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MODELLING OF A PACKED BED REACTOR FOR DRY REFORM OF METHANE

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Abstract: In the present article, the mathematical modeling of a fixed bed reactor to produce synthesis gas (mixture of hydrogen and carbon monoxide) through the dry reforming reaction of natural gas was performed. This product is an important intermediary of the petrochemical industry, being used as reagent in the production of a vast amount of chemicals, fuels and solvents. Reforming with carbon dioxide (dry reforming) has a significant environmental bias, as it uses two of the largest greenhouse-enhancing agents to produce products of interest to the chemical industry. Thus, an adiabatic bed-type reactor (with Ni/Al_2O_3 as catalyst) was modeled in order to trace the conversion, temperature and pressure profiles in the equipment and to size it. The three ordinary differential equations of the mass, temperature and pressure balances were simultaneously solved by the numerical method of Euler (in Microsoft Excel), resulting in an equipment with 3 ton of catalyst and a minimum length of 3.15 m.

Key Words: Chemical Reactor, Dry Reform of Methane, Synthesis Gas, Packed-Bed Reactor, Natural Gas.

Introduction

The industrial equipment responsible for the processing of chemical reactions is the chemical reactor. Of the many ways to classify those reactions, one of the most useful is by the number and type of phases involved, so that there are two major groups: homogeneous reactions, where the reaction takes place in a single phase or heterogenous reactions, where two (or more) phases are present. There are also the catalytic reactions, whose reaction rate is altered by means of the insertion of a component, the catalyst, which accelerates the whole process by reducing the reaction activation energy (that is, the minimum energy required for the conversion of reactants into products). The catalyst does not alter the equilibrium and does not allow thermodynamically unfavorable reactions to occur. It is recovered at the end of the reaction, not being consumed by it [1].

The packed bed reactor (PBR) is one of the most widely used types of catalytic reactors in chemical processing, especially in gaseous reactions. It is referred to as a fixed bed (or packed) reactor because it is a tubular reactor filled with a bed of solid catalyst. It provides the highest conversion between catalytic reactors. Temperature control is difficult, and there may be hot spots. A catalyst with low catalytic activity should not be used, since the replacement of the catalyst is hampered. As one works with a bed, high pressure losses and preferential flow paths may occur in this equipment [2]. In Fig. 1 it is possible to visualize a schematic drawing of an “adiabatic bed”, a type of PBR.

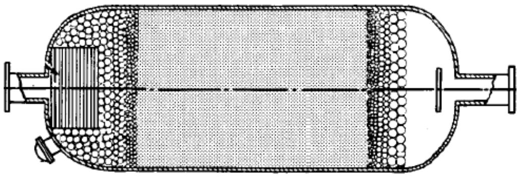

Figure 1 - Adiabatic fixed bed reactor [3].

Synthesis gas is a mixture of hydrogen and carbon monoxide, with a stoichiometry set at 2:2. Any material that has carbon may become the raw material for synthesis gas, some of them are: coal, coke, petroleum and its derivatives, natural gas, among others [4, 5]. The main methods of obtaining this chemical compound are: steam reforming of natural gas, dry reforming of natural gas, partial oxidation, autothermal reforming and coal gasification [4, 6, 7].

The dry reform parts of the reaction between carbon dioxide and methane (CH4). These are two of the main gases responsible for intensifying the greenhouse effect. Its excessive emission, resulting from industrial processes and human activities, causes global warming and the elevation of the planet's average temperature. The consequences of rising temperatures on the planet are the extinction of species, the melting of glaciers and the increase of the sea’s temperature and level. An alternative to reduce the emissions, therefore, is the application of these gases in the industry for the synthesis of certain materials. Reforming methane with carbon dioxide in catalytic reactors allows the synthesis gas to be obtained, as shown in Eq. 1 [8].

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (1)$$

There is a great economic interest in the production of synthesis gas from carbon dioxide (dry reform), since its demand has increased due to its potential in many applications, as in the Fischer-Tropsch synthesis, where the gas is converted into various liquid fuels, or in the production of methanol, dimethyl ether and oxo-alcohols. A drawback in these reactions is the need to work with high temperatures, approximately 1025 K, and a positive point are the low pressures, around 101 kPa, both necessary to obtain high selectivity and conversion rates [7, 9].

The general objective of the present work is the mathematical modeling of a fixed bed reactor (PBR) in order to process the dry reform reaction of the natural gas, aiming the production of synthesis gas. The modeling involved the simultaneous development of the molar, energy and pressure balances in order to trace the conversion, temperature and pressure profiles of the equipment and start to size it.

Experimental

The modeled chemical reactor is responsible for the production of synthesis gas, a mixture of hydrogen gas (H_2) and carbon monoxide (CO), an important product for the petrochemical industry. It is a PBR (packed-bed reactor), a tubular reactor equipped with a fixed bed of catalyst. The reaction’s slow, and limiting, step is the activation of methane to form a CH_x compound and the reaction of that and the oxidant (the carbon dioxide itself). This process is described by Eq. 1, the reaction considered for the development of the process’ balances.

The present reaction is processed at a temperature of 750 °C (1,023.15 K) and at atmospheric pressure (101,325 Pa). In regards of the catalyst, nickel ones have been the most used, since they have desirable characteristics such as: high reactivity and lower price when compared with noble metal-based catalysts [9-11]. When supported on aluminum oxide, their mechanical strength is improved, they grant high surface area and good metal dispersion. Consequently, Ni/Al_2O_3 was chosen for the dry reforming, same as it was done by [12].

The limiting reactant was assumed the CO_2, as its obtainment is considerably harder than methane (natural gas). Its conversion in a reactor using nickel supported on aluminum oxide as catalyst is 95% [10]. The reaction’s kinetics is complex and follow the Langmuir-Hinshelwood mechanism. The complete development of the reaction kinetics and the calculation of the kinetic constants that govern the expression of the reaction rate (at different temperatures) can be found in references [9, 12, 14].

The dimensioning of any catalytic reactor requires the simultaneous resolution of the molar, energy and pressure loss balances. Unlike the ideal homogeneous reactors, in which simpler integrated analytical equations can be obtained, the heterogeneous reactors require the numerical resolution of differential equations that represents such balances. The temperature dependence (as a consequence of the reaction being endothermic) prevents the resolution of the molar balance without the simultaneous analysis of the energy balance. Because it is a fixed bed, there is a significant drop in pressure throughout the equipment, so that the differential equation for the calculation of pressure drop in a particle bed is also required [2].

According to [2], for the PBR reactor, the design equation (molar balance) is similar to the tubular reactor, PFR, but with the volume of the reactor being replaced by the mass of the catalyst, W. This balance is represented by Eq. 2.

$$\frac{dX}{dW} = \frac{r'_{CO_2}}{F_{A0}} \tag{2}$$

Where r'_{CO_2} refers to the reaction rate for the limiting reactant. It was acquired from the literature and can be written by means of Eq. 3 [9, 12].

$$-r_{CO2} = k_2\left[C_{CO2}.C_{H2} - \frac{C_{CO}.C_{H2O}}{K_{EQ}}\right] + k_3.C_{CO2} \tag{3}$$

The concentrations of the other present components in the rate equation must be described in terms of the initial concentration of the CO_2, the limiting reactant, by means of their stoichiometric ratios. The chemical reaction engineering's literature refers to the limiting reactant as "component A". Therefore, Eq. 1 can be rewritten as: $A + B \rightarrow 2C + 2D$. With A as CO_2, B as CH_4, C as H_2 and D as CO. According to [14], there are parallel reactions in the reactor and water is formed by the so-called reverse shift gas (RWGS) reaction, $H_2 + CO_2 \rightarrow CO + H_2O$. This is the only other product in the sequence of reactions beyond hydrogen and carbon monoxide. Its denomination remained as the "component E" in the rewritten rate expression, Eq. 4.

$$-r_A = k_2\left[C_A.C_C - \frac{C_D.C_E}{K_{EQ}}\right] + k_3.C_A \tag{4}$$

In addition, the volume variation in the reactor must be taken into account, since it is a gas-phase reaction. The variation is represented by the term ε_A, calculated by Eq. 5 [2].

$$\varepsilon_A = \delta.y_{A0} \tag{5}$$

The term δ is the change in the total number of moles of the reaction mixture, calculated by the difference between the stoichiometric coefficients of the products and the reactants. The term y_{A0} is the molar fraction of the limiting reactant in the feed. This molar fraction was found through a mass balance in the equipment, considering an arbitrary production of 68,389.56 kg/h of synthesis gas.

From the knowledge of the volume variation parameter, the outlet concentrations of the components present in the reactor were written in the formats represented by the equations of Table 1.

Table 1 - Concentration of reactants and products in terms of A.

Component	Concentration Expression	Equation Number
A	$C_A = C_{A0}.\frac{(1 - X_A)}{(1 + \varepsilon_A.X_A)}.\frac{P}{P_0}.\frac{T_0}{T}$	(6)
C	$C_C = C_{C0} + \frac{2}{1}.\frac{C_{A0}.X_A}{(1 + \varepsilon_A.X_A)}.\frac{P}{P_0}.\frac{T_0}{T}$	(7)
D	$C_D = C_{D0} + \frac{2}{1}.\frac{C_{A0}.X_A}{(1 + \varepsilon_A.X_A)}.\frac{P}{P_0}.\frac{T_0}{T}$	(8)
E	$C_E = C_{E0} + \frac{1}{1}.\frac{C_{A0}.X_A}{(1 + \varepsilon_A.X_A)}.\frac{P}{P_0}.\frac{T_0}{T}$	(9)

The expression of component B was omitted, as it was not present in the reaction rate expression. Its format would be identical to that of component E. The ratios that precede each expression are the ratio between the stoichiometric coefficients of the component in question by that of A.The pressure and temperature terms in the previous equations deal with the fact that both vary along the equipment, since the reaction is endothermic and there is a significant pressure drop along the catalytic bed. These variations are represented in the three differential equations. The "0" subscript refers to the initial conditions of the reaction.

There are two kinetic constants (k_2 e k_3) and one chemical equilibrium constant (K_{EQ}) in Eq. 4. Their values at different temperatures were reported by the literature [12]. Since the temperature varies along the reaction, it was necessary to open such terms as temperature-dependent expressions using Van't Hoff's equation of chemical equilibrium, Eq. 10, and Arrhenius' of chemical kinetics, Eq. 11.

$$K_{EQ} = K^o . exp\left[\frac{-\Delta H_R^o}{R} . \left(\frac{1}{T} - \frac{1}{T^o}\right)\right] \tag{10}$$

$$k_i = k_{0i} . e^{\frac{-E_i}{R.T}} \tag{11}$$

The term E_i refers to the reaction's activation energy, k_{0i} is the pre-exponential factor (or Arrhenius constant), K is the chemical equilibrium constant, k the kinetic constant, ΔH_R^o is the reaction enthalpy at standard temperature (298.15 K) and R is the ideal gas constant. The "o" sign represented in some variables refers to the standard state, 298.15 K. Since the values of these constants were known at various temperatures, Arrhenius ($\ln(k)$ *versus* $\frac{1}{\mathrm{T}}$) graphs were plotted to determine the values of the activation energies and the pre-exponential factors and leave only the temperature as a variable in the expression of the molar balance.

The reaction's enthalpy value at standard condition was determined with Eq. 12, by knowledge of the standard formation enthalpies of the components, which were acquired from [15]. On Eq. 12, ν_i stands for the stoichiometric coefficients of the species.

$$\Delta H_R{}^o = \sum \left(\nu_i . H_{f,i}{}^o\right)_{Prod} - \sum \left(\nu_i . H_{f,i}{}^o\right)_{Reag} \tag{12}$$

The chemical equilibrium constant at standard temperature, K^o, is calculated by Arrhenius' equation, Eq. 13, which depends on the reaction's Gibbs' Free Energy Variation at standard conditions, ΔG_R^o, that one being calculated by Eq. 14.

$$\Delta G_R{}^o = -R.T.lnK^o \tag{13}$$

$$\Delta G_R{}^o = \sum \left(\nu_i . G_{f,i}{}^o\right)_{Prod} - \sum \left(\nu_i . G_{f,i}{}^o\right)_{Reag} \tag{14}$$

Standard Condition Gibbs' Free Energy Variation depends on the species' Free Energies of Formation at said condition, which was also acquired from [15]. The possession of the kinetic and energy data permitted the use of the energy balance differential equation, Eq. 15 [2, 16]. It is based on the mass of catalyst and is directly linked to the reaction rate expression used in the molar balance, so that the energy balance will also have three variables that vary with the reactor's length: conversion, temperature and pressure.

$$\frac{dT}{dW} = \frac{-r_A . [-\Delta H_R(T)]}{F_{A0} . \left(\sum \theta_i . C_{p,i} + X_A \Delta C_p\right)} \tag{15}$$

The term $\Delta H_R(T)$ refers to the enthalpy of the reaction at a variable temperature. It is calculated by Eq. 16, where T remains as an indeterminate variable.

$$\Delta H_R(Tx) = \Delta H^{\underline{o}}{}_{R,298K} + \int_{298}^{T} \Delta C_p . dT \tag{16}$$

The parameter θ_i is the ratio of the concentration (or molar flow or number of moles) of a component i to the concentration of the limiting reactant, Eq. 17.

$$\theta_i = \frac{C_{i0}}{C_{A0}} = \frac{F_{i0}}{F_{A0}} = \frac{N_{i0}}{N_{A0}} \tag{17}$$

The factor ΔC_p is the difference between the sum of the heat capacities of the products and sum of those of the reagents. The C_p data for each component was acquired from [15] and described in the form of Eq. 18.

$$\frac{C_p}{R} = A + B.T + C.T^2 + D.T^{-2} \tag{18}$$

The values for the constants A, B, C and D are shown in Table 2. By applying the constants in Eq. 18 it becomes possible to calculate the heat capacity at the desired temperature. The resolution of the energy balance equation provided the reaction temperature profile, so that the temperature at the end of the reaction was found. The average temperature between the start and end of the process was calculated and the C_p of the species were determined at that temperature (and taken as its numerical value, not as a function of temperature). The resulting values are also expressed in Table 2.

Table 2 - Specific Heat constants and value at average reaction temperature.

Component	**A**	**10^{-3}.B**	**10^{-6}.C**	**10^{5}.D**	**$C_{p,Tavarage}$(J/mol.K)**
CH_4	1,702	9,081	-2,164	-	72,057
CO_2	5,457	1,045	-	1,157	53,202
CO	3,376	0,557	-	-0,031	32,720
H_2	3,249	0,422	-	0,083	30,623

After the energy balance, it was necessary to apply Ergun's equation (Eq. 19) to calculate the pressure drop in the packed bed [2].

$$\frac{dP}{dW} = \frac{-G.(1-\emptyset).(1+\varepsilon_A.X_A)}{g_c.D_p.\emptyset^3.{\rho_{cat}}^2.A_{ST}.(1-\emptyset).\left(\frac{P}{P_0}\right).\left(\frac{T_0}{T}\right)}.\left[\frac{150.(1-\emptyset).\mu_m}{D_p} + 1{,}75.G\right] \tag{19}$$

Where $\emptyset$ is the porosity of the catalytic bed, g_c is a conversion factor (equals 1.0 for the metric system), D_p is the catalyst particle diameter, ρ_b is the specific mass of the catalytic bed, A_{ST} is the reactor's cross-sectional area, μ_m is the dynamic viscosity of the reactants that flow through the reactor and G is the surface velocity of the components. The latter can be calculated as shown in Eq. 20.

$$G = \rho.v^* = \rho_{mist}.\frac{v_0}{A_{ST}} = \frac{\dot{m}_t}{v_0}.\frac{v_0}{A_{ST}} = \frac{\sum(F_{i0}.MM_i)}{A_{ST}} \tag{20}$$

The three differential equations of the molar, energy and pressure balances can be rewritten in terms of the reactor's length, as in Eq. 21.

$$dW = \rho_{cat}.(1-\emptyset).A_{ST}.dz \tag{21}$$

The resolution of the previous differential equations granted the conversion, temperature and pressure profiles along the equipment's length, allowing to define an optimum, one with the conversion of 95% for CO_2. As it depends on the cross-sectional area of the reactor (cylindrical), it was necessary to choose an initial value for the diameter of the equipment and change it as the final result was a reasonable one for the size of an industrial reactor. The choice and subsequent change in bed porosity and catalyst's particle diameter was performed using the same premise. The literature suggests values between 2 and 5 mm for the catalyst's particle diameter [3].

The input parameters in the reactor are described in Table 3. The properties of mixtures were determined by the weighted sum (by the molar fraction) of the individual properties.

Table 3 - Initial reaction and reactor parameters.

Component A (CO_2)			**Component B (CH_4)**			**Initial Parameters**		
Variable	**Value**	**Unit**	**Variable**	**Value**	**Unit**	**Variable**	**Value**	**Unit**
F_{A0}	1,203.85	kmol/h	F_{B0}	1,633.8	kmol/h	v_0	238,227.81	m^3/h
MM_A	44	kg/kmol	MM_B	16	kg/kmol	T_0	1,023.15	K
ρ_A	0.5241	kg/m^3	ρ_B	0.1906	kg/m^3	P_0	101,325	Pa
$\dot{m}_A$	52,969.57	kg/h	$\dot{m}_B$	26,140.83	kg/h	μ_{mix}	2.879.10^{-5}	Pa.s
v_{A0}	101,066.9	m^3/h	v_{B0}	137,161.5	m^3/h	ρ_{bed}	1,632	kg/m^3
C_{A0}	5.0533	mol/m^3	C_{B0}	6.858	mol/m^3	$D_{reactor}$	1.5	m
y_{A0}	0.4242	-	y_{B0}	0.5758	-	$D_{particle}$	0.025	m
μ_{A0}	4.149.10^{-5}	Pa.s	μ_{B0}	1.943.10^{-5}	Pa.s	$\emptyset$	0.60	-
ε_A	0,8484	-	-	-	-	$A_{cross\ sect}$	1.76625	m^2

The balance equations written in terms of reactor length are represented in Eqs. 22, 23 and 24. The substitution of the data presented in the previous tables results in three differential equations whose variables are the conversion of the limiting reagent (X_A), the temperature of the reaction mixture (T) and its total pressure (P).

$$\frac{dX}{dz} = \rho_{cat}.(1-\emptyset).A_{ST}.\left(F_{A0}{}^{-1}.\left[k_{02}.e^{\frac{-E_2}{R.T}}.\left(\frac{P}{P_0}\right).\left(\frac{T_0}{T}\right)2.C_{A0}{}^{2}.\frac{(X_A - X_A{}^{2})}{(1+\varepsilon_A.X_A)^2} - \frac{\frac{2.C_{A0}{}^{2}.X_A{}^{2}}{(1+\varepsilon_A.X_A)^2}}{K^o.exp\left[\frac{-\Delta H_R^o}{R}.\left(\frac{1}{T}-\frac{1}{T^o}\right)\right]} + k_{03}.e^{\frac{-E_3}{R.T}}.\left(\frac{P}{P_0}\right).\left(\frac{T_0}{T}\right).C_{A0}.\frac{(1-X_A)}{(1+\varepsilon_A.X_A)}\right]\right) \tag{22}$$

$$\frac{dT}{dz} = \rho_{cat}.(1-\emptyset).A_{ST}.\frac{-r_A.\left[\Delta H^{\text{º}}{}_{R,298K} + \int_{298}^{T}\Delta C_p.dT\right]}{F_{A0}.\left(\left[\theta_A.C_{p,A} + \theta_B.C_{p,B} + \theta_C.C_{p,C} + \theta_D.C_{p,D}\right] + X_A.\Delta C_p\right)} \tag{231}$$

$$\frac{dP}{dz} = \frac{-G.(1-\emptyset).(1+\varepsilon_A.X_A)}{g_c.D_p.\emptyset^3.\rho_{cat}.\left(\frac{P}{P_0}\right).\left(\frac{T_0}{T}\right)}.\left[\frac{150.(1-\emptyset).\mu_m}{D_p} + 1{,}75.G\right] \tag{24}$$

The previous differential equations were solved by the numerical method of Euler, also denominated the Taylor Method truncated in the first derivative. This term is related to the way in which the method calculates the various points of the problem function [17]. For a generic function f dependent on x, the Taylor series truncated in the first term is written according to Eq. 25.

$$f(x+\Delta x) = f(x) + \Delta x.\frac{d(f(x))}{dx} \tag{25}$$

The previous equation represents that the function f in the following point (with increment of Δx) can be calculated by adding the function $f(x)$ (at the previous point) with the product of the increment Δx and the derivative of the problem function in said previous point, $\frac{d(f(x))}{dx}$. previous point. From initial data for the function $f(x_0) = x_0$ it becomes possible to determine the function at the next point, f_1, by establishing a pass for the function. The pass is the increment Δx that the function suffers [17].

Adapting to the case of the reactor, the problem functions are conversion, the temperature and the pressure. The initial data for the variables were known, so that the method can be applied. The pass was chosen as 0.05 m. The lower the pass of the function, the greater the precision obtained by the numerical method [17]. For example, Eq. 26 represents the calculation of the first point for the conversion.

$$X_{A,1} = X_{A,0} + (pass).\frac{dX(X_{A,0}, T_0, P_0)}{dz} \tag{26}$$

Results and Discussion

The final conversion of the limiting reagent was known, 95% [13]. In this way, the conversion, temperature and pressure differential equations were solved up to this limit in order to determine the minimum length of the reactor. With that, two curves were generated: conversion-temperature versus length, Figure 2, and pressure versus length, Figure 3.

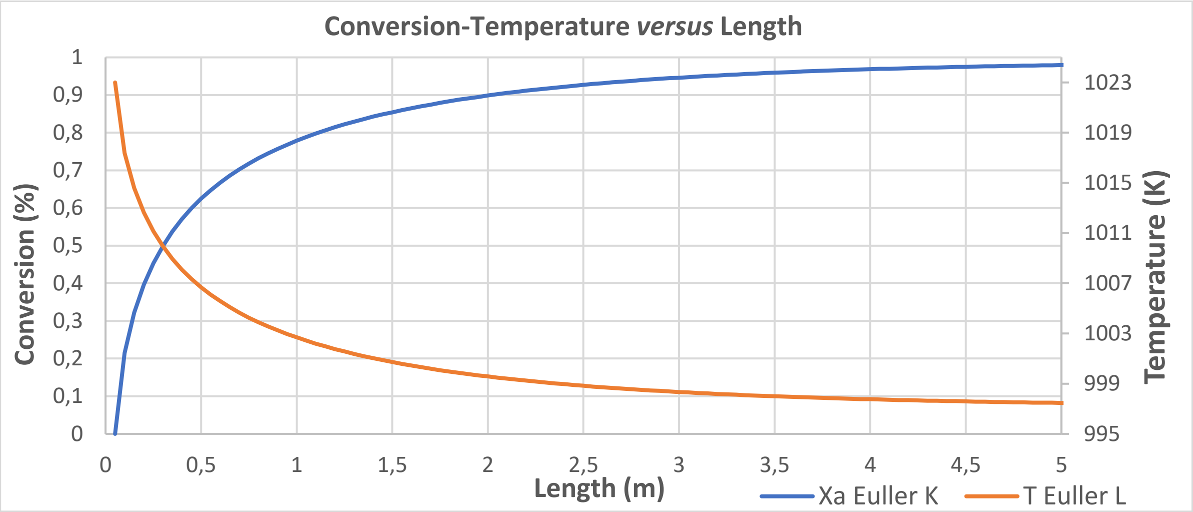

Figure 2 - Conversion-Temperature Profile.

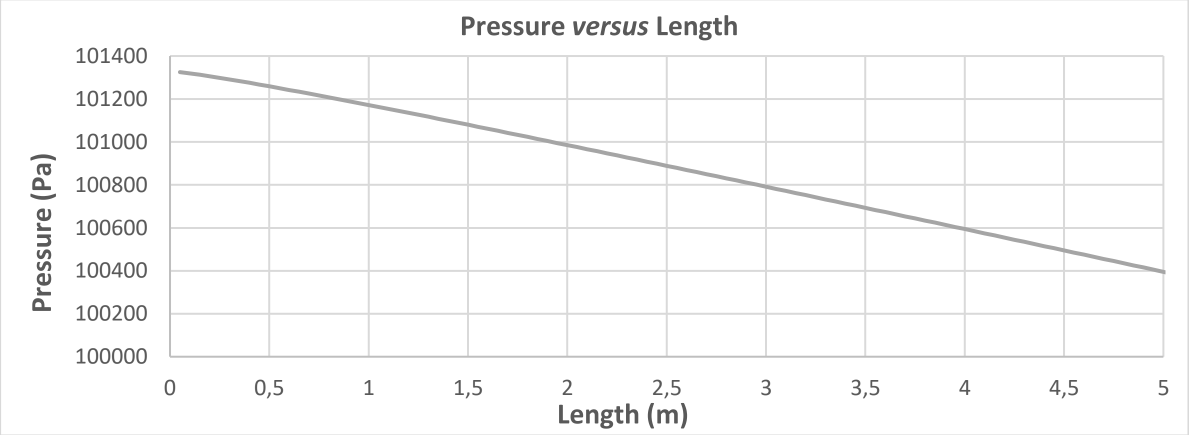

Figure 3 - Pressure Profile.

From the previous curves it was possible to determine that the reactor requires 3.15 m to reach the value of 0.95 for the conversion, the maximum possible for the process. The final design results are compiled in Table 4. The volume of the reactor was taken as that of a cylinder, since the reactor is of the tubular type. This value, however, does not take into account any safety factor over the length, so that it can be seen as a minimum required volume. The mass of catalyst was calculated using an integrated form of Eq. 21. The value for the reactor's diameter was changed throughout the modeling in order to maintain a length-diameter ratio of approximately 2: 1, resulting in 1.5 m.

Table 4 - Reactor Dimensions.

Variable	Valor	Unit
z (bed length)	3.15	m
$D_{reactor}$	1.5	m
W (Mass of catalyst)	3,031.09	kg
$V_{reactor}$	5.56	m^3
T_S (Outlet Temperature)	998.22	K
P_S (Outlet Pressure)	100,762.03	Pa

The large amount of catalyst required is a consequence of the high feed rates and synthesis gas production. An economic evaluation of the catalyst's, the raw materials and the product (synthesis gas) cost would be a counterbalance to re-evaluate the acquired sizing results and attempt to optimize the equipment through a cost-effective bias. Also, since the temperature decrease is small, the type of reactor chosen was the "single catalytic bed", also referred to as adiabatic bed [3]. Thus, there is no need to heat the medium by inserting the reactor inside a furnace (as in the steam reform production route).

It should be noted that the Euler method for numerical resolution of ordinary differential equations is not as accurate as others available in the literature (Runge-Kutta, for example), so that the acquired results should be evaluated with such awareness. In addition, no software simulations (Chemcad® or Aspen®) were made, which could grant more precise and complete results. The previous sizing data are a first approximation for the PBR's design, that have successfully taken into account the complex reaction kinetics and serves as a basis for future projects.

As the outlet pressure is lower than the atmospheric, there would be the need for slight pressurizing of the feed gases in order to avert fluid flow difficulties. Since the pressure drop in the catalytic bed is low, a blower is able to do such service, preventing the need to use a compressor, which is a considerably expensive equipment.

Conclusion

In the present study, the mathematical modeling of a fixed bed reactor for the dry reform of natural gas was performed. The development of the mass, energy and pressure balances were carried out based on the literature, and were expressed in the form of the ordinary differential equations of conversion, temperature and pressure varying with the length of the reactor, aiming the determination of the minimum required length of the catalyst bed, varying the cross-sectional area accordingly. The method of resolution of the ODEs was Euler's, in order to simplify the resolution of the problem, which was made in the Microsoft Excel Software, and to provide preliminary dimensioning data.

The attained results were satisfactory enough, granting an equipment with a length-diameter ratio of 2:1, as desired, and with a moderate amount of catalyst, of approximately 3 tons (consequence of the high process flows). The low temperature reduction, despite the high endothermicity of the reaction, avoid the need to operate the reactor inside a process furnace.

The dry reform is an interesting alternative route that focuses on the environmental bias, since it uses greenhouse gas intensifiers to produce important products for the petrochemical industry, with synthesis gas being one of them. The acquired results can be improved from an economic evaluation of the equipment and also from the implementation of more precise numerical methods. Still, they serve as a start for designing an equipment for the desired reaction and as basis for future projects.

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