Effects of different extraction methods and process condition on fatty acid profile and stability of the avocado oil

By

Shaun Thamsanqa Mgoma

Thesis submitted in fulfillment of the requirement for the degree

Master of Engineering: Chemical Engineering

Department of Chemical Engineering
Faculty of Engineering and Built Environment
Cape Peninsula University of Technology
Bellville Campus

Supervisor: Dr. Moses Basitere
Co-Supervisor: Mr. Vusi Mshayisa

November 2020

“We are only bound by the limits of our own conviction. We can transcend the script of a pre-defined story, and pave the way for the future that we design. We just need to tap that power, that conviction, that determination within us.”
Robert F. Smith

Declaration

I, **Shaun Thamsanqa Mgoma**, declare that the contents of this dissertation/thesis represent my own unaided work, and that the dissertation/thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

17 July 2020

Signed **Date**

Abstract

The avocado fruit is mostly consumed as a fruit rather than being processed to extract its oil. In addition to other constituents it has a content of oil which is the main component of its dry weight; which means that the fruit is found to be important for both food and oil. Avocado oil is important oil in the culinary, cosmetic and pharmaceutical industries. It finds its prominence due to its physicochemical properties in all these three industries. It is important to the food industry because of its high content of unsaturated fatty acids and high levels of antioxidants. In the cosmetic industry it is important because of its fast absorbing properties in the skin and the antioxidants properties, and in the pharmaceutical industry is found to be important as it's a source of many bioactive compounds like sterols and vitamins. All these uses and benefits of the oil can only be employed once the oil is extracted from the fruit. However, the extraction method employed plays a major role on the properties of the oil which influences its application. Therefore, it is crucial to use an extraction method that can offer high yields and good quality parameters of the oil.

In this study different solid-liquid extractions were done to recover the avocado oil from its flesh. The first research chapter explored two pre-treatment method of the avocado flesh, namely the oven drying and the microwave heating. The pretreated avovado probes were subjected to solid-liquid extraction using organic solvents. Both pretreatments were found to be effective and necessary for the process; but microwave heating was found to be the modern practice and requires much less time for pretreatment. Different process conditions were explored to evaluate how each parameter affects the oil yield from the avocado flesh. The selected parameters were the time, the solid to liquid ratio, as well as the modes of pretreatment and the modes of extraction, namely Soxhlet extraction, maceration and microwave aided extraction.

The results found that oil yield increases with increase in extraction time, however, the process reaches equilibrium until there was no increase observed. Then maceration washes were evaluated as a mode of extraction by using fresh solvent with a number of different washes of the avocado flesh, this prevented the extraction reaching equilibrium but used a high quantity of solvent increase a recycling energy need. The optimum solid to liquid ratio found was the ratio 1:2 (w/w) to be best for the extraction, anything more

was a waste of solvent. The pretreatment between microwave and oven drying found that the oil yield was almost similar between the two; however, the microwave heating was done only for 2 hours whilst the oven drying was done over 24 hours. Therefore, it was found that the microwave pretreatment would be best to save overall operational time.

The second research chapter focused on the kinetics and thermodynamics of the extraction of avocado oil. The chapter evaluated how the extraction takes place when heat at different temperatures. It also explained the energy required for the process to take place. The extraction experiments were done at four different temperatures, 40 °C - 70 °C in increment of 10 °C, the results found that as the temperature increased the rate of process increased which resulted in the shorter extraction period. The addition of the heat to the extraction of avocado oil resulted in a positive enthalpy which meant that the process were endothermic. The entropy was also found to be positive which meant that the extraction was irreversible. As result, the Gibbs free energy was found to be negative. However, this meant that the process under those conditions took place spontaneously.

The final research chapter evaluated both the yield of oil with different process conditions; it also further investigated the quality of the oil with different extraction conditions and methods. For the examination of the parameter effects on the extraction process, experimental design method was used. The experimental results were evaluated using response surface methodology (RSM) in order to optimize the extraction process, which aided identifying the optimum extraction conditions with the help of RSM. From the results of the analysis of variance (ANOVA) it was established that the results of the experiments were significant with a p-value < 0.05. This explained that the interaction of process conditions had a significant effect in the yield of the oil produced. The quality of the oil was studied by evaluating the fatty acids and the stability of the oil. The fatty acids results found that the unsaturated fatty acids were a high content in the oil as expected from avocado oil; however, it was also found that the fatty acids of the oil are dependent on the avocado fruit which varies in the content of unsaturated and saturated fats according to its geographical area provenience. The stability of the oil was also found to vary with different extraction methods and process conditions. It was also found that the stability of the oil can be compromised by some elements and compounds that are sensitive and prone to causing lipid oxidation. Hence extra virgin oils are sensitive as they are prone to photo-oxidation due to the content of chlorophylls.

Acknowledgements

I acknowledge all the people who have contributed to such a momentous achievement in completing this great work. I could not have done all of this without the contribution of each and every one of you. I am truly grateful for making this remarkable accomplishment to my career possible.

- To my supervisor: Dr. Moses Basitere for the opportunity he has afforded me trusting me with his time, all his effort and sacrifice. For the incredible support and patience, he had with me. His constant presence and support had a great impact and has made all this work possible and journey bearable. Since the day I came back to advance my studies he has been there to guide and inspire me to work hard and follow through everything.
- To my co-supervisor: Mr. Vusi Mshayisa for the guidance and patience he had with me. His support, presence and encouragement have also had a significant impact into making this work possible. The time he has afforded me and the knowledge he contributed to this work made it a success.
- To my fellow BTech student assistants: Larryngeal Gutu and Luvuyo Hlwempu for the hard work they put in contributing to this work, it meant a lot and made the completion of this work possible.
- To BioERG family: They all had a positive impact in my life especially during this work. All the guidance and different advices they gave me. To Dr. Maxwell Mewa for dedicating and sacrificing his time to teach and train me in using Response surface methodology program for my research.
- To all the laboratory staff: Ms. Hannelene Small, Ms. Ntombi Bingo and Mr. Derick Dlamini for all the technical guidance and support, much needed help and patience with me in the laboratory.
- To AgriFood laboratory staff: Mr. Ndumiso Mshicileli, Bongisiwe Zozo and Nandipha Jingqi for welcoming me in their laboratory. For the training they offered in the analysis of oil and their dedicated work in analyzing the samples in order to complete this work.
- To Cape Peninsula University of Technology: For all the financial support they provided in making my participation in a conference possible resulting in a publication of an article in a conference proceeding.
- To my family and friends: To my parents and family, I truly appreciate all that they have done and sacrificed for my career and personal growth. No words can fully express my gratitude to all of you and what you have done for me. To my friends, I’m grateful for your support and help during the course of this journey.

Dedication

This thesis is dedicated to my family, who has been there for me throughout this journey,

It is a Mngoma thing

And to the memory of my late brother Percy Vuyo Mgoma,

Who never got to celebrate this achievement with me

Layout of Thesis

This research study was conducted at Cape Peninsula University of Technology in the department of Chemical Engineering Bellville campus.

This thesis is divided and laid out in the following chapters:

Chapter one: This chapter gives the background and motivation of the study; it describes the problem statement and research objectives, and further outlines the delineation of the study.

Chapter two: This chapter is the literature reviewed for the study; it focuses on the agricultural practices of the avocado fruit and how these practices affect the fruit; it further describes the post-harvest management and how they affect the quality and lifespan of the fruit. It then elaborates on the oil extraction technology and the physicochemical properties of the avocado oil.

Chapter three: This chapter focuses on the systematic improvement study of the process parameters of the process to have a high yield of extracted oil.

Chapter four: This chapter focuses on the reaction kinetics of the avocado oil extraction process and also the thermodynamic modelling of the system.

Chapter five: This chapter focuses on the optimization of the avocado oil extraction process using response surface methodology. The chapter further explains the effect of extraction temperature on the fatty acid profile and the stability of oil.

Chapter six: This chapter is a summary and conclusion of the study; it contains the summary of all chapters. It then also outlines the recommendations for further study.

Table of Contents

List of Figures

List of Tables

List of symbols

Nomenclature

symbols

A	Arrhenius constant (min^{-1})
C_A	Concentration of avocado oil at time t (g/L)
C_{A0}	Concentration of avocado oil at time 0 (g/L)
e	Euler's number
E_a	Activation energy (kJ/mol)
ΔG	Change in Gibbs free energy (kJ/mol)
ΔH	Change in enthalpy (kJ/mol)
K	Reaction rate constant (min^{-1})
K	Equilibrium constant
N	Process order
R	Universal gas constant (8.3145 J/mol.K)
ΔS	Change in Entropy (J/mol.K)
t	Extraction time (min)
T	Temperature (^oC & K)
X_A	Oil fraction at time t
X_{A0}	Oil fraction at time 0
Y_T	Oil concentration percentage extracted
Y_U	Oil concentration percentage unextracted

CHAPTER ONE

MOTIVATION AND DESIGN OF RESEARCH STUDY

1.1. Introduction

The avocado fruit (*Persea americana* Mill.) originated from Mexico, Central and South America. It is a fruit of a subtropical tree that grows in tropical environments and it is frost sensitive (Woolf et al., 2009). It is a popular fruit and highly consumed because of good taste and texture, as well as for its health benefits. The fruit has a high content of oil; and hence it is also a source of oil for culinary and cosmetic use. This is a fruit with extremely high oil content, which is the main component of its dry weight (Reddy et al., 2012). Avocado oil has chemical properties similar to that of olive oil; having at least about 60% monounsaturated fatty acids and approximately 10% polyunsaturated fatty acids (Woolf et al., 2009). It is also found to contain high levels of antioxidants and phytochemicals; such as carotenoids, chlorophylls, polyphenols, tocopherols and phytosterols (Qin & Zhong, 2016). Its high content of monounsaturated fatty acid and its lipid soluble antioxidants makes it an oil that is found to enhance cardiovascular health in culinary use and anti-aging benefits in cosmetic application (Qin & Zhong, 2016). The use of the oil is predominantly in the cosmetics industry because of its stability, high skin penetration properties and its high content of vitamin E (α-tocopherols). Furthermore, it has a low presence in the culinary circle, but it is continually growing popularity (Woolf et al., 2009). There are different methods used to extract oil from vegetables and plant material, some of these methods are used to extract avocado oil. The avocado oil is produced by extracting the oil from the flesh of the avocado fruit. The oil content varies but it is widely found that the seed contain 1% of the oil and the skin contain about 4% of the oil (Costagli et al., 2015). Although the skin and the seed of the avocado also contain oil, but the oil used is extracted only from the flesh of the fruit. There are traditional extractions methods like aqueous or water extraction process, there are conventional methods like cold pressing, there are also chemical or solid-liquid extraction methods using organic solvents for extraction and there are new non-conventional extraction methods like supercritical fluid extraction with carbon dioxide solvent. All these are the different extraction methods used in practice for avocado oil extraction. These techniques have expanded over time as the new ones are developed and optimised to improve the efficiency and increase the oil yields.

1.2. Research motivation and problem statement

Avocado fruit contain vitamins A, B, C and E, carotenoids and sterols that possess antioxidant property. The fruit is very popular because of these vitamins and health benefits. However, the agricultural and retail industries are challenged by losing a great quantity of this fruit because the fruit is sensitive and susceptible to quality degradation. As a result of this quality loss, businesses in agriculture and retail experience a great economic loss. However, the current avocado oil industry is based on reject avocado fruits from the export and retail industry (Woolf et al., 2009).

According to Reddy et al., (2012), the avocado fruit has a very high oil content ranging (20-35%) by fresh weight and depending on geographic location. However, the fruit is mostly consumed as a fruit rather than being processed to produce oil. Furthermore, it was found that there is very limited information on the effects of extraction methods on the avocado oil produced (Qin & Zhong, 2016). It was also found from the available literature on avocado oil extraction that the methods of extraction are still being developed and optimized. There is also very little information and motivation from literature to prove that avocados, like olives can also be used as one of the main sources of oil; hence now currently avocado is not a fruit that is considered the primary source of oil as oppose to olives (Borges *et al*., 2013). According to Wong et al., (2010) both olive oil and avocado oil are very similar based on composition and properties. The high oil content of avocado fruit opens an opportunity to an industry of great economic importance to the country. This study aims to investigate the effects of different pretreatment and extraction methods on the composition of the avocado oil, with a special focus on the fatty acids profile, stability and nutritional components of the oil. These different extraction methods will enable the design of an optimized avocado oil extraction process for commercial industry. The effect of the postharvest ripening stage of the fruit will also be studied. Furthermore, this study will attempt to find an appropriate use and develop avocado oil-based innovative products which possess its nutritional and health benefits.

1.3. Research questions

- Which extraction methods are the most efficient for the avocado oil extraction?
- Which extraction process conditions are the most effective for the avocado oil extraction?
- What are the extraction kinetics avocado oil extractions from the fruit mesocarp?
- How do the extraction methods affect the quality of the oil?
- Is pretreatment necessary in the oil extraction process?
- Which oil quality profile will be best for Cosmeceuticals applications and which profile will be best for use as culinary oil?

1.4. Research objectives

The objectives of this study were as follows:

- To subject the avocado mesocarp from South African cultivars through four different extraction methods; Cold pressing, batch solid-liquid extraction, microwave-aided solid-liquid extraction and Soxhlet extraction.
- To evaluate at least two pretreatment methods for avocado oil extraction
- Evaluate different process conditions during the extraction process
- Evaluate the extraction kinetics and thermodynamic parameters of the extraction process
- Conduct an optimization study of the avocado oil extraction process with the aid of Response Surface Methodology (RSM)
- Evaluate the fatty acid profiles of the avocado oil from each extraction method
- Evaluate the avocado oil stability from each extraction method
- Identify the correlation between the extraction method and the quality of the oil produced

1.5. Significance of the study and expected outcomes

The part of the significance of this research is to address what is outlined by the research problem, which aim is to contribute to the deficiency and gap found in literature, namely, the effect of different extraction methods on the fatty acid profiles of the obtained oil (Qin & Zhong, 2016). The other element that this research aims to study and address is the effects of the ripening stages on physicochemical properties of oil. According to Ozdemir & Topuz (2003); there are no reports on the fatty acid composition of the avocado during the post-harvest ripening period.

The results of this study aim to help resolve the problem of economic loss experienced in the agricultural and retail businesses by opening the opportunity to produce avocado oil of high quality and value. This study aims to provide empirical data through scientific research with regards to the opportunity found in avocado oil production as a growing sector in the domestic oil industry globally. Therefore, efficient methods of extraction will help stimulate the growth of this industry, making it of economic importance especially in South Africa as it is one of the largest avocado growers in the world. This growth will benefit the farmers grow their market and have confidence in growing their avocado production without fear of loss through waste. The growth in avocado industry will also benefit the communities where avocado is grown in the country by creating employment and entrepreneurship opportunities. According to the report by the Department of Agriculture, the avocado industry helps create employment especially in rural areas where there are avocado farms. This will stimulate economic activity and participation in the rural areas thereby creating sustainable jobs and businesses in this industry.

Furthermore, the data from this study will enable the researcher to optimize the extraction process further and design unit operations and economical processes that can be used to commercialize the avocado oil extraction in industry. The output of this research will also culminate in a MEng dissertation, with information generated for the presentation at conferences in the form of posters or oral presentation. In addition, the results and information from this study may be published in reputable peer reviewed journals and/or conference proceedings.

1.6. Delineation

While the avocado fruit is popular because of pleasant taste, smooth texture and its high content of antioxidants which are important in the stability of the oil, the content of antioxidants was however not analysed due to challenges in analysis. The preliminary attempts of analysis were not successful and challenges were found to have been due to the availability of resources, particularly with the sample preparations. The physicochemical properties of this study therefore only focused on the fatty acid profile and the stability of the oil. The pretreatment methods of the study was only related to oven and microwave drying of the avocado mesocarp, the freeze-drying pretreatment was not effectuate, due to the unavailability of the equipment.

1.7. References

Bill, M., Sivakumar, D., Thompson, A.K. and Korsten, L., 2014. Avocado fruit quality management during the postharvest supply chain. *Food Reviews International*, *30*(3), pp.169-202.

Borges, T.H., Pereira, J.A., Cabrera-Vique, C., Lara, L., Oliveira, A.F. and Seiquer, I., 2017. Characterization of Arbequina virgin olive oils produced in different regions of Brazil and Spain: physicochemical properties, oxidative stability and fatty acid profile. *Food Chemistry*, *215*, pp.454-462.

Chemistry Libretexts. 2019. Available online at https://chem.libretexts.org/Bookshelves/Introductory_Chemistry/Book%3A_The_Basics_of_GOB_Chemistry_(Ball_et_al.)/17%3A_Lipids/17.2%3A_Fats_and_Oils

dos Santos, M.A., Alicieo, T.V., Pereira, C.M., Ramis-Ramos, G. and Mendonça, C.R., 2014. Profile of bioactive compounds in avocado pulp oil: influence of the drying processes and extraction methods. *Journal of the American Oil Chemists' Society*, *91*(1), pp.19-27.

Dreher, M.L. and Davenport, A.J., 2013. Hass avocado composition and potential health effects. *Critical Reviews in Food Science and Nutrition*, *53*(7), pp.738-750.

Moreno, A.O., Dorantes, L., Galíndez, J. and Guzmán, R.I., 2003. Effect of different extraction methods on fatty acids, volatile compounds, and physical and chemical properties of avocado (*Persea americana* Mill.) oil. *Journal of Agricultural and Food Chemistry*, *51*(8), pp. 2216-2221.

Ozdemir, F. and Topuz, A., 2003. Changes in dry matter, oil content and fatty acids composition of avocado during harvesting time and post-harvesting ripening period. *Food Chemistry*, *86*(1), pp.79-83.

Qin, X. and Zhong, J., 2016. A review of extraction techniques for avocado oil. *Journal of Oleo Science*, p.ess16063.

Reddy, M., Moodley, R. and Jonnalagadda, S.B., 2012. Fatty acid profile and elemental content of avocado (*Persea americana* Mill.) oil–effect of extraction methods. *Journal of Environmental Science and Health, Part B*, *47*(6), pp.529-537.

Satriana, S., Supardan, M.D., Arpi, N. and Wan Mustapha, W.A., 2019. Development of methods used in the extraction of avocado oil. *European Journal of Lipid Science and Technology*,*121*(1), p.1800210.

Seymour G.B., Tucker G.A. (1993) Avocado. In: Seymour G.B., Taylor J.E., Tucker G.A. (eds) Biochemistry of Fruit Ripening. Springer, Dordrecht

Wong, M., Requejo-Jackman, C. and Woolf, A., 2010. What is unrefined, extra virgin cold-pressed avocado oil. *Journal of the American Oil Chemists' Society*, *87*, p.1099.

Gaydou, E.M., Lozano, Y. and Ratovohery, J., 1987. Triglyceride and fatty acid compositions in the mesocarp of *Persea americana* during fruit development. *Phytochemistry*, 26(6): 1595-1597. doi: 10.1016/S0031-9422(00)82251-7

León-Camacho, M., García-González, D.L. and Aparicio, R., 2001. A detailed and comprehensive study of amaranth (*Amaranthus cruentus* L.) oil fatty profile. *European Food Research and Technology*, 213(4-5): 349-355. doi: 10.1007/s002170100340

Costagli, G. and Betti, M., 2015. Avocado oil extraction processes: method for cold-pressed high-quality edible oil production versus traditional production. *Journal of Agricultural Engineering*, *46*(3), pp.115-122.

Martinez, N.L. and Moreno, R.V., 1995. Parameters for determining the maturity of avocados. *Industries–Alimentaires et Agricoles*, 112(4): 200-203.

CHAPTER TWO

LITERATURE REVIEW

2.1. Avocado fruit industry in South Africa

Avocado fruit is mostly consumed fresh locally and globally, with its production in South Africa being an export-oriented industry that exports fresh avocados to the European countries (Reddy et al., 2012). However, one of the problems with avocado fruit faced by producers is its short time maturation and oxidation; as a result of this there is a growing industry to extract the oil from the avocado fruit. Avocado oil can be considered to have a commercial importance in the fats and oils industry due to its nutrients and health benefits (Costagli et al., 2015). The avocado tree is a subtropical plant and it grows well under subtropical climate conditions. In South Africa; Limpopo, Mpumalanga and Kwa-Zulu Natal are provinces with subtropical climate conditions. These provinces are located in the north-eastern part of the country and hence most avocado cultivars are found in these provinces.

Avocado fruit is commercially produced in South Africa and its production is mainly aimed at export market to the European countries (Bill et al., 2014). There are about five to six varieties of avocado produced in South Africa with Hass and Fuerte as the predominant ones. According to report by Department of Agriculture, (2017) the Hass variety accounted for 33% and Fuerte 42% of the avocados produced in South Africa that year. These values change and fluctuate over time depending on the yield of that particular year. However, South African avocado growers association (SAAGA) reports that approximately 70% of the avocado trees in South Africa are Hass variety and the remaining 30% comprises of mostly Fuerte, Ryan and Pinkerton varieties (Nelson, 2010).

The avocado industry in South Africa contributes to providing employment in the country with majority of the people employed living in the rural areas. The industry is estimated to employ approximately 23 000 casual workers during its peak season (Department of Agriculture, 2017). The farm workers in the avocado farms are paid according to the baseline set rate of minimum wage rate, with the future years projected to be the current wage rate + CPI (Consumer Price Index) + 1.5% (Department of Agriculture, 2017).

2.2. Ripening of avocado

The avocado fruit tree is one of the trees that bears fruit that ripen when fallen (Reddy et al., 2012). The avocado fruit is unlike other fruits because the softening and ripening of the fruit does not take place during maturity on the tree; but it takes place once the fruit is picked from the tree (post-harvest) (Ozdemir & Topuz, 2004). Avocado is also known to be one of the most rapidly ripening fruits, completing its post-harvesting ripeness within 5-7 days (Seymour & Tucker, 1993). Martinez & Moreno (1995) maintains that the oil increases in the mesocarp of the avocado fruit and changes in composition during maturation of the fruit; concentration of unsaturated fatty acids increase parallel with decreasing amount of saturated fats.

According to Ozdemir & Topuz (2003), as the water content decreases in the mesocarp of the fruit, the oil content increases by the same amount, so that the percentage of water and oil remains constant. This depends on the age of the fruit and is assumed to be taking place during the maturation of the fruit on the tree. The same study indicated that there was no significant difference found in the content of the oil during the first four days after the harvest.

2.3. Post-harvest management

Avocado fruit is sensitive and susceptible to loss in quality. The loss in quality of the fruit is as a result of post-harvest management of the fruit. Post-harvest management operations include harvesting practices, packing operations, temperature management, post-harvest treatment, transporting and storage conditions (Bill et al., 2014). Effects of post-harvest management start with pre-harvest management. Factors that are to be considered during pre-harvest are climate or environmental factors which involve temperature, wind and rainfall; pruning practices, pest and disease control and irrigation (Arpaia et al., 2004). The temperature during the ripening phase of the fruit is one of the most important factors; since temperatures above 30^{o}C have adverse effects whilst temperatures between 20^{o}C and 25^{o}C are favourable for fruit quality (Ericksson & Takaake., 1964 as cited by Bill et al., 2014).

2.4. Avocado quality specifications for retail and exports

Department of agriculture, forestry and fisheries (DAFF) have established standards for compliance for farmers and growers of fruits and vegetables. The standards are to protect the consumers by having safe and quality food for consumption. Local retailers also adhere to these standards when sourcing their fruits and vegetables. To ensure that the fruits and vegetables they source and sell in their outlets are of quality and comply with the food safety standard; the retailers make sure they buy from farmers that are accredited by food safety auditors. The available standards for food safety that are accredited and recognized globally allow local farmers to trade globally by exporting their fruits and vegetables internationally.

Guided by the agricultural products act number 119 of 1990; the food safety auditors are referred to as assignees of/by the minister. Their functions or responsibilities are to perform duties to authorize the quality of the food and grade to be sold. The assignee is given the powers of the minister within their jurisdiction. With the rights granted to them are able to prohibit the sale of the agricultural product if it does not comply with the standards of its class or grade. The auditor or assignee therefore conducts Global Food Safety Initiative (GFSI) certification services. These certifications include:

- BRC Global standards for Agents and Brokers
- BRC Global standard for food safety
- BRC Global standard for packaging and packaging material
- BRC Global standard for storage and distribution
- FSSC 22000 (Food safety systems certification)
- Global GAP (Good Agricultural Practice)
- IFS Food (International featured standard)
- IFS Logistics certificate
- SQF (Safe Quality Food)

These accreditations allows for local and global trading of food in general including agricultural products.

2.5. Oil extraction from avocado fruit

The extraction methods of oil can be classified into three categories; physical, chemical and biological (which is extraction by the use of biological enzymes) (Satriana et al., 2019). Physical extraction methods include crushing, pressing, filtering and centrifuging. Chemical extraction methods include extraction of the oil from the fruit with organic solvents. Biological extraction is a method used to extract oil by means of biological enzymes.

Avocado oil is found primarily on the mesocarp (flesh) of the fruit, the mesocarp consists of parenchyma cells and idioblast cells (Satriana et al., 2019). The parenchyma cells contain finely dispersed oil emulsion whilst the idioblast cells contain oil as droplets covered by thick cell walls. Idioblast cells contain most of the oil because they are thicker than parenchyma cells in diameter. Extraction methods are being developed to efficiently extract most of the oil from these cells. According to Moreno et al., (2003), the different extraction methods can affect the fatty acid profile of the oil produced. However, according to Qin & Zhong, (2016), there is very little information about the effect of different extraction methods on the triglyceride profile of the oil produced.

2.6. Pretreatment of avocado mesocarp (flesh)

The oil extracted from the avocado fruit through pressing is found to be predominantly that which is in the parenchyma cells in the matrix of the avocado fruit. According to Satriana et al., (2019) the idioblast cells appear to be unruptured and intact during the pressing. Qin & Zhong, (2016) describes that the lipids are primarily found in the mesocarp (flesh) of the avocado that is composed of numerous parenchyma cells and evenly scattered idioblast cells. The idioblast cells are the cells which hold most of the oil in the plant cell matrix. Therefore, it was found that in order to get optimal oil yield from the extraction process, the aim of the process is to get to the idioblast cells. Qin & Zhong, (2016) further reiterates that the idioblast cell walls are thicker than the parenchyma cell walls.

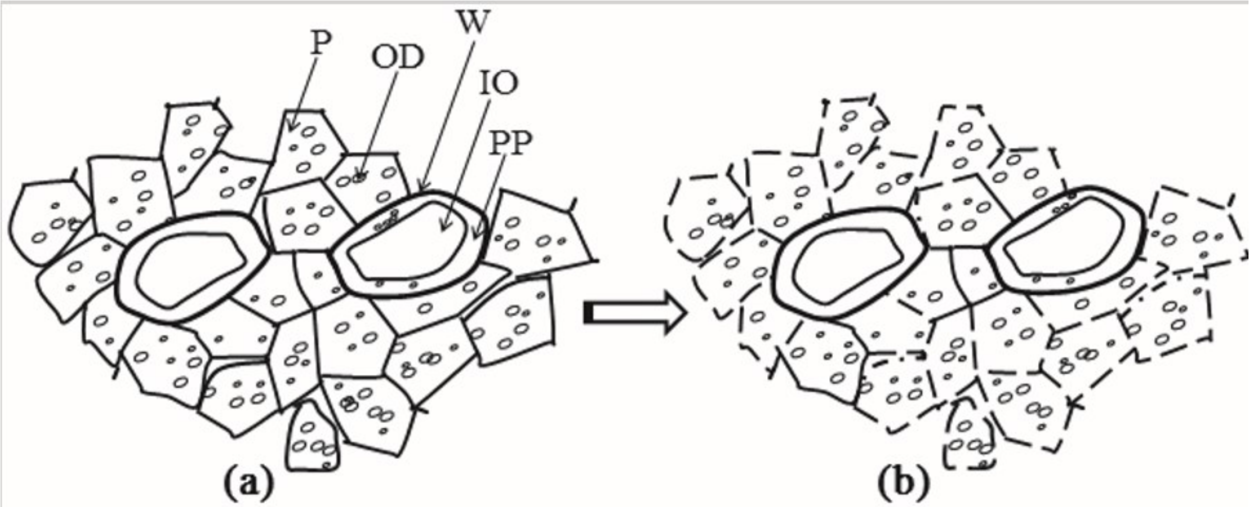

Figure 2.1: Avocado mesocarp cell matrix during ripening **(Qin & Zhong, 2016)**

Figure 1 above illustrates the difference between the unripened and the ripened matrix of the avocado mesocarp. The diagram on (a) is a picture of a matured but unripe avocado and (b) is a picture of a ripened avocado mesocarp. The diagram also shows as labeled P- Parenchyma cells; OD- Oil droplets; W- Wall of idioblast; IO- Idioblast oil sac; PP- Protoplasm. These shows that after ripening, the oil from the parenchyma cells is exposed as the cell walls are porous and the oil droplets are accessible. However, the cell walls of the idioblast are still firmly intact, meaning that the oil sacs are not easily accessible; hence there is a need for the pretreatment stage in the process to obtain optimal oil yield during extraction. This also shows that avocado oil can be easily extracted from the ripe avocado fruit as opposed to the unripe fruit.

Qin & Zhong, (2016) further stressed that pretreatment improves the oil yield and the quality of oil extracted. The pretreatment efforts are all to disrupt the structure of the oil sacs and make it easy to access the oil; this should however not negatively affect the quality of the oil produced. The pretreatment process primarily removes the water content from the mesocarp in order to get to the oil easily. Qin & Zhong, (2016) argues that the water content of the fruit affects the oil yield from the avocado; hence there was an introduction of pretreatment of the avocado fruit prior to extraction. The different approaches to pretreatment of the avocado prior to extraction include slicing or meshing, oven drying or freeze drying, microwave drying/treatment, addition of salts, enzymes or solid additives.

Mostert et al., (2007) made a study of the effect of different pretreatments and ripeness on the avocado oil yield. The study looked at the effect of freeze drying and oven drying on both ripe and unripe avocado fruits. Extraction of the oil was done using two methods, the supercritical CO_2 and the hexane solvent extraction. The results of the study showed that freeze drying was the best pretreatment method as it gave higher oil yield with both extraction methods and even both ripe and unripe avocado fruits. Ortiz Moreno et al., (2003) suggests that reason for a lower oil yield from oven drying pretreatment is due to denaturation and crosslinking of protein and gelatinization followed by dehydration of starch that may lead to formation of a physical barrier around the oil cell. Mostert et al., (2007) further reported that this may cause the increase to the mass transfer resistance during extraction between the surface and the extracting fluid. Mostert et al., (2007) further reiterates that the bigger particle size formation formed through hardened structure of the mesocarp from oven drying makes it less porous and exposes less oil to the extracting fluid. Freeze drying on the other hand makes the material brittle and powdery, which have much smaller particle sizes and more porous compared to those of oven-dried particles. According to Mostert et al., (2007) smaller particles sized results in higher oil yield due to larger surface area on extraction.

The microwave pretreatment of the avocado mesocarp prior to extraction is a recent and modern technology. There have been several researches made on the technology and it is becoming more popular as it may save more time than freeze drying and oven drying. From the study by Ortiz Moreno et al., (2003), they reported that a higher oil yield was obtained with microwave and solvent extraction, but oil of higher quality was obtained with microwave and squeezing (which we can relate to pressing). This confirms what Qin & Zhong, (2016) argues when they say it depends on the objective of the extraction whether is higher yield or a higher quality. Satriana et al., (2019) further reiterates that a more extensive pretreatment is required to improving both the oil yield and the quality of the oil. Ortiz Moreno et al., (2003) found that the intensity of the energy of the microwave applied to the avocado mesocarp affects the oil yield. In that study it was found that there was an optimal energy that gave a highest yield, but the energy above that or lower that it decreased. (Ortiz Moreno et al., 2003) reported 1.8 kJ/g as the amount of energy optimal for microwave pretreatment that gave highest oil yield.

2.7. Cold pressing

Cold pressing is a method where oil is pressed out of the plant material by squeezing or by mechanical screw press or hydraulic press (Qin & Zhong, 2016). This method is mainly used and was developed for seed oils. It is still a popular extraction method to produce seed oil commercially in industries. Cold pressing is a low energy process which does not require any heating during extraction, solvent recovery is not required or even evaporation of these solvents. This process however requires a sequence of multiple steps before and after pressing (Satriana et al., 2019). Cold pressing is a process which produces the least amount of oil and hence the process itself has been developed and modified over time to increase the yield of oil. This has been done by combination of methods or steps during the extraction process. According to Satriana et al., (2019) chemicals like calcium chloride and formaldehyde can be added in the process to increase the yield of oil produced during the pressing. In some instances where unit operations like centrifuging is applied; enzymes can be added to the avocado paste before separation of the oil to increase the oil yield.

Cold pressed oil, which is also referred to as extra virgin oil is found to have a higher content of chlorophyll. The high level of chlorophyll in the oil may have a negative effect on the oxidative stability of the oil due to its easy photo-oxidation when exposed to light and oxygen (Qin & Zhong, 2016); thereby also having a negative effect on the shelf life of the oil.

2.8. Organic Solvent

Solvents are organic liquids which are used to dissolve or dilute other substances or material. They may also be used as fuels, intermediaries and components of other substances or products (ILO, 2014). Likewise; organic solvents are used for lipids extraction from plants and vegetables. Hence this form of extraction is known as solvent extraction. In this extraction process, the solvent dissolves the oil from the plant or vegetable and result in an oil-solvent solution. In this case the oil is the solute and the plant material is the solid.

2.9. Solvent extraction

Avocado extraction by organic solvents is a conventional lipid extraction method that has been used in practice. It is known to be the most common method to separate oils from plant-based oil sources. In chemistry it is found that lipids are hydrophobic and thus also makes them non-polar compounds; and it is also known that hydrophilic compounds are polar compounds. According to Kumar, (2015) like dissolves like based on polarity, this means that the non-polar compounds are dissolved more by non-polar solvents. Kumar, (2015) further explains that the physical properties of a solvent such as polarity, dipole movement, polarizability and hydrogen bonding decide which class of compounds it can dissolve and with which other solvents it is miscible. This makes the choice of solvents a very important process to follow and consider to achieve optimum yield during extraction.

The criteria of the choice of solvent also needs to consider the boiling point of the solvent for easy recovery, the toxicity of the solvent, reusability, the economic value and availability (Kumar, 2015). Therefore, the choice of solvent plays an important role to affect the efficiency of the extraction and the economics of the process. The efficiency of a solvent extraction process requires total penetration of the solvent into the lipid membranes with the solvent and desired compounds match in polarity (Satriana et al., 2019). Satriana et al., (2019) further explain the importance of the pretreatment of the plant material or fruit in the instance of avocado; that it is very important that the solvent come into direct contact with the lipids. This efficiency will ensure maximum amount of oil extracted from the plant thereby also improving the economics of the process. The efficiency further goes to the recovery of the solvent for reusability and the economics that are associated with both cost recovery and cost of new fresh solvent.

Oil extraction by use of solvents has a few shortcomings although it is found to be the method which produces a higher yield of oil (Qin & Zhong, 2016). It is found that the oil extracted by solvents contain residual solvent even after recovery, which limits the use of this avocado oil in food and pharmaceutical industries. This then suggests that further refining steps of the oil are needed for application as edible oil, pharmaceutical and cosmetics use (Satriana et al., 2019).

2.10. Solvent extraction by Soxhlet method

Modes of solvent extraction can be with the Soxhlet apparatus which includes the application of heat while extraction takes place. The Soxhlet apparatus includes an Erlenmeyer flask, the thimble which holds the sample, the Soxhlet device and the condenser. The Soxhlet device setup extracts the oil from the sample using the solvent and then the solvent is distilled out and recovered from the oil mixture. The setup includes a heating mantle which heats up the solvent while extraction takes place. Some of the advantages of using the Soxhlet extractor includes 1) the sample phase is continually brought into contact with fresh solvent, ensuring complete extraction; 2) the heat applied to the distillation flask is extended to the extraction cavity to some extent and it relatively keeps the system at a high temperature; 3) the extract need not to be filtered after extraction and; 4) the sample throughput can be increased by performing several parallel extractions concurrently. The oil extraction by solvents has been extensively done using the Soxhlet method because of its many advantages; however, there is also a downside to it. According to Satriana et al., (2019) it was noted that extracting oil at high temperatures may destroy some of the bioactive compounds found in the plant material.

2.11. Solvent extraction by Maceration

The other mode of solvent extraction is known as maceration. This is the simplest form of solvent extraction that does not require a lot of equipment or resources. This method is used industrially for small and large quantities of extraction. The method is also used for both herbal extracts and for oil extraction. The process of maceration is done by placing a grounded or crushed plant material on a beaker/container and pouring the chosen solvent over the material. The mixture is stirred occasionally and after some time the solvent would have extracted/absorbed some of the compound (oil) from the plant material and some equilibrium will be reached; then the plant material and the miscella (solution) will be separated. Then the plant material is washed with fresh solvent to extract more of the oil that still remains in the material. Maceration is repeated until all the oil is removed from the plant material or fruit. The solvent is then recovered by distillation once the plant material/fruit is spent.

Solvent extraction by maceration may be static or dynamic when applied in practice industrially. This method of solvent extraction has an advantage over Soxhlet method because it does not involve any heating and thus extraction takes place at low temperatures. The low temperatures make maceration a more nutritional extraction method because the low temperatures preserve the bioactive compounds including the alpha-tocopherols found in the avocado oil.

2.12. Supercritical carbon dioxide extraction

Extraction of oil by supercritical carbon dioxide is a modern and unconventional method applied in practice today. This is an extraction process that makes use of the carbon dioxide gas in the supercritical state as an extraction fluid. The carbon dioxide is considered a solvent in the process, the solvency of the carbon dioxide fluid can be altered according to the desired state by adjusting the pressure and temperature during extraction (Satriana et al., 2019). This ability to alter the solvency of the fluid makes it very advantageous; this allows the process to be altered to achieve a specific quality of oil extracted by changing the solvency of the fluid during extraction. Supercritical carbon dioxide is considered a green solvent; it is biologically safe, non-toxic and does not leave any residue solvent in the extracted oil/compound. According to Qin & Zhong, (2016) the supercritical carbon dioxide extraction is highly selective, by tuning of the state and solvation power of the carbon dioxide by changing the process parameters (pressure and temperature) can selectively extract or not some bioactives, like chlorophyll.

Table 2.1: Different extraction processes studied from literature

Extraction Method	Extraction Procedure	Oil Yield	Reference
Pressing	Microwave pretreatment→ Extract oil by squeezing	65.20%	(Ortiz Moreno et al., 2003)
Solvent	Freeze dry →Extract unripe Avocado with Hexane	677 g/Kg	(Mostert et al., 2007)
	Oven dry →Extract unripe Avocado with Hexane	629 g/Kg	(Mostert et al., 2007)
	Freeze dry →Extract ripe Avocado with Hexane	720 g/Kg	(Mostert et al., 2007)
	Oven dry→ Extract ripe Avocado with Hexane	702 g/Kg	(Mostert et al., 2007)
	Oven dry→ Extract Hass Avo with Hexane	647.6 g/Kg	(Reddy et al., 2012)
	Oven dry→ Extract Fuerte Avo with Hexane	636.7 g/Kg	(Reddy et al., 2012)
	Microwave pretreat→ Extract Hass Avo with Hexane	699.4 g/Kg	(Reddy et al., 2012)
	Microwave pretreat→ Extract Fuerte Avo with Hexane	609.0 g/Kg	(Reddy et al., 2012)
Supercritical	Freeze dry →Extract unripe Avocado with SC-CO_2	588 g/Kg	(Mostert et al., 2007)
	Oven dry→ Extract unripe Avocado with SC-CO_2	522 g/Kg	(Mostert et al., 2007)
	Freeze dry→ Extract ripe Avocado with SC-CO_2	648 g/Kg	(Mostert et al., 2007)
	Oven dry→ Extract ripe Avocado with SC-CO_2	604 g/Kg	(Mostert et al., 2007)
	Oven dry→ Extract Hass Avocado with SC-CO_2	628.7 g/Kg	(Reddy et al., 2012)
	Oven dry→ Extract Fuerte Avocado with SC-CO_2	595.6 g/Kg	(Reddy et al., 2012)

2.13. Moisture content of the fruit

As the water content decreases in the mesocarp the fruit the oil content increases by the same amount, so that the percentage of water and oil remains constant (Ozdemir &

Topuz, 2004). As discussed with the ripening of the fruit, there will always be water content in the flesh of the avocado fruit.

Hence, mixed extraction methods were introduced which included preparation with a microwave and pretreatment by oven drying and freeze drying. However, according to Landahl et al., (2009), the dry matter and the oil content of the mesocarp do not always correlate; Landahl et al., (2009) and Woolf et al., (2009) argued that depending on the growing areas, the dry matter within the fruit can vary. Furthermore, Hofman et al., (2000) maintained that there are no correlations between the dry matter content, the oil content, and the fruit quality.

2.14. Mass transfer

Mass transfer is the process of transfer of one or more compounds (solute) from the feed plant material to the solvent. The driving force of this mass transfer process is the concentration difference between the solute of the plant material (feed) and the solvent. The concentration of the solute is low in the solvent and high in the feed; which allows the solute to diffuse from the feed material to the solvent. This then shows that the process of diffusion is central to mass transfer by extraction.

Diffusion being central to mass transfer; according to Lloyd & van Wyk, (2011) it was found that there are a number of hindrances to diffusion which in turn hinders mass transfer rate overall. The three interfaces are found during the diffusion which causes resistance to diffusion process:

- The diffusion layer on the feed side
- The resistance to transfer of the interface itself
- The diffusion layer on the solvent side

This process is illustrated by Figure 2.2 below.

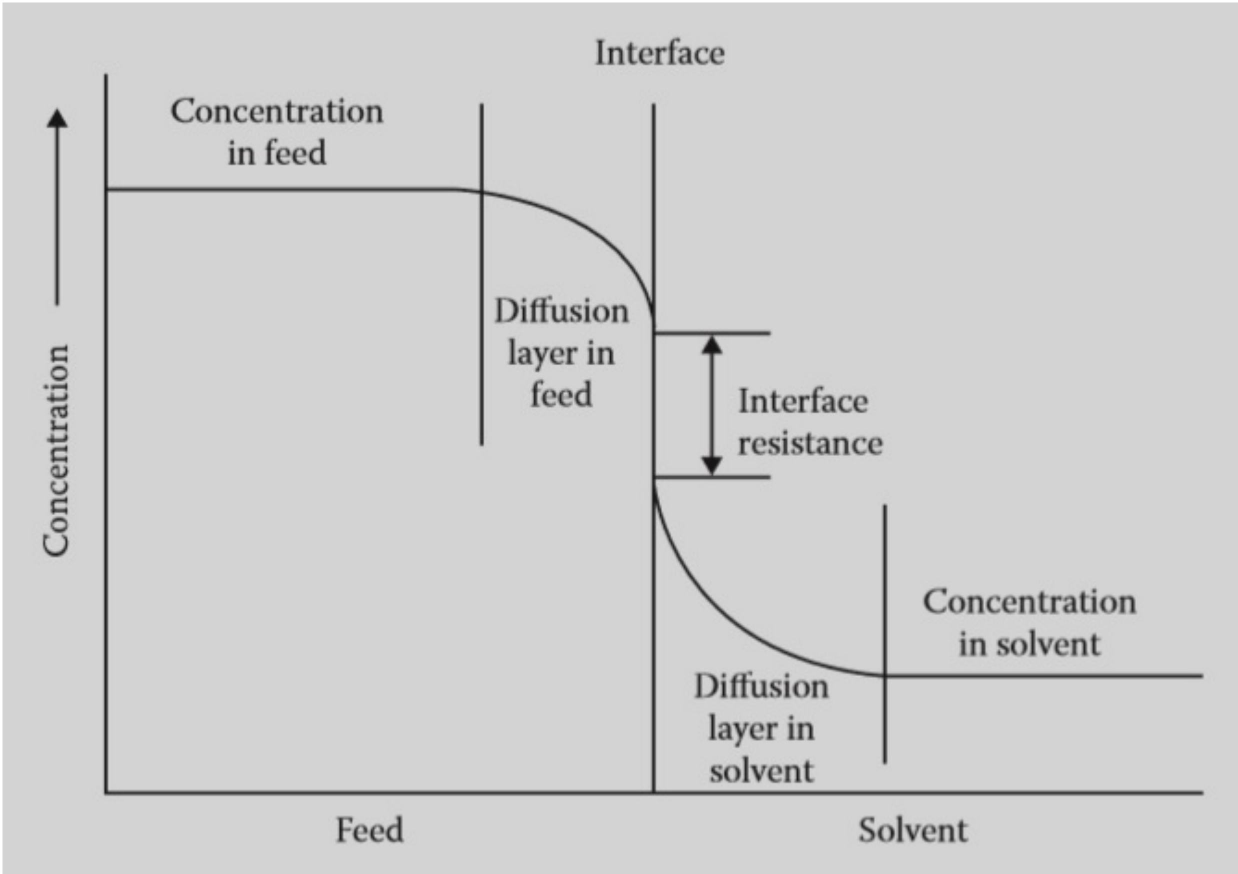

Figure 2.2: Transfer of solute between two phases (Lloyd & van Wyk, 2011)

2.15. Diffusion

Diffusion is a movement or transfer of a compound or material from high concentration to low concentration. In the case of avocado extraction, diffusion takes place from a plant material or the avocado fruit where it is in high concentration of the oil to the solvent where there is low concentration of the oil. Diffusion is defined and explained by Fick's law; which states that the rate of diffusion is directly proportional to both the concentration and the surface area of the solid-liquid interface and is inversely proportional to the thickness of the membrane/liquid film around the solid.

$$\frac{dM}{dt} = \frac{k'A(C_s - C)}{b} \qquad (2.1)$$

Where:

k' – The diffusion coefficient

A – Surface area of the liquid-solid interface

B – The effectiveness thickness of the liquid film surrounding the solid

C_s – The concentration of the saturated solution in contact with the solid
C - Concentration of the solute in the bulk of the solution at time, t.
M – The mass of the solute transferred in time

This shows that the greater the area over which diffusion can take place, the greater the rate of mass transfer (Lloyd & van Wyk, 2011). For a solid-liquid extraction process like avocado oil extraction, to increase the rate of mass transfer from the solid to the liquid phase; the solids must be crushed down to smaller particles to increase the surface area. This principle refers back to the importance of pretreatment, even after the pretreatment step of drying the avocado mesocarp.

2.16. Fatty acids profile of avocado oil

Avocado oil has a high concentration of unsaturated fats and as a result is seen to have health benefits. The avocado oil is added as an ingredient to food products because of the nutritional value of the fatty acids (Satriana et al., 2019). Typical avocado oil contains 76% of monounsaturated fatty acids (palmitoleic and oleic acids), 12% polyunsaturated fatty acids (linoleic and linolenic acids) and 12% saturated fats (stearic and palmitic acids). These values are given as percentages of fatty acids per total fatty acid (Wong et al., 2010).

According to Qin & Zhong, (2016), the fatty acid composition of the oil can be changed by variety of the fruit, the geographical origin of the fruit, the ripening stage as well as extraction method. Avocado oil is considered and characterized to be similar to olive oil because of its fatty acid composition and due to the fact that it has a high composition of monounsaturated fatty acid (oleic acid). Linoleic acid is the main polyunsaturated fatty acid and Palmitic acid is the main saturated fatty acid found in avocado oil.

2.17. Lipid oxidation

Lipid oxidation is defined as the reaction of oil degradation due to a reaction involving heat/thermal energy, exposure to oxygen or a reaction from photo-oxidation activated by exposure to light. These reactions are referred to as thermal oxidation, auto oxidation and photo oxidation (Woolf et al., 2009). These reactions causes degradation of the oil which may result in damaging the essential health substances of the oil (Berasategi et al., 2012). Although some vegetable oils like avocado oil have a high content of chlorophyll which makes it susceptible to photo oxidation, it also have a high content of carotenoids and tocopherols which act as antioxidants for the oil (Woolf et al., 2009). Therefore, lipid oxidation is found to be one of the major causes of quality deterioration in vegetable oils. Hence the shelf-life of the oil is determined by measuring the deterioration of the oil due to lipid oxidation to determine the stability of the oil. Some of these measurements or physicochemical properties used to determine lipid oxidation and shelf-life of the oil are; oxidative stability and peroxide value.

With respect to fatty acids of the oil, unsaturated fatty acids are more prone to oxidation than saturated fatty acids (Berasategi et al., 2012). The study done by Berasategi et al., (2012) on comparison of oil stability between olive oil and avocado oil, found that comparing the fatty acids from the heating treatment experiment the unsaturated fatty acids decreased and the saturated fatty acids increased after 3 hours. This was a result of thermal oxidation, which resulted in the oxidation of both the olive and avocado oil. The practice that is used today industrially in the production of culinary and essential oils is the addition of antioxidants which prevent oxidation of the oil.

2.18. Reaction/Extraction kinetics

There are two types of reactions that may take place in a chemical reaction; there is an irreversible reaction and a reversible reaction. An irreversible reaction is a reaction that takes place in one direction until all the reactants are consumed (Fogler, 1999). A reversible reaction on the other hand it is a reaction that may proceed in both directions (Fogler, 1999). These reactions take place at different rates and the rate at which the reaction takes place is said to be the rate of reaction. The rate at which these chemical reactions take place can be expressed in different ways. It can be expressed in either the rate of disappearance of reactants or the rate of formation of products (Fogler, 1999). Therefore, the basis at which the reaction rate is expressed needs to be consistent throughout all the calculation made.

The reaction kinetics can be determined from the rate law equation because the rate law is based on the reaction taking place. The rate law or the kinetic expression is the equation that relates the rate of reaction to the concentrations of the species involved in the reaction (Fogler, 1999). It may also be said that the rate law gives the relationship between the rate of reaction and concentration.

$$-r_A = [k_A(T)][fn(C_A, C_B ...)] \quad (2.2)$$

The $-r_A$ is the rate of reaction, k_A is the reaction rate constant and the C_A is the concentrations of the reactants. According to the rate law equation, it is found that reaction rate constant is a function of temperature but it is independent of concentration.

2.19. Arrhenius equation

The Arrhenius equation is an equation that relates the reaction rate constant to temperature. According to (Fogler, 1999), the Arrhenius equation is an equation that has been tested and verified empirically to give the temperature behaviour of reaction rate constants over a range of temperatures. The Arrhenius equation is as follows:

$$k = Ae^{-E_a/RT} \quad (2.3)$$

Where:
K is the reaction rate constant
A is the Arrhenius constant (unitless)
E_a is the activation energy in J/mol
R is the universal gas constant = 8.3145 J/mol.K
T is the absolute temperature in kelvin (K)

In this equation, the Arrhenius constant which is also referred to as the pre-exponential factor together with the activation energy are found to be independent of temperature (Laidler, 1996).

The Arrhenius equation is also widely used to determine the activation energy of the system. The activation energy is defined as the minimum amount of energy that is required by the reacting molecules in order for the reaction to take place (Fogler, 1999). There is a relationship between the activation energy and the reaction rate; according to Mills et al, (1993), the higher the activation energy the more temperature sensitive the reaction rate. Activation energy is determined empirically through the Arrhenius equation after running a few experiments at different temperatures.

2.20. Chemical Thermodynamics

Chemical thermodynamics is a study of chemical reactions and its relations with heat, work and internal energy of substances. Thermodynamics is also referred to as a study of the transformation of energy, particularly the conversion of heat energy into work (Elliott, 1991). Furthermore, thermodynamics is a study that makes use of mathematical models to study the chemical methods and the spontaneity of the process (Ott, 2000). The thermodynamics mathematical models help understand the chemical reactions better, which then fives opportunity to optimize the processes. The thermodynamic models are the enthalpy, entropy and Gibbs free energy; all these parameters indicate different behaviour to the reactions of the process. The enthalpy indicates the type of reaction whether is endothermic or exothermic; a positive enthalpy indicates that the reaction is endothermic and a negative enthalpy indicates an exothermic reaction. Entropy specifies the direction of the reaction, positive entropy indicates that the reaction is irreversible and negative entropy indicates that the reaction is reversible (Amin et al., 2010). Gibbs free energy specifies the spontaneity of the reaction; a positive Gibbs energy indicates that the reaction is non-spontaneous and a negative Gibbs energy indicates that the reaction occur spontaneously (Stølen & Grande, 2004).

2.21. References

Aktar, T. & Adal, E. 2019. Determining the Arrhenius kinetics of avocado oil: Oxidative stability under Rancimat test conditions. *Foods*, 8(7): 236. doi: 10.3390/foods8070236

Amarante, R.C.A., Oliveira, P.M., Schwantes, F.K. & Moro, A. 2014. Oil extraction from castor cake using ethanol : kinetics and thermodynamics. *Industrial & Engineering Chemistry Research*, *53*(16): 6824–6829. doi: 10.1021/ie500508n

Amin, S.K., Hawas, S., El Diwani, G.D. & El Rafei, S. 2010. Kinetics and thermodynamics of oil extraction from *Jatropha curcas* in aqueous acidic hexane solutions. *Journal of American Science*, 11(3): 247–253. doi: 10.1155/2015/871236

Berasategi, I., Barriuso, B., Ansorena, D. & Astiasarán, I. 2012. Stability of avocado oil during heating : Comparative study to olive oil. *Food Chemistry*, 132(1): 439–446. doi: 10.1016/j.foodchem.2011.11.018

Ott, J.B., & Boerio-Goates, J. 2000. The first and second laws of thermodynamics In: Ott, J.B. (ed.) *Chemical Thermodynamics: Principles and Applications*, Elsevier Academic Press, Amsterdam.

Bill, M., Sivakumar, D., Thompson, A.K. & Korsten, L., 2014. Avocado fruit quality management during the postharvest supply chain. *Food Reviews International*, 30(3): 169–202. doi: 10.1080/87559129.2014.907304

Costagli, G., & Betti, M. 2015. Avocado oil extraction processes: method for cold-pressed high-quality edible oil production versus traditional production. *Journal of Agricultural Engineering,* 46(3): 115-122. doi: 10.4081/jae.2015.467

Department of Agriculture, F. and F. 2017. *A Profile of the South African Dairy Market Value*.

Elliott, V. 1991. *Introductory Applied Thermodynamics*. Metric Publications.

FAO/WHO. 2018. *JOINT FAO/WHO EXPERT COMMITTEE ON FOOD ADDITIVES Eighty-sixth meeting Geneva, 12–21 June 2018*.

FAO/WHO Expert Committee. 2016. *COMPEDIUM OF FOOD ADDITIVE AND SPECIFICATION*.

Flores, M., Perez-Camino, M.D.C. & Jose, T. 2018. Preliminary studies on composition, quality and oxidative stability of commercial avocado oil produced in Chile.*Journal of Food Science and Engineering*, 4(1), 21–26.

Fogler, H.S. 1999. *Elements of Chemical Reaction Engineering, 3rd ed.* Prentice-Hall Inc., New Delhi.

Hofman, P.J., Jobin-Décor, M. & Giles, J. 2000. Percentage of dry matter and oil content are not reliable indicators of fruit maturity or quality in late-harvested 'Hass' avocado. *HortScience*, 35(4): 694–695. doi: 10.21273/HORTSCI.35.4.694

ILO: Occupational Safety and Health: Solvents and The Workplace 2014. OSH brief 5

Jeon, Y.H., Son, Y.J., Kim, S.H., Yun, E.Y., Kang, H.J. & Hwang, I.K. 2016. Physicochemical properties and oxidative stabilities of mealworm (*Tenebrio molitor*) oils under different roasting conditions. *Food Science and Biotechnology*, 25(1): 105–110. doi: 10.1007/s10068-016-0015-9

Kumar, D.S. 2015. Herbal Bioactives and Food Fortification, CRC Press, Boca Raton.

Landahl, S., Meyer, M.D. & Terry, L.A. 2009. Spatial and temporal analysis of textural and biochemical changes of imported avocado cv. Hass during fruit ripening. *Journal of Agricultural and Food Chemistry*, 57(15): 7039–7047. doi:10.1021/jf803669x

Liauw, M.Y., Natan, F.A., Widiyanti, P., Ikasari, D., Indraswati, N. & Soetaredjo, F.E. 2008. Extraction of Neem oil (*Azadirachta indica* A . Juss) using n-hexane and ethanol: A studies of oil quality, kinetic and thermodynamic. 3(3): 49–54.

Lloyd, P. & van Wyk, J. Introduction to extraction in food processing, pp 1–24. In: Lebovka , N., Vorobiev, E., Chemat, F. (eds.) Enhancing Extraction Process in Food Industry, CRC Press, Boca Raton, 2011.

Mewa-Ngongang, M., du Plessis, H.W., Hutchinson, U.F., Mekuto, L. & Ntwampe Ko, S. 2017. Kinetic modelling and optimisation of antimicrobial compound production by *Candida pyralidae* KU736785 for control of *Candida guilliermondii*. *Food Science and Technology International*, 23(4) 358–370. doi: 10.1177/1082013217694288

Mewa-Ngongang, M., du Plessis, H.W. et al. 2019. Grape pomace extracts as fermentation medium for the production of potential biopreservation compounds. *Foods*, 8(2), 51. doi:10.3390/foods8020051

Mills, I., Cvitas, T. & Homann, K. 1993. *Quantities, Units and Symbols in Physical*

Chemistry. 2nd ed., Blackwell Science Ltd., London..

Mostert, M.E., Botha, B.M., du Plessis, L.M. & Duodu, K.G. 2007. Effect of fruit ripeness and method of fruit drying on the extractability of avocado oil with hexane and supercritical carbon dioxide, J*ournal of the Food Science and Agriculture*, 87(15): 2880–2885. doi: 10.1002/jsfa.3051

Myers, R., Montgomery, D. & Anderson-Cook, C. 2015. *Response Surface Methodology*, 3rd ed., John Wiley & Sons, Hoboken.

Nelson, R.M. 2010. Quality challenges facing the South African avocado industry – An overview of the 2009 South African avocado season. 99. 7–12.

Ortiz Moreno, A., Dorantes, L., Galíndez, J. & Guzmán, R.I. 2003. Effect of different extraction methods on fatty acids, volatile compounds, and physical and chemical properties of avocado (*Persea americana* Mill.) oil. *Journal of Agricultural and Food Chemistry*, 51(8): 2216–2221. doi: 10.1021/jf0207934

Ott, B.J. (ed.) 2000. Introduction pp. 1–36, In: Ott, B.J. (ed.): *Chemical Thermodynamics: Principles and Applications*, Elsevier Academic Press, Asterdam.

Ozdemir, F. & Topuz, A. 2004. Changes in dry matter, oil content and fatty acids composition of avocado during harvesting time and post-harvesting ripening period. *Food Chemistry*, 86(1): 79–83. doi: 10.1016/j.foodchem.2003.08.012

Qin, X. & Zhong, J. 2016. A review of extraction techniques for avocado oil. *Journal of Oleo Science*, 65(11): 881–888. doi: 10.5650/jos.ess16063

Reddy, M., Moodley, R. & Jonnalagadda, S.B. 2012. Fatty acid profile and elemental content of avocado (*Persea americana* Mill.) oil -effect of extraction methods. *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes*, 47(6): 529–537. doi: 10.1080/03601234.2012.665669

Richardson, J.., Harker, J.. & Backhurst, J.. 2002. *Coulson and Richardson's Chemical Engineering*. 5th ed., Butterworth-Heinemann, Oxford.

Dos Santos, S.B., Martins, M.A., Caneschi, A.L., Aguilar, P.R.M. & Coimbra, J.S.D.R. 2015. Kinetics and thermodynamics of oil extraction from *Jatropha curcas* L. using ethanol as a solvent. *International Journal of Chemical Engineering*, doi: 10.1155/2015/871236

Satriana, S., Supardan, M.D., Arpi, N., Aida, W. & Mustapha, W. 2019. Development of methods used in the extraction of avocado oil, *European Journal of Lipid Science and Technology*, *Special Issue: Euro Fed Lipid Highlights 2018*, 121(1): 1800210. doi: 10.1002/ejlt.201800210

Seymour, G.B. & Tucker, G.A. 1993. Avocado. pp. 53–81. In: Seymour, G.B., Taylor, E., Tucker, G.A. (eds.) Biochemistry of Fruit Ripening, Springer Science+Business Media, Dordrecht.

Stølen, S., Grande, T. & Allen, N.L. 2004. Chemical Thermodynamics of Materials Macroscopic and Microscopic Aspects. John Wiley & Sons, Ltd., Chichester.

Sulaiman, S., Aziz, A.R.A. & Kheireddine, M. 2013. Optimization and modeling of extraction of solid coconut waste oil. *Journal of Food Engineering*, 114(2): 228–234. doi: 10.1016/j.jfoodeng.2012.08.025.

Topalla, H. & Gecgel, U. 2000. Kinetics and thermodynamics of oil extraction from sunflower seeds in the presence of aqueous acidic hexane solution. *Turkish Journal of Chemistry,* 24(3) 247–253.

Laidler, K.J. 1996. A glossary of terms used in chemical kinetics, including reaction dynamics. *Pure & Applied Chemistry*, 68(1): 149–192. doi: 10.1351/pac199668010149

Uzoh, C.F., Onukwuli, O.D. & Nwabanne, J.T. 2014. Characterization, kinetics and statistical screening analysis of gmelina seed oil extraction process. *Materials for Renewable and Sustainable Energy*, 3(4). doi: 10.1007/s40243-014-0038-1

Wong, M., Requejo-Jackman, C. & Woolf, A. 2010. What is unrefined, extra virgin avocado oil ?, *AOCS Inform Magazine*

Woolf, A., Wong, M., Eyres, L., McGhie, T., Lund, C., Olsson, S., Wang, Y., Bulley, C., Wang, M., Friel, E. & Requejo-Jackman, C. 2009. Avocado Oil, pp. 73–125. In: Morea, R.A., Kamal-Eldin, A. (eds.) *Gourmet and Health-Promoting Specialty Oils*, AOCS Press Urbana.

CHAPTER THREE

This chapter has been published in a conference proceeding as:

Mgoma, S.T., Gutu, L., Basitere, M. and Mshayisa, V, Effects of Different Extraction Methods and Process Conditions in the Yields of Avocado Oil. ACBES-19, November 2020.
Available online at: https://www.eares.org/siteadmin/upload/1876EAP1119138.pdf

3. Effects of Different Extraction Methods and Process Conditions in the Yields of Avocado Oil

3.1. Introduction

Avocado is a fruit with extremely high oil content, which is the main component of its dry weight. The fruit is highly nutritious, rich in antioxidants and vitamins. These are vitamins A, B, C and E, carotenoids, tocopherols and sterols that possess antioxidant properties. It was shown that these nutritional components are found in its oil also. The use of avocado oil for culinary purpose and for cosmeceuticals use as an essential component makes it a raw material with high economic importance. Because of the economic importance and potential of this oil; it becomes appropriate to further investigate the detailed changes that the oil undergoes when different extraction methods and conditions that are used for obtaining of the oil from fruit (Ortiz Moreno et al., 2003). This study is aimed at providing data of optimal process condition that can help design and optimize oil-producing processes to operate efficiently. Optimization is known as an act of obtaining the best possible results or the effort of achieving the optimal solution under the given set of circumstances (Kumar, 2015). The current avocado oil industry relies on the rejects fruit from the export and retail industry (Woolf et al., 2009); this is due to the costs of oil production with a high-grade avocado. It is therefore important to find the optimal solution for the avocado oil extraction process that will yield more oil with less effort and resources. Qin & Zhong (2016) however argues that a suitable extraction method depends not only on the yield of the oil but also on the chemical composition and quality of the obtained oil.

3.2. Objectives

The objectives of this part of the study were as follows:

- To evaluate the effect of the two types of pre-treatment methods (oven drying and microwave heating) on the oil yield with solid-liquid extraction.

- To extract avocado oil with n-hexane with different parameters; extraction times, different solid-liquid ratio, and different modes of solid-liquid extraction. Finally, the obtained oil yields were compared between these extraction methods.
- Determine favourable conditions at each of the different process parameters and extraction modes.
- Compare the amount of solvent used for extraction to the amount of avocado oil extracted.

3.3. Materials and methods

3.3.1. Fruit Preparation and Pretreatment

The avocado fruit were attained from a fruit and vegetable market wholesale. The avocado fruit kind chosen to be studied was the Hass variety. The fruits were all sourced from local South African farms located in the north eastern part of South Africa (Limpopo, Mpumalanga and Kwa-Zulu Natal). The Hass avocado is the most grown variety in South Africa; according to the South African Avocado Growers Association (SAAGA), approximately 70% of avocado trees in South Africa are Hass variety. This proves to be a variety that has a high potential to supply the oil production industry in South Africa. The fruits were purchased unripe from the wholesale; they were then left in the laboratory for 5 days at ambient temperature to ripen. The ripening of the fruit before extraction was based on a study by Mostert et al., (2007) who studied the yield of oil between ripe and unripe avocados. When the fruits were ripe they were then peeled and deseeded. The oil was extracted from the mesocarp (flesh) of the avocado, while the seed and peels are considered as waste. The mesocarp was meshed up with the blender and a fork to form a paste. The paste then needed to be pretreated to remove most of the moisture before extraction may take place. This increase the rate of extraction. According to Qin & Zhong (2016), the moisture content of the avocado pulp inhibits the extraction of the avocado oil; hence pretreatment is important before extraction takes place. The paste was oven dried using Labotec air draft oven for 24 hours at 70 ^{o}C. The dried avocado mesocarp paste was then stored in a cool dark place at a temperature below 20 ^{o}C.

3.3.2. Choice of Solvent

Therefore, since this study was looking at solvent extraction methods; it was important to first look into the suitable solvent to use for oil extraction. According to FAO/WHO Expert Committee (2016) only 17 organic solvents were allowed to be used for food and personal care products. These solvents are known as GRAS (Generally Regarded as Safe) solvents. According to Kumar (2015) the choice of solvent should be selected based on the availability, price, properties, like boiling point to allow easy recovery with evaporation, toxicity, solvent power and it should be non-hygroscopic. The solvent chosen for this study was n-hexane; this is due to its dielectric coefficient, which makes it a non-polar solvent and favourable to extract non-polar compounds, like oil. The other factor considered in choosing n-hexane was its low boiling point and low latent heat of vaporization and lastly, do by its high selectivity. Therefore, this solvent will dissolve the oil mostly due to its selectivity given by dielectric constant value.

The n-hexane used in this study for extraction was lab grade solvent.

3.3.3. Solvent Extraction

The n-hexane extractions were all performed at room temperature with no heat applied during extraction. The extractions took place in glass Erlenmeyer flasks with just the dried avocado paste and the hexane solvent. All the extractions were done with 50 g avocado sample; the extractions were done at different operating conditions. The extractions were all done in pairs as duplicates, sample A and sample B; to assure the credibility of the experiment and results.

The different conditions that were applied to the extractions were solid-liquid ratios of the avocado and the solvent. The ratios explored were 1:1, 1:2 and 1:3. The other process condition explored was the extraction time, times chosen were 2, 4 and 6 hours, respectively.

The extraction was also done using different methods with n-hexane; these were macerations and microwave-aided extraction. Maceration was done in three (3) stages with one (1) hour extractions. The avocado was placed in a flask and extraction took place for an hour, then the solution was filtered and the solid avocado was placed in another amount of fresh solvent for another hour. This was done in three stages.

The microwave-aided extraction was done by a pretreatment of the avocado in a microwave oven before extraction. The avocado paste was placed over the turning plate inside the oven; the microwave was set on maximum power output of 1000 W for ten (10) minutes. The microwave used was a Samsung model: MS103HCE. After being put out from the microwave, the probe was allowed to cool down. Thereafter was extracted with n-hexane in an Erlenmeyer flask.

In all the experiments performed, the samples were filtered with vacuum to recover the remaining solid after extraction (rafinate). The liquid phase solution of the oil in solvent was then separated using a rotary evaporator, where the n-hexane and the oil were recovered separately.

3.4. Results and discussion

3.4.1. Effect of extraction time

The yield of oil extracted from the avocado paste showed to have had an increase with the increase in time. According to Table 3.1, the results show a significant difference in the amount of oil extracted with difference in time that the avocado is allowed to stay in the solvent. The relationship is also found to be very close to linear according to the yield against time chart shown in Figure 3.1.

Table 3.1: Oil yield (g/kg avocado mesocarp on a dry weight basis) from the avocado fruit after extraction with n-hexane at different extraction times.

Time (hrs)	Yield (g/kg)
2	337 ± 8
4	432 ± 23
6	541 ± 31

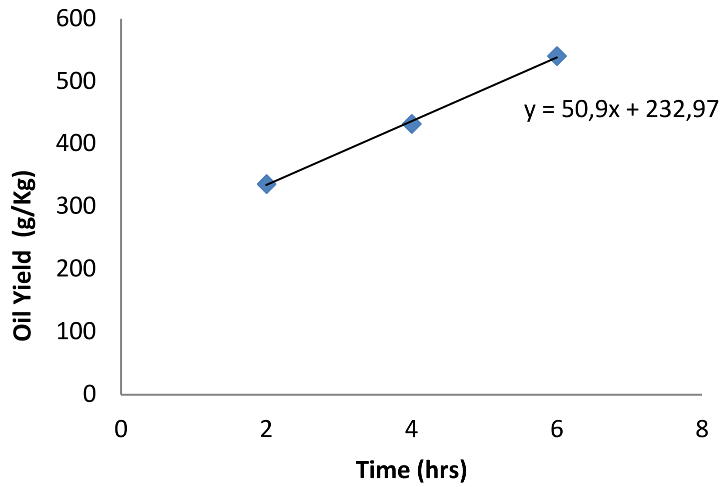

Fig 3.1: Oil Yield vs Extraction time

Although the results show an increase of oil extracted, the data point are found to be few to explain the point of exhaustion, which is the time which releases the maximum amount of oil from the avocado. According to Lloyd & van Wyk (2011) during diffusion; there is high concentration of the solute in the feed and it decreases with time as it diffuses through the solvent over time. It is therefore recommended that further experiments explore the extraction time further than 6 hours. The gradient of the best fit line was found to be 50.9; this then tell us that from these results the rate of oil extraction was approximately 50.9 grams per hour (g/hr).

3.4.2. Effect of solid-liquid ratio

The effect of the solid to liquid ratio of the avocado solid to the n-hexane solvent was explored. The extraction was done keeping constant the extraction time while changing the ratio. All the extractions were done at a constant time of four (4) hours.

Table 3.2: Oil yield (g/Kg of avocado mesocarp on a dry weight basis) from avocado fruit after extraction with hexane at different solid to liquid ratios.

Ratio	Yield (g/kg)
1:1	245 ± 27
1:2	432 ± 23
1:3	272 ± 16

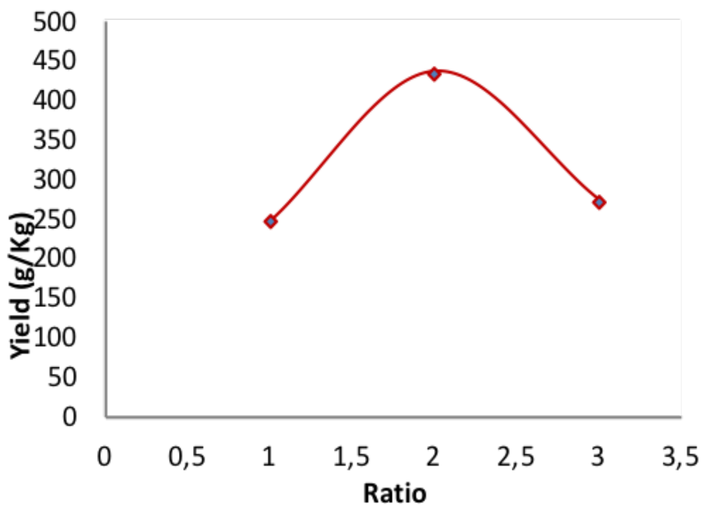

Fig 3.2: Oil Yield vs. Solid/Solvent Ratio

The results show that the solid to solvent ratio of the avocado and the solvents have an optimum ratio of 1:2. This ratio gave the highest oil yield compared to the ratios of 1:1 and 1:3. This proves that there is an optimum solid to liquid ratio in extraction. Therefore, more solvent does not necessarily result in a higher rate of extraction, neither does less solvent. According to Lloyd & van Wyk (2011) diffusion takes place predominantly on the interfaces between the solid material and the solvent known as diffusion layers. They argue that the diffusion layers also act as resistance to diffusion; therefore, even if the solvent is in excess, the rate of diffusion is determined by what takes place at the diffusion layers interfaces.

3.4.3. Oil extraction by macerations

Avocado oil was also extracted by the use of macerations; where a series of extractions are done. After an hour of extraction, the mixture was filtered and fresh solvent was added to the avocado. This was done with a solid to liquid ratio of 1:2, it was kept constant and the extraction time was also kept constant at every 1 hour.

Table 3.3: Oil mass (grams) of oil extracted after every hour of the macerations. The total mass is shown below with the yield (g/Kg of avocado mesocarp on weight basis).

Time (hr)	Mass of oil (g)
1	11.10 ± 0.16
2	3.43 ± 0.25
3	2.48 ± 0.60
Total	17.01 ± 0.15
Yield	340 ± 3 g/kg

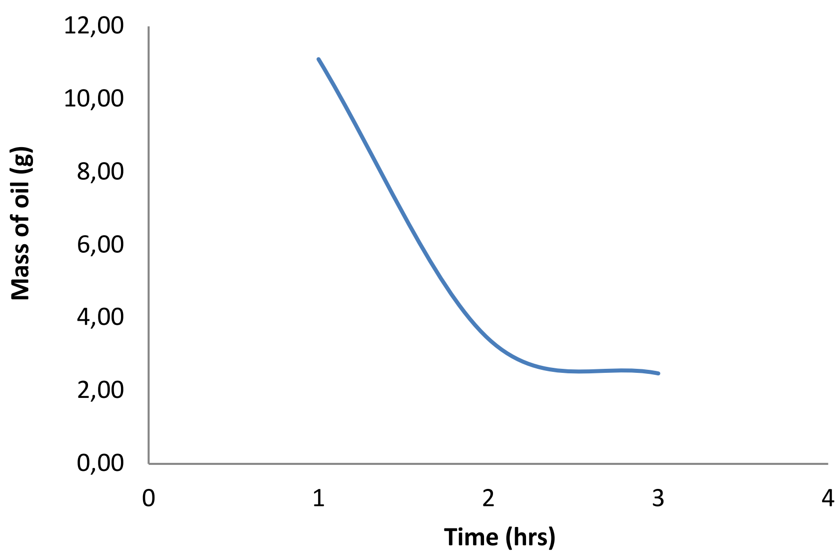

Fig 3.3: Mass of Oil Extracted Over Time

The effect of a different extraction mode with n-hexane shows a slight difference. According to Figure 3.3; using fresh solvent every hour helps observe the rate of extraction over time at every hour. This curve is in concordance with Fick's in diffusion law, that the rate of diffusion is driven by the concentration difference of the solute between feed and the solvent (Richardson et al., 2002). Figure 3.3 shows that more oil was extracted in the first hour of extraction or the first maceration. The rate and mass of extract decreases as the concentration of the solute decreases in the solid phase and increases in the bulk solution (Lloyd & van Wyk, 2011).

3.4.4. Oil yield vs amount of solvent used

The relationship and effect of the amount of solvent used to the oil yield after extraction was studied to help optimize the extraction process. The data was gathered from the different experiments done with the time kept constant while varying the amount of solvent used in that experiment.

Table 3.4: Relationship between the oil yield and the amount of solvent used for extraction

Solvent used (mL)	Yield (g/kg)	Method	Time (h)
76.34	245 ± 27	1:1 Ratio	4 hours
152.67	432 ± 20	1:2 Ratio	4 hours
229.01	272 ± 12	1:3 Ratio	4 hours
458.01	340 ± 3	1:2 ratio macerations	3 x 1-hour macerations

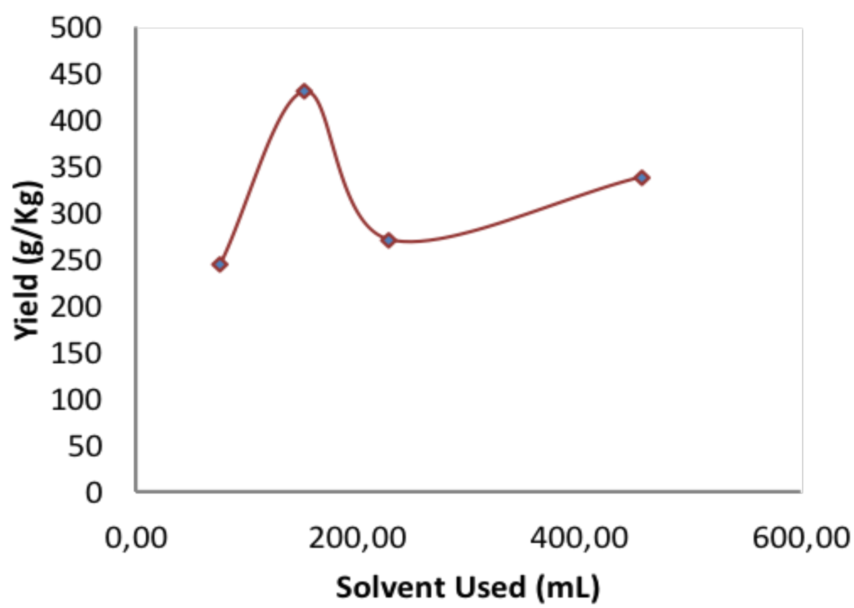

Fig 3.4: Amount of Solvent Used vs. Oil Yield

The data showed no trend or real relationship between the amount of solvent used and the oil yield. Therefore, the more solvent used in the extraction of avocado oil does not guarantee a higher yield of oil. Therefore, from an economic stance, it is wasteful to choose and operate an extraction process that uses any ratio above 1:2. Therefore, with the focus on the study to optimize the extraction process with n-hexane; it is very important to notice the optimum amount of solvent needed for a higher rate of extraction.

3.4.5. Microwave-aided (pretreatment) extraction

The microwave aided solvent extraction was done to evaluate the effect of microwave pretreatment compared to that of oven drying.

Table 3.5: Oil yield (g/kg avocado mesocarp on dry weight basis) after hexane extraction with aid of microwave pretreatment.

Pretreatment	Oil Yield (g/kg)	Solid/liquid ratio	Extraction Time
Microwave (10 min)	329 ± 4	1:2	2 hours
Oven Dried (24 hours)	337 ± 8	1:2	2 hours

The optimum conditions for the microwave pretreatment was taken from a study by Ortiz Moreno et al., (2003) who studied the effect of sample exposure time in the microwave to the yield of the avocado oil. Therefore the optimum exposure time and power conditions used in this study were used (Ortiz Moreno et al., 2003) . In this part of the study, it was aimed to compare the difference in oil yield between oven-dried samples and the microwave pretreated samples after extraction with n-hexane for 2 hours. The results show that on average, the oven dried samples yielded more oil than microwave pretreated samples. However; with the deviation allowances range, the yields are actually the same on average. The oven dried samples are only slightly higher; the difference statistically is not significant.

These results prove that the two pretreatment methods give the same yield of oil when extracted with n-hexane. However; although the oil yield may be similar, according to Ortiz Moreno et al., (2003) oil extracted with aid of microwave pretreatment gave a lower quality oil than that which was oven dried. The microwave-aided extracted oil had higher levels of volatiles than the oil extracted from oven-dried samples. Ortiz Moreno et al., (2003) also found oil extracted from microwave pretreated samples to have lower unsaturated fatty acid content compared to that of oven dried samples.

3.5. Conclusion

The results of this study provide data to aid the design of an efficient solvent extraction process for avocado oil. This process should also be suitable and practical for implementation for commercial production. Therefore, the optimum extraction method and condition is that which will be producing a high yield of oil with fewer resources and must be suitable to use in industry. The suitable extraction method depends not only on the yield of the oil but also on the chemical composition and quality of the oil produced. It is therefore also sensible that in order to receive more value in the oil produced from avocado. The oil must be of high quality in order to be used in food, pharmaceutical and cosmetic industry.

The results of the study found that the pre-treatment step was essential for avocado oil extraction; and the results showed that based on the yields between oven dried and microwave heating, microwave heating pre-treatment was favourable. This is because it requires less time and results in a much shorter pre-treatment process. It was found that it requires 24 hours to dry the avocado flesh in an oven but it requires only 10 minutes to heat up the avocado with the microwave at 1000 watts, causing the rupture of the oil cells and the avocado mesocarp is ready for extraction. The results also showed that the yield was proportional to the extraction time; therefore, from the study, the highest extraction time (6 hours) was found to be the favourable time for extraction. It was also then concluded that the optimum solid/liquid ratio for extraction was 1:2, which is also 1.53 mL of hexane per gram of dry avocado.

It can therefore also be said that from the high oil content of the Hass avocados in South Africa and the high yields found from extraction methods and conditions with n-hexane; the avocado oil industry in South Africa has great potential. These results also prove that avocados may also be considered a primary source of oil for the food and pharmaceutical industries because of its nutritional value and availability in the South Africa. The avocado availability in South Africa does not only depend on the commercial farmers; but it has potential for local farmers in the north eastern part of the country which is known to be a sub-tropical climate.

3.6. Recommendations

The experiments conducted evaluated the process conditions and extraction methods only and not necessarily the costs directly. However, from a general view, the processes that require the use of energy can be estimated and assumed to have a higher cost. Furthermore; the amount of solvent used in the extraction process can be assumed to be proportional to the cost of production. Therefore, from the results of the experiments, it was found that there is an optimum solid to liquid ratio which will help to control the amount of solvent used for extraction. It was also found that a significant yield of oil can be extracted without the aid of heat during extraction process. This reduces the use of energy which can be stored to use for pretreatment and solvent recovery.

3.7. References

Aktar, T. & Adal, E. 2019. Determining the Arrhenius Kinetics of Avocado Oil: Oxidative Stability under Rancimat Test Conditions. *Foods*, 8(7): 236.

Amarante, R.C.A., Oliveira, P.M., Schwantes, F.K. & Moro, A. 2014. Oil Extraction from Castor Cake Using Ethanol : Kinetics and Thermodynamics.

Amin, S.., S, H., GE, D. & SE, R. 2010. Kinetics and thermodynamics of oil extraction from Jatropha Curcas in Aqueous Acidic Hexane Solutions. *Journal of American Science*, 11(3): 247–253.

Berasategi, I., Barriuso, B., Ansorena, D. & Astiasarán, I. 2012. Stability of avocado oil during heating : Comparative study to olive oil. *Food Chemistry*, 132(1): 439–446. http://dx.doi.org/10.1016/j.foodchem.2011.11.018.

Bevan, J. & Science, E. 2000. The First and Second Laws of Thermodynamics The First Law of Thermodynamics. In *Chemical Thermodynamics: Principles and*

Applications.

Bill, M., Sivakumar, D., Thompson, A.K. & Korsten, L., 2014. Avocado fruit quality management during the postharvest supply chain. *Food Reviews International*, 30(3): 169–202.

Choi, E 2008. Notes: *Trans* Fat Regulation: A Legistlative Remedy for America's Heartache, *Southern California Interdisciplinary Law Journal:,* 17*,* 509–544.

Costagli, G., Betti, M., Laval, A., Market, S., Food, U., Oil, O. & Val, T. 2015. edible oil production versus traditional production co m m er ci a l u Avocado fruit and oil extraction se on on co m m er a. , XLVI(1999): 115–122.

Department of Agriculture, F. and F. 2017. *a Profile of the South African Dairy Market Value*.

Elliott, V. 1991. *Introductory Applied Thermodynamics*. Metric Publications.

FAO/WHO. 2018. *JOINT FAO/WHO EXPERT COMMITTEE ON FOOD ADDITIVES Eighty-sixth meeting Geneva, 12–21 June 2018*.

FAO/WHO Expert Committee. 2016. *COMPEDIUM OF FOOD ADDITIVE AND SPECIFICATION*.

Flores, M., Perez-Camino, M.D.C. & Jose, T. 2018. Preliminary Studies on Composition, Quality and Oxidative Stability of Commercial Avocado oil produced in Chile. , (July).

Fogler, H.S. 1999. *Elements of Chemical Reaction Engineering - 3rd Ed.pdf*. Third. New Delhi: Prentice-Hall Inc.

Hofman, P.J., Jobin-Décor, M. & Giles, J. 2000. Percentage of dry matter and oil content are not reliable indicators of fruit maturity or quality in late-harvested 'Hass' avocado. *HortScience*, 35(4): 694–695.

ILO. 2014. What is a solvent ? Where are solvents used ? Industries where solvents are most likely used What are the main health effects ? How can solvents enter your body and make you ill ? What precautions should you take ? Preventing exposure. , (5). http://www.ilo.org/wcmsp5/groups/public/---americas/---ro-lima/---sro-port_of_spain/documents/presentation/wcms_250196.pdf.

Jeon, Y.H., Son, Y.J., Kim, S.H., Yun, E.Y., Kang, H.J. & Hwang, I.K. 2016. Physicochemical properties and oxidative stabilities of mealworm (Tenebrio molitor) oils under different roasting conditions. *Food Science and Biotechnology*, 25(1): 105–110.

Kumar, D.S. 2015. *Herbal Bioactives and Food Fortification*.

Landahl, S., Meyer, M.D. & Terry, L.A. 2009. Spatial and temporal analysis of textural and biochemical changes of imported avocado cv. hass during fruit ripening. *Journal of Agricultural and Food Chemistry*, 57(15): 7039–7047.

Liauw, M.Y., Natan, F.A., Widiyanti, P., Ikasari, D., Indraswati, N. & Soetaredjo, F.E. 2008. EXTRACTION OF NEEM OIL (A zadirachta indica A . Juss) USING N-HEXANE AND ETHANOL : STUDIES OF OIL QUALITY , KINETIC AND THERMODYNAMIC. , 3(3): 49–54.

Lloyd, P. & van Wyk, J. 2011. Introduction to Extraction in Food Processing. : 1–24.

Mewa-ngongang, M., Plessis, H.W., Hutchinson, U.F. & Mekuto, L. 2017. Kinetic modelling and optimisation of antimicrobial compound production by Candida pyralidae KU736785 for control of Candida guilliermondii. *Food Science and Technology International*.

Mewa-ngongang, M., Plessis, H.W. & Ntwampe, S.K.O. 2019. Grape Pomace Extracts as Fermentation Medium for the Production of Potential. : 8–11.

Mills, I., Cvitas, T. & Homann, K. 1993. *Quantities, Units and Symbols in Physical Chemistry*. Second Edi. London: Blackwell Science Ltd.

Mostert, M.E., Botha, B.M., Plessis, L.M. Du & Duodu, K.G. 2007. Short Communication Effect of fruit ripeness and method of fruit drying on the extractability of avocado oil with hexane and supercritical carbon dioxide. , 2885(June): 2880–2885.

Myers, R., Montgomery, D. & Anderson-Cook, C. 2015. *Response Surface Methodology*. Third edit. New Jersey: Wiley.

Nelson, R.M. 2010. Quality challenges facing the South African avocado industry – An overview of the 2009 South African avocado season. : 7–12.

Ortiz Moreno, A., Dorantes, L., Galíndez, J. & Guzmán, R.I. 2003. Effect of different extraction methods on fatty acids, volatile compounds, and physical and chemical properties of avocado (Persea americana Mill.) oil. *Journal of Agricultural and Food Chemistry*, 51(8): 2216–2221.

Ott, B.J. 2000. Introduction 1.1. In *Chemical Thermodynamics: Principles and*

Applications. 1–36.

Ozdemir, F. & Topuz, A. 2004. Changes in dry matter, oil content and fatty acids composition of avocado during harvesting time and post-harvesting ripening period. *Food Chemistry*, 86(1): 79–83.

Qin, X. & Zhong, J. 2016. A Review of Extraction Techniques for Avocado Oil. *Journal of Oleo Science*, 65(11): 881–888. https://www.jstage.jst.go.jp/article/jos/65/11/65_ess16063/_article.

Reddy, M., Moodley, R. & Jonnalagadda, S.B. 2012. Fatty acid profile and elemental content of avocado (Persea americana Mill.) oil -effect of extraction methods. *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes*, 47(6): 529–537.

Richardson, J.., Harker, J.. & Backhurst, J.. 2002. *Coulson and Richardson's Chemical engineering*. Fifth. Oxford: Butterworth Heinemann.

Santos, S.B. Dos, Martins, M.A., Caneschi, A.L., Aguilar, P.R.M. & Coimbra, J.S.D.R. 2015. Kinetics and Thermodynamics of Oil Extraction from Jatropha curcas L. Using Ethanol as a Solvent. *International Journal of Chemical Engineering*, 2015.

Satriana, S., Supardan, M.D., Arpi, N., Aida, W. & Mustapha, W. 2019. Development of Methods Used in the Extraction of Avocado Oil. , 1800210: 1–12.

Seymour, G.B. & Tucker, G.A. 1993. Avocado. : 9–10.

Stolen, S. & Grande, T. 2004. *Chemical Thermodynamics of Materials Macroscopic and Microscopic Aspects*. John Wiley and Sons.

Sulaiman, S., Aziz, A.R.A. & Kheireddine, M. 2013. Optimization and modeling of extraction of solid coconut waste oil. *Journal of Food Engineering*, 114(2): 228–234. doi: 10.1016/j.jfoodeng.2012.08.025.

Topalla, H. & Gecgel, U. 2000. Kinetics and Thermodynamics of Oil Extraction from Sunflower Seeds in the Presence of Aqueous Acidic. , 24: 247–253.

Union, I., Pure, O.F. & Chemistry, A. 1996. COMMISSION ON CHEMICAL KINETICS * A GLOSSARY OF TERMS USED IN CHEMICAL KINETICS , INCLUDING REACTION DYNAMICS. , 68(1): 149–192.

Uzoh, C.F., Onukwuli, O.D. & Nwabanne, J.T. 2014. Characterization, kinetics and statistical screening analysis of gmelina seed oil extraction process. *Materials for*

Renewable and Sustainable Energy, 3(4).

Wong, M., Requejo-jackman, C. & Woolf, A. 2010. *What is unrefined , extra virgin avocado oil ?*

Woolf, A., Wong, M., Eyres, L., McGhie, T., Lund, C., Olsson, S., Wang, Y., Bulley, C., Wang, M., Friel, E. & Requejo-Jackman, C. 2009. Avocado Oil. *Gourmet and Health-Promoting Specialty Oils*: 73–125.

CHAPTER FOUR

Submitted for publication as
Shaun Thamsang Mgoma, Moses Basitere, Vusi Mshayisa. Kinetics and thermodynamics of oil extraction from South African Hass Avocados using hexane as a solvent. Journal of Food sciences, Manuscript number: JFD-2020-1208

4. Kinetics and Thermodynamics of Oil Extraction from South African Hass Avocados using Hexane as a Solvent

4.1. Introduction

Avocado oil is a known product around the world as it has grown with use in different industries. The oil is produced from the avocado fruit, which is a fruit with high oil content, found to have been the main component of its dry weight (Ozdemir & Topuz, 2004). The avocado fruit is mainly consumed as a fruit itself and because of this it was not considered to be grown as a primary source of oil. Therefore, avocado oil have been generally produced from the fruits rejected by the fresh fruit trade (Woolf et al., 2009). The avocado oil has been an important raw material in the cosmetic industry due to its high skin penetration properties and its high vitamin E content (Woolf et al., 2009). Therefore, with the increase in demand of the avocado oil, the production of the oil has been explored with different extraction processes such as traditional mechanical cold pressing, aqueous extraction which uses water and centrifugal force, solid-liquid extraction which makes use of organic solvents and the biological extraction which uses biological enzymes. According to Topalla & Gecgel (2000), solid-liquid extraction is the most common and efficient extraction process for producing vegetable and seed oils. The studies of process kinetics and thermodynamics have been done on extraction of oils from different oil sources (Aktar & Adal, 2019; Amin et al., 2010; Sulaiman et al., 2013; Dos Santos et al., 2015); this study aims to further add and contribute to this existing literature and also compare the kinetics of avocado oil extraction from this study to that of other extraction processes. Topallar & Geçgel (2000) studied the kinetics of extraction of sunflower seed oil and they found an increase in extraction with increase in temperature and they also found that the extraction process was irreversible and spontaneous. Sulaiman et al (2013) studied the kinetics and thermodynamics of oil extraction from waste coconut and found the process to be a first order, also endothermic, irreversible and spontaneous.

The aim of this study was to determine the process kinetics and the thermodynamic parameters of avocado oil extraction through a solid-liquid extraction process with n-hexane solvent. Fick's law and Van't Hoff's model were both selected to test their suitability in describing and explaining the experimental data on the kinetics and thermodynamic parameters of avocado oil extraction process at different temperatures. Fick's law was chosen to prove whether is suitable to explain the theory of diffusion of oil from the avocado solid to the hexane liquid with experimental data? Van't Hoff's model was chosen to prove whether is suitable to describe the relationship between changes in temperature with the change in equilibrium constant with the experimental data of avocado oil extraction? The results of this study were also compared to other research studies to evaluate the models used.

4.2. Objectives

The objectives of this study were as follows:

- To determine the kinetics of the avocado oil solid-liquid extraction process at temperatures between 40 °C, 50 °C, 60 °C and 70 °C.
- To determine the thermodynamics of the avocado oil extraction process and use the parameters to explain the process dynamics.
- Apply Fick's law to explain the avocado oil extraction by diffusion process.
- Apply the Van't Hoff's model to describe the relationship between how the change in temperature affect the reaction equilibrium.

4.3. Methodology / Materials and method

4.3.1. Raw materials

The raw material chosen for this study was the Hass avocado variety grown locally in South African farms. The avocados used in this study were sourced from the market wholesaler kept under controlled temperature to slow the ripening. The avocado fruits were then kept at ambient temperature in the laboratory for 5 days to have a natural ripening. The avocados sourced are of the same brand and grower. The ripened fruits were peeled and deseeded; the mesocarp was meshed up into a paste using a blender as shown in Figure 4.1 below. The paste was placed in pans and dried for 48 hours in an oven at 70 ^{o}C. The dry avocado paste was grounded and stored in a closed cupboard to avoid direct light.

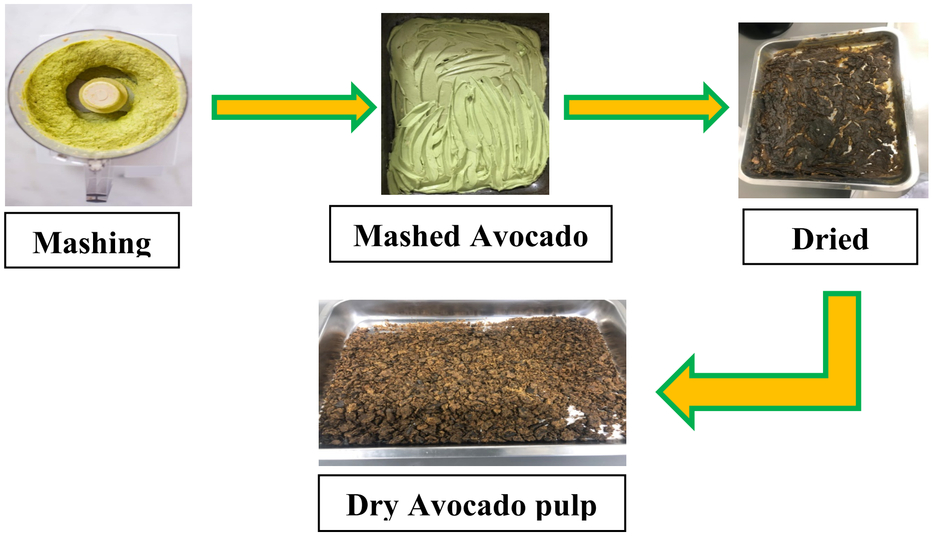

Figure 4.1: Avocado pulp pretreatment process

During the preliminary experiments, the average oil content of the avocados was determined through an exhaustive extraction using the Soxhlet extraction method as shown in Figure 4.2 below. This confirms what Kumar (2015), Satriana et al.(2019), Ozdemir & Topuz (2004) research claim that the Soxhlet extraction was found to be the exhaustive solvent extraction method to give the maximum extraction. According to Kumar (2015), the Soxhlet operation makes use of fresh solvent every time there is contact between solid and liquid since the solvent and the solid are not in constant contact, therefore, the solid and liquid never reach equilibrium. The average maximum amount of oil content found in the Hass avocados at maturity was found to be 67.07% of the fruit dry weight.

Figure 4.2: Soxhlet extractor battery

n-hexane was the organic solvent chosen to be used for extraction in this study. This choice was based on different reasons; the first reason was the eligibility of the solvent, which was based on resolution made by the joint committee of United Nations Food and Agricultural organisation and the World Health Organisation (FAO/WHO). The committee decided that only 17 organic solvents were allowed to be used for food and personal care products. These solvents are known as GRAS (Generally Recognised as Safe) solvents. The other reason will have to do with the chemical characteristics of the solvent. According to Kumar (2015) the choice of solvent should be selected based on the availability, price, properties like boiling point to allow easy recovery with evaporation, toxicity, solvent power and it should be non-hygroscopic.

4.3.2. Oil extraction

The avocado oil extraction was done based on the conditions of the preliminary experiments that were done with Soxhlet extractor prior as shown in Figure 4.2. The avocado oil was extracted with n-hexane at a constant solid to liquid ratio of 3.05 ml hexane/gram of dry avocado, which was found to have been a favourable ratio in the previous research. The three necked 500 ml round flasks were used for batch extraction. One neck was used for the condenser, the other for the thermometer and the third had a stopper which was opened for sampling every 10 minutes. The extractions were done at four different temperatures 40-70 in 10 ^{o}C ramp, and for three hours at each temperature. The runs were done in duplicate to compare and ensure the reliability of results. The concentration of the oil extracted was monitored and recorded over time. The oil concentration in the solution was measured by extracting 3 ml from the solution using a pipette into a glass beaker; the beaker was then placed in an oven to allow the solvent to evaporate. The beakers were then removed from the oven, allowed to cool down and then reweighed. The difference in weight over time was observed and recorded.

The mass of mesocarp used for extractions was 50 g samples with 152.67 mL of hexane as solvent for all experiments. In all the experiments, the solvent was first poured into the flask and heated up to the desired temperature. Then the dried avocado mesocarp would be added and extraction would commence. After three hours of extraction the solid and solution were separated using the Büchner funnel and filter paper with aid of a vacuum as shown in Figure 4.3 below. The liquid solution was also further separated by distilling the solvents using the Büchi rotary evaporator. The oil was collected in a glass beaker and put in an oven to remove any remaining solvent that was not recovered. The oil was then placed in a bottle and kept for the analysis.

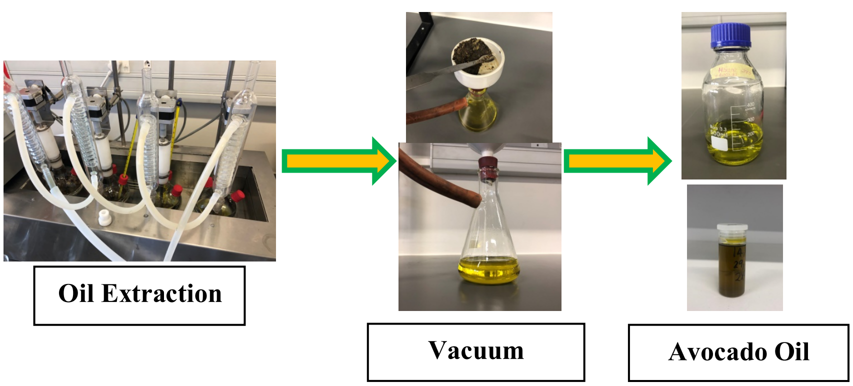

Figure 3.4: Oil extraction under controlled temperatures and separation of oil from solid and solvent

4.4. Results and Discussion

4.4.1. Yield of oil over time at different temperatures

From the preliminary experimental runs done of the oil extraction with n-hexane; the results guided the runs of these sets of experiments. Extraction was done only with South African avocados of the same ripeness as explained in the methodology. The concentration yield of the oil in the liquid phase was compared between the four different temperatures and the plot was generated. Table 4.1 and Figure 4.5 below represent the data from the experiments conducted at four different temperatures over 3 hours each.

Table 4.1: Oil concentration yield over time at different temperatures

Time (min)	Oil Concentration Yield (g.L^{-1})			
	40 °C	50 °C	60 °C	70 °C
0	0	0	0	0
10	75.1250	92.8250	96.3000	113.5500
20	78.0000	114.9500	117.6000	139.9000
30	95.0750	129.6500	132.5250	152.2500
40	106.5000	138.6750	142.1250	168.6500
50	117.1250	142.8500	152.5250	177.5250
60	125.8000	154.1750	159.5750	181.5250
90	143.6750	166.4500	171.7000	196.6500
120	152.2750	174.4500	180.0000	198.7500
150	163.3000	179.7500	188.5250	207.1250
180	169.2000	189.0250	192.6750	210.7250

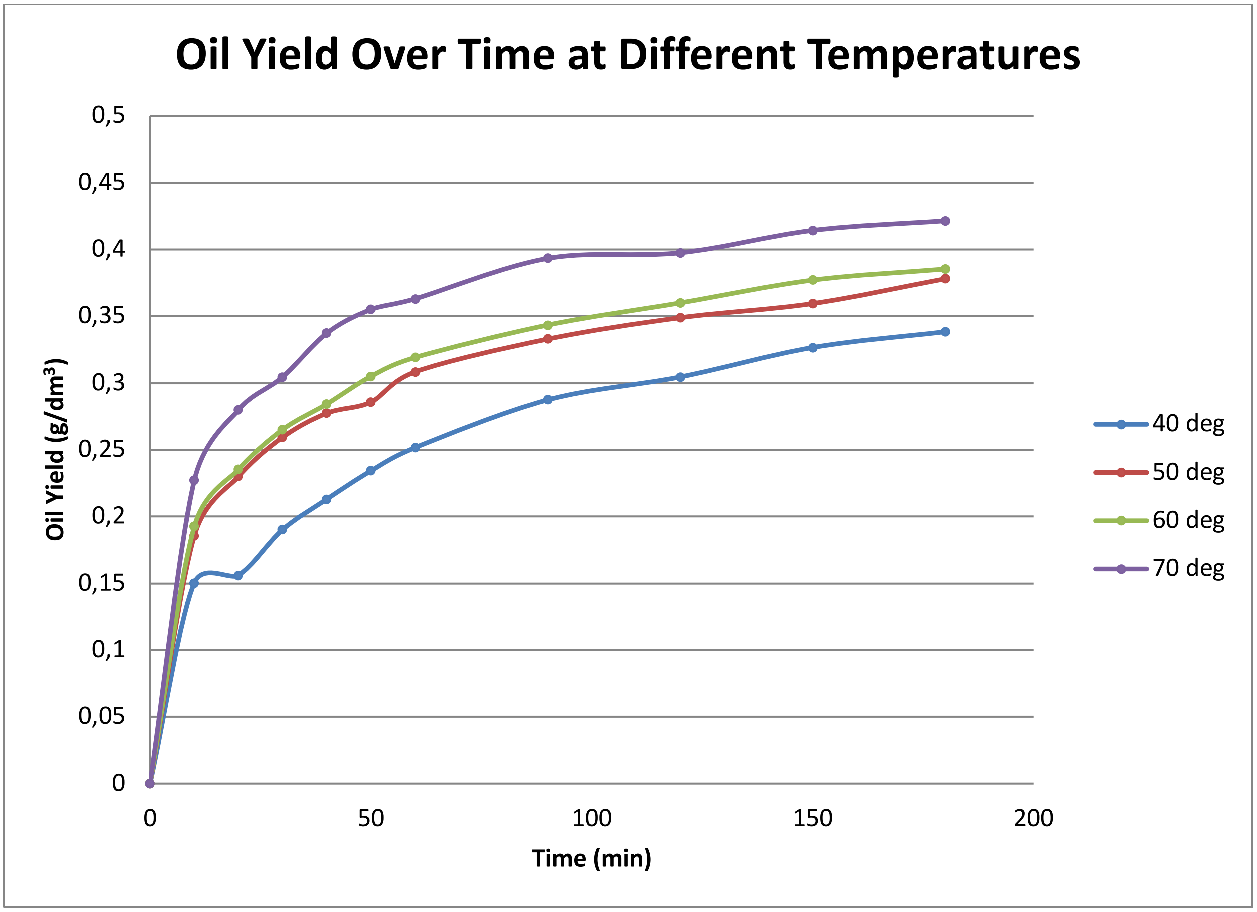

Figure 4.4: Oil Concentration yield over time at different temperatures

4.4.2. Effects of temperature on the oil yield

Figure 4.5 shows the effect of temperature in the extraction process of avocado oil. The results show that the increase in temperature enhances the yield of oil and the rate at which the oil is extracted. This means that the rise in temperature results in the rise in the rate of process, which we can conclude that the temperature is directly proportional to the extraction yield and rate of extraction. As seen in Table 4.1, the rise of temperature from 40 ^{o}C to 70 ^{o}C raised the final oil concentration yield by over 40 g/L, from 169.2 g/L to 210.73 g/L. Furthermore, the rate of extraction is increased by the increase in temperature, the oil extracted in the first 10 minutes of extraction increases from 75.13 g/L at 40 ^{o}C to 113.55 g/L at 70 ^{o}C, which is also the difference of almost 40 g/L.

The solubility of the material which is being extracted will increase with the increase in the temperature as it is being extracted (Richardson et al., 2002). Figure 4.5 also shows the effect of time during the extraction process. The extraction continues in favour of the forward process over time as the oil diffuses from the solid into the liquid phase (Richardson et al., 2002). However, it is also found that as time increases the rate of extraction decreases and the reaction tends to go to equilibrium state. This is elaborated by the shape of the curve, which moves from being steep to become flat. The trend of the plot shows that the concentration gradient decreases as the avocado solid tends to exhaustion over time. This confirms Fick's law in diffusion that the rate of diffusion is driven by the concentration difference of the solute between feed and the solvent (Richardson et al., 2002).

According to the mass transfer mechanism of solid-liquid extraction, the start of the extraction is dominated by washing, which extracts the solute from the exposed surface of the solid. The extraction then further proceeds by diffusion where the solute diffuses from the inside of the solid particles into the liquid phase. This step of diffusion is described and explained by Fick's law, which states that; if a concentration difference exist, the rate of transfer of a component is proportional to the product of the molecular diffusivity and the concentration gradient (Richardson et al., 2002).

4.4.3. Process kinetics

The oil extraction process is controlled by diffusion due by the concentration gradient of the oil in the liquid phase (Dos Santos et al., 2015) which is the driving force for extraction. Since this process is controlled by diffusion it can therefore then be related to Fick's law and as a result Fick's second law equation can be rearranged (equation 4.1) (Dos Santos et al., 2015). This results in the rate of concentration in an unsteady state process as follows:

$$\frac{dC}{dt} = kC^n \qquad (4.1)$$

The equation may also be rearranged into a form that includes the conversion and written as follows:

$$\frac{dC_A}{dt} = k\left[C_{A0}\left(1 - X_A\right)\right]^n \qquad (4.2)$$

Where C_{A0} is the oil concentration in the solid at time 0; and X_A is the oil fraction at time t, retained in the solid phase, k is the extraction rate constant and n is the process order.

However, because the batch extractor was used for this study with constant volume and the data shows that the process is irreversible, with single component. Therefore, an assumption that the process rate is a function of the concentration of only one compound can be made (Fogler, 1999). The process rate can then be determined by the following equation:

$$\frac{dC_A}{dt} = -C_{A0}\frac{dX_A}{dt} \qquad (4.3)$$

To determine the extraction rate constant from experimental data by making use of a differential method of analysis; both the reaction (extraction) rate constant and the reaction order can be calculated (Fogler, 1999). The equation can be linearized by taking a natural logarithm on both sides of the equation to be in the form of a straight line function:

$$\ln\frac{dC_A}{dt} = n\ln C_A + \ln k \qquad (4.4)$$

According to Fogler, (1999), the reaction rate constant can be determined graphically using the differential method. This method makes use of a linearized equation that when simplified be in the form of $Y = mx + C$. Therefore, from the data obtained from experiments it was possible to plot the graphs of the logarithm of the change in concentration over time [ln dC/dt] against logarithm of the concentration [ln C] at different temperatures. The slope of these plots gives us the reaction order and the intercept of the plot gives us the ability to determine the process rate constant. The results of the extraction rate constant obtained at different temperatures are shown in Table 4.2 below:

Table 4.2: Extraction rate constants at different temperatures

Temp (K)	Temp (°C)	k (min^{-1})
313	40	0.0015
323	50	0.0044
333	60	0.0103
343	70	0.1382

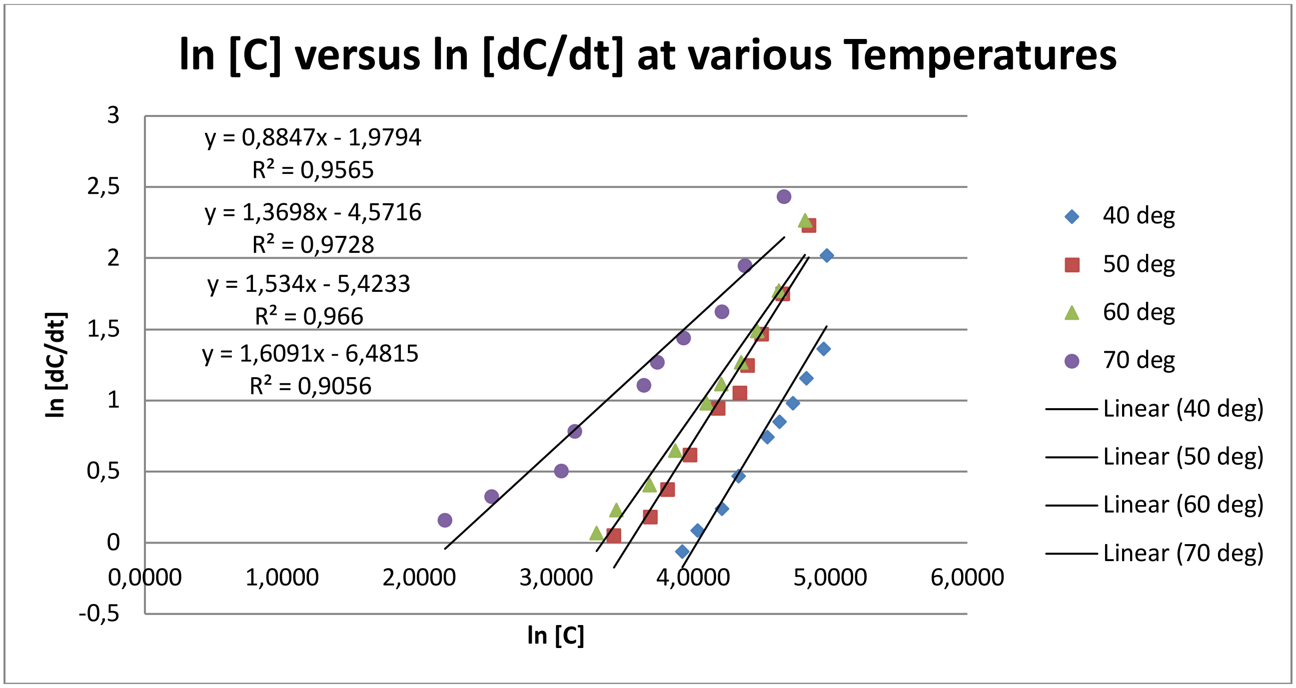

Figure 4.5: Plot of dC/dt against ln C to determine the extraction rate constant and process order

Figure 4.6 at different temperatures shows that the plots have different slopes and intercepts. When comparing these trends it was found that different temperatures have different process rates, which was evident that the increase in temperature led to an increase in extraction rate constant, k. Table 4.2 shows the results of the rate constants at different temperatures, and an increase rate constant was observed with the increase in temperature. According to Amarante et al., (2014) the increase in extraction temperature increases the solubility of the solvent and decreases the viscosity of both the solute and the solvent, which helps facilitate the mass transfer process.

The determination coefficient (R^2) of the all the functions shows the percentage of above 90%, which means that over 90% of the data points on all the functions fall in the regression lines. The results however show that there is a variation in process orders. We see that the extraction at 60 °C and at 70 °C have a first order; whereas the extraction at 40 °C and at 50 °C are still in the first order but they tend to the second order.

4.4.4. Thermodynamic models

The thermodynamic models used in this study were carefully chosen to be those that would be applicable to the conditions of which the experiments were performed. For the conditions of constant volume and constant temperature, the van't Hoff's model (equation 4.5) may be applied to help determine the Enthalpy and the Entropy of a system (Amarante et al., 2014). According to Atkins & de Paula, (2006), van't Hoff's model relates the equilibrium constant of a system to the changes in temperature. From the second law of thermodynamics; the Gibbs' free energy derived from the Gibbs and Helmholtz energies model at constant temperature can be calculated with the use of equation (4.6).

$$\ln K = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (4.5)$$

$$\Delta G = \Delta H - T\Delta S \qquad (4.6)$$

4.4.5. Determining the activation energy

The activation energy of the extraction process can be determined using the Arrhenius equation which is found to be:

$$k = Ae^{-E_a/RT} \qquad (4.7)$$

Where E_a is the activation energy, R is the universal gas constant, A is the Arrhenius constant and T is the temperature where k is the reaction rate constant. The activation energy and the Arrhenius constant can also be determined graphically by linearizing and simplifying the Arrhenius equation (Mills et al., 1993). The linearized Arrhenius equation is found to be in the following form:

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A \qquad (4.8)$$

The equation can be seen to also be having the form of a straight line $Y = mx + C$. Therefore, we can plot (1/T) against ln k. This also means that according to equation 4.8 above, the activation energy can be determined from the slope of the plot and the Arrhenius constant can be determined from the intercept.

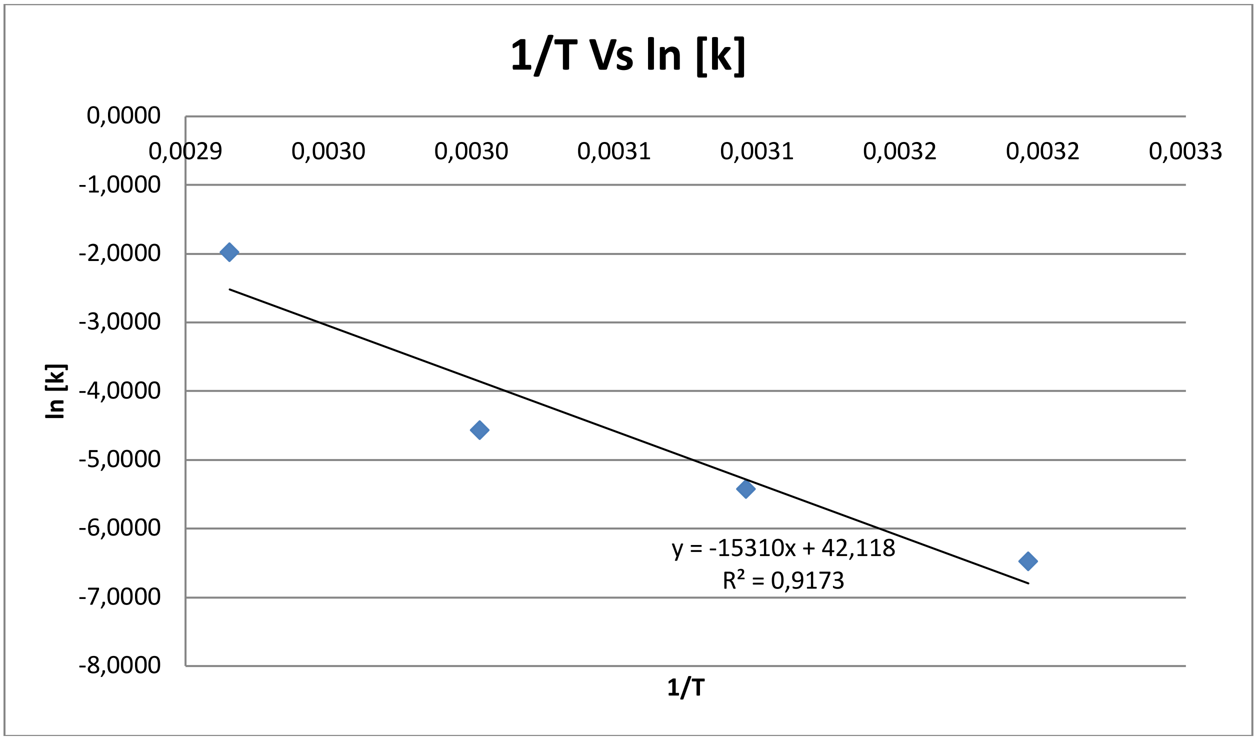

Figure 4.6: Plot of 1/T against ln k to determine the activation energy of the process

Figure 4.7 is a plot of 1/T against ln k; the regression of the plot allowed the activation energy and the Arrhenius constant be calculated. The activation energy was found to be, E_a = 127.2950 kJ/mol and the Arrhenius constant, A = 1.9571×10^{18} min^{-1} , which can transformed to A = 3.2618×10^{16} s^{-1}.

4.4.6. Calculating the activation thermodynamic parameters

These parameters and constants now allow the activation thermodynamic parameters to be determined. The activation thermodynamic parameters were calculated according to the transition state theory using the following equations:

$$A = \frac{RT}{Nh} e^{\Delta S^{\neq} / R} \quad (4.9)$$

$$\Delta H^{\neq} = E_a - RT \quad (4.10)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (4.11)$$

These parameters were calculated according to each absolute temperature and they are as shown in the Table 4.3 below:

Table 4.3: Activation Thermodynamic parameters

Temp (K)	**ΔS≠ (J/mol.K)**	**ΔH≠ (kJ/mol)**	**ΔG≠ (kJ/mol)**
313	70.8185	124.6926	-22.0415
323	70.55702	124.6094	-22.6653
333	70.30351	124.5263	-23.2865
343	70.0575	124.4431	-23.9053

The results in this case show that there is positive entropy and a negative Gibbs free energy. The indication of changes in enthalpy and entropy being positive means that the extraction process is endothermic (Grande, 2004). These activation thermodynamic results during extraction also indicate that there is a rise in the disorder of solid-oil-hexane system because the oil is transferred from a solid phase to a liquid phase (Amarante et al., 2014).

Furthermore, it was also found that the change in activation free energy or the Gibbs free energy calculated using equation 4.6 to be negative. The negative change in Gibbs free energy means that the reaction takes place spontaneously (Amarante et al., 2014). It can therefore then be confirmed that the extraction of oil from the avocado mesocarp with hexane as solvent takes place spontaneously in the temperature range 40-70 ^{o}C.

4.4.7. Calculating the standard thermodynamic parameters

The standard thermodynamic parameters were calculated using the van't Hoff's model with equation 4.5. These parameters were calculated using the equilibrium data of the extraction process.

Table 4.4: Equilibrium data at different temperatures

Temp (K)	1/T (K^{-1})	Y_T	ln Y_T	Y_U	k (s^{-1})
313	0.003195	51.6641	3.9448	15.4059	3.3535
323	0.003096	57.7176	4.0556	9.3524	6.1714
333	0.003003	58.8321	4.0747	8.2379	7.1416
343	0.002915	64.3435	4.1642	2.7265	23.5995

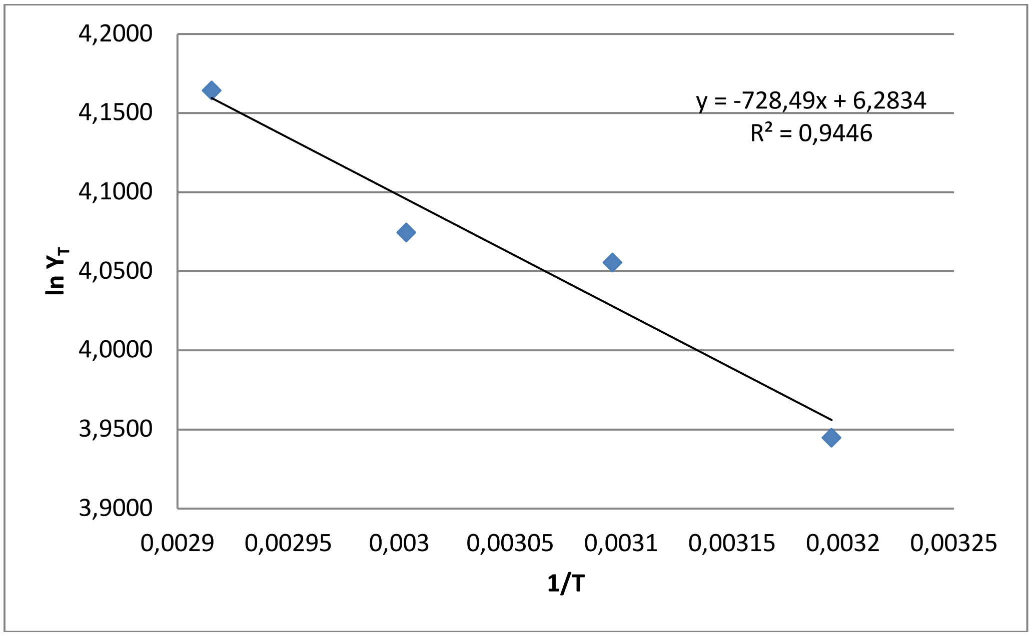

Figure 4.7: Plot of 1/T against the ln Y_T to determine the standard enthalpy of the system

Table 4.4 shows the summary of equilibrium values at different extraction temperatures. This equilibrium data was used to plot the inverse of absolute temperature (in kelvin, K) against the natural log of the oil yield at that temperature. The plot (Figure 4.8) gives a straight line and its slope represents the standard enthalpy of the system, ΔH_R (Amin et al., 2010). The standard change in enthalpy of the system was found to be ΔH = 0.0876 kJ/mol for an avocado oil extraction using *n*-hexane.

Table 4.5: Standard thermodynamic parameters at different temperatures

Temp (K)	K	ΔS **(J/mol.K)**	ΔG (kJ/mol)
313	3.3535	10.3406	-3.1490
323	6.1714	15.4030	-4.8876
333	7.1416	16.6089	-5.4432
343	23.5995	26.5395	-9.0154

Enthalpy ΔH = 0.0876 kJ/mol

According to the results in Table 4.5, which were determined from the van't Hoff's model and the equilibrium constant equation; it was found that the enthalpy was positive, which explains that the avocado oil extraction process is an endothermic reaction; which proves that there was energy applied to the reaction. The study also determined the standard entropy of the extraction process at different temperatures. The results of the entropy found were all positive for the temperatures that were studied. The positive standard entropy of the system confirms that the extraction reaction is an irreversible reaction (Amin et al., 2010; Ott, 2000). The study also found the results of the standard Gibbs free energy to be negative for all the temperatures studied. A negative Gibbs free energy indicates that the extraction reaction is a spontaneous reaction at that temperature (Grande, 2004).

According to the study by (Amarante et al., 2014) and the one done by (Sulaiman et al., 2013); the results of their studies agree with the results of this study with avocado mesocarp. Amarante et al., (2014) studied the extraction of castor oil from waste castor cake and Sulaiman et al., (2013) studied and optimized the extraction of coconut oil from waste coconut. These two studies explored the chemical thermodynamic parameters of the extraction processes and the results of their studies were compared with those of this study with avocado. The comparison of these studies was found to have agreed; which meant that the results of this study agreed with the thermodynamic laws. The extraction reactions were all endothermic because of the positive change in enthalpy, the reactions were all found to have been irreversible because of the positive change in entropy and the reactions were all found to have been spontaneous because of the negative change in Gibbs free energy.

The results of this study were compared with those of Amarante et al., (2014) and Sulaiman et al., (2013) because they were extractions from the fruit/vegetable mesocarp (flesh) and not that of seeds oil. The extractions were all done using organic solvents that are acceptable as GRAS solvents. The studies done by Liauw et al., (2008); Topallar & Geçgel, (2000) and Santos et al., 2015) shows that it was also found that the results of this study also agreed with some of their studies done with seed oils. However, according to Dos Santos et al., (2015), Topallar & Geçgel, (2000) and Liauw et al., (2008); it was found that with seed oils, the particle size and moisture content of the seeds have a significant influence in the Gibbs energy which overall have an influence in the spontaneity of the reaction.

4.5. Conclusion

The study has confirmed the kinetics of the extraction of oil from avocado flesh through a batch solid-liquid process using hexane as a solvent with the solid to liquid ratio of 3.05 ml/g. The process was also found to have been feasible at temperatures between 40-70^{o}C. The study confirmed that the rise in extraction temperature results in a rise in the rate of extraction and the yield of the oil extracted. The kinetic study of the process showed that the increase in temperature gave an increase in the extraction rate constant. The difference of 30^{o}C in temperatures from 40-70^{o}C was found to have had an increase in yield of over 40 g/L from 169.2 g/L to 210.73 g/L. This work also concluded that extraction of avocado oil took place by both washing and diffusion steps; where Fick's law proved to successfully describe the diffusion process of oil from the avocado flesh.

The conclusion was reached that the use of van't Hoff's model proved to be a suitable model and it successfully described the relationship between the changes in equilibrium constant with the change in temperature. The thermodynamic parameters proved that the experimental results agreed with the theory of second and third law of thermodynamics as was expected regarding the change in enthalpy, entropy and Gibbs free energy. At elevated temperatures of 40-70 ^{o}C the change in enthalpy was found to be positive which indicates that the process is endothermic, thus confirming that the energy was added to the system. The change in entropy was also found to have been positive which indicates that the extraction reaction is irreversible. The Gibbs free energy was calculated at all extraction temperatures and were all found to have been negative. This according to the second law of thermodynamics, which is described by the Gibbs and Helmholtz energies, indicates that the extraction reaction is spontaneous. It was also found from the results that the increase in temperature decreases the Gibbs energy; this means that the increase in extraction temperature increases the spontaneity of the reaction.

4.6. References

Aktar, T. & Adal, E. 2019. Determining the Arrhenius Kinetics of Avocado Oil: Oxidative Stability under Rancimat Test Conditions. *Foods*, 8(7): 236.

Amarante, R.C.A., Oliveira, P.M., Schwantes, F.K. & Moro, A. 2014. Oil Extraction from Castor Cake Using Ethanol : Kinetics and Thermodynamics.

Amin, S.., S, H., GE, D. & SE, R. 2010. Kinetics and thermodynamics of oil extraction from Jatropha Curcas in Aqueous Acidic Hexane Solutions. *Journal of American Science*, 11(3): 247–253.

Atkins, P. & de Paula, J. 2006. *Physical Chemistry*. 8th ed., Oxford University Press, Oxford

Bevan, J. & Science, E. 2000. The First and Second Laws of Thermodynamics The First Law of Thermodynamics. In *Chemical Thermodynamics: Principles and Applications*.

Fogler, H.S. 1999. *Elements of Chemical Reaction Engineering - 3rd Ed.pdf*. Third. New Delhi: Prentice-Hall Inc.

Kumar, D.S. 2015. *Herbal Bioactives and Food Fortification*.

Liauw, M.Y., Natan, F.A., Widiyanti, P., Ikasari, D., Indraswati, N. & Soetaredjo, F.E. 2008. EXTRACTION OF NEEM OIL (A zadirachta indica A . Juss) USING N-HEXANE AND ETHANOL : STUDIES OF OIL QUALITY , KINETIC AND THERMODYNAMIC. , 3(3): 49–54.

Mills, I., Cvitas, T. & Homann, K. 1993. *Quantities, Units and Symbols in Physical Chemistry*. Second Edi. London: Blackwell Science Ltd.

Nelson, R.M. 2010. Quality challenges facing the South African avocado industry – An overview of the 2009 South African avocado season. : 7–12.

Ozdemir, F. & Topuz, A. 2004. Changes in dry matter, oil content and fatty acids composition of avocado during harvesting time and post-harvesting ripening period. *Food Chemistry*, 86(1): 79–83.

Richardson, J.., Harker, J.. & Backhurst, J.. 2002. *Coulson and Richardson's Chemical engineering*. Fifth. Oxford: Butterworth Heinemann.

Santos, S.B. Dos, Martins, M.A., Caneschi, A.L., Aguilar, P.R.M. & Coimbra, J.S.D.R. 2015. Kinetics and Thermodynamics of Oil Extraction from Jatropha curcas L. Using Ethanol as a Solvent. *International Journal of Chemical Engineering*, 2015.

Satriana, S., Supardan, M.D., Arpi, N., Aida, W. & Mustapha, W. 2019. Development of Methods Used in the Extraction of Avocado Oil. , 1800210: 1–12.

Stolen, S. & Grande, T. 2004. *Chemical Thermodynamics of Materials Macroscopic and Microscopic Aspects*. John Wiley and Sons.

Sulaiman, S., Aziz, A.R.A. & Kheireddine, M. 2013. Optimization and modeling of extraction of solid coconut waste oil. *JOURNAL OF FOOD ENGINEERING*, 114(2): 228–234. http://dx.doi.org/10.1016/j.jfoodeng.2012.08.025.

Topalla, H. & Gecgel, U. 2000. Kinetics and Thermodynamics of Oil Extraction from Sunflower Seeds in the Presence of Aqueous Acidic. , 24: 247–253.

Woolf, A., Wong, M., Eyres, L., McGhie, T., Lund, C., Olsson, S., Wang, Y., Bulley, C., Wang, M., Friel, E. & Requejo-Jackman, C. 2009. Avocado Oil. *Gourmet and Health-Promoting Specialty Oils*: 73–125.

CHAPTER FIVE

Shaun Thamsang Mgoma, Moses Basitere, Vusi Mshayisa. Systemic process improvement study of avocado oil extraction with hexane. MDPI Journal. Manuscript number: sustainability-880075

SYSTEMIC PROCESS IMPROVEMENT STUDY OF AVOCADO OIL EXTRACTION WITH HEXANE

5.1. Introduction

Avocado (*Persea americana*) fruit originates from Central America, Southern Mexico and belongs to the *Lauraceae* family. It is rich in unsaturated fats, antioxidant and many other health-promoting compounds like plant sterols. The antioxidants rich in avocado helps eliminate free radicals from body cells and may also help prevent and reduce the damage caused by oxidation; plant sterols help prevent and reduce cholesterol and heart disease. These have led to an increase in consumption and growth in cultivars annually. An increase in consumption of avocado fruit and processing has been noticed over the years due to an increased demand of bioactive compounds like antioxidants for human health (Costagli et al., 2015). The avocado fruit is primarily grown for consumption as a fruit; however, it has since been referred to as “butter pear” due to its high oil content.

Avocado oil production has been growing gradually over the recent years. New Zealand is one of the leading producers of avocado oil since its production inception in 2000. Within the years 2008/2009, the country had produced more than 150 000 liters of avocado oil which was expected to increase in the following years (Wong et al., 2010) . According to Wong et al (2010), the leading world producers of avocado oil are New Zealand, Chile, South Africa and Kenya. The current avocado oil industry relies on the rejected avocado fruits from the retailers and export markets (Woolf et al., 2009). However, countries like South Africa and New Zealand have started using dedicated cultivars for avocado oil production, New Zealand is reported to use about 3% of the avocado grown for oil production (Wong et al., 2010).

Avocado oil is used predominantly in culinary and cosmeceuticals industry; the oil used for cosmeceuticals is extracted by solid-liquid extraction method using organic solvents and the oil used for culinary is mostly extracted through a cold press method (Costagli et al., 2015). These two processing methods differ in the yield and quality of oil produced. The avocado oil processing industry applies different methods and pretreatment techniques to improve the efficiency of the oil extraction process.

Pretreatment methods include; oven drying the avocado paste, preheating the paste with microwave and addition of enzymes prior to extraction. Extraction methods applied are cold pressing, solid-liquid solvent extraction and enzymatic extraction. Solid-liquid oil extractions are done using different solvents based on solubility of the solute; solvents frequently used are ethanol, hexane and petroleum ether. Amarante et al., (2014) extracted oil from castor cake using ethanol as solvent and Sulaiman et al., (2013) extracted oil from waste coconut cake using hexane and petroleum ether. There are different modes of solvent extraction applied like batch maceration and Soxhlet extraction. Enzymatic extraction can be done together with physical methods like centrifuging; Qin & Zhong, (2016) reported the use of exogenous enzymes like pectinases, alpha-amylase and celluloses enzymes to degrade the cell walls and expose the oil cells to release the oil. The material would then be ready for centrifuging to extract the oil. These methods are also explored and applied not only to improve the yield of oil but to also improve the quality of oil produced (Reddy et al., 2012). Avocado fruit are prone to spoilage due to its rapid ripening post harvesting. The other problem facing the industry currently is that the entire industry relies on spoilt and rejected avocados from the export and retail sectors. In an attempt to answer this question; can the avocado oil extraction process be efficient enough in order to incorporate more use of fresh avocados in the avocado oil industry? The two objectives of the study aim to address the aforementioned concerns of the avocado oil production.

The first objective considered the effects of the different process parameters in the yield of avocado oil extracted with hexane. A process optimization was conducted using response surface methodology to evaluate the significance of each process parameter on the yield of the oil. The second objective involved the inspection of the quality of oil produced from different methods and process parameters. The quality parameters investigated were the fatty acid profile and the stability of the oil. These objectives were motivated by the problems found both in the avocado fruit and avocado oil industries in South Africa.

5.2. Objectives

The objectives of this part of the study were as follows:

- To determine the optimum process conditions of the avocado oil solid-liquid extraction process.
- To use the response surface methodology to determine the three optimum conditions simultaneously.
- To evaluate the quality of the oil by looking at its fatty acids profile and stability.
- To determine whether the avocado oil industry in South Africa can be grown to have dedicated cultivars for avocado oil.

5.3. Materials and methods

5.3.1. Raw materials

The raw material chosen for this study was the Hass avocado variety grown locally in South African farms in Limpopo province. This variety of avocado was chosen based on its abundance in availability, it is said to be the most grown avocado variety in South Africa

The avocados used in this study were sourced from the market wholesaler kept under controlled temperature of 20 ºC - 24ºC in order to slow the ripening. The avocado fruits were then kept at ambient temperature in the laboratory for 5 days to have a natural ripening.

The ripened fruits were peeled and deseeded; the flesh was meshed up into a paste using a blender. The paste was placed in pans and dried for 48 hours in an oven at 70ºC. The dry avocado paste was grounded and stored in a closed cupboard to avoid direct light.

5.3.2. Oil extraction

Avocado oil was extracted from the flesh of the avocado fruits after the fruit was deseeded and peeled. Preliminary runs of oil extraction were done using different extraction methods. The maximum oil yield was found in the Soxhlet extraction method using hexane (Science World, Cape Town, South Africa) as the solvent. Solid-liquid extraction using organic solvent was an extraction technique chosen and hexane was the solvent selected for these extractions. For optimization of the process, two studies and experimental runs were done in order to make an evaluation. The first study and run of experiments were done to study the reaction kinetics and thermodynamic models of the extraction. The second study was a response surface methodology with a randomized central composite design of experiments.

5.3.3. Thermodynamic and kinetic study

Extraction of oil was done at four different temperatures from the oven dried flesh of the avocado using hexane as the solvent. All the extractions were done with a solid-liquid ratio of 3.05 ml of solvent per gram of avocado. The temperatures used were 40, 50, 60 and 70 °C respectively. Extractions took place in a three-necked round bottomed flasks used as batch reactors. One neck was used for the condenser, one neck was used for the thermometer and the third neck had a stopper and was used to sample the mixture every 10 minutes as the oil diffuses from the avocado solids into the solution. During sampling, 3 ml was collected into a beaker and placed in an oven to evaporate the solvent. The beaker was weighed before and after sampling to determine the weight of the oil at the time of sampling. A trend was observed as the oil is extracted over time at different temperatures.

5.3.4. Response surface methodology

The response surface methodology was used for optimization of the avocado oil extraction process using hexane as a solvent of extraction. The central composite design (CCD) was used for the design of the experiments in this study. This design was adopted from a study done by Mewa-Ngongang et al., (2019) by extracting grape pomace extracts from waste grape pomace. There were three independent variable factors to be evaluated on how they influence one dependent variable to be measured. The independent factors studied were time, temperature and solid-liquid ratio. These were all selected with specified ranges guided by the preliminary runs of experiments. The response evaluated was the oil yield concentration in the oil and solvent mixture. The experimental design gave 20 experiment runs to be conducted with randomized changes in the three independent factors within the given ranges. The experiments were also run as batch reactions in three necked round bottomed flasks with a condenser and a thermometer.

The oil yield response was measured and quantified by the amount of oil (mass) in the mixture (volume) of oil and solvent; which was expressed as grams per liter (g/L). The results of the experiment are shown in table 5.2 below as actual values. An analysis of variance was done, and the data was analysed using a quadratic model. The results of the analysis of variance (ANOVA) generated with the quadratic model was used to explain the effects of each individual and combined parameters on the yield of the oil. The model also generated 3D plots of response surfaces to graphically represent the interactive relationship between two parameters on the oil yield.

5.3.5. Determining the Peroxide value using auto titration

The avocado oil extracted from different methods and conditions was analysed for peroxide value by the method adapted from the American Oil Chemists Society (AOCS) Cd 8-53 method (International Union of Pure and Applied Chemistry Commission on Oils, 1992). The method used an auto-titrator with a platinum electrode (Metrohm, Switzerland). A sample of approximately 2.0 g of oil was weighed in a glass beaker and a 10 ml of acetic acid:1-decanol mixture at a ratio of (3:2) by volume (v/v) that was freshly prepared was also added. The solution was gently stirred for 30 seconds and 0.2 ml of freshly prepared solution of potassium iodide was added to the mixture and stirred. The mixture was placed in the dark for 1 minute and after 50 ml of deionized water was added. The solution was continuously stirred and placed under the auto-titrator, a titration with 0.01 M solution of sodium thiosulfate was performed. A control sample where the oil was replaced by the deionized water was also subjected to the same treatment. The volume of the sodium thiosulfate solution added during the titration was recorded for both the control sample and the oil samples. The Peroxide value was then calculated using the following formula:

$$PV = CV_{01} \times (EP_1 - CV_{02}) \times {}^{Titer}\!/_{COO} \qquad (5.1)$$

Where CV_{01} is 10 for the sodium thiosulfate concentration of 0.01 $mol.dm^{-3}$. EP_1 is the end point volume (ml) of the sodium thiosulfate required to titrate the sample, CV_{02} is the volume (ml) of sodium thiosulfate required for the titration of the control sample. Titre is the titre of the standardized sodium thiosulfate solution, and COO is the weight of the oil sample (g). The results were expressed in milli-equivalents of O_2 per kg sample.

5.3.6. Determining the Oxidative stability using the Rancimat

The Rancimat method was used to determine the oxidative stability of all the avocado oil. This stability was determined by estimating the oxidation induction time using the equipment Metrohm Rancimat model 743 (Metrohm, Switzerland). The oil samples of 5 ml were added to test tubes and heated to a temperature of 110^{o}C. After the oil reached its set temperature of 110^{o}C, purified air at 20 L/h was bubbled into the oil while the increasing water conductivities were continually measured. The volatile compounds result from the air which ran through the heated oil. At the end of the oxidation induction, the stability of the oil against the oxidation was indicated by the induction time in hours.

5.3.7. Fatty acids profiles

The fatty acid profiles of the oil were determined using the gas chromatography (GC) with a flame ionization detector (FID). The avocado oil was derivatized, firstly prepared into fatty acid methyl esters (FAME). The oil was first extracted with diethyl ether and petroleum ether, then it was methylated (AOAC, 2005). The methyl esters were put in tubes and kept in water bath to be ready for analysis. The equipment Agilent 6890 GC – 5973 MS/FID (Agilent Technologies, Santa Clara, CA., USA) system with a DB 23 – Capillary column (60 mm×250 µm, 0.25 µm) was used for this analysis. The equipment used a temperature program of 100– 240^{o}C with a 3 ^{o}C/min ramp gradient. The carrier gas was nitrogen at a flow rate of 24 ml/min and a split ratio of 25:1. The injection temperature of the analysis was 250^{o}C and the detection temperature was 325 ^{o}C. The fatty acids were detected and were identified by comparison of retention times with the reference standards from library.

5.4. Results and Discussion

During the preliminary experiments, the average oil content of the avocados was determined through an exhaustive extraction using the Soxhlet extraction method. According to Kumar (2015), the Soxhlet operation makes use of fresh solvent every time there is contact between solid and liquid since the solvent and the solid are not in constant contact. Therefore, the solid and liquid never reach equilibrium. The average maximum amount of oil content found in the Hass avocados at maturity was found to be 67.07% of the fruit dry weight.

5.4.1. Process conditions optimization using response surface methodology (RSM)

The study evaluated process parameters that have significant effects on the yield of the avocado oil produced. Furthermore, the study correlated these process parameters to the quality of oil. Central composite design (CCD) was used to evaluate the non-linear correlation of time, temperature and solid-liquid ratio on the avocado oil yield. Three independent variables/parameters were selected for the design of the study; Time (A), Temperature (B) and solid-liquid Ratio (C). The model equation was generated representing the relation of individual and combined input variables on the output; the model equation is shown in equation 5.2. The quadratic fitness model was found to be significant to explain the avocado oil extraction system. This was based on the analysis of variance parameters shown Table 5.1 below. The table indicate that the model was found to have $p<0.05$, which proved that the model was significant. The table also indicates that the linear effect of temperature (B) and solid-liquid ratio (C) were significant ($p<0.05$). The individual effect of time (A) and the combined linear effects (AB), (AC), (BC), and the quadratic effects (A^2), (B^2), and (C^2) were found to be insignificant ($p>0.05$). Removing the insignificant variables from the model equation resulted in equation 5.3 below. This was done due to the linear nature of the model according to the analysis.

$$Y = -82.44 + 0.9444A + 4.5665B - 0.6740C + 0.0164AB - 0.0072AC + 0.0649BC - 0.0028A^2 - 0.1072B^2 + 0.0109C^2 \quad (5.2)$$

$$Y = -82.44 + 4.5665B - 0.6740C \quad (5.3)$$

The coefficient of determination (R^2) from the model was 0.82; this indicates that 81.7% of the overall variability of the extraction process system can be explained by the model equation (Myers et al., 2015; Uzoh et al., 2014). The adjusted coefficient of determination (R^2_{adj}) was found to be 0.6523 which was in reasonable agreement with the coefficient of determination (R^2). However, the predicted coefficient of determination was 0.42 which was found not in agreement with both the R^2 and the adjusted R^2_{adj}. The adequate precision ratio of 85.48 was found for the model, the adequate precision of greater than 4 is desired (Uzoh et al., 2014). This high adequate precision of 85.48 demonstrated the adequate signal-to-noise ratio which made the model acceptable in terms of reliability and precision in describing the system (Mewa-Ngongang et al., 2019).

Table 5.1: The analysis of variance (ANOVA) table of the quadratic model for optimization of extraction of avocado oil with hexane using Time (A), Temperature (B) and Solid-liquid ratio (C) as independent variables

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	1.70E+08	9	18833.61	4.96	0.01	significant
A-Time	10466.60	1	10466.60	2.76	0.13	
B-Temp	20889.79	1	20889.79	5.50	0.04	
C-Ratio	91757.53	1	91757.53	24.17	0.00	
AB	5364.32	1	5364.32	1.41	0.26	
AC	3817.56	1	3817.56	1.01	0.34	
BC	11586.86	1	11586.86	3.05	0.11	
A^2	7657.26	1	7657.26	2.02	0.19	
B^2	15541.86	1	15541.86	4.09	0.07	
C^2	2153.26	1	2153.26	0.57	0.47	
Residual	37965.08	10	3796.51			
Lack of Fit	37965.08	5	7593.02			
Pure Error	0.00	5	0.00			
Cor Total	2.08E+08	19				
Std. Dev.	61.62			**R^2**	0.82	
Mean	185.12			**Adjusted R^2**	0.65	
C.V. %	33.28			**Predicted R^2**	0.42	
				Adeq Precision	85.48	

The analysis of variance table gives the data analysis and indicates that the model is significant ($p<0.05$). Although the variable of time was found to be insignificant, but this only meant that the effect of time does not have much effect on the yield of the oil extracted. This means that there will be oil extracted with this process regardless of the process time selected for extraction, provided there is sufficient hexane solvent available for extraction with reasonable temperature. However, the amount of oil extracted can only be maximized with an optimum solid-liquid ratio and a favourable temperature high enough to increase the rate of extraction. According to Topalla & Gecgel, (2000), the rate of extraction is proportional to temperature because the extraction rate constant is defined and explained by the Arrhenius equation, which is a correlation that relates the rate of reaction to the temperature. Hence, the model confirms what was found in kinetics literature by Amarante et al., (2014); Sulaiman et al., (2013) and Dos Santos et al., (2015).

The relationship between all the independent variables were assessed and graphically represented by 3D plots of the response surface (Figures 5.1-5.3). These plots represent the interactive effects between two independent variables on the response (Uzoh et al., 2014). The interaction between temperature and solid-liquid ratio show that there was an optimum condition realized when the ratio of 100% (1:1) and the maximum temperature of extraction is 68 ^{o}C depicted in figure 5.3. This was found to be mainly the washing stage of the mass transfer process as explained by Richardson et al. (2002). The amount of solvent is enough to initiate the extraction process by extracting the oil that is exposed to the surface of the solid and is exposed to the solvent, the process was also found to have taken place rapidly due to the high temperature which aids the high rate of extraction according to the extraction kinetics.

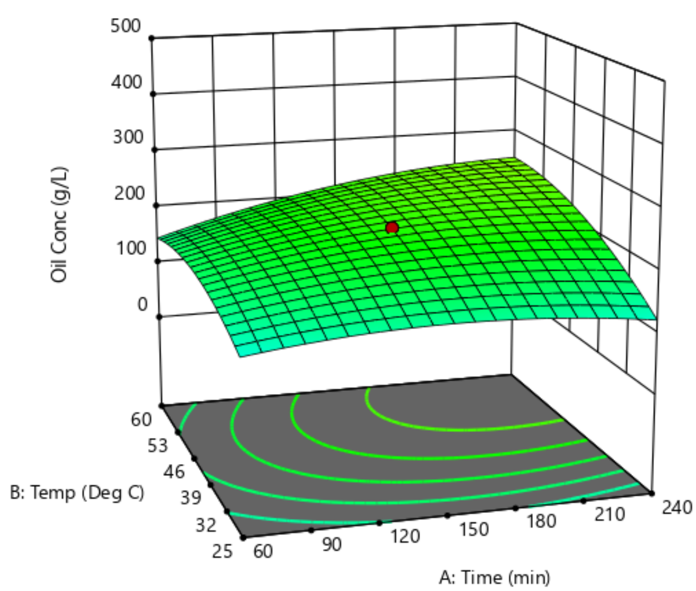

Figure 5.1: A 3D plot of Response surface interaction between Time and Temperature on the oil Yield

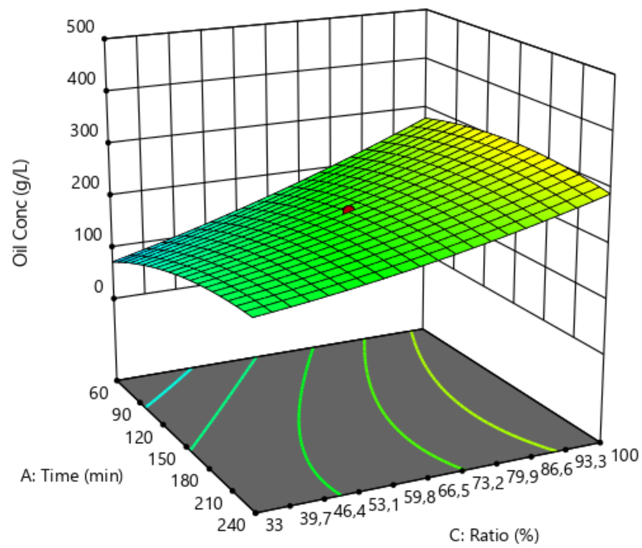

Figure 5.2: A 3D plot of Response surface interaction between Time and Solid/liquid ratio

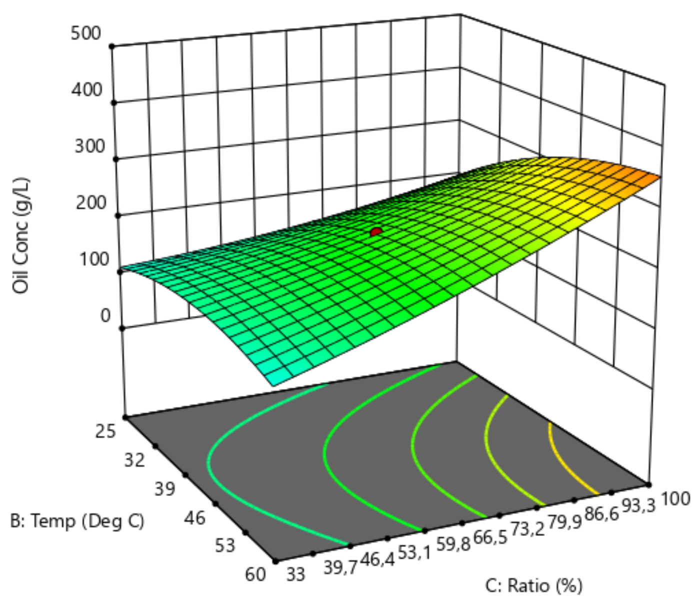

Figure 5.3: A 3D plot of Response surface interaction between Temperature and Solid-liquid ratio

Figure 5.4 is a plot of residuals which shows the normal probability against the studentized residuals. This plot represents a probability assessment of the model to see whether the model follows a linear trend. The points of the actual experimental data were found to be closely along the predicted straight line which confirms that the model is a good fit. This shows that the model follows the linear trend meaning the residuals follow a normal distribution. This confirms that the developed model is adequate and its normality assumptions are satisfactory (Mewa-Ngongang et al., 2017; Myers et al., 2015; Uzoh et al., 2014).

Table 5.2: Table represents the results of predicted and actual oil yield responses

Run Order	Predicted Value (g/L)	Actual Value (g/L)
1	156.02	105.40
2	196.30	247.74
3	214.94	216.42
4	56.28	20.00
5	214.94	216.42
6	362.14	347.92
7	196.13	255.67
8	103.18	0.00
9	214.94	216.42
10	111.89	142.83
11	214.94	216.42
12	214.94	216.42
13	165.78	142.83
14	214.94	216.42
15	1493	102.14
16	187.83	172.37
17	111.66	42.48
18	64.62	115.43
19	298.68	304.32
20	387.37	404.81

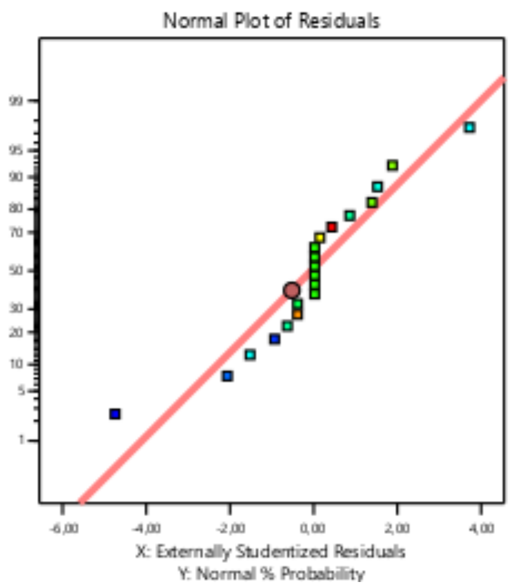

Figure 5.4: A Normality probability versus Studentized Residuals plot of Avocado oil extraction process

The model and the 3D plots were developed by the data of each run of the actual response and assessed against the predicted response. Table 5.2 shows the predicted oil yield responses and the actual experimental responses of the oil yield. The predicted responses are based on the quadratic model generated by the extraction process study and the actual responses are the results from the experiments.

5.4.2. Optimum conditions recommended by RSM

The model generated the optimized solutions according to the results from the experiments; the model generated 52 responses with different parameters and responses. The results found the maximum oil concentration yield of 404.81 g/L which was a response of an alpha plus parameter of solid-liquid ratio which was 1.24 mL/g. The significant parameters from this study were the temperature and the solid-liquid ratio according to the ANOVA in table 5.1 above. From this analysis the solutions proposed by the model were found to have identified the optimum temperature to be 60 ^{o}C and the solid-liquid ratio of 1.53 mL/g, which are found to be consistent in all the optimized solutions. The parameter that was found to be insignificant was time, which was varied in the 52 optimized solutions from the model. Some of the solutions were selected and are shown in table 5.3 below.

Table 5.3: Optimized solutions generated from the RSM model

Time (A) (min)	**Temperature (B) (°C)**	**Solid-liquid ratio (C) (mL/g)**	**Oil yield (g/L)**	**Desirability**
128.04	59.99	1.53	344.35	0.851
191.50	60	1.53	363.19	0.897
198.02	60	1.53	363.83	0.899
205.35	60	1.53	364.26	0.900

Table 5.3 shows that with the optimum temperature and solid-liquid ratio constant, the extraction time was varied to give a slight difference in oil concentration yield. Therefore, the effect of time on the oil concentration yield can be compared and

discussed. The solutions predict that variation by 77.31 minutes of extraction time increases the oil concentration yield by 19.91 g/L with an oil yield from 128.04 g/L to 205.35 g/L. The difference of 19.91 g/L against the energy used to maintain 60 ^{o}C for over an hour. The energy can be calculated according to the following equation:

$$Energy = Power \times time \qquad (5.4)$$

The equation shows that the energy is directly proportional to the power (watts) and time Therefore, the longer the extraction time the higher the energy used; the energy increases in multiple proportion. According to equation 5.4; the comparison of used may not be worth only the increase of 5% in the oil yield. Therefore, the optimum extraction conditions according to the predicted solution can be concluded to be the one with the lowest extraction time. Thus the optimum conditions are the extraction with n-hexane/solid ratio at 1.53 mL/g, at 60 ^{o}C and the extraction time of 128 minutes.

5.4.3. Characterization of the avocado oil

Furthermore, the avocado oils from solvent extraction with different process parameters were analysed to determine its stability and fatty acid profiles. The oils extracted were selected and analysed for fatty acid profile and oxidative stability to compare the quality of the oil produced through the solvent extraction and different process parameters.

Table 5.4: The Fatty Acid Profile of Avocado oil in total fat content (g/100g)

Sample	Total Fats (g/100g)	C12	C14 Myristic	C16 Palmitic	C16:1 Palmitoleic	C18 Stearic	C18:1c Oleic	C18:1t Elaidic	C18:2c Linoleic	C20 Arachidic
Avocado oil - Hex25	24.5119	-	0.1259	9.5317	0.4774	0.2860	7.2715	0.1260	6.3282	0.3651
Avocado oil - Hex40	22.0012	-	-	8.3303	0.3627	0.2615	7.5646	0.1180	5.0546	0.3096
Avocado oil - Hex50	27.8432	-	-	10.9572	0.5001	0.3572	8.9506	0.0627	6.6623	0.3531
Avocado oil - Hex60	21.8046	-	0.1423	9.1658	0.5419	0.2769	5.8009	0.0451	5.3718	0.4599
Avocado oil - Hex70	26.4664	-	-	10.4231	0.4801	0.3324	8.1218	0.0876	6.6155	0.4058
Avocado oil - Ethanol	20.4736	-	-	9.0019	0.7285	0.5587	3.7118	-	6.1137	0.3591
Avocado oil - Soxhlet	22.9040	-	-	10.2157	0.7849	0.4151	5.5742	0.0563	5.4987	0.3590

Table 5.5: The Fatty Acid Profiles of Avocado oil in % fat content

Sample	Total Fats %	C12	C14 Myristic	C16 Palmitic	C16:1 Palmitoleic	C18 Stearic	C18:1c Oleic	C18:1t Elaidic	C18:2c Linoleic	C20 Arachidic
Avocado oil - Hex25	100	-	0.51	38.89	1.95	1.17	29.67	0.51	25.82	1.49
Avocado oil - Hex40	100	-	-	37.86	1.65	1.19	34.38	0.54	22.97	1.41
Avocado oil - Hex50	100	-	-	39.35	1.80	1.28	32.15	0.23	23.93	1.27
Avocado oil - Hex60	100	-	0.65	42.04	2.49	1.27	26.60	0.21	24.64	2.11
Avocado oil - Hex70	100	-	-	39.38	1.81	1.26	30.69	0.33	25.00	1.53
Avocado oil - Ethanol	100	-	-	43.97	3.56	2.73	18.13	0.00	29.86	1.75
Avocado oil - Soxhlet	100	-	-	44.60	3.43	1.81	24.34	0.25	24.01	1.57
Average	**100**	**-**	**0.58**	**40.87**	**2.38**	**1.53**	**27.99**	**0.29**	**25.17**	**1.59**

Table 5.6: Summary of the Total percentage of fatty acids by type

	Saturated Fatty Acids	Monounsaturated Fatty Acids	Polyunsaturated Fatty Acids
% Content	44.57	30.67	25.17
% Total	44.57	55.84 Total unsaturated fats	

5.4.4. Fatty acid profile

The fatty acid profiles of the oils are influenced by the fruit variety, geographic area, harvesting practice and methods of extraction (Reddy et al., 2012). The fatty acid composition of the avocado oil is shown in Table 5.6, the predominant fatty acids found from the avocado oil in this study (in decreasing order) palmitic acid (37.86 - 44.60%) which is the saturated fatty acid; oleic acid (18.13 – 34.38%) which is monounsaturated fatty acid and linoleic acid (22.97 – 29.86%) which is a polyunsaturated fatty acid.

The results were found to have been contrary to the data of previous research done on avocado oil by Ortiz Moreno et al.,(2003) and Qin & Zhong (2016) where oleic acid has the highest content. In this study, palmitic acid which is a saturated, was the predominant fatty acid as opposed to the expected to be oleic acid, which is the monounsaturated fat to be dominant according to previous studies done by Reddy et al., (2012), Ortiz Moreno et al.,(2003) and Qin & Zhong, (2016). It was found that from the average of all the saturated fats in the oil a total of 44.57% were present and total of unsaturated fats were 55.84%, which g a ratio of 1.25:1 of unsaturated fats: saturated fats. This still confirms that the avocado oil is an essential oil as it maintains the high content of essential components of the oil like oleic and linoleic fatty acids.

The fatty acid profile also shows presence of elaidic which is a *trans* fatty acid; trans fats are undesirable as they are known to contribute to the many cases of heart disease (Choi, 2008) . According to Choi (2008), Food and Drug Administration (FDA) in America have restricted the amount of *trans* fatty acids in the oil/food to be <0.5 g/100g. The results of this study confirm that the average of the oils extracted still lies within the guidelines of the FDA and are acceptable to be used as edible oil. However, the oil extracted at 25 ^{o}C and 40 ^{o}C were found to be non-compliant to this standard. This means that the oils may not be used for any food products or drugs. Ortiz Moreno et al. (2003) studied the effect of microwave power on the *trans* fatty acid and found that the increase in energy of the microwave for pretreatment increases the *trans* fatty acid content of the avocado oil. This may be further explored in future studies to optimize the microwave-aided extraction technique for oil that will be compliant with the food and pharmaceutical standards.

Reddy et al. (2012) studied the fatty acid profile of the avocado oil from Hass and Fuerte varieties of South African cultivars. The study found that the Hass variety had a lower content of monounsaturated fatty acids than that of the fuerte variety. It was also observed that the study done by Reddy et al. (2012) with avocados from South Africa, the Oleic fatty acid content was lower than that of other studies done with avocado fruits from other countries with the same variety. Oleic fatty acid content differed with different countries. Ortiz Moreno et al. (2003) found a content of 60 g/100 g with avocados from Mexico; Ozdemir & Topuz (2004) found a content of 53% and (47%-59%) with the avocados from Turkey. Flores (2018) also studied the fatty acids difference in the avocado oil from Chile and the oil they extracted from avocados from Spain of Hass variety. The study showed that the Oleic acid of the oil from Chile was 67.7% and that of avocados from Spain was 65.4%. Reddy et al. (2012) found an Oleic acid content of 41-49% from South African Hass variety.

5.4.5. Lipid oxidation determination

Lipid oxidation was studied by analysis of the avocado oil extracted through different process parameters. The analytic parameters that were evaluated were peroxide value and oxidative stability. The results of these analyses are presented in table 5.7 and table 8 below and these results are further discussed in the subsequent sections.

Table 5.7: Results of the Peroxide Values of Avocado oil

Sample	Peroxide value (mEq/kg)
Avocado oil - Hex25	6.76
Avocado oil - Hex40	13.32
Avocado oil - Hex50	8.89
Avocado oil - Hex60	13.36
Avocado oil - Hex70	10.59
Avocado oil - Soxhlet	7.28

Table 5.8: Results of the Oxidation Induction time of Avocado oil

Sample	Oxidation induction time (h)
Avocado oil - Hex25	0.43
Avocado oil - Hex40	4.58
Avocado oil - Hex50	3.13
Avocado oil - Hex60	5.34
Avocado oil - Hex70	8.59
Avocado oil - Soxhlet	1.98

5.4.6. Peroxide value

The peroxide value analysis is used to measure the oxidative deterioration of the oil. Herein determined by measuring the amount of iodine formed from the iodide reaction with the hydroperoxides found in the oil. Hydroperoxides are formed through autoxidation susceptible to highly unsaturated fats and oils. Table 5.7 above shows the results for the peroxide values of the avocado oil extracted at different temperatures. This parameter together with the oxidative induction time gives an indication of the stability of the oil (Jeon et al., 2016). According to Woolf et al. (2009), higher peroxide value reduces the shelf-life of the oil and thus this can be correlated with the oxidative stability of the oil.

The obtained results in this study showed that no trend was found between the peroxide value and the extraction temperature of avocado oil. The peroxide value was low at temperatures of 25 °C and 50 °C and high at temperatures of 40 °C and 60 °C. The values fluctuate, with no clear trend between extraction temperature and peroxide value.

5.4.7. Oxidative stability

The review of Qin & Zhong, (2016) on avocado oil extraction methods explains that antioxidants and pigments help with keeping the oil stable, albeit some pigments like chlorophyll are sensitive to light and thus induce photo-oxidation. The study further explained experiments conducted at increased temperatures with hexane found that chlorophyll favoured lower temperatures and other unsaponifiable matter are favoured by the higher temperatures. Hence, the oil extracted at lower temperatures in this study was found to have a lower stability. The loss in stability was due to the photo-oxidation induced by the high content of chlorophylls. Furthermore, it can be argued and concluded that the higher stability found from oil extracted at high temperatures was due to the high content of antioxidants found in the unsaponifiables after extraction.

5.5. Conclusion

Avocado oil extraction process efficiency can be improved in both extraction yield and quality of oil produced. The response surface methodology study found the optimum process extraction parameters that will result in a high yield of oil to be at a temperature of 60 °C with 1.53 mL hexane /g avocado for an extraction time of 128 minutes. These parameters were predicted by the RSM model to yield an oil concentration of 344.35 g/L. The study found that a high extraction temperature and lower solid-liquid ratio also favored a higher oil yield. The high solid-liquid ratio was found to lead to equilibrium, whereas the lower ratio favors the forward process more. The quality of oil with respect to stability was found to have increased with increased extraction temperature. Oil with higher stability resulted when the extraction temperature increase. From the fatty acid profile study, it was also found that the oil extracted at higher temperatures had lower *trans* fatty acids content, than the oil extracted at lower temperatures.

Having considered all these observations and findings, from the study it was concluded that the avocado oil industry can be grown to a bigger scale in South Africa since the efficiency of its processing can be improved by simply changing the process parameters. The efficiency of the process will therefore make the industry economically viable by reducing production costs substantially, and thereby the industry do not entirely rely on spoilt or reject avocados. Henceforth there can be avocado farms dedicated for oil processing only with its cultivars grown specifically for production of avocado oil.

It was then recommended that the future study be done to confirm the conclusions made regarding the stability of the oil. Further investigation need to elucidate the exact causes of lipid oxidation in avocado oil at different temperatures and extraction methods. There is still a chasm for exploring more extraction methods and pretreatment methods.

5.6. References

Aktar, T. & Adal, E. 2019. Determining the Arrhenius Kinetics of Avocado Oil: Oxidative Stability under Rancimat Test Conditions. *Foods*, 8(7): 236.

Amarante, R.C.A., Oliveira, P.M., Schwantes, F.K. & Moro, A. 2014. Oil Extraction from Castor Cake Using Ethanol : Kinetics and Thermodynamics.

Amin, S.., S, H., GE, D. & SE, R. 2010. Kinetics and thermodynamics of oil extraction from Jatropha Curcas in Aqueous Acidic Hexane Solutions. *Journal of American Science*, 11(3): 247–253.

Berasategi, I., Barriuso, B., Ansorena, D. & Astiasarán, I. 2012. Stability of avocado oil during heating : Comparative study to olive oil. *Food Chemistry*, 132(1): 439–446. http://dx.doi.org/10.1016/j.foodchem.2011.11.018.

Bevan, J. & Science, E. 2000. The First and Second Laws of Thermodynamics The First Law of Thermodynamics. In *Chemical Thermodynamics: Principles and Applications*.

Bill, M., Sivakumar, D., Thompson, A.K., Korsten, L., Bill, M., Sivakumar, D., Thompson, A.K. & Korsten, L. 2014. Avocado Fruit Quality Management during the Postharvest Supply Chain Avocado Fruit Quality Management during the Postharvest Supply Chain. *Food Reviews International*, 30(3): 169–202. http://dx.doi.org/10.1080/87559129.2014.907304.

Candidate, J.D. & Angeles, L. 2006. NOTES TRANS FAT REGULATION : A LEGISLATIVE REMEDY FOR AMERICA ' S HEARTACHE. : 509–544.

Costagli, G., Betti, M., Laval, A., Market, S., Food, U., Oil, O. & Val, T. 2015. edible oil production versus traditional production co m m er ci a l u Avocado fruit and oil extraction se on on co m m er a. , XLVI(1999): 115–122.

Department of Agriculture, F. and F. 2017. *a Profile of the South African Dairy Market Value*.

Elliott, V. 1991. *Introductory Applied Thermodynamics*. Metric Publications.

FAO/WHO. 2018. *JOINT FAO/WHO EXPERT COMMITTEE ON FOOD ADDITIVES Eighty-sixth meeting Geneva, 12–21 June 2018*.

FAO/WHO Expert Committee. 2016. *COMPEDIUM OF FOOD ADDITIVE AND*

SPECIFICATION.

Flores, M., Perez-Camino, M.D.C. & Jose, T. 2018. Preliminary Studies on Composition, Quality and Oxidative Stability of Commercial Avocado oil produced in Chile. , (July).

Fogler, H.S. 1999. *Elements of Chemical Reaction Engineering - 3rd Ed.pdf*. Third. New Delhi: Prentice-Hall Inc.

Hofman, P.J., Jobin-Décor, M. & Giles, J. 2000. Percentage of dry matter and oil content are not reliable indicators of fruit maturity or quality in late-harvested 'Hass' avocado. *HortScience*, 35(4): 694–695.

ILO. 2014. What is a solvent ? Where are solvents used ? Industries where solvents are most likely used What are the main health effects ? How can solvents enter your body and make you ill ? What precautions should you take ? Preventing exposure. , (5). http://www.ilo.org/wcmsp5/groups/public/---americas/---ro-lima/---sro-port_of_spain/documents/presentation/wcms_250196.pdf.

Jeon, Y.H., Son, Y.J., Kim, S.H., Yun, E.Y., Kang, H.J. & Hwang, I.K. 2016. Physicochemical properties and oxidative stabilities of mealworm (Tenebrio molitor) oils under different roasting conditions. *Food Science and Biotechnology*, 25(1): 105–110.

Kumar, D.S. 2015. *Herbal Bioactives and Food Fortification*.

Landahl, S., Meyer, M.D. & Terry, L.A. 2009. Spatial and temporal analysis of textural and biochemical changes of imported avocado cv. hass during fruit ripening. *Journal of Agricultural and Food Chemistry*, 57(15): 7039–7047.

Liauw, M.Y., Natan, F.A., Widiyanti, P., Ikasari, D., Indraswati, N. & Soetaredjo, F.E. 2008. EXTRACTION OF NEEM OIL (A zadirachta indica A . Juss) USING N-HEXANE AND ETHANOL : STUDIES OF OIL QUALITY , KINETIC AND THERMODYNAMIC. , 3(3): 49–54.

Lloyd, P. & van Wyk, J. 2011. Introduction to Extraction in Food Processing. : 1–24.

Mewa-ngongang, M., Plessis, H.W., Hutchinson, U.F. & Mekuto, L. 2017. Kinetic modelling and optimisation of antimicrobial compound production by Candida pyralidae KU736785 for control of Candida guilliermondii. *Food Science and Technology International*.

Mewa-ngongang, M., Plessis, H.W. & Ntwampe, S.K.O. 2019. Grape Pomace Extracts as Fermentation Medium for the Production of Potential. : 8–11.

Mills, I., Cvitas, T. & Homann, K. 1993. *Quantities, Units and Symbols in Physical Chemistry*. Second Edi. London: Blackwell Science Ltd.

Mostert, M.E., Botha, B.M., Plessis, L.M. Du & Duodu, K.G. 2007. Short Communication Effect of fruit ripeness and method of fruit drying on the extractability of avocado oil with hexane and supercritical carbon dioxide. , 2885(June): 2880–2885.

Myers, R., Montgomery, D. & Anderson-Cook, C. 2015. *Response Surface Methodology*. Third edit. New Jersey: Wiley.

Nelson, R.M. 2010. Quality challenges facing the South African avocado industry – An overview of the 2009 South African avocado season. : 7–12.

Ortiz Moreno, A., Dorantes, L., Galíndez, J. & Guzmán, R.I. 2003. Effect of different extraction methods on fatty acids, volatile compounds, and physical and chemical properties of avocado (Persea americana Mill.) oil. *Journal of Agricultural and Food Chemistry*, 51(8): 2216–2221.

Ott, B.J. 2000. Introduction 1.1. In *Chemical Thermodynamics: Principles and Applications*. 1–36.

Ozdemir, F. & Topuz, A. 2004. Changes in dry matter, oil content and fatty acids composition of avocado during harvesting time and post-harvesting ripening period. *Food Chemistry*, 86(1): 79–83.

Qin, X. & Zhong, J. 2016. A Review of Extraction Techniques for Avocado Oil. *Journal of Oleo Science*, 65(11): 881–888. https://www.jstage.jst.go.jp/article/jos/65/11/65_ess16063/_article.

Reddy, M., Moodley, R. & Jonnalagadda, S.B. 2012. Fatty acid profile and elemental content of avocado (Persea americana Mill.) oil -effect of extraction methods. *Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes*, 47(6): 529–537.

Richardson, J.., Harker, J.. & Backhurst, J.. 2002. *Coulson and Richardson's Chemical engineering*. Fifth. Oxford: Butterworth Heinemann.

Santos, S.B. Dos, Martins, M.A., Caneschi, A.L., Aguilar, P.R.M. & Coimbra, J.S.D.R. 2015. Kinetics and Thermodynamics of Oil Extraction from Jatropha curcas L.

Using Ethanol as a Solvent. *International Journal of Chemical Engineering*, 2015.

Satriana, S., Supardan, M.D., Arpi, N., Aida, W. & Mustapha, W. 2019. Development of Methods Used in the Extraction of Avocado Oil. , 1800210: 1–12.

Seymour, G.B. & Tucker, G.A. 1993. Avocado. : 9–10.

Stolen, S. & Grande, T. 2004. *Chemical Thermodynamics of Materials Macroscopic and Microscopic Aspects*. John Wiley and Sons.

Sulaiman, S., Aziz, A.R.A. & Kheireddine, M. 2013. Optimization and modeling of extraction of solid coconut waste oil. *JOURNAL OF FOOD ENGINEERING*, 114(2): 228–234. http://dx.doi.org/10.1016/j.jfoodeng.2012.08.025.

Topalla, H. & Gecgel, U. 2000. Kinetics and Thermodynamics of Oil Extraction from Sunflower Seeds in the Presence of Aqueous Acidic. , 24: 247–253.

Union, I., Pure, O.F. & Chemistry, A. 1996. COMMISSION ON CHEMICAL KINETICS * A GLOSSARY OF TERMS USED IN CHEMICAL KINETICS , INCLUDING REACTION DYNAMICS. , 68(1): 149–192.

Uzoh, C.F., Onukwuli, O.D. & Nwabanne, J.T. 2014. Characterization, kinetics and statistical screening analysis of gmelina seed oil extraction process. *Materials for Renewable and Sustainable Energy*, 3(4).

Wong, M., Requejo-jackman, C. & Woolf, A. 2010. *What is unrefined , extra virgin avocado oil ?*

Woolf, A., Wong, M., Eyres, L., McGhie, T., Lund, C., Olsson, S., Wang, Y., Bulley, C., Wang, M., Friel, E. & Requejo-Jackman, C. 2009. Avocado Oil. *Gourmet and Health-Promoting Specialty Oils*: 73–125.

CHAPTER SIX

SUMMARY AND CONCLUSION

6.1. SUMMARY AND CONCLUSION

In this study the extraction processes of avocado oil from South African Hass avocado fruit were investigated. The main objective was to investigate the effects of all extraction methods and process conditions on the yield and quality of the oil and then further optimize the extraction process. Three different experimental runs were conducted with different objectives in order to reach an overall objective of the study. The first research chapter (chapter 3) focused on exploring different oil extraction methods and how they affect the yield of the oil. The second research chapter (chapter 4) focused on investigating the kinetics and thermodynamics of the avocado oil extraction process. Finally, the third research chapter (chapter 5) focused on optimization of the oil extraction process using Response Surface Methodology (RSM), furthermore, the study investigated the effect of different extraction methods on the quality of the oil.

Avocado oil production is a growing application in the Food processing and Cosmeceuticals industries. The increase in healthy lifestyle has also resulted in an increase in demand of both, the avocado fruit and its oil respectively. The growth in demand and production has prompted a need for an efficient and improved process that produces high quality oil. The avocado oil industry is currently dependent on the reject avocado fruits from export and retails. This is due to the economic trade-off between selling avocado fruit as it is and the fruit processing, to obtaining oil. The avocado oil industry is therefore very small and growing really slow due to the production costs, and the avocado oil yields found during processing. The predominantly used extraction method for obtaining culinary avocado oil is cold pressing, which results in very low oil yields. The industry is also small because it does not have dedicated cultivars for producing avocado oil. Therefore, the industry has a deficiency in advanced extraction technology which will produce higher yields at lower costs to allow the industry to grow. Therefore, this study aimed at improving the avocado oil extraction technology.

The study therefore explored different extraction methods with different process conditions with the scope to determine the optimal extraction method and conditions for a high oil yield from avocados. This was done by extracting oil from Hass avocados from strictly South African cultivars using different methods and applying different process conditions. The extraction methods that were explored are solid-liquid extraction with hexane solvent and microwave-aided solvent extraction; and solvent extraction with microwave pretreatment The process conditions that were explored are different solid/liquid ratio; different extraction/residence times and continuous extraction with fresh solvent. The efficiency of all these methods and conditions were comparison of their oil yields. The results of this study clearly demonstrate that the extraction process favored high temperature for extraction as it provided a higher yield and the solid/liquid ratio between 1:2-1:1, but not higher. The higher ratio tends to lead the process to equilibrium, which has a low extraction rate. The higher temperature was also established to produce oil of high stability, which meant it had a low oxidative deterioration and consequently higher shelf-life. The high temperatures also found to lead to lower trans fatty acid contents, which are undesired and detrimental for consumption. The fatty acid profiles of oil at higher temperatures were found to be acceptable with high unsaturated fatty acid content. The overall aim of the study was to therefore improve the efficiency of the process by increasing the yield of oil without compromising its quality. The optimum extraction parameters with *n*-hexane solvent were found to be with 1.53 mL/g solvent at a temperature of 60 °C for 128 minutes. These were found according to the RSM with central composite design.

The enthalpy, entropy and Gibbs free energy were the thermodynamic parameters investigated. The extraction was performed at four different temperatures 40-70 °C in 10 °C ramp, respectively. The kinetic model found that the process kinetic order was one, and the increase in temperature increased the oil yield from 169.20 g/L at 40 °C to 210.73 g/L at 70 °C after 3 hours of extraction. The value of the calculated activation energy was E_a = 127.30 kJ/mol, the thermodynamic parameters (from the transition state theory) at 70 °C were $\Delta S^{\neq}$ = 70.06 J/mol.K, $\Delta H^{\neq}$ = 124.44 kJ/mol, $\Delta G^{\neq}$ = -23.91 kJ/mol, respectively The standard thermodynamic parameters of the process at 70 °C were ΔH = 0.09 kJ/mol, ΔS = 70.06 J/mol.K and ΔG = -7.19 kJ/mol. These indicated that the extraction of avocado oil is an irreversible endothermic process. Furthermore, it was proven that the process is spontaneous.

6.1.1. Process engineering significance

The significance of this study was to demonstrate the advantage of the solid-liquid extraction method as an efficient process for the obtaining method of avocado oil. This study proves that the solid-liquid extraction produces a higher yield of oil, furthermore the quality and properties of the oil could be adjusted to the desired specification by changing the solvent, pretreatment method or process conditions during extraction. This extraction method allows an advantage for the economies of scale in industrial production and opportunities for cost efficient process by recovery of the organic solvent by distillation to be re-used in the process. It may also be found as cost efficient by shortage of processing time based on the opportunity cost of production.

6.1.2. Future studies and significance of the study

This study proved that the solid-liquid extraction method is an efficient process for avocado oil extraction. It has proven the average oil yield of Hass avocado with different process conditions; it has also studied the process kinetics and thermodynamics of the extraction. This data may be taken and could be useful in further simulation studies of the avocado oil solid-liquid extraction process with process simulation software. The results from simulations could be then compared with the laboratory experimental data from this study. The data of this study can also be used to further study of the process in a pilot plant, setting the optimal conditions reported in this research obtained through the optimization study with RSM. This can also open opportunities for further investigation of pretreatments of the avocado flesh before extraction. The other opportunity found to further investigate is the effect of all the process conditions and extraction methods on essential bioactive compounds found in the avocado oil.

- The significance of this research is that the proven efficient extraction process of avocado oil enables a significant growth in the industry making it an economically important industry. This becomes economically important because South Africa is one of the leading avocado producers in the world, it can therefore consider avocado as a valuable commodity and take advantage of the opportunity to grow its oil production industry.

- The avocado oil production industry may force to grow the avocado production in the country without incurring any losses in quality for export or retail markets. The growth in avocado production will also help create business opportunities and decrease unemployment especially women in rural areas of the country to be economically involved and empowered.
- All these show the significance of this study socially and economically, which therefore confirm the importance to further explore it.