non-linear parameter estimation, represent well the process behaviour. A process simulator for studies on computer-based operation should have the capacity to represent adequately both intrinsic process characteristics and practical features of process operation. This means, essentially – (i) processing of non-linear dynamical models, including sensors and final control elements, synchronised with real-time; (ii) efficient mathematical treatment of process non-linearities, such as dead-times; (iii) communications through standard analog and/or serial signals; (iv) simulation of noisy measurements; (v) interactivity in real-time with the operation. One such tool has been developed within the research group.

The theoretical non-linear dynamical model of the crystallization process, implemented in the process simulator, includes growth rate dispersion mechanisms and the characterisation of crystal size distribution (CSD) by its first six linear moments. Values of the state variables (internal temperature, brix, vacuum pressure and level), together with those of other key variables (feed and steam properties) are made available as standard analog output signals, as if they came from industrial sensors. Also, standard analog input signals, corresponding in practice to the commands to the control valves, are received and translated as inputs to the integration routines. Noises can be superimposed to the output signals. Process loads and process characteristic parameters can be changed on-line. With such standard communications and working synchronised with real-time, the simulator provides the environment to which any formal industrial control system can be linked. Or, simply, manual operation can be performed. Studies aiming at the development of new strategies for computer-based crystallizer operation and the relevant operator training on the use of new technologies are now possible at low cost and in a safe environment.

New Autocatalytic Oxidations of Primary Alcohols in Cellulose in Phosphoric Acid

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Homogeneous oxidations at 4°C of cellulose dissolved in phosphoric acid with (i) sodium bromate with a small amount of sodium bromide, (ii) sodium chlorate with a small amount of sodium chloride and (iii) sodium chlorite have been studied. With these reaction systems the primary alcohol groups were completely (>95%) oxidised to carboxylic acids. Undesired ketones due to secondary alcohol groups oxidation were reduced with sodium borohydride. The selectivity observed is explained in terms of common autocatalytic oxidation mechanisms involving the positive hypohalous acidium ions, H_2OCl^+ and H_2OBr^+.

New Compounds From Microbiological Products of Sucrose

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A microbial product of sucrose, a high molecular weight levan, is readily made in high yield and high purity from commercial sucrose, sugarcane and sugarbeet juices and molasses.

Several derivatives of this levan have been synthesized. The characteristics and properties of these polymeric derivatives are described. Applications and uses of the compounds are outlined.

New Synthetic Pathways to C-glycosides

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C-glycopyranosyl compounds exhibit antimicrobial, antifungal, and antitumor activities, most probably based on enzyme inhibition, or interference with cell surface recognition and differentiation processes.

C-glycosidic analogues of that component would be metabolically stable, and thus offer enhanced therapeutic value. Synthesis of a configurational variety of e.g. amino (glyco-pyranosyl) methanes is thus an important synthetic goal. The amino group would allow linking the C-glycoside to a variety of scaffolds.

Our first approach has been to C-link a C-N synthon (HCN or CH_3NO_2) to the anomeric carbon of a natural carbohydrate. We have realised this with cyanide on glycal, on per-O-acetyl sugars and on cyclic acetal protected glycosyl fluorides, prepared by a novel method. The catalytic hydrogenation of glycosyl cyanides presented challenges and new synthetic possibilities. With CH_3NO_2, and 4,6-O-alkylidene protected D-glucose or D-mannose derivatives, we obtained very good yields of cyclic Henry condensation products in THF with a novel catalytic procedure.

The novel reduction of the resulting nitro (4,6-O-benzylidene-b-D-glycopyranosyl) methane with Fe°/Ni° in THF/H_2O/CO_2 readily supplied amino (4,6-O-benzylidene-b-D-glycopyranosyl) methane, which was diasterodiversified into D-allo, D-manno, and D-altro C-glycosides. These approaches fail, however, if prerequisite natural carbohydrate precursors are not available in a given case. Thus, a total synthesis scheme was also initiated.

Phtalimido acetaldehyde diethylacetal and 4-penten-2-ol, with $TiCl_4$, form 2-methyl-4-chloro-6-phtalimido-methyl tetrahydropyran, which was functionalized into phtalimido (6-deoxy-b-D,L-hexopyranosyl) methanes. Chiral extensions of this method are possible.

C-"disaccharides" became available from the Ferrier "dimerisation" of glycals, and from the hydrogenation of glycosyl cyanides.

Oxidized and Carboxy-alkylated Carbohydrates and Some Potential Applications

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Converting carbohydrates into carboxylates or polycarboxylates is an obvious way of upgrading renewables. The (poly)carboxylates obtained may display unique properties or may enter the competition with fossil-based materials such as poly-acrylates.

Methods to introduce carboxylate groups include carbohydrate oxidation and carboxy-alkylation.

Progress in oxidation is still substantial. Some old methods are revised (noble metal catalysis, nitrate/nitrite oxidation) and new methods come to the fore. Here, the amazingly selective TEMPO-catalyzed 6-oxidation of low and high molecular mass pyranose systems will be discussed.