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Pilot scale process for hydrodimerization of dimethyl maleate

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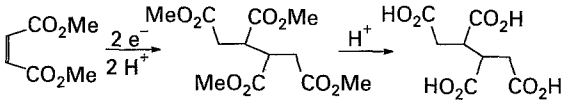
A pilot scale process is described for the electrochemical hydrodimerization of dimethyl maleate to tetramethyl butanetetracarboxylate. The reaction is performed in an undivided bipolar cell using graphite electrodes, methanol as the solvent and sodium acetate as the supporting electrolyte. Several hundred kilograms of product were formed. Electrode lifetimes of four hundred hours were achieved with reasonable selectivity (70%) to the desired product. Dimethyl succinate is a major (20+%) byproduct along with minor quantities of dimethyl methoxysuccinate.

1. Introduction

Butanetetracarboxylic acid (BTCA) is useful as a crosslinking agent for cotton to produce permanent press fabric [1]. The crosslinking agent currently used, DMEU, releases small amounts of formaldehyde into the environment. One way to produce BTCA is shown in Reaction 1.



(1)

Initial efforts to carry out the hydrodimerization of dimethyl maleate (DMM) using the system used for commercial hydrodimerization of acrylonitrile [2] led to poor selectivity to the desired tetramethyl butanetetracarboxylate (TMBTC). Bench scale studies [3] led to a system involving methanol as the solvent, sodium acetate as the supporting electrolyte and an undivided cell with graphite electrodes. This paper details the assembly and operation of a pilot scale electrolysis system for production of approximately a ton of TMBTC.

2. Experimental details

Dimethyl maleate was obtained from Alcolac (Sedalia MO.) methanol from Chemcentral (St. Louis, MO) and sodium acetate from Jarchem Industries (Newark, NJ). Graphite electrodes were AGSX grade obtained from UCAR Co. Gas chromatographic analyses were performed on a Varian 3700 instrument with a Hewlett–Packard 3390A Integrator and TC detector. The column was a DB-1 30 m megabore capillary. The injection port was at 200 °C and the detector was held at 250 °C. The initial temperature of the program was 80 °C for 2 min, then ramped up at 20 °C min^{-1} to 300 °C and held there for 25 min. The order of elution was DMM, dimethyl succinate (DMS), dimethyl methoxysuccinate (MeODMS), and TMBTC (retention times 3.9, 4.1, 5.0 and 9.1 min, respectively). The response factor of TMBTC was sensitive to peak size below a certain level so that minimum sample size of 0.2 μL was required. Diglyme was often used as an internal standard.

The ElectroSyn cell [4] was modified for bipolar operation. The plastic screens were replaced by free floating ones cut from 1 mm thick, 0.64 cm mesh plastic screen. The electrodes were 15.5 cm × 32.7 cm × 0.85 cm (507 cm^2 surface area) to fit snugly in the cell frames. The ends of each electrode were fitted with 0.32 cm thick Teflon sheets which fit in a groove machined into the electrode ends. The Teflon sheets were cut to fit the upper and lower part of the cell frames and served to reduce bypass current. Holes which exist in the frames for electrode contact were plugged with rubber stoppers from the inside. Electrical contact to the end electrodes was made using four 1 mm diameter gold wires for each end electrode. Two gold wires were punched through a small rubber stopper which fit the frame holes. The wires further fit into small holes drilled into the end electrodes. Two pairs of wires contacted each end electrode. The stoppers were held in place by backing washers which were each in turn held in place by two screws which were threaded into the frame. Viton O-rings were severely swelled by the electrolysis solution. However, Buna N O-rings worked well and the large O-rings which sealed the frames together were formed from 0.35 cm Buna N cord which was joined at the ends using Superglue. The cell never leaked at the O-rings.

Cell assembly was accomplished by building up the stack lying on a bench top. The assembled cell was compressed using pipe clamps and wired together through the pilot holes with copper wire. The assembly was then mounted on the frame aided by lab jacks to support it as it was mounted on upper

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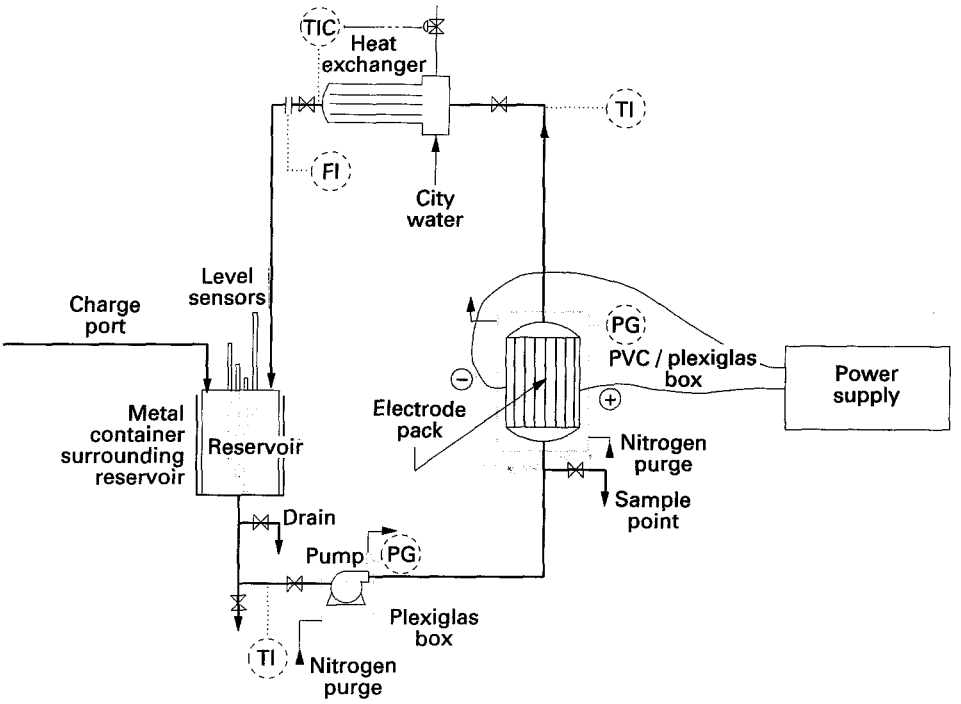

Fig. 1. Diagram of pilot plant system. (PG) Pressure gauge, (TI) thermocouple, (TIC) thermocouple controller and (FI) flow sensor/indicator.

and lower bolts. The front backing plate was added along with nuts and washers on the bolts. After slightly snugging the nuts, the copper wire was removed. Then the cell nuts were torqued to 1.7 N m.

The cell stack was initially operated with eight cells but was quickly expanded to 16 cells. The scale up from eight to 16 cells was linear in all respects.

The pilot process (Fig. 1) included the cell, a pump, a reservoir, a heat exchanger and a variety of sensors. The pump was a March magnetically driven centrifugal pump with Riton head and impeller and was capable of delivering 75 $dm^3 min^{-1}$ of electrolysis solution. The pump and cell were enclosed in plexiglas boxes which were blanketed with 0.5 cm water pressure of nitrogen to prevent ignition of methanol in case a leak occurred. The reservoir was a polyvinyl chloride (PVC) tank 30 cm × 30 cm × 30 cm and was contained in a stainless steel open topped box. The heat exchanger was shell and tube type made of 316 stainless steel. There were 56 tubes 91 cm long with i.d. of 2.9 cm. All piping was 2.54 cm PVC and gasketing was Buna N. The power supply was a Sorensen DCR 150-18B. A Signet paddle wheel flow indicator (magnetic impulse type) was used. Thermocouples were type J, coated with Teflon. The temperature controller was an Omega CN9000 microprocessor to control the water flow to the heat exchanger based on the outlet process fluid temperature from the heat exchanger. A Research control valve was used to control the cooling water to the heat exchanger (air to close, sized for 38 $dm^3 min^{-1}$, 1.27 cm stainless steel, Trim A, $Cv = 1.29$ and 70% of trim A). An I/P transmitted the controller output to the valve. A Molytek EZ-DATA 32 channel recorder logger monitored the cell voltage, current, flow and all temperatures. Three Teflon coated, on/off infrared level sensors were positioned at different depths of the reservoir via the top. There were interlocks which interrupted the current to the cell (a) if the cell temperature exceeded 50 °C, (b) if the flow dropped below 19 $dm^3 min^{-1}$, (c) if nitrogen purge to the boxes around the cell and pump dropped below 0.5 cm water and (d) if the solution level dropped below the lowest level indicator. Once current was interrupted, manual reset was required to resume current flow.

For a typical batch electrolysis, 8 kg of DMS, 15 kg methanol and 0.2 kg of sodium acetate were added to the reservoir. Circulation of solution through the system for a couple of minutes resulted in sufficient mixing of the components. The electrolysis was run at 12.5 A (25 A m^{-2}) and the temperature was maintained at near 25 °C for 10 h. The voltage to the stack was initially 75 V increasing slowly over most of the run but rapidly rising to over 100 V near the end of the run. The resulting solution was drained into metal cans which were later combined with product solution from other runs in drums for transport to another facility for TMBTC recovery. Typical analysis of the electrolysis product (not including solvent) indicated 3% DMM, 73% TMBTC, 19% DMS and 5% MeODMS. The mass balance indicated that typically 2% to 4% of the DMM was not accounted for at the end of each run. Some of that lost material was undoubtedly from handling losses but a small amount of high boiler is likely; in fact, no high boiling material was detected.

TMBTC tends to precipitate from such a solution on cooling, so that the residual solution in the electrolysis unit pipes, etc. would plug the unit if left for a few hours in winter (the explosion resistant enclosure which contained the physical operation

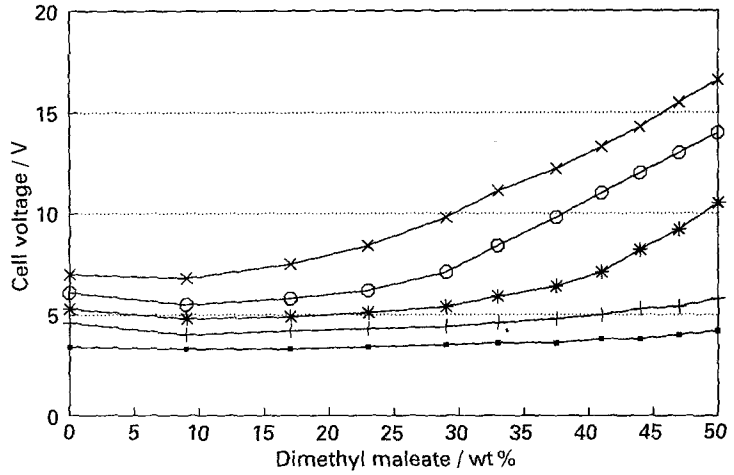

Fig. 2. Cell voltage against payload in a flow cell having graphite electrodes with 1 mm gap. DMM in methanol containing 1 wt % sodium acetate. Current density (■) 12.5, (+) 25, (*) 37.5, (○) 50 and (×) 62.5 mA cm^{-2}.

was not heated). Therefore, if another run was not immediately begun, the methanol for the next run was added immediately and circulated through the system to dilute the residual TMBTC and that mixture was allowed to stand in the system overnight or over the weekend. The system was sufficiently protected by safety interlocks that batches were typically run overnight unattended.

3. Results and discussion

A pilot unit for hydrodimerization of DMM was initially constructed using an Electrosyn cell as originally designed in the monopolar mode of operation with eight cells in the stack. After a few runs it was discovered that the metallic electrode contacts to the graphite anodes had dissolved (presumably by anodic dissolution) in the electrolysis solution. In addition, the high current required for the monopolar operation caused the power supply to be extremely noisy resulting in complaints from other workers in the area. Thus, the cell was modified to be operated in bipolar fashion with initially eight and then 16 cells in the stack as described in the experimental. The current to the stack was reduced from 150 to 200 A to 10 to 15 A with, of course a corresponding increase in stack voltage.

Operating conditions for the unit had been determined in previous bench scale operation [3]. Methanol was the solvent of choice for the reaction and sodium acetate was the optimum choice for supporting electrolyte based on its cost and performance. Optimum payload and current density were determined based on the data shown in Fig. 2 and capital and power cost assumptions.

The pilot unit was operated (typically two batches per day) for several months. Over time, the selectivity of dimerization of DMM to TMBTC decreased relative to the electrohydrogenation of DMM to DMS. Electrodes which no longer produced good selectivities were subjected to many treatments attempting to cause the selectivity to TMBTC to recover. Reversing the current to the cell after a few runs would increase the electrode lifetime somewhat (in terms of good selectivity). A variety of washing techniques (solvents, acids and bases) were ineffective at improving selectivity of used electrodes. The only treatment found to adequately restore selectivity was to scrape away the surface of the graphite exposing fresh material.

One goal of the operation was to be able to operate 1000 h between electrode changes which was considered an acceptable period of time based on the practice of other electrochemical processes. Figure 3 shows the results of 900 h of operation on a single set of electrodes. Data are missing for some of the batches. Note that the selectivity to TMBTC

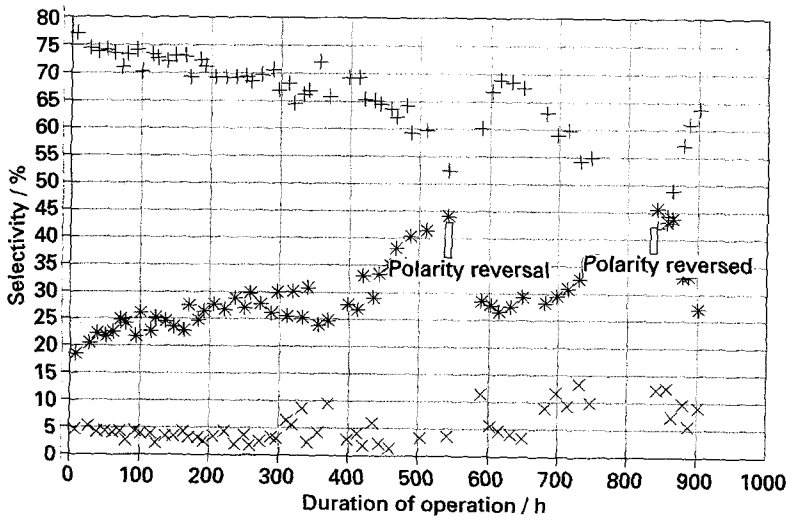

Fig. 3. Electrochemical pilot plant data. Selectivity to (+) TMBTC, (*) DMS and (○) MeODMS in successive batches on a single set of electrodes.

decreases with time with a concomitant increase in DMS production. After 550 h of operation the polarity was reversed resulting in increased selectivity to TMBTC, but the selectivity decreased more rapidly than before. Another reverse after 850 hours again increased the selectivity to TMBTC. The byproduct MeODMS which is formed in the nonelectrochemical reaction of DMM with methanol is produced in larger quantities later in this series of runs. It is believed that MeODMS formation is catalyzed by an unknown contaminant in the system.

Electrochemical power consumption for this process, assuming 94% current efficiency, is about 2 kW hr kg^{-1} of TMBTC or assuming \$0.05 per kW hr, \$0.10 per kilogram of TMBTC.

Recovery of TMBTC from the product solution was accomplished by addition of an equal volume of water and cooling the solution. Purification, saponification and recovery of the resulting BTCA are reported in a separate publication [5] which describes the overall process. Nearly half a ton of BTCA was supplied to a textile firm who found it to be of higher quality (i.e., less colour) than BTCA from other sources, an essential characteristic of material used to make white fabric.

4. Conclusion

The conclusion from this work is that it is possible to produce high quality TMBTC in a very low cost electrochemical cell design and solvent–electrolyte system. Major factors which will influence the cost of production of TMBTC are the electrode lifetime and a market for byproduct DMS.

References

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