DRYING KINETICS AND THE EFFECTS OF DRYING METHODS ON QUALITY (CBD, TERPENES AND COLOR) OF HEMP (*Cannabis sativa* L.) BUDS

By

Sai Kiran Reddy Challa

Submitted in partial fulfilment of the requirements

for the degree of Master of Science

at

Dalhousie University

Halifax, Nova Scotia

March 2020

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Abstract

The hemp industry currently relies on traditional drying methods to preserve and extract the cannabidiol (CBD), but they do not allow a high-quality product. Therefore, effects of two drying technologies, convective drying (isothermal and non-isothermal), and freeze drying on the drying time and product quality (CBD, terpenes, color) were evaluated. An increase of the drying temperatures significantly decreased the terpenes content (above 40 ºC) but, it did not effect the CBD content. The total CBD content was the highest (2.78%) under non-isothermal drying condition (40 °C changed to 70 ºC at 25% moisture content) and was the lowest (1.28%) under freeze-drying. The proposed drying regime reduced the time by 90% compared to control (32 °C) and the CBD increased compared to the fresh material. This is by far the first report to show the behavior of CBD and terpenes as influenced by various drying temperatures and technologies in hemp buds.

List of Abbreviations and Symbols Used

a_w	Water activity
CBCA	Cannabichromenic acid
CBD	Cannabidiol
CBDA	Cannabidiolic acid
CBGA	Cannabigerolic acid
CRD	Completely randomized design
d.b.	Dry basis (gram H_2O/gram dry solids)
D_{eff}	Effective moisture diffusion coefficient (m^2/s)
DOX	Deoxyxylulose pathway
E_a	Activation energy (kJ/mol)
EHD	Electrohydrodynamic drying
EMC	Equilibrium moisture content
ΔE	Total color difference
FD	Freeze drying
FDA	Food and Drug Administration
GAB	Guggenheim-Anderson-de Boer model
GLC	Gas-liquid Chromatography
GOT	Geranylpyrophosphate:olivetolate transferase
GPP	Geranylpyrophosphate
HPLC	High Performance-Liquid Chromatography
k	Drying rate constant

K	Kelvin
MC	Moisture content
M_R	Moisture ratio
OA	Olivetolic acid
PPO	Polyphenol oxidase
PUFAs	Polyunsaturated fatty acids
R	Universal gas constant (J/mol/K)
$\bar{R}^2$	Adjusted coefficient of determination
RH	Relative humidity
RMSE	Root mean square error
THC	Δ9-tetrahydrocannabinol
w.b.	Wet basis (%)
X	Moisture content (% or g/g)

Acknowledgements

This work was supported by Mitacs through the Mitacs Accelerate program (grant IT 16241). I would like to thank the Truro Cannabis Co. for the financial support and for providing the opportunity to do this research.

I would like to express my deep gratitude to Dr. Alex Martynenko my research supervisor for accepting and encouraging me to pursue this master's program and for offering his support and guidance throughout my journey in this university. I feel immense privileged to work with him. His contributions are sincerely appreciated and gratefully acknowledged.

I would like to specially thank Dr. Nrusimha-Nath Misra for his patient guidance, encouragement and useful critics of this project. His knowledge, support and willingness to help made this project to complete successfully on time.

I would like to thank Dr. Rajasekaran Lada for helping me with the term papers, which greatly helped in building my thesis. His useful critics, guidance and immense support towards the project is indeed appreciated. Also, I would like to thank Dr. Peter Havard, for his contribution, support and useful critics to this project.

To all relatives, friends and others who, in one way or another, shared their support, thank you. This thesis is dedicated to all.

Chapter 1. Introduction

1.1. State of Hemp Industry- Products, Uses and Applications

Industrial hemp/ hemp (*Cannabis sativa* L.) of the family "Cannabaceae" is an annual, short day, flowering herb with staminate (male) and pistillate (female) flowers occurring on separate plants (dioecious condition) (Figure 1. Structure of hemp plant. (A). Female plant; (B). Female inflorescence; (C) Male inflorescenceFigure 1). The earliest evidence of using hemp (4000 B.C.) was reported to be in China, where the plant was grown for the fibers and later used for medical purposes (Touw, 1981).

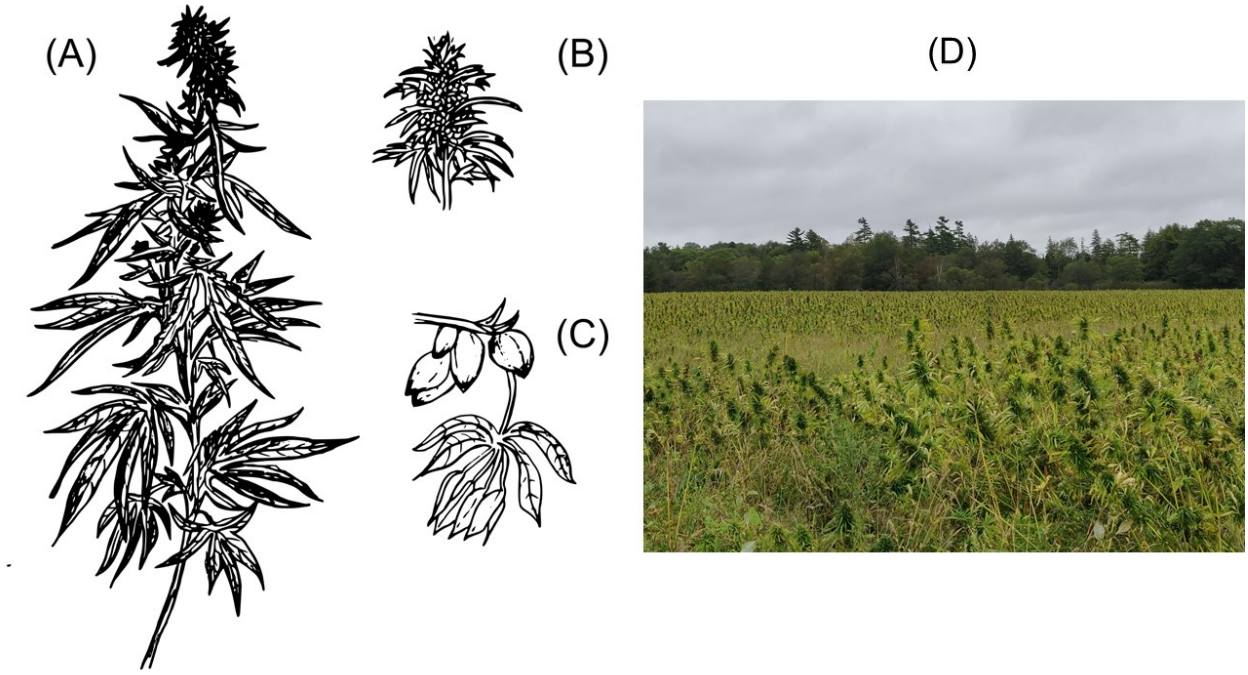

Figure 1. Structure of hemp plant. (A). Female plant; (B). Female inflorescence; (C) Male inflorescence; (D) Hemp field (drawn by Challa).

Among the 30 countries that grow hemp, China is reported to be the leading producer in the world with approximately 162,000 ha (HempToday™, 2019), followed by Canada with 35,000 to 40,000

ha as per 2019 data (HealthCanada, 2019). USA with 31,000 ha, has been estimated to have quadrupled to 206,900 ha in 2020 with 455% increase in the cultivation compared to the 2018 census (Angell, 2019), signaling high interest and investment in the hemp market. France, the Europe's leading grower of hemp, has about 17,000 ha under hemp, making it the fourth leading nation (HempToday™, 2019). Effective cannabis legalization and the shift of hemp production specifically for the cannabidiol (CBD) products, a massive increase in the cultivation of hemp and cannabis in Canada was observed. About 80% of the total hemp in the U.S. and majority of the hemp in Canada was grown for the CBD in the year 2019 (Arnason, 2019; AssociatedPress, 2020). With a total coverage of 12,142 ha, Alberta province was reported to be the leading cultivator of hemp in Canada followed by Saskatchewan with 10,975 ha (Figure 2) (HealthCanada, 2019). Annual sales of CBD from hemp could potentially be larger than those of marijuana, because of the large number of products in which it can be used. The market in North America is expected to grow with annual growth rate of 16.9% from 2018 to 2025 due to increasing CBD oil and fiber-based products (Craig Giammona, 2019).

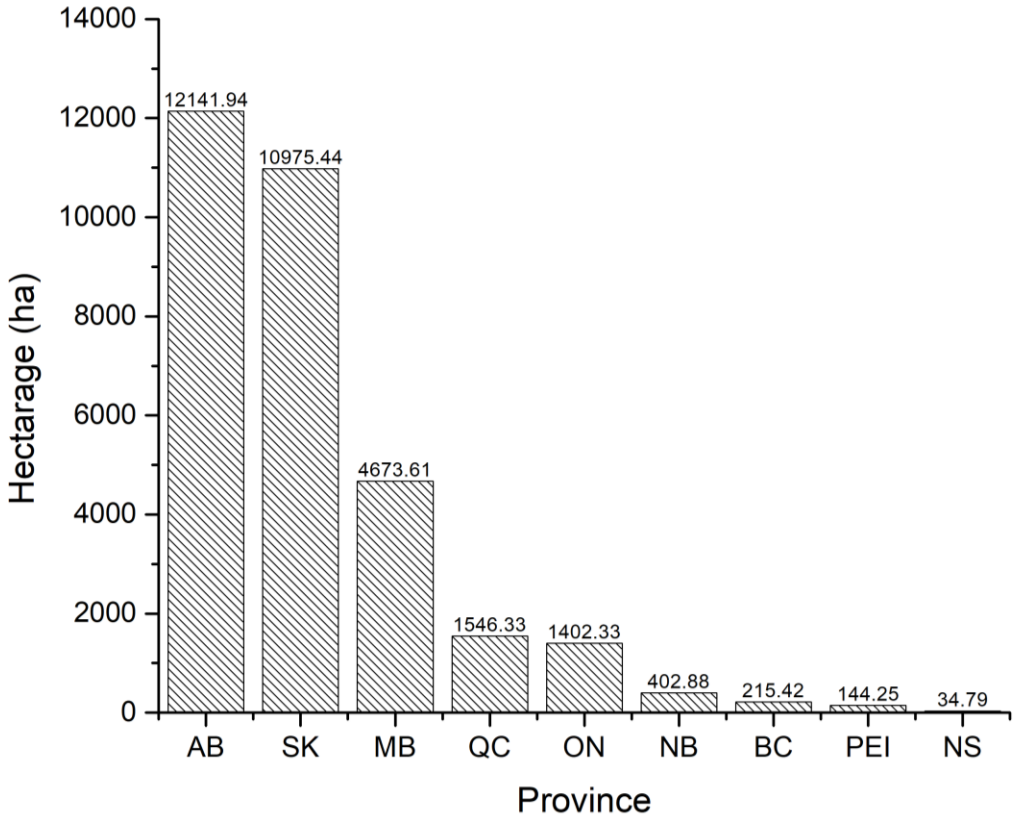

Figure 2 Registered hectarage for cultivation of industrial hemp by Canada province (illustrated by Challa).

Hemp can be used for multiple purposes such as for medicinal, recreational, furniture, paper, textile, as supplements in foods, beverages, and cosmetics with an estimated 25,000 different types of products (Salentijn, Zhang, Amaducci, Yang, & Trindade, 2015) (Figure 3). Each part of hemp, from the seed to the flower, is beneficial to the humans. Hemp seed is a source of food and typically contains over 30% oil and about 25% protein. Hemp seed oil is over 80% in polyunsaturated fatty acids (PUFAs) and is an exceptionally rich source of linoleic acid (omega-6), alpha-linolenic acid (omega-6) and alpha-linolenic acid (omega-3) (Tang, Ten, Wang, & Yang, 2006). Canada exported nearly 5,400 metric tons of hempseed in the year 2018 of which, over 70 per cent went to the U.S. (Jaeger, 2019) followed by European Union (EU) member countries and South Korea. Several food products with hemp and cannabis as an ingredient are

available in the market. Examples include cookies, chocolates, gummies, jellies, candies, and coffee (Benson, Hobbes, Gemmiti, & Platt, 2016; Hospodor, 2012). Similarly, peanut-cannabis butter blend, confectioneries containing cannabinoids derived from hemp products have also made it to the market (CannabisDispensary, 2019). Since, the scientific evidence supporting the safety of CBD in food is limited, the U.S. Food and Drug Administration (FDA) indicated that CBD does not comes under generally recognized as safe (GRAS) for its use in human or animal food, and further issued warnings to the companies that are selling CBD related products (FDA, 2019).

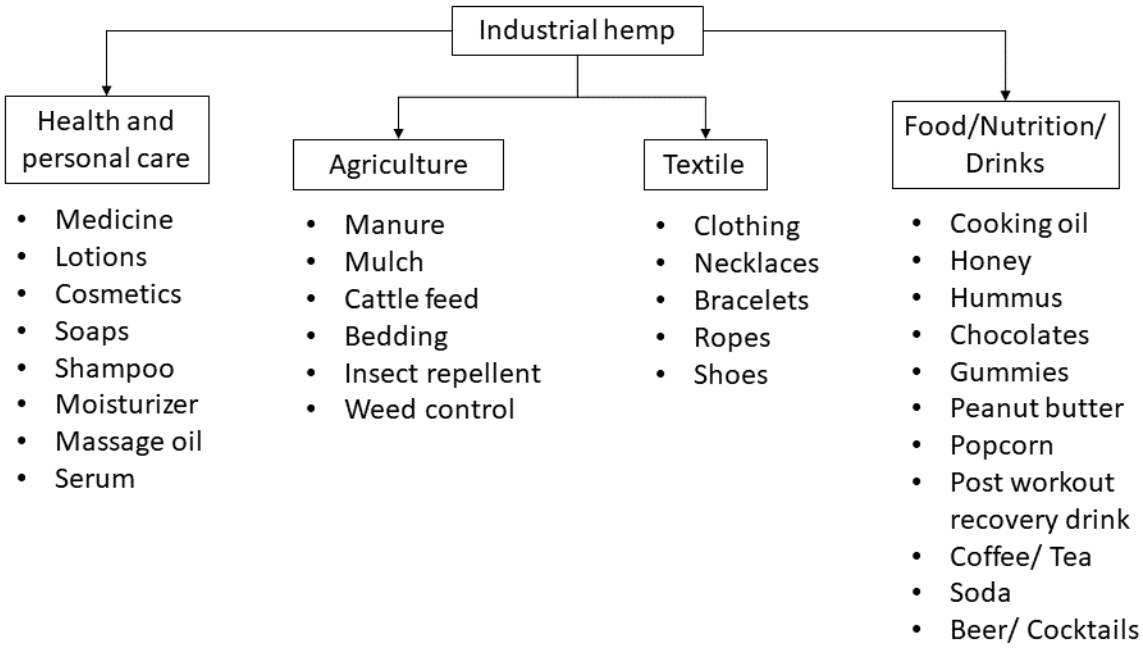

Figure 3 The industrial hemp: sub-markets and products (illustrated by Challa).

Currently, hemp industry is concentrated on the cannabidiol (CBD), the important compound that possesses known medicinal properties beneficial to the humans. The pharmacological characteristics of CBD include anxiolytic, anti-inflammatory, antipsychotic, antispasmodic and analgesic (UNODOC, 2009). Cannabinoid-based medicine is regularly used for treatment of

several illnesses, for example to improve hunger/appetite in AIDS (acquired immuno-deficiency syndrome) patients, to decrease nausea and vomiting in chemotherapy (Tramèr et al., 2001), and for treating muscle spasms and chronic pain (Borgelt, Franson, Nussbaum, & Wang, 2013; Whiting et al., 2015). The use of CBD (Epidolex) for effective alleviation of seizures in children with epilepsy who do not respond to other medications is also well documented (Friedman & Devinsky, 2015). A mixture of Δ-9THC and CBD is approved in Europe and Canada for treating spasticity and neuropathic pain associated with multiple sclerosis (Pertwee, 2012).

Therefore, the multiple uses and applications makes hemp a potential plant to explore in different areas to improve its production and processing. This project mainly explored the literature pertaining to the CBD, the beneficial and commercial compound of hemp, and different aspects of drying technologies, which facilitate CBD retention in the product.

1.2. Hemp Chemistry

Cannabidiol (CBD), being the principle cannabinoid responsible for hemp's unique medicinal properties, information on the areas of CBD production in the plant (via the chemical pathway), its location in the buds, and its role and significance besides other cannabinoids in hemp, is crucial. Hemp and cannabis plants contain several phyto-cannabinoids, which are a class of terpenophenolic compounds that modulate the neurotransmitter release in the brain by acting on the cannabinoid receptors in cells. Among the cannabinoids, Δ9-tetrahydrocannabinol (Δ9-THC/ THC), responsible for the psychotic properties, and cannabidiol (CBD), responsible for medicinal properties are the most potent (Turner, Hemphill, & Mahlberg, 1980). Modern hemp has been selectively bred to produce low levels of THC (0.3% in the dried material) (Small & Marcus, 2002) and high levels of fiber, seed, and, more recently, cannabidiol (CBD) (2-5%) (Hartsel, Eades, Hickory, & Makriyannis, 2016).

The monoterpenoid precursors, predominantly geranylpyrophosphate (GPP), that originate from the deoxyxylulose (DOX) pathway, and the phenolic precursors mostly olivetolic acid (OA), generated by polyketide pathway are subsequently condensed to form cannabigerolic acid (CBGA) by the prenyltransferase enzyme geranylpyrophosphate:olivetolate transferase (GOT) (Fellermeier & Zenk, 1998; Sirikantaramas et al., 2004) (Figure 4). CBGA and its homologues are the central intermediates in the cannabinoid pathway. The CBGA thus formed, undergoes oxidative cyclization reactions to form various alkyl homologues of tetrahydrocannabinolic acid (THCA), cannabidiolic acid (CBDA), and cannabichromenic acid (CBCA) catalyzed by the respective synthase enzymes (Pertwee, 2014).

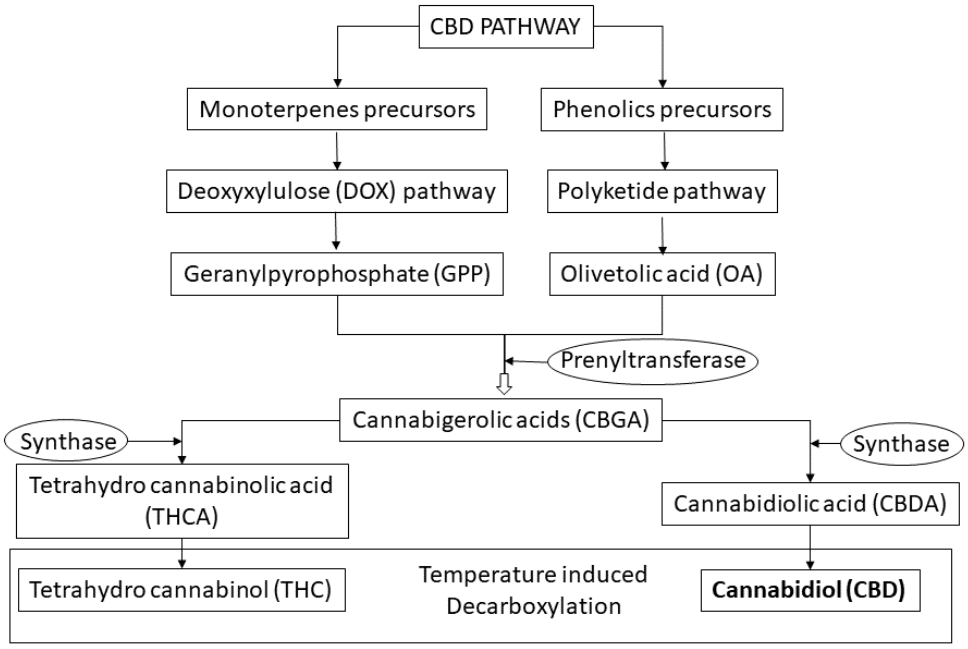

Figure 4 CBD Pathway (illustrated by Challa)

Turner and Mahlberg (1984) conducted experiments on the effect of drying temperature on cannabinoids. Samples were dried for 24 h at 37 °C and 60 °C and CBD content was separated and analyzed using both Gas-liquid Chromatography (GLC) and High-Performance Liquid Chromatography (HPLC). Analyses revealed that samples dried at 60 °C have both acid and

neutral cannabinoids, while only cannabinoid acids were found in samples dried at 37 °C, has shown that decarboxylation occurred only at high (above 37°C) temperature. Hence, in plants, cannabinoids are mainly stored in the form of acids such as, Δ9-tetrahydrocannabinolic acid (THC-A), cannabidiolic acid (CBD-A) (Taschwer & Schmid, 2015), and small amounts of decarboxylated forms, such as THC and CBD that occurred due to spontaneous decarboxylation during the cultivation process.

Total CBD level (w/w %) is typically calculated as:

$$Total\ CBD = (0.877 \times CBDA) + CBD \quad \ldots (1)$$

where 0.877 is the scaling factor accounting for the difference in molecular weight between CBDA and CBD (w/w %). Total CBD content (standard way of reporting) refers to the maximum potential CBD content of a hemp product, assuming 100% decarboxylation of cannabinoid acids (Jikomes & Zoorob, 2018).

Apart from cannabidiol, hemp contains numerous terpenes which are the main contributors to the plant's unique aroma. The fragrance of various plants is mainly due to the monoterpenes, which contribute to distinctive smell of trees (e.g. α- and β-pinene from pines), mints (e.g. menthol from peppermint), fruits (e.g. limonene from citrus) and flowers (e.g. geraniol from roses) (Singsaas, 2000). Among the hemp terpenes, popular and abundant are alpha and beta pinene, myrcene, terpineol, limonene, geranyl acetate and caryophyllene oxide. Out of these, 75% of the volatiles noticed are pinenes and limonene in the surrounding atmosphere, making 7% of the essential oil (Hood, Dames, & Barry, 1973).

1.3. Location of Cannabinoids in Plant

C. sativa shoots bear various types of glandular and non-glandular epidermal appendages called Trichomes (Briosi and Tognini (1894, 1897). These glandular hairs occur in both male and female plants but are found more profusely on pistillate (female) plants. In flowers, morphologically three different types of glandular hairs are observed. They are capitate-stalked, capitate-sessile and bulbous (Figure 5). Bulbous and capitate-sessile type glands can be observed on almost all vegetative and flowering shoots parts, but capitate-stalked glands are limited to flowering regions. As the bracts mature, these glands increase in density, become translucent and store high quantities of cannabinoids. In a gland, cannabinoids are chemically bounded with the cell walls, secretory vesicles and fibrillar material in the secretory cavity of the disc cell (Hammond & Mahlberg, 1973). Cannabinoids are mainly genetically controlled and depend on plant variety. However, there is a significant dependence of cannabinoids formation from the environmental conditions. Reportedly, cannabinoids occurred comparatively abundant in the plants grown under low humidity, less rainfall and sunny climatic conditions (Murari, Lombardi, & Romagnoli, 1988; Pate, 1994; Sharma, 1975).

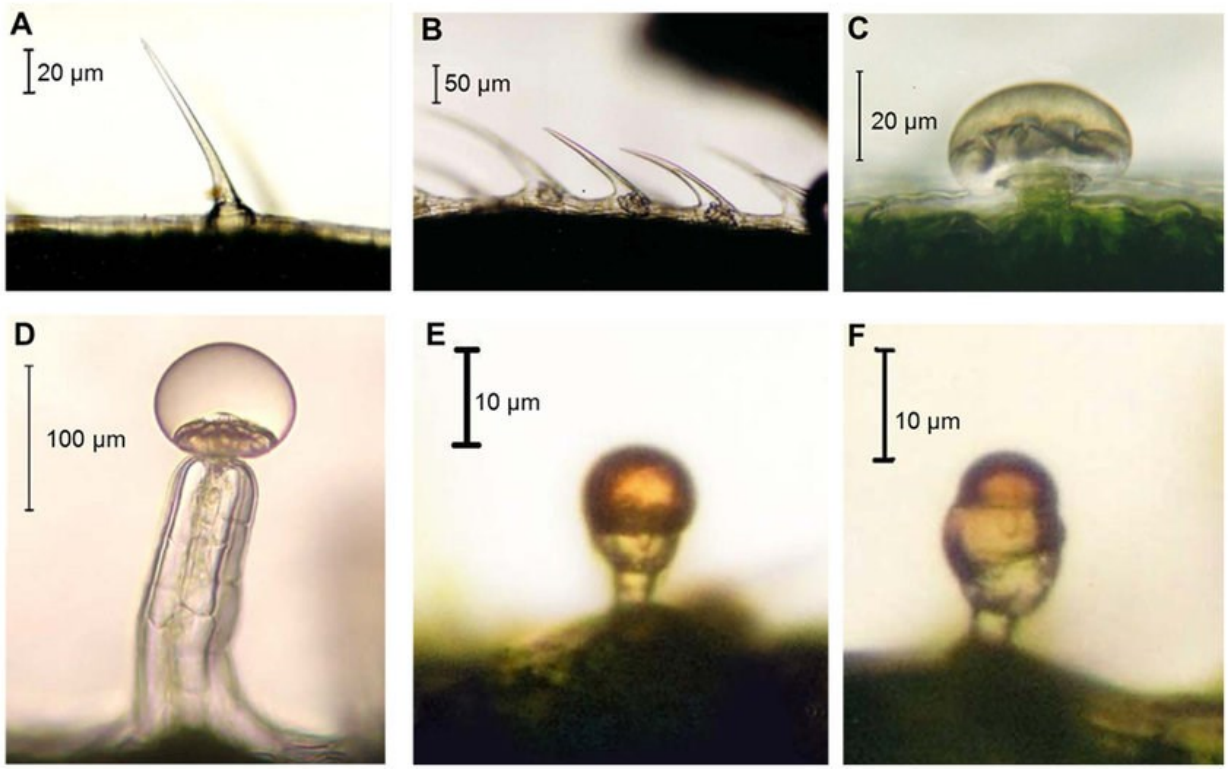

Figure 5 Hemp trichome types. (A) Unicellular non-glandular trichome; (B) Cystolythic trichomes; (C) capitate sessile trichome; (D) capitate-stalked trichome; (E) simple bulbous trichome; (F) complex bulbous trichome. Photographs by Dr. David J. Potter; reproduced from Andre, Hausman, and Guerriero (2016) under Creative Commons Attribution License.

1.4. Physiological Significance of Cannabinoids in Plants

Cannabinoids are the secondary metabolites that are formed specifically in hemp (and cannabis). Their occurrence in plant is found to be a part of plant's defense mechanism. These are often seen as gummy resins exuding on the surface of the plant parts, as a waxy coating that is similar to cacti, serving as a barrier for reducing water loss in xeric conditions (Pate, 1994). Rothschild and Fairbairn (1980) used pure THC (against CBD) on cabbage leaves and described its repellant nature on white cabbage butterfly (*Pieris brassicae*). Terpenes often known for the hemp aroma are also known to possess insect-repellent properties. They may protect the plants by deterring the herbivores and by attracting predators and parasites of herbivores. Also, these cannabinoid sticky

resins are tough for a considerable insect to chew, along with trichomes, thus, acting as a mechanical defense like many other plant species (Levin, 1973).

1.5. Postharvest Processing

Typical processing of hemp for CBD involves, harvesting, drying of harvested product, followed by grinding, extraction, and product development (Figure 6).

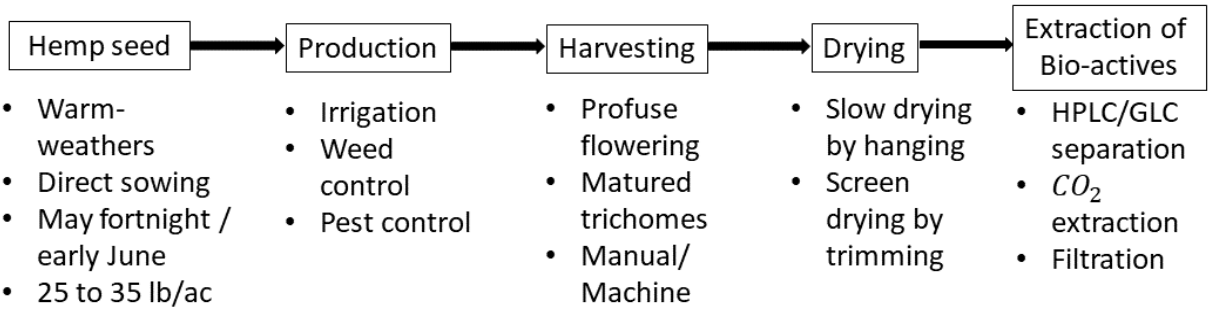

Figure 6 Sequential industrial processing of hemp for CBD (illustrated by Challa).

The first important step in postharvest processing and preservation of hemp involves reduction of the water content in buds through drying. A lower moisture leads to a decrease of the free moisture (active water) availability for microbial growth and enzymatic activity, consequently, preventing the spoilage of the product (Roos, 2007).

1.5.1. Equilibrium Moisture Content (EMC) and Water Activity (a_w)

Equilibrium Moisture Content (EMC) can be termed as the moisture content of a wet material in equilibrium with air of given humidity and temperature (Soysal & Öztekin, 1999). All cultivated crops have diverse physical and chemical structures and therefore, have different EMC under similar conditions. EMC data for a biological material is necessary to understand the safe moisture levels to which the product should be dried for a considerable period of storage and preservation.

Water activity may be defined as the ratio of the vapor pressure (p) of water in food to the vapor pressure (p_0) of pure water at a given temperature (p/p_0). This can be expressed as relative humidity/100 (Al-Muhtaseb, McMinn, & Magee, 2002). Scott (1957), introduced the concept of water activity (a_w) which represents the quality and boundness of the water content available for physical, chemical, and microbiological reactions. Microorganisms require a minimum water activity level for their growth and therefore, a reduction in water activity is a key for controlling microbial growth (Sancho-Madriz, 2003).

Fresh cut plants have a water activity up to 0.95 a_w. According to Labuza, Cassil, and Sinskey (1972), Roos (2007) (Figure 7), molds cannot grow if the water activity in the product is below 0.60 a_w. This concept of water activity will be useful in defining the safety regulations concerning growth of unwanted microorganisms, critical control points, food hazards, standards and packaging requirements of foods (Fontana, 2000).

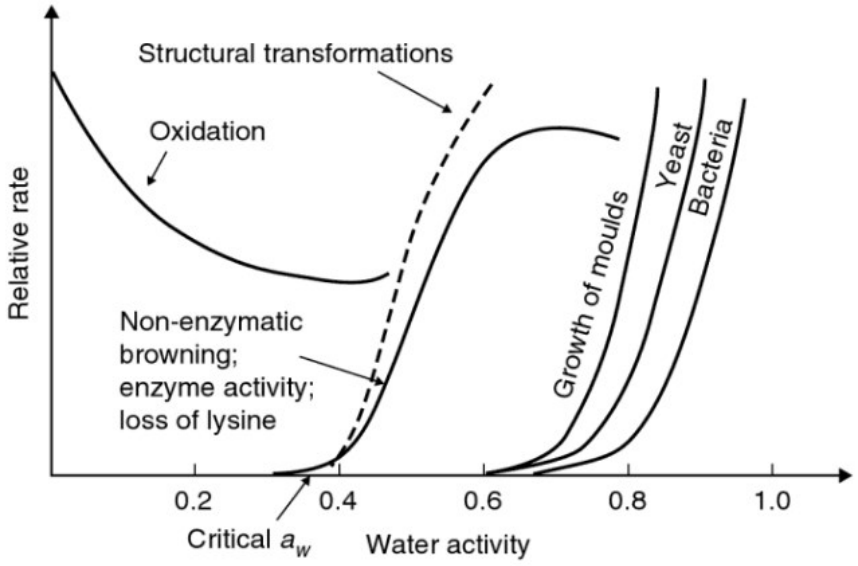

Figure 7 Stability map for food materials, modified from Roos (2002) by (Chen & Mujumdar, 2009).

1.5.2. Moisture Sorption Isotherms

The relationship between the relative humidity (RH)/ water activity (a_w) and the moisture content of a material at equilibrium (EMC) can be graphically exhibited through moisture sorption isotherm (Figure 8). Based on the direction of water transferred from the material, the processes were termed as desorption and adsorption. If a relatively wet material is placed in the constant relative humidity conditions, water from the material gets transferred to the environment. The amount of the material moisture transferred is measured through weight changes of the material. The amount of water drawn depends on the applied relative humidity condition and the moisture content in the material (various relative humidity environments draw various amounts of moisture from the material until both attain equilibrium). Plotting the equilibrium moisture levels against their respective relative humidity conditions gives the desorption isotherm. Similarly, an adsorption isotherm can be determined by placing a relatively dry material at different relative humidity environments, where water is adsorbed into the material, *via* the diffusion phenomena (Labuza, 1968). A sorption isotherm indicates the moisture content of a material for each corresponding RH, at constant temperature.

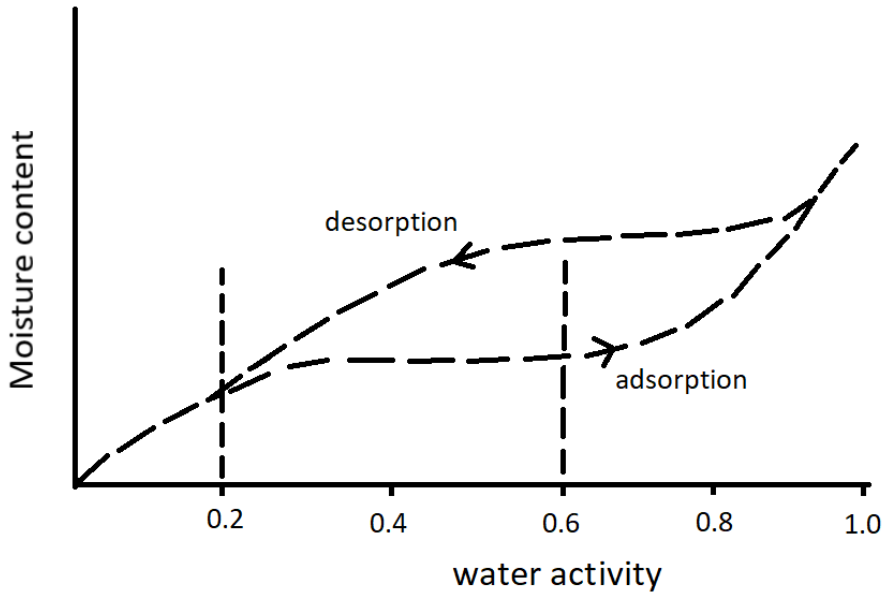

Figure 8 Typical moisture sorption isotherm (drawn by Challa).

Moisture sorption isotherm for a typical food system can be divided into three main regions. Region A (a_w 0.0 to 2.0) denotes strongly bound water and the water molecules in this region are said to be unfreezable. This water is not available for chemical reactions. Region B (a_w 0.2 to 0.6) represents less firmly bound water molecules that are held in the solid matrix by capillary condensation and are present as multilayers above the monolayer. Region C (a_w 0.6 to 1.0) represents water present in macro-capillaries and exhibits nearly all the properties of bulk water. Micro-organisms utilize this water causing the contamination to the product (Al-Muhtaseb et al., 2002).

Owing to this phenomenon, moisture sorption isotherms of most foods are sigmoidal in shape and have been classified as Type II isotherms (Gregg et al., 1967). In this project, only desorption isotherm of hemp was explored to determine the moisture content at 0.6 a_w and EMC for safe preservation.

1.5.3. Industrial Drying of Hemp

Hemp has been so far dried and used predominantly for fiber production. However, with the recent legalization of hemp and cannabis for medicinal and recreational purposes, demand for hemp CBD has been significantly increasing. The substantial growth in the cultivation of hemp demands appropriate drying technology for product preservation and for CBD extraction. Drying of hemp and cannabis has evolved over years as more of an art than technology, perhaps, due to the taboos associated and illegal status in most countries.

The commonly practiced traditional drying method is “slow drying”. In this method, either the whole plant or the branches with flower buds are hung upside down (Figure 9). Consequently, water from the stem slowly migrates into the buds as water evaporates and thus, increases the drying time. A variation of slow drying known as “cage drying”, involves hanging of buds from wire cages instead of static wires is also in practice. This modification allows to move the cages closer or away from dehumidifiers or heaters in a drying room. Drying is carried out in closed and well-ventilated drying rooms that employ dehumidifiers. The average temperature in the drying room is maintained between 18-21 °C, while the relative humidity is set in the range of 50-55%. Under these conditions, the total time required to dry the buds as well as the trims to final moisture content is about 5 to 6 days. Currently, there does not exist any model to predict the endpoint of drying or the overall drying time. Most growers and industries predict that the product is dried based on the texture and crispness of the bud. An issue that is often encountered with current methods of drying is mold growth due to inadequate control over the slow process (Hawes & Cohen, 2015).

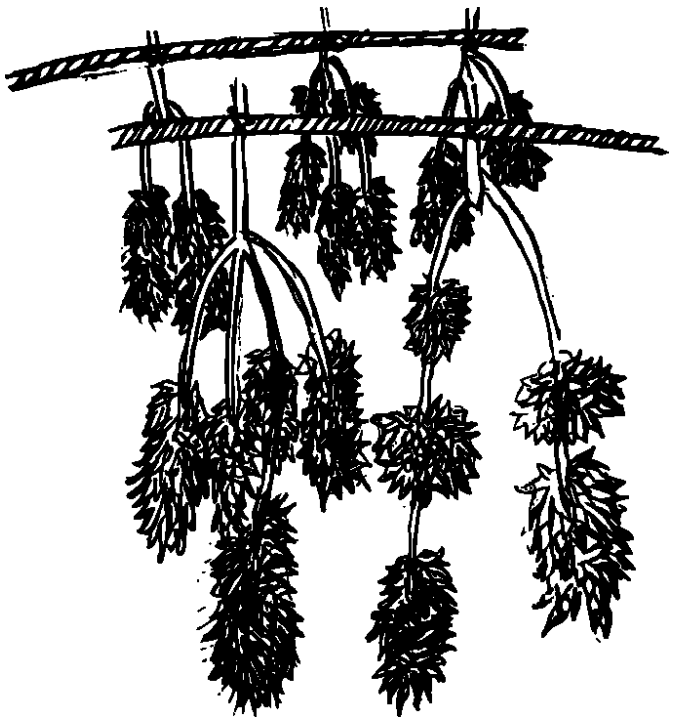

Figure 9 Process of slow drying by hanging the hemp stems upside-down along with buds (drawn by Challa).

The other commonly practiced drying method is “screen drying”. In this method, prior to drying, the flowers (often referred as “cola”) are trimmed, i.e. removal of long palmate leaves (fan leaves) present at the flowering area as well as buds from the stem. The manicured flower or cola typically range between 10 to 15 cm in length, while the trimmed buds fall between the size of particles to 2 cm. The trimmed buds are then placed on the trays/ screens and dried in closed and well-ventilated drying rooms. Drying conditions are similar to the slow drying process except for drying time, which takes 3 to 4 days. It should be noted that the trimmed buds have a much higher effective surface area available for drying as well as a very different diffusivity compared to the untrimmed flower. This implies that the time required to dry the whole flower with stem would be longer than that for an equivalent mass of the buds. Based on this hypothesis, there is ample scope for optimizing the drying conditions separately for the buds to minimize the overall drying time.

1.5.4. Relevant Drying Technologies

1.5.4.1. Convective Drying

Convective drying technology is the most commonly used drying method in the food processing industry due to its simple operation and low cost (Mujumdar, 2014; Müller, 2007). The principle of convective/ hot air drying lies in heat transfer from air to the wet material and consequently, conjugate mass transfer from the material to gas phase (evaporation). Convection systems lower the relative humidity by raising the temperature of the air passing through the product, thereby, creating the gradient for mass transfer. Typical convective dryer is equipped with a heat control unit to regulate temperature, fan, drying chamber with sample trays, instruments for measuring temperature, mass, relative humidity and airflow (Figure 10).

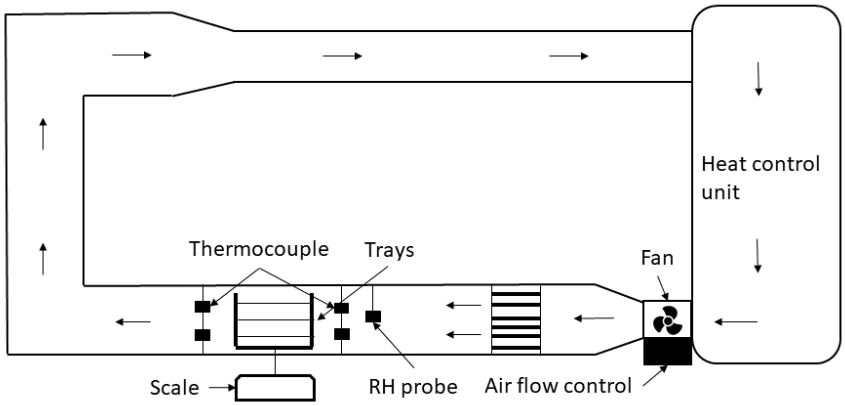

Figure 10 Schematic diagram of convective dryer (illustrated by Challa)

Convective drying mainly takes place at the constant rate and falling rate periods (Mujumdar, 2014). Constant dehydration rate is observed in a fresh material, where the structure is firm and free water is distributed uniformly on the surface and the interior of the material. Moisture transfer occurs as a result of the concentration gradient. Eventually, as the surface gets dried, diffusion of water to the surface decelerates with tightly bound water in the inner surfaces causing falling dehydration rate.

Controlled variables in convective drying are mainly temperature, relative humidity and air velocity. In an earlier study, the effect of air velocity on drying kinetics was observed to be negligible at high air velocities (Berna, Rosselo, Canellas, & Mulet, 1990; Kaymak-Ertekin, 2002; Mulet, Berna, Borr, & Pinaga, 1987). Further, the critical air velocity value at which drying rate is not affected was found to range from 1 to 1.5 m/s. Increase in the air temperature has a significant effect on drying rate and is the major determinant of product quality (Martynenko & Janaszek, 2014; Ozguven, Tarhan, Polatci, & Telci, 2016).

Over 85% of industrial dryers are convective, using either hot air or combustion gases as the media for heat transfer. The traditional methods associated with the drying of hemp are based on the same phenomenon. However, there is no relevant study on the effect of drying temperatures on CBD retention. This void certainly merits to carry out suitable research to determine CBD and terpenes behavior as a function of temperature.

1.5.4.2. Intermittent Drying/ Non-Isothermal Drying

Modern drying technologies like intermittent/ non-isothermal drying, which is proven to reduce drying time at minimum loss of quality and good energy efficiency can be used as an alternative to conventional isothermal drying at low temperatures. Non-isothermal drying involves suitable fluctuation (increase/decrease) of drying conditions (temperature and humidity) to facilitate redistribution of thermal gradients and levelling of moisture within the material (Martynenko & Kudra, 2015). Non-isothermal drying has been successfully applied for the drying of sensitive herbaceous materials that have potential implications for hemp drying. For example, Ozguven et al. (2016) used stepwise drying of peppermint by incremental rise of drying air temperature from 35 °C to 55 °C in 4 hours and then maintained the temperature at 55 °C. This approach not only retained the quality of the product that is similar to 35 °C, but also accelerated drying. Similar

experiments were conducted by Cuervo-Andrade and Hensel (2016), with Lemon balm drying, where a combination of 40 °C and 50 °C, with change point at 20% moisture content showed nearly no change in quality and reduced energy consumption by 10% and drying time by 28.5% compared to standard drying at 40 °C. Therefore, non-isothermal stepwise drying could be a good alternative to traditional convective drying of hemp at constant temperature. In fact, in a recent patent, Hawes and Cohen (2015) describe an intermittent drying process for cannabis involving three stages of drying. They claim that relatively higher initial temperatures (between 50 to 60 °C) and higher humidity (< 80% RH) for up to 5 hours will result in inactivation of mold spores while preventing rapid evaporation from the material. Subsequently, they suggest that in the second stage the temperature and humidity should be dropped to prevent any thermal denaturation, while ensuring constant drying. Finally, the patent suggests further lowering of humidity, while keeping the temperature relatively constant in the final stage of drying to reach the equilibrium moisture content of about 8 to 9%. Noticeably, while the patent by Hawes and Cohen (2015) exploits non-isothermal drying conditions for inactivation of mold spores, it does not shed light on the reduction in the overall drying time or CBD retention. Thus, effect of temperature and moisture content on the overall drying time and CBD retention needs to be further explored.

1.5.4.3. Freeze Drying

Freeze drying is a method of drying materials by sublimation under vacuum (Liapis & Bruttini, 2006). Operating at low temperatures, freeze drying technology potentially reduces the volatile losses, resulting in premium quality dried product. Freeze drying can be divided into primary and secondary drying stages. Primary drying stage involves lowering of pressure, through vacuum, and applying heat, by conduction or radiation, to the material for sublimating ice. The secondary drying stage involves removal of unfrozen water. Temperature will be higher in this phase compared to

primary drying for breaking any physico-chemical interactions formed between the frozen material and water molecules (Liapis & Bruttini, 2006). Essential components of a freeze dryer usually include vacuum chamber, condenser, shelves, refrigeration system, shelf-fluid system, control system, and vacuum system.

Freeze drying is progressively developing into an important preservation method for highly delicate and heat-sensitive biological products, as it retains the quality of the fresh material. Drying is done at low temperatures with a minimum loss of flavor, valuable compounds and minor shrinkage (Gardeli, Evageliou, Poulos, Yanniotis, & Komaitis, 2010). Due to the low processing temperature and less oxygen availability, freeze drying can preserve the product quality better than other drying techniques (Litvin, Mannheim, & Miltz, 1998; Strumillo & Adamiec, 1996).

Energy consumption in freeze drying is a significant factor, with the energy losses and long drying time (usually 10-15 hours) dictating the overall cost-economics. Energy losses include loss of radiant energy to dryer walls, losses within the product, energy dissipation in vacuum pumps, and energy released to the environment from freezers and freeze dryer units (Díaz-Maroto, Sánchez Palomo, Castro, González Viñas, & Pérez-Coello, 2004). The drying time is mostly limited by slow heat transfer. The problem of inefficient heat transfer could be resolved with microwave heating. Microwave Freeze Drying (MFD) is widely recognized due to 50–75% less time to drying vis-à-vis freeze drying (Duan, Zhang, Mujumdar, & Wang, 2010). MFD however, poses challenges for industrial implementation owing to non-uniform heating of the dry zones in product, thereby negatively impacting the product quality (Wang & Shi, 1999). The cost of freeze drying is about four to ten times higher than that of convective hot air drying (Liapis & Bruttini, 2006). Since freeze drying is an expensive process, the use of freeze drying at industrial level is limited

to high-value products, such as hemp. Thus, freeze drying could be another potential technology that can preserve the CBD and terpenes content and therefore necessitates further research.

1.6. Problem Statement

As hemp industry relies on traditional drying practices for CBD extraction, which often take 3 to 4 days, problems such as excessive energy consumption, poor quality product and also, mold development that occurs due to the uneven/ incomplete drying of buds (George-Cosh, 2018). A systematic study is certainly required to understand the effect of different drying technologies on CBD degradation. This leads to the specific research questions: what is the equilibrium moisture content for safe preservation, and how the different drying temperatures and drying time influence the CBD and terpenes retention? Drying of hemp buds for further extraction of bioactive compounds (CBD and terpenes) is a bottleneck to the entire production cycle. Proper research is necessary to address such problems which would help the growing hemp industry to select suitable drying method that enable high throughput.

So, my hypotheses are that desorption isotherm can be used to determine the moisture content at 0.6 a_w and EMC for safe preservation. Quality parameters such as, CBD, terpenes and color behavior against various temperatures aid in selecting an appropriate convective drying temperature. Non-isothermal drying, where an increase in the drying temperature in the middle of the process, could save considerable amount of time and energy besides ensure quality retention. Freeze drying, which is proven to be an effective technology for quality retention, would retain maximum hemp buds' quality.

1.7. Objectives

This study involves objectives to:

1. Determine the desorption isotherm of hemp, and thereby, to determine the equilibrium moisture contents in hemp buds for a safe preservation.
2. Determine the effect of convective drying temperatures (25, 32, 40, 50, 60 and 70 ºC) on drying time and product quality (CBD and terpenes).
3. Determine the best fitted model that expresses drying kinetics of convective drying and the effective moisture diffusivity (D_{eff}).
4. Determine the ability of non-isothermal drying to decrease the drying time with maximum quality retention.
5. Determine the effects of freeze drying on drying time and quality.
6. Compare the effect of convective vs. freeze drying on product quality and specific energy consumption.
7. Evaluate the above drying technologies and identify the best drying condition beneficial for the industry.

Chapter 2. Materials and Methods

2.1. Experimental Setup

All the drying experiments of hemp buds were conducted at a farm site in Middle Musquodoboit (45.053973, -63.127794), NS, Canada (Figure 11) due to the unavailability of a license to grow hemp/ cannabis for research at the university. The temporary research lab was established at a farmhouse near to 100-acre hemp fields. The facility is equipped with an adjustable thermostat for ambient temperature control. Ventilation, relative humidity regulation, commuting to the facility (located 60 km away from the university), food and other resources, were some of the major challenges faced during the research. The drying equipment required for the experiments were transported from Dalhousie University (September 11, 2019) to the research facility. The two convective driers (3926TB 9-Tray food dehydrator, Excalibur, Sacramento, California, USA) and the freeze drier (Harvest Right, Salt Lake City, Utah, USA) were placed in the individual rooms (Figure 12).

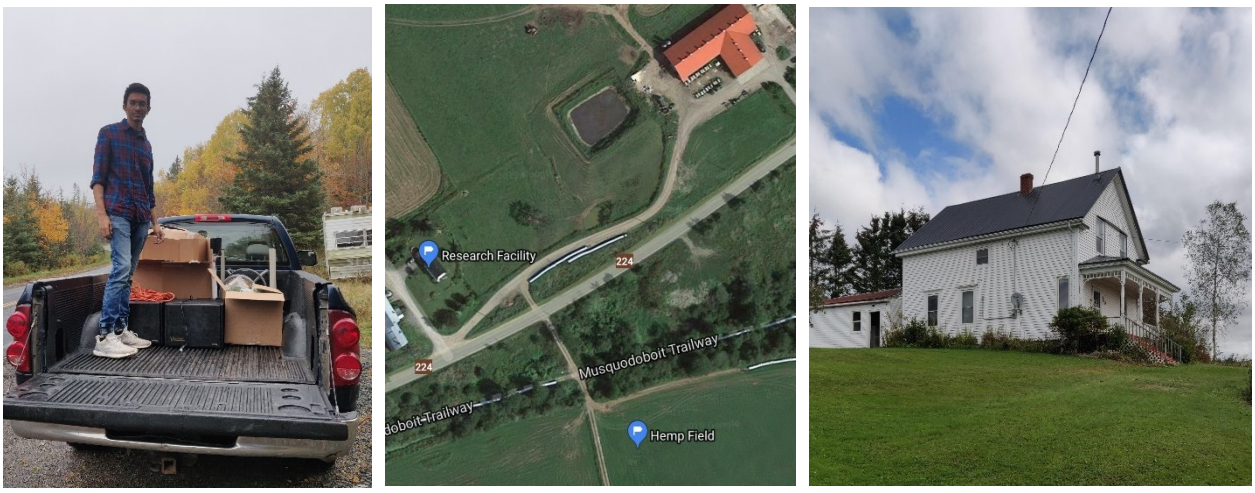

Figure 11 a. Transporting the drying equipment to the research facility; b. Satellite view of the research facility; c. Outer view of the research facility.

Figure 12 Driers arrangment in the research facility

2.2. Samples Preparation

Fresh hemp buds (variety-X-59, source- Inplanta) were obtained from the hemp field located near Middle Musquodoboit early in the morning prior to each experiment. Harvesting of whole flower (often referred as 'Cola') was performed through mechanical cutting with pruning shears. After harvesting, removal of fan leaves and trimming of buds from the stem were carried out manually (Figure 13). Buds harvested (110 – 120 days after sowing) were over matured and possessed seeds that resulted in increase of dry matter (32-38%). Each bud was measured using a ruler and was in the average size of 5×4 sq.cm. For freeze drying, buds were stored in a freezer (-20 ºC) immediately after trimming, for about 36 to 48 hours, before each experiment.

Figure 13 A. Whole Cola (Flower); B. Cola after removing fan leaves; C. Fresh trimmed buds (Clicked by Challa.)

2.3. Desorption Isotherm

For determining the desorption isotherm, static gravimetric method was used, where the moisture content of the material is calculated through measuring its weight. This method is reported to be the standard and the easiest method for determining sorption isotherms (Al-Muhtaseb et al., 2002; Chen & Mujumdar, 2009).

The main requirements to determine the desorption isotherm of a material include, facilitating various constant RH environments and measuring the corresponding moisture content of the material. In this method, seven salt solutions (Fisher Scientific Inc., Massachusetts, USA) (Table 1) (Chen & Mujumdar, 2009), which can maintain seven different RH environments were used and were placed in seven airtight jars (Figure 14). For obtaining around 100% RH (1.0 a_w), fresh water was taken. Inside each jar, a small cuvette was placed over which an aluminum tray was employed that holds the sample. Fresh trimmed hemp buds were weighed and were placed in each jar. The mass of each sample was measured periodically using a digital scale HCB2002 (Adam Equipment, Danbury, CT, USA) with 0.01g accuracy. The jars were sealed with wax and parafilm

to prevent any possible leakage. Temperature inside the room was maintained using the thermostat (22 ± 1 ºC). For calculating the moisture content of the material, weight of each sample was measured periodically until constant weights were observed (24 – 48 h). Constant weight represents that the sample moisture is in equilibrium with the relative humidity of the environment. From the weight measurements, moisture content (mc) on dry basis X_{db} and wet basis X_{wb} of the material was calculated by,

$$X_{db} = \left(\frac{W_w - W_d}{W_d}\right) \text{ (g/g; dry basis)} \quad \ldots (2)$$

$$X_{wb} = \left(\frac{W_w - W_d}{W_w}\right) \times 100 \text{ (\%,wet basis)} \quad \ldots (3)$$

where, W_w is the initial/ final weight of the sample, and W_d is the weight of the sample dry matter. Dry matter was measured by removing the residual moisture in the sample by using the convection oven at 105 ºC for around 24 hours (until constant weight was observed). The experiments were done in three repetitions.

Table 1 Salt solutions used for sorption isotherms

Salts	**Required according to guidelines (1.5 or 2 times than solubility)**	**RH**
Potassium chloride (KCl)	>53g	85%
Sodium chloride (NaCl)	>54g	75%
Sodium Nitrite ($NaNO_2$)	>170g	65%
Magnesium nitrate ($Mg(NO_3)_2$)	>188g	54%
Potassium carbonate (K_2CO_3)	>168g	44%
Potassium acetate (CH_3COOK)	>300	23%
Lithium Chloride (LiCl)	>175	11%

Figure 14 Glass jars used for static gravimetric method (by Challa).

Mathematical Modelling of Desorption Data

For mathematical analysis, the desorption data was fitted with Guggenheim-Anderson-de Boer (GAB), a three parameter model, which has been considered to be the best fit model for many food and agriculture products over a wide range of relative humidity values (Al-Muhtaseb et al., 2002; Chen & Mujumdar, 2009; Prothon & Ahrné, 2004). The GAB equation has been widely adopted throughout the literature to evaluate the sorption phenomena of food systems. GAB equation can be represented by,

$$M = \frac{M_0 C K a_w}{(1-K a_w)(1-K a_w+C K a_w)} \qquad \ldots (4)$$

Where, M is the moisture content of the material on a dry basis (g/g), a_w is the water activity, and M_0, K and C are the three sorption parameters/constants describing sorption properties of the material. To check the suitability of this equation, statistical tools such as $\bar{R}^2$ (adjusted R^2-coefficient of determination), and root mean square error (RMSE) analysis were used (Erbay & Icier, 2010).

Since, the main objective is solely for studying the EMCs at target a_w values, with the available time and resources, the study was limited only to the exploration of the desorption isotherm of hemp buds fitted with the widely used GAB model.

2.4. Drying Experiments

2.4.1. Isothermal Convective Drying

Isothermal convective drying experiments were carried out in Excalibur dehydrator (Figure 15). The dehydrator was equipped with a 7-inch fan that produced an average air velocity of 1.0 m/s, a heating element and a thermostat, all located at the backside of the unit. The dryer can hold 9 trays but only three were used for each experiment. Each tray has a screen to hold the samples and for air exchange. Weight of each tray was measured (HCB2002- Adam Equipment, Danbury, CT, USA) prior to placing the material.

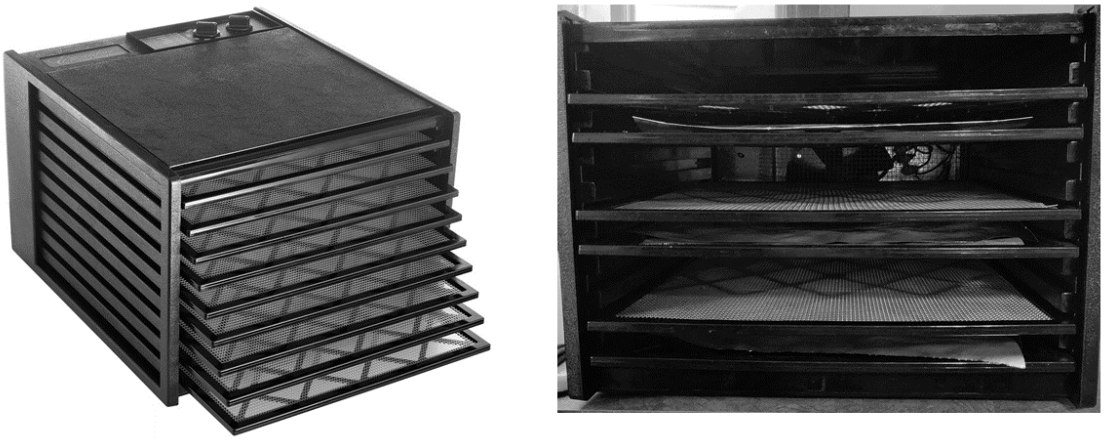

Figure 15 Excalibur 3926TB 9-Tray food dehydrator (excaliburdehydrator.com)

Fresh cut and trimmed buds were placed on three trays (Figure 13, C) and the weights of each sample along with the tray were measured after taring the scale. Trays were then placed inside the drying space at the top, middle and bottom (Figure 15). The dryer was provided with a door which helps in uniform circulation of the air and an adjustable thermostat which can control the

temperature ranging from 32 to 75 ºC. Prior to each drying experiment, temperature of the drying space was measured using infrared thermometer (MasterCraft, Ontario, Canada) with a range of -30 to 480 ºC, ensuring that required temperature was maintained. Drying experiments were carried out at 25, 32, 40, 50, 60 and 70 ºC temperature. A completely randomized design (CRD) was used for the experiments where each drying temperature was randomly assigned and run with two repetitions and with three replicates (samples) in each repetition. Drying at 25 ±1 ºC was made possible by turning off the thermostat of the dryer and adjusting the drying room temperature. Air velocity was measured using an anemometer and was constant through out the experiment (1 ± 0.1 m/s). Temperature of the material and the dryer was checked regularly throughout the experiments by using infrared thermometer. Relative humidity of the drying room was monitored by using a hygrometer (45 – 60%). Experiment was terminated when the material reached approximately the equilibrium moisture content (EMC). One tray of samples was placed inside the convection oven to measure the dry matter. Another two trays of samples were used for quality analysis. Drying at 32 ºC was taken as control, recommended by the industrial partner. The experimental design of isothermal drying was presented in Table 2.

Table 2 Experimental design: Isothermal drying

Experimental units	**Factors**	**Levels**	**Response variables**	**Design**
Fresh hemp buds	Temperature	1. Drying at 25, 32 (control), 40, 50, 60, and 70 ºC. 2. Drying at 32 ºC (control)	Drying time, total CBD and terpenes content, color, energy consumption	CRD Repetitions: 2 Replicates: 3

2.4.2. Non-Isothermal (Stepwise) Drying

In this work, the method of stepwise drying was presented as an alternative to the conventional drying that uses a constant temperature during the whole process. The objective of stepwise drying is to decrease the drying time and thereby, reduce the overall energy consumption with maximum quality retention. Drying of hemp was notably faster in the initial stage compared to the later stages. Hence, higher temperatures were applied during the later stages or falling rate periods thereby reducing the total drying time. The temperature change points chosen in the experiments are based on the moisture content of the product on a wet basis (w.b.) (Table 3). In the first set of experiments, initial temperature was set at 40 ºC and later increased to 70 ºC when the product reached the moisture content of 45% (w.b.). Whereas, in the following set, the temperature was increased (from 40 to 70 ºC) when the product MC reached 25%. Similarly, the temperature was first set at 40 ºC and increased quickly to 60 ºC using the thermostat when the product reached 45%, and 25% (respective moisture contents were predicted using the weight to moisture content data of hemp buds from the preliminary experiments). Drying at 32 ºC was taken as control since it was close to the drying temperature practiced by the industrial partner. Experiments were done in duplicates with three set of samples in each replicate. Non-isothermal drying experiments were done in the same convective dryer that was used for the isothermal drying (Figure 15).

Table 3 Experimental design: Non-isothermal drying

Experimental units	Factors	Levels	Response variables	Design
Fresh hemp buds	Temperature	1. 40 ºC, increased to 70 ºC at 45% moisture content (w.b.). 3. 40 ºC, increased to 70 ºC at 25% moisture content (w.b.). 4. 40 ºC, increased to 60 ºC at 45% moisture content 5. 40 ºC, increased to 60 ºC at 25% moisture content. 6. Drying at 32 ºC (control).	Drying time, total CBD and terpenes content, color, energy consumption	CRD Repetitions: 2 Replicates: 3

2.4.3. Freeze Drying

Freeze drying (FD) experiments were conducted in a laboratory-scale freeze dryer (Harvest Right, Salt Lake City, Utah, USA) (Figure 16). FD experiments were carried out simultaneously along with the convective drying experiments. Freshly cut and trimmed buds were stored in a freezer at -20 ºC for 36-48 hours prior to the drying experiments. Later, buds were removed and spread on three trays in a single layer and their weights along with the tray were measured. Trays were then immediately loaded into the freeze dryer to avoid melting of ice in the product. Drying was carried out for 2, 4, 6, 7, and 8 hours, uninterrupted, to plot the drying kinetics. Final weights were measured at the end of each run to calculate moisture content. However, samples dried for 7 h and 8 h were only considered for quality analysis, where the moisture content of the product was around 7-10% (w.b.). Experiments were done in three repetitions with three replicates in each run.

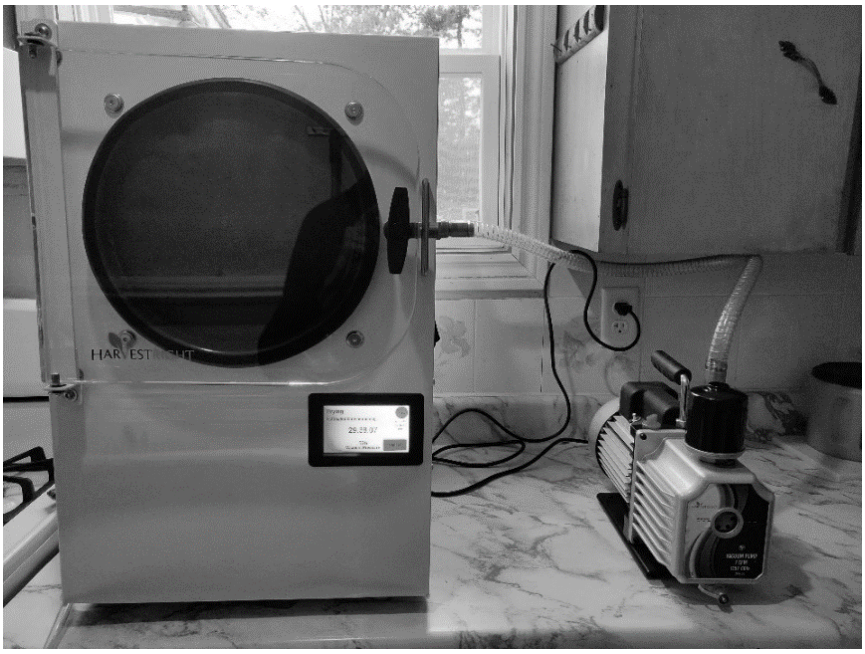

Figure 16 Freeze dryer (Harvest Right, Salt Lake City, Utah, USA).

2.5. Mathematical Modelling of Drying Kinetics

The main objective of the mathematical modelling is to fit the convective drying curves with a suitable equation. Fitted curves can be used as an aid for data visualization, to infer values of a function where no data are available, and to summarize the relationships among two or more variables. To explain the convective drying kinetics of hemp buds, 5 semi-theoretical models, such as Newton model, Page model, Henderson and Pabis, Logarithmic, and Midilli model, were selected (Table 4). The temperature distributed around the material is assumed to be constant. Semi-theoretical models are easier and require fewer assumptions (since they use some experimental data) and are effective within the process conditions applied (Fortes and Okos, 1981; Parry, 1985).

Mathematical models have been developed for convective drying curves of foods and herbs in the literature that examine the relationship between the time (independent variable) and moisture ratio (M_R) (dependent variable). These models use the moisture ratio as the independent variable instead

of the moisture content of the material since, all the respective material might not have the same initial moisture content every time. Moisture ratio (M_R) from the moisture content (g/g) can be calculated by the formula

$$M_R = \frac{X - X_e}{X_0 - X_e} \quad \ldots (5)$$

where, 'X' is the moisture content in g H_2O/ g dry matter at a given time, X_0 is the initial moisture content (g/g), and 'X_e' is the equilibrium moisture content. 'X_e' was assumed to be 0.03 (g/g) for all the drying experiments (since the lowest moisture content recorded was 0.03 g/g).

Table 4 Mathematical models given by various authors for drying curves.

	Model equation	**Model name**	**Reference**
1.	$M_R = \exp(-kt)$	Newton	(O'Callaghan, Menzies, & Bailey, 1971)
2.	$M_R = \exp(-kt^n)$	Page	(Page, 1949)
3.	$M_R = a\exp(-kt)$	Henderson and Pabis	(Hensderson & Pabis, 1961)
4.	$M_R = a\exp(-kt)$+b	Logarithmic	(Rayaguru & Routray, 2012)
5.	$M_R = a\exp(-kt^n) + bt$	Midilli et al.	(Midilli, Kucuk, & Yapar, 2002)

The M_R data is plotted with t, and the non-linear regression analysis was performed with the selected models to determine the constant values that supply the best appropriateness of models. To test the goodness of fit, statistical methods such as root mean square error (RMSE), and the adjusted R^2 (coefficient of determination, $\bar{R}^2$) were used as the primary criterion to select the best equation expressing the convective drying of hemp buds at different temperatures (Ertekin & Yaldiz, 2004; Soysal, Öztekin, & Eren, 2006). The RMSE gives the deviation between the predicted and experimental values. The lower the values of the RMSE, the better the goodness of

fit. The $\bar{R}^2$, on the other hand, gives the percentage of variation explained by the independent variables that affect the dependent variable (shows the proportion of variation explained by the fitted line) and needed to be close to 1 for the better results. These statistical criterions can be calculated as follows:

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}\left(M_{R,cal,i} - M_{R,exp,i}\right)^2\right]^{1/2} \quad \ldots (6)$$

$$\bar{R}^2 = 1 - (1 - R^2)\frac{n-1}{n-p-1} \quad \ldots (7)$$

where 'p' is the total number of explanatory variables in the model (not including the constant term), and 'n' is the sample size. Eq. 7 can also be represented as:

$$\bar{R}^2 = 1 - \frac{SS_{res}/df_e}{SS_{tot}/df_t} \quad \ldots (8)$$

where 'df_t' is the degrees of freedom (n – 1) of the estimate of the population variance of the dependent variable, and 'df_e' is the degrees of freedom ($n – p – 1$) of the estimate of the underlying population error variance.

2.6. Effective Moisture Diffusivity (D_{eff})

Diffusion in solids is an important and the main transport mechanism involved in the moisture removal from foods. The overall diffusion phenomenon is combined into single term and named as effective moisture diffusivity (D_{eff}) (Erbay & Icier, 2010). Initially evaporation of water takes place through capillary action at a constant drying rate which is similar to the drying of free water on a surface. However, as the upper layers dry, a gradient among the upper and the underneath layers arise which leads to diffusion of water. This phenomenon is associated with the increase of product temperature (based on the surrounding temperature) and decline in the drying rate. Certainly, the concave form of drying curves is a result of variation of the moisture content and

D_{eff} during drying. Hence, the slopes of these curves can be derived from linear regression of ln(M_R)-t data (Mujumdar, 2014). D_{eff} varies mainly with the product's internal conditions such as temperature, moisture content, and structure. External factors such as air temperature and velocity on the other hand are insignificant in some ranges compared to the internal conditions. Therefore, for clarifying the drying characteristics of hemp buds, it is important to calculate D_{eff} (Erbay & Icier, 2010).

The analytical solution to Fick's second law was used for estimation of the effective moisture diffusion coefficient D_{eff} in hemp buds (Crank, 1979):

$$M_R = \frac{8}{\pi^2}\sum_{i=0}^{\infty}\frac{1}{(2i+1)^2}\, exp\left(-\frac{(2i+1)^2\pi^2 D_{eff}t}{4L^2}\right) \qquad \ldots (9)$$

where, M_R is the moisture ratio, L is the sample thickness, t is the temperature, and D_{eff} is the moisture diffusivity. The value of D_{eff} was used as an empirical parameter that characterises the drying rate, despite limited restrictions in the diffusion theory in describing the experimental drying data (Hamdami, Monteau, & Le Bail, 2004). The first five terms in the series expansion of Eq. 9 were considered in the least square fitting procedure (i = 0 to 4), since there was no change in the third decimal of $\overline{R}^2$ and RMSE beyond the fifth term (Lebovka, Shynkaryk, & Vorobiev, 2007).

2.7. Activation Energy (E_a)

The amount of energy required to initiate a chemical reaction is termed as activation energy (Martynenko & Janaszek, 2014). Physical and thermal properties of biological products, such as moisture diffusion, and activation energy, are necessary for the standard dryer design (Aghbashlo & Samimi-Akhijahani, 2008). The relationship between drying temperature, effective diffusion coefficient, and activation energy is determined by the Arrhenius model.

$$D_{eff} = D_{\infty} exp\left(\frac{E_a}{RT}\right) \quad \ldots (10)$$

where D_{∞} is the Arrhenius constant, E_a is the activation energy and R is the universal gas constant (8.314 J/mol/K). Therefore, the activation energy of drying was determined from effective diffusion coefficients at two different temperatures (25 ºC and 70 ºC) using the following equation (Martynenko & Janaszek, 2014):

$$\mathrm{E_a} = \mathrm{R} \ln\left(\frac{\mathrm{D_2}}{\mathrm{D_1}}\right).\frac{\mathrm{T_1 T_2}}{\mathrm{T_2 - T_1}} \qquad \ldots (11)$$

where, D_2 and D_1 are the moisture effective diffusion coefficients at 343.15 K (T_2, 70 ºC) and 298.15 K (T_1, 25 ºC) respectively. The value of E_a denotes the sensibility of the diffusivity against temperature. The greater value of E_a represents more sensibility of D_{eff} to temperature (Kaymak-Ertekin, 2002).

2.8. Quality Analysis

2.8.1. Cannabinoids Content

The analytical methods for cannabidiol content and terpenes profile were adopted from the published method of United Nations Office on Drugs & Crime with minor modifications (UNODOC, 2009).

An Agilent 1220 Infinite high-performance liquid chromatography (HPLC) coupled with an Agilent 1260 Infinity II Diode-array detector (DAD) was used for the analysis of cannabinoids.

Parameters:

- Column type: 250x4mm RP-8 (5 µm); pre-column 4x4mm RP-8 (5 µm)
- Injection: 10 / 20 µL
- Column temperature: 30°C
- Gradient Pump: Isocratic

- Mobile Phase: Acetonitrile : water (8:2 v/v).
- Flow: 1 ml/min
- Wavelength detection: 220 to 240 nm

Sample preparation and extraction:

Two grams of representative sample received was placed aside for calculating the moisture content (g/g). The remainder of the representative sample was dipped in liquid nitrogen and frozen before grinding. Then sample was ground and equilibrated to room temperature. One gram of the ground sample was weighed, ensuring that the liquid nitrogen has completely evaporated from the sample, and was added to a 50 mL Falcon tube. This sample was extracted (double extraction, 40x dilution) with 10 - 20 mL methanol/ methanol : chloroform (9:1 v/v) on a vortex for 15 - 20 minutes. The sample was then filtered using Whatman™ filter paper for 15 - 20 minutes. The double methanol extraction results in 99.5% extraction of the cannabinoids.

Calibration:

Stock solution: Nine Standard solutions- 100 µL each of Δ9-THC, CBD, Δ-8THC, CBC, CBG, CBN, THCV, THCA and CBDA.

Dilution 1: 100 µL stock solution in 900 µL methanol = 0.1 mg/ml.

Dilution 2: 100 µL of dilution 1 in 900 µL methanol = 0.1 mg/ml.

Quantifications of cannabinoids were achieved by comparing the ratio of sample/ISTD with the ratio of the external standard (ESTD)/ISTD at the target concentration. Retention time for CBD is 4.9 min at 220 to 240 nm wavelengths. Cannabinoid analysis results were reported individually as CBDA, CBD, and total CBD content (w/w %).

2.8.2. Terpenes Profile

An Agilent 7820A gas chromatographer (GC) coupled with an Agilent 7693 autosampler and flame ionization detector (FID) was used for the analysis of terpenes. An Agilent DB-5 column (30m x 0.250 mm, 0.25 micron) was used for the separation of terpenes.

GC parameters:

- Injection: 5/ 10 µL
- Equilibration time: 1.5 - 2 min
- Oven/column temperature:
    - Initial: 35 °C – hold 4 min
    - Ramp 1: 10 °C/min up to 105 °C – hold 0 min
    - Ramp 2: 15 °C/min up to 205 °C – hold 0 min
    - Ramp 3: 35 °C/min up to 270 °C – hold 5 min

FID:

- Heater: 340 °C
- Compressed gas flow: 400 mL/min
- H2 gas flow: 40 mL/min
- Make-up gas flow: 5 mL/min

Terpene certified reference materials (CRMs) were used as received (2.5 mg/mL, LGC standards and Sigma Aldrich). All gases used were obtained from Air Liquide.

Sample preparation:

Two grams of representative sample received was placed aside for calculating the moisture content (g/g). The remainder of the representative sample was dipped in liquid nitrogen and frozen before grinding. Then sample was ground and equilibrated to room temperature. One gram of the ground

sample was weighed, ensuring that, all the liquid nitrogen has evaporated from the sample, and was added to a 50 mL Falcon tube. This sample was extracted (double extraction, 40x dilution) with 20 mL methanol and vortexed for 20 minutes at 500 rpm. The sample was then filtered using Whatman™ filter paper for 20 minutes. The double methanol extraction results in 99.5% extraction of the cannabinoids. No further dilutions were performed, and 1 mL of the extract was pipetted into a clean GC vial for analysis.

Calibration:

Standards of 35 common terpenes found in hemp and cannabis, (α-pinene, Camphene, Sabinene, β-pinene, Myrcene, α-phellandrene, 3-carene, α-terpinene, p-cymene, Limonene, Eucalyptol, Ocimene, g-terpinene, Sabinene, Hydrate, Terpinolene, Linalool, Fenchol, Camphor, Isoborneol, Borneol, Menthol, α-terpineol, Nerol, Pulegone, Geraniol, Geranyl Acetate, α-cedrene, β-Caryophyllene, α-Humulene, Valencene, Nerolidol, Caryophyllene Oxide, Guaiol, Cedrol, α-bisabolol), were prepared, at 7 different concentrations of 1 to 25 µg/mL to obtain a 7 points calibrations curve for the terpene quantification.

Quantifications of terpenes were achieved by comparing the ratio of sample/ISTD with the ratio of ESTD/ISTD at the target concentration. Terpene analysis results were reported as total terpenes content (w/w%). The methods have been validated by Perennia (www.perennia.ca) in Truro.

2.8.3. Color

Color of medicinal and aromatic plants is considered as a primary quality criterion to the consumers, who prefer the buds with a natural appearance. Degradation of color or browning can be indirectly related to quality deterioration due to enzymatic reactions caused by the activity of polyphenol oxidase (PPO) during postharvest handling (Argyropoulos & Müller, 2014a, 2014b).

For color measurements of food, CIELAB *L*, a*, and b** values were used, where *L** represents the sample lightness and darkness, with 100 being very white and 0 being dark; *a** value measures green to red, with -50 being totally green and +50 being totally red; and b* represents blueness to yellowness on a scale -50 to +50 (Nourian & Ramaswamy, 2003; Siriamornpun, Kaisoon, & Meeso, 2012). The *L, a, b* model was developed such that the amount of numerical change in these values resembles to nearly the same amount of visually perceived change. From the *L*, a*, b** values, the total color difference (ΔE) among fresh material and the products dried at different drying conditions is used (Eq. 12) to quantify the color and its changes. Delta (Δ) symbol represents the difference of the fresh material value from the dried sample measured value.

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad \ldots (12)$$

The L^*, a^*, *and* b^* values were measured by using color grab mobile app (www.loomatix.com, version 3.6.1, 2017). Color measurement was carried out inside a specially designed Styrofoam box (30*15*20 cm) (Figure 17Figure 17 Experimental setup for color measurements) equipped with constant illuminating LED array. The inner walls were completely covered with a black cloth to avoid reflections of light. On the top surface, a small opening was allowed for the mobile camera (OnePlus 6t, 16 + 20 MP Dual camera) to capture the image. Samples were placed inside the box and was covered with the lid. The light intensity was adjusted to 300 lux using a potentiometer and a digital lux meter (HDE, Allentown, Pennsylvania), while the mobile camera was placed at the opening. Measurements of color were done for fresh (control) and dried samples of each treatment each with two repetitions. The total color difference (ΔE), between fresh material and the products dried at different drying conditions, was then calculated from the observed L^*, a^*, b^* values.

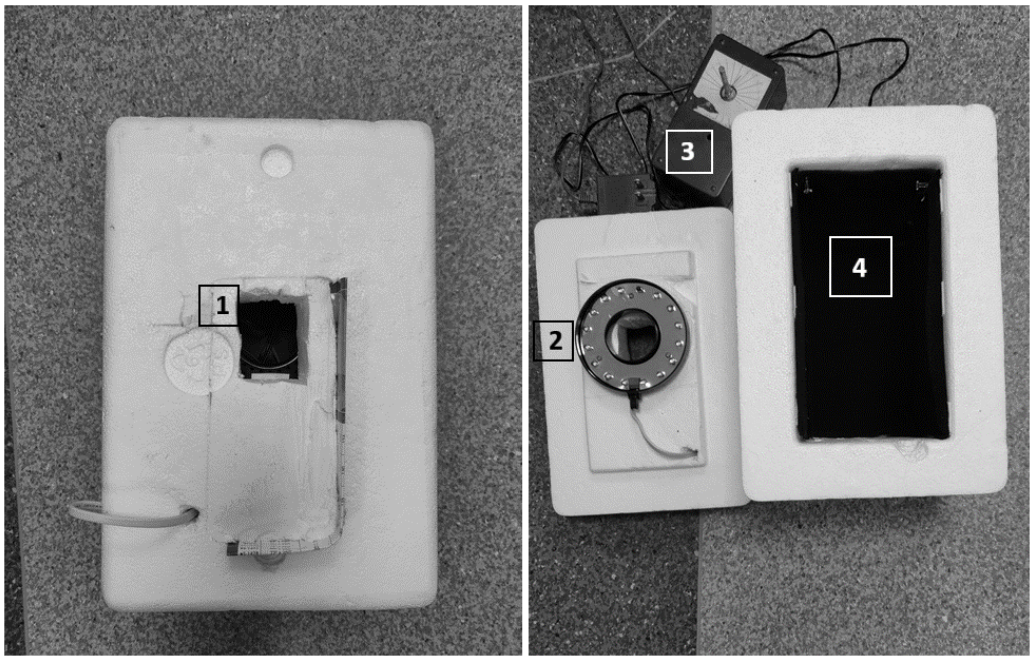

Figure 17 Experimental setup for color measurements; 1. Mobile camera opening, 2. LED array, 3. Power regulator, 4. Black inner walls where samples were placed.

2.9. Specific Energy Consumption

Specific energy consumption is defined as the energy consumed for evaporating 1 kg moisture from hemp buds. It is one of the important parameters that determine drying efficiency when economic aspects are important. It was introduced by (Kudra, 2004) and further used in a number of research publications. It is calculated by the formula (Soysal et al., 2006),

$$Q_s = \frac{t_{on} \times P \times 10^{-6}}{m_w} \qquad \ldots (13)$$

where, Q_s is the specific energy consumption (MJ/kg [H_2O]), t_{on} is total power-on time (s), P is the total power (MJ/s) and m_w is the total mass of water removed (kg).

The specific energy consumption (Q_s) of drying for all the experiments was calculated using the power consumption data measured via a wall power meter (Megapower, China). The Power (W) observed for each drying method and the total drying time have been used to calculate the total energy consumption. The moisture removed from hemp buds from an initial moisture of 65%

(since average initial moisture of hemp buds is ≈ 65%) to a final moisture of 10%, was assumed to be constant in all the drying treatments. The specific energy consumption was thus calculated by dividing the total energy with the total moisture removed (0.055 kg).

2.10. Statistical Analysis

A completely randomized design (CRD) was used to carry out drying experiments. All the isothermal drying experiments at different temperatures were conducted randomly followed by non-isothermal drying experiments. Freeze drying experiments were conducted simultaneously. Considering the short harvest period available, thereby for conducting the experiments, and keeping in mind the costs for analysing CBD and terpenes content, there was very little possibility to conduct experiments with more than two repetitions. However, the results that showed high CBD content were again verified with two replications as mentioned in section 3.5. The effect of the 11 drying conditions on total CBD content (%), and total terpenes content (%) was determined using one-way analysis of variance (ANOVA). The validity of the model assumptions (normal distribution and constant variance of the error terms) for each response was verified by examining the residuals (Montgomery, 2017). To verify the normal distribution assumption, normal probability plot of the residuals and the Anderson–Darling test for normality were used. To verify the constant variance assumption, plot of the residuals vs. fitted values was used. Independence assumption was ensured by randomization. Since the effect of drying temperature on the total terpenes content was significant ($P < 0.05$), multiple means comparison was conducted using Fisher's least significant difference (LSD) test at 5% level of significance to compare the total terpenes content among each treatment. For color, analysis of variance was used to compare the mean ΔE values at 5% significance level. The analysis was carried out using Minitab software (Minitab LLC, 2019).

Chapter 3. Results

3.1. Desorption Isotherm

The mean equilibrium moisture content (EMC) values of the corresponding water activity (a_w) that were determined from a triplicate experiment for the hemp buds are presented in table 5. The average standard deviation for these measurements was calculated to be 0.058 g/g (X_{db}). Overall, the precision of EMCs for all the RH values was satisfactory. Each sample inside the jar was left for more than 24 hours to attain equilibrium with the RH environment with periodic weight measurements. The reason for any considerable deviations could be inferred from the prolonged time to reach equilibrium and minor variations in the room temperatures.

Table 5 Experimental sorption data for hemp buds from triplicate experiment

Water activity (a_w) (RH/100)	Mean EMC (X_{db} - g/g)
1	1.691 ± 0.031
0.85	0.897 ± 0.159
0.75	0.750 ± 0.055
0.65	0.457 ± 0.071
0.54	0.364 ± 0.071
0.44	0.236 ± 0.014
0.23	0.198 ± 0.04
0.11	0.125 ± 0.23

Further, the experimental data was fitted adequately with the GAB equation to estimate the EMCs corresponding to various relative humidity target values. The values of the results (points) and

predicted curves (solid lines) for hemp buds at 22 ± 1 ºC was illustrated in Figure 18 and the parameter values were provided in table 6. The model was in good fit with the experimental data with $\bar{R}^2$ value being 0.96901 and RMSE of 0.09076. The obtained curves represent the characteristic sigmoid shape isotherm indicating the diffusion limited transfer between the material and the environment. The EMC values calculated by the model for the hemp buds at the safe water activity of 0.6 was 0.428 g/g d.b. In other words, to avoid microbial growth during drying at 22 °C, the hemp buds are recommended to be dried to a moisture content of 30% wet basis at the earliest possible time, and further, for a safe preservation at 0.2 a_w, the buds should be dried to a moisture content of 9 % w.b. (or 0.096 g/g) (Argyropoulos, Alex, & Müller, 2011; Roos, 2007). The EMC at 0.6 a_w will drop by about 0.5% for every increase of 10 °C air temperature, at a constant relative humidity of air (Bala & Bala, 1997), however, the extreme a_w values do not have much effect, such as at 0.2 a_w. The reported mold growth in certain cases (George-Cosh, 2018) during drying/ in the end product could be due to a considerable lag period to dry the buds after their harvest. Also, due to the prolonged drying methods, where moisture content of the material is more than 30% for a considerable period encouraging mold growth, or due to the incomplete drying of a fraction of product.

Table 6 GAB model parameters for desorption isotherm

M_0	K	C	Adjusted R^2	RMSE
0.53091	0.8046	0.98518	0.96901	0.09076

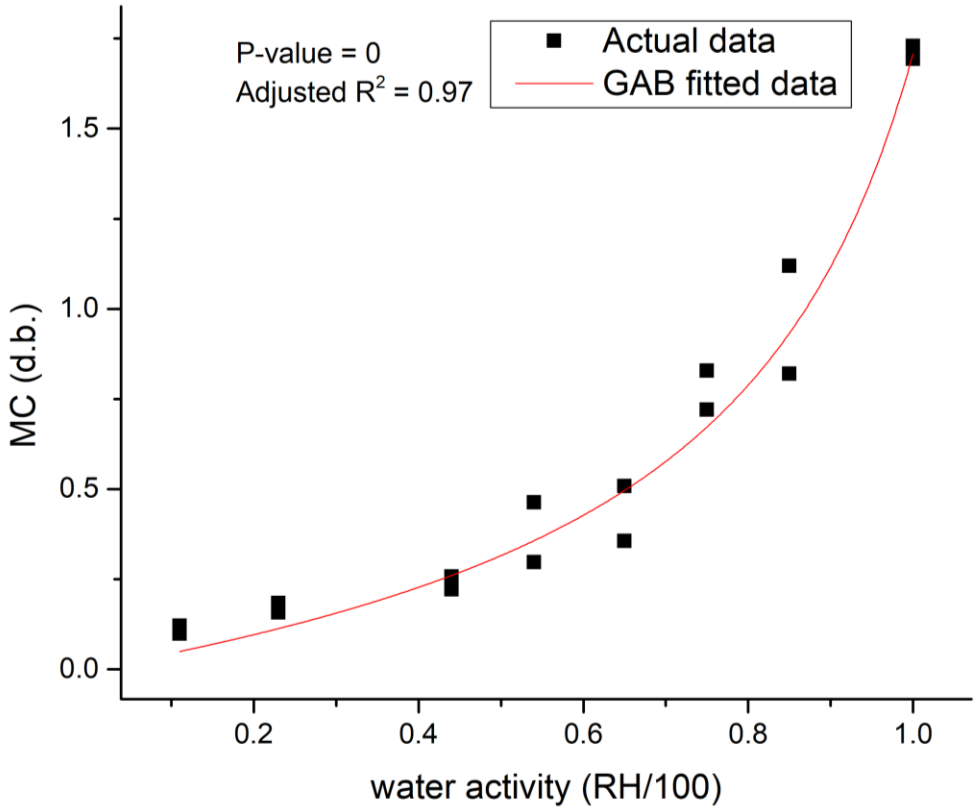

Figure 18 Desorption isotherm of hemp buds at 22 ±1 ºC, fitted using the GAB model.

3.2. Effect of Temperature on the Drying Time

3.2.1. Isothermal Convective Drying

Drying kinetics of hemp buds was presented in Figure 19 as the decrease of the moisture ratio (M_R) versus time (h) as influenced by different temperatures (25, 32, 40, 50, 60, 70 ºC). The models used moisture ratio M_R such that all the samples would have the same initial moisture content. With the increase of temperature by 10 ºC, the drying time to reach the final moisture of 0.10 ± 0.005 g/g nearly reduced to half. It was the longest (51 ± 0.2 h) at 25 ºC and the shortest at 70 ºC (3 ± 0.2 h). Compared to the control (32 ºC), drying at 70º C is 12.6 times shorter, saving 92 % of the time. Drying rate in the initial stages was rapid, loosing considerable amounts of moisture, however, the rate decreased exponentially in the later stages particularly at low temperatures

(below 40 ºC). This exponential behavior of the drying kinetics indicated that moisture transfer of hemp buds is diffusion-limited, governed by Fick's law (Lebovka et al., 2007).

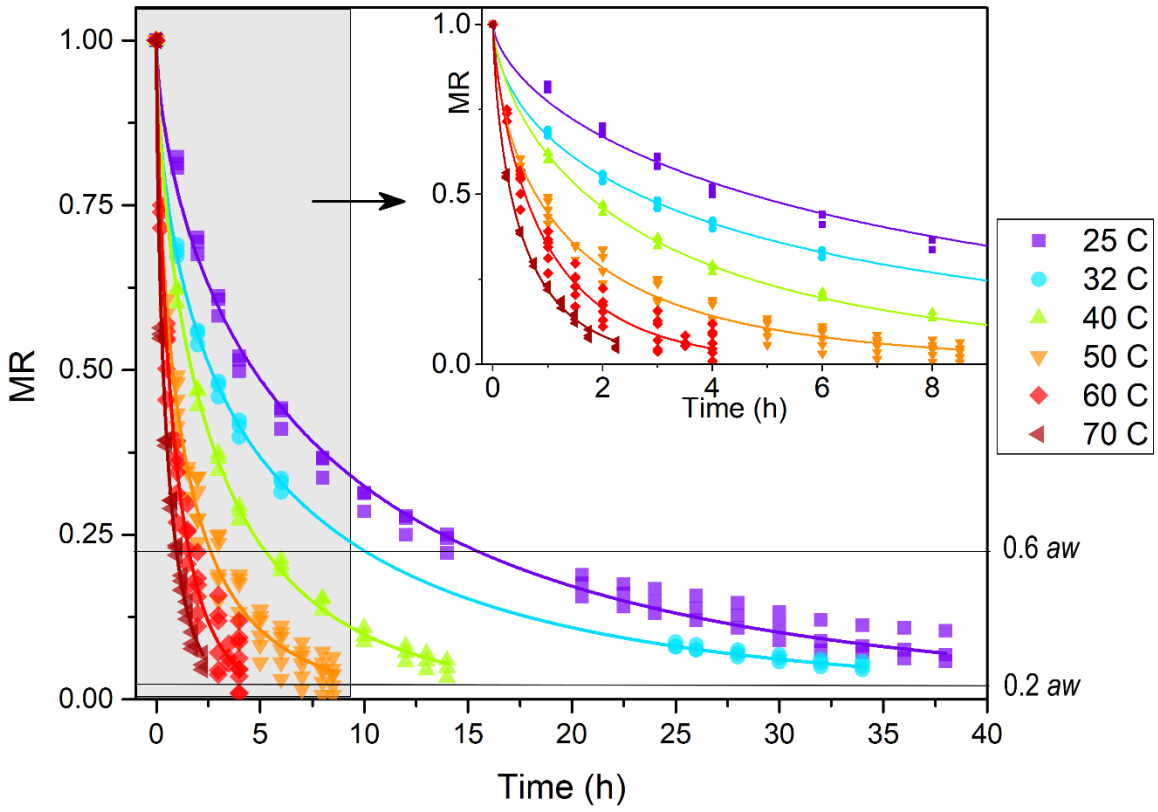

Figure 19 Moisture ratio versus time at different temperatures, comparing experimental curve with the predicted one (—) through Page model [Model 2] for Hemp (*Cannabis sativa* L.) buds.

3.2.1.1. Mathematical Modelling

The results of the statistical computations for the convective drying data are shown in Figure 19, where the dots represent the original data and the curved lines represent fitted values. The fitting ability of 5 drying models expressing the changes in the moisture ratios with drying time are presented in the appendices as the values of the coefficients and statistical parameters found for the respective models. Among all the drying models used in this study, the Page model and Midilli model gave the best fit for all the experimental data point. However, Page model was only

considered since it is simpler among the two. This model represented the experimental values satisfactorily with an average $\bar{R}^2$ value of 0.994 and the RMSE of 0.019. The drying coefficient k increased with the increase of drying temperature. These results agree with the drying rate data, which follow the similar trends.

3.2.1.2. Effective moisture Diffusivity (D_{eff}) and Activation Energy (E_a)

The calculated diffusivity values for each drying temperature were provided in Table 7 and the fitted lines were presented in Figure 20. Diffusivity increased with the increase of drying temperature hitting maximum at 70 ºC. D_{eff} value was observed lowest (2.83×10^{-8} m^2/s) at 25 ºC highest ($4.66\times10^{-7} m^2/s$) at 70 ºC temperature. Therefore, the effect of drying temperature on D_{eff} is critical. These values agree with the diffusivity values of foods that are dried in a convective type batch dryer, where 86.2% of D_{eff} values of the foods were in the region 10^{-10} to 10^{-8} m^2/s (Erbay & Icier, 2010). Whereas the overall D_{eff} values of foods dried using various drying methods were in the range of 10^{-12} to 10^{-6} m^2/s. Since, drying of hemp was carried out at higher temperatures (> 50 ºC) the diffusivity values were comparatively higher.

Table 7 Values of calculated moisture effective diffusion coefficient (D_{eff}) at different temperatures

Drying temp (ºC)	D_{eff} **(m^2/s)**
25	2.83E-08
32	4.35E-08
40	8.40E-08
50	1.61E-07
60	2.77E-07
70	4.66E-07

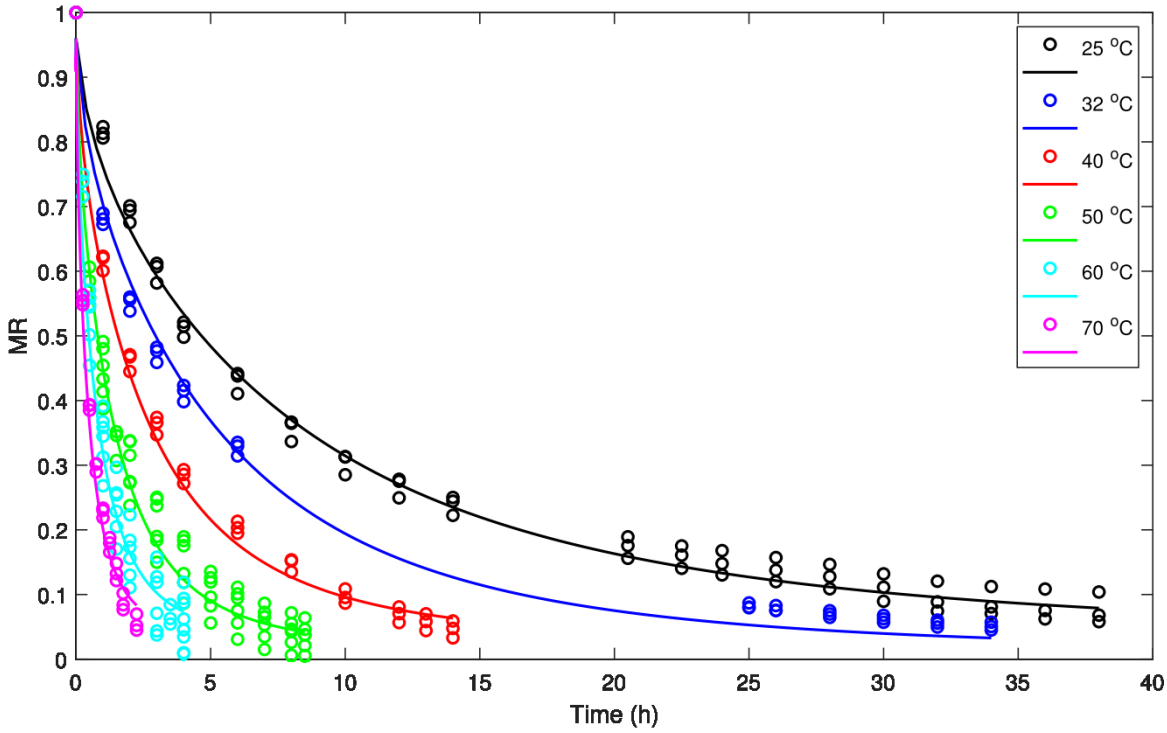

Figure 20 Moisture ratio versus time at different temperatures, comparing experimental curve with the predicted one (—) through Fick's second law for obtaining effective moisture diffusion coefficient 'D_{eff}' for Hemp (*Cannabis sativa* L.) buds.

This explains the reason for the long drying periods at low temperatures and rapid drying at high temperatures in hemp buds.

The activation energy, calculated from eq. 11 for hemp buds was 63.70 ± 1 kJ/mol. This value is relatively high when compared with the values of 41 different food and medicinal products where the activation energies were in the range of 12.32 to 82.93 kJ/mol and of that 80.5 % were accumulated in the range of 18 to 49.5 kJ/mol (Erbay & Icier, 2010). The activation energy of some of the herbs such as for drying thyme (*Thymus vulgaris L.*) was 73.84 kJ/mol (Doymaz, 2011), 43.129 kJ/mol for *Phyllanthus amarus* (Sousa et al., 2018), 53.51 kJ/mol for lemon balm *(Melissa officinalis L.*) (Argyropoulos & Müller, 2014a), 28.36 kJ/mol for carrot (Doymaz, 2004), and 23.42 kJ/mol for apple (Martynenko & Janaszek, 2014). Comparatively, the E_a value of hemp buds is high, showing high sensibility of D_{eff} to temperature (Kaymak-Ertekin, 2002). These

activation energy values are helpful in designing an ideal dryer for hemp and for modelling the mass transfer processes such as dehydration or moisture adsorption during storage.

3.2.2. Non-Isothermal Convective Drying

The drying curves corresponding to standard drying, for drying air temperatures of 40, 60 and 70 °C, and stepwise drying combination of 40/60 °C and 40/70 ºC at two change points, 25% and 45% moisture content (w.b.) are presented in Figure 21 and Figure 22.

A considerable decrease in the drying time in case of stepwise drying was observed, compared to the 16 hour conventional drying at 40 ºC to reach 10% mc. Drying time was observed to be shortest for 40/70 ºC changed at 45% mc which took 4 hours, followed by 40/60 ºC changed at 45% mc that took 4.5 hours. This was followed by 40/70 ºC and 40/60 ºC changed at 25% with 6 h and 7 h respectively. This process is still diffusion limited. Temperature increased the diffusion inside the material, which led to faster drying.

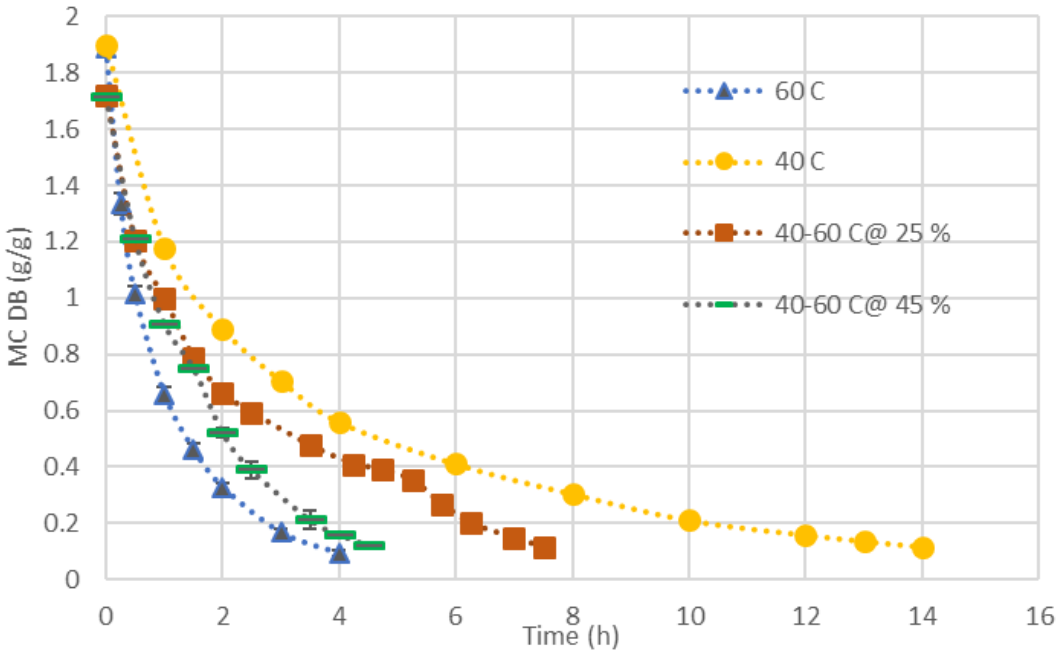

Figure 21 Non-isothermal drying 40/60°C at 25% & 45% moisture content and isothermal convective drying at 40, 60°C.

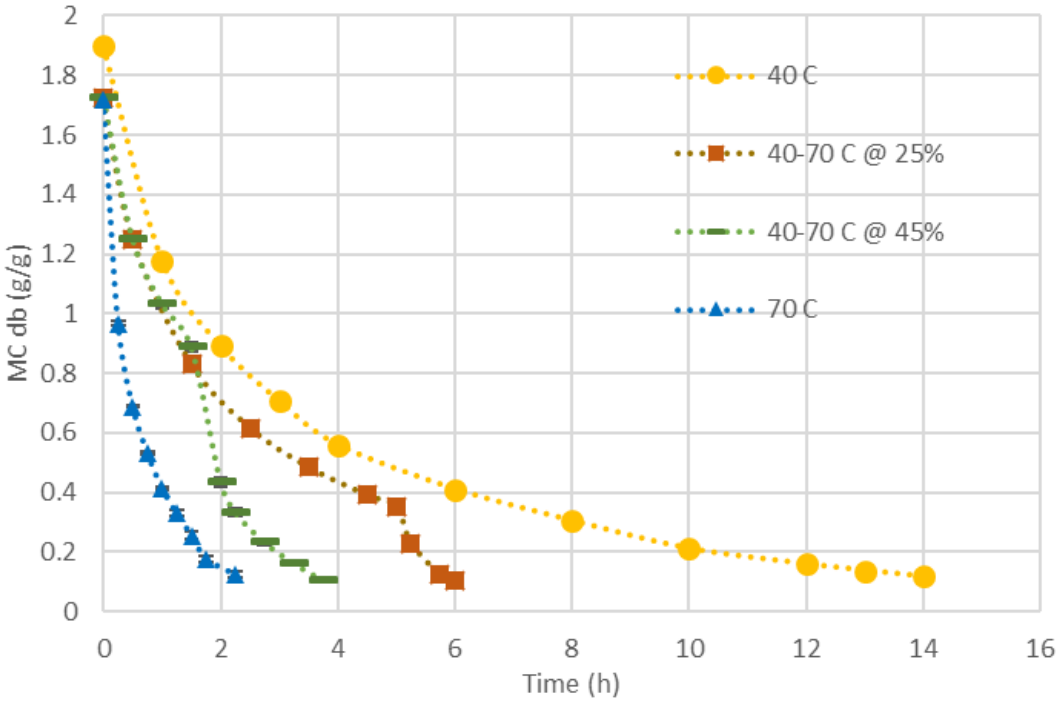

Figure 22 Non-isothermal drying 40/70°C at 25% & 45% moisture content and Isothermal convective drying at 40, 60°C.

3.2.3. Freeze Drying

Effect of freeze drying on drying time was compared with standard convective drying at 32, 40, 60, and 70 ºC temperatures. The moisture content on dry basis (g/g) versus time (h) curves for freeze drying, and convective drying, were shown in Figure 23. Freeze drying which dries the product at relatively lower temperatures (from 15 to 50 °C; at 0.046 to 0.053 kPa pressure) took 7.5 h to reach the moisture content of 10%, whereas in case of convective drying it took 38 h, 16 h, 4 h, and 3 h, at 32, 40, 60, and 70 ºC, respectively.

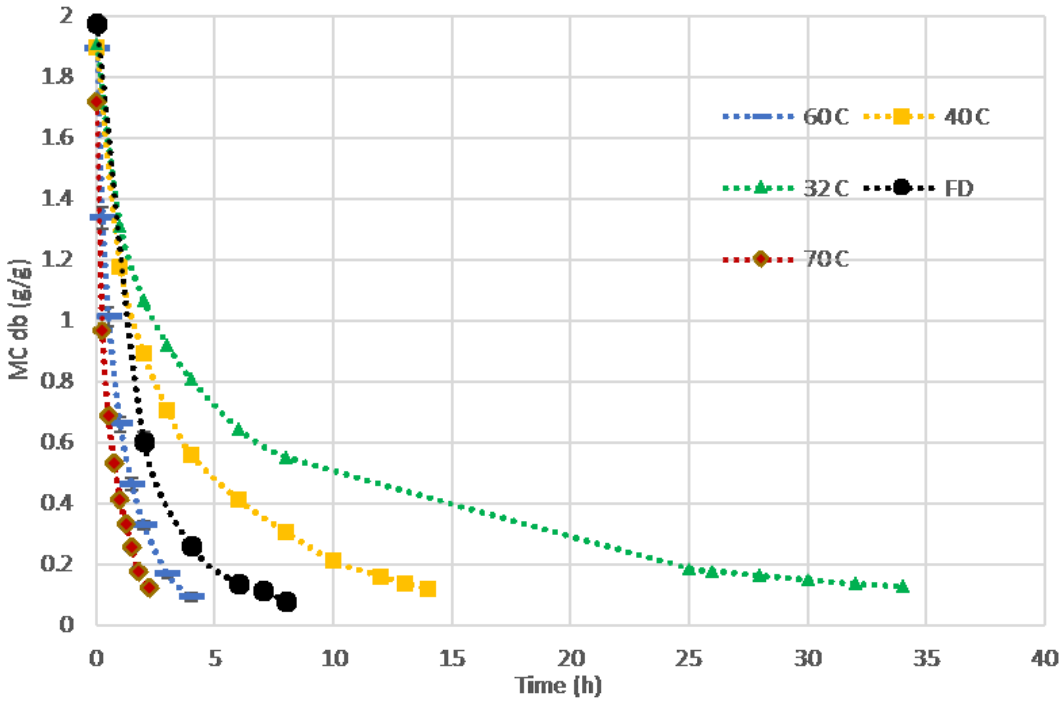

Figure 23 Drying curves (Moisture content on dry basis [g/g] vs. time [h]) of freeze drying as compare to isothermal convective drying at 32, 40, 60, 70 °C.

3.3. Effect of Temperature on the Quality

3.3.1. Cannabidiol (CBD)

The percentage contents of total CBD, which include (CBDA + CBD) in the samples dried at various drying conditions are presented in Table 8. ANOVA results showed no significant difference among the mean total CBD content dried at various temperatures. This shows that drying temperatures do not have a negative effect on the total CBD content as assumed. The total CBD content was observed to be maximum at 70 ºC and least at 50 ºC in isothermal convective drying (Figure 26).

Cannabidiol is the major cannabinoid responsible for the exceptional properties of hemp. Industries have been drying hemp at lower temperatures for 3 to 5 days considering that the CBD

could be lost at higher temperatures. Therefore, these results construct a strong evidence disproving the assumption.

Along with the total CBD (CBDA + CBD) content, CBD alone (decarboxylated/ neutral form) was evaluated individually, since CBD alone showed a steady increase with increase of temperature (Figure 25). ANOVA results showed there is no significant difference among the mean CBD alone values. This concludes that decarboxylation (CBDA to CBD) process occurred with increase of temperature and was maximum at 70 ºC.

CBDA content was also analysed separately using the ANOVA and the results showed no significant difference among the mean values at various drying conditions. CBDA behaviour with drying temperature was similar to the total CBD content with a slight variation due to the change in the proportion of CBDA to CBD (Figure 24). The decarboxylation effect in the product does not play any prominent role, as the ratio of CBD to CBDA has only changed but not the total CBD content. The proportion of CBD to CBDA ((CBD/CBDA)*100) at 32 °C was 4.21 and increased gradually with increase of temperature and was maximum at 70 °C (10.41). Whereas, in fresh material it was observed to be 8.56.

Table 8 Values of essential compounds at different drying conditions; *Fisher's grouping; values that do not share a letter are significantly different at a probability, $P \leq 0.05$.

Sample	CBDA (%)	CBD alone (%)	Total CBD (%) [(CBDA × 0.877) + CBD]	St. dev T. CBD	Terpenes (%)	St. dev Terpenes
Fresh	1.99	0.17	1.91	0.598	0.93^{a*}	0.195
25 ºC	2.09	0.12	1.96	0.487	$0.34^{b,c}$	0.015
32 ºC	2.22	0.09	2.04	0.144	0.38^{b}	0.015
40 ºC	2.23	0.12	2.07	0.152	$0.32^{b,c}$	0.015
50 ºC	1.99	0.16	1.90	0.283	$0.26^{d,e}$	0.03
60 ºC	2.08	0.20	2.02	0.263	$0.25^{e,f}$	0.005
70 ºC	2.52	0.26	2.47	0.479	$0.22^{f,g}$	0.005
FD	1.36	0.08	1.28	0.117	$0.30^{c,d}$	0.015
40/60 ºC at 45%	1.80	0.12	1.69	0.095	$0.22^{f,g}$	0.015
40/60 ºC at 25%	1.82	0.19	1.78	0.264	$0.22^{f,g}$	0.005
40/70 ºC at 45%	1.84	0.23	1.84	0.217	0.21^{g}	0.005
40/70 ºC at 25%	3.03	0.23	2.78	0.121	$0.24^{e,f,g}$	0.005

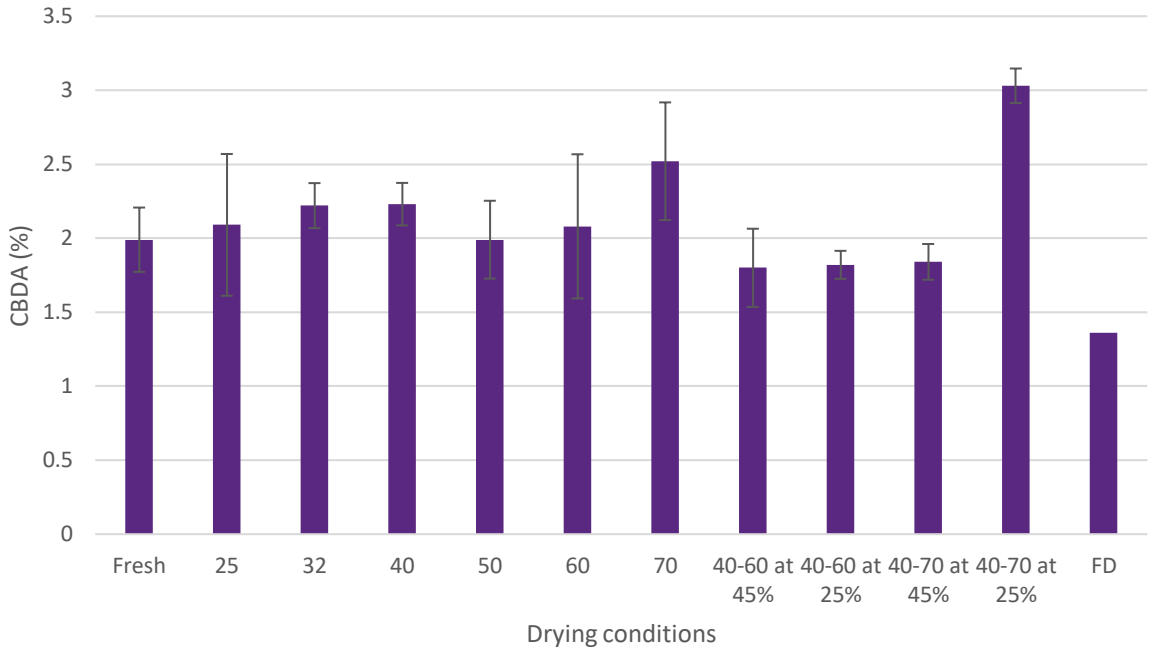

Figure 24 CBDA content (%) at different drying conditions with the standard deviations.

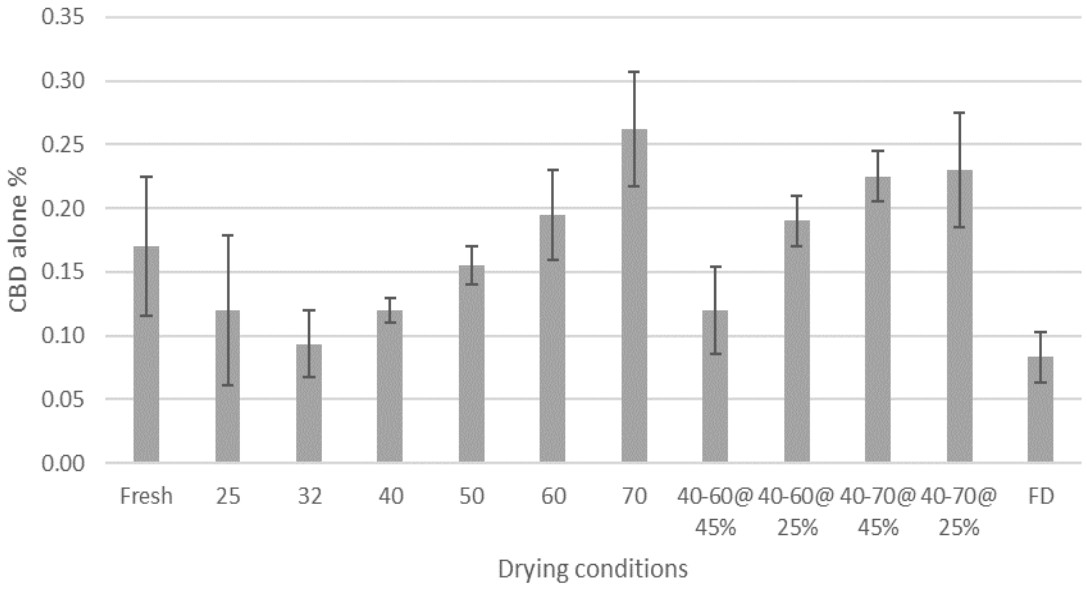

Figure 25 CBD alone content (%) at different drying conditions with the standard deviations.

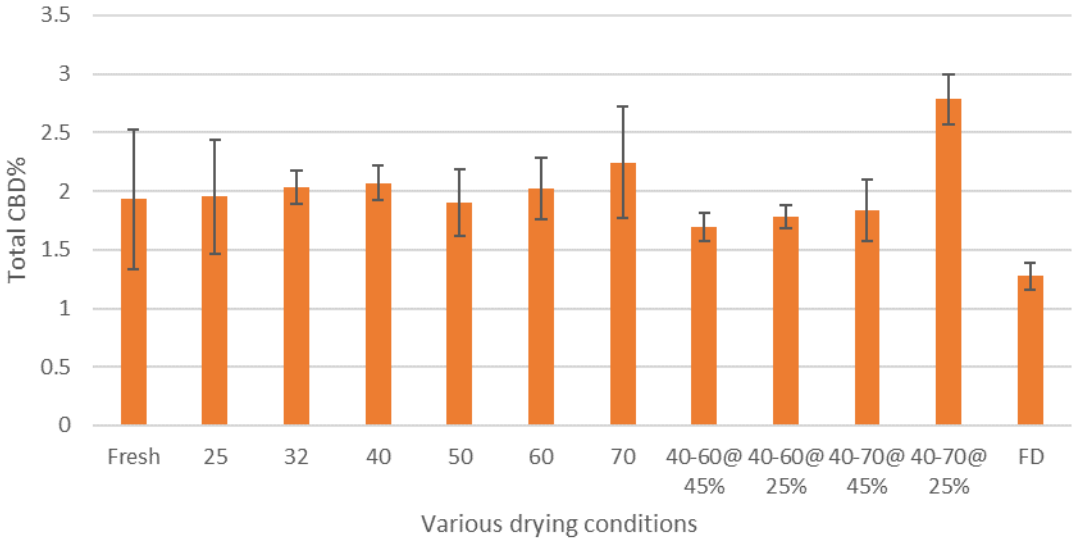

Figure 26 Total CBD content (%) at different drying conditions with the standard deviations

In non-isothermal drying, total CBD along with CBD alone and CBDA followed trends similar to isothermal convective drying (Figure 24, 25, 26). Nevertheless, the total CBD content was maximum (2.78%) at 40 - 70 ºC changed at 25% moisture content, which is the highest compared to all other drying conditions. Total CBD content at other non-isothermal conditions was lower than convective drying at 40, 60 and 70 ºC. CBD alone on the other hand was maximum when temperatures were 40/ 70 ºC at 25% and 45% MC (0.23%, 0.23%). In case of freeze drying, the total CBD, and CBD alone was observed to be the lowest (1.28%, 0.08, respectively).

3.3.2. Terpenes Content

The total terpenes content (%) at various drying conditions was provided in Table 8 and the content of 12 major terpenes observed in fresh hemp against various drying conditions was presented in table 9. Analysis revealed that there is a significant difference among the fresh material and the dried samples. Mean terpenes content in the fresh samples was observed to be 0.925% (Figure 27Figure 27), whereas the highest terpene content in the dried samples stood at 0.38% dried at 32

ºC temperature. As the temperature increased, total terpene content decreased significantly and was observed lowest at 70 ºC. Multiple mean comparisons showed that, there is a significant difference among the terpenes content at low temperatures (25, 32, 40 ºC, and FD) and high temperatures (50, 60, 70 ºC).

The major sesquiterpenes observed in the fresh hemp were caryophyllenes, and the monoterpenes were pinenes, myrcene, limonene and sabinene, which contributed to almost 95% of the total terpenes and of these, 85% were again caryophyllenes. The behaviour of individual terpenes was analysed and were grouped based on their evaporation behavior against drying temperature. Terpenes such as caryophyllene oxide (average content among all the drying conditions is 0.16% or 1.6 mg/g; standard deviation- 0.01%) , sabinene (0.01%; SD- 0.001%), and α-terpinene (0.002%; SD- 0.0002%), ocimene (0.001%; SD- 0.0001%), α-humulene (0.001%; SD- 0.0001%) were decreased with drying but stable with the increase of drying temperature. Terpenes such as, myrcene (0.006%; SD- 0.0005%), terpinolene (0.006%; SD- 0.0002%), α-pinene (0.02%; SD- 0.002%) and β-caryophillene (0.03%; SD- 0.001%) decreased gradually with the increase of temperature. Terpenes such as, Guaiol, Nerlidol, g-terpinene, geranyl acetate, p-cymene, linalool were almost completely evaporated with drying, leading to a significant decrease. All the remaining terpenes that were analysed were not observed in fresh hemp samples itself.

Table 9 List of 12 Major terpenes observed in the hemp buds and their content at various drying conditions (mg/g)

Sample	Caryophyllene oxide	Geranyl acetate	β-caryophyllene	α-terpineol	α -pinene	Sabinene
fresh	5.79	0.62	0.54	0.44	0.41	0.14
FD	1.53	0.02	0.5	0.03	0.31	0.135
25 °C	1.91	0	0.46	0	0.31	0.06
32 °C	1.86	0.225	0.4	0.13	0.2	0.085
40 °C	1.68	0.06	0.38	0.08	0.22	0.09
50 °C	1.43	0.11	0.25	0.1	0.12	0.085
60 °C	1.665	0.02	0.135	0.02	0.1	0.08
70 °C	1.19	0.02	0.1	0.025	0.105	0.085
Sample	**Terpenolene**	**β-pinene**	**Humulene**	**Limonene**	**Myrcene**	**α-terpinene**
fresh	0.135	0.135	0.12	0.1	0.085	0.045
FD	0.19	0	0.25	0.025	0.11	0.015
25 °C	0.03	0	0.095	0	0.1	0
32 °C	0.085	0.055	0.105	0.03	0.1	0
40 °C	0.05	0	0.1	0.03	0.06	0.03
50 °C	0.01	0.01	0.06	0.025	0.015	0.02
60 °C	0.01	0	0.035	0.015	0.005	0.015
70 °C	0.03	0.025	0.035	0.03	0.025	0.025

Hence, it should be noted that, the drying itself has a negative effect on the total terpene content and were significantly low especially above 40 °C. Terpenes play a significant role in the quality especially in building up the aroma of the product. Many customers prefer the product with high terpenes content especially for smoking purposes as they generate the characteristic smell of hemp

(and cannabis). Hence, the whole drying method solely lies on the type of product that is being dried for. If the terpenes are to be considered as a primary quality criterion by the industry, then drying at lower temperatures ideally at 40 ºC is recommended since terpenes losses were significantly high above 40 °C and dried quickly compared to the control (32 °C).

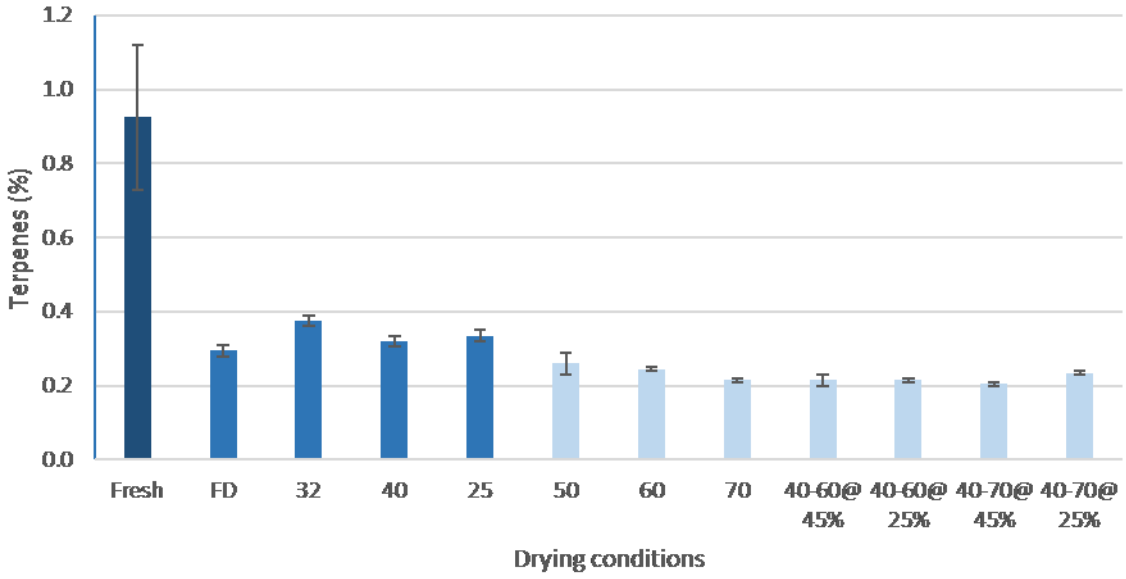

Figure 27 Total terpenes content (%) for various drying conditions with the standard deviations.

3.3.3. Color

Results from color analysis of the fresh and dried hemp buds were provided in Table 10 and the photographs of dried samples at various temperatures was provided in Figure 28**.** Low ΔE values represent low color difference between the fresh and the dried product. ANOVA results showed that, there is no significant difference among the mean L*, a*, b*, and ΔE values. Overall, the mean ΔE values were low at high temperatures and vice versa compared to the fresh material. These results were in accordance to the total CBD content. Since, color deterioration is a measure

of heat sensitive properties, this could also be a potential evidence that, CBD and other bio-actives were retained even at higher temperatures.

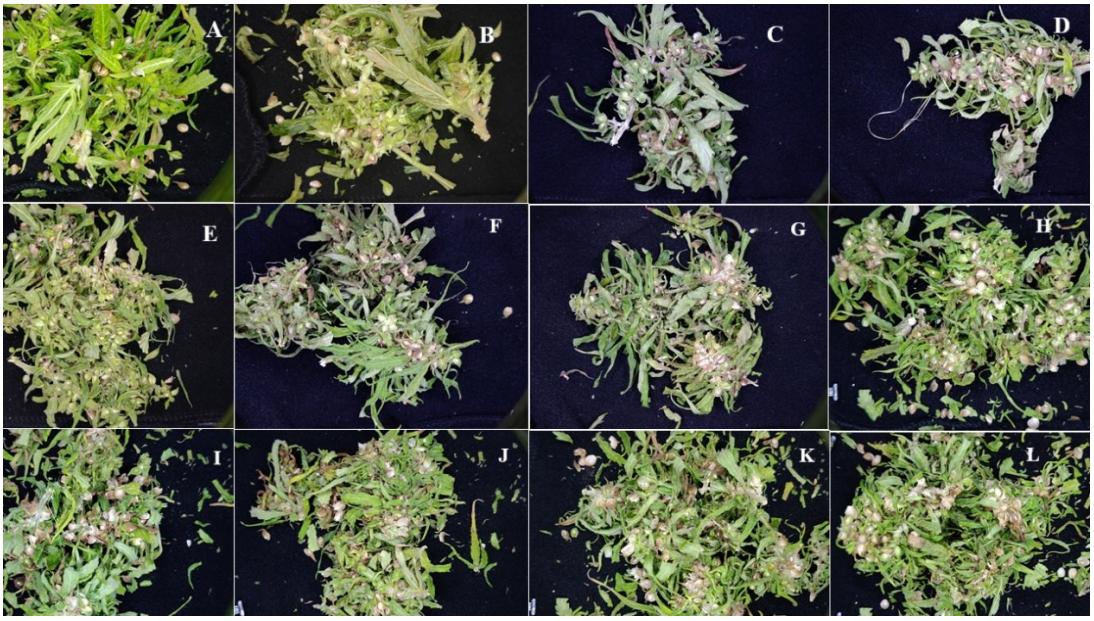

Figure 28 Fresh and dried hemp samples; A. Fresh, B. Freeze dried, C. 25ºC, D. 32ºC, E. 40ºC F. 50ºC, G. 60ºC, H. 70ºC, I. 40/60ºC@25%, J. 40/60ºC@45%, K. 40/70ºC@25%, L. 40/70@45%

Table 10 Mean values of L*, a*, b* and E values for samples dried at different drying conditions

Sample	L*	a*	b*	ΔE
fresh	93.65	-5.05	9.7	
FD	77.8	-9	14.9	17.14249
25 C	87.4	-11.75	22.65	15.86364
32 C	86.1	-3.2	4.55	9.324564
40 C	97	-5.7	12	4.115216
50 C	84.3	-4.05	8.15	9.530215
60 C	92.1	-5.7	10.8	2.008731
70 C	91.5	-5.3	10.7	2.384324
40/60 45%	87.9	-5.5	9.1	5.798707
40/60 25%	83.4	-1.8	11	10.8312
40/70 45%	80.6	-12.6	18.6	17.50757
40/70 25%	79.65	-11.9	20.55	18.99066

Highest mean L* value was observed at 40 ºC and least for freeze dried product. Highest mean a* value was observed at 25 ºC and least at 40/70 ºC at 45% MC. Highest mean b* value was observed at 25 ºC and least at 50 ºC. Overall, the mean total color difference (ΔE) was least for 60 and 70 ºC samples and were highest for 40/70ºC at 25% and freeze-dried samples compared to the fresh sample. Samples dried at 25 ºC, non-isothermal 40/70 ºC @ 25 MC and freeze dried showed a notable variation compared to fresh sample with low L*, a* values and high b* value but were insignificant. However, visually, freeze dried product was observed more relatable with the fresh product compared to other samples (Figure 28).

3.4. Specific Energy Consumption

Specific energy consumption and drying time were analysed by comparing the values for isothermal drying at 32 ºC with other drying conditions (Table 11). It can be observed that both the drying time and energy consumption increased as drying temperature decreased. In non-isothermal drying, drying time and energy consumption are low when change points are at 45% (mc w.b.). For isothermal drying at 32 ºC, the specific energy consumed was 16,291.64 MJ/kg(H_2-O), whereas at 70 ºC and non-isothermal 40/70ºC@25%, the consumptions were 1,286.18 MJ/kg and 2572.4 MJ/kg respectively. The reduced energy consumption is 12.5 and 6.5 times less, with 92.1% and 84.2% savings, respectively. Freeze drying, at a given drying time (7.5 h), consumed double the energy (6381.82 MJ/kg) compared to convective drying (3215.45 MJ/kg).

Table 11 Specific energy consumption (MJ/kg) Power consumed (MJ), and drying time (h) for each drying condition

Drying condition	Drying time (h)	Power (MJ)	Specific energy consumption (MJ/kg)
70 ºC	3	70.7	1286.2
60 ºC	4	94.3	1714.9
40/70 ºC@45%	4	94.3	1714.9
40/60 ºC@45%	4.5	106.1	1929.3
40/70 ºC@25%	6	141.5	2572.4
40/60 ºC@25%	7	165.1	3001.1
50 ºC	9	212.2	3858.6
40 ºC	16	377.3	6859.6
32 ºC	38	896.0	16291.6
25 ºC	51	1202.6	21865.1
FD	7.5	351.0	6381.8

3.5. Verification of the Results

It was expected that, the freeze drying, or low temperature drying methods would possibly show better results since traditional drying methods have adopted low temperatures. Since, the results obtained were in contrast with the literature, fresh samples of hemp buds were again harvested, mixed, and were divided into 8 equal batches (100 g ± 1/ batch). Then convective drying at 70 ºC, 40 ºC/70 ºC at 25% mc, and freeze-drying experiments were carried out in duplicates and were compared with the CBD content of fresh material. The results showed similar trends with maximum CBD content being in non-isothermal 40 ºC/70 ºC at 25% mc condition.

3.6. Discussion

Increase of temperature by 10 ºC in convective drying nearly reduced the drying time to half, to reach the final moisture of 0.10 ± 0.005 g/g of hemp buds. This shows that, temperature had a great influence on the drying rate. These outcomes are obvious and agree with numerous literatures concerning drying of foods. The prolonged exponential behaviour of drying kinetics of hemp buds in the later stages shows that water present in the beneath layers are hard to remove. This could be because water in the underneath layers are tightly bound. When the non-isothermal conditions were applied, where the temperatures were increased after a certain period of drying, the drying rate considerably increased. Further, diffusivity (D_{eff}) values showed that diffusion was rapid with the increase of temperatures. Therefore, the hemp buds should be dried with an additional external force, such as high temperatures or low RH, in the later stages (roughly after 40 ± 5% MC w.b.) to considerably reduce the total drying period. Considering the energy consumption and CBD retention besides drying time, the non-isothermal drying condition: 40 ºC changed to 70 ºC at 25% MC w.b. showed the best results. Freeze drying dried the buds in 7.5 h which is relatively faster than the low temperature convective drying. However, considering the high energy consumption (double than convective drying) and the low CBD retention (least), FD would not be an appropriate technology for drying hemp buds.

The results of CBD content are comparable with the results of Turner and Mahlberg (1984), where cannabis samples were dried for 24 h in oven at 37 °C and 60 °C. They observed that samples dried at 60 °C had both acid and neutral cannabinoids, while at 37 °C only cannabinoid acids were found, showing that decarboxylation took place only at 60 °C. Also, the overall change in the cannabinoid content was insignificant. They also noted an increasing trend in the cannabinoid content with the prolonged drying (past 24 hours). This confirms the non-volatile nature of CBD,

and possibly other sticky resinous cannabinoids at these temperatures. Cannabinoids are secondary metabolites that play a crucial role in plant's defense mechanism. Since, drying is an induced stress, the CBD content might have increased as a part of defense. However, on the other hand, the freeze-dried product showed the lowest CBD. It should be noted that, the fresh material is immediately frozen in the freezer and then allowed for drying under vacuum. Certainly, the production of CBD by the material might be seized due to freezing temperatures. Hence, the stress induced due to high temperature seems to be critical for rapid production of CBD.

Further, the moisture content of the product might also have a significant role in CBD production. If temperature is alone considered as critical factor that increased CBD content, then consequently, the non-isothermal condition 40 ºC/70 ºC at 45% should retain maximum CBD, since, the material is subjected to high temperatures for longer time (40 ºC changed to 70 ºC when product reached 45% moisture). However, the condition 40 ºC/70 ºC at 25% moisture content showed highest CBD content contrasting with the previous assumption.

One possible reason could be an increased function of prenyltransferase enzymes or CBD synthases with the increase of temperature resulting in rapid production of CBD content. However, there is no systematic study on the function of these enzymes with respect to temperature so far. Nevertheless, the cannabinoid content was observed higher in the plants grown in tropical and xeric conditions with low humidity and sparse rainfall (De Faubert Maunder, 1976; Murari et al., 1988; Paris, Boucher, & Cosson, 1975; Sharma, 1975)

Increase of temperature showed a significant negative effect on terpenes indicating their volatile nature. Total terpenes content was analysed, and it was observed that, drying significantly decreased the terpenes content and more significantly above 40 °C. This could be because terpenes are naturally volatile which is a part of plant's defense mechanism such as, for repelling the insects

(Pate, 1994), for the suppression of the growth of surrounding vegetation (C. H. Muller, Muller, & Haines, 1964; W. H. Muller & Hauge, 1967). Terpenes behaviour was described by Hawes and Cohen (2015) who stated that, excess drying and/or drying at high temperatures evaporate some of the volatile oils (terpenes) that give hemp and cannabis its unique taste and aroma. This could be the possible reason for the practice of low temperature traditional drying methods for cannabis. A report by 'The Medical Cannabis Awareness Association (MCAA)' stated that, the most volatile terpenes found in the cannabis/ hemp plant start to evaporate around 21 ºC and can be noticed with pungent aroma in the air.

Chapter 4. Implications and Future Trends

Produced data help industry to design suitable drying methods that ensures rapid drying and maximum quality retention at minimal costs. Proposed drying method accelerates postharvest processing leading to high productivity ultimately conserving energy and expenses.

The project would help in satisfying current demand for health-promoting CBD products. A considerable segment of Canadian society needs CBD-based drugs for medicinal purpose. The outcome from this project will facilitate meeting the consumer demands in a timely manner. Also, an increased export potential and revenue is envisaged. Enabling high throughput of hemp based medicinal products would increase efficiency and support indirect job creation. Drying of hemp for further extraction of bioactive compounds (CBD and terpenes) is a bottleneck to the entire production cycle. The optimal drying technology recommended will reduce quality losses for the industry that will in turn translate into high value product. The effect of drying temperature on the terpene profile helps the cannabis industry to choose appropriate drying temperature. This project would further encourage the hemp industry in building partnership with the Dalhousie university providing access to the expertise of researchers/ engineers.

This research would open doors to the future research in areas of processing of hemp buds and hemp product development. Moisture sorption isotherms of hemp buds at various temperatures fitted with various models would help in prolonged storage and designing various drying technologies. Use of other novel technologies such as microwave-vacuum drying that dry the product at short period of time, various types of intermittent drying, can be explored. Further experiments on convective drying beyond 70 ºC temperatures, outdoor vs. indoor grown hemp, drying at various RH, chemical analysis and production pathway of CBD/ THC as influenced by

drying temperatures, would reveal concealed results. The water that was removed *via* vacuum suction in freeze drying could contain evaporated terpenes. This water can be collected, and the terpenes can be further extracted/ used. Harvesting, that takes three weeks, trimming of buds from the stem, which is laborious and time-taking, thermostable pesticide residues that get concentrated through drying, are some of the other issues being faced by the industry in the processing sector. Besides the technological advancements required, there are other political issues to be addressed. Although cannabis and hemp are legal in Canada, obtaining license for research is challenging and a major limitation to further studies.

Chapter 5. Conclusion

Increase in drying temperature reduced the total drying time of hemp buds by 92% (at 70 ºC) compared to control (32 ºC). Page model fitted the best that explains the drying kinetics of hemp buds. Diffusivity (D_{eff}) increased with the increase of temperatures and activation energy was 63.70 ± 1 kJ/mol. The hemp buds are recommended to be dried to a moisture content of 30% (at 22 °C) wet basis at the earliest possible time to avoid possible microbial growth during drying, and further, for a safe preservation and long term storage, the buds should be dried to a moisture content of 9 % w.b.

Increase of drying temperatures marginally increased the total CBD content with highest (2.783%) being in non-isothermal drying mode (40/70ºC @ 25% moisture content) and lowest (1.276%) in freeze dried product. Decarboxylation process occurred with the increase of temperatures leading to increase in CBD to CBDA ratio. Increase in temperature significantly decreased the total terpenes content. Terpenes were significantly high when dried at low temperatures including FD. In case of color, no significant change was observed at higher temperatures. Isothermal drying at 70 ºC and non-isothermal 40/70ºC @25% consumed 12.5 and 6.5 times less energy than control.

The suitable drying method to be recommended for the hemp buds merely depends on the product of interest developed by the industry. If the product requires only the total CBD content (such as CBD oil, supplements, edibles, body care, drinks), then drying at 70 ºC or 40/ 70ºC @ 25% is recommended. However, if the product (such as for smoking/ recreation which require aroma/ flavor) demands terpenes content along with the CBD, then drying at 40 ºC is recommended, since temperatures above 40 ºC significantly lost terpenes. This project revealed the important characteristics of CBD and terpenes as influenced by drying temperatures and technologies. This

research would help the cannabis industry to optimize the existing drying methods allowing maximum energy savings and product quality.

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Appendix 1

Statistical parameters and the values of the coefficients specific to each model at various drying temperatures of hemp buds.

Model	Drying T (ºC)	*k*	*a*	*b*	*n*	Adj. R-Squared	RMSE
Newton	25	0.117				0.917	0.076
	32	0.240				0.951	0.066
	40	0.325				0.960	0.056
	50	0.638				0.944	0.066
	60	1.034				0.972	0.053
	70	1.658				0.968	0.051
Page	25	0.256			0.643	0.993	0.021
	32	0.396			0.574	0.999	0.007
	40	0.482			0.680	0.998	0.011
	50	0.810			0.633	0.989	0.029
	60	1.051			0.772	0.985	0.03
	70	1.522			0.703	0.998	0.012
Henderson Pabis	25	0.091	0.858			0.947	0.061
	32	0.208	0.922			0.956	0.062
	40	0.291	0.922			0.967	0.051
	50	0.575	0.924			0.951	0.062
	60	0.985	0.962			0.973	0.051
	70	1.545	0.941			0.972	0.047
Logarithmic	25	0.157	0.833	0.111		0.985	0.03
	32	0.250	0.869	0.070		0.984	0.03
	40	0.38	0.88	0.074		0.985	0.034
	50	0.771	0.893	0.069		0.970	0.048
	60	1.227	0.920	0.065		0.983	0.040
	70	2.093	0.889	0.085		0.986	0.033

Midilli et al.	25	0.247	1.010	0.001	0.688	0.994	0.019
	32	0.392	1.001	2.7E-04	0.589	0.994	0.007
	40	0.489	1.001	-0.001	0.654	0.998	0.010
	50	0.81	0.999	-0.008	0.591	0.988	0.029
	60	1.086	1.002	0.006	0.816	0.985	0.037
	70	1.406	1	-0.019	0.636	0.998	0.010