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Technical and Economic Evaluation of Different Reactors for Methanotrophic Cultures for Propylene Oxide Production

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ABSTRACT

A two-stage process for the manufacture of propylene oxide is described. The preliminary economics based on use of methanol as a regeneration factor has resulted in a production cost of $12.10/lb of propylene oxide based on propylene oxide production rate of 40 mg/g-cell/h in conventional reactor. Increasing the propylene oxide production from 40 to 500 mg/g-cell/h resulted in a cost reduction from $12.10 to 5.8/lb of propylene oxide. The granular-activated, carbon-fluidized bed reactor (GAC-FBR) absorbs the propylene oxide and when saturated is eluted with ethyl acetate, and the bed is regenerated by steam to drive off the residual solvents. The estimated manufacturing costs are approx 59% lower (from $12.10/lb in conventional reactors to $5.00/lb for GAC-FBRs) for products that are highly inhibitory such as epoxides. In the GAC-FBR reactor, enhancing the propylene oxide production rate from 120 to 1500 mg/g-cell/h has resulted in the cost reduction to $2.00/lb. Enhancing the production capacity from 1 million lb to 10 million lb/yr has further reduced the cost of production to $1.00/lb.

Index Entries: Propylene oxide; granular-activated carbon; fluidized bed reactor.

INTRODUCTION

Most enzymes are very specific in respect to the carbon source. One of the major incentives for research on the biochemistry of methanotrophs is the potential industrial exploitation of the unusual lack of substrate specificity of the methane monooxygenase enzyme. The ability of this enzyme to insert oxygen into a wide variety of chemicals makes the methane-

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utilizing bacteria of potential economic importance. A wide range of non-growth substrates including alkanes, haloalkanes, alkenes, alicyclics, and aromatics have been evaluated *(1–3)*. For example, propylene oxide can be produced from propylene through a co-oxidative process *(4,5)*. Methane is used to grow the organisms and to regenerate them after the production of propylene oxide. Thus, it is possible to have continuous production of the co-oxidized product because the cosubstrate, methane, provides the energy and carbon requirements of the cell.

In the earlier studies conducted at Institute of Gas Technology (IGT, Des Plaines, IL), a continuous process has been developed for enhancement of methane monooxygenase activity so that higher amounts of propylene oxide can be produced *(6,7)*. The production of propylene oxide has been demonstrated in bench-scale studies *(8)*.

The objective of the proposed economic analysis is to develop the cost of propylene oxide for conventional processes, which involve a continuous production of biocatalyst followed by a batch-reactor process for production of propylene oxide. The goal is to compare the conventional process with the GAC-FBR process. The GAC-FBR process has been investigated in various ground-water applications *(9–11)*. GAC-FBR is a single-stage process in which propylene oxide produced by bacteria is adsorbed on the granula-activated carbon, which results in reduced inhibition on enzyme and bacteria producing it. The cost has been estimated for conventional process and GAC-FBR at several different capacities of production under various propylene-oxide production rates. For technical and economic evaluation, the process parameters achieved by IGT were used to design and economically evaluate a schematic process using conventional stirred tank fermentors and air stripping for propylene oxide recovery. Furthermore, the process parameters achieved by the granular-activated carbon-fluidized bed reactor technology (GAC-FBR) for methanotrophic oxidation for waste treatment of chlorinated hydrocarbons *(12)* were used to design and economically evaluate this GAC-FBR reactor scheme for chemical production by methanotrophs.

RESULTS

Process Description and Economic Evaluation of Conventional/IGT Process for Methanotrophic Co-Oxidation

A schematic of the process is shown in Fig. 1. This process scheme and the yields, rates, and conversion factors were developed, based on the work conducted at IGT.

The stage 1 fermentors produce regenerated cells and oxidations enzyme/cofactors from methane oxidation. In general, it is extremely

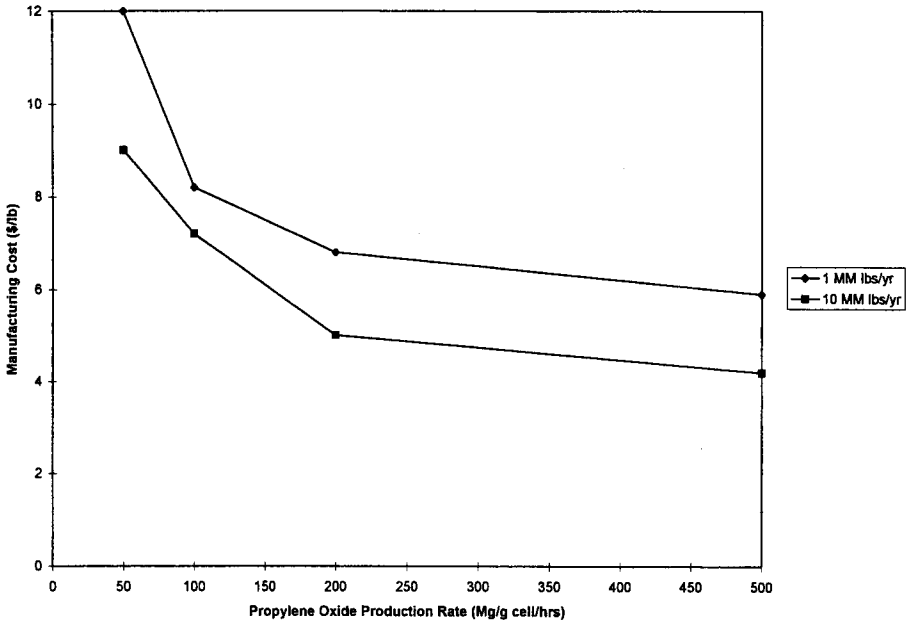

Fig. 1. Schematic of the conventional process of methanotrophic oxidation.

difficult to maintain the sterility of methanogenic cultures, however, under the optimized-nutrient conditions and pH of the reactor, sterile conditions were demonstrated for more than a month of continuous operation *(6)*. In stage 2 fermentors, the cells are used to oxidize propylene to propylene oxide (PO) with methanol as a cofactor regenerant. Air is used in large excess to strip PO from the broth and the stripped PO vapor is adsorbed in granular-activated carbon (GAC) beds. The GAC when saturated with PO is eluted with ethyl acetate (azeotrope composition with water) and the bed is regenerated by steam to drive off the residual solvents. The eluant and regenerant condensate are combined and sent to a series of two distillation columns—the eluant distillation separates and recovers the product PO and the second ethyl acetate column recovers the ethyl acetate azeotrope for recycling and the water, heavies, and some of the unrecoverable ethyl acetate go into the wastewater stream.

The current conventional/IGT process was evaluated. The manufacturing cost to produce one million pounds of propylene oxide was used as a representative example. The estimated manufacturing cost for PO from this process is shown in Table 1 (approx $12.00/lb). This economic analysis was developed based on a material balance from IGT data. Some of the factors important for this analysis are:

Table 1
Manufacturing Base-Cost Process for Methanotrophic Co-oxidation

Item	Quantity, U/lb of product	Price per U, $	Cost per Yr, million	Cost per lb product, $
Raw materials:				
Propylene	0.75	0.14		0.10
Methane	31.88	0.073		2.33
Nutrients	1.28	0.1		0.13
Methanol	0.22	0.06		0.01
Subtotal				2.57
Chemicals, supplies:				
Ethyl acetate	0.21	0.55		0.12
Carbon (GAC)	0.002	0.8		0.00
Miscellaneous			0.10	0.10
Subtotal				0.22
Variable Utilities:				
Steam, 50 psig thousand lb	0.04	3.8		0.15
Water process, thousand gal	0.31	1.5		0.46
Water cooling, thousand gal	4.79	0.1		0.48
Electricity, kWh	65.12	0.05		3.26
Subtotal				4.35
Total variable cost:				7.14
Operating labor	4/shift	@30,000/yr	0.48	0.48
Supervision	0.8/shift	@60,000/yr	0.18	0.18
Maintenance	3% of DFC		0.67	0.67
Plant overhead	75% (labor + supervision)		0.50	0.50
Insurance and taxes	1.5% of DFC		0.33	0.33
Total fixed cost				2.15
Total cash cost (fixed + variable)				9.29
Depreciation (8 yr straight line)			2.78	2.78
Manufacturing cost (cash + depreciation)				12.07

Basis: 1 million lb propylene oxide/yr, 8000 h/yr

1. The large quantity of methane used and the equipment and power needs associated with the process are very important cost factors.
2. This arises primarily because the PO productivity is so low (40 mg/g cell-h as an average productivity achieved by IGT to date). Thus, a large mass of cells have to be regenerated to carry out the reaction.

3. This low productivity is caused by very strong end-product inhibition at low concentration of the PO (or other epoxide products/intermediates).
4. The size of the equipment, particularly, the fermentors is very large. They are to be made of carbon steel and lined where possible and needed (to cut down the cost).
5. These fermentors are conventional and methane and oxygen gas are sparged simultaneously. Mixing of combustible/explosive gases in the fermentors is also a major design and engineering problem.
6. With this large volume and low productivity process it would be very difficult to reduce the costs. It would also be very difficult to scale-up or convince industrial clients to scale-up given the process uncertainties.
7. Process schemes and technical advances that will enable simultaneous separation of the PO end-product, thus reducing the inhibition and also make the equipment volumes lower and less unwidely would have clear advantage.

Process Description and Economic Evaluation of GAC-FBR Process for Methanotrophic Co-Oxidation

A process economic analysis was also conducted based on a GAC/FBR process developed at the Michigan Biotech Institute (MBI) using chlorinated organics (TCE). A schematic for the GAC/FBR process is shown in Fig. 2. Methane and oxygen are dissolved in fresh broth via inverted-cone diffusers, and this broth is pumped up flow through the GAC/FBRs. The methanotrophs form a biofilm on the GAC so that biocatalyst is retained. In the co-oxidation cycle, propylene is oxidized with methanol as a cofactor regenerant. One of the advantages of using GAC-FBR reactor is continuous adsorption of propylene oxide on the bed. This will minimize the inhibition of biocatalyst because of exposure to a reduced amount of propylene oxide. This will lead to a larger conversion cycle of propylene to propylene oxide as compared to the conventional process. The GAC, when saturated with PO, is eluted with ethyl acetate (azeotrope composition with water), and the bed is regenerated by steam to drive off the residual solvents. It is important to mention here that once a bed is in propylene-oxide production mode, the biocatalyst accumulation is done for next bed. The biocatalyst, being dead because of production of propylene oxide, is not recyclable any further. The PO-adsorbed GAC is eluted with ethyl acetate and then regenerated with steam. The ethyl acetate PO separation and ethyl acetate water separation is done by distillation as discussed earlier.

The estimated manufacturing cost for this process scheme is shown in Table 2. This process economic analysis was based on the costs and operation information on GAC/FBRs of MBI. The estimated cost was 41% of the conventional process because of reduced inhibition and the corresponding enhancement in the PO production rates.

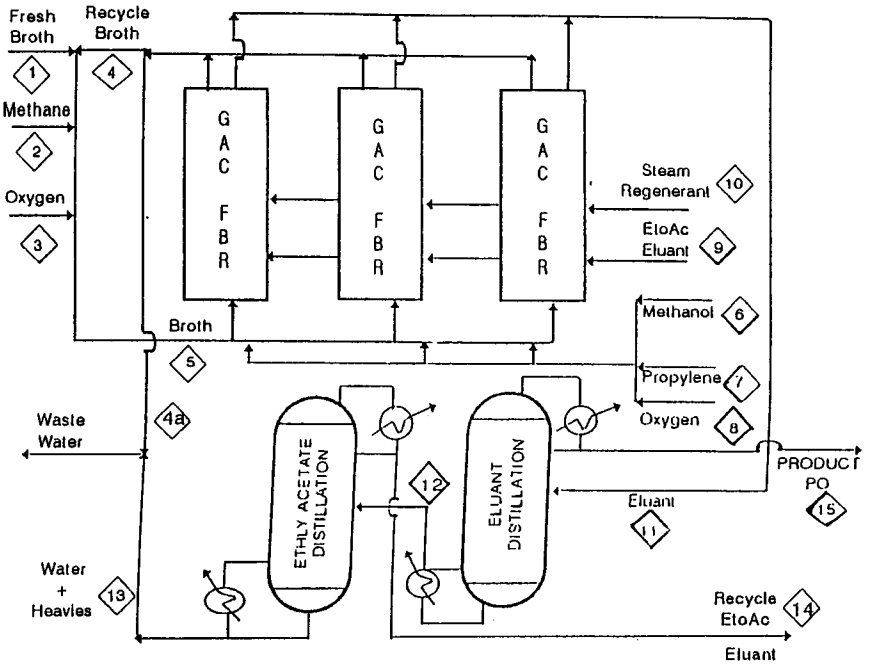

Fig. 2. Schematic of the granular activated carbon/fluid-bed reactor (GAC/FBR) process for methanotroph co-oxidation.

Process Economics—Sensitivity Analysis

Brief sensitivity analyses of the manufacturing cost to changes in production volume 1 to 10 MM lbs/yr and to the organism's rate of production were also conducted. The increase in rate has a very marked effect on the manufacturing cost because the low productivity caused by end-product inhibition increases all costs (Figs. 3 and 4). The increase in production volume reduces the manufacturing cost as expected, because the fixed costs per unit volume are reduced. The GAC-FBR process, because of its ability to adsorb the inhibitory product/intermediate has been assumed to have a threefold increase in corresponding production rate—this assumption is based on a similar decrease in inhibition seen with the methanotrophic oxidation process for waste treatment of toxic halogenated compounds.

This analysis shows that the GAC-FBR process will have a lower cost than the conventional process and at large volumes and high rates (for products that are not very inhibitory), the manufacturing cost can be < \$1.50/lb and be as low as \$1.00/lb. A wide range of specialty or fine chemicals fall in this range of manufacturing costs. Our results suggest that cost of production of propylene is not competitive with the current cost (\$ 0.57/lb). Thus the application of this process needs two important considerations: use higher capacity than demonstrated

Table 2
Manufacturing Cost—GAC/FBR Process for Methanotrophic Co-oxidation

Item	Quantity, U/lb of product	Price per U, $	Cost per Yr, million	Cost per lb product, $
Raw materials:				
Propylene	0.74	0.14		0.10
Methane	7.01	0.073		0.51
Nutrients	0.42	0.1		0.04
Methanol	0.22	0.06		0.01
Subtotal				0.67
Chemicals, supplies:				
Ethyl acetate	0.27	0.55	0.15	
Carbon (GAC)	0.005	0.8		0.00
Oxygen	20.35	0.075		1.53
Miscellaneous			0.05	0.05
Subtotal				1.73
Variable Utilities:				
Steam, 50 psig thousand lb	0.04	4		0.17
Water process, thousand gal	0.05	1.5		0.08
Water Cooling, thousand gal	1.26	0.1		0.13
Electricity, kWh	2.16	0.05		0.11
Subtotal				0.48
Total variable cost:				2.88
Operating labor	3/shift	@30,000/yr	0.36	0.36
Supervision	0.8/shift	@60,000/yr	0.18	0.18
Maintenance	3% of DFC		0.20	0.20
Plant overhead	75% (labor + supervision)		0.41	0.41
Insurance and taxes	1.5% of DFC		0.10	0.10
Total fixed cost				1.25
Total cash cost (fixed + variable)				4.13
Depreciation (8 yr straight line)			0.85	0.85
Manufacturing cost (cash + depreciation)				4.98

in this economic analysis (> 10 million lb/yr.); or determine the ratio of L- and D-forms and purify a single stereospecific form. These products are currently sold at very high prices (> $ 1000.00). Thus, the actual strategy will depend upon the requirement of quantity and type of the product at specific production site.

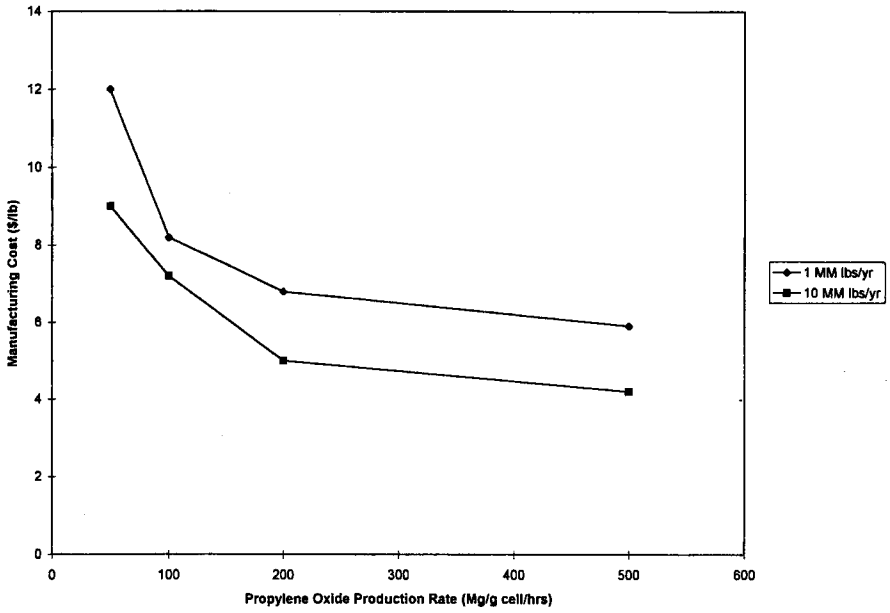

Fig. 3. Effect of propylene-oxide production rates and plant capacity on manufacturing cost in the conventional process.

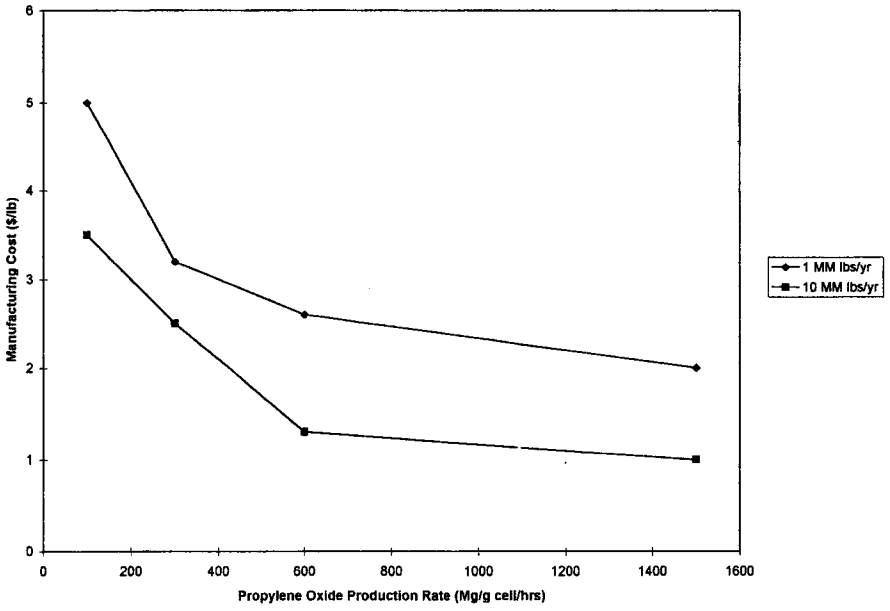

Fig. 4. Effect of propylene oxide production rates and plant capacity on manufacturing cost in the GAC-FBR process.

CONCLUSIONS

The GAC-FBR reactor for propylene oxide production was found to be superior:

1. The estimated manufacturing costs are approx 59% lower (from $12.00/lb in conventional reactors to $5.00/lb) for GAC-FBRs for products that are highly inhibitory such as epoxides, and, considerably lower costs (i.e. < $1.50/lb) are possible for less inhibitory higher productivity products produced in large volumes (> 10 million lbs/yr).
2. The process enables simultaneous conversion and removal of product by adsorption, thus reducing the effect of end-product inhibition on productivity.
3. The capital costs are considerably (3.3-fold) lower in GAC-FBR reactor.
4. The equipment required is not large and unwieldy.
5. Methane and oxygen are dissolved in the media by separated-inverted cone diffusers, hence they do not mix in the gas phase and have explosive/combustible mixtures.
6. The GAC-FBR technology has been scaled-up to very large >2000 GPM reactors and has had a very good track record to-date.

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