Design of a Microfluidic Photocatalytic Reactor for Removal of Volatile Organic Components: Process Simulation and Techno-Economic Assessment

Mariam Alkaabi,∥ Meera Mohamed,∥ Ameera Almanea,∥ Mahra AlShehhi,∥ Khadija Farousha,∥ Ahmed Yusuf, and Giovanni Palmisano∗

ABSTRACT: This study reports on a gas-phase photocatalytic microreactor (MR) employed for the degradation of 2-propanol in indoor air. A process flow diagram was developed and simulated in Aspen Hysys V10, and a techno-economic assessment was carried out based on the simulated results. An economic evaluation was carried out using a fixed and demand-dependent variable cost model. Decreasing the mass flow rate or the initial concentration of the 2-propanol in indoor air and increasing the diameter or length of the MR resulted in a better air remediation efficacy. Sensitivity analysis for the economics of the manufactured MR showed that the optimal plant production volume is 10,000 units per year. At this volume, the total manufacturing cost was 2.8 M$/y with a production cost of $127 per unit and a levelized cost of a MR (LCOM) of about $280 per unit. These findings herein can help bolster research into both technical and economic aspects of MR production for the photocatalytic remediation of air. The resulting design could be applied in air conditioner units and other home ventilation units for the removal of harmful volatile organic compounds in the air.

1. INTRODUCTION

Air quality remains a major concern, as air pollution continues to pose a global threat. The prevalence of adverse environmental effects and the number of affected individuals are on the rise. It is estimated that around 4.5 million deaths occur annually as a consequence of health complications, resulting from air contamination.1 Studies demonstrated that people generally spend 90% of their time in indoor atmospheres, indicating that the majority of health risks associated with air quality are consequences of indoor air pollution.2 Volatile organic compounds (VOCs) are some of the major pollutants that affect air quality. They are of high toxicity and low water solubility and evaporate easily at room temperature. VOC sources include natural sources, industrial processes, household, and office equipment.3 Headaches, allergic reactions, nausea, and fatigue are some short-term effects associated with VOC exposure. Long-term effects include anemia, liver damage, and neurologic problems.4 Some VOCs are also classified as carcinogenic,5 and they can also contribute to ground-level ozone and acid rain. VOCs can also contribute to ground-level ozone and acid rain.6 Therefore, air pollution is an issue that needs to be addressed and resolved globally.

Substantial research has been conducted for VOC removal and degradation in air. Photocatalytic oxidation (PCO) offers a viable new technology that can be used to purify indoor air.6 PCO is also known to be environmentally benign and economically feasible, as it is inexpensive and utilizes solar energy to overcome environmental problems such as air and water pollution. It uses photon energy to trigger a chemical reaction by activation of the catalyst on which the target pollutant is photoadsorbed. The activation of the semiconductor can take place only if it is hit by an energy greater than its band gap energy. In such a case, electrons in the valence band are promoted to the conduction band and create a hole in the valence band. These electron−hole pairs generate oxidation−reduction reactions that decompose various harmful VOCs into harmless substances such as water and carbon dioxide. Titanium dioxide (TiO2) is the most investigated and used photocatalyst due to its high chemical stability, low toxicity, inexpensiveness, and effectiveness for the photo-

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degradation of organic compounds. Photocatalysts can be ineffective when used in conventional reactors due to mass transfer limitations, insufficient exposed active specific surface area, non-uniform light distribution, etc. 

The application of microreactors (MRs) as devices to degrade VOCs has been gaining increasing attention. This is because of their promising features that are compatible with PCO. Utilizing MR technology in photocatalysis has many advantages such as effective light illumination, short diffusion distance, and lack of a photocatalyst recovery step. By immobilizing photocatalysts in MRs, the following can be achieved: better mass transfer, uniform light distribution, reduction in the number of lost photons, and most importantly enhanced separation of the photocatalyst from medium and improved catalyst recovery. Therefore, MR technology provides remarkable features that can potentially enhance the design of heterogeneous photocatalytic processes. The miniaturized size of these photoreactors ensures a high surface-to-volume ratio for short molecular diffusion and improved transport of heat and mass. Photocatalytic MRs also have higher spatial illumination uniformity for good light penetration through the catalyst. The small volume of MRs also reduces environmental burdens, as they are atom-economical and step-economical.

Several studies have demonstrated the design and simulation of gas-phase photocatalytic MRs using computational tools such as COMSOL Multiphysics. These studies focus more on optimizing the kinetics and transport processes involved in VOC degradation. However, in this work, for the first time, we aim to provide insights into the economic feasibility of large-scale production of a gas-phase photocatalytic MR, for application in air purification units, especially as an add-on to air-conditioning units or home ventilation appliances. The study, herein, utilizes Aspen Hysys V10 to model a system that simulates a photocatalytic MR.

A potential solution for the annihilation of hazardous VOCs in the air was devised and evaluated in this study. This work involves designing and simulating a photocatalytic MR device, using 2-propanol as a model VOC. Despite the advantages that MRs offer, these reactors are not close to being commercialized due to the lack of techno-economic assessment data for the evaluation of their economic viability. Techno-economic studies of such systems can potentially serve as a basis for their envisaged commercialization for pollution control. Therefore, this study presents a techno-economic assessment of a photocatalytic MR, with an economic analysis aimed at the estimation of fixed and demand-dependent variable costs. The sensitivity analysis of mass production of the designed photocatalytic MRs was also investigated.

2. PROCESS DESIGN AND SIMULATION

2.1. Process Assumptions. The photodegradation of 2-propanol was assumed to be performed under atmospheric conditions and 2-propanol undergoes complete mineralization to CO and H₂O. Plug flow reactors (PFRs) were used to simulate the microchannels in Aspen Hysys. It was also assumed that there is no pressure drop in the PFRs. To simulate the thermodynamic properties, NRTL was employed as the fluid package. Since the removal of 2-propanol is a heterogeneous photocatalytic reaction in the gas phase, it was incorporated using the elementary reaction in eq 1.

\[ CH_3CHO + 4.5O_2 \rightarrow 2CO_2 + 3H_2O \] (1)

The catalyst was assumed to be supported on the walls of the MR. However, Aspen Hysys has no models for PFR reactors with immobilized catalysts. Therefore, we assumed that the reaction is fast enough for an instantaneous degradation of 2-propanol molecules after they reach the walls and thus adsorb on the immobilized catalyst. The

Figure 1. The process flow diagram (PFD).
degradation was assumed to follow the Langmuir–Hinshelwood (LH) rate, as shown in eq 2.

$$-r_p = \frac{k_p K_p C_p}{1 + K_p C_p} = \frac{275.2 C_p}{1 + 46.9 C_p}$$

where $-r_p$ is the LH rate in mol m$^{-3}$ h$^{-1}$, $k_p$ (5.868 mol m$^{-3}$ h$^{-1}$) is the reaction rate constant of pollutant (2-propanol), $K_p$ (46.9 m$^{-3}$ mol$^{-1}$) is the photoadsorption equilibrium constant of 2-propanol, and $C_p$ is the concentration of the pollutant for TiO$_2$ adapted from ref 13.

It was assumed that the reaction takes place in the presence of UV LED lights, installed on top of the MR. The light intensity effect was assumed to be already integrated into the reaction rate constant. The walls of the microchannels were assumed to be coated with the TiO$_2$ catalyst.

The use of wall-coated microchannels was assumed to avoid pressure drop and overcome both mass and heat transfer limitations associated with packed bed reactor types. Wall-coated microchannels are also less complex than other MRs, such as the monolithic MR, in terms of geometry. This is due to the very irregular matrix structure associated with monolithic designs and their lack of kinetic data. Therefore, wall-coated microchannels require simpler modeling. Microchannels of cylindrical geometry were assumed. Normah et al. reported that unlike rectangular geometries, cylindrical geometries minimize thermal resistance and perform better thermally and hydro-dynamically.

2.2. Process Description. Figure 1 shows the process flow diagram (PFD) that was simulated in Aspen Hysys V10. The initial flow rate of contaminated air was 0.5 kg/h with an initial composition of 0.01% mol fraction for 2-propanol in air. The polluted air stream is then sent to a saturator, which receives water via stream 3 and saturates the feed stream to the specified relative humidity. Only at low relative humidity does water vapor enhance the photodegradation of 2-propanol. The increased formation of hydroxyl radicals increases the degradation rate of 2-propanol. At large concentrations, however, water vapor hinders the process due to competitive adsorption on the catalyst’s sites. As a result, 20% was chosen as the relative humidity value. The stream is then separated into 15 equal streams that enter the PFRs in parallel, after passing through the saturator. A splitter is used to equally divide the flow rates, resulting in streams of equivalent properties. The selection of 15 PFRs was to maintain high conversion (more than 99%) of 2-propanol at the exit of the reactors. Besides, an odd number of microchannels in parallel have low flow maldistribution as reported by Odiba and Olea. The effluent streams were eventually collected using a mixer at the exit of the PFRs, and the resulting stream passes through a valve and is vented out. The effect of process variables, such as initial concentration of 2-propanol, mass flow rate, diameter ($d$), and length ($l$) of the microchannel, was investigated to assess their impact on the rate of removal of 2-propanol from the air.

2.3. Microdevice Design and Fabrication. The photocatalytic microdevice was designed as parallel PFRs (Figure 2). It was assumed that the microdevice is made of stainless steel with a transparent side made of Pyrex glass lid in contact with an array of UV-LED lights to activate the catalyst thin film immobilized in all the microchannels. Pyrex is highly suitable for photocatalytic MRs, as it has good chemical stability and transparency over a broad range of wavelengths. Pyrex and its fabrication costs are also considered inexpensive. The cost of the Pyrex glass attached to the UV-LED was considered to be part of the MR cost. The volume of each PFR was sized as 392.7 μL (see eq 3), with a diameter and length of 0.5 mm and 2 m, respectively. $F_{A0}$ represents the molar flow rate in mol h$^{-1}$, $X$ is the conversion, and $-r_A$ is the reaction rate. The size of the components in the microdevice is shown in Table 1.

$$V_{PFR} = F_{A0} \int_0^X \frac{dX}{-r_A}$$

| Table 1. Size of Microdevice Components | equipment | quantity | size |
|----------------------------------------|-----------|----------|------|
| PFRs                                   | 15        | diameter 0.5 mm and length 2 m with a volume of 392.7 μL |
| compressor                             | 1         | 8.5 μW (centrifugal-type) |

Stainless steel was selected for most parts because it is an excellent choice due to its strength, durability, and versatility. It has a protective film leading to sufficient corrosion resistance required for the system, due to the presence of chromium and the metal’s non-porosity. A study also showed that stainless-steel reactors allow for uniform distribution of the catalyst on its surface when immobilized using the sol–gel method.

MRs can be produced by various types of microfabrication techniques, which are essentially not chemical but manufacturing processes. It has been assumed herein that the MR is made of steel and a transparent (to UV light) side made of Pyrex.
glass attached to an array of small UV-LEDs for effective illumination of the immobilized photocatalyst. Commonly used microfabrication techniques for metallic materials are dry and wet etching based on silicon and other semiconductor technologies.\(^2,23\) Wet and dry chemical etching can be used to achieve different types of channel geometries. In microfabrication, the aspect ratio (ratio between width and depth of a microchannel) is one of the main considerations. A gas-phase stainless-steel MR for heterogeneous-catalyzed reactions has previously been built. This reactor was about 360 \(\mu\)m wide and 130 \(\mu\)m deep.\(^2\) These dimensions are compatible with the type of microchannels studied herein. Therefore, in the economic analysis, it will be assumed that the MRs are produced through the wet etching microfabrication technique.

### 2.4. Economic Analysis

Estimation of capital, operating, and manufacturing expenses was part of the economic evaluation for this study. To study the economic feasibility, a scenario where this photocatalytic microdevice is mass-produced was assumed. This microdevice can be used in ventilation and cooling appliances (such as portable air-conditioning units, humidifiers, etc.) installed in households or common living areas. They can serve as a filtration unit for the purification of air before being circulated into the room. Figure 2 shows a schematic of such a photocatalytic microdevice. This device could be beneficial for the further development of air pollution control strategies, especially in households.

It was assumed that economic analysis is based on mass production of the miniaturized photocatalytic reactor. These MRs were produced using a microfabrication technique known as wet etching. It was assumed that the proposed manufacturing plant will produce at least one thousand units of these reactors. In a typical manufacturing plant such as the one that specializes in microfabrication, several cost components must be taken into account. Due to the non-availability of financial data of a plant producing MRs, herein, the data on manufacturing costs for microsystems or microelectromechanical systems (MEMS) using high-aspect ratio microfabrication techniques similar to those used in MR fabrication were assumed. A previous study by Lawes\(^2,24\) detailed all the cost components associated with microfabrication that was adopted in this study.

Lawes\(^2,24\) investigated the layer-processing costs associated with principal high-aspect ratio micromachining techniques used in microsystems or MEMS fabrication. The work particularly focused on silicon surface micromachining, wet bulk etching (the technique assumed in this study), wafer bonding, deep reactive ion etching, excimer laser micro-machining, UV LIGA, and X-ray LIGA. The study proposed a cost model known as MEMS-COST, which takes into account the financial operational and machine-dependent parameters of different manufacturing techniques as inputs and calculates the layer processing cost at the wafer and chip level as a function of demand volume. The required inputs for the cost model are described as follows:\(^2,24\)

- **Microdevice data:** these are information about the number of the different designs per year and the number of layers processed. For the MR in this work, one layer will be micromachined on steel wafers. The maximum depth and width of the microchannel in the microdevice are 500 \(\mu\)m, and it was assumed that a single microdevice chip (rectangular) has a base area of 100 \(cm^2\).
- **Wafer data:** the steel wafer in which the microchannels were etched was assumed to be about 1.5 mm thick.
- **Operational details:** this includes hours per year for facility operation per operator and the number of machines per operator.
- **Financial assumptions:** the amortization period needs to be inputted and mask cost and salaries of operators. Mask cost is the cost of purchasing the transparent film that allows light to shine through in a defined pattern during the microfabrication process.
- **Microdevice processing technology:** this includes the cost of capital equipment, such as cost of ownership, maintenance, consumables, manpower, and so on, exposure or etching rate of the process for a given material (i.e., steel wafer/h), the cost per steel wafer, the maximum number of steel-wafer etched per year per machine, and the yield of a good MR unit from the process.

The cost of etching microchannels on a single MR (i.e., a steel wafer) can be calculated from eq 4. Wet etching is the assumed technique for microfabrication; the cost of ownership is low because the equipment required are simple mask aligners, resistance handling tools, and wet etching baths. The variable cost was calculated from the hourly cost of operation of the equipment, the time to process a MR, and the cost of throughput-dependent consumables per steel wafer (or MR).\(^2,24\)

\[
C_R = C_F + C_V N_R
\]

where \(C_R\) is the cost of processing a MR in a year ($ per reactor); \(C_F\) is the fixed cost ($ per year); \(C_V\) is the variable cost ($ per reactor); and \(N_R\) is the number of reactor units per year.

Table 2 shows the fixed and variable costs of some microfabrication technologies. The cost presented is based on the processing of a single layer of wafer; to adopt this cost herein, it will be assumed that the processing of a single layer of the wafer is similar to the microfabrication of a MR. Other costs such as test and packaging costs are also important and must be included; this cost can be more than 50% of the cost of manufacturing a microdevice; thus, 50% will be used in this work. Fixed overhead costs such as R&D costs, marketing

### Table 2. Fixed and Variable Costs for Processing a Single Microdevice for Selected Microfabrication Technologies\(^d\)

| Cost components | X-ray LIGA PMMA (scanner only) | wet bulk micromachining (used in this study) | wafer bonding |
|------------------|--------------------------------|---------------------------------------------|---------------|
| Fixed costs     |                                |                                             |               |
| Capital         | $ 1,050,000                    | $ 236,250                                   | $ 134,750     |
| Amortized (5 years; $/year) | $ 210,000 per year | $ 47,250 per year                           | $ 26,950 per year |
| Annual cost (4% of capital) | $ 42,000 per year | $ 9450 per year                            | $ 5390 per year |
| Annual maintenance (0.05 MY) | $ 2800 per year | $ 2800 per year                            | $ 2800 per year |
| Annual total    | $ 254,800 per year            | $ 59,500 per year                           | $ 35,140 per year |
| Variable costs  |                                |                                             |               |
| \(C_V\)         | $ 244.6 per wafer              | $ 2.97 per wafer                            | $ 4 per wafer |

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sales, building, and supervision for typical chemical plants are between 50 and 70% of total expenses for operating labor and maintenance.\textsuperscript{25,26}

Therefore, these overhead costs would be accounted for as 70% of all costs associated with labor in this work. The cost of installing a UV-LED as a cover to the wet-etched MR is important as well. This cost was included as part of the variable costs; the cost of a UV-LED in a rectangular array was assumed to be about $500 per MR, based on the average price found on a merchant website.\textsuperscript{27}

All cost components were from 2007; these costs were converted to the corresponding value of that of 2019 using the chemical engineering plant cost index (CEPCI) value of 607.5.\textsuperscript{28} The project life was assumed to be 10 years, while the discounted rate for cash flow was set at 10%. The equipment’s salvage value was set as zero; depreciation was also assumed to be zero. The taxation rate was considered as 5%, as it is the taxation rate in the UAE. The levelized cost of a microdevice (LCOM) was estimated as the minimum selling price of a MR that recuperates the net present value of the total cost of building and operating the plant over a lifetime of \(n\) years (eq 5).\textsuperscript{29}

The net present value (NPV) is given by

\[
NPV = \sum_{t=1}^{n} \frac{\text{Net annual cash flow}}{(1 + i\%)^t} = 0
\]

where \(i\) is the discount rate, \(n\) is the project or plant lifetime, NPV is in M$, and cash flow is the total annual income after tax in M$/y.

3. RESULTS AND DISCUSSION

3.1. Effect of Process Variables on the Conversion of 2-Propanol. The photocatalytic degradation of 2-propanol was investigated by studying the effect of various process variables, which include inlet mass flow rate, initial concentration, and reactor dimensions. Figure 3a shows that higher values of the mass flow rate resulted in a lower conversion. This observation can be related to the residence time of the reactant in the MR; low flow rate means high residence time and higher conversion and vice versa.

The length (\(l\)) of the microchannels was also examined at a constant flow rate of 0.5 kg h\(^{-1}\). An increase in \(l\) increased conversion as shown in Figure 3b. The trend is expected, as increasing the length (\(l\)) enables a higher residence time, which further enhances conversion. At a length (\(l\)) greater than about 1.5 m, the conversion was 100% for the conditions studied herein. For the effect of changing the diameter (\(d\)), the resulting trend is as shown in Figure 3c (similar to the trend observed for changes in length (\(l\))). It showed that an increase in diameter (\(d\)) also increases the conversion due to an increased volume (or residence time). Increasing the inlet initial concentration decreased the final conversion (see Figure 3d). Increasing the initial concentration usually increases the initial rate of the reaction but results in lower final conversion;
this observation is supported by previous studies on MR modeling. Optimal design parameters were an initial flow rate of 0.5 kg/h and an initial composition of 0.0001 for 2-propanol in the air. For the reactor, the observed length \((l)\) was 2 m and the diameter \((d)\) was 0.5 mm, as previously mentioned.

3.2. Cost Estimation and Sensitivity Analysis. Various cost indicators were estimated for the production of 1000 units of MR using the wet etching technique. The project life was assumed to be 10 years, the net cash flow was discounted, and the NPV at the end of the project life was set to zero to obtain the minimum price each unit can be sold to break even at the end of 10 years. Table 3 shows the results of the estimated costs. The annual total manufacturing cost (TMC) was about 1.4 M$/y; of this amount, the annual variable cost takes the largest share of about 35.5% followed by fixed overheads, cost of testing, and packaging. The fixed costs were only about 2.5% of the TMC since the wet etching technique has been previously ascertained to have cheaper initial capital investment compared to other techniques including X-ray LIGA PMMA. The variable cost took the largest share of TMC because it depends on the total amount of units produced in a year. Besides, the cost of UV LED installation on every MR represents about 99.4% of all variable costs. This shows that the MR production is highly sensitive to the cost of the light source installed and packaged with the MR. In light of this, a sensitivity analysis was carried out on important economic variables.

Table 3. Important Cost Estimates for Production of 1000 Units of MR

| item                        | unit     | value |
|-----------------------------|----------|-------|
| MR                          | units/y  | 1000  |
| fixed costs                 | M$/y     | 0.035 |
| variable costs              | M$/y     | 0.5   |
| testing and packaging       | M$/y     | 0.27  |
| fixed overheads             | M$/y     | 0.378 |
| TMC                         | M$/y     | 1.41  |
| For NPV_{10}                |          |       |
| cost of an MR               | $/unit   | 641.86|
| the selling price of an MR  | $/unit   | 1412.09|

Figure 4 shows the effect of the increase in plant throughput on the TMC, cost of a unit, cost of UV LEDs, and LCOM. It is evident from this sensitivity analysis that the TMC increases with an increase in the volume of the unit. The cost of production of a unit and the LCOM decreases as the volume increases to 10,000 units. From this amount, there was no significant decrease in the cost of production even as TMC increases. The cost of UV-LEDs was a significant economic variable as well; it can be seen that as the cost decreases, other economic variables decrease fast. This shows that a cost-effective light source must be used for production to maximize profit in the long run. The economic trend observed herein is quite similar and in agreement with the results previously reported by Lawes. For the economic analysis in this work,
the optimal volume of production is 10,000 units; volume beyond this value would result in significant loss and waste of resources. At this volume, the cost of production is $127 per unit (when the cost of UV-LEDs is $100 per unit) and the LCOM was $280 per unit.

4. CONCLUSIONS

MR technology is continuously gaining significant interest due to its energy efficiency, fast kinetics, good yield, safety and reliability, scalability, and sustainability. In this work, a photocatalytic MR was designed and simulated (using Aspen Hysys V10) for the removal of 2-propanol in indoor air. The economic assessment was also carried out for a manufacturing plant producing a gas-phase photocatalytic MR. Results show that removal of 2-propanol in a simulated photocatalytic MR increases with increasing diameter and length but decreases with increasing mass flow rate and initial pollutant concentration. For 1000 units produced per year, the TMC cost was 1.41 M$ per year and the LCOM was about 1412 $ per unit. Sensitivity analysis shows that increasing volume of production increases the TMC and decreases the LCOM and cost of production of a unit until a minimum is reached at 10,000 units and no changed is observed. The designed MR herein can be used in several household ventilation systems. It is hoped that the findings from this work will provide a good starting point and help manufacturers and policy makers make appropriate decisions on mass production and integration of photocatalytic MRs in household ventilation products.

Author Contributions

M.A., M.M., A.A., and M.A. contributed equally.

Notes

The authors declare no competing financial interest.

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