

THE SUCROSE FUEL CELL: EFFICIENT BIOMASS CONVERSION
USING A MICROBIAL CATALYST

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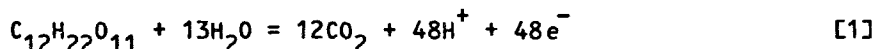
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Sucrose was used as a fuel in a thionine-mediated microbial fuel cell containing *Proteus vulgaris* serving as the biocatalyst in the anode compartment. The measured yields show that under suitable conditions the substrate may be oxidised quantitatively to electricity and carbon dioxide.

INTRODUCTION

In parallel with a renewed interest in conventional fuel cells (Bockris and Srinivasan, 1969), recent reviewers have drawn attention to the biochemical fuel cell as a means of interfacing a biological energy source with conventional electrochemical technology (Aston and Turner, 1984; Wingard, Shaw and Castner, 1982). The 'direct' microbial fuel cell is particularly promising, since it can be used to extract the energy of oxidation of a naturally-occurring fuel such as a carbohydrate with high efficiency (Bennetto, 1984). The mode of action of the fuel cell depends on the use of intact micro-organisms as integral bio-reactors capable of performing a whole range of enzymatic transformations. The organisms operate inside the electrochemical cell under anaerobic conditions, where electrons trapped as intermediates from the degradation of substrate are available for transfer to the anode. These electrons are diverted by a 'redox' mediator to the external circuit, which is completed by a suitable cathode. The result of mediator action is a dramatic increase in the obtainable current.

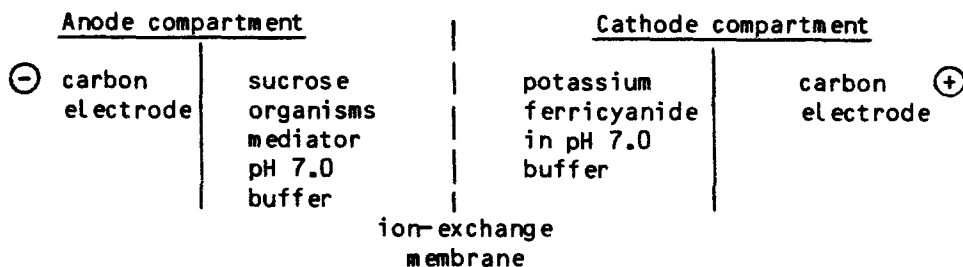
Recent studies have shown that 50-65% of glucose substrate may be oxidatively converted to electricity using *Proteus vulgaris* as a catalyst and thionine as an electron-transfer mediator (Thurston, Bennetto, Delaney, Mason, Roller and Stirling, 1985), while the potential for utilisation of carbohydrate waste products has been demonstrated in *E.coli* fuel cells using lactose in milk whey (Roller, Bennetto, Delaney, Mason, Stirling, Thurston, and White, 1983). In principle, fuel-cell oxidation of sucrose can provide a high electron yield according to the equation



We here present evidence that sucrose can be used most effectively as a fuel, giving coulombic yields which approach the theoretical maximum.

EXPERIMENTAL

The electrochemical cell is formally represented as shown below:



The cell had an anolyte capacity of 15ml. Details of its construction and operation are given elsewhere (Bennetto, 1984; Delaney, Bennetto, Mason, Roller, Stirling, and Thurston, 1984). *Proteus vulgaris* was the preferred biocatalyst on the basis of previous work. The organisms (type B11, NCTC 10020) were prepared as previously (Roller, Bennetto, Delaney, Mason, Stirling and Thurston, 1984) except that the culture medium was enriched with sucrose. Ancillary kinetics studies using thionine as a mediator demonstrated that the organisms can utilise sucrose rapidly and effectively to provide the reducing power needed for application in the bio-fuel cell (Roller *et al.*, 1984). Other sucrose-metabolising organisms were considered for use as a fuel cell biocatalyst, but were found to be unsuitable. *Erwinia carotovora*, for example reduced thionine only *ca.* 0.2 times as fast as *P.vulgaris*, and the coulombic yield from a sucrose-fed fuel cell was only 21%.

The anode compartments were loaded with 30 mg (dry weight) of organism in 0.1M or 0.5M sodium phosphate buffer containing 1 mM

thionine. Cells containing various additions of sucrose in the range 0-30 μmol were discharged at 30°C through standard resistances of 100 ohms (or occasionally 200 ohms). Electrical yields were computed from plots of current vs. time, which gave plateaux in the region of 0.35 V (3.5 mA) as in previous work (Delaney *et al.*, 1984). In preliminary tests on unpurified sugars, cane sugar molasses containing 30% sucrose, with glucose, fructose, oxidised organic material and ash as impurities was used. Carbon dioxide evolved from sucrose oxidation in the fuel cells was flushed from the cells by passage of nitrogen, collected in traps containing 1M potassium hydroxide solution, and estimated by automatic titration as previously described (Thurston *et al.*, 1985).

RESULTS

The efficiency of utilisation of sucrose in the fuel cells was assessed from the coulombic yield, Y per mole of added substrate. According to equation [1] the maximum is 4.63 C μmol^{-1} sucrose. However, the measured coulombic yields (Y_t) require correction for the increment from oxidation of endogenous material of the organisms in the absence of added substrate (Y_e), which was usually 10-15 C but varied from 4-35 C for different batches.

$$Y = \frac{[Y_t - Y_e]}{(\mu\text{mol substrate})} \quad [2]$$

Illustrative results (100 ohm) are presented in the table, where Y is expressed as a percentage of the theoretical maximum from equation 1.

Table: Coulombic yields from sucrose bio-fuel cells

	sucrose (μmol)	total yield Y_t (C)	net yield (corrected) $[Y_t - Y_e]$ (C)	Y (%)
series 1	0.0	4.1	-	-
	5.0	28.4	24.3	105.0
	0.0	4.5	-	-
	5.0	29.7	25.1	108.4
series 2	0.0	35.0	-	-
	2.5	46.0	11.0	95.0
	5.0	57.9	22.9	98.9
	7.5	70.6	35.2	101.4
	10.0	79.4	44.4	95.9

Results for duplicate runs (as in series 1, see table) demonstrate the reproducibility attained in the measurements, though small errors in Y arise from variations in experimental conditions (volume of anolyte, average current/voltage, rate of N_2 -bubbling). It is appropriate (cf. eq.2) to calculate Y from the graph of the corrected yield versus quantity of added sucrose. A plot of this kind, which summarises data from five series of experiments, is shown in fig.1, where the line drawn represents the maximum electrical yield that can be obtained from complete oxidation of sucrose.

From figure 1 it is apparent that, within the experimental errors, the production of electricity from oxidative conversion of added substrate approaches 100% coulombic efficiency, at least for

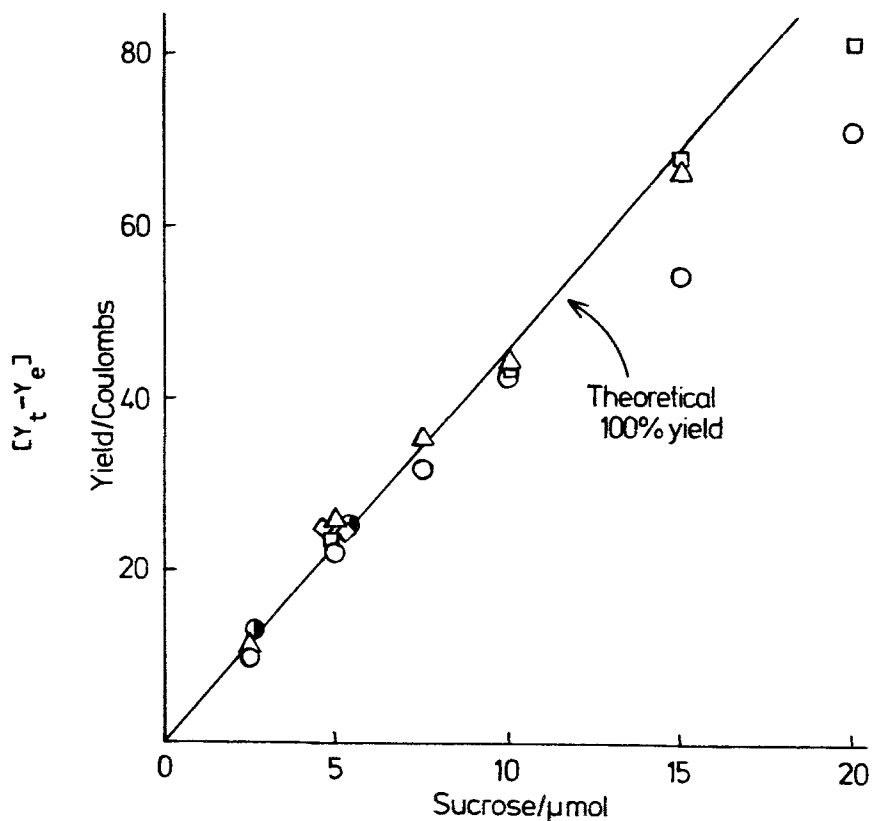


Figure 1 Electrical yield from sucrose-powered fuel cells as a function of sucrose added. \diamond , series 1 (see table); \triangle , series 2; \circ , \bullet , \square , results obtained using organisms giving endogenous yields of ca. 20 coulombs.

smaller amounts of sucrose in the cell. This result is not dependent of the endogenous content of the organisms or the resistive load in the range 100-200 ohm. In some experiments (as in series 1) the 0.1M buffer used was only sufficient to maintain a constant pH when the sucrose oxidised was in the range 0 - 10 μmol . At higher loadings the production of acid in the anode compartment (cf. eq.1) sometimes exceeded the buffering capacity, as indicated by measurements on the cell contents which showed a reduction in pH to 5.5 - 6.0. Where the buffering was insufficient, inhibition of metabolism under acid conditions accounts for some low yields, i.e. points below the line in the range 15 - 30 μmol sucrose. When more concentrated buffer was used (0.5M, as in series 2 above) the pH values remained stable and the linearity of the plot extended to above 20 μmol sucrose. Preliminary tests using molasses suggest that 70% or more of the carbohydrate content is oxidised.

Confirmation of the near complete conversion of sucrose fuel to carbon dioxide and water is provided by results of two series of experiments in which CO_2 was collected (fig.2). In theory, the production of 1 C electricity should be accompanied by release of 2.58 μmol CO_2 at maximum efficiency (equivalent to 12 mol CO_2 per mol sucrose). Within experimental error, the data points in fig.2 fit the theoretical line. An average positive deviation (points above the line) may indicate a small departure from this relationship arising from some release of CO_2 by organisms without concomitant production of electricity, attributable to incomplete scavenging of electrons by the mediator.

From these results it is clear that the sucrose fuel cell could form the basis of a useful biomass conversion device, such as might find application in effluent treatment. Moreover, the degradation of carbohydrate could provide a bonus of usable electrical energy. The more complex assessment of the energetic efficiency of the system will be considered elsewhere, though preliminary estimates are in excess of 50%. Improvements can be expected to result from appropriate immobilisation of organisms (Wiseman, 1985) in a manner which should not increase cell polarisation, and through the application of microprocessor control (Bennetto, Delaney, Mason, Roller, Stirling, Thurston and White, 1984). Important practical problems remaining are pH buffering (which could be overcome with the use of an acid-consuming oxygen cathode), maintenance of the cathode reagent, and transfer of water to the catholyte.

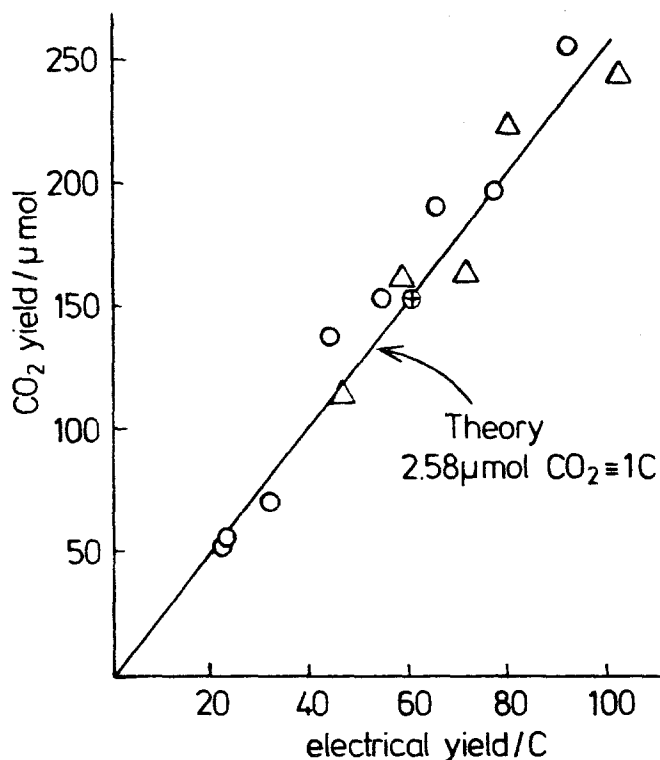


Figure 2 Relationship between CO_2 evolved from the anode compartment of the fuel cell and coulombic yield obtained.

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