PROCESSES FOR LIGHT ALKANE CRACKING TO OLEFINS

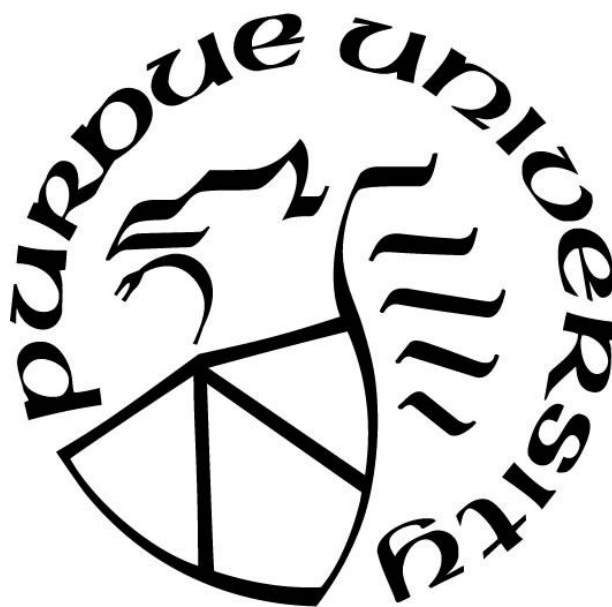by

Wasiu Peter Oladipupo

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THE PURDUE UNIVERSITY GRADUATE SCHOOL
STATEMENT OF COMMITTEE APPROVAL

Dr. Rakesh Agrawal, Chair

Davidson School of Chemical Engineering

Dr. Fabio H. Ribeiro

Davidson School of Chemical Engineering

Dr. Jeffrey J. Siirola

Davidson School of Chemical Engineering

Dr. Mohit Tawarmalani

Krannert School of Management

Approved by:

Dr. John A. Morgan

ACKNOWLEDGMENTS

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ABSTRACT

The present work is focused on the synthesis of small-scale (modular processes) to produce olefins from light alkane resources in shale gas.

Olefins, which are widely used to produce important chemicals and everyday consumer products, can be produced from light alkanes - ethane, propane, butanes etc. Shale gas is comprised of light alkanes in significant proportion; and is available in abundance. Meanwhile, shale gas wells are small sized in nature and are distributed over many different areas or regions. In this regard, using shale gas as raw material for olefin production would require expensive transportation infrastructure to move the gas from the wells or local gas gathering stations to large central processing facilities. This is because existing technologies for natural gas conversions are particularly suited for large-scale processing. One possible way to take advantage of the abundance of shale resource for olefins production is to place small-sized or modular processing plants at the well sites or local gas gathering stations.

In this work, new process concepts are synthesized and studied towards developing simple technologies for on-site and modular processing of light alkane resources in shale gas for olefin production. Replacing steam with methane as diluent in conventional thermal cracking processes is proposed to eliminate front-end separation of methane from the shale gas processing scheme. Results from modeling studies showed that this is a promising approach. To eliminate the huge firebox volume associated with thermal cracking furnaces and allow for a compact cracking reactor system, the use of electricity to supply heat to the cracking reactor is considered. Synthesis efforts led to the development of two electrically powered reactor configurations that have improved energy efficiency and reduced carbon footprints over and compare to conventional thermal cracking furnace configurations.

The ideas and results in the present work are radical in nature and could lead to a transformation in the utilization of light alkanes, natural gas and shale resources for the commercial production of fuels and chemicals.

1. INTRODUCTION

1.1 Background

The work in this thesis is focused on the production of olefins from light alkane resources. Olefins are unsaturated hydrocarbons having one or more carbon-carbon double bonds in their molecular structure. Examples include ethylene, propylene, butylene and butadiene. They are important building blocks for chemicals and fuels production. Producing consumer goods like plastics, detergents, and solvents may not be possible without them. Gasoline fuel is also comprised of 3 – 9% by volume of olefins; and over 25% by volume of higher alkanes that can be derived from the olefins. The wide usage of olefins as raw materials can be attributed to their abilities to participate in many kinds of chemical reactions. Addition, oligomerization, polymerization, and oxidation reactions are some of the reactions that they can participate in. The strong reactivity of the olefins is caused by their possession of doubles bonds. Their double bonds could be broken and rearranged to form new molecules during chemical reactions.

Olefins, which are also known as alkenes, have two or more hydrogen atoms less than the corresponding alkanes. Hence, they can be obtained from the corresponding alkanes by removing one or more hydrogen molecules. For example, one hydrogen molecule may be removed from ethane to produce ethylene as in the below dehydrogenation reaction.

$$C_2H_6 \quad \rightleftharpoons \quad C_2H_4 \quad + \quad H_2$$
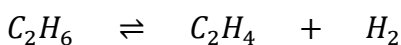
Unlike the olefins, however, alkanes are highly stable hydrocarbon; and do not readily participate in chemical reactions. This is because, in contrast to the olefins, alkanes do not possess any double bonds in their molecular structures. So, high amount of energy has to be employed to convert an alkane into the corresponding olefin. For example, it requires 137 KJ of energy to convert a mole of ethane to ethylene in the dehydrogenation reaction above. Supplying such amount of energy typically means subjecting the ethane molecule to a high temperature thermal decomposition process. Temperatures as high as 900 ^{o}C are employed in industrial ethane cracking plants.

The difficulty in breaking the molecule of ethane to ethylene may be explained thermodynamically with figure 1.1. Figure 1.1 is a plot showing how ethane conversion at equilibrium varies with temperatures for different pressures. From the plot, it is evident that achieving high conversion of ethane per pass requires a correspondingly high temperature for any given pressure. The impact of pressure on conversion is not insignificant either. For a given temperature, higher conversions of ethane are achievable with lower pressures. Hence, a combination of high temperatures and low pressures is generally required to covert a molecule of ethane to ethylene. These operating conditions are typically anywhere between 800 – 900 °C and 1.5 – 2.5 Bar in industrial thermal cracking plants, where about 65% per pass conversion of ethane obtains.
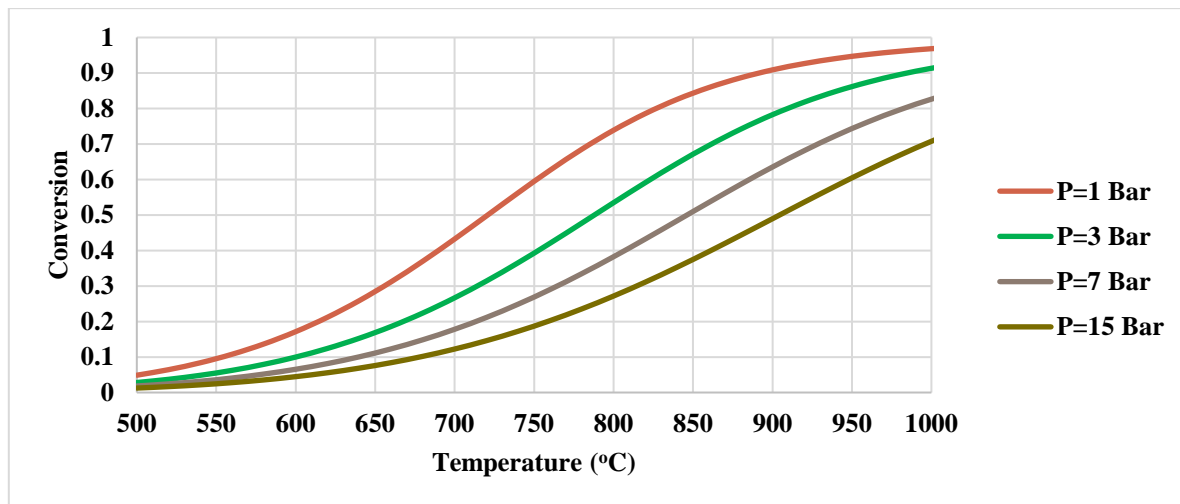
Figure 1.1: Equilibrium Conversions of Ethane at Different Temperatures and Pressures

Apparently, the need for high temperature is a fundamental challenge for ethane conversion to ethylene process. The process of generating, supplying and controlling heat for the high-temperature process is by no means simple. This complexity can be summed up in the fact that in industrial thermal cracking of ethane, heat has to be transferred to the cracking reactor in ultra-seconds, 0.1 – 0.3 seconds, whereas the product stream upon exiting the reactor has to be cooled even within lesser times; below 500 °C in 0.02 – 0.05 seconds. These ultra-seconds time scale requirement of these processes qualifies the difficulty with heat management and control around ethane (and other alkanes) thermal cracking plants. However, the ultra-seconds time scales are required to inhibit unwanted side reactions occurring during the alkanes cracking to olefins.

Indeed, heat management considerations are essential in synthesizing processes for olefin production. However, just as with any other chemical processes, raw material nature will influence process synthesis and design considerations in the first instance. Shale gas is a natural source of ethane and other light alkanes that can be utilized to produce olefins, with the alkanes making up to 30 mol% or more of its composition.

Shale gas is available in abundance and its production continues to rise. Figure 1.3a and 1.3b illustrate this abundance in the United States. By 2040, shale gas production rate in the United States is projected to double the present rate in 2020 (Figure 1.2a); and over the next 20 years, the country will be producing more natural gas than it will be consuming (Figure 1.2b). While crude oil fractions such as naphtha and gas oil are some other raw materials that are typically employed in producing olefins, the continued abundance of shale gas resource and its relatively high light alkane content compare to other kinds of natural gas resource make it especially worthwhile to explore process synthesis options for olefin production using shale gas as raw material.
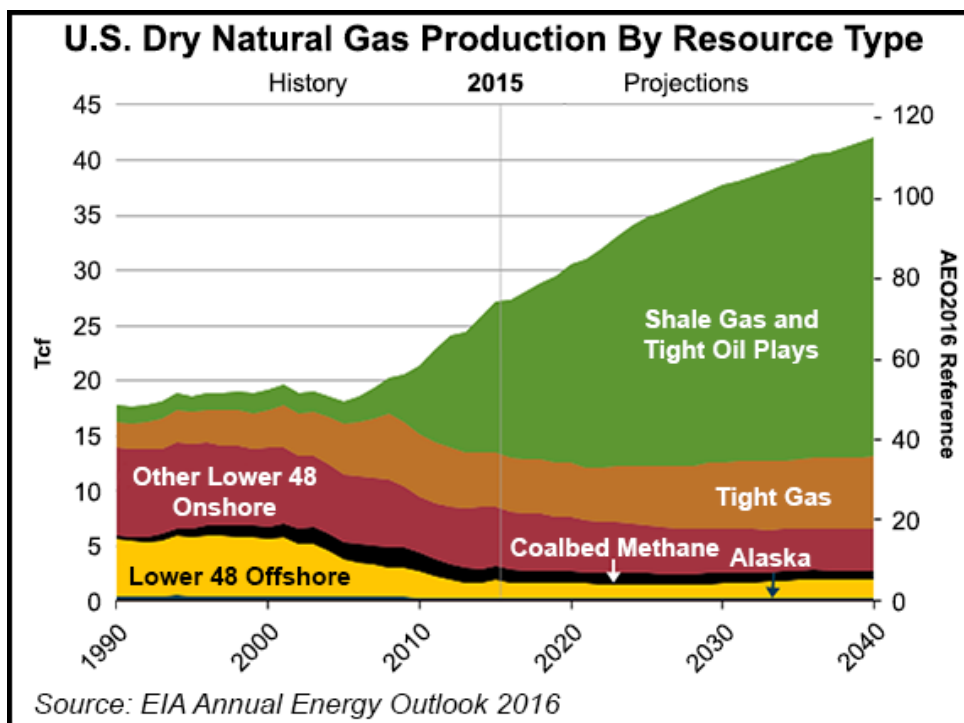
Figure 1.2a: US Dry Natural Gas Production by Resource Type (Source: EIA Annual Energy Outlook 2016)
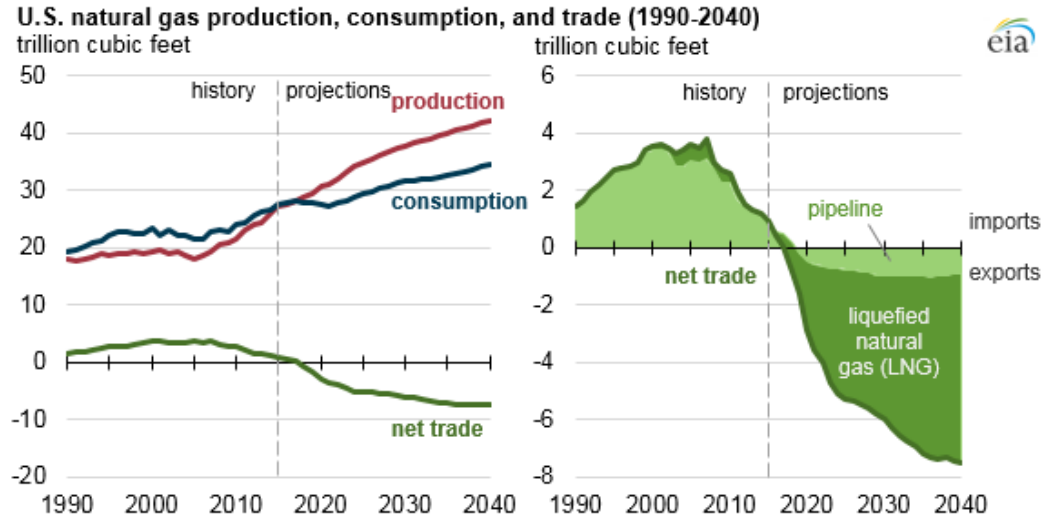
Figure 1.2b: US Natural Gas Production, Consumption and Trade (Source: EIA Annual Energy Outlook 2016)

There are existing commercial technologies for the processing of natural gas resource, including ones for the production of olefins from the gases. The existing gas- to-olefin technologies include steam ethane cracking in which ethane is subjected to high temperature thermal decomposition to ethylene in the presence of steam, and catalytic dehydrogenation technologies where catalysts are utilized to influence the production of on-demand propylene and butylene from propane and butanes respectively.

However, given the nature of shale gas resource, it may not be economically viable to utilize the existing technologies for shale gas processing towards olefin production. These technologies are synthesized and designed to suit large scale processing, a fact which is at variance with the realities regarding the relatively new shale gas resource. Shale gas resources are available in small sized wells, scattered across many different local areas in the United States and other parts of the world. If shale gas resources are to be utilized with existing processes, the gases would have to be transported from their many different local production sites to central processing facilities many miles away. Utilizing pipeline infrastructures to transport the gases from the many different areas to central processing facilities will be cumbersome and could be commercially non-attractive. To take advantage of the abundant shale gas resource, having small-sized processing plants located near gas well-head or local gathering stations has been proposed and shown to be a potentially viable approach [36]. The objective in the present work is to synthesize processes, that are

amenable to small-scale operations or modularization, for the conversion of light alkane resources in shale gas to olefins.

1.2   Thesis Overview

The overarching problem statement for this thesis may be described as follows: *Given a shale gas mixture, how can its light alkane contents be transformed to the most valuable olefins in the simplest way possible, such that, an otherwise and inherently complex gas conversion process, may become amenable to modularization?* To address the stated problem, reaction engineering and thermodynamic principles are employed to unravel and analyze new process concepts and configurations. These will be covered in two chapters. In the next chapter - chapter 2 - a novel chemical process concept is introduced and studied as an alternative to the conventional steam cracking process for olefin production. In chapter 3, energy utilization and heat management considerations were used to develop new process configurations. The process configurations described in chapter 3 are extensions of the process concept introduced in chapter 2.

Graphs and figures in this thesis are in colored prints to distinguish among important components and features where necessary. Accordingly, readers are advised to study this thesis in its colored format.

2. REPLACING STEAM WITH METHANE IN THERMAL CRACKING PROCESSES FOR OLEFIN PRODUCTION

2.1 Introduction

Steam cracking is the current leading technology for the commercial production of olefins. In the steam cracking process, feed material such as ethane and other alkanes are cracked at 750 ºC – 900 ºC and 1.7 Bar – 2.5 Bar using a plurality of reactor tubes that are placed in the radiant section of a thermal furnace. The cracking reactions occur very rapidly at residence time of 0.1 – 0.5 seconds in the presence of steam. Depending on the type of feed, steam to hydrocarbon ratio in the feed could vary from 0.25 – 0.85 Kg steam/Kg hydrocarbon. For steam ethane cracking, in which the hydrocarbon feed is mostly pure ethane, a ratio of 0.3 – 0.35 Kg steam/Kg ethane is typical. Steam presence in the feed has multiple benefits. They are as follows.

1. Steam acts as diluent during hydrocarbon cracking. Since low pressure favors conversion for alkanes cracking or dehydrogenation, having steam in the feed mixture helps to reduce the hydrocarbon (alkanes) partial pressure and consequently improves their conversion. Conversion of ethane in commercial steam ethane cracking plant could be 60 - 75%. [55]

2. Thermal cracking reactions involve series of free-radical reactions; some of which are undesired. Besides olefins, unwanted side products including methane, acetylene, benzene and heavier components are produced as part of the high temperature reactions. Meanwhile, most of the unwanted side products are obtained from reactions that are favored by high pressures. Acting as a diluent, steam helps to reduce the pressure of hydrocarbons during the cracking reactions. Accordingly, the influence of undesired secondary reactions during cracking is reduced while the formation of the desired primary products, olefins, is favored. [55]

3. The presence of steam helps to minimize coke deposition. Coke deposition on the internal walls of reactor tubes during cracking reactions, if not properly managed, could lead to unwarranted shut down of the cracking furnace and financial losses. Although slightly and partially, steam reacts with coke, removing some of it as oxide gases. It also lowers the number of condensation reactions, which are responsible for coke formation in the reactor tubes.

Indeed, the presence of steam as a diluent in the cracking reactor tubes is hugely beneficial for olefin production. However, a careful look at the composition of shale gas inspires new curiosity. Consider Table 2.1, which provides examples compositions of shale gas from three different regions in the United States. As in the table, methane typically makes up over 50% by mole of the components in shale gas. It is a natural and abundant constituent of shale gas.

Table 2.1: Shale Gas Composition for Three Well Regions in the United States

Species	Mole Percentage (%)		
	Barnett Region	Eagle Ford Region	Bakken Region
Methane	85.5	74.3	57.8
Ethane	6.6	13.8	20.0
Propane	1.9	5.4	11.4
Butanes	1.3	2.8	3.8
Higher Alkanes	0.3	3.0	1.3

And, methane is the most thermally stable of hydrocarbons up to 1027 ºC [13]. Accordingly, it may be argued that methane will not crack nor be decomposed under thermal cracking conditions typical for the pyrolysis of light alkanes. If that is the case, how about using methane as the diluent for light alkane cracking rather than steam (that is replacing steam with methane)? This is a worthwhile question to consider given the potential impacts/benefits such possibility could have for olefin production using the light alkane resources in shale gas.

1. If shale gas were to be the starting raw material in a conventional steam cracking facility, then there will be a need for an upstream demethanizer to remove methane from the natural gas mixture. Methane separation from natural gas is an energy-intensive process; and may not be suitable for modularization. Meanwhile, methane is an undesired byproduct of the cracking process and is typically separated from the steam cracker product stream. So, with a feedstock already containing methane that need to be removed prior to it being fed to the reactor, methane would have to be removed in two different stages – before and after reaction. Apparently, this will be quite a complex process. Having a process scheme with less separation difficulty; where methane is to be removed in only one stage - after reaction, will make for a simpler and a more modularizable process for producing olefins using light alkane

resource from shale gas. More so, removing methane at a downstream stage after light alkanes have been converted to heavier compounds (olefins etc.) will be simpler than separating methane from the light alkanes.

2. In a world troubled with water scarcity in some of its parts, eliminating the need for diluent water in thermal cracking facilities will help to relieve the pressure on the global need for water, reduce energy consumption for water production, and enhance long-term environmental sustainability.

3. Water has a high latent heat that must be supplied to convert it to steam. Converting water to diluent steam, therefore, involves the use of high amount of energy. Methane, on the other hand, need not undergo any phase change to be used as a diluent. It is already a gas even at ambient conditions.

Given the potential benefits highlighted above, the benefits of replacing steam with methane as diluent in thermal cracking of light alkanes sourced from shale gas are quite apparent. However, it is not clear what the chemistry for the thermal cracking process will be in the presence of methane. On the other hand, the kinetics and product distribution patterns for the thermal cracking of alkanes in the presence of steam are well known. How will replacing steam with methane change the narratives? What will the product distribution look like with a methane diluent? Will methane perform as well as steam in suppressing unwanted secondary reactions and coke formation? Providing answers to these questions will be the focus of the rest of this chapter.

2.2   Literature Review

There has been a lot of research works and study for hydrocarbon cracking over the past decades. A lot of studies have focused on understanding the product distribution and determining the reaction mechanisms for single-component cracking, including the cracking of methane, ethane, propane and butanes, as well as mixture cracking such as cracking of ethane-propane mixture. In what follows, the accounts of some of the relevant works that have been done in the literature regarding the chemistry of thermal cracking processes are provided.

Sundaram and Froment are among the popular workers who carried out extensive studies for the cracking of ethane, propane, butane and their mixtures using both experimental and mathematical modeling techniques. Their works are widely accepted as the standard for describing

the pyrolysis (or cracking) of light hydrocarbons. In their first paper of a series [45], Sundaram and Froment developed molecular reaction schemes from observed experimental product distributions to describe the thermal cracking of ethane, propane and their mixtures. The experiments were carried out at reactor outlet temperatures of 780 ºC – 850 ºC and pressures of 1.5 – 2 atm. Their molecular model (including kinetic parameters) is comprised of five reactions to describe the cracking of ethane; nine reactions to describe the cracking of propane and ten reactions to describe ethane-propane mixture cracking.

In another paper by Sundaram and Froment [46], a more detailed reaction scheme involving free-radical species were provided to explain light alkane cracking. A total of 133 free-radical reactions, with kinetic parameters, were provided to explain single-component as well as mixture cracking of ethane, propane, n-butane, isobutane, ethylene and propylene.

Sundaram and Frenandez-Baujin provide a qualitative analysis to describe the impact of methane and hydrogen presence on the thermal cracking of light alkane [43]. They carried out experiments to determine the product distribution when different mixtures of steam, methane and hydrogen are considered as diluents in the pyrolysis of ethane, propane and butane. Their results indicated that methane and hydrogen presence decrease the yield of ethylene but enhances that of propylene for ethane cracking. For the cracking of a mixture of ethane and propane, the presence of methane and hydrogen enhances the yield of ethylene but decreases that of propylene. For the cracking of a mixture comprising ethane, propane, and butanes, methane and hydrogen presence enhances the yield of ethylene but decreases that of propylene. While the results from Sundaram and Frenandez-Baujin provide some understanding of the impact of methane presence in light alkane cracking, their work did not consider methane as a lone diluent. Methane was used as a component in a mixture of diluent comprising steam, methane and hydrogen in their experimental runs. Understanding the impacts when methane is the lone diluent is necessary for the consideration in the present work.

In 1991, Holmen et al investigated the impact of adding ethane and propane as additives on the thermal cracking of methane in the temperature range of 1000 ºC – 1200 ºC at atmospheric pressure. It was observed that the presence of ethane and propane enhances the conversion of methane due to the free-radical nature of the reactions. Ethane is formed as a primary product in in the cracking of methane. While the formation of radicals from methane is slow, ethane readily decomposes to ethylene and hydrogen at high temperatures. This leads to chain reaction that

culminates in more cracking of methane. Hence, the presence of ethane enhances methane cracking. However, this study is carried out at temperatures greater than what is required for light alkane cracking viz. 750 – 900 ^{o}C. For a temperature of 1200 ^{o}C, Holmen et al recorded a methane conversion of 5.8% in 0.19 seconds.

Some other studies have proposed reaction mechanisms to describe the cracking of methane as a lone component at temperatures of 1000 ^{o}C and below. Olsvik and Billaud proposed a detailed 35-step reversible free radical reactions to explain the formation and consumption of the species formed during the early stages of the thermal cracking of methane at 1000 ^{o}C, with methane conversions ranging from 0.05% to 0.69% at residence times of 0.27 - 2.12 seconds. Keipi et al also adopted a 37-step reaction mechanism to describe the thermal decomposition of methane at temperatures of 797 ^{o}C – 1177 ^{o}C.

In all of the above and to the best of our knowledge, there is no product distribution analysis or details of chemistry to carry out same for a case where methane is treated as a lone diluent for light alkane cracking. The closest to such analysis is the work done Sundaram and Fernadez-Baujin [43]. Even at that, details of reaction mechanisms and/or product distributions were not provided by Sundaram and Frenandez-Baujin. Only qualitative explanation of the impact when a mixture containing methane is used as diluent was provided. It is the objective in the present chapter to determine the impacts and product distribution when methane is the lone diluent for light alkane cracking.

2.3   Methods

Ethane, propane and butanes are the light alkane resources that are considered for the present study. Since reaction mechanisms and kinetic parameters for the cracking of feed mixture comprising methane and light alkanes are unavailable, available data for single-component cracking of each of the component are obtained from different literature sources and superimposed. Such method of superimposition was also used by Sundaram & Fromnent to explain the cracking of ethane-propane mixture [45]. Given their completeness and wide acceptability, the free-radical reaction mechanisms for single-components cracking of ethane, propane and butanes published by Sundaram and Froment were adopted [46]. The Sundaram and Froment's free-radical model is comprised of 49 reactions for ethane-only cracking; 80 reactions for propane-only cracking; 86

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reactions for n-butane-only cracking; and 86 reactions for iso-butane-only cracking. For methane-only cracking, the 37 free-radical reactions used by Keipi et al was adopted.

The adopted kinetic models were superimposed and categorized into two sets: *Model A* and *Model B*. With Model A, it was taken that methane influence under light alkane cracking conditions (less than 1000 ^{o}C and ultrafast) can be ignored; that methane is completely non-reactive. Accordingly, only reaction sets and kinetic parameters from Sundaram & Froment for ethane, propane and butanes cracking were considered in Model A. Cumulatively, Model A contains 95 free-radical reactions to explain the cracking of ethane-propane-butane mixture. With Model B, it was assumed that methane participates slightly in the cracking reactions. Accordingly, the reaction sets from Keipi et al were superimposed with those for the cracking of ethane-propane-butane mixture in Model A. Cumulatively, Model B has 129 reactions.

Two classes of cracking, *single-component cracking* and *mixture cracking* were studied. A study of ethane-only cracking was adopted for the single-component cracking. For the mixture cracking, studies involving the cracking of ethane-propane-butane mixture was adopted. The two classes were studied with methane as the diluent on the one hand, and with steam as the diluent on the other hand. Using steam as a diluent, on one part, is necessary to compare the performance of the present approach with the conventional steam cracking process. Table 2.2a and 2.2b provide the details of the feed composition for the cases involving steam as a diluent and the ones involving methane as a diluent respectively.

Table 2.2a: Cracker Feed Compositions for when Steam is the Diluent

Component	Feed Mole Fraction	
	Single-Component Cracking (Ethane Only)	*Mixture Cracking (Ethane, Propane & Butane)*
Steam	*0.785*	*0.622*
Ethane	0.215	0.215
Propane	0.000	0.122
Butane	0.000	0.041
Total	**1.000**	**1.000**

Table 2.2b: Cracker Feed Compositions for when Methane is the Diluent

Component	Feed Mole Fraction	
	Single-Component Cracking (Ethane Only)	Mixture Cracking (Ethane, Propane & Butane)
Methane	0.785	0.622
Ethane	0.215	0.215
Propane	0.000	0.122
Butane	0.000	0.041
Total	1.000	1.000

ANSYS Chemkin Pro, a software tool for modeling gas phase and surface chemistry, was used to carry out product distribution studies. In addition to reaction mechanisms and kinetic parameters, other information needed as inputs in Chemkin are reaction conditions, reactor profile, feed profile, and thermodynamic data. These thermodynamic data include heat of formation, entropy, and heat capacities for every gas-phase specie participating in the reactions. There are 39 species, including compounds and free radicals, involved in all the reactions considered. The thermodynamic data for some of the species, especially for compounds, are available in Chemkin. For some of the free radicals, the data are not available. The unavailable data are obtained from the literature. Further details are provided in the appendix. The cracking reactions are modeled in Chemkin as plug flow with isothermal temperature profile for a reaction temperature of $850\,^{\circ}C$ and pressure of 2 Bar. Product distributions at different residence times are obtained for the different feed cases considered.

2.1 Results and Discussion

2.1.1 Product Distribution and Analysis

Figure 2.1a: Product Distribution Obtained Using Model A for Ethane-Only Cracking Carried Out with Steam Diluent

Figure 2.1b: Product Distribution Obtained Using Model A for Ethane-Only Cracking Carried Out with Methane Diluent

Figures 2.1a and 2.1b are product distribution plots for ethane-only cracking using steam and methane as diluents respectively, obtained from applying Model A to carry out the studies in Chemkin. The main products formed, ethylene, hydrogen and methane, as well as unconverted ethane, diluent steam and diluent methane are indicated on the plots. Comparing the two figures, it is observed that the product distribution profile is the same either steam or methane is used as diluent. The mole fraction of ethylene and that of hydrogen follow similar trends in both cases. The difference between the two plots is in the profiles for steam and methane, the diluents. In figure 2.1a, the composition of steam diluent in the product decreases slightly with residence time, a consequence of increases in the compositions of products that are being formed as cracking reaction proceeds. In figure 2.1b, the composition of methane diluent decreases less slightly than the way steam diluent's composition decreases in figure 2.1a. This is because, methane is itself one of the products that are being formed during cracking. Hence, the profile of methane in figure 2.1b represents that for a combined composition of methane initially present as diluent and new ones that are being formed as reaction proceeds. In figure 2.1a, where steam is the diluent, the profile for the slight amount of methane being formed as part of reaction products is indicated.

Figure 2.2a: Product Distribution Obtained Using Model A for Ethane-Propane-Butane Cracking Carried Out with Steam Diluent

Figure 2.2b: Product Distribution Obtained Using Model A for Ethane-Propane-Butane Cracking with Methane Diluent

Figures 2.2a and 2.2b are product distribution plots for mixture cracking of ethane, propane and butane using steam and methane diluents respectively, obtained from applying Model A to carry out the studies in Chemkin. In addition to ethylene, hydrogen and methane, other key products indicated on these plots include propylene and butadiene. Profiles for unreacted steam, methane, ethane and propane are also indicated on the plots. Like in the previous cases for single-component cracking, it is observed from figures 2.2a and 2.2b that the product distribution profile when steam is used as diluent is the same as the profile when methane is the diluent. Again, the difference between the two plots is in the profiles for steam and methane - the diluents. In figure 2.2a, the composition of steam diluent decreases slightly as reaction proceeds. In figure 2.2b, on the other hand, the composition of methane diluent increases slightly as reaction proceeds. Although, it is expected that methane will be formed as a product during cracking and will contribute to the observed composition profile of methane on the plots, the noticeable increases (unlike in figure 2.1b) is a result of the formation of high quantity of methane from the cracking of propane and butane. In figures 2.1a and 2.1b, methane formation results from the cracking of ethane only. However, for mixture cracking in figures 2.2a and 2.2b, the formation of methane results from not only the cracking of ethane but also from the cracking of propane and butane.

Figure 2.2a, in particular, when compared to figure 2.1a, indicates how the cracking of propane and butane leads to huge formation of methane. These results are consistent with the product distribution patterns in the literature for the conventional steam cracking process [45, 46, 55].

From the foregoing, it is seen that, in general, the product distribution profiles when methane is used as a diluent is not different from the profiles when steam is the diluent.
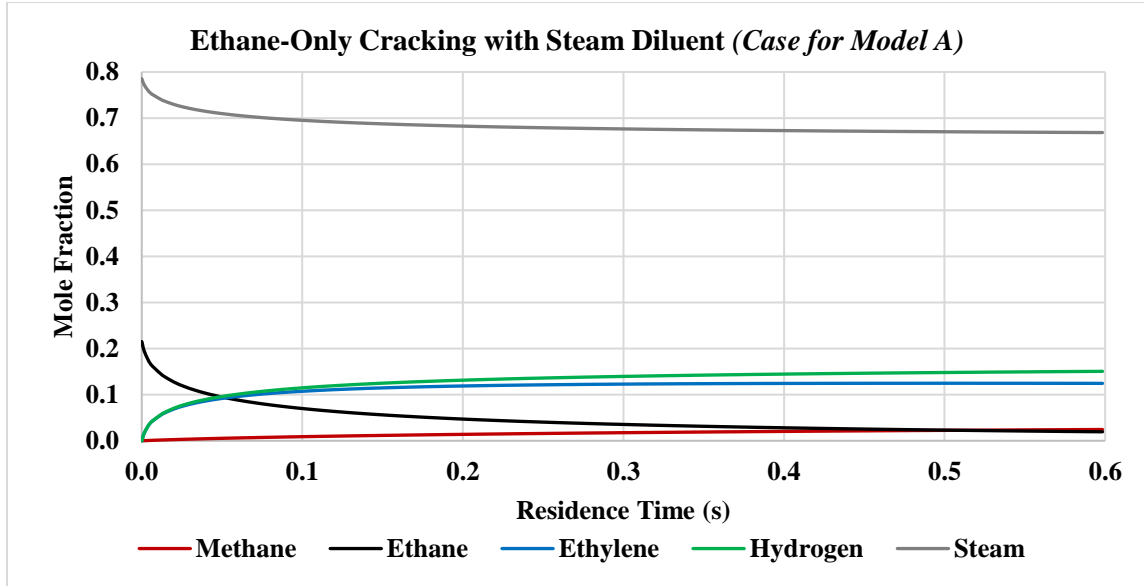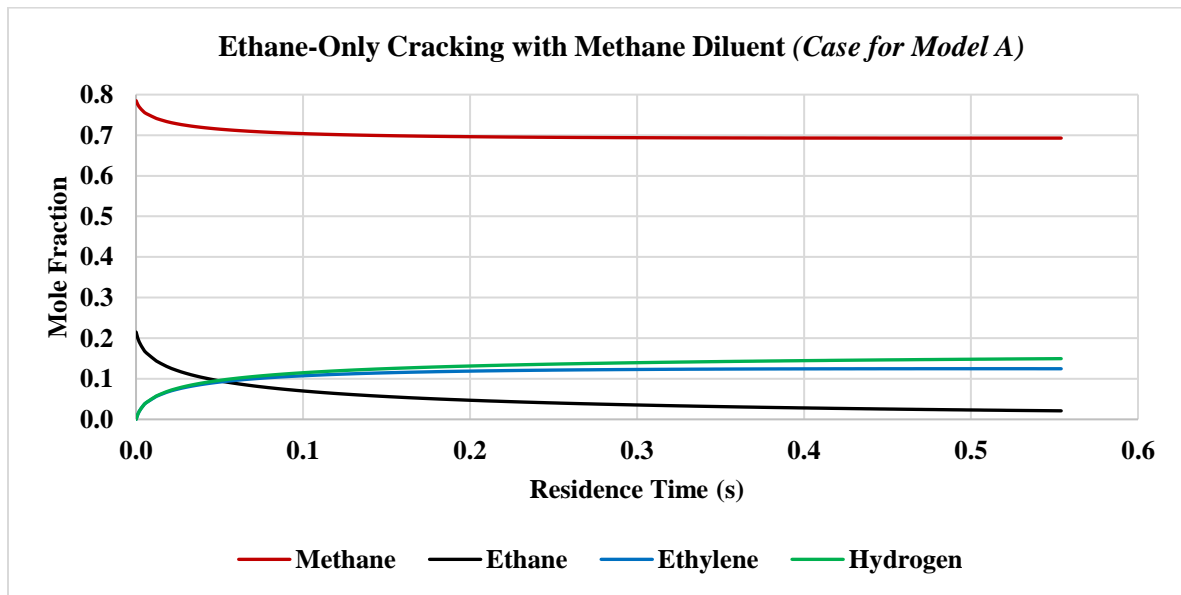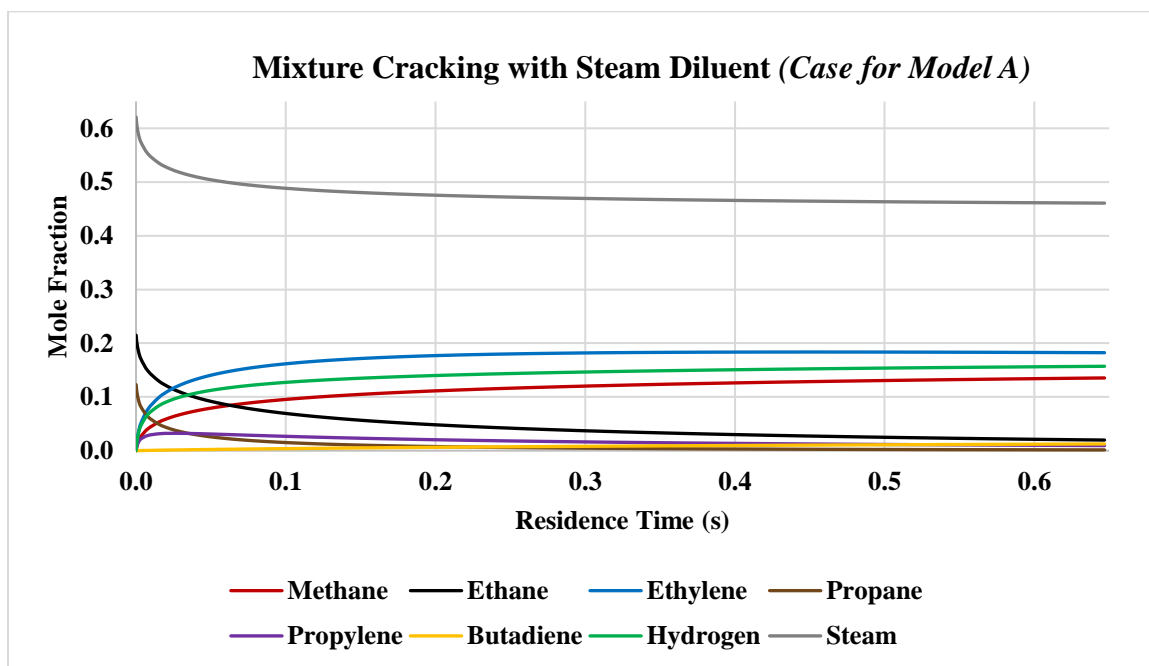

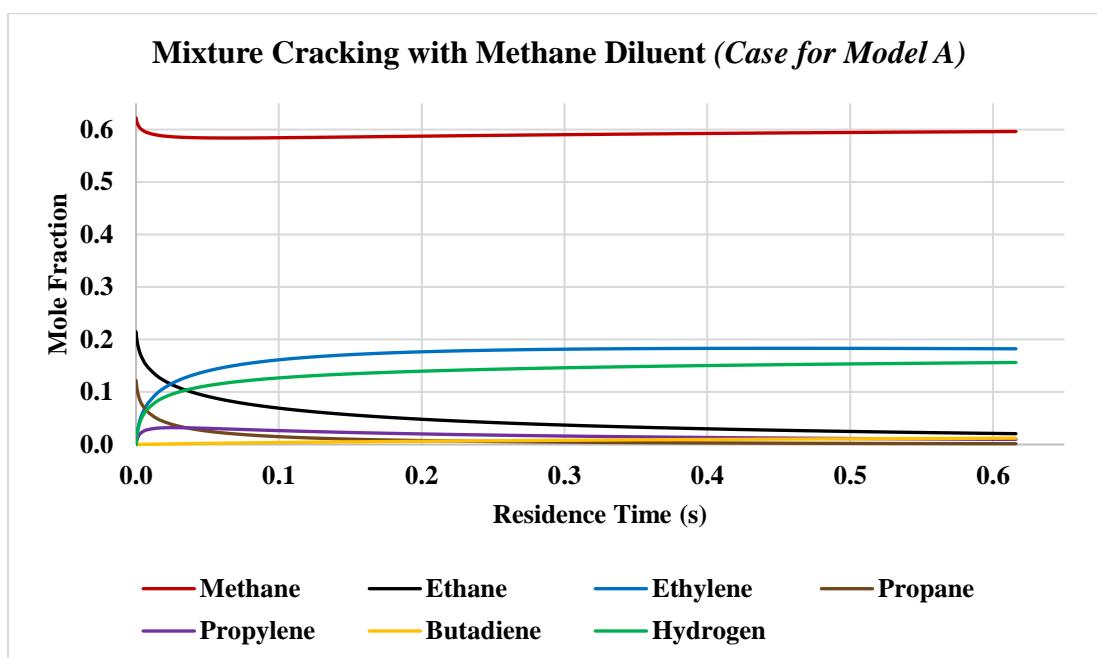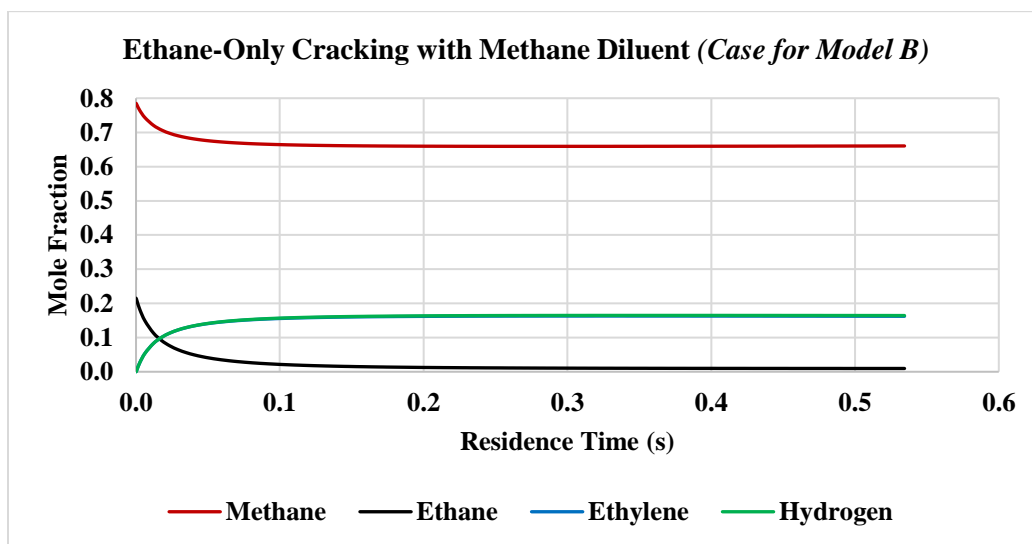Figure 2.3a: Product Distribution Obtained Using Model B for Ethane-Only Cracking Carried Out with Methane Diluent
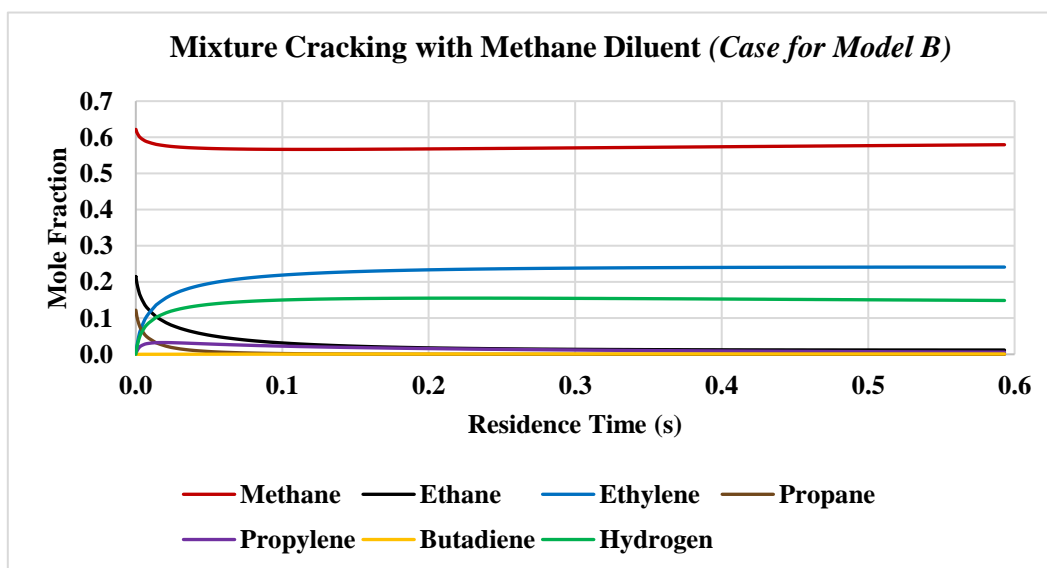
Figure 2.3b: Product Distribution Obtained Using Model B for Ethane-Propane-Butane Cracking with Methane Diluent

What about *Model B*, where methane cracking kinetics are superimposed with those for the light alkanes? What would the product distribution profiles look like with *Model B*, when methane is the diluent? Figures 2.3a and 2.3b provide answers to this question. Ethylene and hydrogen remain the key product for the single-component cracking case (figure 2.3a), while for the mixture cracking case (figure 2.3b), the products also remain ethylene, propylene, butadiene, and hydrogen. So, with Model B, the product components remain the same as when Model A is used.

However, a careful comparison of the plot in figure 2.3a with its counterpart in figure 2.1b is revealing. Observe that a higher yield of ethylene, the desired product, is profiled in the plot in figure 2.3a that the one in figure 2.1b. In figure 2.3a, the profile curve for ethylene yield intersects the profile curve for hydrogen yield, indicating that ethylene and hydrogen have about the same composition in the product stream even as reaction proceeds. In figure 2.1b, on the other hand, the profile curve for hydrogen lies above that for ethylene, implying higher compositions of hydrogen than ethylene. Table 2.3a provides further clarifications regarding this observation. The table provides details of compositions at a specific residence rime of 0.2 seconds for ethane-only cracking using methane diluent, with separate columns for the compositions when Model A and Model B are applied. The table also provides the composition for the case where steam is the diluent. While the mole fraction of ethylene is 0.119 when Model A is applied either using steam or methane diluent, the corresponding mole fraction of ethylene when Model B is used is 0.162. Accordingly, there is a 36% increase in the concentration of ethylene in the product distribution when Model B is used compared to the result when Model A is used. Evidently, there is also a decrease in the production of the undesired methane byproduct with Model B. This result demonstrates the favorability of using methane as a diluent even when it is considered that methane is slightly participating in the reaction.

Table 2.3a: Product Distribution for Ethane-Only Cracking at 0.2 Seconds

Components	Mole Fraction at 0.2 s for Cracking of Ethane		
	With Steam Diluent	*With Methane Diluent (Model A)*	*With Methane Diluent (Model B)*
Steam	0.682	-	-
Methane	0.013	0.696	0.660
Ethane	0.047	0.046	0.013
Ethylene	0.119	0.119	0.162
Butadiene	0.003	0.003	0.000
Hydrogen	0.132	0.132	0.164
Total	**0.996**	**0.996**	**0.999**

Figure 2.3b is the plot for the case of mixture cracking when methane is the diluent. Similar argument made for the single-component cracking also applies here. Applying Model B results in the yield of more ethylene than applying Model A. There is a 32% increase in the concentration of ethylene in the product distribution when Model B is used over Model A. However, the yield of the higher olefins including propylene and butadiene are suppressed. Although, in general, ethylene - being the most stable of the olefins at high temperatures - is the predominant olefin compound that result from thermal cracking reactions irrespective of feed composition, using Model B leads to a further suppression in the yield of the higher olefins. Table 2.3b provides more specific details of the compositions at a residence time of 0.2 seconds. Methane, when used as a diluent and considered to be slightly reactive, is favorably influencing the cracking of light alkane mixtures in such manner that ethylene production is greatly enhanced, while suppressing the formation of other products.

Between the two predictions with model A and model B, it may be argued that using methane as diluent in light alkane cracking is promising.

Table 2.3b: Product Distribution for Ethane-Propane-Butane Cracking at 0.2 Seconds

Components	Mole Fraction at 0.2 s for Ethane-Propane-Butane Cracking		
	With Steam Diluent	*With Methane Diluent (Model A)*	*With Methane Diluent (Model B)*
Steam	0.475	-	-
Methane	0.112	0.587	0.568
Ethane	0.048	0.048	0.018
Propane	0.007	0.008	0.000
Butane	0.001	0.001	0.000
Ethylene	0.177	0.177	0.234
Propylene	0.020	0.020	0.016
Acetylene	0.001	0.001	0.000
Butadiene	0.006	0.006	0.000
Hydrogen	0.140	0.140	0.155
Total	**0.987**	**0.988**	**0.991**

2.2   Conclusion

In this chapter, methane has been proposed and studied as a diluent to replace steam in thermal cracking, in an attempt to come up with a simple and modularizable process for the conversion of light alkane resources in shale gas to olefins. The proposed approach was evaluated using ANSYS Chemkin Pro. The results from the studies showed that using methane as a diluent is promising. Product distribution profiles indicate that, with methane as a diluent, similar or more favorable yields of desired products will result compare to when steam is the diluent. Also, ethylene remains the major olefin product that can be expected from the cracking of light alkanes at $750 - 900\ ^{o}C$ irrespective of feed composition.

The impact on coke formation of replacing steam with methane has not been accounted for in the present study. Indeed, coke deposition is an important consideration in thermal cracking. But a conclusion may not be reached on whether methane diluent will perform lass favorably or more favorably than its steam counterpart in limiting coke formation. Coke formation phenomenon in thermal cracking process is complex. It is predominantly a surface phenomenon involving reactor tube skin and the species in the gas phase cracking reactions. Accordingly, a homogeneous-only study, as in the present study, may not be adequate to investigate the consequences when methane is used as a diluent rather than steam. A rigorous study involving a combined surface and gas phase chemistry may be necessary to reach any conclusion.

3. PROCESS SYNTHESIS AND HEAT INTEGRATION AROUND LIGHT ALKANE CRACKING SYSTEM

3.1   Introduction

Thermal cracking of alkanes are high temperature processes, with typical reactor temperatures of 750 – 900 ℃, as well as operating pressures of 1.7 – 2.5 Bar and residence times of 0.1 – 0.5 seconds. There are three primary steps that must be carefully designed, controlled and integrated to ensure effective cracking operation. Process synthesis and heat management considerations must revolve around these steps. The three steps are feed preheating, cracking reactions, and cracked gas quenching; and are illustrated in figure 3.1.
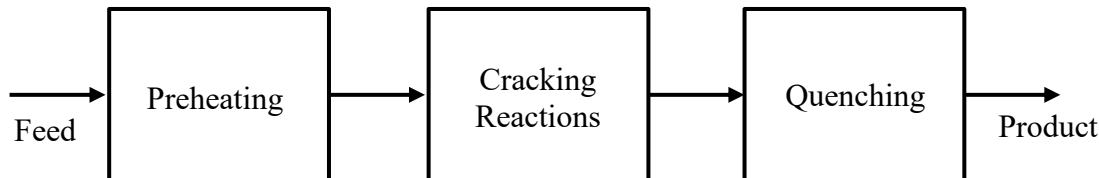
Figure 3.1: Basic Process Steps involved in Light Hydrocarbon Cracking

Feed Preheating: Depending on feed type, the mixture entering the cracking reactors are heated to incipient temperatures of 500 – 650 ℃, temperature points just before the commencement of the ultra-fast cracking reaction. In conventional thermal cracking processes where steam is used as diluent, the feed preheating is carried out in stages. Water is converted to steam, while hydrocarbon feed is first heated alone to high enough temperatures. The two streams are then mixed and continued to be heated until the mixture is at the desired inlet temperature.

Cracking Reactions: Within 0.1 – 0.5 seconds and at 750 – 900 ℃, gas-phase cracking reactions are carried out in tubular reactors (reactor coils) in thermal cracking plants. Short residence time is appropriate to control the cracking reactions. Prolonged residence time will result in undesired cracking reactions and formation of undesired heavier products, including coke. Coke formation is a critical concern is the operation of thermal cracking plants. As cracking reaction progresses, coke forms and deposits on the internal walls of the reactor coils. Besides loss of hydrocarbon material to coke formation, the direct impact of coke deposit includes increased pressure drop along the length of the reactor and increased inefficiencies in transferring heat to the

reactor internals. Accordingly, thermal cracking plants are often shut down every 20 – 90 days for decoking operation. Uncontrolled coke deposition on reactor walls could lead to severe consequences including unplanned plant downtime and revenue losses for operators.
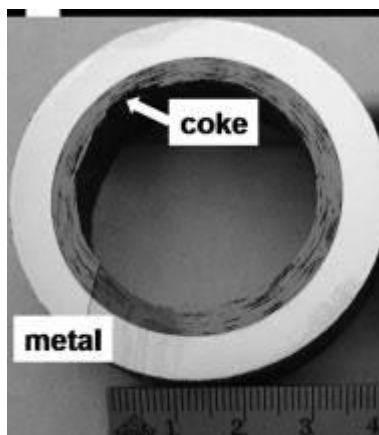
Figure 3.2: Pyrolysis Reactor Tube with Deposited Coke Layer [22]

Cracked Gas Quenching: To stop further reactions and limit the formation of undesired products and coke, the cracked gas (product stream) exiting the cracking reactor have to be cooled rapidly to temperatures below $500\,^{o}C$ within 20 - 50 milliseconds. Modern cracker plants employ transfer line exchangers (TLE) for this quenching process. The TLE, which is similar in design to a shell and tube heat exchanger, employs water for quenching. The cracked gas exchanges heat with a high-pressure saturated water stream. The saturated water extracts, at a minimum, an amount of heat equivalent to its latent heat of vaporization from the cracked gas; culminating in rapid cooling of the cracked gas.

3.1.1 Thermal Furnace System

Conventional thermal cracking furnaces are comprised of two sections: radiation section and convection section. The furnace employs hydrocarbon fuel burners to produce high temperature combustion heat. Radiant heat from the burners are transferred to reactor coils placed in the radiation section of the furnace to rapidly increase the temperature of the feed to reactor operating temperature, and then to supply the endothermic heat of reaction needed for cracking. Heat from the spent flue gas exiting the radiation section are then transferred by convection to streams that are being passed through the convection section of the furnace. Preheating of reactor feed mixture,

and thermal conditioning of boiler feed water for quenching are carried out in the convection section. The flue gas exiting the convection section are then discharged to the atmosphere at 100 – 150 ºC [39]. Figure 3.3 is an example of a furnace configuration with heat balances around it.
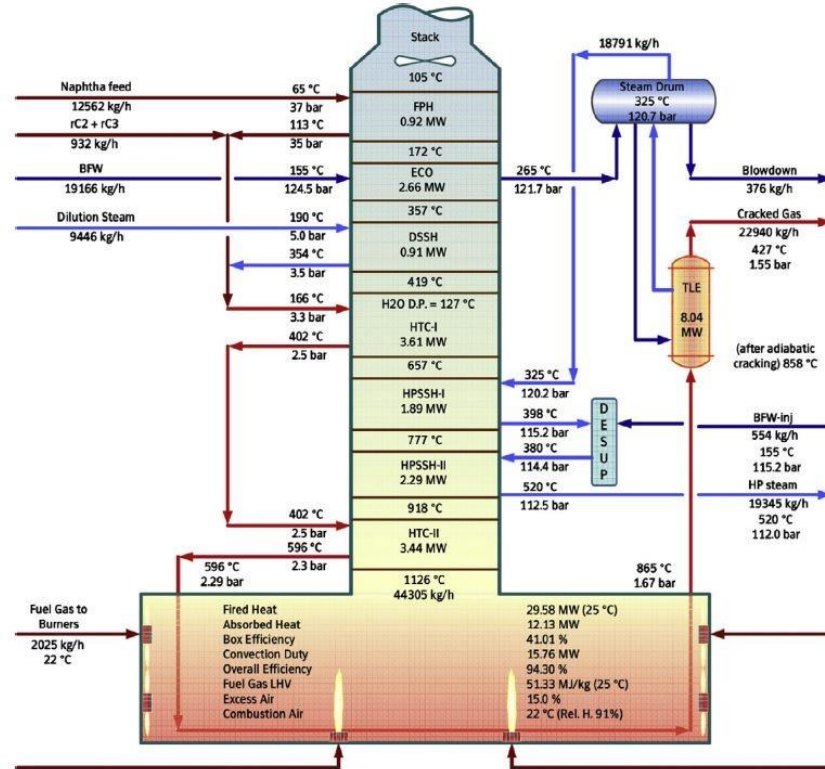
Figure 3.3: Thermal Cracking Furnace Design [39]

One limitation with conventional thermal cracking furnaces is that not more than 42% of the heat generated by combustion at the burners can be utilized in the radiation section [39]. Although, the overall energy efficiency of a furnace can be up to 95% depending on how effectively the energy in the spent flue gas stream are utilized in the convection section. Regardless, the fact that not more than 42% of the energy from the combustion can be utilized in the radiant section, where the cracking reactions takes place, is a concerning limitation. The consequence of this limitation is that the amount of hydrocarbon fuel or any other such fuel needed to process a unit quantity of reactor feed is fixed by how much of the energy from the fuel can be utilized in the radiant section. Thus, the quantity of fuel to be supplied to the furnace burners must be at least $\frac{1}{0.42}$ of the quantity needed to produce an amount of energy equivalent to the maximum amount of heat that can be utilized in the radiation section of the furnace.

Moreover, industrial thermal cracking furnaces are cumbersome structures with huge firebox volume that are designed to allow for effective distribution and optimal utilization of heat; and can be designed for production capacity up to 1500 Ktonne/Annum of Ethylene. Figure 3.4 depicts an example. Implementing such a huge structure for a small scale or modular process system, with an estimated capacity of 30 – 40 Ktonne/Annum of Ethylene, may not be feasible.

From the foregoing, if a thermal cracking process is to be adopted for small-scale or modular production of olefins using light alkane resources in shale gas, there is then a need to revamp existing design or process configurations for thermal cracking. Such a redesign is not only necessary to ensure structural compactness but to also ensure energy savings or less burning of fuel, and consequently less release of greenhouse gases.

Figure 3.4: Structural Image of an Industrial Thermal Cracking Furnace [56]

3.1.2   Objective

In this chapter, alternate means for the supply of heat to thermal cracking reactors are considered and studied for light alkanes cracking to olefins. The objective is to come up with process configurations with inherent structural compactness, and superior performance to conventional furnace systems in terms of energy utilization, energy savings, and reduction in carbon footprint.

3.2   Methods

Wismann et al carried out a detailed study, including experimental and computational analysis, of a steam methane reforming system, employing electricity to supply heat energy to its reactors. Their results indicate that by electrically heating the reforming reactor, achieving a reformer structure that is 100 times smaller than conventional reformer system is possible. Not only that, their design is also able to achieve reduced energy consumption and CO_2 emissions as waste heat streams that are associated with conventional reformer systems are eliminated [52]. The Wismann et al idea is extended to the analysis of light alkane cracking in the present work. This is a reasonable extrapolation given the fact that reformer system and thermal cracking system are governed by the same thermodynamic principles. Just as thermal cracking of light alkanes requires the supply of heat energy at high temperature, steam methane reforming similarly requires the supply of heat energy at high temperature to catalytically convert methane to syngas.

ASPEN Plus, a process simulation software, was used to carry out the analysis. First, base case flowsheets for the cracking of light alkane using the conventional furnace systems were simulated. Energy balance information around a thermal cracking furnace were obtained from the literature and adapted for the simulation [39]. The conceptual understanding resulting from this simulation efforts are then utilized in simulating new flowsheets where electrical energy are applied in supplying heat to the thermal cracking reactor. The cracking reactor was modeled with a RYield block in ASPEN Plus. Yields were calculated using the product distribution profiles obtained from the studies with Chemkin at a temperature of 850 ºC, pressure of 2 bar and residence time of 0.2 seconds for the cracking case in which methane is the diluent. The less optimistic kinetic model, Model A, was employed to generate the product distribution in Chemkin.

3.2.1   Base Case Simulations

Table 3.1 provides details of the feed composition and flowrates for all simulations in the present study. The configuration in figure 3.5a is the first of two base case flowsheets that are simulated, *Base Case A*. Combustion of methane produces the needed heat energy for the thermal furnace in this case. A total of 20.4 MW of heat is fired from the furnace burners. 8.57 MW of the fired heat (representing the maximum 42% utilization rate) is transferred to the cracker (cracking reactor) via radiation. The spent flue gas preheats the cracker feed and the boiler feed water.

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Table 3.1: Details of Cracking Reactor Feed Composition and Flowrates

Feed Components	Mole Fraction	Flowrate (Kmol/Hr)
Methane	0.622	309.8
Ethane	0.215	107.1
Propane	0.122	60.8
Butane	0.041	20.4
Total	**1.000**	**498.1**
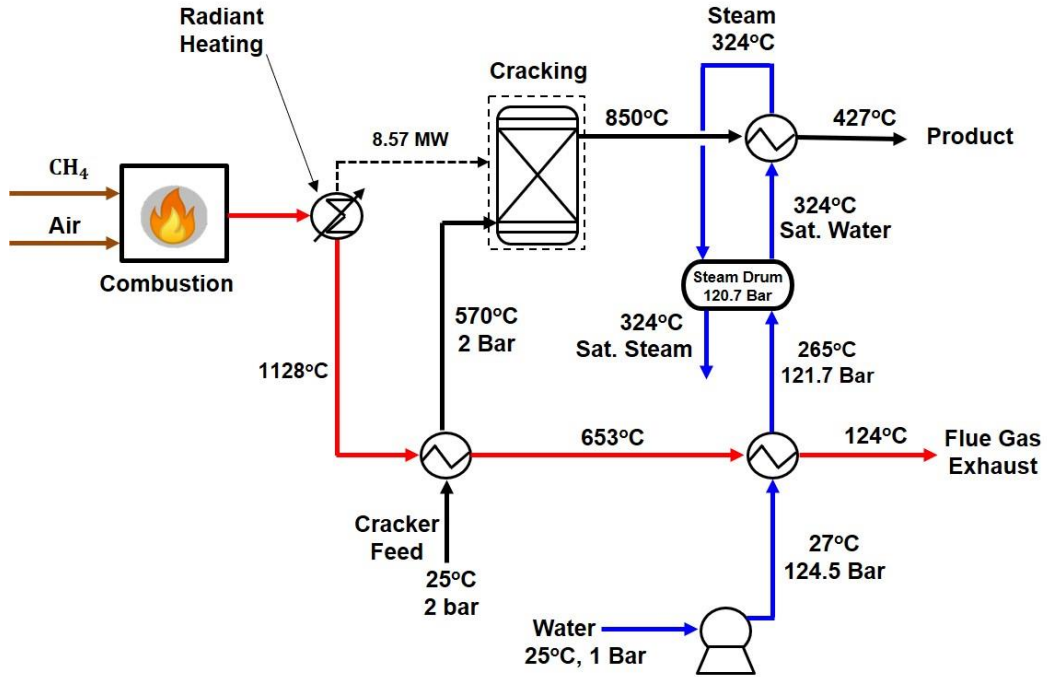
Figure 3.5a: Base Case A –Thermal Cracking Configuration with Conventional Furnace System using Methane as Fuel in the Burner

Figure 3.5a depicts another base case configuration, *Base Case B*. Here, a mixture of methane and hydrogen undergoes combustion in the furnace burner to supply needed heat to the cracking reactor. The hydrogen in the fuel mixture is obtained from the cracked gas (product stream), since hydrogen is one of the products of light alkane cracking. As with base case A, a total of 20.4 MW heat is fired in the furnace in base case B. Of this total, 14.4 MW results from the burning of methane, while approximately 6 MW results from the burning of hydrogen. Accordingly, the quantity of methane being burnt in base case B is 29.4% lower than in base case A. Except for a reduction in carbon footprint by 29.4%, however, the configuration in base case B

is the same as in base case A. Both have a maximum 42% energy utilization rate for cracking and same structural pattern.
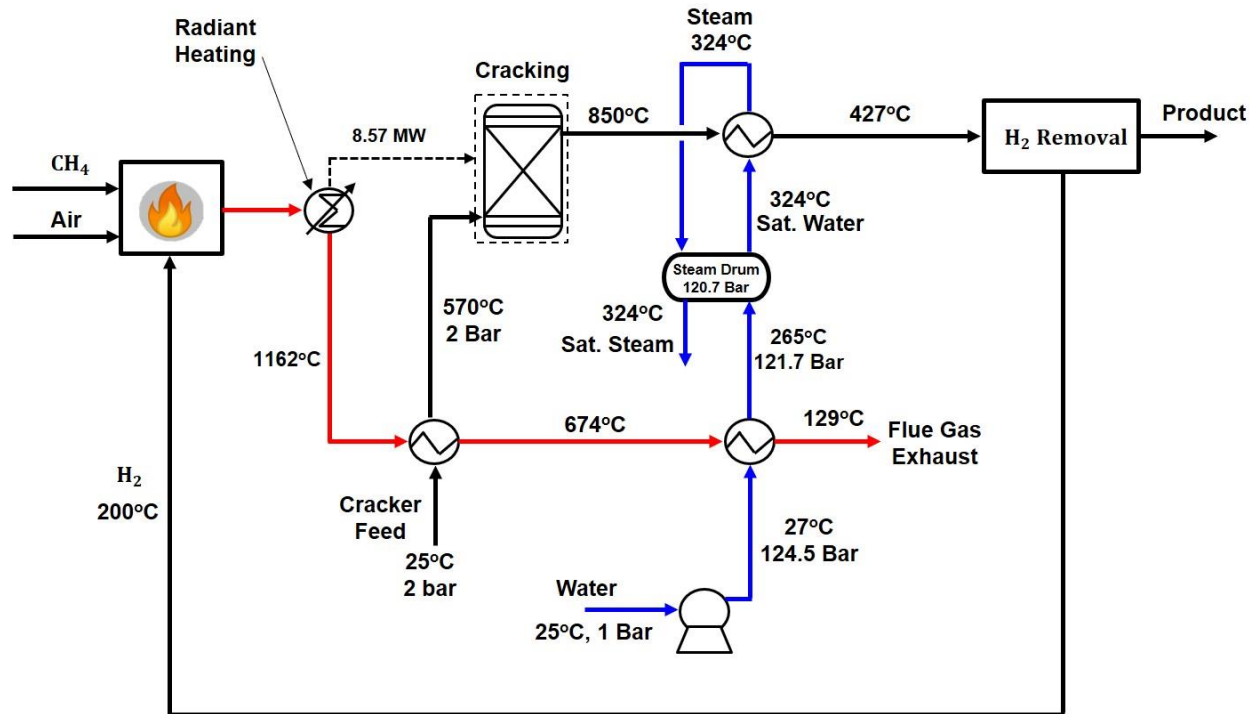
Figure 3.5b: Base Case B - Thermal Cracking Configuration with Conventional Furnace System using a Mixture of Methane and Hydrogen as Fuel in the Burner

3.3   Results and Discussions

Four new cases, in which electricity is employed to supply heat to the cracking reactor, are synthesized and studied. In each case, the goals are to ensure structural compactness and achieve more than 42% utilization of inputted energy for the primary cracking reaction, so that modularization, energy savings and less carbon footprint can result. In discussing the results, comparisons will be made with base case B. This is because all the four new configuration cases involve the use of hydrogen, in one way or the other, as fuel in generating electricity. And of the two base cases illustrated under the methods section, it is only in base case B that hydrogen burning occurs in providing heat energy, through a furnace, to the cracking reactor. Thus, base case B will be used for comparisons. Going forward, base case B will be referred to as the *reference case*.

Case 1: Using Electricity from Gas Turbines to Power the Cracking Reactor
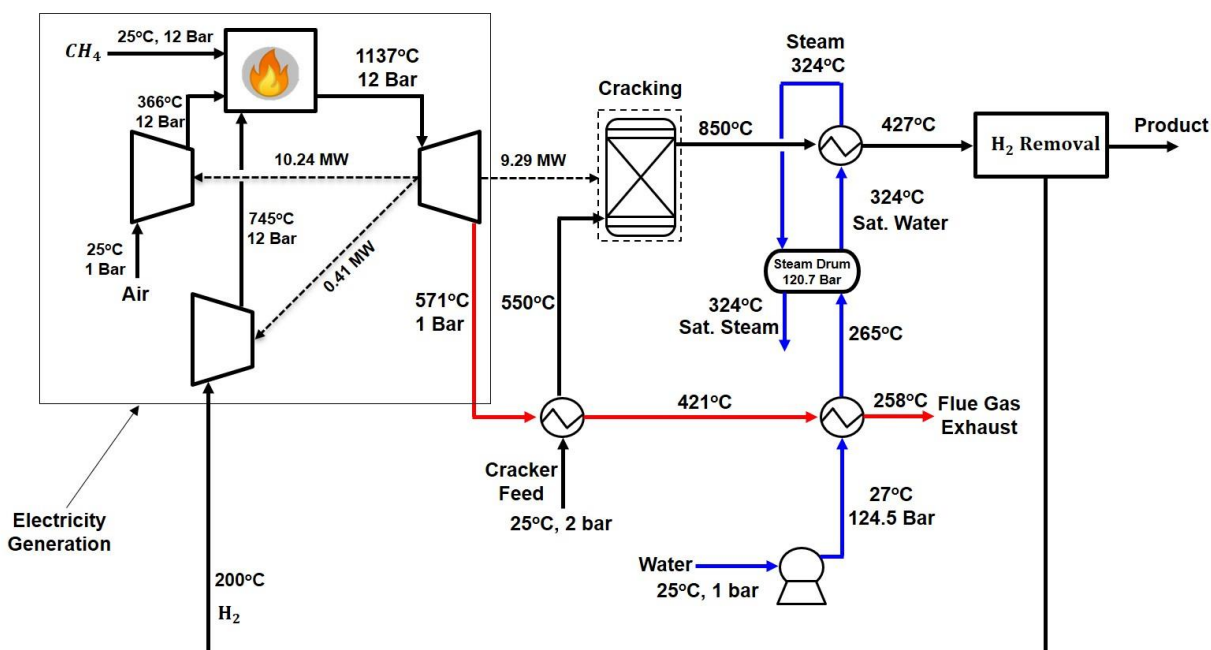
Figure 3.6: Case 1 – Using Electricity Obtained from a Gas Turbine System to Power the Cracking Reactor

In the configuration in figure 3.6, the need for a furnace is eliminated. Electricity is employed to supply heat to the cracking reactor. A gas turbine, burning a fuel mixture of methane and hydrogen, generates the required electrical energy. The hydrogen in the fuel mixtures is

obtained from the cracked gas (product) stream. The energy in the flue gas exiting the turbine preheats the cracking reactor feed to required inlet temperature, and also preheats the high-pressure water needed to quench the cracked gas. A thermal efficiency of 35% is attained in the gas turbine and an efficiency of 95% for the conversion of electrical energy to heat energy in the reactor is assumed. A total of 27.05 MW of energy, comprising 21 MW of energy from methane fuel and 6.05 MW from hydrogen fuel, was inputted into the gas turbine system. The cracking reactor consumes 9.29 MW of heat which is transferred to it as electrical energy. The '27.05 MW' energy input in case 1 is 32% more energy input than that for the reference case where a thermal furnace is employed. The 21 MW of energy sourced from methane also means that 46% more hydrocarbon fuel is being burnt in case 1 than in the reference case. The portion of inputted energy that is utilized for cracking in case 1 is also 34%; 8% less than the '42% utilization' in the reference case. From the foregoing, though it is the more structurally compact one, case 1 configuration involves the use of more energy, burning of more fuel and a higher carbon footprint than the reference case.

Case 2: Using Electricity from a Combined Gas Turbine and Fuel Cell Systems to Power the Cracking Reactor
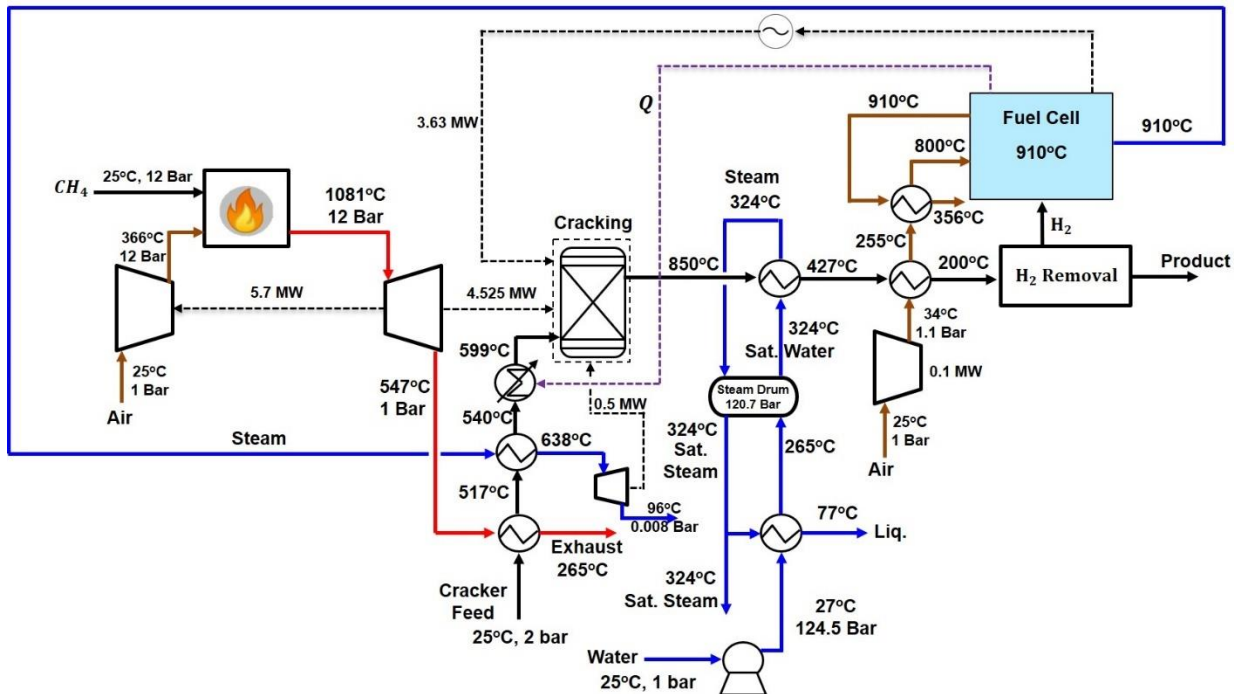
Figure 3.7: Case 2 – Using Electricity from a Combined Fuel Cell and Gas Turbine System to Power the Cracking Reactor

In case 2, (figure 3.7), the cracking reactor requires 8.66 MW of electricity. A hydrogen fuel cell is employed together with a gas turbine to co-produce electricity. Fuel cells are known to be more energy efficient than turbines. With an assumed efficiency of 60% in the fuel cell, 3.63 MW of electrical energy is produced from it. A steam turbine utilizes the steam exiting the fuel cell system to produce an additional 0.5 MW of power. So, only 4.5 MW of power needed to be produced from the gas turbine to meet the cracking reactor need. A portion of the steam from the quenching operation preheat the fresh water entering the quencher in what looks like a cyclic process. This eliminates the need to use heat from the exhaust flue gas stream to preheat the fresh water entering the quencher, as in the reference case. The percentage energy utilization for cracking in case 2 is 45.3%, a 3.3% improvement over the conventional approach in the reference case. The energy input from methane is also 13 MW; implying a 10% reduction in hydrocarbon burning compared to the reference case. The present configuration is demonstrably more energy efficient that the one in the reference case and has lower carbon footprint, besides being more structurally compact.

Case 3: Using Electricity from Grid Combined with that from Fuel Cell to Power the Cracking Reactor
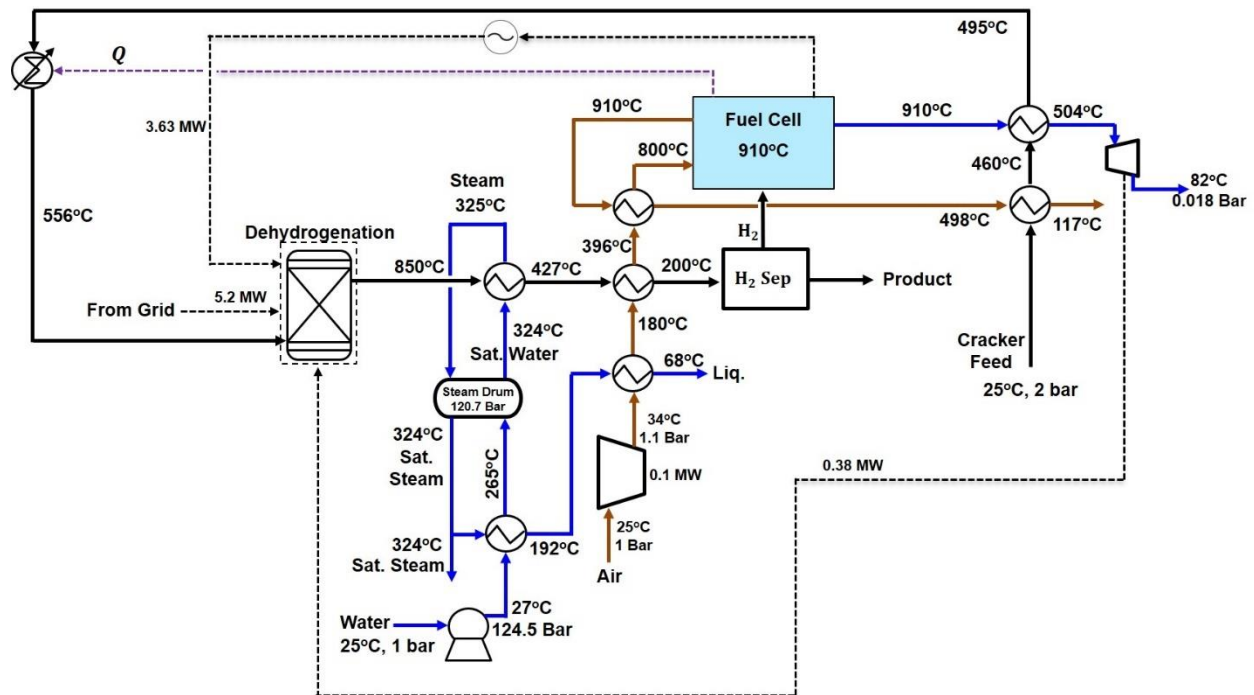
Figure 3.8: Case 3 - Using Electricity from Fuel Cell and an External Grid to Power the Reactor

In the configuration in figure 3.8 (case 3), the need to burn hydrocarbon fuel to generate electricity within the process is eliminated. The hydrogen fuel cell system supplies 3.63 MW of electricity, which is only a portion, precisely 41%, of the total electrical energy required to be supplied to the cracker. The cracker requires 8.83 MW of electricity. The deficit of 5.2 MW is supplied from an external grid. The hot streams exiting the fuel cell preheat the cracker feed. The percentage of energy utilized for cracking with this configuration will depend on the efficiency of the external plant supplying the grid power. Assuming a modest efficiency of 45% for an external grid's combined cycle power plant, then the percentage energy utilization for cracking with the present configuration will be 50%; 8% improvement over the conventional configuration in the reference case. The energy input from hydrocarbon (if used to supply all the inputted energy into the combined cycle plant) will be 11.8 MW; representing 18% reduction in carbon footprint compared to the reference case. Therefore, case 3 is also more energy efficient than the reference case, besides being more structurally compact.

Case 4: Using Only Electricity from Grid to Power the Cracking Reactor

Figure 3.9: Case 4 – Using Only Electricity from Grid to Power the Cracking Reactor

In figure 3.9 (case 4), there is no in-process power generating system whatsoever. All the needed electrical power for the electrified cracking reactor (8.75 MW) comes from an external grid. The hydrogen in the cracked gas (product stream) is burnt to provide energy to preheat the feed. With a 45% efficient grid power-producing plant, the energy utilized for cracking in the present configuration will be 34.3% of total input; 7.7% lower than what is obtainable with the reference case. The carbon footprint in the configuration in case 4 will also be higher than that in the reference case by 35% if it is assumed that all the inputted energy into an external grid's power plant comes from hydrocarbon source(s). This is because 19.44 MW of hydrocarbon-sourced energy would have been inputted into the power plant, compared to the 14.4 MW of hydrocarbon-sourced energy inputted in the reference case. While it may be less energy efficient and results in more carbon footprint than the reference case, the configuration in case 4 is a very simple one. It may be the most adaptable towards modularization and small-scale processing of all the cases considered. There is less heat integration around it compared to cases 1,2 and 3.

3.4 Conclusions

Table 3.2: Energy Comparison for Different Configuration Cases

Configuration Cases	Energy Input from HC Fuel (MW)	Percentage of Input Energy Utilized for Cracking	Carbon Footprint Relative to Reference Case
Reference Case	14.4	42%	1.00
Case 1	21.0	33%	1.46
Case 2	13.0	45%	0.90
Case 3	11.8	50%	0.82
Case 4	19.4	34%	1.35

HC = Hydrocarbon. [Case 3 and Case 4 are based on an assumed 45% efficiency of a CGC Power Plant]

Table 3.3 provides a summary of the results discussed for the different cases. Two cases, (cases 2 and 3) are demonstrably more energy efficient and results in less carbon footprint than the reference case, besides being more structurally compact. Cases 1 and 4 are also more structurally compact than the reference case, though less energy efficient.

The present study has led to the discovery of simple and energy-efficient thermal cracking configurations, that are amenable to modularization, for olefins production. These results, combined with the ones discussed in chapter 2, could lead to a transformation in the utilization of light alkanes and shale resources for the commercial production of fuels and chemicals.

APPENDIX

Further details regarding the chemistry and thermodynamics in this appendix may be found in the papers by Holmen et al [19, 20], Keipi et al [23], Sundaram and Froment [46], and Xu et al [53].

1.0   Supplementary Thermodynamic Data for Use in Chemkin

THERMO ALL

   300.000 1000.000 5000.000

N2   J-9-65N 2   G   300.000 5000.000 1651.00   1
 2.99595345E+00 1.23650803E-03-3.70307884E-07 5.05346607E-11-2.62980289E-15   2
-9.13275934E+02 5.68044098E+00 3.26021756E+00 5.91317648E-04 2.24046943E-07   3
-1.95572836E-10 3.61873219E-14-9.99926012E+02 4.27471787E+00   4

H2   J-3-61H 2   G   300.000 5000.000 1372.00   1
 2.80745773E+00 1.05566826E-03-2.75154709E-07 3.13764993E-11-1.31833174E-15   2
-7.56604815E+02-3.36900751E-01 3.53708090E+00-3.54734803E-04 6.80901911E-07   3
-2.27080447E-10 1.93615941E-14-1.04438982E+03-4.36829600E+00   4

H   J-6-74H 1   G   300.000 5000.000 1000.00   1
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 2.54747466E+04-4.65341317E-01 2.50104422E+00 0.00000000E+00 0.00000000E+00   3
 0.00000000E+00 0.00000000E+00 2.54747466E+04-4.65341317E-01   4

CH2   J12-72H 2C 1   G   300.000 5000.000 1358.00   1
 3.42504406E+00 3.00835428E-03-1.03082425E-06 1.60128149E-10-9.29054353E-15   2
 4.52226365E+04 2.77263987E+00 4.11616695E+00-7.72574732E-04 4.51949310E-06   3
-3.01358785E-09 6.24607712E-13 4.52499362E+04-8.58779324E-02   4

CH2S   J12-72H 2C 1   G   300.000 5000.000 1993.00   1
 3.44498208E+00 3.14193588E-03-1.11876327E-06 1.78884595E-10-1.06027384E-14   2

4.98233800E+04 1.55704872E+00 3.71072329E+00 1.05249922E-03 2.28817331E-06   3
-1.84118043E-09 3.92349813E-13 4.98869752E+04 6.77208108E-01   4

CH3   J-6-69H 3C 1   G 300.000 5000.000 1389.00   1
 3.51281373E+00 5.11412616E-03-1.67632051E-06 2.52495177E-10-1.43302925E-14   2
 1.61238028E+04 1.62436127E+00 3.43858162E+00 4.07752666E-03 3.19830965E-07   3
-9.47669373E-10 2.21828163E-13 1.63164018E+04 2.52807406E+00   4

CH4   J-6-69H 4C 1   G 300.000 5000.000 1369.00   1
 2.71850414E+00 8.46951151E-03-2.86170881E-06 4.40328507E-10-2.53773215E-14   2
-1.05576197E+04 3.79320756E+00 2.91521312E+00 3.23795334E-03 6.91220825E-06   3
-5.84273795E-09 1.33208116E-12-1.00717942E+04 4.55719556E+00   4

C2H2   H 2C 2   G 300.000 5000.000 1407.00   1
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 2.52697118E+04-5.81321385E+00 2.06742667E+00 1.46568506E-02-1.52947063E-05   3
 8.30965761E-09-1.72932175E-12 2.59578589E+04 8.62758672E+00   4

C2H3   H 3C 2   G 300.000 5000.000 1395.00   1
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 3.37134093E+04-3.39792712E+00 1.25329724E+00 1.56258370E-02-1.07803879E-05   3
 4.18054634E-09-7.01360362E-13 3.50634118E+04 1.71341661E+01   4

C2H4   H 4C 2   G 300.000 5000.000 1395.00   1
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 3.59383137E+03-7.47789234E+00 2.33879687E-01 1.96334647E-02-1.16833214E-05   3
 3.64246453E-09-4.77442715E-13 5.45482795E+03 1.97084228E+01   4

C2H5   ---HHCH 5C 2   G 300.000 5000.000 1386.00   1
 5.66493785E+00 1.05521743E-02-3.56342205E-06 5.48309761E-10-3.16078826E-14   2
 1.18038472E+04-7.05382280E+00 1.40260633E+00 1.83031419E-02-8.31872369E-06   3

1.58802205E-09-6.24798169E-14 1.35593673E+04 1.67109914E+01   4

C2H6   H 6C 2   G 300.000 5000.000 1384.00   1
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 2.08340901E-09-5.29868617E-14-1.12345534E+04 2.11648750E+01   4

C*C*C   H 4C 3   G 300.000 5000.000 1395.00   1
 7.72656830E+00 9.36653958E-03-3.18633443E-06 4.92833501E-10-2.85166316E-14   2
 1.98863470E+04-1.91891052E+01 9.04627493E-01 2.54935880E-02-1.80277971E-05   3
 6.83164810E-09-1.08512767E-12 2.22562951E+04 1.74142208E+01   4

C#CC   H 4C 3   G 300.000 5000.000 1361.00   1
 7.82375971E+00 9.40009504E-03-3.31992737E-06 5.26581431E-10-3.10092843E-14   2
 1.83958734E+04-1.97410978E+01 2.36172918E+00 1.71141946E-02-4.77661324E-06   3
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C*CC   H 6C 3   G 300.000 5000.000 1388.00   1
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CCC   H 8C 3   G 300.000 5000.000 1387.00   1
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 4.95900425E-09-4.55919788E-13-1.41148884E+04 2.41087380E+01   4

C#CC.   H 3C 3   G 300.000 5000.000 1380.00   1
 7.88591315E+00 6.65864168E-03-2.34157567E-06 3.70338401E-10-2.17650188E-14   2
 3.75766518E+04-1.85822699E+01 2.07875733E+00 2.00336132E-02-1.45703340E-05   3
 5.70232469E-09 -9.5228527E-13 3.96645659E+04 1.27620341E+01   4

C*C.C   H 5C 3 G 300.000 5000.000 1382.00 1

7.37492443E+00 1.17510061E-02-4.00021283E-06 6.18947395E-10-3.58215018E-14 2

2.72874911E+04-1.43478655E+01 2.17916644E+00 2.03826623E-02-7.91413834E-06 3

4.76906187E-10 2.70398536E-13 2.94895338E+04 1.48785684E+01   4

C*CC.   H 5C 3 G 300.000 5000.000 1386.00 1

8.86768772E+00 1.09012389E-02-3.80094606E-06 5.97727066E-10-3.49892618E-14 2

1.61006315E+04-2.50850368E+01-3.34024311E-01 3.22991878E-02-2.33490952E-05 3

8.99835085E-09-1.46327673E-12 1.93614921E+04 2.44623002E+01   4

CCC.   H 7C 3 G 300.000 5000.000 1386.00 1

8.87891888E+00 1.51926066E-02-5.19821700E-06 8.07099695E-10-4.68244711E-14 2

7.21999864E+03-2.29020523E+01 4.89680103E-01 3.17745383E-02-1.69420751E-05 3

4.27222899E-09-3.88106071E-13 1.04955773E+04 2.33241310E+01   4

CC.C   H 7C 3 G 300.000 5000.000 1999.00 1

7.09059577E+00 1.70219362E-02-5.94894999E-06 9.40795995E-10-5.53826830E-14 2

6.75883699E+03-1.26909429E+01 6.38704055E-01 2.84865544E-02-1.14329581E-05 3

8.81112868E-10 3.15683673E-13 9.22131415E+03 2.30629265E+01   4

CC#CC   H 6C 4 G 300.000 5000.000 2002.00 1

8.60406095E+00 1.71534809E-02-6.32700416E-06 1.03618677E-09-6.24642424E-14 2

1.29670725E+04-2.23443927E+01 2.65416244E+00 2.37241191E-02-3.54896794E-06 3

-3.98445583E-09 1.30374564E-12 1.56563258E+04 1.21063985E+01   4

C*CC*C   H 6C 4 G 300.000 5000.000 1398.00 1

1.11633789E+01 1.37163965E-02-4.69715783E-06 7.29693836E-10-4.23486203E-14 2

7.79039770E+03-3.69847949E+01-1.43095121E+00 4.78706062E-02-4.15446800E-05 3

1.91549552E-08-3.57158507E-12 1.17551314E+04 2.90825833E+01   4

C*C*CC   H 6C 4   G 300.000 5000.000 1390.00   1
 1.05039680E+01 1.41242631E-02-4.80637221E-06 7.43634992E-10-4.30400365E-14   2
 1.44239603E+04-3.16247069E+01 1.13142053E+00 3.44939157E-02-2.14418290E-05   3
 6.84195879E-09-8.94244064E-13 1.78579480E+04 1.92969683E+01   4

C*CCC   H 8C 4   G 300.000 5000.000 1392.00   1
 1.13508668E+01 1.80617877E-02-6.16093029E-06 9.54652959E-10-5.53089641E-14   2
-5.97871038E+03-3.64369438E+01-8.31372089E-01 4.52580978E-02-2.93658559E-05   3
 1.00220436E-08-1.43191680E-12-1.57875035E+03 2.95084236E+01   4

CC*CC   H 8C 4   G 300.000 5000.000 1384.00   1
 1.07864376E+01 1.84629194E-02-6.28289490E-06 9.72052191E-10-5.62579166E-14   2
-7.33793717E+03-3.44892763E+01 6.69213599E-01 3.76839941E-02-1.85689683E-05   3
 3.69571062E-09-1.03095209E-13-3.33819338E+03 2.14868169E+01   4

CCCC   H 10C 4   G 300.000 5000.000 1389.00   1
 1.25055526E+01 2.17524393E-02-7.43384946E-06 1.15331684E-09-6.68749762E-14   2
-2.19479302E+04-4.44902356E+01-5.95684476E-01 4.89605743E-02-2.82670269E-05   3
 8.13598060E-09-9.29098102E-13-1.69934308E+04 2.71845212E+01   4

C*C.CC   H 7C 4   G 300.000 5000.000 1389.00   1
 1.07092407E+01 1.61102825E-02-5.49846133E-06 8.52304018E-10-4.93905022E-14   2
 2.31874323E+04-3.07648054E+01 9.64124370E-01 3.66781354E-02-2.17105448E-05   3
 6.55880219E-09-8.11791145E-13 2.68423270E+04 2.24365633E+01   4

CC*CC.   H 7C 4   G 300.000 5000.000 1385.00   1
 1.16018486E+01 1.57505666E-02-5.46376126E-06 8.56295369E-10-5.00066835E-14   2
 1.06487145E+04-3.86778976E+01-1.15881716E-01 4.13379755E-02-2.68395034E-05   3
 9.08882895E-09-1.29712052E-12 1.49645427E+04 2.50016070E+01   4

CCCC.   H 9C 4   G 300.000 5000.000 1389.00   1

43

1.20744111E+01 1.96194736E-02-6.70869362E-06 1.04121341E-09-6.03910407E-14   2
3.12417345E+03-3.86189978E+01 2.15101842E-01 4.42132965E-02-2.55006473E-05   3
7.32080770E-09-8.32495567E-13 7.61325140E+03 2.62751123E+01   4

CCC.C   H 9C 4   G 300.000 5000.000 1373.00   1
1.18293992E+01 1.94203812E-02-6.55835141E-06 1.00989031E-09-5.82693176E-14   2
1.79315973E+03-3.68210535E+01 7.70280140E-01 3.86280904E-02-1.57100260E-05   3
7.16860110E-10 7.00801289E-13 6.28812837E+03 2.49106490E+01   4

CY13PD   H 6C 5   G 300.000 5000.000 1387.00   1
1.36543234E+01 1.52623059E-02-5.38999640E-06 8.55032202E-10-5.03603129E-14   2
8.91096357E+03-5.54058745E+01-5.12257957E+00 5.97969364E-02-4.59592394E-05   3
1.77718567E-08-2.77548707E-12 1.53464279E+04 4.51716467E+01   4

CYC5H8   H 8C 5   G 300.000 5000.000 1398.00   1
1.27525879E+01 2.01602949E-02-6.86564327E-06 1.06303695E-09-6.15663048E-14   2
-3.09810152E+03-4.85501459E+01-5.44615258E+00 6.33154620E-02-4.59351514E-05   3
1.71229729E-08-2.58907474E-12 3.11839629E+03 4.88944865E+01   4

C*CC.C*C   H 7C 5   G 300.000 5000.000 1390.00   1
1.39666270E+01 1.73382242E-02-6.05769915E-06 9.54008293E-10-5.59044772E-14   2
1.75830681E+04-5.22086625E+01-3.69004112E+00 5.97581971E-02-4.57690635E-05   3
1.82005947E-08-2.97538155E-12 2.36302311E+04 4.22584443E+01   4

CY13PD5.   H 5C 5   G 300.000 5000.000 1380.00   1
1.06503882E+01 1.49464087E-02-5.20404629E-06 8.17478318E-10-4.78123546E-14   2
2.62331598E+04-3.58023979E+01 2.08894920E+00 3.37631637E-02-2.23117862E-05   3
8.63437149E-09-1.52814693E-12 2.95117492E+04 1.09127048E+01   4

CYPENE3.   H 7C 5   G 300.000 5000.000 1393.00   1
1.26277707E+01 1.83191561E-02-6.36198040E-06 9.97993461E-10-5.83248243E-14   2

```
                                  1.37991416E+04-4.86756039E+01-5.60258714E+00 6.08014232E-02-4.41262848E-05    3
                                  1.62584973E-08-2.42658937E-12 2.01220162E+04 4.92393171E+01              4


CYC5H9.          H  9C  5      G  300.000 5000.000 1378.00     1
 1.24946381E+01 2.23549938E-02-7.51362241E-06 1.15415415E-09-6.65065318E-14    2
 6.45390040E+03-4.65796398E+01-5.78089755E+00 5.92878731E-02-3.26281412E-05    3
 7.06409844E-09-1.75407888E-13 1.32581249E+04 5.34176945E+01              4


C*CCCC*C          H 10C  6      G  300.000 5000.000 1395.00     1
 1.67186191E+01 2.30179407E-02-7.81866308E-06 1.20831815E-09-6.98826125E-14    2
 1.74306625E+03-6.19565928E+01-1.80013527E+00 6.71111879E-02-4.84054490E-05    3
 1.84055726E-08-2.89367813E-12 8.10249521E+03 3.72242052E+01              4


BENZENE          H  6C  6      G  300.000 5000.000 1391.00     1
 1.37969112E+01 1.75463970E-02-6.14454458E-06 9.69199960E-10-5.68574315E-14    2
 2.61691889E+03-5.64845457E+01-5.47111685E+00 6.44195230E-02-5.05526465E-05    3
 2.04451595E-08-3.37591343E-12 9.14055839E+03 4.63686277E+01              4


CHD14          H  8C  6      G  300.000 5000.000 1369.00     1
 1.76883674E+01 2.00067698E-02-7.14996880E-06 1.14314548E-09-6.76953796E-14    2
 3.45242039E+03-8.02538079E+01-5.49947822E+00 6.82134483E-02-4.29985903E-05    3
 1.21493314E-08-1.16666693E-12 1.20744433E+04 4.63551821E+01              4


CHD13          H  8C  6      G  300.000 5000.000 1396.00     1
 1.53625259E+01 2.08675112E-02-7.19203048E-06 1.12251633E-09-6.53733380E-14    2
 4.62118283E+03-6.26703913E+01-5.81337476E+00 7.22248431E-02-5.52161741E-05    3
 2.16975324E-08-3.46304555E-12 1.17578006E+04 5.03398935E+01              4


CYC6H10          H 10C  6      G  300.000 5000.000 1392.00     1
 1.60811950E+01 2.53669984E-02-8.74760281E-06 1.36572651E-09-7.95518468E-14    2
-9.52829324E+03-6.79771626E+01-6.42702467E+00 7.69721740E-02-5.37392770E-05    3
```

1.91548574E-08-2.77729519E-12 -1.6203119E+03 5.32418985E+01   4

C*CCC.C*C   H 9C 6   G 300.000 5000.000 1395.00   1
 1.63325383E+01 2.13113595E-02-7.25043627E-06 1.12181536E-09-6.49365392E-14   2
 1.88315603E+04-6.04214178E+01-2.15219686E+00 6.55925871E-02-4.81557025E-05   3
 1.84581470E-08-2.90301780E-12 2.51322407E+04 3.84483853E+01   4

C*CC*CC.C   H 9C 6   G 300.000 5000.000 995.00   1
 1.36288339E+01 2.45055787E-02-8.07546311E-06 1.23042786E-09-7.08589527E-14   2
 1.27234636E+04-4.54653810E+01 2.56830777E+00 2.90638735E-02 4.52075606E-05   3
-7.47713655E-08 2.91501468E-11 1.69000816E+04 1.77668995E+01   4

MECYPE2.   041206H 11C 6   G 300.000 2500.000 1000.00   1
 3.43704060E+00 5.25429550E-02-2.74113740E-05 7.00181070E-09-7.10219100E-13   2
 7.03728910E+03 4.92897220E+00-2.52635050E+00 5.88077490E-02-4.78416000E-06   3
-3.49249800E-08 1.82926730E-11 9.00699610E+03 3.77690890E+01   4

MECY3PE2.   -THERMH 9C 6   G 300.000 5000.000 1399.00   1
 1.60019772E+01 2.23767730E-02-7.69541000E-06 1.19917356E-09-6.97554910E-14   2
 8.00888196E+03-6.43262066E+01-6.26683807E+00 7.81434505E-02-6.20920380E-05   3
 2.56610022E-08-4.31523883E-12 1.53621677E+04 5.39324477E+01   4

CYC6H5.   H 5C 6   G 300.000 5000.000 1393.00   1
 1.26714475E+01 1.57716661E-02-5.48965219E-06 8.62345100E-10-5.04424280E-14   2
 3.41167244E+04-4.61178992E+01-4.21717254E+00 5.91434680E-02-4.95004867E-05   3
 2.16411668E-08-3.84655064E-12 3.96389820E+04 4.32773003E+01   4

CYC6H7   H 7C 6   G 300.000 5000.000 1399.00   1
 1.48952230E+01 1.86446019E-02-6.40880880E-06 9.98505156E-10-5.80800835E-14   2
 1.74517869E+04-5.85128201E+01-5.53952555E+00 7.04351030E-02-5.73920116E-05   3
 2.40513712E-08-4.06716243E-12 2.41107691E+04 4.97426193E+01   4

CYC6H9   H   9C   6   G   300.000 5000.000 1396.00   1
 1.57757308E+01 2.29119263E-02-7.86274116E-06 1.22355692E-09-7.11069741E-14   2
 1.41828333E+04-6.30151719E+01-5.51570747E+00 7.45070998E-02-5.62467883E-05   3
 2.20897753E-08-3.54975415E-12 2.13847403E+04 5.06632363E+01   4

END

2.0   Reaction Mechanisms for Use in Chemkin: MODEL A

ELEMENTS H C END

SPECIES CH CH2 CH3 CH4 C2H C2H6 C2H4 C2H2 C2H3 C2H5 CCC. CC.C C*C*C C#CC
C3H8 H2 C*C.C C*CC. C#CC. C3H6 C4H4 C4H5 C4H6 C4H10 C4H8 C6H6 H C5 CC*CC.
CCCC. CCC.C C5H10 C5H11 C5H12 C6H10 C6H12 C7H12 C8H14 C(S) END

REACTIONS
!Units are in cm3-mole-sec-cal

!Free-Radical for Ethane Pyrolysis (Sundrama & Froment - 1978)
 C2H6=>2CH3   4.0E16   0.00   87500.0
 C3H8=>C2H5+CH3   2.0E16   0.00   84500.0
 C4H10=>2C2H5   1.5E16   0.00   82100.0
 C4H10=>CCC.+CH3   9.0E16   0.00   85400.0
 C4H8=>C*CC.+CH3   8.0E16   0.00   74000.0
 C2H4+H=>C2H3+H2   8.0E11   0.00   4000.0
 C2H6+H=>C2H5+H2   1.0E14   0.00   9700.0
 C2H4+CH3=>C2H3+CH4   1.0E13   0.00   13000.0
 C2H6+CH3=>C2H5+CH4   3.8E14   0.00   16500.0
 C2H4+C2H5=>CH3+C3H6   3.0E12   0.00   19000.0
 C2H3=>C2H2+H   2.0E09   0.00   31500.0

C2H5=>C2H4+H	3.2E13	0.00	40000.0
C*CC.=>C2H2+CH3	3.0E10	0.00	36200.0
CCC.=>C2H4+CH3	4.0E13	0.00	32600.0
CCC.=>C3H6+H	2.0E13	0.00	38400.0
CC*CC.=>C4H6+H	1.2E14	0.00	49300.0
CC*CC.=>C2H4+C2H3	1.0E11	0.00	37000.0
CCCC.=>C2H4+C2H5	1.6E12	0.00	28000.0
CCCC.=>C4H8+H	1.0E13	0.00	36600.0
C5H11=>C5H10+H	5.0E13	0.00	36600.0
C5H11=>C4H8+CH3	3.2E13	0.00	31500.0
C5H11=>C2H4+CCC.	4.0E12	0.00	28700.0
C2H2+H=>C2H3	4.0E13	0.00	1300.0
C2H4+H=>C2H5	1.0E13	0.00	1500.0
C3H6+H=>CCC.	1.0E13	0.00	2900.0
C3H6+H=>CC.C	1.0E13	0.00	1500.0
C4H6+H=>CC*CC.	4.0E13	0.00	1300.0
C2H4+CH3=>CCC.	2.0E11	0.00	7900.0
C2H4+C2H3=>CC*CC.	5.0E10	0.00	7000.0
C2H4+C2H5=>CCCC.	1.5E10	0.00	7600.0
C3H6+C2H5=>C5H11	1.3E10	0.00	7500.0
C2H4+CCC.=>C5H11	2.0E10	0.00	7400.0
C2H3+H=>C2H4	1.0E13	0.00	0.0
C2H5+H=>C2H6	4.0E13	0.00	0.0
C*CC.+H=>C3H6	2.0E13	0.00	0.0
CCC.+H=>C3H8	1.0E13	0.00	0.0
CC*CC.+H=>C4H8	2.0E13	0.00	0.0
CCCC.+H=>C4H10	1.0E13	0.00	0.0
C5H11+H=>C5H12	1.0E13	0.00	0.0
CH3+CH3=>C2H6	1.3E13	0.00	0.0
C2H5+CH3=>C3H8	3.2E12	0.00	0.0
C*CC.+CH3=>C4H8	3.2E12	0.00	0.0

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CC*CC.+CH3=>C5H10          3.2E12    0.00      0.0
C2H3+C2H3=>C4H6            1.3E13    0.00      0.0
CC*CC.+C2H3=>C6H10         1.3E13    0.00      0.0
C2H5+C2H5=>C4H10           4.0E11    0.00      0.0
C2H5+C2H5=>C2H4+C2H6       5.0E10    0.00      0.0
CC*CC.+C2H5=>C6H12         3.2E12    0.00      0.0
CC*CC.+C*CC.=>C7H12        1.3E13    0.00      0.0
CC*CC.+CC*CC.=>C8H14       3.2E12    0.00      0.0
C2H2=>2C(S)+H2             5.0E12    0.00   62000.0


!Exclusive Additions Towards Propane Pyrolysis
C3H6+H=>C*CC.+H2           2.5E12    0.00    1100.0
C3H8+H=>CCC.+H2            1.0E14    0.00    9700.0
C3H8+H=>CC.C+H2            9.0E13    0.00    8300.0
C4H8+H=>CC*CC.+H2          5.0E13    0.00    3900.0
C3H6+CH3=>C*CC.+CH4        2.0E12    0.00   12200.0
C3H8+CH3=>CCC.+CH4         3.4E13    0.00   11500.0
C3H8+CH3=>CC.C+CH4         4.0E12    0.00   10100.0
C4H8+CH3=>CC*CC.+CH4       1.0E11    0.00    7300.0
C3H6+C2H3=>C*CC.+C2H4      3.0E12    0.00   14500.0
C3H8+C2H3=>CCC.+C2H4       3.0E12    0.00   18800.0
C3H8+C2H3=>CC.C+C2H4       1.0E12    0.00   16200.0
C3H6+C2H5=>C*CC.+C2H6      1.0E11    0.00    9200.0
C3H8+C2H5=>CCC.+C2H6       1.2E12    0.00   12600.0
C3H8+C2H5=>CC.C+C2H6       8.0E11    0.00   10400.0
C3H8+C*CC.=>CCC.+C3H6      1.0E12    0.00   18800.0
C3H8+C*CC.=>CC.C+C3H6      8.0E11    0.00   16200.0
CC.C=>C3H6+H              2.0E13    0.00   38700.0
CCC.C=>C3H6+CH3           2.5E13    0.00   31900.0
CCC.C=>C4H8+H            2.0E13    0.00   39800.0
C4H8+H=>CCC.C             1.0E13    0.00    1200.0
```

C3H6+CH3=>CCCC.	3.2E11	0.00	9100.0
C2H4+CC.C=>C5H11	1.3E10	0.00	6900.0
CCCC.=>CCC.C	5.2E14	0.00	41000.0
CC.C+H=>C3H8	1.0E13	0.00	0.0
CCC.C+H=>C4H10	1.0E13	0.00	0.0
CCC.+CH3=>C4H10	3.2E12	0.00	0.0
CC.C+CH3=>C4H10	3.2E12	0.00	0.0
C*CC.+C2H5=>C5H10	3.2E12	0.00	0.0
CCC.+C2H5=>C5H12	8.0E11	0.00	0.0
CC.C+C2H5=>C5H12	8.0E11	0.00	0.0
C*CC.+C*CC.=>C6H10	3.2E12	0.00	0.0

!Exclusive Additions Towards Butane Pyrolysis

C4H10+H=>CCCC.+H2	1.5E14	0.00	9700.0
C4H10+H=>CCC.C+H2	9.0E13	0.00	8400.0
C4H10+CH3=>CCCC.+CH4	3.5E13	0.00	11600.0
C4H10+CH3=>CCC.C+CH4	3.5E12	0.00	9500.0
C4H10+C2H3=>CCCC.+C2H4	1.0E12	0.00	18000.0
C4H10+C2H3=>CCC.C+C2H4	8.0E11	0.00	16800.0
C4H8+C2H5=>CC*CC.+C2H6	2.0E11	0.00	8300.0
C4H10+C2H5=>CCCC.+C2H6	2.0E12	0.00	12600.0
C4H10+C2H5=>CCC.C+C2H6	4.5E11	0.00	10400.0
C4H10+C*CC.=>CCCC.+C3H6	4.0E11	0.00	18800.0
C4H10+C*C.C=>CCCC.+C3H6	8.0E11	0.00	16800.0
C4H10+CCC.=>CCC.C+C3H8	2.0E11	0.00	10400.0
C4H10+CC.C=>CCCC.+C3H8	2.0E11	0.00	12600.0
C3H6+CH3=>CCC.C	3.2E11	0.00	7400.0

END

3.0   Reactions Mechanisms for Use in Chemkin: MODEL B

ELEMENTS H C N END

SPECIES CH CH2 CH3 CH4 C2H C2H6 C2H4 C2H2 C2H3 C2H5 CCC. CC.C C*C*C C#CC
C3H8 H2 C*C.C C*CC. C#CC. C3H6 C4H4 C4H5 C4H6 C4H10 C4H8 C6H6 H C5 CC*CC.
CCCC. CCC.C C5H10 C5H11 C5H12 C6H10 C6H12 C7H12 C8H14 C(S) N2 END
REACTIONS
!Units are in cm3-mole-sec-cal

!Adapted Mechanism for CH4 Pyrolysis as Discussed by Keipi et al

CH4=CH3+H	3.51E15	0.00	104000.0
CH4+H=CH3+H2	2.25E04	3.00	8768.0
!CH3+CH3=C2H6	1.01E15	-0.64	0.0
!C2H6+H=C2H5+H2	5.54E02	3.50	5174.0
!C2H6+CH3=C2H5+CH4	0.55E00	4.00	8296.0
!C2H5=C2H4+H	2.00E13	0.00	39700.0
CH3+CH3=C2H4+H2	1.00E16	0.00	32000.0
!C2H4+CH3=C2H3+CH4	6.62E00	3.70	9512.0
!C2H4+CH3=CCC.	2.00E11	0.00	7170.0
!C2H4+H=C2H3+H2	1.32E06	2.53	12258.0
!C2H3=C2H2+H	1.93E28	-4.783	51123.0
CH3+C2H3=C3H6	1.00E13	0.00	0.0
!CCC.=C3H6+H	1.58E16	0.00	38000.0
C3H6=>C*CC.+H	1.00E15	0.00	88000.0
!C*CC.=C2H2+CH3	1.16E10	0.00	43200.0
C*CC.=C*C*C+H	5.00E13	0.00	35000.0
C*CC.+H=C*C*C+H2	1.00E13	0.00	0.0
!C3H6+H=C*CC.+H2	5.00E12	0.00	1500.0 !Turn on for C3
!C2H3+C2H3=C4H6	1.26E13	0.00	0.0
C2H3+C2H4=C4H6+H	5.00E11	0.00	7315.0

C2H2+H=C2H+H2   6.02E13   0.00   22300.0

C2H2+CH3=C2H+CH4   1.81E11   0.00   17300.0

C4H6+H=C4H5+H2   1.00E14   0.00   15000.0

C4H5=C4H4+H   1.00E14   0.00   41400.0

C2H+H=C2H2   1.81E14   0.00   0.0

C2H3+C2H2=C4H5   1.10E12   0.00   4000.0

CH3+CH3=C2H5+H   1.80E12   0.00   10400.0

C4H5+C2H2=>C6H6+H   6.02E12   0.00   9000.0

C2H4=>C2H3+H   1.00E16   0.00   108000.0 !Only Fwd-C2C3 Py

C2H5+C2H2=C2H6+C2H   2.71E11   0.00   23400.0

!C2H5+H=C2H6   3.07E13   0.00   0.0

C2H4=C2H2+H2   7.94E12   0.44   88760.0

C2H3+H=C2H2+H2   9.64E13   0.00   0.0

C2H2+CH3=C#CC+H   6.20E11   0.00   20000.0

C3H6=C#CC+H2   8.00E12   0.44   81150.0

!C3H6+CH3=C*CC.+CH4   1.58E12   0.00   8800.0 !Turn on for C3

C2H=>2C(S)+H   4.68E15   0.00   62000.0

!Free-Radical for Ethane Pyrolysis (Sundrama & Froment - 1978)

C2H6=>2CH3   4.0E16   0.00   87500.0

C3H8=>C2H5+CH3   2.0E16   0.00   84500.0

C4H10=>2C2H5   1.5E16   0.00   82100.0

C4H10=>CCC.+CH3   9.0E16   0.00   85400.0

C4H8=>C*CC.+CH3   8.0E16   0.00   74000.0

C2H4+H=C2H3+H2   8.0E11   0.00   4000.0 !Rev Add for CH4

C2H6+H=C2H5+H2   1.0E14   0.00   9700.0 !Rev Add for CH4

C2H4+CH3=C2H3+CH4   1.0E13   0.00   13000.0 !Rev Add for CH4

C2H6+CH3=C2H5+CH4   3.8E14   0.00   16500.0 !Rev Add for CH4

C2H4+C2H5=>CH3+C3H6   3.0E12   0.00   19000.0

C2H3=>C2H2+H   2.0E09   0.00   31500.0

C2H5=>C2H4+H   3.2E13   0.00   40000.0

C*CC.=C2H2+CH3	3.0E10	0.00	36200.0 !Rev Add for CH4
CCC.=>C2H4+CH3	4.0E13	0.00	32600.0
CCC.=>C3H6+H	2.0E13	0.00	38400.0
CC*CC.=>C4H6+H	1.2E14	0.00	49300.0
CC*CC.=>C2H4+C2H3	1.0E11	0.00	37000.0
CCCC.=>C2H4+C2H5	1.6E12	0.00	28000.0
CCCC.=>C4H8+H	1.0E13	0.00	36600.0
C5H11=>C5H10+H	5.0E13	0.00	36600.0
C5H11=>C4H8+CH3	3.2E13	0.00	31500.0
C5H11=>C2H4+CCC.	4.0E12	0.00	28700.0
C2H2+H=>C2H3	4.0E13	0.00	1300.0
C2H4+H=>C2H5	1.0E13	0.00	1500.0
C3H6+H=>CCC.	1.0E13	0.00	2900.0
C3H6+H=>CC.C	1.0E13	0.00	1500.0
C4H6+H=>CC*CC.	4.0E13	0.00	1300.0
C2H4+CH3=>CCC.	2.0E11	0.00	7900.0
C2H4+C2H3=>CC*CC.	5.0E10	0.00	7000.0
C2H4+C2H5=>CCCC.	1.5E10	0.00	7600.0
C3H6+C2H5=>C5H11	1.3E10	0.00	7500.0
C2H4+CCC.=>C5H11	2.0E10	0.00	7400.0
C2H3+H=>C2H4	1.0E13	0.00	0.0
C2H5+H=C2H6	4.0E13	0.00	0.0 !Rev Add for CH4
C*CC.+H=>C3H6	2.0E13	0.00	0.0
CCC.+H=>C3H8	1.0E13	0.00	0.0
CC*CC.+H=>C4H8	2.0E13	0.00	0.0
CCCC.+H=>C4H10	1.0E13	0.00	0.0
C5H11+H=>C5H12	1.0E13	0.00	0.0
CH3+CH3=>C2H6	1.3E13	0.00	0.0
C2H5+CH3=>C3H8	3.2E12	0.00	0.0
C*CC.+CH3=>C4H8	3.2E12	0.00	0.0
CC*CC.+CH3=>C5H10	3.2E12	0.00	0.0

C2H3+C2H3=C4H6   1.3E13   0.00   0.0 !Rev Add for CH4

CC*CC.+C2H3=>C6H10   1.3E13   0.00   0.0

C2H5+C2H5=>C4H10   4.0E11   0.00   0.0

C2H5+C2H5=>C2H4+C2H6   5.0E10   0.00   0.0

CC*CC.+C2H5=>C6H12   3.2E12   0.00   0.0

CC*CC.+C*CC.=>C7H12   1.3E13   0.00   0.0

CC*CC.+CC*CC.=>C8H14   3.2E12   0.00   0.0

C2H2=>2C(S)+H2   5.0E12   0.00   62000.0

!Exclusive Additions Towards Propane Pyrolysis

C3H6+H=C*CC.+H2   2.5E12   0.00   1100.0 !Rev Add for CH4

C3H8+H=>CCC.+H2   1.0E14   0.00   9700.0

C3H8+H=>CC.C+H2   9.0E13   0.00   8300.0

C4H8+H=>CC*CC.+H2   5.0E13   0.00   3900.0

C3H6+CH3=C*CC.+CH4   2.0E12   0.00   12200.0 !Rev Add for CH4

C3H8+CH3=>CCC.+CH4   3.4E13   0.00   11500.0

C3H8+CH3=>CC.C+CH4   4.0E12   0.00   10100.0

C4H8+CH3=>CC*CC.+CH4   1.0E11   0.00   7300.0

C3H6+C2H3=>C*CC.+C2H4   3.0E12   0.00   14500.0

C3H8+C2H3=>CCC.+C2H4   3.0E12   0.00   18800.0

C3H8+C2H3=>CC.C+C2H4   1.0E12   0.00   16200.0

C3H6+C2H5=>C*CC.+C2H6   1.0E11   0.00   9200.0

C3H8+C2H5=>CCC.+C2H6   1.2E12   0.00   12600.0

C3H8+C2H5=>CC.C+C2H6   8.0E11   0.00   10400.0

C3H8+C*CC.=>CCC.+C3H6   1.0E12   0.00   18800.0

C3H8+C*CC.=>CC.C+C3H6   8.0E11   0.00   16200.0

CC.C=>C3H6+H   2.0E13   0.00   38700.0

CCC.C=>C3H6+CH3   2.5E13   0.00   31900.0

CCC.C=>C4H8+H   2.0E13   0.00   39800.0

C4H8+H=>CCC.C   1.0E13   0.00   1200.0

C3H6+CH3=>CCCC.   3.2E11   0.00   9100.0

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C2H4+CC.C=>C5H11           1.3E10      0.00    6900.0
CCCC.=>CCC.C               5.2E14      0.00   41000.0
CC.C+H=>C3H8               1.0E13      0.00      0.0
CCC.C+H=>C4H10             1.0E13      0.00      0.0
CCC.+CH3=>C4H10            3.2E12      0.00      0.0
CC.C+CH3=>C4H10            3.2E12      0.00      0.0
C*CC.+C2H5=>C5H10          3.2E12      0.00      0.0
CCC.+C2H5=>C5H12           8.0E11      0.00      0.0
CC.C+C2H5=>C5H12           8.0E11      0.00      0.0
C*CC.+C*CC.=>C6H10         3.2E12      0.00      0.0


!Exclusive Additions Towards Butane Pyrolysis
C4H10+H=>CCCC.+H2          1.5E14      0.00    9700.0
C4H10+H=>CCC.C+H2          9.0E13      0.00    8400.0
C4H10+CH3=>CCCC.+CH4       3.5E13      0.00   11600.0
C4H10+CH3=>CCC.C+CH4       3.5E12      0.00    9500.0
C4H10+C2H3=>CCCC.+C2H4     1.0E12      0.00   18000.0
C4H10+C2H3=>CCC.C+C2H4     8.0E11      0.00   16800.0
C4H8+C2H5=>CC*CC.+C2H6     2.0E11      0.00    8300.0
C4H10+C2H5=>CCCC.+C2H6     2.0E12      0.00   12600.0
C4H10+C2H5=>CCC.C+C2H6     4.5E11      0.00   10400.0
C4H10+C*CC.=>CCCC.+C3H6    4.0E11      0.00   18800.0
C4H10+C*C.C=>CCCC.+C3H6    8.0E11      0.00   16800.0
C4H10+CCC.=>CCC.C+C3H8     2.0E11      0.00   10400.0
C4H10+CC.C=>CCCC.+C3H8     2.0E11      0.00   12600.0
C3H6+CH3=>CCC.C            3.2E11      0.00    7400.


END
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