KINETICS, CATALYSIS, AND REACTION ENGINEERING

Stochastic Simulation and Single Events Kinetic Modeling: Application to Olefin Oligomerization

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In order to handle a tractable network for complex reaction systems such as oligomerization, stochastic tools are applied to reduce the reaction mechanism. The particularity of this work is that quantitative single event kinetic modeling constants are used to generate a network which correctly describes the dynamic behavior of the studied reacting system. By using the stochastic method, which is based on a probabilistic approach, we can avoid the generation of improbable reaction paths in order to reduce the network expansion. Comparison with a classical limited network shows that the proposed network generation technique can be more reliable. Alongside, the stochastic simulation algorithm can be used as a method of simulation instead of the deterministic method because of the huge size of the oligomerization network.

Introduction

Hydrocarbon chemistry on acid catalysts, although well-known since the description of the carbocation chemistry, still remains complex, mainly due to the huge number of reactions and species that can take place in a reactor. For light cut to middle distillates, a single event methodology was an appropriate answer to the challenge of keeping the models to a tractable size through the generation of the exhaustive network by computer algorithm, the reduction of kinetic parameter numbers via the single event concept, and the reduction of the material balance equations via the rigorous lumping of thermodynamically equilibrated species. These three points are the keys to modeling the majority of the refinery processes.

Solutions for two of these points were even developed for hydrocracking modeling, allowing the calculation of a lumping coefficient without the formal generation of the whole network. In oligomerization, the numbers of reactions and species grow much faster than other refinery processes (hydrocracking, for example). Moreover, no similar lumping is possible i.e. no real thermodynamic equilibrium between species can be considered. However, the exponential expanding of such a network makes it challenging to solve the problem with present computing power. In the present work, a partial nonexhaustive network was generated, thanks to a step by step stochastic algorithm integrating some qualitative kinetic information.

In the next sections, brief descriptions of oligomerization, single event kinetic modeling, and the stochastic simulation method are presented.

Oligomerization

Olefin oligomerization consists of the production of heavier olefins, via the alkylation of a few monomers (typically 2−5 monomers—essentially propene and butenes). The product is sulfur, oxygenate, and nitrogen free, which respects the environmental specifications, together with a high research octane number, allowing its use as a component for future new reformulated gasoline. Oligomerization reactions were studied essentially in the 1980s on ZSM-5. This catalyst is characterized by shape selectivity. Oligomerization reactions are characterized by the fact that first the main oligomers appear and then a disproportionation reaction and cracking reactions create species with intermediates carbon numbers leading to a continuum of species by carbon number and boiling point (Figure 1).[1]

Thermodynamic studies yield correlations for the predictions of the main properties of the isomer groups.[2–5]

Several kinetic models were developed. The Mobil model[6] describes the kinetics network as a combination of oligomerization, cracking, and disproportionation reactions (Figure 2). Isomers with the same carbon number are lumped together. In this model, a reactivity is affected to each lump and the oligomerization kinetic constant is equal to the product of both reactivities. Reactivities depend on the carbon number via a correlation and on the temperature via a pseudo activation energy.

An explanation of the concept of lump reactivity is available.[7] However due to the rough lumping by carbon number, such a model is not detailed enough in order to predict chemical properties

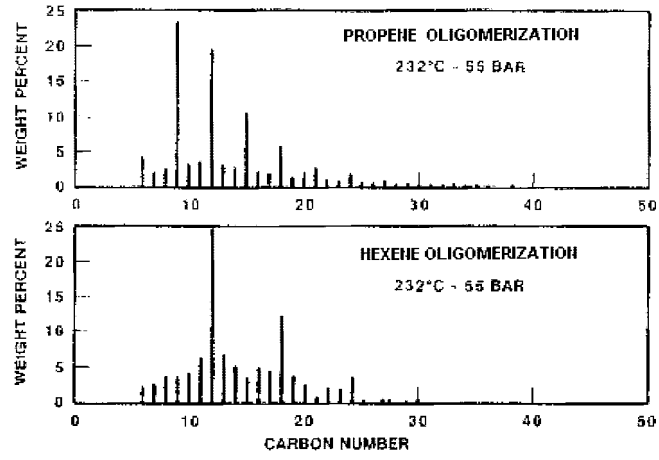

Figure 1. Typical product distribution by FIMS for propylene and 1-hexene reaction over ZSM-5.[1]

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10.1021/ie071215l CCC: $40.75
Published on Web 06/05/2008

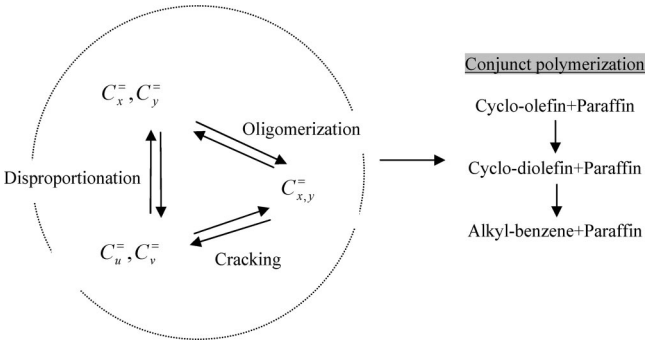


Figure 2. Catalyzed olefin reaction pathway proposed by Quann et al.[6]

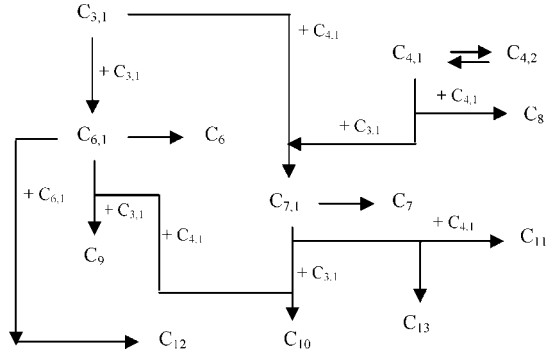


Figure 3. Typical lumped reaction pathway.[8]

of the product, particularly the research octane number (RON) and other transportation specification. Moreover, the reactivities of species are very different according to the branching numbers. This is linked to carbocation chemistry and will be developed in the next part. For example, isobutene is much more reactive than the *n*-butenes. On IFP amorphous silica−alumina catalyst, isobutene is quite fully converted as soon as the temperature is higher than 40 °C, while *n*-butenes begins to be significantly converted over 100 °C. This implies the need of introducing at least two kind of lump according to the reactivity. Such a model can be used for a simplified network (Figure 3).[8]

Single Event Microkinetic Modeling

The single event microkinetic modeling is now well established for the kinetic modeling of the acid catalyzed refinery process. It has been successfully applied to processes like isomerization,[9] reforming, and hydrocracking[10,11] but also the methanol to olefin[12] and alkylation process.[13,14] The methodology consists in taking into account the whole detail of the kinetic network, the reduction of a kinetic constant number via a few assumptions, and the lumping of species in order to reduce the number of ordinary differential equations (ODE) to be solved. The complete methodology can not be directly applied to our case study but can be adapted.

Table 1. Cumulative Number of Olefins by Carbon Number—Step by Step Generation[15]

olefins	step 1	step 2	step 2 bis[a]	step 3	step 4
C_3	0	0	0	0	1
C_4	3	3	3	3	3
C_5	0	0	0	3	5
C_6	0	0	0	9	13
C_7	0	0	0	21	27
C_8	2	14	25	57	62
C_9	0	0	0	119	139
C_{10}	0	0	0	117	291
C_{11}	0	0	0	356	643
C_{12}	6	30	30	972	1623
C_{13}	0	0	0	1117	3664
C_{14}	0	0	0	2394	7478
C_{15}	0	0	0	6213	19071
C_{16}	18	96	96	15678	46847
total	29	143	154	27059	79867

[a] *n*-Butane initiation with secondary−secondary reactions.

Carbenium Ion Chemistry. Single event kinetic modeling can be considered as microkinetic modeling, in the way reactions are regarded at the elementary level. For oligomerization process, several types of elementary reactions can be considered: alkene protonation and deprotonation, PCP branching, alkyl shift, hydride shift, oligomerization (alkylation), and cracking.

For oligomerization modeling, it has been shown that the number of species and reactions explodes exponentially.[15] A methodology with step by step generation, including some qualitative knowledge in the generation, allowed to obtain a large network (see Table 1). However, the number of reactions and species remains gigantic, all the more since no lumping is possible, because isomers by branching numbers are not close to equilibrium as it is the case for reforming and hydrocracking. Compared to the classic single event methodology, there are two bottlenecks: the generation of the network (no exhaustive network possible) and the simulation of the systems (no tractable ODE set). However, the concept of single events allows the description of the elementary steps with a finite number of intrinsic parameters (see Figure 4).

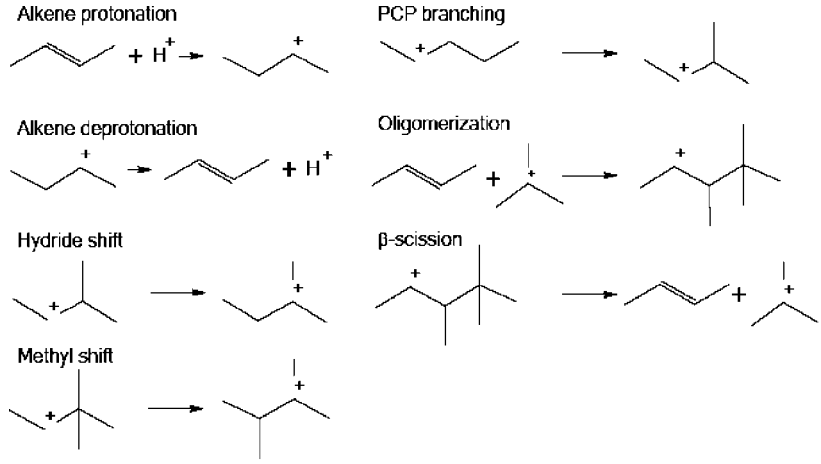


Figure 4. Reaction pathway of alkylcarbenium ions for alkylation process.[16]

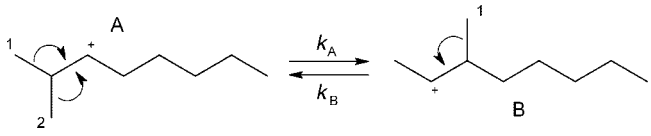


Figure 5. Decomposition of an elementary step into a single event.

Single Event Concept. The notion of the single event was formalized in refs 17–19. The key concept is to decompose an elementary step into so-called "single events" which are described with an intrinsic kinetic. Consider the example of the methyl shift as in Figure 5. From A to B, there are two ways of executing the methyl shift, whether there is a migration of the methyl labeled 1 or there is a migration of the methyl shift labeled 2 with kinetic k_A. From B to A, there is only one possible way of migration with kinetic k_B. If the kinetic of the migration of a methyl shift is denoted k then it follows that $k_A = 2k = 2k_B$.[18]

Each of the possible migration shifts is called a single event and k is the intrinsic kinetic single event constant. In the previous equation, $n_e = 2$ is the number of single events. This number depends on the geometry of the reactant and activated complex.

The definition of the single event number can be formalized from the Eyring law:[17]

$$k = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^{0\#}}{RT}\right) = \frac{k_B T}{h} \exp\left(+\frac{\Delta S^{0\#}}{R}\right) \exp\left(-\frac{\Delta H^{0\#}}{RT}\right)$$

where k is the single event kinetic constant, k_B is the Boltzmann constant ($= 1.38065 \times 10^{-23}$ J/K), h is Planck's constant ($= 6.6261 \times 10^{-34}$ J·s), R is the universal gas constant ($= 8.314$ J/mol·K), T is temperature (K), ΔG is the standard Gibbs free energy of reaction, ΔH is the standard enthalpy of reaction, and ΔS is the standard entropy of reaction. According to statistical thermodynamics, the enthalpy term is quite intrinsic and depends only on the molecular structure of the reacting species. The standard entropy of a component is determined by several contributions associated with the various motions of the component such as translation, vibration and rotation.

$$S^0 = S^0_{trans} + S^0_{vib} + S^0_{rot}$$

The rotational contribution is composed of two terms: the intrinsic value ($\hat{S}^0$) and a term due to symmetry (σ), i.e.

$$S^0_{rot} = \hat{S}^0_{rot} - R \ln(\sigma)$$

Accounting for the effect of chirality, the rotational contribution S^0_{rot} is given by

$$S^0_{rot} = \hat{S}^0_{rot} - R \ln\left(\frac{\sigma}{2^n}\right)$$

The expression in the parentheses, that quantifies all symmetry contributions of a species, is called the global symmetry number and is represented by σ_{gl},

$$\sigma_{gl} = \frac{\sigma}{2^n}$$

The difference in standard entropy between reactant and activated complex due to symmetry changes is given by

$$\Delta S^{0\#} = \Delta S^{0\#}_{int} + \Delta S^{0\#}_{sym}$$

$$\Delta S^{0\#}_{sym} = R \ln\left(\frac{\sigma^r_{gl}}{\sigma^{\#}_{gl}}\right)$$

where the superscripts r and # refer to the reactant and activated complex, respectively.

Substituting this contribution into Eyring expression leads to

$$k = \left(\frac{\sigma^r_{gl}}{\sigma^{\#}_{gl}}\right) \frac{k_B T}{h} \exp\left(\frac{\Delta \hat{S}^{0\#}}{R}\right) \exp\left(-\frac{\Delta H^{0\#}}{RT}\right)$$

As a result, the rate coefficient of an elementary step (k) is a multiple of the single event rate coefficient ($\tilde{k}$) in such a way that only those structural effects associated with the stability of the carbenium ions remain present:

$$k = n_e \tilde{k}$$

The number of single events (n_e) is the ratio of the global symmetry numbers of the reactant and the activated complex,

$$n_e = \frac{\sigma^r_{gl}}{\sigma^{\#}_{gl}}$$

Calculation of the Number of Single Events. Application of the single-event concept requires the number of single events for each elementary step. The calculation starts with the numerical representation of the molecule or ion by a Boolean matrix. The external symmetry number is calculated from the molecular topology.[20] The method is based on the identification of the symmetry centers, by recursively removing layers of atoms. Simple rules applied to each layer yield contributions to the external symmetry number, that depend on the hybridization state (sp^2 or sp^3) of each carbon atom. Although determination of the basic general structure of the transition state can be challenging, recently a summary of the proposed short cut model formulas is proposed in ref 14.

Single Event Kinetic Intrinsic Constant. The number of rate coefficients required to predict the product distribution of cracking, oligomerization, or other very complex systems needs to be derived. Froment et al.[18] proposed some simplifying assumptions in order to reduce the number of single events rate parameters.

Assumption 1: Methyl- and primary carbenium ions are so unstable that they can be disregarded in the construction of reaction networks.

Assumption 2: Only the type of carbenium ion (secondary or tertiary), not the identity (number of carbon atoms), determines its activity in the isomerization single events.

Consequently, only the following single event rate coefficients have to be considered in the isomerizations: (a) for hydride shift $\tilde{k}_{HS}(s;s)$, $\tilde{k}_{HS}(t;s)$, $\tilde{k}_{HS}(s;t)$, $\tilde{k}_{HS}(t;t)$; (b) for methyl shift $\tilde{k}_{MS}(s;s)$, $\tilde{k}_{MS}(s;t)$, $\tilde{k}_{MS}(t;s)$, $\tilde{k}_{MS}(t;t)$; (c) for PCP isomerization: $\tilde{k}_{PCP}(s;s)$, $\tilde{k}_{PCP}(s;t)$, $\tilde{k}_{PCP}(t;s)$, $\tilde{k}_{PCP}(t;t)$.

Assumption 3: The rate coefficient of protonation is independent of the olefin.

Consequently, the rate coefficient for protonation amounts to two only: $\tilde{k}_{Pro}(s)$ and $\tilde{k}_{Pro}(t)$.

Assumption 4: The rate coefficient of deprotonation depends upon both the carbenium ion and the olefin: $\tilde{k}_{dep}(s,O_{ref})$, $\tilde{k}_{dep}(t,O_{ref})$.

Assumption 5: The rate coefficient for cracking is independent of the produced olefin.[19]

As a result, the number of rate coefficients would then be limited to four: $\tilde{k}_{cr}(s;s)$, $\tilde{k}_{cr}(s;t)$, $\tilde{k}_{cr}(t;s)$, $\tilde{k}_{cr}(t;t)$.

Assumption 6: The rate coefficient for alkylation is independent of the reacted olefin.

Consequently, the rate coefficients would then be: $\tilde{k}_{alk}(s;s)$, $\tilde{k}_{alk}(s;t)$, $\tilde{k}_{alk}(t;s)$, $\tilde{k}_{alk}(t;t)$.

More reduction of the number of single events rate coefficients through thermodynamic constraints can be achieved for

protonation/deprotonation, isomerization, and cracking/alkylation reactions.

Consequently, by introduction of single event concept, the rate of each elementary step can be computed with a limited number of kinetic constants.

Stochastic Simulation

The stochastic simulation approach is completely different of the deterministic approach, in the way it describes the phenomenon at the microscopic scale. While the deterministic approach models reaction as a continuum, the stochastic approach models them as discrete event that follows with a probability distribution. Stochastic modeling was lately developed compared to deterministic approach.[21]

Consider the volume V, which contains molecules of N chemically active species S_i ($i = 1, \ldots, N$), and possibly molecules of several inert species as well. Let

$$X_i \equiv \text{current number of molecules of chemical species } S_i \text{ in } V, \quad (i = 1, \ldots, N)$$

We are further given that these N chemical species S_i can participate in M unidirectional chemical reactions R_μ ($\mu = 1, \ldots, M$), each characterized by a numerical reaction parameter c_μ in which $c_\mu \delta t \equiv$ average probability, to first order in δt, that a particular combination of R_μ reactant molecules will react accordingly in the next time interval δt.

Now the propensity function which reflects the probability of each reaction in volume V is defined

$$a_\mu = h_\mu c_\mu$$

where h_μ is the number of distinct molecular reactant combinations for reaction R_μ.

In order to find a mathematical expression for probability function, one can consider that one possible route from $\vec{X}_0$ to $\vec{X}$ is for *no reaction* to occur in $[t, t + \mathrm{d}t)$, another possible route is *exactly one* R_μ *reaction* to occur in $[t, t + \mathrm{d}t)$. The chemical master equation (CME) is a t-evolution equation for the probability function and is the basis of stochastic modeling:[21]

$$\frac{\partial}{\partial t} P(\vec{X}, t|\vec{X}_0, t_0) = \sum_{\mu=1}^{M} \{P(\vec{X} - \vec{v}_\mu, t|\vec{X}_0, t_0) \times a_\mu(\vec{X} - \vec{v}_\mu) - P(\vec{X}, t|\vec{X}_0, t_0) \times a_\mu(\vec{X})\}$$

However, the application of CME is restrained due to its complexity, especially for a large reactional network.

Stochastic Simulation Algorithm (SSA). Gillespie[22,23] made stochastic modeling applicable with the introduction of the stochastic simulation algorithm (SSA).

By introducing the *reaction probability density function* $P(\tau,\mu)$, one should know when the next reaction will occur and what kind of reaction it will be. These two requirements can be mathematically determined from the set of random pairs, whose probability density function is $P(\tau,\mu)$. It turns out that there is a simple, rigorous way of doing this on a computer; a unit interval uniform random number (URN) generator is a computer subprogram which calculates and returns a random number r from the uniform distribution in the unit interval.[23]

Gillespie's direct method is based on the fact that any two-variable probability density function can be written as the product of two one-variable probability density functions, a procedure known as conditioning:[22]

$$P(\tau, \mu) = P_1(\tau) \times P_2(\mu|\tau)$$

where, by some calculations, one can find

$$P_1(\tau) = a \exp(-a\tau) \quad (0 \le \tau < \infty)$$

$$P_2(\mu|\tau) = \frac{a_\mu}{a} \quad (\mu = 1, 2, \ldots, M)$$

where

$$a = \sum_{\mu=1}^{M} a_\mu = \sum_{\mu=1}^{M} h_\mu c_\mu$$

A random value τ may be generated by simply drawing a random number r_1 from the uniform distribution in the unit interval and taking

$$\tau = \frac{1}{a} \ln \frac{1}{r_1}$$

Then, a random integer μ may be generated by drawing another random number r_2 from the uniform distribution in the unit interval and taking μ to be that integer for which

$$\sum_{\nu=1}^{\mu-1} a_\nu < r_2 a \le \sum_{\nu=1}^{\mu} a_\nu$$

i.e., the successive values $a_1, a_2, \ldots$ are cumulatively added until their sum is observed to be equal to or to exceed $r_2 a$, where upon μ is then set equal to the index of the last a_ν term added.[22]

Stochastic Simulation Algorithm for Network Generation. It seems that the application of stochastic simulation algorithm does not require the total reaction network. It means that for applying the method of Gillespie directly, it is necessary to know just the whole of possible reactions at the moment t. The number of possible reactions at time t grows exponentially with the number of molecules included. While the population becomes larger, determination of the possible reactions channels are required. By applying the proposed method, there is a compromise to find a size of the network which sufficiently represents the population from the statistical point of view and which at the same time is sufficiently restricted considering the computing time.

In order to use the stochastic simulation approach, calculation of the propensity function for each reaction path is required. While deterministic kinetic constant and stochastic propensity constant are connected together, the stochastic propensity constants identified to the single event kinetic constants and number of single events of each reaction. Application of single event theory enables us to generate a detailed network with limited numbers of kinetic constants. For unimolecular reactions, the single events kinetic constants are equal to stochastic propensity constants, so the propensity function for protonation is

$$a_j = ne_j \tilde{k}_j X_O$$

For deprotonation, alkyl shifts, PCP-branching, and beta-scission we have

$$a_j = ne_j \tilde{k}_j X_C$$

and for bimolecular reaction, i.e., oligomerization,

$$a_j = ne_j \tilde{k}_j \frac{X_O X_C}{V}$$

where X_O and X_C are the number of molecules of olefin and carbenium ions, respectively, and V refers to the volume of the chemically reacting system.

In order to simplify the application of stochastic simulation algorithm, we use three random numbers for selecting the next reaction time and the reaction which should be fired.

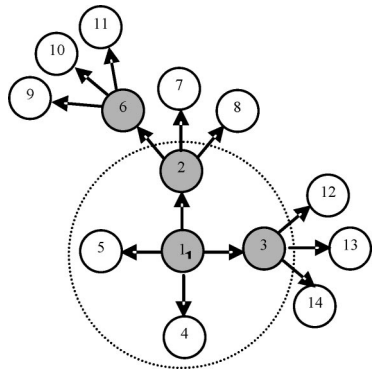


Figure 6. Illustrative step by step network generation.

We define the propensity function for each component equal to summation of propensity of all possible reaction which can be done in the moment t,

$$a_i = \sum_{j=1}^{M_i} a_j$$

where M_i refers to the number of possible reactions of component i in time t.

The total propensity function in original stochastic simulation algorithm of Gillespie is considered as

$$a_0 = \sum_{i=1}^{N} a_i$$

where N is the total number of component at time t.

The probability of selecting molecule i from all components is equal to

$$P_i = \frac{a_i}{a_0} = \frac{\sum_{j=1}^{M_i} a_j}{\sum_{i=1}^{N} a_i}$$

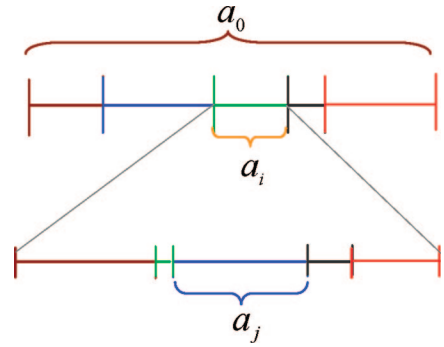
After selecting a component which reacts, it is now necessary to select a reaction for this molecule, so we need a third random number: the probability of reaction j of molecule i to take place is equal to

$$P_j = \frac{a_j}{a_i} = \frac{a_j}{\sum_{j=1}^{M_i} a_j}$$

While the generated random numbers are generated independent, the probability of selecting one reaction of all possible reactions in the network is equal to the probability of selecting a molecule multiplied by probability of selecting a reaction of this molecule, so

$$\mathcal{P}_{ij} = \mathcal{P}_i \times \mathcal{P}_j = \frac{a_i}{a_0} \times \frac{a_j}{a_i} = \frac{a_j}{a_0} = \frac{a_j}{\underbrace{\sum_{i=1}^{N}\sum_{j=1}^{M_i} a_j}_{all-reactions}}$$

It should be noted that each carbenium ion has its propensity function related to deprotonation, hydride shift, methyl shift, PCP branching, and beta-scission, except for alkylation whose propensity function is calculated by both carbenium ion and olefin populations (so for each component which undergoes alkylation, the propensity function is multiplied by $^1/_2$). For each olefin, the propensity function is calculated by summation of protonations propensity and $^1/_2$ of alkylations propensity.



According to the Gillespie method, the time of the next reaction is

$$\tau = \frac{1}{a_0} \ln \frac{1}{r_1}$$

The next component i which undergos the next reaction can be determined by

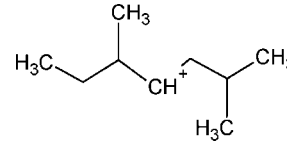
$$\sum_{v=1}^{i-1} a_v < r_2 a_0 \leq \sum_{v=1}^{i} a_v$$

One reaction of the selected component is determined by third random number:

$$\sum_{v=1}^{j-1} a_v < r_3 a_i \leq \sum_{v=1}^{j} a_v$$

After firing a reaction by the stochastic method, it should be checked for the network modification. If the product(s) of selected reaction(s) are new, i.e., the population of product(s) becomes one for the first time, then all possible elementary reactions for new molecule(s) should be generated as illustrated in Figure 6. It should be noted that we do not consider cyclic and aromatic compounds which can be produced via isomerization reactions; our network generation program produces linear hydrocarbons.

For example, consider the molecule of 2,5 dimethyl,4-heptyl as shown below.



If this molecule is a new product, resulting from a fired reaction, then the following reactions should be added to network

- one hydride shift (s,t)
- one hydride shift (s,s)
- two deprotonation (s)
- one methyl shift (s,s)
- one beta-scission (s,s)
- three PCP (s,t)
- three PCP (s,s)
- n_s alkylation (s,s)
- n_t alkylation (s,t) where n_s and n_t are numbers of secondary−secondary and secondary−tertiary possible alkylations, respectively.

Figure 7 presents the schematic of stochastic simulation algorithm with step by step network generation. In fact, there

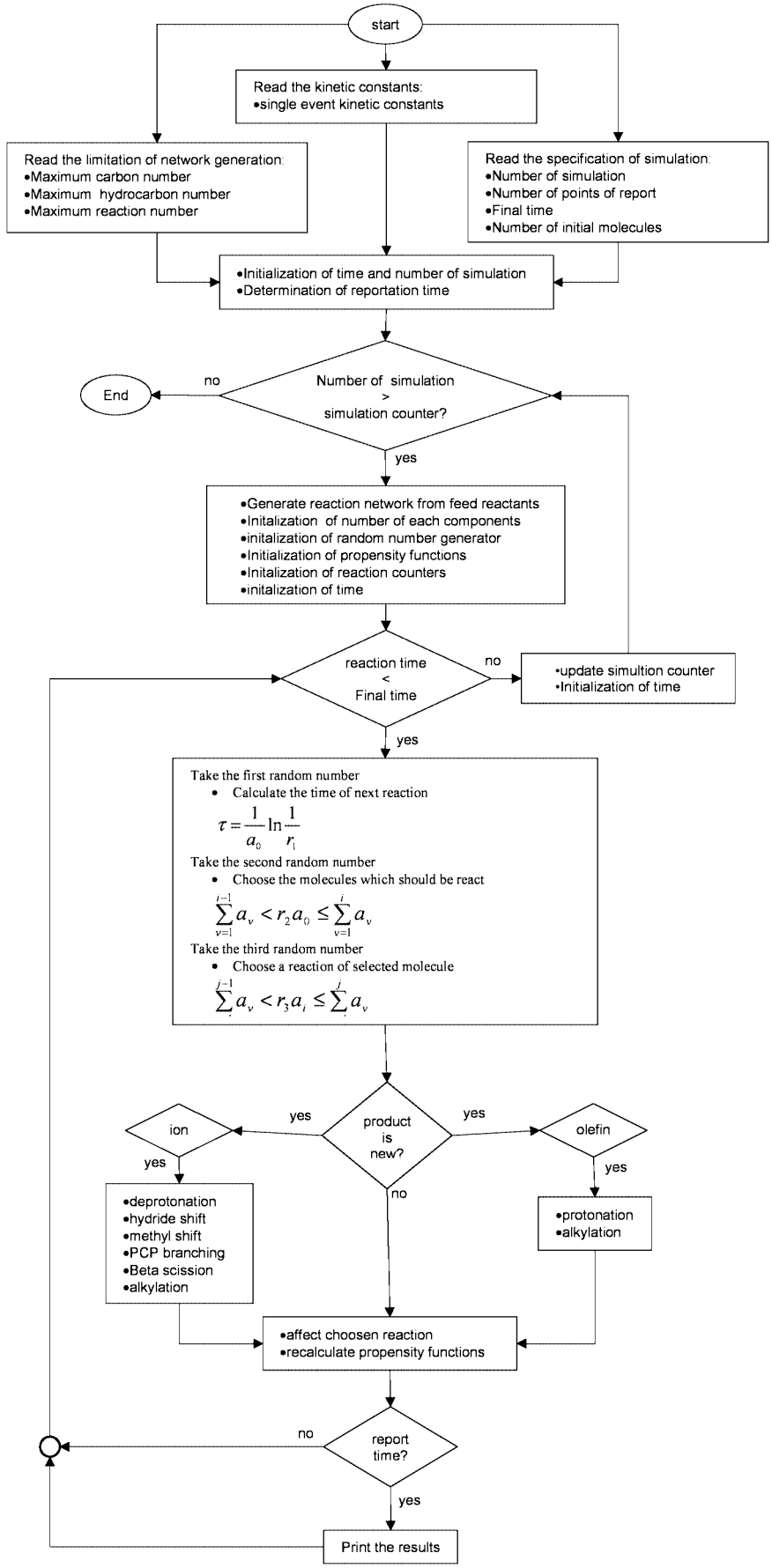


Figure 7. Schematic of step by step network generation by stochastic approach.

are three loops in the main program. The outer loop repeats the stochastic method several times to have average results; the second loop allows the stochastic modeling while the time is not over the predefined final time of simulation; the inner loop

Table 2. Relative Kinetic Rates of Hydrocracking Modes[24,25]

beta-scission type	ions	relative rate
A	t−t	170−1050
B1	s−t	2.8
B2	t−s	1
C	s−s	0.4
D	s−p	∼0

Table 3. Comparison of Number of Molecules and Reactions in Stochastic Step by Step Network Generation and Simulation

	$t = 0.1^a$	$t = 0.5^a$	$t = 4.0^a$
olefins	2260	3606	3806
carbenium	2674	3022	3060
protonation	1950	5115	5802
deprotonation	3124	5547	5917
hydride shift	2192	3941	4210
methyl shift	954	1498	1523
PCP-branching	7970	13810	14246
beta-scission	1015	1686	1803
oligomerization	1649	1817	1817

[a] The time dimension is $D_t = [1/c_r]$.

is used to report the population of components in predefined time intervals.

We use the C++ programming language and compiler to code our algorithm. There are more than 12 500 lines of coding whereas 11 000 lines are related to elementary reaction creation and calculation of the number of single events. Nearly 1500 lines of C++ code are added to the network generation program in order to combine the network generation and stochastic kinetic simulation together.

Because, at this moment, our object is to verify the mathematical ability of simulation of differently generated limited networks, the arbitrary kinetic constants of single events are used by considering the reactivity of carbenium ions and relative rates of hydrocracking[24] (see Table 2). The right values should be directly determined from experimental data or could be predicted by some theoretical rules and available theories.

However, the direct application of SSA imposes the presence of all reactions with different rate scales because it handles molecules and not lumps.

In future work, we will introduce additional assumptions analogous to that of the rate determining step in the deterministic method. Then stochastic simulation will be applied to lumps and no longer to molecules. This will be the object of a future communication.

Results

The proposed model is applied for modeling of oligomerization network where C_4 olefins are used as feed. In this step, we considered all elementary reactions and the maximum carbon number limit is set to 12. Full network generation for this system results in 3835 olefins and 3062 carbenium ions and over than

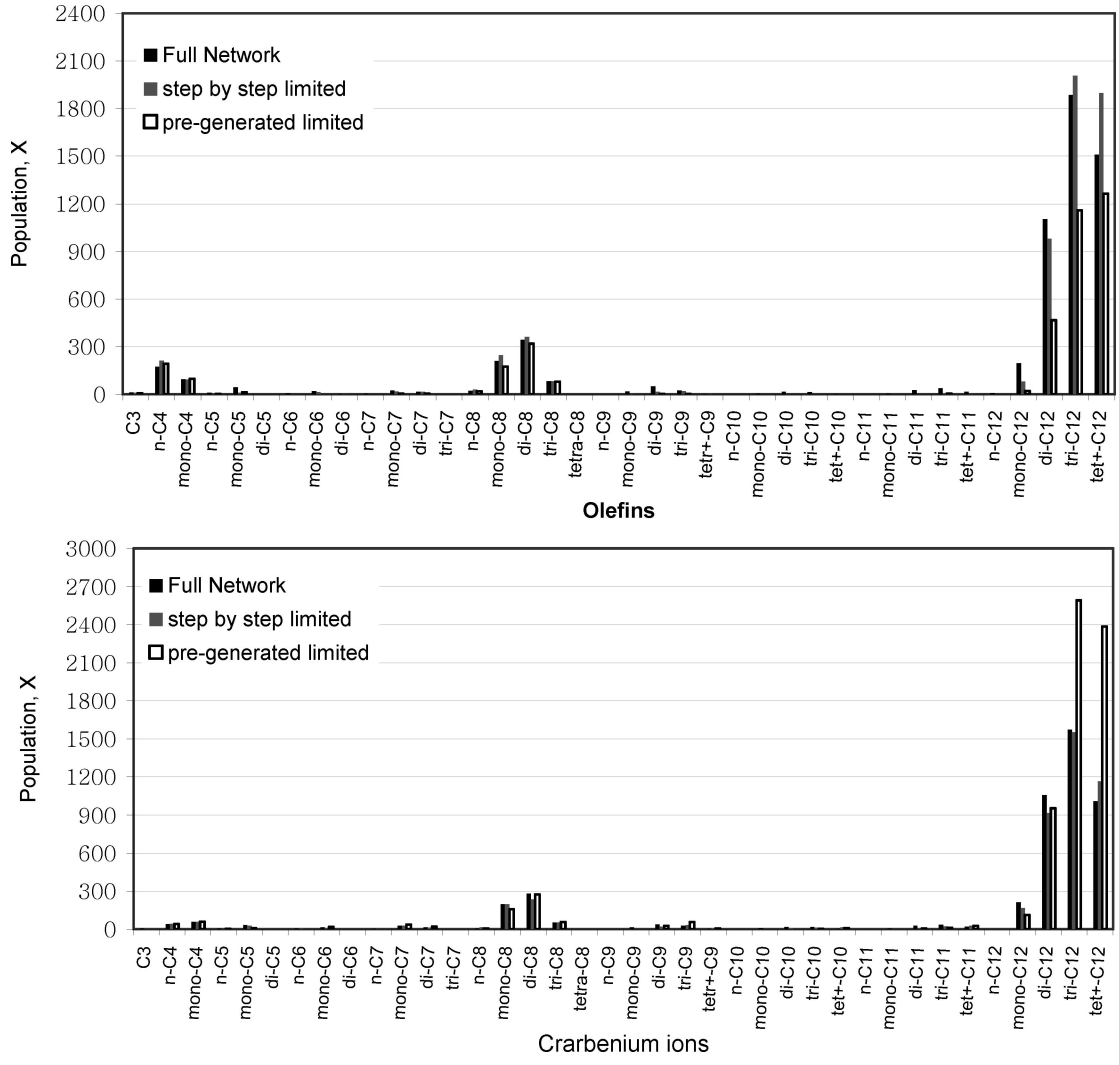


Figure 8. Comparison of limited network generations with full network generation for oligomerization of C_4 olefins up to C_{12}.

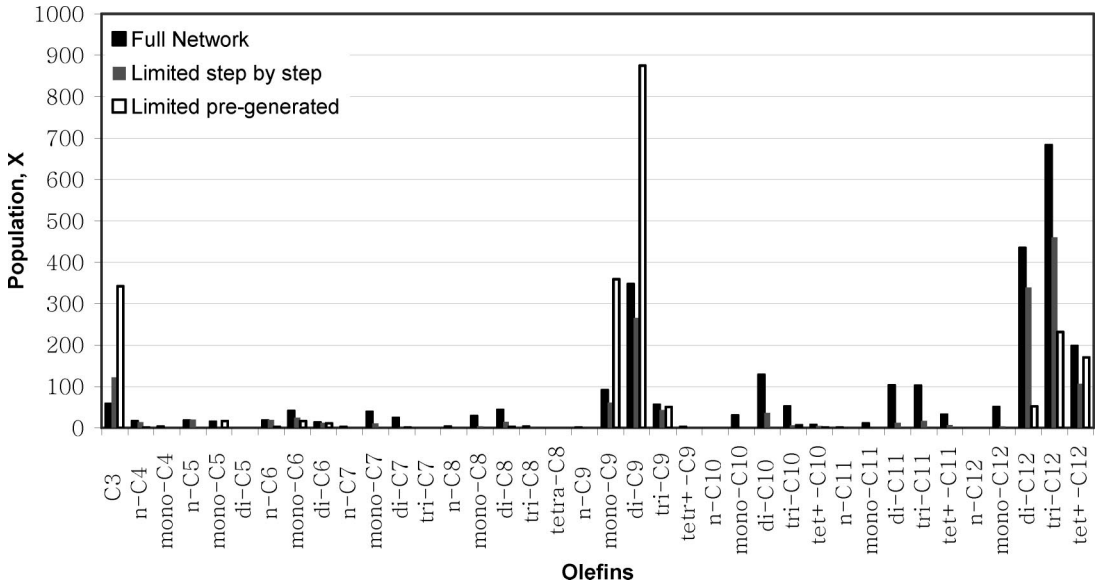


Figure 9. Comparison of limited network generations with full network generation for oligomerization of C_3 olefins up to C_{12} with $N_0(C_3) = 10\,000$, limit = 2000 molecules, at time = 500 (high conversion).

35 000 elementary reactions. Considering that the dimension of reaction time, D_t, is related to the stochastic constant dimension i.e., $1/[c_r]$, the time scale, in this work, depends on kinetic constants considering the relative kinetic rates in Table 2. For a typical run of stochastic molecules by molecule network generation and simulation at time $0.1[D_t]$, we have 2674 carbenium ions and 2260 olefins which are created by the model. Only 1590 carbenium ions and 1253 olefins have nonzero population. While reactions proceed, the network becomes larger and larger. For the same typical run after time $0.5[D_t]$ we have 3022 carbenium ions and 3606 olefins. At time $t = 4[D_t]$, 3060 carbenium ions and 3806 olefins can be observed in the network. Table 3 gives an example of time dependent molecule by molecule network generation.

The main objective of our work is to show that the step by step simulation and generation with limitation criteria is more satisfactory than the simulation of a pregenerated limited network. In order to avoid the technical problems of creating a large reaction network, a limit is set to the number of hydrocarbons. In a typical case, we allow a maximum hydrocarbon number of 2000 whereas the full network consists of 3835 carbenium ions. This limit is also applied for the classical generation of network (without considering probability) and after the stochastic model is used to simulate this pregenerated network. On the other hand, the step by step generation and simulation which is proposed in this work is used. Figure 8 compares the simulation of these two limited networks with the full network results. It is obvious that the proposed model is more satisfactory than a pregenerated network and is more reliable.

It can be seen that at the beginning of the oligomerization reactions the most important reactions are protonation of olefins and oligomerization of C_4 molecules to C_8; hereafter, the isomerization reactions (hydride shift, methyl shift, and PCP-branching) and deprotonation of C_8 carbocations begin to take place. As reactions proceed, C_8 molecules can be oligomerized with C_4 components giving C_{12} species. After formation of considerable amount of C_{12} molecules, the probability of beta-scission reactions rise, as a consequence some intermediate carbon numbers such as C_6, C_9, C_{10}, and C_{11} appear. The step by step simulation is capable of predicting the intermediate olefins, while the limited pregenerated network does not. Another example is shown in Figure 9 which compares the mentioned methods for oligomerization of C_3-C_{12}. In this example, protonation/deprotonation reactions are considered more rapid than other elementary reactions. In other words, equilibrium is assumed between protonation and deprotonation.

Conclusion

Detailed kinetic modeling of oligomerization, comprising all species and elementary reactions of such a complex system, results in a huge network. Since rigorous lumping criteria cannot be applied, the technical limitations, like compiling problems and the execution time of a deterministic solution, remain considerable. It seems that the application of stochastic simulation algorithm for step by step network generation method could be an advisable solution for network creation of complex systems. Using the stochastic simulation approach allows us to have the most probable reaction paths at each moment. Using such a model enables us to direct the network growth toward the most important and experimentally observed products, and the unimportant part(s) of the reaction network can be eliminated. The greatest disadvantage of the proposed model is its high execution computer time. However, it should be noted that, for stochastic simulation algorithm (SSA), the CPU time depends directly on reaction conversion, i.e., the final time of simulation, and the number of initial molecules. For example, considering conversion of propylene up to C_{12} under conditions of Figure 9, the CPU time for a single run with a given machine (2.66 GHz) for our work is 1.71 h, whereas for a full and pregenerated network, they are 7.22 and 2.15 h, respectively. Both stochastic simulation approach and detailed kinetic modeling are time-consuming, and thus, the combination of these two models results in more CPU time usage for simulation and network generation at the same time.

Acknowledgment

This work was supported by the TOTAL scholarship program.

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Received for review September 10, 2007
Revised manuscript received March 12, 2008
Accepted March 12, 2008

IE071215L