A SURVEY OF VALUE ADDITION IN THE SUGAR INDUSTRY

WALFORD S N and MOREL du BOIL P G

Sugar Milling Research Institute, c/o University of KwaZulu-Natal,
Howard College Campus, Durban, 4041, South Africa
swalford@smri.org pduboil@smri.org

Abstract

A review of the global status of value addition (other than fuel ethanol and co-generation) in the sugar industry shows that several value-added commodity chemicals are currently produced from sugar feedstocks. These include sucrose acetate isobutyrate (primarily food applications), surfactants (food and cosmetic sector), organic acids such as citric and gluconic acid (mainly food applications), lactic acid (mainly food applications but increasingly biodegradable polymer applications) and polyols (food and pharmaceutical applications). A number of products are produced on a smaller scale due to the cost of production limiting the potential market. These include polysaccharides (e.g. xanthan gum and pullulan), oligosaccharides (e.g. fructose oligosaccharides – FOS) and industrial chemicals (e.g. itaconic acid). Development of the biorefinery concept has resulted in lignocellulose feedstocks such as bagasse being targeted to produce strategic platform chemicals that have been identified as replacements for petrochemical products.

Keywords: value addition, biorefinery, lignocellulose feedstocks, review, platform chemicals

Introduction

The global sugarcane industry is a mature commodity-based industry that is faced with the reality that sugar, molasses and bagasse can no longer be regarded as the final products from a sugar mill. Value addition and diversification are increasingly being investigated as possible routes to new markets and making the industry less dependent on a single commodity. This review covers current and potential products and their uses but excludes fuel ethanol and co-generation as these have been adequately covered previously (Wienese, 1999; CaBEERE, 2004; Wienese and Purchase, 2004).

A South African historical overview

The South African sugar industry and ancillary industries relying on sugar or its by-products have been involved in value-added products for many years. A number of these enterprises have been previously reviewed (Cleasby, 1968; Andrews, 1977; Bernhardt, 1993) and typical applications are discussed below.

Fermentation derived products

Fermentation of sugars has been a mainstay of the South African sugar industry since its inception in the 1850s and a variety of products have been, and are, currently made by fermentation techniques. These include:

- *Alcohol.* This was first made from final molasses in the 1860s at the Umgeni Distilleries (*Historical Overview of the South African Chemical Industry: 1896-2002. The Chemical* *and Allied Industries Association*. http://www.caia.co.za/chsahs04.htm). Natal Cane By-Products (NCBP) was established in 1917 to produce commercial alcohol, methylated spirits and ether (Anon, 1931). Some of the commercial alcohol was used in a motor fuel known as 'Natalite' (a blend of 60% of 96% alcohol and 40% ether) between 1917 and 1927. This was superseded by 'Union Motor Spirit' – a blend of 50% absolute alcohol and petrol (Anon, 1937) that was available until the 1960s (Hayes, 1977). National Chemical Products (NCP), based in Germiston, also produced alcohol from molasses which was used in a fuel mixture sold by SATMAR, in the then Transvaal. Alcohol was also used for vinegar production by fermentative oxidation (*Historical Overview of the South African Chemical Industry: 1896-2002. The Chemical and Allied Industries Association*. http://www.caia.co.za/chsahs04.htm). Diversification by NCP resulted in molasses being used as the basis for an acetone-butanol-ethanol (ABE) fermentation using *Clostridium acetobutylicum*. This plant was closed in the late 1980s due to the cheaper solvents that resulted from the commissioning of the Sasol plants at Secunda. Liquid waste streams from these types of fermentations (known as vinasse or dunder) are rich in salts (particularly potassium) and other organic matter. Disposal can be a problem. Dunder can be used directly as a form of fertilizer or evaporated to give concentrated molasses solids (CMS) and sold for use as concentrated liquid fertilizer (Turner *et al*, 2002).

- *Food yeast,* or Baker's yeast, has been made on a commercial scale in South Africa since the early 1920s (Anchor Yeast, 2005, http://www.anchor.co.za). Currently South African yeast products are used locally and exported for a diverse range of industries including baking, brewing, wine and whiskey. Some of the waste stream is broken down to release soluble amino acids and proteins and concentrated to yield edible spreads such as Marmite®.
- *Single cell protein* (SCP) is the microbial biomass or proteins obtained from processes in which bacteria, yeasts, other fungi or algae are cultivated in large quantities for use as a protein supplement in animal feed or human nutrition. The most common process is based on the utilisation of torula yeast (*Candida utilis*). NCBP produced food yeast from molasses on a commercial scale, for both human and animal consumption, from 1955 until the mid-1990s. A two-ton per day pilot plant, based on hydrolysed bagasse, was erected and run at Malelane. SCP was produced for animal feeding trials and for estimation of the capital investment required for a full-scale plant (Bernhardt and Proudfoot, 1990).
- *Lysine* is an essential amino acid required in the diet of mono-gastric animals such as chickens and pigs. Locally, synthetic lysine is produced using a fermentation route based on a classically mutated micro-organism at the SA Bioproducts plant completed in 1995 in Umbogintwini, Durban (this was previously the AECI plant). Feedstocks for this fermentation are corn steep liquor and low ash High Test Molasses (HTM) produced by Hulref (van Walsem and Thompson, 1997). Some research into other suitable carbohydrate sources within the sugar industry has been reported (Bernhardt, 1998; Fechter *et al*, 2001).

Bagasse derived products

Bagasse has been used as the raw material for a number of products and further processing. These include:

- *Animal feed.* Bagasse is a source of roughage which compares favourably with lucerne, ground maize cobs and cottonseed hulls in terms of digestibility. The absorbent properties of dried, milled bagasse make it an ideal carrier for molasses, a relatively inexpensive energy source containing minerals and vitamins. Two commercial animal feed producers use combined bagasse and molasses. Voermol Feeds was commissioned adjacent to the Maidstone mill in 1963 (Anon, 1963) and Molatek Feeds adjacent to the Malelane mill. NCBP produced a dried molasses powder marketed under the name 'Kalori 3000' for many years (Anon, 1979a).

- *Pulp and Paper*. Although bagasse is not as good as timber for the production of paper due to the higher ash content and shorter fibres, the first pulp and paper operation was commissioned in 1956 at the Ngoye Paper Mill adjacent to the Felixton sugar mill. After a particularly well-documented study (Bruijn *et al*, 1974) this plant undertook one of the first industrial applications of the Ritter biopulping treatment of bagasse fibre to avoid deterioration (Andrews, 1977). The mill is today part of the Mondi group. The world's first commercial production of coated paper from bleached bagasse pulp was brought on stream at the Stanger Pulp and Paper mill in 1976 (Anon, 1975; Andrews, 1977). This paper mill, which also produces tissue, is attached to the Gledhow sugar mill that provides some of the bagasse for depithed fibre. The paper mill is now part of the Sappi group.
- *Particle board* is conventionally made from timber products (chips and wood dust). Bagasse fibre can be bound together with resin to form bagasse particle board. This was produced by Hulsakane Ltd (a Hulett company) from 1972 to 1975. The plant was located at the Amatikulu sugar mill that provided depithed bagasse. The board was used in the construction industry (Anon, 1972) until the factory ceased production due to mechanical and profitability constraints. At around the same time, a second board plant came on stream producing a board having smooth surfaces on both sides in contrast to the Hulsakane board (Andrews, 1977). It is currently made by Ultrabord from bagasse at the Malelane mill and is used in furniture making as backing board (Anon, 1978).
- *Furfural*. The only plant in South Africa making chemicals directly from bagasse is the furfural (2-furfuraldehyde) plant that was commissioned in 1972 at Sezela by Smithchem (Pty) Ltd (Anon, 1973; Andrews, 1977). A furfuryl alcohol factory was commissioned in 1980 (Anon, 1979b) and most of the furfural produced is converted to the alcohol and exported (Bernhardt, 1993). Furfural has recently been registered for use as a nematicide (CropGuard®) by Illovo and further use is envisaged (About us. http://www.cropguard.co.za/aboutus/index.htm). Other chemicals isolated and further processed include diacetyl, acetoin and 2,3-pentanedione (Our Products – Description of downstream products. http://www.illovo.co.za/ourproducts/downstreamproducts.htm). Bagasse residue is fed back to the sugar mill boilers as fuel.

Other products

Other value-added applications that have had varied success locally, include:

- *Waxes* have historically been recovered from the filter mud of milling factories processing green cane using simple solvent extraction. These muds contain about half the wax present in cane. Solvents used have included benzene, toluene and petroleum ethers. Extraction from muds rather than from bagasse has been preferred because lower volumes are processed. One of the reasons for the establishment of NCBP in 1917 was for the commercial scale extraction of cane wax at the Esperanza mill. Further plants were installed at Renishaw, Illovo and Tongaat with a central refining plant at Umgeni (Anon, 1947), which later became uneconomic. A pilot scale plant was erected at Darnall in the late 1950s. This burnt down and was never replaced (Anon, 1955; Mitchell, 1979).
- *Sugar alcohols* including sorbitol, mannitol and xylitol are prepared by the hydrogenation of glucose, fructose and xylose. These alcohols can also be used as the starting point for

the preparation of glycols and other chemicals. NCPB erected a sorbitol and mannitol plant in 1980 (Anon, 1984) that ceased production in the early 1990s. TSB were partners in the Polyol Partners consortium that researched glycols production from molasses in the 1990s. A pilot plant was established at Malelane with funding from the Industrial Development Corporation (Friobjarnarson *et al*, 2003; Analysis of polyol production through the use of green renewable technology vs petrochemical technology. http://202.66.146.82/listco/hk/globalbiochem/ cpresent/pre041027a.pdf).

The international perspective

The biorefinery concept

Priority is being given in the research direction of many of the world's leading countries to implementing solutions to the problem of global warming. The implementation of the biorefinery concept is one of the main themes of these solutions. This concept is also central to many of the diversification routes being investigated by biomass-based industries (including the sugarcane industry). A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power and chemicals from biomass and to maximise the value derived from the biomass (Ohara, 2003; Edye *et al*, 2004; Bohlmann, 2005). The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum. This concept is not new. The processing of primary agricultural commodities into a variety of co-products such as food, drink and animal feed (e.g. sugar, alcohol and animal feed, all from sugarcane or molasses) constitutes a biorefinery. The current usage of the concept is that of a processing plant that integrates the essential conversion technologies to produce a range of industrially useful intermediates with less pollution than that associated with petrochemical production (Figure 1, reproduced from http://www.nrel.gov/biomass/biorefinery.html).

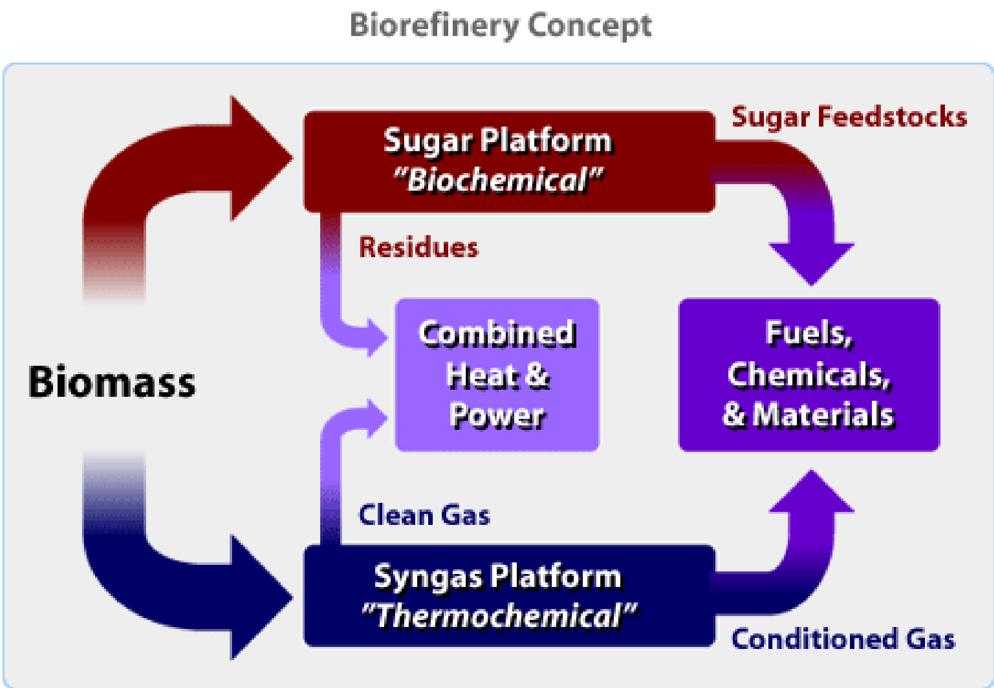

Figure 1. Biorefinery concept.

Value added chemicals from sustainable resources such as plants are integral to this biobased economy (Canuc, 2000; Fahrenkamp-Uppenbrink, 2002; Cargill and Codexis launch research collaboration to develop industrial bioproducts platform. http://www.cargill.com/today/releases/2003/03_05_19codexis.htm; Biopolymers as viable alternatives to common plastics materials. http://www.lactic.com; Werpy and Petersen, 2004). Most of the envisaged chemical streams are based on some form of biotransformation – either fermentation of sugar streams or direct enzymatic transformation of sugars or polymers such as cellulose, hemicellulose or lignin. The sugar-derived building blocks identified as the basis for further traditional chemical processing are shown in Table 1.

Table 1. Identified sugar building blocks (Werpy and Petersen, 2004).

Building block
1,4-diacids (succinic, fumaric, malic)
2,5-furan dicarboxylic acid
3-hydroxy propionic acid
aspartic acid
glutaric acid
glutamic acid
itaconic acid
levulinic acid
3-hydroxybutyrolactone
glycerol
sorbitol
xylitol / arabinitol

Global trends in the sugar industry

The main countries supporting innovative research on by-products from sugarcane include Australia and the USA, with Cuba showing signs of re-establishing by-products research. Brazil and India are showing some interest in expanding on traditional by-products routes. The development of high-value by-products would probably require a co-ordinated effort by both industry and government, and would involve institutions outside the sugar industry.

- *Australia.* Most research funding into the sugar industry has been from the Australian government's Sugar Research and Development Corporation (SRDC). One of the aims of the Corporation is to 'diversify the income stream from the products of sugarcane, primarily by broadening the product base' (SRDC http://www.srdc.gov.au). Diversification projects undertaken over the last 10 years include:
  - the evaluation of the ZeaChem ethanol process. (Blinco *et al*, 2003; Edye *et al*, 2004; Lavarack *et al*, 2004).
  - the evaluation of the Ecopulp process (Lavarack *et al*, 2005).
  - extraction of aconitic acid using supported liquid membranes and the recovery of organic acids from fermentation broths (McMurray and Griffin, 2002; Blinco and Doherty, 2005).
  - acid hydrolysis of sugarcane bagasse (Lavarack *et al*, 2002).
  - cane separation technology (Allen *et al*, 1997).
  - preparation of bagasse pulp (Rainey and Clark, 2004).
  - cane wax extraction and refining (Askew *et al*, 1999; Valix, 2004).

An alliance of university, sugar industry research groups, federal and state governments and commercial expertise (Co-operative Research Centre for Sugar Industry Innovation through Biotechnology – CRC SIIB) was formed in 2003. The objective was 'to add new value to Australian sugarcane'. It is strongly biotechnology oriented, but projects relevant to sugarcane value-addition (CRC SIIB – Programme 2 http://www.crcsugar.com) focus on:

- assessing the feasibility of lactic acid production in the sugarcane industry as an intermediate for polymer and plasticiser production.
- the utilisation of bagasse for the production of lignin-based products.
- the use of sucrose phosphorylase for the conversion of sucrose to biodegradable detergents.
- surveys of sugar factory products and by-products for commercially interesting bioactive flavonoids for nutraceutical and pharmaceutical applications.

The CRC SIIB Biorefinery philosophy is outlined in Figure 2 (reproduced from http://www.crcsugar.com/?p=3.2) with a demonstration pilot plant biorefinery planned for 2006 (Edye *et al*, 2005).

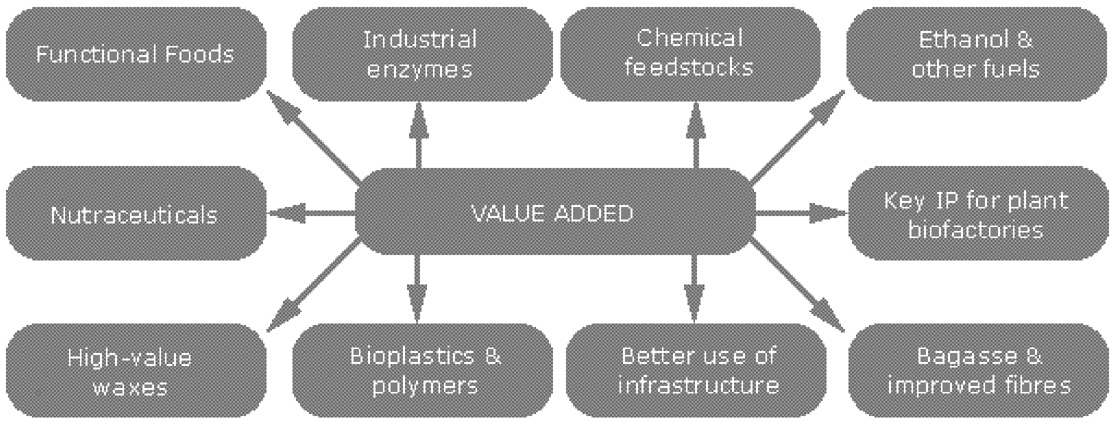

Figure 2. CRC SIIB Sugarcane biorefinery programme.

- *United States.* Scientists from Audubon Sugar Institute (ASI) have participated in by-product applications for many years and have filed several patents in this area. These include the hydrolysis of biomass (Day and Workman, 1984), chromatographic techniques for improving sugar quality (Saska and Lancrenon, 1995; Saska, 2000, 2001; Saska and Chen, 2002), recovery of glycerol or inositol (Kampen, 1993a,b; Saska and Diack, 1996), the production of dextranase (Day and Koenig, 1988), the production of clinical-grade dextran (Day and Kim, 1993) and the production of isomaltooligosaccharide nutraceuticals (Day and Chung, 2004). Their overall by-product strategy outlined in Figure 3 (Taylor, 2000) has many similarities with the Australian direction outlined above.

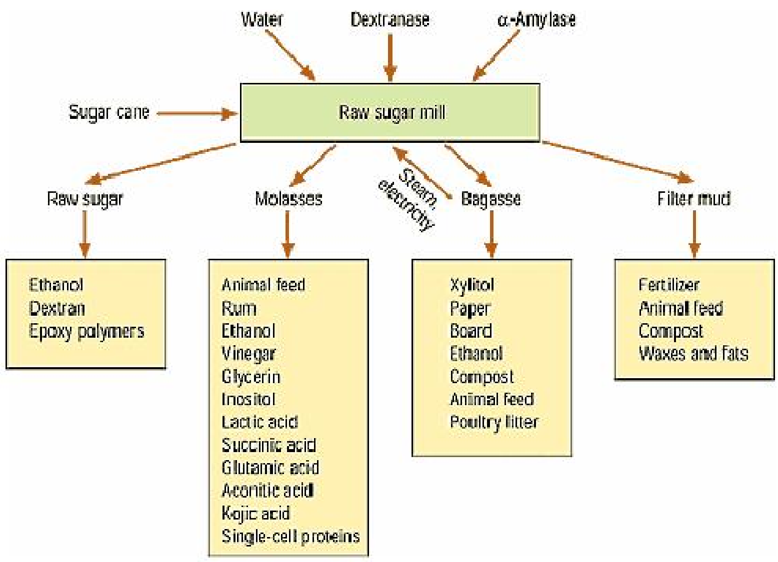

Figure 3. ASI Biorefinery concept.

The AgCenter at Louisiana State University (LSU) has shown that bagasse can be used to make value-added non-woven textiles by carding and needle-punching pre-treated bagasse fibre (Producing nonwoven materials from sugarcane. *Louisiana Agric Mag* (Fall) http://www.agctr.lsu.edu/en/communications/publications/agmag/Archive/2002/Fall/Producing+Nonwovent+May+Materials+from+Sugarcanehtm; Chen *et al*, 2004; Anon, 2005a). The product is suitable for horticulture (degradable pots and erosion mats) and animal bedding. ASI has received a federal grant (shared with Michigan Biotechnology Institute) from the US Department of Energy (DOE) to study the conversion of sugarcane by-products into products of significant value, such as fuel replacement and speciality chemicals. Progress has been presented recently (Tiedje *et al*, 2005). Currently ASI is investigating polymers and polysaccharides from sugarcane. This includes the development of new technology for the pilot plant production of glucooligosaccharides and lactic acid (Anon, 2005b).

- *Cuba.* Although once strong in by-product research, activity at the Cuban Institute for Research on Sugarcane Derivatives (ICIDCA) has recently focused on pharmaceutical research such as policosanol. ICIDCA is in the process of diversification and drawing on its knowledge base. Current research includes developing by-products from bagasse and molasses. These include animal feed, yeast, bagasse board, paper pulp, furfural and dextran. Power generation is receiving attention.
- *Brazil.* Although Brazil's main focus has been on the production of ethanol (fuel and potable), small by-product industries have been established (pulp/paper, lactic acid, citric acid, animal feed and monosodium glutamate (MSG)) and there is currently a research shift to diversify into other by-products (BCG report to Canegrowers: Review of constraints on Industry competitiveness and innovation. *Boston Consulting Group*. http://www. canegrowers.com.au/FileLib/BostonPowepoint.pdf). Copersucar operated a pilot plant producing 50 tonnes/year of polyhydroxyalkanoates (PHA) and has recently announced plans for a 4000 tonnes/year factory (From fuel to plastic, Brazil unveils future of sugarcane. *Truth about trade and technology*. http://www.truthabouttrade.org/article.asp?id=5481).
- *India* has a number of plants producing a variety of by-products, many of these on a small scale. There are up to 560 plants in India making use of bagasse, molasses or filtercake to produce paper, particle board, ethanol, yeast, citric acid, lactic acid and ephedrine (Rao, 1999).

- *Taiwan's* sugar industry has lost most of its former vitality as the state-run Taiwan Sugar Corporation (TSC) and has diversified into areas other than sugar (Chiu and Huang, 2000). Some research is conducted by the Products Development Department where the only sucrose-based value-added product currently produced is fructooligosaccharides (FOS) (Yang, 2001; Liou, 2003).

Review of sugar derived chemicals

Sucrochemicals

Sucrochemistry is that branch of science and technology that aims to bring added market value to sucrose by chemical methods. It has long been known that sucrose is the world's purest large volume tonnage organic chemical. The American sugar industry created the Sugar Research Foundation (SRF) in 1943 that had as one of its original purposes the creation of new markets for commodity sugar. A comprehensive review of the work of this Foundation alludes to the many applications for which sugar can be, and is, used (Kollonitsch, 1970).

The basis for the reactivity of sucrose is the eight hydroxyl groups present on the molecule (see Figure 4). Three are in primary positions (-CH_2OH) and five in secondary positions (-CHOH-). In general the three primary hydroxyls have greater reactivity but prove difficult to react exclusively. This has been a major drawback in sucrochemistry.

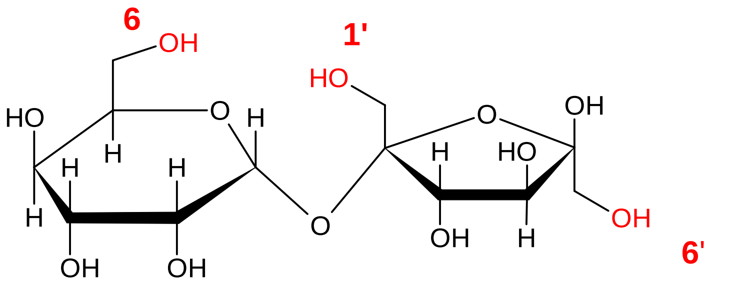

Figure 4. Sucrose structure showing the three primary hydroxyl groups (6, 1', 6').

Synthesis of an enormous number of sucrose derivatives is possible. Substitution with just one type of group could theoretically give 255 different compounds and with mixed groups the number becomes astronomical. The alcohol group can undergo a number of derivatisation reactions that can lead to the formation of esters, ethers and substitution derivatives (Figure 5). Sucrose is readily degraded by acids, oxidizing agents, alkalis and catalytic hydrogen to compounds of lower molecular weight.

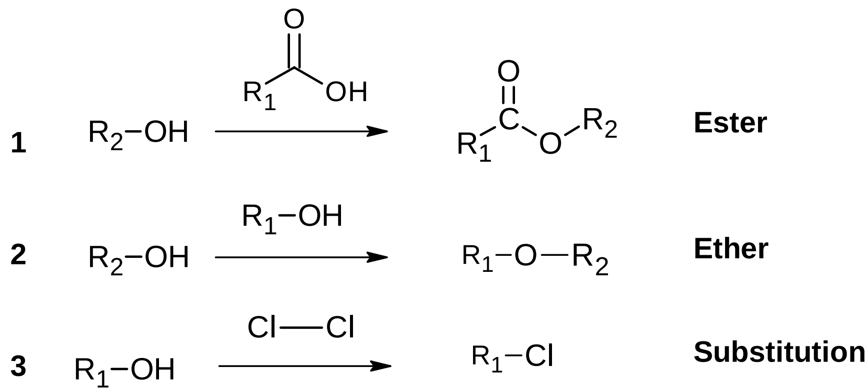

Figure 5. Possible derivatisation reactions of the alcohol group.

The following gives an indication of the current value-added compounds made from sucrose on a commercial basis.

- *Sucrose esters* are ideal non-ionic surfactants (a type of compound that can greatly reduce the surface tension of water when used in very low concentrations). The main sugar molecule is hydrophilic, whilst the attached fatty esters are hydrophobic. Two distinct processes have been adopted for the preparation of the esters.

  The process of using a solvent in which both the sugar and methyl esters of fatty acid are mutually soluble was first described in the 1950s and 1960s (Osipow *et al,* 1956; Hass *et al*, 1959; Meith and Linow, 1967; Iwatsuki, 1968). Solvents include pyridine, dimethyl formamide (DMF), dimethyl sulphoxide or propylene glycol. These solvents are expensive and toxic. After reaction is complete, purification of the final product to remove traces of these solvents becomes expensive. The most common solvent used is DMF, and the process of interesterification using potassium carbonate as catalyst is known as the Hass-Snell process. A modification of this is the Nebraska-Snell process in which a microemulsion of sucrose is formed in a propylene glycol solvent and treated with methyl esters of fatty acids (Kammerlohr, 1968).

  In the solventless process, a heterogeneous mixture of the reactants is reacted to form a final viscous mass that is a mixture of esters, sucrose glycerides and soaps. This can be used directly in detergent formulations. The yields of the esters are lower, which makes isolation and purification of the final product a tedious job. A number of variations exist, including the USDA and Zimmer methods (Kosaka and Yamada, 1977) and the TAL® process (Parker *et al*, 1977).

  Sucrose esters are non-toxic and biodegradable. Food grade esters include sucrose stearate, palmitate, laurate, behenate, oleate and erucate with the quality and application dependent on the level of mono-ester content (1 to 80%). They are used as emulsifiers, stabilisers, thickening agents and preservatives in baking, confectionery, canned foods and beverages (Kawamata, 1968; Various applications of sugar esters to foods. http://www.mfc.co.jp/ english/infor.htm). Applications in the cosmetics field include use in shampoos, creams, lotions and toothpaste (Hill, 2001). Mixed sucrose esters formulated with the sodium salt of carboxymethylcellulose (known as TAL Prolong® and Semperfresh®) have been used as a coating for edible fruit (especially apples and bananas), vegetables and fungi so as to increase the stability during shipping, storage and retail display, and thereby extend the shelf-life (Olorunda and Aworh, 1984, Millera and Krochtab, 1997).

  Recent advances in biotechnology have led to considerable interest in the development of enzymatic methods for the production of surfactants (Plou *et al,* 2002). The most common enzymes used are the lipases, normally in non-aqueous media. Biocatalytic routes for the preparation of sucrose based esters promise to be economical, efficient and environmentally benign (Yan, 2001; Gulati *et al,* 2003; Ferrer *et al*, 2005).
- *Sucrose acetate isobutyrate (SAIB)* is a mixture of esters of sucrose with a composition approximating sucrose diacetate hexaisobutyrate. Approximately 100 000 tons per annum is synthesized for use in the industrial, food, cosmetic and pharmaceutical sectors (Godshall, 2002). Industrial uses include plasticisers in printing inks, in automotive paints and as a clarifier and transparency agent for paper (Anon, 2004). SAIB has been used in the food industry for over 30 years in many countries as a 'weighting' or 'density-adjusting' agent in non-alcoholic carbonated and non-carbonated beverages (Reynolds and Chappel, 1998). SAIB also helps 'fix' fruit juice aroma oils in beverages (Merkt *et al,* 2004). Cosmetic applications include nail coatings, shampoos (Adams, 1976),

conditioners, lipsticks and fragrance fixation that helps prolong the odour of fragrance ingredients (Anon, 1999). SAIB is finding increasing use in the pharmaceutical field in the area of controlled release formulations.

- *Polyurethane* is a resilient, flexible and durable polymer that can take the place of paint, cotton, rubber, metal and wood in thousands of applications across all fields. The principal method of manufacture has been the reaction of a polyol (produced from sucrose) with diisocyanate (see Figure 6).

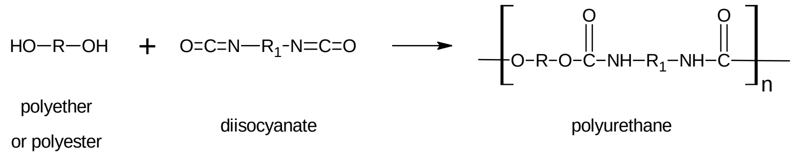

Figure 6. Basic reaction for the formation of a polyurethane polymer.

Depending on the diisocyanate and polyol constituents used, the resulting polyurethane could be a liquid, a foam or a solid form. Sucrose, in combination with an alkylene oxide (such as ethylene, propylene or butylenes oxide) to produce the required polyol, produces rigid urethane foams. These can be used for packaging, furniture and insulation in refrigerators (Frisch and Kresta, 1976; Meath and Booth, 1976; Fuzesi, 1976; Smith, 2000). Commercial products include Veranol® (Dow Polyurethanes) and Pluracol® 975 Rigid Polyol (BASF Chemicals). The high sucrose content, when combined with suitable flame retardants, produces foams having low smoke and good char-forming characteristics (Anon, 2001).

Fermentation products

Fermentation performs complex transformations on organic materials to produce a desired product, by using the metabolic activity of micro-organisms. A biocatalyst (either a cell or an enzyme) converts the organic material to the desired product. Sugars are often used as the raw material for transformation. Advantages of fermentations over normal chemical synthesis include product specificity, lower energy costs and higher yields. The biorefinery concept is dependent on biotransformation using fermentation as the process of choice to produce chemicals for further processing. Some of the important chemicals produced by fermentation techniques are discussed below. Figure 7 summarises this information and highlights the most important uses of the products.

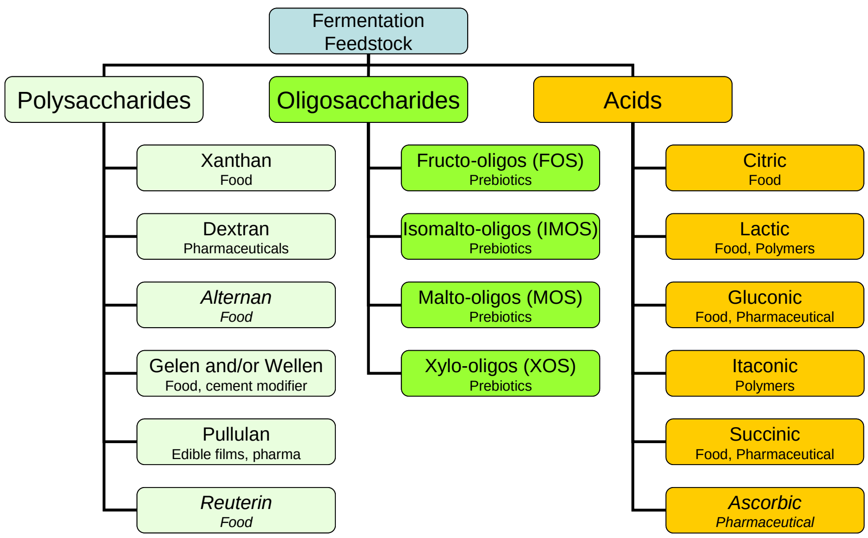

Figure 7. Fermentation products by compound type (compounds in italics are not currently commercially available).

- *Citric acid* is an approved flavouring and preservative used in foods and beverages (E330). Its buffering capacity is used to control pH in household cleaners and pharmaceuticals. Approximately 50% of the production is used by the beverage and soft drinks industry, 20% in the food processing industry and 10% in the pharmaceutical industry, where citric acid is used as an acidulant, buffering agent, taste enhancer and synergist in antioxidant mixtures. The remaining 20% is split between technical applications in various industries as a complex-forming agent, cleaning agent, softening agent, decalcifying agent, derusting agent, as a synergist in antioxidant mixtures and a component in washing powders and detergents. Lastly, small fractions are used in special applications such as citrate buffering of whole blood samples for transfusion. A submerged fermentation using *Aspergillus niger* is used with sucrose or molasses (beet or cane) as the substrate (Kristiansen *et al,* 1999; Pazouki *et al*, 2000).
- *L-Ascorbic acid,* or vitamin C, is produced by the Reichstein chemical synthesis based on d-sorbitol sourced from sugar as the starting raw material. Over the past decade there have been increasing environmental concerns and legislative pressure to develop alternatives to this process. The recent development of an efficient fermentation process for the synthesis of 2-keto-gluconic acid (an intermediate in the Reichstein process) using sucrose and glucose has provided a catalyst for change (Hancock and Viola, 2002; Ascorbic Acid / Vitamin C Technology. http://www.enco.ch/ascorbic.htm).
- *Lactic acid* can be manufactured by chemical synthesis or fermentation. Chemical methods produce a racemic mixture (D and L forms). Catalysed degradation of molasses and sugar has been used for this method (Montgomery and Ronca, 1953; Narayanan *et al*, 2004). Technical grade acid from this process has been used in the textile, tanning and resin and metal industries. The fermentation method of manufacture can produce either the L or D form exclusively. Sucrose, molasses and corn syrup have been the historically preferred raw materials (Inskeep *et al*, 1952; Narayanan *et al*, 2004; Needle and Aries, 1949). However most fermentations are now based on corn syrup as the substrate of choice. Until recently, lactic acid was used primarily in the food industry as a preservative, flavour enhancer, and acidulant for which the global market has been estimated to be about 100 000 tons/year.

  In 1997, Cargill Dow polymers (now NatureWorks) constructed a 140 000 ton/year polylactic acid (PLA) plant based on fermentation of glucose from corn syrup. The PLA is used in fibres and packaging (Canuc, 2002). NatureWorks has recently announced the building of a second plant.
- *Gluconic acid* is formed by the oxidation of glucose. It has been prepared by the inversion of sucrose followed by chemical or electrolytic oxidation of the glucose followed by separation of the acid and unreacted fructose (Docal, 1947; Prescott *et al,* 1953). The current method of preparation is a bioprocess based on glucose syrup employing *Aspergillus niger* in a process similar to citric acid production. However, unlike the citric acid process, where glucose is taken up by the organism, converted to citric acid and exported, gluconic acid is produced extracellularly (Magnuson and Lasure, 2004). It is approved for use in food (E574), feed and pharmaceutical applications. The chelating properties of the acid are useful for use as an industrial chemical. Applications include an additive to improve cement hardening, scale removal in metal cleaning and metal finishing, use in industrial and household cleaning compounds and in the paper and textile industries.
- *Itaconic acid. Aspergillus terreus* is employed for itaconic acid production in a process similar to that for citric acid. Both processes were invented about the same time (Kane *et al*, 1945; Batti and Schweiger, 1963), and both can be conducted in the same manufacturing facility. By contrast with citric, gluconic and lactic acids, itaconic acid is

used exclusively in non-food applications. Its primary application is in the polymer industry, where it is employed as a co-monomer at a level of 1 to 5% for certain products. Itaconic acid is also important as an ingredient for the manufacture of synthetic fibres, coatings, adhesives, thickeners and binders.

- *Succinic acid* and its derivatives are widely used as speciality chemicals for applications in foods, pharmaceuticals and cosmetics. The acid has been highlighted as a potentially important chemical precursor due to its similarity to the petrochemically derived maleic acid and maleic anhydride. It is currently prepared biochemically from glucose using an engineered form of *Anaerobiospirillum succinicproducens* (Guettler and Jain, 1994).
- *Sugar alcohols*, or polyols, are generally made by the hydrogenation of sugars using Raney nickel as the catalyst. However, they can also be prepared by fermentation routes and there has been a general trend away from chemical synthesis towards enzymatic fermentation. Polyols are widely used as low calorie sweeteners and in food applications where the Maillard reaction is undesirable. About 40% of production is used in food processing. The rest is evenly split amongst the pharmaceutical, cosmetic and chemical industries. Commercially produced polyols include erythritol, xylitol, mannitol, sorbitol, maltitol and isomalt.
- *Polysaccharides* and oligosaccharides occur naturally, but many can also be produced from sucrose or inverted sucrose (i.e. glucose and fructose) using suitable micro-organisms (enzymes, bacteria or fungi) and properly selected fermentation conditions, *viz* aerobic/anaerobic, substrate concentration and reactor temperature. They have many applications in the nutritional, medical, food or industrial sectors, e.g. as thickeners, emulsifiers, personal care products, adhesives *etc*. Several polysaccharides have commercial value or potential. Progress in genetic modification of microorganisms has given rise to a host of enzymes that are more tolerant of industrial conditions and often give increased product yield, faster than older methods. Typical polysaccharides include:
  - *Xanthan*. This was one of first polysaccharide thickeners to be tested as a food additive by the then US Food and Drug Agency (now the Food and Drug Administration) and is now a well-developed commercial product. Xanthan is produced extracellularly by the bacterium *Xanthomonas campestris* and has applications from drilling muds to salad dressings – the viscosity is only slightly temperature dependent. Commercially, glucose or starch is fermented in batch culture, but sucrose is also an efficient substrate and molasses has been used as feedstock (Papagianni *et al*, 2001). The gum is recovered from the culture by precipitation with alcohol. Xanthan gum is widely used as a rheology control agent in aqueous solutions and as a stabiliser for emulsions and suspensions, as well as a component of cosmetic and personal care products.
  - *Dextran*. This is a polysaccharide produced from sucrose by *Leuconostoc mesenteroides* or related species. Cuba produces about 400 tonnes/year in a single factory (Almazan *et al*, 1999). The main application is as a blood plasma extender. Dextran was manufactured in South Africa for a short period after World War 2 (Anon, 1951). Day and Kim (1993) have patented a process for the production of dextran polymers of controlled molecular weight by using a mixed culture of *Leuconostoc mesenteroides* and *Lipomyces starkeyi* in the presence of sucrose. The concurrent production and degradation of dextran controls the size of dextran produced and obviates the usual chromatographic fractionation. Clinical grade dextran is formed (Kim *et al*, 1996). Dextran derivatives such as iron dextran (e.g. InFed, DexFerrum, Iron-Dex) are used for parenteral iron therapy, both in human and veterinary fields (Silverstein and Rodgers, 2004). Sulphated dextrans have been proposed as anti-HIV agents (Tandon and Chhor, 2005). Ferucarbotran is a dextran magnetite used as an MRI diagnostic agent. Dextrans are also being developed as a

fibrous non-woven textile for speciality end-uses, such as wound dressings. Dextran is also used in the photographic industry to enhance silver formation and in mining operations as a lubricant.

- *Alternan*. These polysaccharides are glucans with alternating α-(1-6) and α-(1-3) linked glucose residues in the main chains, and are synthesised by alternansucrase expressed by *Leuconostoc mesenteroides*. They are not yet in commercial production, but can mimic gum arabic's bulking action, and patents covering their production exist (Leathers *et al*, 1997; 1998).
- *Gellan*. This is produced by *Pseudomonas elodea* or *Sphingomonas* spp using a fermentation process from sucrose or other carbohydrates (Kanari *et al*, 2002). The presence of acyl substituents influences the gel properties and this allows some degree of tailor-making in the downstream processing and blending. Gellan gels tend to be firm and brittle (similar to agar-agar gels) compared to the soft elastic gels formed by xanthan, and are effective at low concentration. Apart from gelling, it is also used as a suspending agent and texture modifier in a range of foods. Gellan (and some other hydrocolloids) can act as fat-barriers and so be used for oil reduction in fried foods. This polysaccharide is now approved for food use in the USA and European Union, as well as Canada, South Africa and Australia. Trade names include Kelcogel, a constituent of air freshener gels.
- *Welan. Sphingomonas* spp also produce welan – a branched gellan in which the anionic side chains stabilise the helical conformation. As a result, welan gum has excellent thermal stability and viscosity retention at elevated temperatures and high pH. The polysaccharide is available from CP Kelco as K1A96 and has application as a pigment suspender for concrete and as a component of de-icing fluids.
- *Pullulan.* A polysaccharide produced by *Aureobasidium pullulans*. Beet molasses and jaggery have been used as substrates (Roukas, 1998; Roukas and Serris, 1999; Roukas and Liakopoulou-Kyriakides, 1999; Lazaridou *et al*, 2002; Goksungur *et al*, 2004; Vijayendra *et al*, 2001). Fermentation conditions necessary for the production of very high molecular weight pullulan have been described (Thorne *et al*, 2000, 2002). Commercially, it is manufactured by Hayashibara Biochemicals Ltd from various feedstocks including waste product streams. Industrial, food and medical grades are produced. The purified polymer is odourless, tasteless, and non-hygroscopic under normal atmospheric conditions, and can be moulded into three-dimensional solids or very thin films that are glossy, tenacious, resistant to oil/grease, non-toxic, biodegradable, edible, heat-sealable, unaffected by small changes in temperature and practically impermeable to oxygen. It can be used as an edible film, e.g. as the carrier for breath fresheners such as Listerine® PocketPaks. Cade *et al* (2003) and Scott *et al* (2005) have filed patents relating to pullulan film compositions. Pullulan finds applications in foods, pharmaceuticals, cosmetics, chromatographic enzyme purification and in hydrometallurgical processes. The polymer can be woven into fibres and has potential in the production and strengthening of fabrics. Special fishing lines and bulletproof vests are some of the products that contain this polysaccharide. Pullulan has been used to provide the polymer matrix for anion-exchange membranes (Synthesis of anion-exchange membranes using interpenetrating polymer networks with pullulan as polymer matrix. http://academic.sun.ac.za/unesco/PolymerED2002/private/Nguyen%20(4).pdf) and to prepare cross-linked nanoparticles for drug delivery (Gupta and Gupta, 2004). Leathers (2003) has summarised aspects of the production and applications of pullulan and points out that increased demand for pullulan could justify expanded production, resulting in new market niches.
- *Reuteran*. A branched α-glucan produced by *Lactobacillus reuteri* growing on sucrose. Lactic acid bacteria (LAB) are food-grade organisms with GRAS (generally

regarded as safe) status, and *L. reuteri* is able to synthesise large amounts of high molecular weight fructans and glucans. The structure as described by van Geel-Schutten *et al* (1999) and by Kralj *et al* (2005) appears to be very similar to that of the polysaccharide sarkaran first identified by Bruijn (1973) and recently shown to be produced by the fungus, *Phaeocytostroma sacchari* (Morel du Boil *et al*, 2005). However, production from the bacterial source would probably be faster than from a fungal source. Branched chain α-glucans have potential in the field of body weight management (Ekhart *et al*, 2005). Although not in commercial production, it has been suggested that the glucans and fructans produced by *L reuteri* have possible applications in the food industry owing to their bioactive properties.

- *Oligosaccharides.* Physiologically functional oligosaccharides (prebiotics) are mass-produced from sucrose, lactose, maltose and starch derivatives using specific microbial enzymes. Prebiotics are non-digestible food ingredients that beneficially affect the host by selectively stimulating the growth and activity of one species or a limited number of species of bacteria in the colon. These functional oligosaccharides are usually not absorbed in the small intestine, but are fermented in the colon and so provide less energy than carbohydrates in general. Important oligosaccharides include:
  - *Fructose oligosaccharides (FOS).* Commercial forms of fructose oligosaccharides are created by extraction (and hydrolysis) from natural food sources such as inulin from chicory or Jerusalem artichoke (e.g. Raftilose, Raftiline, Frutafit, Frutalose) (Gibson *et al*, 1994; Franck, 2002) or by enzymatic synthesis from sucrose (e.g. Neosugar, Meioligo, Profeed, Actilight, Nutraflora) (Schiweck *et al*, 1991). FOS are widely used to add fibre to food without adding viscosity. They are sometimes added to yoghurt to add a prebiotic effect to a food already containing probiotics (e.g. Bonlé yoghurt range). FOS and other oligosaccharides have been proposed for supplementation of pet, livestock and poultry diets (Doyle, 2001; Flickinger and Fahey, 2002).
  - *Isomaltooligosaccharides (IMOS).* IMOS have application in food, cosmetics and pharmaceuticals. They can be prepared using dextransucrase with sucrose and glucose or maltose as substrates. The molecular weight of IMOS can be influenced by combining dextransucrase and dextranase, analogous to the procedure described above for preparing clinical dextran (Day and Kim, 1993). IMOS can also be prepared by hydrolysing dextran to give a mixture of isomaltooligosaccharides. Such branched glucans are promising replacements for antibiotics in the production of *Salmonella*-free poultry and swine. Researchers at Audubon Sugar Institute, amongst others, have been active in promoting similar applications (Anon, 2002; Anon, 2003; Day *et al*, 2001; Chung and Day, 2002; 2004; Day and Chung, 2004). It is claimed that the technology using a unique strain of micro-organism grown on sugar in the presence of specific inhibitors, results in rapid growth of oligosaccharides at about 1% of the current cost of producing such oligosaccharides (Sugar product may substitute for antibiotic in animal feed. *Louisiana Agric Mag* (Fall). http://www.agctr.lsu.edu/en/communications/publications/agmag/Archive/2001/Fall/Sugar+Product+May+Substitute+for+Antibiotic+in+Animal+Feed.htm). Meito Healthy Friend (MHF) is a mixed feed produced by Meito Sangyo containing dextran, oligo- and polysaccharide fermentation products and has significant effects on weight gain and prevention of *Salmonella* bacteria in poultry and livestock.
  - *Maltooligosaccharides (MOS).* Maltooligosaccharides are linear glucose oligomers and have historically been produced by partially hydrolysing starch (either enzymatically or by using acid). They are more commonly known as glucose syrups and have extensive application in the food and brewing industries. Selection of

different enzymes and hydrolysis conditions enables many tailor-made compositions to be produced (Marchal *et al*, 1999).

- *Xylooligosaccharides (XOS).* Xylooligosaccharides are sugar oligomers made up of xylose units. XOS are non-digestible and have pre-biotic activity. The production costs are comparatively high. XOS can be obtained from processing residual vegetable biomass, e.g. bagasse. Chemical and enzymatic processing is used to effect xylan solubilisation which is then chemically degraded (preferably by steam or autohydrolysis treatments) to yield XOS. Vacuum evaporation is used to concentrate the solution and to remove volatile acids and flavour precursors. The growing demand for functional foods opens promising markets for XOS in many fields such as pharmaceuticals, food and feed applications (Alonso *et al*, 2003).
- *Polyhydroxyalkanoates (PHA).* PHAs are biodegradable polymer materials accumulated intracellularly by bacteria under conditions of nutrient stress. Polyhydroxybutyrate (PHB) is the most common type of PHA, and studies on it have triggered commercial interest in this class of polymers. Bacterially produced polyhydroxybutyrate (and other PHAs) have sufficiently high molecular mass (50 000 to 1 000 000 Da, depending on the bacterium) to have characteristics that are similar to conventional plastics such as polypropylene. PHB can be blended and compounded to give copolymers with many applications. Moulded items include bottles and golf tees. In the form of plastic sheeting they can be used for diaper backings. PHAs have been processed to fibres to create non-woven products and they have application in the food industry. They also have potential, after chemical hydrolysis, to provide monomers such as β-hydroxyacid esters, which can be converted to biodegradable solvents. The monomer units are all in D(-) configuration, owing to the stereospecificity of biosynthetic enzymes. The incorporation of different monomers into PHAs results in a potentially wide range of new polymers with different characteristics. Zeneca and Monsanto used bacterial fermentation to produce poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) commercially using *Ralstonia eutropha* or *Alcaligenes eutrophus* (Biopol), but the high cost of PHA production as a result of high purification cost and low recovery has restricted its widespread production. The production of PHB requires 3 kg of sucrose per kg of final product. In an attempt to reduce the cost of carbon source, various trials using molasses feedstock have been undertaken (Yimaz and Beyatli, 2005; Celik *et al*, 2005; Mercan and Beyatli, 2005).

Other processes

- *Waxes, lipids and sterols.* Sugarcane wax occurs mainly on the outer surfaces of the stalk (rind) and leaves. The wax coating is usually most evident just below the node where it forms a wax ring. The wax is believed to function as a protective coating against moisture loss. Wax content is generally dependent on variety and Rutherford *et al* (1993) demonstrated a correlation between cuticular wax and resistance to *Eldana saccharina* Walker (Lepidoptera: Pyralidae) infestation.

  Although there is probably no longer a market for crude or refined cane wax, there is some interest in isolating the lipid or sterol fractions. Plant sterols (known as phytosterols) have therapeutic value and are used to help lower cholesterol levels. The isolation of sterols from sugarcane skin and bagasse is described by Ito *et al* (1989) and Empie *et al* (2004). Research is continuing in this field.

There has recently also been increased interest in isolating the long-chain alcohol fraction from cane wax. Sugarcane wax alcohols (SCWA) are produced following saponification of a waxy extract of *Saccharum officinarum*. Policosanol is the generic name for a highly concentrated and standardised mixture of five higher primary aliphatic alcohols that occur together in sugarcane wax. Policosanol production was pioneered in Cuba and vaunted as a major success story (Development Cuba: Sugarcane's new promise. *Interpress Service News Agency (Tierramerica)* http://www.havanajournal.com/business_comments/A2379_0_4_0_M). Several patents exist (Dalmer Laboratories, 1999, 2002). The pharmaceutical is reputed to lower cholesterol, amongst other claims, and has been marketed in many countries.

Australian researchers have been focusing on extracting a superior wax and have recently patented a procedure for extracting food grade wax from mill mud (Valix, 2004). The optimisation of cane wax production and the evaluation of its chemistry are on-going research topics (Askew *et al*, 1999). Lower alcohols, rather than petroleum solvents, are generally preferred for the extraction of higher grade waxes (Miyagi *et al*, 1991; Valix, 2004). Supercritical fluid extraction has also been proposed (Inada *et al*, 1987).

- *Pyrolysis.* This is a process in which biomass material, such as bagasse, is rapidly heated to high temperatures in the absence of air. The bagasse decomposes into a combination of solid char, gas, vapours and aerosols. When cooled, most of the volatiles condense to a liquid refered to as 'BioOil'. The properties of 'BioOil' produced from bagasse have been compared to wood-based products (Morris, 2001). The composition of the bagasse 'BioOil' was found to be similar to that of the wood-based product. A patented pyrolysis technique was used in this study (Piskorz *et al*, 1998).
- *Activated carbon* is a widely used adsorbent to purify, decolorise, deodorise, and dechlorinate a variety of liquid and gas streams. It is widely used as a decolourising agent in the sugar industry. Many lignocellulosic agricultural by-products have been successfully converted into activated carbons. Granular and powdered activated carbons have been produced from sugarcane bagasse (Xia *et al*, 1998; Lavarack, 1997; Marshall *et al*, 2000). Activated carbons have been produced on a laboratory scale from compressed South African sugarcane bagasse in a pyrolysis furnace (Devnarain et al, 2002).

Conclusion

The South African sugar industry has a long history of, generally, simple value addition to a variety of output streams from the sugar mill. The production of most of these commodities has matured. As the industry faces the challenge of operating in a mature commodity market, the addition of newer value-added commodities will have to be considered in order to increase the revenue streams. In doing so, the industry will need to embrace the skills required to research and produce these biobased products.

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