IENICA

SUMMARY REPORT FOR EUROPEAN UNION

CARBOHYDRATE CROPS

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7.1 Introduction

Starch, unlike cellulose, exists in a granular structure and is typically bimodal and polydisperses, both at the granular and molecular level. This underscores the uniqueness of starch. The molecular bimodal nature of starch refers to the major molecular components, namely the high molecular weight branched amylopectin and the more linear material, amylose. The ration of these two components varies depending upon the source of the starch and everything from 100% amylopectin to 100% amylose has been reported as occurring in nature or as a result of classical plant breeding. This is particularly the case with maize where the full range has been reported. Amylose typically occurs at levels between 20 and 30% but apart from maize, elevated levels of amylose have also been reported in barley and pea (40% and 60% respectively). High amylopectin sources have been reported in barley, wheat, pea and rice as well as maize.

Whilst virtually all plants contain carbohydrate in one form or another, it is primarily those which store carbohydrate which can later be extracted which are reported here.

Table 7.1 shows a breakdown of carbohydrate producing crops grown by the EU-15 member states that have reported in this project. Wheat, Maize, particularly in central southern Europe, sugar beet and chicory are the dominant carbohydrate sources in the EU, but only a small percentage of total production is used by the industrial market. In addition, starch potatoes are grown solely for the industrial starch market. While sugar beet processing facilities are well distributed, facilities for other crops are more variable, particularly potatoes, which has a significant impact on crop demand and production potential. Some types of peas have application for the production of starch because of their high content of amylose but no commercialisation has been reported. There is interest in sweet sorghum in southern Europe, apart from this there are few new species under investigation.

A significant quantity of carbohydrate processed and used in Europe particularly maize starch, is imported.

Table 7.1 : Carbohydrate Crop Plants in EU15 by Species and Country

PLANT SPECIES BY COUNTRY **Carbohydrate Crops**	**Austria**	**Belgium**	**Denmark**	**Finland**	**France**	**Germany**	**Greece**	**Ireland**	**Italy**	**Netherlands**	**Portugal**	**Spain**	**Sweden**	**UK**
Wheat		✓	✓	✓ C	✓ C	✓ C	✓ C		✓ C			✓	✓ C	✓ C
Maize	✓ C	✓		✓	✓ C	✓	✓ C		✓ C			✓ C		✓
Sugar beet	✓ C	✓ C	✓ C	✓ C	✓ C	✓ C	✓ C		✓ C	✓ C		✓ C	✓ C	✓ C
Potato	✓ C	✓	✓ C	✓ C	✓	✓ C	✓ C		✓	✓ C		✓	✓ C	✓
Chicory		✓ C		✓					✓	✓ C			✓	✓
Barley		✓	✓	✓ C	✓	✓	✓		✓			✓	✓	
Oat				✓										✓
Quinoa			✓		✓	✓				✓				✓
Jerusalem artichoke		✓			✓	✓			✓	✓				✓
Pea		✓				✓	✓							✓
Sweet sorghum		✓				✓	✓ P	✓	✓			✓		

‘C' denotes commercial production ‘P' denotes at pilot stage, ‘✓' denotes scientific interest/development,

7.2 Scientific and Technological Aspects

Starch is unique amongst the polysaccharide-based hydrocolloids because it is versatile in a function both of its polydispersity and its granular nature. These features provide useful functionality, particularly in food, and also enable highly purified chemically derivatised starches to be made economically. To exploit the wider range of opportunities requires a broad spectrum of skills from plant breeding and molecular genetics on the one hand to modification and processing skills and the application know-how on the other. The basic biosynthetic pathway involves three basic steps:

(i) monomer synthesis (ADP-glucose pyrophosphorylase)
(ii) polymer synthesis (granular bound and soluble starch sythetase)
(iii) polymer branching (branching enzymes)

The generation of the active monomer ADP-glucose is catalysed by the action of the ADP glucopyrophosphorylase. These monomers are then polymerized into a backbone of starch via granular bound and soluble starch synthetases and branched via the action of starch branching enzymes. With this information Dutch and Swedish scientists have been able to generate an amylose-free or amylopectin-rich potato using antisense techniques to inhibit the synthesis of granular bound starch synthetase.

High amylopectin maize, or waxy maize as it is known because of the reference to the waxy appearance of the kernel, has been available for nearly a century. High amylose versions of cornstarch are more recent, being developed within the last 40 years. Most common and commercially available are those hybrids, which contain either 50% or 70% amylose. Within the last five years, plant breeders have been able to develop a new hybrid, which is essentially free of amylopectin (<5%). This material is unique and has properties that are not typical of the high amylose starches. It rapidly produces gels with storage modulus (G'); gels which are stable over a period of time and which show considerably less syneresis than a typical high amylose starch. The biochemical and genetic basis of this novel starch is not yet understood but it is known that low levels of expression of the starch branching enzyme, SDE II, is a feature of this hybrid. SBE I appears to be less critical in controlling the starch composition. At the molecular level, it is known that an absolute requirement of high amylose hybrids in maize is the presence of the ae gene. On its own, the levels of amylose can be raised from the typical levels of 27% to approximately 40%. More elevated levels require the presence of a number of modifier genes. To date, the primary source of high amylose is maize but in addition to the examples already given, British scientists have developed a high amylose potato using antisense technology to a newly discovered branching enzyme.

Due to the high level of co-operative hydrogen bonding that can occur between the essentially linear chains of amylose, little or no swelling of the granule occurs in water and consequently, it is not possible to cook out the starch granule under normal conditions. The applications of amylose starches are rarely in the granular form but in a dispersed state, generated by special cooking conditions using a combination of high temperature and shear. Under these conditions, the amylose chains can be separated and then allowed to re-associate under controlled conditions, finding applications as films, foams, barriers, adhesives and a way to control the digestion of starch as a food ingredient. These latter applications refer to RS-2 and RS-3, forms of resistant starch which were first reported in the early eighties and which can now be isolated in commercial quantities. These materials resist digestion in the small intestine and are fermented in the colon by mixed acid fermentative micro-organisms producing butyrate in preference over acetate and propionate. The digestion of the starch granule is both a function of the source of the starch as well as the subsequent processing and provides unique physiological benefits, in terms of colonic health.

In contrast, regular starch or the amylose-free forms are more readily hydrated and the swollen granules provide a range of viscosity profiles, which find wide applications particularly in food. These inherent properties can be and are further amplified by the post treatment of the extracted starch - these include chemical, enzymic and physical modification. For food applications, this allows control over a number of textural and processing attributes. Chemical cross-linking builds structural integrity into the granule and prevents the breakdown of the swollen granule and the inherent viscosity. Substitution of the starch backbone controls retrogradation of the linear regions of the polymer and finds particular application in chilled or frozen products where syneresis is prevented. Understanding the factors that influence retrogradation has allowed plant breeders to control the chain length of the outer branches and build in “natural” freeze-thaw stability. This has been achieved by insertion of the *su*2 gene into a *wx* background and allows the application scientists to control the association of the chains without chemical modification.

For industrial applications a wider range of chemical modifications has been developed including cationic, anionic and amphoteric substitutions, as well as hydrophobic starches and novel aldehyde chemistry, allowing wide applications in such industries as paper making, textiles and biodegradable/re-pulpable packaging products in response to environmental pressures. These chemistries are particularly applicable in the paper industry where modified starches find application as retention and drainage aids as well as providing both set and dry strength. The biodegradable applications make use of high amylose starch from maize and are extruded to produce a material competitive with expanded polystyrene.

Clearly, a huge potential for the application of starches lies “simply” in modifying the structure at source once the link between application, enzymes and genes can be made. Such starches develop functional properties of their own and provide a rich source of raw material in both dispersed and granular form.

The science and technology supporting traditional starch markets - for example, sizing of papers and boards; adhesives; sizing of textiles, is all well explored and reported. However, a number of newer areas are well under investigation and justify exploration. These include novel polymers from starches; development of ‘designer’ starches; paints and surface coatings.

7.3 Markets

EU starch markets are currently dominated by a number of well-established players, mainly multinational companies. These include:

- Amylum
- National Starch
- Cerestar
- Avebe
- AKY I/S
- Cargill

7.31 Starch Market

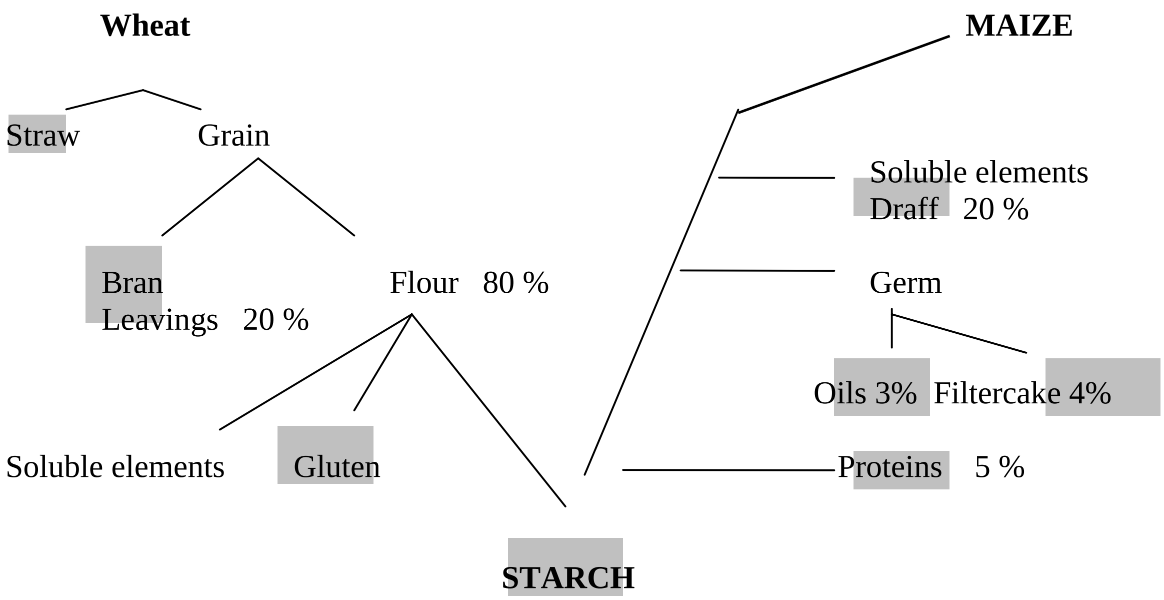


Figure 7.1 By-products from starch processing of cereals

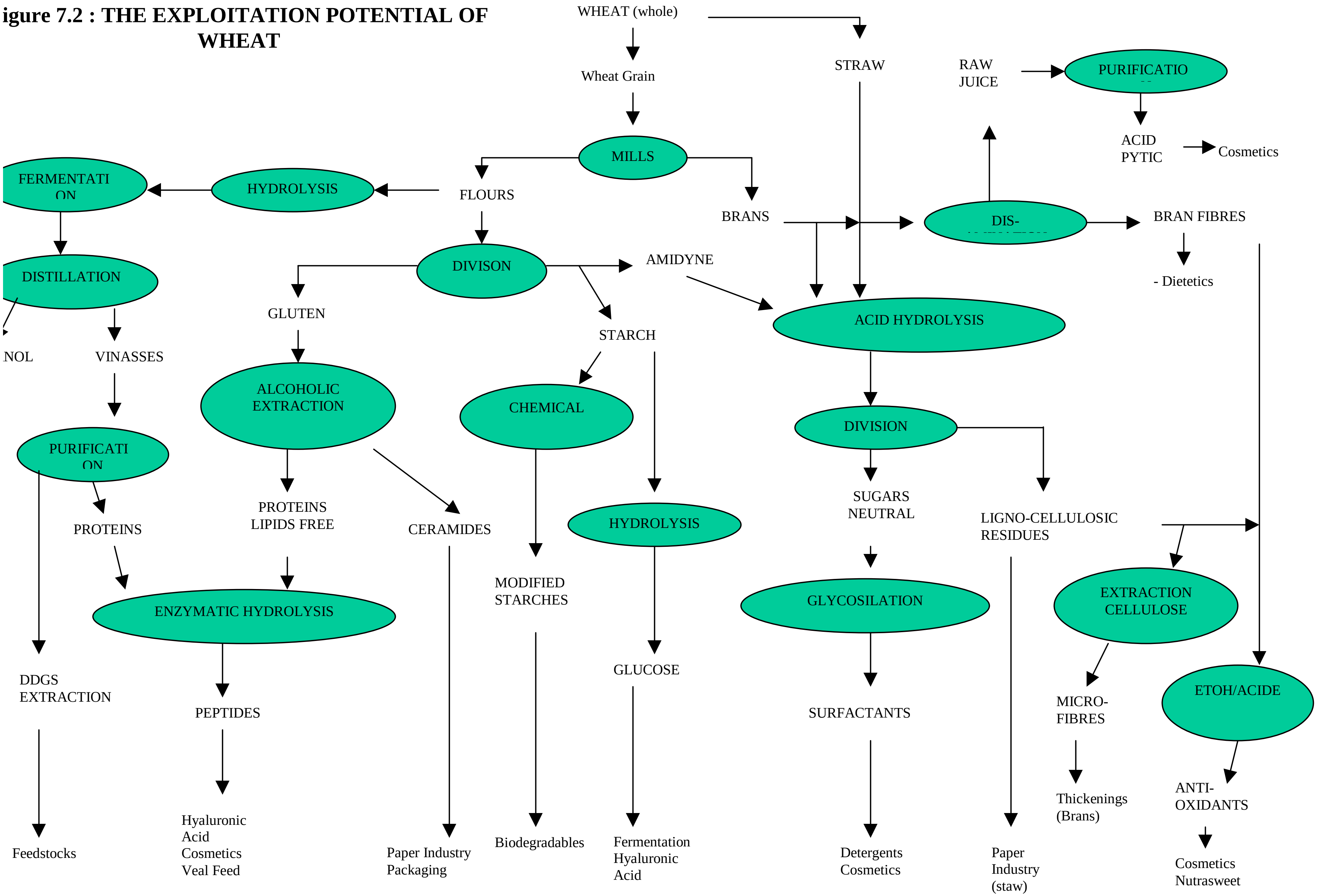
All starch/sugar extraction processes produce by-products (see Fig 7.1) The by-products are currently sold to the animal feed industry, but many other applications with higher added value are now being developed.

Non food uses of flours
Certain direct applications of grain flours are being developed
1. ROVERCH in France produces POLYNAT, a bioplastic with characteristics close to those of polyethylene or polypropylene made from rye flour by gelling and plastifying with natural alcohols.
2. ARD is developing packing boats from wheat flour.

Non food uses of by-products
Work is in progress to develop potential applications for starch by-products in the medium term. The aim is to make industrial processing profitable by creating value from all components of the feedstock, by targeting high added-value sectors such as cosmetics, where the demand is low in volume but very strong for so-called "green" products.

Figure 7.2 illustrates the potential as seen by ARD for obtaining valuable products from wheat by-product. This company is working on conversion of beet pulp in the same manner.

igure 7.2 : THE EXPLOITATION POTENTIAL OF WHEAT



The overall use of starches for non-food markets in Europe falls into 5 significant areas (See Fig 7.2).

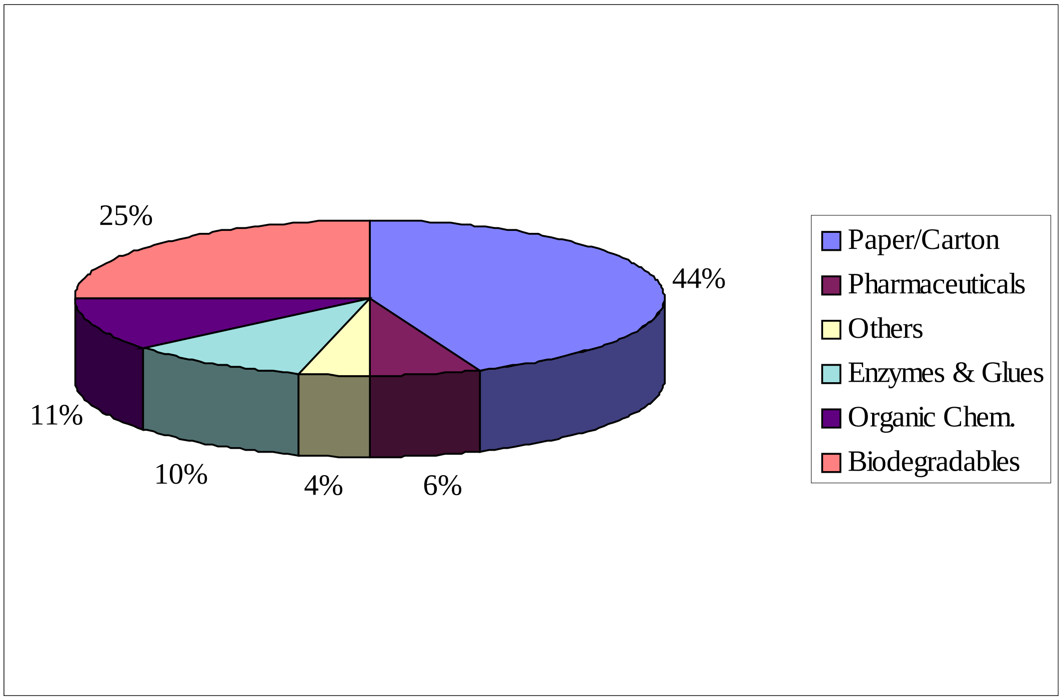


Figure 7.1 : A global overview of the non-food uses of starch in Europe (from: Spelman, 1994)

Starch products include:

7.3.1 Adhesives

Starch-based adhesives are primarily used for paper bonds, the most important sector being in corrugated board. Traditional, starch-based adhesives have faced competition from high performance synthetic products. To maintain their current share of the adhesive market, they must be cost and performance competitive. Some observers consider this unlikely.

7.3.2 Agrochemicals

In the agrochemical industry starches are used as encapsulation agents for pesticides and for the production of aqueous base pesticide formulations. The future potential in this application is unclear.

7.3.3 Cosmetics and Toiletries

The use of sorbitol in toothpaste is an example of a well established use of starch and starch derivatives in this sector. There is potential to develop a wide range of uses in this type of this type of high value, low volume markets.

7.3.4 Detergents

Consumer concern over environmental issues, particularly related to phosphates, has led to an increasing interest in starch-derived products for the detergent industry. Surfactants are the primary cleaning components in formulated detergents. Plant-derived carbohydrates may be used to provide the water-soluble potion of surfactants and to form APGs (alkylpolyglucosides). These are non-ionic surfactants made by combining an oleochemical based oil soluble group and a water soluble group based on glucose derived from starch, thereby producing an entirely ‘natural’ product.

Builders and co-builders or sequestering agents buffer a wash medium, soften the water and disperse dirt particles, which are removed during washing. Starch-derived products have shown satisfactory technical qualities but currently there is lack of a suitable economic process for their production.

Studies have shown that 60 to 75% of washing powders could be replaced by biodegradable products

7.3.5 Paper Making Additives

The paper and board industry is the biggest non-food starch-using sector, taking about 44% of EU industrial starches.

Starch is used in several aspects of the paper manufacturing process but primarily in surface sizing and at the ‘wet end’. Both modified and unmodified starches can be used for coating; increasing amounts are used in paper as a filler.

7.3.6 Pharmaceutical

Pharmaceutical industry uses glucose hydrolysates or their derivatives as fermentation substrate in order to produce several active compounds (vitamins, antibiotics, hormones). Cyclodextrins stabilise aromas as chelating agent or move bitterness from citrus fruits. They also trap cholesterol and enter the preparation of lightened butter. Inulin from chicory is used as a substrate for pharmaceuticals preparation as it displays beneficial effects on kidney functions, due notably to its rapid excretion. Starch can be used in the pharmaceutical industry for coating and dusting tablets and binding the components of the tablets. These are high value, low volume market with good growth potential.

7.3.7 Paints

Based upon either acrylic or vinyl monomer lattices, it has been possible to replace up to 25% of the petroleum-based monomer by native starch from potato, maize, waxy maize or wheat. It is likely that starch-based paints are as economic as synthetic coatings and could have novel properties. Also, they are more environmentally friendly – the feedstocks are sustainable and leftovers could be recycled thereby moving towards the target of zero waste.

Potato, wheat and maize starch-based paints are just as durable, glossy and liquid as synthetic paints. They are potentially biodegradable after disposal, but durable in use. However, current formulations are less water-resistant and take longer to dry than synthetic paints.

Starch has been used in emulsions and alkyds, the two most common types of decorative paint. In emulsions, starch replaces up to 35% of the normal acrylic or vinyl monomers which polymerise to form the finished product. In alkyd paints, oil-derived polyols are replaced by modified starch. The starch is converted into polyols in a novel process which appears economically viable.

7.3.8 Textiles

Starch is used for sizing (potato starch), printing (cereal starch) and finishing (dextrins and degraded starches). This is a very small market and declining, since the synthetic alternatives currently have superior performance, even though more expensive.

7.3.9 Water Purification

Starch based products have traditionally been used by the water treatment industry as a coagulant or flocculate aid. Potato starch is preferred because of its high potassium content. However, starch-based products have been replaced to a large extent by synthetic polyelectrolytes because of their superior performance and lower dosage rates. The biodegradability of starch may also be undesirable because it increases biological oxygen demand.

7.3.10 Biodegradable plastics

Starch can be used in this type of material in three different ways:

- adjunct in conventional plastics (6% starch)
- blended with synthetic polymers (60 to 75% starch)
- as a thermoplastic starch itself (75 to 95% starch + other grain-derived compounds).

These biodegradable plastics are suitable only for short-life-cycle applications, i.e. 20% of the total market for plastics, along with a strategy for recycling synthetic plastics, which have qualities that are indispensable for many applications. Currently production of biodegradable plastics stands at a few tens of thousands of tonnes world-wide, but could reach one million tonnes by 2000 if new regulations governing the use of fossil carbon or non-biodegradable packaging are adopted.

7.3.11 Super-absorbent products

Grafted starches that retain up to 1,000 times their weight in water, in disposable nappies, as a talc substitute, or root coating in semi-arid zones.
The potential market is estimated to reach 100,000 t/year in Europe in 2000.

Table 7.2 : Estimated potential market for starch in EU-15 during 2000

Potential Markets	Millions tonnes per annum Starch
Paper making	1.4
Plastics/detergents	1.1
Fermentation	1.2

7.3.12 Sugar Market

The most important chemical-pharmaceutical application for low-molecular carbohydrates like saccharose and glucose is based on the fermentative conversion of the carbohydrates by micro-organisms into industrial usable products. Results of the bioconversion by the enzymes of bacteria and yeast are alcohols (ethanol and others), organic acids (citric acid and others), the biopolymers polyhydroxybutanoic acid (PHB) or polylactic acid (PLA), antibiotics, vitamins and others products. Beside the production of synthetic materials, especially polyurethane, and of sugar surfactants like alkyl polyglucosides, production of N-methyl-glucamides and saccharose fatty-acid ester is significant. Alkylpolyglucosides and N-alkylglucamides are used in considerable quantities as surface-active components in modern detergents and washing-up liquids and saccharose fatty-acid ester is mainly used in the cosmetic field. However at current oil prices, sugar-based products are often uneconomic compared to petrochemical products.

The direct chemical modification opens up further possibilities of refining sugar. The most interesting aspect for the production of synthetics is its polyfunctionality. The large number of reactive hydroxyl groups predestines sugar among others for the synthesis of polyester or polyurethane. Examples are the use of saccharose or its derivatives as prepolymers for polyurethane HR-foams.

Inulin is extracted from chicory in a similar way as saccharose from sugar beet roots.
Non-food uses require inulin transformation either by fermentation or enzymatic treatment or chemical modification to ethanol, acetone-butanol, polymers, surfactants, plastics, stains, etc. Fructose dehydrogenation produces the 5-hydroxymethylfurfural (HMF) interesting for furanic oligomers, which are used as sun protectants, anti-fungal or anti-microbial compounds. HMF re-hydration leads to levulinic acid formation, useable as herbicide, as motor

additive precursor and enables the production of polyesters and polyamides. Isolated by chemical oxidation, dicarboxy inulin can replace polyphosphates in detergents.

7.4 Barriers to Progress

7.4.1 Crop production

It has been postulated (section 7.3) that European demand for carbohydrates is increasing and that there is potential to replace imported products. There appear to be few scientific limitations to the increased production of existing carbohydrate crops in Europe but significant EU imposed constraints. General increase in productivity has consistently occurred as the result of plant breeding and improved agronomy. It is important that sufficient input continues to improve productivity and reduce inputs through an improved understanding of individual crop physiology. New plant breeding techniques need to be adopted to speed up the production of crop types containing a high content of specific carbohydrate products to ensure changing market requirements can be met. A specifically target should be to elucidate the precise roles and relative importance of the enzymes responsible for controlling starch synthesis in order for the variability in starch types (primarily the ratio of amylose and amylopectin) to be exploited commercially. In potatoes the creation of a type which produces pure amylose starch is a high priority. An increased crop area is likely to be the most positive method of increasing production.

Chicory is much less developed crop than sugar beet and needs a greater improvement to enable it to become as productive. The number of carbohydrate crops are limited, the expansion of existing knowledge on barley, oats and peas and the development of new crops such as quinoa and sweet sorghum would improve biodiversity on the farm, with rotational benefits in terms of maintaining soil fertility and pest and disease control.

To improve attractiveness to processors, attention should be given to meeting crop quality criteria, uniformity and volume of supply.

The carbohydrate extraction industry is largely based on old technology, with high-energy requirement, the development of improved extraction technology needs to offer cost savings, improved environmental practice and the ability to handle an increasing range of product types.

The overall value of carbohydrate crops depends on the market for crop by-products. Traditionally these have been used as animal feed but increasingly higher value by-products need to be produced to ensure the economic efficiency of the whole crop.

7.4.2 Industrial Use

While a considerable number of industrial uses for carbohydrate crops have been identified, increasing effort is needed to develop higher value products and to improve the efficiency of industrial conversion processes. This should include optimisation of fractionalisation of all crop components. Particular emphasis is needed in the development of 'green products'. There is a need for stronger collaboration between the chemical industry and carbohydrate experts to develop product technologies to deliver new product and production processes.

7.4.3 Economic

Price is a major barrier to development. European carbohydrate prices are not competitive in comparison with the world market prices and fossil fuel sources of carbon.

The impact of Agenda 2000 on the production of non-food carbohydrate is likely to be negative for agricultural producers but positive for carbohydrate processors. The end result could be a reduction in the availability of European produced materials.

7.4.4 Environmental

Carbohydrate crops produced by gene transfer, offer a potential to meet industry demands but are currently unacceptable to the general public. It will be necessary to devise acceptable environmentally friendly production practices to minimise pollen transfer and public anxiety to enable commercialisation of these types.

Much of the benefits of products derived from crop carbohydrates are built on biodegradability. These benefits must be seen to be maintained in all new products and consistency of biodegradability improved.

The environmental benefits of products derived from crop carbohydrates are poorly communicated to the general public. Education coupled with EU wide schemes to label environmental friendly products [as already exist in some countries] would enhance consumer demand.

7.4.5 Legislative

To enhance the development of crop derived carbohydrates and to meet International Agreements on Climate Change and Biodiversity an EU legislative framework should be established. This would be particularly aimed at extending the legislation with regard to identifying sustainable and biodegradable products and taxation of non-biodegradable packaging.

European List of Notifiable Chemical Substances Regulations (ELINCS) and the European Inventory of Existing Commercial Chemical Substances Regulations (EINECS), are a major burden and constraint on industrial development and exploitation of new feed stocks from plants. Consideration should be given to ameliorating its impact for large and small-scale industries, otherwise R&D investment in new products will be seriously impaired.

7.4.6 EC Actions

Review impact of Agenda 2000 on carbohydrate production and processing industry with a view to stimulating production.

Ensure ongoing rebate mechanism for starch production and use.

It would be helpful to long term research and investment by industry if the EU could produce a definitive long-term status governing industrial crops and ensure integration of policy making in EC.

There is continuing need for EU support of research and development, particularly to help overcome scientific/technical barriers. More of this support should be directed towards pilot projects to bridge the gap between scientific small-scale developments and full commercialisation.

7.4.7 Communication

Communications between the main participants in the non-food carbohydrate, farmers, seed vendors, storage operators, research bodies, crusher, refiners and industrial users need improvement. Only by multi-path communication will confidence and requirements of all parties be defined and understood.

Communication of the new carbohydrate products and their environmental benefits to industrial and domestic users will overcome the lack of knowledge and enhance product demand.