END USE FUNCTIONALITY OF CEREAL AND PSEUDOCEREAL COMPONENTS

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INTRODUCTION

The seeds of cereals and pseudocereals are potentially a very rich source of functional ingredients for a wide variety of applications. Rather than try to deal in some general way with all pseudocereals and cereals, examples will be drawn from the pseudocereals amaranth and quinoa and the cereals sorghum and millet. It is hoped however that these examples will point towards generic possibilities and problems.

Before dealing with specific components it is important to consider the economics of component extraction, since no matter how interesting or potentially useful a component is, it will only find its way into commercial use if the economics of the production process are viable.

Some possibilities for component extraction from seeds are illustrated in Figure 1.

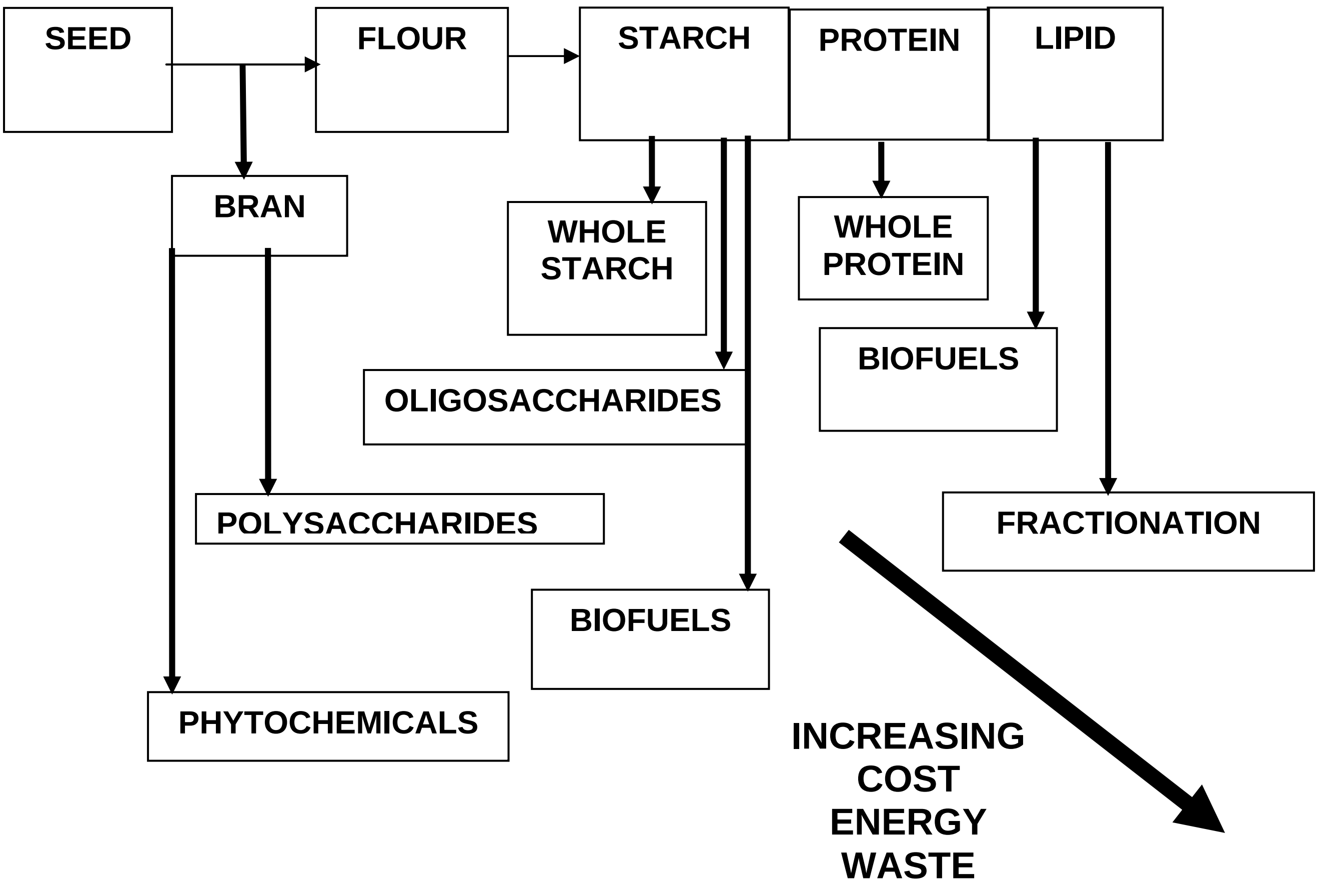

Figure 1. Potential products from seeds

The Figure illustrates the main components that can be isolated from a seed. Clearly depending on the specific nature of the seed and the extraction process there may be other components available. Whatever the details it is generally true that as the refinement of the extracted material increases costs will rise in terms of energy consumed, waste produced and chemical and plant investment and running costs. To illustrate this Figure 2 considers in more detail the extraction of protein products from flour.

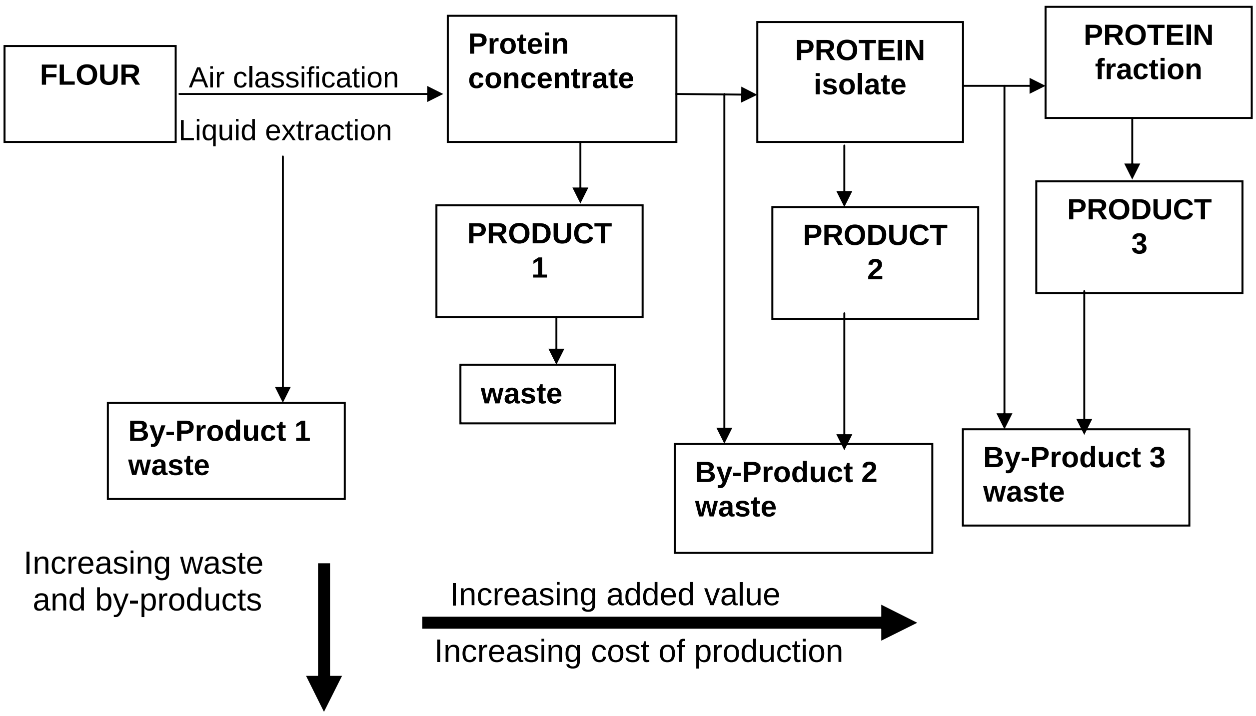

Figure 2 The extraction of protein from flour.

In the Figure three possible extracts are considered although there may in practice be more. The first stage is crude concentrate merely enriched in protein, the second stage is an isolate, such as soya isolate that may be used for wide variety of functions and the third stage is the fraction of a specific protein or group of proteins. At each stage waste and cost increase as does the added value of the product. The sum of costs must equal the value of the products and profits.
Thus:

(Value of products 1 + 2 + 3) + (Value of by-products 1 + 2 + 3)
= (cost of production of 1 + 2 + 3) + (cost of disposal of waste) + profit

Typically, very high value products will require considerable input to isolate or prepare them. The equation shows that even if a product has very high value its extraction will only be worthwhile if the associated costs can be met. Conversely if the product has a high value and can be obtained at relatively low cost, a penalty of low value products and by-products can be sustained. The point here is that no product has a value or cost that can be considered in isolation from the remainder of the processes involved. This economic truth has sometimes led the disappointment of scientists who see a scientifically exciting scheme but do not appreciate the economic realities.

THE FUNCTIONALITY OF SEED COMPONENTS

Lipids

In some plants lipids are the main energy storage medium and in these plants the quantity of lipid is such that they are useful as sources of biofuels. In the cereals and pseudocereals however lipid levels are typically of the order of 3 to 10% of seed weight and thus are not present in sufficient quantities to be suitable as biofuels. The range of lipids available from cereals and pseudo cereals is extensive: examples are given in Table 1.

SPECIES	SORGHUM	QUINOA	AMARANTH
LIPID CONTENT(%)	5	9.7	8
14:0	0	0.2	0
16:0	18.3	9.9	20.7
16:1	0.82	0.1	16.6
18:0	1	0.8	3.8
18:1	41.8	24.8	23.6
18:2	35.9	52.3	35.3
18:3	2.14	5.4	ND
20:0	0	0.7	ND
20:4	0	0	0.48
squalene	0	0	6.2

Table 1 Fatty acid and lipid composition of sorghum, quinoa and amaranth. Data taken from (Berghofer & Schoenlechner, 2003); (Taylor & Belton, 2003); (Taylor & Parker, 2003)

The range of functionalities of the diverse mixtures fatty acids and triglycerides that are available is very wide in terms of melting point, crystal habit and so on. However as the lipid content of the seeds is low fractionation is not likely to be a viable option, as there are many other plant lipid sources with much higher lipid contents. The most likely use of these lipids is therefore as a whole lipid fraction which is extracted after milling and might be used as a dietary supplement or specialist cooking oil. One exception to this possible is the occurrence of squalene in amaranth. Squalene has uses in the cosmetics industry and as a specialised lubricant (Berghofer & Schoenlechner, 2003). It is not clear however that the amount of squalene present is sufficient to make its extraction economically viable.

Polymeric components

The main components of the rest of the functional fractions of the seeds are polymeric and thus have number of important features in common. All polymers are intrinsically viscoelastic in melts and solutions. In general they will readily form gels when cross linked by external reagents or because of the intrinsic polymer /polymer interactions that can occur. Polymers can also form glasses and rubbers. These properties make then valuable as structural materials and historically they have been used in a wide variety of applications well outside the food area, but the advent of synthetic plastics has to a very large extent replaced this traditional use. The increasing concern about the environmental impact of synthetic materials and the long term sustainability of petrochemical supplies has caused a renewed interest in the potential of plant derived biopolymers as sources of functional materials. However, currently, with the exception of starch and cellulose, most of the uses of plant biopolymers are still in food applications.

Bran

The term bran here is meant to include all plant cell wall residues from milling. These are a source of an extremely rich group of hetero-polysaccharides. Three main types may be recognised, cellulose, pectin and arabinoxylans. These are already widely exploited in the food industry as is shown in Table 2 but there are increasing numbers of papers on the potential for these as biodegradable plastics.

Polysaccharide type	**Derivatives**	**Example uses**
Cellulose	powdered	Bulking agent
	microcrystalline	Anticaking agent
	colloidal	thickener
	methyl Cellulose	emulsifier
	hydroxy methyl cellulose	stabiliser
	methyl ethyl cellulose	Gelling agent
Pectin		Biodegradable films and pharmaceutical applications[1,2]
	high methyl pectin	Gelling agent
	low methyl pectin	Gelling agent in low sugar products
	amidated pectin	Gelling agent
Arabinoxylans		
		Gums gelling agents
	from maize hulls	Biodegradable film[3]

Table 2 The uses of plant cell wall polysaccharides, The table is based in part on data from (Harris & Smith, 2006). 1(Zsivanovits et al., 2005), 2(Liu et al., 2003), 3(Zhang & Whistler, 2004)

One of the problems of extraction from bran is the chemical complexity of the plant cells walls. Pectin is relatively straightforward to extract but arabinoxylans require more careful extraction, especially if degradation is to be avoided. Plant cell walls are also potentially valuable sources of phenolics compounds such as ferulic acid.

Starch

In many ways starch is the simplest of the seed components, it is a homo-polymer of glucose. However, this is complicated by the occurrence of branched form of the polymer called amylopectin and straight chain form called amylose. These may occur in wide range of different ratios. Starch is stored in granules which may vary considerably in size ranging from as small as 0.5 microns in some varieties of amaranth (Berghofer & Schoenlechner, 2003) to as much as 30 microns in sorghum (Taylor & Belton, 2003). A further complication is the crystalline state of starch in the granule. Starch may occur in the A, B or C forms (Buleon & Colonna, 2007). In pseudocereals the A form occurs alone and in cereals both A and B forms can exist, but the A form predominates. Starch behaviour may be characterised in a number of different ways depending on the applications required. Amongst the most important of these is the melting temperature, which is highly dependent on the water content, and the pasting curves which represent the changes in viscosity during a heating and cooling cycle. Differences in behaviour make different starches suitable for different applications. For example, comparison of the pasting curves of amaranth and quinoa (Taylor & Parker, 2003) show dramatic differences in the viscosity of the two starches during the heating cycle. Quinoa has a much higher viscosity at the gelling point than amaranth and its viscosity continues to rise quite sharply on cooling.

The end use applications of starch are very wide it is used as a whole material in wide variety of thickening, coating and filing applications. One of the most important potential applications for starch is a component of biodegradable plastics. Starch is readily available and may be easily extruded it thus has attracted a great deal of attention. Starch on its own however has problems notably associated with its hydrophillicty. However, formulation in composites and mixtures offers considerable promise (Averous, 2004; Rouilly & Rigal, 2002).

<u>Proteins</u>

The storage proteins of the pseudocereals consist mainly of 11S globulins. These are very widespread in dicotyledonous plants and typically are hexameric proteins of molecular weight of the order of 330,000-450,000 (Shewry, 2003). These proteins are therefore similar to the soya storage proteins and would be expected to have similar versatile functionality. However, a limitation of the use of soya protein is the associated bean flavour which is not favoured by some consumers. On the positive side soya is about 20% oil and 40% protein which makes the extraction of the protein relatively easy and the economics of the process attractive. The possible advantage of globulins isolated from pseudocereals is that they may have a more acceptable flavour. The disadvantage is that typical protein contents of amaranth and quinoa are between 13 and 18% of seed weights and the energy storage chemical is starch, which is more difficult than oil to separate from the protein. The exploitation of these proteins therefore will depend on economic extraction process and/or some additional functionality that makes them competitive with soya.

In contrast to the pseudocereals, cereals contain prolamins. These are glutamine and proline rich proteins that are not water soluble but are soluble in alcohol water mixtures. The prolamins of sorghum and millets are highly homologous with the zein proteins from maize; they are about 40% alpha helical and 60% beta sheet (Belton et al., 2006). Latest results suggest that alpha zein is a triple super helix that is able to bind lutein in its core. It is to be expected that kafirin, the prolamin of sorghum and pennisetins, the prolamins of millets, are similar in structure (Momany et al., 2006). Kafirin is unique amongst the prolamins as being the most hydrophobic (Belton et al., 2006). It there may therefore be some interesting properties to be exploited from this material that are not shown by other prolamins of the same type. Zeins have been used as the basis of biodegradable films and plastics for some considerable time (Padua & Wang, 2002) more recently investigations into the behaviour of plastics and films from Kafirin have begun and the materials have shown considerable promise (Da Silva & Taylor, 2005). Relatively little has been reported on the functional properties of pennisetins. Since the extractability and occurrence of these proteins is similar to that of zein it may well be that they do have a similar economic potential.

CONCLUSIONS

The pseudocereals and less common cereals have been relatively unexplored in terms of their potential as sources of novel functional components. Enough is known to be sure that all of them have at least some valuable properties or components. At this stage it is not clear that they are of sufficient value to be exploitable on their own. They may have value as by products of processing. In particular the proteinatious material left over from cereal brewing may provide useful feed stock for protein extraction and utilisation. Another potential future source could be the residue from biofuel production exploiting the starch content of the seeds.

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