LED-Based Photocatalytic Reactor Design
Optimization on Cost Preassessment

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by

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The objective of this thesis, undertaken from October 2014 until June 2015 at Delft University of Technology, was to check the methodology in the LED-based photocatalytic reactor design by minimizing the reactor cost. In the end, the methodology is provided and several parameters, namely reactor length, the number of LED and power of LEDs, etc., are examined to determine which parameter plays more important role in determining reactor cost.

The degradation of toluene in the air is chosen as a chemical reaction model. The methodology concerns annular reactor with three cylinders where the catalyst locates in the outermost wall while LEDs are fixed in the most inner tube. Commercial software, gPROMS, is used to conduct both the simulation and optimization. A three-dimensional model in cylindrical coordinates system is shown in this study. The model is further simplified to a two-dimensional one, on which the optimization design bases. Both models are built up based on the mass balance of toluene, momentum balance of the fluid, radiation field of LEDs and heterogeneous photocatalytic reaction scheme.

In chemistry, photocatalysis is the acceleration of a photocatalytic reaction in the presence of a catalyst. In this work, the photocatalysts is the titanium dioxide, TiO2, which is widely used in theoretical and practical studies. The reaction mechanism shown in the reaction model is called chain propagation. The mechanism follows the Langmuir Hinshelwood reaction model which involves a series of chemical reactions of toluene, water and titanium dioxide. Based on this reaction mechanism, a simplified expression of reaction rate is available. This reaction rate is also taken as boundary condition in solving the governing equations.

Following the chemical model, a light profile is in need to show the irradiation strength absorbed by catalysts. As is known, the photocatalysts require light energy to activate the chemical reaction rate. It is essential to give the light profile to calculate the intensity of the reaction. Two three-dimensional models are provided to study the parameters in determining the light profile. The light emitting diode (LED) is used in the work as the light source. As a matter of that LED concentrates energy in narrow small radiation angle, it receives more attention and preference as the light source in photocatalysis studies.

Mass and momentum balances are also required to describe the fluid field as parts of the reactor model. A simplified model of the fluid is introduced based on the assumption that the fluid studied is under full development condition. Based on this assumption, a steady state Poiseuille fluid model can be established as the momentum balance to get the velocity profile. After acquiring the velocity profile, a mass balance model can be established which is also considered as the governing equations. The mass balance model describes the mass distribution and the mass transportation phenomenon of toluene in the fluid.

After the establishment of the model, simulation and optimization of the reactor can be performed. The target of optimization is to offer optimized geometric structure of the reactor to get a lower cost of the reactor. It was achieved by changing the geometric variables such as reactor length, radius, and the number of LEDs and power of LEDs with the commercial software gPROMS. gPROMS is selected because it is particularly suitable and convenient for optimization activity. The analysis, in the end, gives an optimized value for the number of LEDs, power and reactor length which shows the reliability of this method for the tubular reactor.
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## Contents

1 **Introduction**     
1.1 Photocatalysis ....................................................... 2  
1.2 Photocatalysts. ..................................................... 3  
1.3 Light sources. ....................................................... 4  
1.4 Challenges and limitations ......................................... 5  
1.5 Photocatalytic reactor optimization .............................. 7  
1.6 Objective of the project .......................................... 8  

2 **Reactor Model**  
2.1 Configuration of photocatalytic reactor .......................... 10  
2.2 Momentum and Mass balances. ...................................... 11  
2.3 Irradiation Model. .................................................... 13  
2.4 Photocatalysis kinetic model ....................................... 15  
2.5 Optimization formulation .......................................... 21  
   2.5.1 Formulation of the objective function ....................... 21  
   2.5.2 Formulation of the optimization process .................... 24  
   2.5.3 Introduction to gPROMS ...................................... 26  
2.6 Summary and comments ............................................. 27  

3 **Optimization**     
3.1 Two variable optimization ......................................... 29  
   3.1.1 Result of the two-variable optimization ................. 30  
   3.1.2 Analysis of the two-variable optimization .............. 31  
3.2 Three-variable optimization .................................... 33  
   3.2.1 Result of the three-variable optimization ............. 33  
   3.2.2 Analysis of the three-variable optimization .......... 35  
3.2 Four-variable optimization ...................................... 37  
   3.2.1 Result of the four-variable optimization .............. 37  
   3.2.2 Analysis of the four-variable optimization .......... 39
3.3 Summary and Comments ........................................... 41

4 Conclusions and comments ........................................ 42
  4.1 Conclusion ....................................................... 42
  4.2 Recommendation .............................................. 43
    4.2.1 Validation with experimental results .................. 43
    4.2.2 Further study on the objective function ............... 43
    4.2.3 Numerical solution with higher order ................. 44

Bibliography .......................................................... 45

Appendices ........................................................... 48
  .1 Parameters assessment ........................................ 48
    .1.1 Depreciation coefficient of catalysts, \( d_{\text{catalysts}} \) ... 48
    .1.2 Power of LED and Depreciation coefficient of LEDs, \( d_{\text{LED}} \) ... 48
    .1.3 Price of material, \( P_{\text{material}} \) .......................... 48
    .1.4 Depreciation coefficient of material, \( d_{\text{material}} \) .......... 49
    .1.5 Price of electricity ........................................... 49
    .1.6 Price of photocatalysts ..................................... 49
  .2 Code of gPROMS model ......................................... 50
    .2.1 Code of the MODEL entity .................................. 50
    .2.2 Code of the PROCESS entity ............................... 54
    .2.3 Code of the OPTIMIZATIONS entity ....................... 56
  .3 Notation ......................................................... 57
Introduction

As a promising technology, photocatalysis shows its unique advantages and potential in many disciplines, from hydrogen production, indoor and outdoor air purification [1], remediation of non-biodegradable molecular in the factory [2], to the organic synthesis with high selectivity. In recent years, photocatalytic semiconductor process has shown a high potential for the contaminated air remediation [3]. Compared with conventional technology, photocatalysis in pollutant degradation shows advantages as a low-cost, environmentally friendly and sustainable treatment technology [3] to align with the ‘zero’ waste scheme. Therefore, photocatalytic reactor, an application of photocatalysis, received great focuses from both theoretical and practical fields.

However, the industrial application of photocatalysis also suffers the challenges and limitations in many fields. As it is concluded in the recent study [4], the kinetic performance of the reactor which concerns both mass and photo transfer is considered as one of the major limitations. As a general limitation in the chemical industry, the contact between the activated catalysts and reactants plays a major role in limitation of mass transfer [4]. Apart from the mass transfer, the kinetic performance of the reactor is also limited by the poor photon utilization which leads to the reactor design with a large volume. The limitations of both transfers eventually contribute to a high cost, which hindered the applications of the photocatalysis. Therefore, the optimization study on the photocatalysis is receiving more attentions.

The optimization of photocatalysis involves studies in many disciplines from the performance of the reactor, optimal light distribution to the improvement of catalysts efficiency. The optimal working conditions of the catalysts [5] [6] (PH, light intensity, and wavelength) in the different applications have received many investigations. In addition, many efforts have been devoted to the optimization studies on the optimal light profile [7], which enhance the energy efficiency of the reactor. On the contrary, although hundreds of reports are published each year concerning the promising possibility of photocatalysis in commercialization, few reports are available on the optimization of the photocatalytic reactor design.

The studies of the photocatalytic reactor involve many disciplines: performance of different light sources and catalysts, methodology in reactor design and optimization, and the kinetic study of photocatalytic reaction. The mathematical model based optimization method has shown great advantages in the reactor design by applying with several software. This method
has been utilized in many studies like the optimizations of light profile [7], kinetic behavior [8] and operation conditions [9]. In this study, a mathematical model of the titanium dioxide ($\text{TiO}_2$) based photocatalytic reactor is introduced with UV LED as light sources. As a widely used photocatalysts, $\text{TiO}_2$ shows its advantages of as a cheap, stable and nontoxic catalyst for photocatalytic application. UV LED, which is a viable light source over many conventional lamps, has the potential of lower cost, higher energy efficiency and smaller size.

In this chapter, several fundamental knowledge of the photocatalytic reactor optimization is introduced from photocatalysis, light and catalysts used in this study, to the optimization principle of the reactor design. So an overview of the basic knowledge that the optimization bases on is shown in this part.

### 1.1. Photocatalysis

Photocatalysis implies the acceleration of a photoinduced reaction in a presence of a catalyst. The semiconductor catalysts have been widely used as photocatalysts to induce a series of degradative and oxidative reactions on its surface [3]. The distinct lone electron characteristic around the nucleus contributes to the foundation of the photocatalysis. Once the catalysts absorb the photon with energy equal or larger than the bandgap of photocatalysts, the lone electron is excited to the empty conduction band consequently. The photonic excitation of the electron leaves a positive hole in the valence band in the photocatalysts, and thus creating an electron-hole pair. The figure below shows the schematic mechanism of the electron-hole pair formation.

![Figure 1.1: Schematic mechanism of electron-hole pair formation [3]](image)

In this figure, an oxidation degradation reaction is taken as an example to show the mechanism. This electron-hole pair is considered as the energy carriers in the semiconductor [10]. The migration of the energy carriers eventually transfers the energy to activate the photocatalytic reaction. As it is shown in the figure, photocatalysts are very important in this mechanism as it transfer the energy from the photon to activate the reaction while remaining unchanged. The next section shows the development of the study on the photocatalysts in the recent studies.
1.2. Photocatalysts

The study on photocatalysts dates back to the 1970s and kinetic study of the photocatalytic reaction has been well achieved. A handful catalysts like \( TiO_2 \), ZnO, ZrOs and CeO\(_2\) were investigated and compared\([11]\) based on the attempt of the photocatalytic degradation of a wide variety of reactants. It is commonly accepted that the factors in control of the photocatalytic activities include the efficiency of electron-hole pair generation and their separation on the catalysts surface\([12]\).

In the study from Serpone et al.\([11]\), \( TiO_2 \) and ZnO showed the highest activity among all types with a higher efficiency above mentioned. However, comparing with ZnO, \( TiO_2 \) is of chemical stability in the large range of PH condition and cheap to acquire\([13]\) with higher energy conversion\([14]\). In the recent studies, special attentions have been focused in the field of heterogeneous photocatalysis using \( TiO_2 \) as photocatalysts with a variety of applications. Choina et al.\([15]\) showed the high potential of \( TiO_2 \) as long lifetime photocatalysts in the dyes decomposition. In addition, \( TiO_2 \) was also implemented in the pollutant degradation\([16]\) and air purification\([17]\).

According to the study of Kaneco\([16]\), \( TiO_2 \) also has the advantage of higher efficient, cheaper and suitable for varieties of light sources. Moreover, \( TiO_2 \) is also a non-toxic catalyst which makes it suitable for different type of reactor in water of air purification industry\([18]\). As a matter of fact that \( TiO_2 \) is more environmentally friendly, this semi-conductive catalyst is becoming widely used in both theoretical and practical studies. In the study from Chong et al.\([3]\), they summarized the feasibilities and advantages of \( TiO_2 \) in the heterogeneous reaction. \( TiO_2 \) can work under ambient operating temperature and pressure condition without secondary pollution from the intermedia compounds. In addition, the thermal stability and strong mechanical properties of \( TiO_2 \) prompt it with a wide industries as it is mentioned above.

Based on the reviews on varieties of photocatalysts, \( TiO_2 \) shows many advantages in the heterogeneous photocatalytic reaction with higher energy efficiency, cheaper cost, better stability, etc. So in this study, \( TiO_2 \) was selected as the catalyst in the reactor optimization.
1.3. Light sources

The photoinduced reactions require both semiconductor and sufficient light energy. The optimal light profile is necessary for the kinetic study. Many studies focused on the different types of light sources providing the light energy. The early studies of comparison between solar energy and artificial light source dated back to the early 1990s. Sunlight and artificial light showed different advantages in practical use. Rashed et al.[19] claimed that sunlight is of better performance in degradation of methyl orange over the conventional UV lamp [19]. However, in the study done by Neppolian et al.[20], they found out that the UV lamp showed much better performance in photocatalytic degradation with a large variety of the organic components. Although sunlight is more abundantly available and can be utilized at a smaller cost, the fluctuation character makes it less competitive comparing with the UV light source. In addition, UV irradiation is of great help in preventing the recombination of the electron–hole, which is thought to be a major problem in the photocatalysis process, at the activated catalytic surface [20].

More studies were conducted regarding the comparison of different types of UV light sources. In general, UV LED shows better quality in lower energy consumption, longer lifetime and smaller size for assembly than many conventional UV light sources (incandescent light and gas discharge UV lamp)[21]. In addition, UV LED also shows high potential in photocatalysis process. Shie et al. [22] studied in the comparison among three main types of UV light: Ultraviolet long-wave (UVA), Ultraviolet short-wave (UVC), and UVLED. They compared the performance of the three UV light with two primary factors, decomposition efficiency, and energy effectiveness. They found out that the UVLED can save much more energy than the conventional UV light source as UVA and UVC while reaching similar decomposition efficiency.

In addition, two studies from C.C. Wong et al. [23] and Jeong et al. [24] raised the comparison of different monochromatic UV LEDs with the various wavelengths. They pointed out that the UV light with the wavelength around 300 nm is of the best performance regarding the degradation and selectivity in the volatile organic components purification like toluene. A recent study by Levine et al. [25] compared the performance of UV LED with the UV BLB (a fluorescent black light blue lamp) by regarding several efficiency factors (photocatalytic oxidation efficiency, reaction quantum efficiency, energy efficiency). They found out that UV LED had the potential to achieve equally high efficiency as UV BLB by applying uniform irradiance. It showed that UV LED was a viable photon source regarding the efficiencies aforementioned.

Based on the past studies on different types of light sources, UV LEDs shows a good performance in photolysis with higher energy efficiency and photon yield over the sunlight and some conventional UV light sources. In addition, UV is safer and environmentally friendly than some conventional light source like mercury UV lamp. The UV LEDs assembly can also offer a better uniform light distribution on the catalysts layer based on the study of Wang et al.[7] in the reactor design. With all the advantages above mentioned, UV LED shows great potential in replacing conventional light sources.
1.4. Challenges and limitations

As it is shown in the past two sections, the LED and TiO$_2$ are both receiving great attentions in theoretical and practical studies. However, the challenge and limitation still exist for the photocatalysts and LED source. In a recent study on the review of the recent development of photocatalysis, Qu [19] pointed out several kinetic challenges and limitations that photocatalysis technology faces. On one hand, most photocatalysts can only work under the condition of ultraviolet (UV) or near UV light with limited efficiency. And the only a small fraction of photogenerated electrons and holes can be separated and available to activate the photocatalytic reaction. On the other hand, undesired reactions can be ignited due to the low selectivity of the semiconductor. So a stable and highly selective semiconductor with small band gap becomes the frontier of the catalysts study.

For the UV LED light source, it also faces the challenges and limitations. A recent study done by Steele [26] summarized the development of the commercial LED in the past decades. He pointed the two major limitations of LEDs which referred to a relative higher cost of LED compared with the conventional light sources and low light output per emitter. As Levine et al. [25], shows in his study, a large number of LEDs has a positive effect on improving the performance of UV LED regarding the efficiency. However, it also increases the total cost of the reactor and difficulties in heat management.

In addition to the challenges and limitations for the photocatalysts and light sources, photocatalysis technology also faces the challenges in commercialization and practical purpose. Several engineering limitations of the photocatalytic process were categorized into two types in the study done by Gerven et al. [25]. On one hand, the limitations of photon transfer partially concern the light profile design mentioned in the last paragraph. On the other hand, the limitation of mass transfer in reactor design is a common obstacle in the chemical engineering, especially in the scale-up stage. Several potential methods of improvement of mass transfer are provided in their study. One method is to increase the contacts between catalysts and reactants by slurry or rotation. The other way is to use reactor with high surface-to-volume value.

From the review of the analysis of limitation and challenge, it is concluded that optimizations are in need in many disciplines. The optimization of the light profile is essential to the performance of photocatalytic reactor concerning the performance efficiency factors aforementioned. Combining with the economic analysis shown above, the optimization guidelines are available and usable for the further commercialization.
1.5. Photocatalytic reactor optimization

The optimization study on the photocatalytic reactor can be classified into two broad categories. The first category mainly concerns the kinetic performance of the reactor, which refers to several performance efficiencies factors (quantum yield, photonic efficiency, photochemical thermodynamic efficiency factor).

In the study by Singh et al. [27], an optimal design of the monolithic reactor was introduced. In their study, the optimal objective of high photonic efficiency and better uniformity of radiation profile can be obtained by changing the configuration parameters (number of LEDs, proximity between lamps, etc.). Duran et al. [8] studied on the optimization of energy consumption based on the annular reactor. In the study, they pointed out that the hydraulic diameter ratio (a geometric ratio between reactor radius and rib height) had an influence on the energy consumption and reactor performance efficiency. The optimal balance between energy consumption and reactor performance was achieved by applying repeated ribs on the catalysts. It is concluded that the geometric parameters have great influence on the performance of the photocatalytic reactor regarding the several performance factors above mentioned. Van Gerven et al. [4] summarized the past studies on the optimization of the photocatalytic reactor to overcome the major limitations of the photocatalysis technology. Their study mainly focused on the influence that different type of reactors has on to the reactant-catalyst contact which determines the efficiencies above mentioned.

Apart from the studies concerning the optimization of various kinds of the reactor, the methods of the optimization also received a lot of attentions. Chong et al. [3] made a review of the past studies on the different methods of the optimization process. They compared the methods between the conventional experimental design (ED) and the multi-variable (MV) optimization principle. The ED method which is also called the one-factor-at-a-time approach was widely used in the past, especially for the optimal experiment condition analysis. This method is validated by assuming the performance parameters are independent. In the study of Natarajan et al. [18], the optimal operation parameters were obtained by changing the parameters one at a time. However, in the recent studies, the conventional method was replaced by the multi-variable method as the assumption is not validated every time. Another reason has to do with the fact that the former principle is very time and effort consuming [3]. For example, Duran et al. [8] achieved the optimal energy consumption by changing various variables (e.g., reactor geometry, the number of UV lamps and power output). Therefore, the MV optimization method was also used in this research in optimization with gPROMS.

The other category of the optimization study combines both the kinetic and the economic performance of the reactor. In the recent studies done by Loponov et al. [9], the economic analysis was taken as the objective function in the optimization process. In the study, they compared the kinetic performance of the three types of reactor and then optimized several variables to minimize the reactor cost. Using a robust reactor model with an objective cost function, he found the most relevant parameters in optimizing the microchannel reactor. Compared with the past studies, Loponov et al. [9] illustrated the possibility of reactor optimization with a cost objective function by changing the design parameters. Two studies
from Munoz [28] and Gernjak [29] implied the life cycle assessment (LCA) principle on the economic performance of the reactor using solar energy. Similarly, the objective function of these two studies was the annual reactor cost including electrical energy cost, fixed and operation cost, performance and chemical costs. The optimization of minimizing the annual reactor cost was achieved by varying the geomatic parameters. Although the optimization results showed the photocatalytic reactor was still costly, the study offered a method of the reactor optimization in the scale-up process based on the economic view.

In conclusion, the optimization combining both kinetic and economic performances of the photocatalytic has been shown based on the past studies. A multi-variables methodology is preferable in the optimization process by optimizing the design parameters.
1.6. **Objective of the project**

In general, the objective of this work is to achieve the model-based optimization of the photocatalytic reactor by minimizing the total reactor cost. With the mathematical model provided, simulation and optimization can be achieved with the help of gPROMS, a commercial software used in this work. As it is aforementioned, optimization strategy of this study combines the economic and kinetic performances. The optimization results are regarded to give an instruction on the annular reactor design based on both economic and kinetic views.

Based on the comprehensive optimization method mentioned above, the optimal reactor is defined as the one with the lowest cost while reaching a required conversion of the reactant. Therefore, this optimal goal follows the principle of combining both kinetic and economic performance. Based on the literature review on optimization, a multiple variables (MV) methods is involved in this process. The basic idea of this strategy is to achieve the objective by changing several controlling variables concurrently.

After the optimization activity in gPROMS, a set of optimal parameters can be achieved as the optimization results. Then, a comparison and analysis of the optimal results were conducted to check which parameters play significant roles in achieving an optimal annular tube reactor. In the optimization process, the procedure starts from the two-variable optimization and gradually reaches to more sophisticated optimization with four variables. In the two-variable optimization, the reliability of the model and software is examined. In the most sophisticated optimization with four variables, four parameters are selected as the controlling variables. Then more complex optimization entities can be performed as follows.

As this study contributes to the Light-generating Photocatalysts and Intensified Reactor project in TU Delft, the conclusion drawn will be used to compare with the experiment results in the future study of Maryam (Fatemeh) Khodadadian who works as the main researcher on this project. In the last chapter, a summary of the analysis of the conclusion is conducted and comments on the future investigation are also included.
In this chapter, the model of the photocatalytic reactor is introduced in detail by following the sequence from reactor configuration, governing mass and momentum balance model, reaction kinetics, irradiation profile, to the optimization expression.

An introduction to the configuration of the reactor and the governing equations is firstly shown. Two sections consist of this part. The first section is the geometry of the reactor, which displays the shape of the reactor with several geometric parameters. The second part shows the governing model by concerning both mass and momentum transfer phenomena. In addition, the assumptions that the model bases on are also well introduced in this part. In the end, the boundary conditions for solving the systematic differential equations are provided based on the kinetic model and light profile in the following parts.

Following the introduction of the mass and momentum balance, a brief summary on the kinetics of the chemical reaction is shown. As aforementioned, the degradation of toluene is taken as the reaction model. A chain reaction kinetics mechanism is used to build up the model for a series of complex photocatalytic reactions. This robust reaction model can be simplified by following the strategy proposed by M.J.Munoz and A. Kubacka [2]. A brief summary of the simplification process is discussed and shown. In the end, the expression of the reaction rate of toluene at the catalysts layer was shown, which is used as one boundary condition.

As it is mentioned that reaction rate is determined by the light obtained by the catalysts, the irradiation model is illustrated in detail. In this part, two three-dimensional models are presented in both Cartesian and cylindrical coordinates systems. The development of the irradiation model is briefly shown in this section. In addition, several simulations of the irradiation model were performed to illustrate the relationship between irradiation profile and design parameters. In the end, a two-dimensional model was simplified from the three-dimensional model in the cylindrical coordinates based on the configuration of the reactor shown in the previous section. The last model needed to be introduced is the optimization model which concerns the economic assessment of a four-year pilot reactor. A brief summary of the optimization principle is shown first. The objective function is illustrated later after the brief summary of the past studies on economic assessment.
2.1. Configuration of photocatalytic reactor

In this study, an annular reactor is chosen as the basic configuration. The LEDs are located within the reactor so that the energy can be fully utilized. As aforementioned that the model studied is a two-dimensional one, the geometric configuration of the reactor is shown below in figure 2.1.

As is shown in the figure 2.1, the reactor consists of three cylinders. The first part is the outermost wall where the catalysts locate. The catalysts layer is the nontransparent material to the light, which means this material can absorb all the light energy reaching the catalysts layer. Contradictory to this wall, the thin inner wall, which is marked with blue color, is entirely transparent to the light. The second part is the concentric annular tube through which the gas passes. The last part has to do with the most inner tube where all the LEDs are evenly distributed. The LEDs in the picture are marked with red color. The gas flows through the annular tube region between $r_1$ and $r_2$.

According to the figure 2.1 above, several geometric parameters can be figured out to describe the shape of the reactor: reactor length $L$, radius of the most inner wall $r_0$, radius defining the fluid region $r_1$ and $r_2$, thickness of each wall $t$, and distance between two LEDs along axial axis in sequence. As a matter of fact that all these parameters are related to the material cost, these parameters can also be treated as variables in determining the total cost of the reactor.
2.2. Momentum and Mass balances

Based on the configuration shown above, the mathematical model can be formulated by applying the mass and momentum balances in the cylindrical coordinate system. The momentum balance is required to describe the velocity profile in the reactor. The mass balance expression shows the concentration profile also along the flow direction. Several assumptions and theories are introduced so as to establish the mathematical expression:

1. Assuming the air is treated as the Newtonian, incompressible and isothermal fluid with constant physical properties, the model is axially symmetric. All the azimuth partial differential and azimuthal terms are dropped out. Besides, the model is also simplified as laminar flow so the vortex term in Naiver-Stokes can be neglected;

2. The fluid is in the stationary situation as this model is only used to simulate and optimize the performance in the steady state condition. All the time derivative terms are dropped out;

3. Chemical reaction at the catalysts wall has no impact on velocity profile which means the velocity is only determined by geometric parameters;

4. Flow in the reactor is considered as the one in the fully developed region. In other words, an unidirectional axial flow is obtained with constant pressure drops between the entry and outlet of the reactor;

5. Although always dilute, the only species that could change its concentration along the axial direction measurably in percentages is toluene. The diffusion along the radial direction can be treated as primary mass transfer mechanism from the gas to the catalysts layer. The convective mass transfer can be neglected. Moreover, the mass change along the axial direction is only driven by the flow.

Based on the first assumption, two sets of Naiver-Stokes equations can be established in the cylindrical coordinate system with constant physical properties. The first of a set of N-S equation is used to calculate the velocity of flow. The development of velocity expression starts from the continuity equation,

\[
\frac{\partial U_r}{\partial r} + \frac{\partial U_z}{\partial z} = 0
\]  

(2.1)

As it is assumed that the fluid is in the fully developed region, the partial differential term \( U_r \) over axial coordinate, \( z \), should be zero. There is no velocity gradient along the radial direction, which can be applied to the simplification of the velocity expression in motion equations. Applied with the assumptions that no velocity gradients along the radial direction, we can simplify the expression by dropping out the term with radial velocity. The Naiver-Stocks equation in the axial component is the only validated expression in this simplification. The final expression of velocity is,
After achieving the velocity expression, the development of governing model which shows the mass transfer within the gas phase can be formulated. The differential equations are also developed from the general Navier-Stokes equation. Comparing with the velocity expression, the gradients of the toluene concentration along both radial and axial direction are observed. Based on the assumptions above mentioned, a set of simplified mass balance expression is shown as follows,

\[ \rho U_z \frac{\partial U_z}{\partial r} = -\frac{\partial P}{\partial z} + \mu \frac{\partial}{\partial r} \left( r \frac{\partial U_z}{\partial r} \right) \]  

(2.2)

Wherein, \( D_{\text{eff}} \) stands for the effective diffusion coefficient of toluene which is derived based on the ideal situation where only diffusion is concerned in the mass transfer. \( C_{(r, z)} \) is the concentration at each specific position in the reactor. The term on the left hand side shows the concentration change along the fluid while term on the right side is the one relating to the pure diffusive mass transfer in the radial direction. The change of toluene in quantity along axial direction is equal to the amount transferred to the catalytic layer along radial direction. Eventually, the toluene reacts and is consumed at the catalysts layer.

In order to get the expression of velocity and concentration, several boundary and initial conditions are introduced based on facts and assumptions. Under the fully developed fluid condition, two boundary conditions confine the Newtonian, incompressible fluid. The first condition is that the fluid is stationary at both walls of the annular reactor. The other boundary condition has to do with the fact that radial velocity gradient is equal to zero at the central position of the reactor. Moreover, the volumetric flow rate, \( Q \), at the entry is taken as the initial condition. In summary, the mathematical expressions of these boundaries are,

\[ U_z \big|_{r=r_1,r_2} = 0 \]
\[ \frac{\partial U_z}{\partial r} \bigg|_{r=(r_1+r_2)/2} = 0 \]
\[ U_z \big|_{z=0} = \frac{Q}{\pi (r_2^2 - r_1^2)} \]  

(2.4)

Applied with these conditions, an explicit expression of velocity is achieved as follows,

\[ U_z = \frac{Q}{\pi r_2^2} \ln \left( \frac{r_1}{r_2} \right) \left[ \begin{array}{c} 1 - \left( \frac{r_1}{r_2} \right)^4 \ln \left( \frac{r_1}{r_2} \right) + 1 - \left( \frac{r_1}{r_2} \right)^2 \left( 1 - \frac{r_1^2}{r_2^2} \right) \ln \left( \frac{r_1}{r_2} \right) \\ 1 - \left( \frac{r_1}{r_2} \right)^2 \left( 1 - \frac{r_1^2}{r_2^2} \right) \ln \left( \frac{r_1}{r_2} \right) \\ 1 - \left( \frac{r_1}{r_2} \right)^2 \left( 1 - \frac{r_1^2}{r_2^2} \right) \ln \left( \frac{r_1}{r_2} \right) \end{array} \right] \]  

(2.5)
Comparing with the velocity expression, it is impossible to get an explicit expression of toluene concentration. The boundary conditions for solving mass transfer equation are shown as: 1. concentration gradient at the catalysts layer is equal to the reaction rate; 2. the gradient at the inner wall of the annular reactor is zero as chemical reaction only happens at the catalysts layer. In addition, an entering concentration is provided as the initial condition. The conditions are shown below,

$$\frac{\partial C_{z,t}}{\partial r} \bigg|_{r=r_1} = 0$$

$$D \frac{\partial C_{z,t}}{\partial r} \bigg|_{r=r_2} = r_{toluene}$$

(2.6)

Wherein, $r_{toluene}$ stands for chemical reaction which is related to the toluene concentration at the layer. The boundary conditions show that an implicit algebraic expression of the concentration can be developed, which can be solved numerically with the help of programming software.

### 2.3. Photocatalysis kinetic model

As it is mentioned in the introduction, photocatalytic degradation of toluene is considered as a promising and sustainable method as the reaction can be activated with normal temperature and pressure. Therefore, a kinetic model which is used to simulate the reaction at the catalysts is required. The general scheme can be described as a chain reactions mechanism, which is also called as Langmuir Hinshelwood model, with several intermediates among the reactions. The figure 2.2 below gives an overview of the reaction mechanism of oxidation of toluene based on the chain reaction model.

![Figure 2.2: Simplified diagram of the toluene degradation reactions](image)

Based on the study from Hennezela [30] and Munoz [2], they offered a methodology in simplifying the expression of the kinetic mechanism. The general idea of this simplification procedure can be summarized as three steps. In the first step, the expressions of reaction rates for toluene and other intermediary reactants can be developed with specific concentrations. In the second step, based on the assumption of steady state condition, a further expression of
toluene reaction rate can be achieved; In the final step, according to the experiment conducted by Hennezele [30], several terms can be dropped out as the values were subtle comparing with the other terms. The simplified expression of the reaction [2] rate of toluene was shown as follows,

$$ r_{C_{6}H_{5}CH_{3}} = -\sqrt{e_{\lambda}^{a,s}} \left( \frac{\alpha_1 C_{C_{6}H_{5}CH_{3}} + \alpha_2}{1 + C_{C_{6}H_{5}CH_{3}} K_{C_{6}H_{5}CH_{3}} + C_{H_{2}O} K_{H_{2}O}} \right) $$

(2.7)

According to the study done by Imoberdorf et al.[31], the irradiance has an influence on the local surface rate of electron-hole. Based on their studies, a linear relationship between irradiation strength and local surface generation rate of electron-hole under the condition of high irradiation. Therefore, the simplified expression of photocatalytic reaction rate of toluene can be achieved as,

$$ r_{C_{6}H_{5}CH_{3}} = -\alpha_1 \sqrt{e_{\lambda}^{a,s}} C_{C_{6}H_{5}CH_{3}} $$

(2.8)

In summary, an overview of the simplification method of the reaction rate expression is shown in this section. Based on the several assumptions and chain reaction theory, the complicated series of chemical reactions can be simplified to one simple expression. This expression showed a linear relationship between reaction rate of toluene and irradiance under the high irradiation condition. This expression is essential in solving the differential equations as is treated as one boundary condition. However, as it is shown above, the reaction rate is only determined by two variables which are not assumed by ones in defining shape or performance of the reactor. In the later part, the method of calculation of radiant intensity which is closely impacted by the shape of the reactor is introduced. Then the link between the chemical reaction rate and parameters that define the shape and performance of the reactor can be formulated.
2.4. Irradiation Model

In this section, an overview of the irradiation model is introduced. A three-dimensional schematic diagram, figure 2.3, shows the model of irradiation profile in the cylindrical coordinate system. In the figure, the red dots are the positions of one LED lamp and P is one point on the catalysts surface. \( n^2(\cos \phi_i, \sin \phi_i, z_i) \) stands for the normal vector of one LED, S. In this three-dimensional irradiation model, the UV LEDs are evenly distributed in a \( n \times N \) matrix in which \( n \) is the number of LEDs along the annular direction and \( N \) is the number of LEDs axially. The coordinates of each point in this system are expressed by radial distance \( r \), azimuth \( \phi \), and axis \( z \).

![Figure 2.3: Three-dimensional irradiation model in cylindrical coordinate](image)

The model of light profile starts from the irradiation distribution from single LED. Moreno et al. [32] came up with a phenomenological model for LED light pattern by concerning main phenomena. They developed a detailed expression of radiant intensity regarding the radiant flux. Based on the assumption that air is entirely transparent to the light. The energy lost in the fluid region is neglected. Therefore, a general expression describing the relationship between irradiance and radiant intensity of one single LED is shown as follows,

\[
E_{(z,r,\phi,z_i,r,\phi_i)} = \frac{I_{(z,r,\phi,z_i,r,\phi_i)}}{D^2} 
\]  
(2.9)

Wherein, \( D_{ij} \) and \( \theta \) are the distance and viewing angle from light source S to the specific point \( P(z,r,\phi) \) on the catalysts layer, respectively. By applying the approximation of radiant intensity from Moreno et al. [32], the radiant intensity at the point \( P \) can be expressed as the equation,

\[
I_{(z,r,\phi,z_i,r,\phi_i)} = I_0 \cos^n(\theta_{i,j}) 
\]  
(2.10)
In the formula, $I_0$ is the absolute radiant intensity from single LED lamp. Assuming there is a surface perpendicular to the normal vector of LED, $n^*(\cos \phi_{ij}, \sin \phi_{ij}, z_{ij})$, where the point P is located. $S'$ is the projection point of S in this surface. It is easy to calculate the distance from LED to this surface, $|SS'|$, and $D_{ij}$, respectively.

$$D_{ij} = r^2 + r_i^2 - 2rr_i \cos(\phi - \phi_{ij}) + (z - z_{ij})^2$$

The cosine value of the viewing angle from single LED S to the specific point, P, on the catalysts layer is available. Henceforth, the expression of radiant intensity received by the catalyst P from single LED is obtained as follows,

$$\cos \theta_{ij} = \frac{|SS'|}{D_{ij}} = \frac{r \cos(\phi - \phi_{ij}) - r_i}{\sqrt{r^2 + r_i^2 - 2rr_i \cos(\phi - \phi_{ij}) + (z - z_{ij})^2}}$$

$$E_{(x,y,x_i,y_i,x_i,y_i)} = I_0 \left( r \cos(\phi - \phi_{ij}) - r_i \right)^m \left( r^2 + r_i^2 - 2rr_i \cos(\phi - \phi_{ij}) + (z - z_{ij})^2 \right)^{(m+4)/2}$$

Based on the assumption that the attenuation of reflection of light through the gas phase is neglected, the irradiance strength received by the catalysts is equal to the energy from all LEDs. The irradiance of each point at the surface is equal to the accumulation of energy from all types of light. The expression of irradiation at catalysts layer can be achieved by accumulating the irradiation from all the LEDs. The expression is shown as follows,

$$E_{(z,r,\phi)} = \sum_{i=1}^{N_s} \sum_{j=1}^{n} \frac{I_0 \left( r \cos(\phi - \phi_{ij}) - r_i \right)^m \left( r^2 + r_i^2 - 2rr_i \cos(\phi - \phi_{ij}) + (z - z_{ij})^2 \right)^{(m+4)/2}}{\sqrt{r^2 + r_i^2 - 2rr_i \cos(\phi - \phi_{ij}) + (z - z_{ij})^2}}$$

Based on the expression above, the irradiation strength received by the catalysts is determined by the positions of catalyst surface and the number of LEDs. One thing needs to point out is that all the variables in the expression, like radius and number of LEDs, are taken as the geometric parameters of the reactor. Therefore, the irradiation profile is expected to be determined by the parameters aforementioned.

To validate this expectation that irradiation profile is determined by the geometric parameters, two sets of simulations are conducted. The first set of simulations is performed based on the three-dimensional irradiation model in cylindrical coordinates. Several simulations of irradiation model were performed as shown in figure 2.4. In this set of simulations, different irradiation profiles are obtained by changing the number of LEDs in the angular direction. From these four graphs, we can find that increasing the number of LEDs also increases the irradiance received by the catalysts. In addition, from the figure a to d, less fluctuated irradiation profiles were observed with the increase of the number of LEDs. The light profile is dramatically influenced by the number of LEDs. Based on the simulation results, the number of LEDs is essential to the light profile and intensity of irradiance received at the catalysts layer.
Figure 2.4: Irradiation intensity profile at catalyst layer with a different number of LEDs in angular coordinate: a. Irradiation; b. Intensity profile with n=2; c. Irradiation intensity profile with n=4; c. Irradiation intensity profile with n=6; d. Irradiation intensity profile with n=8
Apart from the number of LEDs, the other geometric parameters are also essential in determining the light profile. A new three-dimensional model in Cartesian coordinate system is introduced for this purpose. The configuration of the three-dimensional model in the Cartesian coordinates is shown in figure 2.5. The configuration of the model is made up of two layers. In the upper layer, LED lamps are evenly distributed in a 3x9 matrix. The catalyst is located at the bottom layer which is fixed to the height equal to zero.

Based on the general irradiance expression from the study done by Moreno et al. [32], the expression of irradiance (2.14) reached to the bottom layer in Cartesian coordinates is achieved as follows,

\[
E_{(x,y,0)} = \sum_i \sum_j \frac{I_0 \cos^m(\theta_{i,j})}{D_{ij}^2} = \sum_i \sum_j \frac{I_0 \cdot z_{ij}^m}{\left( (x - x_{i,j})^2 + (y - y_{i,j})^2 + z_{ij}^2 \right)^{(m+4)/2}}
\]  

(2.14)

Wherein \(E_{(x,y,0,x_{i,j},y_{i,j},z_{i,j})}\) stands for the irradiation strength received at a specific point at the catalysts layer from the LEDs located in the upper layer. \(I_0\) is the radiant intensity on axis of single LED. From this expression, we can see that the irradiation strength is also influenced by the positions of the two layers. As the height of bottom lay is fixed as 0, \(z_{ij}\) also stands for the distance between the two layers. So we can expect that the irradiation strength received by catalysts is closely related to the distance between the LEDs display and the catalyst layer.

The second series of simulations were performed in Matlab. The figures 2.5 show the different irradiation profile at catalysts layer with the changing distance between two layers. As it is shown in the graphs 2.5, the irradiation profile is becoming more uniform with the increase in the distance. However, the irradiance strength decreases at the same time, which can be observed with the peak value. The reason is that the power is concentrated mainly in a small radiation angle. The overlapping area between two adjacent LEDs is small when the distance between two layers are very close. We can see that a larger distance between LED display and catalyst of benefit to a uniform irradiation profile. Combining the simulation results obtained in the last series, the geometric parameters have influences on the irradiation profile and the irradiance at the catalysts layer.
Figure 2.6: Irradiance received at catalyst layer with different distances between two layers: a. Irradiance strength with d=10mm; b. Irradiance strength with d=20mm; c. Irradiance strength with d=30mm; d. Irradiance strength with d=40mm; e. Irradiance strength with d=50mm
In the previous section, the configuration of reactor model is built up in two dimensions based on the assumption that it is entirely azimuthal symmetry. Assuming that a uniform light profile is obtained in the annular cross section, the irradiation profile model can also be simplified to the two-dimensional one. Therefore, the irradiance at the catalysts surface can be calculated by expression below,

$$E_{(z,r,\phi)} = \sum_{i=1}^{N} \frac{I_0 \left( r - r_{i,j} \right)^m}{\left( \left( r - r_{i,j} \right)^2 + \left( z - z_{i,j} \right)^2 \right)^{(m+4)/2}}$$

(2.15)

In this expression, the term \((r - r_{ij})\) stands for the distance between the catalysts layer and the most inner wall where the LEDs locate. The irradiance strength is determined by geometrical parameters, reactor length, and the distance of catalyst surface to LEDs array, \(d\), and the number of LEDs.
2.5. Optimization formulation

Economic feasibility of the photocatalytic reactor has been proved to be promising comparing with the conventional technology. In the recent studies, we see a trend of obtaining the optimal reactor in both kinetic and economic ways. Based on the study done by Lopnov et al., the economic assessment can be integrated with the kinetic performance of the reactor. In their study, the reactor performance factor, conversion of the pollutant, is applied to the cost function. The objective of the optimization process can be summarized as minimizing the reactor cost while obtaining sufficient conversion of the reactant. Several parameters were adjusted separately to achieve the optimal reactor.

2.5.1. Formulation of the objective function

In this work, a similar optimization principle is applied. On one hand, the optimal reactor should obtain good kinetic performance by achieving required toluene conversion. On the other hand, the reactor cost should be minimized as much as possible by adjusting the design parameters. The expression of the photocatalytic reactor cost is used as the objective function. Since the objective function only involves the major costs, the total cost can be divided into three sections,

\[ C_{total} = C_{catalyst} + C_{material} + C_{operation} \]  \hspace{1cm} (2.16)

Where, \( C_{catalyst} \), \( C_{material} \), and \( C_{operation} \) stand for the catalysts cost, material cost and operational cost, respectively. This objective function concerns both the fixed and operational costs. The first two terms on the right-hand side contribute to the fixed cost. Instead of only considering the initial investment, the cost function also takes the effect of depreciation of the facility into consideration. A comprehensive cost function is applied to a four-year reactor. The specific expression for each term is shown as follow,

\[ C_{catalyst} = d_{catalyst} \cdot P_{catalyst} \cdot m_{catalyst} \]
\[ C_{material} = d_{material} \cdot P_{material} \cdot m_{material} \]
\[ C_{operation} = d_{LED} \cdot P_{LED} \cdot N + \frac{P_{elect} \cdot P}{d_{LED} \cdot t} \]  \hspace{1cm} (2.17)

The meaning and unit of all of the terms in the functions are referred to the notification in the appendix. In summary, the fixed cost mainly concerns the overall cost, which includes the installation and amendment, of the material and catalysts. The operation cost only involves the energy cost from the light sources. One thing that needs to point out is that the terms of the price and depreciation coefficient are fixed as unchangeable parameters in the model. The cost of each section is only determined by the design parameters including geometric (reactor length, radius, etc.) and operation parameters (power of LEDs),
By replacing the mass of material and catalyst in the function 2.17 with the expressions above, the total cost expression, which is determined by geometric parameters, is obtained as follows,

\[
C_{\text{total}}(r_2, L, N) = d_{\text{catalyst}} \cdot P_{\text{catalyst}} \cdot (2\pi \cdot r_2 L a) + d_{\text{material}} \cdot P_{\text{material}} \cdot \pi \rho_{\text{material}} \left( (r_2 + \text{th})^2 - r_2^2 \right) L \quad (2.19)
\]

Table 2.1 shows the summary of all the terms used in the model formulation, which includes the explanation and unit for each term. The value of the parameters used in the objective function are shown in the table in the Notation section. In summary, the objective function concerns the total cost for the photocatalytic annular reactor, which includes major investments spent in fixed and operational costs. One thing that needs to point out is that the depreciation factors are brought into this cost expression. The depreciation coefficients terms bring in the idea of the time effect in determining the annual cost. This idea follows the life cycle assessment principle as time is an essential factor in economic assessment. However, based on the assumption that only steady state situation is studied in this work, time is not considered as the variable in this model. The depreciation coefficients are only regarded as parameters instead of variables. The total cost of the photocatalytic reactor is only determined by several design parameters.
<table>
<thead>
<tr>
<th>Symbol of term</th>
<th>Explanation of the term</th>
<th>Unit</th>
<th>Symbol of term</th>
<th>Explanation of the term</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>weight of catalysts</td>
<td>kg/m²</td>
<td>P&lt;sub&gt;catalyst&lt;/sub&gt;</td>
<td>price of catalyst</td>
<td>$/kg</td>
</tr>
<tr>
<td>C&lt;sub&gt;in&lt;/sub&gt;</td>
<td>concentration of toluene at the entrance</td>
<td>mol/m³</td>
<td>P&lt;sub&gt;material&lt;/sub&gt;</td>
<td>price of material</td>
<td>$/kg</td>
</tr>
<tr>
<td>C&lt;sub&gt;out&lt;/sub&gt;</td>
<td>concentration of toluene at the outlet</td>
<td>mol/m³</td>
<td>P&lt;sub&gt;LED&lt;/sub&gt;</td>
<td>price of LED</td>
<td>$</td>
</tr>
<tr>
<td>C&lt;sub&gt;total&lt;/sub&gt;</td>
<td>total reactor cost</td>
<td>$/y</td>
<td>P&lt;sub&gt;elect&lt;/sub&gt;</td>
<td>price of electricity</td>
<td>$/y</td>
</tr>
<tr>
<td>C&lt;sub&gt;catalyst&lt;/sub&gt;</td>
<td>catalysts cost</td>
<td>$/y</td>
<td>P</td>
<td>power of LED lamp</td>
<td>W</td>
</tr>
<tr>
<td>C&lt;sub&gt;material&lt;/sub&gt;</td>
<td>material cost</td>
<td>$/y</td>
<td>Q</td>
<td>volumetric flow rate</td>
<td>m³/s</td>
</tr>
<tr>
<td>C&lt;sub&gt;operation&lt;/sub&gt;</td>
<td>operational cost</td>
<td>$/y</td>
<td>r</td>
<td>radius/radial vector</td>
<td>m</td>
</tr>
<tr>
<td>C&lt;sub&gt;z,r&lt;/sub&gt;</td>
<td>concentration rate of</td>
<td>mol/m³</td>
<td>r&lt;sub&gt;2&lt;/sub&gt;</td>
<td>radius of outermost wall</td>
<td>m</td>
</tr>
<tr>
<td>C&lt;sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;&lt;/sub&gt;</td>
<td>concentration of toluene</td>
<td>mol/m³</td>
<td>r&lt;sub&gt;1&lt;/sub&gt;</td>
<td>radius of the middle wall</td>
<td>m</td>
</tr>
<tr>
<td>dz</td>
<td>number of steps in axial direction</td>
<td>y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>r&lt;sub&gt;0&lt;/sub&gt;</td>
<td>radius of most inner wall</td>
<td>m</td>
</tr>
<tr>
<td>d&lt;sub&gt;catalysts&lt;/sub&gt;</td>
<td>depreciation coefficient of catalysts</td>
<td>y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>r&lt;sub&gt;c&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;&lt;/sub&gt;</td>
<td>reaction rate of</td>
<td>mol/s</td>
</tr>
<tr>
<td>d&lt;sub&gt;material&lt;/sub&gt;</td>
<td>depreciation coefficient of material</td>
<td>y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>th</td>
<td>thickness of wall</td>
<td>m</td>
</tr>
<tr>
<td>d&lt;sub&gt;LEDs&lt;/sub&gt;</td>
<td>depreciation coefficient of LEDs</td>
<td>y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>V</td>
<td>reactor volume</td>
<td>m³</td>
</tr>
<tr>
<td>D&lt;sub&gt;eff&lt;/sub&gt;</td>
<td>effective diffusion coefficient</td>
<td></td>
<td>U&lt;sub&gt;r&lt;/sub&gt;</td>
<td>radial velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>E</td>
<td>irradiance</td>
<td>W/m²</td>
<td>U&lt;sub&gt;z&lt;/sub&gt;</td>
<td>axial velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>I</td>
<td>radianc intensity</td>
<td>W/sr</td>
<td>z</td>
<td>axial coordinate</td>
<td></td>
</tr>
<tr>
<td>I&lt;sub&gt;0&lt;/sub&gt;</td>
<td>absolute radianc intensity</td>
<td>W/sr</td>
<td>φ</td>
<td>angular coordinate</td>
<td></td>
</tr>
<tr>
<td>m</td>
<td>radianc intensity</td>
<td>W/sr</td>
<td>θ&lt;sub&gt;i,j&lt;/sub&gt;</td>
<td>viewing angle</td>
<td></td>
</tr>
<tr>
<td>m&lt;sub&gt;catalyst&lt;/sub&gt;</td>
<td>mass of catalyst</td>
<td>kg</td>
<td>ρ</td>
<td>density of air</td>
<td>kg/m³</td>
</tr>
<tr>
<td>m&lt;sub&gt;material&lt;/sub&gt;</td>
<td>mass of material</td>
<td>kg</td>
<td>ρ&lt;sub&gt;material&lt;/sub&gt;</td>
<td>density of material</td>
<td>kg/m³</td>
</tr>
<tr>
<td>N</td>
<td>number of LEDs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.5.2. Formulation of the objective function

The formation of the optimization assignment starts from the objective declaration, controlling variable selection to the defining of the constraint variables. As it is shown in the previous section, the reactor cost was taken as the objective function in the optimization assignment. In this study, the objective is to minimize the cost function by changing several controlling variables, such as geometric parameters, the power of LED, volumetric flow rate, etc.

In the gPROMS, the controlling variables need to be declared in the OPTIMIZATIONS entity. These variables are predefined in the MODEL entity and then changed in the optimization process. The table below 2.1 shows the summary of the variables used in different optimization assignment from the two-variable optimization to the four-variable optimization.

<table>
<thead>
<tr>
<th>Optimization</th>
<th>Assignment</th>
<th>Controlling variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-variable optimization</td>
<td>Simulation assignment</td>
<td>Reactor length</td>
</tr>
<tr>
<td></td>
<td>Full optimization assignment</td>
<td>Number of LEDs, Reactor length</td>
</tr>
<tr>
<td>Three-variable optimization</td>
<td>Assignment 1</td>
<td>Number of LEDs, Reactor length, Power or LED</td>
</tr>
<tr>
<td></td>
<td>Assignment 2</td>
<td>Number of LEDs, Reactor length, Radius of the outermost wall</td>
</tr>
<tr>
<td>Four-variable optimization</td>
<td></td>
<td>Number of LEDs, Reactor length, Radius of the outermost wall, Volumetric flow rate</td>
</tr>
</tbody>
</table>

In addition to the objective function which concerns the economic view, the kinetic performance is also included in the OPTIMIZATIONS entity as the constraint variables. Constraint variable, which is also predefined in the MODEL entity, confines the optimization by meeting the requirement of this type of variable. Both equality and inequality constraint variables can be assigned to this section. Based on the complexity of the optimization and practical purpose, several constraint variables are proposed for different purposes. The first constraint variable is the conversion of the toluene which shows the kinetic performance of the reactor. The expression is shown as follows,

\[
Conversion = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\% \tag{2.20}
\]

Based on the optimization principle aforementioned, the reactor should achieve required conversion of the toluene. In this study, this value is set as fifty percent. However, in the optimization assignments with three and four variables, the conversion is declared as the inequality constraint variable considering the practical purpose of convergence in the numerical solving. A small range of the conversion is assigned from 50 percent to 50.1
percent. In addition to the conversion of toluene, the Reynolds number is proposed as the other inequality constraint variable in the three and four-variable optimization assignments. The expression of the Reynolds number is shown as follows,

\[ \text{Re} = \frac{Q}{\pi \mu (r_2 + r_1)} \]  

(2.21)

This constraint variable is introduced by considering the different flow pattern due to the change of radius of the reactor and volumetric flow rate. However, the fluid should remain under the laminar flow condition so that the model is still validated. Based on the practical purpose of convergence, an inequality constraint variable is provided for the Reynolds number. The range of the constraint variable is limited between 10 and 100 to keep the laminar flow condition. After the setting of the constraint variables, the optimization process can be performed based on the model introduced in the former entities. In conclusion, the optimization activity can be summarized as follows 2.2,

<table>
<thead>
<tr>
<th>Given</th>
<th>Variables defined in the CONTROLS section: geometric parameters of the reactor and power of LEDs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimize</td>
<td>The total cost of the photocatalytic reactor</td>
</tr>
<tr>
<td>So as to</td>
<td>Minimize the total cost</td>
</tr>
<tr>
<td>Subject to</td>
<td>Process constraints: Inequality constraints such as conversion of toluene and standard deviation of irradiance at the catalysts surface</td>
</tr>
</tbody>
</table>

**2.5.2. Formulation of the objective function**

The whole optimization model was formulated and performed in the commercial multi-entities based software, gPROMS model builder. Several entities consist of this model builder. In this study, VARIABLE TYPES, MODEL, PROCESS and OPTIMIZATIONS entities are used in the model formulation. In summary, the governing model is built up in the MODEL section based on the variable types defined in the VARIABLE TYPE entity. Simulation can be conducted in the PROCESS entity with the initial values and boundary conditions assigned. Combined with the OPTIMIZATIONS entity, the optimization process can be performed.

gPROMS model builder is a powerful platform which is well accepted by both the academic researchers and pioneer companies. Several advantages are shown below, which also gives the reasons why gPROMS is chosen in this study,

1. gPROMS Model Builder can properly be implemented for the dynamic simulation of the models with over 100,000 differential and algebraic equations [35], which is adequate for this work;
2. The same model can be used for both simulation and optimization activity, which means the model does not have to be re-written with changing set of input specifications [36];

3. gPROMS is implanted with several sophisticated conditional discrete methods and numerical solvers [36] for the different numerical operations. In this study, an MINLP (mixed integer non-linear programming) solver is utilized to solve the differential equations;

4. The multi-variable method is selected to perform the optimization process in this work. gPROMS makes it possible to change several controlling variables concurrently to achieve the optimization objective.

One thing needs to point out is that MINLP plays the essential role in the numerical solving issue. The first reason is that a nonlinear system of equations is introduced as the governing model. The second reason has to do with the iteration computation that both integer (number of LEDs) and continuous variables (reactor length) are present as controlling variables. The iteration computation process can be summarized in two steps. In the first step, a continuous nonlinear iteration is performed by treating the discrete variable as the continuous one. For the second step, the optimization proceeds with the discrete variable being rounded to the nearest integer. So a mixed integer solver is required when both integer and continuous variables are chosen as the controlling variable in the optimization assignment.

To solve the nonlinear algebraic system of equations, the finite differences and a discretization scheme are in need in both radial and axial directions. Several conditional discretization methods are embedded in this software. In this study, two discretization methods are applied based on different boundary conditions available. Along the axial axis, the back forward discretization method is used with simple boundary conditions. However, in the radial direction, a more complex method, central forward discretization method, is applied with an implicit boundary condition of reaction rate at the catalysts layer. Based on the advantages mentioned above, gPROMS is chosen as the platform to formulate and optimize the model for the photocatalytic reactor.
2.6. Summary and comments

In this chapter, the model of the photocatalytic reactor is introduced in detail from the configuration of the reactor, governing model, reaction kinetics, irradiation profile, to the optimization formulation. The essential theories and assumptions that each sub-model bases on are introduced in detail.

A two-dimensional governing model which concerns the primary mass and momentum transfer phenomenon is shown with the annular tube reactor configuration. The simplification process of the governing model is shown based on several core assumptions and hypotheses. Following the introduction of the governing model, the models for irradiation and photoreaction are shown independently. The chain reaction kinetics is proposed as the chemical reaction model based on the degradation of toluene. A simplified expression of reaction rate, which is proportional to the toluene concentration, is achieved. In addition, simplified irradiation models were also introduced to investigate the light profile. Several simulations were performed based on the irradiation models. The simulation results show the impact that geometric parameters have on to the light profile. It shows the possibility that the optimization of the reactor can be achieved by changing the geometric parameters. These variables are also used in the optimization assignment which is shown in detail in the next chapter.

Following the introduction of the mathematical models, the optimization formulation is presented in this chapter. The formulation starts from the objective function which is determined by several geometric parameters concurrently. Instead of changing the parameters one at a time, a multi-variable method is proposed for the optimization by changing several variables simultaneously. Based on this approach, commercial software, gPROMS, is introduced to perform the multi-variable optimization. The brief introductions to the optimization process and gPROMS are also shown in this section. The criteria of the optimal reactor are illustrated from both kinetic and economic perspectives.

In summary, the model for an LED-based annular photocatalytic tube reactor is presented in this chapter. The core principles of for each sub-model in the model building are introduced and analyzed in detail. In the last section, the optimization method and objective function are shown based on the multivariable optimization principle. The formulation of the optimization is introduced briefly by focusing on how gPROMS performs the optimization assignment. The constraints and objective function are introduced in detail based on the optimal reactor criteria from both kinetic and economic perspectives. In the next chapter, the optimization results are shown and analyzed in detail based on the optimization model introduced in this chapter.
Optimization results and analysis

Based on the mathematical model introduced in the last chapter, the optimization model is conducted in the gPROMS. In this chapter, the optimization activity is presented based on several assignments with different numbers of controlling variables. The chapter starts with the simple optimization assignment with two variables to the more sophisticated three and four-variable assignments.

With the increase in the number of variables, several geometric design parameters are involved including reactor length, number and power of LEDs, the radius of the reactor and the volumetric flow rate. Three type of optimization activities were conducted based on the number of variable declared. The activities are briefly introduced with the purposes of each assignment and key elements (the range of controlling variable). In addition to the introduction of each assignment, the optimization results are also analyzed to show the specific impact that each design parameter has on to the cost function.

Moreover, the increase of the number of variables also leads to the increase of complexity which can be proved by the CPU time of each optimization assignment. The simulation in the two-variable optimization only took around 100 seconds of CPU time. However, the computation time increases to more than 9000s to finish one four-variable optimization assignment with gPROMS. The increase of the complexity of the optimization model also leads to the difficulty in the numerical solving for the algebraic differential equations, which is discussed in detail in two and four-variable optimization results analysis sections.
3.1. Two-variable optimization

The first reactor optimization activity is a series of simulations and optimizations with two variables. The variables are the number of LEDs and reactor length. Two types of assignments contribute to the two-variable optimization. The first type of the assignment is related to a series of simulations in which only reactor length is taken as controlling variable. For a given series of the number of LEDs, correlated reactor cost and lengths are obtained to meet the required conversion of toluene. The other type is the assignment with both variables being declared as controlling variables. Therefore, the simulation and optimization are conducted by optimizing the reactor length and number of LEDs to minimize the cost, which is also constraint by the specific conversion of toluene.

Two purposes are examined based on these two optimization assignments. The first purpose is related to the relationship between reactor length and number of LEDs in optimizing the reactor cost. The other purpose is to check whether these two optimization assignments can obtain the same or similar results. The first purpose can be examined by several simulation results obtained in the first type of assignment. By changing the number of LEDs in the PROCESS entity, the change of both reactor length and the cost are observed concurrently. In addition, the lowest reactor cost can also be visualized with the series of results. This lowest reactor cost is taken as the optimal value to compare with the optimum results obtained in the other type.

The second purpose can be examined by comparing the optimization results with the lowest reactor cost obtained in the simulations. As it is aforementioned, the lowest cost of the reactor can be found among the simulation results obtained with the different number of LEDs given. In the second type of assignments, several optimum reactor costs can be obtained by being offered various initial guesses of the controlling variables. The comparison between the lowest reactor cost of the simulation results and optimum reactor costs can be achieved.
3. Optimization result and analysis

3.1.1. Result of the two-variable optimization

As it is introduced, twenty simulation assignments were performed first to show the change of reactor cost and length with an increasing number of LEDs. The number of LEDs which is assigned in the PROCESS entity varies from 90 to 135. Moreover, the range of the controlling variable, the reactor length, is from 0.5m to 15m. Two results, reactor cost ($C_{total}$) and length (L) are obtained in each assignment. Therefore, based on the twenty groups of results, a figure which shows how reactor cost and length change is obtained as follows,

![Figure 3.1: reactor cost ($/y$) as a function of the number of LEDs and the optimized reactor length with a conversion of toluene of fifty percent](image)

In the figure 3.1, the red curve stands for the optimal value of reactor length while the blue curve is the optimal reactor cost with given number of LEDs. It is evident to see that the reactor length decreases with the increasing number of LEDs. In addition, the figure shows a concave curve of the reactor cost with an increasing number of LEDs. So the optimal reactor cost was found at the lowest point of the concave curve where the number of LEDs is 114. Following the simulation results, the optimization assignments with two controlling were conducted. The results of these assignments are given in the table 3.1. Eleven assignments were performed with the same range of reactor length as the simulation assignment. Moreover, the range of the number of LEDs is from 5 to 1000. In each assignment, three optimal results, N, L and $C_{total}$ are obtained.

From the table 3.1, we can find that different initial guesses for both variables lead to different optimization results in the two-variable optimization. However, the optimization results are close to the lowest reactor cost obtained in the first type of assignment, which is shown in table 3.2. The reasons are discussed and analyzed in the next section.
Table 3.1 Optimum results of the two-variable optimization by using number of LEDs and reactor length as controlling variable to minimize the reactor cost with the conversion of toluene of 50%

<table>
<thead>
<tr>
<th>Initial guess</th>
<th>Optimized result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor length (m)</td>
<td>Number of LED</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>1</td>
<td>150</td>
</tr>
<tr>
<td>15</td>
<td>150</td>
</tr>
<tr>
<td>20</td>
<td>150</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
</tr>
<tr>
<td>15</td>
<td>200</td>
</tr>
<tr>
<td>25</td>
<td>200</td>
</tr>
<tr>
<td>25</td>
<td>250</td>
</tr>
</tbody>
</table>

3.1.2. Analysis of the two-variable optimization

According to the results presented in the last section, the optimization can always be achieved for both types of optimization assignments. It shows the reliability of the model to perform the optimization with a conversion of toluene of fifty percent. In addition, it proves that the geometric parameters have the impacts on the reactor cost, and the optimal result can be achieved by changing these parameters. The reactor length keeps reducing with an increase in the number of LEDs. Therefore, the first purpose of checking the relationship between two geometric parameters is achieved by the accomplishing several simulation assignments.

From the simulation results, the lowest reactor cost was observed when the number of LEDs is 114. In the two-variable optimization assignment, different initial guesses of the controlling variables give different sets of optimum results. Three reasons lead to the differences in the optimum results. The first reason is related to the default tolerance for the numerical solver. In the figure 3.1, a flat region of the curve of the reactor cost is observed around the lowest point. The relative errors of the optimal reactor costs obtained from the second optimization to the optimal result of the simulation is shown in table 3.2. From the table 3.2, the relative errors of all the optimization results are smaller than 2 percent. The relative error is calculated based on the equation [3.1],

\[
Error_{rel} = \frac{|C_{total, full} - C_{total, partial}|}{C_{total, partial}} \times 100\%
\]  

Where, \(C_{total, refer}\) is the lowest reactor cost obtained in the simulation assignments. \(C_{total}\) is the optimum reactor cost obtained in each two-variable optimization assignment. Since the default value of relative tolerance of MINLP solver is 0.1, the optimization results are accepted by the solver. A more accurate optimization result can be obtained based on a
smaller tolerance. However, a lower tolerance also leads to the difficulty in convergence and higher computational cost. Therefore, a proper tolerance is essential in the numerical solving issue.

Table 3.2 Comparison between optimal simulation result and two-variable optimum results

<table>
<thead>
<tr>
<th>Optimization assignment</th>
<th>Initial guess</th>
<th>Optimized result</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reactor length (m)</td>
<td>Number of LED</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>150</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>150</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>150</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>200</td>
</tr>
<tr>
<td>9</td>
<td>15</td>
<td>200</td>
</tr>
<tr>
<td>10</td>
<td>25</td>
<td>200</td>
</tr>
<tr>
<td>11</td>
<td>25</td>
<td>250</td>
</tr>
<tr>
<td>Simulation result</td>
<td>5</td>
<td>-</td>
</tr>
</tbody>
</table>

The second reason is due to the local minimum issue of the numerical solution. As it is introduced in chapter two, the differential equations system of the governing model is highly nonlinear which required numerical solving method. For the MINLP solver used in the optimization, a local optimum solution search is preferable and conducted first in the continuous domain. Therefore, the local optimum issue is observed especially when it comes to more variables optimization. In addition, the numerical method used to solve the differential equations. The Newton-raphson method is utilized in gPROMS to perform the numerical algebraic solving activity. The initial guess for the variable has a great impact on both convergence and the iteration results. The chances are high that different initial guess gives different iteration result because of this numerical method.

In summary, two purposes are checked based on the simulation and two-variable optimization assignments. The optimal reactor cost exists which is shown by the results of the simulation assignments. Based on the two-variable optimization assignments, the optimum results can also be found by changing the geometric parameters. The model is proved as the reliable method to perform more sophisticated optimizations with more controlling variables. However, the optimization results are highly initial-guess dependent, which means different initial guess results in the different optimum result. Several possible reasons are discussed in this analysis among which the flat region around the optimal value is thought to the major cause of this issue. Therefore, a change of tolerance of the solver is suggested to get a more accurate optimization result.
### 3.2. Three-variable optimization

Based on the results of the two-variable optimization, the optimization model is proved to be reliable for the reactor optimization. After the two-variable optimization assignment, more complicated three-variable optimization assignments are performed. The purpose of this three-variable optimization is to check the impact that more variables have on to the optimization results. In addition, the impacts that the power of LED and radius of the outermost wall have on to the optimal results are also compared.

Two sets of the assignments contribute to this three-variable optimization section. In addition to the number of LEDs and reactor length, one more variable needs to be declared as controlling variable. In the first set of optimization assignments, the power of LED was chosen as the third variable. The other set of optimization assignments is performed with the outermost radius, \( r \). The impact that both parameters have on to the cost function are shown and analyzed. The optimization assignment is carried out by following the same process as the full two-variable optimization. The initial values are given for the controlling variables and four optimum values are achieved as one set of optimization result. The optimization results of both assignments are shown in the next section.

#### 3.2.1. Result of the three-variable optimization

In the first optimization assignment, the power of LED is selected as the third controlling variable. The range of this variable, \( P \), is from 0 to 0.06W based on the instruction of the product. In addition, the constraint condition is still the conversion of toluene to a value of fifty percent. The table below shows the optimization results of this three-variable assignment.

<table>
<thead>
<tr>
<th>Initial guess</th>
<th>Optimization results</th>
<th>Constraint variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of LEDs</td>
<td>Power of LED (W)</td>
<td>Reactor length (m)</td>
</tr>
<tr>
<td>150</td>
<td>0.01</td>
<td>15</td>
</tr>
<tr>
<td>150</td>
<td>0.05</td>
<td>15</td>
</tr>
<tr>
<td>150</td>
<td>0.05</td>
<td>1</td>
</tr>
<tr>
<td>150</td>
<td>0.05</td>
<td>25</td>
</tr>
<tr>
<td>300</td>
<td>0.05</td>
<td>5</td>
</tr>
<tr>
<td>300</td>
<td>0.05</td>
<td>25</td>
</tr>
<tr>
<td>50</td>
<td>0.05</td>
<td>15</td>
</tr>
<tr>
<td>50</td>
<td>0.05</td>
<td>20</td>
</tr>
<tr>
<td>50</td>
<td>0.05</td>
<td>5</td>
</tr>
</tbody>
</table>
From the table 3.3, the optimal result of the power is always 0.06W with different initial guesses given. This value is equal to the maximum power of each LED. In addition, the optimization results of the number of LEDs and reactor length are similar to the two-variable optimization result. Different initial guesses for all variables gave different optimum results, which is quite similar to the results of the two-variable optimization assignment, which is referred to the table 3.1.

After the three-variable optimization with power as the third controlling variable, another three-variable optimization assignment is performed. Instead of using the power of LED, another geometric parameter, the radius of the outermost wall, is selected as the third controlling variable in this assignment. The range of the radius varies from 0.016 to 0.1m which is based on the practical purpose that the outermost radius is larger than the radius of the inner cylinders. The table 3.4 below shows the optimization results. From this table, we can see that different initial guesses lead to different optimization results. Three assignments give the results of smaller reactor cost and the last one shows a higher cost comparing with the former three-variable optimization. In addition, the three optimal results of reactor length reach to the lower bound and the other one is also very close to the bound. The analysis of this observation is shown in the next section.

<table>
<thead>
<tr>
<th>Initial guess</th>
<th>Optimization results</th>
<th>Constraint variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of LEDs</td>
<td>Radius r2 (m)</td>
<td>Number of LEDs</td>
</tr>
<tr>
<td>----------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>15</td>
<td>0.02</td>
<td>149</td>
</tr>
<tr>
<td>15</td>
<td>0.04</td>
<td>112</td>
</tr>
<tr>
<td>30</td>
<td>0.04</td>
<td>141</td>
</tr>
<tr>
<td>50</td>
<td>0.01</td>
<td>214</td>
</tr>
</tbody>
</table>

Reynolds number is brought in as another constraint variable for the optimization assignment with volumetric flow rate as the third controlling variable. The reason to add this constraint is that the change of radius also leads to the change of velocity profile in the fluid region. However, the fluid should remain under the laminar flow condition so that the model is still validated. The Reynolds number is limited within a range as $10 \leq \text{Re} \leq 100$. 

Table 3.4: Optimum results of the three-variable optimization by using the radius of the reactor, number of LEDs and reactor length as controlling variable to minimize the reactor cost with the conversion of toluene of 50%.
3.2.2. Analysis of the three-variable optimization

From the table 3.3, we can find out that the power of the LED reaches the standard power which is also the upper bound of this controlling variable. Since the lifetime of the LED is shorter with an increase in power, the standard power is assumed to be the maximum power available under the standard working condition. In addition, from the table 3.4, the number of LEDs and reactor length share the similar optimization results as the full two-variable optimization results. This leads to a conclusion that power plays a less role in determining the reactor cost comparing with the other two variables.

Two reasons are proposed regarding this conclusion. The first reason is that sufficient energy is required by the catalysts to meet certain reaction rate. As it is shown in the kinetic reaction model, the energy provided by the LEDs and the concentration have the direct impact on the reaction rate which determines the conversion of toluene. Therefore, a set of LED assembly with high power is preferred based on kinetic purpose. The other reason has to do with the fact that the price of electricity is very low. As it is shown in the appendix, the annual electricity price for the light source is 0.816 $/W·y which is ten times smaller than the price of LED. Since number and power of LEDs are the only two parameters in determining the total input energy, it is more economical to increase the power of LED instead of number of LEDs.

Based on the results in table 3.4, the decrease of the reactor cost is observed in three sets of optimization results comparing with the lowest cost obtained in the two-variable optimization. It is evidently shown that the radius has the influence in determining the reactor cost. The outermost radius is essential in optimization design of this reactor as it determines the distance between LEDs and catalysts layer. As it is shown in the second chapter, the distance influences the light profile which determines the energy received by the catalysts. A larger distance is of benefit to a uniform light profile while a smaller distance increases the energy received by the catalysts. Based on the optimization results in table 3.4, it indicates that the optimal radius reaches to the lower bound of the range. Therefore, a small radius is accepted by the model to minimize the cost while reaching fifty percent of the toluene conversion.

In addition to the impact on the light profile, the distance from catalysts to the light display also influences the mass transfer along the radial direction. As it is shown in the second chapter, diffusion is the major mass transfer phenomenon along the radius direction. Therefore, the radius of the outermost wall directly influences the mass transfer resistance of diffusion. The equation 2 below shows the expression of mass transfer resistance from catalysts layer to the light display,

\[
R_{\text{diffusion}} = \frac{\Delta C}{F} = \frac{(r_2 - r_1)^2}{D_{\text{eff}}}
\]  

(3.2)

In the expression above, \(R_{\text{diffusion}}\) is the resistance of diffusion, \(\Delta C\) is the concentration difference and the \(F\) stands for diffusion flux. Based on the expression, a small radius of the outermost wall is beneficial to the smaller mass transfer resistance which increases the
intensity of the mass transfer through diffusion. Therefore, the optimal result of radius, $r_2$, is obtained with a small value close to the lower bound for the range. So we can draw a conclusion that the radius is important in determining the reactor cost and a relatively smaller radius is preferred with this model. Two reasons are proposed to explain this optimal result as a small radius is beneficial to the energy received by the catalysts and the mass transfer intensity through diffusion.

One thing needs to point out is that the increase in the number of controlling or constraint variables leads to a more complex numerical issue. A higher complexity of the numerical issue makes it harder to get convergent while solving the differential equations. Several methods were taken to solve this difficulty. One method is to give easier constraints in the optimization assignment. For example, the equality constraint condition can be replaced by the inequality constraint with a larger range. Another method is to increase the tolerance of the solver so that an easier convergent requirement can be achieved. However, a trade-off is required in the process since a larger tolerance would lead to inaccurate optimization result. In the three-variable assignments, both methods were applied to obtain the optimization results.
3.3. Four-variable optimization

Based on the three-variable optimization, three major geometric parameters are introduced in determining the reactor cost. In the analysis of the three-variable optimization results, a small radius of the outermost wall is preferable. By adding one more controlling variable, a four-variable optimization assignment is proposed based on the former optimization.

In the four-variable optimization assignment, another controlling variable, volumetric flow rate, is declared. The volumetric flow rate is closely related to the flow pattern. It determines the velocity profile in the reactor which affects both the concentration and residence time of the toluene. As it is shown, the concentration and residence time of the toluene determines the conversion of toluene as a result. In addition, the volumetric flow is also an indicator of the reactor’s performance as it shows the amount of toluene consumed by the reactor. However, in the above optimization activities, the criteria of the optimal reactor only concern the conversion of the toluene as the performance factor. The actual capability of the reactor is not shown in the criteria. Therefore, the purpose of adding volumetric flow rate as controlling variable is to check the impact that this design parameter has on the optimization. Based on the study from Lopnov [22], an amendment is proposed to the objective function by combining the actual performance of the reactor with cost assessment. The function is shown as follow,

$$ C_{total,new} \equiv \frac{C_{total}}{\bar{v}_e \cdot C_{m} \cdot \text{Conversion}} $$

(3.3)

Where, $C_{total,new}$ is the new reactor cost with a unit of $/mol$ which shows the cost spent to convert one molar of toluene. $T$ is the working time of the reactor in seconds, $Q$ stands for the volumetric flow rate and $C_{total}$ is the former objective function. In summary, the new cost function is introduced based on the idea as follows,

New reactor cost = Annual reactor cost / mole of toluene converted per year

Based on this objective function, the four-variable optimization assignment was performed. The next section shows the optimization results of the four-variable assignment.

3.3.1. Result of the four-variable optimization

In table 3.5, the results of the four-variable optimization assignments for different initial guesses are shown. Different initial guesses lead to different optimization results, which is similar to the three-variable assignments. The optimum reactor costs based on the new objective function are shown in the column with the name ‘Molar reactor cost’. The last column shows the reactor cost based on the original objective function of annual reactor cost.
Table 3.5: Optimum results of the four-variable optimization by using the radius of reactor, number of LEDs, reactor length and volumetric flow rate as controlling variables to minimize the reactor costs with the conversion of toluene of 50%

<table>
<thead>
<tr>
<th>Initial guess</th>
<th>Optimization results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor length (m)</td>
<td>Number of LEDs</td>
</tr>
<tr>
<td>10</td>
<td>500</td>
</tr>
<tr>
<td>10</td>
<td>500</td>
</tr>
<tr>
<td>1</td>
<td>500</td>
</tr>
<tr>
<td>10</td>
<td>500</td>
</tr>
<tr>
<td>10</td>
<td>500</td>
</tr>
<tr>
<td>20</td>
<td>500</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
</tr>
</tbody>
</table>
In addition to the results of four-variable optimization, the optimum reactor costs of three-variable optimization based on the new objective function were shown in table 3.4. In the three-variable optimization, the volumetric flow rate is fixed, which means there is no change to the optimum results of the number of LEDs, reactor length and radius in principle. Therefore, the reactor costs in the last column are obtained by dividing the results in the ‘annual reactor cost’ column with the term \( Q \cdot C_{in} \cdot Conversion \).

Table 3.6: Comparison of the optimal reactor costs of three-variable optimization based on two objective functions

<table>
<thead>
<tr>
<th>Number of LED</th>
<th>Radius ( r_2 ) (m)</th>
<th>Reactor length (m)</th>
<th>Annual Reactor cost ($/y)</th>
<th>Molar Reactor cost ($/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.02</td>
<td>5</td>
<td>664</td>
<td>1218</td>
</tr>
<tr>
<td>15</td>
<td>0.04</td>
<td>5</td>
<td>670</td>
<td>1229</td>
</tr>
<tr>
<td>30</td>
<td>0.04</td>
<td>5</td>
<td>653</td>
<td>1198</td>
</tr>
<tr>
<td>50</td>
<td>0.01</td>
<td>10</td>
<td>789</td>
<td>1447</td>
</tr>
</tbody>
</table>

3.2.2. Analysis of the four-variable optimization

From the table 3.5, a small radius is still preferable to the objective function as the optimal radius achieved is close to the lower bound. The radius is proved to be essential in the reactor optimization. However, compared with the results of the two and three-variable optimization activities, the optimal results obtained in the four-variable optimization deviate a lot. The results in the first three assignments are far different from the rest four. The reason for this deviation is presumed to be the local minimum issue in the numerical solving process. As it is mentioned in the two-variable optimization result analysis, the algebraic differential equations are highly nonlinear ones. The numerical solver, MINLP, in use to solve the equations prefers the local optimal result search in the continuous variable region. Therefore, a method of achieving global optimum is recommended in solving the algebraic differential equations.

As it is shown in table 3.6, two objective functions give opposite results of the optimal reactor cost. Both strategies give reasonable results based on different purposes of the optimization. For the original objective function, the annular reactor cost is the focus which only concerns the money spent to meet this criterion. Therefore, a small reactor is preferable to minimize the cost. However, for the amended objective, the performance of the reactor is also involved in the expression. The reactor with a large volume is preferred if a large consumption of toluene is required. The third optimum result, marked with red color in table 3.5, gives a better solution with relatively lower costs for both objective functions. It offers a potential method for the reactor optimization by concerning both two types of costs. However, more optimization assignments are required to validate this method in the future studies.

From the results shown in table 3.6, the optimum reactor costs of three-variable optimization were higher than the counterparts of four-variable optimization. It shows that the volumetric flow rate is influential in minimizing the reactor cost. In addition to the optimum reactor costs,
the two optimization assignments also present different optimum results in the number of LEDs and reactor length. More LEDs and longer reactor length were observed in the four-variable optimization results.

The volumetric flow rate shows the capacity of the reactor which makes it cheaper to use larger equipment to convert the toluene. The radical reason is related to the residence time for the toluene in the reactor. In addition to the intensity of reaction, the residence time also determines the amount of the toluene converted by the reactor. Sufficient residence time is required to convert the specific amount of toluene. Moreover, as it is mentioned that diffusion is the major mass transfer phenomenon along the radial direction, it also requires sufficient residence time to transfer the toluene radially to the catalysts layer. A higher volumetric flow leads to the increase in velocity of the flow, which makes the residence time smaller if the reactor length remains the same. Therefore, a longer reactor is in need to meet the sufficient time requirement.

In conclusion, two new design parameters are proved to be essential in the reactor optimization. A revised objective function is proposed based on the amendment of the first objective function. The comparison between the two objective functions is performed. Based on this comparison, a possible solution of combining these two strategies is proposed for a further analysis.
3.4. Summary and Comment

In summary, three types of optimization activity were conducted in this study based on the model introduced in chapter two. Several design parameters are declared as the controlling variables in the optimization assignments. The number of variables increases from two to four with the increase in the complexity of the optimization model. The optimization results are also presented and analyzed in detail in this chapter. Based on these results, several parameters are brought up as the major determining factors in the reactor optimization.

The optimization activity starts with a simpler assignment with two controlling variables, the number of LEDs and reactor length. In this part, several simulation were performed and the optimal reactor cost is visualized with the optimal number of LEDs and reactor length. Similar optimization result was also achieved with the two-variable optimization which shows the reliability of the model. In addition, the number of LEDs and reactor length are both proved to be essential to the reactor optimization. Based on the two-variable optimization, the power of LED and radius of the reactor were examined in the three-variable optimization assignments. The conclusion drawn is that higher power of LED and small radius are preferable in achieving the goal of minimizing small reactor cost.

Following the three-variable optimization, a four-variable optimization assignment is presented by adding volumetric flow rate as the fourth controlling variable. In addition to adding one more variable, an amendment was made to objective function by adding the volumetric flow rate to the function. The new objective function combines the reactor cost with the capacity of the reactor to show the cost spent in converting the toluene. Two conclusions were drawn in this part. The volumetric flow rate is proved to be essential in the optimization. And the other conclusion shows that the reactor with higher annular cost gives a lower cost based on the new cost function.

In summary, the number of LEDs, reactor length, the radius of the cylinder and the volumetric flow rate all play essential roles in the reactor design based on this optimization model. gPROMS is also proved to be a reliable platform to obtain the optimal reactor design. However, more efforts are still needed for the further studies. As it is mentioned in the three variables optimizations, the increase of controlling and constraint variables also leads to the difficulty in the convergence of the numerical solution. In the four-variable optimization, we have seen a large deviation among the optimization results which is presumed to be the local minimum issue in numerical solution. So more efforts are needed to investigate the MINLP solver and discretization method. In addition, a new optimization function is brought out by adding the volumetric flow rate into the original objective function. A further study of the combining the two types of reactor cost is thought to be valuable by following the same strategy introduced aforementioned.
4. Conclusions and Recommendations

4.1. Conclusion

The objective of this study is to provide an optimization methodology of the annular photocatalytic reactor via a mathematical model. A set of numerical equations contributes to the mathematical model in the optimization model of the annular photocatalytic reactor. The algebraic equations describe the governing model of the reactor while the optimization model shows the process of optimal reactor design.

Several submodels consist of the governing model, which starts from the two-dimensional configuration of the reactor, kinetic models of reaction and light profile, to the mass and momentum governing equations. The photocatalytic degradation of toluene is taken as the reaction model. As aforementioned, the optimization goal of the methodology is to minimize the reactor cost while receiving required conversion of the toluene. The optimization model is formulated with the objective function and several constraints. The optimal reactor is defined based on both economic and kinetic views. This optimization goal was achieved by changing several design parameters, such as geometric parameter and power of LEDs, etc., concurrently in the optimization model.

Based on the optimization model, three sets of optimization assignments with different numbers of variables were conducted. Several design parameters were introduced and compared to check the impact that each parameter has on the objective function. Therefore, the geometric parameters and volumetric flow rate were proposed as the primary determining parameters in the reactor optimization. In the two-variable optimization, the optimal reactor cost is observed in a series of simulations and the optimum result is obtained by the two-variable optimization assignments. In the three and four-variable optimizations, volumetric flow rate and radius were examined to be more influential in determining reactor cost over the power of LED. In addition, a new objective function is proposed and analyzed based on the purpose of evaluation of the cost spent to convert one molar toluene. However, with an increase of the number of the controlling variables, the complexity of the mathematical model also increases. The increase in complexity of the model leads to the difficulty of the convergence in solving the algebraic equations system. Several possible methods of solving this issue are proposed by relaxing the constraints and offering a larger
tolerance of the solver.

In conclusion, a multivariable mathematical model is introduced in this study as the methodology. And the model formulated in gPROMS is proved to be reliable in the photocatalytic reactor optimization. In addition, several design parameters are proposed as the main factors in reactor design.

4.2. Recommendations

4.2.1. Validation of experimental results

Although the gPROMS model is proved to be reliable by the optimization results, experimental results are still required to validate the mathematical governing model. The validation includes the light profile at the catalysts layer and experimental data of the toluene conversion with the same configuration of the reactor. Once the model is validated by the experiment, the conclusion of drawn in this study can be utilized as the methodology in reactor design.

4.2.2. Further study on the objective functions

As it is shown in the four-variable optimization section, a new type of cost function is present by considering the cost spent to convert per molar toluene. Instead of optimizing the annual cost, this function shows a different strategy in optimization which gives different optimal reactor design. The optimization results show that a reactor with a large volume is of benefit in reducing the cost spent in converting toluene. However, based on the original objective, a small reactor is preferable to the annual cost reduction.

The two functions are both reasonable. For the original objective function, it considers the conversion of toluene as the performance factor. Nevertheless, the new objective involves the capacity of the reactor which shows the amount of toluene converted. A further study is required to take both aspects into consideration. One recommendation is proposed by combining the two functions together as one function. So a compromised optimization result can be achieved with relatively lower cost in both two types of cost.

4.2.3. Numerical solution with higher order

As it is discussed in the previous section, with the increase of the controlling variables in the optimization activity, it is getting more difficult in obtaining convergent results for the algebraic equations. Although several methods have been taken in the three and four-variable optimizations, failures still exist in the numerical solving process. In addition, the accuracy of the results is also required to solve the local minimum issue. More studies need to be offered on this topic based on the mixed integer nonlinear solver embedded in the gPROMS. As the solver implemented in gPROMS is still under developing, it can be expected that higher order of numerical solver will be available.
4. Conclusions and recommendations

4.2.4. Alternative software of model building

As it is shown in the previous chapter, several numerical difficulties occurred during the differential algebraic equations solving process. The major cause was related to the local minimum issue which is brought out by the MINLP solver utilized in gPROMS. Therefore, the alternative solver achieving global optimum is recommended in the analysis of the result of four-variable optimization section. The state-of-the-art software in the model building, namely General Algebraic Modeling System (GAMS), can be used as the alternatives to continuing the study.
Bibliography


Appendices

.1. Parameters assessment

.1.1. Depreciation coefficient of catalysts, $d_{\text{catalysts}}$

The prediction of catalysis lifetime is based on the research done by Tasbihi et al. [37]. In this book, a batch reactor is used to predict the half lifetime for supported $TiO_2$ photocatalysts. And the conclusion is that the catalysis reaches to its half lifetime after ten cycles with 40 min in each cycle. So the total lifetime for $TiO_2$ based photocatalysts is 1000 min with no regeneration. Several assumptions are needed to determine depreciation factor for catalysts:

1. Regeneration can fully recover the catalysts to its initial working performance
2. Regeneration time is not included in the working time
3. Reactor works 16 hours a day which is also the lifetime of catalysts.
4. Catalysts are replaced every month after 30 regenerations.

So the depreciation factor of this type of catalysts is 12, which means the catalyst is replaced 12 times a year.

.1.2. Power of LED and Depreciation coefficient of LEDs, $d_{\text{LED}}$

The light source used in this study is the LED lamp from Nichia, version NSSU100CT. The figure below 2 shows the schematic principle of the irradiation at the surface. The standard working condition is also laid out with the current of 30mA and voltage of 3V. So the standard power which is also the maximum power obtained is 0.06W.

Based on the instruction from NICHIA (the manufacturer of standard LED) [6] the average lifetime for LED under the standard working condition is 1000 hours. In addition, the standard working power of this LED is 0.06W. Based on the assumption that the reactor works 16 hours per day, the depreciation factor of LED, $d_{\text{LED}}$, can be calculated and rounded to 6 as follows,

$$
d_{\text{LED}} = \left| \frac{365}{1000/16} \right| = 6
$$

.1.3. Price of material, $P_{\text{material}}$

The material of the reactor mainly concerns the one at the outer wall of the reactor. So the price of material is the cost of stainless steel. The method used here is factoring approach proposed by Peters et al. [38] which predicts the fixed-capital investment cost in the end. This approach covers the costs of labor, fitting, amendment and installation.

In general, the raw material and labor cost contribute to 13 percent of the total cost of piping and pipe related equipment in the coarse estimation. Since the reactor works under the normal pressure and temperature condition, the standard material with a lower cost is sufficient in
this case. Based on this reason, the stainless steel with type 304 is selected for the outermost wall. With the help of auxiliaries’ graph [39] an estimation cost, 10 dollars per kilogram, is settled. So the total fixed cost for the pipe-shaped wall is 77 dollars per kilogram.

**1.4. Depreciation coefficient of material, d\text{material}**

The depreciation coefficient of the material concerns the lifetime of the reactor. Based on the assumption that the reactor works until the end of its lifetime, the depreciation coefficient of the material is equal to the reciprocal of the lifetime. The lifetime of this photocatalytic reactor is presumed to be four years in this study. So the depreciation coefficient \(d\text{material} \) is equal to 0.25.

**1.5. Price of electricity, \(P_{\text{ele}}\)**

The average electricity prices in the past three years in the euro were obtained from the website Eurostat [40], the official website for European statistics. The values of electricity price from the year 2011 to 2013 are marked with red circle in the figure [2] below.

The electricity price we select for this study is the industrial one in the year 2013, 0.127 euro/kWh. So the annular electricity price can be obtained based on the assumption that the LED works 16 hours per day, which is shown as the equation below,

\[
0.127(\text{euro/kWh}) \times 16(\text{h/d}) \times 365(\text{d/yea}) \times 1.1(\$/\text{euro})/1000 = 0.816(\$/\text{W/yea})
\]

![Figure 2: Electricity price of main European countries from the year 2011 to 2013](image)

**1.6. Price of photocatalysts, \(P_{\text{material}}\)**

The price of photocatalysis is obtained from the website, sigma-aldrich [34], one of the largest catalysis manufacturers. The price range is from 68 to 160 based on different components and structure, which are differentiated based on the function of the catalysts. In the model, the highest market price, 160 euro/kg, is selected for the coarse cost estimation.
.2. Code of the gPEOMS model

.2.1. Code of the MODEL entity

PARAMETER

\begin{align*}
m & \text{ AS REAL} \quad \# \text{ LED directionality} \\
\text{radial}_\text{Diffus} & \text{ AS REAL} \quad \# \text{ diffusion coefficient} \\
\text{reaction}_\text{rate}_\text{constant} & \text{ AS REAL} \quad \# \text{ reaction rate constant (m3/s.W)} \\
\text{photon}_\text{exponent} & \text{ AS REAL} \quad \# \text{ exponent of superficial rate of photon absorption} \\
\text{counter} & \text{ AS INTEGER} \quad \# \text{ Number of LEDs axially and is calculated } N = \text{floor}(L/s)+1 \text{ in Matlab (or counter)} \\
a & \text{ AS REAL} \quad \# \text{ kg cat per surface area of the reactor} \\
P_\text{cat} & \text{ AS REAL} \quad \# \text{ cat cost} \\
P_\text{mat} & \text{ AS REAL} \quad \# \text{ material cost} \\
P_\text{LED} & \text{ AS REAL} \quad \# \text{ LED and electricity cos} \\
P_\text{elec} & \text{ AS REAL} \quad \# \text{ electricity cost} \\
t & \text{ AS REAL} \quad \# \text{ reactor jacket thickness} \\
d_{\text{dens}} & \text{ AS REAL} \quad \# \text{ reactor jacket density} \\
d_{\text{dens}} & \text{ AS REAL} \quad \# \text{ catalyst density} \\
d_{\text{dep}} & \text{ AS REAL} \quad \# \text{ depreciation factors} \\
d_{\text{dep}} & \text{ AS REAL} \quad \# \text{ depreciation factors} \\
d_{\text{dep}} & \text{ AS REAL} \quad \# \text{ depreciation factors} \\
d & \text{ AS INTEGER} \quad \# \text{ grid numbers} \\
\end{align*}

DISTRIBUTION_DOMAIN

\begin{align*}
\text{axial} & \quad [0:1] \quad \# \text{ axial has been normalized} \\
\text{radial} & \quad [0:1] \quad \# \text{ radial has been normalized } r_\text{prime} = r^*(R_\text{out}-R_\text{in})+R_\text{in} \& 0<r<1, R_\text{in} < r_\text{prime} < R_\text{out} \\
\end{align*}

VARIABLE

\begin{align*}
\text{max_int} & \quad \text{AS no_type} \quad \# \text{ reactor Length} \\
\text{reactor}_\text{length} & \quad \text{AS length} \\
R_\text{in} & \quad \text{AS length} \quad \# \text{ the outer radius of inner tube} \\
R_\text{out} & \quad \text{AS length} \quad \# \text{ the inner radius of outer tube} \\
R_\text{light} & \quad \text{AS length} \quad \# \text{ the radius of LED assembly tube} \\
d & \quad \text{AS length} \quad \# \text{ distance of LEDs from catalyst surface radially} \\
\text{Cin} & \quad \text{AS concentration} \quad \# \text{ inlet concentration @ z=0} \\
\text{residence}_\text{time} & \quad \text{AS residence_time} \quad \# \text{ residence time} \\
\end{align*}
vol\_flow\_rate AS flow\_rate # Volumetric flow rate
u AS DISTRIBUTION (radial) OF velocity
radius\_ratio AS no\_type # inner to outer radius ratio

N AS no\_type # number of LEDs
s AS length # LED-to-LED space in axial direction
z\_0 AS ARRAY(counter) OF length # position of each LED on z coordinate and calculated in matlab as linspace(0,L,N)
P AS power # LED power

e\_as\_z0 AS DISTRIBUTION (axial, counter) OF photon\_absorption\_rate # irradiance from every LED at any point
e\_as AS DISTRIBUTION (axial) OF photon\_absorption\_rate # local superficial rate of photon absorption
e\_as\_ave AS photon\_absorption\_rate # average of irradiance in the reactor
STDE AS no\_type # standard deviation to show the level of uniformity of light

molar\_reaction\_rate AS DISTRIBUTION(axial) OF reaction # reaction rate
molar\_reaction\_rate\_ave AS reaction # average of reaction rate along the reactor length
molar\_conc AS DISTRIBUTION (axial,radial) OF concentration # reactor concentrations

Cout AS concentration # outlet concentration
conversion AS no\_type # conversion
Photonic\_efficiency AS no\_type # objective function
cost AS cost

BOUNDARY # Boundary condition equations
# @ z=0
FOR r:= 0 TO 1 DO
   molar\_conc(0,r)= Cin;
END

# @ r=R\_in
FOR z:=0\|+ TO 1 DO
   -radial\_diffus\*PARTIAL(molar\_conc(z,0),radial)/(R\_out-R\_in)= 0;
END

# @ r=R\_out
FOR z:=0+ TO 1 DO
    -radial_diffus*PARTIAL(molar_conc(z,1),radial)/(R_out-R_in) = e_as(z) ^ photon_exponent
    *reaction_rate_constant*molar_conc(z,1);
END

EQUATION

radius_ratio=R_in/R_out;       # inner to outer radius ratio
d=R_out-R_light;            # distance of LEDs from catalyst surface

residence_time=3.14*(R_out^2-R_in^2)*reactor_length/vol_flow_rate;   # volumetric flow rate
for a given residence time and reactor geometry

# Velocity profile
FOR r:= 0 TO 1 DO
    u(r)=2*vol_flow_rate/(3.14*R_out^2)*log(radius_ratio)/(1-radius_ratio^4) * log(radius_ratio)
    +(1-radius_ratio^2)^2*(1-((r*(R_out-R_in)+R_in)/R_out)^2-(1-radius_ratio ^2) / log(radius_ratio)
    *Log((r*(R_out-R_in)+R_in)/R_out));
END

# molar Balance
FOR z:=0+ TO 1 DO
    FOR r:= 0+ TO 1- DO
        molar_conc(z,r)=-u(r)*PARTIAL(molar_conc(z,r),axial)/reactor_length
        +radial_diffus*PARTIAL(molar_conc(z,r),radial,radial)/(R_out-R_in)^2
        +radial_diffus*(1/(r*(R_out-R_in)+R_in))
        *PARTIAL(molar_conc(z,r),radial) /(R_out-R_in);
    END #FOR r
END # FOR z

s=reactor_length/N+0.000001;          #LED-to-LED space

# every LED's location on the z coordinate
FOR i:=1 TO counter DO
    z_0(i)=(1-(N-1)*s/reactor_length)/2+(i-1)*s/reactor_length;
END # FOR i

IF i < N THEN
    e_as_z0(z,i)= max_int*((d)^m/((d)^2+(reactor_length*(z-z_0(i)))^2)^((m+2)/2));
ELSE
    IF i = N THEN
        e_as_z0(z,i)= max_int*((d)^m/((d)^2+(reactor_length*(z-z_0(i)))^2)^((m+2)/2));
    ELSE

e_as_z0(z,i)=0;
END
END
END

FOR z:=0 TO 1 DO
   e_as(z)= SIGMA(e_as_z0(z, ));
END

e_as_ave= SIGMA (e_as())/(dz+1); # average of irradiance in w/m2 & photon/m2

STDE=sqrt(SIGMA((e_as()-e_as_ave)^2)/(dz+1)); # standard deviation (to show the uniformity)

# Reaction rate
FOR z:=0 TO 1 DO
   molar_reaction_rate(z)=(e_as(z))^{photon_exponent}*reaction_rate_constant*molar_conc(z, 1);
END

molar_reaction_rate_ave=SIGMA(molar_reaction_rate())/(dz+1); # average reaction rate

Cout=INTEGRAL(r:=0:1;(R_out-R_in)*(r*(R_out-R_in)+R_in) *u(r)*molar_conc(1,r))/
INTEGRAL(r:=0:1;(R_out-R_in)*(r*(R_out-R_in)+R_in)*u(r)); # Toluene concentration at reactor outlet

conversion=100*(Cin-Cout)/Cin; # Toluene conversion

photonic_efficiency=vol_flow_rate*(Cin-Cout)/e_as_ave*10^6;

#objective_function=conversion-a*(reactor_length/s+1);

cost=dep_cat*(P_cat*a^2*3.14*R_out*reactor_length)+3.14*dep_reactor*(P_mat*dens_mat*((R_out+t)^2-R_out^2)*reactor_length)+dep_LED*(P_LED*N)+(N*P*P_elec); #$/year
max_int = P*(9.4E-2/6);
.2.2. Code of the PROCESS entity

UNIT

reactor AS Opt_4_3_15_Real_Parameters

SET

WITHIN reactor DO

m := 1.5;
radial_Diffus := 8.4E-6; # m2/s
reaction_rate_constant := 1E-5; # m3/s.W
photon_exponent := 0.5;
axial := [BFDM,2,dz];
radial := [CFDM,2,20];
a := 0.002; # [kg/m2]
P_cat := 160;
P_mat := 15/0.13;
P_elec := 0.128*16*365/1000; # [$/w.year]
P_LED := 0.5;
t := 0.005; # [m]
dens_cat := 4230; # [kg/m3]
dens_mat := 7955; # [kg/m3]
dep_reactor := 0.2; # [1/year]
dep_cat := 12; # [1/year]
dep_LED := 6; # [1/year]
dz := 500; # grid numbers
counter := 300;
END # within reactor

ASSIGN

WITHIN reactor DO

reactor_length := 13.585; # m
R_in := 0.015; # m
R_out := 0.025;  # m
R_light := 0.008;  # m

N := 50;
P := 0.06;  # LED poser[Watt]

vol_flow_rate := 1.33E-6;  # [m3/s]
Cin := 3.9;  # [mmol/m3]

END # within reactor

INITIAL

STEADY_STATE

# SCHEDULE
# OperationSchedule
SOLUTIONPARAMETERS
DOSolver := "CVP_SS" [
  "MINLPSolver" := "OAERAP" [
    "NLPSolver" := "NLPSQP" [
      "OptimisationTolerance" := 1
    ]
  ]
]
]
2.3. Code of the OPTIMIZATIONS entity

```
PROCESS Process_4_3_15_Real_Parameters

TIME_INVARIANT
  reactor.react_length

INITIAL_VALUE
  20.0 : 0.5 : 50.0

ENDPOINT_INEQUALITY
  reactor.conversion
  50.0 : 100.0

MINIMISE
  reactor.cost
```
## 3. Notation

<table>
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<tr>
<th>Parameter (Unit)</th>
<th>Value</th>
</tr>
</thead>
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</tr>
<tr>
<td>$C_{in}$ (mol/m$^3$)</td>
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<tr>
<td>$P$ (W)</td>
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<td>$P_{material}$ ($/kg$)</td>
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<td>$P_{catalyst}$ ($/kg$)</td>
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<tr>
<td>$P_{elect}$ ($/y$)</td>
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<td>$d_{catalysts}$ (y$^{-1}$)</td>
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<tr>
<td>$d_{material}$ (y$^{-1}$)</td>
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<tr>
<td>$d_{LEDs}$ (y$^{-1}$)</td>
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<tr>
<td>$a$ (kg/m$^2$)</td>
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<tr>
<td>$\rho_{material}$ (kg/m$^3$)</td>
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</tr>
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<td>$th$ (m)</td>
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</tr>
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<td>$r_0$ (m)</td>
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</tbody>
</table>