Entropy Generation Analysis of a Thermal Cracking Reactor

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ABSTRACT: The present paper analyzes the entropy generation of a tabular thermal cracking reactor with propane feed, as well as the molecular mechanism of the reaction. The reaction model is obtained and the flow, reaction, momentum, and energy are determined with knowledge of the outer wall temperature. Then, the equations of entropy generation in the tabular reactor are solved and the rate of entropy generated by three sources along the reactor is determined. After that, the temperature of the tube or reactor is changed using the reference results, and the results and procedures are replicated. The results obtained for two states show that the three factors are in the order of chemical reactions, heat transfer, and pressure loss in terms of their contribution to entropy generation. The decrease in input feed temperature does not influence the weight percent of the products considerably, but when the wall temperature is reduced, as is the case with the optimal wall temperature state, the conversion percent in the reactor is reduced. The entropy generated by heat transfer in reactors with lower feed temperature is much higher at the beginning of the reaction. These variations do not affect the pressure-induced entropy considerably. The variation of input feed temperature does not affect the entropy generated by the chemical reactions, but the entropy produced in the reactor with optimal wall temperature is the lowest. At the inlet of the reactor, the entropy is higher when the wall has optimal temperature, which can be attributed to its higher rate of reactions than the other two states of input feed temperature.

1. INTRODUCTION

Thermal cracking of hydrocarbons is the most common way of olefin production and extensive research has predicted that thermal cracking will be the prevailing technology for this process in future too. The thermal cracking of propane is done by a radical mechanism. This mechanism has been described and analyzed by different researchers over time. Zhou et al. presented a radical model for the pyrolysis of propane composed of 10 reactions. Due to computational problems, the molecular model of the reactions is widely used to simulate the process of propane thermal cracking. According to Van Damme et al. and Sundaram et al., a molecular model has been developed for nine reactions with nine components. Masoumi et al. explored a one-dimensional steady-state model for tabular plug flow reactors for the thermal cracking of naphtha. The study used a schematic of free radical reaction composed of 90 components and 543 reactions. The objective was to optimize the steady state for maximum operation profit. Gao et al. optimized the steady-state model of naphtha cracking using the HYSYS software package. The optimization improved the operation profitability remarkably. They assessed the processes under steady-state conditions, but in the real world, the coke formation is a function of time and influences the efficiency. However, they ignored the impact of coke thickness on the coefficient of heat transfer. Ghasemi et al. focused on an ethylene furnace by using a three-dimensional (3D) model and computational fluid dynamics. Gao et al. implemented a one-dimensional dynamic model of naphtha cracking using the gPROMS software package. Their model included the dynamic state in mass balance equations, energy balance, and coke formation. Then, the steady-state optimization was done to gain optimal performance. Ghasghae and Karimzadeh studied the dynamic model of thermal cracking in furnaces in an attempt to explain and predict the unsteady-state behavior of cracks during start-up run. The mathematical model was composed of four submodels—convection model, cylindrical coil, combustion chamber model, and shell and tube model. Using these submodels, the researchers modeled a two-dimensional (2D) zone for predicting fuel consumption, heat transfer rate, and cracking temperatures at start-up run. Zheng et al. performed a 3D modeling and analysis of CFD for a thermal cracking reactor and furnace. The temperature distribution and heat flow were
Figure 1. Diagram of the hydrocarbon thermal cracking process.

calculated using a computer and were compared by spectrometry. The effect of coil outlet temperature on the feed-to-product conversion percentage was examined in a one-dimensional model by Barazandeh et al.10 Two industrial case studies have been reviewed and validated by Roudgar Saffari et al.11 Through numerical analysis, the amount of pollutant production was reduced using the re-burning method. The entropy induced by heat transfer has been investigated by many researchers. The study entropy generation by Nummedal and Kjelstrup12 in a thermodynamic equipartition of force (EOF) has been used to study entropy generation by two methods: EOF and EOEP. Several other studies18–20 have applied the governing equations of the system to study entropy generation. Nummedal and Kjelstrup12 investigated the heat transfer process and entropy generation by two methods: EOF and EOEP. Sauar et al.13 and Kjelstrup et al.14 extended the concept of EOF theory in the chemical reactors. The main problem is the nonlinear relations of the flow and force related to the chemical reactions. The theory has been applied as a suitable method for the analysis of the reactors.12 Likewise, Wilhemsen et al.22 conducted a comprehensive study on a steam reformer that is used to produce hydrogen.

Considering the temperature as the control variable and using the governing equations in the problem of plug flow reaction and SO2 oxidation, Johannessen and Kjelstrup23 applied the optimal control theory to minimize the entropy generation in the reactor. Kingston et al.24 explored the entropy generation in CSTR and PLUG reactors. The temperature and pressure were examined in entropy production.25

Chen et al.24 addressed CO2 hydrogenation for light olefin production and focused on minimizing the entropy production. Resjorde et al.25 addressed entropy production minimization in the process of propane dehydrogenation. This process included different components of a tower condenser reactor and exchanger. The principles of the structural theory have also been used in modeling and minimizing the entropy generation in a reactor.26 Abdous27 analyzed the entropy generation in helically coiled tubes in the flow boiling condition under a constant heat flux. Kurnia et al.28 replicated this analysis for various cross sections.

There has been some research on the entropy generation in other reactors but not in olefin or ethylene production reactors. The importance of olefin production is so great because in the petrochemical industry olefin is regarded as the heart of petrochemicals and the olefin production reactor in the olefin unit is regarded as the heart of the production. Studies already done on the thermal cracking reactor have been based on the principles of conservation and the governing equations of energy and chemical reactions and flow. These laws are based just on the first law of thermodynamics and do not consider entropy production as adequate and appropriate for the design and implementation of a process. However, the second law of thermodynamics and entropy production rate can be considered to supplement these laws to find competitors for the processes that generate olefins. Acquiring the sources of entropy generation and the underpinning factors and alleviating its generation will result in the size and performance optimization of the process and, consequently, its economization. Accordingly, this paper simulates a conventional reactor for the thermal cracking process to collect its products and use them to explore the factors underpinning entropy generation and their effectiveness in the process of entropy generation.

2. THERMAL CRACKING PROCESS

In this process, the hydrocarbon feed passes through the thermal cracking reactor at 800–900 °C with dilution steam at very high speed and it is transformed to lighter products. The main outputs of the reactor are ethylene and propylene. Besides, butadiene, olefin, and aromatics are produced. To stop unwanted reactions and hinder their progress, the output products of the reactor are rapidly cooled down to 300 °C in a transfer line exchanger. The energy produced by this process is applied to produce high-pressure steam in a steam drum. In the next step, the products are cooled down to almost room temperature by direct injection of oil and water, and their heavy components are separated. The output products of this step are fed into a compression section, where their pressure is increased to as high as 35 bars. Then, they are transferred to the fractionation section and finally, the main products are separated from one another.1
the production efficiency to find out the optimal operational parameters and control them within the determined values.

The heat that is required for the progression of the reactions is supplied by the thermal cracking furnace within which the reactor is located. Since thermal cracking reactions are endothermic, the temperature in the reactor is a key parameter in thermal cracking. The rise of temperature, i.e., the increase in heat flux, on the outlet surface of the reactor to as high as the allowed level can increase the quantities of the products, among which the production of the unwanted product, coke, is increased more severely. Hence, the reactor temperature should be set at a level that increases the desirable production efficiency and reduces the quantities of the undesirable products. The temperature is increased with respect to limitations arising from the material of the reactor outlet, whereas a uniform heat should reach the reactor along the reactor axis. It should be noted that overheating generates hot spots on the surface of the reactor and causes the formation of local coke at the reactor surface.

In thermal cracking furnaces, the reactors are placed in the furnace in different ways. They can be parallel or perpendicular to the floor in terms of the furnace type. Also, the reactor diameter can be fixed or variable depending on the feed type. Variable-diameter reactors are conventionally used for liquid feeds and the fixed-diameter ones are used for gaseous feeds. The number of reactor paths inside the furnace can also be varied depending on the technical knowledge of the technology owners.

### 2.1 Reactor Specifications

To validate the results, we use the same reactor as in ref 29. The feed of the reactor is pure propane. The specifications are presented in Table 1. The scale of the olefin unit does not allow experimental validation, and also this work has been done on an industrial scale. A comparison has also been made with the work of Berreni et al.29 In this regard, there are various works that show that validation can be done based on the work of others or compared with industrial data. There are more industrial data for validation such as Roudgar Saffari et al.11

#### Table 1. Specifications of the Reactor Used in the Study

| parameters/variable | value |
|---------------------|-------|
| length of the coil in the radiant section | 95 [m] |
| length of the straight portion of the coil | 8.85 [m] |
| length of the bends | 0.554 [m] |
| radius of the bends | 0.178 [m] |
| tube internal diameter | 0.108 [m] |
| wall thickness | 0.008 [m] |
| total feed per coil | 0.7635 [kg/s] |
| steam dilution rate | 0.4 [kg steam/kg propane] |
| inlet pressure | 3 [bar] |
| inlet temperature | 873.15 [K] |

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3. **MATHEMATICAL MODEL OF THE THERMAL CRACKING REACTOR**

The mathematical model of the study is based on ref 30. Figure 2 displays a simplified schematic to better understand the problem.

#### 3.1 Mass Balance Equation

Mass balance for the jth component of the reaction mix along the dz length of the reactor is written as

\[ \frac{dF_j}{dz} = \frac{R}{4} \pi d_j^2 \left( \sum \alpha_i f_i \right) \frac{\pi d_j^2}{4} \]

in which \( r_i \) denotes the speed of the ith reaction that is calculated by

\[ r_i = K_i \prod \alpha_i \]

To use the law of speed, the concentrations should be related to the molar flow rate and pressure. If all gases are assumed to be ideal, according to the general gas law, we have

\[ \alpha_j = \frac{P_j}{RT} = \frac{y_j P_j}{RT} \]

Replacing the molar ratio as \( y_j = \frac{P_j}{R} \) in this equation, we have

\[ \alpha_j = \frac{F_j P_j}{RT} \]

3.2 Energy Balance Equation

Energy balance along the reactor is calculated by eq 5.

\[ \frac{dT}{dz} = \frac{1}{\sum_j F_j c_p \left( \frac{I}{\sum_j} \pi d_j^2 \right)} \left( \sum_j F_j c_p \left( \frac{I}{\sum_j} \pi d_j^2 \right) \frac{\pi d_j^2}{4} \sum_i r_i (\Delta H_i) \right) \]

Readers can find the details of the procedures to calculate different components by this equation in the appendix.

#### 3.3 Momentum Balance

The equation for pressure is as below

\[ \frac{dp}{dz} = \alpha \left[ 2F_j \frac{\pi d_j^2}{4} \rho u^2 + \alpha \rho u \frac{dF}{dz} \right] \]

The first term on the right side shows the friction-induced pressure loss and the second term denotes the pressure loss induced by momentum change. According to the continuity equation, since the gas flow is assumed to be ideal, we have

\[ G = pu = \text{const} \]

\[ \rho = \frac{M_m P_i}{RT} \]

\[ u = \frac{G}{M_m \frac{RT}{P_i}} \]

\[ \frac{dF}{dz} = \left[ \frac{G R}{P_i} \left( 1/M_m + \frac{1}{M_m} \frac{dT}{dz} \right) \right] - \frac{G R T}{M_m P_i} \frac{dP}{dz} \]

By replacing the equations, we have

\[ \frac{dP}{dz} = \frac{1}{M_m P_i} \left( \frac{G R}{P_i} \left( 1/M_m + \frac{1}{M_m} \frac{dT}{dz} \right) + F_r \right) \]

\[ \frac{dt}{dz} = \frac{1}{M_m P_i} \left( \frac{G R}{P_i} \left( 1/M_m + \frac{1}{M_m} \frac{dT}{dz} \right) + F_r \right) \]
in which the friction function for the straight part of the tube is as follows

$$\text{Fr} = \frac{2f}{d_t} = 0.092\text{Re}^{-0.2/d_t}$$  \hfill (12)

and the equation for bends is as below

$$\text{Fr} = 0.092\text{Re}^{-0.2/d_t} + \zeta/\pi R_b$$  \hfill (13)

$$\zeta = \left(0.7 + \frac{\Lambda}{90^\circ} \times 0.35\right)\xi$$  \hfill (14)

$$\xi = 0.051 + 0.19\frac{d_t}{R_b}$$  \hfill (15)

Instead of $\frac{d(1/M_m)}{dz}$ in the pressure equation, the following equation can be used

$$\frac{d(1/M_m)}{dz} = \frac{d}{dz} \left(\frac{\sum F_i}{G\Omega} - \frac{\sum F_i}{G\Omega}\right)$$  \hfill (16)

### 3.4. Calculation of Convection Heat Transfer in Reactor Outlets

Convection heat transfer is calculated by

$$q = hA(T_w - T_p)_{irr}$$  \hfill (17)

$$T_b = \frac{\int_0^L 12\pi \rho dr U_c P_T}{\int_0^L 12\pi \rho dr U_c}$$  \hfill (18)

$$q = mC_p(T_{bo} - T_{bc})$$  \hfill (19)

$$Nu = 0.023\text{Re}^{0.8} Pr^n$$  \hfill (20)

in which $n = 0.4$ for the outlet heating, $T_w > T_{bo}$, $L/D > 60$, and $6000 < \text{Re}_D < 10^7$.

### 3.5. Entropy Generation in the Thermal Cracking Reactor

Since the reactor is supposed to be in a steady state, the system entropy balance has three other terms than entropy generation. Furthermore, there are two entropy factors induced by heat transfer to the system. Then, the equation of entropy generation is written as below by applying entropy balance for the control volume

$$\left(\frac{ds}{dt}\right)_{irr} = s_{out} - s_{in} + \Delta s_u$$  \hfill (21)

For a small element $dz$, we have $\Delta S_u = -\pi d_i j_i(z)/T_u(z)dz$. The final equation for entropy generation by entropy balance is as follows

$$\left(\frac{ds}{dt}\right)_{irr} = s_{out} - s_{in} - \pi d_i \int_0^L \frac{j_i(z)}{T_u(z)} dz$$  \hfill (22)

$$\left(\frac{ds}{dz}\right)_{irr} = \int_0^L \left(\frac{ds}{dz} - \pi d_i \frac{j_i(z)}{T_u(z)}\right) dz$$  \hfill (23)

$$\sigma = \frac{ds}{dz} - \pi d_i \frac{j_i(z)}{T_u(z)}$$  \hfill (24)

Using the following equations

$$v = \frac{(F_l/\Omega)RT}{P}$$  \hfill (25)

$$\Delta \left(\frac{1}{T}\right) = \frac{1}{T(z)} - \frac{1}{T_i(z)}$$  \hfill (26)

The local entropy generation can be written as

$$\sigma = \pi d_i j_i(z)\Delta \left(\frac{1}{T}\right) + \Omega \left(-\frac{1}{T} \frac{dp}{dz}\right) + \frac{\pi d_i^2}{4} \sum_i \left(-\frac{\Delta G_i}{T}\right)$$  \hfill (27)

As can be inferred from the equation, three events are the sources of entropy in a chemical reactor: chemical reactions, heat transfer to the reactor wall, and pressure loss. All terms in eq 28 are formed by multiplying the thermodynamic flux and the relevant force. The first term is the result of the heat flux $j_i(z)$ multiplied by its thermodynamic force $\Delta (1/T)$, the second term is the result of velocity flux multiplied by its thermodynamic force $\left(-\frac{1}{T} \frac{dp}{dz}\right)$, and the last term is the result of the velocity flux of the reaction $r_i$ multiplied by its thermodynamic force $\left(-\frac{\Delta G_i}{T}\right)$.

The total entropy production is obtained by integrating $\sigma$ over the reactor length.

$$\left(\frac{ds}{dz}\right)_{irr} = \int_0^L \sigma dz$$  \hfill (28)

### 3.6. Kinetic Model Selected for the Research

We have used a molecular mechanism here. It has been presented by Sundaram and Froment and colleagues. This reactor is fed with propane and water steam and then, they are converted to 12 components in 11 reactions. The reaction of the water steam and other components is, however, neglected. These reactions, as well as the activation energy and the Arrhenius equation factor, are presented in Table 5. In our study of the entropy generation, we ignored coke formation. The specific velocity of the reaction $K$ depends on temperature and is related to this factor as below

$$K = A \exp\left(-\frac{E}{RT}\right)$$  \hfill (29)

in which $A$ denotes the coefficient of the exponential function, or frequency factor, $E$ represents the activation energy (J/mol or cal/mol), $R$ is the ideal gas constant, and $T$ shows the absolute temperature ($K$).

### 3.7. Assumptions and Problem-Solving Procedure

This section deals with solving the reactor model presented in the previous section. We use the results for temperature, pressure, and weight percent for individual components along the reactor length to calculate and examine the entropy. Prior to simulating the reactor, the assumptions should be specified.

The following assumptions have been made for reactor simulation:

- The gas flow inside the reactor is supposed to be PLUG flow. This commonly accepted assumption is quite reasonable because the axial dispersion of the reactor can be ignored due to the high velocity of gas inside the reactor that is within the limits of turbulent flow and also due to the high ratio of reactor length to its diameter.
- Coke deposition is ignored, and the reactor is assumed to be in steady state.
- There is merely a mix of steam and gas inside the reactor.

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The integral generated in the reactor can be calculated. The last equation of this temperature is presented in the following sections in terms of the length of the reference reactor.29 The last equation is derived from the energy balance. These equations are solved in the MATLAB software package with the function ode15s. This function can solve hard differential equations by the GEAR method. After the mixture temperature, pressure, and weight percent of each individual component are derived in terms of the reactor length, the integral generated in the reactor can be calculated. Therefore, we have 12 differential equations with known initial conditions. These equations are solved in the MATLAB software package with the function ode15s. This function can solve hard differential equations by the GEAR method. The ideal gas law is applied to derive concentrations.

To simulate the reactor, the molar balance, energy balance, and momentum balance equations should be solved along the reactor simultaneously. To solve the energy equation, we need to know the temperature of the input feed (Table 2). The energy in the equation is a function of the outer surface of the pipe. The profile of this temperature is presented in the following sections in terms of the length of the reference reactor.29 The last equation results from the pressure loss for which the initial condition, i.e., the input pressure, is known. The properties of the gas mixture are calculated by the equations in the appendix. Therefore, we have 12 differential equations with known initial conditions. These equations are solved in the MATLAB software package with the function ode15s. This function can solve hard differential equations by the GEAR method. After the mixture temperature, pressure, and weight percent of each individual component are derived in terms of the reactor length, the integral generated in the reactor can be calculated.

4. RESULTS AND ANALYSIS

4.1. Results for the Reactor in the Reference State. The key goal of the propane thermal cracking reactor is ethylene production. The main outputs of the reactor include methane, ethylene, propylene, propane, and hydrogen. The values used for temperature, pressure, molar flow rate of feed, and steam feed ratio in the inlet of the reactor are given in Table 3. Propane conversion percent and the weight percents of the products are derived to compare the results of the simulated reactor with those of the industrial reactor.

As Table 3 shows, the simulation results and the empirical results of the industrial reactor are highly consistent despite ignoring coke formation. The highest difference is 12%, related to propylene C3H6 weight percent. This difference is as low as 4% for the other components and falls to about 0.01% for conversion percent, which is the key goal of the problem. The reason why the coke formation is very limited is that the results of the industrial reactor have been recorded at an early running time before the formation of coke.

The temperature profile of the outer wall of the tube that is used for calculations is illustrated in Figure 3. This is derived from ref 29 and is, indeed, the reactor surface temperature in the industrial specimen.

Table 2. Reactions Involved in the Thermal Cracking of Propane

| no. | reaction        | \(A\) (1/S, m³/kmol-s or kg-s/mol-m) | \(E\) (kJ/mol) | \(\Delta H\) (kJ/mol@298 K) |
|-----|-----------------|-------------------------------------|----------------|--------------------------|
| 1   | \(C_3H_8 \rightarrow C_2H_4 + CH_4\) | \(4.692 \times 10^{10}\) | 211.7 | 82.66 |
| 2   | \(C_3H_8 \leftrightarrow C_2H_6 + H_2\) | \(5.888 \times 10^{10}\) | 214.6 | 124.68 |
| 3   | \(C_3H_8 + C_2H_4 \rightarrow C_2H_6 + C_2H_2\) | \(2.536 \times 10^{13}\) | 241.7 | −11.64 |
| 4   | \(2C_3H_6 \rightarrow 3C_2H_4\) | \(1.514 \times 10^{11}\) | 233.5 | 117.5 |
| 5   | \(2C_3H_6 \leftrightarrow 0.5C_6H_6+3CH_4\) | \(1.423 \times 10^{7}\) | 190.4 | −14.48 |
| 6   | \(C_3H_8 \leftrightarrow C_2H_2 + CH_4\) | \(3.794 \times 10^{11}\) | 248.5 | 96.4 |
| 7   | \(C_3H_8 + C_2H_4 \rightarrow C_2H_6 + CH_4\) | \(5.553 \times 10^{14}\) | 251.1 | −11.24 |
| 8   | \(C_3H_8 \rightarrow C_2H_4 + H_2\) | \(4.652 \times 10^{15}\) | 272.8 | 136.32 |
| 9   | \(C_3H_8 + C_2H_4 \rightarrow C_2H_6 + C_2H_2\) | \(1.026 \times 10^{12}\) | 172.6 | −133.42 |
| 10  | \(C_3H_8 \rightarrow C_6\) | \(6.92 \times 10^{7}\) | 143.6 | 83.42 |

Table 3. Comparison of the Products of Simulated and Industrial Reactors

| component | weight percent (wt %) of the simulated reactor | weight percent (wt %) of the industrial reactor |
|-----------|----------------------------------------------|-----------------------------------------------|
| conversion coefficient | 90.61 | 90.60 |
| CH₄ | 22.89 | 24.00 |
| C₂H₄ | 36.82 | 34.50 |
| C₂H₆ | 12.89 | 14.70 |
| C₃H₈ | 9.38 | 9.30 |
| H₂ | 1.67 | 1.20 |

Figure 3. Temperature profile of the outer surface of the reactor with industrial wall temperature.

Using the outer wall temperature of the reactor illustrated in Figure 3, the results presented in Table 3, and the governing equations, the temperature profile of the gas mixture is calculated as depicted in Figure 4. The gas mixture temperature is 873.15 K at the beginning of the inlet. As is evident in Figure 4, the outer temperature of the reactor products approaches the wall temperature as heat is transferred along the tube and the chemical reactions proceed.

Figure 5 shows the reactor conversion percent along the reactor. Also, the weight percent profile of each product is displayed in Figure 6 for the above-mentioned data aggregates. The pressure profile for the gas mixture that is calculated in the program is shown in Figure 7.
Figure 8 presents the profile of the heat flux transferred to the gas mixture along the reactor.

So far, some basic calculations have been made to determine the entropy generated in the reactor. Then, we derive the data required for calculating the entropy generation rate. The entropy generation rate is estimated by analyzing the entropy generation as described in the equations of the previous sections. The results that are obtained for entropy generation result from the three factors heat transfer, pressure loss, and chemical reactions as presented in Table 4. The values obtained by the two methods of entropy balance and non-equilibrium thermodynamics are highly consistent.

Table 4. Values Derived for the Entropy Generation in the Reactor with Industrial Wall Temperature

| Entropy generation cause | Generated entropy [J/(K·s)] |
|--------------------------|-----------------------------|
| heat transfer            | 66.1642                     |
| chemical reactions       | 582.47                      |
| pressure drop            | 47.3889                     |
| total entropy generated by non-equilibrium thermodynamics | 696.0231 |
| total entropy generated by entropy balance | 696.0856 |

It is observed in Table 4 and Figure 9 that the share of entropy generated by the chemical reactions is more than the other factors. The next rank is for heat transfer followed by pressure loss in the generation of entropy. Figure 9 illustrates the circular graphs to show the share of each factor in entropy generation.
Drawing the local entropy generated along the tube by these three factors can provide useful information about the relationship between entropy generation and the profile of temperature, pressure, and conversion percent. Figure 10 depicts the local entropy generation by the three factors and their sum.

The results obtained using the optimal wall temperature profile for the weight percent of the products are shown in Table 5.

### Table 5. Weight Percent of the Products of the Reactor with Optimal Wall Temperature and that with Industrial Wall Temperature

| component | weight percent (wt %) of the simulated reactor | weight percent (wt %) of the industrial reactor |
|-----------|-----------------------------------------------|-----------------------------------------------|
| conversion coefficient | 90.61 | 84.06 |
| CH₄ | 22.89 | 20.77 |
| C₂H₄ | 36.82 | 33.38 |
| C₃H₆ | 12.89 | 15.12 |
| C₃H₈ | 9.38 | 15.93 |
| H₂ | 1.67 | 1.56 |

In this condition, the results for the temperature of the gas mixture are as shown in Figure 12.

Figure 12. Temperature profile of the gas mixture for the reactor with optimal wall temperature.

The weight percent of the products under optimal wall temperature is shown in Figure 13. The pressure profile derived for the optimal wall temperature state is displayed in Figure 14. In this state, the heat flux along the reactor is as shown in Figure 15. Using these results for the reactor with optimal wall temperature, the entropy generation rate induced by each factor is presented in Table 6 and Figures 16 and 17.
Also, to explore the impact of other parameters on entropy generation, the inlet propane temperature is studied as an effective factor. To compare the results, all calculations are carried out for the reactor feed with propane at the temperatures of 800 and 840 K. The following sections address the results and compare the generated entropy and its impact on the variations of reactor efficiency.

4.3. Comparison of the Results. Here, the effects of reactor wall temperature and input feed temperature are studied to help better understand the impact of various parameters on entropy generation. So, in addition to the calculations already done (with optimal wall temperature and the wall temperature of an industrial representative reactor), the calculations are repeated for a reactor fed with input propane at the two temperatures of 840 and 800 K. The results are presented below.

Figure 18 shows the conversion percent for all cases versus the tube length. The weight percent of the product (methane, propane, propylene, and ethylene) is shown in Figures 19−23 for the four cases. It can be observed in Table 7 that the decline of input feed temperature does not influence the weight percent of the main products considerably, but the decline of wall temperature as compared to its optimal temperature results in remarkable loss of the reactor’s conversion percent, which is not desirable. The impact of the variations on gas mixture temperature along the reactor is illustrated in Figures 24 and 25.

As the temperature of the input feed declines, the gas mixture temperature decreases at the inlet of the reactor, but it then starts...
to match the graph for the industrial reactor as the chemical reactions proceed.

Table 7. Comparison of the Weight Percents of the Reactor Products

| components | weight percent (wt %) in the main reactor | wt % in the reactor with optimal wall temperature | wt % in the reactor with inlet temperature of 840 | wt % in the reactor with inlet temperature of 800 |
|------------|------------------------------------------|-------------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| CH₄        | 22.89                                    | 20.77                                           | 22.52                                         | 22.11                                         |
| C₂H₆        | 36.82                                    | 33.38                                           | 36.32                                         | 35.76                                         |
| C₃H₆        | 12.89                                    | 15.12                                           | 13.33                                         | 13.80                                         |
| H₂          | 9.38                                     | 15.93                                           | 10.39                                         | 11.55                                         |

Figure 23. Graph comparing the weight percents of ethane.

Figure 24. Graph comparing the gas mixture temperatures for temperature variation.

Figure 25. Graph comparing the gas mixture temperature with the outer wall temperature of the reactor.
As is evident in Figure 26, the variations of the studied parameters do not influence the pressure loss along the reactor considerably. Given the fact that the impact of such parameters as the path changes can be ignored when the pressure loss is calculated, or indeed the frictional pressure loss is calculated, and also considering that the gases have very close viscosities to one another, the pressure graphs are well-matched to each other.

4.4. Effect of Variations on the Entropy Generation.

The entropy is generated along the reactor by the three factors of heat transfer, pressure loss, and chemical reactions. The variations of each of these parameters due to the variations of the conditions influence the entropy generation rate. The following sections address the effect of each individual factor as affected by the change in the conditions.

4.4.1. Entropy Induced by Heat Transfer. Figure 27 shows the rate of heat transfer along the reactor under the studied conditions. As is evident, the rate of heat transfer is increased with the reduction of input feed temperature of the reactor. This increase can be related to the difference in the temperature of the gas mixture and wall temperature. Also, at optimal wall temperature, a slight decrease is observed in the rate of heat transfer due to the decrease in the temperature difference between the gas mixture and the wall. Given the governing equation of the problem, the increase or decrease in heat transfer is expected to directly influence the entropy generation by heat transfer, as can be observed in Figure 27. Since the heat transfer in the reactor with the wall temperature of the industrial representative reactor is very close to that in the reactor with optimized wall temperature, their generated entropies are almost equal, but the heat transfer-induced entropy in reactors with lower feed temperature is much higher. Figure 28 shows the comparison of entropy generated by heat transfer.

4.4.2. Entropy Induced by Pressure Loss. As mentioned earlier, the variations of the conditions do not influence pressure loss considerably. So, it is expected that the entropy generated by the pressure loss is almost the same under these conditions, which is depicted in Figure 29.

4.4.3. Entropy Induced by Chemical Reactions. In short, it can be inferred that the amount of entropy generated during the chemical reactions is a function of the type of chemical reactions, their extent, and the type of the products in addition to the conditions governing the problem as expressed in the thermodynamic equations. Therefore, the weight percent of the reactor products shows the entropy generated by the chemical reactions. As expressed, the chemical reactions and the products are close to one another in cases in which just the input feed temperature is changed. Thus, the entropies induced by chemical reactions are expected to be close to one another in these three states. This is evident in Figure 30. But, in case of the optimal wall temperature of the reactor, it can be said that since the conversion percent and, consequently, the number of chemical reactions are lower than those of the industrial representative reactor, the generated entropy is lower too.
entropy at the inlet of the reactor is higher under optimal wall temperature than when the input feed temperature is 800 or 840 K because the conversion percent at the inlet of the reactor is higher under optimal wall temperature. The same event happens at the outlet of the reactor, which may be associated with the pressure and temperature distribution.

4.5. Total Entropy. Figure 31 and Table 8 present the total entropies generated by heat transfer, pressure loss, and chemical reactions for each problem state. It is observed that the decrease in inlet feed temperature of the reactor has a slight effect on mitigating the entropy, but the application of optimal wall temperature reduces it remarkably at most points of the reactor, which is mainly related to the decrease in entropy generated by the chemical reactions.

5. CONCLUSIONS

The thermal cracking reactor with propane and water steam as the input feed and methane, ethylene, propylene, propane, and hydrogen as the main products was studied in terms of entropy generation, the governing equations, and the effect of factors such as input feed temperature and reactor wall temperature ignoring the formation of coke and the time effects in a steady state by the two methods of entropy balance and non-equilibrium thermodynamics. The following is the summary of the results:

- The three factors are in the order chemical reactions > heat transfer > pressure loss in terms of their contribution to entropy generation.
- The entropy generated by the pressure loss is almost uniform along the reactor.
- The entropy generated by the heat transfer has a descending trend along the reactor. This is related to the decrease in the temperature difference between the fluid inside the reactor and the reactor wall temperature and consequently the decrease in heat transfer, in which case the process approaches the quasi-equilibrium state.
- The entropy generated by the chemical reactions is low at first, then it sharply increases as the reactions are triggered, and then, it starts falling because the chemical reactions are less intensive at the inlet and outlet of the reactor.
- The decrease in input feed temperature does not influence the weight percents of the products considerably, but when the wall temperature is reduced—as is the case in the optimal wall temperature state—the conversion percent in the reactor is reduced.
- The gas mixture temperature is reduced along the reactor when the input feed temperature is reduced at the beginning of the reactor and then, it matches the industrial graph as the chemical reactions happen.
- The variations of these parameters have no great effect on pressure loss along the reactor tube.
- The rate of heat transfer is increased as the input feed temperature is reduced. This can be due to the higher temperature difference between the gas mixture and wall temperature.

Table 8. Amount of Entropy Generated in Different States

| entropy generation cause | industrial reactor | reactor with optimal wall temperature | inlet temperature of 840 | inlet temperature of 800 |
|--------------------------|--------------------|---------------------------------------|--------------------------|--------------------------|
| heat transfer            | 66.16              | 66.43                                 | 76.15                    | 90.15                    |
| chemical reactions       | 582.47             | 534.099                               | 574.98                   | 566.36                   |
| pressure drop            | 47.38              | 43.08                                 | 46.22                    | 45.01                    |
| total entropy            | 696.02             | 643.61                                | 697.36                   | 701.52                   |
| generated by non-        |                    |                                       |                          |                          |
| equilibrium thermodynamics |                  |                                       |                          |                          |

Figure 30. Graph comparing the entropy generated by chemical reactions for the temperature variation state.

Figure 31. Graph comparing the locally generated entropy.
Since the heat transfer in the reactor with industrial wall temperature is very close to that in its counterpart with optimal wall temperature, this heat transfer generates almost similar amounts of entropy in both reactors.

- The entropy generated by heat transfer in reactors with lower feed temperature is much higher at the beginning of the reactor.
- These variations do not affect the pressure-induced entropy considerably.
- The variation of input feed temperature does not affect the entropy generated by the chemical reactions, but the entropy produced in the reactor with optimal wall temperature is the lowest.
- At the inlet of the reactor, the entropy is higher when the wall has the optimal temperature, which can be attributed to its higher rate of reactions than the other two states of the input feed temperature.

In this study, entropy production factors were investigated. The effect of the parameters on entropy production was shown. In future work, entropy production can be minimized. It is also possible to produce entropy in different types of industrial coils inside the furnace and select the most suitable coil with higher production performance conditions.

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**Notes**

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**NOMENCLATURE**

| Symbol | Definition |
|--------|------------|
| J      | jth component |
| dz     | length |
| $F_j$  | intensity of molar flow of the jth component |
| $\alpha_j$ | stoichiometric coefficient of the jth component in the ith reaction |
| $R_j$  | overall velocity of the production and/or consumption of the jth component |
| $r_j$  | velocity of the ith reaction |
| $K_i$  | specific velocity of the ith reaction |
| $c_i$  | molar concentration of the jth component |
| $y_i$  | molar ratio |
| $\Delta H_j$ | heat of the ith reaction |
| $J_q(z)$ | heat flux transferred from outer heat source to reaction flow in the location z of the reactor |
| $C_{pj}$ | heat capacity of the jth component |
| $A$    | unit conversion factor |

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