

Development of a Molecular Kinetic Model and Tuning of its Required Kinetic Parameters for Thermal Cracking of Light Hydrocarbons

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Abstract

Thermal cracking of light hydrocarbons was studied in which a molecular kinetic model for light hydrocarbons, and their mixture was developed. Required kinetic parameters were calculated and tuned by error minimization between several real reactors measured data and results of their simulation. Reactors were simulated as a one-dimensional plug flow reactor. Simulation consists of a reactor model and heat transfer from an external hot surface of the reactor. Nonlinear regression method was used to minimize the errors of simulation results and optimization of the kinetic model parameters. The kinetic and reactor models were verified by comparing their results with the measured data of several real reactors. Required experimental data were collected through the literature survey. Accuracy of the simulation results showed that the developed kinetic model and the reactor simulation can be applied for the operational analysis of cracking furnaces, operating parameters optimization, and industrial plant profitability improvement.

Keywords: *Thermal Cracking, Molecular Kinetic Model, Kinetic Parameters, Light Hydrocarbon*

1. Introduction

Light hydrocarbons such as ethane, propane, butane, LPG, naphtha and their mixture can be used as feedstock for production of ethylene and light olefins. The processes used for these purposes are named thermal or steam cracking. During these processes, large hydrocarbon molecules are broken into smaller ones. Cracking processes include endothermic reactions, so require a huge amount of energy. The process often takes place in a long tubular reactor and energy

requirements of the process are supplied by a gas-fired furnace. Feed and steam are preheated and mixed typically up to 500-600°C, and then fed to the reactor. Reactor absorbs the required heat by the radiation mechanism from the hot combustion gases and the refractive walls. Temperature at the outlet of the reactor is in the range 800-900°C. The process is performed at the lowest pressure possible because higher pressures affect the products selectivity, for example, it reduces the selectivity of

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ethylene in ethylene plants [1]. Steam is used when an increase in the process pressure is required. Steam acts as a diluent and lowers the partial pressure of hydrocarbons to reduce secondary reactions such as condensation reactions between light hydrocarbons and coke formation [2]. In addition, steam reduces coke formation by the reaction between H₂O and carbon [3]. Residence time of the reactor is not enough to reduce and control the severity of the cracking [4]. A combination of hydrogen, paraffins, olefins, aromatics, and other heavier hydrocarbons are produced during the process. Cracked gases, leaving the reactor, are cooled rapidly in a heat exchanger to stop the undesired reactions and heat recovery.

Optimization of cracking processes is one of the most important goals for managers of industrial plants due to energy cost and process economic aspects. Performing an optimization process on an industrial plant is not a reliable method because of its huge cost and time requirements. In addition, there are numerous cracking process variables that must be tuned. For example, a change in feed composition alters the process optimum point, and it is necessary to retune all variables. Results of experimental setup and pilot plants cannot be fully utilized in main plants because of their differences [5]. Therefore, a good mathematical model of hydrocarbon cracking will be an attractive tool for optimizing the feedstock selecting and mixing, process control, production plan, plant design and revamping of the reactor. However, modeling of cracking processes has several complexities:

1. Although large thermo-chemical and

kinetic data exist for cracking reactions, the process is understood reasonably well and most final products are defined, but many of them are individual and can only be used for their special case, especially for the kinetic parameters. The extent of the reaction system and many intermediates and minor species whose concentrations are very low and unmeasured make the process very complex. Perhaps, this is one of the reasons for the different behaviors of cracking of hydrocarbons in laboratory, pilot plant, industrial plant reactors and simulation results [5]. Finally, there is not a model accurate enough to relate them. So a reaction mechanism that covers more cracking products and process variables is needed.

2. Variations in heat transfer rate along the reactor tube can affect the product distribution. An accurate model is needed to study heat transfer effects. The energy flows through the tube wall of the reactor depend on gas flow inside and outside the reactor, tube wall material, coke and deposition, and rate of heat generation and its distribution outside the reactor tube [5-8]. Radial temperature gradient and radiation heat transfer inside the reactor tube affects the product distribution too [9-10].

3. Accurate modeling requires minimizing the simplifying assumptions in model equations. This makes the model very complex and difficult to solve [9-10]. Simplifications and regular assumptions such as neglecting the effect of some parameters or dimensions in modeling of reactor, using inaccurate but simple

equations to estimate physical and chemical properties of fluids or heat and mass transfer coefficient are unavoidable [11], but reduce the results' accuracy and must be minimized.

2. Experimental data

In modeling of a cracking process, kinetic parameters are the basic data. Measuring of kinetic parameters by experimental methods is very difficult and sometimes nearly impossible. Usually, required kinetic parameters are prepared by literature survey. Many authors also tune their required parameters. Such parameters are often suitable for their mechanism only, and can not be used directly for a different one because of differences between their setup and reaction conditions. To generalize a model, the errors of its estimations for many different conditions must be minimized. For this purpose a suitable set of experimental data is required, which can be collected from the literature.

2-1. Collection of experimental data

To generalize the mechanism, tuning of the parameters must be performed for many reactors that work with different feedstock and process conditions to minimize the errors of the reactor model results due to kinetics. Many data sets exist in literature but the sizes of the used reactors or their reaction conditions are not reported or are not clear enough. Therefore, the model cannot be solved for them, they cannot be used in kinetic parameters tuning or mechanism, nor the model results validation, unfortunately. So, required sets of experimental data were adapted from references [5, 14–16, 22].

Towfighi et al. [11] have conducted some experiments on cracking of pure propane, n-butane and i-butane to study cracking of light hydrocarbon and LPG. Their data and results were used to validate the model and kinetic mechanism.

3. Kinetics and modeling

3-1. Selecting the reaction mechanism

Thermal cracking reactions characteristically take place based on the radical mechanism and free radicals have a basic role in formation and distribution of the products. During thermal cracking process bond cleavage takes place along the molecule and rebounding produces reactions products. Bond breaking is probable for each bond in the molecule. These probabilities at process condition determine the products distribution. Hits between reaction mixture species and their internal vibrations and oscillations are the main reasons for radical formation. Radicals are very unstable and very attractive to other species in reaction mixture. They convert to a stable molecule and more stable radical, or react with the nearest species in access very fast. For example, an ethyl radical converts to ethylene as molecular product and an H^{\bullet} as a more stable radical. So, their concentrations in reaction mixture reduce to as low a level as their net rate of formation and concentration seems to be negligible. Radicals with one free-bound (preliminary radicals) are formed during one-step effective hits between reaction mixture species, while formation of radicals with more free-bounds (secondary radicals) needs more hitting steps, except for very high temperatures. At very high temperatures,

molecules or radicals may be destroyed due to internal vibrations and oscillations, in addition to hits between them. Therefore, formation of preliminary radicals is more probable than secondary radicals. For example, if n-butane molecule is exposed to thermal cracking, the radicals such as H^\bullet , CH_3^\bullet , $C_2H_5^\bullet$, $C_3H_7^\bullet$, $C_3H_7-CH_2^\bullet$, $CH_3-CH^\bullet-C_2H_5$ are primary radicals and many others with fewer H atoms will be the secondary radicals. Hence, complete mechanisms that have been based on radicals have many reactants and will be very complex. To avoid this complexity, different types of the reaction mechanism for the cracking of hydrocarbons have been recommended in the literature. The mechanisms are categorized in three groups, free-radical, molecular, and lumped mechanisms.

When the number of reactants and products are low, and the most effective radicals and reactions can be determined, free radical mechanism is the best choice and produces the most accurate results, but an extent mechanism is often required [11-14]. Presence of primary radicals seems to be more probable and it is better for reaction mechanism to be based on them. If there are some components in products that seem to be produced from secondary radicals, it is more probable that they have been formed from molecular products of primary radicals, because their concentration may rise more than primary radicals as a result of their stability. These assumptions can reduce the extent of reaction mechanism.

Molecular mechanism is more useful when the number of reactants and products are increased. Such a mechanism can cover all reactants and products with the lower number

of reactions. If suitable reactions are selected, the results will have enough accuracy [15-16].

When feed or products have complex or undefined composition or unusual components are present, utilizing radical or molecular mechanisms is not reliable. In such cases, reactants and products are divided into cuts or mixtures with defined characteristics that are named bulk components. These cuts are used as pure materials and a semi-molecular mechanism is generated with them. Results of this method have less accuracy than the above mechanisms [17].

In the cracking of light hydrocarbons, feed and product compositions can be defined and measured accurately. The number of reactants and products is not too high, so a radical or molecular mechanism is suitable to represent the process. As explained above, when reaction mechanism is written based on radicals, reaction system becomes quite complex with a great number of reactions. To reduce the complexity it is recommended that a molecular mechanism be applied. It is better that such mechanism be adapted from radical mechanism. A good molecular mechanism must have a molecular replica for each radical. Molecular mechanism must recommend reliable reactions for feed and product components. For example, reactions with molecularity more than three are not reliable because it needs to hit more than three species to each other at the same time, which is not very probable. A well developed molecular mechanism has some advantages to the radical mechanism:

1. Results of several radical reactions can be achieved with the lower number of

molecular reactions, so modeling equations have less complexity. For example, if it is supposed that the radical mechanism shown at the left side of the Table 1 is part of an overall one, it can be represented with smaller molecular mechanism at the right side.

- Each radical requires its algebraic or differential mass balance equation in reactor mathematical model. When a molecular mechanism is used in place of the radical mechanism several equations can be eliminated.
- All the rate kinetic parameters (frequency factors and activation energies) need some tuning to achieve good estimation results by the model, so less reaction requires fewer kinetic parameters.
- Radical mechanisms insert radical properties into the calculations with unknown physical property equations. Therefore, more approximations are required in the calculations and these decrease the calculations accuracy. By choosing a molecular mechanism one can eliminate such problems. For example, utilizing an equation of state such as Peng-Robinson (PR) requires T_c , P_c and ω of the component, and such properties cannot be measured for a radical. However it has been observed that the

concentrations of the free radicals are very low [14] and eliminating them does not have a considerable effect on the physical property estimation.

As mentioned above, when composition of reactor feed is well known, especially for light hydrocarbons, radical mechanisms are recommended. In such a case the numbers of main products are also limited. Light hydrocarbon is often referred to as hydrocarbons with carbon number up to C_5 . But a slight amount of heavier ones may be present in feed mixtures. On the other hand, during cracking processes heavier compounds like higher paraffins, olefins, aromatics, and ... may be produced by condensation reactions. Some of the main components of light hydrocarbon feeds and their cracking products are listed in Table 2. Feedstock is mainly mixtures of saturated hydrocarbons. Liquefied petroleum gas (LPG) can be an important feed for the thermal cracking. It mainly consists of propane, butane, i-butane, propylene and butene with a small amount of higher hydrocarbons. The cracking products mainly consist of light olefins and paraffins, acetylenes, hydrogen and light aromatics such as benzene and toluene [5, 14-16]. Coke is formed in a small amount during the reaction.

Table 1. Number of reactions required in radical and molecular mechanism for similar reactant and products.

Radical Mechanism		Molecular Mechanism	
1.	$R-CH_2-CH_2-R' \leftrightarrow R-CH_2-CH_2^{\cdot} + \cdot R'$	1.	$R-CH_2-CH_2-R' \leftrightarrow R-CH=CH_2 + R'H$
2.	$R-CH_2-CH_2^{\cdot} \leftrightarrow R-CH=CH_2 + H^{\cdot}$	2.	$R-CH=CH_2 + H_2 \leftrightarrow R-CH_2-CH_3$
3.	$R-CH_2-CH_2^{\cdot} + H_2 \leftrightarrow R-CH_2-CH_3 + H^{\cdot}$		
4.	$2 H^{\cdot} \leftrightarrow H_2$		
5.	$R'' + H^{\cdot} \leftrightarrow R'H$		

Table 2. Typical compound existing in light hydrocarbon feeds and cracking products [5, 14-16].

Component	Feed	Products
H ₂	✓	✓
CH ₄	✓	✓
C ₂ H ₆	✓	✓
C ₃ H ₈	✓	✓
C ₄ H ₁₀	✓	✓
C ₅ H ₁₂	✓	✓
C ₆ H ₁₄	--	✓
C ₇ H ₁₆	--	✓
C ₂ H ₄	✓	✓
C ₃ H ₆	✓	✓
C ₄ H ₈	✓	✓
C ₅ H ₁₀	--	✓
C ₆ H ₁₂	--	✓
C ₇ H ₁₄	--	✓
C ₂ H ₂	✓	✓
C ₃ H ₄	--	✓
C ₄ H ₆	--	✓
Benzene	--	✓
Toluene	--	✓
Styrene	--	✓
Ethyl benzene	--	✓
Carbon	--	✓
Xylene	--	✓

If all components present in feed or products are considered in mechanism, its complexity increases, especially for the radical mechanisms. In such cases some components of feed or products with low concentrations can be eliminated. Selecting a component for these purposes depends on its yield during the reaction. If a component with a high yield is eliminated, yield of remained components must be increased for mass balance. Therefore, tuning of kinetic parameters cannot eliminate the estimation errors of the model. Some components are very active and their rate of production and consumption are very high, but their yields are low, elimination of such components reduces the

mechanism accuracy and generalization.

A free-radical mechanism was developed by Sundaram et al. for cracking of light hydrocarbons [14]. The main recommended mechanism consists of 133 radical and molecular reactions. In addition, they recommended an extracted mechanism with fewer numbers of reactions for pure light paraffins such as ethane, propane and so on. For mixed feeds, one must use the main mechanism. Main mechanism has been developed for hydrocarbons with carbon number less than 6 and higher hydrocarbons have been lumped in C₅⁺. Aromatics and naphthenics have not been considered due to lack of relevant kinetic data. With these summarizations, the mechanism consists of 133 reactions between 13 radicals and 14 molecules. So, if some of the higher hydrocarbons, aromatics and naphthenics are required to be added to the mechanism, it becomes more and more complex. The mechanism adds 13 continuity equations due to free radicals to model equation set and 13 sources of error in physical property estimation are added to the model too. Another example is the free-radical mechanism with 144 reactions recommended by Towfighi et al. (2006) for LPG cracking [11]. They have considered more molecular species like aromatics in their mechanism. According to reported compositions for cracking products of light hydrocarbons, and as shown in Table 2, carbon numbers up to C₇ must be considered for saturated and unsaturated hydrocarbons. Five light aromatics must also be covered by the mechanism. As previously explained, primary radicals are more probable and enough to be utilized in mechanism

development. Table 3 shows the primary radicals of selected paraffins. In the same manner, Table 4 shows the primary radicals of selected olefins. If olefins listed in this table are considered to be the primary radicals of paraffins, the primary radicals of these will be the secondary radicals of paraffins. Some reactions can be expected for

aromatics, so their radicals have been shown in Table 5. All these radicals must be considered in every radical mechanism. So, at least 91 reactions are required to represent their formation. Reactions between them rapidly increase the number of required reactions.

Table 3. Light paraffins and their radicals and molecular replica of radicals.

No.	Component	Primary Radicals	Molecular Replica
1	H ₂	H [•]	H ₂
2	CH ₄	CH ₃ [•]	CH ₄
3	C ₂ H ₆	C ₂ H ₅ [•]	C ₂ H ₄
4	C ₃ H ₈	C ₂ H ₅ CH ₂ [•] , CH ₃ CH [•] CH ₃	C ₃ H ₆
5	C ₄ H ₁₀	C ₃ H ₇ CH ₂ [•] , C ₂ H ₅ CH [•] CH ₃	1-C ₄ H ₈ , 2-C ₄ H ₈
6	C ₅ H ₁₂	C ₄ H ₉ CH ₂ [•] , C ₃ H ₇ CH [•] CH ₃ , C ₂ H ₅ CH [•] C ₂ H ₅	1-C ₅ H ₁₀ , 2-C ₅ H ₁₀
7	C ₆ H ₁₄	C ₅ H ₁₁ CH ₂ [•] , C ₄ H ₉ CH [•] CH ₃ , C ₃ H ₇ CH [•] C ₂ H ₅	1-C ₆ H ₁₂ , 2-C ₆ H ₁₂ , 3-C ₆ H ₁₂
8	C ₇ H ₁₆	C ₆ H ₁₃ CH ₂ [•] , C ₅ H ₁₁ CH [•] CH ₃ , C ₄ H ₉ CH [•] C ₂ H ₅ , C ₃ H ₇ CH [•] C ₃ H ₇	1-C ₇ H ₁₄ , 2-C ₇ H ₁₄ , 3-C ₇ H ₁₄

Table 4. Light olefins and their radicals and molecular replica of radicals.

No.	Component	Primary Radicals	Molecular Replica
9	C ₂ H ₄	C ₂ H ₃ [•]	C ₂ H ₂
10	C ₃ H ₆	CH ₃ CH=CH [•] , CH ₃ C [•] =CH ₂ , CH ₂ [•] CH=CH ₂	C ₃ H ₄ , 1,2-C ₃ H ₄
11	1-C ₄ H ₈	C ₂ H ₅ CH=CH [•] , C ₂ H ₅ C [•] =CH ₂ , CH ₃ CH [•] CH=CH ₂ , CH ₂ [•] CH ₂ CH=CH ₂	1-C ₄ H ₆ , 1,2-C ₄ H ₆ , 1,3-C ₄ H ₆
12	2-C ₄ H ₈	CH ₃ CH=CHCH ₂ [•] , CH ₃ CH=C [•] CH ₃	2-C ₄ H ₆ , 1,2-C ₄ H ₆
13	1-C ₅ H ₁₀	C ₃ H ₇ CH=CH [•] , C ₃ H ₇ C [•] =CH ₂ , C ₂ H ₅ CH [•] CH=CH ₂ , CH ₃ CH [•] CH ₂ CH=CH ₂ , CH ₂ [•] CH ₂ CH ₂ CH=CH ₂	1-C ₅ H ₈ , 1,2-C ₅ H ₈ , 1,3-C ₅ H ₈ , 1,4-C ₅ H ₈
14	2-C ₅ H ₁₀	C ₂ H ₅ CH=CHCH ₂ [•] , C ₂ H ₅ CH=C [•] CH ₃ , C ₂ H ₅ C [•] =CHCH ₃ , CH ₃ CH [•] CH=CHCH ₃ , CH ₂ [•] CH ₂ CH=CHCH ₃	1,2-C ₅ H ₈ , 2-C ₅ H ₈ , 2,3-C ₅ H ₈ , 1,3-C ₅ H ₈
15	1-C ₆ H ₁₂	C ₄ H ₉ CH=CH [•] , C ₄ H ₉ C [•] =CH ₂ , C ₃ H ₇ CH [•] CH=CH ₂ , C ₂ H ₅ CH [•] CH ₂ CH=CH ₂ , CH ₃ CH [•] C ₂ H ₄ CH=CH ₂ , CH ₂ [•] C ₃ H ₆ CH=CH ₂	1-C ₆ H ₁₀ , 1,2-C ₆ H ₁₀ , 1,3- C ₆ H ₁₀ , 1,4-C ₆ H ₁₀ , 1,5-C ₆ H ₁₀
16	2-C ₆ H ₁₂	C ₃ H ₇ CH=CHCH ₂ [•] , C ₃ H ₇ CH=C [•] CH ₃ , C ₃ H ₇ C [•] =CHCH ₃ , C ₂ H ₅ CH [•] CH=CHCH ₃ , CH ₃ CH ₂ [•] CH ₂ CH=CHCH ₃ , CH ₂ [•] C ₂ H ₄ CH=CHCH ₃	1,2-C ₆ H ₁₀ , 2-C ₆ H ₁₀ , 2,3- C ₆ H ₁₀ , 2,4-C ₆ H ₁₀ , 1,4-C ₆ H ₁₀
17	3-C ₆ H ₁₂	C ₂ H ₅ CH=CHCH ₂ CH ₂ [•] , C ₂ H ₅ CH=CHCH ₂ [•] CH ₃ , C ₂ H ₅ CH=C [•] C ₂ H ₅	1,3-C ₆ H ₁₀ , 2,3-C ₆ H ₁₀ , 3- C ₆ H ₁₀
18	1-C ₇ H ₁₄	C ₅ H ₁₁ CH=CH [•] , C ₅ H ₁₁ C [•] =CH ₂ , C ₄ H ₉ CH [•] CH=CH ₂ , C ₃ H ₇ CH [•] CH ₂ CH=CH ₂ , C ₂ H ₅ CH [•] C ₂ H ₄ CH=CH ₂ , CH ₃ CH [•] C ₃ H ₆ CH=CH ₂ , CH ₂ [•] C ₄ H ₈ CH=CH ₂	1-C ₇ H ₁₂ , 1,2-C ₇ H ₁₂ , 1,3- C ₇ H ₁₂ , 1,4-C ₇ H ₁₂ , 1,5-C ₇ H ₁₂ , 1,6-C ₇ H ₁₂
19	2-C ₇ H ₁₄	C ₄ H ₉ CH=CHCH ₂ [•] , C ₄ H ₉ CH=C [•] CH ₃ , C ₄ H ₉ C [•] =CHCH ₃ , C ₃ H ₇ CH [•] CH=CHCH ₃ , C ₂ H ₅ CH [•] CH ₂ CH=CHCH ₃ , CH ₃ CH [•] C ₂ H ₄ CH=CHCH ₃ , CH ₂ [•] C ₃ H ₆ CH=CHCH ₃	1,2-C ₇ H ₁₂ , 2-C ₇ H ₁₂ , 2,3- C ₇ H ₁₂ , 2,4-C ₇ H ₁₂ , 2,5-C ₇ H ₁₂ , 1,5-C ₇ H ₁₂
20	3-C ₇ H ₁₄	C ₃ H ₇ CH=CHCH ₂ CH ₂ [•] , C ₃ H ₇ CH=CHCH [•] CH ₃ , C ₃ H ₇ CH=C [•] C ₂ H ₅ , C ₃ H ₇ C [•] =CHC ₂ H ₅ , C ₂ H ₅ CH [•] CH=CHC ₂ H ₅ , CH ₃ CH [•] CH ₂ CH=CHC ₂ H ₅ , CH ₂ [•] C ₂ H ₄ CH=CHC ₂ H ₅	1,3-C ₇ H ₁₂ , 2,3-C ₇ H ₁₂ , 3- C ₇ H ₁₂ , 3,4-C ₇ H ₁₂ , 2,4-C ₇ H ₁₂ , 1,4-C ₇ H ₁₂

Table 5. Light aromatics and their radicals and molecular replica of radicals.

No.	Component	Primary Radicals	Molecular Replica
21	C ₆ H ₆	C ₆ H ₅ [•]	C ₆ H ₆
22	C ₇ H ₈	C ₆ H ₅ CH ₂ [•] , 2-C ₆ H ₄ [•] CH ₃ [†] , 3-C ₆ H ₄ [•] CH ₃ [†] , 4-C ₆ H ₄ [•] CH ₃ [†]	C ₇ H ₈
23	o-C ₈ H ₁₀	CH ₃ C ₆ H ₅ CH ₂ ^{•†} , 3-C ₆ H ₄ [•] (CH ₃) ₂ [†] , 4-C ₆ H ₄ [•] (CH ₃) ₂ [†] , 5-C ₆ H ₄ [•] (CH ₃) ₂ [†] , 6-C ₆ H ₄ [•] (CH ₃) ₂ [†]	o-C ₈ H ₁₀
24	m-C ₈ H ₁₀	CH ₃ C ₆ H ₅ CH ₂ ^{•†} , 2-C ₆ H ₄ [•] (CH ₃) ₂ [†] , 4-C ₆ H ₄ (CH ₃) ₂ ^{•†} , 5-C ₆ H ₄ (CH ₃) ₂ ^{•†} , 6-C ₆ H ₄ (CH ₃) ₂ ^{•†}	m-C ₈ H ₁₀
25	p-C ₈ H ₁₀	CH ₃ C ₆ H ₅ CH ₂ ^{•†} , 2-C ₆ H ₄ [•] (CH ₃) ₂ [†] , 3-C ₆ H ₄ [•] (CH ₃) ₂ [†]	p-C ₈ H ₁₀

One of the main reactions of radicals with at least two carbon in chain is elimination of H[•] from the nearest C-H group to their free bound and formation of a double bound. Therefore, it seems that an olefin with unsaturated bound at the position of free bound of radical is the best selection for replication. Double bounds are very active, so many reactions of radicals can be expected for them. On this basis, Tables 3, 4 and 5 show some molecular replications for paraffins, olefins and aromatics.

A radical mechanism consists of many cracking and condensation reactions. All reactions are reversible and cracking reactions act in the opposite direction of condensation reactions. Condensation reactions may take place between radicals or radicals and molecules. The left side of Table 1 shows a symbolic form and a part of radical reaction mechanism. The forward side of Reaction 1 defines dissociation of every C-C bound in a molecule and creation of two radicals, and the backward one covers all condensation reaction between radicals to form heavier hydrocarbon. Reaction 2 shows the elimination of an H atom from the nearest carbon to free bound of radical and formation of an unsaturated compound. The reverse

side of this reaction can cover all reactions that are precursors to form saturated radicals from unsaturated compounds that can be followed by the reaction 3 to form saturated compounds. Reactions 4 and 5 show formation of hydrogen and hydrocarbon molecule from their radical and vice versa. If the free bound of radical has not posed at one end of its carbon chain, through reactions similar to reactions 1 and 2, branched hydrocarbon and n-olefins (n≠1) can be created. In the same manner cyclization and aromatization reactions can be defined. Now, if all of the possible radicals are inserted to such a mechanism, an overall and complete mechanism can be created.

The right side of Table 1 defines replicable molecular reactions. If required reactions for cyclic, aromatic and acetylenic compounds according to radical mechanism are added to them, a suitable molecular mechanism is created. By replication of the components listed in Table 2 in the final symbolic molecular mechanism, required molecular mechanism for light hydrocarbons is prepared. Unfortunately, the position of double bound in olefin products of cracking processes has not been reported in much of the literature. On the other hand, branched

hydrocarbons are also not reported. In such cases, all olefins have been considered as 1-olefin and branched hydrocarbons change with linear hydrocarbons. The final mechanism has been shown in Table 6. In this mechanism, all the reactions have been considered to be reversible to achieve flexibility against pressure and reactants

concentration variations. All the reactions have been assumed to be elementary and reactions have been selected so that their molecularity is less than or equal to 3. The rate of reactions has been given by equation (1) and rate orders have been adapted from reaction molecularity:

Table 6. Molecular reaction mechanism for light hydrocarbons cracking.

No.	Reaction	$k_{oF} \times 10^{-8} \dagger$	$E_{aF} \times 10^{-5}$ (kJ/kgmole)	$k_{oR} \times 10^{-8} \dagger$	$E_{aR} \times 10^{-5}$ (kJ/kgmole)
1	$C_2H_6 \leftrightarrow C_2H_4 + H_2$	1.14564	1.48321	2.46764	1.27170
2	$C_3H_8 \leftrightarrow C_3H_6 + H_2$	0.95266	1.38546	0.95001	1.23999
3	$C_4H_{10} \leftrightarrow 1-C_4H_8 + H_2$	1.19897	1.32462	1.89572	1.02889
4	$C_5H_{12} \leftrightarrow 1-C_5H_{10} + H_2$	2.29627	1.26762	2.10376	1.05170
5	$C_6H_{14} \leftrightarrow 1-C_6H_{12} + H_2$	2.19996	1.32735	0.96519	1.14999
6	$C_7H_{16} \leftrightarrow 1-C_7H_{14} + H_2$	2.59439	1.26281	2.04018	0.96343
7	$C_2H_6 + H_2 \leftrightarrow 2 CH_4$	2.21316	1.41069	0.97243	1.37065
8	$C_3H_8 \leftrightarrow C_2H_4 + CH_4$	1.79216	1.40754	0.95001	1.13451
9	$C_4H_{10} \leftrightarrow C_3H_6 + CH_4$	4.08187	1.29696	1.44406	1.00220
10	$C_5H_{12} \leftrightarrow 1-C_4H_8 + CH_4$	5.49995	1.20001	2.99997	0.99971
11	$C_6H_{14} \leftrightarrow 1-C_5H_{10} + CH_4$	1.00002	1.29352	2.99997	0.90001
12	$C_7H_{16} \leftrightarrow 1-C_6H_{14} + CH_4$	3.82172	1.17073	4.33714	1.17482
13	$C_4H_{10} \leftrightarrow C_2H_6 + C_2H_4$	0.95002	1.49999	1.06659	1.22529
14	$C_5H_{12} \leftrightarrow C_3H_8 + C_2H_4$	1.35469	1.41875	4.99348	1.00974
15	$C_6H_{14} \leftrightarrow C_4H_{10} + C_2H_4$	1.00077	1.49999	1.08984	1.44994
16	$C_7H_{16} \leftrightarrow C_5H_{12} + C_2H_4$	1.60406	1.15326	3.37203	1.40910
17	$C_6H_{14} \leftrightarrow C_3H_8 + C_3H_6$	2.21463	1.06030	3.25468	0.99705
18	$C_7H_{16} \leftrightarrow C_4H_{10} + C_3H_6$	1.39081	1.29662	4.71072	0.90543
19	$C_4H_8 \leftrightarrow 2 C_2H_6$	3.14452	1.32329	0.95001	1.30049
20	$C_5H_{10} \leftrightarrow C_3H_6 + C_2H_4$	4.26441	1.44999	1.54744	1.00082
21	$C_6H_{12} \leftrightarrow 1-C_4H_8 + C_2H_4$	1.20852	1.20496	2.61834	0.97111
22	$C_7H_{14} \leftrightarrow 1-C_5H_{10} + C_2H_4$	1.53749	1.40029	3.57016	1.04772
23	$C_2H_4 \leftrightarrow C_2H_2 + H_2$	2.06107	1.44222	2.99997	0.86407
24	$C_3H_6 \leftrightarrow C_3H_4 + H_2$	1.85016	1.69998	5.49995	0.90045
25	$C_3H_6 \leftrightarrow C_2H_2 + CH_4$	7.47344	0.86532	2.21021	1.35898
26	$C_2H_4 + C_2H_2 \leftrightarrow 1,3-C_4H_6 + H_2$	1.05702	1.59597	1.22452	1.44999
27	$1,3-C_4H_6 + C_2H_2 \leftrightarrow \text{Benzene} + H_2$	59.99946	0.85022	4.94812	1.05369
28	$1,3-C_4H_6 + C_3H_4 \leftrightarrow \text{Toluene} + H_2$	59.79097	0.92765	1.00048	1.44999
29	$\text{Benzene} + CH_4 \leftrightarrow \text{Toluene} + H_2$	5.58691	1.49999	0.95041	1.44999
30	$\text{Benzene} + C_2H_2 \leftrightarrow \text{Styrene}$	26.54795	0.92904	2.02054	1.26130
31	$\text{Styrene} + H_2 \leftrightarrow \text{Ethyl benzene}$	12.15356	1.01571	1.58057	1.25564
32	$i-C_4H_{10} \leftrightarrow C_3H_6 + CH_4$	1.00026	1.24482	1.50951	1.25893
33	$i-C_4H_{10} + H_2 \leftrightarrow C_3H_8 + CH_4$	2.72583	1.23911	1.03628	1.44999
34	$2-C_4H_8 + H_2 \leftrightarrow C_4H_{10}$	4.99996	0.95628	1.00001	1.44999
35	$2-C_4H_8 + CH_4 \leftrightarrow i-C_5H_{10}$	1.06867	0.98331	1.38417	1.38193
36	$i-C_5H_{10} \leftrightarrow C_3H_6 + C_2H_6$	5.99995	1.29772	1.00044	1.44998
37	$2-C_4H_8 + 1,3-C_4H_6 \leftrightarrow o\text{-Xylene} + 2 H_2$	2.81241	1.09177	1.11378	1.26461

† Unit of frequency factors depends on reactions molecularity, sec^{-1} , $\text{m}^3.\text{kgmole}^{-1}.\text{sec}^{-1}$ and $(\text{m}^3)^2.(\text{kgmole})^{-2}.\text{sec}^{-1}$ for molecularities 1, 2 and 3 respectively.

$$(-r_A)_i = -\frac{dC_A}{dt} = kC_A C_B \quad (1)$$

k, the rate equation constant, is assumed to obey the Arrhenius Equation:

$$k = k_o \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

It should be noted that this mechanism covers all the components shown in Table 2 only by 37 reactions for 24 molecular components, hence a much shorter mechanism is developed compared with the free-radical mechanisms represented above. The mechanism developed in this work is similar to Belohlav et al's. (2003) reaction system for cracking of light hydrocarbons [5]. As they have also recommended and emphasized, the reactions used in their mechanism are adapted from free radical reactions.

3-2. Reactor modeling

Several configurations for the cracking reactors have been utilized. In lab scale and small pilot plants, the reactor is a one pass bare tube surrounded by an electrical heater. A lab scale reactor can be modeled by a straight tube surrounded with a hot surface. Fig. 1 shows a differential element of such a reactor. Since all data collected for tuning of kinetic parameters are obtained by laboratory setups, such a model is considered for their reactors. In the large-scale pilot plants and industrial plants tubular shape reactors and coils are used that hang in the middle of the fired heaters. Simulation of such reactors is difficult, but in a simplified form it can be

simulated as several straight tube reactors in series surrounded by a constant heat flux from the burners.

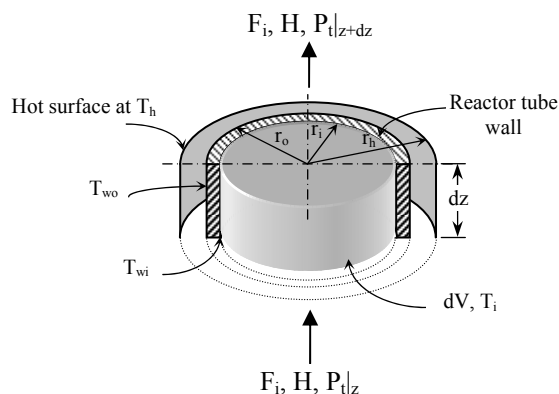


Figure 1. Reactor differential elements.

Modeling of a cracking reactor is accompanied by several difficulties. In general, three balance equations, named Mass, Energy and Momentum balance equations must be solved simultaneously. Transport phenomena inside and outside the reactor tubes accompanied by a complex reaction system, make these equations very stiff. So, all the authors consider some assumptions to simplify model equations. Here, the following assumptions have been considered:

1. One dimensional flow inside the reactor.
2. Plug flow and laminar regime inside the reactor and no entrance region effects.
3. No radial concentration gradients and axial dispersion.
4. Reactor tube wall heat resistance is negligible $T_{wi} \approx T_{wo} = T_w$
5. Reaction Energy requirements are supplied by the radiation mechanism from a hot surface at constant-temperature surrounding the reactor.

6. Reactions are elementary, and the rate order corresponds to the reaction molecularity.
7. The rate coefficients obey the Arrhenius relationship at reactor condition.
8. Dilution agents act as inert.

Model equations for a volume element of the reactor are as follow:

Mass balance: For each component in feed or product one mass balance equation must be considered:

$$\frac{dF_i}{dV} = \sum_i v_{ij} (-r_A)_i \quad (3)$$

where $(-r_A)_i$ is given by Eq.(1). For each component $C_i = cy_i$, and Eq. (1) can be rewritten as follows:

$$(-r_A)_i = -\frac{dC_A}{dt} = kc^2 y_A y_B \quad (4)$$

and c is the molar density of process fluid.

Energy balance: balance of energy for the volume element is given by:

$$\frac{dH}{dV} = \frac{dQ}{dV} + \sum_i v_{ij} (-r_A)_i [-\Delta H_{rj}] \quad (5)$$

dQ/dV is heat absorbed by process fluid from the heat source. Due to high temperature, heat absorption takes place with two mechanisms, convection and radiation. Convection heat transfer can be calculated by usual methods, but utilizing Stephan-Boltzmann law for radiation is not accurate enough. Radiation heat transfer between gases and a surface is considerably more complex. Gases are transparent to radiation

in many cases, except for CO_2 , H_2O , and various hydrocarbons. These radiate to an extent. Hottel method [20, 21] is applied to consider the absorptivity and emissivity effects of gases. Although this method is used for flue gas, ($\text{H}_2\text{O}+\text{CO}_2$), at the atmospheric pressure, the cracking processes also take place at low pressure, and the absorptivity and emissivity of hydrocarbons are often greater than CO_2 , for example, absorptivity of CH_4 for infrared radiation is much greater than CO_2 and has stronger greenhouse effect. Hence heat transfer inside the reactor tube can be given by:

$$\frac{dQ}{dV} = \frac{2h_i}{r_i} (T_w - T_i) - \frac{2\varepsilon_s \sigma}{r_i} [\varepsilon_g (T_i) T_i^4 - \alpha_g (T_w) T_w^4] \quad (6)$$

ε_g and α_g depend on concentration of water and hydrocarbons. Due to lack of data for calculation of this parameter for hydrocarbons, utilizing the data for CO_2 seems to be a good replacement.

T_w in Eq. (6) is unknown, hence another relation is needed. Required relation is prepared by heat transfer outside the reactor tube. For reactors with electrical heater or hot surface as energy source the following relation can be used:

$$\frac{dQ}{dV} = \frac{2\sigma(T_h^4 - T_w^4)}{r_o \left[\frac{1}{\varepsilon_s} + \frac{r_o}{r_h} \left(\frac{1}{\varepsilon_h} - 1 \right) \right]} = C_1 (T_h^4 - T_w^4) \quad (7)$$

Momentum balance: balance of momentum inside a tube is given by the following relation:

$$dP_t + \frac{f\rho u^2}{2D_t A} dV + \rho u du = 0 \quad (8)$$

From overall continuity equation:

$$\rho u A = GA = \text{const.} \quad (9)$$

A is the cross section of reactor tube and assumed to be constant, hence after differentiation and rearranging:

$$u du = -u^2 \frac{d\rho}{\rho} = -\frac{G^2}{\rho^3} d\rho \quad (10)$$

By substituting Eq. (11) into Eq. (9) and rearranging:

$$\frac{dP_t}{dV} = -G^2 \left[\frac{d}{dV} \left(\frac{1}{\rho} \right) + \frac{f}{2D_t \rho A} \right] \quad (11)$$

Knutzen et al. gave the friction factor by [9, 18]:

$$Fr = \frac{f}{2D_t} = 0.092 \frac{Re^{-0.2}}{D_t} \quad (12)$$

For the straight parts of the reactor coils and

$$Fr = \frac{f}{2D_t} = 0.092 \frac{Re^{-0.2}}{D_t} + \frac{\zeta}{\pi R_b} \quad (13)$$

For the tube bends. Nekrasov gave ζ by [9, 19]:

$$\zeta = \left(0.7 + 0.35 \frac{\Lambda}{90} \right) \left(0.051 + 0.19 \frac{D_t}{R_b} \right) \quad (14)$$

Where R_b and Λ are tube bend radius and bend angle, respectively.

The above mentioned equations should be solved simultaneously to get the model results for reactor.

3-3. Model solution method

Reactor governing equations are a set of nonlinear first-order differential equations, and hence cannot be solved analytically. Runge-Kutta 4th order method was utilized to solve the system of differential equations. The model outputs are the yields or composition of products, temperature profiles of cracked gas and skin temperature along the reactor tube. ρ and c , mass and molar density, C_p , and Enthalpy of cracked gas for each element in Runge-Kutta method along the reactor tube are calculated by Peng-Robinson equation of state. Other required physical properties are calculated based on contribution methods and their related mixing rules.

3-4. Estimation of kinetic parameters

Estimation of kinetic parameters for the proposed mechanism is the basic step in modeling of a cracking process. Usually, required kinetic parameters are prepared by literature survey. Measuring of kinetic parameters by experimental methods is very difficult because isolation of a cracking reaction is almost impossible. So, all authors tune their required parameters. Such parameters are only suitable for their mechanism and cannot be applied for another mechanism. Hence, the differences in developed mechanism, modeling equations, and solution methods may cause greater

discrepancy between the results and reduce the accuracy of the model estimations.

To generalize the mechanism, tuning of the parameters must be performed for many reactors with different feedstock and process conditions to minimize the errors of the reactor results. The objective function that should be minimized is the sum of square of error percents (EPSS), and can be defined as:

$$EPSS = \sum_i \sum_k \left[\frac{Y_{ik,model} - Y_{ik,experiment}}{Y_{ik,experiment}} \times 100 \right]^2 \quad (15)$$

Error minimization must be performed for all of the reactors simultaneously. $Y_{ik,experiment}$ can be any result of i component for reactor k that can be measured such as products yield, mole fraction, conversion, and so on. $Y_{ik,model}$ is the same data that is estimated for each variation in kinetic parameters ordered by error minimization method and compared with $Y_{ik,experiment}$ for the new error computation. Nonlinear regression method has been used to minimize the errors due to the nonlinearity of the equations applied in the model. Some of the initial kinetic parameters have been adapted from the literature [5, 15–16], and then tuned to minimize the errors. Table 6 shows the mechanism and final kinetic parameters.

4. Results and discussion

The accuracy of the model is the most important goal of the process simulation. In simulation of cracking process, in addition to the reactor modeling, an accurate and acceptable reaction mechanism is required too. An acceptable reaction mechanism must be the shortest one that uses more real

reactions, covers a greater number of the reactant and products and also gives results with enough accuracy, not only at the reactor exit but also along the reactor length. On the other hand, the proposed mechanism must be flexible enough against variations of pressure and component concentrations along the reactor due to variations in feed rate, composition, temperature, pressure and reactor specifications and characteristics.

Table 6 presents the reaction mechanism developed in this work for the simulation of the thermal cracking reactors. On the basis of the reactor model and the reaction mechanism, required kinetic parameters were calculated and tuned for several different reactors. Many data sets exist in literature but the sizes of the used reactors or their conditions are not reported or not clear enough. Therefore they cannot be used in kinetic parameters tuning or mechanism and model results validation, unfortunately. Required sets of experimental data for this process were adapted from the literature [5, 11, 14–16, 22]. The reaction mechanism and reactor model are used to estimate product concentrations of four different reactors that are used in the kinetic parameters tuning. Required data are adapted from reference [5] and the results are presented in Table 7. In this table the results of the model utilized by Belohlav et al. [5] are also presented for comparison. They developed a molecular mechanism similar to that recommended above. Results show the advantage of recommended model. Accuracy of the results of developed model, specially for the main components like H_2 , CH_4 , C_2H_6 , C_2H_4 is very good and for the others is acceptable. It must be noted that one of the sources of the errors

is the unbalance in atomic moles of elements per unit mass of products with the same for feeds. On the other hand, Table 7 shows that the reported experimental data have not been normalized correctly. These types of measurement errors have a considerable effect on parameters tuning and achieving

acceptable estimation error, especially for components with low concentration in products. So, acceptable error range must be wider. The estimation errors of the concentration of aromatics or heavier compounds in Table 7 may be affected by these types of errors.

Table 7. Advantages of the recommended model compared with Belohlav *et al.* [5] model.

Component	Reactor 1						Reactor 2					
	Feed wt.%	Cracking Products				Feed wt.%	Cracking Products					
		Experiment wt.% [5]	Belohlav et al. [5] wt.%	Err%	This work wt.%		Err%	Experiment wt.% [5]	Belohlav et al. [5] wt.%	Err%	This work wt.%	Err%
H ₂	0.0	4.2	4.1	-2.4	4.286	2.0	0.0	3.8	3.7	-2.6	3.668	-3.5
CH ₄	0.0	5.4	5.1	-5.6	4.375	-19.0	0.0	3.7	4	8.1	3.275	-11.5
C ₂ H ₆	99.9	32.7	34.1	4.3	31.832	-2.7	99.6	41.3	39.7	-3.9	41.461	0.4
C ₂ H ₄	0.1	49.7	49.2	-1.0	51.209	3.0	0.4	45.7	47.2	3.3	45.051	-1.4
C ₂ H ₂	0.0	0.4	1.2	200.0	0.363	-9.2	0.0	0.3	1.1	266.7	0.296	-1.5
C ₃ H ₈	0.0	0.2	0.3	50.0	0.267	33.4	0.0	0.2	0.2	0.0	0.190	-5.2
C ₃ H ₆	0.0	1.5	0.9	-40.0	1.515	1.0	0.0	1.3	0.8	-38.5	1.471	13.1
C ₃ H ₄	0.0	0.1	0	-100.0	0.119	19.0	0.0	0.1	0	-100.0	0.104	4.1
C ₄ H ₁₀	0.0	0.2	0	-100.0	0.188	-6.1	0.0	0.3	0	-100.0	0.221	-26.4
C ₄ H ₈	0.0	0.3	0.8	166.7	0.387	29.0	0.0	0.3	0.5	66.7	0.342	13.9
C ₄ H ₆	0.0	2	1.3	-35.0	2.454	22.7	0.0	1.5	0.9	-40.0	1.903	26.9
Benzene	0.0	1.8	2.5	38.9	1.728	-4.0	0.0	0.9	1.5	66.7	1.088	20.9
Toluene	0.0	0.9	0	-100.0	0.421	-53.3	0.0	0.4	0	-100.0	0.202	-49.4
Xylene	0.0	0	0	--	0.001	--	0.0	0	0	--	0.001	--
E-benzene	0.0	0	0	--	0.024	--	0.0	0	0	--	0.012	--
Styrene	0.0	0	0	--	0.041	--	0.0	0	0	--	0.022	--
C ₅	0.0	0.6	0	-100.0	0.481	-19.8	0.0	0.4	0	-100.0	0.439	9.8
C ₆	0.0	0	0	--	0.100	--	0.0	0	0	--	0.083	--
C ₇ ⁺	0.0	0.1	0.5	400.0	0.208	108.4	0.0	0	0.3	--	0.172	--
Sum / Err. SOS	100	100.1	100	274671.0	100	18330.0	100	100.2	99.9	123177.7	100	4954.7
Component	Reactor 3						Reactor 4					
	Feed wt.%	Experiment wt.% [5]	Belohlav et al. [5] wt.%	Err%	This work wt.%	Err%	Feed wt.%	Experiment wt.% [5]	Belohlav et al. [5] wt.%	Err%	This work wt.%	Err%
H ₂	0.0	1.4	1	-28.6	1.348	-3.7	0.0	1.4	0.8	-42.9	1.155	-17.5
CH ₄	0.0	25.7	25.8	0.4	24.917	-3.0	0.0	23.9	25	4.6	22.760	-4.8
C ₂ H ₆	4.0	4.3	6	39.5	3.296	-23.4	4.0	4.2	4.3	2.4	4.345	3.4
C ₂ H ₄	0.0	33.8	32.7	-3.3	31.810	-5.9	0.0	30.2	30.9	2.3	29.786	-1.4
C ₂ H ₂	0.0	0.8	0.9	12.5	0.887	10.9	0.0	0.7	0.8	14.3	0.776	10.8
C ₃ H ₈	35.0	3.7	3.7	0.0	3.278	-11.4	25.0	2.9	3.6	24.1	3.018	4.1
C ₃ H ₆	1.0	13.2	13.5	2.3	14.425	9.3	1.0	14	14.2	1.4	14.269	1.9
C ₃ H ₄	0.0	0.9	0.6	-33.3	0.806	-10.4	0.0	1	1.1	10.0	0.747	-25.3
C ₄ H ₁₀	60.0	0.9	0.3	-66.7	0.932	3.6	60.0	1.2	0.3	-75.0	1.130	-5.8
C ₄ H ₈	0.0	1.9	2.6	36.8	1.908	0.4	10.0	2.7	3.4	25.9	3.022	11.9
C ₄ H ₆	0.0	2.9	2.3	-20.7	2.752	-5.1	0.0	3.4	2.5	-26.5	2.736	-19.5
Benzene	0.0	4.4	5.3	20.5	6.272	42.5	0.0	6.4	6	-6.3	7.401	15.6
Toluene	0.0	1.5	1	-33.3	1.977	31.8	0.0	2.2	1.4	-36.4	2.579	17.2
Xylene	0.0	0.1	0	-100.0	0.010	-90.4	0.0	0.1	0	-100.0	0.098	-1.7
E-benzene	0.0	0	0	--	0.075	--	0.0	0.1	0	-100.0	0.109	8.9
Styrene	0.0	0.4	0	-100.0	0.394	-1.5	0.0	0.5	0	-100.0	0.522	4.4
C ₅	0.0	1.9	2	5.3	2.570	35.3	0.0	2.3	2.2	-4.3	2.733	18.8
C ₆	0.0	0.6	0.6	0.0	0.623	3.8	0.0	0.8	0.8	0.0	0.782	-2.2
C ₇ ⁺	0.0	1.6	2	25.0	1.719	7.5	0.0	2.2	2.8	27.3	2.032	-7.6
Sum / Err. SOS	100	100	100.3	32074.7	100	13392.2	100	100.2	100.1	41879.6	100	2738.1

To eliminate the effects of such errors, tuning of kinetic parameters must be performed for many other reactors with different operating conditions and feed compositions of the same light hydrocarbons. It is a logical expectation that, the more reactor data used in kinetic parameters tuning, the more generalized the model.

For an example of the accuracy of our model, its results were compared with the experimental data published by Froment *et al.*

Froment *et al.* performed several experiments on cracking of Propane [22]. One set of their results is on cracking of propane at 800°C and 1atm. The data represent the effect of

space time (V/F_0) on the propane conversion and yield (weight of product/weight of feed) of main cracking products. Fig. 2 compares the results of our simulation with their data. A good agreement is seen between their experimental data and model results.

Froment *et al.* also performed another set of experiments on cracking of ethane. To better check the performance of our model, Fig. 3 compares the results of ethane conversion at different temperature versus V/F_0 , obtained by our model with the data published by Froment *et al.* [15]. Fig. 3 shows good agreement between the data and model results again.

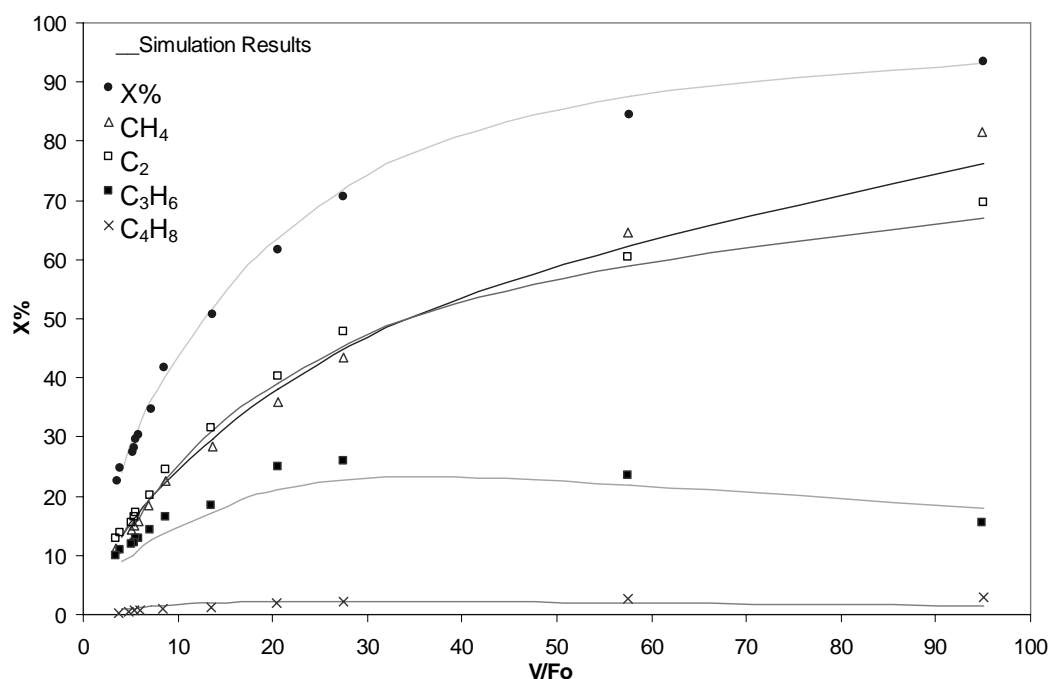


Figure 2. Total conversion of propane and conversion to primary products as a function of V/F_0 at 800°C [22].

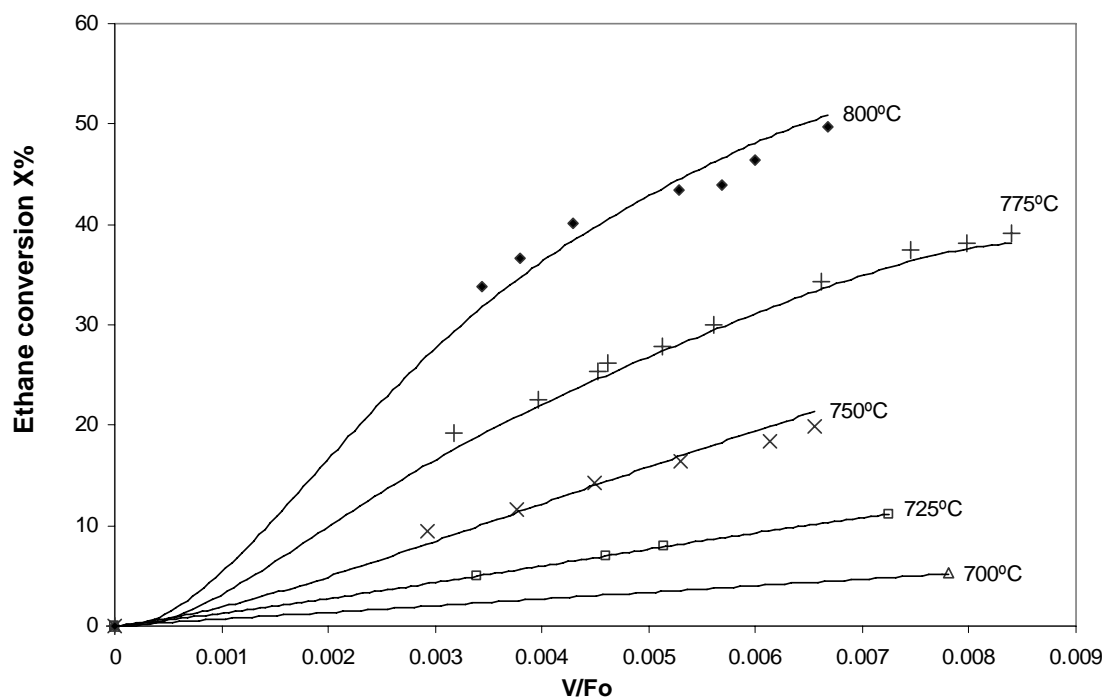


Figure 3. Conversion of ethane as a function of V/F_o predicted by the model (lines) and experimental data (Points) [15].

The above results can validate the kinetic mechanism and reactor model used for modeling and simulation of light hydrocarbons cracking. The model was used to predict the results of cracking of propane that was performed in cracking setup by Towfighi et al. [11]. Fig. 4 shows the results of experiments for propane cracking, predictions of the Towfighi et al. [11] model with radical mechanism and the results of molecular mechanism and reactor model recommended in this work. As these figures show, the recommended molecular mechanism can predict reactor product compositions as good as the radical mechanism used by Towfighi et al. [11] and achieve acceptable results. Hence with smaller molecular mechanism and lower reactants number the same advantages can be achieved.

On the other hand, in spite of many models being used for cracking of light hydrocarbons that focus on main products [5, 14-16, 22], the recommended model tries to cover heavier compounds like higher saturated and unsaturated hydrocarbon and aromatics in addition to main components with acceptable estimations. Figs. 5a, 5b, and 5c show the yield (weight of determined product per weight of feed) of various ethane cracking products along the reactor. Fig. 5a shows the conversion of ethane and variations in concentration of main products of its cracking along the reactor. Fig. 5b shows the variations in concentration of aromatic compound and their source reactants along the reactor. According to this figure, production of toluene increases when production of methyl acetylene increases and the concentration of propene begins to

decrease. Fig. 5c shows some of the remained trace products of cracking of ethane. In spite of other products, in the reactor condition, concentration of butane increases to a maximum and then decreases. This may be due to the reaction between ethane and its primary product, ethylene. The concentration of i-butane, i-pentane, 2-butane, o-xylene and ethyl benzene are also

predicted by the model and are very low. This is in agreement with the experimental data because such trace materials are often undetectable or not reported.

Fig. 5d shows the temperature profile along the reactor for ethane cracking process. According to this figure, no considerable reaction takes place up to the temperature 700°C. This is in agreement with Fig. 3.

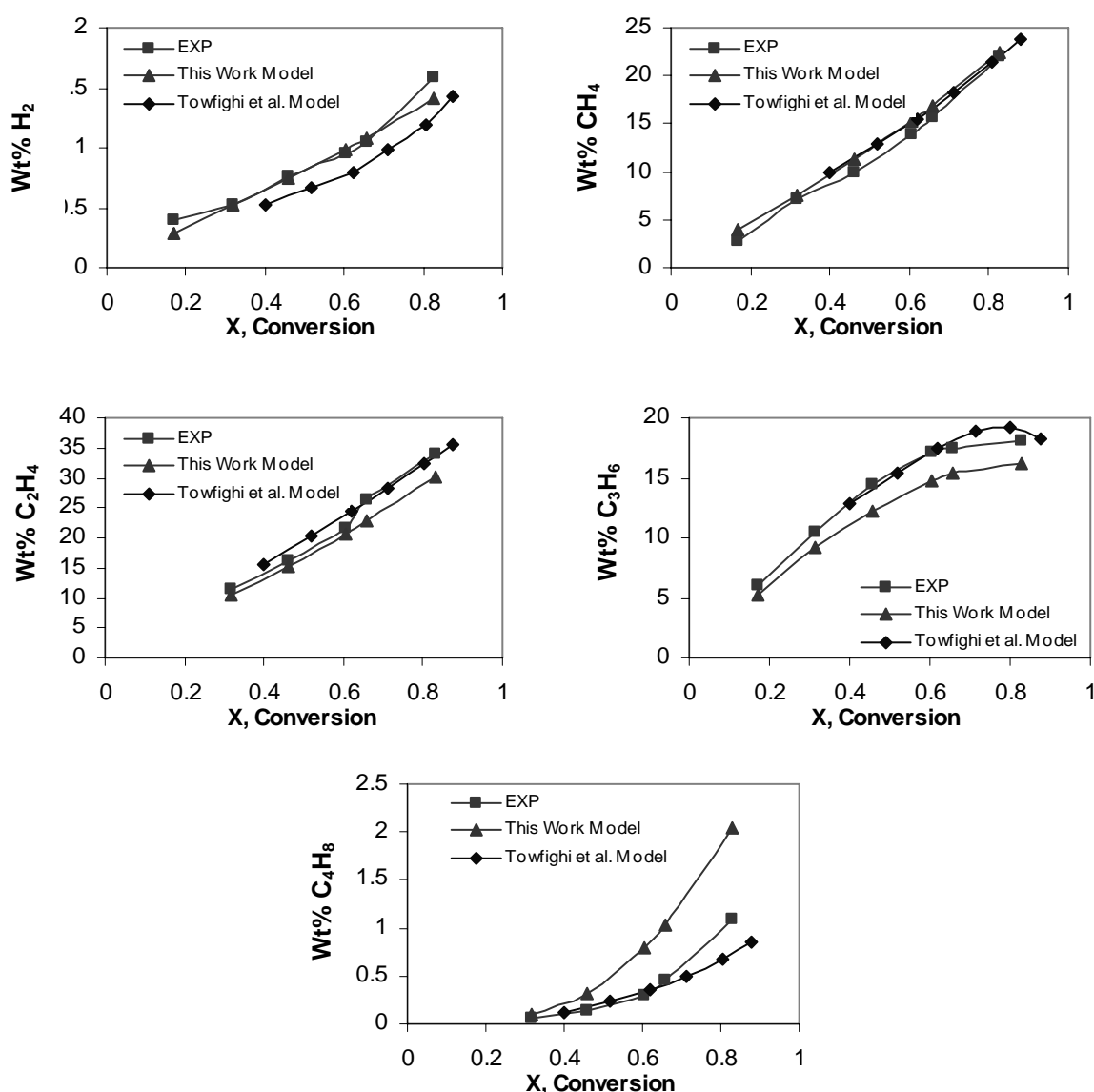
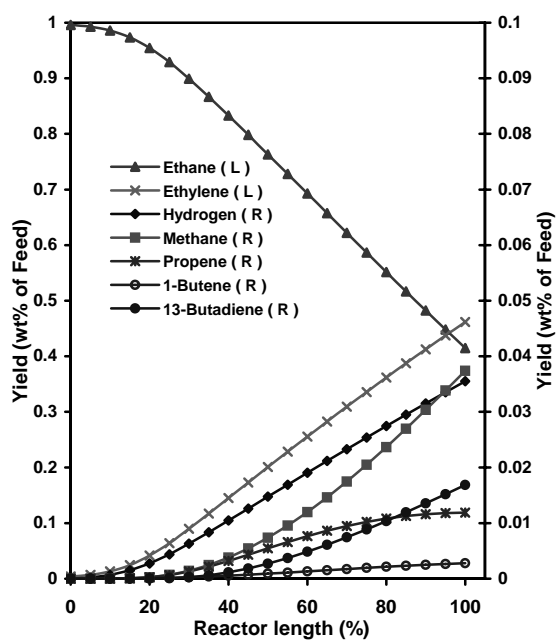
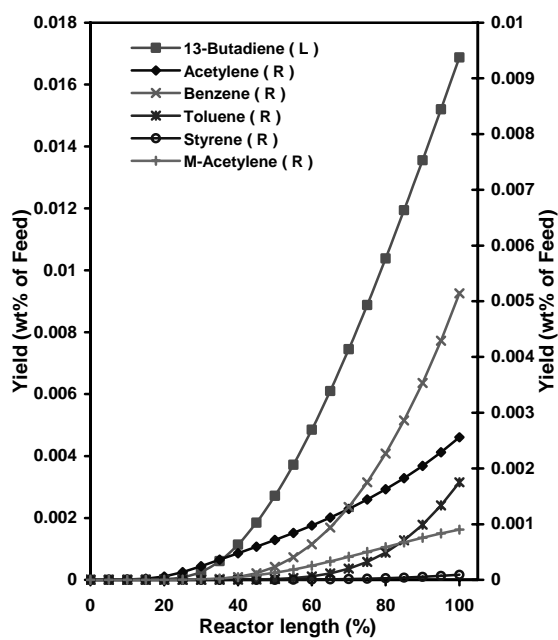


Figure 4. Comparison of experimental & model product yields (weight of product/weight of feed) distribution in thermal cracking of propane [11].

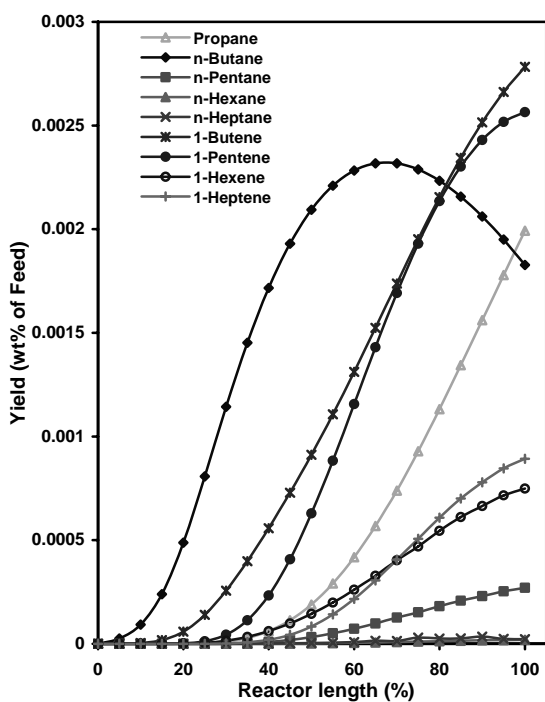
Development of a Molecular Kinetic Model and Tuning of its Required Kinetic Parameters for Thermal Cracking of Light Hydrocarbons



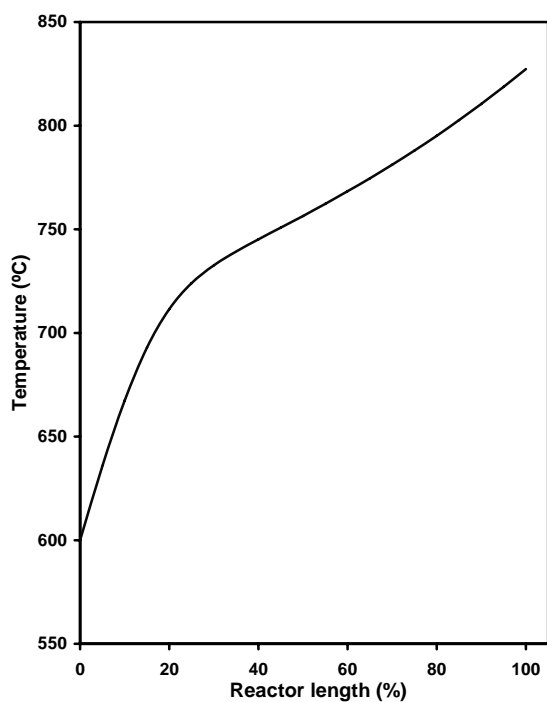
(a) Main Products



(b) Aromatics and their source reactant



(c) Other Products

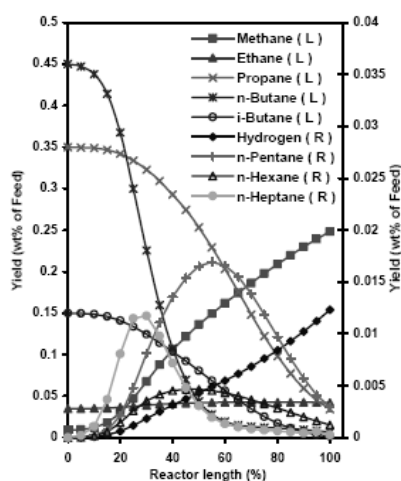


(d) Temperature Profile

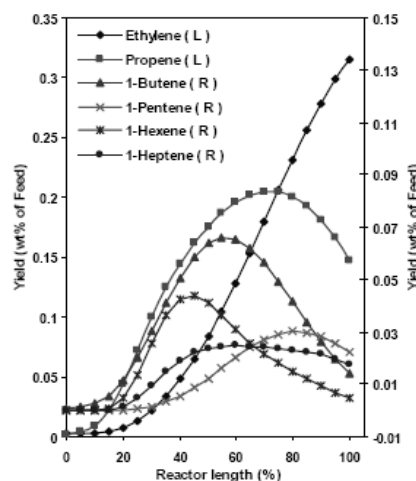
Figure 5. Yield of various Ethane thermal cracking products and temperature profile along the reactor (Reactor data adapted from Ref. [5], feedstock 4 and its reactor conditions). (R) and (L) refer to Right and Left Y axis.

The same results can be obtained for cracking of LPG. Figures 6a, 6b, 6c illustrate the results for thermal cracking of LPG. Fig. 6a shows the conversion of Feed components and production of paraffinic products along the reactor. Fig. 6b shows production of olefinic products along the reactor. According to these figures all the paraffinic and olefinic products increase to a maximum and then decrease while methane, ethylene and hydrogen continuously increase along the reactor and this means that lower

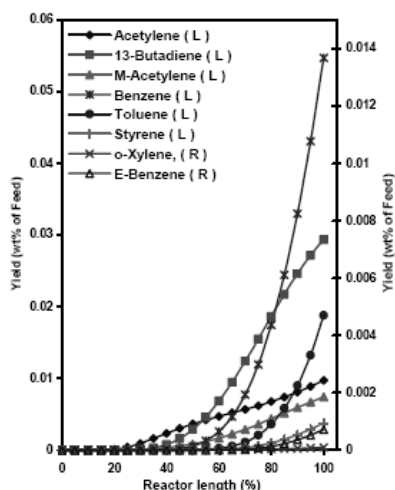
temperature and residence time increase the selectivity of such products. Fig. 6c shows the production of aromatics and their source reactants. When the concentration of ethylene and acetylene and temperature increase enough the concentration of aromatics begins to increase rapidly. As shown in Fig. 5b and Fig. 6c this phenomena takes place at 60% of length of the reactor and at this length, according to Fig. 5d and Fig. 6d process fluid temperature is in the range 700-750°C, approximately.



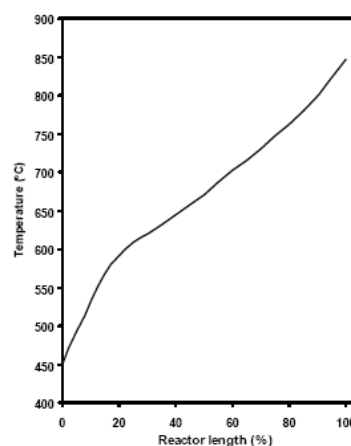
(a) Paraffinic feeds and Products



(b) Olefinic products



(c) Aromatics and their source reactant



(d) Temperature Profile

Figure 6. Yield of various LPG thermal cracking products and temperature profile along the reactor (Reactor data adapted from Ref. [5], feedstock 3 and its reactor conditions,). (R) and (L) refer to Right and Left Y axis.

Figure 6d presents the temperature profile along the reactor. In spite of ethane, LPG cracking is started at 575°C and preheating up to 600°C or higher means that some cracking took place in the preheater.

5. Conclusions

The molecular reaction mechanism recommended in this work, on the basis of reactor modeling results, can estimate products of light hydrocarbons with higher accuracy and cover a larger extent of compounds. Results of model solving for several feeds show that one can confine to estimations not only at the end of the reactors, that kinetic parameters are tuned by them, but also yield of products in the middle points of reactors. Adding a coke thickness estimation procedure to the model will complete the simulation and the simulation can be utilized for process studies and optimization, specially for olefin production plants that want to use light hydrocarbons as feed.

Nomenclature

A reactor tube cross section area [m]
 C molar density of cracking gases (mole/m³)
 C_i, C_A, C_B molar concentration of process gases (mole/m³)
 C_p heat capacity [J/mole · K]
 D_t tube diameter [m]
 E_a activation energy [J/mole]
 E_{aF} forward reaction activation energy [J/mole]
 E_{aR} reverse reaction activation energy [J/mole]
 F molar flow rate [mole/hr]
 f friction factor

G total mass flux of the process gas [kg/m²s]
 H enthalpy of process gas
 h_i inside heat transfer coefficient [W/m².K]
 h_o outside heat transfer coefficient [W/m².K]
 k reaction rate constant [depend on reaction rate order 1/s or m³/s]
 k_o frequency factor [depend on reaction rate order 1/s or m³/s]
 k_{oF} forward reaction frequency factor [depend on reaction rate order 1/s or m³/s]
 k_{oR} reverse reaction frequency factor [depend on reaction rate order 1/s or m³/s]
 R universal gas constant [J/mole.K]
 P_t total pressure [kPa]
 Q heat flux [W/m²]
 R_b radius of the tube bend [m]
 Re Reynolds number
 r_i reactor tube inside radius [m]
 r_o reactor tube outside radius [m]
 r_h hot surface radius [m]
 T_i process gas temperature [K]
 T_h hot surface temperature [K]
 T_{wi} reactor tube wall inside temperature [K]
 T_{wo} reactor tube wall outside temperature [K]
 T_w reactor tube wall average temperature [K]
 u process gas velocity [m/s]
 V volume (m³)
 y_i, y_A, y_B mole fraction of process gas
 z reactor axial coordinate (m)
 $(-r_i)$ reaction rate in pyrolysis process [mole/m³.s]
 $[-\Delta H_r]$ heat of reaction [J/mole]

Indices

i	component counter
j	reaction counter
k	reactor counter

Greek Letters

α_g	process gas emissivity
ν_{ij}	stoichiometry coefficient
A	angle of bend [degree °]
ρ	density [kg/m ³]
σ	Stephan-Boltzmann constant [W/m ² . K ⁴]
ε_g	process gas emissivity
ε_s	reactor tube wall emissivity

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