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OPTIMIZING ETHYLENE PRODUCTION THROUGH THERMAL CRACKING: A COMPREHENSIVE STUDY

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KEYWORD

Olefin, ethylene, cracking,
Steam cracking
Polyethylene,
thermal cracking,
coke formation

ABSTRACT

Ethylene, an essential olefin in the petrochemical sector, is predominantly manufactured via the thermal decomposition of hydrocarbons like Ethane, naphtha, and gas oil. The academic research analyses the ethylene production process through thermal cracking, emphasizing the fundamental principles, technological advancements, and economic factors utilizing an enhanced kinetic molecular model in PETRO-SIM. The research utilized this model to assess the influence of different operational variables on ethylene output and overall product distribution. The cracking procedure occurs within elongated, tube-shaped reactors vertically aligned in a gas-heated furnace, with the addition of steam as a diluent to lower the partial pressure of hydrocarbons and inhibit undesired side reactions. The furnace consists of a convection segment for initial heating and a radiant segment where the majority of cracking reactions occur. The formation of coke, a secondary product of hydrocarbon dehydrogenation, is managed through periodic decoking employing air and steam. The model development incorporated simplified assumptions, such as disregarding bending impacts, focusing solely on molecular species, and presuming steam diluent to be chemically inactive. The radiant coils were simulated as a singular plug-flow reactor utilizing PETRO-SIM's integrated PFR module with the Peng-Robinson property package. Two models were postulated. The investigation of the temperature profile within the reactors was carried out for both categories of models. A simulation was executed in order to comprehend the impacts of different parameters such as reactor length, inlet temperature, coil output temperature, and steam-to-ethane ratio on the outlet composition of the reactor.

1 Introduction

The global economic growth and rising consumer demand have significantly increased the need for olefins, particularly ethylene. Olefins are hydrocarbons with a double bond, also known as alkenes. Ethylene, the simplest alkene with only two carbon atoms connected by a single, double bond, is a crucial olefin in the petrochemical industry, with a global nominal capacity of approximately 155 million tons per year. The majority of ethylene production is utilized in the manufacturing of polyethylene, but it also plays a role in the production of ethylene oxide, ethylene dichloride, and ethylbenzene. The production process primarily involves cracking, a process that has evolved over the past century to meet the growing global demand for ethylene-based materials. Steam cracking of feedstocks such as Ethane, naphtha, and gas oil is the primary method of producing ethylene. Thermal cracking is a high-temperature process in which hydrocarbons are exposed to temperatures ranging from 800°C to 900°C in the presence of steam, resulting in the formation of smaller molecules, primarily ethylene.[1]

2 Industrial Thermal Cracking Process

Figure 1 depicts the process of ethylene production. Cracking is carried out in long, tube-shaped reactors, also known as radiant tubes, arranged vertically in a rectangular gas-fired furnace.[2] A typical coil consists of several straight tubes connected by bends, and an industrial furnace may contain multiple such coils. Burners heat the coils to provide the necessary heat for the endothermic cracking reactions.[3] The primary purpose of steam in the process is fourfold: it lowers the partial pressure of high-molecular-mass aromatics, reduces the likelihood of condensation reactions, increases the conversion of desired products, and reduces coke formation and buildup. Steam is added as a diluent to the process to reduce the partial pressure of hydrocarbons and limit undesirable side reactions.

The furnace used in this process comprises a convection section followed by a radiant section. In the convection section, the feedstock is mixed with steam and preheated to a temperature of between 773 and 923 K. The temperature of the flue gases generated by the radiation burners in the firebox can reach as high as 1200 K[2]. The heat produced by the flue gases is utilized to preheat the hydrocarbon feedstock and the dilution steam and to facilitate thermal cracking in the radiation section.

After passing through the convection section, the gas enters the radiant section of the furnace, where most of the cracking occurs. As the conversion in the radiant section is highly endothermic, a high energy input is required[4]. The radiant coil is heated directly by burners, ensuring that the process gas obtains sufficient thermal energy for cracking, which typically occurs in a temperature range of 1050 to 1160 K. During the time in the radiant section, the feedstock is cracked into smaller and lighter products, such as ethylene and propylene.

The mixture is then quenched to stop the reactions and avoid the formation of other side products. It is then compressed and cooled in the liquid phase. Then, the mixture is fed into fractionation (separation) towers, which separate the liquid into ethylene and other components.[5]

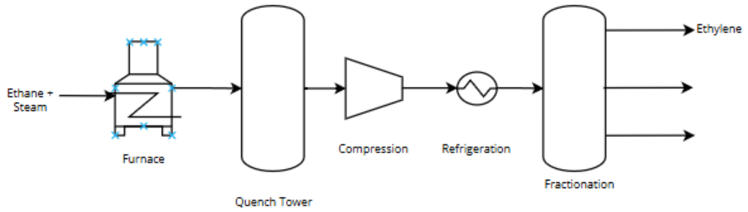


Figure 1. Ethylene production process flow diagram

3 Coke Formation

The dehydrogenation of hydrocarbons within the reactor results in the formation of coke, which solidifies on the internal surface and acts as an additional resistance, decreasing heat transfer[6]. This also causes a significant pressure drop between the inlet and outlet of the reactor as the cross-section for the flow of the feed is decreased. Furthermore, it may increase the partial pressure of the hydrocarbon, which would lead to a decrease in the ethylene yield. Sundaram et al. 1981[7] proposed the following model for coke formation. C4+ includes all hydrocarbons heavier than C_3H_8 From eq. (2) butadiene is responsible for coke formation.

$$C_2H_6 \rightarrow products \qquad (1)$$

$$C_4^+ \rightarrow coke \qquad (2)$$

Decoking is carried out by burning the coke using a mixture of air and steam, usually heated to 1173–1273 K, producing hydrogen and carbon dioxide.[2] Various parameters, such as wall temperature, steam-to-ethane ratio, and residence time, can be controlled to decrease coke formation. This research paper delves into the intricacies of ethylene production via thermal cracking, examining the fundamental principles, technological advancements, and economic considerations via an improved kinetic molecular scheme using PETRO-SIM. The model was used to analyze how different process factors affected the yield of ethylene and the overall composition of the product distribution.

4 Model Development

Two distinct reaction mechanisms can represent hydrocarbon cracking. The first mechanism is the free radical reaction scheme, which comprises numerous steps and reactions and is difficult to model [8]. The molecular reaction scheme is preferred to overcome this complexity. Although ethane cracking is known to follow a free radical reaction scheme, most researchers use a simplified molecular reaction scheme to represent the ethane cracking process.

The following assumptions have been made in the development of the ethane cracking model.[3]:

- **i.** Effects due to the bending and other hydrodynamic parameters were neglected, and the entire set of coils was modelled as a single plug-flow reactor (PFR).
- **ii.** No chemical reactions occur before the reactant enters the radiant section (i.e., before the PFR).
- **iii.** The product list considers only molecular species; free radicals and their corresponding reactions are not included in the simulation.
- **iv.** Since the formation of coke is not considered, the reactor core temperature was assumed to be the same as the reactor wall temperature.
- **v.** The steam diluent in the feed is assumed to be inert, and reactions involving steam are not considered.

A PFR mode could well describe the process in the radiant coils of the pyro cracker. PETRO SIM's built-in PFR module was selected for this purpose. Peng-Robinson was the property package selected as it is the most suitable property package for a hydrocarbon system.

Priyesh Ranjan et al.[3] proposed the temperature scheme and reactor dimensions, which served as the base case simulation for assessing the effect of the temperature profile. The process took place in a furnace, also known as a firebox, measuring 11m in height, 11m in length, and 2.5m in width. The firebox housed six sets of radiant coils, with each set comprising eight inlet tubes, resulting in a total of 48 tubes. [3] The furnaces were designed to crack gaseous fresh and 100% pure ethane feed with a steam-to-hydrocarbon ratio of 0.3. The dilution steam served the dual purpose of lowering the hydrocarbon partial pressure and reducing the coking rate in the radiant coils. The feed was fed at a temperature of 953 K and a pressure of 2.2 bar, with a flow rate of Ethane at 7000 kg/hr and steam at 3000 kg/hr.

The plug flow reactor (PFR) configuration included 48 tubes with a length of 10.5m, an inner diameter of 0.085m, and a total diameter of 0.085 m [3]. The modules present in the scheme were C_2H_6, C_2H_4, C_3H_8, C_2H_2, CH_4, C_3H_6, and C_4H_6. The simulations use a proposed improved molecular reaction scheme. [9]. Tables 1 and 2 show the forward and reverse reactions, along with the pre-exponential constant and activation energy.[10]

Table 1.: **Molecular reaction scheme for Ethane cracking Kinetic data**

No.	Reactions	Pre exponential constant (lt/mol.min or min^{-1})	Activation Energy (KJ/mol)
1	$C_3H_8 \rightleftharpoons C_3H_6 + H_2$	3.16 x 10^{10}	216.1
2	$C_2H_6 \rightleftharpoons C_2H_4 + H_2$	2.04 x 10^{13}	270.0
3	$C_3H_6 \rightleftharpoons C_2H_2 + CH_4$	9.33 x 10^{11}	246.0
4	$C_3H_8 \rightarrow C_2H_4 + CH_4$	5.50 x 10^{10}	214.2
5	$C_3H_8 + C_2H_4 \rightarrow C_3H_6 + C_2H_6$	1.15 x 10^{14}	245.0
6	$2C_3H_6 \rightarrow 3C_2H_2$	1.45 x 10^{11}	233.5
7	$C_2H_4 \rightarrow C_2H_2 + C_4H_6$	7.41 x 10^{10}	174.1
8	$2C_2H_6 \rightarrow C_3H_8 + CH_4$	2.18 x 10^{14}	267.0

Table 2. : Equilibrium constant parameters for reversible reactions

No.	Pre exponential constant	Activation Energy (KJ/mol)
1	1.64×10^5	91.7
2	1.42×10^8	137
3	8.64×10^6	108

The simulation was conducted in two steps. The initial approach involved utilizing a single reactor model, while the subsequent method employed a dual reactor model. Within the single reactor model, both the convection and radiation sections were integrated into a unified reactor design. A linear increase in temperature gradient was observed, as shown in Figure 2a. A similar temperature trend was also documented in the research paper authored by Yam M.[11]

The dual reactor's configuration exhibits identical reactor design and kinetic parameters to those of the single reactor model. Although the dual reactor model is similar to the single reactor model, the primary distinction is in the allocation of length.

The outlet temperature at the convection reactor is 1070 K, with the outlet temperature in the radiation section slightly higher at 1100 K. To maintain consistency with the single reactor model, a mass flow rate of 95 tons/hr (where Ethane is measured at 71.5 tons/hr and steam at 28.5 tons/hr) was introduced. The model environment is depicted in **Figures 2 and *3*.**

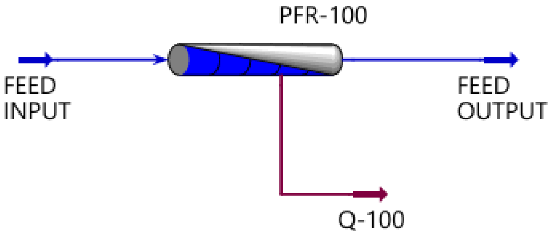


Figure 2. Single reactor model

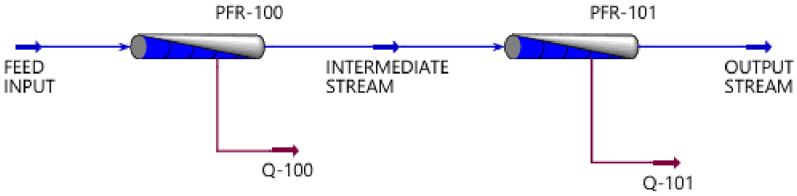
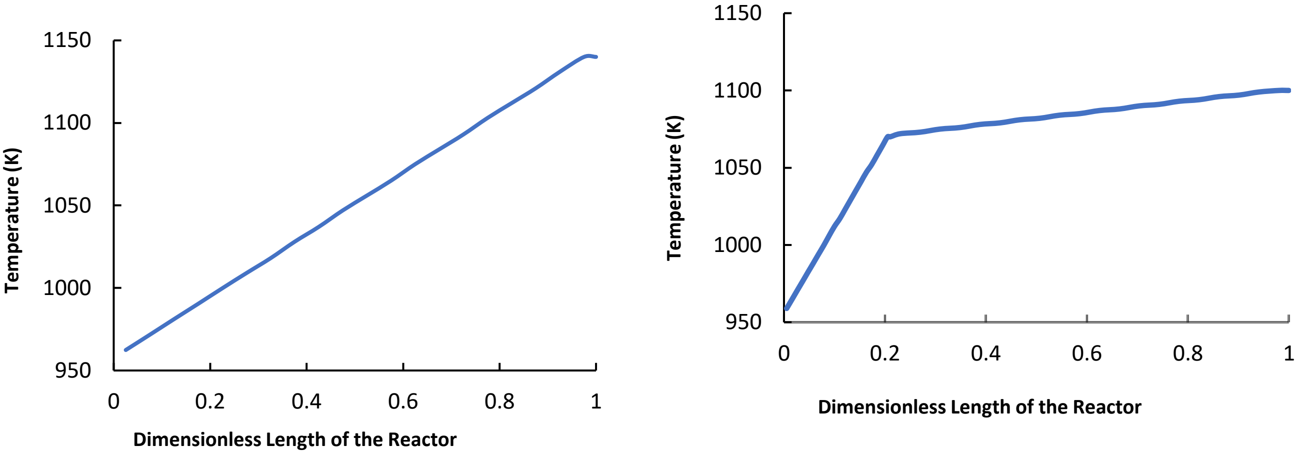


Figure 3. Dual reactor model

5. Result and Discussion

The temperature distribution within the reactors of both models is comprehended. As articulated in the Development section of the model, both models exhibit non-isothermal characteristics. This information can be comprehended by examining Figure 4(a) and Figure 4(b) provided below. The temperature distribution obtained through simulation closely resembles the findings of previous studies by Gao et al. [12] and Gujarathi et al.[13]



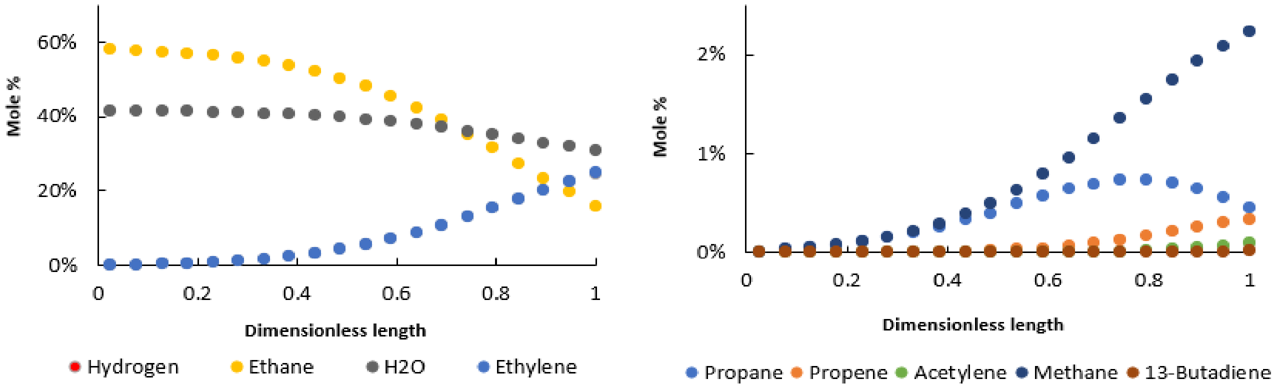
(a) (b)

Figure 4. Temperature Distribution throughout the reactor (a) Single reactor model (b) Dual reactor model

The exit composition data can be found in ***Table 3 and Table 4*** for single and dual reactor models, respectively. Similarly, the mole fraction distribution of all individual components involved in the simulations can be effectively examined and analyzed through the graphical representation presented in Figure 5(a) and Figure 5(b) below, which offers a visual depiction of the relative proportions of each component within the system for both types of simulation scenarios.

Table 3. Outlet composition of the single reactor model

No.	Components	Mole (%)
1	Propane	0.659
2	Propene	0.4927
3	Hydrogen	35.94
4	Ethane	23.37
5	Ethylene	36.12
6	Acetylene	0.1387
7	Methane	3.25
8	13-Butadiene	0.0308



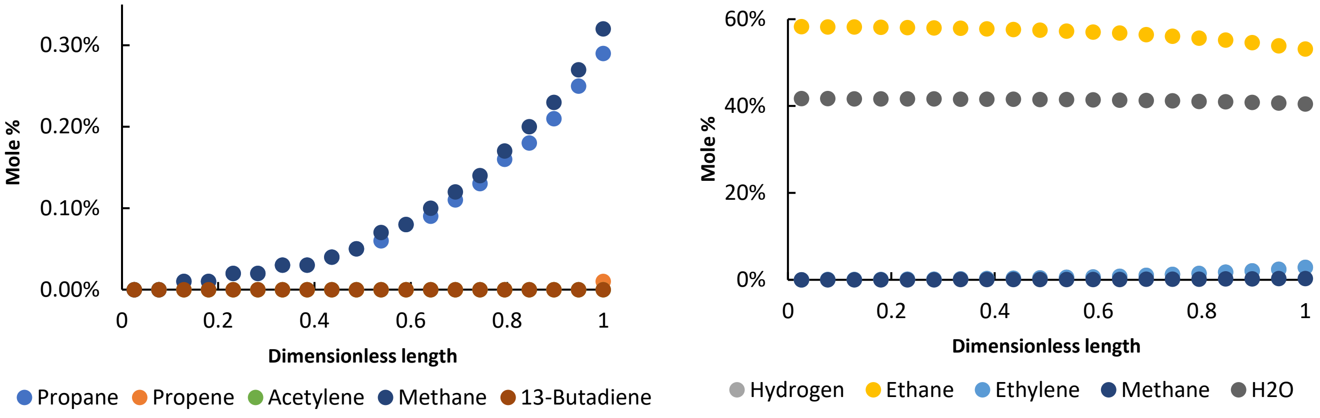
(a) (b)

Figure 5. (a) and (b) Mole fraction distribution of component throughout the reactor

Ethylene and hydrogen display nearly identical mole compositions in a single reactor model. The ethane conversion remains consistent throughout the entire reactor length. Propene is observed in the latter section of the reactor. Acetylene and 1,3-butadiene are formed towards the end of the reactor. The presence of methane is limited to a maximum of 3.25 mole %.

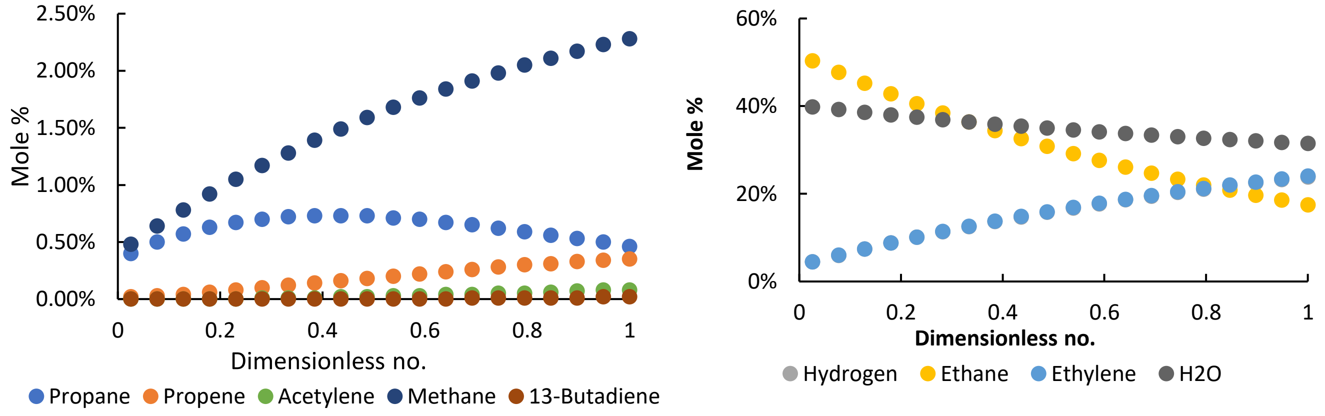
Table 4. Outlet composition of the Dual reactor model

No.	Components	Mole (%) of the outlet from Reactor 1	Mole (%) of the outlet from Reactor 2
1	Propane	0.004794	0.6757
2	Propene	0.000112	0.5133
3	Hydrogen	0.04837	34.8008
4	Ethane	0.8929	25.507
5	Ethylene	0.04849	35.03
6	Acetylene	1.73E-06	0.1233
7	Methane	0.005374	3.327
8	1,3-Butadiene	6.55E-09	0.0283



(a) (b)

Figure 6. (a) and (b) Mole fraction distribution of components throughout the convection reactor



(a) **(b)**

Figure 7. (a) and (b) Mole fraction distribution of components throughout the radiation reactor

In the dual-reactor model, the primary reactor functions as a convection reactor and is responsible for the preheating process. The reaction rate is relatively low during the preheating phase, leading to the generation of minimal products. This phenomenon is observable in the illustrations provided in Figure 7 and Figure 8. Initially, a small amount of ethylene, hydrogen, and propane is produced at the beginning of the reactor, followed by the generation of propene and methane at distances of around 19.5 m and 2.5 m, respectively. Acetylene and 1,3-butadiene are not generated in this particular reactor model.

The subsequent reactor, referred to as the radiation reactor, facilitates the majority of the reactions, resulting in a gradual rise in the formation of ethylene along the length of the reactor. Similarly, the formation of all other components also increases as the reactor continues. Initially, the reactions responsible for propane formation are dominating. As the temperature increases, propane cracking also. The production of methane is limited to 3.327 mole %. The data derived from the simulation is then compared with results from previous work in the literature.

Table 5. Comparison of simulation and industrial data

Components	Product mole (%)			
	Simulation with Sundaram et al. Reaction scheme [10]	Industrial data	Present scheme with single reactor model	Present scheme with dual reactor model
H_2	40.67	36.79	35.94	34.80
CH_4	3.32	3.83	3.25	3.327
C_2H_4	37.69	34.34	36.12	35.03
C_2H_6	15.11	22.36	23.37	25.25

Further elaboration on these models is presented in subsequent sections of this paper.

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5 Sensitivity Analysis

In the industrial operation of the pyro cracker, the critical, independent process variables include the COT, steam-to-hydrocarbon ratio, and feed flow rate/composition. These parameters may be adjusted to optimize the yield of the process. Any modifications to these variables should be made with careful consideration of the economic and environmental implications. Throughout the comparative analyses undertaken in this study, only the levels of essential elements like hydrogen, methane, ethylene, and Ethane were considered. The examination in this article focused exclusively on the composition of these molecules and elements. The simulation enables us to recognize the impacts of various parameters on the cracker. The subsequent analysis is elaborated upon in greater detail ahead.

5.1 Coil Output Temperature for Single Reactor Model

The coil output temperature, which is denoted as the temperature of the reactor's output, plays a crucial role in the overall performance of the system. It serves as a key indicator of the thermal dynamics within the reactor, reflecting the energy exchange processes taking place. Moreover, the extent of the reaction within the reactor is intricately linked to the temperature variations observed in the coil output. As the temperature rises, there is a corresponding increase in the reaction rate, leading to a more pronounced impact on the system's behaviour and efficiency. This particular parameter holds a substantial influence on the final composition of the reactor's output. In the conducted simulation, various outlet temperatures were tested, ranging from 953 K to 1200 K, while maintaining all other process parameters at the same levels as the base case scenario. Analysis of the results depicted in Fig. 8 reveals a notable trend: as the temperature rises, there is a corresponding increase in the concentration of ethylene within the output. Initially, the concentration of ethylene surpasses that of hydrogen until reaching 1140 K, at which point the hydrogen concentration begins to rise and eventually equals that of ethylene. Moreover, the concentration of methane also experiences an increase, albeit at a slower rate, with the maximum observed increment being 3.645% at 1200 K. It is worth noting that this increase is below the 5% threshold, which is considered the upper limit for methane formation. Hence, the temperature for Ethane cracking above 1140 K is considered unfeasible due to economic factors.

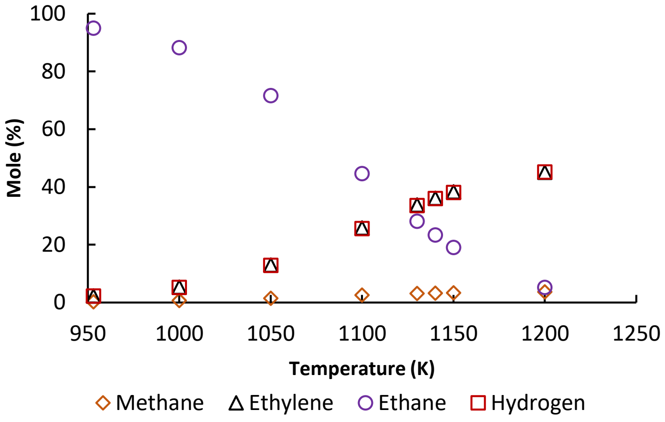

Figure 8. Effect of COT on product distribution in single reactor model

5.2 Steam to Ethane ratio

Steam is utilized for dilution within the pyro cracker, as previously mentioned. Simulations were conducted across various steam-to-ethane ratios, ranging from 0.1 to 1. The impact of the steam-to-ethane ratio in the pyro cracker is depicted in Figure 9. Analysis of Figure 9 reveals that the proportions of ethylene and hydrogen exhibit similar trends, gradually increasing with higher dilution. The highest methane content, at 4.42%, is observed at a steam-to-ethane ratio of 0.11. According to the data plotted in the graph, a steam-to-ethane ratio of around 0.42 (ethane - 0.7 and steam 0.3 mass fraction) is notably favoured, as lower ratios may result in excessive methane formation. Increasing the steam-to-ethane ratio above 0.42 is considered disadvantageous for this procedure.

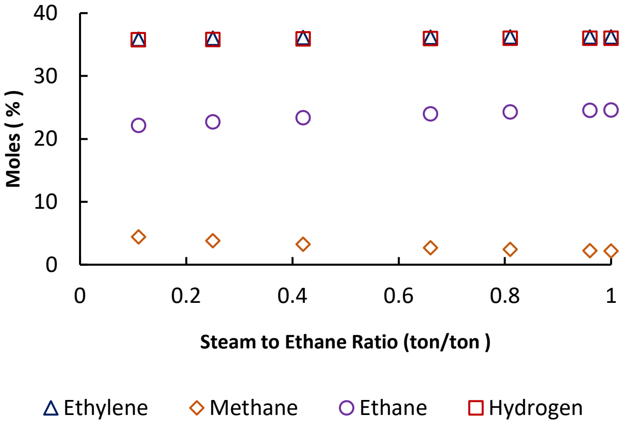

Figure 9. Effect of Steam to Ethane Ratio on product distribution

5.3 Inlet Temperature

The impact of inlet temperature plays a crucial role in determining the outlet composition. The simulations entailed adjusting the reactor's input temperature while keeping all other parameters constant, mirroring the base case scenario. Analysis of the simulation results facilitated the generation of a graph illustrating the observed composition trends in Figure 10. The graph highlights a marked increase in ethylene and hydrogen composition with rising temperatures, in contrast to methane, which exhibits a slower rate of increase. This phenomenon can be attributed to the initial reactor section's preheating process, which enhances ethane consumption. Excessive coke formation and disruption of the reactor's temperature distribution should be averted by avoiding high inlet temperatures. Consequently, based on the findings from the graph analysis, an optimal inlet temperature of approximately 943 K is recommended to achieve a production yield of around 36.12 mole % ethylene while restricting methane production to 3.43 mole %.

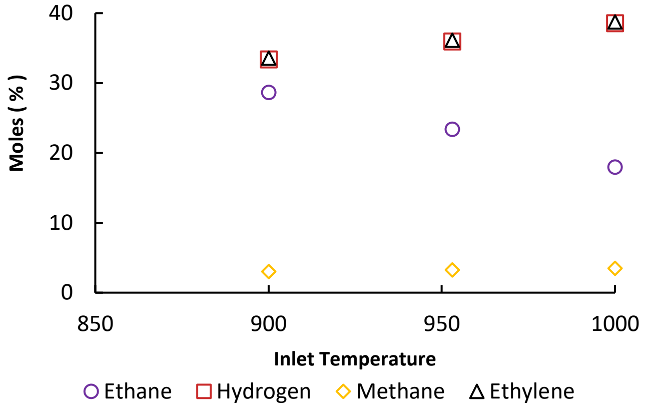

Figure 10. Effect of Inlet Temperature on product distribution

5.4 Reactor Length

The reactor's length significantly impacts the residence time, which in turn affects the composition of the output materials. In this simulation, the design and kinetic parameters were maintained consistent with the base case, while the reactor's dimensions were varied to study their effect on residence time. As depicted in Figure 11, the concentrations of ethylene and hydrogen increased with longer residence times or extended reactor lengths. Initially, ethylene was observed in slightly higher concentrations than hydrogen; however, with increased residence time, a marginal rise in hydrogen concentration was noted.

The temperature profile along the reactor's length follows a hyperbolic trend. As the reactant mixture progresses through the reactor, both the residence time and temperature increase, enhancing ethylene yield. However, elevated ethylene concentrations at higher temperatures may also encourage coking reactions, necessitating more frequent decoking. This study concludes that a reactor length of approximately 15 meters provides optimal performance, achieving an ethylene yield of around 41.54% while restricting methane formation to 3.764%.

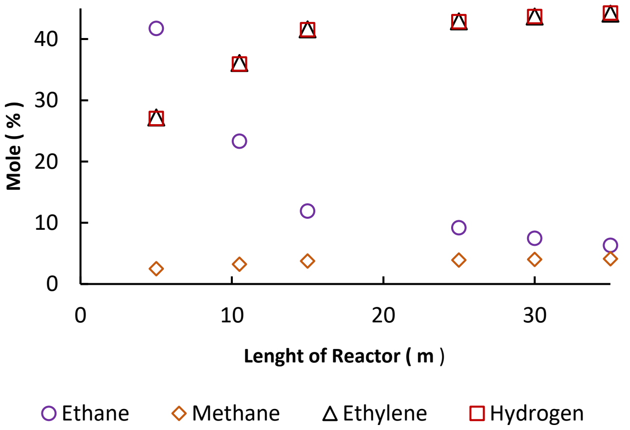

Figure 11. Effect of reactor length on product distribution

5.5 Coil Output Temperature of Dual Reactor Model

In the dual reactor, the temperature of the effluent from the second reactor, known as the radiation reactor, is modified while maintaining all other parameters constant, as in the reference case. The consumption rate of Ethane exhibits a continuous increase along the length of the reactor. Similarly, the production rates of ethylene and hydrogen also experience a steady rise along the reactor's length.

Analysis of the graph reveals an initial predominance of ethylene composition over hydrogen; however, as the temperature surpasses 1100 K, there is a significant surge in hydrogen composition, reaching a peak of 56.45% at 1200 K. The higher temperatures lead to increased methane formation, with a gradual rise observed as the temperature exceeds 1000 K. The highest yield of methane achieved under these conditions is 3.8 mole %. To optimize ethylene production, it is recommended to maintain the COT at approximately 1100 K.

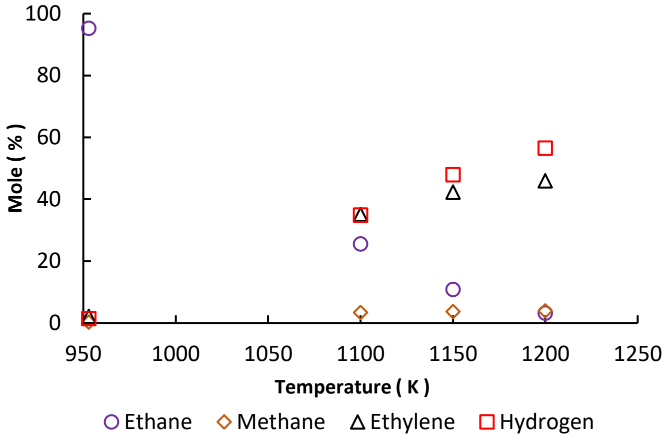

Figure 12. Effect of COT on product distribution in Dual reactor model

6 Conclusion

The developed and simulated process model of an industrial ethane cracker using PETRO-SIM is presented in this study. The radiant section of the pyro cracker is identified as the primary site for significant cracking reactions. Incorporating a molecular reaction scheme with eight reactions provides a more accurate depiction of Ethane cracking kinetics compared to previous models. Due to the unavailability of actual temperature data within the radiant coils, various temperature profiles from the literature were analyzed through the model. Validation of the model was achieved by comparing the simulated results with existing industrial data.

Moreover, the study conclusively demonstrates that the simulation results utilizing the enhanced reaction scheme align well with industrial data. The impact of key process parameters such as COT, steam-to-ethane ratio, reactor length, and inlet temperature on product composition was investigated using the validated model. Noteworthy findings from the sensitivity analysis indicate that:

1. The COT should be approximately 1140 K for a single reactor model and approximately 1100 K for dual reactor mode.
2. The steam-to-ethane ratio should be around 0.42 (ethane - 0.7 and steam 0.3 mass fraction)
3. The inlet temperature should not be higher than 1000 K.

The model's ability to predict optimal conditions for the cracking unit is successfully demonstrated, potentially impacting industrial pyro cracker economics. The methodology for modelling and simulation showcased in this work is easily interpretable and reproducible for future dynamic simulation processes.

7 Acknowledgement:

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