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Optimal Design of an Autothermal Membrane Reactor Coupling the Dehydrogenation of Ethylbenzene to Styrene with the Hydrogenation of Nitrobenzene to Aniline

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Abstract:

Coupling the dehydrogenation of ethylbenzene to styrene with the hydrogenation of nitrobenzene to aniline in a catalytic fixed bed membrane reactor has the potential for significantly improving both processes (Abo-Ghander et al. 2008). In a continuing effort to realize this potential, an optimal design is sought for a co-current flow, catalytic membrane reactor configuration. To achieve this objective, two conflicting objective functions, namely: the yield of styrene on the dehydrogenation side and the conversion of nitrobenzene on the hydrogenation side, have been considered. The total number of the decision variables considered in the optimization problem is twelve, representing a set of operational and dimensional parameters. The problem has been solved numerically by two deterministic multi-objective optimization approaches: the normalized normal constraint method and the normal boundary intersection method. It was found that the integrating reactor can be run to produce a maximum styrene yield of 97% when production of styrene is emphasized and a maximum of 80% of nitrobenzene conversion when nitrobenzene conversion is emphasized. The resulting sets of Pareto optimal solutions obtained by both techniques have been found to be identical. In addition,

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qualitative explanations have been provided for the effect of the decision variables on both objectives.

Keywords: membrane fixed-bed reactor; bi-objective optimization; normalized normal constraint method; normal boundary intersection method; optimal design; coupling of reactions.

1. Introduction

Styrene and aniline are important intermediate products in the petrochemical industry. Styrene is used in the production of the polystyrene, acrylonitrile-butadiene-styrene resins (ABS), and a variety of other polymers. Its commercial production is performed by the dehydrogenation of ethylbenzene. This dehydrogenation reaction is reversible and but it is thermodynamically limited with a maximum achievable conversion of about 50% (Elnashaie et al. 2000). Aniline, on the other hand, is used in, e.g. the synthesis of methylene diphenyl diisocyanate (MDI) and as an additive in rubber processing. About 85% of global aniline is produced via a catalytic process using metal-supported catalysts (Sangeetha et al. 2009). Because of their industrial importance, styrene and aniline manufacturing plants have large capacities (estimated as 100,000 tons/year for styrene). Hence, the investment cost in those plants is high, so that any small enhancement in the process could yield significant financial rewards (Babu et al. 2005, Li et al. 2003).

To overcome the thermodynamic limitation on the dehydrogenation of ethylbenzene to styrene, novel process designs involving membrane reactors have been proposed in recent years. In these reactors, the reaction of interest is promoted by hydrogen-selective membrane walls which remove hydrogen from the reaction chamber to a separate compartment where hydrogen is either extracted by a sweep gas (Abdalla and Elnashaie, 1993, Abdalla and Elnashaie, 1994, Abdalla and Elnashaie, 1995, Hermann et al. 1997) or reacted separately to generate another useful product (Elnashaie et al. 2000, Moustafa and Elnashaie, 2000, Abo-Ghander et al. 2008). The enhancements in conversion of ethylbenzene and yield of styrene were predicted to be considerable. Among these possible membrane reactors, the configuration proposed by Abo-Ghander et al. (2008) is

of special interest because it allows the coupling with a second important industrial process. To improve the production of styrene in such membrane reactors, it is crucial to seek an optimal design which considers both geometry and operational variables, since a small improvement could provide high dividends to the petrochemical industry and consumers.

In view of this aim, mathematical models and optimization techniques are valuable tools. However, this configuration involves several key elements to model the reactor, for example heat transferred across the membrane walls by conduction, as well as diffusion of hydrogen from the dehydrogenation side to the hydrogenation side.

Therefore, this paper addresses the model based optimization of the design of the co-current flow configuration of the fixed bed membrane reactor introduced by Abo-Ghander et al. (2008). A bi-objective optimization problem with twelve (12) parameters is formulated and solved to obtain a Pareto set. Afterwards, the designer will be able to select one design out of this set of equally good reactors, based on his preferences. The optimization problem solved in this paper is unique because it concerns the coupling of reactions in fixed bed membrane reactors, as well as the production of two main chemical products, namely styrene and aniline.

The structure of the paper is as follows. Section 2 reviews some interesting results reported in literature with respect to model based reactor design optimization. Sections 3, 4 and 5 introduce for the fixed bed membrane reactor under study: the reactor configuration, the reaction kinetics and the mathematical reactor model, respectively. Sections 5 and 6 describe the optimization problem formulation and provide some details about the numerical solution strategy. Section 7 discusses the obtained numerical results. Finally, Section 8 summarizes the main conclusions.

2. Literature review

In optimization problems, feasible solutions are sought which correspond to extremes of one or more objective functions. This is important in early design stages of any chemical

process where decision variables have to be within certain limits and to satisfy certain constraints imposed by, e.g. safety and environmental legislations. This type of problems has been addressed in the literature by a number of researchers. For example, Sheel and Crowe (1969) modeled an existing ethylbenzene dehydrogenation reactor and optimized its performance using a profit function defined as the difference between the gain due to the production of styrene and fuel gases, i.e. methane and ethylene, and the loss due to steam usage and by-products, i.e. toluene and benzene. In the same study, the case of a double bed reactor was also considered. The decision variables considered were the steam temperature, steam rate and reactor depth. It was concluded that the reactor would work better if the constraints on both the temperature and steam flow were relaxed. Clough and Ramirez (1976) studied the effect of injecting steam into a styrene reactor at a point downstream of the reactor inlet. Optimization was performed to find the best injection point considering a profit objective function defined as the difference between the market value of the products and the utility cost. A styrene pilot plant was constructed and the results confirmed the improvement predicted by the model.

In all of the previous studies, only a single objective was considered. However, in practice often multiple and conflicting objective functions are present (see, e.g., Bhaskar et al. (2000) for an overview until the year 2000). These optimization problems differ conceptually from the single objective optimization problems. As a result of the conflicting objectives, there is no single optimal solution, but rather a set of solutions which best satisfy all objectives. These solutions are referred to as Pareto-optimal solutions. Broadly speaking, a feasible point is a Pareto-optimal solution if it is impossible to improve one objective function without worsening at least one of the others. The exact mathematical description can be found in, e.g. Das and Dennis (1998), or Miettinen (1999).

For instance, Lim II et al. (2001) optimized the production of methyl ethyl ketone (MEK) from the dehydration of sec-butyl alcohol considering bi-objective functions, i.e. profit and environmental functions. The problem was solved by an improved version of the normal boundary intersection (NBI) method (Das and Dennis, 1998) which combined the

original NBI method with the summation of weighted objective functions. The enhanced method gave evenly-distributed Pareto points and reliable optimization results, even in a non-convex region of the Pareto curve. Li et al. (2003) treated the same problem as addressed by Clough and Ramirez (1976), but with two objective functions. Both the adiabatic and steam-injected styrene reactors were considered, while styrene production and styrene selectivity were taken as the objective functions of the optimization problem. The problem was solved using a non-dominated sorting genetic algorithm (NSGA) (Srinivas and Deb, 1995). Optimization of the reactor showed that the production and selectivity of styrene could be improved compared to the current operating conditions after obtaining reliable NSGA results. The multi-objective differential evolution algorithm was introduced by Babu et al. (2005). This algorithm was applied to the optimization of the styrene reactor, and the results were compared with those obtained from the NSGA. In the optimization problem, three objective functions were considered, i.e. styrene production, styrene yield, and styrene selectivity. The Pareto set based on the new algorithm was found to be much better than that obtained by the NSGA, as reflected in the profit function. Tarafder et al. (2005a) studied the optimization of a double-bed styrene manufacturing reactor and compared the results with those for a single bed and steam-injected reactor. Three objective functions were considered, i.e. styrene molar flowrate, styrene selectivity and total heat duty required by the process. The problem was solved using elitist NSGA-II (Deb et al. 2002), which works more efficiently and quickly than NSGA. The production of styrene in the double-bed reactor was higher than in the other two reactors. The production of ethylene in an industrial ethylene reactor was investigated by Tarafder et al. (2005b) considering two and three objective functions, i.e. conversion of ethane, selectivity of ethylene, and flow of ethylene. The elitist NSGA-II algorithm was used to solve the problem. 100% ethane conversion and more than 90% ethylene selectivity were reported.

For catalytic membrane reactors, a multi-objective optimization problem was studied by Cheng et al. (2008) for a methanol reactor and a hydrogen production reactor. The elitist NSGA-II algorithm was again used to obtain an optimal solution with three objective functions, i.e. product flowrate (methanol or hydrogen), reactant flowrates (hydrogen or

methane), and exergy loss of the reactor. The problem was solved to evaluate the effect of key membrane characteristics like membrane thickness and membrane area per unit length on these objective functions. More recently, Logist et al. (2009) have reported the efficient generation of Pareto sets for several (bio)chemical processes described by ordinary differential equations based on a combination of (i) novel deterministic multiple objective optimization routines (i.e. Normal Boundary intersection and Normalized Normal Constraint (Messac and Mattson, 2004)) and (ii) an advanced deterministic multiple shooting optimization approach (Leineweber et al. 2003a, Leineweber et al. 2003b)

3. Reactor Configuration

Figure 1 depicts a conceptual drawing of the membrane reactor, with only one hydrogenation tube portrayed for simplicity. There are two compartments separated by a hydrogen perm-selective membrane. The outer compartment is for the dehydrogenation of ethylbenzene to styrene, while the hydrogenation reaction of nitrobenzene to aniline takes place in the inner compartment. The external wall of the outer shell is assumed to be adiabatic.

In simple fixed bed reactors in which ethylbenzene is continuously dehydrogenated, styrene, hydrogen, and secondary products like benzene and toluene are produced, and the temperature drops along the reactor due to the endothermic reaction. In the membrane reactor considered in Figure 1, hydrogen produced in the outer shell, diffuses across the hydrogen-selective membranes to the inner compartment under the influence of the difference in hydrogen partial pressures on the two sides. Inside the tubes, the diffused hydrogen encounters nitrobenzene and steam in the presence of a hydrogenation catalyst, where it reacts via an irreversible exothermic hydrogenation reaction. Heat produced by this reaction is transferred from the tube compartment through the hydrogen-selective membrane walls to the shell compartment where it provides the endothermic heat of the dehydrogenation of ethylbenzene. The transfer of hydrogen from the shell compartment to the tube compartment, while heat flows in the opposite direction, promotes the

formation of more styrene. However, the heat transferred from the tube compartment decreases the temperature and as a result lowers the rate of reaction.

4. Chemical Reactions and Kinetic Expressions

The main reactions taking place in the outer chamber are listed below.

The first reaction is the principal reaction in the shell, producing one mole of styrene per one mole of ethylbenzene. This reaction is endothermic and reversible. It is favoured by high temperatures and low pressures (Le Chatellier's principle). In most modern designs, this process is carried out in three reactors in series, with heat supplied either by heating the reactants entering each stage or by injecting hot steam with the feed stream. By applying this procedure, the forward reaction can be boosted. In addition to producing styrene, there are two side products, benzene and toluene, resulting from thermally cracking ethylbenzene at high temperatures. These side reactions reduce the selectivity to styrene. On the other side of the integrated reactor (tube side), a single reaction takes place where the diffused hydrogen reacts with the feed steam consisting of nitrobenzene and steam in order to produce aniline.

This hydrogenation reaction is irreversible and exothermic, with three moles of hydrogen reacting with one mole of nitrobenzene in order to produce each mole of aniline. The heats of reaction and the kinetic expressions for the reactions on both sides of the integrated reactor are summarized in Tables 1 and 2.

5. Mathematical Reactor Model

To derive the model equations for the membrane reactor, a slice of infinitesimal length is considered on both sides of the coupled reactor. Mass, energy and momentum balances are then derived based on the following assumptions.

1. Steady state operation.
2. Ideal gas behavior on both sides.
3. Plug flow for the fixed beds on both the shell and tube sides.
4. Pseudo-homogeneous one-dimensional model.
5. Catalyst deactivation is neglected.
6. Pressures along both compartments are calculated based on Ergun's equation.

The resulting mole, energy and pressure equations for both sides of the integrated reactor are summarized in Table 3. The heat transfer across the membrane per unit length is estimated assuming a composite circular tube with a convective heat resistance on the tube side, followed by a conductive heat resistance due to the presence of a layer of stainless steel with a thickness of 0.0012 m, followed by another conductive heat resistance due to the presence of a palladium layer with a thickness of 20×10^{-6} m, and finally a convective resistance on the shell side (Abo-Ghander et al. 2008). The convective heat transfer coefficients on both sides of the reactors are calculated using the correlations accompanying the heat transfer equation in Table 3, assuming that the reacting mixture on the dehydrogenation side is always heated, while that on the hydrogenation side is always cooled (Froment and Bischoff, 1990).

5. The Optimization Problem

In the current paper, two objective functions are considered and split between the dehydrogenation and the hydrogenation sides. On the dehydrogenation side, the requirement is to maximize the yield of styrene, whereas that on the hydrogenation side is to maximize the conversion of nitrobenzene. The two objective functions may then be defined as:

$$\text{Maximize: } Y_{\text{ST}} = \frac{\text{Moles of Styrene Produced}}{\text{Moles of Ethylbenzene Fed}} = \frac{n_{\text{ST}}(\text{L}) - n_{\text{ST}}(0)}{n_{\text{EB}}(0)} \quad (16)$$

$$\text{Maximize: } X_{\text{NB}} = \frac{\text{Moles of Nitrobenzene Reacted}}{\text{Moles of Nitrobenzene Fed}} = \frac{n_{\text{NB}}(0) - n_{\text{NB}}(\text{L})}{n_{\text{NB}}(0)} \quad (17)$$

Maximization of the conversion of nitrobenzene on the hydrogenation side results in maximizing the production of aniline on the same side. Twelve decision variables are considered, i.e. the feed molar flowrate of ethylbenzene on the dehydrogenations side $n_{\text{EB}0}$, the steam-to-ethylbenzene ratio SOR, the feed temperature on the dehydrogenation side T_f , the feed pressure on the dehydrogenation side P_f , the feed molar flowrate of nitrobenzene on the hydrogenation side $n_{\text{NB}0}$, the steam-to-nitrobenzene ratio SOR', the feed temperature on the hydrogenation side T'_f , the feed pressure on the hydrogenation side P'_f , the number of hydrogenation tubes N , the net diameter of the dehydrogenation side D , the diameter of the membrane tube D_t , and the reactor length L . However, the solutions of the above mentioned problem are required to satisfy the several constraints:

1. The feed molar flowrate of ethylbenzene on the dehydrogenation side is taken to be between -25% and 10% of the nominal value of 10.24 moles/s. These bounds are consistent with the industrial case since the plant can operate at a much lower capacity, but not at a much higher capacity (Yee et al. 2003).

$$7.66 \leq n_{\text{EB}0} \leq 11.27 \quad \text{moles/s} \quad (18)$$

2. The lower limit on the steam-to-ethylbenzene ratio is set as 7 to prevent coke formation on the catalyst surface. At the same time, too much steam cannot be

used because it would make the process economically unfeasible. As for industrial practice, the upper limit is set to 20 (Yee, et al, 2003).

$$7 \leq \text{SOR} \leq 20 \quad (19)$$

3. The lower bound on the feed temperature on the dehydrogenation side is set at 780 K to ensure that the reacting mixture is not too cold for the reaction to occur, while the upper limit is set at 915 K to protect the membrane.

$$780 \leq T_f \leq 900 \text{ K} \quad (20)$$

4. Although the dehydrogenation of ethylbenzene to styrene is favoured at lower pressures, it is important to work at a relatively higher pressure to create a favorable driving force for hydrogen permeation through the membrane. The lower limit on the feed pressure is chosen as 1.0 bar while its upper limit is set at 4.0 bar to prevent violation of the ideal gas law and to avoid costly pressure vessel designs.

$$1.0 \leq P_f \leq 4.0 \text{ bar} \quad (21)$$

5. The maximum amount of hydrogen which can be produced based on these bounds (18) is 11.27 moles/s. From the stoichiometry of the hydrogenation equation, each mole of nitrobenzene needs to react with three mole of hydrogen arriving from the dehydrogenation side. Hence, the maximum amount of nitrobenzene that can react with the diffused hydrogen is around ~3.77 moles/s. The molar flowrate of nitrobenzene in a single hydrogenation tube, considering an average of 1750 tubes, is around 0.002 moles/s. This limit neglects the hydrogen produced from side reactions, i.e. reactions (4), (5), and (6). Consequently, the upper limit is set at 0.005 moles/s to allow for any additional hydrogen produced, so that:

$$0.002 \leq n_{\text{NB}_0} \leq 0.005 \text{ moles/s} \quad (22)$$

6. Bounds on the steam-to-nitrobenzene ratio are set so that:

$$2.0 \leq \text{SOR}' \leq 4.0 \quad (23)$$

7. Bounds on the feed temperature on the hydrogenation side are chosen as:

$$780 \leq T'_f \leq 900 \text{ K} \quad (24)$$

8. Bounds on the feed pressure on the hydrogenation side are established at:

$$1.0 \leq P'_f \leq 4.0 \text{ bar} \quad (25)$$

9. To enhance the rate of heat transfer from the dehydrogenation side to the hydrogenation side, the number of hydrogenation tubes is bounded by:

$$1000 \leq N \leq 2500 \quad (26)$$

10. The net diameter of the dehydrogenation side vessel is set to be within the limits chosen by Li et al. (2003a):

$$1.95 \leq D \leq 3.0 \text{ m} \quad (27)$$

11. Bounds on the diameter of the hydrogenation tube are specified as:

$$2.5 \times 10^{-2} \leq D_t \leq 5.5 \times 10^{-2} \text{ m} \quad (28)$$

12. To limit the (dimensionless) reactor length, we require that:

$$1.5 \leq L \leq 4.0 \quad (28)$$

13. To ensure that heat is always transferred from the hydrogenation side to the dehydrogenation side, the following constraint is adopted:

$$T_f - T'_f < 0.0 \text{ K} \quad (29)$$

14. To ensure that hydrogen is always transferred from the dehydrogenation side to the hydrogenation side, we stipulate that:

$$P'_f - P_f < 0.0 \text{ bar} \quad (30)$$

15. Palladium membranes are currently limited to temperatures lower than about 923 K. Hence, the temperature along the hydrogenation side is required to be less than or equal to 915 K in order to ensure the durability and sustainability of the membranes.

$$T'_{\max}(z) - 915.0 \leq 0.0 \text{ K} \quad (31)$$

$0 \leq z \leq 0$

16. It is important to achieve autothermality on the dehydrogenation side. This leads to the following nonlinear equality constraint to ensure that the outlet temperature of the dehydrogenation side is equal to the feed temperature of the dehydrogenation side:

$$T_f - T(L) = 0.0 \text{ K} \quad (32)$$

The entire optimization problem can now be formulated as the following multiple objective dynamic optimization problem.

$$\begin{aligned}
 &\text{Maximize:} && \mathbf{J}(\mathbf{p}) \\
 &\text{Subject to:} && \frac{d\mathbf{x}}{dz} = \mathbf{f}(\mathbf{x}, \mathbf{p}) \quad \text{with} \quad \mathbf{x}(z=0) = \mathbf{x}_0 \\
 &&& \mathbf{p}^L \leq \mathbf{p} \leq \mathbf{p}^U \\
 &&& \mathbf{A}\mathbf{p} \leq \mathbf{0} \\
 &&& \mathbf{c}_{\text{eq}}(\mathbf{p}) = \mathbf{0} \\
 &&& \mathbf{c}_{\text{ineq}}(\mathbf{p}) \leq \mathbf{0}
 \end{aligned}$$

where:

$$\mathbf{p} = [n_{\text{EBo}}, \text{SOR}, T_f, P_f, n_{\text{NB0}}, \text{SOR}', T'_f, P'_f, N_t, D, D_t, L]^T,$$

$$\mathbf{J}(\mathbf{p}) = \begin{bmatrix} Y_{\text{ST}} \\ X_{\text{NB}} \end{bmatrix},$$

$$\frac{d\mathbf{x}}{dz} = \mathbf{f}(\mathbf{x}, \mathbf{p}) \text{ is the reactor model described by equations (8) to (13),}$$

$$\mathbf{p}^L = [7.66, 7, 780, 1.0, 0.02, 2.0, 780, 1.0, 1000, 1.95, 2.5 \times 10^{-2}, 1.5]^T$$

$$\mathbf{p}^U = [11.27, 20, 900, 4.0, 0.05, 4.0, 900, 4.0, 2500, 3.0, 5.5 \times 10^{-2}, 4.0]^T$$

$$\mathbf{A} = \begin{bmatrix} 0 & 0 & 1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \end{bmatrix},$$

$$\mathbf{c}_{\text{eq}}(\mathbf{p}) = T_f - T(L)$$

$$\mathbf{c}_{\text{ineq}}(\mathbf{p}) = T_{\max}(z) - 915.0 \quad 0 \leq z \leq L$$

All other variables not included in the decision variable vector $\mathbf{p}$ are maintained at their industrial values as specified in Table 4.

6. Details of the Numerical Solution

To solve the above mentioned problem numerically, a number of approaches can be tried. The most common approach is the weighted sum (WS) method. It starts by linearly combining all objective functions of interest using weight vectors, and then solving the system considering the constraints. However, the WS fails to obtain solutions in non-convex regions of the Pareto set, and the Pareto optimal solutions generated are not necessarily evenly-distributed (even if the weight is varied evenly (Das and Dennis, 1997)).

Alternatively, evolutionary strategies (Deb, 2001) have been successfully adopted by a number of researchers. However for the current case study, a genetic algorithm (GA) has been found to produce dominated (i.e. non-Pareto optimal) solutions, whereas an evolutionary algorithm (EA) based on the GA, failed to generate well-distributed Pareto solutions.

Hence, the Normalized Normal Constraint (NNC) method and the Normal Boundary Intersection (NBI) method, introduced by Messac and Mattson, (2004), Messac et al. (2003) and Das and Dennis, (1998), have been used to solve the bi-objective optimization problems under study. These deterministic methods are easy to implement and able to produce evenly-distributed (local) Pareto solutions in a limited amount of time. Both methods suffer, however, from producing non-Pareto optimal solutions, but these can be removed by applying a Pareto filter.

To solve the problem at hand, both the NNC and NBI methods have been implemented in Matlab to obtain the Pareto frontier. A Pareto filter has been applied to remove all non-Pareto points. Since optimization solvers are mostly designed for minimization problems, the problem of maximizing the objective functions defined in equations (16), and (17) has been first transformed into a minimization problem by introducing the following generic functions for both objectives:

$$J_{SY} = \frac{1}{1 + Y_{SY}} \quad (34)$$

$$J_{NB} = \frac{1}{1 + X_{NB}} \quad (35)$$

Minimization of equations (34) and (35) results in maximizing the styrene yield on the dehydrogenation side and the nitrobenzene conversion on the hydrogenation side. To evaluate the generic function defined by equations (34), and (35), model equations (8) to (13) have been solved numerically considering equations (14), and (15). For the co-current configuration of the catalytic reactor, these model equations form a set of initial value problems which can be solved by any integrating subroutine for given initial conditions. The Matlab integrator `ode15s` has been employed with a relative tolerance of 1×10^{-10} to ensure accuracy. To apply the NNC and NBI methods, it was required that anchor points be found which correspond to the best possible values for the respective individual objectives. Then, the utopia point was found which corresponds to all objectives simultaneously being at their best possible values. While the utopia point was used to normalize the system objective functions defined by (34) and (35), the anchor points have been used to construct the utopia line. This utopia line was divided into forty (40) segments, with an optimization problem solved at each segment. Two commercial solvers purchased from Tomlab have been utilized to solve the resulting optimization problems. Each solution cycle was started with the global `glbDirect` solver, and was finished with the local `snopt` solver. At the beginning, the global solver `glbDirect` was run for 100 iterations, and then its output was used to initiate the local solver `snopt` which converged to the feasible solution. It should also be noted that the solutions with both techniques, i.e. NNC and NBI, have been obtained independently, with the same problem solved assuming that no solution was at hand, i.e. none of the solutions have been used to provide a starting guess for any other technique.

7. Results and Discussion

The optimization study has been carried out on an industrial scale catalytic membrane reactor integrating the dehydrogenation of ethylbenzene to styrene with the hydrogenation of nitrobenzene to aniline. Catalyst properties, such as bulk densities and particle diameters for both reactions, have been assumed to be uniform on both sides of the integrated catalytic membrane reactor. The molar flowrates of other components in the dehydrogenation feed stream, i.e. styrene, benzene, and toluene, have been treated as impurities at their industrial levels, as shown in Table 4.

To confirm the optimization results, two numerical techniques have been implemented, namely the NNC and NBI methods. The results from both numerical techniques have been filtered using a Pareto filter in order to remove all non-Pareto optimal points from the solution set.

The Pareto optimal solution set corresponding to the simultaneous maximization of styrene yield and nitrobenzene conversion is plotted in Figure 2. Both NNC and NBI methods gave the same Pareto optimal set which is a favorable sign of confirmation for both the reliability and correctness of the results. It can be also seen that along the Pareto set, while one objective improves, the other worsens, causing none of the solutions to dominate over the others. This makes all solutions of the Pareto set equally good. Hence, the final decision of the reactor design and operating point should be based on additional information which normally depends on either experience or site specifications. From the results, it is possible to optimally design the integrated catalytic membrane reactor to provide a 97% styrene yield and 20% nitrobenzene conversion at one extreme, and a 47% styrene yield and 80% nitrobenzene conversion at the other extreme. In between, a gradual evolution of both costs is mostly observed, whereas a gap in the conversion of nitrobenzene is present when the yield of styrene is about 0.55. Hence, this indicates that there exist two intrinsically different types of reactor designs.

To quantify the role of the decision variables in realizing the objectives, the decision variables are plotted in Figures 3 to 6. Although the general trend is always clear, some ‘scatter’ may be present in some plots. Its presence reflects the fact that in certain regions,

some of the decision variables have a limited influence on the cost functions, which makes the exact determination of the optimal values hard. However, it should be emphasized that, as their influence on the costs is only limited, an exact determination is not required for industrial practice.

In Figure 3a and 3b, the styrene yield and nitrobenzene conversion are plotted against the feed molar flowrate of ethylbenzene, illustrating the conflicting nature of both objectives. The styrene yield decreases sharply at a low ethylbenzene flowrate, scatters after that for a wide spectrum of ethylbenzene flowrates with a styrene yield mean value of 65%, and finally decreases sharply at higher flowrates. A qualitative explanation is that as the molar flowrate of ethylbenzene increases, the rates of the side reactions become significant because their reaction rates are directly proportional to the partial pressure of ethylbenzene. Also, the residence time decreases, leading to an unfinished reaction, negatively affecting the styrene yield on the dehydrogenation side. On the other hand, increasing the ethylbenzene flowrate has a positive effect on nitrobenzene conversion. This increase continues until a level of 50% nitrobenzene conversion is reached where the effect becomes almost insignificant. Then, at higher flowrates the nitrobenzene conversion increases sharply until an upper ceiling of about 80% nitrobenzene conversion is reached. This is because when the molar flowrate of ethylbenzene increases, the production of hydrogen becomes significant due to the contribution from the side reactions. Consequently, more hydrogen is available for transfer to the hydrogenation side.

In Figures 3c and 3d, the yield of styrene and the nitrobenzene conversion are plotted against the steam-to-ethylbenzene molar ratio. High styrene yields can be favored by operating the dehydrogenation side at a low ratio of 7.0, whereas high nitrobenzene conversions are induced by operating the dehydrogenation side at a high ratio of 20.0. The styrene yield is high at low steam-to-ethylbenzene ratios because the production of hydrogen from the steam reactions becomes insignificant, in turn suppressing the backward reaction of the main reaction producing styrene. The nitrobenzene conversion is favored by a high steam ratio on the dehydrogenation side because there will be more

hydrogen produced in that reaction chamber, leading to increasing the amounts of hydrogen transferred to the hydrogenation side.

The effects of the dehydrogenation feed temperature on styrene yield and nitrobenzene conversion are plotted in Figures 3e and 3f. The feed temperature on the dehydrogenation side shows a conflicting effect on both objectives: as the feed temperature on the dehydrogenation side increases, the styrene yield increases, whereas the nitrobenzene conversion decreases. The styrene yield approaches the limit of 97% because the forward reaction producing styrene is favored by high temperatures as well as by receiving heat from the hydrogenation chamber transferred from the hydrogenation reaction. Although this phenomenon helps breaking the endothermality of the dehydrogenation side, and producing a high styrene yield, it also creates a drop in temperature inside the hydrogenation side, leading to low nitrobenzene conversions.

The feed pressure on the dehydrogenation side also shows a conflicting effect on both objectives as shown in Figures 4a and 4b: as it increases, the styrene yield increases, but the nitrobenzene decreases. This occurs because increasing the feed pressure creates a significant driving force for the transfer of hydrogen from the dehydrogenation side to the hydrogenation side leading to higher styrene yields. However, as the styrene is produced on the dehydrogenation side, the temperature drops, creating a significant temperature gradient between the two compartments and helping to transfer more heat from the hydrogenation side, which reduces the nitrobenzene conversion.

The effect of the feed molar flowrate of nitrobenzene on both objectives is plotted in Figures 4c and 4d. As the molar flow of nitrobenzene on the hydrogenation feed stream increases, the styrene yield increases because of a larger heat transfer between the two compartments. However, the heat transfer has a negative effect on the conversion of nitrobenzene as it reduces the temperature inside the tubes, causing the hydrogenation reaction to take place at a lower temperature. Increasing the molar flowrate of nitrobenzene in the feed stream of the hydrogenation side leads to an unfinished reaction which reduces the nitrobenzene conversion.

The effect of steam-to-nitrobenzene ratio plotted in Figures 4e and 4f shows no effect, as this parameter mainly reduces the temperature along the hydrogenation side and maintains it below 915.0 K by diluting the reacting mixture on the hydrogenation side.

The effect of the feed temperature of the hydrogenation feed on both objectives is the same as that of the dehydrogenation side and is plotted in Figures 5a and 5b. As the feed temperature of the hydrogenation side increases, more heat is produced on the hydrogenation side due to the reaction. However, the heat produced transfers across the membrane to break the endothermality inside the dehydrogenation side, resulting in a high styrene yield and a lower conversion of nitrobenzene (due to a lower production of aniline on the hydrogenation side). The similar behavior of the feed temperature of the dehydrogenation and the feed temperature of the hydrogenation side may result from applying too many constraints on the temperatures on both sides, i.e. constraints (29), (31), and (32). These constraints favor optimal designs in which both sides of the reactor operate at the same feed temperature.

In Figure 5c and 5d both objectives are plotted against the pressure of the hydrogenation feed. There is scatter visible with respect to both objectives. A low feed pressure on the hydrogenation side of 1.0 bar is preferred in order to increase the yield of styrene to around 75%, while a styrene yield of 97% can be achieved at a pressure of about 4.0 bars. For the nitrobenzene conversion, it is preferable to operate the reactor at a pressure as low as 1.0 bar in order to achieve a conversion of 80%. A higher pressure lowers the conversion to 20%.

The effect of the number of hydrogenation tubes with regard to both objectives is depicted in Figures 5e and 5f. The values are scattered, with an increasing trend in general for the yield of styrene as a function of the number of tubes. For the nitrobenzene conversion, the trend is also scattered but reversed, i.e. increasing the number of hydrogenation tubes decreases the nitrobenzene conversion. A qualitative explanation is that, as the number of the hydrogenation tubes increases, the rate of the heat transfer

across the membrane increases, leading to more styrene production on the dehydrogenation side. However, this transfer of heat decreases the conversion of nitrobenzene on the hydrogenation side.

In Figure 6a and 6b, the effect of the net diameter of the dehydrogenation side is plotted against both objectives. For the yield of styrene, there is scatter, with an increasing trend in general. To increase the yield of styrene on the dehydrogenation side, a higher net diameter is required, leading to a higher residence time. However, increasing the net diameter of the dehydrogenation side leads to decreasing the conversion of nitrobenzene because more heat will be transferred to break the endothermality of the dehydrogenation side.

The effect of the hydrogenation tube diameter on both objectives is displayed in Figures 6c and 6d. The behavior is scattered with mixed trends. The yield of styrene increases in general as the diameter of the hydrogenation tubes increases, whereas the nitrobenzene conversion decreases. Increasing the diameter of the hydrogenation tube enhances the rate of the heat transfer across the membrane from the hydrogenation side to the dehydrogenation side leading to higher styrene yields. However, this transferred heat causes the hydrogenation compartment to cool down leading to a lower nitrobenzene conversion.

In Figure 6e and 6f, both objectives are plotted against the length of the catalytic reactor. Both show no trend with this variable, so it is favorable to adopt the maximum reactor length.

To illustrate the differences in optimal designs of the membrane reactor, three solutions located along the Pareto set have been chosen. For these solutions, the reactor profiles for the styrene yield, the nitrobenzene conversion and the temperatures on both sides have been plotted in Figure 7a and 7b. The three solutions, whose numerical values are listed in Table 5, represent the case where: (i) styrene is the product of overriding importance (solution A), (ii) both styrene and aniline are equally important (solution B), and finally

(iii) aniline is the product of overwhelming importance (solution C). For solution A, the yield of styrene increases monotonically along the reactor on the dehydrogenation side until it reaches around 97%, while the conversion of nitrobenzene cannot achieve more than 21% on the hydrogenation side. The temperature along the dehydrogenation reaction decreases in the first part of the reactor due to the endothermality of the reactions, but it then recovers as a result of the transfer of heat from the hydrogenation side to the dehydrogenation side through the hydrogen membrane wall. The exit temperature of the dehydrogenation side is exactly the same as the feed temperature, indicating the satisfaction of the imposed nonlinear autothermality constraint. The temperature on the hydrogenation side increases at the beginning of the reactor due to the reaction with diffused hydrogen, but it decreases later due to the transfer of the heat to the dehydrogenation compartment.

For solution B, the styrene yield and nitrobenzene conversion increase on both sides of the reactor compartments until a styrene yield of 56% and a nitrobenzene conversion of 55% are achieved. The temperature profiles on both sides of the reactor are similar to those in solution A. For solution C, the production of aniline is higher than that of styrene, i.e. 80% nitrobenzene conversion and 49% styrene yield, with no structural differences observed in the temperature profiles on both sides of the reactor compared to solutions A and B. Note that the maximum temperature on both sides of the reactor does not exceed 915 K, thereby protecting the durability of the membranes.

8. Conclusions

In this work, an optimal design of a catalytic membrane coupling dehydrogenation of ethylbenzene to styrene with hydrogenation of nitrobenzene to aniline has been obtained. To achieve this goal, a bi-objective optimization problem with linear and nonlinear constraints has been formulated. The focus has been on maximizing the styrene yield on the dehydrogenation side while simultaneously maximizing the nitrobenzene conversion on the hydrogenation side. Bounds and constraints with real industrial values have been imposed on both operational and design variables. Two numerical techniques- the normalized normal constraints (NNC) method and the normal boundary intersection

(NBI) method- have successfully solved the problem giving evenly distributed Pareto solutions after applying a Pareto filter. Both techniques gave the same Pareto set although the optimization problems have been solved independently. From this Pareto set, it is seen that there exist two classes of reactor designs with styrene yields and nitrobenzene conversions going from values of about 50% and 80% when nitrobenzene conversion is focused on, to values of about 97% and 20% when the styrene yield is emphasized. The different optimal designs have been illustrated for the coupled catalytic fixed bed membrane reactor and the effects of different decision variables have been explained qualitatively. From the present Pareto optimal results, the designer will be able to select one design for the coupled reactor based on his personal preferences. Hence, these results are very valuable for the procedure of designing a reactor in which both reactions are integrated.

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Notation

a_i	constant, 1 for hydrogen, 0 otherwise, [-]
$\mathbf{A}$	matrix of linear constraints.
A_{cs}, A'_{cs}	cross sectional area of shell and tube side, [m ²]
$C_{pi}, C_{p'i}$	heat capacity of component i on shell and tube side, [$\frac{J}{mole \times K}$]
$\mathbf{c}_{eq}(\mathbf{p})$	vector of nonlinear equality constraints, [-]
$\mathbf{c}_{ineq}(\mathbf{p})$	vector of nonlinear inequality constraints, [-]
D	net diameter of the shell side, [m]

D_p, D'_p	diameter of catalyst particle on shell and tube side, [m]
D_t	diameter of tube, [m]
E_j	activation energy of reaction j on shell side, $[\frac{J}{\text{mole} \times K}]$
E'	activation energy of the hydrogenation reaction on tube side, $[\frac{J}{\text{mole} \times K}]$
H_i, H'_i	enthalpy of component i on shell and tube side, $[\frac{J}{\text{mole}}]$
$\mathbf{J}(\mathbf{p})$	vector of objective functions, [-]
J_{NB}	nitrobenzene conversion generic function, [-]
J_{SY}	styrene yield generic function, [-]
k_{i0}	reaction i pre-exponential factor, $[\frac{\text{mol} \times K^m}{\text{kg cat} \times \text{s} \times \text{bar}^n}]$, (for k_1 and k_2 , $m=0$, $n=1$; for k_3 and k_5 , $m=0$, $n=2$; for k_4 , $m=0$, $n=1.5$; for k_6 , $m=3$, $n=3$)
k_i	reaction i rate constant, $[\frac{\text{mole} \times K^m}{\text{kg cat} \times \text{s} \times \text{bar}^n}]$, (for k_1 and k_2 , $m=0$, $n=1$; for k_3 and k_5 , $m=0$, $n=2$; for k_4 , $m=0$, $n=1.5$; for k_6 , $m=3$, $n=3$)
L	total length of reactor, [m].
N	number of tubes in hybrid reactor, [-]
n_{EBo}	feed molar flowrates of ethylbenzene on shell side, $[\frac{\text{mole}}{\text{s}}]$
n_{NB0}	feed molar flowrates of nitrobenzene on tube side $[\frac{\text{mole}}{\text{s}}]$
n_i, n'_i	molar flow rate of component i on shell and tube side, $[\frac{\text{mole}}{\text{s}}]$
J_i	molar flux of component i, $[\frac{\text{mole}}{\text{m}^2 \times \text{s}}]$
p_i, p'_i	partial pressure of component i on shell and tube side, [Pa] partial pressure of component i on tube side, [Pa]
P, P'	total pressure on shell side and tube side of reactor, [bar]

P_f, P'_f	feed pressure on shell side and tube side, [bar]
$\mathbf{p}$	vector of decision variables, [-]
$\mathbf{p}^L$	lower bound vector of decision variables, [-]
$\mathbf{p}^U$	upper bound vector of decision variables, [-]
Q	heat transferred from tube side to shell side, [$\frac{J}{m}$]
Q_o	pre-exponential constant of hydrogen membrane, [$\frac{\text{mole}}{m \times s \times \text{bar}^{0.5}}$]
r_j	rate of reaction j on shell side, [$\frac{\text{mole}}{\text{kg cat} \times s}$]
r'	rate of reaction on tube side, [$\frac{\text{mole}}{\text{kg cat} \times s}$]
r_1	inner radius of hydrogenation tube, [m]
r_2	outer radius of hydrogenation tube, [m]
r_3-r_2	thickness of palladium membrane, [m]
SOR	steam-to-ethylbenzene ratio, [-]
SOR'	steam-to-nitrobenzene ratio, [-]
T, T'	temperature on shell and tube side of reactor, [K]
T_f, T'_f	feed temperature on shell and tube side of reactor, [K]
X_{NB}	conversion of nitrobenzene on tube side, [-]
Y_{ST}	yield of styrene, [-]
z	axial coordinate inside reactor, [m].
$[\Delta H(T)]_j$	heat of reaction j at temperature T on shell side, [J/mole].
$[\Delta H'(T')]$	heat of reaction at temperature T' on tube side, [J/mole].
Δz	thickness of differential element, [m]
ρ_s, ρ'_s	catalyst solid density on shell and tube side, [$\frac{\text{kg}}{\text{m}^3}$]
σ_{ij}	stoichiometric coefficient of reactant i in reaction j, [-]
δ_{H_2}	thickness of hydrogen permeation membrane, [m]

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Table 1: Summary of stoichiometric equations, heats of reactions and reaction rate expressions.

Chemical Reaction	Heat of Reaction	Kinetic Equation	Reference
1. Reactions on Dehydrogenation Side ^a			
$C_6H_5CH_2CH_3 \rightleftharpoons C_6H_5CHCH_2 + H_2$	$\Delta H_{298} = 117.6 \frac{\text{kJ}}{\text{mole}}$	$r_1 = k_1 \left(p_{EB} - p_{ST} \frac{p_{H_2}}{K_A} \right)$	(Elnashaie et al., 1993; Abo-Ghander et al., 2008)
$C_6H_5CH_2CH_3 \rightarrow C_6H_6 + C_2H_4$	$\Delta H_{298} = 105.4 \frac{\text{kJ}}{\text{mole}}$	$r_2 = k_2 p_{EB}$	(Elnashaie et al., 1993; Abo-Ghander et al., 2008)
$C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4$	$\Delta H_{298} = -54.6 \frac{\text{kJ}}{\text{mole}}$	$r_3 = k_3 p_{EB} p_{H_2}$	(Elnashaie et al., 1993; Abo-Ghander et al., 2008)
$2H_2O + C_2H_4 \rightarrow 2CO + 4H_2$	$\Delta H_{298} = 210.2 \frac{\text{kJ}}{\text{mole}}$	$r_4 = k_4 p_{H_2O} p_{C_2H_4}^{1/2}$	(Elnashaie et al., 1993; Abo-Ghander et al., 2008)
$H_2O + CH_4 \rightarrow CO + 3H_2$	$\Delta H_{298} = 206.1 \frac{\text{kJ}}{\text{mole}}$	$r_5 = k_5 p_{H_2O} p_{CH_4}$	(Elnashaie et al., 1993; Abo-Ghander et al., 2008)
$H_2O + CO \rightarrow CO_2 + H_2$	$\Delta H_{298} = -41.2 \frac{\text{kJ}}{\text{mole}}$	$r_6 = k_6 \left(\frac{P}{T^3} \right) p_{H_2O} p_{CO}$	(Elnashaie et al., 1993; Abo-Ghander et al., 2008)
2. Reaction on Hydrogenation Side ^b			
$C_6H_5NO_2 + 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$	$\Delta H_{298K} = -443.0 \frac{\text{kJ}}{\text{mole}}$	$r' = \frac{k' K_{NB} K_{H_2} p'_{NB} \sqrt{p'_{H_2}}}{\left(1 + K_{NB} p'_{NB} + K_{H_2} \sqrt{p'_{H_2}} \right)^2}$	(Amon et al., 1999)

^a partial pressures are given in (bar)

^b partial pressures are given in (kPa)

Table 2: Numerical values of kinetic pre-exponential constants and activation energies.

Reaction	k_{i0}^a	E_i (kJ/kmol)	Reference
1 ^b	8.32×10^3	0.909×10^5	(Elnashaie, et al, 1993)
2	4.23×10^9	2.080×10^5	
3	6.13×10^3	0.915×10^5	
4	3.95×10^3	1.040×10^5	
5	1.42×10^2	0.657×10^5	
6	5.80×10^{12}	0.736×10^5	
7 ^c	1.86×10^{-4}	10.0×10^3	(Amon, et al, 1999)

^a $k_i = \frac{10}{36} k_{i0} \exp\left(-\frac{E_i}{RT}\right)$, where k_{i0} is the pre-exponential factor (units, check the notations), for $1 \leq i \leq 6$

$k_i = 10^3 k_{i0} \exp\left(-\frac{E_i}{RT}\right)$, for $i = 7$.

^b The equilibrium constant is calculated by: $K_A = \exp\left(\frac{-\Delta F}{RT}\right)$, where: $\Delta F = a + bT + cT^2$,

$a = 122725.16$, $b = -126.27 / K$, $c = -2.194 \times 10^{-3} / K^2$

^c $K_{NB} = 1.51 \times 10^{-2} \text{ kPa}$, $K_{H_2} = 0.14 \text{ kPa}^{-0.5}$

Table 3: Model equations for integrated catalytic membrane reactor.

Balance Equations	Mathematical Expressions	Equation
Dehydrogenation Side		
Mole	$\frac{dn_i}{dz} = \sum_{j=1}^6 \sigma_{ij} r_j (1-\varepsilon) A_{cs} \rho_s - 2\pi r_3 N a_i J_i$	(8)
Energy	$\frac{dT}{dz} = \frac{\sum_{j=1}^6 [-\Delta H(T)]_j r_j (1-\varepsilon) A_{cs} \rho_s + Q}{\sum_{i=1}^{10} n_i C_{p_i}}$	(9)
Pressure	$\frac{dP}{dz} = -\frac{G}{\rho_g g_c D_p} \left(\frac{1-\varepsilon}{\varepsilon^3} \right) \left[\frac{150(1-\varepsilon)\mu_g}{D_p} + 1.75G \right]$	(10)
Hydrogenation Side		
Mole	$\frac{dn'_i}{dz} = \sigma'_i r'_i (1-\varepsilon') A'_{cs} \rho'_s + 2\pi r_3 a'_i J_i$	(11)
Energy	$\frac{dT'}{dz} = \frac{(2\pi r_3) \sum_{i=1}^i a'_i J_i \int_{T'}^T C_{p_i} dT + [-\Delta H'(T')] r'_i (1-\varepsilon') A'_{cs} \rho'_s - Q}{\sum_{i=1}^4 n'_i C_{p'_i}}$	(12)
Pressure	$\frac{dP'}{dz} = -\frac{G'}{\rho'_g g_c D'_p} \left(\frac{1-\varepsilon'}{\varepsilon'^3} \right) \left[\frac{150(1-\varepsilon')\mu'_g}{D'_p} + 1.75G' \right]$	(13)
Hydrogen diffuses per unit length		
Diffusion of Hydrogen Across the Membrane	$J_{H_2} = \frac{Q_o \exp\left(-\frac{E_{H_2,P}}{RT}\right)}{\delta_{H_2}} \left(\sqrt{P_{H_2}} - \sqrt{P'_{H_2}} \right)$ <p>where: $Q_o = 7.29 \times 10^{-03} \text{ (mol.m)/(m}^2\text{.min.atm}^{0.5}\text{)}, \delta_{H_2} = 25 \times 10^{-6} \text{ m}$ $E_{H_2,P} = 20.5 \times 10^3 \text{ J/mol}$</p>	(14)
Heat transfer per unit length		
Heat Transferred Across the Membrane from Hydrogenation to Dehydrogenation Side	$Q = \frac{2\pi r_1 (T' - T)}{\left[\frac{1}{h'} + \frac{r_1}{k_{ss}} \ln\left(\frac{r_2}{r_1}\right) + \frac{r_1}{k_{pd}} \ln\left(\frac{r_3}{r_2}\right) + \frac{r_1}{r_2 h} \right]}$ <p>where: $k_{ss} = 22.88 \text{ W/m}\times\text{K}, k_{pd} = 93.3 \text{ W/m}\times\text{K}$ $\frac{hD_t}{k_g} = 0.813 \left(\frac{D_p G}{\mu_g} \right)^{0.9} \exp\left(-\frac{6D_p}{D_t}\right)$ $\frac{h'D'_t}{k'_g} = 3.50 \left(\frac{D'_p G'}{\mu'_g} \right)^{0.7} \exp\left(-\frac{4.6D'_p}{D'_t}\right)$</p>	(15)

Table 4: Values of constant variables in the optimization problem.

Dehydrogenation Side		
Item	Value	Unit
Styrene molar feed flowrate	0.1861	mol/s
Benzene molar feed flowrate	0.0306	mol/s
Toluene molar feed flowrate	0.2444	mol/s
Catalyst density	2146.3	kg/m ³
Catalyst particle diameter	4.7×10^{-3}	m
Bed void	0.48	---
Hydrogenation Side		
Catalyst density	1400	kg/m ³
Catalyst particle diameter	3.6×10^{-3}	m
Bed void	0.46	---

Table 5: Representative solutions for the Pareto frontier.

Parameter		Optimal Solution A		Optimal Solution B		Optimal Solution C	
		Value	Unit	Value	Unit	Value	Unit
Dehydrogenation Side	Feed Molar of Ethylbenzene	7.66	mol/s	9.36	mol/s	11.27	mol/s
	Steam-to-Ethylbenzene Ratio	7.00	---	7.00	---	20.00	---
	Feed Temperature on Shell Side	825.41	K	780.00	K	820.02	K
	Feed Pressure on Shell Side	4.00	bar	2.52	bar	4.00	bar
Hydrogenation Side	Feed Molar of Nitrobenzene	0.005	mol/s	0.002	mol/s	0.002	mol/s
	Steam-to-Nitrobenzene Ratio	4.00	---	4.00	---	4.00	---
	Feed Temperature on Tube Side	825.41	K	780.00	K	820.02	K
	Feed Pressure on Tube Side	3.62	bar	1.00	bar	1.00	bar
Dimensional Variables	No. of Hydrogenation Tubes	2500	tubes	1582	tubes	1000	tubes
	Net Diameter of Dehydrogenation Side	3.00	m	2.39	m	1.95	m
	Diameter of Hydrogenation Tube	0.048	m	0.035	m	0.040	M
	Reactor Length	4.00	m	4.00	m	4.00	M
Objective functions	Yield of Styrene	0.9747	---	0.5644	---	0.4909	---
	Conversion of Nitrobenzene	0.2113	---	0.5548	---	0.7957	---

Figure 1: Conceptual design of integrated catalytic membrane reactor coupling dehydrogenation of ethylbenzene with hydrogenation of nitrobenzene.

Figure 2: Pareto optimal set obtained by simultaneous maximization of styrene yield and nitrobenzene conversion.

Figure 3: (a, b) Feed molar flowrate of ethylbenzene; (c, d) Steam-to-ethylbenzene on dehydrogenation side; and (e, f) Feed temperature on dehydrogenation side corresponding to the Pareto optimal set.

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Figure 4: (a, b) Feed pressure on dehydrogenation side; (c, d) Molar feed of nitrobenzene on hydrogenation side; and (e, f) Steam-to-nitrobenzene on hydrogenation side corresponding to the Pareto optimal set.

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Figure 5: (a, b) Feed temperature on hydrogenation side; (c, d) Feed pressure on hydrogenation side; and (e, f) Number of hydrogenation tubes corresponding to the Pareto optimal set.

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Figure 6: (a, b) Net diameter of dehydrogenation side; (c, d) Hydrogenation tube diameter; and (e, f) Length of reactor corresponding to the Pareto optimal set.

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Figure 7: (a) Styrene yield and nitrobenzene yield along the membrane reactor at three different optimal Pareto solutions; (b) Temperature profiles on both shell and tube sides of the membrane reactor at three different optimal Pareto solutions.

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