

**EFFECTS OF ELECTROSTATIC SPRAY DRYING ENCAPSULATION ON  
FLAVORS AND ITS COMPARISON WITH TRADITIONAL SPRAY DRYING**

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## **Dedication**

This Master's thesis is dedicated to my parents. I wouldn't be here today if it weren't for the example you've set. Your unwavering passion, ambition, and leadership have undoubtedly shaped me and influenced my career.

## ABSTRACT

This study compared the flavor encapsulation properties of electrostatic spray drying (ESD) with traditional spray drying (TSD). Four flavor compounds—limonene, citral, cinnamaldehyde, and t-2-hexenal—were encapsulated using two different carrier system formulations: one with gum acacia and maltodextrin (Formulation 1), and another with HICAP-100 (a chemically modified starch) and maltodextrin (Formulation 2). The physical characteristics of the spray-dried flavors were assessed by measuring total oil, particle size, surface oil, and the formation of oxidation products over a 21-day accelerated storage period. ESD was performed at various atomizer voltages (+18, -18, +2, and -2 kV) to investigate how these voltages influenced the physico-chemical properties of the flavor encapsulant. Oxidation levels of the flavor compounds were determined using gas chromatography with flame ionization detection.

ESD has been proposed as an alternative to traditional spray drying for encapsulating bioactive and volatile compounds due to its lower inlet temperatures and the use of nitrogen gas as drying medium. The particle size of TSD was found to be larger than that of any of the ESD samples, with no significant variation in particle size across different voltage settings. The total limonene content in the spray dried formulation with HICAP was similar for both TSD and ESD samples, except for the +18 kV sample, which exhibited the lowest oil content. Similarly, for the formulation with gum acacia, there was no significant difference in total oil content between TSD and ESD. However, oxidation levels of the flavor compounds were higher in ESD samples compared to TSD, which could be attributed to the higher surface oil content in ESD. Oxidation was evident immediately after spray drying in all ESD samples, though the degree of oxidation remained consistent across the different voltages. Further research is required to explore the underlying causes of unexpectedly high rate of oxidation in ESD samples.

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### **List of abbreviation**

- i. SD – Spray drying
- ii. ME – Microencapsulation
- iii. SEM – Scanning electron microscopy
- iv. TSD – Traditional spray dryer
- v. ESD – Electrostatic spray dryer
- vi. GC- FID – Gas Chromatography flame ionization detector
- vii. GA – Gum Acacia

## CHAPTER 1. LITERATURE REVIEW

### Introduction

Flavoring agents responsible for the aroma of foods are generally volatile organic compounds. These compounds play a crucial role in influencing human sensory perception and consumer acceptance of food products (Premjit et al., 2022; Reineccius, 2004). However, during storage and processing, it is essential to protect flavors from harsh environmental conditions and undesirable interactions with other ingredients, as most flavoring agents are volatile liquids that are prone to rapid evaporation and potentially, chemical degradation (i.e. oxidation). Maintaining flavor stability at a manageable level is a significant challenge for food processors. Moreover, flavors are highly sensitive to factors such as pH, moisture, acidity, salt, and enzyme activity, which can cause them to lose their intended profile or cause off-flavor.

Encapsulation is one of the most effective and widely used methods to enhance flavor stability and reduce deterioration. It reduces the oxidative degradation that may occur during storage periods at elevated temperatures. Encapsulation involves enclosing an active component within a wall material, coating material, or encapsulant to shield it from oxygen exposure. This process forms a protective barrier around the flavor droplets, shielding the flavor compounds from oxygen, the most common means of flavor deterioration. Moreover, encapsulation improves product functionality by enabling variable characteristics such as particle size, structure, and form, facilitating easier handling, and ensuring controlled or triggered flavor release under specific conditions (Charve & Reineccius, 2009; Reineccius, 1988, 1989, 2004).

### SPRAY DRYING

For many years, the spray-drying (SD) technique has been employed to encapsulate various food components, including flavors, and lipids. This technique was first utilized industrially in the 1920s; however, the demand generated by the surplus milk production in the post-World War II era accelerated the development of spray drying technology (Bhandari, 2008). Today, SD is widely used across a diverse range of industries, including the production of food powders, fragrances, enzymes, nutraceuticals, probiotics, antibiotics, blood plasma, both inorganic and organic chemicals, detergents, ceramic powders, and fertilizers

(Celik and Wendel, 2005; Filková and Mujumdar, 1995). The widespread adoption of this method can largely be attributed to its efficiency and simplicity. Spray drying facilitates the continuous production of uniformly spherical granules, agglomerates, or free-flowing powders from liquid feed (Samborska et al., 2022). When properly executed, spray drying is recognized as a method capable of producing powders with precisely controlled physicochemical properties. This technique is particularly advantageous for materials that are highly sensitive to heat, owing to the cooling effect produced by evaporation and the extremely brief exposure (lasting only milliseconds or seconds) of the atomized droplets to the heated drying medium (Bellinghausen, 2019).

SD of food products is particularly advantageous because food powders are more stable than their aqueous counterparts, thereby lowering the costs associated with storage, packaging, and transportation. The primary factors contributing to the high stability of SD food powders include their low water activity, which helps prevent oxidative degradation, enzymatic activity, hydrolytic reactions, browning, and microbiological spoilage, (Samborska et al., 2024). SD is a widely preferred technique to produce health-enhancing products, including functional foods and nutraceuticals, due to its ability to better preserve heat-sensitive bioactive compounds compared to other drying methods. This method is recognized for its practicality, and cost-effectiveness and is commonly employed in industrial settings to generate large quantities of powder. This is made possible using drying towers, or large-scale drying chambers, which facilitate high-throughput processing. The continuous nature of the spray drying process allows for significant productivity, making it suitable for large-volume applications (Selvamuthukumaran et al., 2019).

## **PRINCIPLE OF SPRAY DRYING**

The principle of SD involves four key stages, which are organized based on the design and function of the dryer, as well as the physicochemical properties of the feed solutions: (1) preparation of the feed material (2) atomization, (3) evaporation, and (4) powder recovery. The fundamental concept underlying this technique is the rapid evaporation of water from the atomized liquid material, which forms fine droplets

upon contact with a heated air stream within the drying chamber (Bellinghausen, 2019; Reineccius, 1988, 2004).

Solution preparation constitutes the first step in the SD process, with the feed material potentially taking the form of an emulsion, suspension (e.g., for microencapsulation), or solution, depending on the specific application. The composition of the feed solution plays a critical role in determining both the processability and the final product characteristics, necessitating careful consideration of several factors (Miller et al., 2022):

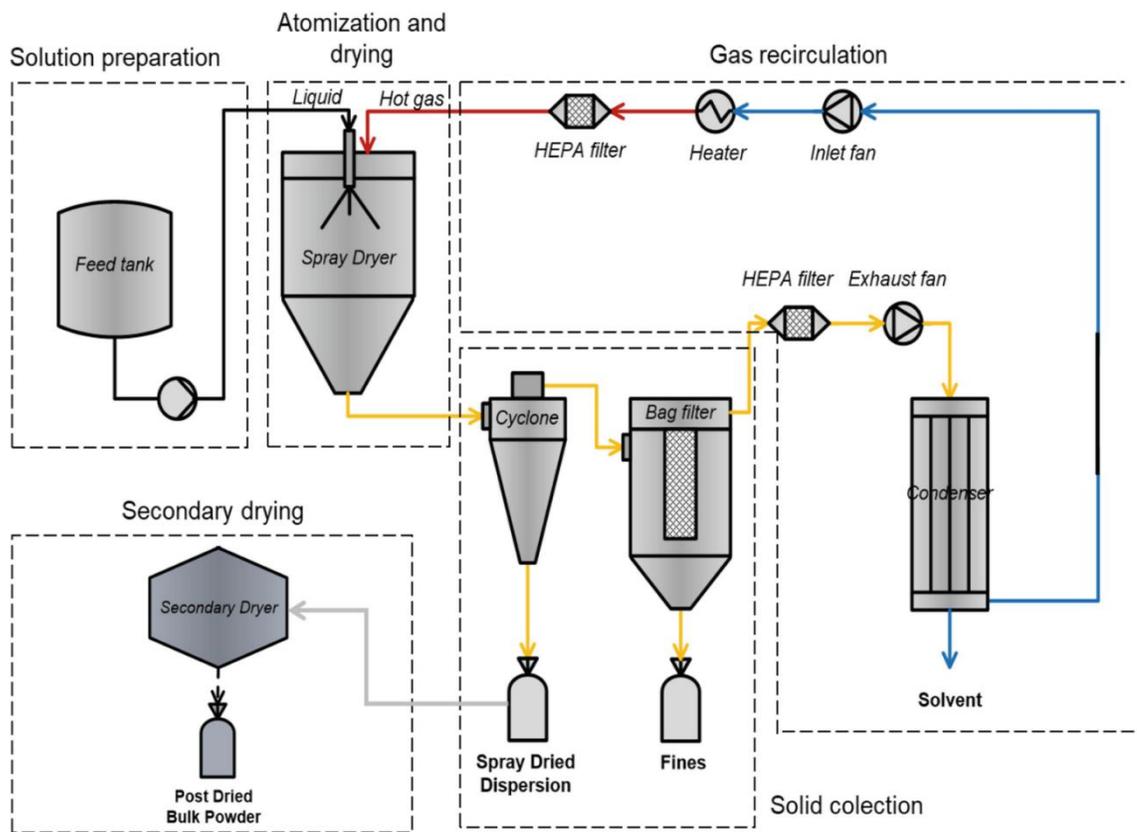


Figure 1.1 Spray drying process. (Source: (Miller et al., 2022))

- **Solids Content:** The concentration of solids is constrained by the solubility of the components within the solvent (water). Higher solid concentrations typically result in the formation of larger, denser particles, as increased evaporation of the liquid phase and more limited solute diffusion occur within the droplets.

- **Rheological Properties:** The concentration and composition of the feed solution, including the water and solutes, influence its surface tension, viscosity, and overall rheological behavior. These properties significantly affect droplet formation and drying dynamics, particularly when dealing with non-Newtonian fluids.
- **Stability:** The chemical composition of the solution must remain stable throughout the spray-drying process. The combination of active ingredients, solvents, polymers, and other excipients may pose challenges to the chemical stability of the formulation. This issue becomes particularly critical in large-scale manufacturing, where batch durations can range from several hours to days. During this extended processing time, the reactivity of the components in the solution can lead to drug degradation, precipitation, or the formation of impurities.

Secondly, atomization plays a crucial role in the SD process, as it directly affects drying kinetics, the quality of the final powder, and the energy efficiency of the process. As such, it is often regarded as the central element of spray drying. The atomizer, or droplet-generating device, is therefore a key component of the SD. A primary goal of atomization is to increase the surface-to-volume ratio, enabling ultra-rapid drying. This is achieved by breaking down a bulk liquid into fine droplets, which allows for quick drying and minimizes the degradation of heat-sensitive compounds while preserving the desired morphology and physicochemical properties of the particles. Centrifugal atomizers and high-pressure single-fluid nozzle atomizers are typically employed in large-scale spray-drying operations, while smaller installations may utilize electrostatic, ultrasonic, or pneumatic (twin-fluid) nozzle atomizers. Centrifugal wheel and pressure or two fluid nozzle atomizers are the most commonly used in commercial food applications. Electrostatic atomizers, however, are infrequently used in food processing due to their very low feed flow rates. The selection of atomizers is one of the important factors that impacts the quality and properties of the final spray-dried product. The choice of atomizer is influenced by factors such as production scale, the physical properties of the liquid feed (e.g., viscosity), and the specific requirements of the product (Selvamuthukumar et al., 2019).

After the preparation and atomization stages, the next step in the spray-drying process involves mixing the atomized droplets with hot air (or inert gas), facilitating both heat and mass transfer. The atomized droplets typically remain saturated during this phase. Despite the high temperature of the incoming air, the droplet temperature stays close to the wet bulb temperature (WBT) due to evaporative cooling. As drying progresses, the rate of water diffusion from the core to the surface decreases, resulting in a lower evaporation rate and an increase in droplet temperature. Toward the end of the process, drying slows significantly, and the droplet temperature approaches that of the outlet air. The drying rate and moisture diffusivity are influenced by the solids content of the feed. The drying time generally ranges from 5 to 100 seconds, although some particles may have longer residence times due to recirculation, with up to 2–10 minutes required to collect all the dried powder (Filková & Mujumdar, 1995).

Three main types of air–droplet contact systems are used: co-current, counter-current, and mixed-flow. In a co-current system, the feed is introduced in the same direction as the drying air, which is particularly suitable for heat-sensitive materials. In this configuration, the wet product is initially exposed to the driest, hottest air, while the partially dried product is exposed to cooler air. This arrangement is common in systems using wheel and nozzle atomization. In a counter-current system, the feed enters opposite the drying air, which can expose the driest particles to the hottest air, potentially causing thermal damage. This system is more appropriate for heat-stable ingredients and is typically used with nozzle atomization. The mixed-flow system is used for producing coarse powders and is considered the most energy-efficient option for heat-resistant materials. The uniformity of the hot air flow throughout the drying chamber and the chamber design itself is crucial for ensuring consistent powder quality. The design should minimize the presence of wet or overheated particles and prevent excessive particle contact with the chamber walls (Filková & Mujumdar, 1995; Miller et al., 2022; Samborska et al., 2024).

The drying air temperatures and airflow rates are adequately adjusted to ensure optimal conditions for producing a dry powder. Dry separators, such as cyclones and bag filters, are used to recover the powder. Cyclones operate by using centrifugal force to direct larger particles to the cyclone surface, where they are separated by gravity, while the air flows upwards. Cyclones are efficient for separating larger particles, but

for particles around 1  $\mu\text{m}$ , bag filters are more effective. In bag filters, the air passes through the filter, leaving the powder trapped on the surface. Regular cleaning of the filter is necessary to maintain efficiency. The selection of filters depends on product properties and air temperature (Miller et al., 2022; Reineccius, 1988, 2004; Samborska et al., 2024). Electrostatic precipitators are effective for collecting sub-micron particles, but due to their high cost, they are generally not used in large-scale spray drying. Wet scrubbers, applied after dry collectors, use water to separate particles from the air. In a wet scrubber, the air is injected at high velocity through a venturi inlet, where it interacts with water spray to dissolve fine particles. The cleaned air is then released, reducing environmental pollution and improving hygienic handling. The resulting powder consists of particles formed from spherical droplets that shrink during drying, with particle structure varying between compact or hollow based on droplet composition (Gharsallaoui et al., 2007).

### **Encapsulation**

Ingredients are incorporated into food for various purposes, with a growing trend toward minimizing the use of synthetic food additives and substituting them with naturally derived alternatives. However, natural ingredients often face challenges in terms of potency and functional application when compared to their synthetic counterparts. A promising strategy to overcome these limitations and enhance the efficacy and versatility of natural ingredients is through microencapsulation (ME). This technique involves encasing an ingredient within a protective coating or capsule, which can modify or preserve its properties, making it possible to incorporate ingredients that would otherwise be impractical for certain food formulations (Shahidi & Han, 1993).

ME technology first conceptualized in the 1930s and commercially introduced in 1954, initially saw widespread use in the production of carbonless copy paper. Over time, it has found extensive application in the food industry, where it serves multiple purposes. These include protecting sensitive ingredients from environmental factors such as light, oxygen, and moisture; controlling the release rate of active compounds; and improving the handling characteristics of ingredients. The benefits of ME include reducing ingredient reactivity, facilitating uniform mixing, preventing evaporation, masking undesirable flavors, and even

enabling the conversion of liquids into solids for easier storage and handling. In essence, microcapsules offer food manufacturers advanced methods to protect delicate ingredients, preserve flavors, prevent nutrient degradation, and create more nutritious, stable, and consumer-appealing products. This technology provides considerable flexibility, making it possible to develop innovative food products that align with the evolving demands of modern consumers (Renaldi & Samakradhamrongthai, 2024; Shahidi & Han, 1993).

One of the primary reasons for encapsulating active substances is to enhance their stability both during processing and in the final product. For example, probiotics are highly sensitive to environmental factors such as mechanical stress, pH changes, transport conditions, and exposure to digestive enzymes in the stomach. Probiotics, which are live microorganisms with proven health benefits when consumed in adequate amounts, require protection to maintain their effectiveness and viability. Encapsulation also helps to reduce the evaporation and degradation of volatile active compounds, such as flavors, which often consist of a mixture of volatile and odorous organic molecules. This is particularly beneficial for protecting delicate aromatic substances, which are typically expensive and essential to the sensory qualities of food products. Food manufacturers are particularly concerned with preserving these aromatic compounds to ensure the longevity and cost-effectiveness of flavors in their products. Thus, encapsulation provides a critical means of safeguarding these sensitive ingredients while maintaining the desired sensory experience for consumers (S. M. Jafari et al., 2008; Nedovic et al., 2011; Piñón-Balderrama et al., 2020). Encapsulation also serves as a protective barrier for food compounds such as aromas, safeguarding them from evaporation, chemical reactions (e.g., flavor-flavor interactions, oxidation, and light-induced degradation), and migration. The protective coating helps preserve the integrity of these compounds. Additionally, encapsulation is employed to mask undesirable sensory characteristics, such as the bitterness or astringency of polyphenols and other bioactive substances with potent antioxidant properties. Preserving the stability, bioactivity, and bioavailability of polyphenols is crucial for maintaining their health benefits. Encapsulating polyphenols, rather than using free forms, can effectively address several of these challenges, enhancing their performance in food systems (Bell, 2000).

A key challenge limiting the use of many phenolic compounds at higher concentrations is their unpleasant taste. Encapsulation addresses this issue by preventing undesirable interactions with other food ingredients, such as oxygen or water, which can degrade the compound or alter its sensory characteristics. This is particularly important for compounds like essential oils, which are only sparingly soluble in water and can impart their strong taste and odor to the surrounding medium. Essential oils are complex mixtures containing terpenes, phenols, alcohols, aldehydes, esters, ketones, and other bioactive substances. They exhibit a range of biological activities, including antimicrobial effects that inhibit the growth of bacteria, yeasts, and fungi. To enhance the antibacterial efficacy of essential oils, they are often encapsulated into various nanospheres, which serve as controlled-release delivery systems with site-specific targeting capabilities. Encapsulation is also critical for improving the handling of active ingredients, such as converting liquid actives (e.g., plant extracts) into solid forms like powders, thereby facilitating easier storage, transportation, and incorporation into food products (Nedovic et al., 2011).

#### **SPRAY DRYING MICROENCAPSULATION OF FLAVORINGS**

Flavor plays a crucial role in food quality and consumer acceptance, and ensuring the stability and integrity of flavoring components is vital for developing distinctive functional foods. Most flavoring compounds are low-molecular-weight, volatile substances that are highly sensitive to air, light, and heat. Their inherent volatility and poor dispersibility in hydrophilic matrix systems pose significant challenges to stabilization during food preparation and storage, leading to potential loss or degradation. To mitigate these issues, encapsulating flavoring compounds before their incorporation into dry foods or beverages is a beneficial strategy as it helps preserve their quality and stability throughout processing. Encapsulation of food ingredients is typically achieved through various methods, most of which involve drying processes, as the encapsulating agents are often in liquid form. Encapsulation involves the transfer of one substance, or a mixture of substances, into another material or system to protect and control the release of the active ingredient. In the food industry, ME is more commonly applied than nanoencapsulation (Renaldi & Samakradhamrongthai, 2024).

ME refers to the process of enclosing active substances, such as food oils and flavors, within a secondary material (the wall material). The resulting encapsulated particles are classified based on their size into three categories: macro ( $>5000\ \mu\text{m}$ ), micro ( $1.0\text{--}5000\ \mu\text{m}$ ), and nano ( $<1.0\ \mu\text{m}$ ). Particles smaller than  $1.0\ \mu\text{m}$  are often referred to as "nanocapsules" and are typically produced using specialized nanoencapsulation techniques. Microcapsules can be further divided into two main types: single-core and multiple-core. Probably 95 % of dry flavorings are multiple cores – small flavor droplets dispersed in a larger dry particle. Single-core microcapsules typically have a high core loading (e.g., up to 90% of the total capsule weight) and are generally produced through more complex methods such as coacervation, fluidized bed drying, droplet co-extrusion, or molecular inclusion. These techniques enable precise control over the encapsulation process, ensuring the protection and controlled release of the core material. In multiple-core microcapsules, the core material is dispersed throughout the wall material, with the space between the particles forming the central area of the capsule. Multiple-core microcapsules generally have a lower core loading, typically around 20–30% of the total capsule weight, compared to single-core capsules. To study the internal and external structures of microcapsules, various analytical techniques can be employed, with scanning electron microscopy (SEM) being one of the most used methods. SEM allows for high-resolution imaging of the microcapsule surfaces and cross-sections, providing detailed insights into their morphology and structural properties. Each method offers unique advantages, and the choice of method depends on the specific challenges associated with the active ingredients, such as flavor stability and dispersibility (S. M. Jafari et al., 2008; Madene et al., 2006; Murúa-Pagola et al., 2009; Sultana et al., 2017).

Spray drying encapsulation (SDE) is a cost-effective technology that has been in use for decades and is extensively employed in the food industry. The most commonly used materials for SDE include natural gums such as gum arabic (GA), low-molecular-weight carbohydrates like mesquite gum (MG), maltodextrins (MD), cellulose, gelatin, lipids, and proteins such as soy and whey proteins. Additionally, modified starches, such as n-octenylsuccinate-derivatized starch, are also utilized. These materials are widely available, affordable, and recognized for their safety, with a range of structural and functional properties. Their versatility and natural origins make them particularly suitable for use in food formulations,

where they can protect sensitive ingredients and enhance the stability of active compounds (S. Jafari et al., 2023).

The flavor industry employs a variety of spray dryer types, each with specific differences in size, shape, airflow configuration, and atomization techniques. However, all spray dryers share common fundamental components. These include the need for heating incoming air, atomizing the material to be dried into the heated air, providing a drying chamber, and incorporating a system to separate the resulting powder from the air—typically through a filter house or cyclone separator. Direct firing with natural gas is the most efficient method for heating drying air, as it burns cleanly and provides the necessary heat for the drying process. When the flavoring material is water-insoluble, a high-shear mixer is employed to emulsify the components and form an emulsion. The feed material for drying is typically prepared separately in a mixing tank to ensure uniformity and optimal conditions for atomization (Charve & Reineccius, 2009). As previously discussed, the infeed material is typically introduced into the atomizer after it has been homogenized. The atomization process is commonly achieved using centrifugal wheels or single-fluid high-pressure spray nozzles. While less common in the flavor industry, two-fluid nozzles are used in specific applications. These nozzles are advantageous for processing particulate or crystalline materials that might clog a single-fluid nozzle, as they have a larger aperture and can handle more challenging feed materials. Centrifugal wheel atomizers offer the benefit of effectively handling highly viscous, abrasive, or particulate feed materials. In contrast, pressure spray systems, such as single-fluid nozzles, provide greater flexibility in controlling the spray pattern and the physical properties of the resulting powder. One advantage of the single-fluid nozzle over the centrifugal wheel atomizer is its ability to produce a larger average particle size. In the flavor industry, both centrifugal and single-fluid atomizers are used almost equally, with the choice depending on specific process requirements and desired product characteristics (Anker & Reineccius, 1988; Reineccius, 1988, 2004).

In the flavor industry, the majority of spray dryers are designed with a concurrent flow configuration, meaning that the product and drying air move in the same direction. This configuration promotes rapid drying and reduces the exposure of the flavoring to excessive heat compared to

countercurrent drying systems. In concurrent dryers, the temperature of the spray-dried product does not exceed the temperature of the exit air, as the atomized feed is initially cooled by water evaporation, and only reaches the exit air temperature when the drying rate decreases. The shape of the drying chamber is typically cylindrical, with either a conical or flat-bottomed design, though some box-shaped dryers are still in use, producing acceptable results. Cylindrical, conical, and flat-bottomed designs are most common in the industry, with box dryers remaining in use in certain applications. In cylindrical and flat-bottomed dryers, dry product accumulates at the bottom, where it is periodically removed through air conveyance or mechanical scrapers. These dryers subject the product to higher heat (time and temperature) than cone-bottom dryers, which can lead to thermal degradation, especially for thermally sensitive flavoring materials such as natural flavors derived from tomato, cheese, or fruit juices. While the additional heat may alter the flavor, this change may be either beneficial or detrimental. In some cases, heat-induced changes contribute positively to the characteristic flavor of certain foods, which would be considered undesirable if not for this thermal treatment (Reineccius, 2004).

Some spray dryers are equipped with both bottom and side powder take-offs. Larger or agglomerated particles are collected from the bottom of the dryer, while smaller, lighter particles are extracted through side air outlets. The dried product is collected either directly from the bottom or, in the case of side outlets, passed through cyclone collectors to separate the drying air from the powder. In some cases, bag houses are still used for collection. After separation, the powder is sieved and packaged in moisture-resistant containers. The exit air from the dryer typically requires treatment to comply with local pollution control regulations. Older dryers often use gas incineration systems for this purpose, but due to rising energy costs, these systems have become less economical to operate. Newer installations generally use scrubbing systems, such as aqueous or chemical sprays, to remove entrained solids and volatile flavor compounds from the exhaust air (Reineccius, 2004).

## **FACTORS AFFECTING SPRAY DRYING ENCAPSULATION OF FLAVORS**

Spray drying (SD) is a widely employed technique in the food and flavor industries, commonly used for producing dry beverages such as instant coffee and tea, as well as flavorings for use in dry mixes and gelatins. Its widespread adoption can be attributed in part to its pioneering role in the flavor industry for producing “encapsulated” flavorings. The continued popularity of spray drying is supported by several key advantages, including the availability of specialized equipment, cost-effectiveness, a range of suitable carrier materials, effective retention of volatile compounds, and enhanced stability of the final flavoring products (Reineccius, 1988, 2004). However, spray drying typically requires high inlet and outlet temperatures, which can present challenges. Flavor retention is generally satisfactory when the process parameters are carefully optimized. To improve flavor retention, it is beneficial to use a feed solution with a high solids concentration ~~and viscosity~~. Additionally, maintaining optimal inlet temperatures (usually between 160 and 210°C) and elevated exit air temperatures (above 100°C) can further enhance flavor retention. The use of high-molecular-weight flavor compounds has also been shown to improve retention which one cannot control. Moreover, the shelf life of oxidizable flavor compounds is heavily influenced by the choice of the carrier material, which plays a critical role in protecting the flavors from degradation over time (Reineccius, 1988, 2004).

### **CORE MATERIAL:**

An important factor influencing the effectiveness of encapsulation and the surface oil content is the relationship between the wall-to-core ratio and the oil/flavor load in the feed emulsion. These two parameters are inversely related. Instability in the emulsion, droplet coalescence, and a low wall-to-core ratio, often resulting from a high oil/flavor concentration, lead to the formation of larger emulsion droplets. According to (S. M. Jafari et al., 2008), the breakdown of these larger droplets during atomization increases the surface oil content in the spray-dried microencapsulates, ultimately reducing encapsulation efficiency. Additionally, a high oil load places more core material closer to the drying surface, shortening the diffusion path for the encapsulated oil or flavor to reach the air-particle interface. This proximity increases the core

material's susceptibility to oxidation and evaporative loss during the early stages of spray drying, further compromising the stability and efficiency of the encapsulation process.

Reineccius, (2004) suggests that the optimal wall-to-core ratio for effectively encapsulating volatile compounds is 4:1. This ratio is also considered ideal for wall systems based on gum acacia (GA) and other carbohydrate-based materials, as noted by (Touré et al., 2011). A sufficiently high wall-to-core ratio is essential to ensure that the core compound is adequately covered by the wall material during the spray drying process. Increasing the wall content helps minimize volatile loss by shortening the duration of the early stages of drying, which are typically associated with significant evaporation. Additionally, a higher total solid content (TSC) results from an increased wall material, which reduces the internal circulation within the droplets, thus accelerating the formation of the crust around the core.

The retention of essential oils and flavor compounds within solid dispersion encapsulation is influenced by the physicochemical properties of the core material (active or filler), including factors such as molecular weight (MW), relative volatility, and compound polarity (Samborska et al., 2022). A higher MW of the encapsulated compounds (e.g., limonene, MW = 136; carvacrol, MW = 150; menthol, MW = 156) contributes to enhanced retention by reducing the tendency of these substances to diffuse out of the matrix during the encapsulation process. This is achieved by strengthening the interaction between the compounds and the surface of the atomized droplets. Consequently, the retention of volatile compounds is more effective when their relative volatility is lower, as this reduces the rate at which they escape from the encapsulating matrix (S. M. Jafari et al., 2008; Samborska et al., 2022). Thus, lower volatility leads to greater retention of essential oils and flavor compounds. Polar compounds, which exhibit higher solubility in water, are more prone to volatile loss, particularly among monoterpenes, hydrocarbons, and phenolic compounds. During the initial stages of the drying process, the water phase can permeate through the selective membrane, which facilitates the migration of volatiles. As the water solubility of the compounds increases, the loss of volatiles becomes more pronounced, since these compounds are more easily leached out in the presence of water (Nguyen et al., 2021).

## **WALL MATERIALS:**

The first step in encapsulating a food ingredient, particularly for flavor or oil encapsulation, is selecting an appropriate wall material, which serves as a film-forming biopolymer. This material is chosen from a broad range of natural or synthetic polymers, depending on the core material and the desired properties of the final microcapsules. For flavor and oil encapsulation, the ideal wall material should possess several key characteristics: it should have emulsifying properties, form a stable film, exhibit low viscosity at high solids concentrations, and have low hygroscopicity. Additionally, the wall material should allow for the controlled release of flavor upon reconstitution in a final food product. It should also be cost-effective, have a neutral taste, be readily available, and provide sufficient protection for the encapsulated flavor or oil during processing, storage, and use in the final product (S. M. Jafari et al., 2008; Madene et al., 2006). The retention of flavor in encapsulated systems is influenced by several factors, including the chemical composition of the core material, such as its molecular weight, chemical functionality, polarity, and volatility. The properties of the wall material, as well as the type and parameters of the encapsulation process, also play critical roles in determining the extent of flavor retention. A thorough physicochemical understanding of the mechanisms involved in encapsulation and the subsequent release of active compounds is essential for the rational design of effective encapsulation systems. This knowledge allows for the optimization of both the encapsulation process and the choice of materials to achieve the desired stability, protection, and controlled release of flavors (Madene et al., 2006; Reineccius, 1988; Whorton & Reineccius, 1995).

Polysaccharides are commonly used as wall materials in encapsulation due to their large molecular structure, which allows them to effectively entrap and protect flavors. These polymers can be derived from a variety of sources, including microbes (e.g., xanthan gum, dextran, cyclodextrins), plants (e.g., pectin, starches, and gums), animals (e.g., chitin, chitosan), and algae (e.g., agar, carrageenan, and alginate). The functionality of polysaccharides can be influenced by factors such as temperature, pH, pKa, and the surrounding electrical charge, which can cause them to adopt different charge states, including neutral, anionic, or cationic forms. For instance, octenyl-succinate anhydride (OSA) starch, a modified starch,

contains octenyl succinate groups that allow it to interact and bind with flavor compounds. Additionally, the helical structure of amylose, a component of native starch, can absorb and bind flavor chemicals within its cavity, further enhancing its capacity to protect and encapsulate flavors. These polysaccharides, through their structural characteristics and chemical reactivity, play a significant role in the stability and controlled release of encapsulated flavorings (X. Chen et al., 2023; Ghandehari-Alavijeh et al., 2024). Maltodextrins, which contain oligosaccharides and polysaccharides, have a high molecular weight and a melting point of 240°C, offering good thermal stability due to their elevated melting point. In contrast, gum arabic solutions, which are Newtonian fluids, exhibit viscosities that increase exponentially with concentration. Gum Arabic with a lower molecular weight and melting point has been shown to result in lower encapsulation efficiency. In emulsions such as oil-in-water, an emulsifier or wall material surrounds the core oil or essential oils (EOs). The total amount of oil used in the process, known as the core oil, refers to the entire quantity of oil after the spray drying process. Surface oil represents the portion of oil that remains on the exterior of the wall material and is not encapsulated. The total entrapped oil is the amount of oil that is successfully incorporated within the wall matrix (total oil minus surface oil). A higher percentage of surface oil results in lower encapsulation efficiency, while minimizing surface oil leads to improved efficiency (Phanse & Chandra, 2024). Recent studies have demonstrated that a spray drying process using a mixture of maltodextrin and Persian gum can achieve high encapsulation efficiency for cinnamon essential oil. The enhanced efficiency was likely due to hydrophobic interactions and the formation of hydrogen bonds between the Persian gum and the EO (Noghabi et al., 2023).

Proteins are a key class of materials used in encapsulation, with sources including animals (e.g., gelatin, casein, albumin, and whey proteins), bacteria, fungi, plants (e.g., glycinin, soy protein, zein, and wheat gliadin), algae, and microalgae. Due to their unique properties, proteins play a critical role in flavor encapsulation. They possess emulsifying capabilities, can form gels and hydrogels, and have high water-binding capacity. Additionally, proteins are capable of foam production, stabilization of emulsion droplets, and the formation of molecular coacervates. Their ability to form films and create nano- and micro-structures further enhances their suitability for encapsulating flavors. These properties are particularly important in

encapsulation, as they allow proteins to protect sensitive flavor compounds, stabilize emulsions, and facilitate the controlled release of the encapsulated materials (Ghandehari-Alavijeh et al., 2024; Premjit et al., 2022). Recent studies have explored the use of "coral-like" soy protein isolate (SPI)-tannic acid complexes for the encapsulation of flavor compounds such as limonene, demonstrating high encapsulation efficiency (EE) and loading capacity (Wu et al., 2023). Additionally, a variety of flavor compounds, including vanillin, limonene, and menthol, have been successfully encapsulated using proteins of both animal and plant origin. These proteins include sodium caseinate, zein, pea protein, and soy protein. These studies highlight the versatility and effectiveness of different protein types in enhancing the stability and delivery of volatile flavor compounds through encapsulation (Francisco et al., 2022; Kim & Peterson, 2021; Qi et al., 2022; Xu et al., 2021).

Lipid-based wall materials are highly effective for encapsulating a broad range of flavor compounds, including hydrophilic, amphiphilic, and lipophilic substances. These materials offer several advantages, such as protecting volatile compounds, enhancing their solubility and encapsulation efficiency (EE), controlling their release behavior, reducing volatility and toxicity, and improving both biocompatibility and biodegradability (Assadpour & Jafari, 2019; Kumar et al., 2018). Recent research has concentrated on utilizing vegetable oils, fatty acid esters, and surfactants to develop lipid-based nano delivery systems, including nano-liposomes, nano-emulsions, solid lipid nanoparticles (SLNs), and nanostructured lipid carriers (NLCs), to improve the delivery of flavor compounds. For example, d-limonene, a hydrophobic compound, has been successfully encapsulated in lipid-based nanocarriers, enhancing its solubility and bioaccessibility within the gastrointestinal tract (Akhavan-Mahdavi et al., 2022). In another study, Tween 80 was used as a surfactant to encapsulate cinnamon essential oil in nanostructured lipid carriers (NLCs) containing oils such as cocoa butter, sesame, and almond oil. According to (Bashiri et al., 2020), these NLCs significantly improved the stability of cinnamon essential oil in beverages.

#### **EMULSIFICATION STAGE:**

After selecting the appropriate wall materials, the second step in the encapsulation process involves preparing the emulsion, which consists of both the core and wall materials. To achieve a coarse dispersion or emulsion, the core material is introduced into the suspension of the wall material through high-speed mixing. The core material may either be dissolved in a suitable solvent or directly added to the dispersion of the wall material. Dissolving the essential oil (EO) prior to incorporation into the wall material suspension reduces its viscosity, which facilitates the formation of smaller droplets and promotes effective coating by the wall material. EOs can be integrated into the wall material suspension through the emulsion process, and the duration of stirring must be carefully controlled to ensure optimal dispersion and stability of the mixture. The stability of the emulsion is a critical factor influencing the success of SD encapsulation for EO (Altay et al., 2024; S. M. Jafari et al., 2008). Liquids with medium to high viscosities are typically emulsified using rotor-stator systems. It is crucial to determine the appropriate rotor/stator configuration, gap width, and rotational speed early in the process to optimize both droplet size and production costs. In general, cooling is required to mitigate temperature increases resulting from the operation of colloid mills. These systems are capable of producing emulsions with droplet sizes ranging from 1 to 5  $\mu\text{m}$  (Mukurumbira et al., 2022; Samborska et al., 2022).

Essential oil (EO) solutions are commonly prepared using mechanical homogenization, ultrasonic treatment, and the incorporation of emulsifiers. These methods aim to reduce the size of oil droplets and promote their dispersion across both lipid and aqueous phases, resulting in a more uniform distribution of EOs within the solution. In a study involving the microencapsulation of green coffee oil via spray drying (SD), a combination of modified starches (Hi-Cap, Capsul, N-lok), gum arabic (GA), and maltodextrin (MD) were used as encapsulating agents, alongside two emulsion homogenization techniques: Ultra-turrax and high-pressure homogenization. The authors found that all combinations of encapsulating materials led to improved emulsion characteristics, including a reduction in droplet size and enhanced kinetic stability. Furthermore, the encapsulation efficiency (EE) of coffee oil in the microparticles was higher when high-pressure homogenization (50 MPa) was employed (ranging from 98.6% to 84.9%), compared to the results obtained using Ultra-turrax (ranging from 87.6% to 82.3%) (Silva et al., 2014).

## ATOMIZATION FACTORS

Centrifugal wheel atomizers and spray pressure nozzles are the most commonly used atomizers for flavor and oil encapsulation, while twin fluid nozzles have limited applications in large-scale processes. Atomization is a critical stage in spray drying, as it can promote volatile loss prior to crust formation. However, process engineers can mitigate this risk by selecting appropriate atomizer types and conditions for specific applications. Volatile loss during atomization occurs when the feed forms a liquid sheet before breaking into droplets, creating a period of lower resistance to mass transfer. To minimize this, two strategies can be employed: reducing the surface tension of the feed by adding emulsifiers and homogenizing the mixture prior to drying or increasing the atomization energy by using higher spray pressures or wheel speeds. Both approaches shorten the time the feed remains as a liquid sheet, thus reducing volatile loss (Reineccius, 1988, 2004).

Papadakis & King, 1988 observed that high nozzle pressures impart greater momentum to the atomized feed emulsion, which, in turn, draws in more hot air into the spray system. This leads to faster drying and the quicker formation of a protective membrane around the droplets. A similar effect is observed with higher wheel speeds in centrifugal atomizers. The goal is to optimize atomization parameters to enhance encapsulation efficiency and maximize core retention.

Regarding surface oil content, (Finney et al., 2002) found that centrifugal atomization produced microencapsulated orange oil with a higher surface oil content compared to spray nozzle atomization. They suggested that this difference was due to the larger particle sizes produced by the spray nozzle, as larger particles have a smaller surface area, leading to lower surface oil content. Atomization is a key factor influencing the particle size of microencapsulates. Larger particles produced by spray nozzles may result from the entrapment of air within the droplets during atomization. When combined with a higher drying air temperature, this effect leads to early crust formation, limiting moisture loss at an early stage and thus preventing significant particle shrinkage in later stages of the spray drying process. As a result, larger particle sizes are obtained.

## SPRAY DRYING PARAMETERS

The optimization of the SD process is primarily influenced by several factors, including the characteristics of the feed material (such as total solids content and viscosity), feed temperature, inlet air temperature, outlet air temperature, and feed rate (Samborska et al., 2022). The effects of these variables are typically evaluated using various statistical methods, with particular emphasis on response surface methodology, full factorial design, and completely randomized design (which typically considers one factor at a time). It is essential to carefully control both the air inlet temperature and flow rate during the spray drying process (Altay et al., 2024; Reineccius, 2004). The two primary factors that influence the determination of the air inlet temperature are the temperature at which the product can be safely processed without degradation and the relative cost of the heat sources. The outlet air temperature can serve as an operational control index for the spray dryer. However, predicting the outlet temperature for a specific product is challenging, as it is influenced by the drying characteristics of the feed solution. It has been reported that the outlet air temperature, unlike the inlet air temperature, cannot be pre-set and typically ranges between 50–80°C for sensitive components such as aroma compounds and essential oils (EOs). Since EOs are heat-sensitive, exposure to the high temperatures during the encapsulation process can lead to degradation reactions and loss of volatile components (Altay et al., 2024).

The SD process is influenced by several interrelated factors, including viscosity and total solids concentration in the feed solution. High viscosity tends to promote the formation of larger and heavier droplets, which can lead to prolonged drying times, larger powder particle sizes, and increased moisture retention. Additionally, high viscosity can negatively impact atomization efficiency and pumping capabilities. Similarly, a feed liquid with a higher total solid content often exhibits increased viscosity, which can reduce the time required for the formation of particle shells and hinder the diffusion of water during the drying process. This behavior was documented by (Fernandes et al., 2014) in their study on the microencapsulation of rosemary essential oil using gum arabic (GA) as the encapsulating material. Their findings indicated that the optimal spray drying conditions were a moderate feed flow rate (0.7 L/h), a low inlet air temperature (135°C), and a moderate wall material concentration (24%).

(Ren et al., 2020) investigated the effect of SD temperature (ranging from 110 to 190°C) on the physical properties of citrus oil microparticles containing polymethoxyflavones (PMF). Their study identified 150°C as the optimal inlet air temperature. Within this temperature range, the encapsulation efficiency (EE) was observed to decrease from 75.8% to 45.2%. This reduction was primarily attributed to the chemical degradation of PMF and its adherence to the surfaces of the drying chamber at elevated drying temperatures. The physical properties of microencapsulates are significantly influenced by the feed flow rate. Maskat et al., 2014 investigated how the spray-drying of roselle extract was affected by variations in feed flow rate (280, 350, and 420 mL/h) and inlet air temperature (150, 160, and 170°C). Their findings indicated that these two factors had a substantial impact on the yield, color, moisture content, and anthocyanin levels of the spray-dried roselle. Specifically, an increase in the feed flow rate resulted in reduced moisture content and promoted the degradation of anthocyanins.

#### **ELECTROSTATIC SPRAY DRYING OF FLAVORS:**

Studies have highlighted several potential negative effects of spray drying on food products due to their reliance on heat. These include browning caused by Maillard reactions, the loss of bioactivity in biological compounds such as vitamins, enzymes, and live bacteria, and protein denaturation (Dantas et al., 2024). Furthermore, high energy consumption is another limitation associated with this drying method, as noted by (Coelho et al., 2022).

Electrostatic spray drying (ESD), a recent advancement in the field, operates continuously at the lowest feasible inlet temperature. This process utilizes both a drying gas and an electrostatic charge to atomize feed solutions through a bi-fluid nozzle. Similar to conventional spray drying, ESD involves atomizing a feed solution within a chamber, but with the addition of an electric voltage and nitrogen gas. In this process, droplets are expelled from the charged sample jet, which is introduced into a chamber with a strong electric field. The electrostatic effect enhances solvent diffusion at the droplet surface, facilitating moisture evaporation without the need for excessive heat. The electrostatic charge plays a crucial role during atomization by influencing the stratification of the components within the droplets. This charge not only

stabilizes the droplets but also helps preserve the properties and bioactivities of the microcapsules or microparticles over time. Additionally, the electrostatic effect prevents premature shell formation and eliminates the falling-rate drying phase, thus enhancing the efficiency and stability of the process (Beaupeux et al., 2024). Additionally, molecular stratification promotes effective microencapsulation. The use of nitrogen gas as an inert drying medium further accelerates solvent evaporation during atomization, while the cyclonic gas flow enables continuous evaporation, thereby extending the residence time of the droplets in the drying chamber (Beaupeux et al., 2024; Szczap & Jacobs, 2023).

### **SETUP AND PRINCIPLE OF ELECTROSTATIC SPRAY DRYER**

In electrostatic spray drying, an electrostatic charge is applied to the fluid nozzle, as illustrated in Fig. 4. The presence of this charge facilitates the atomization of the feed solution, aided by the drying gas. Similar to conventional spray drying, the process of electrostatic spray drying occurs in four main stages. First, the feed solution is pumped through the nozzle, where an electric voltage is applied. Then, heated pressurized gas is introduced through the nozzle to assist in atomization. After the formation of dry particles, they move in a spiral motion toward the separation plenum. Finally, the charged dry particles are collected and neutralized by a collector (Jayaprakash et al., 2023).

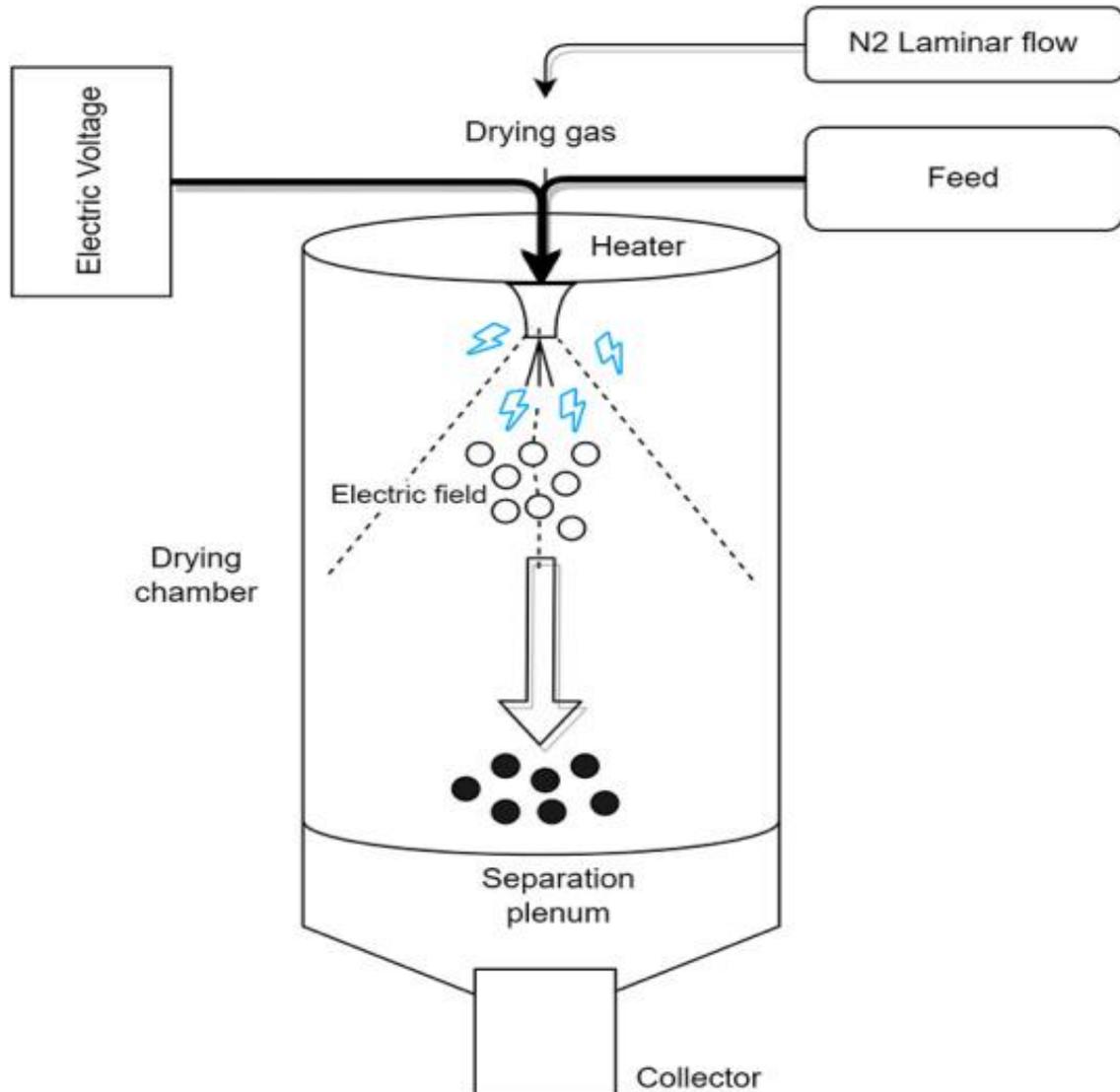


Figure 1.2 Electrostatic spray dryer (Source: (Jayaprakash et al., 2023))

Scaling up traditional research processes can be achieved by simplifying certain aspects of the system. When compared to conventional spray drying, electrostatic spray drying incorporates key differences, including the use of nitrogen, the application of electric voltage, and the inclusion of a separating plenum. An electrostatic force is generated within the droplet and maintained until the particles are fully dried by applying an electric voltage across the system. In the presence of this electrostatic force, the solvent, which typically exhibits the largest dipole moment, is pushed toward the outer surface of the drying droplet, while the bioactive substance, which has a lower dipole moment, resists this movement. As a result, the feed

solution is effectively driven to the droplet's surface. The complete drying process occurs smoothly and without the occurrence of a falling-rate period, provided that the droplet is exposed to the lowest possible drying temperature. This approach allows for the formation of dried particles at significantly lower temperatures (<90°C), in contrast to conventional spray drying, which typically operates at temperatures exceeding 160°C. As a result, electrostatic spray drying aims to achieve superior microencapsulation while minimizing the degradation of bioactive compounds. Additionally, this technique enhances the hydration and flowability of the dried particles, offering improved functional properties compared to traditional methods (Jayaprakash et al., 2023; Masum et al., 2022).

Each of the components of an emulsion in microencapsulation: an active substance (such as oil, vitamins, or other bioactive compounds), a carrier (e.g., starch or other high-molecular weight polysaccharides), and a solvent (usually water or another appropriate solvent) exhibits different polarity. The active substance, being less polar, has a smaller electric dipole compared to the more polar solvent and carrier, which have stronger dipoles. Due to their stronger electric dipoles, the solvent and carrier tend to move to the outer surface of the drying droplets, while the active ingredient remains at the center of the droplet (as illustrated in Fig. 5). This arrangement allows for effective drying at moderate temperatures, preventing premature shell formation around the droplets and preserving the integrity of the encapsulated active substance.

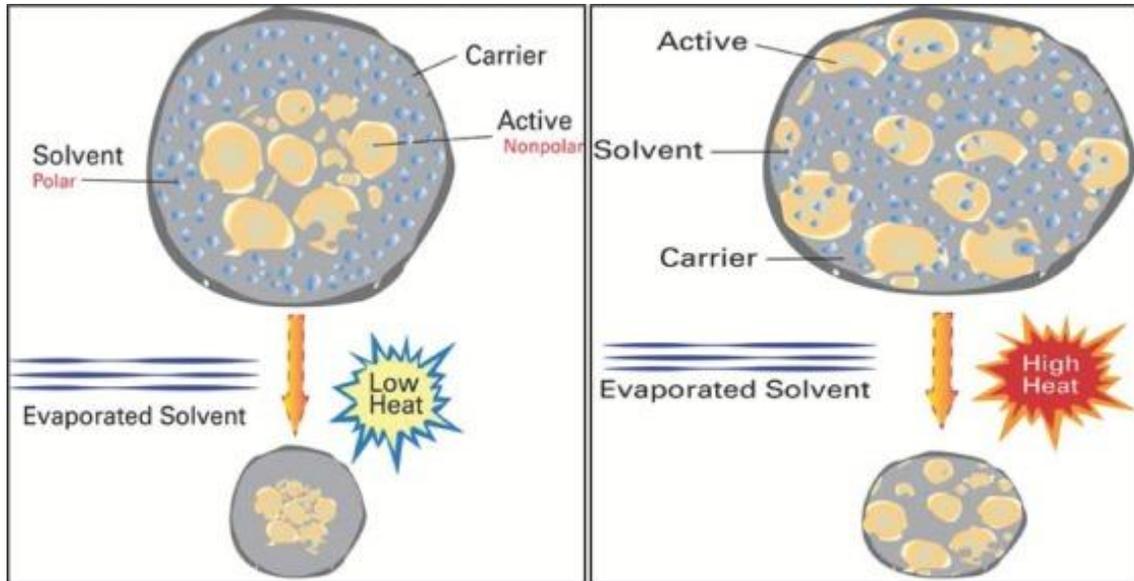


Figure 1.3 Comparison of Atomized Droplet Components in Low-Heat Electrostatic Spray Drying vs. High-Heat Traditional Spray Drying (Source: (Masum et al., 2022))

### RECENT RESEARCH IN ESD

The encapsulation of monoclonal antibodies using an electrostatic spray drying technique was conducted at an inlet temperature of 70 °C, with an applied voltage of 5 kV (Mutukuri et al., 2021). This process was compared to conventional spray drying (without electrostatic charge) under identical operating conditions, where it was observed that drying did not reach completion in the non-charged spray drying setup. The electrostatic spray-dried powders demonstrated favorable moisture content, exhibited a uniform particle distribution, and enhanced physical stability. In a separate investigation, various milk types, including whole, skim, and infant formula milk, were processed via electrostatic spray drying at an inlet temperature of 90 °C and an applied voltage of 10 kV, and compared to powders produced through conventional spray drying at 180 °C. Both spray drying methods resulted in powders with comparable moisture contents (less than 4%) and water activities (below 0.25). The morphology of the particles produced by both techniques was predominantly spherical and agglomerated. Additionally, Maillard reaction analysis revealed a reduced extent of browning in the electrostatic spray-dried powders when compared to those dried using conventional spray-drying methods.

Electrostatic spray drying (ESD) was applied to whole milk, skim milk, and infant milk formula (IMF) wet mix, utilizing the standard operating parameters. The size of the droplets produced during the process was found to be inversely proportional to the applied pressure, with higher pressures resulting in smaller droplets and lower pressures producing larger droplets. The pressure required to achieve atomization of the liquid feed ranged from 100 to 300 kPa, while the electrostatic charge varied from 1 to 30 kV. According to (Masum et al., 2019, 2020), the IMF powder was formulated to contain approximately 59% lactose (w/w), 15% protein (w/w), and 26% fat (w/w). For comparative purposes, identical formulations of whole milk, skim milk, and IMF were also processed using conventional high-heat spray drying techniques under conditions documented in the existing literature, allowing for a comparison of the physicochemical properties of the resulting powders.

In another example, an electrostatic spray dryer (Model 001, PolarDry Electrostatic Spray Dryer, Spraying Systems Co., Naperville, IL, USA) was employed to dry liquid colostrum and lactoferrin at two distinct inlet temperatures, 150 °C and 90 °C. The active IgG content in colostrum powders and the active lactoferrin content in lactoferrin powders were quantified using the ELISA Quantitation method (ELISA Kit, Catalog No. E10-126, Bethyl Laboratories, Montgomery, TX, USA). The results indicated that colostrum powders dried at the lower inlet temperature of 90 °C exhibited significantly better retention of immunomodulatory components, with approximately 16% higher bioactive yield compared to powders dried at the higher temperature of 150 °C (Masum et al., 2022). In a study, 10% solids (w/w) skim milk was fermented to a pH of 4.8 prior to being dried using an electrostatic spray dryer at inlet temperatures below 95 °C. The viable cell counts (cfu/mL) of *Streptococcus thermophilus* and *Lactobacillus delbrueckii* subsp. *bulgaricus* in the resulting yogurt powders were assessed. The results showed that the drying process did not lead to any loss of cell viability, indicating successful preservation of microbial activity in the powder (Koc et al., 2010; Masum et al., 2022).

For several decades, the food and pharmaceutical industries have employed spray drying as a common method for encapsulating oils in powder form. At an inlet air temperature of 220 °C, vegetable oils can be successfully spray-dried, resulting in powders with an oil encapsulation efficiency of approximately

30 to 50%. These powders are often encapsulated in a solid matrix composed of maltodextrin and acacia gum (Turchiuli et al., 2005; Fuchs et al., 2006). The encapsulation efficiency of vegetable oil in emulsions containing starch, sodium caseinate, and maltodextrin, processed at lower operational temperatures, was demonstrated in this study using electrostatic spray drying (ESD). Various combinations of constituent ratios were used to produce emulsions with an oil loading capacity ranging from 50% to 70%. The ESD powders exhibited a water activity ( $a_w$ ) of less than 0.20 and a moisture content below 2.5%. The surface-free fat content was found to be less than 1.5%. Powders with an oil load of 50–60% achieved an encapsulation efficiency of approximately 98%. In contrast, powders with a 70% oil load demonstrated an encapsulation efficiency of around 80% (Masum et al., 2022).

(~~C~~-Wang et al., 2022) utilized ESD and other drying technologies to produce an instant Pu-erh tea, a distinct post-fermented tea made from *Camellia sinensis* var. *assamica*. A sensory evaluation revealed that the electrostatic spray-dried tea exhibited sensory characteristics comparable to those of freeze-dried tea, based on a descriptive analysis. However, the electrostatic spray-dried tea outperformed both vacuum-dried and conventional spray-dried teas in terms of sensory attributes. Specifically, the electrostatic-dried tea exhibited significantly higher intensities of fruity, sweet, stale, woody, and floral notes compared to the spray-dried sample. Furthermore, the electrostatic-dried tea contained a greater number of odor-active compounds, with 17 compounds showing an odor intensity  $\geq 5$ , in contrast to only 7 compounds in the spray-dried tea.

(Jiang et al., 2021) demonstrated the advantages of electrostatic spray drying (ESD) as a microencapsulation method for *Bifidobacterium lactis* BL03, showing that ESD outperformed traditional spray drying and freeze-drying techniques. The study evaluated several parameters, including post-encapsulation survival rates, embedding efficiency, and survival rates following exposure to simulated gastrointestinal conditions. The ESD-encapsulated bacteria exhibited a high post-encapsulation survival rate of 89.26%. In contrast, survival rates for bifidobacteria encapsulated using conventional spray drying ranged from 70.58% to 75.68% (Fritzen-Freire et al., 2013; Simpson et al., 2005). Moreover, (Jiang et al., 2021) reported that the ESD-encapsulated bacteria maintained a survival rate of over 70% after 12 months of

storage at 25 °C, significantly higher than the viabilities observed by (Verruck et al., 2019), found that spray-dried microencapsulated cells stored at 25 °C for 120 days showed survival rates ranging from approximately 30% to 57%, depending on the carrier agent used. Additionally, the survival rate of ESD-encapsulated *Bifidobacterium lactis* BL03 after 4 hours under simulated intestinal conditions was found to be 75%.

Beaupeux et al., 2024 conducted a study comparing electrostatic spray drying (ESD) with traditional drying methods—spray drying (SD) and freeze-drying (FD)—for encapsulating sensitive actives such as oils, lactic acid bacteria (LAB), and enzymes, while also performing a life cycle assessment (LCA) to evaluate the sustainability of these processes. The results showed that ESD provided superior encapsulation efficiency, particularly in oil, reducing degradation and oxidation compared to SD. It also preserved LAB viability better than SD, with comparable results to FD, although FD had a higher environmental impact, particularly in terms of climate change. For enzymes like  $\beta$ -galactosidase, ESD maintained enzyme activity effectively by reducing thermal stress due to lower drying temperatures. The study highlighted the importance of formulation, process parameters, and scale in determining the final product quality and concluded that ESD is a promising, energy-efficient, and environmentally sustainable alternative for drying heat-sensitive materials, offering results similar to FD but with a lower environmental footprint.

## **Chapter 2: Objective and Hypotheses**

### **Objective**

The objective of this study was to encapsulate four flavor compounds—limonene, cinnamaldehyde, citral, and t-hexanal—using two different wall material formulations: gum acacia and maltodextrin, and HICAP-100 and maltodextrin. These materials were encapsulated using electrostatic spray drying (ESD) at four different voltage levels (+18, -18, +2, -2 kV), and the results were compared to traditionally spray-dried (TSD) flavors with the same formulations in terms of shelf life, total oil content, particle size, and structure.

### **Hypotheses**

1. ESD samples will retain flavor compounds better than traditional spray drying.
2. ESD samples will exhibit less oxidation than TSD samples in manufacture and storage due to the lower inlet temperature and the use of nitrogen gas during the spray drying process.

## CHAPTER 3: MATERIALS AND METHODS

### Materials

Gas chromatographic (GC) grade acetone (Sigma Aldrich Inc., St. Louis, MO, USA) was used for GC analysis. (+)-limonene oxide (97%, mixture of cis and trans), citral [5392-40-5], (*E*)-2-hexenal [6728-26-3], and (*E*)-cinnamaldehyde [104-55-2] were purchased from Aldrich Chemical Co. (Sigma/Aldrich, St. Louis, MO) and Acros Organics (Fisher Scientific, Pittsburgh, PA), respectively. Single-fold cold-pressed Valencia orange oil (McCormick FONA, IL, USA) was used as the encapsulation load material. Gum acacia (GA) (TIC Gums, White Marsh, MD, USA), HI-CAP®100, (octenyl succinic anhydride, OSAn, substituted modified starch) (Ingredion, Westchester, IL, USA), and Maltodextrin (10 DE) (Ingredion, Westchester, IL, USA) were used as carrier materials. 2-octanone (Alfa Aesar, Lancs, UK) was used as an internal standard. Magnesium Chloride (MgCl<sub>2</sub>) was obtained from Sigma Aldrich (St. Louis, MO). Other organic reagents that were used for analysis were all analytical grades and the water used for the gas chromatography analysis was deionized.

### Preparation of emulsion

The experimental procedure involves the preparation of two distinct emulsions for encapsulation formulation, each consisting of specific ingredients in defined proportions for a traditional spray dryer. Formulation 1 was composed of 0.2 kg of gum acacia (GA), 0.4 kg of 10 DE maltodextrin, 0.12 kg of a flavor blend, and 1.3 kg of water. Formulation 2 was comprised of 0.2 kg of modified starch (HI-CAP), 0.4 kg of 10 DE maltodextrin, 0.12 kg of the same flavor blend, and 1.3 kg of water. The flavor blend utilized in both matrices consisted of 80% orange oil, with 5% each of *t*-2-hexenal, citral, limonene, and cinnamaldehyde.

The carrier material for each formulation was dissolved in ambient temperature deionized water and thoroughly mixed using a high-shear mixer (Greerco Corp., Hudson, NH, USA) until complete dissolution was achieved. The HICAP carrier material solution was allowed to hydrate overnight at ambient temperature, whereas the gum acacia was not subjected to overnight hydration. Before the spray drying

process, the flavor blend was incorporated into each carrier material formulation and mixed for 3 min using the high-shear mixer (Greerco Corp., Hudson, NH, USA). Since the ESD has a smaller spray drying capacity than a traditional spray dryer, the total formulation was reduced by half, and all the ingredients were weighed accordingly before spray drying.

Table 3.1 Composition of spray dryer infeeds.

Formulation	Water (g)	Maltodextrin (g)	Gum Acacia (g)	HICAP (g)	Flavor blend				
					Orange oil (g)	Limonene (g)	Citral (g)	Cinnamaldehyde (g)	t- Hexanal (g)
Traditional spray dryer									
GA emulsion	1300	400	200	x	96	6	6	6	6
HiCap emulsion	1300	400	x	200	96	6	6	6	6
Electrostatic spray dryer									
GA emulsion	650	200	100	x	48	3	3	3	3
HiCap emulsion	650	200	x	100	48	3	3	3	3

## **Spray drying:**

### **Traditional spray dryer:**

Spray drying was done in the pilot plant of the Department of Food Science and Nutrition at the University of Minnesota with a Niro Utility dryer (Niro, Inc., Columbia, MD, USA). This dryer uses a centrifugal wheel atomizer (24.5 cm diameter rotary vane wheel rotating at 22,400 rpm), is gas heated, has a mass airflow of about 360 kg/h; drying chamber of 1.2 m diameter, 0.75 m cylindrical height, the cone angle of 60°; cyclone collector 0.3 m diameter; and powder collection container of 20 l capacity. Operating at an inlet air temperature of 200°C and an exit air temperature of 100°C resulted in a feed rate of ~330 ml/min (varied in order to maintain outlet temperature). After drying, the powders were cooled to ambient temperature and stored in poly bags at room temperature until analysis.

### **Electrostatic spray dryer:**

An electrostatic spray dryer (PolarDry® Model 001, Fluid Air, Naperville, IL, USA) was employed to perform electrostatic spray drying. The parameters are listed in Table 3.1. Usually, spray drying has been done at inlet temperatures between 120-140°C (Bowen et al., 2012; Chen et al., 2021b). In this study, inlet temperatures of 80°C and outlet temperatures of 40°C were chosen to investigate the effects of low-temperature drying. The preliminary data showed that traditional spray drying with an inlet temperature of 70°C did not form dry powders due to insufficient drying with droplets dripping to the bottom of the drying chamber. However, electrostatic spray drying with a 5kV charge at the inlet temperature of 70°C successfully formed the powder which was collected in the filter sock. The voltages used were two positive and two negative voltages (+18, -18, +2, and -2kV).

### **Yield of spray dried powder**

Yield is defined as the ratio of the weight spray-dried product collected from the cyclone to the total solids in the solution fed into the spray dryer.

$$\text{Yield (\%)} = \frac{\text{Weight of spray dried product collected from the cyclone}}{\text{Weight of total solids in the solution fed into the spray dryer}} * 100$$

### **Particle Size of Spray-Dried Material**

To determine the average particle size of the spray-dried powders, a Horiba LA 960 Laser Particle Size Analyzer (HORIBA Scientific, Edison, NJ, USA) was used. Approximately 0.5 g of each powder was added to the instrument at (Air pressure: 0.15 mPa, Feeder: 100% (Automatic), Refractive Index: 1.67) and the particle size was reported as the mean size based on 95 measurements per run. Particle size was analyzed in duplicate.

### **Volatile Retention by Clevenger Distillation**

The total volatile retention of the spray-dried material was determined by Clevenger Distillation. Spray-dried powder (20 g) was dissolved in 150 mL of distilled water in a 500 mL round-bottom flask. Then, ca. 0.1 mL of vegetable oil was added to the flask as an antifoam agent. The Clevenger trap was connected to the sample flask, and a water-cooled condenser was placed on top of the Clevenger trap. The heat source for distillation was adjusted so that approximately one drop of distillate was achieved every second or two. The distillation was carried out for 2 h, and the apparatus was allowed to cool to ambient temperature and then the volume (mL) of distilled oil was read directly from the collection arm. The volume of oil was converted to mass by multiplying by the density of the oil (0.82-0.86 g/mL) as determined gravimetrically at 20°C (Merck and others 2000). The volatile oil or aroma retention during spray drying was calculated as follows: Volatile oil retention % = [(Measured oil content)/ (theoretical oil content)] X 100%

### **Dry product evaluation:**

The volatile components are highly susceptible to oxidation during storage, leading to an off-flavor. Oxidation is the primary reaction that contributes to the limited shelf life of the product. All the samples were placed in an open container (in a thin layer) and stored in desiccators flushed with nitrogen at 40 °C under controlled water activity (saturated MgCl<sub>2</sub> solution, *a<sub>w</sub>* = 0.33) for 3 weeks to achieve equilibrium. Once equilibrium was reached, the amount of aroma compounds remaining in the powders was measured at different storage times. Samples were withdrawn from the stored powders on days 0, 4, 7, 14, and 21, and the model flavor compounds were quantified by gas chromatography Flame Ionization Detector (FID). For each compound, the remaining amount was expressed as a percentage of the initial amount after drying the considered material.

### **Evaluation of oxidation products by Gas Chromatography (GC)**

The extent of oxidation was measured by gas chromatography. Approximately 0.15 g of each of the spray-dried powders was dispersed in 8.5 ml of water and was mixed using a vortex mixer. Then, 4 g of an acetone solution containing 2-octanone as an internal standard (0.100 mg/g acetone) was added to the vial and mixed again. After mixing and allowing the powder-water-internal standard and acetone solution to settle for 1 h, approximately 1 mL of the supernatant was transferred to 2 mL vials and loaded into an HP7673A automatic sampler (Hewlett-Packard, Wilmington, 23 DE). Using an HP5890 series II GC containing HP-5MS capillary column (30 m x 0.25 mm x 0.25  $\mu$ m) (J&W Scientific, Folsom, CA) and a flame ionization detector (FID), 2  $\mu$ L of each extract was automatically injected into the GC in split mode (20 to 1). The following operating conditions were used: hydrogen carrier gas at 55 kPa head pressure, 20 mL/min total carrier flow, 50°C initial oven temperature, ramping at 10 °C/min to 140 °C with 2 min hold, then 30 °C/min to 220 °C with 2 min hold 220°C; injection port temperature, 250°C. Data collection and peak area integrations were performed. Limonene oxide was reported as the sum of its two major isomers (cis and trans). The oxidative stability of limonene was reported as mg of limonene oxide formed per g of limonene. Similarly, the formation of benzaldehyde and hexanoic acid was determined to monitor the oxidation of cinnamaldehyde and t-2-hexenal.

#### **Evaluation of surface oil by Gas Chromatography (GC)**

A 2 g sample of sample powder was mixed with 4 g of an acetone solution containing 2-octanone as an internal standard (0.25 mg/g acetone) in a sealed test tube. The mixture was agitated for 10 min in a shaker to ensure thorough extraction. The resulting mixture was transferred to a GC vial and analyzed using GC-FID under the same conditions used for the evaluation of oxidation products.

#### **Determination of iron content in SD powders**

The iron content of the spray-dried powders was determined by the Research Analytical Laboratory at the Crops Research Building, University of Minnesota. The method employed for iron determination involved microwave-assisted nitric acid digestion followed by analysis using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The iron content was measured for the emulsions of both GA and HiCap emulsions, as well as for TSD and ESD (+18 kV) samples.

**Table 3.2 Electrostatic spray dryer operating condition (Polar Dry Model 001, Naperville, IL)**

Sr. No.	Parameters	Conditions
1.	Vane	Present
2.	Feedstock Agitation/Heating/Cooling	Agitation
3.	Collection Volume (liters)	1
4.	Evaporation Rate (kg/hr)	1
5.	Nitrogen Blanket (SCFH)	5.0
6.	Filters	5 Micron Cartridge
7.	Nozzle	0.020" / 0.064"
8.	Tubing	1.6 mm
9.	Gas flow (Nm <sup>3</sup> /hr)	25
10.	Inlet Drying Gas Temp (°C)	80
11.	Atomizing Gas Pressure (kPa)	250
12.	Atomizing Gas Temp (°C)	35
13.	Chamber Pressure (kPa)	0.2
14.	Average Spray Rate (kg/hr)	7.0
15.	Average Outlet Temp (°C)	40 ± 0.7
16.	Average Product Temp (°C)	43 ± 0.7
17.	Voltage (kV)	(-18), 18, (-2), 2

## Chapter 4: Result and Discussion

### Infeed solid levels

The primary factor affecting flavor retention during spray drying is the concentration of infeed solids (Reineccius, 1989). A semi-permeable barrier forms rapidly in the drying particles when the infeed solids concentration is high, functioning to retain volatile flavor components. The flavor system should be introduced only after the carrier has dissolved. In spray drying, a typical practice is to load the flavor at 20% of the infeed solids (Reineccius, 1989).

It has long been recognized that the level of solids in the dryer infeed influences volatile retention. Higher solid levels are typically believed to reduce the mobility of fragrance compounds within the wall material, leading to a quicker formation of a protective shell around the compounds. These conditions result in better flavor retention (Leahy et al., 1983; Reineccius & Bangs, 1985, Charve and Reineccius, 2009). Charve & Reineccius, 2009 observed that oxidation was also more pronounced when materials were spray dried at lower infeed solids levels (10%), particularly for gum acacia and modified starch, while the highest flavor retention was observed for gum acacia (94%) at 35% solids and modified starch (88%) at 40% solids. Based on these findings, we chose to encapsulate the flavor with 35% infeed solids for both formulations 1 and 2 to maximize flavor retention while minimizing the formation of oxidation products. Fig. 4.1 shows that the yield of spray-dried powders was similar for GA and HiCap emulsion in both TSD and ESD, as well as across different samples in ESD. Interestingly, volatile retention was only marginally better when SD was at low temperatures.

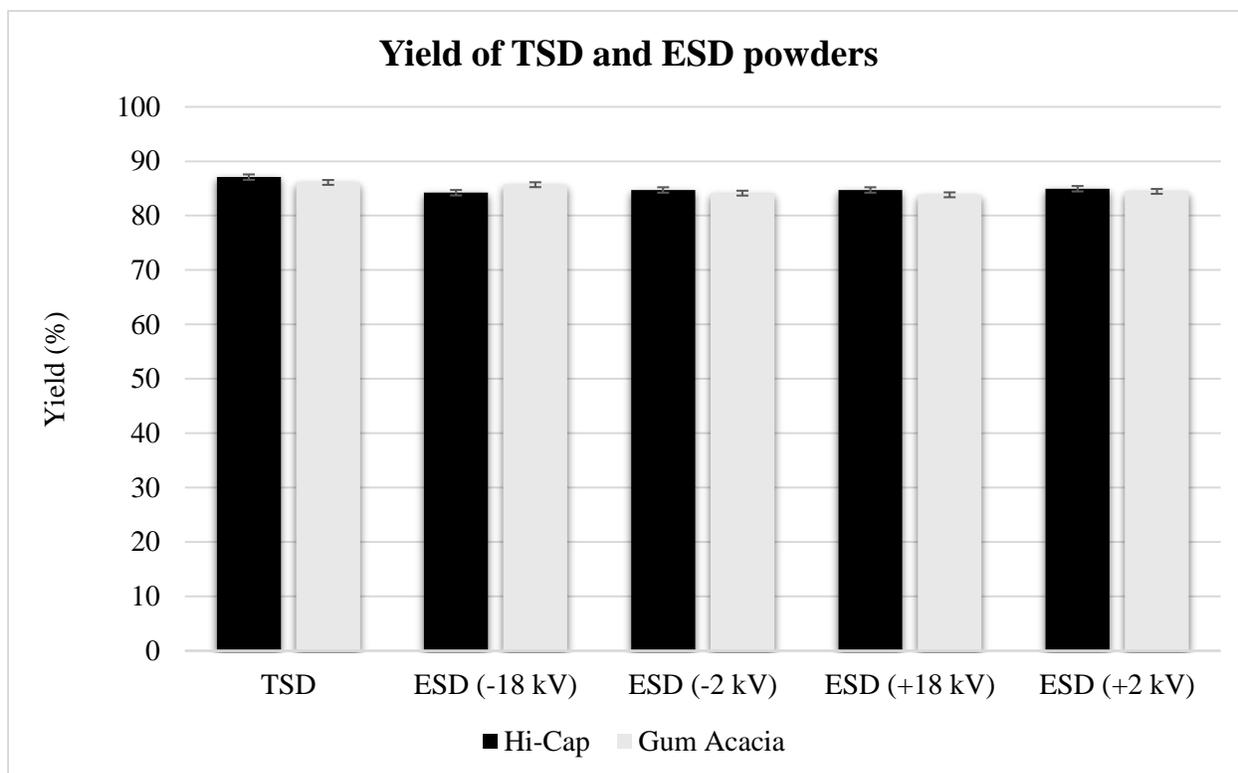


Figure 4.1 Yield of TSD and ESD powders for formulations 1 and 2

### Resultant Powder Particle Size

The infeed solid emulsion has a strong influence on determining flavor retention during drying. The infeed emulsion is always homogenized prior to spray drying; however, considerable process variation exists within the industry in this respect. Anker & Reineccius, 1988 have shown that there is a direct relationship between the degree of homogenization and the retention of orange peel oil during spray drying. Therefore, it appears advantageous to efficiently homogenize the dryer infeed material.

Reineccius, (2004) highlighted that the molecular weight of the flavoring largely determines its diffusion through the particle wall materials and thus its loss during drying. Larger molecules have a slower diffusion rate, thereby preventing volatiles from reaching the particle surface for evaporation. Additionally, the vapor pressure of flavor components is directly related to the volatility of aroma compounds. Vapor pressure indicates the likelihood of

the compound evaporating before an impermeable crust forms on the surface of the drying droplet, and it also affects retention during the encapsulation process. The flavoring microencapsulation process is influenced by a range of factors, including the choice of wall materials, emulsion properties, and drying parameters. It is widely recognized, however, that smaller emulsion droplet sizes enhance efficiency and help retain volatile compounds. This is because fewer flavoring components are lost during the process, ultimately reducing manufacturing costs.

Cristina Ferrer Carneiro et al., 2022 found that during the spray drying of passion fruit flavor and orange oil, the emulsion particle size distribution of passion fruit flavoring ( $D_{4,3} = 36.9 \mu\text{m}$ ) was significantly smaller than that of orange flavoring ( $D_{4,3} = 44.1 \mu\text{m}$ ), with a p-value of less than 0.05. This difference was attributed to the smaller droplet size distribution of the orange oil emulsion, which resulted in higher emulsion stability and encapsulation efficiency. Based on these findings, we aimed to maintain the droplet size as small as possible for formulations 1 and 2 in this study for ESD and TSD powders.

The effect of dryer infeed emulsion droplet size on the retention of d-limonene, a water-insoluble flavor, during spray drying was illustrated by (Soottitantawat et al., 2003). As the emulsion droplet diameter increased, the retention of d-limonene decreased across all carriers' solid combinations of GA and MD. The flavor retention was notably lower, especially in the 0.5–2.0  $\mu\text{m}$  mean emulsion size range. This indicates that smaller emulsions are more stable during atomization and the spray drying process. Furthermore, it implies that the size of emulsion droplets is a critical factor in flavor retention, provided appropriate wall materials are used. Similar findings by (Anker & Reineccius, 1988) also showed that a smaller emulsion size leads to higher retention of orange oil. For ESD, the droplet size varied between 1 to 2  $\mu\text{m}$  for GA emulsion and 0.5 to 1  $\mu\text{m}$  for HiCap emulsion. In the GA emulsion, the droplet size remained consistent across different voltage settings, and a similar pattern was noted for the HiCap emulsion.

The physical characteristics of the infeed emulsion, including viscosity and solids concentration, along with the atomization operating parameters, such as wheel diameter and rotational speed for centrifugal atomization, or orifice size and pressure for nozzle atomization, are key factors that determine the particle size of the powder.

Additionally, infeed solids and operating temperatures can influence particle size. In practice, particle size can be partially controlled through these factors, depending on the design of the spray dryer (Reineccius, 2004).

Several studies have highlighted that larger particle sizes in spray-dried powders are associated with improved flavor retention and lower surface oil content. For instance, (S. M. Jafari et al., 2007) encapsulated fish oil and d-limonene in maltodextrin matrices combined with surface-active biopolymers (modified starch or whey protein concentrate) at 40% solids w/w. Their findings demonstrated that larger particles (>63  $\mu\text{m}$ ) retained more volatiles than smaller particles (<38  $\mu\text{m}$ ). Similarly, (Soottitantawat et al., 2005) observed that when using gum arabic, with or without maltodextrin as the carrier, the aroma stability of d-limonene improved upon storage as the particle size (typically between 10 and 150  $\mu\text{m}$ ) and emulsion size increased. This improvement was likely due to a reduction in surface area, which limited exposure to oxidative conditions. In line with these findings, our results showed that TSD powders had larger particle sizes than all the ESD samples, suggesting that TSD powders had lower surface oil content. This lower surface oil content likely made TSD powders less susceptible to oxidation compared to ESD powders, which exhibited higher oxidation levels. Therefore, beneficial in minimizing oxidation, supporting the hypothesis that increased surface area in smaller particles (such as those produced by ESD) contributes to a greater extent of oxidation.

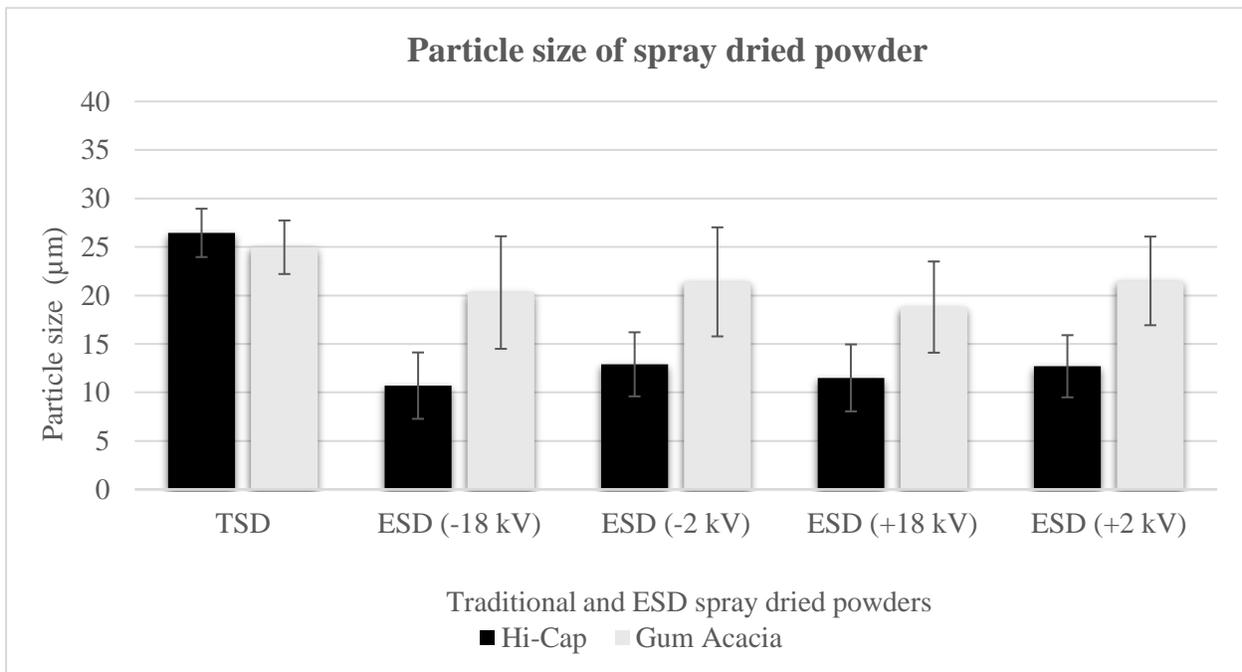


Figure 4.2 Particle size of TSD and ESD powders.

### **Total oil and surface oil:**

The retention of volatiles and the effectiveness of microencapsulation are key characteristics of the process, primarily depending on the total amount of oil retained within the matrices after spray drying and the amount of oil encapsulated within the microcapsules. Low volatile retention indicates a greater loss of the active ingredient to the environment during processing, prior to the storage or transportation of the final powdered product. Consistent with previous studies, carrier systems containing an emulsifier demonstrated better oil retention during spray drying compared to carrier wall material formulations composed solely of maltodextrin with varying dextrose equivalencies (Reineccius, 2004). Soottitantawat et al., 2003 observed a correlation between volatile retention and emulsion particle size, with volatile retention decreasing as the infeed emulsion particle size increased. This reduction in volatile retention is likely due to the high shear forces generated during the atomization of coarser emulsions, which exposes the volatile components to greater evaporation during the drying process. Additionally, factors such as the type of carrier wall material, viscosity, solids content, and the ratio of carrier wall material to flavor material (all held constant) also influence volatile retention.

Baranauskienė et al., (2006) studied the effect of different wall materials on the total oil content of encapsulated peppermint essential oil. Out of all the wall materials, ENCAPSUL 855-emulsified peppermint oil product contained the lowest total oil content of 13.5 g per 100 g, HICAP was 15.03g per 100 g, while the CIEmCap 12633-emulsified product had a total oil content of 15.2 g per 100 g. The emulsification efficiency of peppermint essential oil in the liquid emulsions for both the ENCAPSUL 855 and CIEmCap 12633 products ranged from 88.8% to 99.7%. This demonstrates that the retention of volatiles is strongly influenced by the type of ~~solid matrix~~ carrier solids used. The combination of gum acacia and maltodextrin effectively enhanced the retention of total oil, as demonstrated by Charve & Reineccius (2009), who found that the retention of the highly volatile (E)-2-hexenal increased approximately 20-fold when higher solids were used with gum acacia and modified starch. This finding aligns with other studies, such as those by Reineccius & Bangs, 1985, who observed a significant improvement in the retention of highly volatile compounds when higher solids content was applied, facilitating rapid membrane formation.

GA and HiCap emulsion demonstrated good volatile retention due to the high infeed solids content, with HiCap emulsion showing better retention of total oil than GA emulsion. In the case of GA emulsion, both TSD and ESD at -2 kV exhibited similar volatile oil retention (89.3% and 90.5%), while other voltages resulted in lower total oil retention, with +2 kV showing the lowest. For HiCap emulsion, TSD and ESD samples exhibited similar total oil retention, with +18 kV being the only exception, showing the lowest retention at 82.9%. It can be concluded that for gum acacia, +18 kV yielded the highest total oil retention, while for HI-CAP, total oil retention remained consistent across different voltages of ESD and TSD, except for +18 kV. Voltage variation did not significantly affect the total oil retention in the HiCap emulsion, whereas, for the GA emulsion, a change in total oil retention was observed.

The extent of oxidation is directly related to the extent of surface oil. High surface oil content and poor flavor retention during drying are primarily caused by particle shrinkage and cracking. When particles crack during drying, it leads to significant flavor losses and elevated levels of surface (or extractable) oil (Reineccius, 1989). For GA emulsion, TSD exhibited 57.6 mg/kg of surface oil, while ESD showed a significantly higher surface oil content, with -2 kV yielding the highest at 85 mg/kg. Similarly, for HiCap emulsion, TSD had 60 mg/kg of surface oil, while +18 kV resulted in the highest surface oil content at 98 mg/kg. The higher surface oil observed in ESD samples can be attributed to their smaller particle size, whereas TSD samples exhibited larger particle sizes. Larger particles typically result in lower surface oil content because they have a smaller surface area relative to their volume. Since surface oil is determined by the outer surface of the particles, larger particles offer less surface area for oil to accumulate compared to smaller particles (surface to volume/mass ratio). Furthermore, larger particles generally undergo less shrinkage and cracking during drying, reducing the exposure of internal oil to the surface. Consequently, larger particles tend to have a more intact surface, leading to lower surface oil content, while smaller particles are more susceptible to cracking and oil/flavor loss.

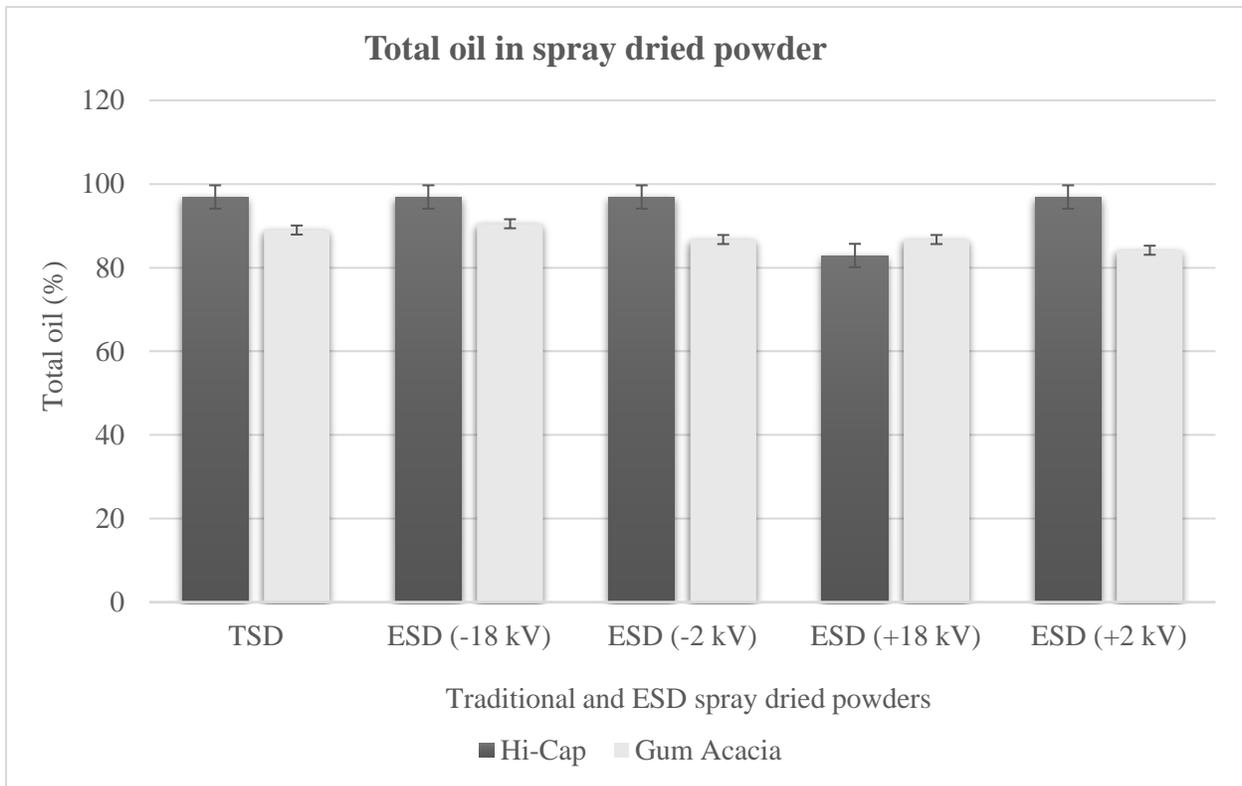


Figure 4.3 Total oil content in TSD and ESD powders by Clevenger.

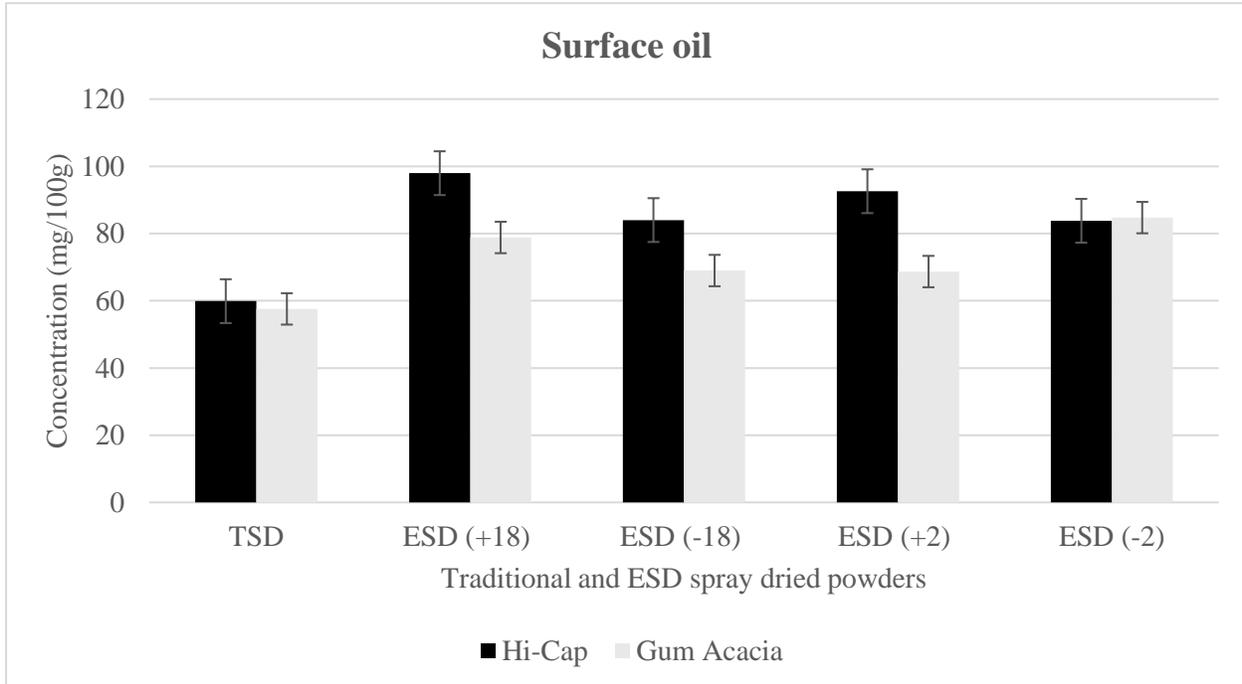


Figure 4.4 Surface oil content for TSD and ESD powders

## **Formation of oxidation products during shelf-life study**

Several factors affect the oxidative stability of spray-dried flavorings, and extensive research has been conducted on this topic. Key elements include the inlet and outlet temperatures of the dryer, the humidity of the drying air, the atomization method, as well as the particle size and formulation of the infeed emulsion. Previous studies on heat damage have shown that higher dryer inlet temperatures accelerate the oxidation process. Additionally, dryer air temperatures impact powder characteristics such as moisture content, surface oil, and the total oil content in the final product. Based on several previous studies, limonene oxide was selected as the oxidation product of orange oil to examine its formation across both TSD and ESD samples (Charve & Reineccius, 2009; Cristina Ferrer Carneiro et al., 2022; Reineccius, 1989; Reineccius & Bangs, 1985). The formation of limonene oxide was chosen as an oxidation product to measure. To evaluate the oxidation of limonene, the ratio of the areas of limonene oxide to limonene was analyzed, and the formation of limonene oxide was monitored over a 21-day storage period. Given the lower inlet and outlet temperatures in the ESD process and the use of nitrogen gas during spray drying, it was anticipated that ESD samples would exhibit lower oxidation product formation during the storage study compared to TSD samples.

At day 0, the level of limonene oxide was higher in both GA and HiCap emulsion for the ESD samples vs TSD. Over the 21 days, the oxidation trend for GA emulsion remained consistently high in all ESD samples, regardless of voltage, compared to TSD samples. The oxidation levels across the different voltages in the ESD samples were similar, except for the -18 kV setting, which exhibited slightly lower oxidation than the other ESD samples. For the HiCap emulsion, ESD samples showed increased limonene oxide formation on day 0, indicating that oxidation primarily occurred during the drying process, with little to no additional oxidation during storage compared to TSD. However, no further oxidation was observed in the HiCap emulsion during the subsequent 21-day study for both ESD and TSD samples. This contrasts with the findings of Sobel et al., (2022), who reported that ESD samples had a reduced formation of limonene oxide compared to TSD, although their analysis was based on headspace odor analysis. In contrast, our study utilized solvent extraction with acetone followed by GC-FID to determine the total concentrations of limonene and limonene oxide. The powders were essentially washed with acetone to get surface oil. Solvent extraction coupled with GC-FID is more effective for quantifying these compounds due to the distinct physicochemical properties of limonene and limonene oxide. GC-FID offers superior sensitivity, allowing for accurate

separation and quantification of both compounds, even at low concentrations, by efficiently extracting them from the sample matrix. Headspace analysis, in contrast, is constrained by the volatility of these compounds and may not fully capture the entire range of limonene and limonene oxide, particularly in encapsulated systems where these compounds may not be prevalent in the gas phase. Furthermore, solvent extraction ensures the comprehensive recovery of both limonene and limonene oxide, providing more accurate and representative measurements than headspace analysis, which may suffer from compound loss or interference from other volatiles. The higher formation of limonene oxide in ESD samples can be attributed to the increased surface oil and reduced particle size, as higher surface oil indicates that the more “unprotected” oil gets readily exposed to oxygen resulting in more oxidation.

We also evaluated the oxidation of citral, cinnamaldehyde, and t-2-hexenal for further study of the effect of ESD and its different voltages and its comparison to TSD. Benzaldehyde was monitored to measure the oxidation of cinnamaldehyde. (H. Chen & Ji, 2011; Luo et al., 2024; Yu et al., 2020). The ratio of neral to geranial was used to monitor the oxidation of citral while hexanoic acid was the indicator of t-2-hexenal oxidation. (Bicas et al., 2009; Karahadian & Lindsay, 1989; Kimura et al., 1983; Nik-Abdul-Ghani et al., 2018; Ohashi et al., 2021; Vandemoortele et al., 2020; S. Wang et al., 2024). A similar oxidation trend was observed for cinnamaldehyde, citral, and t-2-hexenal as was seen for the oxidation of limonene. (Figs 4.7- 4.12).

For HiCap emulsion, oxidation was higher after spray drying in the ESD samples than in the TSD samples. That result is very unexpected. The observation that the products manufactured at Fluid Air were more oxidized than those prepared under higher temperature drying conditions is contrary to expectations and thus, prompted an investigation into reasons why this occurred. One option is that Fluid Air used a blender in emulsion formation that may contain iron as a pro-oxidant. We tested that hypothesis by measuring the iron content in both the TSD and ESD powders. However, it was found that the iron levels in the ESD samples were approximately four times lower than in the TSD samples! This would result in the opposite effect than observed. We do not have an answer as to why the ESD samples oxidized more quickly than those prepared at the UMN however, all sample formulations, indicators of oxidation, and drying methods consistently indicated that the ESD resulted in greater oxidation than the TSD powders. This issue is being investigated by another researcher at the UMN for it makes no sense.

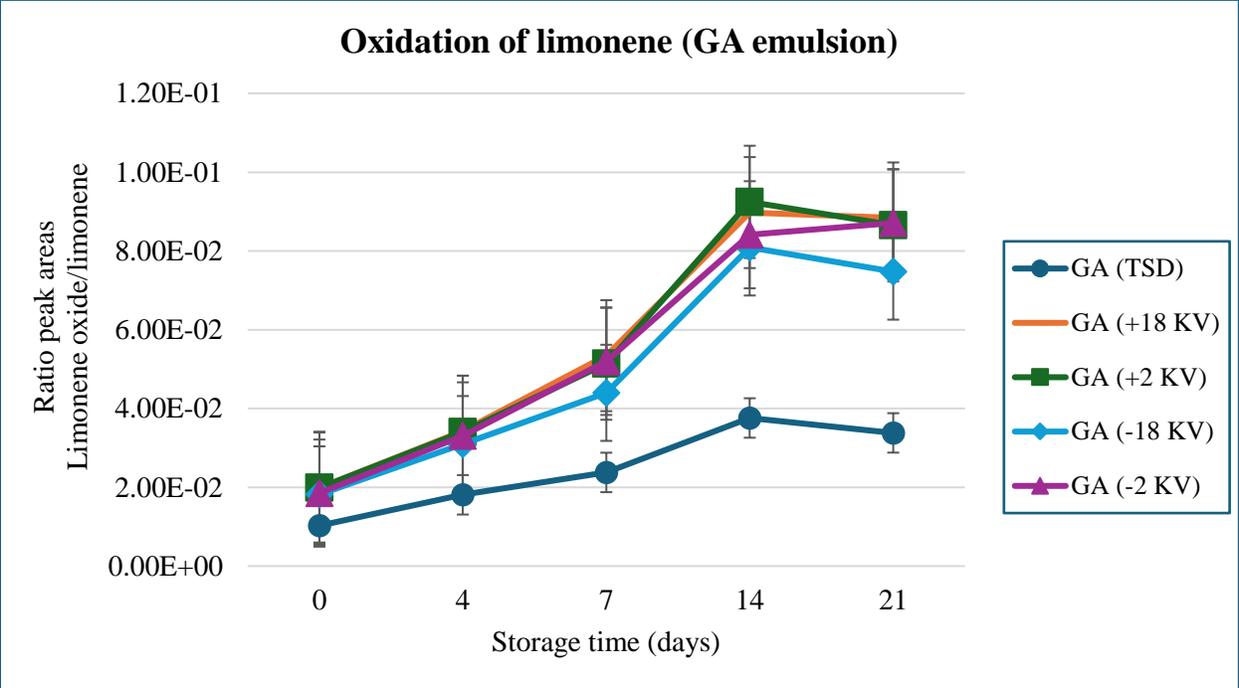


Figure 4.5 Oxidation of limonene over 21-day shelf life study for TSD and ESD (GA emulsion)

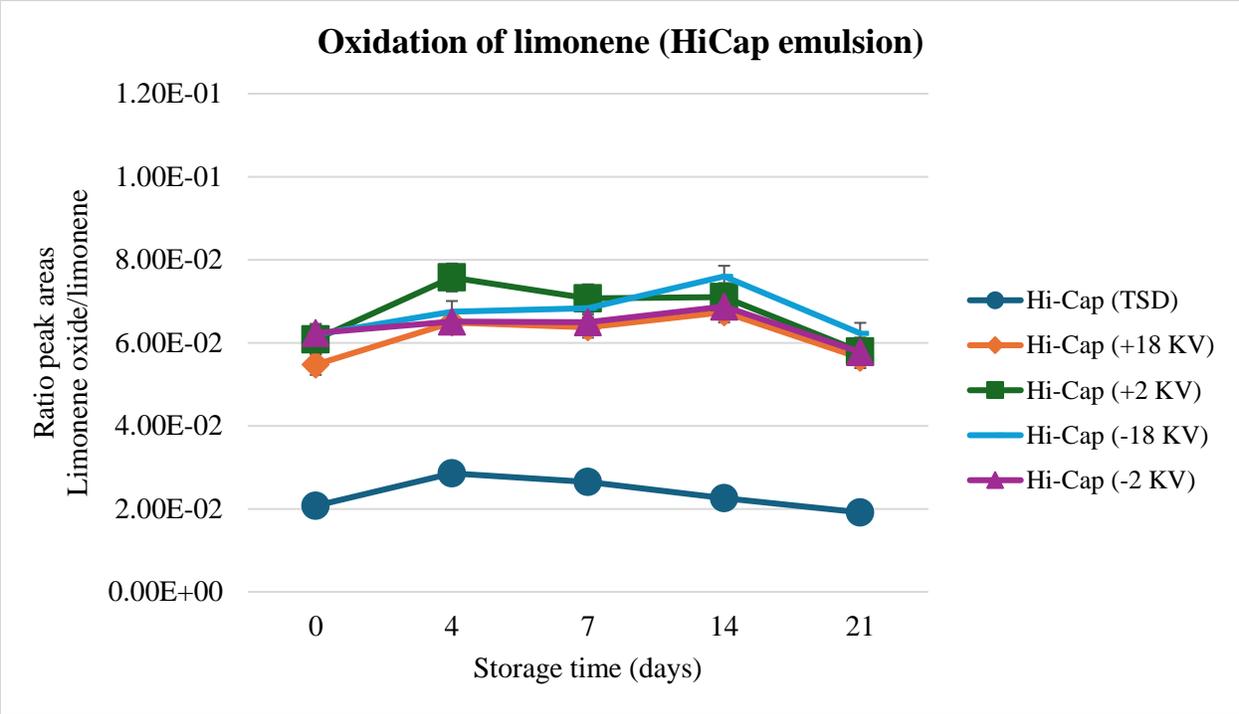


Figure 4.6 Oxidation of limonene over 21-day shelf life study for TSD and ESD (HiCap emulsion)

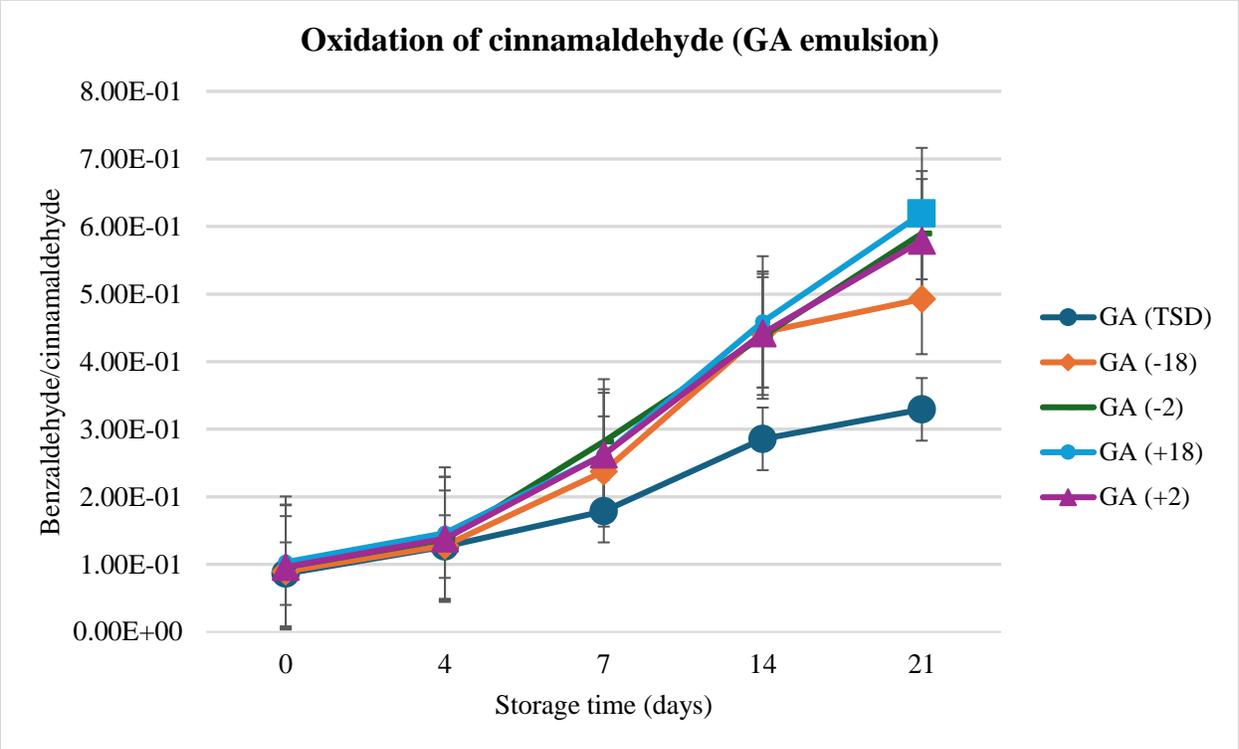


Figure 4.7: Oxidation of cinnamaldehyde over 21-day shelf life study for TSD and ESD (GA emulsion)

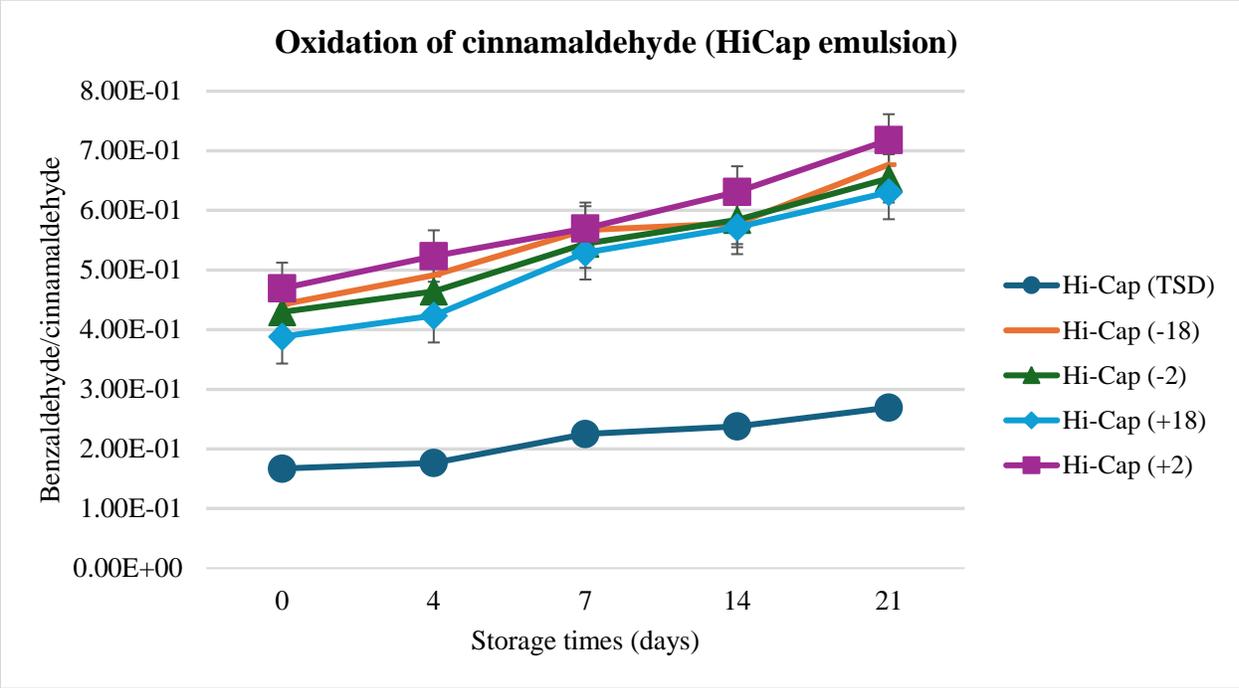


Figure 4.8 Oxidation of cinnamaldehyde over 21-day shelf life study for TSD and ESD (HiCap emulsion)

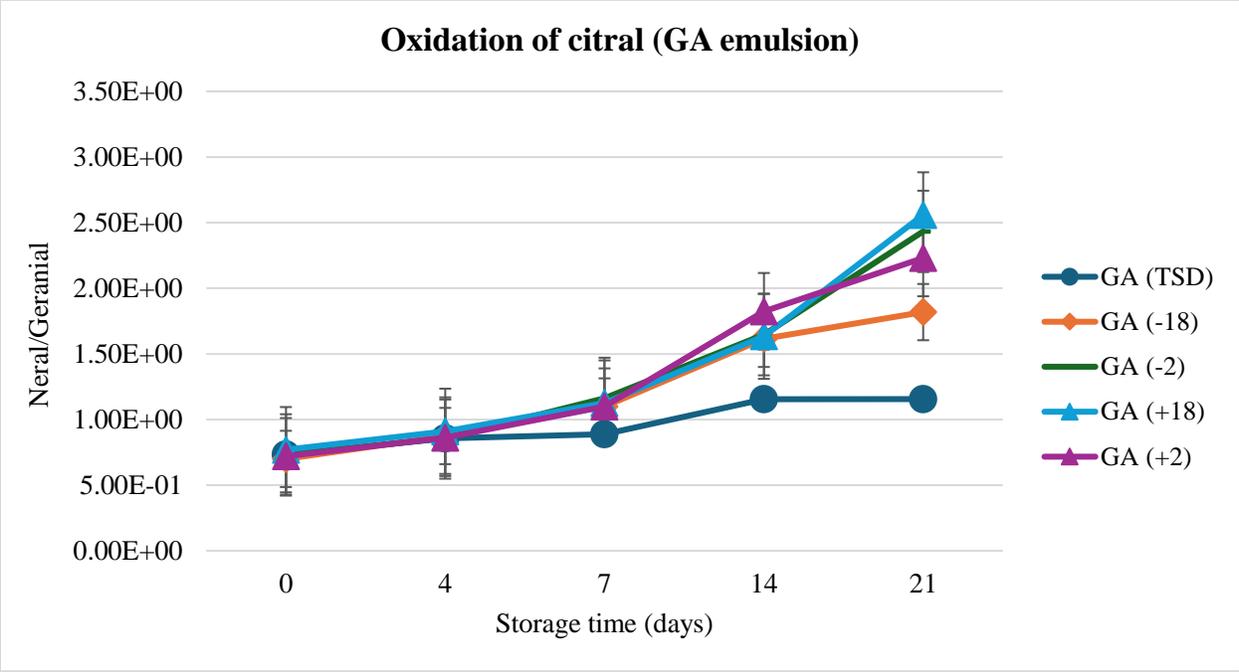


Figure 4.9 Oxidation of citral over 21-day shelf life study for TSD and ESD (GA emulsion)

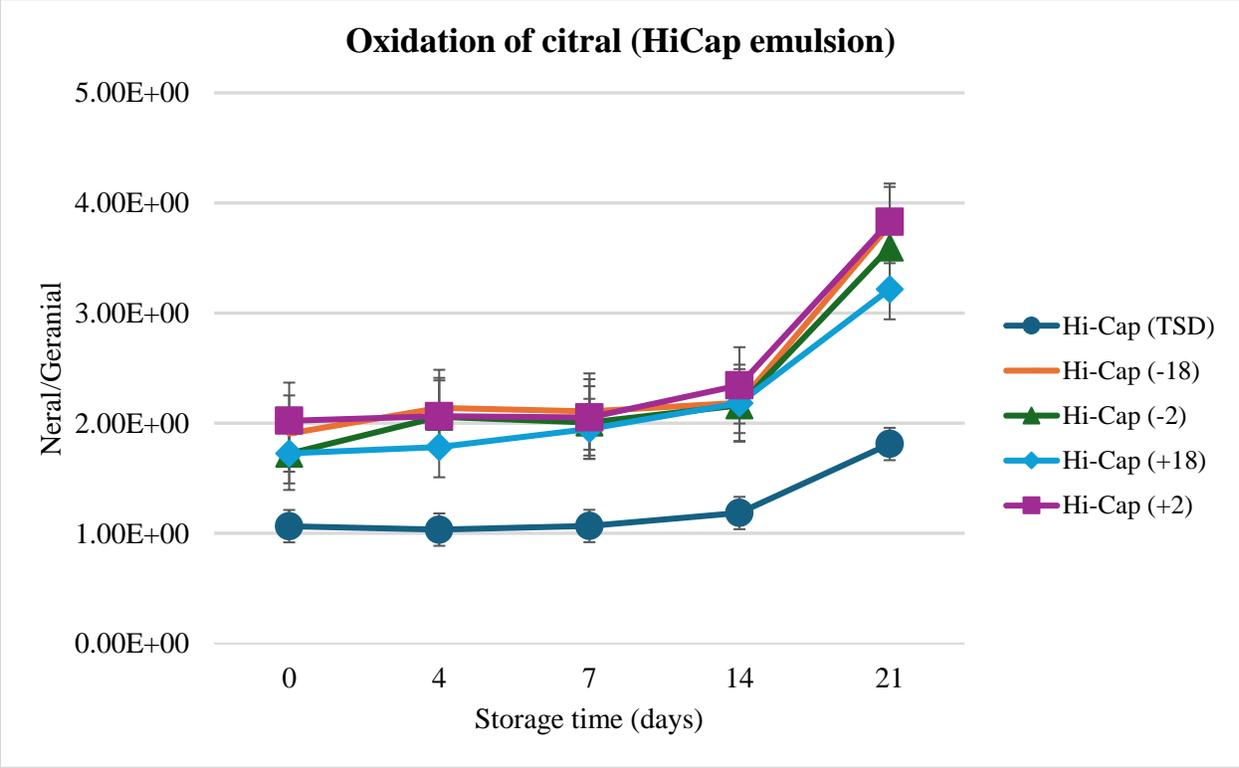


Figure 4.10 Oxidation of citral over 21-day shelf life study for TSD and ESD (HiCap emulsion)

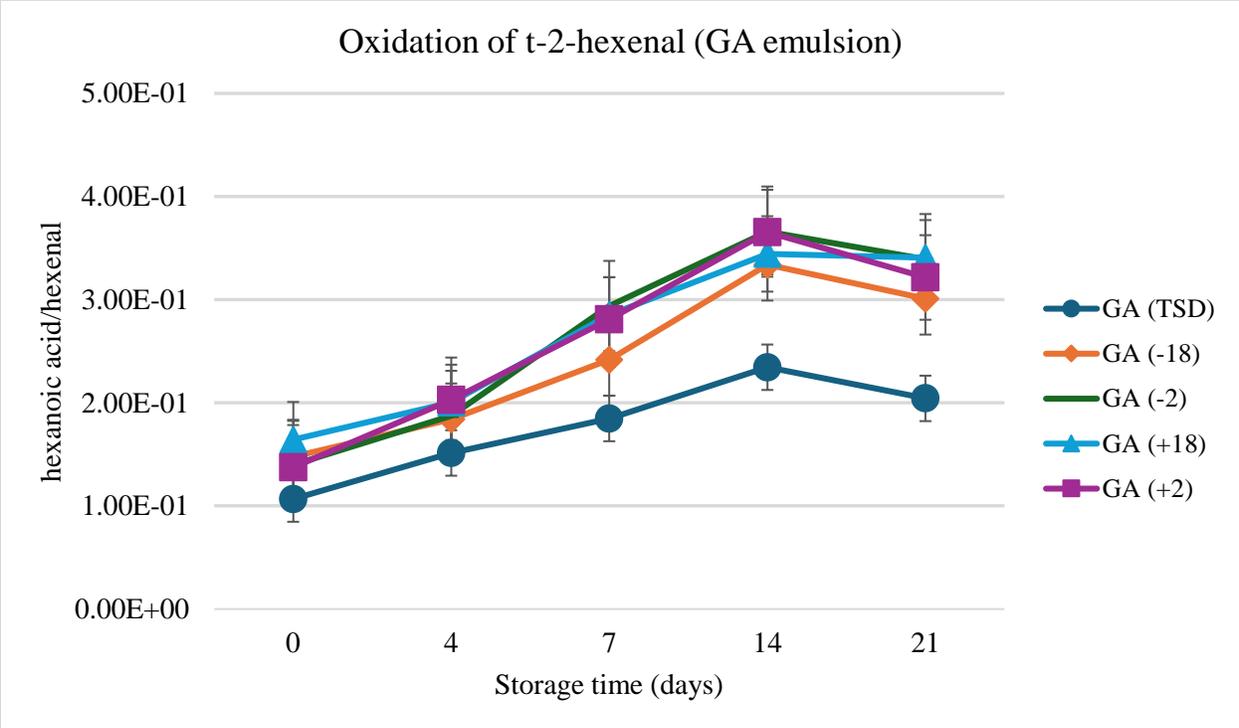


Figure 4.11 Oxidation of t-2-hexenal over 21-day shelf life study for TSD and ESD (GA emulsion)

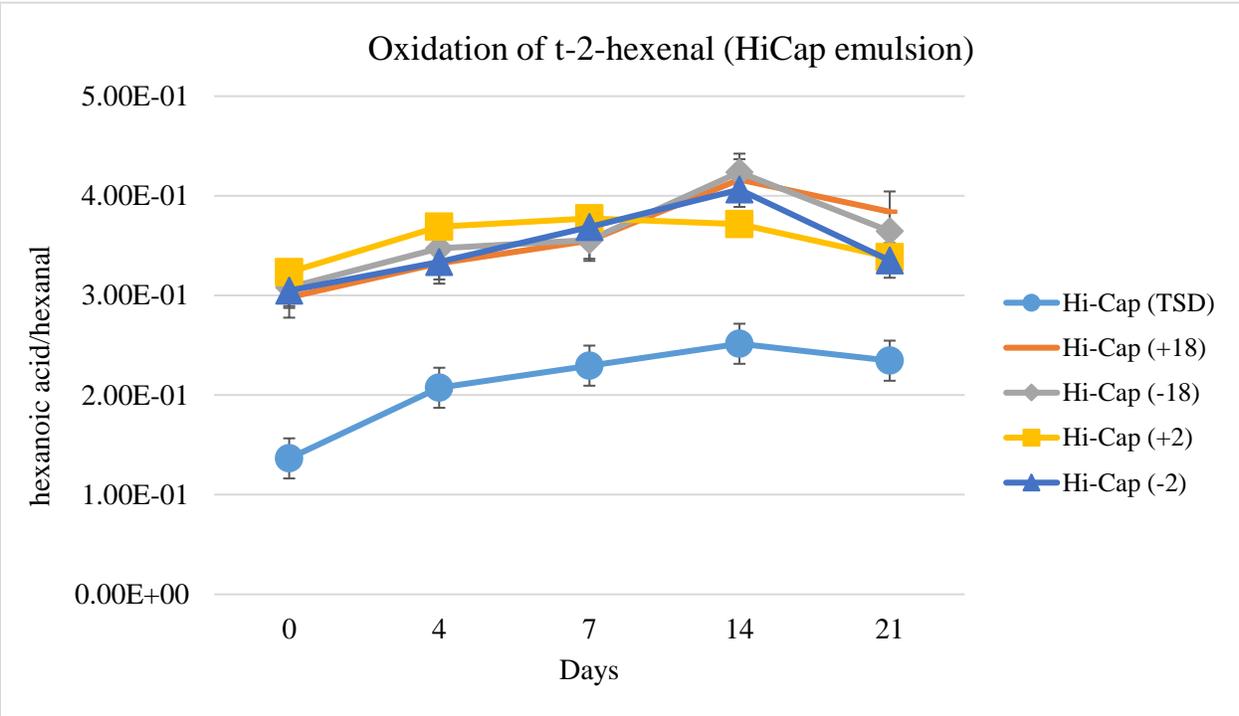


Figure 4.12 Oxidation of t-2-hexenal over 21-day shelf life study for TSD and ESD (HiCap emulsion)

## Chapter 5: Discussion

The GC-FID analysis, which detects oxidation products from all four indicator flavor compounds, indicates that spray dried flavorings prepared by ESD undergo more oxidation than ESD at time 0 TSD immediately after spray drying and during the 21-day shelf life study. In GA emulsion, ESD displays signs of oxidation starting from day 0. For HiCap emulsion, a significant difference is observed in the ESD samples, but the oxidation trend remains consistent across the various ESD samples over the 21 days.

The oxidation observed at Day 0 suggests that the emulsification step or spray drying, is contributing to the oxidation. However, the operating principles of the electrostatic spray dryer (ESD) suggest otherwise. ESD involves lower inlet (90°C) and outlet (45°C) temperatures, along with nitrogen gas (an inert gas) inside the drying chamber, which should reduce oxygen exposure and minimize oxidation. Additionally, the varying voltages in the ESD process do not significantly affect the extent of oxidation. Although earlier studies suggested that heat during spray drying is the primary cause of flavor oxidation, the findings from this study imply that oxidation is more prominent with low-temperature spray drying.

A hypothesis to explain the unexpected data could be related to the homogenization process/equipment involved in emulsion formation at the Fluide Air pilot plant facility. The pilot plant operator at Fluide Aire needed to homogenize the infeed emulsion system much longer than was required at the UMN pilot plant. Excessive homogenization leads to heat generation and the inclusion of higher levels of oxygen in the emulsion. Furthermore, a different type of homogenizer was used between facilities. We proposed that the homogenizer used at Fluide Aire was not of the desired quality (stainless steel) which may have added iron (a potent pro-oxidant) to the emulsion. We had our samples analyzed for iron content and found no difference in iron levels between UMN and Fluide Air - contributing to oxidation in the final spray-dried powders. To test this theory, it is crucial to measure the concentration of oxidation products and the oxidation of flavor compounds through GC-FID analysis.

Since ESD and TSD were conducted at different locations using different equipment, a hypothesis was proposed that heat generated during the emulsion mixing process and/or the presence of heavy metals from the mixer could contribute to oxidation through catalytic reactions. To test this, the iron content of the powders was measured

in a TSD sample, an ESD sample, and the emulsion for both formulations 1 and 2. However, the results revealed that the ESD samples contained approximately four times less iron than the TSD samples and the corresponding emulsions. These findings eliminate the possibility that iron from a mixer or another piece of equipment at Fluide Aire caused oxidation. We did not measure copper or magnesium levels in the powders or emulsions, but these metals are rare in any food processing environment. We have no logical explanation for the observed results. We will be employing an individual (PhD researcher) to continue work on understanding the observed results.

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## Chapter 6: Appendices

### Appendix 1 (Chapter 4)

Table 6.1 Yield of TSD and ESD powders for GA and HiCap emulsion.

Composition	Voltage (kV)	Yield of SD powders (%)
ESD		
GA emulsion	(-18)	85.7%
	(-2)	84.1%
	(+18)	83.8%
	(+2)	84.5%
HiCap emulsion	(-18)	84.2%
	(-2)	84.7%
	(+18)	84.7%
	(+2)	84.9%
TSD		
GA emulsion	-	86.1%
HiCap emulsion	-	87.1%

Table 6.2 Particle size distribution of GA and HiCap emulsion for both TSD and ESD powders.

Composition	Voltage (kV)	Particle size (Dv 50 microns) (µm)
ESD		
GA emulsion	(-18)	20.3
	(-2)	21.4
	(+18)	18.8
	(+2)	21.5
HiCap emulsion	(-18)	10.7
	(-2)	12.9
	(+18)	11.5

	(+2)	12.7
TSD		
GA emulsion	-	24.97
HiCap emulsion	-	26.45

Table 6.3 Total oil retention for GA and HiCap emulsion in TSD and ESD powders

Formulation	Volume of oil (ml)	Voltage (kV)	Volatile oil retention (%)
GA emulsion	3.5	-	89.3
	3.4	+18	86.7
	3.3	+2	84.2
	3.6	-18	90.5
	3.4	-2	86.73
HiCap emulsion	3.8	-	96.9
	3.3	+18	82.9
	3.8	+2	96.9
	3.8	-18	96.9
	3.8	-2	96.9

Table 6.4 Concentration of iron (ppm) in emulsion, TSD and ESD powder

Formulation	Voltage (kV)	Concentration of iron (ppm)
GA emulsion	TSD	11.442
	ESD (+18kV)	4.447
	Emulsion	10.033
HiCap emulsion	TSD	10.709

	ESD (+18kV)	2.560
	Emulsion	6.135

Table 6.5 Oxidation of spray dried orange oil stored at water activity of 0.33 aw over 3 weeks

Formulation	Spray drying process	Limonene oxide/limonene				
		Day 0	Day 4	Day 7	Day 14	Day 21
GA emulsion	TSD	1.03E-02	1.81E-02	2.38E-02	3.76E-02	3.38E-02
	ESD (+18 kV)	1.98E-02	3.43E-02	5.34E-02	8.98E-02	8.84E-02
	ESD (-18 kV)	1.82E-02	3.10E-02	4.40E-02	8.09E-02	7.48E-02
	ESD (+2 kV)	1.99E-02	3.41E-02	5.14E-02	9.25E-02	8.65E-02
	ESD (-2 kV)	1.85E-02	3.31E-02	5.20E-02	8.41E-02	8.71E-02
HiCap emulsion	TSD	2.08E-02	2.86E-02	2.65E-02	2.26E-02	1.91E-02
	ESD (+18 kV)	5.47E-02	6.48E-02	6.37E-02	6.74E-02	5.64E-02
	ESD (-18 kV)	6.20E-02	6.75E-02	6.83E-02	7.60E-02	6.23E-02
	ESD (+2 kV)	6.08E-02	7.57E-02	7.07E-02	7.10E-02	5.79E-02
	ESD (-2 kV)	6.24E-02	6.51E-02	6.50E-02	6.87E-02	5.77E-02

Table 6.6 Oxidation of spray dried cinnamaldehyde stored at water activity of 0.33 aw over 3 weeks

Formulation	Spray drying process	Benzaldehyde/cinnamaldehyde				
		Day 0	Day 4	Day 7	Day 14	Day 21
	TSD	8.63E-02	1.26E-01	1.79E-01	2.86E-01	3.29E-01

GA emulsion	ESD (+18 kV)	1.03E-01	1.46E-01	2.62E-01	4.59E-01	6.19E-01
	ESD (-18 kV)	8.98E-02	1.28E-01	2.37E-01	4.43E-01	4.93E-01
	ESD (+2 kV)	9.61E-02	1.38E-01	2.62E-01	4.42E-01	5.79E-01
	ESD (-2 kV)	9.60E-02	1.37E-01	2.82E-01	4.37E-01	5.90E-01
HiCap emulsion	TSD	1.67E-01	1.76E-01	2.25E-01	2.38E-01	2.69E-01
	ESD (+18 kV)	3.88E-01	4.24E-01	5.29E-01	5.72E-01	6.31E-01
	ESD (-18 kV)	4.42E-01	4.91E-01	5.67E-01	5.78E-01	6.77E-01
	ESD (+2 kV)	4.69E-01	5.24E-01	5.70E-01	6.31E-01	7.18E-01
	ESD (-2 kV)	4.30E-01	4.64E-01	5.44E-01	5.84E-01	6.54E-01

Table 6.7 Oxidation of spray dried citral stored at water activity of 0.33 aw over 3 weeks

Formulation	Spray drying process	Neral/geranial				
		Day 0	Day 4	Day 7	Day 14	Day 21
GA emulsion	TSD	7.33E-01	8.56E-01	8.88E-01	1.15E+00	1.16E+00
	ESD (+18 kV)	7.70E-01	9.10E-01	1.13E+00	1.63E+00	2.56E+00
	ESD (-18 kV)	7.00E-01	8.74E-01	1.10E+00	1.61E+00	1.82E+00
	ESD (+2 kV)	7.20E-01	8.61E-01	1.10E+00	1.82E+00	2.23E+00
	ESD (-2 kV)	7.30E-01	8.59E-01	1.16E+00	1.65E+00	2.43E+00
HiCap emulsion	TSD	1.07E+00	1.03E+00	1.07E+00	1.18E+00	1.81E+00
	ESD (+18 kV)	1.73E+00	1.78E+00	1.95E+00	2.18E+00	3.22E+00
	ESD (-18 kV)	1.91E+00	2.14E+00	2.11E+00	2.19E+00	3.80E+00

	ESD (+2 kV)	2.02E+00	2.07E+00	2.05E+00	2.34E+00	3.83E+00
	ESD (-2 kV)	1.72E+00	2.06E+00	2.01E+00	2.16E+00	3.60E+00

Table 6.8 Oxidation of spray dried t-2-hexenal stored at water activity of 0.33 aw over 3 weeks

Formulation	Spray drying process	Hexanoic acid/t-2-hexenal				
		Day 0	Day 4	Day 7	Day 14	Day 21
GA emulsion	TSD	1.07E-01	1.51E-01	1.85E-01	2.34E-01	2.04E-01
	ESD (+18 kV)	1.64E-01	2.00E-01	2.85E-01	3.44E-01	3.41E-01
	ESD (-18 kV)	1.48E-01	1.84E-01	2.42E-01	3.34E-01	3.01E-01
	ESD (+2 kV)	1.37E-01	2.03E-01	2.81E-01	3.66E-01	3.22E-01
	ESD (-2 kV)	1.40E-01	1.87E-01	2.94E-01	3.66E-01	3.39E-01
HiCap emulsion	TSD	1.36E-01	2.07E-01	2.30E-01	2.52E-01	2.35E-01
	ESD (+18 kV)	2.98E-01	3.32E-01	3.55E-01	4.16E-01	3.84E-01
	ESD (-18 kV)	3.08E-01	3.47E-01	3.55E-01	4.24E-01	3.65E-01
	ESD (+2 kV)	3.23E-01	3.69E-01	3.77E-01	3.72E-01	3.38E-01
	ESD (-2 kV)	3.05E-01	3.33E-01	3.69E-01	4.06E-01	3.35E-01

Table 6.9 Total surface oil for GA and HiCap emulsion in TSD and ESD powders

Formulation	Spray drying process	Surface oil (mg/100g)
GA emulsion	TSD	59.9
	ESD (+18 kV)	98.0
	ESD (-18 kV)	84.0
	ESD (+2 kV)	92.6
	ESD (-2 kV)	83.8
HiCap emulsion	TSD	57.6
	ESD (+18 kV)	78.8
	ESD (-18 kV)	69.0
	ESD (+2 kV)	68.7
	ESD (-2 kV)	84.7

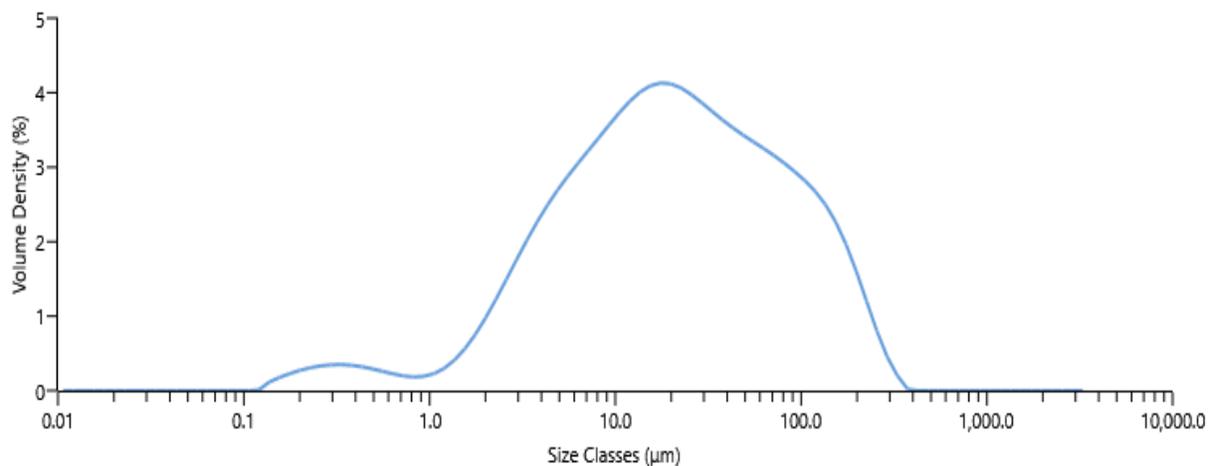


Figure 6.1 Particle size of GA emulsion at -18 kV

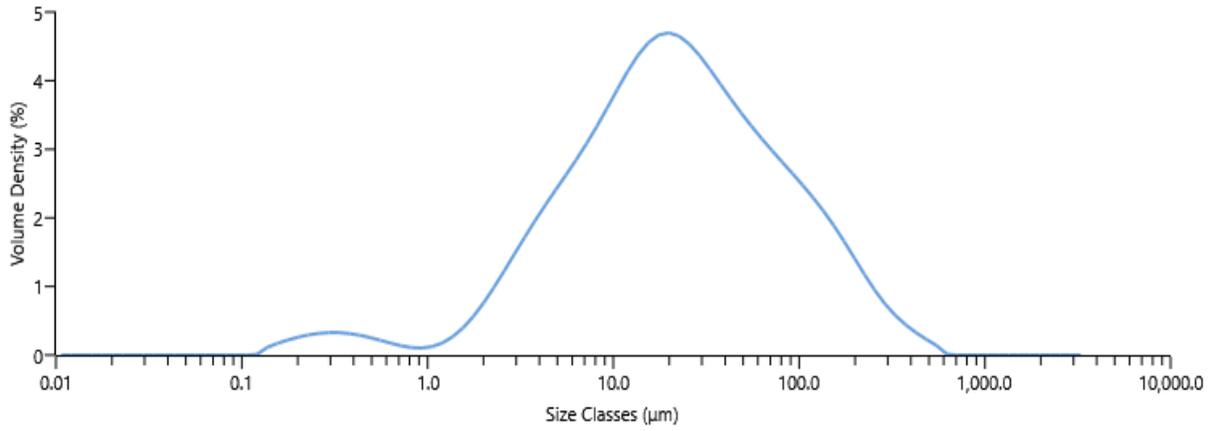


Figure 6.2 Particle size of GA emulsion at -2 kV

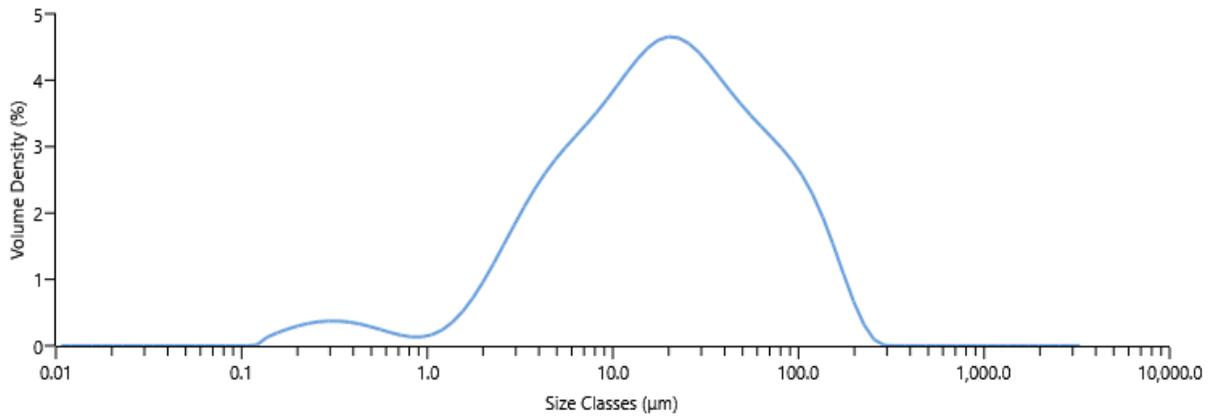


Figure 6.3 Particle size of GA emulsion at +18 kV

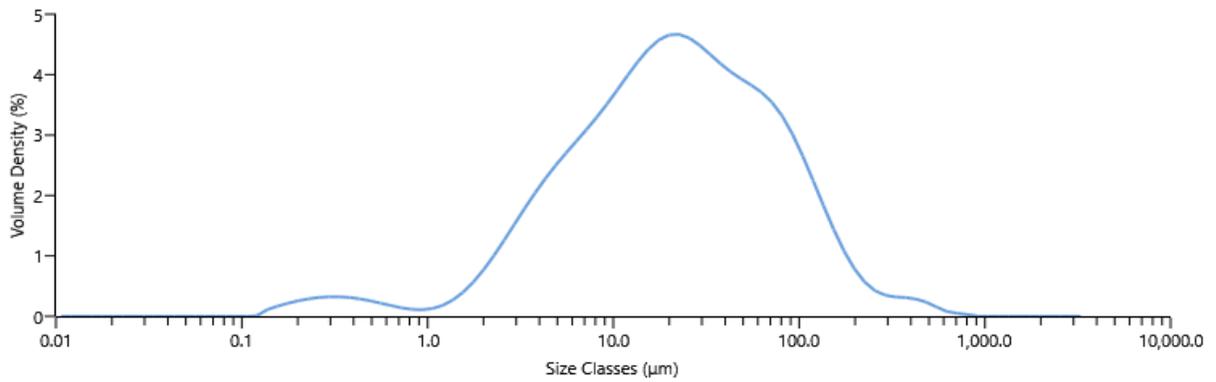


Figure 6.4 Particle size of GA emulsion at +2 kV

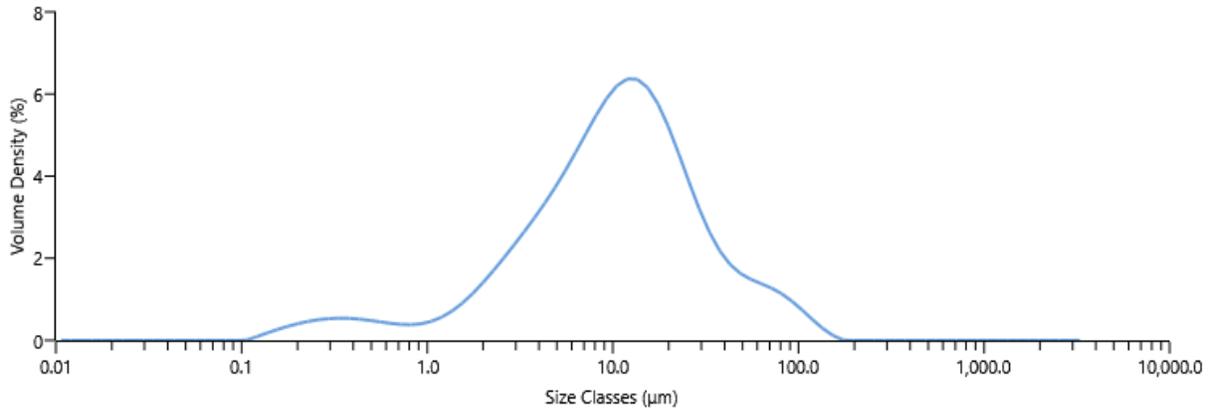


Figure 6.5 Particle size of HiCap emulsion at -18 kV

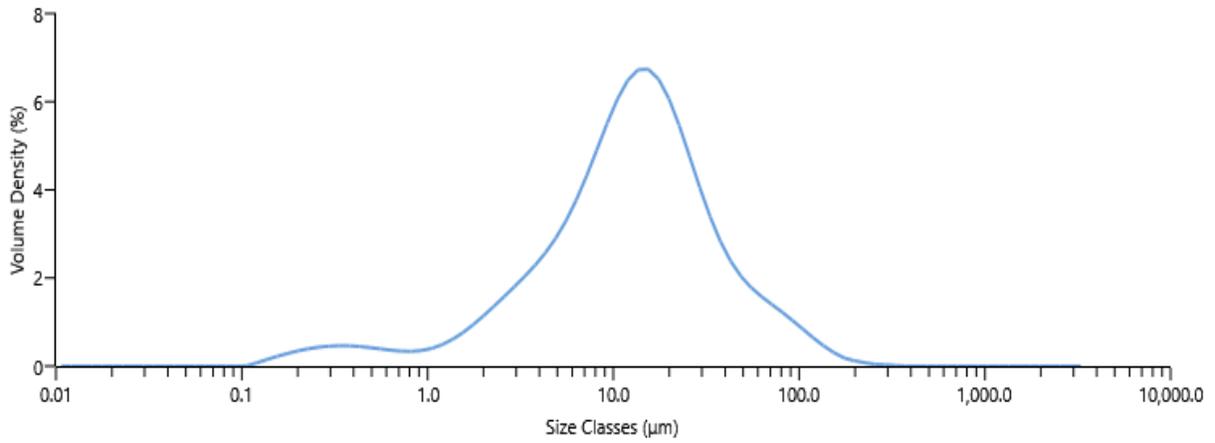


Figure 6.6 Particle size of HiCap emulsion at -2 kV

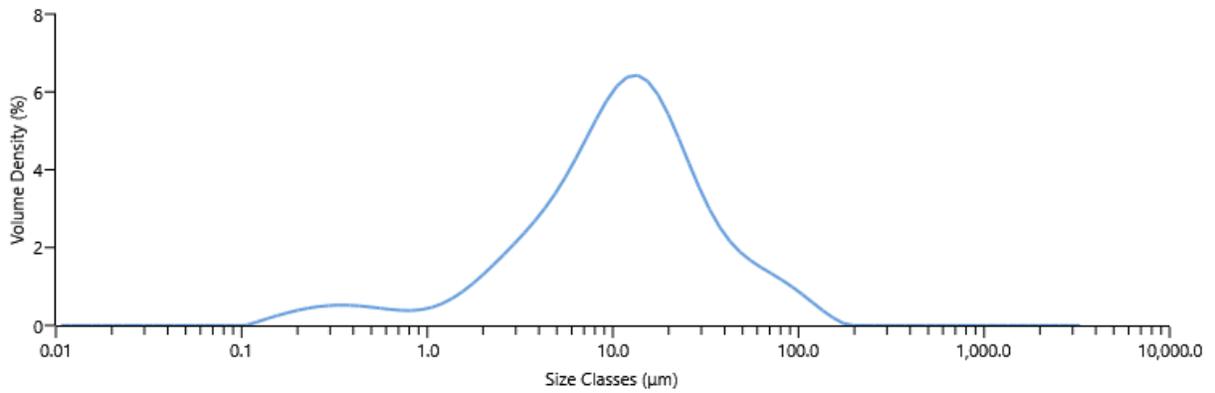


Figure 6.7 Particle size of HiCap emulsion at +18 kV

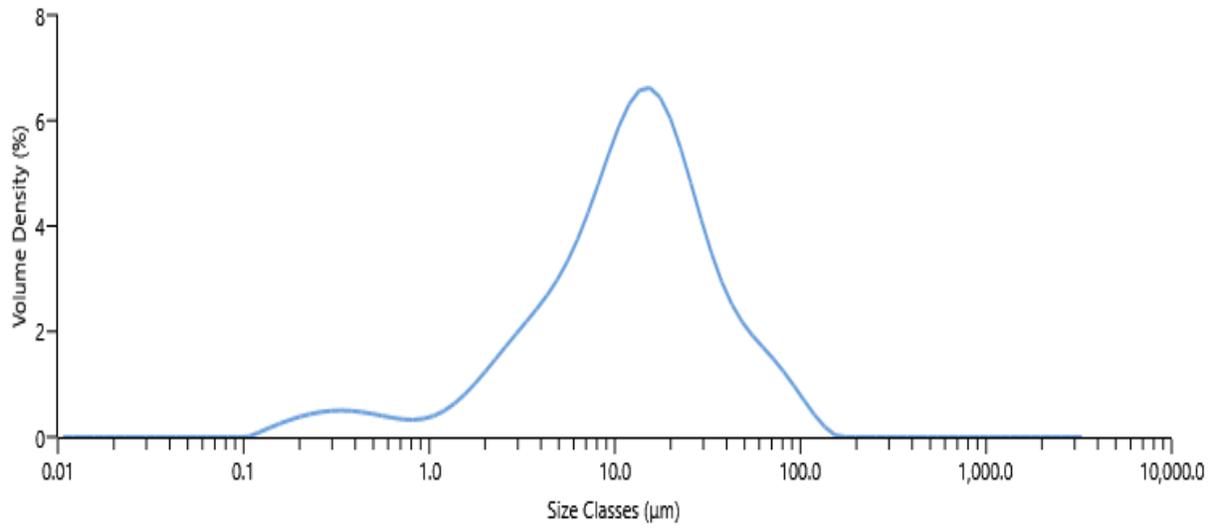


Figure 6.8 Particle size of HiCap emulsion at +2 kV

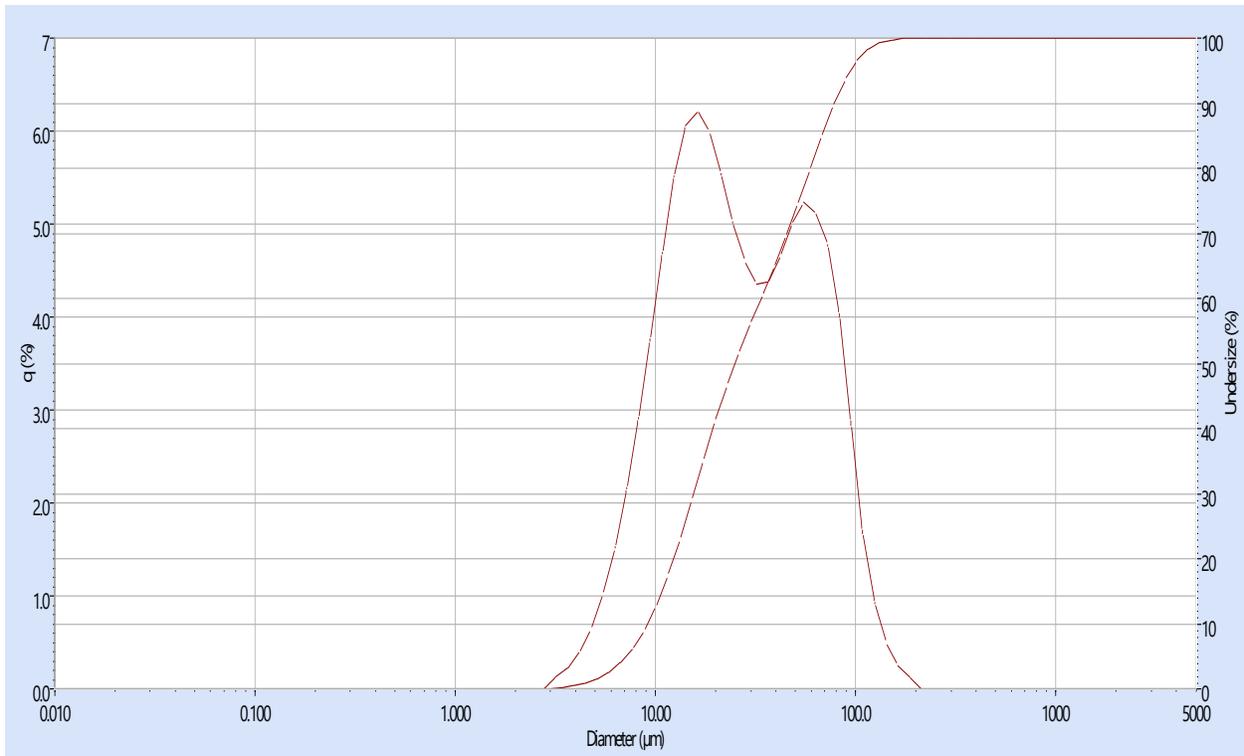


Figure 6.9 Particle size of TSD HiCap emulsion

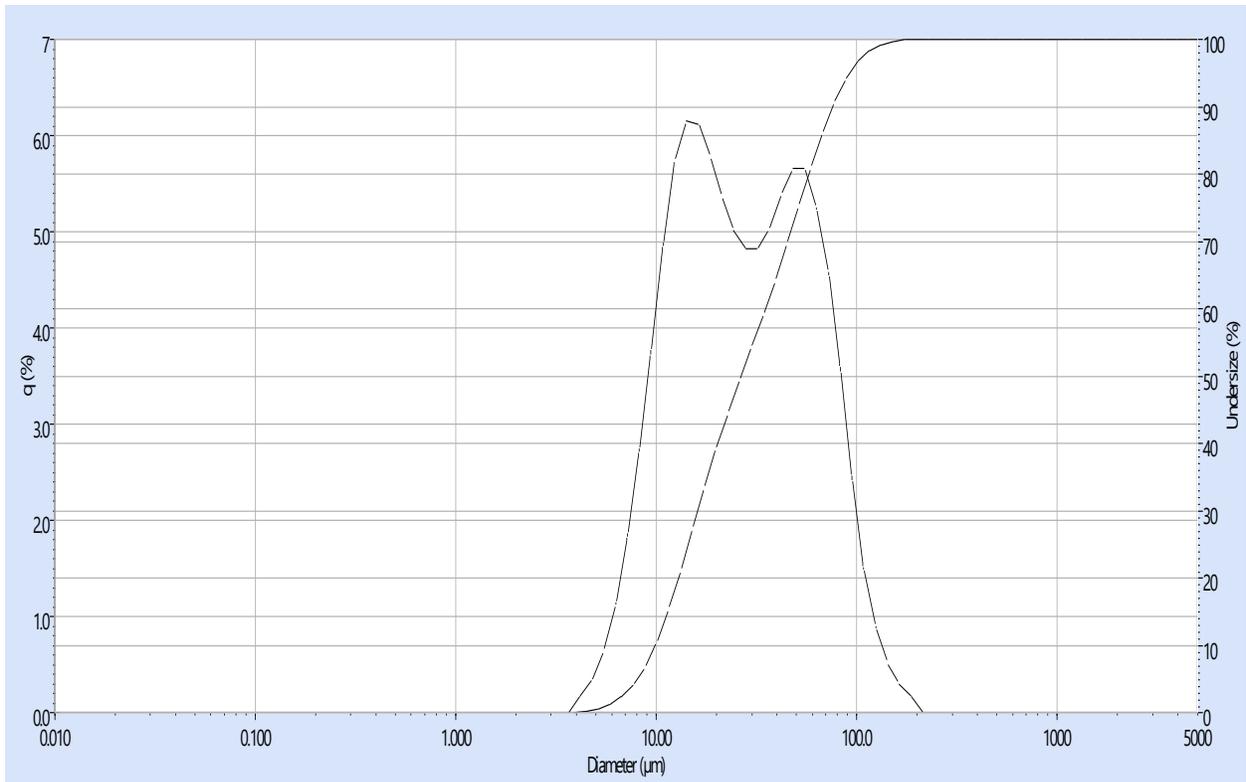


Figure 6.10 Particle size of TSD GA emulsion