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Insights into Propane Cracking: A Simulation and Comparative Study

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Abstract

The thermal cracking of propane is a crucial chemical process with wide-ranging industrial applications, including the production of valuable chemicals and fuels. This research paper presents a comprehensive exploration of the thermal cracking of propane using simulation techniques and comparative studies. The primary objective of this study is to enhance our understanding of the reaction mechanisms, product distributions, and the influence of key parameters on the process. In this paper we employ advanced computational methods to simulate the thermal cracking of propane, providing insights into the reaction kinetics and pathways involved. By employing detailed kinetic models and sophisticated reaction mechanisms, we investigate the effects of temperature, pressure, and residence time on the yield of various products. Through this simulation, we aim to elucidate the mechanisms that govern the formation of critical products like propylene and ethylene. Ultimately, this research contributes to the advancement of the thermal cracking of propane processes by offering critical insights into the optimization of reaction conditions for desired product yields. The findings can be instrumental for industrial processes, enabling more efficient production of valuable chemicals and energy resources. This research bridges the gap between simulation and experimentation, offering a holistic perspective on the thermal cracking of propane and paving the way for future innovations and improvements in this essential chemical engineering domain.

Keywords: Propane Cracking, Tubular Reactor, PetroSIM, DWSIM, Catalytic Cracking, Simulation

Introduction

The process of cracking is essential in the petrochemical industry for breaking down large hydrocarbon molecules into smaller and more valuable components. This can be achieved through either thermal cracking, conducted at high temperatures and pressures without a catalyst, or catalytic cracking, which occurs at lower temperatures and pressures with the presence of a catalyst. The source of these large hydrocarbon molecules is typically the naphtha or gas oil fractions obtained during the fractional distillation of crude oil.

Cracking doesn't involve a single, well-defined reaction. Instead, it breaks hydrocarbon molecules in a somewhat random manner, generating mixtures of smaller hydrocarbons, some of which may contain carbon-carbon double bonds. Modern high-pressure thermal cracking is conducted at approximately 7,000 kPa. The process leads to disproportionation, where lighter, hydrogen-rich products are formed at the expense of heavier molecules that condense and lose hydrogen. This reaction is known as homolytic fission and produces alkenes, which are fundamental for polymer production. The thermal cracking of propane is a pivotal process within the field of chemical engineering, with significant implications for the

production of essential chemicals and fuels. This research paper embarks on an exploration of this intricate process, employing simulation techniques and comparative studies to delve deeper into the mechanisms governing propane thermal cracking. By utilizing computational simulations and comparing their outcomes with experimental data, this study seeks to unravel the complexities of propane cracking, thereby offering invaluable insights for industrial applications and process optimization. The significance of this research is underscored by the growing demand for propylene and ethylene, key products derived from propane thermal cracking. Understanding the reaction pathways and product distributions under varying conditions, such as temperature, pressure, and residence time, can enable engineers and researchers to fine-tune their processes for enhanced yield and energy efficiency.

In this pursuit, the paper draws upon a wealth of knowledge, including detailed kinetic models and radical cracking schemes, to simulate the propane pyrolysis reactor. The analysis extends to comparative studies involving different reactor configurations and experimental setups, where insights are drawn from modelling studies and pilot plant data. These endeavours collectively aim to bridge the gap between theoretical simulations and practical application, offering a holistic perspective on propane thermal cracking, and ultimately fostering innovations in this vital field. By blending theoretical and practical approaches, this research paper aspires to propel the industry forward, addressing challenges and maximizing the potential of propane thermal cracking for sustainable and efficient chemical production. Early pioneers, such as William Merriam Burton and C.P. Dubbs developed thermal cracking processes in the early 20th century, paving the way for the use of these techniques in many refineries until the advent of catalytic cracking in the early 1940s.

Software's Used

In this study majorly 2 software's were used namely PetroSIM and DWSIM.

PetroSIM

Petro-SIM is a comprehensive process simulation software platform designed for the oil and gas industry. It serves as a valuable tool for improving plant performance and productivity in the petrochemical and refining sectors. Developed by KBC Global, Petro-SIM offers both steady-state and dynamic simulation capabilities, allowing engineers and operators to model and optimize various aspects of their processes. Here's a detailed summary of Petro-SIM, including its advantages and disadvantages:

Key features and components of Petro-SIM include a solid engineering framework, integration with digital platforms, and the incorporation of artificial intelligence. It provides specialized reactor models for refining and can link to other software solutions, such as FEESA Maximus and Schlumberger PIPESIM. Petro-SIM also offers a Reactor Suite simulation software, simplifying complex data, automating model calibration, and evaluating the impact of refinery processing. This software's capabilities make it an essential tool for analyzing, modelling, and optimizing complex chemical and process engineering operations. Its integration with digital platforms and Artificial Intelligence enhances its functionality, making it a valuable resource for professionals in the oil and gas industry.

Advantages of Petro-SIM:

a. Accurate Process Simulation: Petro-SIM provides highly precise and accurate process simulation results, making it a reliable tool for modelling complex refinery operations.
b. Rich Functionality: It offers rich process analysis functionality, allowing engineers and operators to analyse and optimize various aspects of their processes effectively.

c. Integration: Petro-SIM is integrated with KBC, a leading provider of consulting and software services for the energy and chemical industries. This integration enhances its capabilities and provides access to best-in-class solutions.
d. Customization: The software can be adapted to the specific needs of different users by adjusting unit operations, utility options, and default stream property lists, making it flexible for various applications.

Disadvantages of Petro-SIM:

a. Cost: Petro-SIM is a premium software solution, and its cost can be a significant factor for smaller organizations or projects with budget constraints.
b. Learning Curve: Due to its advanced capabilities, Petro-SIM may have a steep learning curve for new users. Extensive training and expertise are often required to fully harness its potential.
c. Resource Intensive: Running simulations with Petro-SIM may demand considerable computational resources, potentially limiting its use on less powerful hardware.

In summary, Petro-SIM is a powerful tool for process simulation and optimization in the oil and gas industry, offering high accuracy and rich functionality. However, its cost, learning curve, and resource requirements can be potential challenges for some users.

DWSIM

DWSIM is a prominent open-source chemical process simulator that offers a versatile and cost-effective solution for simulating and optimizing chemical and petrochemical processes. It is designed to facilitate the modelling of complex chemical systems, making it a valuable tool for engineers and researchers in the field of process engineering. Here's a detailed summary of DWSIM, including its advantages and disadvantages:

Key features of DWSIM include a user-friendly graphical interface, compatibility with Windows, Linux, and macOS, and compliance with the CAPE-OPEN standard. It provides a wide range of simulation capabilities, allowing users to conduct experiments, analyse and optimize processes, and generate hypothetical components. DWSIM's open-source nature makes it accessible to a broad user base, offering an alternative to expensive commercial simulation packages. This software is highly adaptable, and its multiplatform support makes it suitable for a variety of operating systems. Whether you're a student, researcher, or professional in the field of chemical engineering, DWSIM serves as a powerful and cost-effective resource for process simulation and analysis.

Advantages of DWSIM:

a. Open Source: DWSIM is open-source software, making it freely available to users. This offers a cost-effective alternative to expensive commercial simulation packages.
b. CAPE-OPEN Compliance: DWSIM complies with the CAPE-OPEN standard, ensuring interoperability and compatibility with various other process simulation software.
c. Versatile: It offers a wide range of capabilities for process modelling, including the simulation of chemical processes, thermodynamics, unit operations, and more.
d. Community Support: DWSIM has an active user community and provides support through forums and resources to help users learn and troubleshoot issues.

Disadvantages of DWSIM:

a. Learning Curve: Due to its extensive capabilities, DWSIM may have a learning curve for new users, requiring time and effort to become proficient.
b. Limited Documentation: While DWSIM offers community support, it may have limited official documentation compared to some commercial software.
c. Resource Intensive: Running complex simulations with DWSIM may require significant computational resources, which could be a limitation for users with less powerful hardware.

In summary, DWSIM is a versatile and cost-effective open-source chemical process simulator that offers compatibility with industry standards and a supportive user community. However, it may require some time to learn and master its features, and resource-intensive simulations could be challenging for some users,

Simulation Details

In the both the software's the simulation was done independently. In order to validate the model, industrial data from Sundaram and Froment (1979) is used.

Reactor Details

The reactor used for the following simulations is a Plug Flow Reactor (PFR). The major distinguishing properties of tubular reactors is their distributed-parameter nature, that is, variables like temperature and components (reactant, product) change with physical dimensions as well as with time. In a regular plug flow reactor system, we assume its vessel is cylindrical. Fluid will flow down word direction across the reactor length, and also the velocity profile is flat. So that no axial mixing will happen, and that radial gradients will not exist in composition or temperatures. The PFR is an empty vessel if no catalyst is used. If any catalyst is packed inside the reactor, then it is called a packed bed reactor. And also, the catalyst will affect the dynamic behaviour of the reactant because the process fluid has lower thermal capacitance than the catalyst mainly in the gas-phase system. The temperatures of both the catalyst and the process fluid vary with time. Under steady-state conditions the two temperatures are equal at any axial position. The table below shows the sizing and conditions of the PFR used.

Table 1: Dimensions of Reactor

Total Volume	0.8702 m3
Length	103.5 m
Diameter	0.108 m
Number of tubes	1
Wall thickness	0.00500m
Pressure Drop	1 bar

Input And Flowsheet

The flowsheet for the simulation process was designed as per Figure 1. In the figure the streams 1 and 2 are the feed streams whose compositions and properties are represented in Table 2. The feed is inputted into the reactor PFR-100. The dimensions and specifications of the same are given in Table 1. The reactions occurring in the reactor are tabulated in Table 3. All the elements used in the sheet are standard and already present in the software's.

The other important part of the flowsheet is the adjuster. The Adjust operation varies the value of one stream variable (the independent variable) to meet a required value or specification (the dependent variable) in another stream or operation. In a flowsheet, a certain combination of specifications may be

required, which cannot be solved directly. These types of problems must be solved using trial-and-error techniques. To solve flowsheet problems that fall into this category, the Adjust operation can be used to automatically conduct the trial-and-error iterations for you. The Adjust operation is flexible. You can use it to link stream variables in the flowsheet in ways that are not possible using ordinary physical unit operations. It can be used to solve for the desired value of just a single dependent variable, or multiple Adjusts can be installed to solve for the desired values of several variables simultaneously. The Adjust operation can perform these functions: l Adjust the independent variable until the dependent variable meets the target value. l Adjust the independent variable until the dependent variable equals the value of the same variable for another object, plus an optional offset.

1. To add an Adjust operation to your simulation, from the Home tab, open the Operations, Logical palette (or press F4).
2. Double-click Adjust (or click and drag it to the flowsheet). An Adjust operation is added to the active flowsheet.
3. Optionally, enter a new name in the Adjust Name field.
4. To start or initialize the Adjust operation, do one of the following:

- Provide values for ALL fields on the Design tab, Parameters page to automatically begin the Adjust operation calculations. With the exception of the Minimum and Maximum values of the independent (Adjusted) variable, all parameters are required before Adjust begins its calculations
- Omit one or both values in the Minimum and Maximum fields for the independent variable, and then click the Start button to begin the calculations. The Start button only appears in the initialization stage of the Adjust operation. It disappears from the property view as soon as it is pressed. Any changes made to Adjust or other parts of the flowsheet automatically trigger the Adjust calculation.

5. When the error value is less than the Tolerance, the status bar displays the OK message in green. If adjust reaches the maximum number of iterations without convergence, the reached iteration limit without converging message displays in red onthe status bar. If you click the Start button when all of the required parameters are not defined, the status bar displays an Incomplete message in yellow and calculations cannot begin.

Figure 1: Flowsheet for Simulation

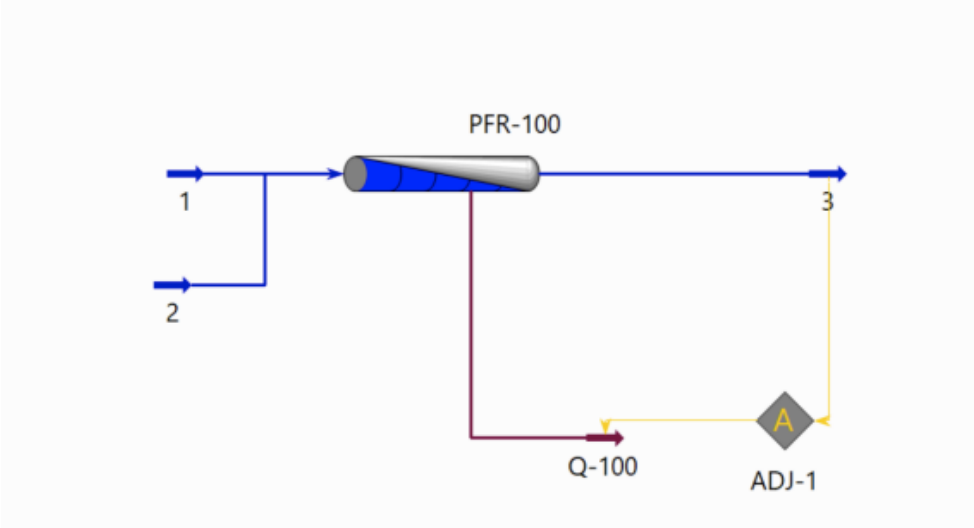


Table 2: Compositions of feed streams

Material Properties	Stream 1(Propane)	Stream 2(Water/Steam)
Vapour / Phase Fraction	1	1
Temperature(C)	599.9	599.9
Pressure (kPa)	300	300
Molar Flow (kgmole/h)	62.33	45.86
Mass Flow(kg/h)	2749	826.2
Std Ideal Liq Vol Flow (m3/h)	5.425	0.827
Molar Enthalpy (kJ/kgmole)	-33100	-2.21E+05
Molar Entropy (kJ/kgmole-C)	276.6	154.7
Heat Flow (kJ/h)	-2063000	-1.01E+07
Liq Vol Flow @Std Cond (m3/h)	5.423	0.8145

The following reactions were used for the simulation (Table 3). The reactions are of the kinetic type and the A (Pre-Exponential Factor) and E (Activation Energy) data was entered manually. Not all reactions lead to the final product but have to be included in the total process simulation.

Table 3: Reactions used in the Simulations

Reaction No.	Reaction	A (s^{-1} or $*kmol^{-1}m3\ s-1$)	E(kJ/mol)
1	$C_3H_8 = C_2H_4 + CH4$	2.56144E+10	211.7
2	$C_3H_8 = C_3H_6 + H_2$	3.7887129E+10	214.6
3	$C_3H_8 + C_2H_4 = C_3H_6 + C_2H_6$	1.267115E+14	247.1
4	$2C_3H_6 = 3C_2H_4$	7.088750E+10	233.5
5	$C_3H_6 = C_2H_2 + CH_4$	4.62985E+11	248.5
6	$C_3H_6 + C_2H_6 = C_4H_8 + CH_4$	2.055E+14	251.1

7	$C_2H_6 = C_2H_4 + H2$	2.48254E+12	272.8
8	$C_2H_2 + C_2H_4 = C_4H_6$	8.48778E+10	172.75

Results And Discussion

All the results in this section were obtained by the simulation of the PFR according to the aforementioned conditions and properties. The results of the exit stream (Stream 3) are tabulated in Table 4. The properties of each individual component are tabulated in Table 5.

Table 4: Output Stream Properties

Material Properties	Stream 3
Vapour / Phase Fraction	1
Temperature:(C)	826.9
Pressure: (kPa)	200
Molar Flow (kgmole/h)	152.7
Mass Flow(kg/h)	3575
Duty	7.594e+06 kJ/h
Molar Enthalpy(kJ/kgmole)	-30080
Molar Entropy (kJ/kgmole-C)	236.8
Heat Flow (kJ/h)	-4591000
Liq Vol Flow @Std Cond (m3/h)	9.15

From the table below we can see that the main components present in the output streams are ethylene, steam and unreacted propane. The current conversion of propane is comparatively low but this point can be easily manipulated by changing the reactor parameters like temperature, pressure, the feed composition and rates. This is addressed in further sections.

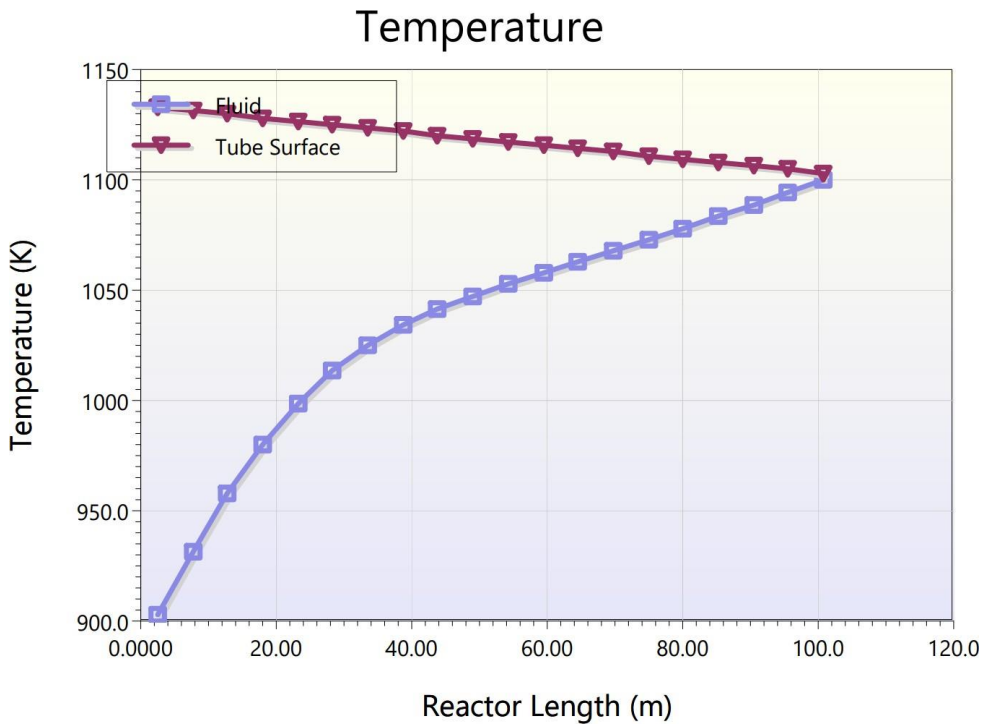
Table 5: Output Stream Composition

COMPONENTS	MOLAR FLOW (kgmole/h)	MOLE FRACTION	MASS FLOW (kg/h)	MASS FRACTION
Methane	22.1823	0.1453	355.8678	0.0995
Ethane	0.0261	0.0002	0.784	0.0002
Propane	20.6203	0.1351	909.2937	0.2544
1-Butene	0	0	0.0003	0
Ethylene	22.5962	0.148	633.9084	0.1773
Propene	17.921	0.1174	754.1246	0.211
Hydrogen	21.4734	0.1407	43.2904	0.0121
Acetylene	1.9711	0.0129	51.3236	0.0144
1,2-Butadiene	0	0	0	0
H2O	45.8615	0.3004	826.2	0.2311
1,3-Butadiene	0.0001	0	0.0033	0
Total	152.6519	1	3574.796	1

The profile of temperature versus reactor length (Figure 2) and pressure versus reactor length (Figure 3) have also been plotted. From the profile of temperature and reactor length it can be observed that as the we go from the start of the reactor to the end the temperature of the fluid increases whereas the temperature of the tube surface decreases. The pressure also decreases from starting of the reactor to the end. This can be possibly due to the reduction in the total number of moles of the gases present.

The next graphs plotted were for mole fraction of various components present with respect to the reactor length (figure 4 and 5). From the figures it is clearly visible that the mole fraction of all components increases except the mole fraction of propane. This is as propane is the main reactant and is getting consumed during the process. Though the mole fractions of the other components increase there is a drastic increase in the mole fraction of propene, ethylene and methane. Ethylene and methane are the main products whereas all others are side products. One observation that can be made from the figure 4 is that the propene mole fraction increases up until a maximum point and then decreases as it breaks down into ethylene. We can infer from this that at around 1000-1100˚C propene breaks down into ethylene.

Figure 2: Temperature versus Reactor Length



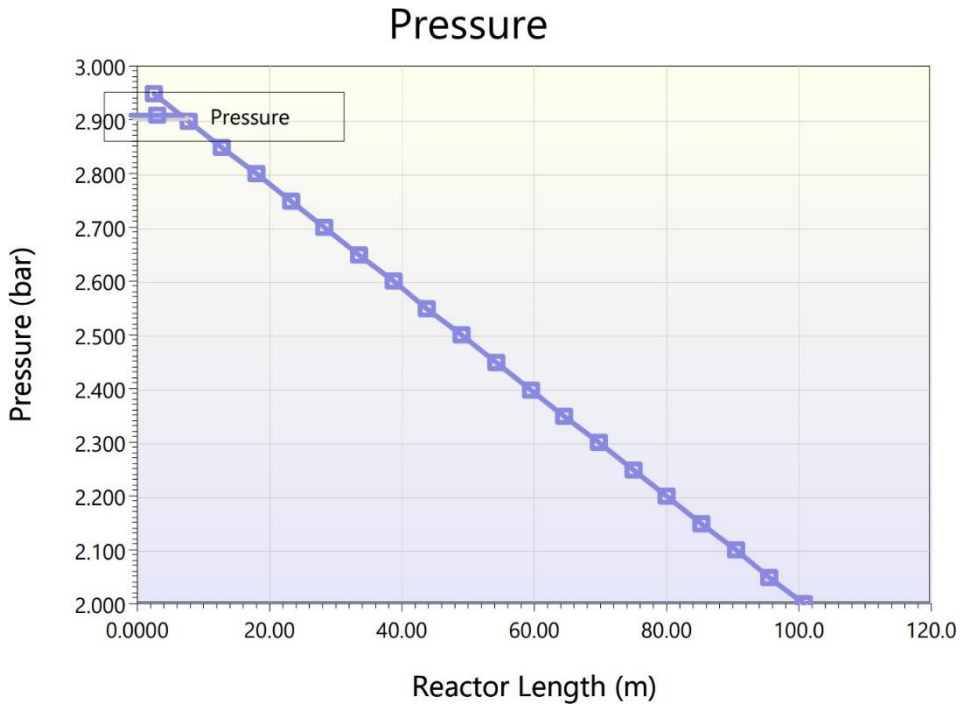


Figure 3: Pressure versus Reactor Length

Figure 4: Mole Fraction versus Reactor Length

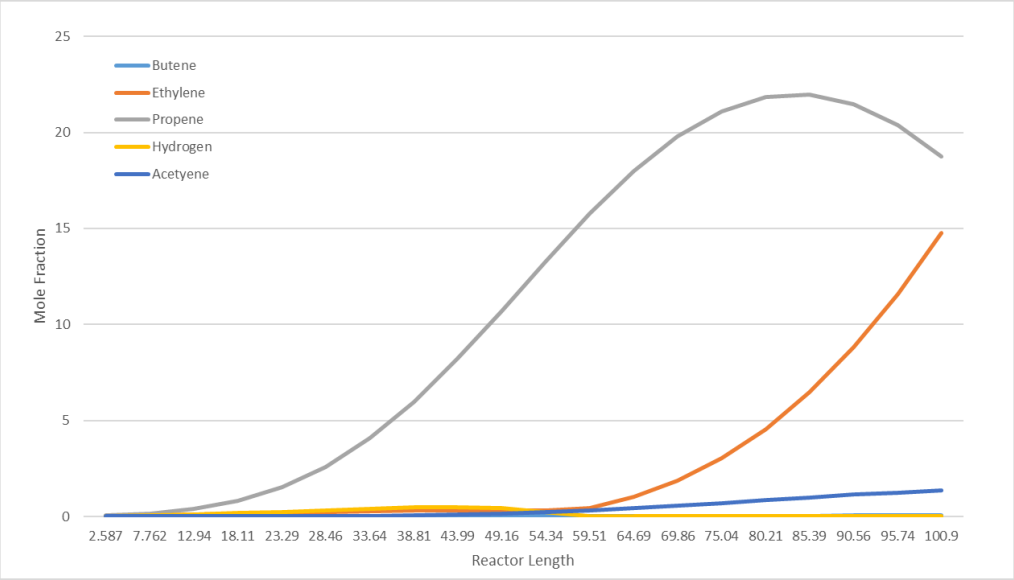
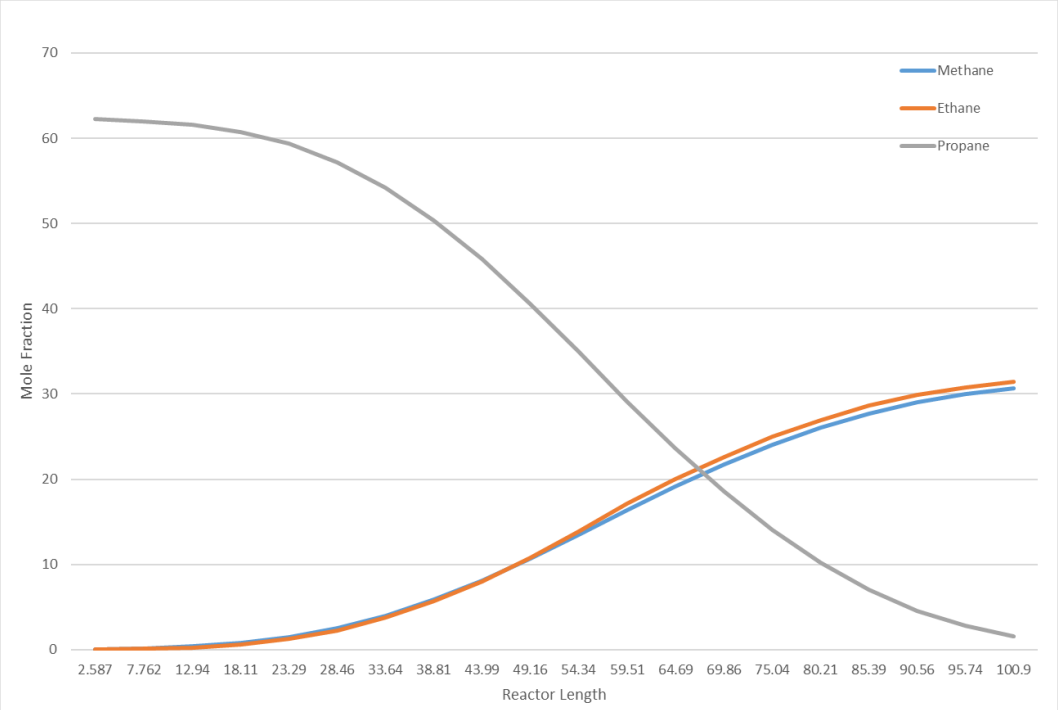


Figure 5: Mole Fraction versus Reactor Length



Comparison of results obtained from PetroSIM and DWSIM

Table 6: Data obtained from software's compared to Industrial Data

Cao (kmol)	Ca(kmol)	Xa	Temperature	Software
62.33	1.5621	97.4938	1200	PetroSIM
62.33	24.5212	60.6590	1100	PetroSIM

62.33	7.3674	88.1800	1154	PetroSIM
62.33	6.233	90	1100	Industrial Data
62.33	34.6735	44.3710	1100	DWSIM
62.33	15.7101	74.7952	1154	DWSIM
62.33	6.67	89.3000	1200	DWSIM

From the above table we can observe that results obtained from both the software's are very close to the industrial data. Minor differences can be observed in both cases due to the differences in the types of calculations that are performed by both the software's and also a deviation from the industrial data may be due to the difference in the type of reactor that was used. From this data it can also be observed that as we increase the temperature of the system the conversion of the reactants increases.

Conclusion

In conclusion, the comparison of PetroSIM and DWSIM simulation software for thermal cracking of propane reveals that both packages offer unique advantages and disadvantages for users. PetroSIM is a commercial software package that offers powerful tools for analyzing complex chemical processes, including thermal cracking of propane. It provides users with a user-friendly interface, and its high-level capabilities and robust simulation capabilities make it an ideal tool for large-scale industrial processes. However, its high cost may limit its accessibility to certain users.

DWSIM, on the other hand, is an open-source simulation software package that is available for free, making it more accessible to a wider range of users. It offers a wide range of features and a customizable interface, allowing users to tailor their simulations to their specific needs. However, its accuracy and reliability may be compromised due to the lack of experimental data and verification.

Hence the choice of simulation software for thermal cracking of propane will depend on the user's specific needs, including the size and complexity of the system, the level of accuracy required, and the available resources. Both PetroSIM and DWSIM offer unique advantages and disadvantages, and users must weigh these factors to determine which software package is best suited for their simulation needs.

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