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A BRIEF HISTORY OF THE APPLICATION OF ULTRASONICS IN FOOD PROCESSING

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ABSTRACT
Investigations into the potential value of ultrasound as an adjunct to food processing operations date back to the 1920"s. But it was only in the 1950"s that the first applications in industry appeared for equipment cleaning and homogenisation. Since then applications have appeared in cutting, package sealing, fouling prevention, foam control and facilitating mould release. In the patent literature, however, there are applications associated with most unit operations in food processing and for applications as diverse as removing toxins and allergens, pasteurising and freezing and thawing. Given the large number of patents using ultrasound in food processing it is perhaps surprising that there are not more applications in commercial use. This disparity is in part due to the limited availability of equipment suited to the industry, and problems associated with scaling up to commercial production rates. Another issue is the high standard of accomplishment required for food industry processes, for example 99.9% of change is not enough when food safety is at issue. Consumers are not very tolerant of error when it comes to the food they eat. The issues are reviewed and the applications in food processing where the use of ultrasound is likely to succeed are outlined.

THE MECHANISMS OF ULTRASOUND AS THEY APPLY TO FOOD PROCESSING APPLICATIONS

A brief chronology of the commercial use of ultrasound sees the advent of ultrasonic cleaning baths in the 1940s, limitations in the ability to generate even moderate ultrasonic intensities mean that the technology is confined to cleaning hard materials, and it is not effective on soft substrates such as found in food materials. In the 1950s and ultrasound is used for homogenisation and dispersion and emulsification using hydro-dynamic technologies [1]. The late 1960's and 70's saw the commercial adoption of ultrasonic cutting particularly in the confectionery industry, where it demonstrated particular advantages in cutting and forming sticky materials. In the 1990s ultrasound was applied to the sealing of packaging materials, and the welding of plastic items used in the food industry. The 21st century, we see the application of piezoelectrically generated ultrasound to this disintegration of food materials, homogenising and extraction. The first patents on the application of my ultrasound food-processing appeared in the 1920s. Since then 6-700 patents (Published in the Derwent patent index) have appeared on the application of ultrasound in food-processing or in food-processing related activities. The early patenting activity in ultrasonic food processes relates primarily, perhaps not surprisingly, to cleaning food materials, and to the modification of food surfaces, particularly in the, breaking down of tough surfaces that can occur during acceleration of drying roasting and frying operations.

While the technology has been adopted for applications such as cleaning equipment, for cutting and moulding sticky confectionery items and cheese, and then ancillary areas such as welding plastic packaging the uptake is comparatively small in relation to the number of patents. Processing operations, where ultrasound has been claimed to be beneficial include detoxification of aflatoxin[2], allergen and reduction[3], freezing[4][5], thawing[6-10], homogenising[11], encapsulation[12;13], developing structure in food materials[14-17], viscosity modification and reduction[11;15;18;19], spray drying[20], extraction and infusion[21][22-33], cleaning and sanitising food materials[34-40], cooking and peeling vegetables[41], humidification[42-44], fat refining[45], cleaning packaging[46], compounding ingredients such hydrocolloids, mixing and dispersing, rapid dissolving of ingredients like sugar,[14;47-52], prevention of blocking[53], catalysis regulation[54-56], low-temperature evaporation and dehydration[57], fouling prevention[58], ice removal[59], killing microbes[60;61] and deodourising and fatting fish[62]. So the question is why ultrasound found hasn't wider application in the food industry.

Historically, shortcomings in the capacity to generate ultrasound have been a limitation. However, this has largely been overcome with recent developments in electronic engineering. There is a disconnection between engineers who understand ultrasound technology and food engineers. Ultrasonic processes are often seen as a technologically difficult and unreliable and capable of producing unwanted free-radicals. Quoting from a recent discussion with a research and development manager from the food industry, "ultrasound is viewed as a technology that shows great promise, but does not deliver". In fact, many of the food industry research and development centres have played with ultrasonic systems using laboratory equipment and it is the background of playing that leads to this perception. Laboratory equipment often models a limited range of what is now possible with industrial ultrasonic equipment and scaling the economics of potential commercial processes from lab experiments is usually unduly pessimistic. As there can be significant energy gains in moving to larger scale processes. Food Science Australia, has had experience bridging this gap between the technology and the process. Some of the issues are outlined here.

Ultrasound in liquid systems.

It is likely that ultrasound and sonochemistry were present in the formation of the stuff of life. Sonochemistry in the aqueous medium of the oceans in particular would have led to chemistry that fixes nitrogen and carbon dioxide and from the atmosphere into the creation of the basic organic molecular building blocks that life is created from [63]. In the 20th century Sonochemistry was first discovered in 1927 [64], and in 1933 [65] it was found that ultrasound could form dextrins from starch and could coagulate egg whites. However, it was not until the 1980s that had developed as a serious area for research[66]. The first endeavours in the study of Sonochemistry revolved around basic chemistry, rather than the impact on the biological chemistry of biomaterials.

Food systems can be regarded as being heterogeneous in terms of understanding Sonochemistry. The implications of this are that lower levels of ultrasonic intensity can be used to drive sonochemical processes[67]. In food systems, we are often dealing with cavitation at the surfaces of colloidal particles, which act as cavitation sites. When cavitation occurs at surfaces and the cavitation bubble typically becomes asymmetric and collapses with a high velocity jet pointed to the surface. Whether the cavitation bubble becomes asymmetric depends on the hydrophobicity of the surface in question[68]. If the colloidal particles surface is hydrophilic the cavitation nucleates at the surface and the cavitation jet will modify the surface of the particle and catapult the particle off the bubble at very high speeds. Hydrophobic particles while not propelled by cavitation jets become entrained in high-speed micro streams, which also lead to potential high velocity collisions, between particles[69].

Sonochemistry in water provides both strong oxidants and reductants, which can be used to drive secondary reactions[70]. The generation of free radicals in aqueous systems is conditional on frequency, intensity and temperature. At 20 kHz few free radicals are formed, but the quantity increases as the frequency increases up to a maximum at approximately 400 kHz[71]. Higher than this frequency, the yield of free radicals declines. Below 400 kHz the radical generation is driven by the population of cavitation bubbles, above 400 kHz the bubble population is more stable, and the duration of bubble expansion is such that the amount of water vaporising into the bubbles is restricted. Where oxidation is not required or desired antioxidants such as ascorbate can be used to stabilise against secondary reactions, or the inclusion of small amounts of ethanol can be used to quench the production of free radicals by lowering the cavitation temperature.

The presence of large co-polymer molecules in food systems creates opportunity for structural modifications by physical forces induced by micro streaming resulting in polymer cleavage and recombination into new co-polymer structures. In the context of the emulsions shelled droplets are created from proteins and dextrins, leading to very stable emulsions [72].

Sonochemistry is capable of markedly increasing the catalytic activity of metals[70] and analogously it can also increase biocatalytic activity involving enzymes[73-76].

Ultrasonic processing should be well suited to large scale food processing. The systems are heterogeneous, and by implication, low intensities are required. The energy is conveyed through the liquid phase, which is often present in food processing operations and undesired sonochemical effects are controllable.

In liquid food systems and ultrasound can affect change via physical and chemical means. Physical effects result largely from intense nano and micro scale streaming induced by the ultrasonic vibrations and the oscillation and collapse of cavitation bubbles. Intense local sheer can modify non-covalent chemical associations in food structures by disrupting Van der Waal's forces, hydrophobic-hydrophilic interactions, rearranging electrostatic bonding and aqueous associations. It can break up or form aggregates of protein molecules, for example, and modify the way they perform in food products[77][78]. In other cases, particles can be driven together to coalesce by fusion or uniting within common water shells or be driven on to surfaces that can act as templates[79]. In the extreme polymer molecules can be pulled apart to generate free radical ends on the broken polymer[80]. These ends can undergo secondary chemical reactions to form a modified polymer structures. As well as chemical processes initiated by polymer breakage, sonochemistry based on reactions initiated by the sonochemical breakdown of water can occur. Volatile food components can also cross the surface boundary into cavitation bubbles, where they can be broken down by pyrolysis and surface active materials can deposit on cavitation bubbles surfaces, where they are first in line for modification by a free radicals generated within the bubble[81-84]

Ultrasound in solid food systems

Many food systems are made up from either living or dead, tissues or cells. The interaction of ultrasound with these materials is complex and varied[85]. At the lowest level of intensity, ultrasound simply increases the rate of metabolic processes in living cells and tissues, which can be used for example in speeding up the rate of fermentations. At slightly higher intensities ultrasound can induce hormetic or stress responses in the cells or tissue. In post-mortem meat tissues, in situ enzymes can be stimulated, for example to induce tenderising[86]. At somewhat higher intensities, ultrasound can be used to enhance mass transfer through inter cellular spaces or across cell walls for more efficient infusion or osmotic dehydration[87][88]. Increasing the intensity further can lead to the disruption of intracellular structures leading to cell death. In increasing intensity higher than this lead to the cell wall poration[89], which can be used to facilitate extraction processes, or for killing microorganisms[90]. Still further increases in intensity, lead to the disruption of cellular structure, the dispersion of cell wall materials, and the development of colloidal suspensions[91].

Ultrasound propagation through gases

In food processing operations such as dehydration, and breaking foams[92;93][94;95]. It is useful to apply airborne ultrasound. In this case, the increased mass transfer in dehydration or foam breaking is achieved by inducing high levels of turbulence in the air to solid or liquid interface. The engineering challenges in these applications are, overcoming the high impedance to ultrasound transmission between the generating surface and the air, the attenuation during passage through the air and thus getting efficient energy transfer and in containing the sound energy within the processing zone.

REQUIREMENTS OF FOOD PROCESSING OPERATIONS, AND HOW THESE MIGHT APPLY TO ULTRASOUND.

The following examples illustrate that it is not straightforward to take laboratory methods and expect them to work in commercial food-processing.

Microbial inactivation

Because ultrasound is widely used in laboratories for the lysis of microbial cells it raises the fairly obvious possibility that ultrasound could be used to achieve pasteurisation or sterilisation of food products. In food-processing often a high degree of certainty that the process has been accomplished, is required, for example in pasteurisation. A reduction in the number of viable cells by 99.99% is not an acceptable standard of pasteurisation. Pasteurisation is defined in terms of the amount of heat treatment, but typically, the destruction of viable cells is in the order of 10^6 to 10^8 log reduction. The standards for sterilisation are higher and destruction of microbial spores is also required. Processes that confer a degree of stability against microbial proliferation (eg. dehydration) must also be accomplished to required standards. However, in practice, such demanding levels of accomplishment are not easy to accomplish using ultrasound in continuous processes. It is necessary to ensure that the entire product receives the same ultrasonic treatment to have certainty that all of the microbial cells have been damaged to the point of being unviable. Attempts to scale up from the laboratory ultrasonic horns to flow through cell configurations, have not been very successful as in practice it is difficult to ensure that the entire product receives equal treatment with this technology. And although the ultrasonic treatment can be of high intensity using this technology the product is in the zone of high intensity for a very brief period of time. A better approach may be to pass the product through a larger volume of lower intensity for a longer exposure time, but ensuring evenly distributed cavitation field. The process objective is to ensure a high probability that a cavitation bubble will nucleate on the surface of every bacterial cell. Regardless of the technology used to apply the ultrasound. It has been found that the killing effectiveness is increased by the inclusion of heat in the process, at temperatures somewhat below those generally regarded as necessary for pasteurisation. The mechanism of heat in this case, probably involves softening microbial cell wall polymers and associated cell membranes to facilitate the sonoporation of the cell surface.

Extraction

Currently ultrasound is frequently used in the laboratory for extraction in analytical preparation. In commercial application, ultrasound has yet to become a commonly used technique for aiding extraction. At Food Science Australia, we have investigated ultrasound for extracting both water soluble and hydrophobic compounds from food materials. Hydrophilic components can be successfully extracted at relatively low ultrasonic energy intensities, if the particle size of the material being extracted is small enough, but the temptation to use higher intensities to extract larger pieces of material should be avoided as typically hydrophilic compounds such as flavinoids are readily denatured by the ultrasonic process. Particular value is seen, in using ultrasound to extract hydrophobic materials in an emulsified form as an alternative and friendlier technique to solvent extraction. Heated carrot mash for the example can be pumped around a radially emitting ultrasonic horn in a flow cell to achieve effective extraction of carotene, with a relatively low sacrifice in extraction efficiency compared to solvent systems.

While this is an interesting concept, it does not stand alone as a commercial process, but rather as one in a sequence of processes that achieve an end product. It is necessary to consider what this end product might be in order to achieve a correct application of the ultrasonic process. In the case of carotene, it is typically marketed as a carotene powder, which is used in the nutritional supplements industry as an ingredient in tablet formulations and in the food industry as an ingredient to enhance nutritional benefit, and also as a colorant. Creation of carotene in the powdered form typically involves some making an emulsion of carotene in an aqueous solution with an encapsulating ingredient such as maltodextrin, protein or glycoprotein material. This solution is then spray dried, or perhaps concentrated and then spray dried to create a powder. The encapsulant effectively protects the carotene from oxidation as well as maintaining it in a convenient powdered form. By using ultrasonic extraction, we already have the carotene in an emulsified form. So to convert the carotene to a powder it remains to add the encapsulating material, and then go through the concentrating on spray drying steps. It is possible; given the nature of carrots that there will be components extracted with the carotene, for example protein and perhaps pectin and sugars, which could be used to provide an encapsulating material. In this example of ultrasound is offering the benefits and of emulsification and extraction and should offer a superior product and a more energy efficient process through its relative simplicity compared to recovery by solvent extraction then emulsifying as a process. So it can be seen that the real benefit of using ultrasound, cannot be deduced by considering the ultrasonic processing step in isolation, but rather from considering the whole process and the product outcome to determine the real commercial benefit of using the ultrasound.

SOME SUCCESSFUL APPLICATIONS OF ULTRASOUND IN FOOD PROCESSING OPERATIONS.

An example where it has been possible to scale up ultrasound from a laboratory process using ultrasonic horn technology in food-processing involves using ultrasound to pulverise residual cell wall material in a previously heat treated vegetable puree or juices to achieve significant modification and the restoration of the textural and rheological properties of the puree[15]. In this instance, it is not essential that all of the residual cell wall material is completely pulverised in order to achieve the desired effects. The mechanism involves releasing the residual pectin bound up in the cell wall residue so that it can form a continuous matrix.

Another example where the ultrasound has successfully been used to as a pulverising technique is in the preparation of biomaterials for further processing by fermentation or enzyme digestion[96;97]. Here the ultrasonic disintegration of the plant cell matrix facilitates the release of substates or nutrients to the microorganisms and prepares the substrate for ready digestion by microbial enzymes. In industrial fermentations, gentle periodic application of ultrasound can be used to break out clumps and of microbial cells to increase the fermentation efficiency[98-102].

Emulsification using ultrasound, has not been widely adopted in the food industry due largely to the availability of relatively inexpensive mechanical homogenising equipment. However, where ultrasound has been used in the emulsifying food materials, droplet sizes of less than 1 µ have been accomplished[103;104], which is not so easy to do using mechanical equipment. Using ultrasonic equipment very stable emulsions are possible through the formation of covalently stabilised shells of surfactant surrounding the droplets, particularly when proteins are used as a surface active material[105-107].

An example of an ultrasonic processing approach, which could probably be used in the food industry, and is not in general use, is in the formation of stable fat crystal forms[108-111]. The reasons probably have little to do with the merits or otherwise of the ultrasonic process itself but rather the investment in pre-existing technologies and skill in using them; technologies which are also long-lived and require infrequent replacement.

In summary there are more opportunities for ultrasound to be used in commercial food processing than are currently being used, but a lack of appreciation by industry of the potential and the skills in industry to successfully use the technology are inhibiting the uptake of a potentially valuable technology.

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