Simulation of ethane steam cracking with severity evaluation

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Abstract. Understanding the influence of operating parameters towards cracking severity is paramount in ensuring optimum operation of an ethylene plant. However, changing the parameters in an actual plant for data collection can be dangerous. Thus, a simulation model for ethane steam cracking furnace is developed using ASPEN Plus for the assessment. The process performance is evaluated with cracking severity factors and main product yields. Three severity factors are used for evaluation due to their ease of measurement, which are methane yield (Ymet), Ethylene-Ethane Ratio (EER) and Propylene-Ethylene Ratio (PER). The result shows that cracking severity is primarily influenced by reactor temperature. Operating the furnace with coil outlet temperature ranging between 850°C to 950°C and steam-to-hydrocarbon ratio of 0.3 to 0.5 has led to optimum main product yield.

1. Introduction
Ethylene is one of the major petrochemical products in the world as it is a primary building block in the production of many other chemicals and products. Common feedstocks of steam cracking are ethane, ranges of naphtha, and other range of hydrocarbons. Steam cracking process took place in a furnace with tubes of plug flow reactor passing through the furnace firebox. Prior to entering the reactor, the hydrocarbon feed is preheated in the convection section of the furnace, and then mixed with superheated steam at a specific ratio. After that, the mixed feed enters the radiant section, which is the furnace firebox, where it is heated to a range of targeted reaction temperature by radiation and reaction rapidly take place. Cracked gas exiting the radiant section is cooled rapidly by Transfer Line Exchanger (TLE) to below reaction temperature in order to stop primary reactions and minimize side reactions. The cracked gas is fed to cracked gas compressor and delivered for further purification and recovery, including recovery of unreacted feed, methane, and C3+ product. The unreacted feed is typically recycled and mixed with fresh feed while methane and C3+ is typically used as fuel gas. From the description, it can be concluded that steam cracking is an energy intensive process. Figure 1 shows simple schematic of steam cracking furnace.

Ethane, being the simplest feedstock, requires the highest temperature (800°C – 900°C) to crack and thus, it utilizes huge amount of energy to operate. Other than temperature, critical process parameters that affect steam cracking performance are reactor pressure and steam-hydrocarbon ratio [1]. Operating the cracking furnace at optimum operating envelope is paramount in order to maintain optimum equipment efficiency, maximizing ethylene yield, while minimizing operating cost. Evaluation of cracking process also requires understanding of the cracking reaction kinetic. It is mainly accepted that cracking is most accurately represented by free-radical reaction mechanism [2]. Since free-radical reaction scheme consist of several hundreds of reactions, most researchers use molecular reaction scheme to simplify the computation in order to determine cracking reaction products [3, 4].
Another important factor to consider is the cracking severity, which determines the extent of cracking reaction and cracking product distribution. Maintaining cracking severity at target is important to avoid over-cracking as it yields unwanted products (heavier hydrocarbons and coke formation) and to avoid under-cracking as it will not crack enough hydrocarbon feed to produce valuable product. To control the cracking severity, industry typically uses Coil Outlet Temperature (COT) as indicator. Maintaining the COT at a target temperature region that favour ethylene yield is correlated with cracking severity control. However, it has been reported that referring solely on COT does not accurately indicate the cracking severity [5, 6]. It needs to be used in tandem with other factors. Thus, the study incorporate methane yield (Ymet), Ethylene-Ethane Ratio (EER), and Propylene-Ethylene Ratio (PER) in the assessment of cracking severity.

2. Model Development

Having a process model will enable offline analysis of plant under various operating conditions and operating strategies in order to understand the impact of making parameter changes prior to implementation at actual plant. It is also useful as a tool to familiarize the plant personnel with the process behaviour during training. Using ASPEN Plus, the steam cracking furnace is modelled as plug flow reactor with ethane and superheated steam as feed streams. No recycle feed is included in the model to simplify process analysis. Using the molecular reaction scheme proposed by P. Ranjan et al [7], the reactor has a length of 10.5 m with 48 tubes and an inner diameter of 0.085 m. Maximum reactor operating pressure is 2.2 barg and steam-to-hydrocarbon ratio between 0.3 – 0.5.

Using the molecular reaction scheme proposed by P. Ranjan et al. [7], the reactions and kinetic parameters are incorporated in the model, as per Table 1. Coke formation reactions are not included in the model.
In the literature, Gujarathi et al. [4] proposed a reactor temperature profile that shows a nonlinear temperature distribution along the reactor with outlet temperature of 840°C. Using the proposed profile (as shown in Figure 2) and a constant reactor temperature profile of 840°C, evaluation of thermodynamic property methods are done. There are six property methods that are suitable to be used for modelling ethylene production system, which are Peng-Robinson, SYSOP0, SRK, UNIFAC, UNIQUAC, and GRAYSON. Selection of property method is done by comparing the resulting product compositions calculated from each method. The result, as shown in Figure 3, shows that all property methods estimated similar percentage of hydrogen, ethylene, ethane, and methane in the reactor product, at both temperature profiles. Since the result using all six property methods is the same, any property method can be used in the simulation. Thus, GRAYSON property method is selected as it is also recommended by ASPEN for ethylene production system. As for temperature profile, constant reactor temperature profile is selected to be used in the study.

**Figure 2**: Optimal temperature profile proposed by Gujarathi et al.

**Figure 3**: Prediction of cracking products using different thermodynamic property methods

Figure 3a (left) – Comparison using Gujarathi et al profile
Figure 3b (right) – Comparison using isothermal profile at 840 C

| No | Reactions : Order | Order | Forward reaction A (s⁻¹) or (L (mol.s)⁻¹) E (kJ mol⁻¹) | Reverse reaction A (L (mol⁻¹)) E (kJ mol⁻¹) |
|----|------------------|-------|---------------------------------------------------|------------------------------------------|
| 1  | C₂H₆ ↔ C₂H₄ + H₂ | 1     | A=4.6 x 10¹⁹ E=272.8                              | A=8.49 x 10⁷ E=136.5                      |
| 2  | C₂H₆ ↔ C₂H₂ + CH₄| 1     | A=7.2 x 10¹₂ E=274.2                              | A=3.81 x 10⁶ E=147.2                      |
| 3  | C₂H₄ + C₂H₄ → C₂H₆| 2     | A=1.0 x 10¹⁵ E=172.6                              |                                          |
| 4  | C₂H₄ + C₂H₆ → C₂H₆ +2H₂ | 2    | A=8.3 x 10¹² E=144.6                              |                                          |
| 5  | C₂H₆ ↔ C₂H₆ + H₂  | 1     | A=5.8 x 10¹⁰ E=214.6                              | A=9.03 x 10⁷ E=93.5                       |
| 6  | C₂H₆ + C₂H₄ → C₂H₆ + C₂H₆| 2  | A=2.5 x 10¹⁶ E=247.1                              |                                          |
| 7  | 2C₂H₆ → 3C₂H₄     | 1     | A=7.3 x 10¹² E=268.5                              |                                          |
| 8  | 2C₂H₄ → C₂H₆ + CH₄| 1     | A=3.8 x 10¹¹ E=273.0                              |                                          |
| 9  | C₂H₁₀ ↔ C₂H₆ + H₂  | 1     | A=1.6 x 10¹² E=260.9                              | A=1.78 x 10⁷ E=135.1                      |
| 10 | C₂H₄ + C₂H₆ → C₂H₆ + CH₄ | 2  | A=7.0 x 10¹⁶ E=252.8                              |                                          |
| 11 | C₂H₆ + C₂H₆ → C₂H₆ + CH₄ | 2  | A=1.0 x 10¹⁷ E=251.1                              |                                          |
3. Process parameter analysis

3.1. Effect of reactor temperature.

Cracking is an endothermic reaction, and thus, require continuous energy input for the reaction to be activated. Stopping the heat supply to the system will cease the reaction almost immediately. Figure 4 shows the effect of reactor temperature to the product composition and different measure of severity applied to it. From Figure 4, it is observed that at 650°C, minimal ethane conversion occurs. Only at 700°C, the reactions start to take place as ethane molecules gain more energy from the heat. Ethane conversion rapidly occur producing ethylene and other products. Ethylene production maximizes between 850°C – 950°C. Beyond that range, ethylene production starts to drop and methane is seen to increase, even though ethane conversion continues. This is primarily due to side reactions activated at higher temperature causing ethane and ethylene to react with other components producing more methane and other by-products [6]. Thus, valuable product is loss while fresh feed and energy is still consumed, reducing the profitability of the plant. To maximize ethylene yield, normal operating strategy is to bring the COT towards higher limit of the optimum temperature range. To minimize further ethylene conversion into other products, immediately after exiting the reactor, cracked gas is cooled down below 650°C.

As shown in Figure 4b, COT is linearly proportional to EER and methane yield, and as shown in Figure 4c, with respect to ethylene yield, COT also exhibit similar patterns as other severity factors. As reactor operating temperature increases, ethylene yield and methane yield rapidly increases. PER, EER, and methane yield indicate high activity at high temperature region, although after certain temperature, ethylene yield start to decrease even with increasing trend of EER and methane yield. This is mainly due to ethane rapid conversion and slow conversion of ethylene into methane and other by-products [6], leading to increasing EER. Reduction in PER also indicate that propylene disappear at higher temperature together with ethylene. Analysing all four severity factors provide an idea of the product distributions of the cracking at any stage and also the optimum severity region that needs to be maintain to ensure optimum ethylene yield.

![Figure 4](image-url)

**Figure 4.** Assessment at different COT. Figure 4a (top left) – Effect of COT to product yield. Figure 4b (top right) – Methane yield, EER, and PER at varying COT. Figure 4c (bottom left) – Relationship between PER and EER with Methane yield. Figure 4d (bottom right) – Comparison of different severity factors with respect to ethylene yield.
3.2. Effect of steam to hydrocarbon ratio.
Cracking of ethane into ethylene and hydrogen is a reversible reaction. In order to keep the reaction favourable towards ethylene, partial pressure of ethane need to be reduced. Thus, steam is introduced into the feed stream to reduce the partial pressure of ethane. Since steam is inert (no reaction with ethane or other components), its presence does not produce by-products. Figure 5 shows the effect of steam to hydrocarbon ratio to the product composition and different measure of severity applied to it. From the results in Figure 5, increasing the steam to hydrocarbon ratio (S/HC) beyond 0.3-0.5 does not contribute to economic benefits in terms of ethylene yield. All severity factors exhibit linear proportional pattern with each other at varying S/HC. Further increasing S/HC is shown to reduce cracking activities. Thus, maintaining steam only between 0.3-0.5 is sufficient to reduce partial pressure in order to keep the reaction equilibrium towards ethylene and reduces reversal to ethane.

4. Summary
Three severity factors were evaluated together with COT and the results showed that temperature plays the most important role in the process. Reactor temperature heavily influence the product distribution from the cracking process compared to steam to hydrocarbon ratio. It is also found that operating at higher temperature region led to high ethane consumption. Moreover, by-products and methane have been produced due to ethylene consumption. Analysis shows that operating at a temperature range of 850°C – 950°C and steam to hydrocarbon ratio of 0.3-0.5 produces maximum ethylene yield while minimizing byproducts. Analysis of multiple severity factors enables engineers to evaluate the cracking performance at every angle and the effect on several products simultaneously. To further improve the accuracy of the model, coke formation can be incorporated together with

Figure 5: Assessment at different S/HC ratio.
Figure 5a (top left) - Effect of S/HC to product yield. Figure 5b (top right) - Methane yield, EER, and PER at varying S/HC. Figure 5c (bottom left) - Relationship between PER and EER with Methane yield. Figure 5d (bottom right) - Comparison of different severity factors with respect to ethylene yield.
addition of recycle feed. This will enable analysis of cracking process under the presence of impurities from the recycle stream and the effect to cracking severity.

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