonesia. Some other noted hybrids are Devamachy and S795 family (from India), Hibrido de Timor (Timor), and C387 (Brazil). Some mutant coffee varieties have also been known, i.e. mocha and purpurascens from *C. canephora*, and caturra, laurina (var. *bourbon*) and maragogype (var. *typica*) from *C. arabica* (Willson, 1999; Charrier & Eskes, 2004).

2.1.3. Bean

Components of coffee fruit (and bean) are illustrated in Fig. 2-1. The most outer part is the fruit skin (exocarp). Below the skin is the fruit pulp, which makes 40-42% of the total weight of the fruit. It can be utilised as an ingredient of animal feed (Cleves, 2004). Just below the pulp there is a slippery and semi-transparent layer of mucilage called pectin layer. Next is parchment (endocarp) that covers the bean. Between the parchment and the bean (endosperm) there is a thin layer of skin (spermoderm) called silver-skin. Usually it still remains on the bean surface after the postharvest processing.

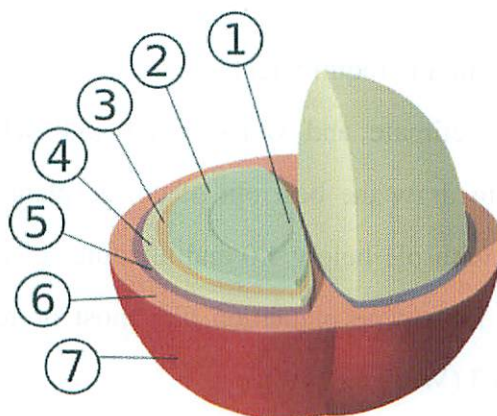


Fig. 2-1. Structure of coffee berry and beans (Wikipedia, 2007)

1. centre cut, 2. bean (endosperm), 3. silver skin (testa, epidermis), 4. parchment (hull, endocarp), 5. pectin layer, 6. pulp (mesocarp), 7. outer skin (pericarp, exocarp).

Table 2-2. Chemical composition of green bean (Farah, 2012)

Component	Concentration (g/100 g)	
	Arabica	Robusta
Sucrose	6.0–9.0	0.9–4.0
Reducing sugars	0.1	0.4
Polysaccharides	34–44	48.0–55.0
Lignin	3.0	3.0
Pectin	2.0	2.0
Protein	10–11	11–15
Free amino acids	0.5	0.8–1.0
Caffeine	0.9–1.3	1.5–2.5
Trigonelline	0.6–0.2	0.6–0.7
Coffee oil	15–17	7–10
Diterpenes	0.5–1.2	0.2–0.8
Minerals	3.0–4.2	4.4–4.5
Chlorogenic acids	4.1–7.9	6.1–11.3
Aliphatic acids	1.0	1.0
Quinic acids	0.4	0.4

2.1.4. Cultivation

2.1.4.1. Soil and climatic requirements

Hot-moist climate and well-drained soil rich in nutrients are two elements needed to draw the best out of coffee plants (Keable, 1923). Even though acid soils with pH below 4.0 and alkaline soils with pH up to 8.0 can still be exploited for coffee plantation, the most preferable is soils with pH between 5.2 and 6.3 (Willson, 1999).

C. arabica grows best on tropical highlands (600–1500 m above sea level) like commonly found in Brazil, whereas *C. canephora* is more adapted to tropical lowlands (0–800 m) (Charrier & Eskes, 2004) which are common in

Vietnam and Indonesia. The required rainfall is about 1400–2000 mm per year for Arabica and 2000–2500 mm per year for Robusta (Descroix & Snoeck, 2004). Optimum temperature for Arabica ranges from 15 to 24 °C, whereas for Robusta it is 22–30 °C (Willson, 1999; Descroix & Snoeck, 2004).

2.1.4.2. Propagation

Coffee can be propagated by seed propagation, which is the cheapest and easiest method, or vegetatively by grafting, stem-cutting, or *in-vitro* propagation, depending on the coffee species and the goals of the project. In propagation by seed, seeds can be sown in a nursery or directly in the field. In nursery, seedlings can be raised in beds, plastic sleeves, or polybags. Vegetative propagation is usually used only when plants that conform to the mother plant cannot be produced by seed propagation. Even though it is more complicated, it allows exploitation of genetic heterozygotic material, thus is helpful in plant selection (Wintgens & Zamarripa, 2004; Willson, 1999).

The young plants are transplanted to a permanent plantation after they have grown to one or two feet high (Keable, 1923). Arabica coffee is usually planted at a higher density (1350 tree/ha) than Robusta (1000 tree/ha). Presence of cover crops or intercropping practice, as well as other technical considerations must be taken into account when deciding the planting distance (Wilson, 1999).

2.1.4.3. Post-planting treatments

After the seedlings have been planted, some measures are needed to make sure the plants grow well. Fertilisers are given in dosages depending on the cultivar and the level of nutrients contained in the soil (Wintgens & Zamarripa, 2004). In dry season, early irrigation stimulates strong vegetative growth. Since coffee plants originated from forest area, where the plants were under shade, such condition must be recreated in the plantation. Leguminous are usually used to provide the shading (Willson, 1999). Coffees with good quality like Blue Mountain coffee of Jamaica and some Brazilian coffees were

said to need no shading (Keable, 1923).

Weeding, and pest and disease control are other important issues, as in such plantation area weeds grow vigorously and pests come easily. Pests commonly found in coffee trees are leaf miners, caterpillars, bugs, nematodes, and mites; whereas the common diseases are leaf rust brown eye spot, and coffee berry disease, which mostly attack Arabica coffees (Wilson, 1999). Weeds that grow only during raining season are less harmful to the plants, compared to perennial weeds (Lambot & Bouharmont, 2004). Mulching can help prevent weed growth, reduce soil moisture loss, and increase the organic matters in the top-soils. It can also serve as an erosion control measure (Descroix & Wintgens, 2004).

In coffee farming, the most important operation is most likely pruning. Without pruning the tree will continue growing, only few (if no) braches will grow, and the number of fruits will be limited. Scheduled pruning helps remove diseased and over-age woods. Open environment that allows light and air to reach all parts of the tree can also be maintained. Besides, pruned crop is space-saving and more easily harvestable (Willson, 1999).

2.1.5. Harvesting

Coffee fruits can be harvested when their colour turns dark crimson, indicating they are ripe. Harvesting is usually done manually by hands of labours that are also called pickers (Keable, 1923). Use of harvesting machine has been introduced since 1967, although is still limited to big plantations (Willson, 1999). The cherries can be harvested selectively of non-selectively. In selective harvesting, only ripe cherries are picked from the trees, whereas in non-selective harvesting, also called stripping or milking, all cherries are removed and later sorted to separate damaged and unripe fruits (Brando, 2004; Clarke, 1985).

2.1.6. Postharvest handling

2.1.6.1. Drying and peeling

Once the coffee cherries are harvested and sorted, the beans must be

separated from the fruit pulp and dried to avoid an uncontrolled fermentation of mucilage. The type of processing method of whether the fruit is dried together with the beans will determine the flavour characteristics of the coffee (Leloup, *et al.*, 2004; <http://www.casabrazilcoffees.com/learn/processing/>, 2014).

A processing method where the fruit is dried together with the bean before separation is called *dry method*, with the drying process usually lasts for 3–9 days (Oestreich-Janzen, 2010). Because the fruit is already dry, it can be peeled from the bean easily through mechanical separation only. The flavour tends to be sweet and full bodied. If not carried out carefully, dry method may result in a higher risk of defects.

The other method where the fruit is peeled from the bean before drying is called *wet method*. Since the cherry is still wet, normal mechanical separation cannot really remove the whole fruit, especially the slippery mucilage (pectin layer). Fermentation is the common way of overcoming this problem. During the process, it is only the mucilage that gets fermented. Fermentation in a water basin can last from 15 hours up to 3 days, depending on how much pectin layer remaining on the surface of bean's parchment. The fermentation may bring out variations in aroma and flavour (Mazzafera & Purcino, 2004), depending on the variety. Wet method yields coffees with less body, higher acidity, and more aroma than the dry method (Mazzafera & Purcino, 2004).

Another type is *semi-dry processing*, which comprises components of the dry and wet processes (Teixera, *et al.*, 2005). It gives a coffee with intermediate body (Duarte, *et al.*, 2010).

2.1.6.2. Hulling (and polishing)

Hulling is an operation where parchment shell is removed from dried coffee bean (Clarke, 1985). A number of different hulling machines are available. Many are based on the original Smout peeler, which uses long rotating screw. Polishing after hulling is also practiced in some plantations to remove the silver-skin (Brando, 2004).

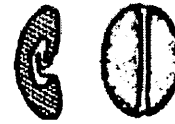
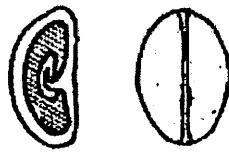
DRIED COFFEE CHERRY**PARCHMENT COFFEE****GREEN COFFEE**

Fig. 2-2. Illustration of some terms used for coffee fruit and bean (Brando, 2004)

Table 2-3. Defect count for sun-dried (natural) coffee

Type of defect	Defect count
1 black bean	1
2 sour or rancid beans	1
2 beans in parchment	1
1 cherry	1
1 large husk	1
2-3 small husks	1
3 shells	1
1 large stone/earth clod	5
1 medium-sized stone/earth clod	2
1 small stone/earth clod	1
1 large stick	5
1 medium-sized stick	2
1 small stick	1
5 broken beans	1
5 green or immature beans	1
5 insect damaged beans	1

2.1.6.3. Bean sortation

Green beans are sorted before they are packed and shipped. Sortation is usually based on the shape of bean (half-elliptical or rounded), size, colour, density, and presence of defects (Brando, 2004). Mostly sortation is done using sorting machines. In the last step where beans with defects are separated, the job is handled by some labours trained specially. Basically coffee is classified based on the target markets. First class beans are usually half-elliptical, heavy, and non-defective.

Based on the latest edition of Coffee Exporter's Guide (International Trade Centre, 2011), beans are classified based on the defect count (see Table 2-3).

2.2. Production of coffee beverages

Production of coffee beverage includes a series of processes, and the route of production depends on what kind of product desired. Complete production chain starting from green bean is given in Fig. 2-3.

2.2.1. Blending

The first step is coffee blending. Here, some varieties of coffee beans are blended with a certain composition based on a recipe of the producer. The varieties used can be one or more, depending on the desired flavour. After the beans are blended, they are roasted at a set roasting condition. The order of these 2 processes can be in opposite, depends on producer experience and preference. Mixing the beans after roasting can be a good way since optimal roasting conditions for different bean varieties are different (Sunarhanum, *et al.*, 2014).

2.2.2. Roasting

As previously explained in Chapter 1, coffee beans are roasted to bring out the desired flavour and aroma of coffee beverages.

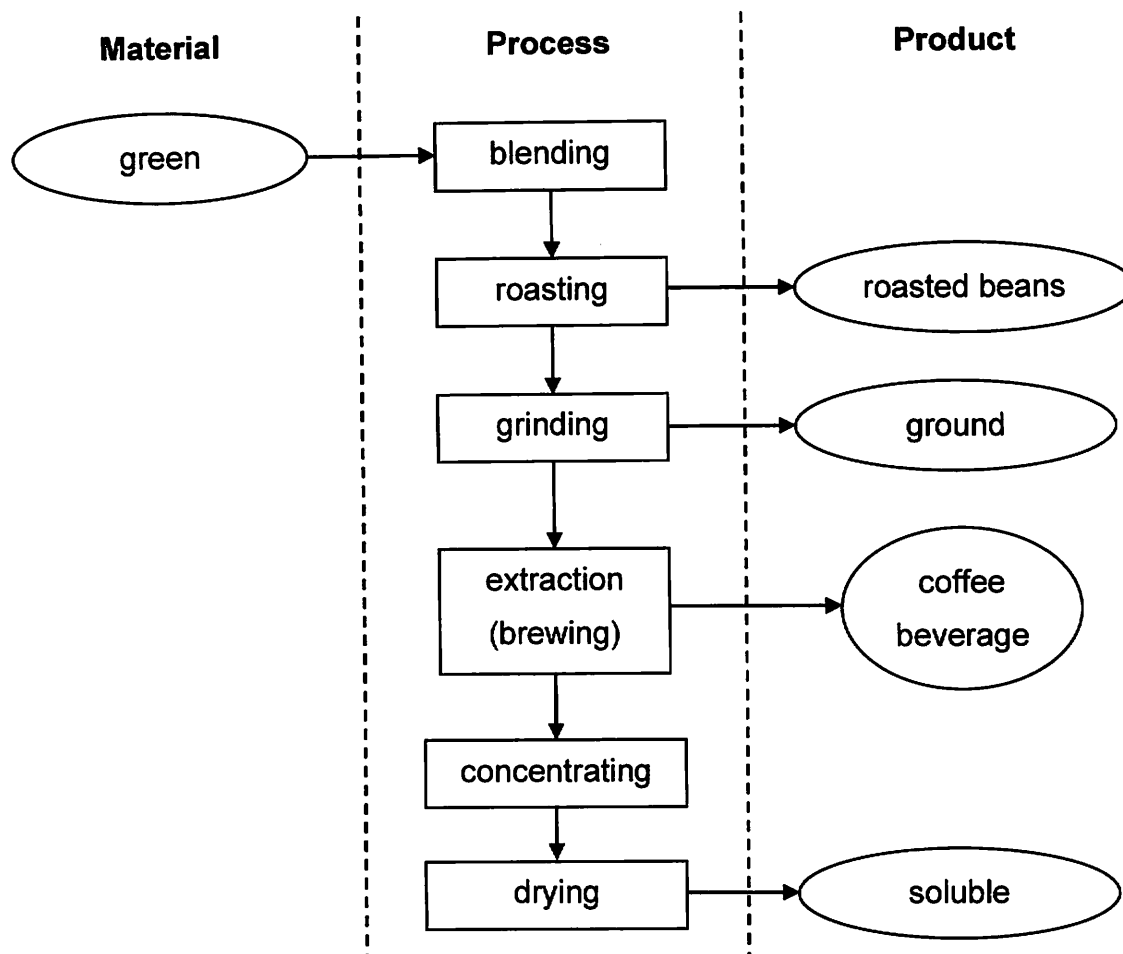


Fig. 2-3. Flowchart of production of coffee beverages

2.2.3. Grinding

The next step right after roasting is grinding. Fineness of ground coffee should be controlled based on the desired flavour and aroma. If the grind is too fine the coffee will have bitter taste and the low volume due to over extraction during brewing. In opposite, too coarse grind will decrease the extractable flavour due to lesser surface area, and result in a weak and bland brew (Andueza, *et al.*, 2003). Coarse particle has been found to help lower the concentration of ochratoxin A (Oliveira, *et al.*, 2013). The ground beans can be packaged directly and sold as ground bean products for home consumption.

2.2.4. Brewing

For liquid coffee products such as canned coffee beverages, coffee liquid is extracted from the ground beans, on which the process is called brewing. Different

aroma profiles of coffee origins are easily noticeable due to lower concentration of aromatic compounds (Bhumiratana, *et al.*, 2011). After brewing the extracted coffee liquid can be mixed with milk, sugar, or other additives as desired, before finally packaged and distributed as liquid coffee product.

There are a number of brewing methods, as given by Petracco (2001):

2.2.4.1. Decoction methods

Used in the making of boiled, Turkish, percolator, & vacuum coffees, decoction methods involve continuous contact of soluble solid and water at a certain temperature and for a certain time, for allowing the soluble to concentrate in the liquid. Higher temperature gives higher extraction rate and yield. Boiling water before brewing results in much better taste due to less volatile loss.

2.2.4.2. Infusion

Ground beans (coarse grind is preferred) are soaked in hot (not boiling) for a time period before filtering. The resulted flavour is milder, with more acid and rich. Infusion method is applied in the making of filter coffee and *Napoletana* coffee.

2.2.4.3. Pressure methods

In these methods, pressure and heat are applied on the beans and fluid percolates through the pores of ground coffee bed. Common applications are espresso, French press (using plunger), and moka.

2.2.5. Soluble coffee making

The extracted coffee liquid is concentrated and dried to make soluble coffee (powdered instant coffee), before packaged and released to the market. Common drying methods used in the industry are spray drying (result in powder or granules) and freeze drying (granules only). The instant coffee products obviously have higher solubility than ground coffee.

2.3. World coffee trade

Some people have been estimating of how many cups of coffee are consumed per day. In overall, at least hundred millions of cups are consumed every day (Daviron & Ponte, 2005; Bond, 2011). Coffee has been an international commodity for hundreds of year, since the 17th century (Willson, 1999). It is now the most widely traded tropical agricultural commodity, with total exports estimated at US\$ 15.4 billion in 2009/2010 (ICO, 2014).

The world coffee trade is governed by a main intergovernmental organisation called the International Coffee Organization (ICO), where exporting and importing governments gather to overcome the challenges facing world coffee industry and market (<http://www.ico.org/>, 2014). About 94% of world coffee production and over 75% of world coffee consumption are represented by the organisation's member governments. Its members per 2013 include 39 exporting members and 6 importing members (27 Europe Union countries are together regarded as one member under the EU).

At first the ICO was formed in 1962 to prevent the coffee price from falling to low through the establishment of the first International Coffee Agreement (ICA) (Willson, 1999). Attempts to control the international coffee trade have actually been made since the beginning of the 20th century (Daviron & Ponte, 2005). To control the coffee price, the ICO set a range of price within which all deliveries of coffee should be sold, and nowadays it publishes the ICO daily indicator price. After several collapses in the agreements, in 2007 the ICO released its 7th and latest ICA that serves as a legal framework of the organisation's activities. It emphasises on developing small and medium scale coffee producers by providing fund and access of information, encouraging research and training, as well as enhancing the market reach and transparency (<http://www.ico.org/>, 2014).

Several countries like Brazil, Vietnam, Indonesia, and Colombia are well-known as world's main coffee producers (see Fig. 2-4). Brazil shares almost one third of the world production (FAOSTAT, 2014), with Arabica coffees as its main commodity (Willson, 1999). Vietnam has taken the second position from Indonesia in last 15 years,

establishing the country as the world largest producer of Robusta coffees (Fig. 2-5). However, the total coffee consumption of Vietnam is still far below that of Indonesia (Fig. 2-6), indicating the production is mostly intended for export. Shares of Robusta coffees in world production fluctuated in about 30% in last 50 years, with the trend increasing in last 20 years (Daviron & Ponte, 2005).

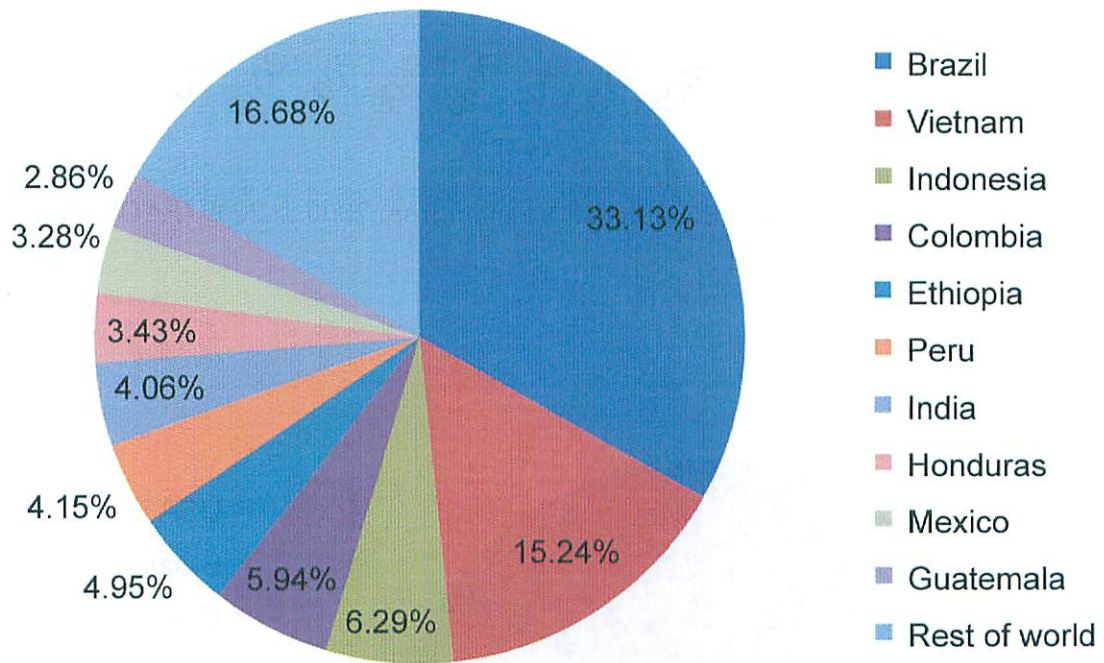


Fig. 2-4. Share of world coffee production in 2011 (FAOSTAT, 2014)

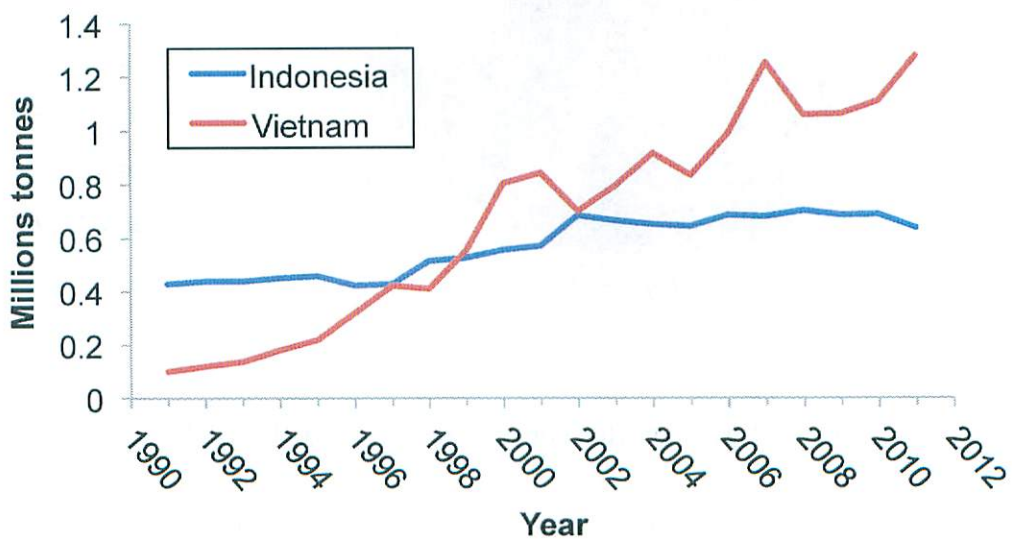


Fig. 2-5. Coffee productions of Indonesia and Vietnam from 1991 to 2011 (FAOSTAT, 2014)

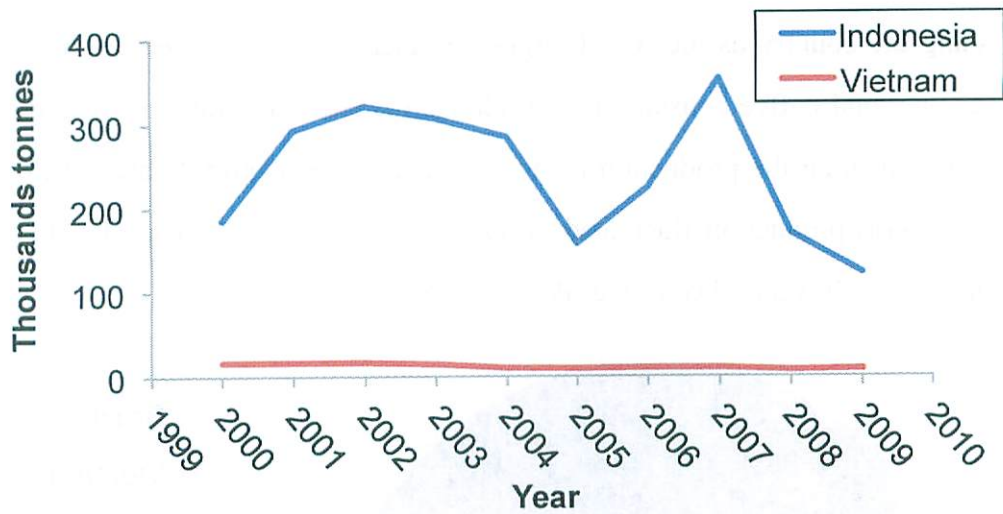


Fig. 2-6. Coffee supplies of Indonesia and Vietnam from 2000 to 2009 (FAOSTAT, 2014)

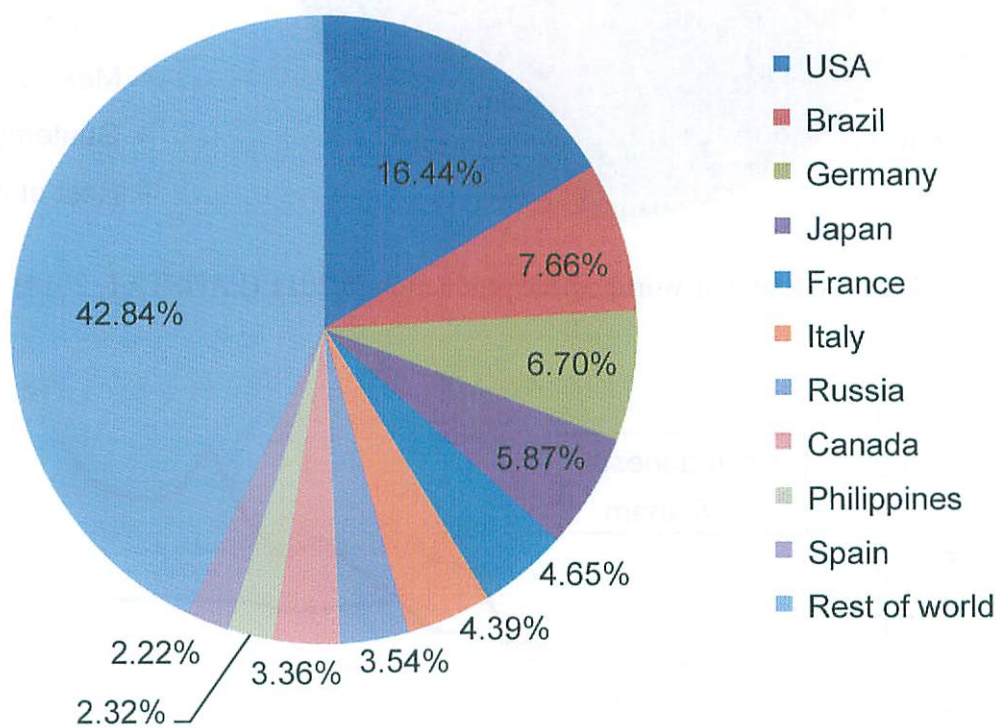


Fig. 2-7. Share of world coffee consumption in 2011 (FAOSTAT, 2014)

While southern hemisphere countries dominate the coffee production, the majority of coffee consumers are northern hemisphere countries (Daviron & Ponte, 2005). Leading consumers of coffee are the USA, Brazil, Germany, Japan, and France

(Fig. 2-7). Brazil is a major exception of top producers that is also one of the main consumers, while most of the top consumers are not producers.

2.4. Effects of coffee on health

Coffee is often claimed to be beneficial for health. The potentially healthy effects are largely influenced by the choice of variety (Mills, *et al.*, 2013). For example, coffee has been found to have a protective effect on non-viral hepatitis related to cirrhosis mortality (Goh, *et al.*, 2014). A small but significant reduction in periodontal bone loss associated with higher coffee consumption by adult men has also been reported (Ng, *et al.*, 2014). However still there are some grey areas in the matter of whether coffee is in overall beneficial for human health. For example, high coffee consumption (more than 4 cups per day) may reduce the risk of overall prostate cancer while at the same time is also associated with fatal and high-grade prostate cancer (Lu, *et al.*, 2014). No clear evidences have been found of adverse effects of coffee on health-related quality of life and harmful effect on chronic disease and mortality causes (Lopez-Garcia, *et al.*, 2014).

The presence of caffeine inside the coffee beverage is one attractive point for coffee drinkers. Caffeine is known to help decrease the level of tiredness and headache (Bruce, *et al.*, 1986), thus increases alertness and allows body to stay awake longer (Smith, 2002). Moderate amount of caffeine intake, about 51 to 322 mg per cup of coffee, has been considered safe (Institute of Food Technologists' Expert Panel on Food Safety and Nutrition, 1987; Crozier, *et al.*, 2012), except for pregnant women and those with a need to restrict caffeine consumption (Lean & Crozier, 2012). However, caffeine intake should not be judged from the coffee consumption. It is a common mistake that may mislead in studies of disease occurrence related to coffee consumption, when caffeine is the actual exposure of interest (Brown, *et al.*, 2001).

Besides the benefits of moderate caffeine intake, some negative effects of caffeine have actually been noted. For example, caffeine has been shown to increase anxiety and impair sleep (Smith, 2002). Caffeine intake also potentially lessens the options that can be generated in unconstrained real-life decision-making situation as

well as the onset times of the generation process (Häusser, *et al.*, 2014). However, little evidence has been found on common belief that caffeine (or coffee) intake increases risks of infarction, sudden death, or arrhythmia (Chou & Benowitz, 1994). Fear of the bad effects of caffeine recently makes decaffeinated coffee popular.

Chapter III

Study of Coffee Roasting under Various Temperature Conditions

3.1. Background and objectives

Roasting is one of food processing methods where heat is applied to food materials. The purposes of applying heat (or cooking) are usually the denaturation of protein and deactivation of bacterial. The heat causes not only change in food structure, but also removal of moisture from the material. Removal of moisture, or dehydration, is one of the oldest methods of food preservation. Method of drying (dehydration) itself varies depending on food products, as it has a challenge of maintaining and manipulating the quality of the product.

Based on those facts, it is reasonable to argue that roasting is a special form of drying. It is special because its very first purpose is not for food preservation, but rather for manipulation of the product, and because there is not only moisture removal but also a series of chemical reactions taking part on it. The flavour and aroma of coffee are produced there, making it the core of coffee beverage production chain. It is interesting to investigate roasting from drying point of view and take a look at the phenomena that happen during the process. The term 'dehydration' instead of 'drying' is used not to confuse between the normal drying process and the drying process that happens during roasting.

Analyses of data of physical phenomena require information of initial properties of the material being studied. In case of food products, moisture content, dimension, and density are some of the most important properties one needs to know. The objectives of the experiments were to measure the initial moisture content and density of coffee beans, to investigate the dehydration process during roasting, and finally to investigate the effect of roasting temperatures on the changes in mass fractions of the beans. The beans and experimental oven used in this thesis are also introduced in this chapter.

3.2. Material and methods

3.2.1. The coffee bean

The main material used in this research is Colombia coffee beans (*Arabica*) with excelso grade. The beans were sorted to exclude beans with defects and round-shaped beans. Round-shaped beans are often regarded as second-class beans. Defects have been found to affect how Arabica coffee beans change during roasting, thus they may affect the process and end-product quality (Franca, *et al.*, 2005). In case of Robusta coffees, there are no significant differences between defective and non-defective beans (Mendonça, *et al.*, 2009).

Table 3-1. Data of coffee bean used for experiment

Species	<i>Coffea arabica</i>
Origin	Colombia
Grade	Excelso
Port arrival date	02/05/2013
Sending date	16/05/2013
Non-defective beans	81.61%
Defective beans	18.39%

3.2.2. Experimental oven

An oven developed to continuously measure the changes in the mass of beans with an electric scale (Shimadzu UW4200H) placed on the top of the oven (see Fig. 3-1) was used for the experiments. It was actually a superheated steam oven designed for drying, but in current study only the heaters were used. The superheated steam generator was set to idle condition. In this oven there is no blower mechanism, thus heat was transferred to the bean directly from the heaters through mechanism of radiation and natural convection.

A sample holder was hung on to the scale, using a wire through a hole made on the top of the oven. The holder was made of aluminium, for it had to withstand high

temperature of roasting and should be safe for use with food products. To minimize the effect of conduction from the holder to the beans, perforated holder was used. Mass of the beans was measured on-line with the electric balance connected to a computer.

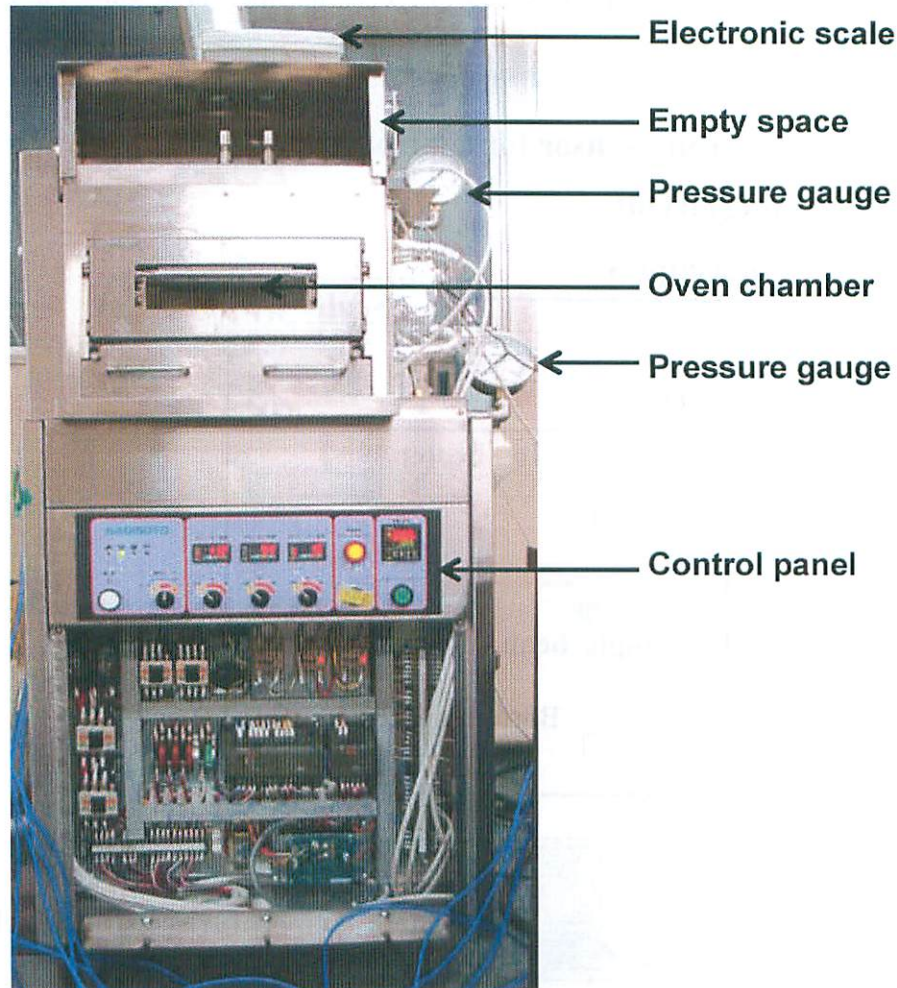


Fig. 3-1. Appearance of the experimental oven

Schematic diagram of the experimental oven and measurement system is given in Fig. 3-2. K-type thermocouples were used to measure temperature of some places. The thermocouples were located at the surfaces of top and bottom heaters inside the oven, the centre of the oven, the air near the surfaces of beans (approximately 0.5 cm above the beans) and the core of a bean hanging in a separate place (see Fig. 3-2 and Fig. 3-3). As for the last one, the thermocouple was inserted into the bean, as shown in Fig. 3-3. So far there have been no clear definitions of ‘roasting temperature’ and ‘product temperature’ (Eggers & Pietsch, 2002). Therefore in this study the term ‘roasting temperature’ refers to the temperature of the air near the bed of beans after it

became constant. This was mean to avoid false measurement caused by the temperature distribution inside the oven. All the thermocouples inside the oven were connected to the computer through a data logger (Keyence NR-1000). The data logger (and the electric scale) can be programmed to record the measured values at set time interval.

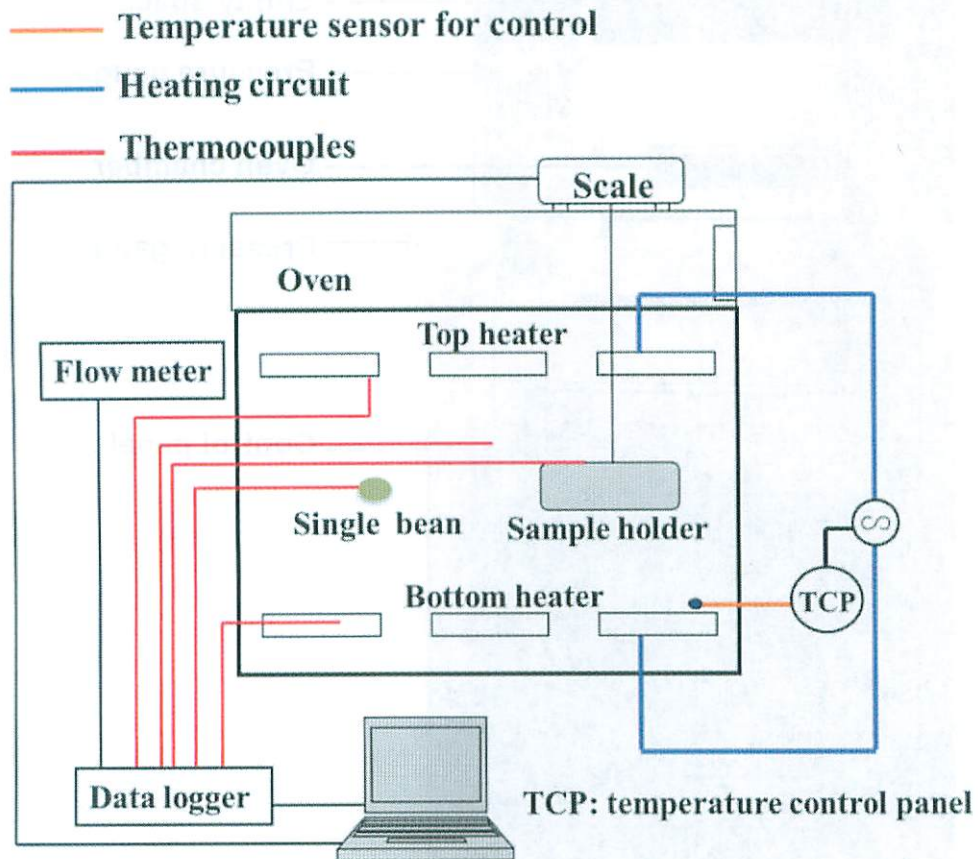


Fig. 3-2. Schematic diagram of the experimental oven and measurement system

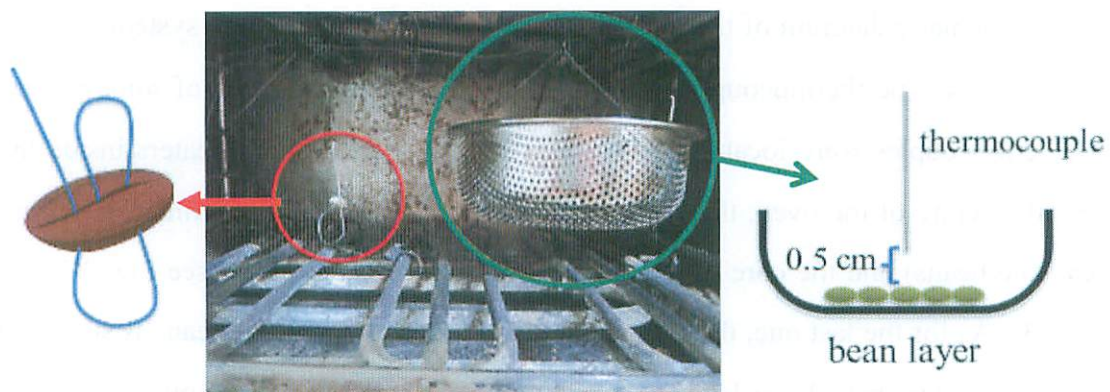


Fig. 3-3. Thermometric points by using thermocouples during drying and roasting experiments

3.2.3. Measurement of initial moisture content

Even though the effect of the bean initial moisture content has been found weak on roasting (Hernández, *et al.*, 2007), data of the initial moisture content of the bean is needed as basic information for every analysis in this research. There are some measurement methods of moisture content of green coffee beans given by the International Organization for Standardization: ISO 1446 (2001), ISO 1447 (1978), and ISO 6673 (1983). The ISO 6673 has been found well suited for routine measurement of moisture content, since the results obtained are independent of the climate conditions and the presence of forced ventilation (Reh, *et al.*, 2006). According to ISO 6673, approximately 10 g of beans should be dried with forced air ventilation controlled at 105.0 ± 1.0 °C for 16 ± 0.5 h. Bean's initial moisture content (X) is calculated in dry basis as follows:

$$X = (m_w - m_d)/m_d \quad (3-1)$$

A characteristic drying curve was then obtained by analysing the data of change in mass, and plotting drying rate (rate of water reduction) as a function of moisture content. The drying rate (R_w) was calculated as follows:

$$R_w = |(m_2 - m_1)/(t_2 - t_1)| \quad (3-2)$$

Fig. 3-4 shows a theoretical illustration of a characteristic drying curve. A full process of drying starts from preheating stage (from A to B). Period from B to C is the period of constant rate drying, whereas from C to E is the falling rate drying period (dotted curve). Sometimes there are two stages of falling rate drying (straight curve from C to D, to E).

In this study 10 g of coffee beans were dried in the oven with the air temperature near the bean surfaces set at 105 °C. Since there was no forced air ventilation used, drying time was extended up to 24 h to make sure the bean mass really reaches the equilibrium state. Even though heat is applied to the beans, it is assumed that no chemical reaction occurs and properties of bean remain unchanged, just like in freeze drying of green coffee beans (Nunes, *et al.*, 2012). The experiment

was conducted in triplicate.

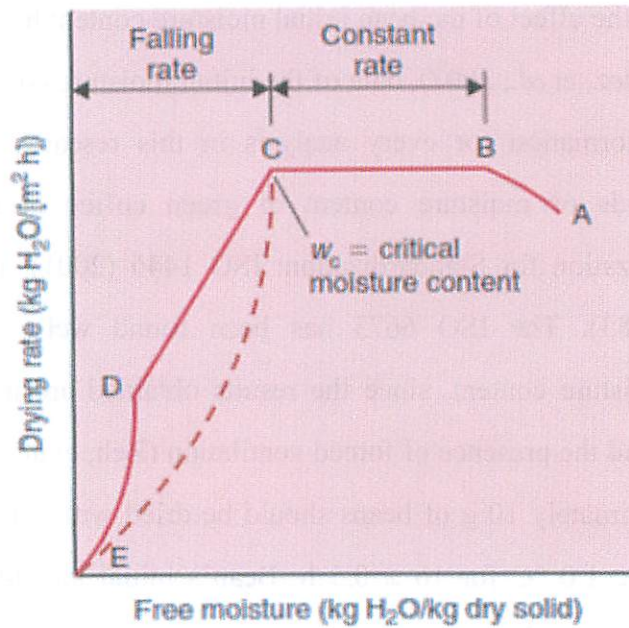


Fig. 3-4. Periods of drying illustrated in a characteristic drying curve (Singh & Heldman, 2014)

3.2.4. Measurement of bean dimension and density

Bean dimension was measured in 3-axis length using a vernier calliper, considering the bean as a half ellipsoid. Measurement was carried out on 50 coffee beans that were picked randomly. Using Fig. 3-5 as basis, the dimension of measured length is then $L_1 = 2c$, $L_2 = 2b$, and $L_3 = a$, with $L_1 > L_2 > L_3$. Volume of a single bean (V_b) is then given by

$$V_b = \frac{1}{2} \left(\frac{4}{3} \pi abc \right) = \frac{\pi L_1 L_2 L_3}{6} \quad (3-3)$$

and its surface area (A_b) is given as follows, with $p = 1.6075$.

$$A_b \approx 2\pi \left(\frac{L_3^p (0.5L_2)^p + L_3^p (0.5L_1)^p + (0.5L_2)^p (0.5L_1)^p}{3} \right)^{1/p} + \frac{\pi}{4} L_2 L_1 \quad (3-4)$$

Average mass of a single bean was measured from the mass of 100 beans. The measurement was carried out for 10 sets of sample (100 beans each). Density of a single bean was then obtained from its mass and volume.

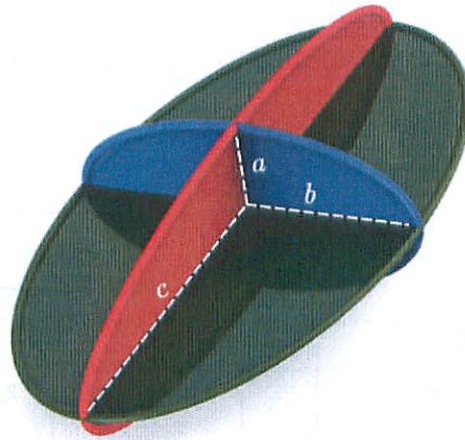


Fig. 3-5. Illustration of an ellipsoid (Wikipedia, 2012)

3.2.5. Investigation on dehydration process of roasting

About 5.5 g of beans were used for the roasting experiments. The small amount used here was meant to reduce the non-uniformity that may be resulted from temperature distribution inside the oven due to the small size of the oven. Beans were roasted at 200 °C using the experimental oven described in the previous sections, and to observe the preheating stage, the beans were heated up together with the roasting air, starting from room temperature. Another drying experiment was carried out in same way (starting from the preheating stage) to compare the dehydration process happening in roasting and that of normal drying condition (at 105 °C).

In dealing with drying kinetics data, cubic splines have been found effective for processing moisture-time data. However, wrong results may still be obtained even with a right method (Kemp, *et al.*, 2001). In this research, Bezier spline was used to deal with the drying kinetics data. The function of Bezier spline was programmed using Visual Basic for Application (VBA) in the Microsoft Excel (source of code: <http://www.xlrotor.com/>). The programming code is given in Appendix 1.

Fig. 3-6 illustrates how bean mass components change during roasting. From t_0 to t_1 beans undergo drying process only and solid remains constant ($m_{s0} = m_{s1}$). From t_1 to t_2 roasting accompanies and solid mass decreases as well. Finally, all the water is removed and solid mass continues to decrease. This was used as the basic assumption for calculating changes in moisture content and solid content. Actually during roasting

there is some moisture resulted from reactions of carbohydrate combustion. It was assumed that the moisture evaporate directly right after it is produced, due to high temperature.

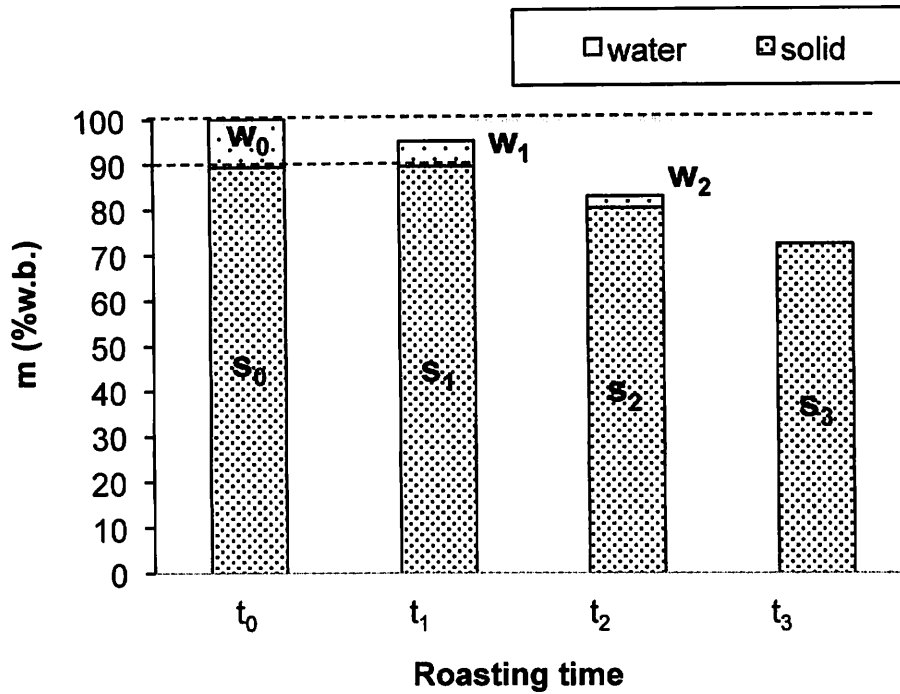


Fig. 3-6. Change in bean components during roasting.

Change in moisture content during roasting was measured by taking samples at some selected time points and drying them using another oven at 105 °C for 24 hours. Drying, or dehydration, rates in both conditions were calculated based on initial mass of solid (dry basis), in a similar way given in Eq. 3-1 & 3-2. Decreases in bean solid mass and whole bean mass after time t were also calculated based on the initial mass of bean solid. The general equation is as follows.

$$C_t = (m_{C_0} - m_{C_t}) / m_{S_0} \quad (3-5)$$

The rates of change at time t were similarly calculated in a same manner with Eq. 3-2 for the purpose of plotting them all in the same graph.

3.2.6. Roasting experiments at different temperatures

Coffee beans (± 5.5 g) were roasted for 24 h, and to investigate pre-roasting and over-roasting conditions several constant temperatures ranging from 140 to 300 °C, namely 140, 180, 200, 220, 260 and 300 °C, were employed. Roasting temperatures ranging from 180 to 300 °C are commonly used in coffee roasting (Franca, *et al.*, 2009; Heyd, *et al.*, 2007; Basile & Kikic, 2009; Wang & Lim, 2014). In this research, temperatures of 140 °C and 300 °C were assumed able to represent the under-roasting and over-roasting conditions.

To obtain the samples for measurement of bean dimension and analysis of moisture content, roasting experiment was repeated from the beginning up to certain time periods for each temperature (see Table 3-2). These repetitive experiments were meant to avoid sampling during experiments. Of the samples taken at each sampling time, 20 beans were randomly picked and their dimensions were measured. The measurements and analyses were performed in the same way explained in section 3.2.4. Measurements of moisture content were carried out by drying the samples in an electrical oven at 105 °C. All experiments were conducted in triplicate.

Table 3-2. Sampling time for each roasting temperature

T (°C)	Sampling time (min)
140	15, 30, 60, 120, 240, 480
180	5, 10, 20, 30, 60, 120
200	3, 5, 8, 11, 20, 40, 60, 120
220	3, 5, 10, 20, 30, 60
260	1, 2, 3, 4, 5, 10, 20
300	0.5, 1, 2, 3, 4, 5

3.3. Results and Discussion

3.3.1. Measurement of initial moisture content

The initial moisture content of green beans was found approximately 12.0%

(SD: 0.29%). A characteristic drying curve of coffee beans during drying at 105 °C for 24 h revealed that there existed only the falling-rate drying period during the drying process of green coffee beans (see Fig. 3-7). It is because the beans had actually been dried during the postharvest handling and before they were stored. The constant rate drying most likely existed there.

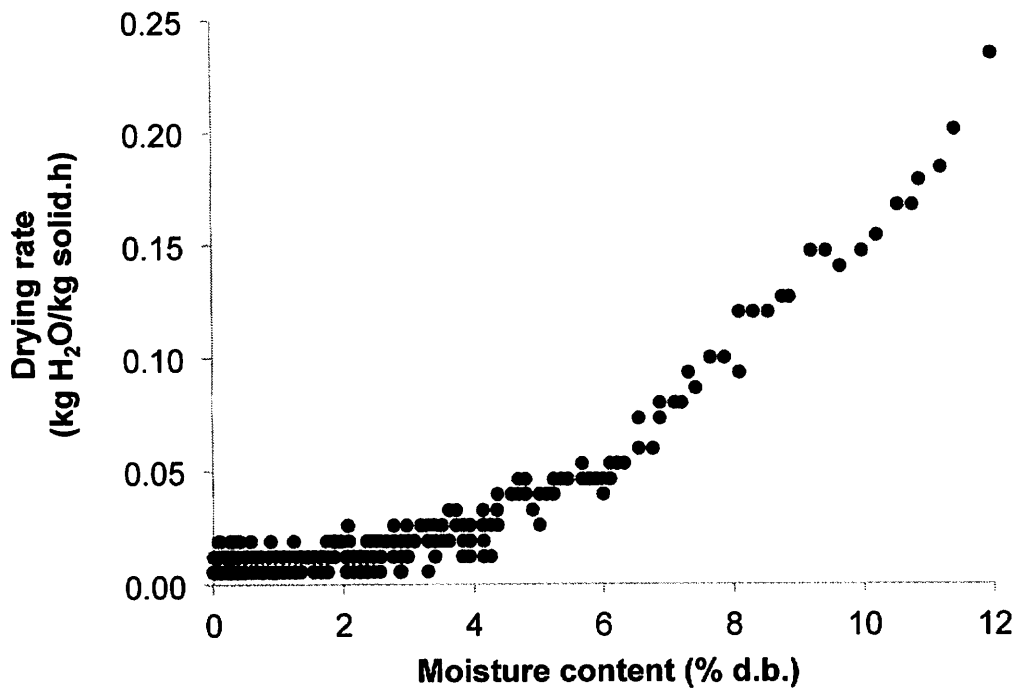


Fig. 3-7. Characteristic drying curve of coffee beans dried at 105 °C for 24 h

3.3.2. Measurement of bean dimension and density

Measurement showed average mass of a single bean was 159.6 mg (SD: 4.59 mg) and its volume 136.4 mm³ (SD: 22.25 mm³), thus its density was 1169.83 kg m⁻³. Another calculation was also performed, with an assumption of the bean being an equivalent sphere of same volume. The data was used for modelling of heat and mass transfer, to make the calculation simpler. Summary of the calculation is given in Table 3-3. It can be seen that assuming bean as an equivalent sphere could actually underestimate the surface area of beans. Since surface area plays an important role in heat transfer from and to the bean, this underestimation might affect the result of a process modelling.

Table 3-3. Physical properties of Arabica coffee beans (Colombia excelso)

Bean form assumed	Half-ellipsoid	Equivalent sphere
Mass	159.6 ± 4.59 mg	
Dimension	$L_1 = 0.981 \pm 0.83$ cm	$r_b = 0.318 \pm 0.017$ cm
	$L_2 = 0.706 \pm 0.38$ cm	
	$L_3 = 0.375 \pm 0.34$ cm	
Surface area	1.577 ± 0.161 cm ²	1.278 ± 0.136 cm ²
Volume	0.136 ± 0.022 cm ³	
Density	1169.83 kg m ⁻³	

3.3.3. Investigation on dehydration process of roasting

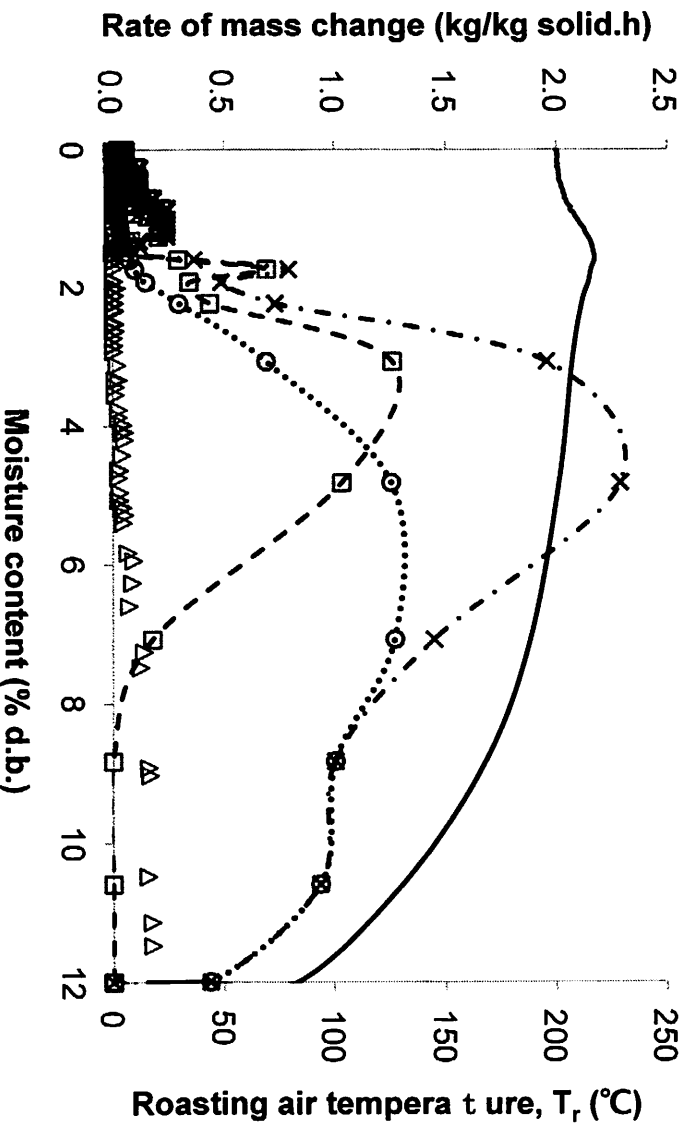


Fig. 3-8. Characteristic dehydration curves of coffee in normal drying condition at 105 °C (Δ) and in roasting at 200 °C (O marks, with dotted curve •••). Similarly, roasting curves of whole bean mass (\times , dot-dashed curve —•—•) and solid mass (\square , dashed curve —•—•) are presented for comparison. Solid line (————) indicates the temperature of the air near bean layer's surface.

Fig. 3-8 shows characteristic dehydration curves of the comparative experiments of roasting at 200 °C and drying at 105 °C. The triangle marks (Δ) indicate the data of normal drying condition at 105 °C, whereas the dotted curve (with \circ marks) indicates the dehydration rate of beans during roasting as a function of moisture content. The dot-dashed curve (\times marks) indicates mass change rate of the whole bean mass, and the dashed curve (\square marks) indicates the rate of change in solid mass of beans, which corresponds to the difference between the dot curve and the dot-dashed curve.

From the figure, it can be seen that the dehydration rate of the samples roasted at 200 °C was much faster than that of the samples dried at 105 °C, obviously. At the beginning of the roasting process ($X \geq 8\%$ d.b.), water evaporation dominated over the reduction of solid and subsequently the rate of solid mass reduction began to increase. The reduction in solid mass was found to start even before drying process slowed down. It indicates the bean temperature keeps increasing and the beans enter roasting stage before all moisture evaporates.

A small peak in the rate of solid mass degradation was found when the moisture content dropped to about 2%. At that time, a short peak of the roasting air temperature was also observed. This happened when the roast loss reached 14–15%. It might be associated with the cracking of the beans, where a large amount of CO_2 and other chemical compounds was released as a result of pressure build-up (Eggers & Pietsch, 2001; Wang & Lim, 2014). Some compounds are released violently when bean cracks, while some are released continuously (Yeretzian, *et al.*, 2002).

3.3.4. Roasting experiments at different temperatures

Change in bean volume during roasting is presented in Fig. 3-9. Bean volumes were found to expand in most roasting conditions, except at temperature 140 °C, where there was a very little, if no, increase in volume found. Since roasting usually starts when bean temperature reaches around 160 °C, it could be concluded that bean expansion is fully governed by roasting process.

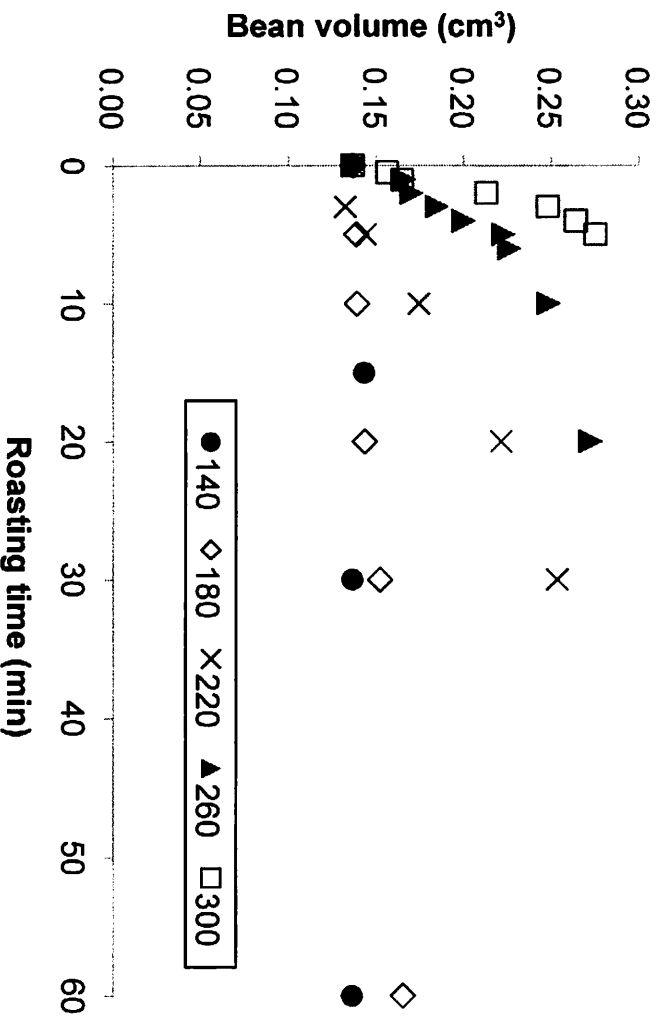


Fig. 3-9. Change in bean volume at different roasting temperature

Changes in coffee bean mass at different roasting temperatures are presented in Fig. 3-10. Even though the data shown were only some representatives, generally the gaps between final masses of the samples roasted at 220 °C and 260 °C were bigger compared to those of the others, which means there might be some phenomena in between those temperatures. Some exothermic reactions are said to occur at approximately 245–250 °C and contribute to increase in heating kinetics and bean burning (Strežov & Evans, 2005; Heyd, *et al.*, 2007; Basile & Kikic, 2009), which cause more carbohydrates and other constituents to react and change into mostly water and CO₂.

In the early stage of over-roasting at 260 °C and 300 °C much oil was found on the surface. More breakups of oleosomes at higher temperatures have been reported (Schenker, *et al.*, 2000), along with more porous structures created by more gas desorption and bean swelling, as shown in Fig. 3-9. These promoted more oil migration to the bean surface, and as the roasting continued the oil evaporated. The greater releases of oil as well as water and CO₂ from the reactions of carbohydrates and other compounds are what contributed to the greater mass decrease.

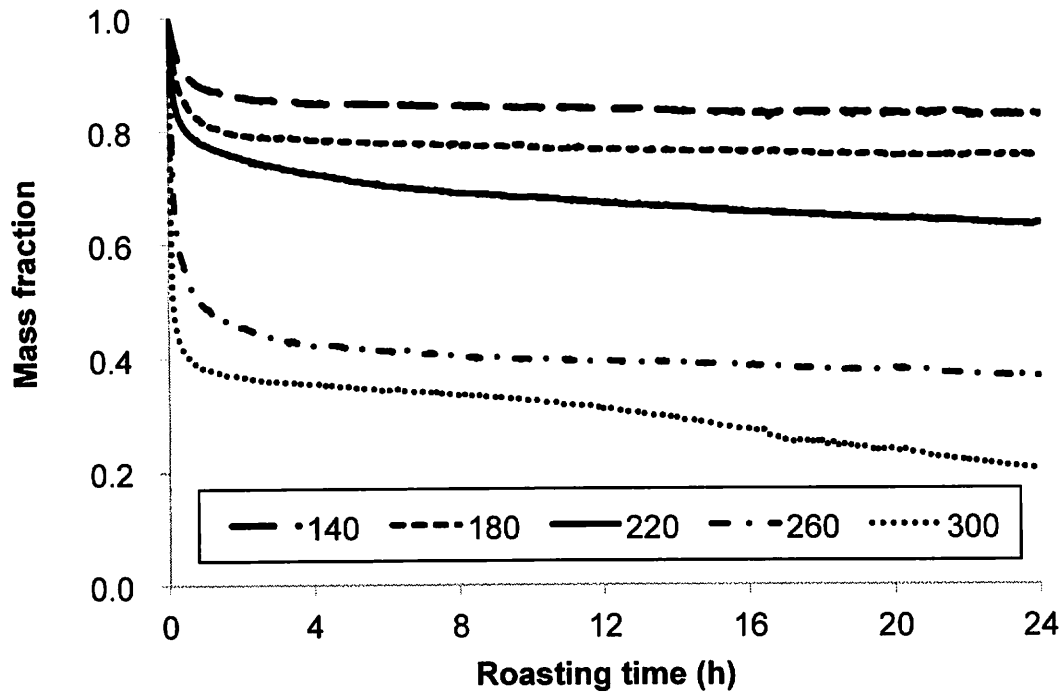


Fig. 3-10. Kinetics of coffee bean mass during 24 h of roasting

Since the roasting time employed was unusually long, it can be assumed that all reactions that could occur at each roasting temperature had finished when the experiments ended. Considering that the bean mass stabilised at different mass fraction, it can be said that at lower roasting temperature there might be some fractions of solid that could not transform to volatiles. In other words, there might be more reactions that convert more solids to volatiles at higher roasting temperature. Even if the results of the temperatures above 250 °C were not taken into account, this fact is still visible from the figure. Thus, it might be concluded some roasting reactions require certain ranges of temperature to start, not only the activation energy. Further investigation is needed to provide more detail information on this matter.

Roast loss (RL) is defined in this study (and also in Wang & Lim, 2014) as the ratio of the difference between weight of green beans and that of roasted beans to the initial mass of beans, which is given as follows.

$$RL = [(m_{gb} - m_{rb})/m_{gb}] \times 100\% \quad (3-6)$$

Wang & Lim (2014) found that the change in rate of mass change occurs at

roast loss of about 15% when the roasting temperature ranged between 220 and 250 °C. Roast loss of 15% is often referred as medium roasting degree (Schenker, 2000; Wang & Lim, 2014). The value corresponds to the result of this study at the same temperature, 220 °C. However, in this study broader range of temperature is used, and the results have shown changes in the rate of mass decrease actually vary with the temperatures.

Change in roast loss over the first hour of roasting for each roasting temperature is presented in Fig. 3-11. Both Fig. 3-10 and Fig. 3-11 support the result of previous studies that coffee roasting has a two-stage phenomenon of how fast bean mass decreases. Assuming that roasting will not be economically beneficial if it continues to the second stage, one can pay attention to the first stage of roasting only, and a linear relationship between roast loss and time can be recognised. Gradient of the regression lines was found to be an exponential product of roasting temperature (see Fig. 3-12), and the roast loss (RL) can be expressed as a function of roasting temperature and time, as follows.

$$RL = 0.0282 t \exp(0.0183T_r) \quad (3-7)$$

The gradient ($k = 0.0282 \exp(0.0183T_r)$) indicates the rate of mass reduction, or the overall reaction rate of roasting. The result is in agreement with that of a previous study, where rate constant of the first stage of roasting could be modelled with Arrhenius equation, as proofed with a linear relationship between $\ln k$ and $1/T_r$ (Wang & Lim, 2014). Basile & Kikic (2009) has found that the roast loss can also be expressed as a function of bean's initial mass and temperature only, based on the data presented by Eggers & Pietsch (2000). However, the range of temperature was not as wide as the one used in this study.

It is important to keep in mind that in this research heat was delivered to the beans through the mechanism of radiation and natural convection, and also some effect of conduction from the sample holder. In real practice where common roasters such as drum roaster, fluidised (spouted) bed roaster, and packed bed roaster are used, the situation is different as forced convection (sometimes with conduction) is usually the

main mechanism of heat transfer (Eggers, *et al.*, 2001; Wang & Lim, 2014; Schwartzberg, 2002; Fabri, *et al.*, 2011; Bottazzi, *et al.*, 2012; Nagaraju, 1997). However, the linear relationship at the first stage of roasting can also be expected, similarly.

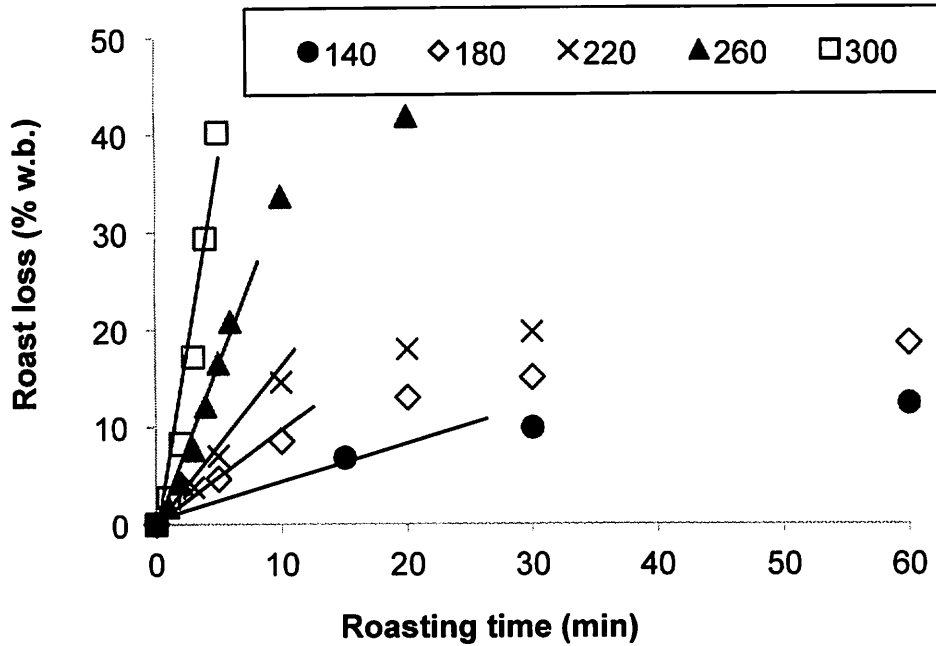


Fig. 3-11. The roast loss for the first hour of roasting at different temperatures.

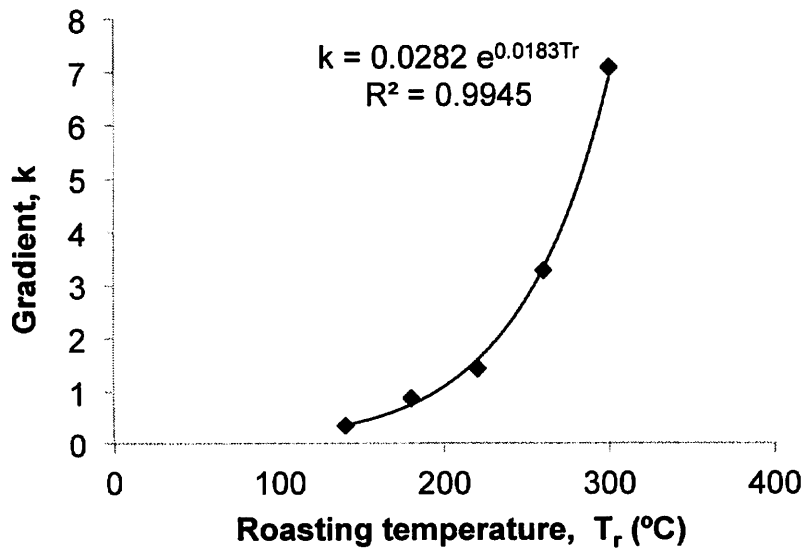


Fig. 3-12. Gradient, of linear regression line of roasting time-loss relationship (see Fig. 3-11) as function of roasting temperature.

Characteristic roasting and dehydration curves of roasting temperatures from 140 to 300 °C are given in Fig. 3-13, 3-14, 3-15, 3-16, and 3-17. It can be seen that increasing roasting temperature shifted the peaks of solid mass reduction towards lower moisture content. Another phenomenon is that the surrounding air temperature tends to stagnate below the set roasting temperature before the dehydration slowdown. It is caused by the both the reduction in supply of sensible heat and the cooling effect of moisture evaporation. The stagnation is more clearly visible when the rate of moisture evaporation is higher. No crack indicating-small peaks were found on the curves of coffee roasted at higher temperatures than 200 °C. Most likely the changes of temperature and mass were not recorded during the phenomena due to relatively long time interval for data recording (every 1 min).

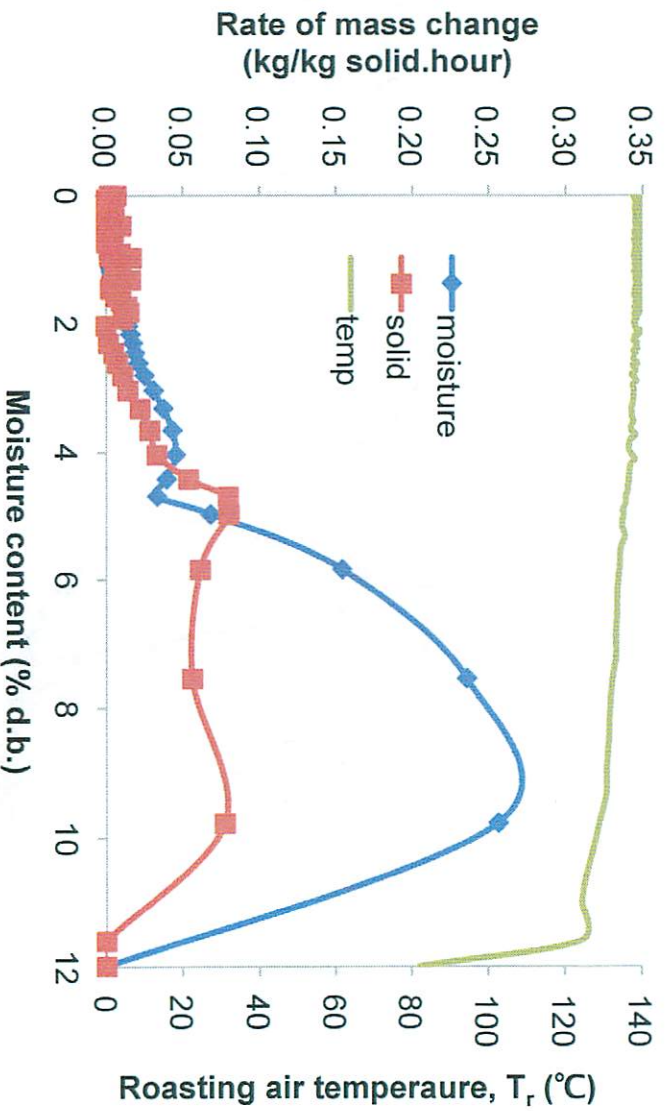


Fig. 3-13. Characteristic dehydration and roasting curves of coffee at 140°C

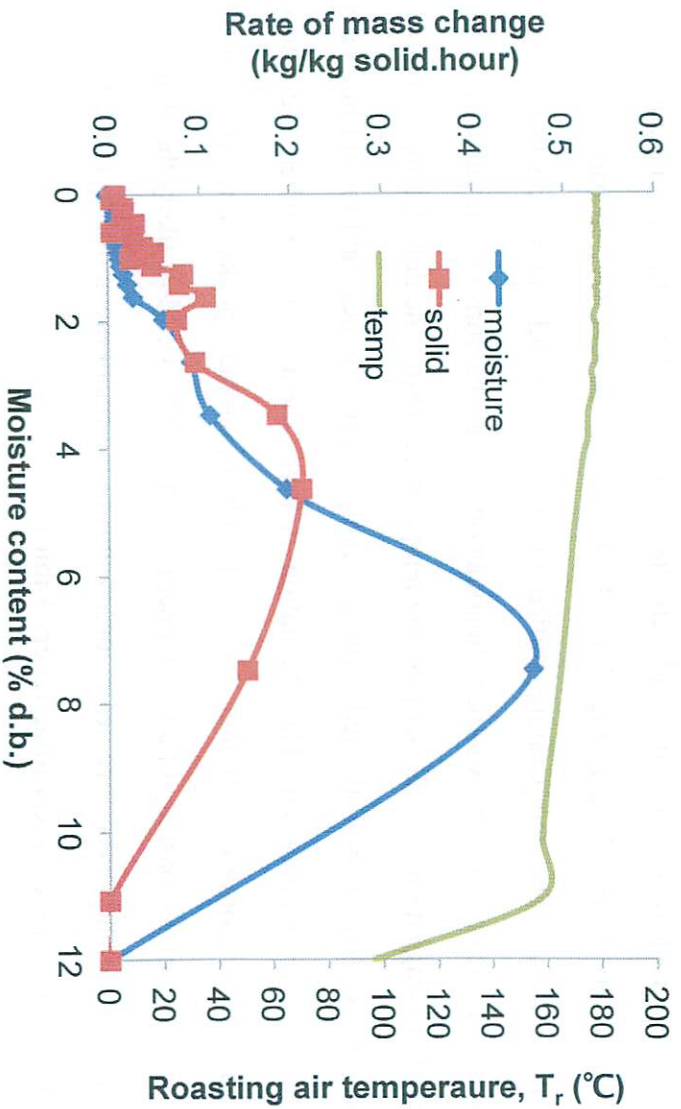


Fig. 3-14. Characteristic dehydration and roasting curves of coffee at 180°C

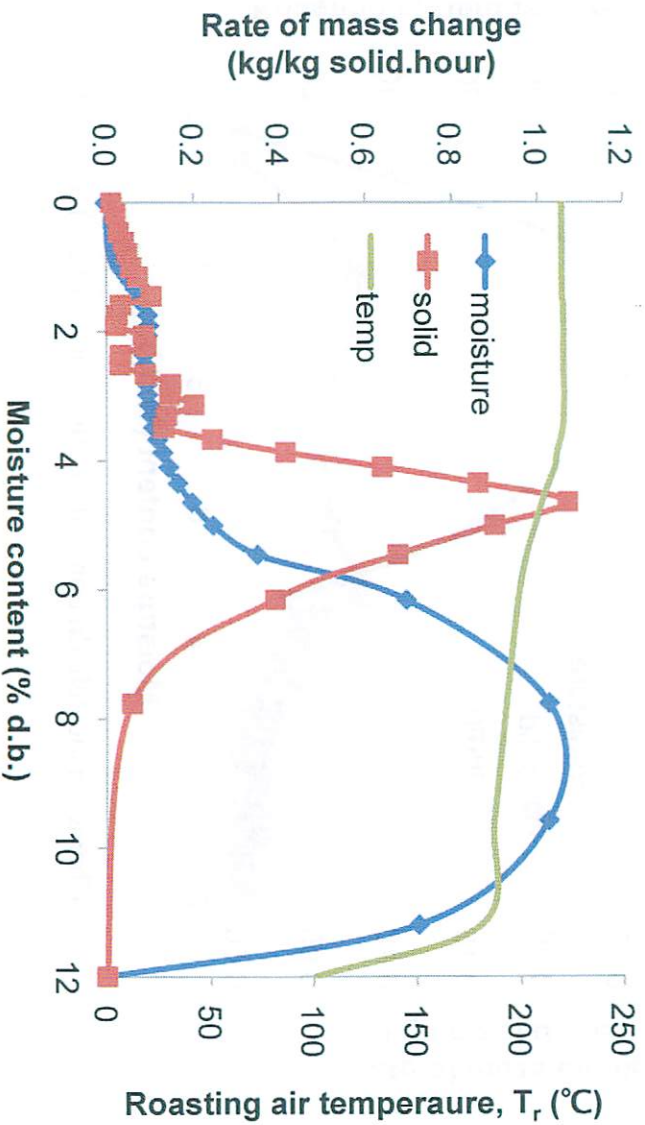


Fig. 3-15. Characteristic dehydration and roasting curves of coffee at 220°C

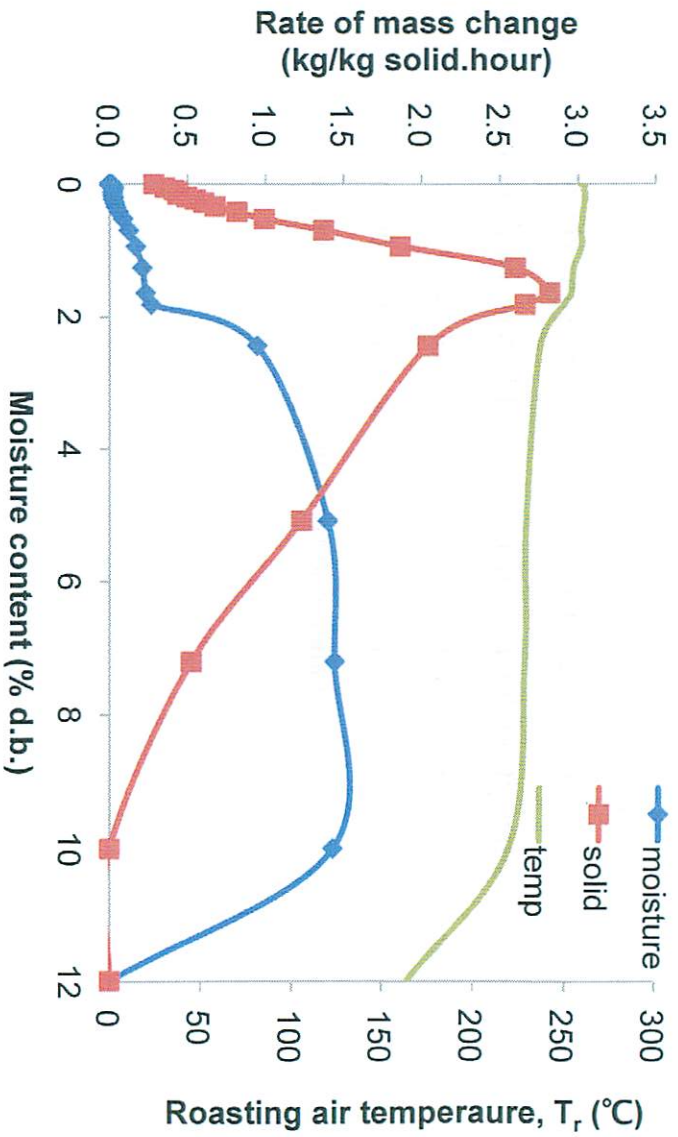


Fig. 3-16. Characteristic dehydration and roasting curves of coffee at 260°C

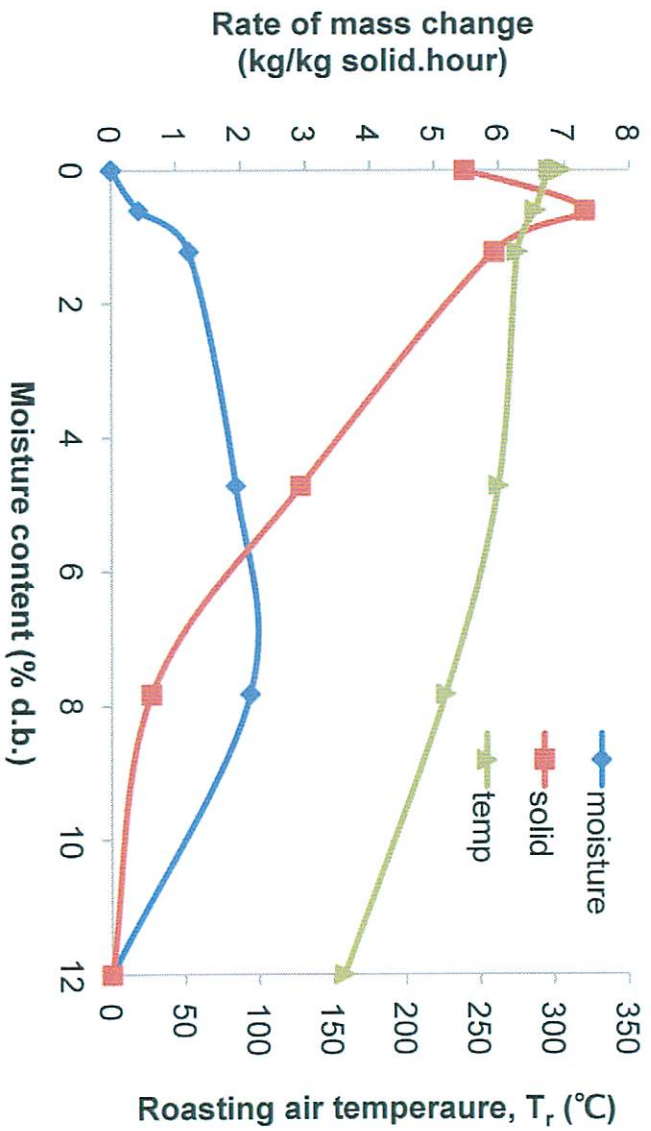


Fig. 3-17. Characteristic dehydration and roasting curves of beans at 300°C

3.4. Conclusions

1. Expansion of bean is fully governed by roasting reactions.
2. Changes in rate from the first to the second stage in roasting kinetics were found to happen at different conditions of roast loss for different roasting temperatures.
3. Roasting reactions require certain ranges of temperature to start, not only the activation energy, as shown by the fact that the fractions of solid that could transform to volatiles are smaller at lower temperatures than at higher ones.

Chapter IV

Colour Change during Roasting

4.1. Background and objectives

Colour, flavour and aroma are important sensory parameters of coffee. How the flavour and aroma are developed is determined by how chemical compounds change during roasting. Colour is usually the main indicator of whether the desired roasting degree has been achieved, as direct measurement of flavour or aroma during roasting is difficult (Franca, *et al.*, 2009). Classification of roast type in most practice is purely based on colour, as aforementioned (NCAUSA, <http://www.ncausa.org/>).

Colour parameters can also be a criterion for discrimination between Arabica and Robusta beans, as long as the beans are not defective. Such colour-based characterisation is applicable in the case of green and roasted coffee (Mendonça, *et al.*, 2009). For Arabica beans, colour saturation tends to increase with the decrease in coffee quality. For Robusta coffee, the colour tends to be brownish, regardless of the bean quality. Luminosity does not significantly differ in Arabica and Robusta coffees of same quality (Mendonça, *et al.*, 2009).

Importance of colour has led to demands on colour monitoring systems, which have been proposed in some studies. For example, Hernández, *et al.* (2008a) used an on-line system to monitor continuously the surface colour of coffee beans undergoing roasting. Grey value, an average of the RGB values, of the beans was used as the control parameter. Two neural network models were proposed to predict the brightness (grey value) and the surface area kinetics of coffee beans during roasting (Hernández, *et al.*, 2008b), and the models were found satisfactory. However, it still takes time for them to become fully applicable in the industry.

Assessment of roasting degree actually cannot rely on only colour and roast loss, but also the roasting temperature. It is because different roasting temperatures lead to different volatile profiles, as the pathways of reactions and product removal are different (Schenker, *et al.*, 2000). Therefore, it is important to understand the colour change in response to roasting temperature. Some studies have been conducted on the

colour kinetics of coffee roasting (Gökmen & Şenyuva, 2006; Wang, *et al.*, 2014). Unfortunately, the roasting conditions were the ones commonly employed and thus the effects of pre-roasting and over-roasting stages were not really understood. The objectives of this study are to measure colour change during roasting at different temperatures and to investigate the relationships among colour parameters, as well as between them and other roasting parameters, for predicting their changes during the process.

4.2. Materials and methods

Coffee beans were roasted at various temperatures, as explained in the Chapter III. The experiments were carried out repetitively and the beans were taken 3 times as a set of samples at the sampling time given in Table 3-1. The samples were ground using an electric grinder of a coffee maker. Each ground sample was divided into three, and the colour was measured. The measurements were performed using handy spectrophotometer NF-333 (Nippon Denshoku, Ind. Co. Ltd.), and the colour was presented in CIELAB colour space shown in Fig. 4-3 (CIE, 2007). Regression analyses were done using statistical software JMP Pro 10 (SAS Institute Inc., 2012).

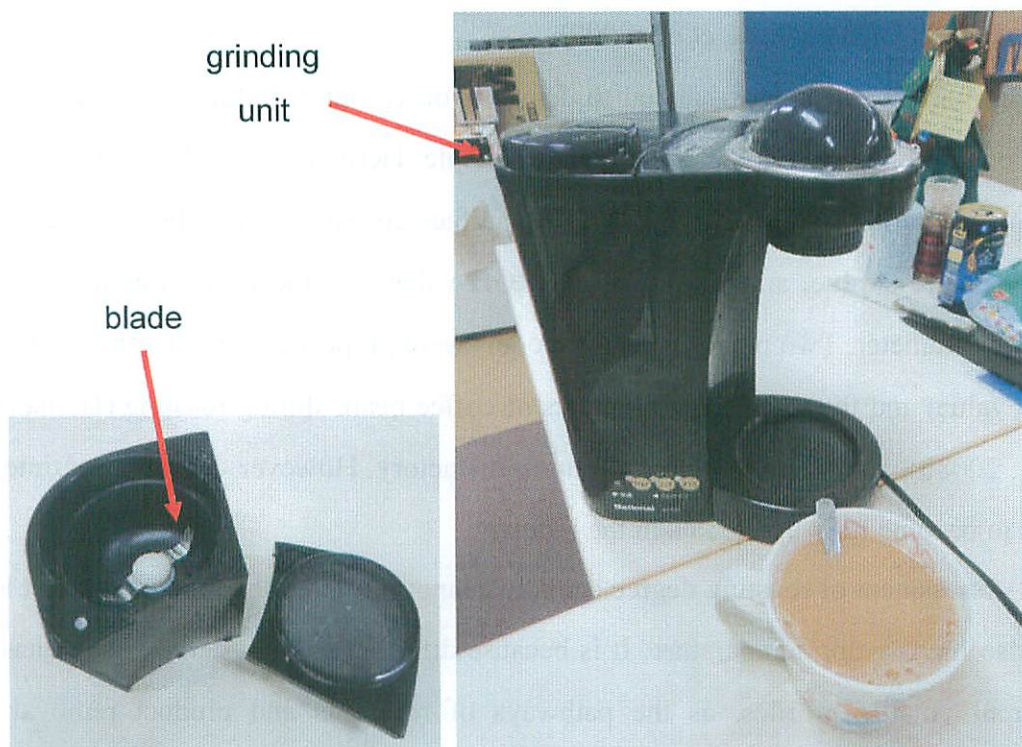


Fig. 4-1. Beans were ground using the electric grinder of a coffee maker

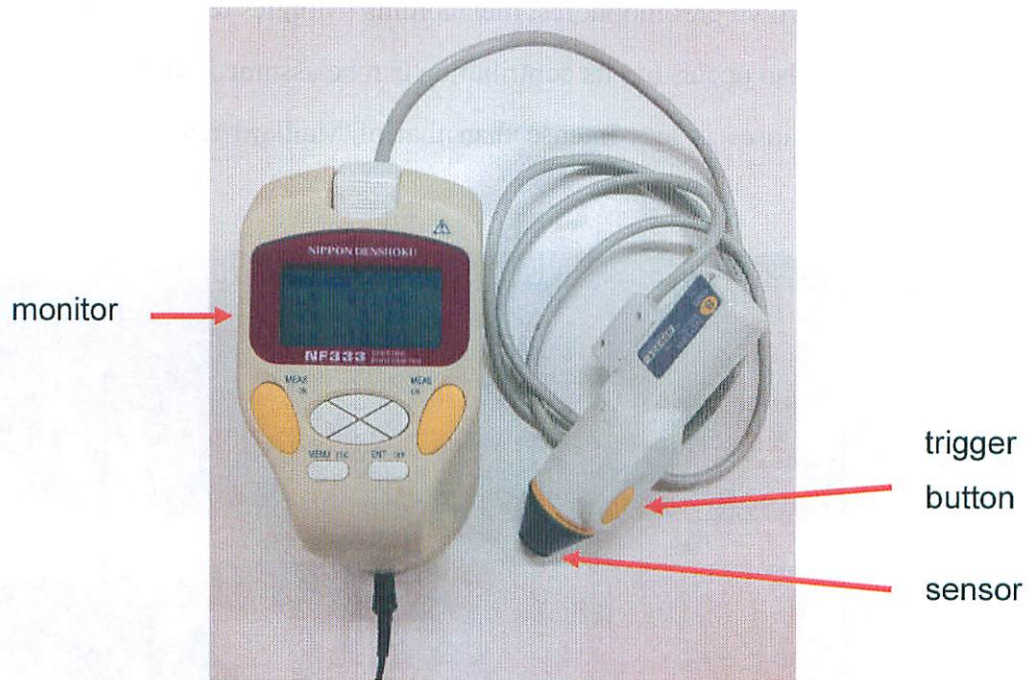


Fig. 4-2. Handy spectrophotometer NF-333 (Nippon Denshoku, Ind. Co. Ltd.)

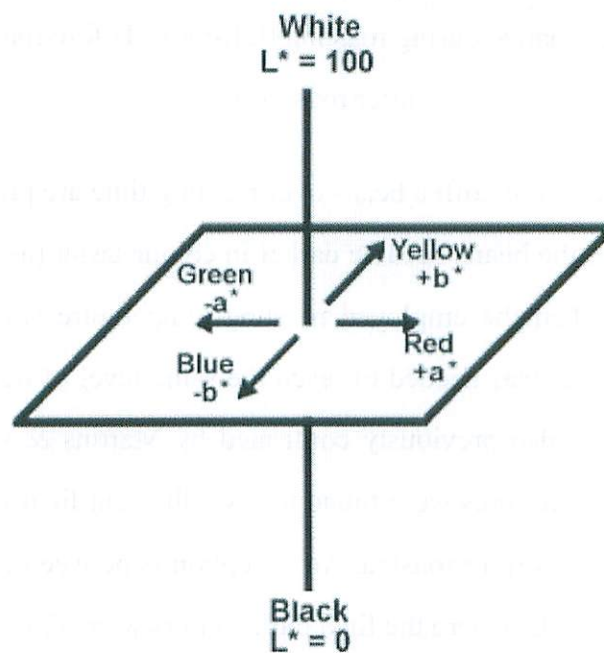


Fig. 4-3. The CIE Lab colour space

(<https://sites.google.com/site/sachidanandabs/colorspace>)

4.3. Results and discussion

As beans undergo roasting process, Maillard reactions take place and cause the colour of beans to change (see Fig. 4-4). The darkening in colour is a result of

accumulation of the brown chromophores, melanoidins (Morales & van Boekel, 1998). Caramelisation may also occur, but its contribution can be assumed limited because the colour formation it causes is less intense than that of Maillard reactions (Bekedam, 2008).



Fig. 4-4. Bean colour change during roasting (left-most: before roasting, right-most: after roasting).

Changes in lightness of coffee beans over roasting time are presented in Fig. 4-5. As seen on the figures, the beans became darker in colour faster (as indicated by lower lightness value, L^*) when the employed roasting temperature was higher. At lower temperatures, longer time was needed to reach the same level of lightness with that of higher temperatures, as also previously confirmed by Martins & van Boekel (2003). However, different temperatures were found to give different final lightness values, no matter how long the beans were roasted. An exception is between the beans roasted at 260 °C and those of 300 °C, where the final dark colours were about the same.

There are two possible explanations to this finding. First, at lower temperature the maximum amount of melanoidins that can be accumulated was limited compared to those at higher temperatures. In other words, at higher temperatures more melanoidins were produced. Most likely, certain melanoidins are resulted at certain range of temperatures, which is in agreement with the results of Bekedam, *et al.* (2008b). Some that can be produced at higher temperatures cannot be resulted from reactions

occurring at lower temperatures. The possible reason is the reactants of melanoidin formation are different, or at higher temperatures the reactants are produced by other reactions that occur there. The type or products formed during the Maillard reactions is determined by the reaction conditions, so consequently the pathways of melanoidin formation can also be different (Tressl, *et al.*, 1995). The second possibility is that the melanoidin populations formed are very different and thus the resulted end-colours are different, even though the amounts of accumulated melanoidins could be the same. The existence of browner melanoidins has been confirmed by Nunes, *et al.* (2012). As aforementioned, different melanoidin populations can possess different characteristics due to different composition of materials. Both of these two possibilities could be correlated and take place at the same time.

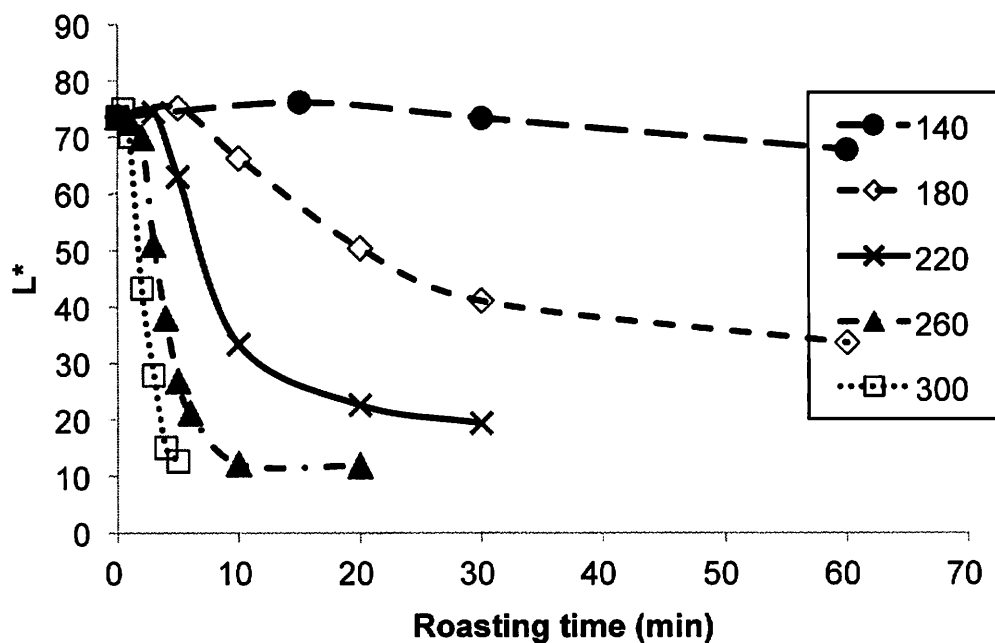


Fig. 4-5. Change in bean lightness (L^*) as a function of roasting time

The data of change in colour given in CIELab colour space (L^* , a^* , b^* values) were plotted into a 3D diagram (Fig. 4-6). From the diagram it can be seen that colour change of the samples due to roasting followed the same curve-like path regardless of the roasting temperature. This phenomenon was also found in baking of white bread (Onishi, *et al.*, 2011). The path, or the curve, is called “characteristic colouring curve” (see Fig. 4-7), which is unique for every variety of food material (Kure, *et al.*, 1997).

Based on the results in Fig. 4-5, the higher the roasting temperature will make the colouring curve longer.

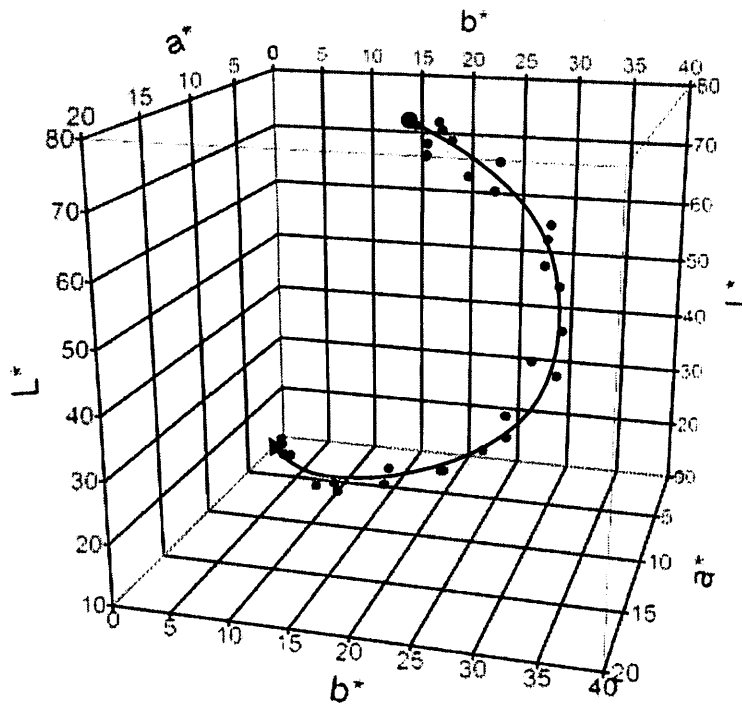


Fig. 4-6. Colour data of coffee beans of all roasting temperatures plotted into 3D diagram. The change in colour follows a certain path.

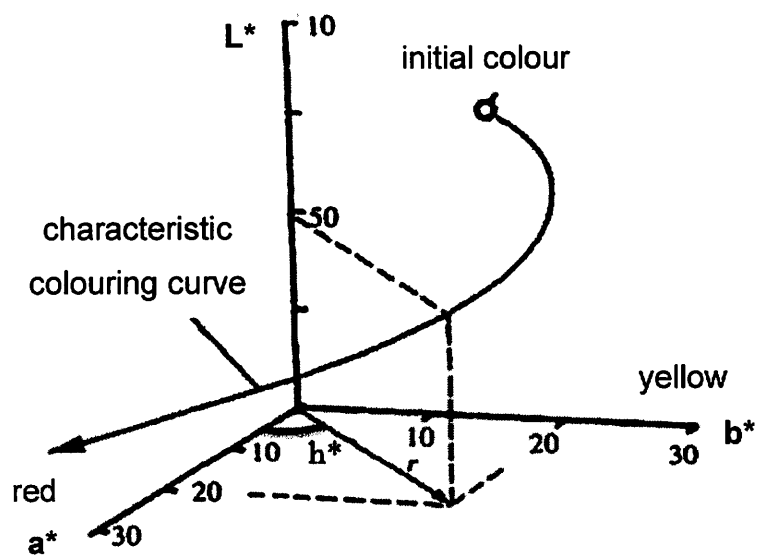


Fig. 4-7. Characteristic colouring curve in a CIELab colour space (Kure, *et al.*, 1997)

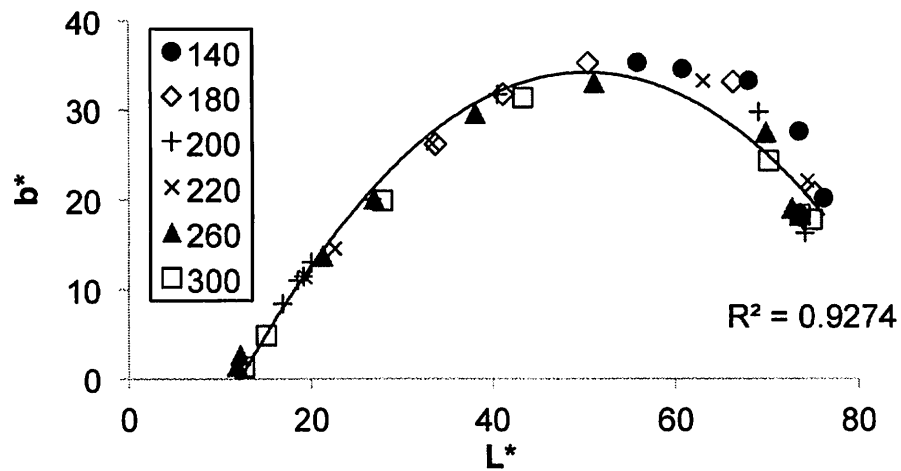
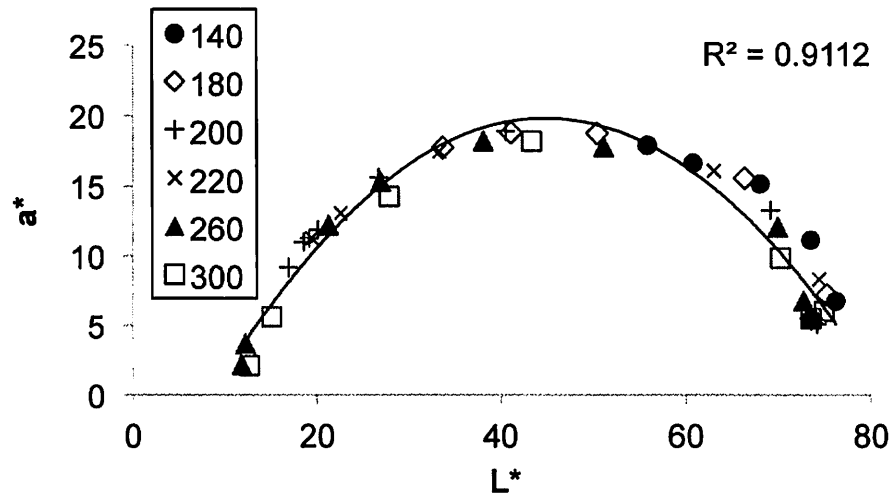


Fig. 4-8. Parabolic relationships found between L^* and a^* (upper) and b^* (lower)

The plots of L^* against a^* and against b^* were found to lie on curved lines (see Fig. 4-8). Assuming that the relationships are parabolic, using regression they can be expressed by the following equations:

$$a^* = 17.39 + 0.05 L^* - 0.014 (L^* - 43.16)^2 \quad (4-1)$$

$$b^* = 18.44 + 0.33 L^* - 0.023 (L^* - 43.16)^2 \quad (4-2)$$

If the values of a^* and b^* are plotted against each other (Fig. 4-9), angle between a^* and b^* values at a coordinate point is the hue (h_{ab}), which is given by the following equation.

$$h_{ab} = \tan^{-1}(b^*/a^*) \quad (4-3)$$

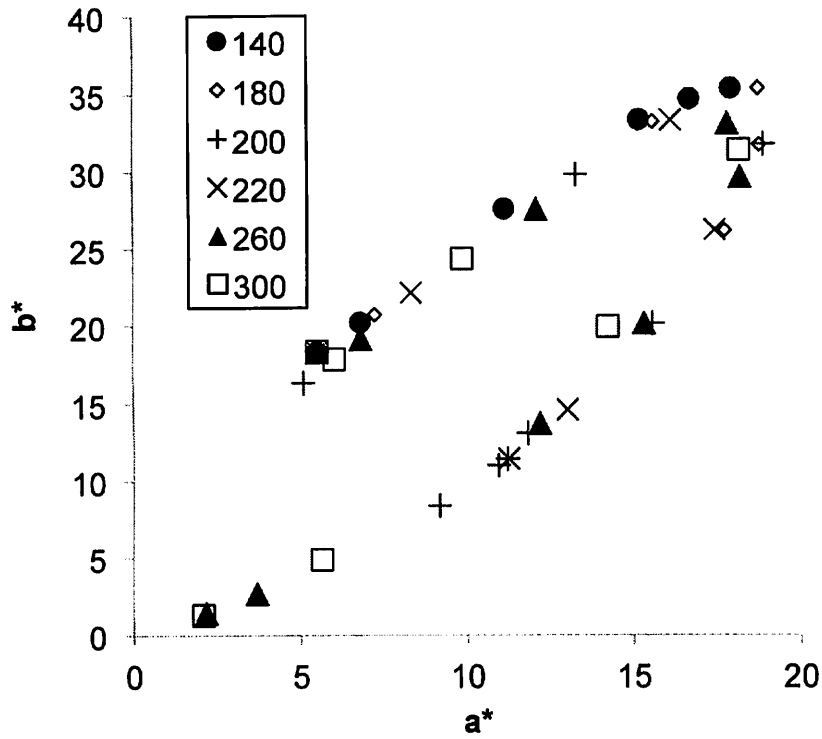


Fig. 4-9. Relationship between a* and b* in coffee roasting

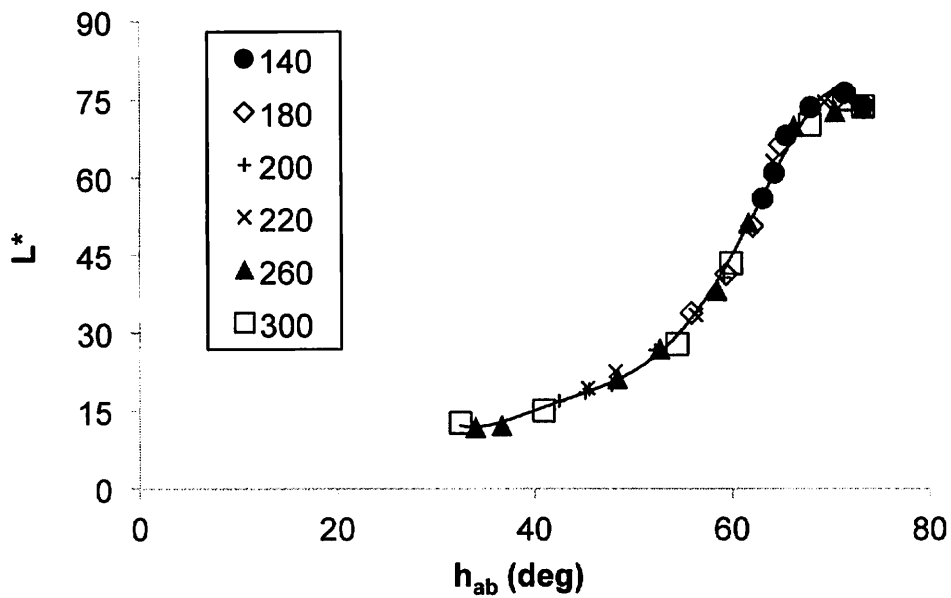


Fig. 4-10. Relationship between lightness value and hue angle

The hue values are plotted against the lightness values in Fig. 4-10. Using regression, the relationship was found to follow polynomial equation empirically (for $32^\circ \geq h_{ab} \geq 74^\circ$, $R = 0.996$).

$$L^* = -9E-06 h_{ab}^5 + 0.002 h_{ab}^4 - 0.208 h_{ab}^3 + 9.742 h_{ab}^2 - 224.21 h_{ab} + 2043.1 \quad (4-4)$$

In white bread baking, where change in colour due to Maillard reactions also occurs, the relationship was found linear (Onishi, *et al.*, 2011), in spite of the similarities found in parabolic relationship between L^* and each of a^* and b^* .

From the relationships among colour values shown by the characteristic colouring curve, it is noticeable that by having only L^* values, a^* and b^* values can be calculated using Eq. 4-1–Eq. 4-4. Bean lightness has been found to be linearly related to with the radical scavenging capacity of coffee (Summa, *et al.*, 2007) even though depending on the product the antiradical capacity may become constant while the browning is still continuing (Morales & Jiménez-Pérez, 2001). L^* value can be also used to indicate residual CO_2 in any roasting condition (Wang & Lim, 2014). Another study found that darker coloured coffee has higher probability to contain less acrylamide than the lighter one does, and the relationship between acrylamide concentration and a^* value is linear (Gökmen & Şenyuva, 2006). As the changes in colour and other sensory parameters of coffee are determined by the chemical reactions occurring inside the beans during roasting, the characteristic colouring curve might be used for elucidating the relationship among the parameters. The colour parameters can be useful information for quality design of the final product. Furthermore, the curve might be also useful for elucidating the mechanism of the chemical reactions.

The kinetic transition of L^* value and that of roast loss has been found similar, thus the parameters could be related (Wang & Lim, 2014). Fig. 4-11 shows the plot of L^* values against roast loss of each roasting temperature. In the early stage of roasting, L^* values slightly increased (means bean colour became brighter) due to moisture removal. After that they decreased continuously before reaching constant values. At temperatures below 220°C the L^* values decreased in lower pace relatively to the roast loss, and the temperature affected how fast the decrease was. For the temperatures of 220°C and above, all variations seems to follow a single characteristic curve. However, if examined more carefully, among the temperature dependent variations, there were still some differences. At higher temperature, L^* decreases more quickly at the

beginning (after the small rise), but its pace gets slower after some time. As also seen in Fig. 4-5, the differences of the minimum lightness values that can be achieved at different temperatures became smaller as the temperatures got higher, especially from 220°C above. The results of this study confirm the temperature dependence of the variations of L^* versus roast loss. In other words, roasted beans of same colour may have different roast loss if roasted at different temperatures. Therefore, compound profiles of roasted coffee cannot be evaluated based on only the roasting degree (which is judged by colour), as also mentioned in previous studies (Franca, *et al.*, 2009; Wang & Lim, 2014).

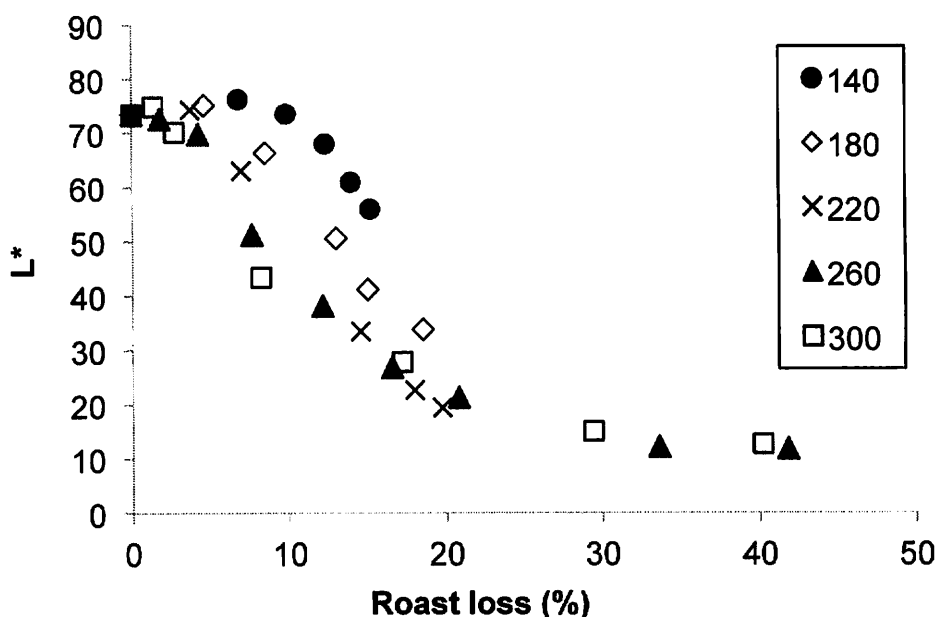


Fig. 4-11. Relationship between L^* and roast loss at various roasting temperatures.

4.4. Conclusions

1. Changes in bean colour during roasting follow a certain path, regardless of the roasting temperature.
2. Roasting degree and achieved quality of coffee cannot be determined from only colour or only roasting loss, because temperature affects how fast bean colour changes relatively to the roasting loss.

Chapter V

Measurement of Specific Heat Capacity using Differential Scanning Calorimetry

5.1. Background and objectives

This chapter is a prelude to the next chapter which is about heat and mass transfer model. Specific heat capacity is an important variable in designing a food processing system. The specific heat capacity of coffee bean itself plays important role in a heat and mass transfer model as a thermal property that will determine how the bean temperature will evolve due to the heat received by the bean during roasting. In most materials, specific heat capacity (in constant pressure) is influenced by temperature and the material's phase. Therefore, it is also important to investigate how specific heat capacity changes as bean temperature increases. However, it is not easy to measure the specific heat capacity of a food material like coffee bean.

A method that can be used to measure specific heat capacity is the differential scanning calorimetry (DSC). DSC measures difference of heat applied to increase temperatures of two materials a same rate. In measurement of specific heat capacity, two materials are used as sample: one is a material that has known specific heat capacity (reference material), whereas the other one is the material being investigated (the sample). DSC can also give information of the type of chemical process that occurs during a thermal process, through the heat difference.

The objectives of the study are to measure the change in specific heat capacity of coffee beans during roasting and to elucidate the phenomena that occur inside the bean due to thermal process.

5.2. Theory of Differential Scanning Calorimetry

As aforementioned, DSC measures the difference of heat applied to increase temperatures of two materials at a same rate. One material is a reference material and the other one is a sample being investigated. Fig. 5-1 gives an illustration of the DSC measurement. For example, a sample is put into the DSC cell 1 and a reference

material is inside the DSC cell 2. The difference of applied heat is given as:

$$\Delta \frac{dq}{dt} = \left(\frac{dq}{dt} \right)_1 - \left(\frac{dq}{dt} \right)_2 \quad (5-1)$$

$(dq/dt)_1$ and $(dq/dt)_2$ are the rate of heat flowing to the cell 1 and cell 2, respectively.

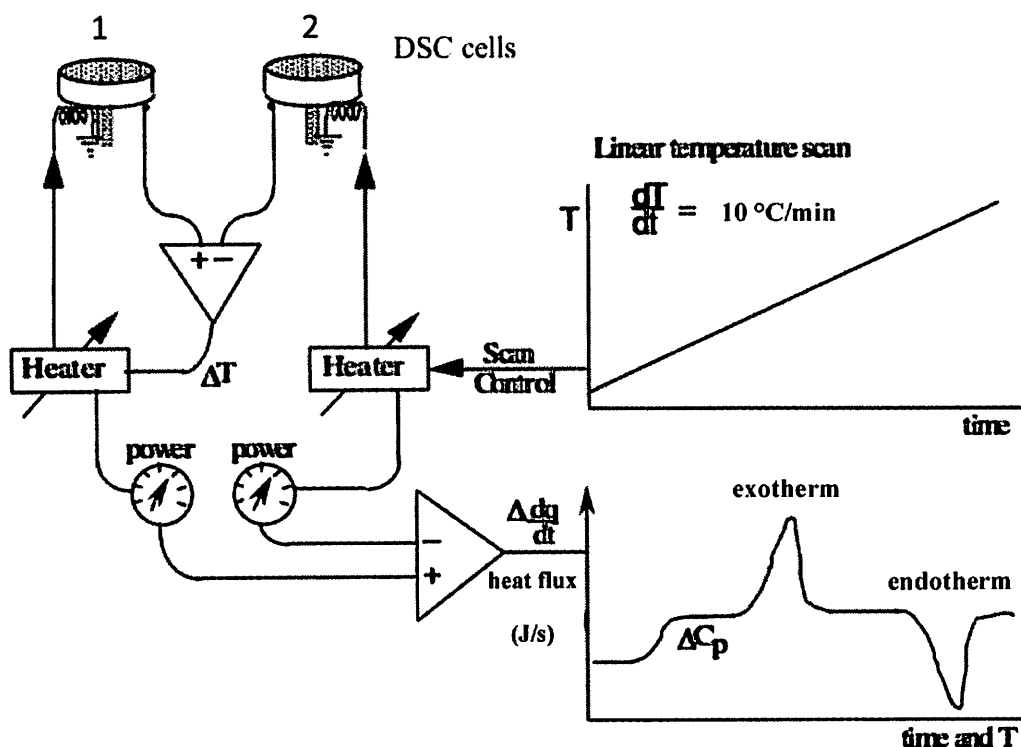


Fig. 5-1. Schematic illustration of the differential scanning calorimetry (Department of Chemistry of Colby College, 2007)

The DSC can be used to explain the phenomena occurring during a thermal process. There are two opposite peaks are shown in Fig. 5-1. If the reference material does not undergo any chemical or phase change, the peak in which the heat difference becomes larger indicates an occurrence of endothermic reactions in the sample material. Here the heat is needed not only for increasing the temperature but also to fuel the reactions. The opposite peak indicates the occurrence of exothermic reactions, where the reactions help supplying heat to increase temperature. The heat that must be applied to the sample material is then reduced.

In measurement of specific heat capacity, DSC measurements are performed on

two sample materials. The first one is a material with known heat capacity that is used as a reference, and the second one is a material that is investigated. The procedure of measurement is as follows.

1. Two empty cells are put into the DSC machine and scanned to obtain the “empty cell” curve, as shown in Fig. 5-2.
2. One of the empty cells was replaced by a cell containing the material used as reference, and scanning is performed to obtain the DSC curve of the reference material.
3. After the two basic curves are obtained, the cell of reference material is replaced with a cell containing the sample, and DSC measurement for the sample is performed.
4. Since the rates of temperature increase are same, specific heat capacity of the sample (C_{p_b}) can be calculated by the following equation.

$$C_{p_b} = \frac{m_a h_b}{m_b h_a} C_{p_a} \quad (5-2)$$

C_{p_a} is specific heat capacity of the reference material. m_a and m_b denote mass of the reference material and mass of the sample being investigated, whereas h_a and h_b are their respective heat flow difference with that of the empty cell (see Fig. 5-2).

Common assumptions used in the measurement are: (1) only increase in temperature takes place and (2) the materials' composition and phase do not change during the measurement. However, during roasting not only the temperature that changes, but also the internal composition and total mass of bean due to physical processes and chemical reactions taking place. Hence, these assumptions are not suitable for coffee bean if the bean temperature increases to the range of roasting temperature. The heat applied to increase bean temperature can give misleading information of the real heat capacity of the bean. Therefore, the measurement will only give information of apparent specific heat capacity.

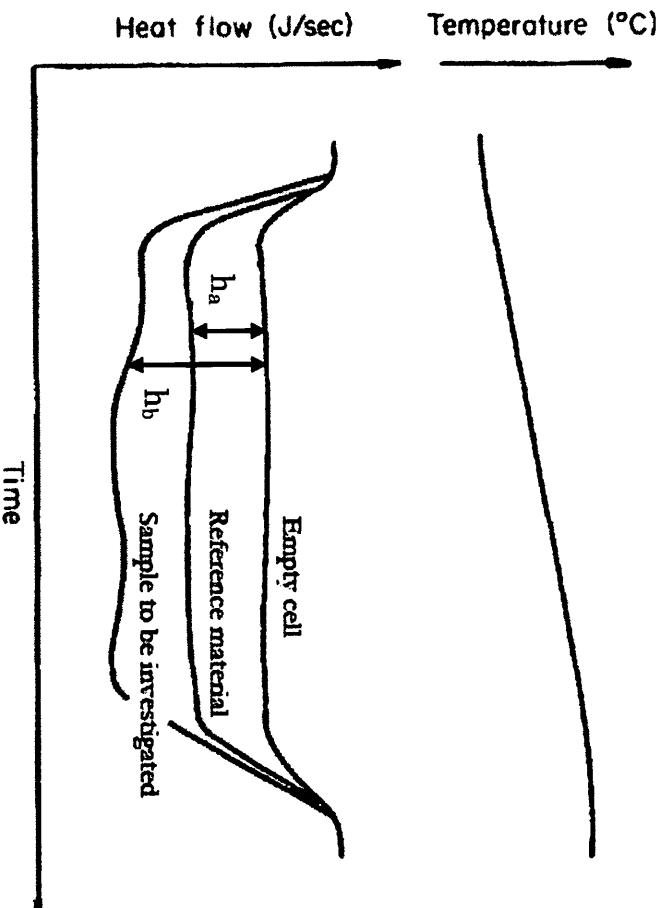


Fig. 5-2. Specific heat determination by measurements of heat differences (Raemy & Lambelet, 1982)

5.3. Materials and methods

About 10 mg of ground green coffee bean was used as sample. Size of the ground bean particles was made as small and uniform as possible. The experiments were carried out using Shimadzu DSC-50 (Fig. 5-3) and DSC cells (vessels) made of aluminium. The scanning rate was set to 10 °C/min, and the upper temperature was set to 300 °C. It is important that the scanning rate and holding time must not be changed during the set of experiment, because different experiment conditions require different basic curves. All measurements were conducted in triplicate.

Since mass of the bean sample inside the cell changes during the experiment, measurement of the sample mass is necessary for analysing the DSC data. The change in mass of bean sample during scanning was measured by repeating the scanning process up to certain temperatures, which were 140, 180, 220, and 260 °C. Each measurement started from the beginning, or the starting temperature that was about 50°C. It was assumed that the trend of change in mass did not really differ one to another. Values in between two sampling temperatures were estimated using Bezier spline function.

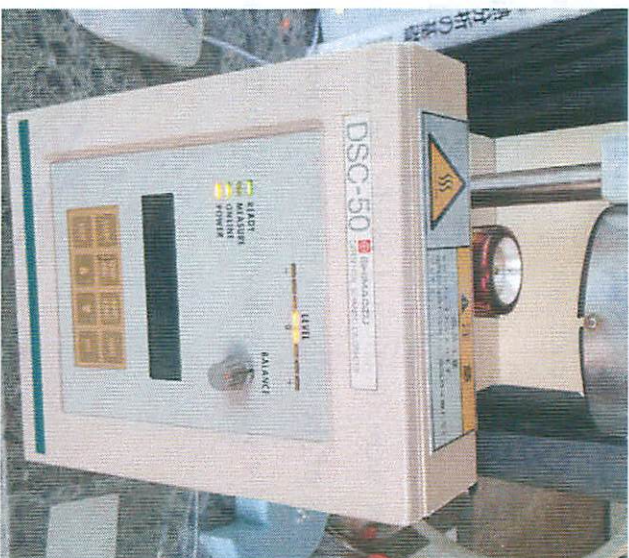


Fig. 5-3. Differential scanning calorimeter (Shimadzu DSC-50)

Al_2O_3 in its crystalline polymorphic phase α -alumina was chosen as the material for comparison, because it is a ceramic material, which is good electrical insulator, with a relatively high thermal conductivity. Data of specific heat capacity of Al_2O_3 was obtained from JIS 7123 (Japanese Industrial Standards Committee, 1987), and made into a function of temperature for calculation purpose (see Fig. 5-4).

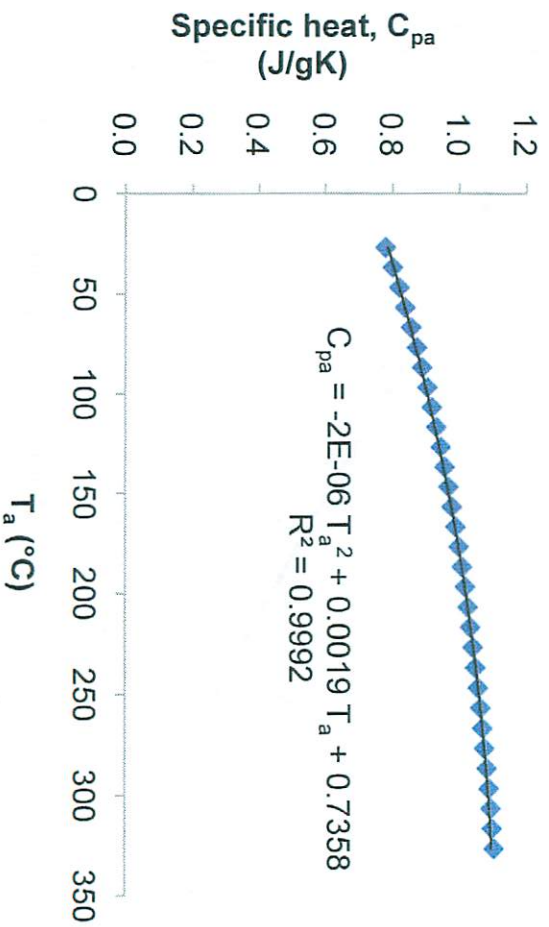


Fig. 5-4. Specific heat capacity of α -alumina

5.4. Results and discussion

Fig. 5-5 compares two raw (unprocessed) data of DSC measurement on green coffee bean (ground). The major difference was in the peak in which endothermic reactions occur. In the top chart, the peak was narrow but high, while in the bottom chart the peak appeared earlier and was wide but shorter. The difference might be caused by how bean samples were distributed inside the cells, because the DSC actually measures temperatures of the cells and not the samples temperature directly and the heat applied to the cells were not always equal to the heat applied to the sample.

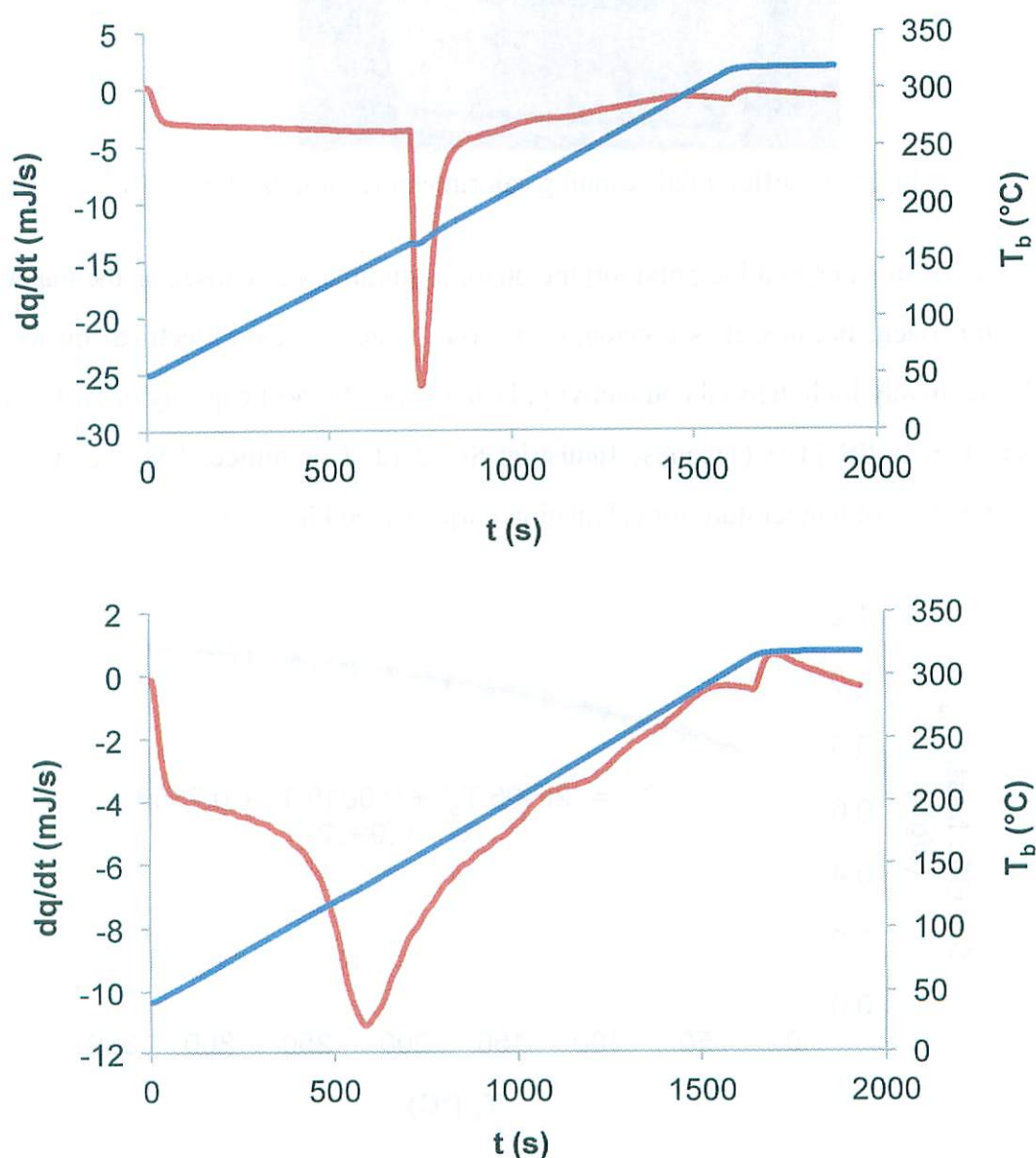


Fig. 5-5. Two types of data of the DSC measurement on green coffee bean

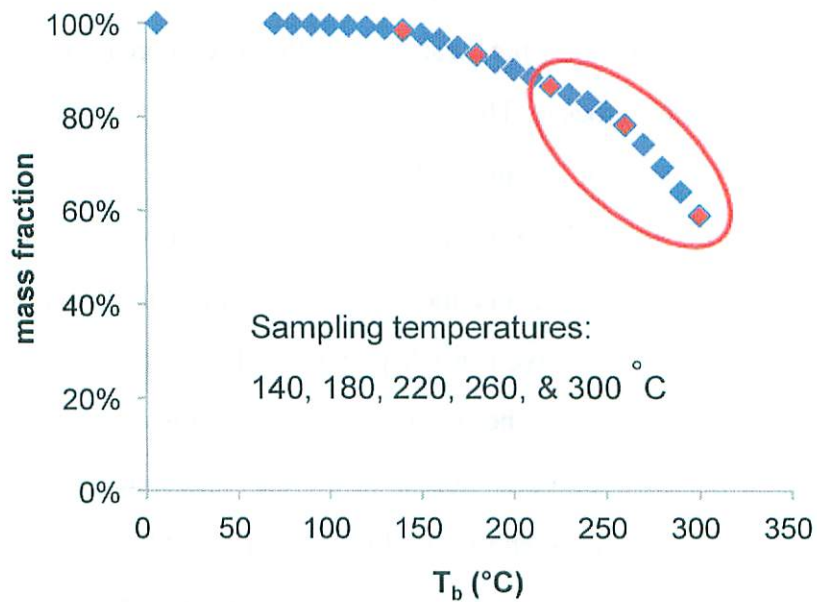


Fig. 5-6. Change in bean mass during the DSC measurement

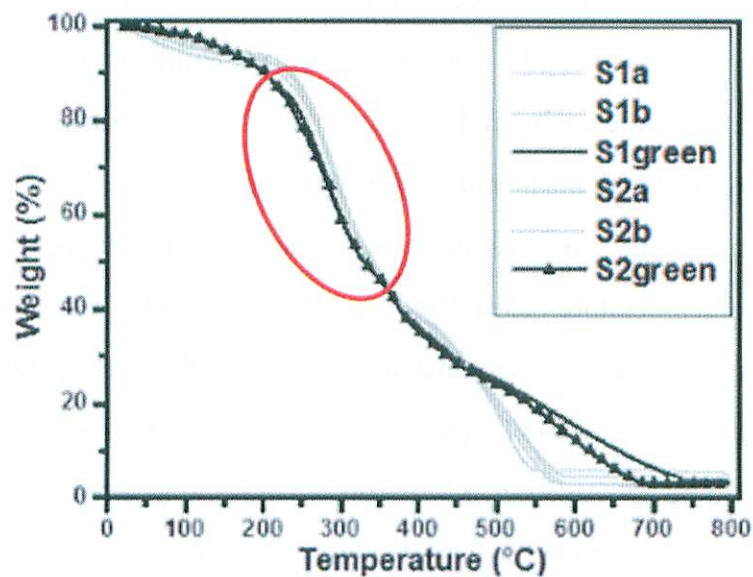


Fig. 5-7. TGA spectra of sets of coffee samples (Rivera, *et al.*, 2011)

Change in bean mass during the DSC measurement is presented in Fig. 5-6. The red data points are the mass at the sampling temperatures, whereas the blue points are the values obtained using Bezier spline function. As comparison, Fig. 5-7 presents a mass data obtained by Rivera, *et al.* (2011) using thermo-gravimetric analysis (TGA) with same heating rate. From both figures, it can be seen that the decrease in mass became faster when the temperature reached 200–210 °C.

The results of analysed DSC data are presented in Fig. 5-8. After bean temperature went above 100 °C, the heat flow difference increased, indicating an occurrence of endothermic process. The peak was found to be at temperature ranging from 140 to 170 °C in both studies. The endothermic process was mostly the evaporation of moisture inside the bean, which continued even when the bean entered the temperature range of roasting, and the formation of phenols (Strezov & Evans, 2005). This confirms the result given in Chapter III: solid mass started to decrease, indicating the beginning of roasting, before the dehydration finished.

The shape of the DSC curve is similar to the curve obtained by Rivera, *et al.* (2011) for green bean, which is shown in Fig. 5-9. The authors mentioned some important phases of coffee roasting based on the obtained DSC data. The most significant transformation happening inside the bean occurs in the temperature range between 208 and 230 °C, and the decrease in mass becomes faster until 289 °C. This range of temperature marked the occurrence of exothermic process, where a large amount of volatile organic compounds is formed, mostly from non-volatile compounds, and released intensively (Franca, *et al.*, 2009; Yeretizian, *et al.*, 2002).

If one assumes that no moisture is evaporated and no chemical changes occur inside the bean at temperature below 100 °C, from the Fig. 5-8 it can be concluded that normally bean specific heat capacity increases linearly with the temperature, following relationship $C_{p_b} = 10.9 T_b + 1457.6$ ($R^2 = 0.9973$), with T_b in °C and C_{p_b} in $J\ kg^{-1}\ K^{-1}$. Thus, the C_{p_b} will be $2547.6\ J\ kg^{-1}\ K^{-1}$ at 100 °C, close to an average value of $2500\ J\ kg^{-1}\ K^{-1}$ for temperature range 25–210 °C obtained by Small & Horrel (1993). Since the initial moisture content is 12.0% in dry basis and the average specific heat of water under 100 °C is $4190\ J\ kg^{-1}\ K^{-1}$, then the specific heat capacity of bean solid is given by $C_{p_s} = 10.9 T_b + 955.1$ (in $J\ kg^{-1}\ K^{-1}$).

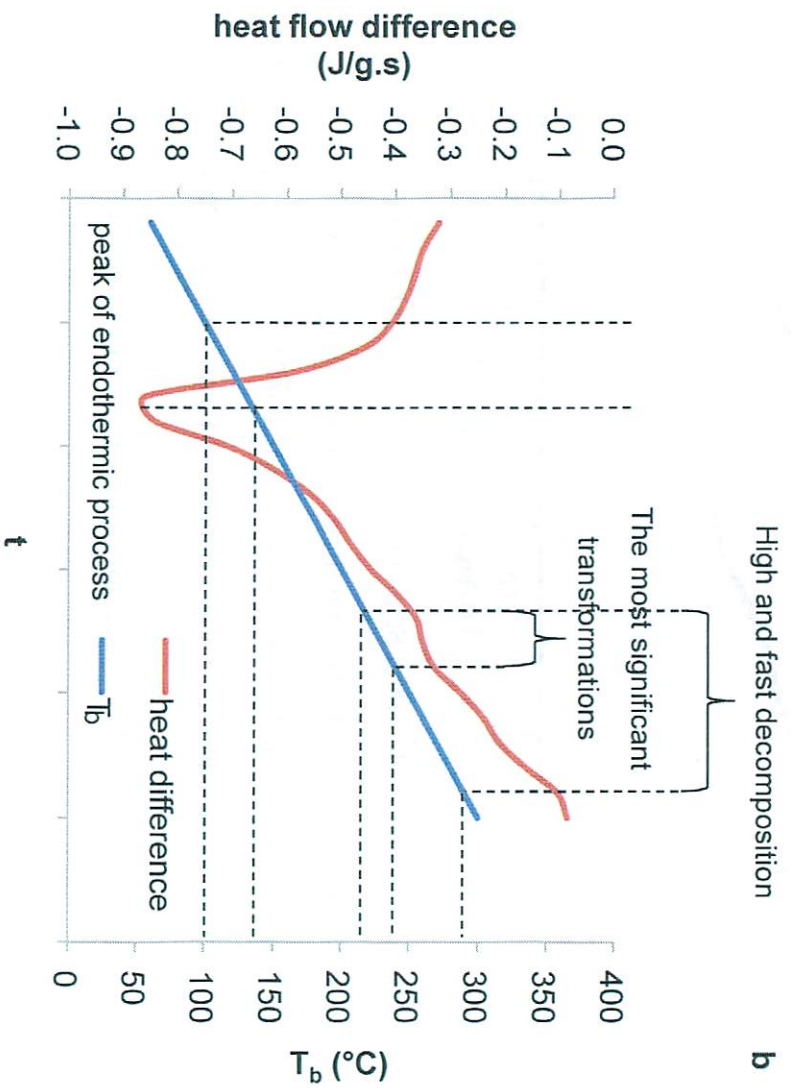


Fig. 5-8. **a.** Change in apparent specific heat capacity; and **b.** Heat difference during the DSC measurement

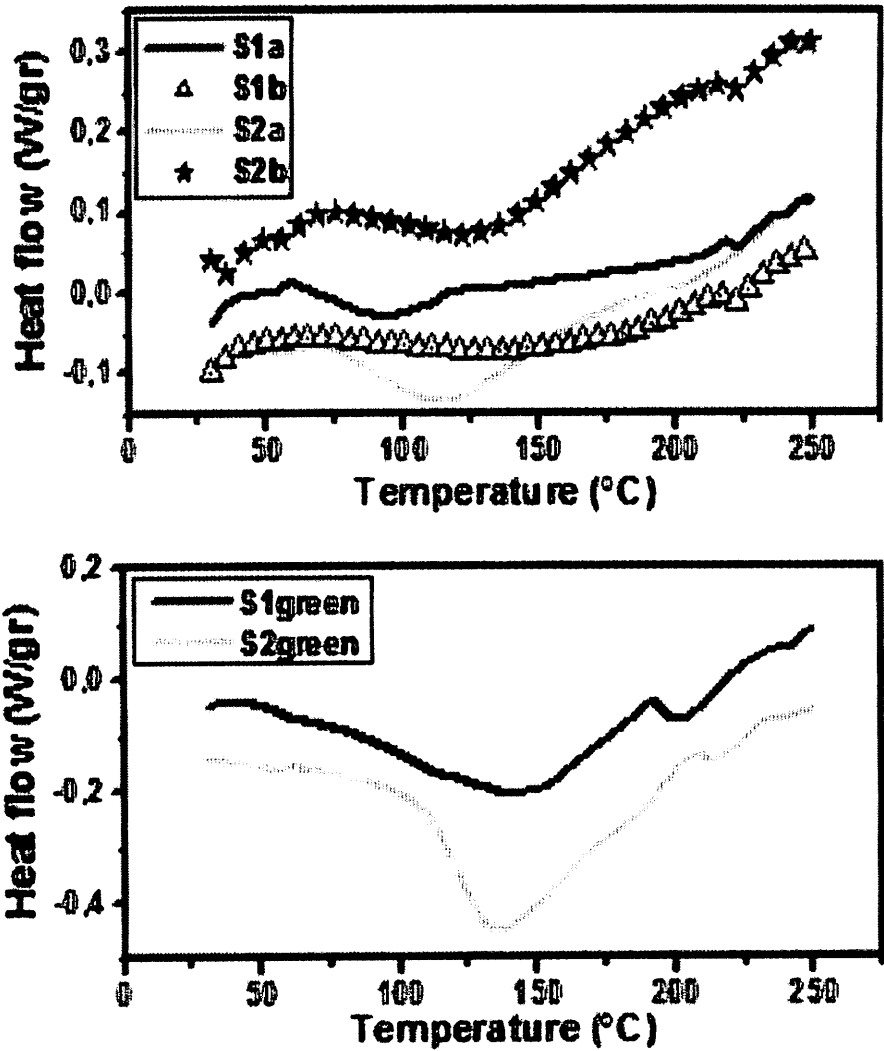


Fig. 5-9. Modulated Differential Scanning Calorimetry (MDSC) spectra of coffee samples, with scanning rate of 5 °C/min (Rivera, *et al.*, 2011). Above: the samples S1a roasted to 210 °C, S1b roasted to 230 °C, S2a roasted to 210 °C, S2b roasted to 230 °C. Lower: the samples without roasting: S1 green and S2 green.

Some equations have been used to express the specific heat capacity of coffee bean in some works. Schwartzberg (2002) has proposed and used the following empirical equation for C_{p_b} .

$$C_{p_b} = \frac{7 T_b + 1099 + 5000 X}{1 + X} \quad (5-3)$$

The C_{p_b} obtained here is not a lumped specific heat capacity. The heats absorbed and generated during endothermic and exothermic chemical reactions are not accounted in

this equation, but are separated in an equation of dT_b/dt .

Since the fraction 5000 X is contributed by bean moisture, the C_{p_s} is then given by $7 T_b + 1099$. This linear relationship is similar to the one obtained in this study ($C_{p_s} = 10.9 T_b + 955.1$), but the effect of temperature is smaller. This equation could result in overestimation of C_{p_s} value at high roasting temperature above 240 °C, as observed in the study by Hernández, *et al.* (2007) that used Schwartzberg's equations (see Fig. 5-10). The predicted temperature increase was slower than the real temperature increase in the experiment at roasting temperature of 300 °C. This is most likely because the predicted specific heat capacity was overestimated. It is quite obvious since the roasting temperatures employed by Schwartzberg's when proposing the equation were actually lower.

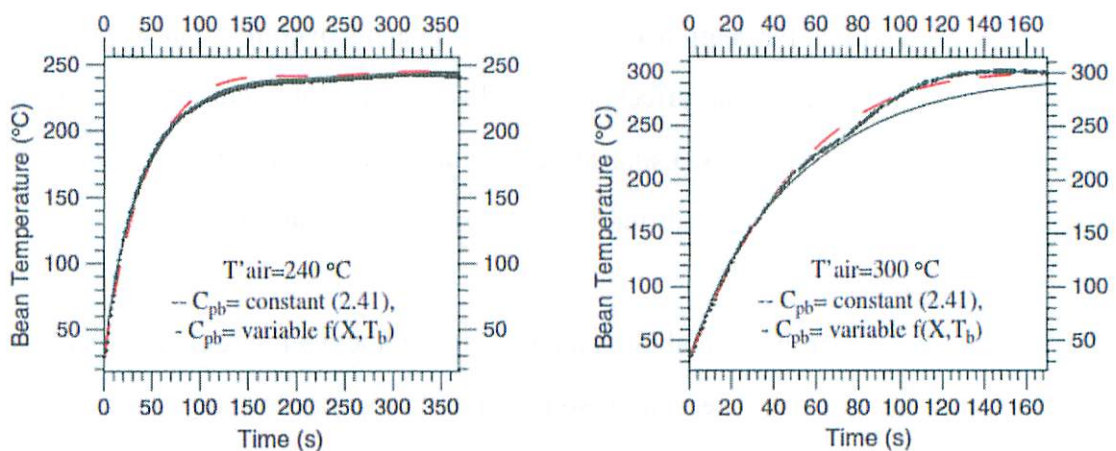


Fig. 5-10. Estimated bean temperature at roasting temperature 240 °C and 300 °C (Hernández, *et al.*, 2007). Red dotted curves indicate result of model using constant C_{p_b} , whereas the thin black curves indicate that of the model using Eq. 5-3.

Experimental data are indicated by the thick black curves.

The analysis of heat and mass transfer in Hernández, *et al.* (2007) also used a constant value of lumped specific heat capacity of $2.41 \text{ kJ kg}^{-1} \text{ K}^{-1}$, which accounted the heat of exothermic and endothermic reactions. Using the equation obtained here, that value is the specific heat capacity at 87.4 °C. Because roasting temperature is far higher, normally ranging from 200 to 300 °C, if the behaviour of specific heat capacity is always increasing with temperature, then the constant value will be too low at the

temperature range of roasting.

The Fig. 5-10 shows the constant lumped specific heat capacity gave better agreement with the experimental data at higher roasting temperature (300 °C). However, mass of bean solid was assumed constant, not decreasing in the model. This overestimation solid mass might possibly have counterbalanced the underestimation of specific heat capacity, so that the obtained result was arguably satisfactory.

Another empirical equation has also been given by Fabbri, *et al.* (2011). The specific heat capacity was given as a function of moisture content only, and the effect of temperature was not taken into account.

From the comparison of results it is clear that estimating specific heat capacity of coffee bean during roasting is not an easy task. With higher gradient, the linear equation obtained in this study will definitely over-estimate the value of C_{p_s} at high temperature even more. Estimation of reaction heat using overall balance has been found inappropriate because the effects of specific heat do not occur simultaneously (Eggers & Pietsch, 2001). Thus, using an all-round estimation of specific heat may always lead to failure because different processes happen at different times and different temperatures.

A possible solution when making a model is to set a temperature range where the linear relationship can be used, and some other temperature ranges with their respective equations. Judging from the analysed DSC data, the empirical equation obtained in this study can be used for estimating the specific heat capacity of bean before the beans enter the stage of roasting, which is before 140–160 °C. Latent heat of moisture evaporation should be considered in the model from 100 °C, when water evaporation starts. When the beans enter roasting stage especially at relatively high temperatures, the linear equation cannot be used anymore. Since the constant value performed better at high roasting temperature (300 °C), and arguably fitted the experiment data at lower temperature (240 °C), it might be more useable at that temperature range of roasting.

5.5. Conclusions

1. DSC has been shown useful for measuring the apparent specific heat capacity of coffee bean and understanding the thermal process inside the bean.
2. Specific heat capacity of coffee bean can be expressed in a linear equation for the temperature below or equal to 100 °C.
3. Using an all-round estimation of specific heat may always lead to failure because different processes happen at different times and different temperatures.

Chapter VI

Towards Modelling of Heat and Mass Transfer in Roasting

6.1. Background and objectives

The importance of reaction pathways in roasting has led to a great importance of an accurate process control that can result in the expected process and end product. The process control requires a model that can accurately simulate the real situation during the process. It has been discussed in the previous chapters that the temperature evolution within the bean matrix due to heating determines the reaction pathways and governs the development of coffee flavour and aroma. Therefore, the model must be able to predict how the bean temperature responds to the heating. Because the heat received by the beans is not only used to increase the bean temperature but also to fuel the roasting reactions, then the temperature increase is also affected by how the composition of bean changes due to the reactions. The model should base on the heat and mass transfer from and to the beans. However, the knowledge on how chemical compounds change inside the bean during roasting is still not enough for the model development, thus putting some limitations on the model.

This chapter discusses the efforts on the modelling of heat and mass transfer of coffee roasting. Some previously proposed models are first reviewed and a simple model of heat and mass transfer based on the current research is presented. The objectives of this study are to investigate the limitations faced by the current models and to look at possible measures needed to improve the quality of modelling.

6.2. Review on previous works

The first model of heat and mass transfer in coffee roasting was proposed by Schwartzberg (2002). Heat transferred to the beans by the gas is calculated by subtracting heats used to heat up the components of roaster from the total heat given by the roasting air. Other heats transferred indirectly through the hot components of the roaster as well as the heat from exothermic reaction are taken into account when

calculating the total heat received by the beans. As explained in Chapter V, specific heat capacity of the bean is calculated empirically based on bean moisture content. The decrease in moisture content is calculated empirically based on some assumptions.

The model by Schwartzberg was first implemented by Hernández, *et al.* (2007), in an experimental batch roaster where heat transfer from air to roaster's metal and contact between beans and the metal were assumed negligible. The model showed some limitations, and the predictions did not fit especially for high roasting temperatures. The first drawback is in specific heat capacity calculation as explained in the previous chapter. The decrease in moisture was calculated using Schwartzberg's equation, despite the fact that in Schwartzberg's experiments the bean temperature did not exceed 250 °C. The types of roaster used were also different as Schwartzberg used rotating-bowl roaster, thus the results did not fit. The rate of exothermic heat was also calculated from the beginning of roasting, which does not reflect the real situation of roasting. Some other limitations are the assumption of constant solid mass and bean equivalent diameter, as well as uniformity of bean temperature and moisture content.

Schwartzberg's model was improved by Heyd, *et al.* (2007) for the case of spouted bed roaster. The non-stationary moisture and temperature profiles due to high external heat transfer were considered. Rate of moisture loss was governed by a diffusion equation, and the apparent water diffusivity was adjusted to fit the experimental data of beans roasted with gas inlet temperature set at 210 and 250 °C. However, the heat from exothermic reactions, moisture produced by the reactions, and heat transported by water inside the bean were neglected in the calculation. Consequently, the predicted results for bean roasted at 250 °C, where the exothermic reactions were most likely occurring, did not fit the data.

Bottazzi, *et al.* (2012) also applied Schwartzberg's model to the case of rotating drum roaster. Just like the previous authors, radiation heat transfer was neglected, as well as the conduction between the roaster wall and the beans. Dimensionless numbers were calculated by considering the profiles of the cylinder. However, in the modelling and experiments the drum rotational speed was set to zero. In his study, Schwartzberg actually did not mention the rotational velocity of the bowl and did not take it into

account. Another drawback of the model is the one dimensional assumption, which does not reflect the real roasting situation as shown by the measurement data.

Basile & Kikic (2009) found that uniformly distributed temperature within the bean can only be assumed in the case of drum roaster, but not in spouted bed and fluidised bed roasters. A lumped specific heat capacity approach was then used to predict the non-stationary thermal profile of coffee bean during roasting. The lumped specific heat capacity was given as a function of bean temperature, initial moisture content, and degradation rates of solid and moisture. The model first considered the bean as an equivalent sphere, but later a mesh model of half-ellipsoid was also built for the analyses. The model was found really good for predicting the average bean temperature as well as the evolution of the thermal gradient within the beans. The main drawback of this model is the temperature dependences of some properties and phenomena were neglected. For example, the external heat transfer coefficient was assumed constant and estimated to fit experimental data. In addition, no clear explanation was provided regarding the rate of moisture loss.

A lumped specific capacity approach was also used by Fabbri, *et al.* (2011), but the variable was given as a function of moisture content. The study used two models of coffee bean: a half-elliptical geometry and a digitised geometry based on real bean shape. However, in the estimation of dimensionless numbers the bean was still assumed as an equivalent sphere. Beside the specific capacity, other variables such as bean density, conductivity, and thermal diffusivity were also calculated empirically as functions of moisture content only, and the dependences on temperature were negligible. Moisture loss was calculated based on diffusion equation, just like found in Heyd, *et al.* (2007). However, the diffusivity was calculated using an equation proposed by Hernández-Díaz, *et al.* (2008), where it was expressed as an empirical function of temperature and ration of moisture content. The equation was actually based on experimental data of coffee drying, which is normally performed at much lower temperature than roasting. Since the roasting experiment was conducted at 200 °C the prediction result could still fit the data, but when a high temperature is employed then the prediction accuracy cannot be guaranteed.

From the studies on heat and mass transfer of coffee roasting conducted so far, it can be concluded that the assumptions were used to make modelling much easier, but at the same time they limit the predicting ability and thus lower the accuracy.

6.3. Development of the heat and mass transfer model of current study

A simple heat and mass transfer model of the roasting condition of current study is constructed here. To make equation writing simple, new denotations are used for some variables, replacing the ones used in previous chapters.

6.3.1. Heat balance

The basic of heat transfer is the principle of energy conservation. If one assumes that there is no energy released to the environment from the bean, then the main equation becomes

$$Q_{\text{received}} = Q_{\text{consumed}} \quad (6-1)$$

Since there is no fan or blower used in the experiments, heat is transferred to the bean through radiation and convection mechanisms. When the bean enters the temperature range of roasting, the heat arising from exothermic reactions is assumed to be fully absorbed by the bean. Neglecting the heat from other sources such as heat from the bean holder and thermocouples, the total heat absorbed by the bean is given as

$$Q_{\text{received}} = Q_{\text{conv}} + Q_{\text{rad}} + Q_{\text{react}} \quad (6-2)$$

In this model the bean shape is assumed equivalent sphere. The heat transferred through natural convection is calculated as follows.

$$Q_{\text{conv}} = 4\pi r_b^2 h_{\text{conv}}(T_a - T_b) \quad (6-3)$$

Heat radiated by the oven heating wall can be calculated using Eq. 6-4. Depending on the situation, if it is assumed that the temperature distribution inside the oven is negligible and no heat escapes from the oven, then the wall temperature can be considered equal to the air temperature.

$$Q_{\text{rad}} = 4\pi r_b^2 \sigma \varepsilon_b (T_w^4 - T_b^4) \quad (6-4)$$

If it is assumed that emissivity coefficients of plants and plant based materials do not vary a lot, the emissivity of coffee bean can be set to 0.98 (Chen & Zhang, 1989; López, *et al.*, 2012).

Exothermic reactions release heat that helps heat up the bean. The basic equation of the reaction heat has been proposed by Schwartzberg (2002) based on a study conducted by Raemy & Lambelet (1982). The assumptions used in the equation are:

- a. The rate of heat generation is proportional to the rate of exothermic reactions.
- b. The rate is proportional to an Arrhenius-type reaction coefficient and remaining concentration of the reactants, with the reactants are fully consumed in the reactions.
- c. Concentration of the reactants are proportional to the ratio of the remaining heat to be generated per kg of dry solid to the total heat to be generated per kg of dry solid.

Thus, the equation becomes

$$Q_{\text{react}} = m_s \dot{Q}_r = m_s f_A \frac{H_{\text{et}} - H_e}{H_{\text{et}}} \exp\left(-\frac{H_a}{RT_b}\right) \quad (6-5)$$

In this study, the exothermic reactions are assumed to occur only after the bean temperature rises above 160 °C.

Because the total heat absorbed by the bean is mainly used to increase the temperature and to evaporate moisture, then the total heat consumption of the bean can be calculated as follows.

$$Q_{\text{consumed}} = C_{p_b} m_s (1 + X) \frac{dT_b}{dt} - m_s L_{\text{vap}} \frac{dX}{dt} \quad (6-6)$$

Combining Eq. 6-1 to Eq. 6-6, and with some modification, the equation of bean temperature change can be obtained.

$$\frac{dT_b}{dt} = \frac{4\pi r_b^2 (U(T_a - T_b) + \sigma \epsilon_b (T_w^4 - T_b^4)) + m_s (\dot{Q}_r + L_{vap} \frac{dX}{dt})}{Cp_b m_s (1+X)} \quad (6-7)$$

6.3.2. Mass transfer: moisture diffusion from the bean

The mass transfer from beans to surrounding environment consists of moisture evaporation and volatilisation of solid compounds. The reduction in solid is hard to predict theoretically because different condition will lead to different reaction pathways. So far there has not been any model that is able to determine the rate of solid volatilisation to roasting temperature. Thus, only the loss of moisture is accounted and the solid mass of the bean is assumed constant in most cases (including the current study). Another approach has been used by Basile & Kikic (2009) in their model, where a lumped specific heat capacity is used and loss in bean mass was calculated as a single unit, not separated between solid and moisture.

Moisture loss from the bean is assumed to follow gas diffusion mechanism in a sphere. Flux of gas A diffusing from surface of a sphere (position 1) into gas B (position 2) is given by Eq. 6-8 (Geankoplis, 1983). For diffusivity of moisture inside the bean, it is assumed that p_A at bean surface is small compared to P so that $P \approx P_{BM}$.

$$N_{A1} = \frac{D_{AB} P}{r_1 P_{BM}} (C_{A1} - C_{A2}) \quad (6-8)$$

For the case of diffusivity of moisture inside the coffee bean, assuming $P \approx P_{BM}$, the equation becomes

$$N_{wb} = \frac{D_{wb}}{r_b} (c_w - c_{we}) \quad (6-9)$$

The diffusivity of moisture inside the coffee bean is assumed to be affected by the diffusivity of water vapour in air. Moisture concentration is defined here as the amount of water per unit of bean volume.

$$C_w = \frac{m_w}{V_b} = \frac{X m_s}{\frac{4}{3}\pi r_b^3} \quad (6-10)$$

The amount of moisture leaving the bean per unit time is then given by the following equation.

$$\frac{dX}{dt} m_s = N_{wb} 4\pi r_b^2 \quad (6-11)$$

Substituting Eqs. 6-9 & 6-10 to Eq. 6-11, the rate of moisture loss is then given by

$$\frac{dX}{dt} = D_{wb} \frac{3X}{r_b^2} \quad (6-12)$$

6.3.3. Determination of coefficients and dimensionless numbers

To determine the coefficients needed in the model is not an easy task. The coefficients are mostly temperature dependent, thus measurement of the coefficients is sometimes nearly impossible in a complicated process like coffee roasting.

Effective heat transfer coefficient of convection and Biot number

Theoretically the effective convective heat transfer coefficient can be calculated from the Biot number and convective heat transfer coefficient of the roasting air at the given temperature. The following equation was derived by Basile & Kikic (2009) based on assumption assuming bean to be an equivalent sphere.

$$h_{conv} = \frac{h_a}{1+0.2 Bi} \quad (6-13)$$

The Biot number can be calculated from bean radius, convective heat transfer coefficient of the roasting air, and heat conductivity of the bean. Later in his work the Eq. 6-13 was modified to fit the data obtained from a closed form model where the bean shape was assumed to be half elliptical.

The Biot number, which is the ratio between internal and external heat transfer resistances, determines the distribution of temperature inside the bean. In the case of drum roaster, external convective heat transfer is not so large and thus the temperature

distribution is negligible. In spouted bean roaster, as also found in other fluidised-bed roasters, external convective heat transfer is very large compared to internal heat conduction, so distribution in moisture content and temperature takes place inside the bean (Heyd, *et al.*, 2007). The heat transferred to coffee beans tends to stagnate on bean surface (Basile & Kikic, 2009), and due to bean's real shape heat transfer from roasting gas to a bean occurs first (and faster) at the corners of the bean (Fabbri, *et al.*, 2011). Temperature of bean surface (T_s) can be expressed as a function of overall bean temperature, roasting temperature, and the Biot number (Basile & Kikic, 2009).

$$T_s = \frac{\frac{T_b + T_a}{Bi + 5}}{\frac{1}{Bi} + \frac{1}{5}} \quad (6-14)$$

Dimensionless numbers of the natural convection around the bean

Nusselt number is required to calculate the conductive heat transfer coefficient of roasting air. There is not only one equation that can be used as some researchers have worked on natural convection around a sphere. The choice of equation depends on the range of Prandtl number (Pr) and Grashof number (Gr) of the process. Yuge (1960) proposed an equation to calculate the Nusselt number for natural convection around a sphere for $Gr Pr \leq 10^8$. The equation is as follows.

$$Nu = 2 + 0.43 Gr^{0.25} Pr^{0.25} = \frac{h_a d_b}{k_a} \quad (6-15)$$

The Prandtl and Grashof numbers can be calculated from temperature, density, dynamic viscosity, heat conductivity, and specific heat capacity of the roasting air, as well as the bean temperature.

Specific heat capacity

The specific heat capacity is based on the segmentation approach proposed in Chapter V. Below 160 °C, it is $C_{p_s} = 10.9 T_b + 955.1 + 4200 X$ (in $J kg^{-1} K^{-1}$), whereas from 160 °C the constant value of $2410 J kg^{-1} K^{-1}$ is used.

Conductivity of coffee bean

So far there has not been any reliable estimation of coffee bean's conductivity (Eggers & Pietsch, 2001). Change in conductivity of coffee bean during roasting is difficult to measure. During roasting bean's chemical composition changes due to the temperature increase, making the bean a totally different thing with different thermal conductivity. Direct on-line measurement during the roasting process is arguably the most ideal way to measure bean conductivity. Fabbri, *et al.* (2011) empirically estimated bean conductivity as a function of moisture content only, neglecting the effect of temperature.

$$k_b = 5.556 \times 10^{-4} \rho_b \left(\frac{x}{1+x} \right) + 0.0713 \quad (6-16)$$

Moisture diffusivity inside the bean

Just like the conductivity, moisture diffusivity inside the bean is very difficult to measure. It also depends on temperature and the composition of bean, but the presence of bean pores seems to play a more important role. During roasting beans undergo some changes in size, structure, and porosity. Obviously it becomes easier for water vapour to escape from the bean after the roasting reactions start and beans become more porous.

Schwartzberg (2002) proposed an equation of rate of moisture loss based on some used assumptions, which are:

- a. The moisture loss is diffusively regulated, thus the rate of loss is inversely proportional to d_b^2 .
- b. Diffusivity coefficient depends on temperature in an Arrhenius-type correlation.
- c. Driving rate for moisture loss is proportional to current moisture content.
- d. Diffusivity is also proportional to the current moisture content.

Besides those assumptions, in this study it is also assumed that water will not evaporates below 100 °C.

If the equation is assumed equal to the theoretical one (Eq. 6-12), then moisture diffusivity inside the bean is given by Schwartzberg as

$$D_{wb} = \frac{4.32 \times 10^3 X^2}{d_b^2} \exp\left(-\frac{9889}{T_b}\right) \quad (6-17)$$

However, the constants were obtained by fitting the prediction data to experimental data, with bean diameter being 6 mm and the beans roasted in a rotating-bowl roaster. Under different roasting conditions, the results obtained by equation were unable to fit to experimental data (Hernández, *et al.*, 2007) even though the bean temperatures calculated based on the moisture loss showed quite good agreement with the experimental data.

Coefficients for exothermic and endothermic heat calculation

Schwartzberg (2002) used $H_a/R = 5500$ K, $f_A = 1.162 \times 10^8$ J kg⁻¹ s⁻¹, and $H_{et} = 2.32 \times 10^5$ J kg⁻¹ for the variables in Eq. 6-5. He also estimated a value of 2.79×10^6 J kg⁻¹ for the latent heat of bean moisture evaporation (Eq. 6-6). This value is bigger compared to the latent heat evaporation of water at 100 °C and 1 atm (2.257×10^6 J kg⁻¹). The latent heat evaporation of water normally becomes lower if the temperature (and pressure) increases.

6.3.4. Results and discussion

The model is simulated in step-wise fashion with one second Δt steps (Schwartzberg, 2002) using a Microsoft Excel spreadsheet. Fig. 6-1 to 6-5 show how bean temperature and moisture content change during roasting, based on the model developed here and the experiments previously explained in Chapter III. The bean temperature in actual roasting, as shown by the experimental data, never really reached the roasting temperature. This was also found in previous studies (Hernández, *et al.*, 2007; Bottazzi, *et al.*, 2012). In real experiment the air temperature inside oven chamber was not likely able to reach equilibrium, and since the air temperature was measured not exactly at the position where the bean was, the effect might have been bigger than expected. Circulation of air inside the chamber is unpredictable, because there was no clear input output mechanism of roasting air that is commonly found in real roaster.

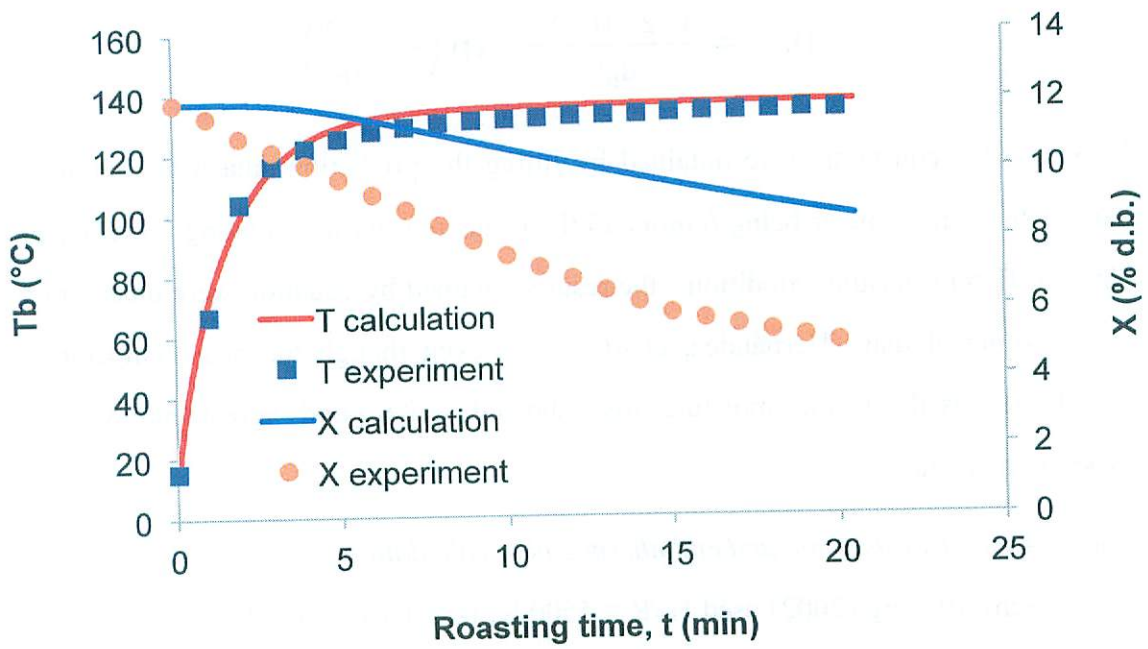


Fig. 6-1. Changes in temperature and moisture of bean roasted at 140 °C

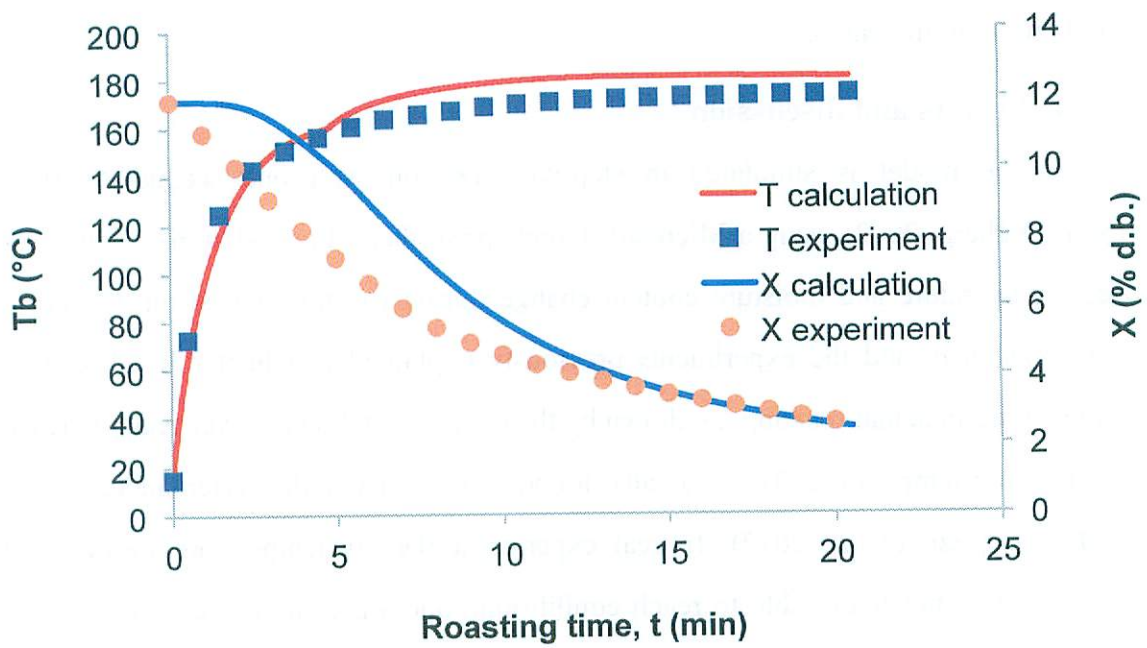


Fig. 6-2. Changes in temperature and moisture of bean roasted at 180 °C

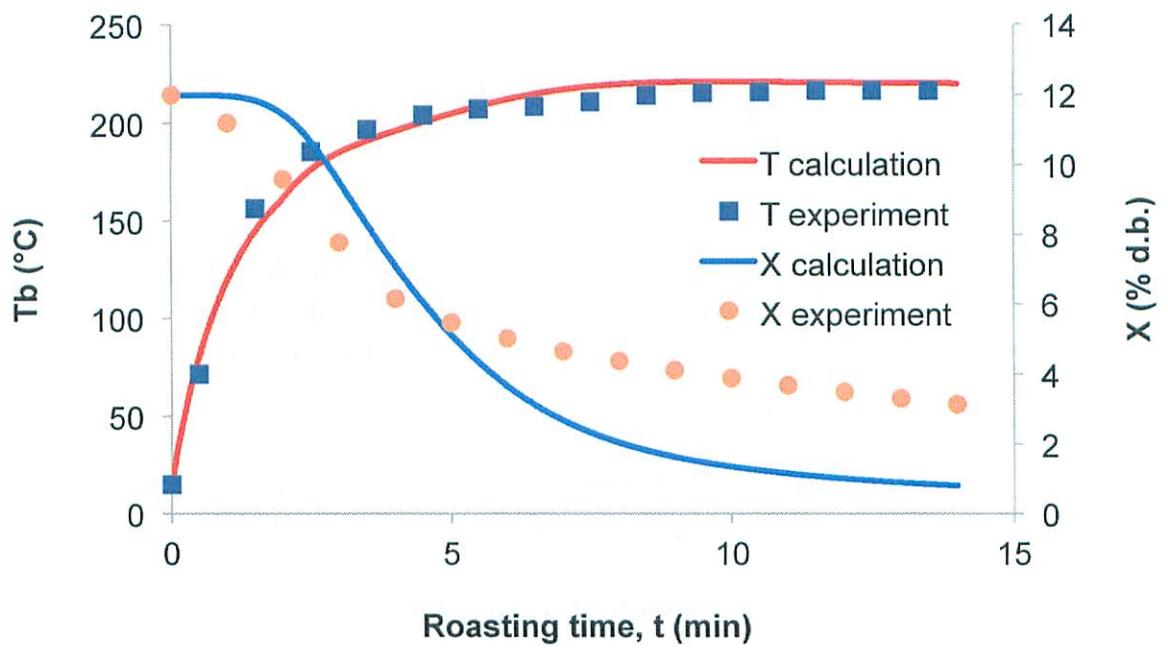


Fig. 6-3. Changes in temperature and moisture of bean roasted at 220 °C

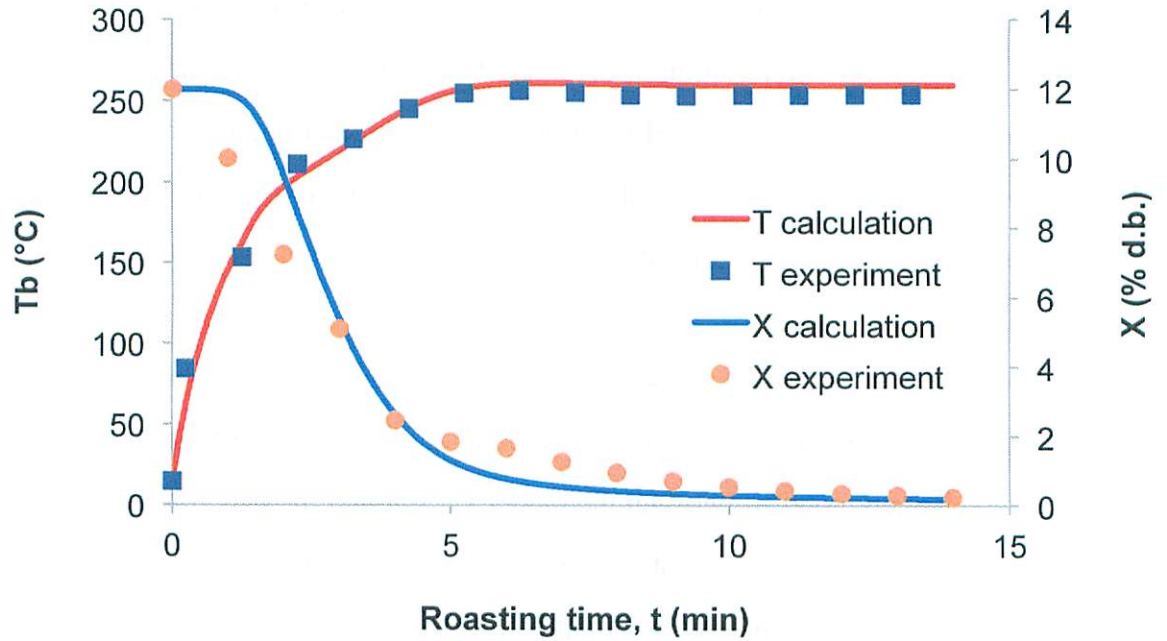


Fig. 6-4. Changes in temperature and moisture of bean roasted at 260 °C

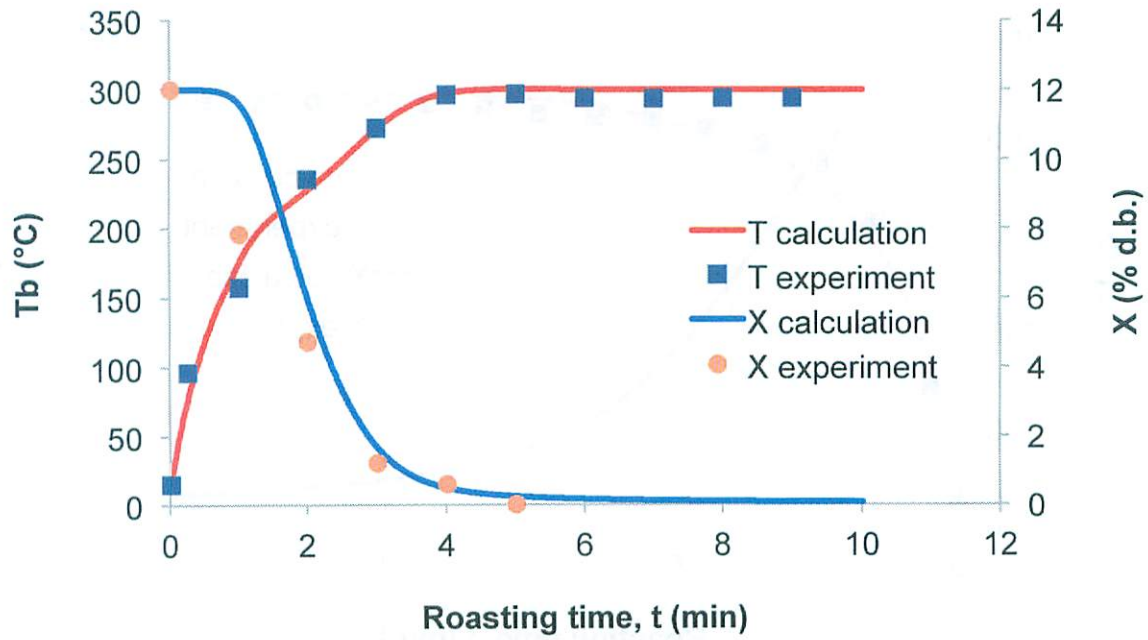


Fig. 6-5. Changes in temperature and moisture of bean roasted at 300 °C

From the figures it can be seen clearly that the model failed to predict accurately the behaviour of bean moisture. From the shape of the experimental data curves, it seems that the dependence moisture diffusivity on bean temperature is not really an Arrhenius-type correlation. Most likely the assumption was made in the first place by considering the time needed for water to start evaporating, and thus the water evaporation was underestimated actually. Even if the assumption was correct, the lag of decrease (where the water does not start evaporating) would last only for a very short time.

Because the increase in bean temperature was calculated based on the calculation of the moisture loss, then the validity of the model can be questioned, despite the relatively good fit between the model's result and the experimental data of bean temperature. Then there might have been some counterbalances that helped the model to fit the experimental data. Another explanation is that water evaporation successfully overcame the roasting reactions and temperature increase in term of heat consumption priority because of lower activation energy (the energy needed by the H₂O molecule to escape from the liquid surface) than those of the roasting reactions (Small & Horrel, 1993). Deeper investigations are needed on this matter.

6.4. Possible measures to improve modelling of coffee roasting

The review of previous works and the discussion on the model built in this study show that the coefficients of heat and mass transfer really affect the performance of a model, and thus should be measured accurately. Complexity of roasting process is obviously a big obstacle for the measurement, as one phenomenon will affect the others and they cannot be separated easily. Even so, roasting process can be divided into some more detailed process based on the fact that the reactions need certain temperatures to occur, not only the activation energy. What is needed is to clarify the segmentation of the whole coffee roasting process into sub-processes, and their regions of occurrence. Separation of the processes that occur at the same time, if possible, will make the calculation of mass balance better. Deeper understanding on mechanism of the coffee roasting, especially the kinetics and pathways of all chemical reactions occurring there, will definitely help a lot.

Therefore, the first thing that needs to be done is to analyse how the chemical compounds change during the roasting. Such analysis will not only help in the estimation of the bean properties through the bean composition, but may also bring insights on how roasting condition influences the reactions. Furthermore, it may enable development of a pathway dependant model of the reactions. This kind of model takes into account many variables of roasting, and thus could give better accuracy in predicting the process. It could be also incorporated with the heat and mass transfer model, and thus could be connected directly to the process control. However, the development of such model will rely on the progress of studies in the chemical compounds and reactions, as it is not simple to understand the reactions from merely the chemical compound data.

Chapter VII

Conclusions and Future Perspectives

The effects of time and temperature of coffee roasting covering pre-roasting and over-roasting condition have been investigated. Bean swelling was fully governed by roasting process, and higher roasting temperature led to greater expansion (Chapter III). The reduction in solid mass that indicates the start of roasting reactions was found to start before the water evaporation completely finishes. A large gap in mass loss during roasting between the samples roasted at 220 °C and those roasted at 260 °C indicates more intense reactions of chemical compounds and oil migrations at higher roasting temperatures. The fact that the fractions of solid that could transform to volatiles are smaller at lower temperatures than at higher ones (Chapter III) proved some roasting reactions require certain ranges of temperature to start, not only the activation energy.

Coffee roasting process has been shown to have a two-stage phenomenon of kinetics. However, the changes in rate were found to happen at different conditions of roast loss for different roasting temperatures (Chapter III). At the first stage of kinetics, before the mass loss became slower, the relationship between roast loss and roasting time could be assumed linear and the slope was determined by the roasting temperature.

The changes in bean colour during roasting were found to follow a certain path, regardless of the roasting temperature (Chapter IV). The path is called the characteristic colouring curve and it may differ for different varieties of coffee beans. Since from the curve it can be indicated that for a certain L^* value each of a^* and b^* has a specific value, the change in colour during roasting can be predicted by understanding the relationships among the parameters. The characteristic colouring curve might be used as basic information for determining the relationship among sensory parameters, and for elucidating the mechanism of chemical reactions occurring during roasting.

By relating the colour and roast loss data it was also confirmed that compound profiles of roasted coffee beans cannot be determined only from the colour-based

roasting degree, as the roasting temperature affects how fast bean colour changes relatively to the change in mass (Chapter IV).

The data of DSC measurement showed that roasting starts after an endothermic process peaking at around 160 °C. From a temperature of about 240-250 °C the exothermic heat production becomes more intense, indicating more exothermic reactions occur. The process takes place after the most important stage of roasting and is associated with fast decomposition of solid. Differential scanning calorimetry has been shown as an ideal method for measuring the specific heat capacity of coffee bean (Chapter V). The specific heat capacity is linearly influenced by temperature and moisture content. However, the equation is only valid before the beans enter the stage of roasting.

In modelling of heat and mass transfer of coffee roasting, the coefficients of heat and mass transfer really affect the performance of a model, and thus should be measured accurately (Chapter 6). Assumptions used to make modelling easier can actually limit the predicting ability and the accuracy of the model. Even seemingly right assumptions may cause some underestimations and overestimations that may have counterbalanced each other in a seemingly accurate model. A segmentation of the whole process is suggested rather than the use of an all-round estimation in measurement and modelling.

The experiment design used in this study has been shown able to help understand better the effect of roasting time and temperature. The same design can be used for investigating the chemical reactions through measurements of the changes in chemicals and composition of the bean, as well as the volatiles that are released during roasting. A comprehensive research will lead to a better insight on the reactions and relationships among phenomena. Obviously, fundamental researches on each chemical reaction, regardless of whether it is directly related to the roasting process, will definitely help in discussing and perceiving the result of measurement.

References

- Alessandrini, L.; Romani, S.; Pinnavaia, G.; Dalla Rosa, M. 2008. Near infrared spectroscopy: an analytical tool to predict coffee roasting degree. *Analytica Chimica Acta* Vol. 625, 95–102.
- Andueza, S.; de Peña, M.P.; Cid, C. 2003. Chemical and sensorial characteristics of espresso coffee as affected by grinding and torrefacto roast. *Journal of Agricultural and Food Chemistry* Vol 51(24), 7034–7039.
- Bagdonaite, K.; Derler, K.; Murkovic, M. 2008. Determination of acrylamide during roasting of coffee. *Journal of Agricultural and Food Chemistry* Vol. 56, 6081–6086.
- Baggenstoss, J.; Poisson, L.; Luethi, R.; Perren, R.; Escher, F. 2007. Influence of water quench cooling on degassing and aroma stability of roasted coffee. *Journal of Agricultural and Food Chemistry* Vol. 55, 6685–6691.
- Basile, M.; Kikic, I. 2009. A lumped specific heat capacity approach for predicting the non-stationary thermal profile of coffee during roasting. *Chemical and Biochemical Engineering Quarterly* Vol. 23(2), 167–177.
- Bekedam, E.K. 2008. Coffee Brew Melanoidins: Structural and Functional Properties of Brown-Colored Coffee Compounds. Ph.D. thesis. Wageningen University, Netherlands.
- Bekedam, E.K.; Schols, H.A.; Cämmerer, B.; Kroh, L.W.; van Boekel, M.A.J.S.; Smit, G. 2008a. Electron spin resonance (ESR) studies on the formation of roasting-induced antioxidative structures in coffee brews at different degrees of roast. *Journal of Agricultural and Food Chemistry* Vol. 56(12), 4597–4604.
- Bekedam, E.K.; Loots, M.J.; Schols, H.A.; van Boekel M.A.J.S.; Smit, G. 2008b. Roasting effects on formation mechanisms of coffee brew melanoidins. *Journal of Agricultural and Food Chemistry* Vol. 56(16), 7138–7145.
- Bhumiratana, N.; Adhikari, K.; Chambers IV, E. 2011. Evolution of sensory aroma attributes from coffee beans to brewed coffee. *Lebensmittel-Wissenschaft*

- und Technologie – Food Science and Technology Vol. 44, 2185–2192.
- Bicho, N.C.; Leitão, A.E.; Ramalho, J.C.; de Alvarenga, N.B.; Lidon, F.C. 2014. Impact of roasting time on the sensory profile of Arabica and Robusta coffee. *Ecology of Food and Nutrition* Vol. 52 (2), 163–177.
- Bond, T.J. 2011. The origins of tea, coffee and cocoa as beverages. In *Tea, Cocoa and Coffee: Plant Secondary Metabolites and Health*; Crozier, A.; Ashihara, H.; Tomas-Barber, F., Eds.; 1–24. Oxford: Blackwell Publishing.
- Bottazzi, D.; Farina, S.; Milani, M.; Montorsi, L. 2012. A numerical approach for the analysis of the coffee roasting process. *Journal of Food Engineering* Vol. 112, 243–252.
- Brando, C.H.J. 2004. Harvesting and Green Coffee Processing. In *Coffee: Growing, Processing, Sustainable Production*; Wintgens, J.N., Ed.; 604–715. Weinheim: Wiley–VCH.
- Brown, J.; Kreiger, N.; Darlington, G.A.; Sloan, M. 2001. Misclassification of Exposure: Coffee as a Surrogate for Caffeine Intake. *American Journal of Epidemiology* Vol. 153 (8), 815–820.
- Bruce, M.; Scott, N.; Lader, M.; Marks, V. 1986. The psychopharmacological and electrophysiological effects of single doses of caffeine in healthy human subjects. *British Journal of Clinical Pharmacology* Vol. 22, 81–87.
- Buffo, R.A.; Cardelli-Freire, C. 2004. Coffee flavour: an overview. *Flavour and Fragrance Journal* Vol. 19, 99–104.
- Burmester, K.; Eggers, R. 2010. Heat and mass transfer during the coffee drying process. *Journal of Food Engineering* Vol. 99, 430–436.
- Cannell, M.G.R. 1985. Physiology of the Coffee Crop. In *Coffee: Botany, Biochemistry, and Production of Beans and Beverage*; Clifford, M.N., Willson, K.C., Eds.; 108–134. London: Croom Helm Ltd.
- Charrier, A.; Berthaud, J. 1985. Botanical Classification of Coffee. In *Coffee: Botany, Biochemistry, and Production of Beans and Beverage*; Clifford, M.N., Willson, K.C., Eds.; 13–47. London: Croom Helm Ltd.
- Charrier, A.; Eskes, A.B. 2004. Botany and Genetics of Coffee. In *Coffee: Growing,*

- Processing, Sustainable Production; Wintgens, J.N.; Ed.; 25–56. Weinheim: Wiley–VCH.
- Chen, J.-M.; Zhang, R.-H. 1989. Studies on the measurements of crop emissivity and sky temperature. *Agricultural and Forest Meteorology* Vol 49, 23–34.
- Chou, T.M.; Benowitz, N.L. 1994. Caffeine and coffee: effects on health and cardiovascular disease. *Comparative Biochemistry and Physiology Part C: Pharmacology, Toxicology and Endocrinology* Vol. 109 (2), 173–189.
- CIE. 2007. Colorimetry - Part 4: CIE 1976 L* a* b* Colour Space. CIE Draft Standard 014-4.3/E:2007.
- Clarke, R.J. 1985. Green Coffee Processing. In *Coffee: Growing, Processing, Sustainable Production*; Wintgens, J.N.; Ed.; 230–250. Weinheim: Wiley–VCH.
- Cleves, R.S. 2004. Ecological Processing of Coffee and Use of Byproducts. In *Coffee: Growing, Processing, Sustainable Production*; Wintgens, J.N.; Ed.; 716–730. Weinheim: Wiley–VCH.
- Crozier, T.M.W.; Stalmach, A.; Lean, M.E.J.; Crozier, A. 2012. Espresso coffees, caffeine and chlorogenic acid intake: potential health implications. *Food and Function* Vol. 3, 30–33.
- Daglia, M.; Papetti, A.; Aceti, C.; Sordelli, B.; Gregotti, C.; Gazzani, G. 2008. Isolation of high molecular weight components and contribution to the protective activity of coffee against lipid peroxidation in a rat liver microsome system. *Journal of Agricultural and Food Chemistry* Vol. 56, 11653–11660.
- Daviron, B.; Ponte, S. 2005. *The Coffee Paradox: Global Markets, Commodity Trade and the Elusive Promise of Development*. London: Zed Books Ltd.
- Davis, A.P.; Govaerts, R.; Bridson, D.M.; Stoffelen, P. 2006. An annotated taxonomic conspectus of the genus *Coffea* (Rubiaceae). *Botanical Journal of the Linnean Society* Vol. 152, 465–512.
- de Oliveira, F.C., Coimbra, J.S.v-R.; de Oliveira, E.B.; Zuñiga, A.D.G.; Rojas, E.E.G. 2014. Food protein-polysaccharide conjugates obtained via the Maillard

reaction: a review. *Critical Reviews in Food Science and Nutrition*. *in press*.
<http://dx.doi.org/10.1080/10408398.2012.755669>.

Department of Chemistry of Colby College. 2007. Differential Scanning Calorimetry: First and Second Order Transitions in Polymers. <http://www.colby.edu/chemistry/PChem/lab/DiffScanningCal.pdf>. Accessed 28th of May 2014.

Descroix, F.; Snoeck, J. 2004. Environmental Factors Suitable for Coffee Cultivation. In *Coffee: Growing, Processing, Sustainable Production*; Wintgens, J.N.; Ed.; 163–177. Weinheim: Wiley-VCH.

Descroix, F.; Snoeck, J. 2004. Establishing a Coffee Plantation. In *Coffee: Growing, Processing, Sustainable Production*; Wintgens, J.N.; Ed.; 178–245. Weinheim: Wiley-VCH.

Duarte, G.S.; Pereira, A.A.; Farah, A. 2010. Chlorogenic acids and other relevant compounds in Brazilian coffees processed by semi-dry and wet post-harvesting methods. *Food Chemistry* Vol. 118 (3), 851–855.

Dutra, E.R.; Oliveira, L.S.; Franca, A.S.; Ferraz, V.P.; Afonso, R.J.C.F. 2001. A preliminary study on the feasibility of using the composition of coffee roasting gas for the determination of the degree of roast. *Journal of Food Engineering* Vol. 47, 241–246.

Eggers, R.; Pietsch, A. 2001. Technology I: Roasting. In *Coffee Recent Developments*; Clarke, R.J., Vitzthum, O.G., Eds.; 90–107. Oxford: Blackwell Science Ltd.

Eric, K.; Raymond, L.V.; Huang, M.; Cheserek, M.J.; Hayat, K.; Savio, N.D.; Amédée, M.; Zhang, X. 2013. Sensory attributes and antioxidant capacity of Maillard reaction products derived from xylose, cysteine and sunflower protein hydrolysate model system. *Food Research International* Vol. 54(2), 1437–1447.

Eskes, A.B.; Leroy, T. Coffee Selection and Breeding. In *Coffee: Growing, Processing, Sustainable Production*; Wintgens, J.N.; Ed.; 57–86. Weinheim: Wiley-VCH.

Fabbri, A.; Cevoli, C.; Alessandrini, L.; Romani, S. 2011. Numerical modelling of heat

and mass transfer during coffee roasting process. *Journal of Food Engineering* Vol. 105, 264–269.

FAOSTAT. 2014. <http://faostat3.fao.org/>

Farah, A.; de Paulis, T.; Trugo, L.C.; Martin, P.R. 2005. Effect of roasting on the formation of chlorogenic acid lactones in coffee. *Journal of Agricultural and Food Chemistry* Vol. 53(5), 1505–1513.

Farah, A. 2012. Coffee Constituents. In *Coffee: Emerging Health Effects and Disease Prevention*; Chu, Y.; Eds.; 21–58. Oxford: Willey-Blackwell.

Franca, A.S.; Mendonça, J.C.F.; Oliveira, S.D. 2005. Composition of green and roasted coffees of different cup qualities. *Lebensmittel-Wissenschaft und Technologie – Food Science and Technology* Vol. 38(7), 709–715.

Franca, A.S.; Oliveira, L.S.; Oliveira, R.C.S.; Agresti, P.C.M.; Augusti, R. 2009. A preliminary evaluation of the effect of processing temperature on coffee roasting degree assessment. *Journal of Food Engineering* Vol. 92, 345–352.

Ferraz, M.B.M.; Farah, A.; Iamanaka, B.T.; Perrone, D.; Copetti, M.V.; Marques, V.X.; Vitali, A.A.; Taniwaki, M.H. 2010. Kinetics of ochratoxin A destruction during coffee roasting. *Food Control* Vol. 21, 872–877.

Fito, P.J.; Castelló, M.L.; Argüelles, A.; Fito, P. 2007. Application of the SAFES (systematic approach to food engineering systems) methodology to roasted coffee process. *Journal of Food Engineering* Vol. 83, 211–218.

Geankoplis, C. J. 1983. *Transport Processes and Unit Operations* 2nd Ed. Boston: Allyn and Bacon, Inc.

Ginz, M.; Balzer, H.H.; Bradbury, A.G.W.; Maier, H.G. 2000. Formation of aliphatic acids by carbohydrate degradation during roasting of coffee. *European Food Resource Technology* Vol. 211, 404–410.

Ginz, M.; Engelhardt, U. 2001. Identification of new diketopiperazines in roasted coffee. *European Food Research and Technology* Vol. 213(1), 8–11.

Gloess, A.N.; Vietri, A.; Wieland, F.; Smrke, S.; Schönbacher, B.; López, J.A.S.; Petrozzi, S.; Bongers, S.; Kozirowski, T.; Yeretizian, C. 2014. Evidence of

- different flavour formation dynamics by roasting coffee from different origins: On-line analysis with PTR-ToF-MS. *International Journal of Mass Spectrometry* Vol. 365–366, 324–337.
- Goh, G.B.; Chow, W.; Renwei-Wang; Yuan, J. Koh, W. 2014. Coffee, alcohol and other beverages in relation to cirrhosis mortality: the Singapore Chinese health study. *Hepatology. in press.*
- Goodman, B.A.; Pascual, E.C.; Yeretjian, C. 2011. Real time monitoring of free radical processes during the roasting of coffee beans using electron paramagnetic resonance spectroscopy. *Food Chemistry* Vol. 125(1), 248-254.
- Gökmen, V.; Şenyuva, H.Z. 2006. Study of colour and acrylamide formation in coffee, wheat flour and potato chips during heating. *Food Chemistry* Vol. 99, 238–243.
- Häusser, J. A.; Schlemmer, A.; Kaiser, S.; Kalis, A.; Mojzisch, A. The effects of caffeine on option generation and subsequent choice. *Psychopharmacology. in press.*
- Hećimović, I.; Belščak-Cvitanović, A.; Horžić, D.; Komes, D. 2011. Comparative study of polyphenols and caffeine in different coffee varieties affected by the degree of roasting. *Food Chemistry* Vol. 129, 991-1000.
- Hernández, J.A.; Heyd, B.; Irlés, C.; Valdovinos, B.; Trystram, G. 2007. Analysis of the heat and mass transfer during coffee batch roasting. *Journal of Food Engineering* Vol. 78, 1141–1148.
- Hernández, J.A.; Heyd, B.; Trystram, G. 2008a. On-line assessment of brightness and surface kinetics during coffee roasting. *Journal of Food Engineering* Vol. 87, 314–322.
- Hernández, J.A.; Heyd, B.; Trystram, G. 2008b. Prediction of brightness and surface area kinetics during coffee roasting. *Journal of Food Engineering* Vol. 89, 156–163.
- Hernández-Díaz, W.N.; Ruiz-López, I.I.; Salgado-Cervantes, M.A. Rodríguez-Jimenes, G.C.; García-Alvarado, M.A. 2008. Modeling heat and mass

- transfer during drying of green coffee beans using prolate spheroidal geometry. *Journal of Food Engineering* Vol. 86 (1), 1–9.
- Heyd, B; Broyart, B.; Hernández, J.A. Valvodinos-Tijerino, B. Trystram, G. 2007. Physical model of heat and mass transfer in a spouted bed coffee roaster. *Drying Technology* Vol. 25, 1243–1248.
- Holscher, W.; Steinhart, H. 1992. Investigation of roasted coffee freshness with an improved headspace technique. *Zeitschrift für Lebensmittel-Untersuchung und Forschung* Vol. 195(1), 33–38.
- Institute of Food Technologists' Expert Panel on Food Safety and Nutrition. 1987. Evaluation of caffeine safety: a scientific status summary. *Food Technology* Vol. 41 (6), 105-115. Chicago: Institute of Food Technologists.
- International Trade Centre. 2011. *The Coffee Exporter's Guide*, 3rd Ed.
- ISO International Standard. 1978. Green coffee – determination of moisture (routine method). ISO 1447:1978.
- ISO International Standard. 1983. Green coffee – determination of loss in mass at 105 °C. ISO 6673:1983.
- ISO International Standard. 2001. Green coffee – determination of moisture (basic reference method). ISO 1446:2001.
- Japanese Industrial Standard Committee. 1987. Testing Methods for Specific Heat Capacity of Plastics. JIS 7123. Nihon Kōgyō Kikaku. (in Japanese)
- Jokanovic, M.R.; Džinić, N.R.; Cvetković, B.R.; Grujić, S.; Odžakovic, B. 2012. Changes in physical properties of coffee beans during roasting. *Acta Periodica Technologica* Vol. 43, 21-31.
- Keable, B.B. 1923. *Coffee, from Grower to Consumer*. Pitman's Common Commodities and Industries Series. New York: Sir Issac Pitman & Sons, Ltd.
- Kemp, I.C.; Fyhr, B.C.; Laurent, S.; Roques, M.A.; Groenewold, C.E.; Tsostas, E.; Sereno, A.A.; Bonazzi, C.B.; Bimbenet, J.; Kind, M. 2001. Method for processing experimental drying kinetics data. *Drying Technology* Vol. 19(1),

15–34.

- Kure, K.; Sagara, Y.; Seo, Y. 1997. Characteristic colour change and its prediction for the surface of white bread during baking processes. *Nippon Shokuhin Kagaku Kogaku Kaishi* Vol. 44(1), 31–37. (in Japanese)
- Lambot, C.; Bouharmont, P. 2004. Soil Protection. In *Coffee: Growing, Processing, Sustainable Production*; Wintgens, J.N.; Ed.; 270–283. Weinheim: Wiley-VCH.
- Langner, E.; Rzeski, W. 2014. Biological properties of melanoidins: A review. *International Journal of Food Properties* Vol. 17, 344–353.
- Lean, M.E.J.; Crozier, A. 2012. Coffee, caffeine and health: what's in your cup? (guest editorial). *Maturitas* Vol. 72, 171–172.
- Leino, M.; Lapveteläinen, A.; Menchero, P.; Malm, H.; Kaitaranta, J.; Kallio, H. 1991. Characterisation of stored Arabica and Robusta coffees by headspace-GC and sensory analyses. *Food Quality and Preference* Vol. 3 (2), 115–125.
- Leloup, V.; Gancel, C.; Liardon, R.; Rytz, A.; Pithon, A. 2004. Impact of Dry and Wet Process on Green Coffee Composition and Sensory Characteristics. *Proceeding of the 20th International Scientific Colloquium on Coffee (ASIC)*, Bangalore, 10-15 Oct 2004; 93–101.
- Liu, Y.; Kitts, D.D. 2011. Confirmation that the Maillard reaction is the principle contributor to the antioxidant capacity of coffee brews. *Food Research International* Vol. 44(8), 2418–2424.
- Lopez-Garcia, E.; Guallar-Castillon, P.; Leon-Muñoz, L.; Graciani, A. 2014. Coffee consumption and health-related quality of life. *Clinical Nutrition* Vol. 33, 143–149.
- López, A.; Molina-Aiz, F.D.; Valera, D.L.; Peña, A. 2012. Determining the emissivity of the leaves of nine horticultural crops by means of infrared thermography. *Scientia Horticulturae* Vol. 137, 49–58.
- Lu, Y.; Zhai, L.; Zeng, J.; Peng, Q.; Wang, J.; Deng, Y.; Xie, L.; Mo, C.; Yang, S.; Li, S.; Qin, X. 2014. Coffee consumption and prostate cancer risk: an updated

- meta-analysis. *Cancer Causes and Control* Vol. 25 (5), 591–604.
- Lyman, D.J.; Benck, R.; Dell, S.; Merle, S.; Murray-Wijelath, J. 2003. FTIR-ATR analysis of brewed coffee: Effect of roasting conditions. *Journal of Agricultural and Food Chemistry* Vol. 51, 3268–3272.
- Martins, S.I.F.S.; Jongen, W.M.F.; van Boekel, M.A.J.S. 2001. A review of Maillard reaction in food and implications to kinetic modelling. *Trends in Food Science & Technology* Vol. 11 (9–10), 364–373.
- Martins, S.I.F.S.; van Boekel, M.A.J.S. 2003. Melanoidins extinction coefficient in the glucose/glycine Maillard reaction. *Food Chemistry* Vol. 83, 135–142.
- Martins, S.I.F.S.; van Boekel, M.A.J.S. 2005. A kinetic model for the glucose/glycine Maillard reaction pathways. *Food Chemistry* Vol. 90, 257–269.
- Mazzafera, P.; Purcino, R.P. 2004. Post-Harvest Processing methods and Physiological Alterations in the Coffee Fruit. *Proceeding of the 20th International Scientific Colloquium on Coffee (ASIC), Bangalore, 10-15 Oct 2004*; 811–819.
- Mills, C.E.; Oruna-Concha, M.J.; Mottram, D.S.; Gibson, G.R.; Spencer, J.P.E. 2013. The effect of processing on chlorogenic acid content of commercially available coffee. *Food Chemistry* Vol. 141, 3353–3340.
- Mendonça, J.C.F.; Franca, A.S.; Oliveira, L.S. 2009. Physical characterisation of non-defective and defective Arabica and Robusta coffees before and after roasting. *Research note. Journal of Food Engineering* Vol. 92, 474–479.
- Moon, J.; Shibamoto, T. 2009. Role of roasting conditions in the profile of volatile flavour chemicals formed from coffee beans. *Journal of Agricultural and Food Chemistry* Vol 57, 5823–5831.
- Morales, F.J.; Jiménez-Pérez, S. 2001. Free radical scavenging capacity of the Maillard reaction products as related to colour and fluorescence. *Food Chemistry* Vol. 72, 119–125.
- Morales, F.J.; van Boekel, M.A.J.S. 1998. A study on advanced Maillard reaction in heated casein/sugar solutions: colour formation. *International Dairy Journal* Vol. 8, 907–915.
- Moreira, A.S.P.; Nunes, F.M.; Domigues, M.R.; Coimbra, M.A. 2012. Coffee

- melanoidins: structures, mechanisms of formation and potential health impacts. *Food and Function* Vol. 3, 903–915.
- Nagaraju, V.D.; Murthy, C.T.; Ramalakshmi, K.; Srinivasa Rao, P.N. 1997. Studies on roasting of coffee beans in a spouted bed. *Journal of Food Engineering* Vol. 31, 263–270.
- Naidu, M.M.; Sulochanamma, G.; Sampathu, S.R.; Srinivas, P. 2008. Studies on extraction and antioxidant potential of green coffee. *Food Chemistry* 107, 377–384.
- National Coffee Association of United States of America. 2014. Roasting Types. <http://www.ncausa.org/i4a/pages/index.cfm?pageid=74>. Accessed 4th of June 2014.
- Ng, N.; Kaye, E.K.; Garcia, R.I. 2013. Coffee consumption and periodontal disease in men. *British Dental Journal*. *in press*.
- Nguyen, T.N.H.; Byun, S.Y. 2013. Combined changes of process conditions improved aromatic properties of Vietnamese Robusta. *Biotechnology and Bioprocess Engineering* Vol. 18, 248–256.
- Nunes, F.M.; Cruz, A.C.S.; Coimbra, M.A. 2012. Insight into the mechanism of coffee melanoidin formation using modified “in bean” models. *Journal of Agricultural and Food Chemistry* Vol. 60, 8710–8719.
- Oestreich-Janzen, S. 2010. Chemistry of Coffee. In *Comprehensive Natural Product: Chemistry and Biology, Vol. 3*; Mander, L.; Liu, H.B.; Eds.; 1085–1117. Elsevier Ltd.
- Oliveira, G.; da Silva, D.M.; Pereira, R.G.F.A.; Paiva, L.C.; Prado, G.; Batista, L.R. 2013. Effect of different roasting levels and particle sizes on ochratoxin A concentration in coffee beans. Short communication. *Food Control* Vol. 34, 651–656.
- Onishi, M.; Inoue, M.; Araki, T.; Iwabuchi, H.; Sagara, Y. 2011. Characteristic colouring curve for white bread during baking. *Bioscience, Biotechnology and Biochemistry* Vol. 75, 255–260.
- Oosterveld, A.; Voragen, A.G.J.; Schols, H.A. 2003. Effect of roasting on the

- carbohydrate composition of *Coffea Arabica* beans. *Carbohydrate Polymers* Vol.54, 193–192.
- Petisca, C.; Pérez-Palacios, T.; Farah, A.; Pinho, O.; Ferreira, I.M.P.L.V.O. 2013. Furans and other volatile compounds in ground roasted and espresso coffee using headspace solid-phase microextraction: Effect of roasting speed. *Food and Bioproducts Processing* Vol. 91(3), 233–241.
- Petracco, M. 2001. Technology IV: Beverage Preparation: Brewing Trends for the New Millennium. In *Coffee Recent Developments*; Clarke, R.J., Vitzthum, O.G., Eds.; 140–164. Oxford: Blackwell Science Ltd.
- Pittia, P.; Dalla Rosa, M.; Lerici, C.R. 2001. Textural changes of coffee beans as affected by roasting conditions. *Lebensmittel-Wissenschaft und Technologie – Food Science and Technology* Vol. 31, 168–175.
- Pittia, P.; Sacchetti, G.; Mancini, L.; Voltolini, M.; Sodini, N.; Tromba, G.; Zanini, F. 2011. Evaluation of microstructural properties of coffee beans by synchrotron X-ray microtomography: a methodological approach. *Journal of Food Science* Vol. 76 (2), E222–E231.
- Pizarro, C.; Esteban-Diez, I.; González-Sáiz, J.; Forina M. 2007. Use of near-infrared spectroscopy and feature selection techniques for predicting the caffeine content and roasting color in roasted coffees. *Journal of Agricultural and Food Chemistry* Vol. 55(18), 7477-7488.
- Raemy, A.; Lambelet, P. 1982. A calorimetric study of self-heating in coffee and chicory. *Journal of Food Technology* Vol. 17, 451–460.
- Reh, C.T.; Gerber, A.; Prodolliet, J.; Vuataz, G. 2006. Water content determination in green coffee – Method comparison to study specificity and accuracy. *Food Chemistry* Vol. 96, 423–430.
- Reineccius, G. 1995. The Maillard reaction and coffee flavour. *Proceeding of the 16th International Scientific Colloquium on Coffee (ASIC), Kyoto*; 811–819.
- Ribeiro, J.S.; Augusto, F.; Salva, T.J.; Thomaziello, R.A.; Ferreira, M.M.C. 2009. Prediction of sensory properties of Brazilian Arabica roasted coffees by headspace solid phase microextraction–gas chromatography and partial least

- squares. *Analytica Chimica Acta* Vol. 634(2), 172-179.
- Rivera, W.; Velasco, X.; Gálvez, C.; Rincón, C.; Rosales, A.; Arango, P. 2011. Effect of the roasting process on glass transition and phase transition of Colombian Arabica coffee beans. In the 11th International Congress on Engineering and Food (ICEF11). *Procedia Food Science* Vol. 1, 385–390.
- Rubayiza, A.B.; Meurens, M. 2005. Chemical discrimination of Arabica and Robusta coffees by Fourier transform Raman spectroscopy. *Journal of Agricultural and Food Chemistry* Vol. 53, 4654–4659.
- Sacchetti, G. Di Mattia, C.; Pittia, P.; Mastrocola, D. 2009. Effect of roasting degree, equivalent thermal effect and coffee type on radical scavenging activity of coffee brews and their phenolic fraction. *Journal of Food Engineering* Vol. 80(1), 74–80.
- SAS Institute Inc. 2012. JMP® Pro 10.0.2 64-bit Edition.
- Schenker, S.; Handschin, S.; Frey, B.; Perren, R.; Escher, F. 2000. Pore structure of coffee beans affected by roasting conditions. *Journal of Food Science* Vol. 65 (3), 452–457.
- Schenker, S. 2000. Investigations on the Hot Air Roasting of Coffee Beans. Ph.D. thesis. Swiss Federal Institute of Technology, Zurich.
- Schönberg, A.; Moubacher, R. 1951. The Strecker degradation of α -amino acids. *Chemical Reviews* Vol. 50(2), 261–277.
- Schwartzberg, H.G. 2002. Modelling bean heating during batch roasting of coffee. In *Engineering and Food for the 21st Century*; Welte-Chanes, J.; Barbosa-Canovas, G.; Aguilera, J.M., Eds.; London: CRC Press LCC.
- Singh, R.P.; Heldman, D.R. 2014. *Introduction to Food Engineering*, 5th Ed. Massachusetts: Academic Press.
- Small, L.E.; Horrel, R.S. 1993. High yield coffee technology. *Proceeding of the 15th International Scientific Colloquium on Coffee (ASIC)*, Paris; 719–726.
- Smith, A. 2002. Effects of caffeine on human behaviour. *Food and Chemical Toxicology* Vol. 40, 1243–1255.
- Speer, K.; Kölling-Speer, I. 2006. The lipid fraction of the coffee bean. *Brazilian*

Journal of Plant Physiology Vol. 18(1), 201-216.

- Strezov, V.; Evans, T.J. 2005. Thermal analysis of the reactions and kinetics of green coffee during roasting. *International Journal of Food Properties* vol. 8, 101–111.
- Summa, C.; Wenzl, T.; Brohee, M.; de la Calle, B.; Anklam, E. 2006. Investigation of the correlation of the acrylamide content and the antioxidant activity of model cookies. *Journal of Agricultural and Food Chemistry* Vol. 54, 853–859.
- Summa, C.A.; de la Calle, B.; Brohee, M.; Stadler, R.H.; Anklam, E. 2007. Impact of the roasting degree of coffee on the in vitro radical scavenging capacity and content of acrylamide. Research note. *Lebensmittel-Wissenschaft und Technologie – Food Science and Technology* Vol. 40, 1849–1854.
- Sunarhanum, W.B.; Williams, D.J.; Smyth, H.E. 2014. Complexity of coffee flavor: A compositional and sensory perspective. Review paper. *Food Research International* Vol. 62, 315–325.
- Teixeira, A.A.; Brandao, C.H.J.; Thomaziello, R.A.; Teixeira, R. 2005. Processing of the harvest. In Ch. 3, The raw bean, in *Espresso Coffee: The Science of Quality*; Illy, A.; Viani, R.; Eds.; 91–95. London: Elsevier Academic Press.
- Tressl, R.; Nittka, C.; Kersten, E. 1995. Formation of isoleucine-specific Maillard products from [1-¹³C]-D-glucose and [1-¹³C]-D-fructose. *Journal of Agricultural and Food Chemistry* Vol. 43, 1163–1169.
- van der Vossen, H.A.M. 1985. Coffee Selection and Breeding. In *Coffee: Botany, Biochemistry, and Production of Beans and Beverage*; Clifford, M.N., Willson, K.C., Eds.; 48–96. London: Croom Helm Ltd.
- Wang, X.; Lim, L. 2014. A kinetics and modelling study of coffee roasting under isothermal conditions. *Food and Bioprocess Technology* Vol. 7, 621–632.
- Wasserman, G. 1992. Coffee. In *Kirk-Othmer Encyclopedia of Chemical Technology* Vol. 6; Kirk-Othmer; Eds.; John Wiley & Sons, Inc.
- Wikipedia. 2007. Coffee Bean Structure (image). In *Coffee Production*. Licensed under the Creative Commons Attribution-Share Alike 3.0 Unported license.

- http://en.wikipedia.org/wiki/Coffee_processing. Accessed 4th of June 2014.
- Wikipedia. 2012. Triaxial Ellipsoid (image). In Ellipsoid. Licensed under the Creative Commons Attribution-Share Alike 3.0 Unported license. <http://en.wikipedia.org/wiki/Ellipsoid>. Accessed 4th of June 2014.
- Willson, K.C. 1999. Coffee, Cocoa, and Tea. Crop Production Science in Horticulture Series Vol. 8. Cabi Publishing: Oxfordshire.
- Winston, E.; de Laak, J.O.; Marsh, T.; Lempke, H.; Chapman K. 2005. Arabica coffee manual for Lao-PDR. FAO Corporate Document Repository. Bangkok: FAO Regional Office for Asia and the Pacific. available online at <http://www.fao.org/docrep/008/ae939e/ae939e00.htm#Contents>.
- Wintgens, J.N.; Zamarripa, A. 2004. Coffee Propagation. In Coffee: Growing, Processing, Sustainable Production; Wintgens, J.N.; Ed.; 87–136. Weinheim: Wiley-VCH.
- Yeretzian, C.; Jordan, A.; Badoud, R. 2002. From the green bean to the cup of coffee: investigating coffee roasting by on-line monitoring of volatiles. European Food Resource Technology Vol. 214, 92–104.
- Yuge, T. 1960. Experiments on heat transfer from spheres including combined natural and forced convection. Journal of Heat Transfer Vol. 82(3), 214–220.
- Zhou, L.; Khalil, A.; Bindler, F.; Zhao, M.; Marcic, C.; Ennahar, S.; Marchioni, E. 2013. Effect of heat treatment on the content of individual phospholipids in coffee beans. Short communication. Food Chemistry Vol. 141, 3846–3850.

References from websites

- <http://www.xlrotor.com/>. Accessed 27th of November 2013.
- <http://en.wikipedia.org/wiki/Ellipsoid>. Accessed 30th of January 2014.
- <http://www.casabrazilcoffees.com/learn/processing/>. Accessed 24th of May 2014.
- <http://www.ncausa.org/>. Accessed 24th of May 2014.
- <http://www.ico.org/>. Accessed 27th of May 2014.
- <http://ecocrop.fao.org/ecocrop/srv/en/cropView?id=751>. FAO-Ecocrop datasheet. Accessed 27th of May 2014.

<http://www.coffeelabequipment.com/>. Accessed 2nd of June 2014.

<https://sites.google.com/site/sachidanandabs/colorspace>. Accessed 2nd of June 2014.

<https://www.scaa.org/>. Accessed 14th of June 2014.

Appendix 1. VBA Codes of Bezier Spline

Module 1

Option Explicit

Type XYZ

 x As Double

 y As Double

 z As Double

End Type

Function FEvaluate_Bezier(xarr, yarr, i0%, i1%, i2%, i3%, t#, chtname\$) As Variant

Dim pt As XYZ, d01#, d12#, d23#, d02#, d13#, f#

'Excel uses a 4 control point bezier when drawing smooth curves

'This routine computes the xy coordinates of one point on the bezier curve.

'The inputs to this routine are:

' xarr = array of charted x values

' yarr = array of charted y values

' i0-i3 the indexes of 4 chart points in xarr/yarr

' t = value between 0 and 1, inclusive, t=0 returns point i1, t=1 returns point i2

' xrtn = x value for point on bezier curve "t" units from point i1 to point i2

' yrtn = y value for point on bezier curve "t" units from point i1 to point i2

'The 4 "chart points" are used to determine 4 "control points" for drawing a Bezier curve from chart point i1 to chart point i2.

'The tricky part is figuring out the locations of the 4 control points.

'bz(0) = i1 always

'bz(1) = on a line through i1 parallel to i2-i0, at a distance from i1 = 1/6th the length |i2-i0|

'bz(2) = on a line through i2 parallel to i1-i3, at a distance from i2 = 1/6th the length |i1-i3|

'bz(4) = i2 always

'bz(1) and bz(2) are also subject to additional modification as follows:

'for bz(1), limit [1/6th the length of i2-i0] to never be more than 1/2 the length of |i2-i1|

'for bz(2), limit [1/6th the length of i1-i3] to never be more than 1/2 the length of |i2-i1|

'in cases where just bz(1) is being limited to $|i2-i1|/2$, for bz(2) reduce the length of $[i1-i3]/6$ by

'replacing it with $(i2-i1)/2 * |i3-i1|/|i2-i0|$

'in cases where just bz(2) is being limited to $|i2-i1|/2$, for bz(1) reduce the length of $[i2-i0]/6$ by

'replacing it with $(i2-i1)/2 * |i2-i0|/|i3-i1|$

'Also, endpoint intervals (designated by $i0=i1$ or $i2=i3$) are handled a little differently.

'In this case use $1/3$ instead of $1/6$.

Dim cht As Chart

Set cht = ActiveSheet.DrawingObjects(chtname).Chart

ReDim pts(0 To 3) As XYZ 'used for the 4 chart points

ReDim bz(0 To 3) As XYZ 'used for the 4 control points

pts(0) = CreateXYZ(ChtToShpX(xarr(i0), cht), ChtToShpY(yarr(i0), cht))

pts(1) = CreateXYZ(ChtToShpX(xarr(i1), cht), ChtToShpY(yarr(i1), cht))

pts(2) = CreateXYZ(ChtToShpX(xarr(i2), cht), ChtToShpY(yarr(i2), cht))

pts(3) = CreateXYZ(ChtToShpX(xarr(i3), cht), ChtToShpY(yarr(i3), cht))

d01 = XYZDist(pts(0), pts(1))

d12 = XYZDist(pts(1), pts(2))

d23 = XYZDist(pts(2), pts(3))

d02 = XYZDist(pts(0), pts(2))

d13 = XYZDist(pts(1), pts(3))

bz(0) = pts(1)

If (d02 / 6 < d12 / 2) And (d13 / 6 < d12 / 2) Then

'this is the normal case where both $1/6$ th vectors are less than half of $d12$

If $i0 < i1$ Then

f = 1 / 6

Else

f = 1 / 3 'for endpoint intervals

End If

bz(1) = XYZAdd(pts(1), XYZMult(XYZSub(pts(2), pts(0)), f))

If $i2 < i3$ Then

f = 1 / 6

Else

f = 1 / 3 'for endpoint intervals

```

End If
bz(2) = XYZAdd(pts(2), XYZMult(XYZSub(pts(1), pts(3)), f))
Elseif (d02 / 6 >= d12 / 2) And (d13 / 6 >= d12 / 2) Then
    'this is the case where both 1/6th vectors are > than half of d12
    bz(1) = XYZAdd(pts(1), XYZMult(XYZSub(pts(2), pts(0)), d12 / 2 / d02))
    bz(2) = XYZAdd(pts(2), XYZMult(XYZSub(pts(1), pts(3)), d12 / 2 / d13))
Elseif (d02 / 6 >= d12 / 2) Then
    'for this case d02/6 is more than half of d12, so the d13/6 vector needs to be
reduced
    bz(1) = XYZAdd(pts(1), XYZMult(XYZSub(pts(2), pts(0)), d12 / 2 / d02))
    bz(2) = XYZAdd(pts(2), XYZMult(XYZSub(pts(1), pts(3)), d12 / 2 / d13 *
(d13 / d02)))
Else
    bz(1) = XYZAdd(pts(1), XYZMult(XYZSub(pts(2), pts(0)), d12 / 2 / d02 *
(d02 / d13)))
    bz(2) = XYZAdd(pts(2), XYZMult(XYZSub(pts(1), pts(3)), d12 / 2 / d13))
End If
bz(3) = pts(2)
pt = Bezier4(bz(0), bz(1), bz(2), bz(3), t)
FEvaluate_Bezier = Array(ShpToChartAxesX(pt.x, cht), ShpToChartAxesY(pt.y,
cht))
End Function

```

```

Function Bezier4(p1 As XYZ, p2 As XYZ, p3 As XYZ, p4 As XYZ, mu#) As XYZ

```

```

' Four control point Bezier interpolation
' mu ranges from 0 to 1, start to end of curve

```

```

Dim mum1#, mum13#, mu3#

```

```

Dim p As XYZ

```

```

    mum1 = 1 - mu

```

```

    mum13 = mum1 * mum1 * mum1

```

```

    mu3 = mu * mu * mu

```

```

    p.x = mum13 * p1.x + 3 * mu * mum1 * mum1 * p2.x + 3 * mu * mu * mum1 *
p3.x + mu3 * p4.x

```

```

    p.y = mum13 * p1.y + 3 * mu * mum1 * mum1 * p2.y + 3 * mu * mu * mum1 *

```

```
p3.y + mu3 * p4.y
' p.z = mum13 * p1.z + 3 * mu * mum1 * mum1 * p2.z + 3 * mu * mu * mum1 *
p3.z + mu3 * p4.z
```

```
Bezier4 = p
```

```
End Function
```

```
Function XYZAdd(a As XYZ, b As XYZ) As XYZ
```

```
XYZAdd.x = a.x + b.x
```

```
XYZAdd.y = a.y + b.y
```

```
End Function
```

```
Function XYZSub(a As XYZ, b As XYZ) As XYZ
```

```
XYZSub.x = a.x - b.x
```

```
XYZSub.y = a.y - b.y
```

```
End Function
```

```
Function XYZMult(a As XYZ, b#) As XYZ
```

```
XYZMult.x = a.x * b
```

```
XYZMult.y = a.y * b
```

```
End Function
```

```
Function XYZDist(a As XYZ, b As XYZ) As Double
```

```
XYZDist = ((a.x - b.x) ^ 2 + (a.y - b.y) ^ 2) ^ 0.5
```

```
End Function
```

```
Function CreateXYZ(a, b) As XYZ
```

```
CreateXYZ.x = a
```

```
CreateXYZ.y = b
```

```
End Function
```

Module 2

Option Explicit

```
Public Function ShpToChartAxesX(x, thechart As Chart) As Double
```

```
    Dim dzoom#, t#
```

```
    Dim dMin#, dMax#
```

```
On Error Resume Next
```

```
    Call myPlotAreaInsideLTWH(thechart)
```

```
    dzoom = ActiveWindow.Zoom / 100
```

```
    With thechart.axes(xlCategory)
```

```
        dMin = .MinimumScale
```

```
        dMax = .MaximumScale
```

```
        t = (x - PA.left) / PA.width
```

```
        ShpToChartAxesX = dMin + (dMax - dMin) * t
```

```
    End With
```

```
End Function
```

```
Public Function ChtToShpX(x, thechart As Chart) As Double
```

```
    Dim dzoom#, t#, dMin#, dMax#
```

```
On Error Resume Next
```

```
    Call myPlotAreaInsideLTWH(thechart)
```

```
    With thechart.axes(xlCategory)
```

```
        dMin = .MinimumScale
```

```
        dMax = .MaximumScale
```

```
        t = (x - dMin) / (dMax - dMin)
```

```
        ChtToShpX = PA.left + PA.width * t
```

```
    End With
```

```
End Function
```

```
Public Function ChtToShpY(y, thechart As Chart) As Double
```

```
    Dim dzoom#, t#, dMin#, dMax#
```

```
On Error Resume Next
```

```
    Call myPlotAreaInsideLTWH(thechart)
```

```
    With thechart.axes(xlValue)
```

```
        dMin = .MinimumScale
```

```
        dMax = .MaximumScale
```

```
        t = 1 - (y - dMin) / (dMax - dMin)
```

$\text{ChtToShpY} = \text{PA.top} + \text{PA.height} * t$

End With

End Function

Public Function ShpToChartAxesY(y, thechart As Chart) As Double

Dim dzoom#, t#

Dim dMin#, dMax#

On Error Resume Next

Call myPlotAreaInsideLTWH(thechart)

dzoom = ActiveWindow.Zoom / 100

With thechart.axes(xlValue)

dMin = .MinimumScale

dMax = .MaximumScale

t = 1 - (y - PA.top) / PA.height

ShpToChartAxesY = dMin + (dMax - dMin) * t

End With

End Function

Sub myPlotAreaInsideLTWH(cht)

Dim dzoom#, t#

dzoom = ActiveWindow.Zoom / 100

With cht.PlotArea

PA.left = .InsideLeft

PA.width = .InsideWidth

PA.top = .InsideTop

PA.height = .InsideHeight

t = PointsPerPixelX / dzoom

PA.left = Round(.InsideLeft / t) * t

PA.width = Round((.InsideWidth + .InsideLeft - PA.left) / t) * t

t = PointsPerPixelX

PA.left = Round(PA.left / t) * t

PA.width = Round(PA.width / t) * t

t = PointsPerPixelY / dzoom

PA.top = Round(.InsideTop / t) * t

```

        PA.height = Round(.InsideHeight / t) * t
        t = PointsPerPixelY
        PA.top = Round(PA.top / t) * t
        PA.height = Round(PA.height / t) * t
    End With
End Sub

```

Module 3

```

Public Type PA_type
    left As Double
    top As Double
    width As Double
    height As Double
End Type
Public PA As PA_type

```

'API's for getting the factors to convert points to pixels

```

Declare Function GetDC Lib "user32" ( _
    ByVal hwnd As Long) As Long

```

```

Declare Function GetDeviceCaps Lib "Gdi32" ( _
    ByVal hDC As Long, _
    ByVal nIndex As Long) As Long

```

```

Declare Function ReleaseDC Lib "user32" ( _
    ByVal hwnd As Long, _
    ByVal hDC As Long) As Long

```

```

Public Const LOGPIXELSX = 88
Public Const LOGPIXELSY = 90

```

'The width of a pixel in Excel's userform coordinates

```

Function PointsPerPixelX() As Double

```


Dim hDC As Long

hDC = GetDC(0)

'A point is defined as 1/72 of an inch and LOGPIXELSX returns

'the number of pixels per logical inch, so divide them to give

'the width of a pixel in Excel's userform coordinates

PointsPerPixelX = 72 / GetDeviceCaps(hDC, LOGPIXELSX)

ReleaseDC 0, hDC

End Function

'The width of a pixel in Excel's userform coordinates

Function PointsPerPixelY() As Double

Dim hDC As Long

hDC = GetDC(0)

'A point is defined as 1/72 of an inch and LOGPIXELSX returns

'the number of pixels per logical inch, so divide them to give

'the width of a pixel in Excel's userform coordinates

PointsPerPixelY = 72 / GetDeviceCaps(hDC, LOGPIXELSY)

ReleaseDC 0, hDC

End Function