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Nonlinear Operability of a Membrane Reactor for Direct Methane Aromatization

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Abstract: This paper presents the first operability studies for the computation of catalytic membrane reactor feasible regions for process design and control. The equilibrium-limited direct methane aromatization conversion process to hydrogen and benzene is addressed as the application. For the operability analysis, a nonlinear model that describes the membrane reactor system is derived. This analysis is performed for different reactor designs, membrane characteristics and flow configurations. The obtained results demonstrate the capabilities of the nonlinear operability approach to provide novel findings on the design of emerging energy systems.

Keywords: operability, nonlinear systems, membrane reactor, direct methane aromatization, system analysis, constraints.

1. INTRODUCTION

According to the U.S. Energy Information Administration (EIA, 2012), the year of 2012 showed a record in U.S. natural gas production of approximately 24.1 trillion cubic feet. There are currently over 2,000 companies associated with the natural gas industry, in which over 530 plants are dedicated to natural gas processing. According to the Gas Processors Association, one of the key areas of research needed consists of developing specialized software tools that can provide technical and economic assessment of the light hydrocarbon processing and utilization facilities (GPA, 2010).

Current challenges of natural gas utilization processes correspond to designing new emerging and flexible systems that can produce chemicals, fuels, power, and heat. However, these technologies are typically operated in highly constrained and integrated processes that are represented by complex nonlinear and high-dimensional models. As an approach for the design of chemical processes, process operability emerged in the last decades. In particular, process operability enables the verification of a design's ability to achieve the feasible region of operation associated with process specifications, considering the physical limitations of the process design (Vinson and Georgakis, 2000). Operability describes the relationship between the input (manipulated and/or disturbance) and output variables through a linear/nonlinear mapping obtained by employing the process model (Georgakis et al., 2003).

This paper presents the first process operability study to analyze the achievable spaces for a membrane reactor (MR) system. Specifically, it addresses the computation of feasible regions for the design and control of the direct methane aromatization (DMA) conversion process of natural gas to fuels and chemicals as an alternative to petroleum. In this case, we focus on the equilibrium-limited production of hydrogen (H_2) and benzene (C_6H_6) from methane (CH_4) using a catalytic membrane reactor. MR systems studies lack of systematic approaches to determine the output (e.g., specifications on reaction conversions and production rates) ranges that are achievable, considering the limited ranges available for the process inputs (e.g., operational variables and membrane characteristics) due to the physical limitations of the process design. In the past, the concept of attainable region was applied to the oxidative dehydrogenation of 1-Butene membrane reactor considering one input and two output variables (Milne et al., 2004).

MRs are emerging systems that enable process intensification by combining phenomena of two unit operations (reaction and separation) in one process, resulting in higher efficiencies and lower costs (Drioli et al., 2011; Brunetti et al., 2012). MRs allow higher conversions than conventional packed-bed reactors due to the reaction equilibrium shift towards the products caused by the selective removal of one

of these products through the membrane. Specifically, in the DMA process, the reaction equilibrium is shifted towards products as H_2 is removed through a H_2-selective membrane (ion transport-based). Restrictions on process target specifications, such as reaction conversions and production rates, as well as multiple challenges associated with controlling temperatures and compositions, make the problem of designing and controlling MRs for the DMA process a challenging area of research.

For the operability calculations, the variables that define the available input set (AIS) for the MR are the reactor tube diameter and pressure; and for the membrane are the selectivity and permeance. Based on the defined input specifications, the operability calculations provide an achievable output set (AOS) for the following performance variables: methane conversion and benzene production rate. The outline of this paper is as follows. First, the basic concepts of process operability are presented. Then, a general description of the reaction kinetics and mass balances used in the membrane reactor model is introduced. Finally, the membrane reactor operability studies are performed focusing on the relationship between the *AIS* and *AOS* for cocurrent and countercurrent flow configurations.

2. PROCESS OPERABILITY CONCEPTS

The main contributions on operability for linear and nonlinear systems have been detailed in Lima et al. (2010) and Georgakis et al. (2003). A summary of the concepts from these references that will be necessary for the approach development is shown here.

To perform the operability analysis, the process model that describes the relationship between the input (manipulated and/or disturbance) and output variables need to be known (Georgakis et al., 2003). This model (M) can be represented by:

$$\mathrm{M} = \begin{cases} \dot{\mathrm{x}} = \mathrm{f}(\mathrm{x}, \mathrm{u}, \mathrm{d}) \\ \mathrm{y} = \mathrm{g}(\mathrm{x}, \mathrm{u}, \mathrm{d}) \\ \mathrm{h}_1(\dot{\mathrm{x}}, \mathrm{x}, \mathrm{y}, \dot{\mathrm{u}}, \mathrm{u}, \mathrm{d}) = 0 \\ \mathrm{h}_2(\dot{\mathrm{x}}, \mathrm{x}, \mathrm{y}, \dot{\mathrm{u}}, \mathrm{u}, \mathrm{d}) \geq 0 \end{cases} \quad (1)$$

in which $\mathrm{x} \in R^r$ are the state variables of the process. Also, $\mathrm{u} \in R^m$, $\mathrm{d} \in R^q$ and $\mathrm{y} \in R^n$ are the vectors of the manipulated inputs, the disturbances and the output variables, respectively. The time derivatives of x and u are denoted by $\dot{\mathrm{x}}$ and $\dot{\mathrm{u}}$, respectively, and f and g represent the nonlinear maps. Finally, h_1 and h_2 include the process constraints associated with production, environmental and safety specifications.

In particular, the manipulated inputs, u, can take values in the available input set (*AIS)*, based on the design of the process that is limited by the process constraints (Vinson and Georgakis, 2000):

$$AIS = \{\mathrm{u} \,|\, \mathrm{u}_\mathrm{i}^{\min} \leq \mathrm{u}_\mathrm{i} \leq \mathrm{u}_\mathrm{i}^{\max}; 1 \leq i \leq m\} \quad (2)$$

Additionally, the disturbance variables, d, which can represent the process uncertainties such as ambient conditions, catalyst activity, or uncontrolled compositions of feed streams, present values inside the expected disturbance set (*EDS*) as follows:

$$EDS = \{\mathrm{d} \,|\, \mathrm{d}_\mathrm{i}^{\min} \leq \mathrm{d}_\mathrm{i} \leq \mathrm{d}_\mathrm{i}^{\max}; 1 \leq i \leq q\} \quad (3)$$

Based on the steady-state model of the process, the achievable output set (*AOS*) for a fixed disturbance value can be achieved using the inputs inside the *AIS*:

$$AOS(\mathrm{d}) = \{\mathrm{y} \,|\, \mathrm{y} = \mathrm{M}(\mathrm{u}, \mathrm{d}); \mathrm{u} \in AIS, \mathrm{d} \text{ is fixed}\} \quad (4)$$

3. MEMBRANE REACTOR MODEL

To illustrate the nonlinear operability concept, a MR for the DMA conversion to H_2 and C_6H_6 is addressed in this section. Fig. 1 shows a schematic representation of the MR cocurrent and countercurrent flow configurations. The following 2-step reaction mechanism (adapted from Li et al., 2002) is assumed for this process:

Step 1:

$$2\,\mathrm{CH_4} = \mathrm{C_2H_4} + 2\,\mathrm{H_2} \quad (5)$$
$$r_1 = k_1\,\mathrm{C_{CH_4}}\left(1 - \frac{k_1'\,\mathrm{C_{C_2H_4}}\,\mathrm{C_{H_2}^2}}{k_1\,\mathrm{C_{CH_4}^2}}\right)$$

Step 2:

$$3\,\mathrm{C_2H_4} = \mathrm{C_6H_6} + 3\,\mathrm{H_2} \quad (6)$$
$$r_2 = k_2\,\mathrm{C_{C_2H_4}}\left(1 - \frac{k_2'\,\mathrm{C_{C_6H_6}}\,\mathrm{C_{H_2}^3}}{k_2\mathrm{C_{C_2H_4}^3}}\right)$$

in which $\mathrm{C_{CH_4}}$, $\mathrm{C_{C_2H_4}}$, $\mathrm{C_{H_2}}$, and $\mathrm{C_{C_6H_6}}$ are the concentrations in the gas phase of methane, ethene, hydrogen, and benzene, respectively. Also, r_1 and r_2 represent the reaction rates of steps 1 and 2, respectively, and k_1, k_1', k_2, and k_2' correspond to the reaction rate constants (where the symbol ´ denotes the inverse reaction).

Considering the shell and tube MR design in Fig. 1, in which CH_4 feeds the reaction side (tube packed with catalysts) and the sweep gas (e.g., helium) flows

in the permeation side (shell), the H_2 produced in the tube permeates to the shell through the membrane layer that is placed on the surface of the tube wall. The produced outlet streams from the tube (retentate) and shell (permeate) are rich in C_6H_6 and H_2, respectively.

The design of MRs using process operability tools will be performed by mapping the feasible regions between process inputs and output variables using the derived nonlinear MR process model at steady state. For this purpose, the following mass balances are considered for the DMA reaction system.

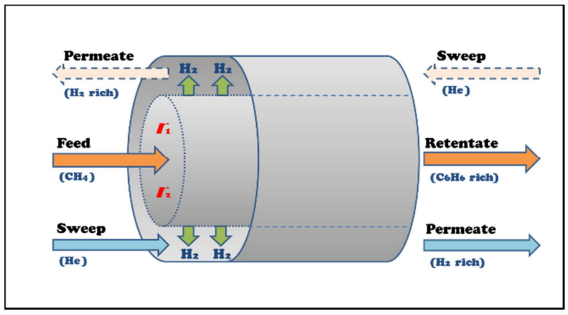

Fig. 1. Membrane reactor: cocurrent (continuous line) and countercurrent (dotted line) configurations.

Molar balances inside tube: (7)

$$\frac{dF_{t,CH_4}}{dz} = r_1 A_t - \frac{Q}{\propto_{H_2/CH_4}}\left(P_{t,CH_4}^{1/4} - P_{s,CH_4}^{1/4}\right)\pi\, d_t$$
$$\frac{dF_{t,C_2H_4}}{dz} = -\frac{r_1}{2}A_t + r_2 A_t - \frac{Q}{\propto_{H_2/C_2H_4}}\left(P_{t,C_2H_4}^{1/4} - P_{s,C_2H_4}^{1/4}\right)\pi\, d_t$$
$$\frac{dF_{t,H_2}}{dz} = -r_1 A_t - r_2 A_t - Q\left(P_{t,H_2}^{1/4} - P_{s,H_2}^{1/4}\right)\pi\, d_t$$
$$\frac{dF_{t,C_6H_6}}{dz} = -\frac{r_1}{3}A_t - \frac{Q}{\propto_{H_2/C_6H_6}}\left(P_{t,C_6H_6}^{1/4} - P_{s,C_6H_6}^{1/4}\right)\pi\, d_t$$

Molar balances inside shell: (8)

$$\frac{dF_{s,CH_4}}{dz} = \frac{Q}{\propto_{H_2/CH_4}}\left(P_{t,CH_4}^{1/4} - P_{s,CH_4}^{1/4}\right)\pi\, d_t$$
$$\frac{dF_{s,C_2H_4}}{dz} = \frac{Q}{\propto_{H_2/C_2H_4}}\left(P_{t,C_2H_4}^{1/4} - P_{s,C_2H_4}^{1/4}\right)\pi\, d_t$$
$$\frac{dF_{s,H_2}}{dz} = Q\left(P_{t,H_2}^{1/4} - P_{s,H_2}^{1/4}\right)\pi\, d_t$$
$$\frac{dF_{s,C_6H_6}}{dz} = \frac{Q}{\propto_{H_2/C_6H_6}}\left(P_{t,C_6H_6}^{1/4} - P_{s,C_6H_6}^{1/4}\right)\pi\, d_t$$

in which $F_{t,i}$ and $F_{s,i}$ correspond to the molar flow rate of component i (CH_4, C_2H_4, H_2 and C_6H_6) inside the tube and shell, respectively. Also, z, d_t, and A_t are the differential length, diameter and cross-sectional area of the reactor, respectively. The membrane flux expression with a relationship proportional to the transmembrane partial pressure gradient of the species with a ¼ dependence is considered (Li et al., 2011), where Q is the H_2 permeance through the membrane and $\propto_{H_2/i}$ is the selectivity between H_2 and component i. Finally, $P_{t,i}$ and $P_{s,i}$ are the partial pressures of components i in the feed and permeate sides of the membrane, respectively.

4. MEMBRANE REACTOR OPERABILITY STUDIES

This section presents the first step on the application of nonlinear operability tools to enable the design of stand-alone MR units. Both MR simulation setups, for cocurrent and countercurrent flows in the shell, consider the following set of conditions: volumetric feed flow of CH_4 of 8 [cm^3 min^{-1}], tube diameter of 0.5 [cm], and total pressure inside the tube of 1 [atm]. Also, k_1 , k_2 , k_1', and k_2' take the values of 0.04 [s^{-1}], 4.2 [s^{-1}], 6.4×10^6 [cm^3/s-mol], and 56.38 [cm^3/s-mol], respectively. Additionally, for the shell side, we define a flow rate of sweep gas (He) of 10 [cm^3 min^{-1}], a total pressure of 1 [atm], and a diameter of 3 [cm]. Isothermal reaction operation at a temperature of 900°C due to the presence of the oven is also considered. The operability studies assume four input variables to specify the *AIS*: membrane selectivity and permeance, tube diameter, and pressure inside the tube. Mathematically, the cocurrent case addressed here corresponds to an initial value problem that can be solved using the MATLAB (MathWorks, Inc.) subroutine "ode15s"; for the countercurrent case, a boundary value problem was formulated using the MATLAB subroutine "bvp4c".

4.1. Cocurrent configuration

For the first case, membrane selectivity and permeance are the input variables that define the *AIS*. Also, the total pressure inside the tube, 1 [atm], and the inner tube diameter, 0.5 [cm], are assumed as constant parameters. This case serves the purpose of determining the set of membrane characteristics that should be obtained in the laboratory so that the desired process specifications can be achieved. Such specifications that define the *AOS* correspond here to the CH_4 conversion and the production rate of C_6H_6.

Fig. 2 shows the *AIS* considered and the *AOS* calculated in this case. Particularly, the vertex "d" in the *AIS* figure is associated with the highest values of membrane permeance and selectivity, 0.01 [mol/(s m^2 $atm^{1/4}$)] and 10^5, respectively. This point corresponds to the best production rate of benzene (≈ 26 mg/h). However, the highest conversion of methane (around

45%) occurs at point "c", where the loss of benzene through the membrane is also the highest, due to the low selectivity value at that point, shifting the equilibrium of reaction step 2 even further. This result indicates that for this MR, increasing the conversion of methane does not necessarily imply a higher production of the desired benzene product. For the segment from the points "a" to "b", which shows a constant low permeance value (10^{-4} [mol/(s m^2 $atm^{1/4}$)]) for gradually increasing selectivities (from 200 to 10^5), only slight changes in methane conversion and benzene production rate are obtained.

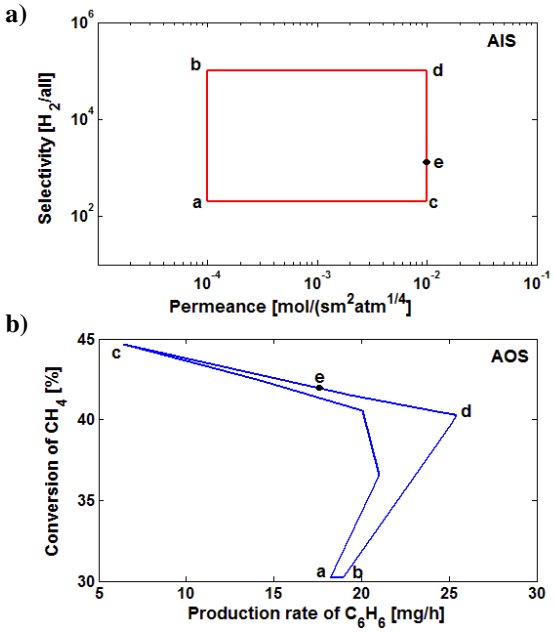

Fig. 2: *AIS* cocurrent - membrane permeance and selectivity (a). *AOS* cocurrent - conversion of methane and production rate of benzene (b).

When the permeance is increased though to 0.01 [mol/(s m^2 $atm^{1/4}$)], from points "b" to "d", both production rate and conversion present positive changes. Thus, the performed operability analysis suggests that: (i) the permeance parameter is more critical for obtaining a high reaction conversion when compared to the selectivity; and (ii) for a high permeance, a sufficiently high selectivity value is also needed for optimal MR production rates. Finally, point "e" represents a case with membrane properties that would be expected in the lab, such as a permeance of 0.01 [mol/(s m^2 $atm^{1/4}$)] and a selectivity of 10^3. For this point, the production rate of benzene is about 17 mg/h and the methane conversion about 42%. The performance improvement starting from this point will be analyzed in the next operability study by changing the reactor design and conditions.

For the second case, we now fix the membrane permeance and selectivity at point "e". Fig. 3 shows the *AIS* and the *AOS* plots for this case, in which the tube diameter and pressure are now the input variables.

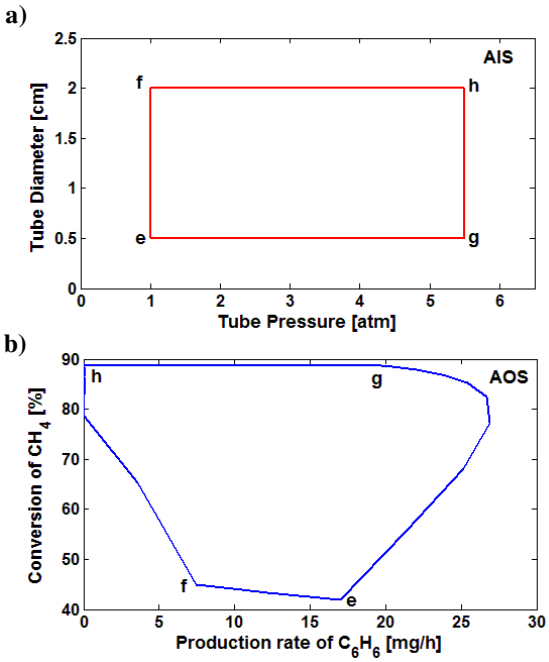

Fig. 3: *AIS* cocurrent - pressure and diameter inside the tube (a). *AOS* cocurrent - conversion of methane and production rate of benzene (b).

According to Fig. 3, the points with the highest pressure of 5.5 [atm], "h" and "g", reach the highest conversion of methane (≈ 89%). For such points, as the diameter decreases from 2 to 0.5 [cm], the benzene flow in the retentate increases from approximately 0 to 20 mg/h. This happens due to the smaller permeation of benzene through the membrane for smaller membrane surface areas. This result shows that a higher pressure does not necessarily translate to higher production rates of benzene. For the lower pressure value of 1 [atm], points "e" and "f" present methane conversions within the small range between 42 and 45%. Additionally, the production rate of benzene follows a similar trend with diameter changes as explained above. These results indicate that a process engineer could manipulate the reactor design for a certain membrane with fixed characteristics to obtain high degrees of methane conversion and benzene production according to the desired specifications. In

this case, the path from "g" to "e" (closer to "g"), i.e. at a tube diameter of 0.5 [cm] for different pressures can be followed.

4.2. Countercurrent configuration

For the countercurrent operability analysis, similar to the cocurrent case, we start with the membrane selectivity and permeance as the input variables that define the *AIS*, as shown in Fig. 4. The total pressure inside the tube, 1[atm], and the inner tube diameter, 0.5 [cm], are also initially assumed as constant parameters. For the purpose of comparison between this configuration and the cocurrent system, the specifications that define the *AOS* correspond here to the CH_4 conversion and the production rate of C_6H_6. Also as previously, point "e" presents a permeance of 0.01 [mol/(s m^2 $atm^{1/4}$)] and a selectivity of 10^3.

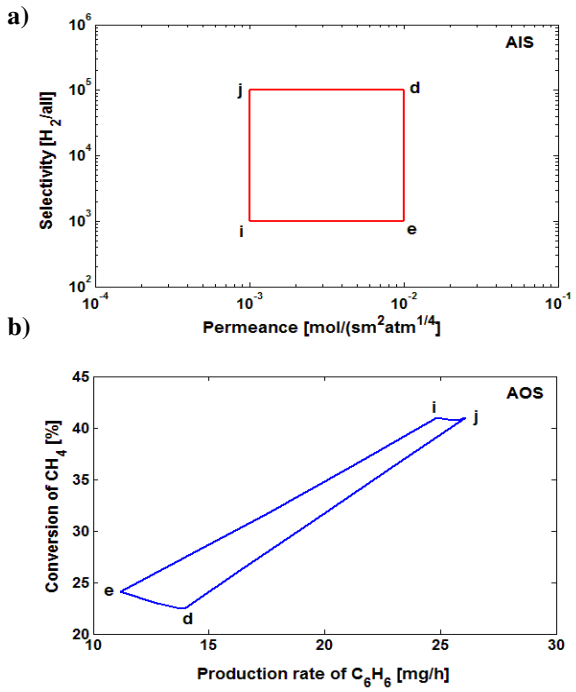

Fig. 4: *AIS* countercurrent - membrane permeance and selectivity (a). *AOS* countercurrent - conversion of methane and production rate of benzene (b).

Fig. 4 also depicts the *AOS* calculated as a function of the defined *AIS*. Note that the highest methane conversion (≈ 41%) occurs at points "i" and "j", which are associated with the lowest value of membrane permeance in the *AIS* figure. In particular, point "j", with higher selectivity, presents the highest production of benzene among all points, due to smaller losses of benzene through the membrane. The path between points "d" and "e" shows the lowest conversion of methane and production rate of benzene, due to the greater permeance, which causes additional losses of methane and benzene through the membrane. Thus, this analysis suggests that the highest production of the desired benzene product is obtained for the scenario with high selectivity and low permeance.

Fig. 5 shows the operability analysis when the membrane permeance and selectivity are fixed at point "j". In this case, the tube diameter and pressure are the input variables. Note that point "o" represents the highest conversion of methane and production rate of benzene, where the tube diameter and pressure are 1[cm] and 1.03 [atm], respectively. For this figure, it is also important to note that increasing the pressure may cause positive or negative effects on methane conversion and production rate (see paths between "l" and "o" and "o" and "n"). The nature of these effects will depend on the relationship between pressure and membrane surface area.

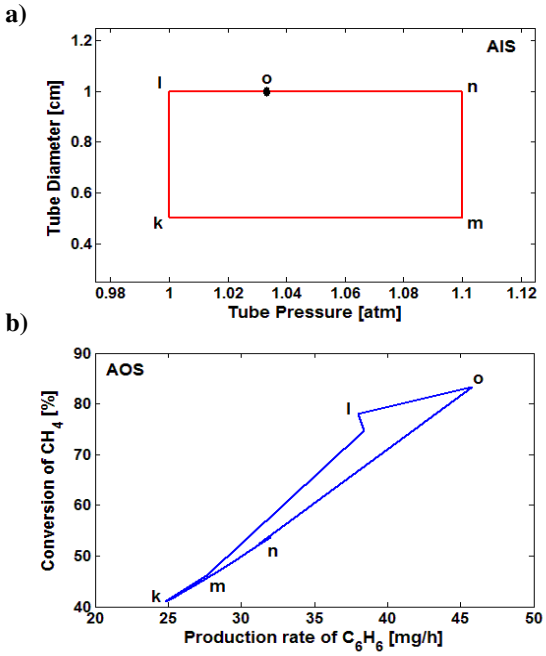

Fig. 5: *AIS* countercurrent - pressure and diameter inside the tube (a). *AOS* countercurrent - conversion of methane and production rate of benzene (b).

When the pressure is kept constant, in the segments from points "k" to "l", and "m" to "n", the change in the tube diameter presents an important effect on the conversion and production rate. This result differs from the cocurrent configuration, in which the

diameter presented a small effect on the conversion of methane (see Fig. 3). Comparing the production rates of benzene in Figs. 3b and 5b, note that the countercurrent configuration shows a performance improvement of approximately 70% from the cocurrent system, from 27 [mg/h] to 46 [mg/h].

5. CONCLUSIONS

This paper presented nonlinear operability analyses for the design (and potentially control) of membrane reactors. In particular, we focused on the direct methane aromatization application for the equilibrium-limited production of hydrogen and benzene. The performed operability analysis for the cocurrent reactor configuration suggested the following conclusions: (i) the membrane selectivity was not a critical design parameter when low permeance values were studied; however, for a high permeance parameter, a high selectivity was essential to tailor the methane conversion and production rate of benzene according to specifications; and (ii) increasing the methane conversion did not necessarily imply a higher production of the desired benzene product. Additionally, for the countercurrent case: (i) the tube diameter presented a greater effect on the methane conversion when compared to the cocurrent configuration; (ii) pressure increments caused positive or negative effects on the output variables depending on the relationship between pressure and membrane surface area; and (iii) the production rate of benzene showed an approximate improvement of 70% from the cocurrent to the countercurrent configuration. The obtained results demonstrated the promising capabilities of the proposed process operability approach to provide guidelines for experimental research, in terms of determining the set of membrane characteristics that should be obtained in the laboratory so that desired process specifications can be achieved. We are currently investigating the application of nonlinear operability approaches to high-dimensional processes. We are also analyzing the incorporation of the membrane reactor economic significance into the operability studies.

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