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To my dear daughter Maria Sophie

… live long and prosper!

Preface

This thesis is submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy (PhD) at the Norwegian University of Science and Technology (NTNU). The work was carried out in the Food Technology group in the Department of Energy and Process Engineering supervised by Professor Trygve Magne Eikevik and co-supervised by Professor Turid Rustad.

The PhD was created and funded by NTNU, with additional financing provided from the Research Council of Norway through the project "New Marine Feed Resources" (172641/S40), which mainly examined the use of the zooplankton species *Calanus finmarchicus*. Our Food Technology group at NTNU investigated how this aquatic raw material can be used by the industry. My contribution and this thesis are focused on one aspect of the processes we examined: Atmospheric Freeze Drying (AFD). The study investigated the use of AFD with zooplankton as well as an examination of additional candidate products for this process and also included more general aspects of AFD. Additional work included the measurement and modelling of the thermal properties of *Calanus finmarchicus*, applying a new method developed by NTNU/SINTEF.

In the last year of my PhD research the focus was on the application of ultrasound in atmospheric freeze drying and the development of a more widely applicable model for this process. Both topics include new ideas and conclusions in this field, and are outlined in this thesis.

Acknowledgement

First of all I want to thank my supervisor, Professor Trygve Magne Eikevik, for the opportunity to work on this interesting project. I really appreciated the opportunity to develop my own ideas and enjoyed working with you and your group. Without your support I would never have “settled” in Trondheim or Norway and without your guidance this thesis would not have developed. A special thanks goes also to Professor Turid Rustad, my co-supervisor. My non-biotechnology background meant that I had a lot of questions, which might normally not have been asked by another student. Your doors were always open to me. Again, thanks to both of you for this project!

I also want to thank the food technology staff from NTNU and SINTEF for their support and friendship during my time here in Trondheim. I enjoyed having you as my colleagues and your support made this work possible. This thanks also includes all the personnel in the laboratory. I hope I was not too “eager” when it came to the progress of my projects. The administration crew from NTNU also needs to be thanked for providing the framework for this project. The crew from the M/S Gunnerus has further earned my thanks during our numerous zooplankton fishing trips. Now we know where to find Calanus!

I want to offer an individual thanks to my fellow PhD student Maria Bergvik from NTNU - Sealab. Again: as a process engineer with a non-biological background, I posed some challenges to you. A big “thank you” as well to interns Françoise Pomerlau, Christopher Rundel, Marlene Kreutz and Anton Grüttner. When you read this thesis you will surely see how important your work was.

I would also like to say a special thank you to all the people who helped me over the last four years – it is hard to include all of you on this one page.

Last but not least, I would like to say “Thank you for everything” to my family. To the family I left behind in Germany: It is not easy to see a close son and brother leaving to explore the world, but without you I would not have had the strength to do so. And to the family I found here in Norway: You are the best! This is particularly true for Liv-Stephanie and our daughter Maria Sophie!

Abstract

Atmospheric or convective freeze drying (AFD) is a dehydration process mostly employed in the food industry. It is also a promising process for the freeze drying of high-end products in the biological and pharmaceutical industry. Proteolytic and lipolytic activity as well as changes in lipid classes and lipid oxidation for products from AFD were investigated and the general potential of the drying method is described.

The drying rate in AFD is generally low. In order to accelerate the drying process, the application of high intensity, airborne ultrasound in AFD (US-AFD) was investigated for different products and under different drying conditions. The drying rates obtained in AFD and US-AFD show that both processes occur in the falling drying rate period and no drying period with a constant drying rate occurs. A modification of the Weibull model was developed and showed high accuracy for modelling and evaluating drying rates in AFD and US-AFD.

In general, US-AFD investigations showed a faster drying rate than AFD. The effective mass transfer for the sublimation of pure ice particles increased by 38% and the effective diffusion for peas is increased by 24.7% at an approach velocity of 1 m sec^{-1}. Airborne ultrasound increased AFD processes especially at low temperatures and low approach velocities during the first hours of drying. Even a minor ultrasonic field increased the effective diffusion significantly. The product quality (shrinkage and colour) is not affected by the application of the ultrasonic field.

A higher mass transfer rate at the solid-gas interface, caused by a reduced boundary layer due to a higher turbulent interface, is identified as the cause for the higher effective diffusion in US-AFD. Hence high intensity, airborne ultrasound has great potential to accelerate drying rates and reduce investment and production costs associated with AFD. It can be expected that other low temperature processes that are based on convective heat and/or mass transfer (such as blast freezing) can be improved in presence of airborne ultrasound.

List of Papers

This thesis is based on the following papers, referred to in the text by Roman numerals.

I. Bantle, Michael, Trygve M. Eikevik and Turid Rustad, Atmospheric Freeze-Drying of *Calanus finmarchicus* and its effects on proteolytic and lipolytic activities. Proceedings of the 4th Nordic Drying Conference NDC 2009: June 17th to 19th 2009, Reykjavik, Iceland, 2009: Ebook: ISBN 978-82-594-3406-7.

II. Bantle, Michael, Trygve M. Eikevik and Jon Eirik Brennvall, A Novel Method for Simultaneous and Continuous Determination of Thermal Properties during Phase Transition Applied to *Calanus finmarchicus*. Journal of Food Science, 2010. 75(6): p. E315-E322.

III. Bantle, Michael, Maria Bergvik and Turid Rustad, Lipid Changes and Lipid Oxidation in *Calanus finmarchicus* during Vacuum, Atmospheric and Nitrogen Freeze Drying, in Proceedings 17th International Drying Symposium, 2010: Magdeburg, Germany: p. 1907-1914.

IV. Bantle, Michael, Trygve M. Eikevik and Anton Grüttner, Mass Transfer in Ultrasonic Assisted Atmospheric Freeze Drying, in Proceedings 17th International Drying Symposium, 2010: Magdeburg, Germany: p. 763-768.

V. Bantle, Michael, Kjell Kolsaker and Trygve M. Eikevik, Modification of the Weibull distribution for modeling atmospheric freeze drying of food. Manuscript accepted for publication in Drying Technology, an International Journal, March 2011.

VI. Bantle, Michael, and Trygve M. Eikevik, Parametric study of high intensity ultrasound in the atmospheric freeze drying of food. Manuscript submitted to Drying Technology, an International Journal, February 2011.

VII. Bantle, Michael and Trygve M. Eikevik, Kinetics of ultrasonic assisted atmospheric freeze drying of green peas. Paper accepted for Nordic Drying Conference 2011, June 19th to 21st 2011.

Reprints of the papers are provided as Appendices I – VII. A short summary of each paper as well as the author contribution is provided in Chapter 4 “Summary of Papers”.

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Nomenclature

Acronyms

AD	Atmospheric or convective drying	-
AFD	Atmospheric or convective freeze drying	-
b	Root of the Bessel function	-
CF	*Calanus finmarchicus*	-
D_{calc}	Diffusion in the modified Weibull model	$m^2\ sec^{-1}$
D_{eff}	Effective diffusion	$m^2\ sec^{-1}$
FFA	Free fatty acids	-
HP	Heat pump	-
HPD	Heat pump drying	-
HP-AFD	Heat pump assisted atmospheric freeze drying	-
L	Length or characteristic length	m
M	Moisture content	-
MR	Moisture ratio	-
m	Mass	kg
N	Number of experimental data points	-
NFD	Nitrogen freeze drying	-
n	Integer	-
r	Radius	m
R^2	Coefficient of determination	-
SMER	Specific moisture extraction rate	$kg_{water}\ kWh^{-1}$
T	Temperature	°C
t	Time	sec
US	Ultrasound or ultrasonic	-
US-AFD	AFD assisted by ultrasound	-
VFD	Vacuum freeze drying	-
x	Coordinate	-

Greek letters

α	Scale parameter	-
β	Shape parameter	-
χ^2	Chi-square, reduced	-

Abbreviations

eq	Equilibrium	-

1 Introduction

1.1 Atmospheric Freeze Drying (AFD)

Drying is the removal of water from a solid by evaporation using thermal energy, and is one of the oldest methods for the preservation of certain products, as in the convective drying of grains or fish. This type of preservation made it possible for humans to store food for extended periods, which makes drying a key step in the evolution of human cultures. To this day drying is still one of most important industrial preservation process for innumerable products. Industrialization helped to optimize the process of drying, which was conducted under varying but controlled conditions. In [1] 15 different dryer types and more than 20 industrial drying sectors are described. However the basic physical principle is still the same as it was thousands of years ago. For every product a certain drying process has to be evaluated in terms of product quality, extended shelf-life, additional processing, ease of handling, sanitation, cost effectiveness and investment. These varied parameters make it difficult to state general conclusions in drying technology.

Certain products (such as some foodstuff, food raw materials, pharmaceuticals or biological material) cannot tolerate high temperatures and need to be stored and processed while frozen. Convective drying is as well possible when the product is frozen[1]. The water in this situation is present in a solid state (ice) and can be sublimated from the product. This is commonly referred to as atmospheric or convective freeze drying (AFD). Although the AFD process has been used in ancient times in cold regions for food preservation [2], it was only in the 1950s that research slowly started on this topic [3] [2]. Not much has been published about AFD in the scientific literature, even though the process offers several advantages (see Chapter 1.2 “Potential of AFD”).

[1] Convection is the movement of molecules within a fluid. In drying technology the term convective drying is used to indicate when heat and mass transfers are due to temperature or pressure gradients between the drying agent (air) and the drying product. The molecules that move are water molecules that diffuse into the drying agent (fluid).

[2] Vacuum Freeze Drying (VFD) is the most common industrial freeze drying process and is often referred to as freeze drying in the literature without any differentiation made between atmospheric or convective freeze drying (AFD). In VFD the ambient pressure around a product is reduced to under the triple point of water, which is at 611.65 Pa at 0.01℃. Given that enough heat is provided, the ice sublimates and is precipitated on a cold surface in the system.

AFD is performed in three steps:

1. Freezing of the product
2. Phase transition from ice to vapour (sublimation)
3. Vapour removal

As in most convective dehydration processes, AFD is done by bringing air of a certain temperature and low relative humidity in contact with the product to be dried. The product is mostly frozen prior to AFD in a separate freezing system. Since the air is not saturated with water vapour, a pressure gradient is created between the ice surface in the product and the air, forcing the ice to sublimate and diffuse into the air. The sublimation energy needed for the process is provided by the dry air and results in the development of a temperature profile between the ice surface and the drying agent (see Figure 1).

In AFD the sublimation of ice and the removal of vapour occur simultaneously. Since ice cannot flow or move in the frozen layer of the product (in contrast to water in convective drying at higher temperatures), a dry layer forms between the ice-containing structure and the drying agent when sublimation begins. Papers VI and VII as well as Chapter 2.2 shows that the drying rate in AFD (and US-AFD) continuously falls at the beginning of the dehydration process. This means that there is never a constant drying rate during AFD (which is in accordance with [2], [4], [5], [6], [7] and [8]), because of the increasingly thicker dry layer [3]. [9] and [10] on the other hand consider an AFD model that includes an initial drying period with a constant drying rate. However, the model accuracy was not satisfactory, which could be due to the inclusion of this first drying period with a constant drying rate.

Freeze drying is generally classified into two drying stages [2], [11]:

1. Primary drying, which is when the water vapour produced by sublimation travels by diffusion and convection flow through the porous structure of the already dried layer before it passes the boundary between product and drying agent.
2. Secondary drying, which begins when all ice is removed by sublimation (at the end of primary drying). It involves the removal of so-called un-freezable water (absorbed or bound water) [12]. The removal of this bound moisture can be

[3] In the presence of free ice on the surface of a drying product it is possible that a first drying period with a constant drying rate occurs in AFD. Free ice can develop during storage and handling of the product, when e.g. water condenses on the surface of the frozen product. Since this ice layer represents only a minor fraction of the total ice present the first drying period will be short compared to the total drying time.

challenging and the drying time can be even longer than in the primary drying stage, even though bound moisture is normally only a minor fraction of the total moisture.

In nearly all cases AFD involves only primary drying and a certain residual moisture content including the bound water, is considered acceptable. For most products the equilibrium moisture content in AFD is between 10% and 20%, while the so-called bound water content is generally lower [4]. A general one-dimensional physical model of AFD is illustrated in Figure 1. [13] and [14] provide a more recent review of the topic.

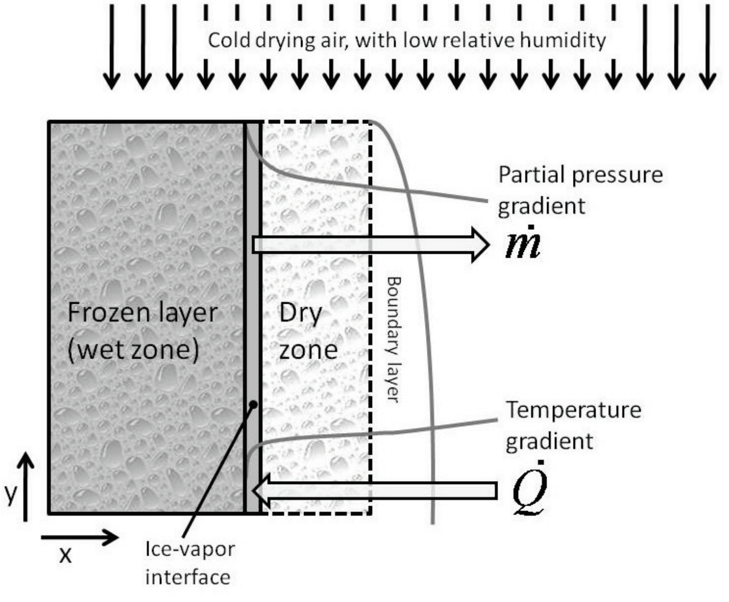

Figure 1: Physical model of Atmospheric Freeze Drying (AFD) [2], [13].

1.2 Potential of AFD

In the general drying literature, the potential of AFD is most often underestimated, or is sometimes not even mentioned. AFD is not an alternative for convective drying at drying temperatures between 0°C and 100°C, because of the lower drying rate and the higher costs involved with AFD, unless the higher product quality from AFD compensates for these drawbacks. But as soon as a drying product cannot tolerate

[4] For zooplankton the so-called bound water was modelled to be 6% (Paper II). Common AFD of zooplankton reaches an equilibrium at a water content of around 10% and therefore involves only primary drying.

even moderate temperatures, freeze drying is used as alternative dehydration method. This is true for certain foodstuff, raw materials, pharmaceuticals and biological materials [11], but AFD is rarely considered as a potential freeze drying method for these products. The main reason for this might be a lack of information in literature about AFD in favour of the more common Vacuum Freeze Drying (VFD) process. The key advantages of AFD, in comparison with VFD, are as follows:

- The process can be designed to be continuous, which results in low operational costs with high productivity [2], [15].
- A heat pump system can be used to recover the drying energy. [16] and [17] investigated this topic and reported a SMER (specific moisture extraction rate) from 1.0 kg_{water} kWh^{-1} for AFD at -5°C and a possible energy saving of 60-80% of the drying energy compared to VFD. In comparison, the SMER for conventional drying (not freeze drying!) is between 0.12-1.28 kg_{water} kWh^{-1}, compared to 0.72-1.2 kg_{water} kWh^{-1} and 1.0-4.0 kg_{water} kWh^{-1} respectively for vacuum drying and heat pump drying (HPD), [18], [19].
- A temperature controlled drying process results in decreases in drying times as well as energy consumption (Paper I, [20]).
- The heat transfer coefficient in fluid bed AFD is about 20-40 times higher compared to VFD [2], [15], [21].
- Inert gases, such as nitrogen, can be used as a drying agent in order to minimize the product degradation caused by oxidation, which makes the product quality comparable to VFD [2], [15] [5].

The main drawback for AFD is generally believed to be the longer drying time in comparison to VFD. However, different investigations have shown that AFD can be faster than VFD, when the product has a certain particle size and/or is dried in a fluid bed (Paper I, III, [6]). It should also be noted that AFD is generally controlled by the internal diffusion or heat conduction of the product, which is true for both VFD and AFD processes. Hence the only remaining drawbacks are the high initial investment costs for a heat pump controlled AFD system and the higher requirements for process control. For the sake of completeness, it should also be noted that these drawbacks are also partially true for VFD.

Paper I investigated the proteolytic and lipolytic activity of zooplankton after it had been dried in an AFD process. As outlined in [22] zooplankton is highly sensitive to degradation, but AFD preserved both protease and lipase during the process. The

[5] Paper III investigated freeze drying under vacuum, air and nitrogen atmosphere. As discussed later the use of nitrogen did not result in a less degraded or oxidized product.

desired activity in the product can be reached by adjusting the drying temperature in AFD (or AD) to the appropriate level. The proteolytic activity for the zooplankton dried in AFD was the same as in the raw material, while the lipolytic activity was slightly reduced. At the same time, the drying rate in AFD was significantly faster than in VFD. Hence AFD can preserve biological activity while also allowing a faster drying process with a higher SMER. Consequently AFD should be considered as an alternative to VFD when it comes to the preservation of biological activity.

Paper III presents a comparison of a heat pump assisted AFD process to common VFD and to freeze drying with inert gas (nitrogen) at atmospheric pressure (NFD) in terms of lipid degradation in zooplankton. The average drying rates were 0.22, 0.10 and 0.04 $kg_{water}kg_{d.m.}^{-1}h^{-1}$ for AFD, VFD and NFD respectively. Free fatty acids [6] accounted for 10, 19 and 32% of the total lipids in AFD, VFD and NFD respectively. This results in a linear relationship between drying rate and free fatty acid content as shown in Figure 2. The figure shows also that the lipid content decreases linearly with the drying rate, which can be mainly explained by hydrolytic reactions during the drying process. In AFD and VFD the phospholipid content was more than halved (57%) compared to the original amount, while in NFD 92% of the phospholipids were lost. No changes were found in the content of omega-3 fatty acids. The rancidity measurement (secondary oxidation) showed the highest value for NFD, which means that the product was rancid after drying. The rancidities for AFD and VFD were similar and within the generally accepted limits. When it comes to lipid preservation AFD and VFD were both suitable preservation methods. The quality reduction was firstly related to the drying time and not to the drying method. Hence, AFD was the fastest drying method in this investigation and showed similar or even better product quality than VFD.

AFD therefore has great potential for industrial freeze drying applications and should be considered more often as an alternative for VFD processes. Future research should focus on this potential in order to overcome the lack of knowledge about AFD. As described, the drying rates, investment and running costs as well as product quality can be similar or even better than for VFD.

[6] Free Fatty Acids (FFA) form when lipids break down (degradation). By measuring the amount of FFA, the lipid degradation can be evaluated.

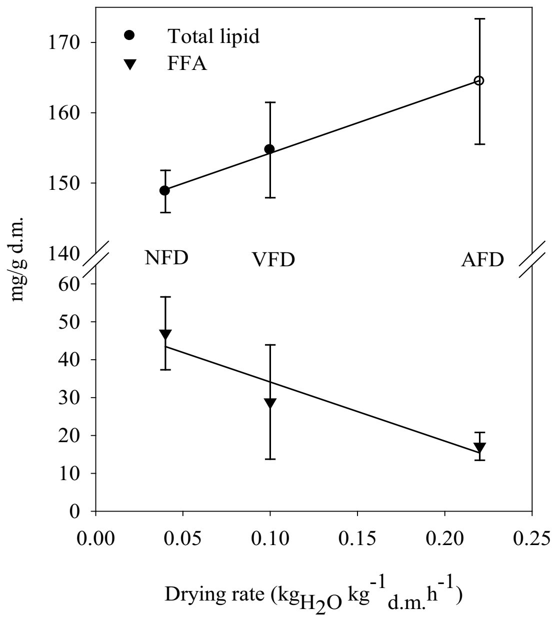

Figure 2: Lipid content and amount of free fatty acids (FFA) as a function of drying rate for dried zooplankton (Calanus finmarchicus) from AFD, VFD and NFD.

1.3 The zooplankton species *Calanus finmarchicus*

NTNU is currently investigating the zooplankton species *Calanus finmarchicus* (CF) and the university's Food Technology group is studying the use of CF as raw material in different processes (project 172641/S40 of the Research Council of Norway). CF has therefore been included in most investigations conducted for this thesis (Papers I – VI) as a heat sensitive raw material. As shown in Paper I and [22], CF is highly sensitive to degradation, which means that CF should be processed and stored when it is frozen. Even when stored in a frozen state, CF will undergo a certain amount of degradation ([22], [23], unpublished material). For this reason, AFD was considered to be a preservation method for CF (Paper I and III).

CF (see Figure 3) is low on the food chain, and is found in high amounts in the Barents and Norwegian Seas. Its annual production potential is estimated to be between 25 and 100 million tons by dry weight, composed of proteins and marine lipids. Currently CF is not exploited as raw material at an industrial scale. Recent developments in harvesting equipment as well as an expected shortage of aquatic proteins and lipids make this zooplankton species a promising marine raw material for the food and feed industry. It is also expected that CF can be harvested in significant amounts without affecting fish stocks at higher trophic levels. However the importance of CF as a link in the food web is known and a liberalization of the current catching ban has to be carefully considered. [24]

Figure 3: The zooplankton species Calanus finmarchicus, which is a potential new raw material for several industrial applications (photo: Jan Ove Evjemo).

A feasibility study at our department investigated an industrial scale separation process for CF. First the raw material was heated to a temperature of 70°C, which stops enzymatic activity. Heating is frequently used to preserve food and it appears that heating CF to 70°C or higher is required to inactivate most of the proteases responsible for degrading proteins (see [22]). The material was then pressed in a belt press and separated into a solid (protein) and liquid fraction. The liquid fraction was further separated using a decanter (gravimetric separation) into a lipid (marine oil) and a water fraction. During heating a significant amount of CF degraded, because the process was time-consuming and slow by nature. Therefore alternative preservation methods, such as freeze drying, should be considered. [25]

The thermal properties of a product are important when it comes to modelling processes (such as the AFD model in [9]) and the dimensioning of equipment (such as the heating process mentioned above). These properties change with temperature, particularly during freezing. In Paper II, all of CF's thermal properties (specific heat, enthalpy, thermal conductivity and density) were measured continuously from -40°C to +20°C using a new method [26] and suitable models were evaluated (Figure 4). The initial freezing point of CF was also determined (-2.3°C).

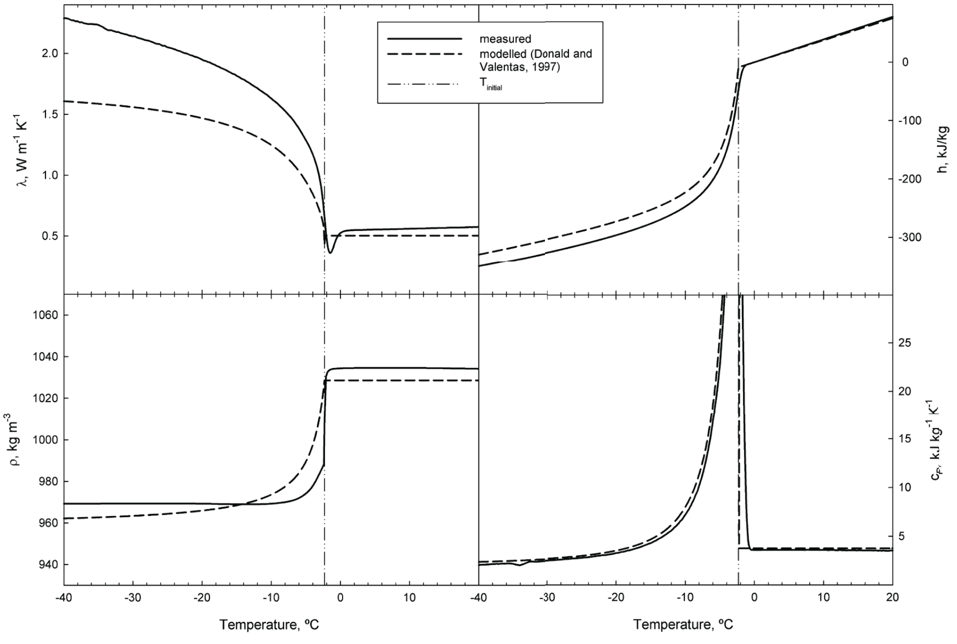

Figure 4: Measured and modelled thermal properties for Calanus finmarchicus related to temperature.

1.4 Ultrasonic drying

Ultrasound is a cyclic sound wave in the frequency range from 20 kHz to 1 MHz, which is above the threshold of the human ear. Examples of ultrasound in nature include the sonar used by whales and the echolocation of bats. Higher ultrasonic frequencies have lower power and are used for diagnostic imaging, whereas lower frequencies are associated with higher power levels and are often referred to as high power or high intensity ultrasound [27]. It should be noted that ultrasound is a type of mechanical or kinetic energy (compared to infrared or microwave radiation which is thermal energy) and requires a resonance media through which the sound wave can move. In an ultrasonic cleaning bath, for example, the resonance media is the water solution.

Recent developments have increased the efficiency of ultrasonic emitters (transducers) which use air as a resonance media to 80% and to intensity levels of

175dB [28]. This so-called high intensity, airborne ultrasound can result in a physical effect when the sound wave is directed into a process. [27] provides a useful review about recent applications of ultrasound in industrial food technology. New applications based on airborne ultrasound are the precipitation of smoke and powder and the destruction of foams [29], improved product quality in freezing [30] and the ability to accelerate drying and dehydration rates [31], [32], [33], [34], [35], [36], [37], Papers IV, VI and VII. However, the use of airborne ultrasound to accelerate drying is not new and was first investigated in the 1950s [38], where the same conclusions were reached as were found in more recent research (see [39] or [40]). However, industrial applications based on airborne ultrasound have been realized only recently [7], most likely because of the availability of efficient ultrasonic equipment.

[41] reviewed the topic of ultrasonic drying and summed up the effects that can lead to an accelerated drying rate:

1. Cavitation effects:
    a. Cavitation breaks down particles, which increases the specific surface area.
    b. Cavitation degases the liquid, which improves the liquid flow.
    c. Cavitation disperses particulates or agglomerations, which improves the particle contact with the drying agent.
    d. Cavitation bubbles caused by US coagulate fibrous and clinging particles (e.g. wood paper pulp). This effect can improve product quality, but not necessary the drying rate.
    e. Cavitation produces free chemical ions.
2. US can change the viscosity or the structural properties of the drying agent.
3. US can clean or clear the surfaces of the product, which will increase the surface area in contact with the drying agent.
4. US can increase the mass transfer at a gas/liquid or gas/solid interface, by affecting the local pressure gradient between the drying agent and product (vapour pressure and saturation vapour pressure).
5. The “sponge-effect”, in which the product is compressed and decompressed in the US field. The water is thereby squeezed out of the product, similar to when a wet sponge is squeezed. The “sponge-effect” was recently used to explain accelerated drying rates [40].

[7] The Australian company Cavitus (www.cavitus.com) offers one of the few industrial system solutions that is based on airborne ultrasound. The ultrasound is used to collapse foam while filling beer and carbonated beverage containers, which significantly accelerates filling rates.

6. US can create high turbulence around the product, which will improve the mass transfer rates between the product and the drying agent.
7. Other effects, such as Oseen forces (a rectified force attributable to the nonlinearity of high intensity waves in air) or Bernoulli forces (forces of attraction due to reduced pressure in a narrowed passageway, such as the movement of gas between stationary objects in close proximity).

Since atmospheric freeze drying has a generally slow drying rate, it is desirable to accelerate the drying process. Ultrasonic drying showed particularly accelerated drying rates at lower temperatures (as reported in [28], [38] or [40]), which suggests that including high intensity, airborne ultrasound in an AFD process **could** result in a higher mass transfer rate. Chapter 2 of this thesis investigates how an AFD process can be assisted by airborne ultrasound (US-AFD), presents the results of the feasibility and parametric study (Papers IV, VI and VII) and evaluates the possible effects from the accelerated drying in US-AFD.

2 Ultrasonic assisted Atmospheric Freeze Drying (US-AFD)

A feasibility study and a more detailed parametric study were performed in order to investigate how ultrasound (US) can increase the drying rate in AFD (Papers IV, VI and VII). This chapter describes the main results and the physics behind US-AFD. Since AFD (and US-AFD) is generally controlled by sublimation and water vapour diffusion in the already dried product structure, the drying rate was evaluated using an empirical effective diffusion model, which was developed and applied for AFD (Paper V).

2.1 Introduction

Ultrasound was successfully used to accelerate drying processes at temperatures between 20°C and 100°C ([27], [31], [33], [34], [38], [40], [41] or [42]). Chapter 1.4 "Ultrasonic drying" (page 8 of this thesis) lists possible reasons for the accelerated drying rate when the process is assisted by ultrasound. These effects were reported in the above-mentioned literature for the drying of a non-frozen product with or without direct contact between the ultrasonic transmitter and product.

In AFD the product is frozen, so the water to be removed is present in the form of ice that is incorporated in the interstices of the product's dry matter. This gives a solid-solid matrix compared to drying in a non-frozen state where the water is present as a liquid in a solid-liquid matrix. Liquid water can move to the surface of the product during drying, which is the premise for the constant drying rate in the first drying period[8]. However, in contrast to ice, liquid water can act as a resonance media for ultrasound. Based on this fundamental difference, some of the effects obtained for US-drying will most likely not occur in US-AFD.

The primary mechanism by which ultrasonic energy is transmitted is cavitation caused by the rapid formation and collapse of microscopic bubbles in the resonance media. The effects caused by cavitation (see [41] and Chapter 1.4) will only occur when liquid water absorbs the ultrasonic wave (by direct contact with the ultrasonic emitter) or when water is used as resonance media, which is only the case for osmotic dehydration. Solid ice is not an adequate resonance media/fluid for ultrasound.

In US-AFD, air is the resonance media, hence the cavitation bubbles will form in the air, or more precisely at the interface between the product and the air. This could influence the structure of the surface and therefore product quality. The energy transmitted during the process could change the viscosity and/or properties of the drying agent, such as the temperature. Since in AFD the drying process is controlled by internal sublimation and diffusion a cleaner surface will not necessarily accelerate the overall drying rate.

[8] As outlined in Chapter 1.1, "Atmospheric Freeze Drying (AFD)" this drying stage will not occur for AFD.

The “sponge-effect” in drying describes a mechanism when liquid water is squeezed out of the product as a consequence of the compressing and de-compressing of the particle structure in the sound wave. This effect cannot occur in US-AFD since ice cannot be squeezed out of the solid-solid matrix of the product. If the ultrasonic sound wave is strong enough to squeeze the solid-solid matrix of the frozen product, this would result in particle breakdown, because of the brittleness of ice.

The cavitation at the interface between the drying air and the product could create more turbulence around the product by disrupting the boundary layer. It is believable that this could cause the local pressure and temperature gradient to increase, which would also improve the mass and heat flux. Other effects, which are described in point 7 in Chapter 1.4, are quite specific and are connected to specific processes or products and are unlikely to be the reason for the in general accelerated drying rate seen in US-AFD.

Based on these theoretical considerations, an accelerated drying rate under US-AFD could be caused by:

1. Changes in the properties of the drying agent (viscosity, temperature, relative humidity).
2. Particle breakdown, which will increase the specific surface area.
3. Better dispersion of the particles.
4. Disruption of the boundary layer, resulting in a more turbulent flow profile around the product to be dried, thereby increasing heat and mass transfer coefficients.
5. Increasing the local pressure and temperature gradient, thereby increasing the heat and mass flux (similar to effect 4).
6. Additional effects that have not been described in the literature.

2.1.1 System for US-AFD

Since ultrasound is a sound wave, its use in a drying system is challenging. In [31] and [35] the complete drying chamber was used as vibrating emitter in order to create an ultrasonic field. A more practical approach for industrial applications is when parts of the drying chamber are open to the ultrasonic sound wave, which is generated by a common transducer, as in [28] or [34]. In order to avoid concentrating sound in one place it makes sense to mix the product continuously instead of changing the position of the ultrasonic transducer.

In order to meet this requirement, a special drying chamber was developed for US-AFD, which was connected to an existing heat pump drying system. The drying process was thus conducted using a fluid or stationary bed. The ultrasonic emitter (transducer) was placed 10 mm underneath the bottom plate of the bed. The bottom plate was perforated with 1 mm holes (clear opening ≈45%), which allowed drying air as well as ultrasonic waves to enter the drying chamber. The transducer we used was modified from an industrial application (Sonotronic, DN 20/200, 20 kHz, diameter 100mm). Using this transducer as the source for high intensity, airborne ultrasound resulted in an efficiency of 20%, which meant that 80% of the energy supplied needed to be conducted out of the system with a separate cooling unit. The efficiency of this equipment is sufficient for research purposes, but any industrial application should use a special airborne ultrasonic transducer (as described in [28]) with an efficiency of up to 80%.

The placement of the transducer altered the original flow profile of the drying air into the chamber. Hence, the transducer was not removed for experiments that did not involve ultrasound in order to maintain the same flow profile for AFD and US-AFD and make the drying conditions comparable. The same procedure was used by [28] and [34], in which the ultrasonic transducer was not removed from the drying system for the experiments that did not involve ultrasound. In [31] and [35] the drying chamber was used as a transducer and therefore the original flow profile of the chamber was preserved. However, this approach requires specially built ultrasonic equipment and would be difficult to realize at an industrial scale. With the ultrasonic system we used (Figure 5), it was possible to compare the drying behaviour for US-AFD and AFD under identical flow conditions for the drying agent and under the same drying conditions.

The drying chamber had a diameter of 200mm and a height of 300mm. It was sealed with a 300µm sieve and could hold approximately 1 kg of product. The weight reduction can be determined with an online weight measurement system using a liquid sealing ring as described in [43]. Since the weight reduction was measured in a fluidized bed, a correction for the changing pressure loss needed to be made (as described in [44]), which reduced the accuracy by approximately 1-2%. However, the drying curve for long drying times (up to several days) can be determined continuously with the online measurement system described here. For a shorter drying time, the chamber was constructed in such a way that the drying process could be interrupted and the weight reduction in the drying chamber determined manually. This is more precise than the online measurement, but requires at the same time more manpower. In the investigations presented here the weight reduction was mainly determined manually in order to provide the most accurate drying rate. The online measurement system was only used for the 24-hour investigation. Figure 5 shows the US-AFD system employed, with more details about the system and the tests that were performed available in Papers I, IV, VI and VII.

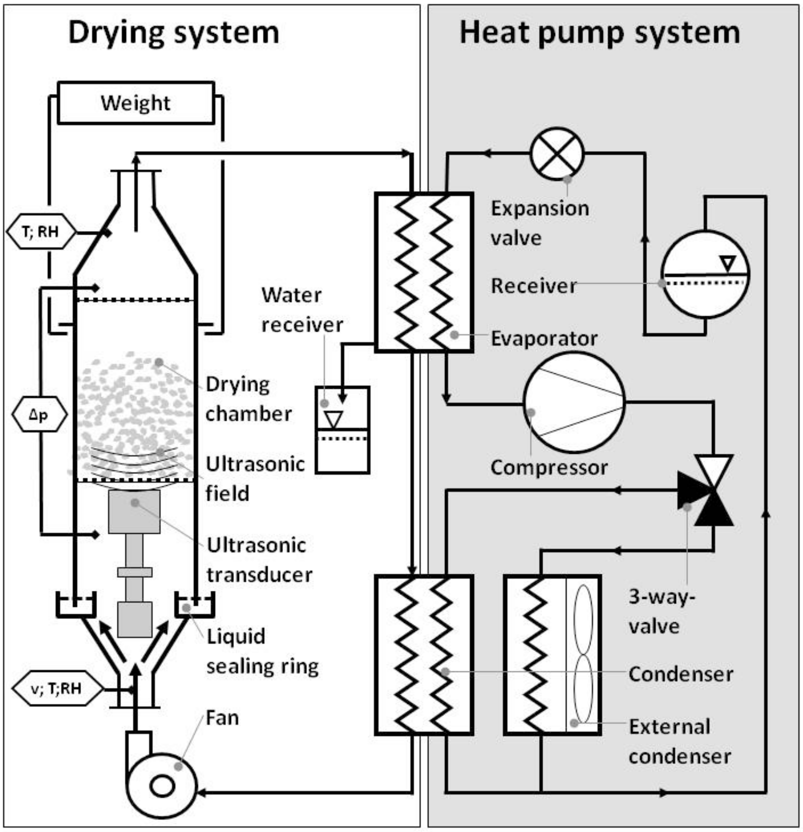

Figure 5: Atmospheric freeze drying system with heat pump energy recovery, online weight measurement and ultrasonic assistance.

2.1.2 Investigations of US-AFD

A feasibility study was performed (Paper IV) in order to see if airborne ultrasound could accelerate AFD. The products that were dried for this study were zooplankton (CF), cod, apple, peas and ice[9]. A more detailed parametric study followed the investigation (Papers VI and VII), using peas as the product to be dried, because of their good fluidization characteristics and their defined particle size and structure. The studies investigated the influence of different drying temperatures, drying times, approach velocities (fluid or stationary bed) and ultrasonic intensities on US-AFD. An

[9] The sublimation of ice particles was included in this study even though it is not strictly speaking a drying process. The sublimation of ice is a process that is only controlled by external heat and mass transfer and therefore offers a useful supplemental investigation in order to determine the principles behind AFD and US-AFD.

overview of all of the investigations performed can be found in Table 1 and a more detailed description is provided in Papers IV, VI and VII. All tests were performed in triplicate and the diffusion for the modified Weibull model (D_{calc} , see Paper V) and the effective diffusion in Fick's law (D_{eff}) were determined from the averaged drying curve. More details about the different models are provided in Chapter 2.3.

Table 1: Products and drying conditions for AFD investigations with and without ultrasound.

Product	Drying temperature	Drying time	Approach velocity	Bed state	US - power in US-AFD
A. Products investigated					
Ice (Sublimation)	-5 °C	1 h	1.2 m sec^{-1}	fluid	74.4 W
Zooplankton	-6 °C	3 h	1.5 m sec^{-1}	fluid	87.3 W
Cod	-6 °C	3 h	1.8 m sec^{-1}	stat./fluid	89.9 W
Apple	-6 °C	3 h	2.5 m sec^{-1}	stat.	87.5 W
Peas	-6 °C	3 h	3.1 m sec^{-1}	fluid	67.6 W
B. Temperature investigation					
Peas	**-6 °C**	3 h	3.1 m sec^{-1}	fluid	67.6 W
	-3 °C	3 h	3.1 m sec^{-1}	fluid	68.2 W
	0 °C	3 h	3.1 m sec^{-1}	fluid	69.9 W
	10 °C	3 h	3.1 m sec^{-1}	fluid	73.2 W
	20 °C	3 h	3.1 m sec^{-1}	fluid	70.7 W
C. Drying time influence					
Peas	-6 °C	**3 h**	3.1 m sec^{-1}	fluid	67.6 W
	-6 °C	**24 h**	3.4 m sec^{-1}	fluid	88.9 W
D. Investigation of approach velocity influence					
Peas	-5.9 °C	3 h	**1.0 m sec^{-1}**	**stat.**	69.9 W
	-6 °C	3 h	**1.8 m sec^{-1}**	**stat.**	69.7 W
	-6 °C	3 h	**2.6 m sec^{-1}**	**stat.**	71.4 W
	-6 °C	3 h	**3.1 m sec^{-1}**	**fluid**	67.6 W
	-6 °C	3 h	**4.7 m sec^{-1}**	**fluid**	72.3 W
E. Investigation of ultrasound intensity influence					
Peas	-3 °C	3 h	3.2 m sec^{-1}	fluid	**0 W**
	-3 °C	3 h	3.2 m sec^{-1}	fluid	**15.3 W**
	-3 °C	3 h	3.1 m sec^{-1}	fluid	**43.1 W**
	-3 °C	3 h	3.1 m sec^{-1}	fluid	**68.2 W**

2.2 Drying rates in AFD and US-AFD

The proposed physical model for AFD (see Figure 1) does not include a drying period with a constant drying rate. In AFD (and US-AFD) the water to be removed is present in the form of ice. In contrast to liquid water, the ice inside the product cannot move to the surface during the drying process. The constant drying rate period is generally characterized by the presence of a sufficient amount of water (or ice) on the surface of the product. It seems sufficient to assume that ice is only in direct contact with the drying agent in AFD for products with ice condensates on the surface or an open or destroyed structure. It is therefore assumed, that this is the only situation in AFD with a short constant drying rate period.

Figure 6, Figure 7 and Figure 8 show some examples of drying rates measured for AFD and US-AFD under different drying conditions. Similar falling drying rate curves were obtained for all investigations performed. The cod cubes used in the experiments (Figure 6) were cut from the filet and the part of the filet that contain ice was exposed directly to the drying air, while the peas (Figure 7 and Figure 8) have an outer shell that can act as a physical barrier to mass transfer. For both products it can be seen that the complete dehydration process for AFD and US-AFD occurs during the period when the drying rate is falling. All of the drying rates decreased continuously with progressing dehydration, which confirmed the initial assumption that the physical model for AFD and US-AFD did not need to include a constant drying rate period. The figures show further that the drying rates obtained for US-AFD are generally higher than for AFD.

In contrast to the drying rates obtained for AFD and US-AFD, the sublimation rates for ice particles with and without ultrasonic assistance (see Figure 9) shows no decrease. Ice particles will get smaller with ongoing sublimation and the effect of the decreasing surface area is considered in the presented sublimation rate in Figure 9. Ice contains no dry matter and therefore no dry layer can be formed when ice is sublimated. Hence, by definition, no internal water vapour transport (or diffusion) can occur. The sublimation rates measured show some variation due to the measurement method but it can be seen that both sublimation processes (with and without ultrasound) occur at a constant rate.

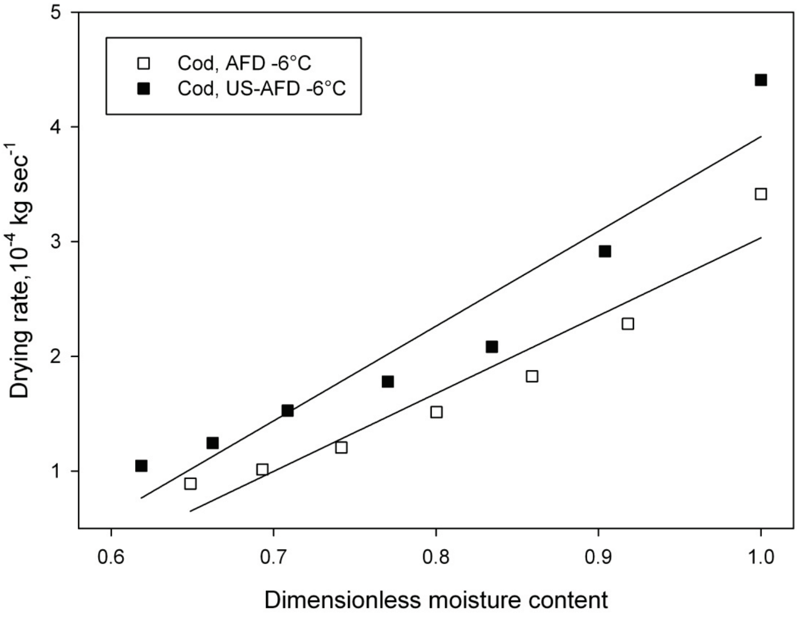

Figure 6: Measured drying rates for AFD and US-AFD of cod cubes at -6℃.

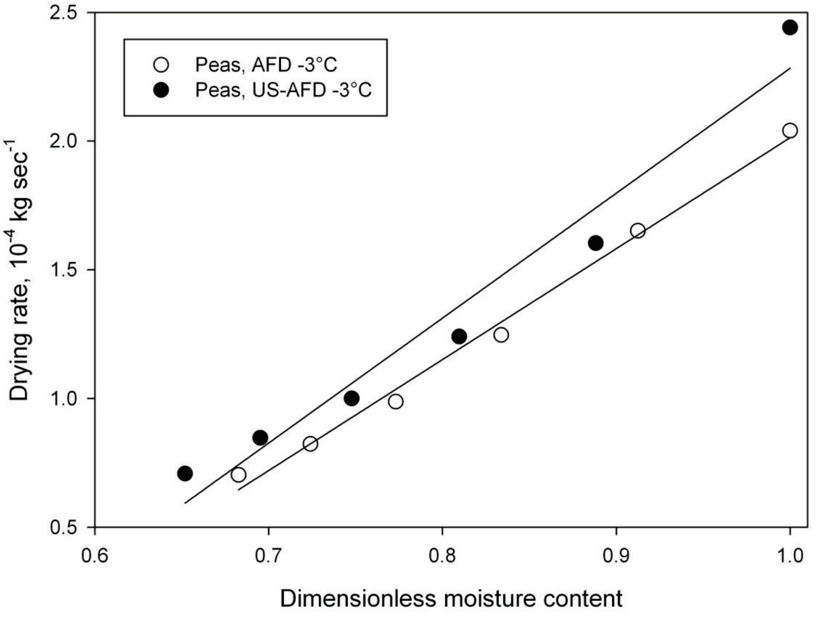

Figure 7: Measured drying rates for AFD and US-AFD of peas at -3℃.

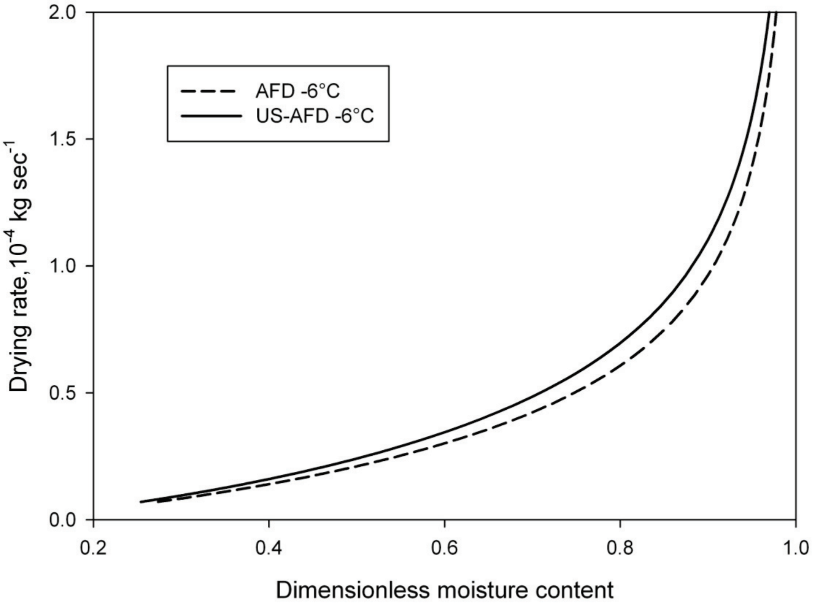

Figure 8: Measured drying rates for 24 hours AFD and US-AFD of peas at -6°C.

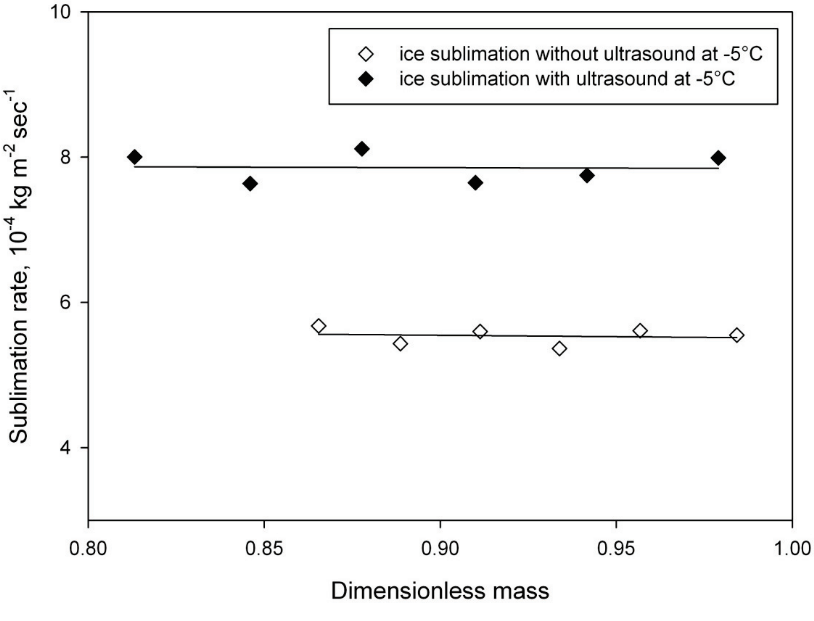

Figure 9: Sublimation rates for ice particles with and without ultrasonic assistance at -5°C with an approach velocity of 1.5 m sec^{-1}.

The drying and sublimation rates obtained (Figure 6 to Figure 9) thus confirm that no constant drying rate period occurs in AFD and US-AFD. For the sublimation of pure ice particles, a constant sublimation period would need to be considered. However the sublimation of ice particles was only included in this investigation in order to evaluate the principles behind US-AFD and no industrial process would sublimate ice in the manner employed for this research. Since the entire dehydration process in AFD and US-AFD occurs during the period when the drying rate is falling, a model for these processes needs only to consider this drying period. Hence, the application of an effective diffusion model (such as the proposed Weibull modification or Fick's law in Chapter 2.3) is justified in the evaluation of the drying behaviour in AFD and US-AFD.

2.3 Modelling AFD and US-AFD

Models that describe a drying process generally predict moisture loss over time, which will give the drying curve. A certain model is often validated for a certain product for constant drying conditions. It is difficult to find a general model that is applicable to for all products, if the drying process is controlled by molecular water vapour diffusion in the already dried product structure. In this situation nearly all models use a product specific parameter, constant or variable in order to adjust for the individual characteristics of the product.

Since it is nearly impossible to find a general model for diffusion controlled drying, the number of models reported in the literature is manifold. There are approximately sixteen models for thin layer drying [45], [46], [47], [48] and [49]; for carrots alone there are 38 model variations [50]. Not many models are reported for AFD. A more recent model is based on the Lewis relation and depends on accurate knowledge of thermal properties and external heat transfer rates [9]. [10] used a similar approach in a CFD model for AFD. Both models have problems with accuracy (deviation of up to 30%, respectively coefficient of determination as low as 80%) which might be caused by the challenging determination of internal heat and mass transfers/diffusions and the implementation of a period with constant drying rate. Also [14] uses thermal properties and a correlation between Nusselt and Sherwood in a model for AFD. An analytical solution for AFD is presented in [51] and [52] where the "Uniform Retreating Ice Front" approach is coupled to the laws of heat and mass transfer. The same approach is used by [7], but the accuracy was not satisfying for the investigations performed (deviation ±10%). [4] based a model for AFD on the Biot number, which describes the relationship between internal and external heat transfer. This study also outlines the importance of the external mass transfer coefficient in AFD on the drying behaviour.

All of these approaches rely on the use of the correct thermal properties, which change significantly in the temperature range in which AFD operates (see Paper II) or rely on numerous equations, variables or constants, all of which also increase the computational time and effort. At the same time these approaches are not generally applicable for AFD and depend on a product-specific parameter, which needs to be determined in an experiment. Hence a simple but accurate empirical model would be desirable (and sufficient) for AFD.

As outlined in Paper VI, Paper VII, Chapter 1.1 and Chapter 2.2 AFD is controlled by internal water vapour diffusion and the drying process occurs only during the period when the drying rate is falling. Figure 1 illustrates the physical model for AFD. The model assumes uniform initial moisture content, one-dimensional moisture movement, no shrinkage, internally controlled moisture transfer in the dried layer, no diffusion in the frozen layer and no voids in the structure of the product. It should be noted that external effects (such as the size of the boundary layer or heat and mass transfer coefficients) can also influence drying behaviour in AFD, even though the process is controlled by diffusion. This is especially true at the beginning of the drying process, when the thickness of the dry layer is still small. A similar conclusion was drawn by [4], who described how the drying rate in AFD can be increased with higher external mass transfer rates, even though the process itself is controlled by diffusion. [7] and [21] also confirm this statement.

A model for AFD can therefore be based on an effective diffusion approach, which can incorporate all drying conditions in one equation. The use of this type of model is sufficient when comparing the drying behaviour for different investigations as long as the boundary conditions are the same. This was the case for the AFD and US-AFD investigations undertaken for this thesis. However, the upscaling of a drying process based on an empirical model of this type needs to be done carefully with respect to maintaining the boundary conditions.

Two empirical model approaches were found to be suitable for AFD and US-AFD:

- a modification of the Weibull model and
- the effective diffusion approach described by Fick's law, which is often used in drying technology.

The modified Weibull model generally showed better accuracy when used for AFD (and US-AFD), but it depends on two parameters: diffusion (D_{calc}) and shape factor (β). Fick's law of diffusion depends on the other hand only on one parameter (diffusion, D_{eff}), but is less accurate for AFD (and US-AFD). However, when comparing the drying behaviour in AFD and US-AFD both models show approximately the same relative increase in diffusion. For the purposes of this thesis it was therefore decided to evaluate and compare all AFD and US-AFD investigations with the effective-diffusion approach (Fick's law), because the drying process can be compared using one parameter only.

2.3.1 Modified Weibull model

The Weibull distribution is one of many probability distribution functions used to describe the behaviour of processes, systems or events that have some degree of variability [53]. The original probability function was described by Waloddi Weibull [54]. The cumulative Weibull distribution is [55]:

$$F_{(t)} = 1 - \exp^{-\left(\frac{t}{\alpha}\right)^{\beta}} \tag{2.1}$$

where t is the time, α is the scale parameter and β is the shape parameter. The model is frequently used in the form of:

$$MR = \exp\left[-\left(\frac{t}{\alpha}\right)^{\beta}\right] \tag{2.2}$$

for air drying [56], [31], rehydration behaviour [57] and water loss under osmotic dehydration [58]. The moisture ratio (MR) is thereby calculated by:

$$MR = \frac{M - M_{eq}}{M_0 - M_{eq}} \tag{2.3}$$

where M is the moisture content of the sample at a certain time, M_{eq} is the equilibrium moisture content of the sample when t = ∞ and M_0 is the initial moisture content. In a preliminary inquiry several other empirical descriptions of a drying process (see list in [59]) were also considered for AFD, but the Weibull model (Equation 2.2) showed the best agreement.

The initial application of the Weibull model showed a good correlation for products dried using AFD, but the empirical model does not account for physical effects (such as diffusion in AFD) or sample dimensions. By substituting the scale parameter β with $L^2 D_{calc}^{-1}$, a simple physical diffusion model can be created [56], [57], [60]:

$$MR = \exp\left[-\left(\frac{D_{calc}\,t}{L^2}\right)^{\beta}\right] \quad 2.4$$

Papers V and VI show that this modification of the Weibull distribution can be used to describe AFD processes in a simple and highly accurate way. The coefficient of determination (R^2) was better than 99.9% and the chi-square (χ^2) lower than $11*10^{-6}$ for all the AFD processes investigated. Hence the drying properties of a certain product can be precisely described with equation 2.4 based on two empirically determined constants (diffusion and shape parameter).

2.3.2 Fick's law of diffusion

Fick's law is one of the most common descriptions for diffusion and is used quite often in association with drying technology. It describes a correlation between the diffusive flux and a concentration field, which means that concentration gradients are the forces for mass transfer when applied to convective drying. The molecular diffusion is thereby described by an effective diffusion coefficient (D_{eff}). One-dimensional mass transfer is hence described as:

$$\frac{\partial M}{\partial t} = D_{eff}\frac{\partial^2 M}{\partial x^2} \quad 2.5$$

where x is the spatial coordinate. Under the assumption of uniform initial moisture content, one-dimensional moisture movement, no shrinkage and an internally controlled moisture transfer (falling drying rate period), the equation can be solved for known geometries. The solution of Fick's law for a sphere, infinite slab and cylinder are [61], [62]:

$$\begin{aligned} &a.)\ MR = \frac{6}{\pi^2}\sum_{n=1}^{\inf}\frac{1}{n^2}\exp\left[-n^2\frac{\pi^2 D_{eff}t}{r_{sphere}^2}\right] && (sphere) \\ &b.)\ MR = \sum_{n=1}^{\inf}\frac{4}{Be_n^2}\exp\left[-\frac{b_n^2 D_{eff}t}{r_{cylinder}^2}\right] && (in.cylinder) \\ &c.)\ MR = \frac{8}{\pi^2}\sum_{n=1}^{\inf}\frac{1}{(2n-1)^2}\exp\left[-(2n-1)^2\frac{\pi^2 D_{eff}t}{L^2}\right] && (in.slab) \end{aligned} \quad 2.6$$

where r is the radius, L is the slab thickness, n is a positive integer and b is the root of the Bessel function. For long drying times, when t is large and r or L is small, only the leading term in these equations needs to be taken into account [61], [62], [63]. This limits the equation to:

$$a.)\qquad MR = \frac{6}{\pi^2}\exp\left[-\frac{\pi^2 D_{eff} t}{r_{sphere}^2}\right]\qquad (sphere)$$

$$b.)\qquad MR = \frac{4}{b_1^2}\exp\left[-\frac{b_1^2 D_{eff} t}{r_{cylinder}^2}\right]\qquad (in.cylinder)\qquad 2.7$$

$$c.)\qquad MR = \frac{8}{\pi^2}\exp\left[-\frac{\pi^2 D_{eff} t}{L^2}\right]\qquad (in.slab)$$

A general form for these solutions can be written in logarithmic form [61], [62], [63]:

$$\ln(MR) = B - A * t \qquad 2.8$$

where the slope of the linear segment will contain the effective diffusion coefficient. In practical engineering the effective diffusion (D_{eff}) can be obtained by plotting the ln(MR) against time and performing a regression analysis in the form of equation 2.8, where A equals the exponential term [61], [62], [63]:

$$a.)\qquad A = \frac{\pi^2 D_{eff}}{r_{sphere}^2}\qquad (sphere)$$

$$b.)\qquad A = \frac{b_1^2 D_{eff}}{r_{cylinder}^2}\qquad (in.cylinder)\qquad 2.9$$

$$c.)\qquad A = \frac{\pi^2 D_{eff}}{L^2}\qquad (in.slab)$$

The moisture ratio is thus mostly obtained from drying experiments of sufficient length. With the modified Weibull model it is possible to determine the effective diffusion in Fick's law by performing the regression analysis described here. Since the complete AFD process can be described with the modified Weibull model, long drying experiments are not needed for the determination of the effective mass diffusion (D_{eff}), (Paper VI).

2.4 Diffusion in AFD and US-AFD

The effective diffusion (D_{eff}) for different investigations comparing AFD and US-AFD (see Table 1) were determined using the method described in Chapter 2.3.2 and are given in Table 2. A non-linear regression analysis was used to determine the effective diffusion.

Two criteria were used to evaluate the accuracy of the estimates: the coefficient of determination (R^2) and the reduced chi-square (χ^2) between the predicted and experimental values. The chi-square was calculated by the expression:

$$\chi^2 = \frac{\sum_{i=1}^{N} \left(MR_{\text{expriment}} - MR_{\text{model}} \right)^2}{N - n} \qquad 2.10$$

where N is the number of experimental data points and n is the number of constants.

The coefficient of determination (R^2) as well as the chi-square (χ^2) and therefore the accuracy for the effective diffusion (D_{eff} in Table *2*) was generally lower than for the diffusion from the modified Weibull model (see Table 2 in Paper V and Table 2 in Paper VI).

The Weibull model generally showed a high accuracy between modelled and measured values (χ^2 less than $24*10^{-6}$, see Papers V and VI) for AFD and US-AFD. The good agreement between modelled and measured values can be illustrated using the example of AFD and US-AFD of peas at -3°C at an approach velocity of 3.1 m sec^{-1} in Figure 10. It is therefore recommended that the modified Weibull model (Paper V) is used to model AFD and US-AFD.

However, the drying behaviour that was found in the different AFD and US-AFD investigations can be compared in one value (D_{eff}) when using Fick's law, whereas the diffusion in the modified Weibull model (D_{calc}) has to be evaluated along with the shape factor (β). It is interesting to note that the increase in effective diffusion as outlined in Table 2 is of the same order and size and shows the same trend as the increase in the diffusion obtained by the modified Weibull model (see increase $D_{eff,Weibull}$ in Table 2 of Paper VI).

Table 2: Comparison of effective diffusion (D_{eff}) for AFD and US-AFD.

Product / Investigation	**AFD**			**US-AFD**			**Increase in D_{eff} with US**
	D_{eff}, 10^{-11} $m^2 sec^{-1}$	**R^2 %**	**χ^2 10^{-6}**	**D_{eff}, 10^{-11} $m^2 sec^{-1}$**	**R^2 %**	**χ^2 10^{-6}**	
A. Products investigated							
Ice (subl.)**	**0.47****	99.25	115	**0.64****	99.83	53	**38.5%**
Zooplankton	**0.84**	99.97	6015	**0.93**	99.97	2729	**9.8%**
Cod	**74.26**	99.79	827	**83.65**	99.80	864	**12.6%**
Apple	**36.68**	99.95	756	**38.44**	99.91	835	**4.8%**
Peas	**4.10**	99.68	709	**4.45**	99.72	556	**8.5%**
B. Temperature investigation							
Peas -6 °C	**4.10**	99.68	709	**4.45**	99.72	556	**8.5%**
Peas -3 °C	**5.87**	99.77	691	**6.90**	99.82	670	**17.5%**
Peas 0 °C	**10.97**	99.91	592	**12.64**	99.48	511	**15.1%**
Peas 10 °C	**15.04**	99.81	4296	**15.08**	99.81	4266	**0.2%**
Peas 20 °C	**19.41**	99.84	6851	**19.61**	99.81	7224	**1.0%**
C. Drying time influence							
Peas 3h	**4.10**	99.68	709	**4.45**	99.72	556	**8.5%**
Peas 24 h	**3.68**	99.70	6179	**4.08**	99.75	6211	**10.8%**
D. Investigation of approach velocity influence							
Peas 1.0 m sec^{-1}	**4.69**	99.87	171	**5.85**	99.91	189	**24.7%**
Peas 1.8 m sec^{-1}	**4.51**	99.78	369	**5.42**	99.87	408	**20.2%**
Peas 2.6 m sec^{-1}	**4.14**	99.67	596	**4.56**	99.65	829	**10.1%**
Peas 3.1 m sec^{-1}	**4.10**	99.68	709	**4.45**	99.72	556	**8.5%**
Peas 4.7 m sec^{-1}	**4.41**	99.78	367	**4.56**	99.79	365	**3.4%**
E. Investigation of ultrasound intensity influence							
Peas 15.3 W	**5.87**	99.77	691	**6.07**	99.76	831	**3.3%**
Peas 43.1 W	**5.87**	99.77	691	**6.91**	99.84	624	**17.7%**
Peas 68.2 W	**5.87**	99.77	691	**6.90**	99.82	670	**17.5%**

**The moisture ratio (MR) for the determination of D_{eff} is based on absolute mass (m) since ice contains no dry matter.

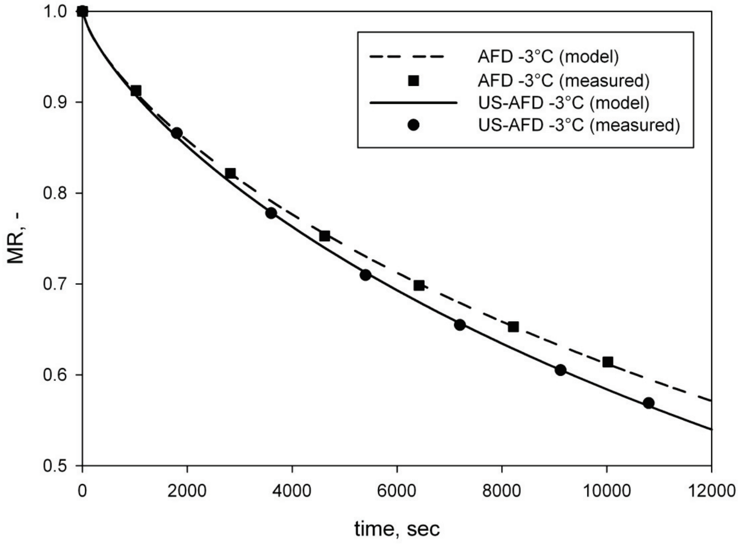

Figure 10: Modelled and measured drying curve for AFD and US-AFD of peas.

The coefficient of determination (R^2) for the effective diffusions (D_{eff}) obtained was at least 99.5% or better while the chi-square (χ^2) did not exceed $7000*10^{-6}$ for all drying experiments.

In general all products showed increased diffusion and faster drying in the presence of an ultrasonic field. The highest increase (38.5%) in effective diffusion was obtained during the sublimation of pure ice particles. Ice is not normally subjected to AFD, because it does not contain any dry matter and no industrial application would sublimate pure ice in the way that we did. The moisture ratio (MR) for ice is therefore based on total mass (m) and not on moisture content (M). However, the “drying” of ice particles is a process in which no internal diffusion occurs, which means that the complete process is controlled by external heat and mass transfer. Therefore, US-AFD of pure ice particles is an interesting undertaking in the overall examination of the principal mechanisms involved in US-AFD.

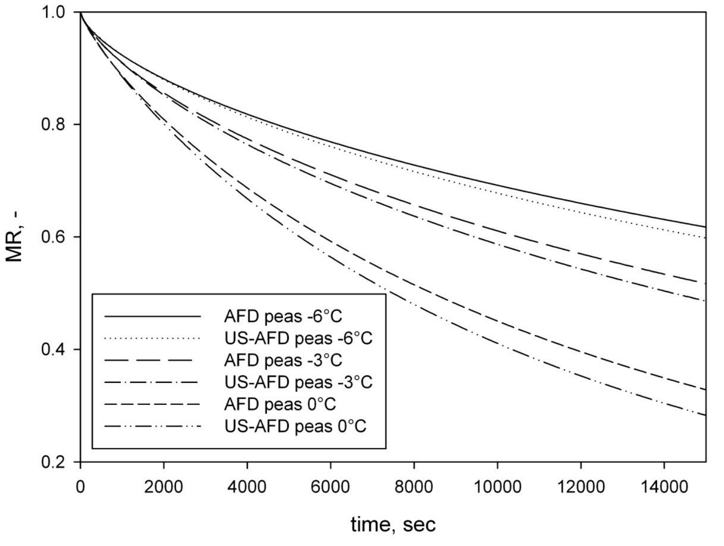

Figure 11: Moisture ratio for AFD and US-AFD of peas at -6℃, -3℃ and 0℃.

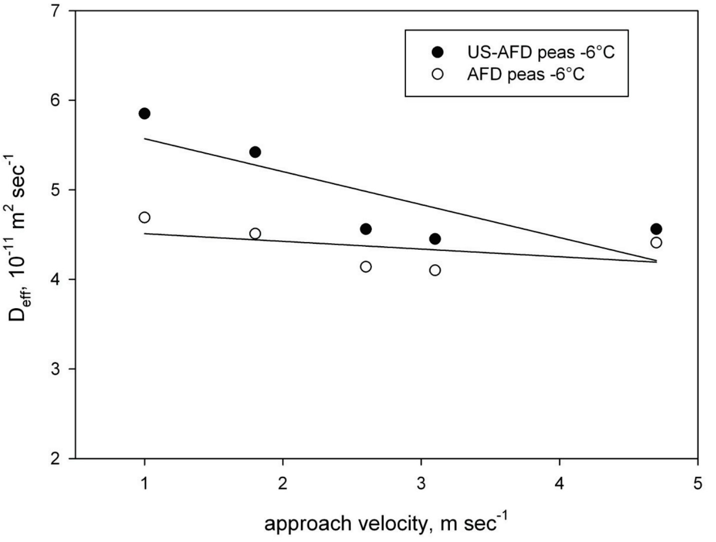

Figure 12: Effective diffusion for AFD and US-AFD of peas at -6℃ and different approach velocities.

The effective diffusion for different drying temperatures increased with temperature (Table 2-B). This is a result of the temperature-dependent vapour pressure of water/ice, which results in faster drying at higher temperatures in general. However, the effective diffusion for drying tests with ultrasonic assistance only increased for drying temperatures below 0℃ (Table 2-B and Figure 11). The highest increase (17.5%) was obtained at a drying temperature of -3℃.

The effective diffusivity for peas in AFD did not vary significantly with different approach velocities in a fluid or stationary bed state respectively (Figure 12 and Table 2-D). The variation obtained is most likely due to the characteristics of the system we used (see Paper VII) and/or the accuracy of the method used to determine the diffusion. It also shows that AFD of peas is in general controlled by internal diffusion and the drying rate is not increased with a higher approach velocity. Applying ultrasound to the system increased the effective diffusion by nearly 25% at an approach velocity of 1 m sec^{-1}. This positive effect was reduced with increasing approach velocity until almost the same effective diffusion in AFD and US-AFD occurs at 4.7 m sec^{-1} in fluid bed state (Figure 12).

Increasing the ultrasonic intensity also increased the effective diffusivity in general (Figure 13 and Table 2-E). However the effective diffusion obtained at 43.1W (around 70% of maximum power) was approximately the same as the effective diffusion at 68.2W.

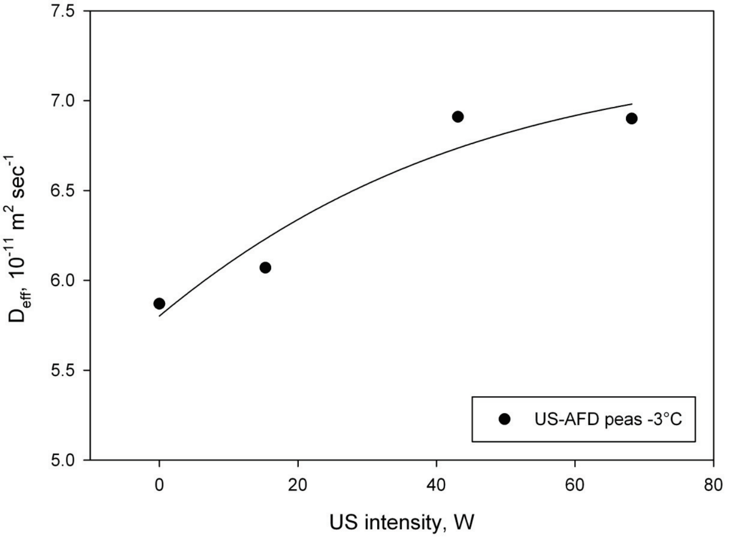

Figure 13: Effective diffusion in US-AFD for peas at -3℃ and different intensities.

The colour of all dried peas did not change significantly for drying with or without ultrasonic assistance (Papers VI and VII). Significant colour changes were only observed for products that showed high effective diffusion as a result of the individual drying conditions. The colour changed with the (final) moisture content, but not due to the application of ultrasound. The d_{50}-diameter was also not affected by the application of ultrasound (Papers VI and VII). Shrinkage occurred from the more rapid dehydration due to the drying conditions, rather than from the application of ultrasound.

No particle breakdown was observed during the tests. Drying conditions (temperatures, relative humidity and velocity) for all tests were recorded and showed no discrepancies between the tests with and without ultrasound. The generally higher sublimation rate for US-AFD did result in a slightly higher relative humidity (≈+2-5%) at the outlet of the drying chamber compared to AFD, whereas the temperature showed no significant or measurable difference. The higher sublimation rate in US-AFD also did not influence the performance of the generously dimensioned heat pump system.

A constant ratio between effective diffusion (D_{eff}) and the diffusion in the modified Weibull model (D_{calc}) as reported in [57] and [60] (see also Paper VI) was not obtained for the tests presented here (Papers IV, VI and VII) and the ratio obtained was not conclusive[10].

The ultrasonic equipment we used had an efficiency of around 20% when employed as source for airborne ultrasound. Taking this as the basis, the specific ultrasonic intensity was between 15 and 20 W $kg_{product}^{-1}$ in the US-AFD investigations performed.

[10] The ratio D_{calc}/D_{eff} obtained in the AFD and US-AFD experiments varied from 11 to 63 depending on drying conditions and product (data not included in this thesis). Therefore this approach was not investigated further.

2.5 Discussion

Atmospheric or convective freeze drying (AFD) has only recently been deployed at an industrial scale. In order to maintain a cold drying agent with low relative humidity, AFD needs to be combined with a heat pump (see Figure 5) [11]. Industrial systems for heat pump drying (HPD) have been successfully designed, dimensioned and installed for drying fish products, with about 70 plants in Norway alone. Hence, the technology for HPD can be scaled up to fit industrial sized plants. Recently [14] and [64] suggested the use of a vortex tube instead of a heat pump system in order to maintain the required conditions for the air used for drying in AFD. [14] provides more detailed information about this system and results from its use. The system proposed here is an attractive alternative that overcomes the drawbacks of existing AFD as well as VFD systems. However, the usage of the proposed vortex tube in an industrial sized-system has yet to be demonstrated. [65] used a simple air cooling system in combination with an adsorbent in order to achieve the desired conditions for the air used in drying in AFD. The industrial scale use of this system also needs to be demonstrated in the future.

Regardless of the system used for air conditioning, the limiting factor for AFD is its relatively low drying rate, which has resulted in an ongoing search for ways to accelerate the sublimation and mass transport [5], [7], [64], [66], [67], [68] or [69]. AFD has great potential and is also currently under investigation for use in spray freeze drying in combination with a freeze concentration process [70] and in combination with bed of adsorbents [6], [65] or [71]. Nevertheless, the common AFD process still remains a focus of research [2], [5], [65] or [72].

There has been a revival interest in the application of ultrasound in drying technology, since economical airborne transducers are now available. The application of ultrasound in AFD has not been investigated to date and is different from the use of ultrasound in normal convective drying at temperatures between 0°C and 100°C, because the product is frozen (Chapters 1.4 and 2.1).

In [35], [36], [73] or [74] the complete drying chamber is used as the vibrating media, which creates an ultrasonic field inside the chamber. In industrial applications this approach is quite difficult to realize, especially since power consumption levels between 1000 to 3000 W $kg_{product}^{-1}$ were used in [35], [36] and [37].

[11] AFD can also be employed without a heat pump in special locations, such as the Lofoten area in Norway, where cold but dry ambient air is traditionally used to produce dried cod, or stockfish. However, changing seasonal temperatures and hygienic requirements as well the need to provide product throughout the calendar year favour industrialized heat pump assisted AFD solutions.

A more practical approach is found in [28] and [34], where an airborne transducer is placed inside the drying system. The product can thus come directly into contact with the vibrating element. However, any industrial application of the direct-contact approach (as described in [28] and [34]) would require an enormous contact area between the product and the ultrasonic transducer, making the system difficult to design, while at the same time reducing the contact area for mass transfer between drying agent and product. A more promising approach for AFD with respect to industrial applications is where the ultrasonic airborne transducer is placed in the drying chamber in such a way that the product is only in contact with the ultrasonic field (also described in [28] and [34]). The system we used for this thesis (Figure 5) made it possible to realize this requirement in a practical and easy way.

As outlined in Chapter 2.2 the operative process that makes AFD and US-AFD work takes place during the period when the drying rate is falling, which means that the process is controlled by diffusion. However, the use of high intensity, airborne ultrasound increased the effective diffusion, which shows that dehydration in AFD can be accelerated, despite the fact that the process is diffusion controlled. This is in accordance with the findings from [4] and [21], where the importance of the external mass transfer coefficient in AFD is described. The accelerating effect of ultrasound occurred only at the beginning of dehydration, when the dry layer of the product was still small. The effect of ultrasound was marginal when the dry layer of the product posed significant resistance to water vapour transport (see Figure 8).

The placement of the ultrasonic transducer altered the original flow profile into the drying chamber used for this research. However, the drying achieved with US-AFD can be compared with AFD since the transducer was not removed for the AFD tests without ultrasound and the drying conditions in AFD were equal to US-AFD. In the investigations performed, the ultrasound was introduced through the bottom plate of the drying chamber in both the fluid and stationary beds. The product in the stationary bed was mixed manually every 30 minutes, so that every product particle was at least near the ultrasonic field during drying. In the fluid bed, the mixing was achieved due to fluidization. Future research should investigate if the ultrasonic transducer can be deployed in the sidewalls of the drying chamber. Additionally, the maximum distance between the ultrasonic transducer and the drying product should be investigated. If the ultrasonic transducer must be close to the product that is being dried, this would limit the industrial usage of this drying technology. An open question is also whether or not there is an optimum angle between the ultrasonic sound wave and the surface of the product. Because this investigation employed a fluid or fixed bed with a good mixing and where the product was close to the ultrasonic transducer, these aspects of ultrasonic assisted drying were not investigated. However the results presented here show that ultrasound can significantly accelerate AFD.

The ultrasonic transducer used had 20% efficiency when employed as an airborne system, which meant that the specific ultrasonic intensity did not exceed 20 Watt per $kg_{product}$ for all investigations. Assuming an 80% efficiency for the airborne transducer and a power consumption of up to 4 kW (as described in [28] and [34]), industrial applications of US-AFD could be realized now with a capacity of 200 $kg_{product}$ per US-unit.

The effects that may be responsible for the accelerated drying rate in the presence of ultrasound are listed in Chapter 1.4. However, more recent research concludes that the faster drying in the presence of airborne ultrasound is caused primarily by two effects [28], [34], [35], [36] or [73]:

1. The product that has been dried is compressed and expanded in the presence of the ultrasonic field. The water inside the product thus diffuses more rapidly than without the use of ultrasound. This effect is commonly referred to as the "sponge-effect".
2. The external mass transfer resistance at the solid – gas interface is reduced. The resulting increased mass transfer rate can be caused by a changing pressure gradient, micro-streaming and/or oscillating velocities, which result in a reduction of the boundary layer and thus higher turbulence around the product.

Chapter 2.1 outlines the possible effects that may occur as a result of the use of ultrasound in AFD. However, the tests performed for this thesis did not show effects such as better particle dispersion, particle breakdown or changes in the properties of the drying agent (see Papers IV, VI and VII). Because of the brittle ice structure, the "sponge-effect" is unlikely to occur in US-AFD. Furthermore, the ultrasonic intensity employed in the experiments was roughly 100 times smaller than in [35], [36] or [37], which seems too small to compress the product mechanically in the manner associated with the "sponge-effect".

The kinetic energy of an ultrasonic wave is generally transferred by cavitation at the interface between the resonance media and the solid [27]. For US-AFD this means that cavitation bubbles will form in the drying air at the interface with the drying product, where a boundary layer exists. Therefore it seems safe to assume that high intensity, airborne ultrasound will especially exert its accelerating effect here. Papers IV, VI and VII concluded that the accelerated effective mass transfer in US-AFD is (most likely) caused by an increased external mass transfer rate due to a reduced boundary layer, which results from higher turbulence at the gas-solid interface.

The results (Table 2) from the experiments conducted using US-AFD support this theory. The highest increase in effective diffusion (38%) was reached during the sublimation of ice particles. Since there is no internal diffusion during the sublimation of ice the process is solely controlled by external effects. In all other products that were investigated, the effective diffusion in US-AFD had a lower increase than with ice, because internal diffusion posed an additional resistance to mass transfer. If US-AFD actually increases internal diffusion, a greater increase in effective diffusion would be expected with US-AFD for products with internal diffusion resistance.

US-AFD with different approach velocities showed the highest increase in effective diffusion at low approach velocities (24.7% at 1m sec^{-1}), where a thicker boundary layer naturally exists (see Figure 14). In the fluid state at an approach velocity of 4.7 m sec^{-1}, the boundary layer is already reduced by the higher turbulence resulting from the approach flow. Hence a further reduction of the boundary layer due to the ultrasonic field only resulted in a minor increase in effective diffusion (+3.4%).

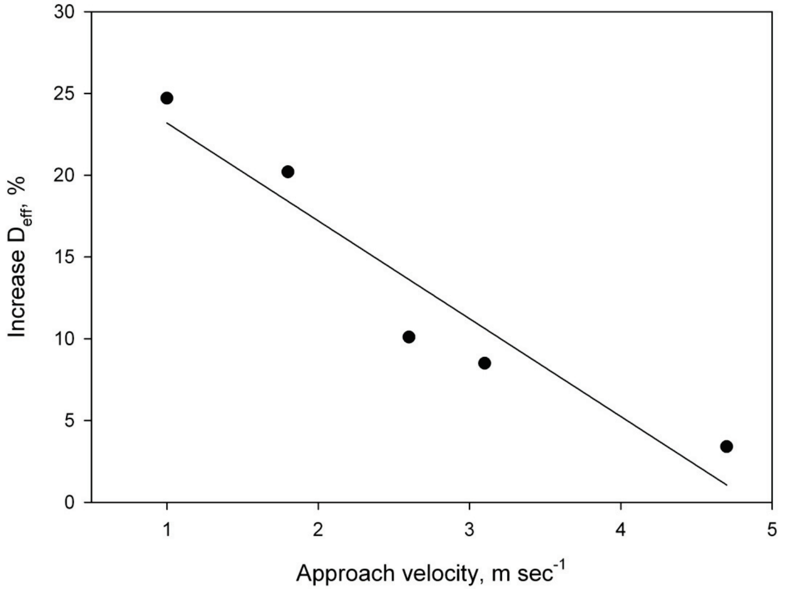

Figure 14: Relative increase in effective diffusion for US-AFD at different approach velocities.

Table 2-E and Figure 13 (see also Paper VI) show that a higher ultrasonic intensity does not necessarily increases the mass transfer. This can be explained by the fact that once the boundary layer is reduced, more ultrasound will not reduce the boundary layer

further at the gas-solid interface. However in [35] and [37], a linear relationship between ultrasonic intensity and the external mass transfer rate was established. Further research on this topic is therefore necessary.

The results obtained from the US-AFD experiments therefore support the conclusion that the ultrasonic field in US-AFD increases the external mass transfer rate. Assuming that this is correct, it is possible to optimize the US-AFD process. Figure 8 shows that the drying rate in US-AFD is similar to AFD towards the end of the drying period. However, when the product begins to dehydrate, US-AFD shows a significantly higher drying rate than AFD. Toward the end of the drying process the internal resistance is naturally higher, because of the increasing thickness of the product's dry layer. That means that ultrasound should only be employed during the beginning of the drying process, because an increased external mass transfer rate will not significantly influence the drying rate when the product already has a thick dry layer.

The specific ultrasonic intensity used in all experiments did not exceed 20 W $kg_{product}^{-1}$ (considering the efficiency of the equipment used), compared to [35], [36] or [37] where the ultrasonic intensity was as much as 100 times higher. This high ultrasonic intensity enabled drying rates in eggplant of up to 70% faster at 40°C [37]. Airborne ultrasound therefore has huge potential to accelerate mass transfer in convective freeze and low temperature drying. However, the additional energy demand for the ultrasonic equipment needs to be taken into account when analysing the drying system. Under certain conditions (see Paper IV) the SMER value can be significantly increased to as much as 0.4 when US-AFD is performed in the manner described here. The use of an energy demanding ultrasonic system in a common convective drying process as described in [35], [36] or [37] would actually significantly decrease the SMER, which means that the drying process would be more expensive or even uneconomic. With respect to energy consumption, the application of ultrasound in a drying system should increase the SMER (or at least not change the SMER), while simultaneously accelerating the drying rate. This requirement was met during all of the experiments performed.

A more detailed discussion of US-AFD can be found in Paper IV, VI and VII.

2.6 Conclusions

The use of ultrasound in a common AFD process generally increased the effective diffusion and therefore the drying rate. The drying rates obtained in AFD and US-AFD show that both processes take place during the period when the drying rate was falling, and are controlled by diffusion. However, external drying conditions also have an influence on the drying rate in AFD and US-AFD, especially at the beginning of the dehydration period, when the dry layer is thin. The effect of ultrasound on the drying rate has to be evaluated together with the product's effective mass diffusion characteristics under certain drying conditions.

With the system used here the effective sublimation can be increased up to 38% for ice, while the effective diffusion for AFD of peas can be increased up to 24.7% at an approach velocity of 1 m sec^{-1}. The accelerated mass transfer rates are significant for AFD (drying temperatures -6°C, -3°C and 0°C), whereas for higher temperatures (10°C and 20°C) the effect of ultrasound was marginal. AFD conducted with products in a fixed bed at low approach velocities (1 to 2.6 m sec^{-1}) significantly accelerated in the presence of ultrasound, while at higher approach velocities (3 to 4.7 m sec^{-1}) with a fluid bed, the accelerating effect of ultrasound was lower. However, even the presence of a moderate ultrasonic field clearly increased the effective diffusion.

The quality of the product, such as the d_{50}-diameter (shrinkage) and colour (L, a and b values) was not affected by the presence of ultrasound in the drying chamber.

A higher mass transfer rate at the solid-gas interface, caused by a reduced boundary layer and a respectively higher turbulent interface, is identified as the cause for the higher effective diffusion in US-AFD.

Airborne ultrasound therefore has high potential for improving atmospheric freeze dying, as well as other processes that are based on convective heat and mass transfer at low temperatures (such as freezing or thawing).

3 Suggestions for further work

The application of ultrasound in AFD was investigated and generally resulted in more rapid drying than drying without ultrasound. However, further research is necessary to understand and evaluate the potential of airborne ultrasound and AFD:

1. US-AFD: The ultrasonic intensity and therefore the additional energy demand for the ultrasonic equipment have to be taken into account when evaluating the drying system in terms of its cost effectiveness (e.g. SMER). One aspect that should be investigated further is, if the effective mass transfer can be accelerated further at higher US intensities. In the investigations performed here the ultrasound did not affect the product quality (colour and shrinkage). Additional quality parameters (such as biological activity, lipid composition, etc.) should be included in future research on US-AFD. In the present investigation the ultrasonic transducer altered the original flow profile of the drying chamber. Other system solutions for US-AFD should be investigated further, in order to evaluate the potential of this technology.

2. Model: The empirical model used for AFD and US-AFD evaluated effective mass transfer/diffusion under different drying conditions. It will provide accurate drying rates as long as the drying and boundary conditions do not change. However, the model should include drying conditions and more product characteristics in order to be applicable under variable conditions and for scale-up. Since ultrasound affects the external mass transfer rate, the model should be further refined in a way that external and internal mass transfer/diffusion can be evaluated.

3. AFD: Industrial AFD is currently only employed in the drying of food. However, based on the results from Papers I and III, AFD holds promise for both pharmaceutical and biochemical drying. AFD (with energy recovery via a heat pump) could be cheaper and an even faster alternative drying method to commercial VFD. Future research on AFD should focus on this potential.

4. US-Freezing: Airborne ultrasound could positively affect other processes such as blast freezing and thawing. The influence of high intensity airborne ultrasound on a blast freezing process has so far not been investigated, even though the technology is considered promising by [27], [75] and [76]. It is possible to accelerate freezing rates for immersion and direct contact freezers with ultrasound (see [30], [75], [76], [77], [78], [79], [80], [81], [82] and [83]) and the same effects could be achieved for ultrasonic blast freezers. Figure 15

shows a possible experimental setup for such an investigation. A parametric study of ultrasonic assisted blast freezing should include different approach velocities, ultrasonic intensities as well as different distances and angles between the ultrasonic transducer and the product. The ice structure of the frozen product should also be analyzed.

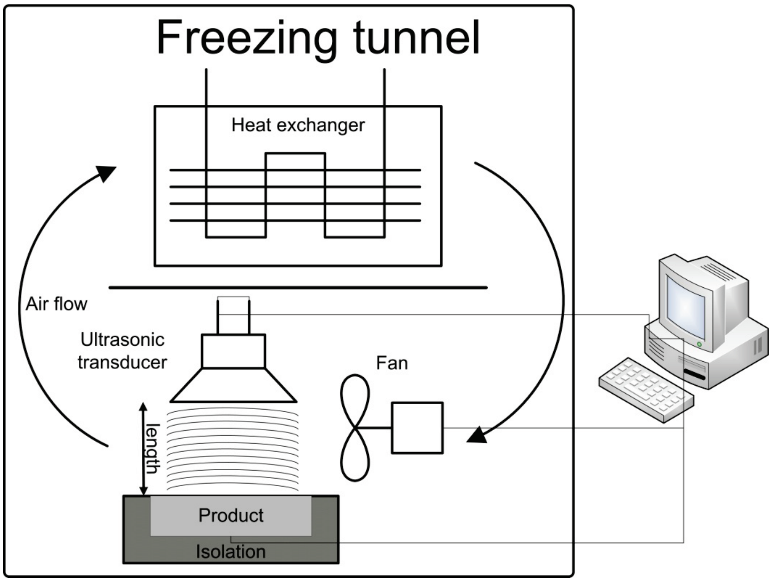

Figure 15: Suggested experimental setup for ultrasonic assisted blast freezing.

4 Summary of Papers

4.1 Paper I

Title: Atmospheric freeze-drying of *Calanus finmarchicus* and its effects on proteolytic and lipolytic activities.

Authors: Michael Bantle, Trygve Magne Eikevik and Turid Rustad.

Published in Proceedings of the 4th Nordic Drying Conference NDC 2009: June 17-19 2009, Reykjavik, Iceland, Ebook: ISBN 978-82-594-3406-7.

Different freeze drying methods for the zooplankton species *Calanus finmarchicus* were evaluated. The proteolytic and lipolytic activity in zooplankton was well preserved under AFD, whereas a temperature controlled AFD/AD process resulted in faster drying but lower activity in the rehydrated product. Sorption isotherms and particle size distribution for zooplankton are given and the drying rate of AFD is compared with VFD.

Contribution: The author (Michael Bantle) organized the trips to collect zooplankton, performed the drying experiments, determined sorption isotherms and particle size distribution. He was further involved in the interpretation of the results, wrote the paper and presented it at the Nordic Drying Conference 2009 in Reykjavik, Iceland.

4.2 Paper II

Title: A Novel Method for Simultaneous and Continuous Determination of Thermal Properties during Phase Transition Applied to *Calanus finmarchicus*.

Authors: Michael Bantle, Trygve Magne Eikevik and Jon Eirik Brennvall.

Published in the Journal of Food Science, 2010, 75 (6): p. E315-E322.

Thermal conductivity, specific heat capacity, enthalpy, density and initial freezing point of the zooplankton species *Calanus finmarchicus* were determined (see Figure 4). Thermal properties were obtained using a new method that allows continuous and simultaneous thermal evaluation of conditions from -40°C to +20°C in one sample. The values obtained were compared with general predictive models. Modelled and measured values agreed well for general engineering purposes, except for the thermal conductivity. Other models were considered for the thermal conductivity of zooplankton and the product specific constant for the best-fit model (Pham and Wilix) was determined.

Contribution: The author (Michael Bantle) improved the existing measurement procedure, performed the measurements, evaluated the data and did the modelling work. He wrote and published the paper in the Journal of Food Science.

4.3 Paper III

Title: Lipid Changes and Lipid Oxidation in *Calanus finmarchicus* during Vacuum, Atmospheric and Nitrogen Freeze Drying.

Authors: Michael Bantle, Turid Rustad and Maria Bergvik.

Published in Proceedings 17th International Drying Symposium, October 4-6 2010, Magdeburg, Germany: p. 1907-1914.

The zooplankton species *Calanus finmarchicus* was dried using 3 different freeze drying processes: in a vacuum, in atmospheric condition and with nitrogen. The drying rate was highest for AFD and lowest for nitrogen freeze drying. Nitrogen freeze drying resulted in a reduced amount of phospholipids and a high amount of free fatty acid content (degradation product), whereas AFD preserved the lipids at a quality similar to VFD. Lipid oxidation was highest in the product from Nitrogen freeze drying, whereas AFD and VFD dried products showed only minor lipid oxidation. The degradation and oxidation of the products showed a linear correlation to the drying rate.

Contribution: The author (Michael Bantle) performed the different freeze drying experiments and was involved in the interpretation of the results. He wrote the main parts of the paper and presented the work at the 17th International Drying Symposium 2010 in Magdeburg, Germany.

4.4 Paper IV

Title: Mass Transfer in Ultrasonic Assisted Atmospheric Freeze Drying.

Authors: Michael Bantle, Trygve Magne Eikevik and Anton Grüttner.

Published in Proceedings 17th International Drying Symposium, October 4-6 2010, Magdeburg, Germany: p. 763-768.

The effect of airborne ultrasound on the drying rate of a common AFD process was studied. A drying system for US-AFD was developed and successfully tested. A feasibility study was presented for different products dried with the system and the effect of ultrasound on AFD was evaluated, based on the total mass reduction over time. US-AFD was in general significantly faster, although the effect varied from product to product. The SMER value of the system increased up to 0.8 for “drying” of ice and up 0.4 for common drying products. The paper demonstrates that even a minor airborne ultrasonic field can significantly accelerate the drying rate. An increased external mass transfer rate was found as the most plausible explanation for this effect.

Contribution: The author (Michael Bantle) planned and built a drying chamber for US-AFD, planned and performed the experiments and evaluated the results. He wrote the paper and presented the work at the 17th International Drying Symposium 2010 in Magdeburg, Germany.

4.5 Paper V

Title: Modification of the Weibull distribution for modeling atmospheric freeze drying of food.

Authors: Michael Bantle, Kjell Kolsaker and Trygve Magne Eikevik.

Manuscript submitted to Drying Technology, An International Journal, December 2010.

The existing Weibull distribution was modified for use in a physical model and its application as an empirical model for AFD processes was demonstrated. Other empirical models were also preliminarily evaluated, but the Weibull model generally showed the best accuracy. Some general aspects of AFD were outlined. The modified Weibull model showed good accuracy for different products dried using AFD at different drying temperatures, approach velocities, particle sizes and drying times. The drying rate for AFD can be described in a simple, fast and highly accurate model, compared to other AFD models.

Contribution: The author (Michael Bantle) performed the AFD tests and evaluated the adaptability of several different models. He modified the best-fit model (Weibull) so it could function as a physical model, evaluated the data, wrote the paper and submitted it to the journal "Drying Technology".

4.6 Paper VI

Title: Parametric study of high intensity ultrasound in the atmospheric freeze drying of food.

Authors: Michael Bantle and Trygve Magne Eikevik.

Manuscript submitted to Drying Technology, An International Journal, February 2011.

A parametric study of US-AFD was conducted using peas. Peas were chosen for drying because of their defined size, structure and shape, even though US-AFD of other products (such as cod) would result in a higher acceleration of the drying rate. An accelerated drying rate in all investigations was achieved. A modification of the

Weibull model was used to evaluate the data. US-AFD showed the highest increase in drying rates at low temperatures and during the first of hours of drying. Even a minor ultrasonic field increased the drying rate significantly. No change in product quality (shrinkage or colour) was found. A higher external mass transfer rate (as a result of a reduced boundary layer) was identified as the possible cause for the higher effective mass diffusion in US-AFD, confirming the conclusions of Paper IV.

Contribution: The author (Michael Bantle) planned and performed the US-AFD investigation. He evaluated the drying behaviour and product quality, wrote the paper and submitted it to the journal “Drying Technology”.

4.7 Paper VII

Title: Kinetics of ultrasonic assisted atmospheric freeze drying of green peas.

Authors: Michael Bantle and Trygve Magne Eikevik.

Paper accepted for Nordic Drying Conference 2011, June 19th to 21st 2011.

Green peas were subjected to atmospheric freeze drying at different approach velocities with and without the assistance of high intensity, airborne ultrasound. The effective diffusion for all AFD processes investigated without ultrasound varied slightly, but the effect on the drying curve was marginal. An accelerated diffusion for US-AFD of up to 24.7% was determined for a stationary bed at an approach velocity of 1 m sec^{-1} and up to 8.5% with fluid bed at an approach velocity of 3.1 m sec^{-1}. It is possible to achieve a higher effective diffusion for US-AFD with a stationary bed than for AFD with a fluid bed. A linear relationship between the increase in effective diffusion and approach velocity was obtained. The quality of the product (colour and shrinkage) was not affected by the presence of ultrasound. This investigation also identified a higher external mass transfer rate (as a result of a reduced boundary layer) as the possible cause for the higher effective mass diffusion in US-AFD.

Contribution: The author (Michael Bantle) planned and performed the US-AFD investigation. He evaluated the drying behaviour and product quality, wrote the paper and submitted it to the Nordic Drying Conference 2011.

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Paper I

Atmospheric Freeze-Drying of *Calanus finmarchicus* and its effects on proteolytic and lipolytic activities

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ABSTRACT

Combining atmospheric freeze-drying (AFD) with a properly designed heat pump system (HP) results in an energy-efficient drying process. This combination makes HP-AFD competitive with vacuum freeze-drying (VFD). The advantages of AFD compared to VFD are lower production costs and the ability to manufacture a similar porous product. The zooplankton species *Calanus finmarchicus* (CF) is attractive for use as aquaculture feed due to its high content of valuable marine lipids and proteins. Atmospheric freeze-drying in a fluidized bed has been evaluated as preservation method for CF. Three different trials of drying techniques were conducted with CF. The drying temperatures were -5ºC, -10ºC and a combination of -5ºC/+20ºC (initial -5ºC for 4 hours and final drying at +20ºC). This paper evaluates the effects of drying conditions on proteolytic and lipolytic activities, and describes particle size distribution and sorption isotherms. Proteolytic activity was reduced for CF dried at a combined temperature of AFD-5ºC/AD+20ºC, while no significant change occurred in CF that was only freeze-dried. All dried CF showed a minor decrease in lipolytic activity. Drying rates for AFD were significantly higher than for VFD.

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Introduction

With an annual production of more than 700 000 tons of farmed fish in 2006, Norway ranks as the ninth-largest aquaculture nation in the world (SSB 2008). Salmon is the main species produced by Norwegian aquaculture (SSB, 2008). In 2006 the aquaculture sector had a turnover of 2.7 billion USD, with double-digit increases in annual production and turnover rates, especially for salmon and rainbow trout (SSB, 2008). The Royal Norwegian Society of Sciences and Letters (DKNVS) and the Norwegian Academy of Technological Sciences (NTVA), (2006 and 1999) have described developing and exploiting biomarine resources in the aquaculture sector as a potential value-added industry that can serve as an alternative to the country's limited natural oil and gas resources. The expectation is that by 2030, the added value from the Norwegian marine industry will be on the order of the size of the oil industry. With its access to clean and protected inshore/near shore waters, its sizable area for growing marine plant biomass and its healthy climate for the production of high-grade seafood, Norway has a natural advantage in the marine industry (DKNVS and NTVA, 2006). It is expected that the traditional capture fisheries industry will not grow significantly in coming decades; instead, the real growth will be fish farming and aquaculture, including the cultivation of new species such as shellfish and algae, biochemical/energy carriers and feed from highly productive ocean areas. The exploitation of new raw materials for fish feed and feed formulation is one main requirement for a sustainable aquaculture industry. DKNVS and NTVA (2006) identified feed from highly productive ocean areas as a new market and predicted an added value of NOK 42.5 billion (around 6 billion USD) by 2030. Their report states further that enormous unexploited resources can be found that ought to be considered for high quality raw materials for fish feed, including small, hard-to-catch or simply unattractive fish and zooplankton.

The zooplankton species *Calanus finmarchicus* (CF) is considered a possible new species for fish feed (Anonymous, 2007). Their lipid composition includes a considerable amount of omega-3 polyunsaturated fatty acids (PUFA) and rare phospholipids (Kattner, 1989). This makes CF interesting not only for aquaculture feed, but also for biomedical purposes and human nutrition. Currently, CF is caught in industrial batches using a fine mesh net similar to that used in trawling for krill. CF is then frozen and sold without further processing, or is subjected to a separation process that isolates the valuable oil first. CF is not currently used for the industrial production of fish feed, but several researchers are investigating this possibility. Olsen et al. (2004) demonstrated that oil from CF can substitute for fish oil in the diet of farmed Atlantic salmon, thus providing long chain omega-3 PUFA. Solgaar et al. (2007) showed high proteolytic activity in CF and identified the high degree of post mortem degradation and a subsequent leaching of highly valuable nutrients as possible problems for the use of CF as feed ingredient. Thus a preservation method is needed to stabilize the raw material.

Drying and frozen storage are considered to be suitable preservation methods for a large number of food and feed products. The base for the formulation of fish feed is mainly dry matter, such as fish meal. Additives, for example fish oil, are mixed into the base with a binding agent, and this material is then extruded as the fish feed pellet. This means that the initial high water content in CF must be reduced if it is to be used as a base for pellets, and a drying process for CF will be needed in the process line. CF should be dried until its water content is low enough to limit water activity. In general, water activity between 0.2 and 0.6 results in reduced lipid oxidation, while water activities below 0.8 respectively 0.6 are recommended to ensure reduced enzymatic activity, and to limit mould and bacteria growth (Shahidi, 2007).

We examined a freeze-drying process for CF as a suitable drying process because CF is sensitive to degradation. While vacuum freeze-drying (VFD) is considered costly (Mujumdar, 2007, chapter 11.5) an atmospheric freeze-drying (AFD) process as described by Claussen et al. (2007a) is more economical and gives product qualities similar to VFD (Donsi et al., 2001). Cost is an important consideration because fish feed must be relatively low cost. Song (1990) developed an AFD process in a fluidized bed that

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involved a specific protocol called a temperature programme. In this procedure the product is first dried with temperatures below its initial freezing point. As soon as the outer shell of the product is stable the temperature of the drying air is increased above the freezing temperature of the product. This results in an accelerated drying process, while the particle structure of the final product is the same as the structure of a product that has been exclusively freeze-dried. The energy efficiency of AFD is significantly increased by circulating and conditioning the drying air with a heat pump (Claussen et al., 2007b). Current efforts include increasing the drying rate further by combining AFD with new technologies such as ultrasonic, microwave, infrared radiation and pulse fluidization (Alves-Filho and Eikevik, 2008).

This paper investigates how CF can be dried in different AFD processes and the effects on the proteolytic and lipolytic activity with regard to the use of CF as fish feed. The sorption isotherms at different temperatures and the particle size distribution for the product were also measured. For the purpose of comparison, the drying rate for CF in VFD was determined.

Materials and Methods

Calanus finmarchicus (CF):

Batches of CF were harvested between the islands of Hitra and Frøya (GPS: 63º30N, 9º55E) outside of Trondheim Fjord, Norway at the end of April 2008. Industrial batches of CF can only be harvested with current technologies during the spring bloom, when their concentration on the surface of the ocean is high. For harvesting, a special surface trawl with a 500µm net was used. The catch consisted mostly of CF at stages four and five, which is in accordance with Tokle (2006). Batches of CF were drained for 15 minutes, vacuumed and frozen in a plate freezer (thickness 5cm). Storage on board was on dry ice (around -80ºC), while on land the batches were stored in a cryogenic freezer at -80ºC. Twelve hours before AFD, the frozen CF plates were placed in a freezer to be temperature conditioned to the initial temperature of the AFD. Therefore the CF temperature and the drying temperature were equal. The Calanus plates were crushed into small particles inside the freezer with a commercial meat grinder two hours before drying.

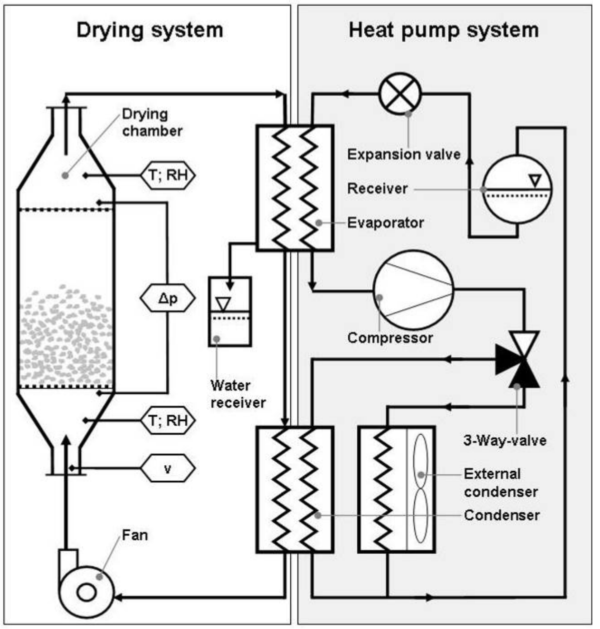

Figure 1: Heat pump assisted atmospheric freeze drying.

Atmospheric Freeze-Drying (AFD):

The AFD system consisted of a cylindrical drying chamber (diameter 20cm, height 35cm). Conditioned air was supplied from the bottom through a 200µm meshed net which was stretched over a supporting structure. The drying chamber was closed with a barred lid that was also spanned by a 200µm meshed net. The drying air was circulated and conditioned with a heat pump (HP) system (Figure 1). The air humidity and temperature was decreased by contact with cold surfaces of the HP evaporator. The dehumidified air was then reheated in the HP condenser.

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An operating unit controlled temperatures in the HP system and the additional external condenser of the drying system, which made it possible to adjust the humidity and temperature of the drying air while recovering energy from the drying system. A ventilator controlled the volume flow of the drying air. Therefore it was possible to have a fixed or stationary and fluidized particle bed in the drying chamber. A fluidized bed requires a high volume flow of drying air but results in a fast drying process, while drying in a fixed bed is slower but needs a reduced volume flow. Three different drying tests were performed in the fluidized bed state. Calanus was dried at -10ºC and -5ºC only. A third test was conducted with an initial drying temperature of -5 ºC for 4 hours and then increased to the final drying temperature of 20ºC after 4 hours until the end of the drying test. This combined AFD-5ºC/AD+20ºC drying method was recommended by Song (1990) and combines the advantages of the porous particle structure of the dried product from AFD with the fast drying rate of conventional atmospheric drying (AD) above the freezing point of the product. For all drying tests the temperature of the heat pump condenser was set to -25ºC. This gave an average relative humidity in the drying air of 17.9% at -10ºC, 17.3% at -5ºC and 2.1% at 20ºC. The average approach velocity of the drying air was 1.9 m/s for all drying tests.

Vacuum Freeze-Drying (VFD):
The vacuum freeze-dryer model "Alpha 1-4 LD" from the company Martin Christ Gefriertrocknungsanlagen, Osterode am Harz, Germany was used for comparative tests with an ice condenser temperature of -60ºC and 0.01mbar pressure. Crushed CF was placed in a neck filter bottle and connected to the vacuum chamber. Weight reduction was determined manually, by disconnecting and weighing the bottle. The VFD apparatus was placed in the laboratory at ambient conditions (≈20ºC), so the heat for sublimation was conducted through the sample bottle.

Determination of proteolytic and lipolytic activity:
Samples of CF were homogenized for 20s in distilled water using an Ultra Turrax, stirred for 10min, and centrifuged at 10400g for 20min at 4^{o}C. The amount of water was double the amount of CF for fresh material while it was 10 times the amount of CF for dried material. The supernatants were filtered through glass wool and the volume of the extract determined. Protein concentrations in the extracts were determined according to Lowry et al. (1951) with bovine serum albumin (Sigma A9647) as the standard.
General proteolytic activity was determined as described by Barret and Heath (1977) with minor modifications. The incubation mixture consisted of 1.2mL of phosphate-citrate buffer (McIlvaine, 1921) and 0.4mL of substrate (bovine hemoglobin Sigma H-2625, 1%). 2mL of 5% w/v TCA (trichloroacetic acid, Merck) was also added to the zero sample. The samples were pre-incubated for 10 min in a water bath at 30^{o}C before 0.4mL suitably diluted enzyme extract was added. Incubation time was 1 hour. The reaction was stopped by the addition of 2mL of 5% TCA. The samples were cooled for 30min and then filtered before the amount of short peptides was determined according to Lowry et al. (1951). Activities were expressed as microgram peptides (cut protein) per gram dry CF per minute. Activity was determined at pH 7 and at 30ºC.
Lipolytic activity was determined by spectrofluorimetry according to the method described by Roberts (1985) and later by Izquierdo and Henderson (1998) with minor modifications. The non-fluorescent substrate 4-methyliumbelliferyl heptanoate was solubilized in a liposomal dispersion of soya lecithin. This substrate was hydrolysed to heptanoic acid and the highly fluorescent compound, 4-methylium belliferone through the action of lipases. Mixtures of 20μL substrate and 40μL of enzyme solutions, suitably diluted in phosphate-citrate buffer (McIlvaine, 1921) at pH 7, were incubated for 15min in water baths at 40ºC. Reactions were stopped by adding 3mL of cold 1mol/l Tris HCl, pH 7.5. For zero time samples, extracts were incubated in water baths at 80ºC for 30 min, centrifuged at 420g for 10min, and diluted and measured as the respective sample. Increase in emission at 450nm (excitation 365nm) was measured using a Perkin Elmer 3000 spectrofluorometer. Activities were expressed as an increase in fluorescence and given in arbitrary units (U) based on the mean of three measurements.

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Sorption Isotherm:

Sorption Isotherms for CF were determined with the water sorption analyser “CISORP” (C.I. Electronics Ltd., Salisbury, UK). The relationship between the CF water content and water activity (a_w) was recorded when reaching equilibrium at constant temperature. The desorption characteristic of fresh CF was measured first, followed by the adsorption characteristic (rehydration) of the same sample. The temperatures were 10ºC and 30ºC. No commercial instrumentation is available to measure sorption characteristics below 0ºC.

Particle Size Distribution (PSD):

The PSD of fresh CF was measured with a standard sieve analyser using frozen CF samples that were ground inside the freeze storage room. The PSD of the dried CF was measured with the same analyser, but at room temperature (≈20ºC).

Results

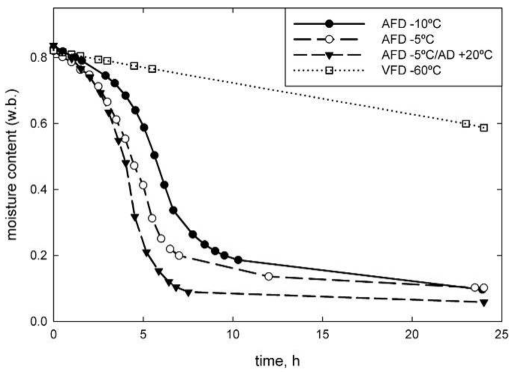

Figure 2: Drying curve for *Calanus finmarchicus* at different temperatures.

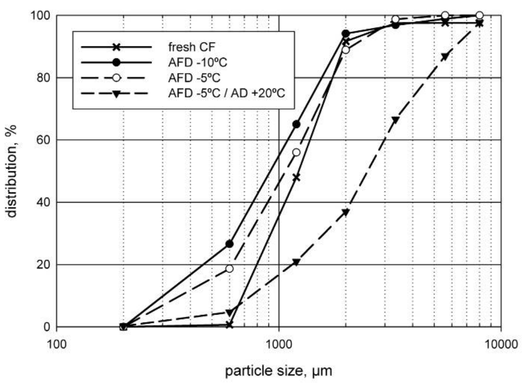

Figure 3: Particle size distribution of *Calanus finmarchicus* before and after drying.

Drying curves for the different AFD tests can be seen in Figure 2. The drying rate was reduced with temperature. During the first 3-5 hours the bulk of CF was in a fixed bed state with channel building rather than in a fluidized bed condition. As the water content was reduced to around 65%, the bed turned into a more fluidized state, which increased mass exchange and the drying rate. At water content of 20% to 25% the drying rate was reduced again. This marked the beginning of the second drying stage. After 24 hours the drying process was stopped. The final moisture content of the product dried at -10ºC and dried at -5ºC was 9.6% (w.b.). The final moisture content of the combined drying process (AFD-5ºC/AD+20ºC) was 5.9% (w.b.). The VFD test showed a much lower drying rate. During the first 24 hours, the moisture content was only reduced to 58% and after 100 hours the final moisture content was 2%. The weight reduction from VFD test showed a linear inclination and it was not possible to distinguish between different drying stages.

The particle size of the CF used was around 1mm (d_{50}-distribution) after crushing the CF plates in the grinder (Figure 3). After the drying process, the purely freeze-dried particles were slightly reduced in size. Size reduction was a result of particle shrinkage and particle breakdown during fluidization. Particles dried with the combined drying process (AFD-5ºC/AD+20ºC) showed an increased particle size distribution. CF particles had a tendency to agglomerate during the first drying stage when they were in an unfrozen condition. Under an optical microscope (60x) all particles showed a homogeneous structure and it was not possible to detect complete single animals. The particle size for product produced using VFD was not measured.

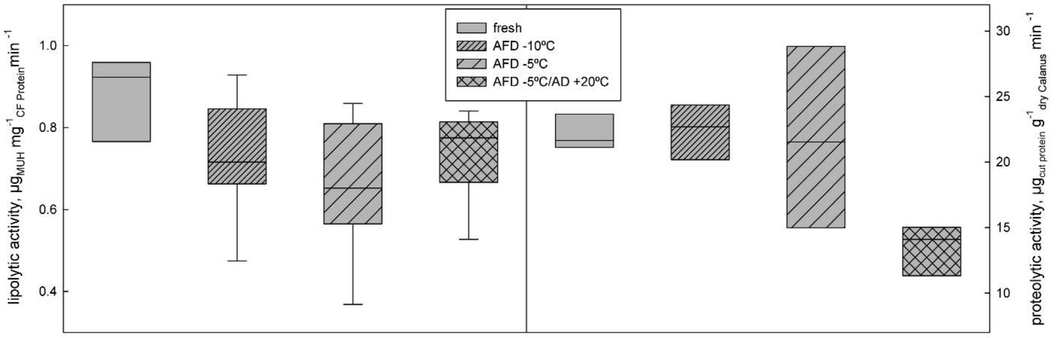

Figure 4: Proteolytic and lipolytic activity of *Calanus finmarchicus* before and after drying.

Figure 4 shows the measured lipolytic and proteolytic activity for fresh and dried CF as median with its variance. Every bar in Figure 4 represents 16 tests (4 measurements performed on 4 samples). The product from VFD was not analysed. All dried CF showed a small decrease in lipolytic activity compared to untreated CF. Proteolytic activity only changed for the product from the combined drying (AFD-5ºC/AD+20ºC). However the proteolytic activity of the product from -5ºC AFD varied over a wide range. A water extract was made for determination of proteolytic and lipolytic activity. The measured activities thereby reflected the activities for rehydrated CF.

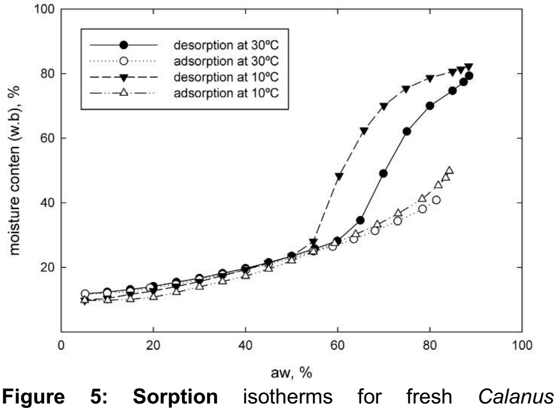

Figure 5: Sorption isotherms for fresh *Calanus finmarchicus* at 30ºC and 10ºC.

Desorption and adsorption isotherms for fresh Calanus at 30ºC and 10ºC are shown in Figure 5. Desorption of fresh CF was a drying process which influenced the product structure (shrinkage) and therefore the water activity for the rehydrated CF (adsorption) was generally lower. Below a moisture content of 25% to 30%, the sorption characteristics for CF did not differ much between adsorption and desorption. Above this moisture content, desorption at 10ºC resulted in a lower water activity than desorption at 30ºC.

Discussion

Freshly caught CF is highly sensitive to degradation. If the raw material is not properly stored and handled its quality plummets rapidly, so that after a few days or even hours the material is not longer usable. The CF for this project was placed in the plate freezer within 1 hour after catching and stored until further processing at -80ºC. This ensured that the material was of defined and high quality which cannot be guaranteed with purchased material, where catching date, duration until freezing, freezing time and storage conditions are not documented. The interpretation of biochemical analyses must be done with regard of the complete process line. This includes catching, freezing and storage conditions. Because of the rapid degradation in CF, a freeze-drying process was chosen as an appropriate dewatering method. The expectation was that at higher drying temperatures the product would lose valuable components and

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the structural changes would be too high. For the same reason mechanical dewatering (e.g. in a press) was excluded, because valuable lipids would be washed out in the liquid phase and structural changes due to the high forces can be expected.
The particle size chosen for the drying process (d_{50} = 1mm) resulted in a high surface area for mass transfer. As reported by Donsi et al. (2001), drying rates in AFD increase with decreasing particle size. The drying rate achieved with the particle size we used was higher for the AFD than for the VFD. Contrary to majority opinion (e.g. Mujumdar, 2007) it is possible for an AFD process to be faster than VFD. It was not possible in AFD to properly fluidize the bulk of the CF that had high water content, because of surface interactions. We suspect that so-called bound or unfrozen water (Wolfe et al., 2002) near the particle surface froze the particles together as soon as the concentration gradient brought the water to the surface. This effect will vanish when a dry front develops towards the particle centre, because the dry part provides a distance to the next particle. The bulk of CF was therefore not in a fluidized state at first, and the drying air streamed mostly on the bulk side or through channels past it. In this state some drying air will remain in contact with the CF, but a laminar flow profile inside the bulk can be expected. The mass transfer will therefore decrease and with it the drying rate. The drying rate will increase when the particles are fluidized properly, because that means every particle can make good contact with the drying air. This explains the accelerated drying towards the end of the first drying stage.
The proteolytic activity was measured for the rehydrated CF and showed the increase of short peptides in the extract. Using CF as fish feed requires a product that is active when it comes in contact with water. The proteolytic activity in freeze-dried CF was comparable to the activity in the fresh material. However, the proteolytic activity in CF dried at -5ºC varied over a wide range. The combined dried CF (AFD-5ºC/AD+20ºC) had a proteolytic activity that was reduced by around one-third. This could be related to the higher drying temperature or the lower water content at the end of the drying. A minor decrease in lipolytic activity occurred for all dried products, but no clear difference was visible for the different drying processes. This indicates that lipase was more susceptible to denaturation during drying. The high remaining enzymatic activity of CF from AFD could be a challenge for its use as standard fish feed, but could be beneficial in starter feeds for aquaculture. Reduced proteolytic activity could be related to drying conditions above the freeze range and should be investigated further.
All material was dried until its final water content was 10% or lower. This resulted in a water activity clearly below 0.1 (Figure 5). In this range, enzymatic activity is very low or non-existent, so protease and lipase will not occur and the product is preserved. However lipid oxidation is generally reduced at water activities between 0.2 and 0.6 (Shahidi, 2007) and will be higher at a water activity below 0.1. Therefore it can be expected that the dried CF has a high susceptibility towards lipid oxidation at this water content. This will influence the quality (rancidity) of the dried product and could be avoided by drying CF to a final water content of around 20% (w.b.). This would result in a water activity around 0.3 (Figure 5), where lipid oxidation has its minimum.
The sorption isotherms show a hysteresis between desorption and adsorption. The explanation can be found in the changed product structure during desorption. Fresh CF was dried slowly during analysis and the equilibrium water activity after a certain time was noted at given temperatures. During this drying process, CF shrank and started to degrade biologically. Adsorption in our measurement was a rehydrating process and since the original structure of CF was diminished, less water than original could be adsorbed. CF that had already been de- and rehydrated once showed no clear hysteresis. Figure 5 shows no differences between desorption and adsorption at different temperatures for low moisture contents and low water activities. Measuring a sorption isotherm takes several days, and as stated earlier, CF is very sensitive to degradation. The reason why no clear difference was measured in this region could be the fact that CF had already started degrading after the time needed for desorption to this low moisture content.
We were able to show with the drying tests that CF has an equilibrium at 20ºC, 5.9% moisture content and 2.1% water activity and at -5ºC/-10ºC, 10% moisture content and ≈17.5% water activity. Lower water content and therefore reduced water activity can generally be reached at higher drying temperatures. Storing CF in a dried condition requires low water activity to prevent quality losses due to enzymatic

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activity, oxidation and rancidity. Adding a drying period with temperatures above the freezing point at the end of an AFD process reduces the water content and water activity of the product significantly. The temperature step must be chosen with respect to the product quality. For CF a drying period with 20ºC after freeze-drying reduced the proteolytic activity by approximately 30%. This has to be tolerated when using CF as fish feed. The reduced water activity could also provide a longer storage period. Since CF can only be caught seasonally, this might be an important advantage. With a combined process the long term storage quality of a freeze-dried product can be improved while the drying time is reduced significantly.

Conclusion

Fish feed is generally a low-cost product, and economic reasons make the use of AFD for CF a good choice. We have shown that AFD did not affect proteolytic activity and only reduced the lipolytic activity of CF to a minor extent. The quality of the freeze-dried and rehydrated product was almost equal to the raw material and also shows the potential of AFD processes in general. Currently, CF can only be caught in industrially significant amounts in the spring, because CF is only present in the surface layer of the sea during their spring bloom. Additionally, CF has a higher lipid composition in the spring season. This suggests the need for optimal long-term storage conditions, because CF is only available seasonally. The quality of fresh and dried CF after different storage times is currently under investigation.

High energy consumption and low drying rates have until recently limited the use of AFD on an industrial scale. Combining AFD with a heat pump made this drying process more competitive with VFD. Depending on the product size, AFD can even achieve higher drying rates than VFD. Future research will concentrate on improving the drying rate with so-called “hybrid” technologies that use ultrasonic, infrared radiation or microwave in AFD (Alves-Filho and Eikevik, 2008). It is believed that AFD can be a cost-effective alternative not only for VFD, but could substitute drying processes for temperature sensitive products, which are currently dried in an unfrozen condition. Because of the low temperature, product quality can be improved with AFD at drying rates that are similar to AD. Thus, AFD offers considerable potential as a future drying technology.

Acknowledgments

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Notation

AD	Atmospheric Drying/Drier
AFD	Atmospheric Freeze-Drying/Drier
CF	*Calanus finmarchicus* (a zooplankton species)
HP	Heat Pump
PSD	Particle Size Distribution
VFD	Vacuum Freeze-Drying/Drier
w.b.	wet base

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Paper II

Is not included due to copyright

Paper III

17th International Drying Symposium (IDS 2010)
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LIPID CLASS CHANGES AND LIPID OXIDATION IN *CALANUS FINMARCHICUS* DURING VACUUM, ATMOSPHERIC AND NITROGEN FREEZE DRYING

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Abstract: Different freeze drying processes (vacuum, atmospheric and nitrogen) were evaluated as preservation methods for the zooplankton species *Calanus finmarchicus*. Changes in lipid composition and lipid oxidation were evaluated for the dried products. The drying rate was highest for atmospheric freeze drying and lowest for nitrogen freeze drying. Nitrogen freeze drying resulted in a reduced amount of phospholipids (92 % loss) and a free fatty acid content of 4.7 % (of dry matter), whereas atmospheric freeze drying preserved the lipids in a quality similar to vacuum freeze drying (57 % loss of phospholipids, and 1.7 and 2.9 % free fatty acids of dry matter).

Keywords: zooplankton, *Calanus finmarchicus*, freeze drying, marine lipids, degradation

INTRODUCTION

Freeze drying is generally employed with food, pharmaceutical and certain biological materials that need to be processed in a frozen condition. The product is dehydrated by sublimation of the frozen water in the product and removal of the vapor. This results in a porous and non-shrunken product structure with good rehydration characteristics and little loss of flavor and aroma. Since no liquid water is present in freeze drying, the product is locally dehydrated very rapidly, which reduces degradation due to enzymatic reactions, protein and lipid degradation and non-enzymatic browning. Freeze drying is increasingly used for dehydrating food such as coffee, certain sea foods, fruits and vegetables (Mujumdar, 2007). Freeze drying is mostly carried out under vacuum at temperatures of -10°C or lower and at pressures lower than 300Pa (VFD). The product is frozen by low temperature cooling, dried by direct sublimation and stored in a dry state under controlled conditions. Due to the use of vacuum and the slow sublimation rates, freeze drying is generally an expensive process.

Recent developments in heat pump technology have made it possible to freeze-dry products at ambient pressures (AFD), where up to 60-80% of the energy can be recovered by circulating and conditioning of the drying air (Strømmen et al., 2002; Colak and Hepbasli, 2009). As shown by Bantle et al. (2009) and Di Matteo et al. (2003), drying rates in AFD can be significantly faster than in VFD when the product is dried as small particles, which improves heat and mass transfer with the drying agent. AFD is normally undertaken at temperatures between -5 °C and -10 °C, where the vapor pressure of water is between 400Pa and 250Pa respectively. It is also possible to dry at temperatures closer to the initial freezing point of the product, where the vapor pressure and sublimation rate are at their maxima. AFD is generally carried out with ambient air as the drying agent, which moderates investment costs. In the case of products that are highly sensitive to oxygen, the drying processes can also be undertaken with inert drying agents (Hawlader et al., 2006). This is also possible in freeze drying when the ambient air can be removed by an inert gas, e.g. nitrogen (NFD).

World aquaculture has grown dramatically in the last 50 years, and has an annual growth rate of 8.7 percent (excluding China) worldwide since 1970. Meanwhile, the world marine fisheries have been overexploited and depleted for the last 10 – 15 years, and the maximum wild capture fisheries potential has probably been reached. (FAO, 2009). Fish meal and fish oil are important ingredients in aquaculture feed as they supply essential amino acids and fatty acids as docohexaenoic acid (DHA) and eicosahexaenoic acid (EPA). If aquaculture continues to grow, alternative feed resources are required. (Naylor et al., 2000). Vegetable sources are most likely to replace parts of the meal and oil because of its availability and low cost. However, the need for n-3 poly unsaturated fatty acids (PUFA) will require a marine source of lipids (Turchini et al., 2009). Also in human nutrition, there has been an increasing awareness of the importance of marine lipids. Many beneficial health effects have been documented from consumption of the omega-3 PUFA, which are mainly provided by marine lipids. DHA (C22:6 n3) and EPA (C20:5 n3) are PUFAs that play a vital role in membrane fluidity, cellular signaling, gene expression, and eicosanoid metabolism. They have been shown to provide positive benefits in coronary heart disease, diabetes, immune response disorders, and mental health (Simopoulos, 1991).

Calanus finmarchicus (CF) is the dominant zooplankton species in the Norwegian and Barents Seas (Planque and Batten, 2000). The annual production of CF in the Nordic Seas is roughly estimated to be 74 million tons by wet weight (Aksnes and Blindheim, 1996). Its high amount of marine lipids includes mainly wax esters (fatty acids esterified with fatty alcohols) and phospholipids, and it contains high amounts of omega-3 long-chained PUFAs, such as DHA and EPA. It also contains high amounts of the omega-3 fatty acid, stearidonic acid (SDA, C18:4 n3) (Sargent and Henderson, 1986). The phospholipids in CF consist mainly of phosphatidyl choline (PC) and phosphatidyl etnanolamine (PE) (Fraser et al., 1989). This makes CF a promising marine resource for proteins and lipids. However, when these highly unsaturated lipids are exposed to air, they give rise to a variety of volatile compounds resulting in an unpleasant rancid product. The oxidation products can also result in possible biological damage. Enzymatic degradation of lipids and proteins leads to formation of free fatty acids, peptides and amino acids. Free fatty acids are more easily oxidized than triacylglycerols, phospholipids and wax esters. Several strategies can be used to avoid oxidation and enzymatic activity. Light, heat, oxygen, and pro-oxidants should be avoided to prevent oxidation, while antioxidants will lower the speed of reactions. Water and temperature have a great influence on enzyme activity (Frankel, 1998; Damodaran et al., 2008).

The current endeavor is to catch and use CF at an industrial scale. Overrein (2010) has shown a high change in lipid- and protein composition *post mortem* due to autolytic enzymes. Solgaard et al. (2007) and Solgaard (2008) have shown the high proteolytic activity of CF and also identified the high degree of *post mortem* degradation and subsequent leaching of nutrients as challenges in processing CF. Grabner et al. (1981) documented similar problems and characteristics for other zooplankton species.

CF is therefore a prime candidate for the use of freeze drying as a dehydration method to stabilize and preserve its proteins and lipids.

For this study, the amount of lipid, PUFA, phospholipids, free fatty acids and lipid oxidation of CF were investigated during freeze drying under vacuum (VFD) and ambient conditions (AFD) as a quality measure. Since the amount and composition of lipids in CF also indicated a high lipid oxidation potential, nitrogen was used as the inert drying agent in an additional freeze drying process (NFD). Lipid changes during the different freeze drying processes were investigated.

MATERIALS AND METHODS

Calanus finmarchicus

Zooplankton can be harvested during the spring season, when their concentration close to the ocean surface is on the increase. A plankton trawl with a 500µm inner net was used to catch industrial-sized batches of CF between the islands of Hitra and Frøya (GPS: 63º30N, 9º55E) outside of Trondheim Fjord, Norway at the end of April 2009. The catch consisted mostly of CF at stages four and five, which is in accordance with Tokle (2006). It was immediately frozen in 0.5cm plates, vacuum-packed and stored on dry ice. The CF plates were stored at -80°C in the laboratory until further processing. Twenty-four hours prior to freeze drying, the CF plates were stored in a -10°C freezing room in order to improve their physical properties before crushing. CF was then crushed to a particle size of d_{50}=2mm with an industrial meat grinder, which was also tempered at -10°C. The bulk of CF was then split into 3 batches and dried using VFD, AFD, and NFD.

Freeze drying

VFD was carried out using an "Alpha 1-4 LD" (Martin Christ Gefriertrocknungsanlagen, Osterode am Harz/Germany) vacuum freeze dryer with an ice condenser temperature of -60ºC. A vacuum of 0.0014 bar was applied, which gives a drying temperature of ≈-17ºC.

Crushed CF (500g) was placed in a neck filter bottle and connected to the vacuum chamber. Weight reduction was determined manually, by disconnecting and weighing the bottle. The VFD was placed in the laboratory at ambient conditions (≈20ºC), so the heat for sublimation was conducted through the sample bottle into the bulk of CF.

For AFD, we used a system as shown in Figure 1 , which allows a SMER (specific moisture extraction ratio) of up to 4 kg_{water} kWh^{-1} (Colak and Hepbasli, 2009). The product was dried in fluidized state, about 10-20% over the minimum fluidization velocity. The drying air was circulated at the condenser and evaporator of a heat pump system. The temperature and humidity of the drying air decreases at the cold surfaces of the evaporator, where the condensation energy is transferred to the refrigerant. The dry air is then heated up again in the condenser of the heat pump system, thereby regaining its own energy. For this study, the temperature in the evaporator was -

30ºC and the condenser temperature was -4ºC. The drying air was therefore conditioned to -6ºC (±0.3K) and 22% (±5%) relative humidity. The removable drying chamber was sealed with a 1mm perforated plate at the bottom and a 300µm mesh at the top. To determine the sublimation rate, the drying process was interrupted at specific time intervals and the weight reduction of the drying chamber, including the product, was determined manually. Crushed CF (1000g) was dried in fluidized bed state during each AFD experiment.

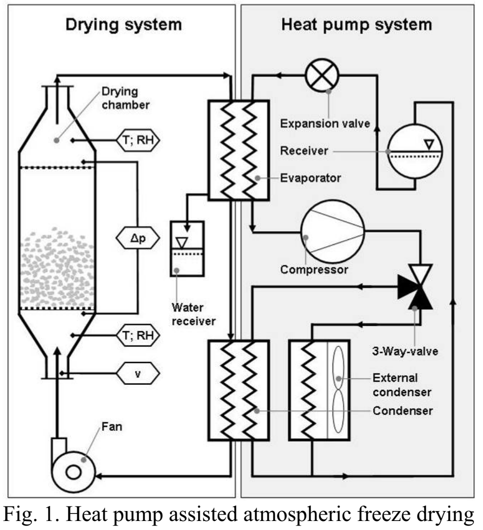

Fig. 1. Heat pump assisted atmospheric freeze drying in a fluidized bed

Nitrogen was used as an inert drying agent in a separate drying chamber (NFD), because it was impossible to replace all the oxygen in the AFD system. Pure nitrogen gas (99.9%) was stored in compressed bottles at -8ºC (±1K) in the freezing room along with the drying chamber. The bottles were connected below the bottom plate of the drying chamber. There was no measurable oxygen content in the drying chamber when the gas bottles were open and the relative humidity of the nitrogen was below the hygrometer's sensitivity of 3%. The moisturized nitrogen was not circulated and was discharged directly to the ambient air. The drying rate was determined by interrupting the drying process, closing the valves, disconnecting the drying chamber, and manually determining the weight reduction in the chamber, including the product. Around 100g of crushed CF was dried in a stationary bed state in each NFD experiment.

Three freeze drying experiments were performed using AFD and VFD and two using NFD. The moisture content of the product before and after drying was determined from the weight reduction of the sample after heating for 24h at 105ºC.

Lipid analysis

Total lipids were determined gravimetrically as described by Bligh and Dyer (1959). All samples were analyzed in triplicates.

Fatty acid methyl esters were prepared according to Metcalfe et al. (1961) and analyzed with a gas chromatograph (Perkin Elmer AutoSystem XL) with TotalChrom. The system was equipped with an auto injector (injection volume of 1 µl, on-column injection, inlet temperature 250 ºC) and a flame ionization detector (FID, 280 ºC). A fused silica capillary column (Varian, 25 m long, 0.25 mm inner diameter) coated with a chemically bonded polyethylene glycol (CP-wax 52CB) was used. The temperature program for the oven was 90ºC for 1 minute, which was then raised to 150ºC at 30ºC/min and finally raised to 225ºC at 3ºC/min and held for 7 minutes. Helium was used as the carrier gas. The retention times of the fatty acid methyl esters were compared to commercial standards (Nu-Chek Prep) and quantified by the use of C19:0 as an internal standard (Nu-Chek Prep) in combination with external standard curves. All samples were analyzed in triplicates.

Lipid classes were analyzed with thin layer chromatography coupled with a flame ionization detector (TLC-FID, Iatroscan MK 6). The detector was operated with an air flow of 2000 ml/min and a hydrogen flow rate of 160 ml/min. Thin quartz rods coated with silica (Chromarods SIII) were used to separate lipid classes. Lipids that were extracted as described were diluted in chloroform and 1µl was applied to the rods with a 5µl syringe (Hamilton). The rods were developed in two different solvent systems. For neutral lipid classes hexane:diethyl-ether:formic acid (85:15:0.04) was used, as described by Fraser et al. (1985). For polar lipid classes chloroform: methanol: water (67:30:3) was used. The rods were held in a chamber with saturated NaCl solution for 8 minutes and developed for 27 minutes. They were then dried for 3 minutes with hot air before burning the rods in the FID to obtain a chromatogram. The scan speed was set at 30sec/rod. Data were collected and integrated with ChromStar. The retention times of the lipid classes were compared with commercial lipid standards (Nu-Chek Prep) and quantified with external standard curves. Natural soy PC and PE (Avanti Polar Lipid) and oleic acid (Nu-Chek Prep) were used to make standard curves. All samples were analyzed in du- or triplicates with four or five rods per replicate.

Lipid oxidation was measured as concentration of secondary oxidation products, thiobarbituric acid reactive compounds (TBARS). TBARS values were determined by the spectrophotometric method as described by Ke and Woyewoda (1979) and analyzed in duplicates. The absorbance values of samples were compared to a standard curve prepared with 1,1,3,3-

tetraethoxypropane for the calculation of TBARS concentrations (µM/g lipid).

RESULTS

The water content of CF before drying was 82% (wet weight basis). Table 1 gives the average final water content from the drying experiments and the mass transfer rate averaged over the total drying time.

Table1. Final moisture content and drying rates for AFD, VFD and NFD

Freeze drying technique	Moisture $\%_{w.w.}$	Drying rate, $kg_{H_2O}kg^{-1}_{d.m.}h^{-1}$
Atmospheric (AFD)	12.7	0.22
Vacuum (VFD)	8.4	0.10
Nitrogen (NFD)	20.0	0.04

AFD showed the highest drying rate and the product reached its final moisture content after 24 hours. VFD needed around 48-60 hours until no further weight reduction was observed. NFD showed the lowest drying rate, in which the product reached a high but stable water content after 120-140 hours (5-6 days). A higher mass flow of drying agent and a reduced product weight in the drying chamber did not increase the drying rate in NFD.

The total lipid in the dried material was 16.4 ± 0.9, 15.5 ± 0.7 and 14.9 ± 0.3 % of dry weight for AFD, VFD and NFD respectively. Before drying, the lipid content was 15.9 ± 0.2 % of dry weight. The total lipid content decreased linearly with the drying rate (Fig. 2A). Free fatty acids were 17 ± 4, 29 ± 15, 47 ± 10 mg/g d.m. in AFD, VFD and NFD respectively and accounts for 10, 19 and 32 % of the total lipid. This gives a linear relationship between drying rate and free fatty acid content as shown in Fig. 2A.

Phospholipids in CF and in the dried samples consisted mainly of PC and PE. Fig. 2B shows that the content was similar for PC and PE in AFD and VFD (1.0 ± 0.3 and 1.0 ± 0.5 mg PC/ g d.m., and 0.7 ± 0.2 and 0.6 ± 0.3 mg PE/g d.m. in AFD and VFD respectively). For NFD, the content of PC and PE was about 0.1 mg/g d.m. There is a small decline in both PC and PE when drying rate goes down. Before drying, the PC and PE content was 22 ± 3 and 15 ± 2 mg/g dry matter. In AFD and VFD the phospholipid content is more than halved (57 %) compared to the original amount, and in NFD 92 % of phospholipids are lost.

A linear relation was also found for FFA and phospholipids (Fig. 3.).

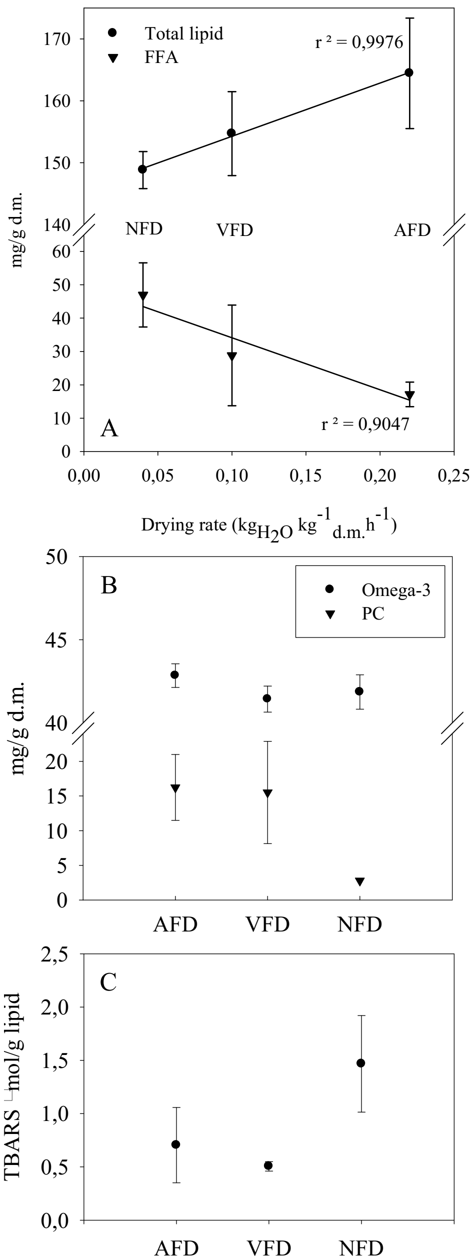

Fig. 2A. Linear regression curve for drying rate ($kg_{H2O}kg^{-1}_{d.m.}h^{-1}$) and total lipid (mg/g d.m.), and FFA (mg/g d.m.) for dried CF from AFD, VFD and NFD. Fig.2B. Content of omega-3 fatty acids and phospholipids PC and PE in dried CF from AFD, VFD and NFD (mg/g d.m.). Fig. 2C. Secondary oxidation products determined as TBARS (µmol/glipid) for dried CF from AFD, VFD and NFD. Values are given as averages ±stdev

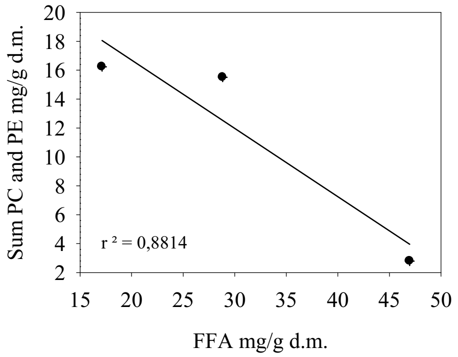

Fig. 3. Linear relation for FFA and phospholipids represented as the sum of PC and PE mg/g d.m. in dried CF from AFD, VFD and NFD. Values are given as averages.

The fatty acid composition was measured and there were no differences in the amount of omega-3 fatty acids among the samples (Fig. 2B). No differences were found in the other fatty acids either (Table 2). Omega-3 fatty acids in the dried samples consist of DHA (C22:6 n3), EPA (C20:5 n3), stearidonic acid (SDA, C18:4 n3) and small amounts of C18:3 n3 and C20:4 n3. They comprise 60 % of the total fatty acids.

Table 2. Fatty acid composition for dried CF from AFD, VFD and NFD (mg/g d.m.). Values are given as averages ± stdev.

Fatty acids	AFD (mg/g d.m.)	VFD (mg/g d.m.)	NFD (mg/g d.m.)
C14:0	8.3 ± 0.4	7.9 ± 0.5	7.3 ± 0.3
C16:0	11.1 ± 0.2	10.9 ± 0.1	10.9 ± 0.2
C18:0	1.0 ± 0.1	1.0 ± 0.0	1.0 ± 0.0
C16:1n7	1.7 ± 0.1	1.6 ± 0.1	1.4 ± 0.1
C18:1n9	1.8 ± 0.1	1.7 ± 0.0	1.6 ± 0.0
C18:1n7	0.4 ± 0.0	0.4 ± 0.0	0.4 ± 0.0
C20:1n9	1.1 ± 0.0	0.9 ± 0.1	0.9 ± 0.1
C22:1n11	1.9 ± 0.0	1.6 ± 0.2	1.5 ± 0.1
C18:2n6	0.9 ± 0.0	0.9 ± 0.0	0.9 ± 0.0
C18:3n3	2.2 ± 0.0	2.1 ± 0.0	2.1 ± 0.0
C18:4n3	13.6 ± 0.3	12.9 ± 0.7	12.8 ± 0.6
C20:4n3	1.0 ± 0.0	1.0 ± 0.1	1.0 ± 0.0
C20:5n3	11.0 ± 0.2	10.9 ± 0.1	11.0 ± 0.2
C22:6n3	15.0 ± 0.4	14.5 ± 0.3	15.0 ± 0.6

The amount of secondary oxidation products was measured for CF dried with the different drying methods (Fig. 2C). NFD showed a higher TBARS value than AFD and VFD. A lipid is considered rancid when its TBARS value is over 1 (Østerlie, 2000). NFD was the only drying method with TBARS that exceeded this value.

DISCUSSION

The significantly lower drying rates for NFD can partly be explained by the stationary state of the bed during drying. A fluidized state would likely result in an increased drying rate for NFD. However, slower drying rates for nitrogen drying were also observed for other products, such as garlic (Rahmann et al., 2009) and might be related to the drying agent. AFD resulted in the fastest drying of CF, as has previously been reported by Bantle et al. (2009).

The lipids are valuable ingredients in CF and must be preserved in the drying process used. The amount of total lipid present in the dried product decreased with increasing drying rate (Fig. 2A) while the content of phospholipids decreased (Fig. 2B) and FFA increased (Fig. 2A). This can be explained by hydrolytic reactions in the drying process. Phospholipases will hydrolyze phospholipids to FFA and lyso-phospholipids. Lysophospholipids are further hydrolyzed by phospholipases and other lipases (Brockerhoff, 1974).

The decrease in phospholipids correlates well with the formation of FFA (Fig. 3.). However, it cannot explain all the formed FFA. In a typical CF phospholipid, about 80 % of the phospholipid is fatty acids. If all the phospholipid in the zero sample (37 ± 6) were hydrolyzed, the theoretical amount of FFA could be about 30 mg/g dry matter. Compared to the measured amount of 47 mg/g d.m. there is an amount corresponding to 1.7 % of dry weight missing. Wax esters can be hydrolyzed to fatty acid and fatty alcohol however they have been shown to be persistent both in CF and also in krill *post mortem* (Overrein, 2010; Saether et al., 1986). Wax esters were not analyzed in this study. The 20 % of the phospholipid that make up the phospholipid backbone (glycerol, phosphate and a nitrogenous group) will give a small total lipid loss but cannot explain the loss found in this study. Overrein (2010) found a high *post mortem* lipolytic activity in CF indicating a high level of active lipases and phospholipases. Also in her study, the loss of phospholipids could not explain the formation of FFA. Rehydrated dried CF has also been shown to have a high lipolytic activity (Bantle et al., 2009). This study seems to indicate that there is some activity in frozen CF.

Drying temperatures of -17°C (VFD), -8°C (NFD) and -6°C (AFD) did not preserve the lipids completely, since free fatty acids were observed in all dried products (Fig. 2A). Enzyme activity during freeze storage is a well established fact. However, they are slowed down with lower temperature. As the water freezes, the other solutes concentrates and can give various effects on enzyme activity in different mediums. An elevated activity during freezing could occur (Damodaran et al., 2008). This indicates that a temperature of -6 ºC could potentially give a higher enzyme activity than 0 ºC. This has not been tested in CF to our knowledge. Lovern and Olley (1962) showed the highest free fatty acid accumulation at -4 ºC in cod flesh.

In VFD no drying agent is present to react with the product and the drying temperature (-17°C) is lower than in AFD and NFD. It was therefore expected that the amount of FFA should be lowest and the lipids preserved best with VFD. Also NFD (inert drying agent and low temperature) should preserve the lipids better than AFD. However AFD showed the lowest amount of FFA after drying (Fig. 2A) despite the high drying temperature (-6°C) and the presence of a reactive drying agent (air). NFD gave the highest FFA content of 32 % of total lipid. The formation of FFA correlates well with drying rate (Fig. 2A) and not with drying temperature and/or drying method. In NFD, the enzymes were active over a longer period and at a higher temperature resulting in more FFA and lower amount of phospholipids. Even though nitrogen is an inert drying agent some oxidative reactions take place during freeze drying according to the TBARS value. These reactions are influenced by factors such as pro-oxidants and light.

The CF was ground before freeze drying. The lipolytic enzymes are then liberated from the tissue and can potentially give a better enzyme-substrate contact and hence more degradation. Saether et al. (1986) showed a higher protein and phospholipid degradation during storage of homogenized krill, compared to whole krill (*M. norvegica*). However, they found no higher degradation in homogenized samples of *Thysanoessa* species. During grinding in this study, a small rise in temperature could also lead to higher enzyme activity and hence some degradation before the drying started.

The omega-3 fatty acids were preserved equally well in the different freeze drying processes and did not seem to be influenced by the drying rate and drying temperature. Fatty acids released from phospholipids by enzymatic activity were found as FFA. However, FFAs are more easily oxidized and the high content of PUFA gives an even higher oxidation potential (Frankel, 1998).

TBARS values in the different drying methods showed no difference between AFD and VFD, even though air is present in AFD. These samples were not rancid, according to the level for rancidity set by Østerlie (2000) at a TBARS value of 1. According to this value, however, the use of NFD resulted in a rancid product. This could be due to the high amount of FFA. However, if the PUFA in the FFA was oxidized, we would expect a lower value of PUFA in NFD.

The high enzyme activity even in frozen condition suggests that CF needs to be stored in deep frozen state or with its valuable lipids separated out. When drying CF, it is necessary to dry the product as rapidly as possible and to store the dried product in a frozen state. To avoid degradation of lipids by enzymes during the drying processes, it is possible to extract the CF lipids directly on board a fishing vessel equipped with a belt press and a decanter. This would also reduce the need for freeze storage capacity, since the process also dewaters the product at the same time. A drying process for the remaining dry matter on shore could then focus on preservation of the proteins. Since industrial protein preservation normally requires heat treatment, CF could then be dried using hot air, which would also accelerate the drying process.

CONCLUSIONS

AFD and VFD are the most suitable preservation methods for phospholipids (PE and PC) and omega-3 long chain fatty acids such as DHA, EPA and SDA in this study. The low drying rate in NFD resulted in a higher amount of free fatty acids and a reduced amount of phospholipids. CF dried by NFD also showed the highest lipid oxidation.

NOMENCLATURE

AFD	Atmospheric Freeze Drying	-
CF	*Calanus finmarchicus*	-
DHA	Docosahexaenoic acid	-
d.m.	dry matter	-
EPA	Eicosapentaenoic acid	-
FFA	Free fatty acids	-
NFD	Nitrogen Freeze Drying	-
PC	Phosphatidyl choline	-
PE	Phosphatidyl etanolamine	-
SDA	Stearidonic acid	-
TBARS	Thiobarbituric acid reactive compounds	-
VFD	Vacuum Freeze Drying	-
w.w.	wet weight	-

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Paper IV

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MASS TRANSFER IN ULTRASONIC ASSISTED ATMOSPHERIC FREEZE DRYING

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Abstract: Mass transfer rates and specific moisture evaporation rates (SMER) for different products were compared for an atmospheric freeze drying process with and without airborne ultrasonic assistance. Mass transfer was increased by as much as 23.2% and with an efficient airborne ultrasonic transducer, additional SMER of 0.1 to 0.4 kg_{water} kWh^{-1} are possible. The improved heat and mass transfer in ultrasonic assisted atmospheric freeze drying is most likely caused by effects at the interface between the product and drying agent. Therefore, airborne ultrasound has not only potential to accelerate freeze drying, but also other processes such as low temperature drying or freezing of food.

Keywords: acoustic drying, low temperature drying, freeze drying, airborne ultrasound

INTRODUCTION

Drying products below their freezing point is a dewatering method for high quality and/or temperature sensitive products. The low temperature protects the product from undesirable enzymatic activity, structural changes during thawing, and also results in a porous product structure with a good rehydration factor. Freeze drying is mainly conducted under vacuum (VFD), below the triple point of water/ice, which is an expensive dewatering method due to its high operational investment. Alternatively, freeze drying can be carried out at ambient pressure (AFD) which results in a product quality that is similar to VFD but with a lower operational investment when energy is recovered in a heat pump system.

Typically, AFD is carried out at temperatures between -5°C and -10°C where the vapour pressure of water is between 400Pa and 250Pa respectively. Depending on the product type, it is also possible to dry near the initial freezing point of the product, where the high vapour pressure of ice results in the highest possible sublimation rate. Drying rates for AFD can be faster than for VFD, as shown by Bantle et al. (2009) and Di Matteo et al. (2003). Drying systems can be combined with heat pumps to recover the evaporation energy (see Fig. 1). The moist air is dehumidified and cooled at the cold surfaces of the evaporator of the heat pump. Energy is thereby transferred to the refrigerant. In the condenser this energy is returned to the drying system by reheating the dehumidified drying air. Strømmen et al. (2002) show that 60-80% of the energy can be saved in heat pump assisted drying (HPD) at the same drying temperature. Colak and Hepbasli (2009a) have reviewed heat pump drying and confirm that in HPD a SMER up to 4 kg_{water} kWh^{-1} can be reached, whereas the SMER for a normal drying system is between 0.12-1.28 kg_{water} kWh^{-1}, compared to 0.72-1.2 kg_{water} kWh^{-1} respectively for VFD. Colak and Hepbasli (2009b) als present HPD applications.

Energy can also be recovered in AFD with a heat pump system, but the low sublimation rates result in long drying times. Accelerated drying can be realized in AFD by crushing the product into fine particles with a high specific surface area and drying it in fluidized or stationary beds (Bantle, et al., 2009). This is also advantageous for products that cannot exist as particles in an unfrozen condition as a result of their physical properties. However the sublimation rate in AFD is the limiting factor and therefore additional sublimation and accelerated mass transfer would be beneficial. In a feasibility study, Alves-Fihlo and Eikevik (2008) outline the potential of ultrasound as an additional energy input into a drying system.

Ultrasound (US) is a cyclic sound pressure wave with a frequency between 20kHz and 1Mhz, which means that it is higher than the frequency of the human sense of hearing. Animals use ultrasound, such as the natural sonar of whales or echolocation of bats. Industrial applications are ultrasonic welding, cleaning, disintegration, humidifiers, particle characterization and non-destructive testing, while in medicine it is used in diagnostics and therapeutics. Ultrasound requires a resonance media, which can be the water in an ultrasonic cleaning bath. Recent developments have increased the efficiency of ultrasonic transducers for air to 80% and to intensity levels of 175dB (Gallego-Juárez et al., 2007). Therefore new applications for so-called airborne ultrasound can be imagined, such as the precipitation of smoke and powder and destruction of foams (Riera et al., 2006), improved product quality under freezing (Xu et al., 2009), and an accelerated drying or dehydration rate when ultrasonic is used (García-Pérez et al., 2006, Khmelev et al., 2006).

Using airborne ultrasound in a drying system was first investigated in the 1950s when researchers such as Boucher (1958) concluded that ultrasound can accelerate drying at lower temperatures. Muralidhara et al. (1985) reviewed ultrasonic drying and identified 10 different effects that can lead to accelerated drying rates with ultrasound. With the recent developments and efficiencies for airborne ultrasonic transducers industrial applications in drying will be profitable. Ultrasound applied prior to drying has also been shown to give accelerated drying rates (Fernandes and Rodrigues, 2008 and Duan et al., 2008). Accelerated drying rates in ultrasonic assisted drying have been reported for lower velocities (García-Pérez et al., 2007) and for lower temperatures (Mulet et al., 2003). Mulet et al. (2003) reported the same diffusivity for ultrasonic assisted drying of carrots at 22°C as for drying without ultrasound at 60ºC. Therefore, lower drying temperatures can be used, which will improve the product quality. The use of ultrasound in a freeze drying process has not been investigated to date, but appears to be a promising technology to accelerate drying rates while preserving product quality.

In this feasibility investigation, different products were dried at atmospheric pressure in a frozen condition with and without ultrasonic assistance in a fluidized or stationary bed. Mass transfer during the first hours of drying with ultrasound is compared with the same drying process without ultrasound.

MATERIALS AND METHODS

The HPD system used in this investigation has previously been described by Bantle et al. (2009). The drying chamber was modified with an ultrasonic transducer (Sonotronic, DN 20/2000, 20kHz, diameter 100 mm, titanium) which was placed 10mm underneath the bottom plate of the fluidized bed (Fig. 1). The bottom plate is a 1mm hole perforated plate. The transducer was modified so it could be used as airborne ultrasonic source. Depending on the product, the power consumption of the transducer is between 80-120W. In earlier tests in cooperation with the supplier the efficiency of the airborne system was determined to be around 20%, which is acceptable since the transducer was originally designed for welding purposes.

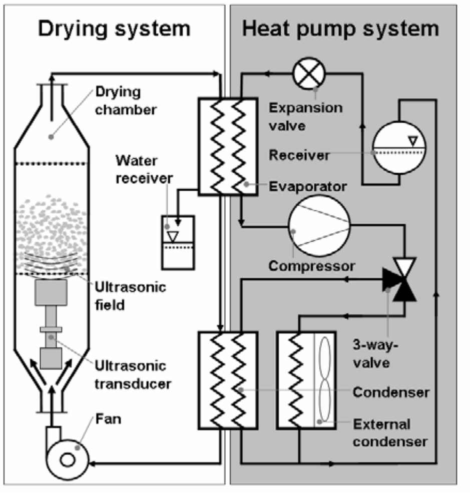

Fig. 1. Drying system with heat pump energy recovery and ultrasonic assistance

The drying chamber had a diameter of 200mm and a height of 300mm. It was sealed with a 300μm sieve and can contain approximately 1 kg of product. The drying tests were performed three times for each product with the same drying time and input weight each time. The weight reduction was determined manually by interrupting the drying process since the ultrasound made it impossible to conduct online weight measurement. The power consumption of the ultrasonic generator, temperatures and the relative humidity of the drying air were recorded below and above the drying chamber. Depending on the fluidization characteristics of the product, drying was performed in a stationary bed with manual mixing during the weight measurement, or in a fluidized bed with a velocity 10-20% higher than the minimum fluidization velocity. The drying temperature was stable at -3°C and -6°C, respectively and therefore below the initial freezing point of the products and in the normal range of AFD. The average mass transfer rates were evaluated from the measured weight reduction over drying time.

The products that were dried were apple, peas and cod, all of which were purchased at a local supermarket. All products were processed (crushed or cut) into particles and frozen in liquid nitrogen and stored at -30°C until drying. The zooplankton species *Calanus finmarchicus* (CF) was included in this investigation. *Calanus finmarchicus* is a small crustacean from the lower levels of the food chain with a size from 0.1mm to 3mm, depending on its stage of development. It represents an enormous amount of biomass in the ocean and is a natural resource for aquatic lipids and proteins. The use of this marine life form is currently being investigated since it can be harvested in industrial batches with newly developed trawls (Bailey et al., 2008). Batches of CF were harvested between the islands of Hitra and Frøya (GPS: 63º30N, 9º55E) outside of Trondheim Fjord, Norway at the end of April 2009, frozen in plates and stored at -80°C. The catch consisted mostly of CF at stages four and five, which is in accordance with Tokle (2006).

In order to determine the sublimation rate of a pure ice surface under AFD, water was frozen, crushed and classified with sieves in a frozen condition. Prior to the AFD the products (ice, CF, cod, apple and peas) were tempered for 24 hours at their drying temperature in a climate chamber. An overview of the products, the particle sizes and drying conditions can be found in Table 1. Three drying experiments were performed for each product with and without ultrasonic assistance. For the drying test without ultrasonic assistance, the transducer was not removed in order to retain the same flow profile in the drying chamber. The average mass reductions from three drying experiments were compared for the different products with and without ultrasonic assistance. SMER values were calculated for the average additional sublimated ice under ultrasound based on the power consumption of the transducer.

Table 1. Product characteristics and drying conditions for the atmospheric freeze drying experiments performed with and without ultrasonic assistance

Product	Size [mm]	Drying time [h]	Drying temp. [°C]	Rel. humidity	Bed condition	Velocity [m/sec]	Input [g] ±2%	Moisture $\%_{wet\ base}$
Ice	$Ø_{50}$= 2 ±1	1	-5 ±0.3	20 ±3 %	fluid	1.20 ±0.12	1000	100
CF	$Ø_{50}$= 3 ±1	3	-6 ±0.4	22 ±5 %	fluid	1.45 ±0.18	800	81.4
Cod	l_{cube}= 14 ±2	3	-6 ±0.3	22 ±5 %	stat./fluid	1.79 ±0.36	1000	82.2
Apple	l_{cube}= 8 ±2	3	-6 ±0.3	24 ±7 %	stat.	2.47 ±0.15	1000	85.8
Peas	$Ø_{50}$= 8 ±1	3	-6 ±0.4	20 ±6 %	fluid	1.49 ±0.20	1000	76.7
Peas	$Ø_{50}$= 8 ±1	3	-3 ±0.3	20 ±6 %	fluid	1.66 ±0.28	1000	76.7

RESULTS

Three drying experiments were performed for each product with and without ultrasonic assistance. Figure 2 shows the averaged drying curves (reduction of moisture with time) for ice particles and cod cubes with and without ultrasonic assistance. The drying time in all tests was 3 hours, respectively 1 hour for the drying of ice. The average sublimation or mass transfer rate was calculated from the weight reduction before and after drying (Table 2). Ice showed the highest sublimation rate and a linear weight reduction over time (Fig. 2), since there is no boundary between the drying agent and ice surface. The other products (CF, cod, apple and peas) had a slower and decreasing sublimation rate over time, because the outer shell of the drying product becomes an ever-thicker barrier to the mass transfer as soon as sublimation begins. This is normal for freeze drying where no first drying stage occurs. During all tests, no significant particle breakdown was observed although there was some minor shrinkage in the partly dried product (see also Bantle et al., 2009). Temperatures and relative humidities for all tests were recorded and showed no discrepancy between the tests with and without US (Table 1). The generally higher sublimation rate in US-AFD did result in a slightly higher relative

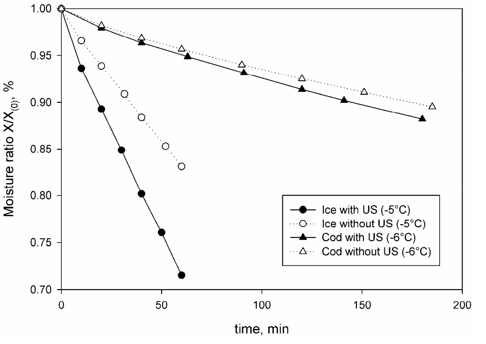

Fig. 2. Drying curve for atmospheric freeze drying of ice particles and cod cubes with and without ultrasonic assistance

humidity (≈+2-5%) compared to AFD, whereas the temperature showed no significant or measurable difference over time. Also the higher sublimation rate in US-AFD did not influence the performance of the generously dimensioned heat pump system.

Table 3 shows the additional SMER values for the tests that were undertaken with an airborne ultrasonic efficiency of 20% for the transducer. The values are based on the average additional sublimation of ice under ultrasound and average power consumption of the ultrasonic generator. Using an airborne ultrasonic transducer with an efficiency of 80% (Gallego-Juárez et al., 2007) would increase this values by the factor of 4. US-AFD of ice results in the highest additional SMER value, followed by the marine products (Cod and CF), peas and apple. The drying temperatures of -6°C and -3°C did not influence SMER values for peas, although a difference in the sublimation rate occurred.

Table 2. Average sublimation rates for different products during atmospheric freeze drying with and without ultrasonic assistance

Product	Sublimation $10^{-1} kg_{ice} kg_{d.m.}^{-1} h^{-1}$		Difference
	without US	with US	
CF	8.54	9.15	7.2%
Cod	6.08	7.15	17.5%
Apple	8.86	9.84	9.9%
Peas$_{-6□C}$	3.37	3.77	11.9%
Peas$_{-3□C}$	4.47	4.74	6.0%
	$10^{-1} kg_{ice} kg_{ice}^{-1} h^{-1}$		
Ice	1.77	2.18	23.2%

Table 3. Additional SMER values for atmospheric freeze drying assisted by airborne ultrasound

Product	Additional SMER for airborne ultrasound $kg_{H_20} kW^{-1} h^{-1}$	
	US efficiency 20%	US efficiency 80%
Ice	0.225	0.899
CF	0.110	0.439
Cod	0.105	0.419
Apple	0.028	0.110
Peas$_{-6□C}$	0.091	0.365
Peas$_{-3□C}$	0.093	0.373

DISCUSSION

US-AFD can increase the sublimation rate up to 23.2% compared to AFD (Table 2) and will also improve the SMER of a system (Table 3). Muralidara et al. (2008) identified several possible effects of the use of US in a drying system:

1. Effects caused by cavitation:
    a. Cavitation breaks down particles, which will increase the specific surface area.
    b. Cavitation degases the liquid, which will improve the liquid flow.
    c. Cavitation disperses particulates or agglomerations, which would improve the particle contact with the drying agent.
    d. Caviation bubbles caused by US will coagulate fibrous and clinging particles (e.g. wood paper pulp). This effect can improve product quality but not necessary drying rate.
    e. Cavitation produces free chemical ions.
2. US changes the viscosity or the structural properties of the drying agent.
3. US cleans or clears the surfaces of the product, which will increase surface area in contact with the drying agent.
4. US can increase the mass transfer at a gas/liquid interface, by affecting the local pressure gradient between the drying agent and product (vapour pressure and saturation vapour pressure).
5. "Sponge" effect: the product is compressed and decompressed in the US field. The water is thereby squeezed out of the product, similar to when a wet sponge is squeezed. The "sponge" effect is often used to explain accelerated drying rates (e.g. Gallego-Juárez et al., 2007).
6. US can create high turbulence around the product, which will improve the mass transfer rates between the product and drying agent.
7. Other effects, such as Oseen forces (a rectified force attributable to the nonlinearity of high intensity waves in air) or Bernoulli forces (forces of attraction due to reduced pressure in a narrowed passageway, such as the movement of gas between stationary objects in close proximity).

Products that are dried in a frozen state have a different physical structure than products dried above the freezing point (hot air drying). In AFD, the water to be removed exists as ice, which will give a solid/solid structure and a mass transfer towards the drying agent. In hot air drying, the liquid water is enclosed in dry matter, which is a solid/liquid system. Therefore a first drying stage with free surface water results in a stable evaporation rate at the beginning of hot air drying. This first drying stage will not occur in AFD, because the ice cannot flow out of the dry matter. Based on this difference, some of the effects that have been observed in hot air drying (Muralidara et al., 2008) are not an issue for US-AFD.

Effects caused by cavitation will most likely only occur when water is present in a liquid form. Cavitation on solid surfaces (like ice) will normally cause damage to the surface. In some cases, this would influence the structure of the surface, but since AFD has no first drying stage it will most likely only change the product quality but not the sublimation rate. For the same reason cleaner surfaces (effect 3) will not increase sublimation rate in US-AFD. However, structural changes on the surface caused by cavitation could be one reason why the sublimation rate of pure ice showed the highest increase in mass transfer under US-AFD.

We did not observe changes in the properties of the drying agent during our tests (effect 2). The temperature and relative humidity of the drying agent showed some variation (Table 1) due to the characteristics of the HP-AFD, but there was no difference between US-AFD and AFD.

US could change the pressure gradient on the surface of the product (effect 4) which could increase sublimation rate. This is similar to effect 6, where a higher turbulence around the product will also increase mass and heat transfer.

The "sponge" effect will most likely not occur in AFD, because the product has a solid/solid matrix and the ice cannot flow out of the product. Also the effects listed under effect 7 (Oseen and Bernoulli forces) will not necessary improve the sublimation rate and are unlikely to be the cause of the faster US-AFD.

Based on these theoretical assumptions the higher sublimation rate in US-AFD is (most likely) caused by an improved heat and mass transfer between the products surface and the drying agent. First, a more turbulent flow profile might minimize the laminar boundary layer, while (second) the pressure gradient between the drying agent and the surface could be improved locally. It can be expected that improved heat transfer would also occur when US is applied in processes which are based on heat transfer by low-temperature air, such as freezing systems for e.g. food.

Future investigations should include the approach velocity as a variable, since flow profiles and laminar boundary layers affect heat and mass transfer.

The SMER values in Table 3 are based on the performance of the ultrasonic equipment and the additional sublimation rate. In our experiment, the additional sublimation did not affect the performance of the (oversized) heat pump system. Therefore the SMER values can be added to the drying system performance. In an industrial HPD, additional evaporation or sublimation will most likely also increase the conditions of the drying agent in a way that will influence the performance of the heat pump. The heat pump system must therefore be designed based on the additional sublimation and the overall performance will give the correct SMER. Based on this investigation, a higher SMER of up to 0.4 kg_{water} kWh^{-1} seems possible, when the HPD is correctly designed.

CONCLUSION

Improved heat and mass transfer caused by a more turbulent flow profile and/or locally changing pressure gradients are identified as the cause for the accelerated sublimation rate in US-AFD. With the US-system used, the SMER values were only slightly improved, but using an airborne US system with an efficiency of 80% would increase SMER values up to 0.4 for the products we tested and up to 0.8 for ice particles. Airborne ultrasound has therefore high potential for improving existing AFD systems, low-temperature driers and also food freezers.

NOMENCLATURE

AFD	Atmospheric Freeze Drying	-
CF	*Calanus finmarchicus*	-
HPD	Heat Pump Drying	-
SMER	Specific Moisture Evaporation Rate	kg_{water} kWh^{-1}
US	Ultrasound or Ultrasonic	-
VFD	Vacuum Freeze Drying	-
d.m.	dry matter	-
l	length	m

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Paper V

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Paper VI

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Paper VII

KINETICS OF ULTRASONIC ASSISTED ATMOSPHERIC FREEZE DRYING OF GREEN PEAS

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Keywords: acoustic field drying, airborne ultrasound, convective freeze drying, fluid bed drying, high intensity ultrasound, mass transfer enhancement

ABSTRACT

Atmospheric freeze drying (AFD) is a dehydration process mostly used for foodstuffs and is a promising technology for the pharmaceutical and biological industries. The challenges posed by AFD are the enhancement of drying kinetics while maintaining the high quality of the final product. High intensity, airborne ultrasound was incorporated in a common AFD system (US-AFD) and the effective diffusion under different approach velocities using both a fluid and stationary bed was determined. An acceleration in diffusion for US-AFD of up to 24.7% was found with a stationary bed while the increase was 8.5% with a fluid bed. It is possible to achieve a higher effective diffusion for US-AFD using a stationary bed rather than with a fluid bed. The quality of the product (color and shrinkage) was not affected by the presence of ultrasound. The higher effective mass transfer is most likely caused by a higher mass transfer rate at the solid gas interface, caused by a reduced boundary layer due to a higher turbulent interface. Hence high intensity, airborne ultrasound has great potential to accelerate AFD, improve product quality and reduce investment and production cost.

INTRODUCTION

Atmospheric Freeze Drying (AFD)

Convective freeze drying at atmospheric pressure (AFD) is a high-end dehydration process, mostly used by the food industry (Claussen et al., 2007). Because the goods are frozen during processing, AFD only results in minor degradation and shrinkage, resulting in high product quality and good rehydration. Bantle et al., 2010a and Bantle et al., 2009 investigated AFD using a highly heat sensitive zooplankton species and showed that the product quality in AFD is similar or better than in vacuum freeze dried products with respect to lipid oxidation, protease and lipase, while at the same time the AFD drying rate was faster than in VFD. This illustrates the potential of AFD, not only for food product, but also for the biological and pharmaceutical industries.

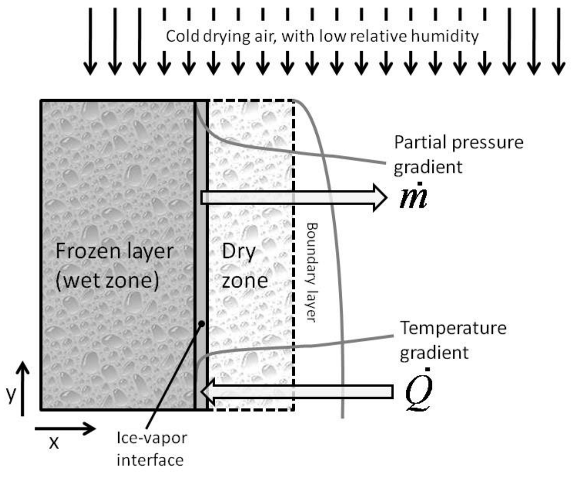

Figure 1: Physical model of Atmospheric Freeze Drying Rhamann and Mujumdar, 2008 ,Claussen et al., 2007.

AFD is done by bringing air of a certain temperature and low relative humidity in contact with the product to be dried. The drying air is brought to its required state (temperature and relative humidity) by circulating the air in a heat pump system (Claussen et al., 2007). However, Rahman and Mujumdar, 2008 showed that a vortex tube can be used instead of a heat pump system in AFD and Reyes et al., 2010 used a simple air cooling system in combination with an adsorbent in order in order to bring the drying air to its desired state.

The product is mostly frozen in a separate freezing system prior to AFD. Since the air is not saturated with water vapor, a pressure gradient is created between the ice surface in the product and the air, forcing the ice to sublimate and diffuse into the air (see Figure 1). The sublimation energy needed for the process is commonly provided by the dry air and results in the development of a temperature profile between the ice surface and the drying agent. Since ice cannot flow or move in the frozen product (in contrast to water in convective drying at temperatures between 0°C and 100°C) a dry layer forms between the ice containing structure and the drying agent when sublimation begins (see Figure 1). This means that there is never a time when there is a constant drying rate period during AFD, because of the increasingly thicker dry layer (Bantle et al., 2009, Bantle et al., 2010a, Bantle et al., 2010b, Heldman and Hohner, 1974, Stawczyk et al., 2007, Di Matteo et al., 2003, Boeh-Ocansey, 1985).

AFD offers several advantages in comparison with VFD:

- The process can be designed to run continuously, which results in low operational costs with high productivity (Rhamann and Mujumdar, 2008 and Li, 2006).
- A heat pump system can be used to recover the drying energy. Strømmen and Kramer, 1994 and Strømmen et al., 2005 investigated this topic and report a SMER (specific moisture extraction rate) of 1.0 kg kWh^{-1} for AFD at -5°C and a possible energy saving of 60-80% of the drying energy compared to VFD.
- A temperature controlled drying process decreases drying times as well as energy consumption (Bantle et al., 2009 and Song, 1990).
- The heat transfer coefficient in the fluid bed is about 20-40 times higher compared to VFD (Rhamann and Mujumdar, 2008 and Li, 2006).
- Different investigations have shown that AFD can be faster than VFD, when the product has a certain particle size and/or is dried in a fluid bed (Bantle et al., 2009, Bantle et al., 2010a, Di Matteo et al., 2003).
- Inert gases, such as nitrogen, can be used as a drying agent in order to minimize the product degradation caused by oxidation, which makes the product quality similar to VFD (Rhamann and Mujumdar, 2008 and Li, 2006).

AFD is generally conducted at temperatures between -10°C and the products initial freezing point, where the frozen water still has a vapor pressure between 260Pa and 611Pa respectively. Consequently the low vapor pressure in AFD results in lower drying rates compared to conventional convective drying at temperatures higher than 0°C. The generally low sublimation rate is the main drawback for AFD and additional sublimation and accelerated mass transfer would be beneficial.

High intensity, airborne ultrasound was suggested as possible hybrid technology for additional sublimation in AFD by Alves-Filho and Eikevik, 2008 and Stawczyk and Li, 2005, while a feasibility study outlined the general potential of the implementation of ultrasound in AFD (Bantle et al., 2010b).

Ultrasonic assisted drying

Ultrasound is a cyclic sound pressure wave with a frequency between 20 kHz and 1 MHz, which means that it is higher than the frequencies that can be detected by the human ear. Industrial applications include ultrasonic welding, cleaning, disintegration, humidifiers, particle characterization and non-destructive testing, while medical uses include diagnostics and therapeutics. Ultrasound requires a resonance media, which can be the water in an ultrasonic cleaning bath. Recent developments have increased the efficiency of ultrasonic transducers which use air as resonance media to 80% and to intensity levels of 175dB (Gallego-Juárez et al., 2007). This so-called high intensity, airborne ultrasound can result in a physical effect when the sound wave is directed into a process (Bhaskaracharya et al., 2009). Airborne ultrasound has the ability to accelerate drying and dehydration rates under certain conditions (e.g. García-Pérez et al., 2006, Khmelev et al., 2006, Gallego-Juárez et al., 1999, Ortuño et al., 2010, Clemente et al., 2010 or Cárcel et al., 2010).

Muralidhara et al., 1985 reviewed the topic of ultrasonic drying and summed up the effects that can lead to an accelerated drying rate. Similar effects were also more recently discussed for ultrasonic assisted drying (see García-Pérez et al., 2006, Khmelev et al., 2006, Gallego-Juárez et al., 1999, Ortuño et al., 2010, Clemente et al., 2010 or Cárcel et al., 2010). A feasibility study investigated ultrasonic assisted AFD (US-AFD) for different products and showed that effective sublimation for AFD can be accelerated by up to 17% in the presence of high intensity, airborne ultrasound (Bantle et al., 2010b). Products that are dried in a frozen state have a different physical structure (solid-solid) than products dried above the freezing point (liquid-solid). Based on these differences some of the effects that can lead to an accelerated drying in the presence of ultrasound Muralidhara et al., 1985 cannot be the reason for accelerated drying in US-AFD. Bantle et al., 2010b assume therefore that the faster drying in US-AFD is caused by a higher mass transfer rate at the solid gas interface, caused by a reduced boundary layer due to a higher turbulent interface.

The ultrasonic assisted atmospheric freeze drying of green peas in a fluid bed dryer was investigated for this paper at different approach velocities and different bed states (fix/stationary or fluid). The influence of the different approach velocities and bed conditions on the effective drying rates were compared with and without ultrasonic assistance, using the effective diffusion approach under Fick's law.

MATERIALS AND METHODS

Drying system

The drying system used in this investigation has previously been described in Bantle et al., 2010a and Bantle et al., 2010b. Figure 2 shows a schematic layout of the drying system with ultrasonic assistance. The drying agent (air) was circulated and conditioned with the help of a separate heat pump system. The drying system was modified with an ultrasonic transducer (Sonotronic, DN 20/2000, 20kHz, titanium), which was placed 10 mm underneath the bottom plate of the fluidized bed. The bottom plate was evenly perforated by 1mm holes and the drying chamber had a diameter of 200mm and a height of 300mm. It was sealed with a 500μm sieve and had a capacity of approximately 1 kg of product for fluid bed drying. The transducer was modified so it could be used as a high intensity, airborne ultrasonic source. The placement of the transducer disturbed the original flow profile of the drying chamber, but the fluid bed condition was sustained. For the

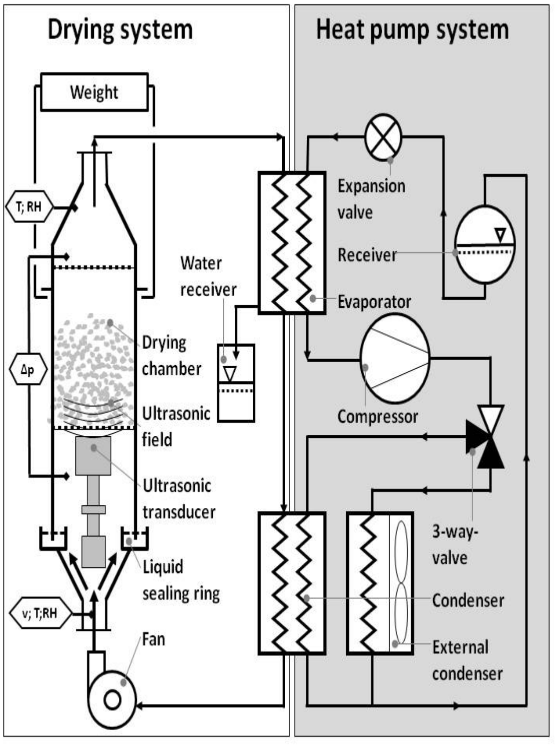

Figure 2: Schematic layout for the atmospheric freeze drying chamber with ultrasonic assistance.

drying tests without ultrasound the transducer was not removed in order to maintain identical flow conditions for the drying air. The power consumption of the ultrasonic generator could be set between 0 Watt (no ultrasound) and its product specific maximum (≈70 Watt for 1 kg of peas). In earlier tests in cooperation with the supplier, the efficiency of the modified transducer was determined to be around 20% when used as an airborne ultrasonic source, which was acceptable for research purposes. Therefore the specific airborne ultrasonic efficiency of the system did not exceed 15 Watt per $kg_{product}$. The drying temperature for all tests was -6°C (average deviation 0.1 K). The drying time for all tests was 3 hours, since ultrasound accelerates AFD, especially during the first hours of drying (Bantle et al., 2010b).

Investigations:

Peas (*Pisum sativum*) were chosen as the product to be dried for this investigation, because they are easy to fluidize, have a stable structure and a defined size and shape. A batch of classified peas was bought from a supplier, frozen in an industrial food freezer and stored at -30°C until further processing. For all drying tests a 1 kg batch of peas with an initial dry matter of 21% and a bulk density of 580 kg/m^3 was used. Twenty-four hours prior to each drying test the batch was tempered in a climate chamber until it reached the drying temperature of the test. The batch of peas was placed in the drying chamber and fluidized for 10 minutes prior to the actual drying test in order to remove condensed ice, smaller particles and deposits. The drying test was started after this pre-treatment, and temperature, relative humidity and approach velocity were measured in the drying chamber. The weight reduction was determined manually by interrupting the drying process at specific time intervals (every 30 minutes). The accuracy of the manual weight determination was ±0.0001% (relative error). The time required to measure the weight of drying chamber was about 15 seconds. Condensation of water during the removal and measuring of the drying chamber was measured gravimetrically and was found to be negligible during this interval. The weight reduction obtained was used to calculate the moisture ratio (MR).

Five different test series with different approach velocities were performed with and without ultrasonic assistance. Fluidization of 1kg of peas in the ultrasonic drying chamber described previously started at an approach velocity between 2.9 and 3.0m sec^{-1}. The approach velocities investigated for the fixed bed were 1.0 m sec^{-1}, 1.8 m sec^{-1} and 2.6 m sec^{-1} and 3.1 m sec^{-1} and 4.7 m sec^{-1} for the fluid bed (average deviation 0.1m sec^{-1}). Because of the changing volume flow of drying air in the heat pump system for the different test series the relative humidity increased from 19% to 25.3% as the approach velocity increased. However, during one test series, the relative humidity was the same for AFD and US-AFD (average deviation 2.0%). The power consumption of the ultrasonic transducer was 70.1 Watt (average deviation 6.8 Watt) for all drying tests with ultrasound. Each test series was performed in triplicate and the reproducibility of the experiment was within ±2%. During AFD using the fixed bed, the product was mixed manually during the

weight determination. At the end of each experiment the dried samples were then placed in an oven at 105 °C to measure the bone-dry weight. The equilibrium moisture content was determined in a separate investigation.
The particle size distribution for each product before and after drying was evaluated by measuring approximately 3-5% of the peas manually with a caliper. The particle size distribution for the peas used in this investigation is narrow (±0.5mm) and evenly distributed, so the d_{50}-diameter described the particle size distribution well. The d_{50}-diameter of the raw material was 8.45mm. Furthermore the color change (L, a, and b value) before and after drying was determined (HunterLab, MiniScan EZ, Virginia, USA). L, a, and b values for the raw material were 49.5 (average deviation 0.4), -16.2 (average deviation 0.5) and 41.6 (average deviation 2.9) respectively.

Determination of effective diffusion in AFD and US-AFD

Fick's law is one of the most common equations used to describe diffusion and is used quite often in drying technology, when the dehydration process is controlled by internal water vapor transport, as in the case in AFD. It describes a correlation between the diffusive flux and a concentration field, which means that concentration gradients are the forces for mass transfer when applied to convective drying. The molecular diffusion is thus described by an effective diffusion coefficient (D_{eff}) under certain drying conditions. One-dimensional mass transfer is hence described as:

$$\frac{\partial M}{\partial t} = D_{eff} \frac{\partial^2 M}{\partial x^2} \quad (1)$$

where x is the spatial coordinate, M is the moisture ratio and t is the time. Under the assumption of uniform initial moisture content, one-dimensional moisture movement, no shrinkage and an internally controlled moisture transfer (falling drying rate period), the equation can be solved for known geometries. The solution of Fick's law for a sphere is (Senadeera et al., 2003 and Sablani et al., 2000):

$$MR = \frac{6}{\pi^2} \sum_{n=1}^{\inf} \frac{1}{n^2} \exp\left[-n^2 \frac{\pi^2 D_{eff} t}{r_{sphere}^2} \right] \quad (2)$$

where r is the radius and n is a positive integer. For long drying times, when t is large and r is small, only the leading term in these equations needs to be taken into account (Senadeera et al., 2003, Sablani et al., 2000 and Okos et al., 2007). This limits the equation to:

$$MR = \frac{6}{\pi^2} \exp\left[-\frac{\pi^2 D_{eff} t}{r_{sphere}^2} \right] \quad (3)$$

A general form for these solutions is logarithmic (Senadeera et al., 2003, Sablani et al., 2000 and Okos et al., 2007):

$$\ln(MR) = B - A * t \quad (4)$$

where the slope of the linear segment will contain the effective diffusion coefficient. In practical engineering the effective diffusion (D_{eff}) can be obtained by plotting the ln(MR) against time and performing a regression analysis in the form of equation 4, where A equals the exponential term (Senadeera et al., 2003, Sablani et al., 2000 and Okos et al., 2007):

$$A = \frac{\pi^2 D_{eff}}{r_{sphere}^2} \quad (5)$$

The moisture ratio obtained from the AFD and US-AFD experiments was used to determine the effective diffusion (D_{eff}), using the method described in equation 4 and 5. The parameters in equation 4 were determined using non-linear regression analysis. Two criteria were used to evaluate the accuracy: the coefficient of determination (R^2) and the reduced chi-square (χ^2) between the predicted and experimental values. The chi-square was calculated by the expression:

$$\chi^2 = \frac{\sum_{i=1}^{N} \left(MR_{\text{expriment}} - MR_{\text{model}} \right)^2}{N - n} \tag{6}$$

where N is the number of experimental data points and n is the number of constants.

It should be noted that AFD is generally controlled by water vapor diffusion in the already dried product structure (see Figure1). However, external drying conditions, such as relative humidity or the size of boundary layer, can also have an effect on the effective diffusion, especially in the beginning of drying when the already dried product structure is small and/or the diffusion is limited.

RESULTS

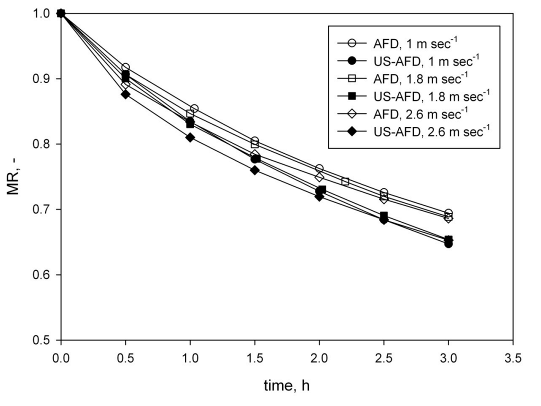

Figure 3: Drying curve for AFD and US-AFD of peas using a fixed bed.

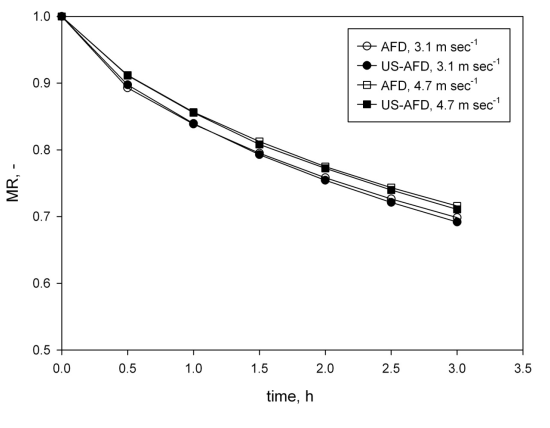

Figure 4: Drying curve for AFD and US-AFD of peas using a fluid bed.

US-AFD showed more rapid drying than AFD under the same drying conditions, in principle. The drying curves for AFD and US-AFD in a fixed and fluid bed state can be seen in Figures 3 and 4, respectively. The presence of ultrasound in the drying system increased the rate of drying especially for AFD in the fix bed state. However, a certain increase in the rate of drying was determined also in fluid state. The effective diffusions for the different AFD and US-AFD test series (Fick's law) are given in Table 1. The coefficient of determination (R^2) was at least 99.65%, while the chi-square (χ^2) did not exceed 829×10^{-6}. The highest increase in effective diffusion (24.7%) was measured in the fixed bed state at an approach velocity of 1 m sec^{-1}. In fluid bed state at an approach velocity of 4.7 m sec^{-1}, the higher effective diffusion for US-AFD diminished to 3.4%. This trend is also illustrated in Figure 6, which shows the increase in effective diffusion for US-AFD at different approach velocities.

The drying rate for US-AFD and AFD is illustrated using the example of the test series with an approach velocity of 1 m sec^{-1}. The drying rate continuously decreases for AFD and US-AFD beginning with dehydration and there was no period where a constant drying rate could be observed for both processes.

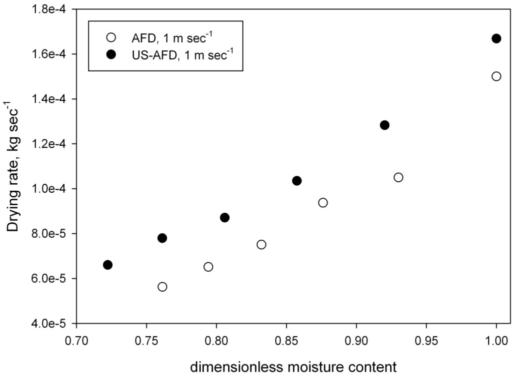

Figure 5: Drying rate for AFD and US-AFD of peas in fix bed state at an approach velocity of 1 m sec^{-1}.

The color of all dried products did not change significantly (Table 2) for drying with and without ultrasonic assistance. Color changes were only observed for products that showed high diffusivity as a result of the individual drying state. The color changed with the (final) moisture content, but not due to the use of ultrasound. The d_{50}-diameater was also not affected by the use of ultrasound (Table 2). Shrinkage occurred from more rapid dehydration due to drying conditions, rather than from the use of ultrasound. Minor changes can also be explained by the uncertainty inherent in the different measurement methods.

Table 1: Average diffusion in the modified Weibull model for drying tests with and without ultrasonic assistance

Investigation	**AFD**			**US-AFD**			**Increase in D_{eff} with US**
	D_{eff} 10^{-11} m^2 sec^{-1}	R^2 %	χ^2 10^{-6}	D_{eff} 10^{-11} m^2 sec^{-1}	R^2 %	χ^2 10^{-6}	
Peas 1.0 m sec^{-1}	**4.69**	99.87	195	**5.85**	99.91	189	**24.7%**
Peas 1.8 m sec^{-1}	**4.51**	99.78	369	**5.42**	99.87	408	**20.2%**
Peas 2.6 m sec^{-1}	**4.14**	99.67	596	**4.56**	99.65	829	**10.1%**
Peas 3.1 m sec^{-1}	**4.10**	99.68	709	**4.45**	99.72	556	**8.5%**
Peas 4.7 m sec^{-1}	**4.41**	99.78	367	**4.56**	99.79	365	**3.4%**

Table 2: D_{50}-diameter and color parameters (L, a, b) for products dried with and without ultrasonic assistance.

	AFD				**US-AFD**			
	D_{50}, mm	L	a	a	D_{50}, mm	L	a	b
Fresh peas	8.45	49.533	-16.167	41.570	-	-	-	-
1.0 m sec^{-1}	8.42	49.280	-14.945	40.375	8.34	48.698	-14.590	39.472
1.8 m sec^{-1}	8.50	49.962	-15.267	38.380	8.45	49.042	-15.493	38.598
2.6 m sec^{-1}	8.40	49.600	-14.478	40.353	8.34	50.428	-13.717	38.303
3.1 m sec^{-1}	8.30	51.383	-15.062	39.550	8.18	50.933	-16.378	40.280
4.7 m sec^{-1}	8.47	49.008	-16.173	41.248	8.42	51.895	-15.147	38.425

DISCUSSION

The effective diffusion approach (Fick's law) used in the present work does not consider a first drying period with a constant drying rate. The constant drying rate period is commonly defined as a sufficient amount of surface water on the product, which is evaporated and removed with the drying air. In AFD the water to be removed is present in the form of ice. In contrast to liquid water, the ice inside the product cannot move to the surface during the drying process and a dry layer will grow in AFD with beginning dehydration (Figure 1). This is why no first drying period was considered and the decreasing drying rates that were obtained (Figure 5) confirm that there is no first stage drying period where a constant drying rate occurs in AFD and US-AFD. The complete dehydration process for AFD and US-AFD took place during the period when the drying rate is falling (the so-called second drying period). When drying occurs during the period when the drying rate is falling, the water is generally moved by water vapor transport through the already dried product structure (diffusion). Hence, the effective diffusion model based on Fick's law can be applied to AFD and US-AFD. In this model all drying conditions that influenced the mass transport are summarized in the effective diffusion value (D_{eff}).

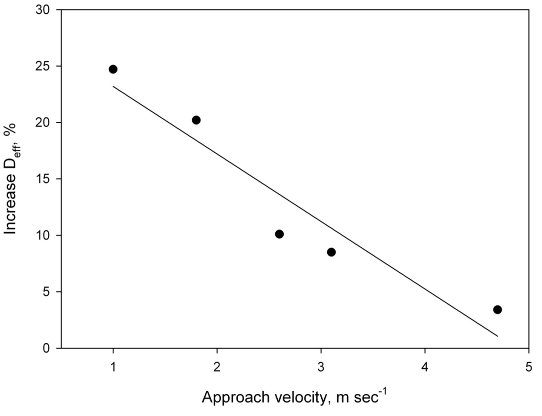

Figure 6: Increase in effective diffusion for US-AFD of peas at different approach velocities.

The drying conditions were stable for all investigations. The average deviation for the approach velocity was 0.1 m sec^{-1}, while it was 2% for the relative humidity and 0.1K for the drying temperature. The reproducibility of the experiments was within 2%. Hence the faster drying in US-AFD must be caused by the presence of the high intensity, airborne ultrasonic field.

The major controlling parameter for AFD and US-AFD is diffusion. Hence, external drying conditions (such as ultrasound) can only affect the overall drying behavior to a certain extend. For this reason, only the first hours of drying were evaluated for this investigation, when the thickness of the dry layer is still small and external drying conditions can have an effect on the effective diffusion. Rahman and Mujumdar, 2008, used a vibro-fluidized bed with adsorbent to accelerate AFD for potato and carrot cubes. The increase in drying rate here (caused by the different drying systems) was also more significant at the beginning of the drying process, whereas towards the end of the AFD process the drying rate was less affected by the system used.

The drying curves for AFD using a fixed bed are given in Figure 3. It can be seen that the drying is slightly faster with increasing approach velocity. With the use of a fluid bed (Figure 4) AFD is actually slower at a higher fluidization velocity. This could be caused by an inefficient contact between particle and drying agent which can occur at higher approach velocities, when parts of the drying agent bypass the fluid bed in channels (see the "bypass"-effect in Martin, 2002). The relative humidity of the drying air increased with the approach velocity, which is caused by the higher volume flow through the heat pump system employed. This might also partly explain the slower drying at higher approach velocities, because the pressure gradient was slightly reduced for AFD and US-AFD at higher approach velocities. However, the influence of the approach velocity was marginal on the final drying curve for AFD. This also indicates that AFD is controlled by diffusion, or more specifically internal water vapor transport. Nevertheless, high intensity, airborne ultrasound clearly increased the drying rate for all US-AFD tests.

The accuracy of the determination of effective diffusion (Table 1) is acceptable for general engineering purposes. The chi-square values (χ^2) obtained were not satisfactory, which shows that the values had a certain discrepancy with the experimentally determined drying curves.

Changes in the properties of the drying agent for US-AFD were not observed compared to AFD. The relative humidity of the drying agent showed some variation due to the characteristics of the heat pump assisted drying system, but there was no difference between drying with and without ultrasonic assistance. The values obtained for effective diffusion show a general trend in the drying behavior, but should not be trusted to the last digit without further evaluation. However, the

proportions of the obtained increase in effective diffusion for US-AFD are correct and also reflect the increase for US-AFD illustrated in Figure 3 and Figure 4.
US-AFD was generally faster than AFD at low approach velocities (see Figure 6). As outlined in Bantle et al., 2010b the faster drying in US-AFD is most likely caused by a higher mass transfer rate at the solid gas interface, caused by a reduced boundary layer due to a higher turbulent interface. Since AFD is controlled by diffusion (internal sublimation and water vapor transport) a higher mass transfer coefficient will only increase the effective diffusion within certain limits. However, in the beginning of drying the dry layer in AFD is relatively small and the diffusion in AFD is generally not high. This means that external effects (such as boundary layer or flow regimes) can also influence the drying behavior to a certain degree. At low approach velocities, there is naturally a thicker boundary layer between the product and drying agent. Hence ultrasound would increase AFD only when a significant boundary layer at the gas-solid interface is an additional resistance to mass transfer. The results (see also Figure 6) therefore support the original assumption of Bantle et al., 2010b, that high intensity, airborne ultrasound can increase the external mass transfer at the gas solid interface.
In the same feasibility study (Bantle et al., 2010b) pieces of zooplankton, cod, apples were dried along with peas using US-AFD. The effective sublimation for peas was increased between 6% and 11.9%, whereas for cod a 17.5% increase was reported. The potential of US-AFD therefore also depends on the product used, or more specifically, the product structure, and it seems possible that higher effective diffusion rates could be achieved for certain products than were obtained here for US-AFD.
The use of ultrasound during the drying process did not affect the quality of the product, such as color (L, a, and b), and particle size (shrinkage) in all investigations. This also illustrates the potential of ultrasound. Ultrasound is kinetic energy (in contrast to microwave and infrared radiation, which are thermal energies) and therefore seems better suited to interact with the heat sensitive products in freeze drying.
In the investigations performed the ultrasound was applied through the bottom plate of the drying chamber with a fluid or stationary bed state. The stationary bed was mixed manually every 30 minutes, so that every product particle was at least near the ultrasonic field. In the fluid bed, mixing is achieved due to fluidization. However the placement of the transducer disturbed the original flow profile of the drying chamber. Future research should investigate if the ultrasonic transducer can be placed in the sidewalls of the drying chamber. The maximum distance between the ultrasonic transducer and the product should also be investigated. The fact that the ultrasonic transducer and product being dried must be in close proximity would limit the industrial usage of this drying technology. There is also a question as to whether or not there is an optimum angle for the relationship between ultrasonic sound wave and the surface of the product. Because this investigation employed a fluid bed or fixed bed with good mixing and the product was close to the ultrasonic transducer, these aspects of ultrasonic assisted drying were not investigated. However the results show that ultrasound can significantly accelerate AFD.
With the US-AFD system used here it was possible to accelerate the effective diffusion by up to 24.7% for the fixed bed at an approach velocity of 1 m sec^{-1} without affecting the quality of the product. Future research should focus on the potential of this high intensity, airborne ultrasound. The aim should to develop this technology further, so it can be used in other dryer types, such as tray dryer or spray dryer.

CONCLUSIONS

The use of ultrasound in an atmospheric or convective freeze-drying process can increase the effective diffusion by up to 24.7%. The higher effective diffusion is significant at low approach velocities (1 m sec^{-1}) with a fixed or stationary bed, whereas in a fluid bed the effect of ultrasound was lower, but still visible. The method used to determine and compare the effective diffusion in AFD and US-AFD was sufficient for this investigation. However, other models should be considered to evaluate AFD and US-AFD in order to achieve greater accuracy. The drying rates obtained show that dehydration in AFD and US-AFD starts with the falling drying rate period. It is assumed that the higher effective diffusion in US-AFD is caused by a higher mass transfer rate at the solid-gas interface, caused by a reduced boundary layer due to a higher turbulent interface. The product qualities, such as the d_{50}-diameter (shrinkage) and color (L, a and b value) were not affected by the presence of ultrasound in the drying chamber. Airborne ultrasound therefore has great potential for improving convective low temperature or freeze drying, as well as other processes that are based on heat and mass transfer rates at low temperatures.

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NOTATION

AFD	Atmospheric freeze drying	-
D_{eff}	Effective diffusion	$m^2\ sec^{-1}$
L	Length	m
M	Moisture content	%
M_e	Equilibrium moisture content	%
MR	Moisture ratio	-
N	Number of data points	-
n	Number of constants	-
R^2	coefficient of determination (regression)	-
r	Radius	m
t	time	sec
US	Ultrasound (airborne) or ultrasonic	-
US-AFD	Atmospheric freeze drying assisted by ultrasound	-
VFD	Vacuum freeze drying	-

Greek Symbols

χ^2	chi-square	-

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