Novel Food Processing Technologies

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Preface

Food Technology is an advanced and vast area of science and technology. It is an interdisciplinary field which encompasses different subjects like food microbiology, food chemistry, food engineering, human nutrition and so on. Though the art of processing and preserving food is well known since ages but the science behind these technologies is still not very clear. The basics of few of these technologies are well established; however, there is a need to overlook these technologies and the newer processing techniques which are developed in the recent past.

Despite the fact that enormous literature prevailing to food science and its basic technique is available world around, the comprehensive book containing knowledge about innovative and emerging technologies of food is rarely found and if available it is scattered in individual units and hard to locate. So, it is the high need of time to compile a book possessing all these recent technologies and their know-how.

Hence, we consider, it is of utmost importance to write the detailed and extensive book offering acquaintance to recent technologies emerged in food processing. We believe, it is a privilege to sum up the advances happening around the world in relation to food technology and its upgradation. The book is likely to cover the innovative technologies such as non-thermal technology, nanotechnology, non-invasive analysis of foods, newer methods of extraction, the recent know-how of food packaging, etc.

This book will be very useful to everyone working in the area of food to upgrade their knowledge regarding various aspects of the latest processing technologies. The compilation, in particular, is not absolutely based on any specific lecture course. However, it will definitely serve as one of the affluent manuscript in supporting too many course outlines related to advanced food technologies prevailing in many academic institutions. This book will generate the interest of many courses including Emerging Technologies in Food Processing, Novel Food Processing

Technologies, Advances in Food Technology, etc. Hence it will fulfill the high demand for food scientists and technologists in upcoming years and will gain popularity throughout the world.

This will be an asset to all the readers thriving to upgrade their knowledge and utilize it for the betterment of mankind. The readers will get acquainted with latest happenings and its details in all aspects of food, thereby will add new dimensions to the basic research strategies. Academicians, researchers and students will get ready references to enhance their proficiency for emerging techniques in processing of foods since it is the compilation of novel technologies with all the details required.

Editors

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1.1 Introduction and Background

In present scenario, the word "extrusion" refers to a process by which dry or semi-moist ingredients with varying in-barrel moisture are forced through varying barrel temperature, screw speed and screw configuration through a die opening of the desired cross section. In other words, extrusion is predominantly a thermo-mechanical processing operation that combines several unit operations, including mixing, coating, kneading, venting, shearing, heating, forming, partial drying or puffing, depending on the material and equipment used.

The origins of extrusion are in the metallurgical industry, where in 1797 Joseph Bramah patented the first extrusion process, wherein a piston driven device was used for making seamless lead pipes. The present understanding of extrusion technology and the developments or improvements in machine design are largely due to research carried out by the plastics industry. In food industry, this technology is in use since 1930 and its popularity is increasing continuously due to its efficiency, continuity and sustainability. In beginning, sausage extruders were developed in the nineteenth century as simple forming machines. One of the original developments which laid the foundation of the food extrusion was the use of pasta press termed as "cold extruder" in mid 1930s.

Furthermore, in the late 1930s, General Mills, Incorporation., Minneapolis, MN, USA, first used a single screw extruder in the manufacture of ready-to-eat (RTE) cereals. Later in 1970s, twin screw extruders were used for the manufacture of moist pet-foods. Twin screw extruders were also adapted from polymer industry, as rising food quality and limitations of single screw extruders were demanding a more versatile process for the newer and higher quality products. After 1970s, the extrusion processing with simultaneous use of heat was popularized as a versatile and highly energy efficient with negligible wastage process. In all these years, number of changes has been noted in the extruder design such as changes in screw design, barrel design and also material used for the manufacture of these materials. Barrel liners availability along with already available segmented screws could further add more economics to the process and increased equipment lifetime. For better wearing characteristics, a number of screw elements of different materials are being used in addition to standard nitrided steel for customized processing needs, such as corrosion and wear resistant surface coated steels, stainless steel, satellite welded and bimetallic HIP (Hot Isostatic Press). JBL Feedscrews Limited, a UK based company recently introduced tungsten carbide coated screw in conjunction with a compatible bimetallic barrel. Likewise, a number of options for barrel metallurgy are available to withstand the higher internal pressure and temperature. Barrels lined with hard cobalt based alloy, typically Xaloy, to give abrasion and chemical resistance are also in use, although, the most common material is carbon steel with a nitride interior. Similarly, steam heated or jacketed barrels were used earlier for cooking purpose which gradually replaced by the electric induction heating elements. These HTST cooking extruders are versatile, highly productive and energy efficient processing machines. They can use a wide variety of raw materials and formulations to produce products with increased shelf-life and convenience.

1.2 Basic Principle of Extrusion Process

Extrusion processing involves a combination of transport processes, including flow of materials within the virtually controlled environment system, thermal energy transfer to and within the material, and mass transfer to and within the material during extrusion. Food ingredients of various types may be processed by extrusion and are referred to as *extrudate.*The basic structure of the extrudate is formed by transforming and manipulating natural biopolymers (of starch, proteins or fibres) as they provide a fluid melt of polymers at high temperatures retain the gases released during the expansion process so as to form expanded foam structures. Puffing of the extrudate is due to the sudden evaporation of the pressurized steamat the die exit. There are generally two main energy inputs to the extrusion process, firstly the energy transferred from the rotation of the screws and secondly the energy transferred from the heaters through the barrel walls. The resulting thermal energy from both the sources causes an increase in the temperature of the material being extrude and subsequently there will be changes in the physical state, such as softening and/or melting of solid material to semisolid fluid.

1.3 Components of an Extruder

A modern cooker extruder has following major components

i) Holding bin & feeding assembly
ii) Pre-conditioner
iii) Extruder assembly: screw, barrel, die and cutter
iv) Driving system

Holding bin provides a buffer of raw material at the inlet so that extruder can operate continuously and without interruption. It should be of appropriate capacity so that extruder can be operating at varying feed rate without any obstruction. The feed rate of modern extruder is typically controlled by a variable speed auger or vibrating feeders to load material at a uniform rate into the barrel. Generally, volumetric and gravimetric feeders are used to feed extruders. A volumetric feeder provides a constant volume of dry ingredients, but cannot guarantee a constant mass flow rate due to changes in feed material density. On the other hand, gravimetric feeder's controls the feed flow rate based on the mass delivered and are, therefore more accurate than volumetric feeders. Addition of liquid feed ingredients can be achieved by using rotameters, fluid displacement meters, differential pressure meters, mass flow meters, velocity flow meters and positive displacement pumps.

Preconditioner constitutes upstream processing step, provides residence time and carries out a continuous mixing, hydration, heat transfer, initiate gelatinization or cooking as well as pasteurization of ingredients depending upon prevailing conditions, equipment design and process demands. Now-a-days, the majority of commercial extruders use preconditioners prior to feeding raw materials into an extruder for various purposes as compared to 30 years ago. Preconditioning results in a lower mechanical energy input requirement for the extruder, this can improve quality and will increase the capacity of and reduce wear on the extruder. Preconditioning may be defined as a prerequisite processing step of blending steam and water with dry ingredients to achieve temperature and moisture equilibrium, which in turn results in more uniform cooking of ingredients and development of "cooked grain" flavor.

The extruder assembly is basically composed of a closed barrel enclosing screw(s), die and cutter at the end of die. Screw is the central part of an extruder that rotates in a grooved cylindrical barrel, made from hard alloys or hardened stainless steel to withstand the frictional wear.For a better understanding of the design of extruders, we need some basic nomenclature terminology forthe extruder parts:

Barrel opening (D_b) – It is a barrel opening in which screw rotates.

Screw diameter (D_s) = Barrel opening (D_b) – screw clearance.

Screw clearance/Clearance – It is the clearance between the flight tips and barrel. It is usually 0.5 mm and will ensure efficient pumping of the material.

Screw clearance = $D_b - D_r$

Screw diameter (D_s)– It is distance between two flights across the screw shaft.

Channel depth/ Flight Height (H) – It is the distance from the top of the flight to the root.

Root diameter (D_r) – The diameter of the root of the screw on which the flights are built.

Root diameter (D_r) = D_b – 2 × *Flight Height (H)*

Shear – A working, mixing action that homogenizes and heats the material.

Pitch/Lead–It is the distance between consecutive flights.

Helix angle – It is the angle between the flight and a line perpendicular to the screw shaft. It usually varies between 12 and 15°.

Axial flight width – It is the width of a screw flight in the axial direction. Axial flight width of a screw is usually 10 % of screw diameter.

Axial channel width – It is the width measured from one side of the flight to the next within the channel perpendicular to the angle of the flight.

Channel – The helical opening that emerges from the feed to discharge end of the screw.

Channel length – It is the length of the screw channel in Z direction, which can be one or more full turn of the screw helix.

Compression ratio – The ratio of screw channel depth in feed zone to that of the metering zone developing the pressure needed to process the raw materials is known as compression ratio.

Barrel length to Diameter ratio (L/D) – It is the ratio of the screw diameter to the length of the barrel.

Barrel is the cylindrical housing that accommodates the rotating screw(s) tightly and should be strong enough to withstand pressure developed and resist wear. Barrels are composed of honed and nitride stainless steel in various L/D ratios. Generally, food extruders have L/D ratios ranging from 1:1 to 25:1. In order to accomplish positive transport, moistened material must slip on the rotating screw and this is enhanced if the barrel wall is grooved. In general, extruder barrel is segmented into 4 heating zones and these segments are jacketed to allow temperature control of individual zones. Heating is typically accomplished with overheated steam, hot oil or band heaters, whereas cooling is achieved with water. Heaters are usually located along the barrel with a thermocouple in each zone to control the heaters and barrel temperature. The most common type of thermocouple used on extruder is the K-thermocouple.

The extruder barrel is capped with a die that contains one or more openings through which the melt flow. These openings shape the final product and provide a resistance against which the screw must pump the extrudate. It plays an important role in deciding product physical properties such as density, expansion, surface texture and final shape of the extrudate. Highly restrictive dies increase barrel fill, retention time and energy input. Final product length is established by using a cutting device mounted to run against the die face. The speed of the cutter and the clearance between the cutter and die is adjusted to the throughput to produce the desired length and shaped product. Driving system/section is to provide power to rotate the extruder screw. It is basically a section where electrical or hydraulic power is converted into rotating power, which drives the extruder shaft(s). The power delivered to the screw shaft is equal to:

Power = Screw speed × Shaft torque

The screw rotation can be clockwise or counterclockwise and is determined by the extruder manufacturer.

1.4 Extrusion Equipment's

Extruders come in a wide variety of shapes, sizes and methods of operation, but can be categorised into one of three main types: piston, roller and screw extruders.

1.4.1 Piston extruders

Piston extruder is the simplest one of these, which consists of a single piston or a battery of pistons within a hollow cylinder that force the material through a capped nozzle or die into a wide conveyor. Piston extruders are designed for precise delivery of viscous, shear sensitive materials and are often used in the confectionery industry to deposit the centre fillings of chocolates, doughnuts, cupcakes centre-filled chewing gums etc.

1.4.2 Roller extruders

Roller extruders consist of two counter-rotating, independently driven drums with narrow space in-between. The gap between the rolls is precisely controlled by hydraulic or advanced closed loop control system and maintained throughout all load conditions. For superior performance, abrasion resistance and long life of rolls, hardened steel layer is used, which can be replaced in the event of damage or wore-out. With the rise of advancements in metallurgy engineering and growing competition, manufacturers provide a variety of options in range and specification for customized needs such as optional programmable logic controller (PLC), low or high throughput designs, varying roll speeds range, grooved or polished rolls, differential roll speeds, sensors to prevent touching of rolls, oscillatory roll scrappers and vibratory discharge end. A variety of product characteristics and shapes can be obtained by altering the rotation speeds and/or gap between the rollers and by changing the roller surface type. This process is used primarily with sticky materials that do not require high-pressure forming. Different types of products such as shaped crackers and hard cookies can be formed by using the desired shape within the rollers and conveying the dough in between the rollers. The dough is forced into the pattern on the roller and the shaped mass is then conveyed to an oven for baking. Excess dough can be collected and integrated to the separate compartment of the in feed hopper for metered use. Roller extruders could also be used for the production of flakes by raising and controlling the roll surface temperature with water cooling system.

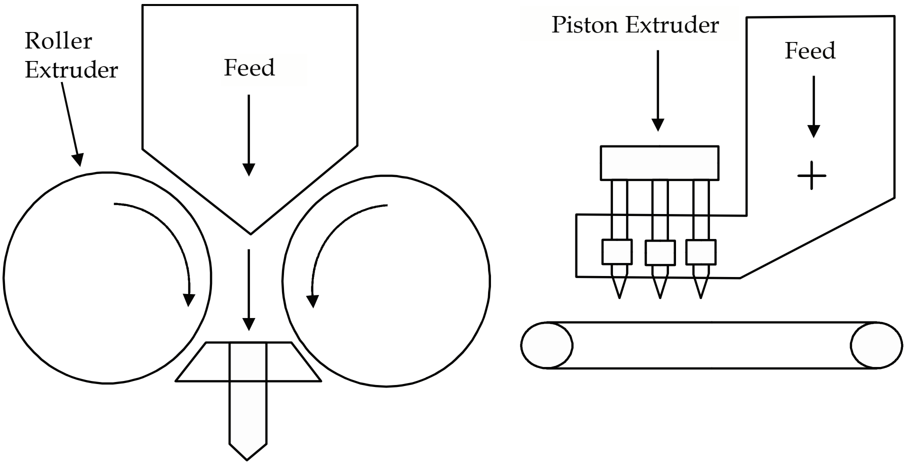

Fig. 1.1 Roller extruder and Piston extruder representation (Dziezak JD, 1989)

1.4.3 Single-screw extruders

The most complex of the three categories of extruder are screw extruders employing single, twin, or multiple-screws rotating in a stationary barrel to convey material forward through a product specific die.

Single-screw extruder means that there is only one screw inside the barrel, and this barrel has grooves over the entire length in order to obtain an improved shear ratio as well as optimum material flow. This hardened stainless steel grooved barrel helps to minimize slip of material inside. The length to diameter ratio (L/D) of the barrel varies between 2:1 and 25:1, depending upon design and company portfolio, such as C.W. Brabender, a German company, provides L/D ratios of 10:1, 15:1, 20:1, 25:1, and 30:1. The single screw extruder consists of three distinct sections in the barrel, i.e., the feed section, the transition section and the metering section. The feed section compresses the feed material and works into dough to the transition section. The feed section has deep flighted screws which aids in conveying the material forward. The transition zone further works the material into dough that is partially cooked and subjected to high pressure. The metering zone function is to receive the compressed feed material, homogenize it and force it through the die at a constant pressure. The small depth of the screw channel and die orifice contributed to the more pressure in this zone as compared to feeding zone. During transport through the extruder, mechanical energy from the rotation of the screw is converted to heat, raising the temperature of the mixture to over 150°C. The resulting plasticised mixture is then forced through the die and the sudden reduction in pressure at the die causes moisture to flash off rapidly as steam results in puffing of the product.

Single-screw extruders have relatively poor mixing ability, therefore, they are often used with materials that have been either premixed or preconditioned.

The single-screw extruder relies heavily upon drag flow to convey the feed material through the spiral or straight ribbed barrel liner of the extruder so as to develop required pressure at the die for puffing. The feed material should not rotate with the rotating screw in order to advance through the barrel. The frictional force between the material and the barrel wall is the only force that can keep the material from turning with the screw and hence most single screw extruders are supplied with grooved barrels for improved adhesion, shearing and net positive transport of material. The rotation of the screw itself in the barrel gives rise to a second flow, called the cross-channel flow, which does not contribute to the net positive movement of material along the barrel but instead re-circulates it within the screw flights and hence is responsible for some of the mixing action of the extruder. Advancement of the material towards die generates another kind of flow, pressure flow, causes backward movement of the material due to higher pressure at the die. The net flow of material should be positive so as to push the material out of the die. Single screw extruders are comparatively cheaper in initial investment and operating cost as compared to twin screw extruders but heavy reliance on drag flow for positive net flow could be a limiting factor in situations where one has to process high fat formulations.

1.4.3.1 Cold forming (Pasta-type) extruders

Among the single-screw extruders, the pasta extruder is one which is generally used for forming various types or shapes of pasta or pasta like products from high moisture dough (>22% wb). It basically involves kneading of the dough to deliver uniform, kneaded and mixed dough at die without the addition of external thermal energy. Cold forming extruders have smooth barrel with no thermal energy, deep flight screw with shear rate of about 4-5 per s, screw diameter to flight height (D/H) of 3-4, and low screw speed (30-60 rpm).Cold extrusion is used to mix, knead, disperse, texturize, dissolve and form a food product or product ingredient for further processing like drying, cooling etc. Typical food products include pastry dough, individual pieces of candy or confections, pasta pieces, hot dogs, and selected pet foods.

1.4.3.2 High-pressure forming extruders

High-pressure forming extruders are low-shear machines with grooved barrels and compressing screws, typically used to compress, mold and extrude pre-gelatinized cereal and other doughs through shaped dies to make pellets for subsequent drying and puffing or frying. This type of extruder has screw diameter to flight height (D/H) of 4.5, shear rate of 10/sec and product moisture of 25%. They are used for the preparation of ready to eat cereals, pellets and second generation snacks.

1.4.3.3 High-Shear cooking extruders

High shear extrusion systems operate at higher screw speeds (>300 rpm), barrel temperature (110 – 180°C), barrel pressure (4000-17000kPa) with shallow flights and grooved barrel surfaces. It usually involves longer barrel to increase residence time and excess heat is removed by cooling. It has screw diameter to flight height (D/H) of 7, barrel length to diameter ratio (L/D) of 2-15 and shear rate in screw of 165/sec. The final product is usually less expanded and requires a final drying step. Used for preparing breakfast cereals, expanded snacks, texturized vegetable protein (TVP) and dried pet foods. Extrudates prepared by using this type of extruder have lower product density (32-160kg/m^3), product moisture (5-8%) whereas higher product temperature (149 °C), barrel temperature (110-180 °C) and barrel pressure (4000-17000 kPa).

1.4.3.4 Low-Shear cooking extruders

It is a continuous type cooker used for high moisture dough's. Generally, low shear extruders will include smooth barrel surfaces, deep flights, low pressure relatively large flow channels, and low screw speeds (>100 rpm). The cooked product can be further processed by drying to achieve desired moisture content in the final product. This type of extruder has screw diameter to flight height (D/H) of 7-15, barrel length to diameter ratio (L/D) of 5-22, shear rate in screw of 20 – 100/sec. Soft-moist foods, starch, soup bases and meat like snacks such as simulated jerky are prepared by using low shear type extruders. Products prepared by using low shear extruders have higher density (320-800kg/m^3), product moisture (25-75%) whereas lower product temperature (<52 °C), barrel temperature (20-65°C) and barrel pressure (550-6000kPa).

1.4.3.5 Collet extruders

Collet extruder is a high shear (140 per s), short barrelled machine and screw with multiple shallow flights that have been used for making puffed snacks. As collet extruders have no external source of thermal energy, the energy for the cooking of the moistened mass comes from the dissipation of mechanical energy. Generally, low moisture (11-16% wb) feed formulation underwent high shear in-barrel conditions due to high screw speed (300 rpm), where temperature raised rapidly, and the starch gets gelatinized and eventually dextrinized.This molten mass loses moisture rapidly at die exit and eventually puffs to form a crisp, expanded curl or collet. This small, irregular finger like product, collet is different from kibble, which is almost reserved for pet food industry especially dog and cat food. This type of machine initially was characterized by an extremely short screw (L/D ratio = 3), but machines with longer L/D ratio of up to 10 that rely heavily on friction-induced heat to produce collets have been developed. This type of extruder has screw diameter to flight height (D/H) of 9, shear rate of 140/sec and end-product moisture of 3-5%.

1.4.4 Twin-screw extruders

Twin-screw extruder means that there are two screws inside the closed barrel. In 1970s, twin-screw extruders were introduced to the food industry as the requirements were increasing for the new, finely structured, higher quality products for which single-screw extruders are no longer satisfactory. From origin, most of the improvements that have evolved in the development of extruders have been incorporated into the modem twin-screw extruders. Clamshell top opening barrel assembly with replaceable barrel liners and slab heaters enclosing durable high torque screws mounted on spline shaft with patented "through-shaft cooling" and user friendly screw ejection unit by a single touch on screen are just a glimpse of technology advancements. Moreover, twin-screw extruders have found a wide application in the chemical and paper industry due to their better process control and versatility, their flexible design permitting easy cleaning and rapid product changeover and their ability to handle a wide variety of formulations.

Twin-screw extruders can be classified on the basis of direction of screw rotation in two categories as counter rotating twin-screw extruders and co-rotating twin-screw extruders.

The screw either rotates in opposite directions (counter rotating) or in the same direction (co rotating). These categories can be further subdivided on the basis of position of the screws in relation to one another as intermesh-ing and non-intermeshing.

1. Co-rotating intermeshing,
2. Co-rotating non-intermeshing,
3. Counter-rotating intermeshing, and
4. Counter-rotating non-intermeshing.

Co-rotating, intermeshing and self-cleaning twin screw extruders are the most commonly utilize in the food industry amid all of the extruders designs available. In intermeshing screw extruder, the flight of one screw engages or penetrates the channels of the other screw resulting in positive pumping action, efficient mixing, and self-cleaning. Intermeshing co-rotating extruders are particularly suited to applications where a high degree of mechanical heat transfer is required but not forced conveyance and thus are widely used for the production of expanded products. The mechanism of flow in twin screw extruders is a combination of both drag and positive displacement. A variety of available screw elements and kneading blocks enhance capacity and mixing ability depending upon the choice and compression of screw elements, thickness and staggering angle of kneading disks. The co-rotating non-intermeshing extruders are used mostly in low viscosity non-cooked products. On the other hand, fully intermeshing counter-rotating are particularly suited to the rubber or plastic industry due to their ability to generate a great deal of pressure with high venting capacity at vent ports. Examples of products suited to this type of extruder include chewing gum, jelly and liquorice confections. By contrast, non-intermeshing screw extruders are outlined as two single-screw extruders sitting side by side with only a small portion of the barrel in common.

The addition of forward- or reverse-conveying discs into the screw configuration alters the pressure profile and barrel fill. These forward-conveying discs push the material forward and reduces barrel fill whereas reverse-conveying discs throw-back material and increases barrel fill. Restrictions are placed for high pressure processes in the screw configuration, where they are tended to wear quickly and replace frequently.

Twin-screw extruders have the following advantages:

- The throughput is independent of feed rate whereas in single screw extruders barrel must be full of material to operate effectively.
- The variety and thickness of kneading blocks such as monolobe, bilobe with varying staggering angle helps in efficient mixing (distributive or dispersive) and kneading of dough.
- Fluctuations in production rate can be accommodated by the positive displacement action of the screws.
- Twin-screw can comparatively handle higher oily (20-25%), sticky or sugary (40%) and moisty materials (45-50%) that undergo slippage in single screw. Thus providing greater flexibility in operation for ingredient use and product formulation.

- Forward or reverse conveying elements with varying pitch could be used to control the pressure and barrel fill inside extruder. Liquorice and fruit gums could be processed by combined action of forward and reverse conveying for generating pressure and venting moisture respectively.
- A short discharge section develops the pressure required for extrusion and thus subjects a smaller part of the machine to wear than in single-screw extruders.
- A mixture of particle sizes, from fine powders to grains, may be used, whereas a single screw is limited to a specific range of granular article sizes.

1.5 Raw Materials for Extrusion Processing

A wide range of raw materials from various sources are used for extrusion cooking. Guy 2001 classified the ingredients by their functional roles as:

i) Structure forming materials
ii) Dispersed phase fillers
iii) Ingredients that act as plasticizers and lubricants
iv) Nucleating agents
v) Colouring materials
vi) Flavouring substances
vii) Others

Structure forming materials constitute the largest group of ingredients among other raw materials used, contain structure forming high starch materials such as maize starch, whole or de-germed flour. Milled cereals, pseudo cereals and tubers such as maize, wheat, rice, sorghum, buckwheat, potato flour are used in the form of flour, meal and decorticated coarse grits for the preparation of extruded food products. All these ingredients are rich in starches and as starches are composed of amylose and amylopectin the proportion of amylose and amylopectin plays an important role in final product texture. Most of the cereal starches have proportion of amylose in the range of 15 – 35%.

Dispersed phase fillers constitute the second largest group of ingredients, contains plant and animal proteins, legume and pulse proteins, meat and marine proteins and plant fiber or bran. Generally, proteins act as filler in continuous matrix but sometime they might have a continuous structure forming role, as in textured vegetable protein. Plasticizers and lubricants, such as water, oils and emulsifiers, lowers the mechanical energy by either reducing the melting point, melt viscosity, hardness and shear. The shearing of natural polymers such as starch, insoluble fibers and/or proteins causes a large dissipation of mechanical energy due to frictional effects. Water, which acts as a plasticizer for the polymers reduces their interactions and causes an exponential decline in energy input. Oil and fats have two functions in extrusion processes. They provide a powerful lubrication effect in the compressed polymer mix and also they modify the eating qualities of the extruded products. Oils and fats produce large effects on the processing of starch even at low levels of 1-2%. Emulsifiers are special forms of lipids which tend to have higher melting points than triglycerides but behave as oils to provide lubrication in extrusion processes. Nucleating agents enhance the number of bubbles in the extrudates and produce finer textures. The ideal types of nucleant are finely powdered food grade materials which remain insoluble during processing and provide surfaces at which bubbles may form. Materials which can help to form bubbles in the fluid melts include the normal types of baking powder made up of sparingly soluble salts of phosphoric acid and calcium (Calcium carbonate) or sodium salts (sodium bicarbonate). Other particulate materials as chalk talc (Magnesium silicate) magnesium carbonates, silicon dioxide and cereal bran's also increase the number of cells and improve the texture of extrudates. Colouring substances, present naturally in raw materials such as corn, tomato and grape pomace, jamun (*Syzygium cumini*) or produce after reaction colors such as reducing sugars and proteins react to produce toasted brown color by Maillard reaction. Flavouring substances, such as salt, sugars, spices, natural and artificial flavours, are usually added either during extrusion or in secondary operations such as post-extrusion treatment. However, post-extrusion flavouring has many disadvantages like uniform application, possibility of contamination, stickiness to consumer's hands and additional cost etc. Others usually include preservatives, antioxidants, vitamins and minerals etc. Dicalcium phosphate is used as source of calcium, tricalcium phosphate is used as anticaking agent whereas trisodium phosphate is used as an antimicrobial agent.

1.6 Extrusion Processing and Nutritional Aspects

Health and nutrition is the most demanding and challenging field in this era and would continue to be in the future as well. Deterioration of nutritional quality, owing to high temperature, is a challenging problem in most traditional cooking methods. Extrusion cooking is preferable to other food-processing techniques in terms of continuous process with high productivity and significant nutrient retention, owing to the high temperature and short time required. The possible effects of extrusion processing on different food ingredients and interactions between them are continually to be an area of interest for researchers. The utilization of extrusion for the development of nutritionally balanced or enriched foods, like weaning foods, dietetic foods makes it necessary to study the nutritional aspects of extruded products.

1.6.1 Carbohydrates

Organically, carbohydrates are the most abundant components of all cereals, pseudo cereals, fruits, vegetables and legumes, consisting of simple sugars to complex molecules like starches and fibres. Milled cereal flours, meals and other starchy materials are widely used as base raw material for the production of extrusion and bakery based products. The physical characteristics such as expansion, hardness, degree of cooking etc., of the melt are predominantly affected by the amount, type and nature of starch present, which usually represents between 50% and 80% of the dry solids in the mixture.

Starch is a unique polysaccharide, occurs naturally as discrete particles called granules, and provides 70-80% of the calories consumed by humans worldwide. Starch granules are composed of an organized mixture of two types of polymers, amylose (linear) and amylopectin (branched). Generally, most native starches contain 20-30% amylose molecules whereas some starches (waxy cornstarch) contain only amylopectin molecules. Corn, rice, wheat and potato are four major sources of starch in the human diet, serving as the major structure forming material for the extruded products. In developing countries, starchy cereals constitute the major portion of meals and daily calories. Generally, starch is a main constituent in extruded foods such as breakfast cereals, snacks, puffs, cereal or lentil analogues, weaning foods etc. Extrusion processing helps to gelatinize starches thus making it more readily digestible to humans and other mono-gastric species. Extrusion cooking uses less water comparatively for gelatinization of these starches and eventually water escapes as steam thus minimized leaching of water soluble nutrients. Increased temperature, screw speed and pressure during extrusion increase the rate of gelatinization, but lipids, sucrose, dietary fibre and salts can retard gelatinization. Gelatinization can be comprehended by a number of methods including thermal methods like Differential Scanning Calorimeter (DSC) and susceptibility to amylases like Visco-amylograph and Rapid Visco Analyser (RVA).

During extrusion cooking, starch molecules found to be broken down into smaller components, such as mono- or di-saccharides, which are more digestible, and due to the branched structure (susceptible to shear) of amylopectin greater molecular weight reductions occurred in larger amylopectin molecules. Extrusion cooking may be used to produce short-chain carbohydrates such as dextrin and/or free glucose for subsequent fermentation or other conversion processes. Lower starch digestibility and reduced glycemic index was reported for high amylose rice based noodles. Starches from the extruded samples dissolved at a significantly faster rate than from native starches and it was an indicative of increase in the amount of linear polysaccharide. Extrusion processing also founds to help in the formation of amylose –lipid complexes. The extent of amylose –lipid complex formation is dependent upon both carbohydrate and lipid type present in the food. Monoglycerides and free fatty acids are more likely to form complexes than are triglycerides, when added to high-amylose starch.

Sugars, such as fructose, sucrose and lactose, are a great source of quick energy. Fine ground sucrose is commonly added to extruded products, particularly in breakfast cereals for toasted colour and flavour etc. The amount of sugar added to a product varies but is typically within the range 6–25 wt% on a final dry product basis. It contributes into binding of other ingredients, flavour development and browning characteristics and is important in controlling texture and mouth feel. Amount of sugars during extrusion is critical for process parameters as well as nutritional and sensory qualities of the products. Incorporation of sugars progressively reduces the expansion whereas increases the bulk density, mechanical strength, crushing force and number of cells per unit area at a high moisture conditions i.e., above 16%.All these changes observed in extrudates have been attributed due to competition of sugars for moisture, inhibition of gelatinization and plasticization of starch-based melts. This effect was noted at sucrose concentrations of as low as 2% when extruding with feed moisture content of 20%. Several investigations have also reported sugar losses during extrusion cooking. High temperature and low moisture cooking conditions (170-210 °C and 13% moisture, respectively) favoured 2–20% of the sucrose loss in the preparation of protein-enriched biscuits. Conversion of sucrose into hexose (glucose) and pentose (fructose) at high temperature with limited moisture conditions and subsequent reaction of these reducing sugars with proteins (Maillard reaction) could be reason for the loss of sucrose. While sucrose loss may affect product colour and flavour development, there is still an opportunity to reduce the content of indigestible oligosaccharides that can cause flatulence. Nutritional quality of extruded legume products can be improved by the destruction of these flatulence-causing oligosaccharides.

The American Association of Cereal Chemists (2001) coined the following description of dietary fibre: ''Dietary fibre (DF) is the edible parts of plants or analogous carbohydrates that are resistant to digestion and absorption in the human small intestine with complete or partial fermentation in the large intestine''. Dietary fibre includes polysaccharides, oligosaccharides, lignin, and associated plant substances. Extrusion reduced the molecular weight of pectin and hemicellulose molecules, resulting in increased water solubility of sugar beet pulp fibre. Many factors influence fibre solubility like acid and alkaline treatment prior to extrusion, such as an increased soluble fibre content in corn bran. Extrusion cooking increased the total dietary fibre of barley flours. The total dietary fibre increase in waxy barley was the result of an increase in soluble dietary fibre. The change in dietary fibre profile during extrusion of barley flour may be attributed, primarily, to a shift from insoluble dietary fibre (IDF) to soluble dietary fibre (SDF), and the formation of indigestible resistant starch and enzyme-resistant indigestible glucans formed by trans-glycosidation.

In summary, extrusion cooking improves starch digestibility and at mild or moderate conditions, extrusion cooking does not significantly change dietary fibre content but it solubilises some fibre components. On contrary, more severe conditions favours the increases in soluble dietary fibre and enzyme-resistant starch fractions.

1.6.2 Proteins

Proteins are large biomolecules consist of covalently linked long chains amino acid residues, which contribute significantly to the functional behaviour and quality of all foods. In the jargon of the food professionals, increasing demand for protein supply by world population and challenges involved with the development of more sustainable novel plant protein products [Novel Protein Foods (NPFs)] will be a crucial topic for discussion in near future. In baking and extrusion, added proteinaceous materials are hydrated to form soft, viscoelastic dough which affects the behaviour of functional properties in food systems. The shearing forces generated in the extruder cause breakage of the large molecular weight proteins into small particles of low molecular weight. Addition of protein reduces the cell size and extensibility of starch polymer and thereby degree of expansion. At higher levels of protein, severely torn regions in the cell walls of the extrudate are noted, indicating a loss of elasticity in the extrusion melt. Increasing screw speed or shear rate led to an increase in viscosity due to unfolding of the protein, involving rupture of covalent bonds or interaction with the starch granules. Increasing feed moisture from 28 to 60% reduces that degree of aggregation and increases the disulphide-H bond, disulphide-hydrophobic interactions significantly in soy protein isolates. The structure of extrudates was found collectively hold by hydrophobic interactions, hydrogen bonds, disulphide bonds and their interactions. The significance of non-covalent bonds outweighs the covalent bonds.

Protein quality is dependent on the quantity, digestibility and availability of essential amino acids. Protein dispersibility Index (PDI) and Nitrogen Solubility Index (NSI) are measures of protein solubility in water after processing. Generally, extrusion processing has higher protein digestibility than non-extruded products. The possible reasons might be exposing enzyme-acting sites, denaturation of proteins and inactivation of anti nutritional factors that impair digestion. Feed ratio was found to have maximum effect on protein digestibility, followed by barrel temperature in the fish–wheat flour blend extrudates. An increase of 2-4% in the digestibility was observed with an increase in the protein proportion. Increase in barrel temperature (100-140 °C) enhances the degree of inactivation of protease inhibitors in wheat flour, and thus, improved the protein digestibility. High temperature conditions encountered during extrusion cooking does not have any adverse effect on protein digestibility, which could be marked to the lesser residence time of melt within the barrel. The effect of other independent process variables, such as length to diameter ratio and screw speed on protein digestibility values appears to be insignificant. Increased screw speed may have increased the protein digestibility of extruded corn-gluten meal, because increasing shear rate in the barrel denatures the proteins more easily, and thus facilitating enzyme hydrolysis. Another advantage of extrusion cooking is the destruction of protein digestibility inhibiting antinutritional factors, such as trypsin inhibitors, haemagglutinins, tannins and phytates. The destruction of trypsin inhibitors increases with extrusion temperature and moisture content. At constant temperature, inactivation increases with increasing product residence time and moisture content. Lectin, a haemagglutinant present in soybeans is relatively heat resistant in almost all traditional methods of cooking. However, extrusion processing has been shown to be very effective in reducing or eliminating lectin activity in legume flour as compared with traditional aqueous heat treatments. Extrusion reduced 88-91% of trypsin inhibitor activity in breadfruit-corn-soy blends. The enzymatic breakdown of proteins improved after extrusion cooking as a result of the inactivation of trypsin inhibitor activity in extruded snacks. During extrusion cooking, pepsin hydrolysis of proteins got enhanced due to the denaturation effect, thus improving the nutritive value by making them more susceptible to pepsin. Another important concern in protein nutrition is the focus on the lysine retention during extrusion process. Lysine is the most limiting essential amino acid in cereals and cereal-based products, extrusion process always modelled in such a way to protect it as possible from destruction. Independent variable such as an increase in screw speed (80-140 rpm) and a reduction of die diameter (10-6mm) enhances lysine retention. Short residence time limits the extent of heat damage to lysine retention. In the extrusion of wheat flour (150°C mass temperature, 5-mm diameter, 150 rpm screw speed) an increase in feed rate (from 200 to 350 g/min) significantly improved lysine retention.

In context of protein rich novel plant protein foods (NPFs), it is important to investigate the structure-function relation for high water holding capacity and better texture. In comparison to animal proteins, water holding capacity of plant proteins was found to be lower (or more hydrophobic), which further initiates the need to understand the big challenge for plant based meat textured foods to achieve the juiciness of meat products without compromising the kinaesthetic and organoleptic qualities.

1.6.3 Fats or Lipids

Christie WW defines lipids as ''a wide variety of natural products including fatty acids and their derivatives, steroids, carotenoids, terpenes and bile acids, which have in common a ready solubility in organic solvents such as diethyl ether, chloroform, hexane, benzene or methanol.'' Among many types of lipids occur in foods, the triglycerides or triacylglycerols are the most common. As name suggests, triglyceride consists of three fatty acid molecules esterified to one glycerol molecule. Although lipids serve as a concentrated form of energy, excess dietary lipid consumption is associated with chronic illnesses, such as heart disease, cancer and obesity.

Fats and oils have basically three functions in formulated recipe for extrusion cooking. Firstly, fats are good source of essential fatty acids, secondly, they are good carrier of fat soluble vitamins, and thirdly, they modify the eating qualities of the final extruded product. In addition to, fats also help with processing in extrusion, they act as lubricant in the extrusion melt. The shearing action of the screw causes the oils to be either dispersed into small droplets or smeared on the polymers. Heating and mixing of starch suspensions in reactive barrel results in the formation of amylose-lipid complexes followed by their disassociation and restructuring once the suspension cooled down. The potential to form starch-lipid complex depends on the amylose level of starch and it was found that among starches potato starch was least able to form complexes. In extrusion processing of cornmeal, two third of free lipids were found bounded as they were not able to extract by hexane. Monoacylglycerols (MAGs) with only one fatty acid attached and diacylglycerols with two fatty acid attached have 2 and 1 free positions, respectively to interact with starches by H-bonding as well as hydrophobic bonding. On contrary, triacylglycerols (TAGs) have no free position to interact by H-bonding, so therefore, TAGs will interact predominantly by hydrophobic bonding and Van der Waals forces. Generally, cereal based extruded products are low in fat content. Cereals such as wheat and corn are typically low in (2%) oils, although oats may contain up to 10% oil. The oil is concentrated in the bran and germ portions of the seed kernel, which are effectively removed during milling to improve storage stability. Single screw extruders can process lipid levels of 12–17%, while twin screw extruders with variable screw configurations can handle feed lipid contents as high as 25%. Generally, extrusion cooking of high-fat materials is not advisable, especially in the case of expanded products, as lipid levels over 5 – 6% impair extruder performance with generating lower shear and mechanical energy. Torque is decreased because the high lipid level reduces friction and thus drags flow within the barrel, resulting in poorer cooking and product expansion. Thus, a highly expanded oat cereal product is difficult to achieve due to its high fat content. The effects of the process conditions on the physical and sensory properties of an extruded oat-corn puff showed that increasing the level of oat flour (and hence fat content) caused an increase in the extrudate bulk density and a reduction in specific length and expansion. At the same time, a small level of lipids like less than 5% facilitates steady extrusion and improves the texture. After extrusion cooking of maize, a decrease in extractable fat has been found with an average of 40% of the original recovered by using different solvents. Lipids might have lost at the die as free oil, when processing high-fat materials, such as whole soy. Another explanation for the lower extractable lipid level is the formation of complexes with amylose or proteins. In an experiment with corn zein and corn oil, interaction of lipid with carbohydrates and proteins was evaluated by the amount of lipid available to extraction by hexane. After extrusion processing, extractable lipids decreased by 66 – 88.5% and this magnitude of decrease was mainly affected by moisture content and interaction of moisture content with barrel temperature conditions. Maximal lipid-macromolecule interaction was observed under low-moisture and high temperature conditions while lipids appear to be entrapped within the carbohydrate-protein network. When extruded foods are digested with acid or amylase and then extracted with solvent, lipid recovery is higher. Only 50% of the extractable lipids in extruded whole wheat were recovered, but total fat was not significantly changed owing to extrusion. The extent of free fatty acids in extruded snacks increases gradually with storage and affect the quality of foods. Free fatty acids are produced in foods from hydrolysis of triglycerides, mainly because of lipase enzymes and high temperatures. Extrusion cooking can prevent free fatty acid release by denaturing hydrolytic enzymes. Oxidation of lipids probably does not take place during extrusion cooking as there is less residence time. However, rancidity is a concern for extruded products during storage. Screw wear is a concern as metals can act as pro-oxidants. Iron content and peroxide values were higher in extruded rice and dhal compared with similar products processed by drying techniques. The presence of antioxidants such as, butylated hydoxyanisole (BHA) and butylated hydroxytoluene (BHT) improves the storage quality of lipids in extrudates. Extrusion cooking was found to enhance the antioxidant activity in tomato pomace blended extruded products and an increasing trend was also reported with an increase in barrel temperature. Oxygen radical absorbing capacity (ORAC) value increases (16 – 30%) with an increase in barrel temperature. The increase in ORAC values might be due to the products formed during Maillard reaction. Maillard reaction products obtained from heated histidine and glucose have peroxyl radical scavenging activity and it relates strongly with ORAC assay.A few published studies and limited research information on other nutritional aspects of lipids such as retention or destruction of health promoting polyunsaturated fatty acids (PUFA) in extrusion processing necessitates more research and work in this area. In extrusion cooking of chum salmon muscle with 10% wheat flour, both docosahexaenoic (DHA) and eicosapentaenoic (EPA) acids were found to be retained and not destructed. Extrusion cooking does not promote significant *cis-trans* isomerisation of unsaturated lipids such as extruded corn and soy blends had 1.5% more *trans*-fatty acids after extrusion.

At the nut shell, factors such as increased surface area of expanded products, addition of pro-oxidants, type and high level of fats, formation of free fatty acids in storage affects the storage stability of extruded products whereas denaturation of hydrolytic enzymes, formation of starch-lipid complex and enhanced or creation of antioxidant maillard compounds improves the stability and quality of products.

1.6.4 Vitamins

Vitamins are essential parts of food and feed. Humans and animals require a certain amount of each vitamin for normal health. Although vitamins do not supply any energy or calories but they do help. Our bodies process carbohydrates, proteins, and fats. Vitamins are essential and complex organic compounds (different than essential amino acids and fatty acids) required in very small quantities by animals and humans for normal metabolism, growth, reproduction, immunity and health. Vitamins, most sensitive to the extrusion process are A and E from fat-soluble vitamins, and C, B_1 (Thiamine), and B_9 (Folic acid) from water-soluble vitamins.

The ability of vitamins to retain its activity during storage and under chemical and/or physical stress conditions is called its stability. There are several factors that affect the stability of vitamins during extrusion. Among the lipid-soluble vitamins, vitamins D and K are fairly stable. Vitamin D is stable to oxidation, acidity, and alkalinity, and unstable to moisture, heat, trace minerals and overtreatment with UV light. Natural forms of vitamin K are stable to heat and unstable to oxidation, alkali, strong acid humidity, irradiation, trace minerals, and processing. Vitamin K adduct, created and stabilized by menadione bisulfite bonded with a suitable ion-exchange resin, is particularly suitable as a vitamin supplement for feeds. The high thermal stability of the vitamin adducts allows us to use it in modern technologies for producing feeds in extruded form. Most of the extruded snacks are deficient in vitamin A and related precursors due to the favourable prevailing conditions such as presence of oxygen and heat leads to denaturation. During extrusion, thermal degradation appears to be the major factor contributing factor to β-carotene losses. Higher destruction of vitamin A (52.5%) was reported in corn/soybean/groundnut blend processed with extrusion as compared to boiling for 2 min (24.9%). Destruction of vitamin A also depends on the source using, such as higher destruction (≈75%) was reported for β-carotene as compared to retinol, vitamin A acetate and vitamin A palmitate (10-50%). High barrel temperature and longer extrusion times are probably more destructive to vitamin A. Extrusion cooking at 180 °C was found to be a more drastic for β-carotene pigments than traditional heating for a long period of time (2 h) at the same temperature. In a study of extruded rice flour fortified with vitamins and minerals, the average vitamin A retention was 48% for dried kernels and 37% for cooked samples. Vitamin D and related tocopherols/tocotrienols reported to be influenced by high temperature short time extrusion cooking. A significant decrease (≈63%) was observed in vitamin E content of buckwheat during extrusion cooking. Gamma and delta tocopherols underwent greater losses (~40%) during extrusion than did alpha and beta forms (23–28%).In extruded cereals, a significant decrease (63 – 94%) in tocopherols and tocotrienols content was reported. The increase in the ratio of tocotrienols to tocopherols after extrusion cooking indicates that tocotrienols are the main residual isomers of vitamin E. Process variables encountered in extrusion processing has huge role on the sensitivity of various forms of vitamin E, such as, a significant decrease in α-tocopherol is reported with an increase in extrusion temperature and a significant decrease in γ-tocopherol with increase in moisture content during extrusion of grass peas.

Among the water-soluble vitamins, thiamine (B_1) is the most susceptible to thermal processing. Vitamin B_1 destruction in extruded wheat flour is a first-order reaction. In extrusion cooking thiamine losses ranges from 5 to 100%. Extrudates obtained from short barrel (90 mm) extruders had a higher retention rate of B vitamin group (44-62%) compared to 20% for long barrel extruders. The destruction and/or retention of vitamins during the extrusion processing is not related to initial levels of the vitamins but varies with the cereal and process type. The retention of thiamine and riboflavin in maize grits during extrusion processing was found to be 54% for thiamine and 92% for riboflavin. An increased degradation was seen in thiamine content with increasing temperature and screw speed whereas an increasing moisture content and screw speed favours riboflavin degradation. Higher feed moisture content and increased throughput improves the stability of B vitamins. Ascorbic acid (vitamin C) is also sensitive to heat and oxidation. This vitamin decreased in wheat flour when extruded at a higher barrel temperature at fairly low (10%) moisture content. The effect of screw speed, compression ratio and die diameter on vitamin C retention was studied and found that losses of vitamin C in extruded potato flakes ranged from 9 to 57%. Larger die and 1/1 screw compression ratio caused less destruction. An increased screw speed and temperature resulted in greater losses. Ascorbic acid may have lost to a limited extent during extrusion, but lose their activity rapidly during storage due to extensive exposure of expanded surface area to oxygen.

In summary, the retention of vitamins in generally decreases with increasing barrel temperature, increasing shear rate and increasing specific energy input while increases with increasing feed moisture content, increasing die opening and increasing throughput.

1.6.5 Minerals

Minerals are inorganic heat-stable solid, crystalline, naturally occurring chemical elements that cannot be decomposed or synthesised by ordinary chemical reactions. As minerals are heat stable, could be added before processing for fortification purposes without any risk of subsequent damage. During extrusion cooking, the mineral content and its bioavailability are generally retained well. In fact, extrusion can improve the absorption of minerals by reducing other factors that inhibit mineral absorption. Phytate may form insoluble complexes with minerals and eventually affect mineral absorption adversely. Extrusion processing helps to hydrolyse phytate to release phosphate molecules. Phytate hydrolysis in extrusion cooking of peas and kidney beans resulted in improved availability of minerals. Extrusion cooking reduces phytate levels in wheat bran flour, but not in legumes processed at low barrel temperature. Extruded rice fortified with micronized ground ferric pyrophosphate was fed to iron-depleted children in India for combating anaemia. The improved bioavailability of minerals after extrusion cooking could be partially attributed to the destruction of polyphenols. Changes in the polyphenol content might result in the binding of phenolics with other organic materials present after thermal treatment. Fibre and fibre components such as cellulose, lignin and some hemicelluloses could affect the mobility of the gastrointestinal tract and interfere with the absorption of minerals. Extrusion cooking does not significantly affect the mineral composition except for iron. After processing, iron content of the extruded potato peels reported to increase by 38% and it was most likely due to the result of wear of metallic pieces of the extruder. Iron content increased with increasing barrel temperature.

1.7 Extrusion Processing and Toxicants/Anti-Nutritional Aspects

Extrusion cooking also improves the nutritional quality of foods by destroying many natural toxins and antinutrients. Enzyme inhibitors (trypsin, chymotrypsin and α-amylase), hormone like compounds, saponins and other compounds could impair growth and development in children, but these same compounds may offer protection against chronic diseases in adults. The utilization of legumes, which are a cheap and valuable potential source of good quality proteins, is limited due to the presence of certain antinutritional factors.

Table 1.1 Antinutrients and toxicants affected by extrusion cooking

Antinutrients	Source	Mitigation strategies
Glucosinolates	Canola	Ammonium carbonate + Extrusion cooking
Glycoalkaloids	Potato	Thiamine
Gossypol	Cottonseed	Higher feed moisture
Allergens	Soy	Starch, Increased shear
Protease inhibitors	Legumes	Higher temperature

Acrylamide	Potatoes and heated foods	Glycine, Glutamine, Cysteine and Lysine, Aspargianse, Low temperature processing
Fumonisins	Cereals	High temperature (>160°C), mixing screws and relatively lower humidity
Aflatoxins	Cereals	Ammonium hydroxide and Ammonium bicarbonate, Calcium hydroxide and hydrogen peroxide, Sodium metabisulfite
Deoxynivalenol	Cereals	Design of the extruder, sodium bisulfite at higher concentrations
Zearalenone	Cereals	High shear rate and temperature
Ochratoxins	Cereals	Higher temperature and moisture content

1.7.1 Acrylamide formation

International Agency for Research on Cancer (IARC) Lyon, France has classified acrylamide as "probably carcinogenic to humans" (class 2A). Its exposure at high levels causes nervous disorders along with reproductive and mutagenic toxicity. It has been found in many foods such as potato chips, french fries, cookies, cereals and bread, which are prepared at a temperature of over 120°C. The main amino acid contributing to the acrylamide formation is asparagine, especially in the presence of reducing sugars, such as glucose, fructose, maltose and galactose, whereas arginine, cysteine, glutamine and aspartic acid produce only trace quantities of acrylamide. As extrusion cooking involves high temperature processing, acrylamide might be formed during the process. Different cereals have different potential for acrylamide formation depending upon their free asparagines content and type. Rye has higher asparagine content in comparison with rice, maize and wheat. The extruded products from rye are found to contain higher acrylamide content. Another important food group from acrylamide point of view are instant baby foods and weaning mixes prepared by extrusion processing. Less varied diet and comparatively lower body weight of children could further add up more worries to the problem. The presence of glycine, glutamine, cysteine and lysine has significant effects on the decrease in acrylamide in the fried products. Antioxidants play minor role in lowering the acrylamide content at low levels. Processing techniques such as blanching, soaking as well as addition of some ingredients, such as citric acid, free amino acids and protein rich components has been reported to lowers the acrylamide content.

At present, extensive research on this topic is undergoing worldwide, which includes mechanism of formation and the mitigation techniques that can reduce or prevent the formation of acrylamide in all kinds of food products. Improved understanding of this issues during extrusion cooking necessitates further research so as to draw concrete conclusions and validate interpretations.

1.7.2 Glucosinolates

Glucosinolates are a group of plant thioglucosides, found primarily among members of the Cruciferae, such as oilseed rape and brassica forages. Glucosinolates are amino acid derived plant metabolites that contain a sulphate and a thioglucose moiety, *per se* considered not harmful but the hydrolysis products have been associated with both auspicious effects on plant defence as well as adverse effects on animal production, such as antithyroid activity (reduce the efficiency of use of meals and slow down the animal growth). From livestock point of view, these adverse effects on animals necessitated the development of varieties of rapeseed with low levels of glucosinolates and erucic acid ("double zero" varieties). In context to processing, extrusion cooking has little effect on retention of glucosinolates. A reduction in total glucosinolates was reported with added ammonia during extrusion processing.

1.7.3 Mycotoxins

Mycotoxins are a risk to human health mainly via the intake of contaminated foods of plant origin, such as corn and wheat, which are consumed worldwide. Mycotoxins are toxic secondary metabolites produced by *Fusarium, Penicillium, Aspergillus* genera colonizing on stressed and badly stored cereals in the field and in storage. Five mycotoxins are considered to be important worldwide are: fumonisins (FB), aflatoxins (AFt), deoxynivalenol (DON or vomitoxin) and derivatives, zearalenone (ZEA) and derivatives and ochratoxins.

High temperature (>160°C), mixing screws and relatively lower humidity due to lower moisture content reported to be favours the fumonisin FB1 and FB2 reduction. Higher temperature with low screw speed significantly reduced the FB1 levels in extruded samples. Higher destruction of mycotoxins was reported at 120°C with mixing screw than that from 140 °C. This might be due to the fact that the residence time is higher at lower temperatures. Die configuration also affects the mycotoxin level significantly. Addition of sodium metabisulfite ($Na_2S_2O_5$) along with moisture content of 15-30% and temperature of 150-180°C was used for study of mycotoxin reduction. Regardless of the moisture content and temperature, losses of 25% were found when sodium metabisulphite was added but only 10–25% without the additive. In another study carried out at 105°C, 50 – 80 % reduction in aflatoxins was reported with extrusion processing alone. Sodium metabisulphite had no significant effect on AFt reduction and neither did sodium bisulphite (SB), calcium hydroxide, hydrogen peroxide or caustic soda. In contrast, ammonium hydroxide and ammonium bicarbonate, at levels ranging from 0.1 to 1.0%, significantly reduced Aft content. In the case of ammonium hydroxide, greater reductions were found at levels of 0.7 and 1%,whereas greater losses were observed at lower concentrations (0.1 and 0.5%) with ammonium bicarbonate since the formation of gases quickly pushed the corn out of the extruder; therefore, aflatoxins did not have enough time to be destroy edduring the extrusion processing. Contrary, in some studies calcium hydroxide and hydrogen peroxide significantly lowered the levels of AFB1, AFM1 and AFB1-dihydrodiol.Extrusion cooking turned out to be an effective process in reducing deoxynivalenol (DON) levels when a moisture content of 15 and 30%, a temperature of 150 and 180 °C and $Na_2S_2O_5$addition of 1% were set up as factors affecting the initial mycotoxin content. The design of the extruder could be a significant factor affecting the residence time and degree of mixing. Sodium bisulphite coupled with extrusion was ineffective for reducing AFB1 content in corn meal whereas quite effective in wheat kernels. Greater reductions were found with 1.5, 2.5 and 5% of sodium bisulphite, statistically higher from those found with 0.5%.In comparison with other methods of thermal processing, extrusion cooking was reported to be more effective for reducing zearalenone (ZEA) concentrations. Detoxification of ZEA was significantly higher by mixing (66–83%) than by non-mixing (65–77%) screws in corn grits. The moisture content of the grits had no significant effect in reduction of this mycotoxin during extrusion with either mixing or non-mixing screws.The higher the temperature and moisture content, the higher theochratoxinx A (OTA) breakdown. The maximum reduction observed for OTA did not exceed 40% even by using 'harsh' conditions.

1.8 Extrusion Processing Techniques and Applications

1.8.1 Co-extrusion

In recent years, extruded snack market has significantly expanded with the advancements in the extrusion design and ancillary equipment engineering. This advancement in metallurgy design and along with improved knowledge of ingredients has helped snack manufacturers to capitalize on innovations and offer more sophisticated products such as co-extruded products. In this process two different materials of contrasting taste, texture and colour are extruded from one die. These two materials can come from two extruders or from one extruder and one pump. Outer layer is processed with a cooker extruder with a die that forms a hollow centre and subsequently the centre is filled with low moisture, viscous filling which will not flow freely at ambient temperatures. The most common snack produced by co-extrusion is a cereal based outer tube with a cheese filling inside.

Co-extruded snacks include a cereal based outer tube, and pumpable fruit pastes, jelly, chocolate, cream, honey, yoghurt, cheese or cereal based filling. Migration of moisture or oil from fillings could be a major problem for texture loss in co-extruded products along with incomplete or less filling and undesired voids. High moisture gradient between cereal based tube and filling could be a reason for moisture migration and care should be taken in formulation selection. Consistent metered flow of the dough and filling at the die exit can prevent such problems. Both of these materials can come from two separate extruders or from an extruder and a pump. These cream feeding pump units has a storage vessel, equipped with a heating jacket and stirrer to maintain the required temperature of the filling for pumping needs. Variable speed screw feeds the filling to the positive displacement pumps, either 4, 6 or 8 pumps in a row with separate precise weight control system, to feed the controlled weight of filling to each co-extrusion stream. It is now possible to pump the filling directly into the centre of the expanded outer product with the use of special dies developed for this process. Die used for co-extrusion has number of openings depending upon the pumps being used, such 4, 6, 8 or 12, for separate concentric streams. Flow to each of co-extruded stream can be individually adjusted for consistency and control. Filling can also be done outside of die exit by adding top or bottom filling onto the U-shaped cereal rope. The required uniformity in cooking and smooth operation (without surging) for co-extrusion process demands twin screw extruder, and therefore, they are mostly used for such processes. After filling, the centre-filled cylindrical ropes pass under a pressing roll for uniform thickness, finishing and space reduction in between filling and outer casing. Cutting of these ropes is achieved by either adjustable, variable speed crimping rolls or reciprocating knives to various shapes. Finally, drying of these pillows or other shapes is achieved by types of driers. Several commercial products consisting of outer layers made by cooking extrusion and filled with pumpable centres have been introduced to the market, such as Kellogg's Krave. Co-extrusion cooking extruders can enhance the research and product development division and continue to meet the demand for innovative snack, cereal, pet foods and candy products.

1.8.2 Supercritical fluid extrusion (SCFX)

The invention or improvement in the extrusion process as supercritical fluid extrusion (SCFX) has prompted the research on the application of supercritical fluids as expanding agent for novel "good for you" snacks. Supercritical fluid extrusion (SCFX), Cornell University patented process, is a sophisticated new technology that uses supercritical carbon dioxide (SC-CO_2) as an expanding agent, minimizes steam driven expansion by cooling the temperature of melt below 100°C. SC-CO_2 could be used for carrying micronutrients, flavourings and colorants soluble in the fluid phase into the melted dough within an extruder.

The SCFX process consists of the following major steps:

i) Formulation with higher feed moisture content is fed into the long barrel extruder, where complete starch gelatinization is achieved but comparatively at lower temperature.

ii) Venting is provided in-between to release steam so as to bring the temperature down and prevent puffing at exit.

iii) Following the venting section, a cooling zone or cooling jacket on the extruder barrel is provided to further decrease the temperature to below 100°C.

iv) Supercritical CO_2 fluid is injected at precise locations through multiple ports in to the viscoelastic melt inside pressurized barrel. Reverse screw elements are used for increasing and maintaining pressure inside barrel. Higher temperature (85-95°C) inside barrel causes reduction in density of fluid and helps in release of carrying solutes such as flavourings, colour etc.

v) Following supercritical CO_2 injection, kneading section helps with the mixing of solutes in the dough.

vi) To keep the supercritical fluid inside, high pressure inside barrel is keep maintained by using reverse screw elements and narrow die openings. Controlled expansion by supercritical CO_2 at lower temperature is achieved as it exits the die.

The requirement of steam as the puffing agent in conventional extrusion for the production of low density expanded snacks may be replaced or avoided with the introduction of another suitable fluid that will also expand upon exiting the extruder die but at lower temperatures. Being easily available, non-toxicity, inert, greater solvency for heat sensitive flavours and vitamins at supercritical stage, makes it a perfect alternative to steam. CO_2 at its critical pressure and temperature [7.48 MPa (1070 psi) and 31°C] behaves both as a liquid and a gas. As supercritical fluids have characteristics of both a liquid and a gas, they facilitate the mass transport of solutes due to higher diffusivity and lower viscosity. Bubble nucleation rate is maximized with the reduction of CO_2 solubility with thermal and pressure changes. The nucleation rate of cells and their growth has shown to be dictated by total amount of soluble CO_2 injected and pressure drop rate. The growth time of nuclei in feed expanded with SC-CO_2 is longer than the growth time of nuclei in feed expanded with steam. The density of extrudates decreases as temperature of extrudates increases from 95 to 105 °C, but a further increase in extrudate temperature does not affect bulk density. Post-extrusion drying is a necessary step in the production of extrudates by SCFX process. During the final drying phase, the extrudate structure would set and settle to achieve a stable internal morphology as sample moisture reduces to the level of final ready to eat product.

Advantages of SCFX

i) Low temperature processing as compared to conventional steam extrusion cooking.

ii) Lower starch and protein degradation owing to lower temperature and high moisture treatment.

iii) Higher retention of heat sensitive flavourings, vitamins and amino acids could be achieved by the combination of high moisture, low shear and injection just before die exit.

iv) Supercritical fluid produces extrudates with smooth surface and more uniform, small and unconnected cells.

v) Less explosive puffing is achieved by SCFX as compared to steam puffing which could be helpful in better texture and storage stability. Highly porous structure is obtained with steam puffing which would allow more moisture infiltration and absorption comparatively to SCFX.

vi) Less porous and closed cell wall structure was obtained with SCFX, which would delay moisture infiltration and thus better bowl life for breakfast cereals.

vii) Modified starches could be produced with SCFX, as transformation of CO_2 to carbonic acid.

Moreover, SCFX is a new process developed at the cutting edge interface of supercritical- fluid and conventional extrusion technologies which offers more flexibility and opportunities for the research arena to develop or work on more nutritious product formulation besides minimizing the associated possible risks.

1.8.3 Pellet technology for third generation snacks (3G)

Pellets or third generation snacks (3G) or indirect expanded products are sometimes referred to as semi or half products. The term "Half-products" means products have been formulated mixed and processed to a stage where a stable, solid, dense, largely cooked product suitable for easy transport and storage. Generally, 3G products are formed at low in-barrel pressure, shear rate to prevent expansion and then dried to a final moisture content of about 10-12% to form a glassy pellet. These non-expanded, pre-gelatinized, dried, dense and storage stable pellets can be shipped to other far locations, stored for longer period of time and distributed to small co-packers or restaurants or retailers. Finally, they are puffed for local markets by frying, microwaving and hot sir stream. Puffed products could be then coated with seasonings or flavours or sugars. Half products are especially valuable to small scale food vendors or retailers, these products provide flexibility to the retailer or restaurant owner to standardize their own recipe based on local rituals and taste.

Process of Preparation

Starch rich cereal base ingredients are mixed with other dispersed fillers and additives in the ribbon blender and conveyed into hopper. Minor ingredients such as salt and baking soda can have useful effects on the final product texture and quality such as salt helps with moisture equilibrium whereas baking soda help with nucleation and puffing during frying or microwaving respectively. Hopper or holding container with predetermined amount of material, functions as a live bottom holding container to prevent bridging of the ingredients. A variable speed feeder screw provides a continuous, uniformly blended metered flow of the blend to the pre conditioner. Pre conditioner is particularly used for precooking and further mixing of dry blend with liquid ingredients such as meat slurries, flavours, oil or colour at the end. Starch gelatinization, typical for pellets, could be achieved in pre conditioner by thermal energy with minimal or no input of mechanical energy. Generally, typical target gelatinization for 3G products is above 90%. Pre-gelatinized material is then gravimetrically conveyed to the extruder. Variety of methods are available to extrude the mixed or blended material into pellets, such as all dry and liquid ingredients could be mixed in ribbon blender and conveyed directly to extruder for starch gelatinization, eliminating pre conditioner section. In all these cases, type of raw material, availability of type of extruder and processing demands dominate the selection method. Low shear forming extruder will be a choice for already pre-gelatinized material, whereas high shear cooking extruder will be choice for non-pre-gelatinized material. Twin screw extruders are commonly used for half product manufacture and starch gelatinization. Undercooking and overcooking of starches may impair the final texture of the product, such as partial cooking of starch granules will lead to a product with uneven expansion in frying whereas overcooking leads to the production of sticky pellets, respectively. Sticky pellets have problems with cutting, finishing and agglomeration during drying. Venting section may be used depending upon whether gelatinization was achieved in pre conditioner or in extruder barrel. For gelatinization in extruder barrel, venting zone reduces temperature of the melt and conveyed the material to forming zone. In forming zone, screw elements are configured to have minimum of restrictions and temperature of the gelatinized mass is reduced to 70-95 °C. The cooled viscoelastic material is pushed through wide opening shaped die to being cut by die face cutter. These shaped pellets now containing 20-40% moisture are ready for drying. Being a critical step for good quality pellets production, humidity controlled dryers are used for drying. Sticky pellets are treated with a pre-drying step, where they are treated with hot air so as to put a layer of skin on them. Pellets with no wet core and surface checking's exits the dryer at final moisture content of 10-12%. Dried pellets can be expanded later by frying or microwaving. At this stage, the pellets can be further processed to produce a finished product or packed in bulk for later processing. The expanded pellets can be seasoned and packaged for finished product distribution.

1.9 Quality Control Parameters for Extrudates

Food quality is difficult to define precisely but it refers to the degree of excellence of a food in all the parameters which play significant role in its overall acceptability in the competitive market. Food quality goes hand in hand with food acceptability and it is important that quality must be monitored from both food safety as well as acceptability standpoint. Quality of a product measures in some form of numbers, for repeatability, preciseness, uniform quality and documentation. Quality parameters for extruded products varies according to final product type and utilization, such as sugar coated or savoury coated snacks, breakfast cereals, puffs, half products etc. Quality of extruded products could be assessed by subjective as well as objective methods as follows.

1.9.1 Subjective methods

Subjective methods require individuals, either trained, semi-trained or not trained, to give their opinion regarding the qualitative or quantitative parameterson some kind of fixed scale by using the sensory organs. *Sensory evaluation* has been defined as a scientific method to evoke, measure, analyse and interpret responses as perceived through the senses of sight, smell, touch and hearing. The shape and size, flavour, hardness and crispnessof the extrudates areimportant parameters that play a significant role in its marketability and acceptance. Sensory evaluation is considered essential for new product development and marketing. Sensory evaluation methods are divided broadly into 3 categories:

(a) Discriminative tests

Discriminative and difference tests are used to determine whether there is a difference between products. These type of tests are used when an existing ingredient is replaced or removed from the formulation. For example, salt reduction in prepared and manufactured foods pushes restaurant owners and companies to reformulate their recipes and try new alternatives. Discriminative tests include triangle test, duo-trio test and paired comparison test. For further information about these tests, look for pages of 'Society of Sensory Professionals'.

(b) Descriptive tests

Descriptive tests are used to determine the extent of differences by generating and collecting the quantitative data among products. Trained, screened panellists with ability to discriminate, rate and identify test samples for similarity, intensity and testes respectively, are used. Trained panels spend several months in training to be qualify for panellists. These tests cannot be used with the consumers.

(c) Affective testing

Hedonic tests are extensively used in the measurement of acceptance. The extruded samples could be evaluated on 9-point hedonic scale or facial hedonic scale with non-trained panellists for acceptability. The results could be easily processed with a mean score and standard deviation for each product. Generally, minimum of 100 consumers are required for meaningful data generation.

1.9.2 Objective methods

Objective methods used for extrudate quality are based on standard scientific tests including physical, chemical, microbiological and instrumental methods. It includes:

Specific Mechanical Energy (SME)

Specific mechanical energy (SME) is a measure of energy going from the drive motor into the process per unit mass. It is a scale independent measure, can be calculated from load on motor or from electrical energy consumption, as given below:

$$SME\left(\frac{KJ}{Kg}\right) = \frac{\frac{T - T_0}{100} \times \frac{N}{N_r} \times P_r}{\dot{m}}$$

where, where T = percent torque, T_0 = no load torque, N = screw speed (rpm), N_r = rated screw speed (rpm), P_r = rated motor power (kW) and m ˪ = mass flow rate (Kg/s)

$$SME\left(\frac{KJ}{Kg}\right) = \frac{\sqrt{3} \times Volts \times (I - I_0) \times cos\emptyset}{\dot{m}}$$

where, where “3 = Amperes load, I = current drawn at full load (amps), I_0 = current drawn at no load (amps), *cos* ˪ = power factor and m ˪ = mass flow rate (Kg/s)

In-barrel moisture

In barrel moisture calculation play important role in extruder performance and final product characteristics. It can be calculated by as follows:

$$In - barrel\ moisture\ (\%) = \frac{Feed\ rate \times Feed\ mc + PC_s + PC_w + Ex_s + Ex_w}{Feed\ rate + PC_s + PC_w + Ex_s + Ex_w} \times 100$$

where, *Feed mc* = feed moisture content, used in fraction.

Expansion indices

Expansion indices measure the degree of puffing undergone by the melt as it exits the die. The amount of expansion in extrudate depends on the amount and type of ingredient being used as well as on pressure differential between the die and the atmosphere. For measurement of expansion, sectional expansion index (SEI) and specific length of the extrudates could be measured with the help of Vernier caliper. The SEI is calculated as the square of the cross-sectional diameter of the extrudate divided by the square of diameter of the die opening, whereas specific length is calculated as extrudate length divided by extrudate mass. For irregular shaped extrudates, thread could be used.

$$SEI = \frac{d^2}{d^{2\ die}}$$

$$Specific\ length = \frac{l_s}{m_s}$$

Bulk Density, Piece Density and Void Fraction

Bulk Density (BD) as expressed as g/cm^3, is an inverse measure of expansion. It is measured for bulk pieces of extrudates by taking them in a defined volume jar or cylinder. For example, 1 litre jar could be used for mass calculation (g/l).

$$Bulk\ Density\ (BD) = \frac{mass^{bulk}}{volume^{bulk}}$$

Piece density is calculated by measuring the mass of a piece of extrudate and volume of that piece (g/cm^3). The diameter and length of the extrudates should be measured by using Vernier calliper.

$$Piece\ Density = \frac{mass_{extrudate}}{volume_{extrudate}}$$

Volume of extrudates can be calculated for geometrical shapes, such as for cylindrical shaped piece, equation is given below:

$$Volume\ of\ cylinderical\ piece\ = {}^{4}/_{\pi}\mathrm{Dia}^2(\mathrm{extrudate}) \times \mathrm{length}$$

For irregularly shaped extrudates, sand displacement or other modified methods can be used to get volume of piece.

Void fraction or porosity of extrudates can be calculated by using equation given below:

$$Void\ Fraction = 1 - \frac{extrudate\ piece\ density}{solid\ density}$$

Absorption and solubility indices

The water absorption index (WAI) measures the ability of uncooked or partial cooked or fully cooked starches or other ingredients such as sugars, gums and proteins particles to hold moisture whereas water solubility index (WSI) measures the amount of solids get solubilise in water respectively. Milled and sieved samples for uniform particle size distribution is used for analysis. Selection of sieve should be as to have

85-95% or more of milled material to pass the screen and do not affect sample composition. Similar sample processing technique could be used for other parameters such as oil absorption index, rapid visco analyser samples etc. WAI measure can be used as an index of gelatinization of starch and porosity characteristics. The WAI increases with the increase in temperature, shear rate and porosity.

$$\mathrm{WAI}(\frac{g}{g}) = \frac{\text{weight gain of gel}}{\text{dry weight of sample}}$$

The WSI is used as an index of degradation of starches or other ingredients due to high shear, temperature and pressure inside barrel.

$$WSI\ (\%) = \frac{weight\ of\ dry\ solids\ in\ supernatant}{dry\ weight\ of\ extrudate} \times 100$$

Oil absorption index (OAI) measures the absorption capacity of the cooked starch to absorb oil. Oil is added into the milled sample in a graduated centrifuge tube and the tube is vortex for 1 min, left for 30 min followed by centrifuge it for 20 min at 700×g, the volume of the free oil calculated. Heated oil may be use to have some idea about oil absorption in frying section.

$$OAI\ \left(\frac{ml}{g}\right) = \frac{volume\ of\ oil\ absorbed\ (ml)}{weight\ of\ the\ sample\ (g)}$$

Colour

Colour is an important parameter of extruded snacks. The high temperature and varying processing conditions favours non-enzymatic browning results in formation of coloured compounds which influence the appearance of the extruded snacks. Changes in colour during extrusion cooking may be used as a measurable indication of the non-enzymatic browning. Different types of colorimeter are available to measure the colour of the extruded snacks.

Pasting properties

Extrusion cooking leads to starch gelatinization, either partial or complete gelatinization, transformation of crystalline structure to amorphous state and resulting in the absorption of water at room temperature, thus formation of cold peak viscosity. Viscoamylograph is best known for evaluating the pasting behaviour of extruded snacks. It involves continuous measurement of shear viscosity during controlled heating and subsequent cooling of an aqueous sample. Rapid Visco

Analyzer (RVA) is another widely used instrument for the study of rheological properties of the starch-based products (Fig. 1.4). Before starting the analysis, decide the sequence of paddle rotation speeds and temperature range or ramp to which sample will supposed to be subjected. Larger particles required longer time to be fully wet by the solvent and for heat energy to flow into or out of the particles, so specify particle size wherever it's important. In RVA, the resistance to the movement of a rotating sensor is electronically detected. During heating in water, starch granules swell and amylose leaches out resulting in increase in viscosity.

Care should be taken in sample preparation; as small samples usually fails to disclose important transitions in viscosity while large samples can mask the small but important transitions. In book, "The RVA Handbook", Pual J. Whalen discussed considerations important for cooked flours and samples in chapter "Extruded products and degree of cook". Author provided sample weights and RVA profiles for raw and cooked samples. For cooked corn, wheat, rice, oats (whole), potato and tapioca, 4.0-5.0, 5.0, 3.5-4.0, 4.0-4.5, 3.0, and 3.0 respectively weights were suggested. Time in-between from sample addition to tower or run should be no more than 30 sec and pre-weighed water should be added first to the canister, followed by sample. For direct-expanded ready to-eat snacks or puffs, rapid moisture uptake and lumping usually causes problems. An inverted number 8 rubber stopper was suggested by the author to break up lumps by shaking vigorously for approximately 30 secs and not by glass or stirrer rod. Standard profiles for raw, unprocessed and processed samples is given below in Table 1.2.

Table 1.2

Unprocessed ingredients		**Processed or cooked products**	
Time (min)	**Temp °C/rpm**	**Time (min)**	**Temp °C/rpm**
0:10	960 rpm	0:10	960 rpm
@0:10	160 rpm (hold)	@0:10	160 rpm (hold)
Idle and 0:00	25 °C	Idle	25 °C
2:00	25 °C	2:00	25 °C
7:00	95 °C	7:00	95 °C
10:00	95 °C	10:00	95 °C
14:00	50 °C	15:00	25 °C
End time 15:00		End time 22:00	

Parameters involved in pasting curve are as:

Pasting temperature – Temperature at which pasting is initiated and varies with type of additives, starch type and processing. This temperature indicates beginning of gelatinization.

Peak viscosity – The maximum viscosity obtained during pasting process.

Breakdown viscosity – It is the difference between the maximum viscosity and the viscosity at the end of the first holding period.

Setback viscosity–It is the difference between the viscosity at the end of the cooling period and the viscosity at the end of the first holding period.

Final viscosity - The viscosity value attained as the paste is cooled to lowest cooling temperature set.

Viscosity is generally measured as RVA units (RVU) or centipoises (cP) units (1RVU = 12 centipoise).

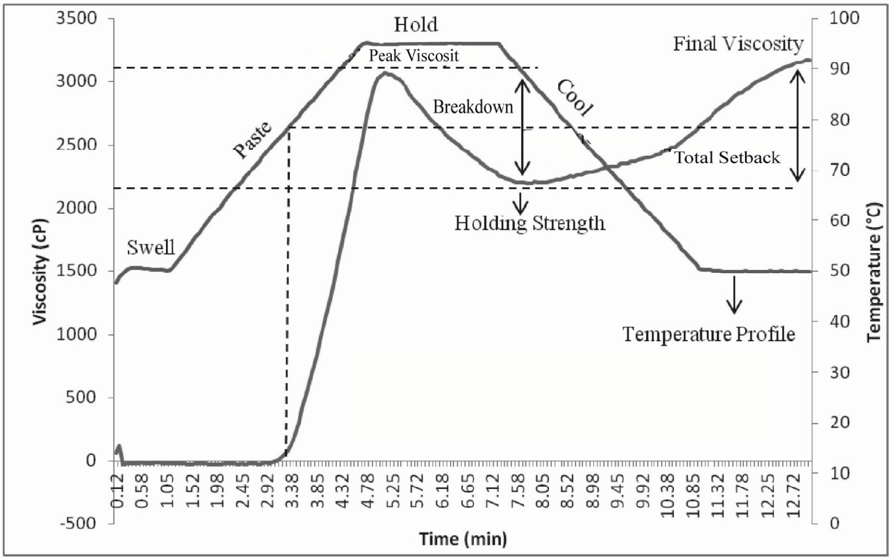

Fig. 1.4. Rapid Visco Analyzer (RVA) viscosity and temperature profile of corn starch

X-ray scattering

X-ray diffraction (XRD) is probably the most popular x-ray scattering technique and has been extensively used to investigate the changes in the crystallographic pattern of starches. XRD has been widely applied in both food starches and starch based biodegradable nanocomposite films or packages. In starches, X-ray measurement detects the semi-crystalline character, which reflects the presence of both the ordered and amorphous regions within the starch granule. X-ray diffraction patterns can help in the identification of starch source(s) used in particular formulation, native starches can be divided into A-type (cereal), B-type (tubers, roots and amylose-rich starches), and C-type (legume) and V-type (swollen granules). Starches, depending upon extent of severity of processing conditions inside barrel, exhibits partially crystalline to fully amorphous X-ray pattern. Loss of crystallinity or ordered structure leads to loss of birefringence. Quick evaporation and drying of moisture at die exit inhibits crystallization of starches, for which longer time required. Studies on the correlation of SME and loss of crystallinity in cereal flours or starches with extrusion processing has been conducted by various researchers. In-barrel temperature of above 80-100 °C has been reported to destroy crystalline pattern completely. V-type pattern could be observed in formulations rich in lipids.

Micro-structural properties

A study of food micro-structure is an important aspect of understanding the functionality or effect of major and minor ingredients on final texture, crushing strength and other properties. Microstructure of food products determines to a large extent the physical, textural and sensorial properties of these products. Food professionals can now apply several techniques for revealing the structural organization that complement microscopic studies. A judicious approach in technique selection can provides data, which would be capable of unmasking structural organization.

Fluorescence Microscopy

Fluorescence is the luminescence of a substance excited by radiation, usually use an ultraviolet light source. It is very sensitive technique, particularly used for studying structures that present in very small concentrations and they cannot be observed by conventional optical microscopy. In fluorescence microscopy, samples are either auto-fluorescent or are caused to fluoresce through the use of fluorescent probes or dyes. Some substance has inherent fluorescence capacity due to the presence of natural fluorescent molecules like aromatic amino acids residues, phenolic acids, lignin, seed coat, elastin and collagen while some need fluorophores to be fluorescent. Thus, fluorescent dyes should be more specific, since they attach only to specific areas of the tissue and leave other unstained. Some fluorescence techniques used for food components are as:

Table 1.3. Fluroscence Techniques for Food Components

Fluorophores	Compatible component(s)
Nile blue	Lipids
Fast green FCF, Texas red, Thiazine red R, Fluorescein isothiocyanate	Proteins
Acid fuchsin	Cereal proteins
Calcofluor white, Congo red	β-glucans
Crystal violet	Lignin
Periodate	Starch

X-Ray Micro-tomography (XMT/XRT)

Foaming or incorporation of bubbles in bio-polymeric materials has a wide range of applications. In view of it, XMT allows high resolution 3-D visualization and characterization (porosity) of different materials. It has been proved to be a very useful technique for the non-invasive visualization and measurement of the internal of microstructure of starch or cereal flours based food products such as porous starchy puffs, starch and pomace based extrudates etc. Extrusion lab in Kansas State University has been pioneer in the use of this advanced, non-invasive technique. XMT can investigate the microstructure of samples non-invasively up to a few millimetres across with an axial and lateral resolution.Contrast between solid and gas phase is based on the difference in absorption of X-rays by the constituents of the sample. XMT allows measurement of close cell structure under environmental conditions without sample disturbing preparations, that are normally used in light and electron microscopy. In comparison to scanning electron microscopy (SEM), it is 3D and non-destructive technique which involved no cutting to expose the cross-section to be viewed thereby no altered structural features. Moreover, 2D images of a sample cross-section does not give accurate information on cell size distribution, as cells are generally sliced off-centre and the diameter measured from the image depend on the depth of cut. Adequate contrast between air and solid phases is difficult to obtain with SEM and other imaging techniques. To overcome all these drawbacks, non-invasive XMT technology proved to have great potential in imaging bio-polymers or food foam structures.

1.10 Conclusion

Wide use of extrusion processing has already shown that is the most efficient and continuous manner of cooking, by which a number of diverse shapes, types, texture can be produced. Extrusion technology provides several different advantages over the traditional methods of food and feed processing like improves digestibility, quick, less water usage, instantaized the product, high production rate and negligible effluents. Novel ingredients, cutting edge extrusion technology and innovative packaging methods need to be combined to yield new and improve already available snacks with having better appearance, texture and mouthfeel, nutrition, and shelf-life. In view of the continuing improvements in the extrusion engineering, new products with controlled glycemic index, thermal or mechanical cooking and final product texture. It has been already proved and established food processing technique which will be used for more innovative applications evident in near future.

Glossary

Axial channel width: It is the width measured from one side of the flight to the next within the channel perpendicular to the angle of the flight.

Axial flight width: It is the width of a screw flight in the axial direction.

Barrel length to diameter ratio (L/D): It is the ratio of the screw diameter to the length of the barrel.

Barrel opening (D_b): It is a barrel opening in which screw rotates.

Breakdown viscosity: It is the difference between the maximum viscosity and the viscosity at the end of the first holding period.

Channel depth/Flight height: It is the distance from the top of the flight to the root.

Channel length: It is the length of the screw channel in Z direction, which can be one or more full turn of the screw helix.

Channel: The helical opening that emerges from the feed to discharge end of the screw.

Clearance: It is the clearance between the flight tips and barrel.

Cold paste viscosity: The viscosity value attained as the paste is cooled to lowest cooling temperature set.

Compression ratio: The ratio of screw channel depth in feed zone to that of the metering zone developing the pressure needed to process the raw materials is known as compression ratio.

Expansion ratio (ER): The ER was calculated as the cross-sectional diameter of the extrudate divided by the diameter of the die opening**.** Expansion indices measure the degree of puffing.

Extrudate: Food ingredients of various types may be processed by extrusion and are referred to as *extrudate***.**

Helix angle: It is the angle between the flight and a line perpendicular to the screw shaft. It usually varies between 12 and 15°.

Hot paste viscosity: Viscosity of sample after heating and cooling cycles are completed or in other words it is the final viscosity reached at the end of cooking.

Nucleating agents: Nucleating agents enhance the number of bubbles in the extrudates and produce finer textures.

Oil absorption index (OAI): Oil absorption index (OAI) measures the absorption capacity of the cooked starch to absorb oil.

Paste viscosity: Instantaneous viscosity of 15 % aqueous sample at 80 °C obtained during pasting process from 25 °C to 95 °C.

Pasting temperature: Temperature at which pasting is initiated.

Peak viscosity: The maximum viscosity obtained during pasting process.

Pitch/Lead: It is the distance between consecutive flights.

Root diameter: The diameter of the root of the screw on which the flights are built.

Screw diameter: It is distance between two flights across the screw shaft.

Setback viscosity: It is the difference between the viscosity at the end of the cooling period and the viscosity at the end of the first holding period.

Shear: Aworking, mixing action that homogenizes and heats the material.

Supercritical fluid extrusion (SCFX): Supercritical fluid extrusion (SCFX) is an elegant new technology that uses supercritical carbon dioxide (SC-CO_2) as a blowing agent, enabling the formation of an expanded structure at comparatively lower temperature i.e., below 100 °C.

Water absorption index (WAI): Water absorption index (WAI) measures the volume occupied by the starch after swelling in excess water.

Water solubility index (WSI): Water solubility index (WSI) measures the amount of free polysaccharides or polysaccharides released from the granule on addition of excess water.

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Supercritical Fluid Extraction in Food Processing

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CONTENTS

2.1 Introduction

Food is one of the complex systems involving many constituents such as carbohydrates, lipids, proteins, vitamins, minerals and other phytochemicals. These all constituents are not present in the same relative proportion in every type of food and thus the foods are categorized and valued according to the presence of these constituents as protein rich foods, fat rich foods, etc. The specific type of food is in abundance with only one or at most two of these constituents and rest of the bulk is not valuable, commercially. So, if these active constituents which are present in the tissue surrounding inactive matrix, are separated, it is of great benefit with respect to increased purity, nutritive value, functional properties, reduction in volume, easy handling and transportation. On contrary some valuable food items contain undesirable constituents generally referred as anti-nutritional factors. Removal of these anti-nutritional factors enhances the food value and commercial utilization. Hence, the separation of phytochemicals and removal of anti-nutrients from the food matrices can be easily carried out by using a unit operation called as extraction.

Extraction involves the separation or isolation of active/desirable components of complex system viz., plant and animal tissues from the rest of inactive/undesirable components by using suitable means such as solvent or mechanical structure. The basic principle involved in the extraction process is partitioning of different components in accordance with the extracting agent. For example, in mechanical extraction, the partitioning is due to pressure and screen/apperature size where as in case of solvent extraction, the portioning of components from mixture takes place due to particular solubilizing power of solvent used.

2.2 Methods of Extraction

Extraction is one of the important unit operations in food processing and finds numerous applications ranging from as simple as juice extraction from fruit tissues to others such as sample preparation, chemical analysis, isolation and purification of nutraceuticals and other functional ingredients, removal of the toxicants, etc. These processes can be accomplished by various types of extractions including mechanical extraction, solvent extraction, microwave assisted extraction, ultrasound assisted extraction, solid phase extraction, sub and super critical fluid extraction.

2.2.1 Traditional methods

The traditional methods used for extraction of suitable component from the food matrix were not selective and were applicable only for particular food components viz., juices and oils. Most of the traditional methods were based on the principle of application of high pressure to macerate the food matrices and squeezing out the liquid component through small perforation. The most common traditional methods of extraction are:

2.2.1.1 Hydraulic press

The hydraulic juice press also known as rack and cloth press is used for the extraction of juice from crushed fruits like pineapple, grapes, oranges and apples etc. In Rack and cloth press, also known as a screw press is a traditional hand-operated machine used to press fruits. Fruits are placed between several layers of rack and cloth, which are called "cheese." A mechanical handle is turned to lower the heavy pressure plate and crush the fruits; the juice is filtered through the rack, cloth and a thin layer of pomace. A rack and cloth press will produce smooth juice.

2.2.1.2 Continuous press

Continuous press are designed as belt presses, screw presses, and roller presses. In belt presses, aperture between two belts decreases, along and disintegrated material is squeezed. In a screw press in a horizontal cylinder, helical screw is rotated. The pitch of the screw flights gradually decreases towards the discharge and exerts higher and higher pressure on the pulp. Screw presses are used to express oils from oil seeds. The roller press is made up of two cylinders in between which pulp is fed. To facilitate liquid flow the cylinders are grooved. The press residue is removed by doctor blade.

2.2.1.3 Maceration

In maceration, the whole or coarsely grinded sample is kept in a stoppered container along with the solvent and is allowed to stand at room temperature for a period of not less than 3 days with repeated stirring until the soluble matter has dissolved. The mixture is filtered, the marc (the damp solid material) is pressed, and the combined liquids are clarified by filtration or decantation after standing.

2.2.1.4 Infusion

Fresh infusions are prepared by macerating the sample for a short period of time with cold or boiling water. Infusions are nothing but the dilute solutions of the readily soluble constituents of a matrix.

2.2.1.5 Digestion

Digestion can be considered as the form of maceration in which mild heat is used during the course of extraction. Digestion process is particularly used in case where the moderately elevated temperature is tolerable. The solvent efficiency of the menstruum in this process is thereby increased due to application of heat.

2.2.1.6 Decoction

In this process, the sample is boiled in a specified volume of water for a defined time; it is then cooled and strained or filtered. This procedure is suitable for extracting water-soluble, heat-stable constituents. This process is typically used in preparation of Ayurvedic extracts called "quath" or "kawath". The starting ratio of crude drug to water is fixed, e.g. 1:4 or 1:16; the volume is then brought down to one-fourth its original volume by boiling during the extraction procedure. The concentrated extract is filtered and used as such or processed further.

This method is popularly used for extraction of liquid coffee from the coffee beans. The coffee seeds are roasted, undergoing several physical and chemical changes. They are roasted to various degrees, depending on the desired flavor. They are ground and brewed to produce liquid coffee which is also known as coffee decoction.

In beer industry, decoction in its basic form is the scooping-up of a certain volume of mash slurry, placing it into a smaller boiling pot, boiling, and then returning it to the mash tun. This hot addition will raise the overall temperature of the mash, add some flavors, and confer a few other benefits as well. The word decoction literally means "to return cooked" so in brewing it is the returning of cooked mash back to the mash tun.

There are two benefits of decoction First, decoction adds flavor and darkens color as the result of caramelized maltose and maillard compounds. Second, decoction improves the efficiency of the mashing process by opening up grains for greater conversion.

2.2.1.7 Percolation

Percolation process is oftenly used to extract active ingredients in the preparation of tinctures and fluid extracts. The solid ingredient is moistened with a suitable amount of specified menstruum and is then allowed to stand for about 4 h in a well-closed container, after which the mass is packed and the top of the percolator is closed. Extra menstruum is added to form a thin cover above the mass, and the mixture is allowed to macerate in the closed percolator for 24 h. The liquid contained in the percolator is allowed to drip slowly by opening the percolator exit channel. Extra menstruum is added as required, till the collected percolate volume makes about three-quarters of the required volume of the finished product. The marc is hard-pressed and the expressed liquid is added to the percolate. Enough menstruum is added to make the requisite volume, and the mixed liquid is clarified by filtration or by standing followed by decanting.

Some of the other methods of extraction are:

- Aqueous alcoholic extraction
- Distillation
  - Hydrodistillation
  - Water and Steam Distillation
  - Distillation with steam
  - Distillation with cohobation
- Headspace trapping extraction
  - Static headspace trapping
  - Dynamic headspace trapping

2.2.2 Recent methods of extraction

The modern methods of extraction of specific component from the complex system involve more precise conditions and/or use of organic solvent in contrast to the traditional methods. Some of the modern methods of extraction are outlined briefly.

2.2.2.1 Conventional Soxhlet extraction

Classical techniques for the solvent extraction of solute from plant matrices are based on the choice of solvent coupled with the use of heat and/or agitation. Existing classical techniques used to obtain solute from plants include: Soxhlet, hydrostillation and maceration with an alcohol–water mixture or hot fat.

In a conventional Soxhlet system the plant material is placed in a thimble-holder, and filled with condensed fresh solvent from a distillation flask. When the liquid reaches the overflow level, a siphon aspirates the solution of the thimble-holder and unloads it back into the distillation flask, carrying extracted solutes into the bulk liquid. In the solvent flask, solute is separated from the solvent using distillation. Solute is left in the flask and fresh solvent passes back into the plant solid bed. The operation is repeated until complete extraction is achieved.

2.2.2.2 Solid phase extraction (SPE)

The principle of solid phase extraction is similar to that of liquid-liquid extraction (LLE), involving a partitioning of solutes between two phases. However, instead of two immiscible liquid phases, as in LLE, SPE involves portioning between liquid (sample matrix or solvent with analytes) and a solid (sorbent) phase. This sample treatment technique enables the concentration and purification of analytes from solution by sorption on a solid sorbent and purification of extract after extraction. The general procedure is to load a solution onto the SPE solid phase, wash away undesired components, and wash off the desired analytes with another solvent into a collection tube.

2.2.2.3 Sonication-assisted extraction (SAE)

Sound waves, which have frequencies higher than 20 kHz, are mechanical vibrations in a solid, liquid and gas. Unlike electromagnetic waves, sound waves must travel in a matter and they involve expansion and compression cycles during travel in the medium. Expansion pulls molecules apart and compression pushes them together. The expansion can create bubbles in a liquid and produce negative pressure. The bubbles form, grow and finally collapse. Close to a solid boundary, cavity collapse is asymmetric and produces high-speed jets of liquid. The liquid jets have strong impact on the solid surface.

Two general designs of ultrasound-assisted extractors are ultrasonic baths or closed extractors fitted with an ultrasonic horn transducer. The mechanical effects of ultrasound induce a greater penetration of solvent into cellular materials and improve mass transfer. Ultrasound in extraction can also disrupt biological cell walls, facilitating the release of contents. Therefore, efficient cell disruption and effective mass transfer are cited as two major factors leading to the enhancement of extraction with ultrasonic power.

2.2.2.4 Microwave-assisted extraction (MAE)

Microwaves are electromagnetic radiations with a frequency from 0.3 to 300 GHz. Domestic and industrial microwaves generally operate at 2.45 GHz, and occasion-ally at 0.915 GHz in the USA and at 0.896 GHz in Europe. Microwaves are transmitted as waves, which can penetrate biomaterials and interact with polar molecules such as water in the biomaterials to create heat. Consequently, micro-waves can heat a whole material to penetration depth simultaneously.

There are two types of commercially available MAE systems: closed extraction vessels under controlled pressure and temperature, and focused microwave ovens at atmospheric pressure. The closed MAE system is generally used for extraction under drastic conditions such as high extraction temperature. The pressure in the vessel essentially depends on the volume and the boiling point of the solvents. The focused MAE system can be operated at a maximum temperature determined by the boiling point of the solvents at atmospheric pressure.

2.2.2.5 Accelerated solvent extraction (ASE)

Accelerated solvent extraction (ASE) is a solid–liquid extraction process performed at elevated temperatures, usually between 50 and 200ºC and at pressures between 10 and 15 MPa. Therefore, accelerated solvent extraction is a form of pressurized solvent extraction that is quite similar to SFE. Extraction is carried out under pressure to maintain the solvent in its liquid state at high temperature. The solvent is still below its critical condition during ASE. Increased temperature accelerates the extraction kinetics and elevated pressure keeps the solvent in the liquid state, thus achieving safe and rapid extraction. Also, pressure allows the extraction cell to be filled faster and helps to force liquid into the solid matrix. Elevated temperatures enhance diffusivity of the solvent resulting in increased extraction kinetics.

2.3 Need and Importance of Supercritical Fluid Extraction

The extraction methods described above differ greatly with respect to efficiency (yield of extract) and efficacy (potency/purity of the extract).

Of these extraction methods, mechanical extraction has extreme low efficiency and efficacy. Whereas though microwave and ultrasound assisted extraction methods yield extract of high purity and in greater amount, these methods are not techno-economically feasible due to their high cost. These traditional extraction methods thus suffer from various disadvantages; thus, they are time consuming, laborious, have low selectivity and/or low extraction yields.

Solvent extraction method is of great choice in food industry specifically for analytical purposes. Nevertheless, this method cannot be used in isolation and purification of nutraceuticals and functional ingredients owing to use of toxic chemical solvents.

Increased public awareness of the health, environment and safety hazards associated with the use of organic solvents in food processing and the possible solvent contamination of the final products restricts applications of solvent extraction method in food industry. Further, the solvents used in this method are very costly. Hence, increasingly stringent environmental regulations together with the new requirements of the medical and food industries for ultra-pure and high added value products have pointed out the need for the development of new and clean technologies for the processing of food products.

Supercritical fluid extraction which uses harmless solvents (commonly CO_2) has provided an outstanding substitute to the use of chemical and toxic solvents. Over the past three decades, supercritical CO_2 has been used for the extraction and isolation of valuable compounds from natural products.

For the past three decades, the commercial application of supercritical fluid technology remained restricted to few products due to high investment costs and for being new and unfamiliar operation. With advances in process, equipment and product design and realization of the potentially profitable opportunities in the production of high added value products, industries are becoming more and more interested in supercritical fluid technology. The extraction is carried out in high-pressure equipment in batch or continuous manner. In both cases, the supercritical solvent is put in contact with the material from which a desirable product is to be separated. The supercritical solvent, now saturated with the extracted product, is expanded to atmospheric conditions and the solubilized product is recovered in the separation vessel permitting the recycle of the supercritical solvent for further use.

2.4 History of Supercritical Fluid Extraction

In 1879 Hannay and Hogard reported that changes in pressure caused inorganic salts like cobalt chloride to dissolve in or precipitate from ethanol at a temperature above the critical temperature of ethanol. Later, Villard (1986) demonstrated that gases such as methane, ethylene, carbon dioxide and nitrous oxide dissolve a number of liquid or solid compounds, such as camphor, stearic acid or paraffin wax.

The interest shown in supercritical fluids during the first half of the twentieth century's involved process operations and not analytical chemistry. A process for deasphalting lube oils using subcritical propane introduced by Wilson et al. in 1936 is still used today. The Solexol process developed by Dickinson and Meyers (1952) for the separation and purification of vegetable and fish oils uses propane as a solvent.

A few years later, purification and separation process of vegetables and fish oils was developed. The process concentrated the polyunsaturated triglycerides in vegetable oils and the vitamin A from fish oils using propane as a selective solvent.

Zosel (1971) reported the decaffeination of green coffee with CO_2. His famous method has provided significant changes in supercritical fluid extraction technology. The process was accomplished by soaking the beans in water and then immersing them in supercritical CO_2. The presence of water was essential for the efficient extraction of the caffeine from within the bean and as results of that, currently over a dozen of patents have been issued that concerns the decaffeination of coffee. Since 1980, there has been rapid development of supercritical fluid extraction (SFE) from natural products, polymers and fish oils. The use of supercritical fluids in chemical reaction and synthesis of polymers and organic chemicals and removal of nicotine from tobacco are under study.

2.5 What is Supercritical Fluid (SCF)

A pure component is considered to be in a supercritical state if its temperature and its pressure are higher than the critical values (Tc and Pc, respectively). At critical conditions for pressure and temperature, there is no sudden change of component properties. The variation of properties with conditions of state is monotonous, when crossing critical conditions, as indicated in Fig. 2.1. Yet the magnitude of the variation can be tremendous, thereby causing different effects on solutes and reactants within neighbouring conditions of state. Similar effects to that of the supercritical state can in some cases be achieved at near critical temperatures in the liquid state of a substance for $p > p_c$ and $T < T_c$.

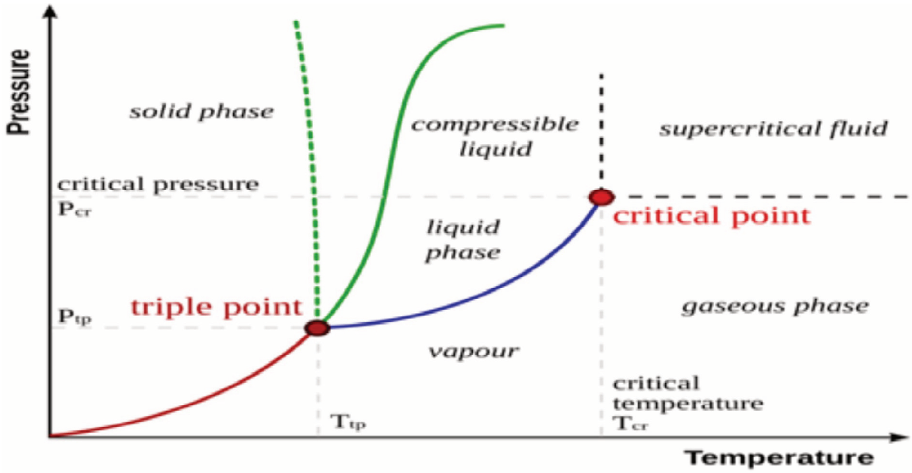

Fig. 2.1 Phase diagram of water showing supercritical region

2.6 Properties of Supercritical Fluids

A phase diagram for an SF is shown in Fig. 2.1. CO_2 is considered an SCF when temperature exceeds its critical temperature (Tc) of 31°C and pressure exceeds its critical pressure (Pc) of 1070 psi or 72.9 atm. At temperatures above Tc and pressures above Pc, CO_2 has properties of both liquid and gas. The distinction between liquid and gas phases is removed in the supercritical region. Under other conditions of temperature and pressure, CO_2 may exist as a solid, liquid, or gas.

Near their critical point and above, super critical fluids have a dissolving power similar to that of liquids, because their density is near that of a liquid. With adjustments in either temperature or pressure above their critical points, changes in the density of super critical carbon dioxide are induced, which in turn changes its viscosity, diffusivity, solubility, and bulk dielectric constant, allowing improved solubility of a component. The density of CO_2 at ambient temperature and atmospheric pressure is only 0.002 g/cm^3. At its critical point, the density of CO_2 is 0.469 g/cm^3. Some properties of a gas, SCF, and a liquid are compared in Table 2.1. Because of its gas-like nature, an SCF has lower viscosity and higher diffusion coefficients than conventional liquid solvents, facilitating its ability for extraction. At this point, density and solubility are sensitive to small changes in temperature (T) and pressure (P). Therefore, the solvent strength of the SCF can be tuned as needed through small changes in T and P to vary solvent properties between those of a liquid and a gas without crossing phase boundaries. The low, critical temperature of super critical carbon dioxide is also an advantage in processing, not only for energy savings, but also for minimization of heat-induced damage to the substrate.

2.6.1 Density and solvent power

The solvating power of the supercritical fluid is dependent on temperature and pressure. At low pressure, the solvent power of CO_2 surprisingly decreases with rising temperature whereas at high pressure it increases. The density, not pressure, is proportional to the solvent power of the supercritical fluid. Solvent power of a supercritical fluid increases with; density at a given temperature; and temperature at a given density. However, solvent with high solvent power have a lower selectivity because more compounds from a mixture of components are soluble whereas solvent with low solvent power have higher selectivity.

2.6.2 Diffusivity and viscosity

In the supercritical state, liquid-like densities are approached, while viscosity is near that of normal gases, and diffusivity is about two orders of magnitude higher than in typical. As was the case for density, values for viscosity and diffusivity are dependent on temperature and pressure. The viscosity and diffusivity on the supercritical fluid approach those of a liquid as pressure is increased, whereas an increase in temperature leads to an increase in viscosity of a gas, the opposite is true in the case of supercritical fluids. Diffusivity, on the other hand will increase in accordance with the rise in temperature.

Characteristic values for the gaseous, liquid, and supercritical state are listed in Table 2.1. In the supercritical state, liquid-like densities are approached, while viscosity is near that of normal gases, and diffusivity is about two orders of magnitude higher than in typical liquids.

Table 2.1 Comparison of Properties of Liquid, SCF and Gas

S.No.	Properties	Liquid	SCF	Gas
1	Density (g/cm^3)	1000	200 – 800	1
2	Viscosity (mPa.s)	0.5 – 1.0	0.05 – 0.1	0.01
3	Diffusivity (cm^2/s)	10^{-5}	10^{-4} – 10^{-3}	0.1

2.7 Choice of Supercritical Fluid

Several solvents are used in supercritical fluid extraction. In fact, any solvent can be used as a supercritical solvent; however, the technical viability (critical properties), toxicity, cost, and salvation power determine the best suited solvent for a particular application. Carbon dioxide is the most used solvent in SCF because it is safe, non-toxic and generally available at a reasonable cost. Nevertheless, other solvents have been investigated as SCF solvents, such as propane, ethane, hexane, pentane and butane. In spite of the toxicity of certain solvents, their use has been advocated because at or near supercritical conditions the amount of solvent used is much smaller than the required amount of any extraction process done at low pressure. Selected supercritical solvents and their properties are enlisted in Table 2.2.

Table 2.2 Comparison of Properties of Liquid, SCF and Gas

S.No.	Substance	Tc (^{0}C)	Pc (atm)
1	Carbon dioxide	31.1	72.8
2	Methane	-82.1	45.8
3	Ethane	32.3	48.2
4	Propane	96.7	41.9
5	Argon	-122.3	48
6	Nitrous Oxide	36.5	72.5
7	Water	374.1	218.3

Among these solvents, carbon dioxide is the most common supercritical fluid solvent, and has been extensively studied for its potential applications in many different fields, including the food processing industries. Due to the low critical temperature and pressure, low cost, wide availability, non-flammability and environmentally friendliness, supercritical CO_2 is the most acceptable supercritical solvent in food applications as well as in other applications without any declaration.

2.8 Co-solvent for Supercritical Fluid Extraction

Co-solvents are the substances added in supercritical fluids in less quantity (5 – 20%) to enhance the solubility power of supercritical fluids. These are also called as modifiers or entrainers. Even at high densities, CO_2 has a limited ability to dissolve high polarity compounds. The addition of modifiers to CO_2 can improve the extraction efficiency by increasing the solubility of the solute. The effects of modifier addition on the matrix and the extraction of such compounds in supercritical conditions have been studied by several researchers. A number of mechanisms have been proposed to explain the effects. It is believed that the reason for the enhancement of the process is the solute –co-solvent interaction. Another explanation is that the matrix swelling facilitates the contact of the solute by the solvent. An important factor in the solubility enhancement is the increase in solvent polarity when a co-solvent is added.

The predominant effect in the extraction will depend on the type of co-solvent, solid matrix, and target solute. Following are the commonly used co-solvents.

i) Water
ii) Methane
iii) Ethane
iv) Acetone
v) Butanol

2.9 Principle and Phenomenon of Supercritical Fluid Extraction

The extraction is carried out in high-pressure equipment in batch or continuous manner. In both cases, the supercritical solvent is put in contact with the material from which a desirable product is to be separated. The supercritical solvent, now saturated with the extracted product, is expanded to atmospheric conditions and the solubilized product is recovered in the separation vessel permitting the recycle of the supercritical solvent for further use.

2.9.1 Principle of supercritical extraction

The extraction of desired solute from solid phase or liquid phase takes place owing to its solubility in the supercritical fluid at critical temperature and pressure. At these conditions, the supercritical fluid diffuses through the matrix with extreme diffusivity due to its high density and low viscosity, solubilizing the solute and taking it along in expansion zone where the SCF undergoes expansion thus making solute immiscible and thus separation. The solvent is conditioned and again reused. The four primary steps in supercritical fluid extraction are extraction, expansion, separation and solvent conditioning.

2.9.2 Extraction

A simple Supercritical fluid extraction process consists basically of two major steps: (1) extraction of the soluble substances from the solid substratum by the SCF solvent and (2) separation of these compounds from the supercritical solvent after the expansion. The extraction process is as illustrated in Fig. 2.2. First the solvent is fed into (solvent pump and heat exchanger) the extractor and uniformly distributed throughout the fixed bed formed by the solid substratum. During the extraction, the solvent flows through the fixed bed and dissolves the soluble compounds. The solute-solvent mixture is separated in the flash tanks (separators) by