First Principles based Reaction Network for Thermal Cracking

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Abstract

In a continued search for higher performance, increased selectivity and faster development of new processes, the chemical industry requires accurate models with a wide range of applicability. An accurate kinetic description of the reaction chemistry in combination with a carefully chosen reactor model is essential for such models. This is of particular importance for the thermal cracking process. An automatically generated reaction network is developed using the Boolean relation matrix concept. The kinetic parameters were obtained by a first principles based group additive method (Saeys et al., 2004). Further expansion of the reaction network and improved quantum chemical calculations have resulted in accurate simulation results for feedstocks ranging from ethane till n-butane. A graphical user interface created with Visual Basic.Net made the program user friendly.

Keywords: **Thermal cracking, kinetic modeling, network generation, first principles**

1. Introduction

Thermal cracking of hydrocarbons is one of the main processes in the petrochemical industry. In tubular reactors hydrocarbons are cracked into commercially more interesting products such as ethylene and propylene. Feedstocks range from ethane to complex mixtures such as naphthas, gas oils and even vacuum gas oils (VGO). The temperatures in the tubular reactors vary from 900 K at the reactor inlet till 1200 K at the outlet. Profit margins become narrower and narrower and therefore the petrochemical industry is continually searching for higher performance and increased selectivity. In this search accurate mathematical simulation models are an indispensable tool. These models account for both the chemical reactions and the physical transport phenomena. Only fundamental kinetic models are able to simulate the chemical kinetics over a wide range of process conditions and for a wide range of feedstocks (Froment, 1992). Also in other chemical processes large-scale detailed kinetic models find increasing use: e.g. for the modeling of combustion processes, atmospheric chemistry, soot formation… Because such models may have thousands of reactions and species, constructing them by hand can be tedious and error-prone. Therefore many research groups have developed computer tools to automatically generate such mechanisms (Chinnick, et al., 1988; Chevalier, et al. 1990; Froment, 1991; DiMaio and Lignola, 1992; Quann and Jaffe, 1992; Blurock, 1995; Ranzi, et al., 1995; Broadbelt, et al., 1996; Prickett and Mavrovouniotis 1997; Battin-Leclerc et al., 2000; Song et al., 2003). At the Laboratory of Petrochemical Industry in Ghent University a new network generation tool has been developed especially for the thermal cracking process.

2. Results and Discussion

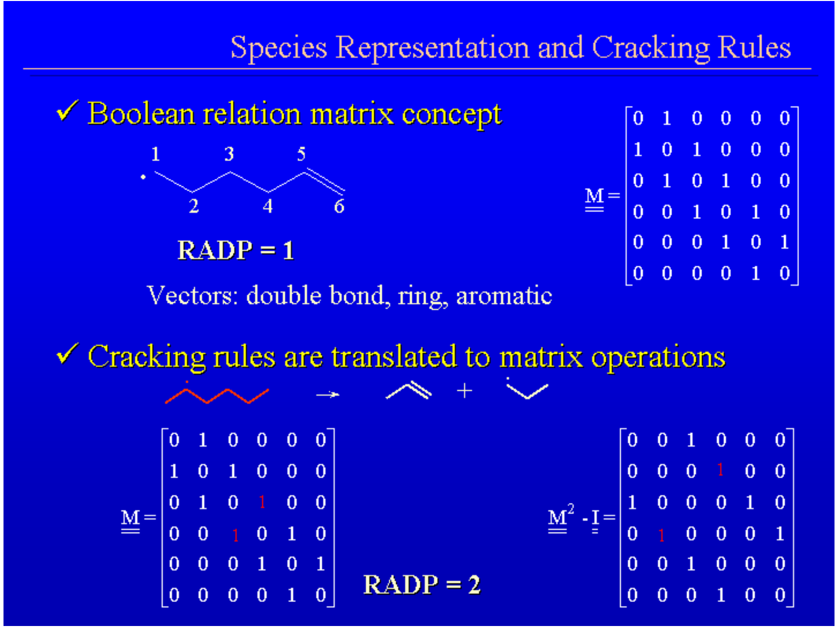
2.1 Network Construction

For an accurate description of chemical kinetics applicable over a wide range of process conditions and feedstocks, a detailed kinetic model is required. Due to the large number of radical intermediates and elementary reactions, building such a kinetic model is a computationally challenging task. Fortunately it can be safely accepted that for thermal cracking monomolecular reactions dominate for species with more than 5 carbon atoms (Ranzi et al., 1983). This allows to distinguish between two networks: the monomolecular μ-network and the β-network, which contains both uni- and bimolecular reactions. The kinetics for the former can be described by analytical expressions based on the Pseudo Steady State Approximation for the radical reaction intermediates. For species with 5 or less carbon atoms this is no longer possible, making it necessary to stock their reactions in a separate sub-network; the β-network.

Thermal cracking of hydrocarbons is known to proceed through a free-radical mechanism and three important families of reactions can be distinguished:

1. Carbon-carbon and carbon-hydrogen bond scissions and the reverse radical-radical recombinations
2. Hydrogen abstraction reactions, both intra- and intermolecular
3. Radical addition to olefins and the reverse β-scission of radicals, both intra- and intermolecular

For the species with 5 or less carbon atoms all reactions from these three families are considered in the β-network. This results in a large number of radical intermediates and elementary reactions. Therefore a computer program has been developed which generates the β-network automatically based on the binary relation matrix concept. In this concept the cracking rules are translated into matrix operations performed on the Boolean relation matrix, representing the species structure (Hillewaert et al., 1988), see Figure 1.



Species Representation and Cracking Rules

✓ Boolean relation matrix concept

RADP = 1

Vectors: double bond, ring, aromatic

$$\underline{\underline{M}} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix}$$

✓ Cracking rules are translated to matrix operations

$$\underline{\underline{M}} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix}$$

RADP = 2

$$\underline{\underline{M}}^2 - \underline{\underline{I}} = \begin{bmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix}$$

Figure 1: Illustration of the Boolean Matrix concept and translation of cracking rules into matrix operations

The buildup of the reaction network is illustrated in Figure 2. Starting from an initial pool of molecules possibilities for scission reactions, hydrogen abstraction reactions and addition reactions are identified. Cyclization reactions are considered as intramolecular additions, while isomerization reactions are considered as intramolecular hydrogen abstractions. For every forward reaction introduced in the network the corresponding reverse reaction is also incorporated in the network. These reactions result in a number of formed radicals and molecules. The new radicals are added to the radical pool and the molecules are added to the molecule pool. In the next iteration the new species react with each other and with other species of the radical and molecule pool and the network is constructed gradually. To limit the number of reactions a carbon count stop criterion is applied (Broadbelt at al., 1994), i.e. species are only added when they have less than n_m carbon atoms for a molecule, and n_r carbon atoms for a radical. Here, both n_m and n_r are set equal to 5; hence the largest species in the reaction network have 10 carbon atoms. The resulting β-network comprises more than 2000 reactions and over 500 species.

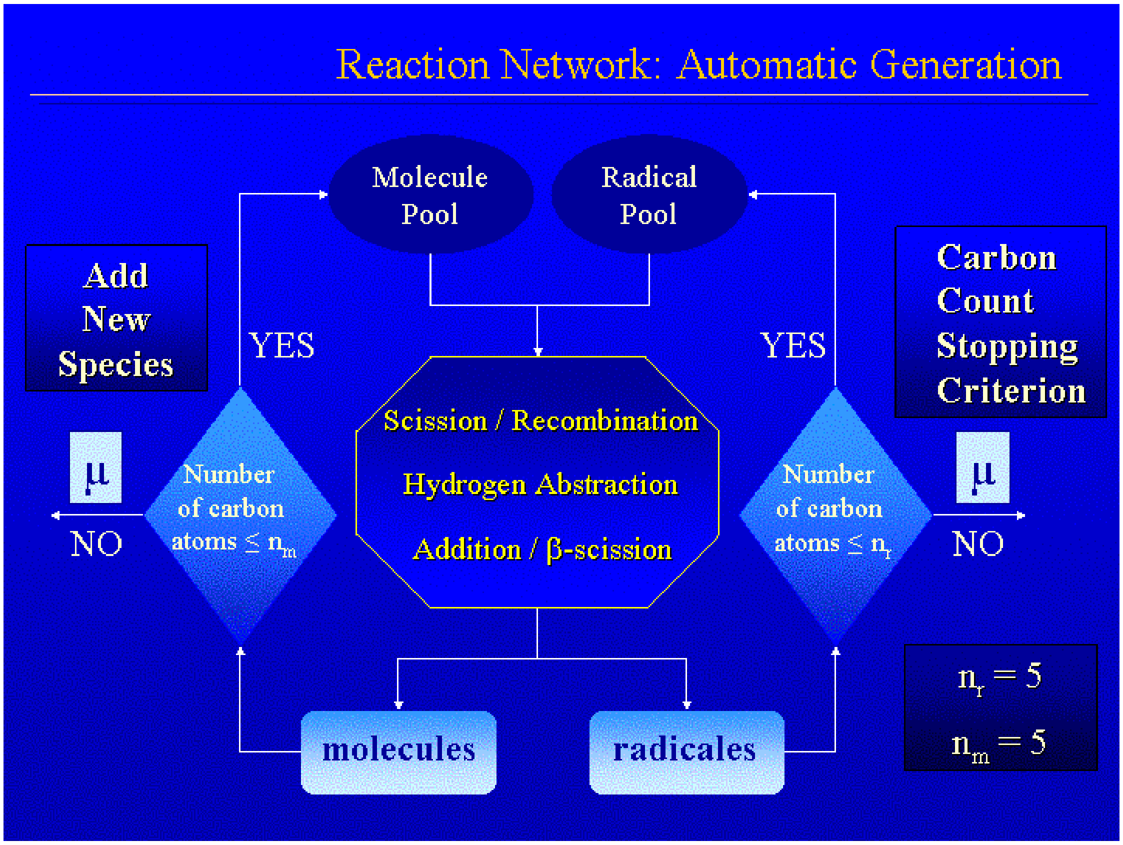


Figure 2: Algorithm for the automatic generation of the reaction network

In the μ-network different reaction schemes are developed for a molecule starting from 3 different primary reactions:

- reaction schemes out of initiation
- reaction schemes out of H-abstraction
- reaction schemes out of radical addition

In Figure 3 a reaction scheme for a C-C scission reaction of decane is shown. If a radical is formed which has only a μ-character the concentration of this radical can be easily calculated if the pseudo steady state for this radical is assumed. This can be illustrated for both the 1-nonyl radical (μ_1) and the 5-nonyl radical (μ_2) formed in the reaction scheme in Figure 1. The 1-nonyl radical (μ_1) is formed directly during the scission reaction; the 5-nonyl radical (μ_2) is formed after the isomerization of the 1-nonyl radical.

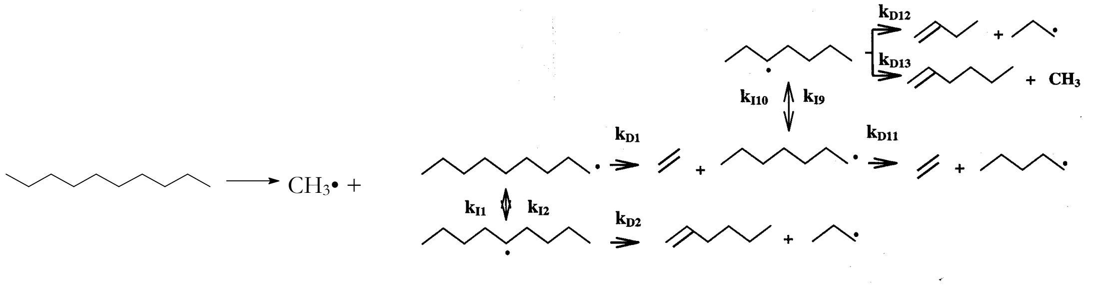


Figure 3: Reaction scheme for decane starting from a C-C scission reaction

The net formation rate of both radicals can be written as:

$$r(\mu_1) = k_1.C_M + k_{I_2}.C_{\mu_2} - \left(k_{I_1} + k_{D_1}\right).C_{\mu_1} \qquad (1)$$

$$r(\mu_2) = k_{I_1}.C_{\mu_1} - \left(k_{I_2} + k_{D_2}\right).C_{\mu_2} \qquad (2)$$

Assuming the pseudo steady state allows the calculation of the concentrations from the remaining algebraic continuity equations. In this example the concentration for the 1-nonyl radical (μ_1) is given by:

$$C_{\mu_1} = \frac{\left(k_{I_2} + k_{D_2}\right).k_1}{\left(k_{I_1} + k_{D_1}\right).\left(k_{I_2} + k_{D_2}\right) - k_{I_1}.k_{I_2}}.C_M \qquad (3)$$

The knowledge of the concentrations of the μ-radicals makes it possible to eliminate these radicals from the reaction scheme. The decomposition of the formed μ-radicals is stopped when only olefins and radicals from the β-network remain. The generated reaction scheme of a component starting from a certain primary reaction is then reduced to a simpler form, which contains the component and the products, which can be formed through unimolecular reactions.

In contrast to previous work (Clymans and Froment, 1984), no global reactions have been included, not even to describe the formation of aromatic compounds. Kopinke et al. (1983) found that under the standard conditions of thermal cracking (T = 700 –800°C, P = 0.1 –0.2 MPa, res. time 0.1 – 1 s) Diels-Alder reactions and other molecular reactions are not the main route for the formation of aromatic compounds. Instead aromatic compounds are formed via additions of radicals to olefins en di-olefins, see Figure 4. Another important route for the formation of aromatic compounds is the propargyl-propargyl route (Miller and Klippenstein 2003).

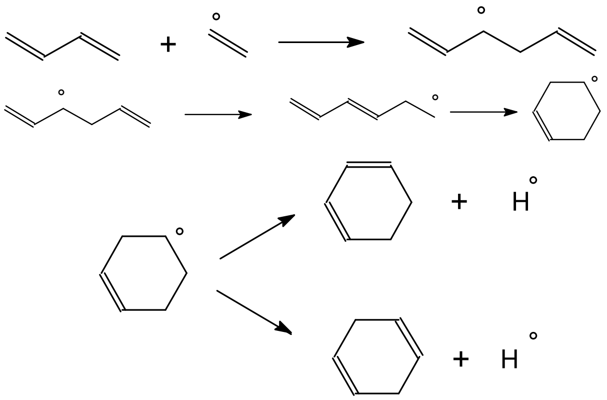
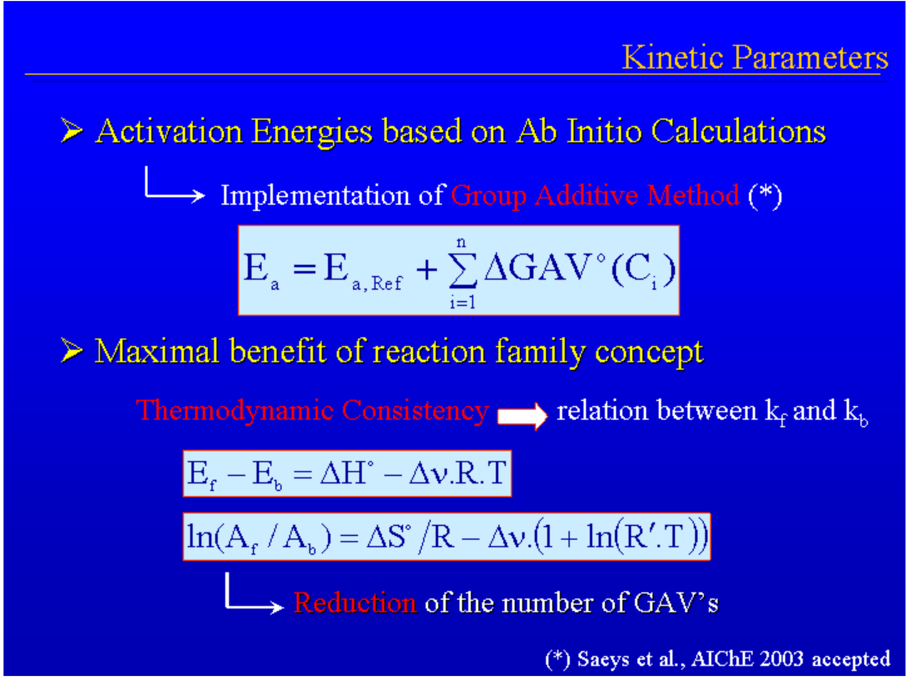


Figure 4: formation of aromatic molecules

2.2 Kinetic parameters

The generated reaction network consists solely of elementary reactions. Hence, the kinetic parameters can in principle be calculated from first principles. The recently proposed first principles based group contribution method [Saeys et al., 2003] was applied to calculate the kinetic parameters. Saeys' method is a consistent extension of Benson's group additivity concept (1976) to transition state theory and takes maximum benefit of thermodynamic consistency and the reaction family concept. Hence, only a limited number of kinetic parameters have to be calculated from first principles. In Figure 5 more detail is given about how the proposed group additive method works.



Kinetic Parameters

- Activation Energies based on Ab Initio Calculations

  → Implementation of Group Additive Method (*)

$$\boxed{E_a = E_{a,Ref} + \sum_{i=1}^{n} \Delta GAV^\circ(C_i)}$$

- Maximal benefit of reaction family concept

  Thermodynamic Consistency ⇒ relation between k_f and k_b

$$\boxed{E_f - E_b = \Delta H^\circ - \Delta\nu.R.T}$$

$$\boxed{\ln(A_f / A_b) = \Delta S^\circ / R - \Delta\nu.(1 + \ln(R'.T))}$$

  → Reduction of the number of GAV's

(*) Saeys et al., AIChE 2003 accepted

Figure 5: Group additive method for calculation of kinetic parameters

2.3 Validation of the model

With the first principles based reaction network, a good agreement is obtained with pilot and industrial data for feedstocks ranging from ethane to n-butane. For an industrial reactor such as a traditional single coil configuration a 2-dimensional reactor model has been applied because of the importance of the radial temperature gradients (Van Geem et al., 2004). In Table 1 the simulation conditions are given for an industrial ethane cracking experiment in a Lummus SRT-I reactor. The latter is a traditional single coil reactor with a diameter of 0.124 m and a reactor length of 100.96 m. The simulation results in Table 2 show the good agreement with the experimental data.

Table 1: Operating conditions for the reactor coil

Total hydrocarbon flow (ton/hr)	3.5
Composition (wt%)	
ethane	97.7
ethene	0.9
propene	1.4
Steam dilution (kg steam/kg feed)	0.35
Inlet temperature (°C)	600
Inlet pressure (MPa)	0.34

Table 2: Comparison between Simulated weight fractions and experimentally observed weight fractions for the thermal cracking of ethane in a Lummus SRT-1 reactor

	Simulated Yield (wt %)	**Experimental Yield (wt %)**
H_2	3.17	3.06
CH_4	2.04	2.20
C_2H_4	41.55	41.50
C_2H_6	49.77	48.90
C_3H_6	0.22	0.81
C_4H_6	0.01	0.58

In a pilot plant the radial temperature gradients are less pronounced, making a 1-dimensional model sufficient. In Figure 6 the parity plots for a set of pilot plants experiments with n-butane as feedstock are shown. A good agreement with the experimental data is observed.

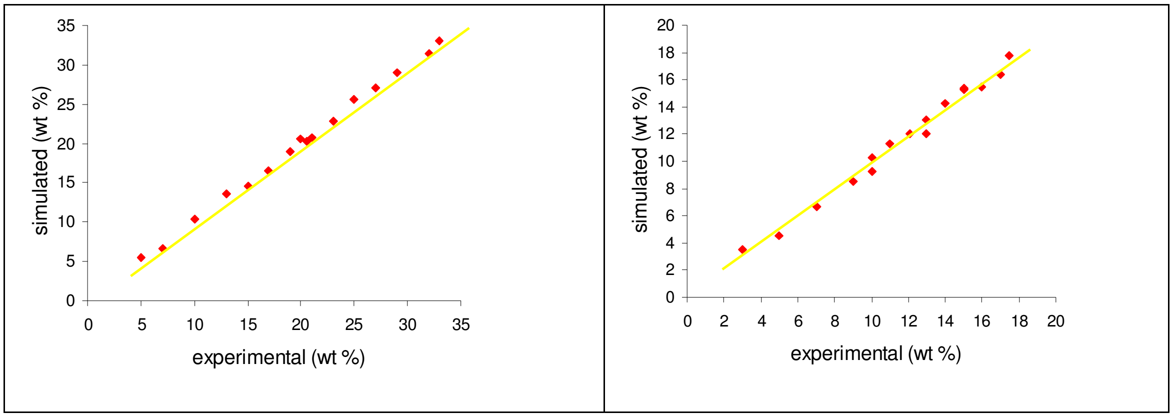
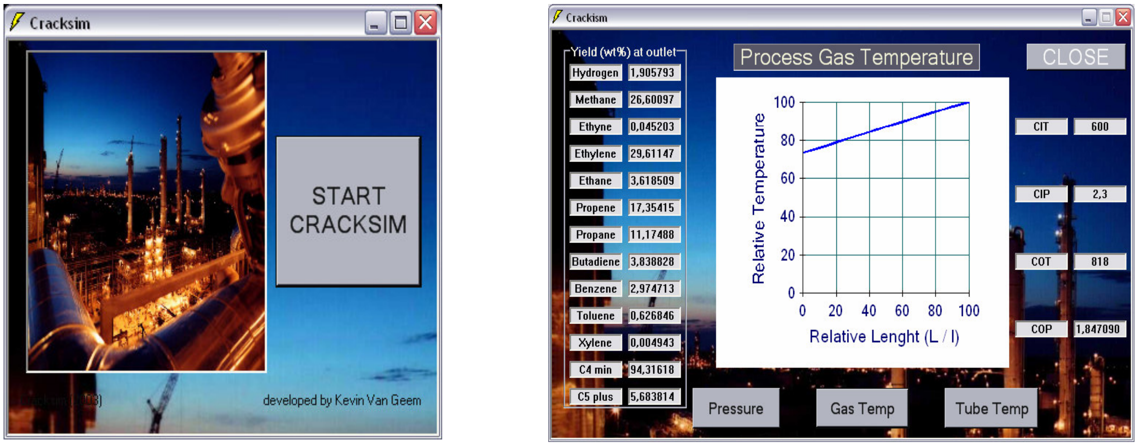


Figure 6: Parity plots for the ethylene (left) and propylene yield (right) using a 1-dimensional reactor model for a set of pilot plant experiments with n-butane as feedstock

2.4 Graphical User Interface



Yield (wt%) at outlet

Hydrogen	1,905793
Methane	26,60097
Ethyne	0,045203
Ethylene	29,61147
Ethane	3,618509
Propene	17,35415
Propane	11,17488
Butadiene	3,838828
Benzene	2,974713
Toluene	0,626846
Xylene	0,004943
C4 min	94,31618
C5 plus	5,683814

CIT	600
CIP	2,3
COT	818
COP	1,847090

Figure 7: Start-up screen (left) and results screen (right) of the GUI

A graphical user interface has been created using Visual Basic.Net. This program has been chosen over other solutions because it is easy to use, has huge possibilities and the user friendliness is very high. The backbone of the program still remains a FORTRAN code, compiled with a Visual

Fortran compiler creating an executable. The Graphical user interface creates the input files and let the program run on the background. The results are visualized using the GUI, see Figure 7.

3. Conclusion

A first principles based reaction network for thermal cracking of hydrocarbons has been developed. Based on the Boolean relation concept the β-network was automatically generated. This fully elementary reaction network includes no global reactions, not even for the formation of aromatic compounds. The kinetic parameters for all reactions are calculated from a first principles group contribution method. Yet, the yields of the major products, ethene and propene are accurately simulated.

4. Acknowledgments

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