Harvesting the sun

Gerald van Engelen, general manager, and **Harry Raaijmakers**, R&D manager at **Cosun Biobased Products** introduce carboxymethyl inulin

In the near future more sustainable resources will replace fossil-based raw materials on a huge scale. A very important sustainable, or better renewable, source for chemicals and materials will be biomass.

The biobased economy, in which biomass is used on a large scale as a raw material for energy and chemicals, will have a major influence on markets and business in many industrial sectors and thus also on agro-food companies like Royal Cosun. This article covers Royal Cosun's strategy and activities in this field.

Royal Cosun has been processing agricultural raw materials into food ingredients for over 100 years. Side streams are sold as feed or valorised as non-food products like bio-ethanol, bio-methane, starch derivatives, fertilisers, speciality chemicals and raw materials for the chemicals industry. Within the agro-food industry, there is a growing interest in non-food application of agricultural raw materials and products in the biobased economy.

Biobased economy

The environment and sustainability are of growing concern and increasing awareness in society and governments. This is related to climate change, the environment in general, future scarcity and costs of fossil-based raw materials and dependence on politically unstable regions for the supply of these raw materials, plus the need for rural development in both developed and poor countries and the impact of economic development in upcoming regions.

All this is leading to policy and legislation at both regional and global level to stimulate a more sustainable sourcing and supply of food products, energy, chemicals and materials. Renewable energy sources like solar and wind power and biomass for energy, chemicals and materials are essential to meet these objectives.

In addition to legislative and political drivers, increasing market demand for more sustainable products is driving this development autonomously. Examples include the detergents markets in Europe and the US, which are becoming more and more 'green', and the water treatment industry, which is increasingly using environmentally friendly chemicals.

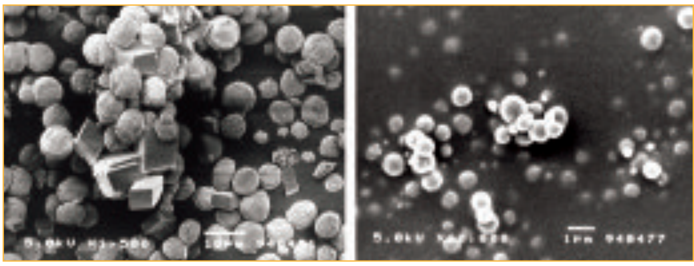

Figure 2 - Crystal growth inhibition with CMI

The biobased economy is unstoppable. It will seriously affect current supply chains and business structures and will push technology and market development in all global regions. In a few centuries time, mankind might look back on the fossil-based era as nothing more than a short interruption of the biobased economy.

Strategic aspects

In order for a region to be a successful player in the biobased economy, various strategic aspects are of importance. Firstly, in those areas where the costs of production of raw materials are high, like the Netherlands, it is crucial to focus on high value products and to develop biorefinery concepts that lead to 100% utilisation of the raw materials.

Secondly, it is evident that R&D investments are needed for the development of the necessary technological competences, know-how and IP position. For instance, pre-treatment technologies for biomass, selective (molecule-targeted) separation and conversion technologies are all relevant.

Finally, the simultaneous technology and market development is complex and requires strategic partnerships with companies throughout the whole value chain from crop via industry to consumer. Complementary technological competencies and combined market knowledge are required to generate synergies, reduce risk and costs and speed up technology and business development.

True innovations are essential for Europe and the US to stay ahead of the growing competition from Asia. The biobased economy is offering new opportunities for innovative products and new business concepts.

Cosun Biobased Products

Cosun Biobased Products was established to develop and operate the business activities in line with the development of the biobased economy for Royal Cosun. Its business scope is the development, manufacturing and marketing of plant derived products for non-food applications. The company's portfolio products are in different stages of development: from technological research to a combination of technology and market development, and finally to day-to-day business.

Some examples of products Cosun is working on are carbohydrate-based plasticisers, natural microfibre-reinforced composite materials and

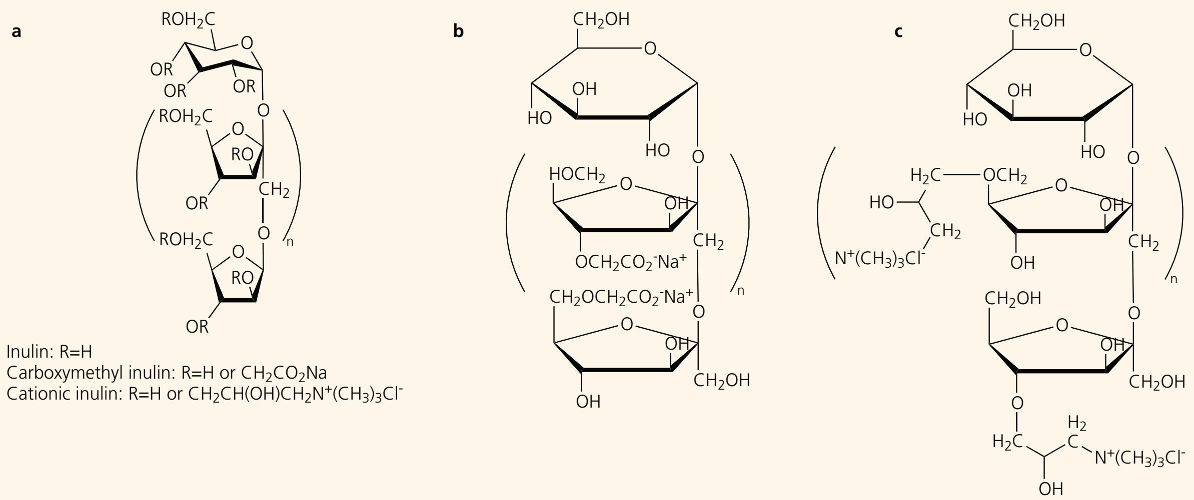

Figure 1 - Structures of inulin (a), carboxymethyl inulin (b) & cationic inulin (c)

furan building blocks for new polymers. Among those already marketed and commercially available are bio-ethanol, bio-methane, green fertilisers, soil topping based on potato peel and starch derivatives which are used as wallpaper glues, in paper and carton and in drilling muds.

Cosun is commercialising inulin derivatives such as carboxymethyl inulin and cationic inulin, which are based on the polysaccharide inulin, extracted from the chicory root. Inulin is a linear polydisperse polysaccharide consisting mainly, if not exclusively, of D-fructose molecules linked by β(2-1) bonds.

A glucose molecule typically, though not necessarily, resides at the end of the fructose chain linked by an α(1-2) bond. Figure 1a shows the structure of inulin. The chain lengths of these inulin molecules range from two to 60 units, with an average degree of polymerisation of about ten.

The D-fructose units of the inulin molecule contain three reactive hydroxyl groups per monosaccharide unit. The reactivity of these groups is much higher than those of starch or cellulose, so it is possible to prepare highly functionalised inulin derivatives in just one step using water as solvent.

In addition, inulin derivatives are more flexible than their corresponding starch and cellulose derivatives, thanks to the higher conformational flexibility of the inulin backbone which arises from a methylene group in the glycosidic linkage between the D-fructofuranose units. This extra flexibility contributes to the physical properties of the inulin derivatives.

Inulin derivatives

The chemistry of inulin has been explored for several years. There are numerous ways to synthesise inuline derivatives, mostly by applying modification techniques already know from cellulose and starch derivatisation. Examples are: esters, ethers, oxidised products and cross-linked derivatives.[1] Table 1 shows most of the inulin derivatives described in the literature.

Table 1 - Inulin derivatives

Inulin ethers	Inulin esters	Oxidation products	Miscellaneous
O-Carboxymethylinulin	Amino acid esters (glycine and lysine)	Dialdehyde-inulin	Inulin carbamate (long chain aliphatic)
O-Cyanoethyl inulin	Acetylated inulin	Dicarboxy-inulin	Inulin xanthate
O-Carboxyethyl inulin	Acetylated O-carboxymethylinulin	6-carboxy-inulin	Inulin phosphate
O-aminopropyl inulin	(Partial) long chain aliphatic acid esters		6-amino 6 deoxy-inulin
O-(3-amino-3-oxopropyl)-inulin	Methacrylate esters		Inulin sulfates
O-(3-hydroxyimino-3-aminopropyl)-inulin	Trans 4,6-cyclic carbonate esters		
O-allyl inulin	(partial) aliphatic Alkenylsuccinic acid esters		
O-(2-hydroxyalkyl)-inulin			
O-(2-hydroxypropyl-3-(trimethylammonium chloride) inulin			
O-(Diethylaminoethyl) inulin			
O-methyl ether			
Inulin-O-3-propylimino-bismethylene phosphonic acid			

The best known inulin derivative is carboxymethyl inulin (CMI, Figure 1b), which Cosun markets under the brand name Carboxyline. CMI is produced via a reaction of inulin with monochloroacetate under alkaline conditions.[2]

In this classical Williamson's etherification reaction, products with various degrees of substitution (DS) are made, ranging from an average of 1.5-2.5 carboxymethyl groups per monosaccharide unit. Sodium glycolate and disodium diglycolate are the main by-products after sodium chloride. Reaction efficiencies of 67-86% are obtained for CMI, with a DS of 2.5 and 1.5 respectively.

Generally, the higher the DS the more functional groups and the better the performance of the molecule. CMI is an excellent threshold scale inhibitor for various types of scaling due to its three main functionalities: complexing of metal ions, crystal growth inhibition and dispersancy.

Figure 2 shows the clear effect the presence of CMI has on the amount, size and morphology of $CaCO_3$ crystals being formed. The mechanism behind this phenomenon is that CMI is able to adsorb on the surface of the growing crystal, thus causing severe steric hindrance on the growth layers of the crystal.[3]

Carboxyline CMI has been applied for many years as a scale inhibitor against carbonate and sulphate in various industrial applications, such as detergents, oil and gas, water treatment, paper and pulp and drinking water. Its excellent safety profile, renewable origin, biodegradability and being both phosphorus- and nitrogen-free are all clear advantages in terms of sustainability and will help to prevent future legislative issues arising.

The synergies obtained fron CMI with other ingredients have led to cost-efficient formulations. And, with the inevitable future scarcity of phosphate rock and the near end of cheap crude oil, prices for fossil-based products are expected to increase further, resulting in an even better competitive cost-performance for CMI.

Another inulin derivative making its first steps into the market is cationic inulin with the brand name Catin (Figure 1c). This is produced via a reaction of inulin with chlorohydroxypropyl trimethyl ammonium chloride (CHPT), which, like carboxymethylation, is carried out in water under alkaline conditions.

The reaction proceeds through the rapid formation of a reactive epoxide (glycidyl trimethylammonium chloride), which is opened by the attack of a nucleophilic alkoxy group of the inulin molecule. Reaction efficiencies of 85-95% are obtained for products with a DS ranging from 0.35-1.5, due to the high reactivity of the inulin molecule.

Cationic inulin has, like other cationic polymers, the ability to adsorb on surfaces and consequently charge a surface positively or to neutralise negatively charged surfaces. Hence, its obvious fields of application are fabric care (softening) and hair care (conditioning), but it can also by applied as coagulant in water treatment and separation processes.

Conclusion

The growing interest in sustainability is manifesting itself in many ways. Besides legislation and increasing market demand for environmentally friendly products, all kinds of concepts now qualify the environmental impact of products and companies. Terms like cradle-to-cradle, carbon footprint, carbon-neutral, climate-friendly, green, life cycle analysis and so on all refer to one key aspect: the drive for sustainability.

All these principles generally try to deliver an overall sustainability score based on multiple indicators: biodegradability, toxicity, energy and water consumption for manufacturing, CO_2 balance, renewability, etc. Of these indicators renewability is the only one guaranteeing future supply. For energy, mankind can rely on several renewable resources, like wind energy, solar power and biomass. For the sustainable supply of chemicals the future is inevitably biobased.

References

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