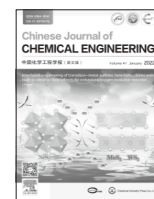




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Computer generation of detailed reaction networks in hydrocracking of Fischer-Tropsch wax



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ABSTRACT

Fischer-Tropsch synthesis (FTS) wax is a mixture of linear hydrocarbons with carbon number from C7 to C70+. Converting FTS wax into high-quality diesel (no sulfur and nitrogen contents) by hydrocracking technology is attractive in economy and practicability. Kinetic study of the hydrocracking of FTS wax in elementary step level is very challenging because of the huge amounts of reactions and species involved. Generation of reaction networks for hydrocracking of FTS wax in which the chain length goes up to C70 is described on the basis of Boolean adjacency matrixes. Each of the species (including paraffins, olefins and carbenium ions) involved in the elementary steps is represented digitally by using a $(N + 3) \times N$ matrix, in which a group of standardized numbering rules are designed to guarantee the unique identity of the species. Subsequently, the elementary steps are expressed by computer-aided matrix transformations in terms of proposed reaction rules. Dynamic memory allocation is used in species storage and a characteristic vector with nine elements is designed to store the key information of a $(N + 3) \times N$ matrix, which obviously reduces computer memory consumption and improves computing efficiency. The detailed reaction networks of FTS wax hydrocracking can be generated smoothly and accurately by the current method. The work is the basis of advanced elementary-step-level kinetic modeling.

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1. Introduction

Syngas derived from coal, biomass and natural gas can be converted into a series of hydrocarbons by Fischer-Tropsch synthesis (FTS) technology. However, it is difficult to control the selectivity for desired liquid fuels with a narrow range of carbon numbers in the current low- and medium- temperature FTS processes [1] in which the product selectivity is close to an Anderson-Schulz-Flory distribution [2]. FTS wax (heavy fractions of FTS products) is a mixture of linear paraffins with chain length from C7 to C70+ characterized by GC analysis. It contains no sulfur, nitrogen and aromatics compared to traditional crude oil and could be a promising material to produce clean diesel by way of hydrocracking technology [3,4].

We noticed that the current kinetic models for FTS wax hydrocracking were still lumped models [5,6] although some advanced

models had been developed in elementary step level in crude oil hydrocracking [7–9]. The challenge in developing such kind of kinetic models in elementary step level is the complexity of the reactions involved in hydrocracking. Froment and co-workers creatively solved the problems by computer generating the reaction networks and single event concept in rate coefficient modeling [10]. A detailed reaction network is the key basis of advanced kinetic modeling. Over the past few decades, researchers had made a lot of efforts in generating reaction networks in several fields. Clymans and Froment [11] generated a reaction network for thermal cracking reactions by Boolean adjacency matrixes for the first time. Soon afterwards, reaction networks based on carbenium ion mechanism were developed for hydroisomerization and hydrocracking reactions [12,13]. Park and Froment extended the concept into methanol to olefin (MTO) reactions [14,15]. Recently, a reaction network of oligomerization was developed by alternating fast and slow reactions, and qualitative kinetic information was added into the reaction network by Guillaume [13,16]. Hereafter, Olefins oligomerization reaction network was automatically generated by

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Jin [17]. A two-dimension vector with three rows and N columns was used to store key characteristic information of the species. Numbering the nature of each carbon atom of the hydrocarbon and carbenium ion species was stressed to discriminate aromatic carbon atoms, naphthenic carbon atoms and bridgehead carbon atoms. Alternating usage between a two-dimension vector and a Boolean adjacency matrix proceeded to implement the elementary steps.

To further extend this concept into FTS wax hydrocracking and improve the accuracy of kinetic models in predicting the product selectivity at a wide range of operating conditions, here we generate a practical reaction network for FTS wax hydrocracking according to the real cracking characteristics. Methods on reducing memory consumption and accelerating computation are described. This work will be very useful in detailed-mechanism kinetic modeling and reactor simulation of the process.

2. A Brief Description of the Elementary Steps in FTS Wax Hydrocracking

It is widely accepted that the hydrocracking catalyst used is a bifunctional catalyst, meaning two types of active sites which are metal sites and acid sites. Dehydrogenation of paraffins and hydrogenation of olefins occur on metal sites. Elementary steps concerning carbenium ions are carried out on acid sites.

A more specific reaction process of FTS wax hydrocracking is as follows: paraffin molecules with given carbon number can be converted into corresponding olefins on metal sites by dehydrogenation. Subsequently, the olefins in adsorbed state migrate from metal sites to acid sites, capture protons and form corresponding carbenium ions in terms of the positions of the double bonds of the olefins by protonation. Carbenium ions generated will continue going through isomerization such as hydride-shift (HS), methyl-shift (MS) and protonated cyclopropane branching (PCP-branching) to form other isomeric carbenium ions and obtain short chain olefins and carbenium ions by cracking reaction (β -scission). Cyclization and aromatization of the carbenium ions are not considered here because the selectivity of the cycloalkanes and aromatics is negligible in our experiments, as exhibited in Fig. 1.

There are only characteristic peaks of n -paraffins and iso -paraffins in the product spectrum (as shown in Fig. 1). New paraffin molecules are formed by deprotonation of the carbenium ions on acid sites and hydrogenation of the corresponding olefins. The possible elementary steps that occur on the acid sites for FTS wax hydrocracking are shown in Fig. 2.

To avoid explosive increases in reaction paths for long chain FTS wax hydrocracking, some rules are designed to eliminate unstable species and reactions less likely to occur on the surface of the catalysts according to carbenium ion chemistry and real product spec-

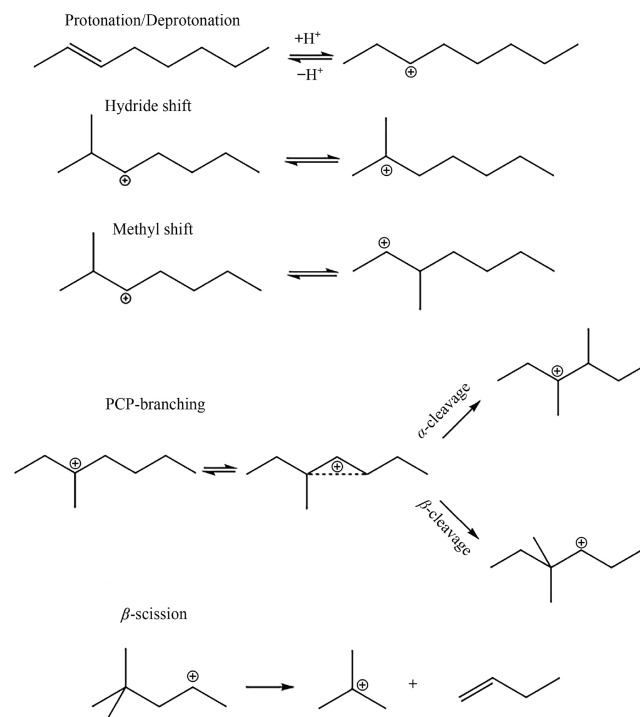


Fig. 2. Elementary steps on acid sites for FTS wax hydrocracking.

trum in Fig. 1. The specific rules for reaction network generation are as follows:

- (1) Methyl carbenium ions and primary carbenium ions are not considered due to instability;
- (2) Isomers are limited to methyl branches and no more than three branched chains;
- (3) The protonated cycloalkyl branching goes through PCP-branching step exclusively;
- (4) Bimolecular reactions such as hydride transfer and alkylation are not considered;
- (5) Cyclization and aromatization are not considered in this reaction system;

3. Digital Representation of the Species and Elementary Steps

3.1. Digital representation of hydrocarbon molecules and carbenium ions

A hydrocarbon molecule or a carbenium ion is randomly numbered and the carbon skeleton structure of the species can be

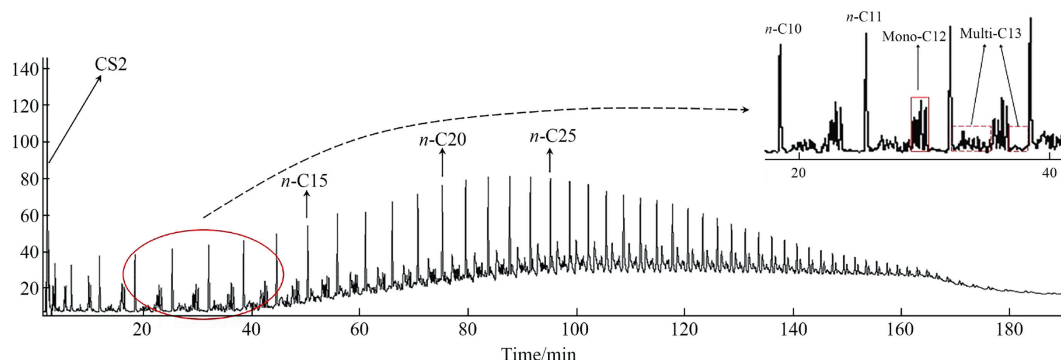


Fig. 1. A typical product spectrum of FTS wax hydrocracking by GC analysis.

described by a two-dimensional $N \times N$ Boolean adjacency matrix (symmetric sparse matrix). N is the total number of carbon atoms of the species. The value of each element in the $N \times N$ matrix reflects the relationship between any two carbon atoms of the species and it is determined as follows:

$$\begin{cases} m_{ij} = m_{ji} = 1 & (\text{having a bond between atom } i \text{ and atom } j) \\ m_{ij} = m_{ji} = 0 & (\text{having no bond between atom } i \text{ and atom } j) \\ m_{ii} = 0 \end{cases}$$

in which m_{ij} is on behalf of an element in row i and column j of the Boolean adjacency matrix. Whatever it is a paraffinic, an olefinic or a carbenium ion species, the values of the corresponding element m_{ij} and m_{ji} in the $N \times N$ matrix are 1 if there is a C-C σ bond between carbon atom i and carbon atom j , otherwise the values of them are 0. Moreover, the values of the diagonal elements in the Boolean adjacency matrix are all 0, meaning there is no any chemical bond between the carbon atom itself. It should be noted that the $N \times N$ matrix of the carbon chain skeleton structure can not directly reflect some more detailed information of the species such as the type of the species, the series and nature of each carbon atom. Therefore, an auxiliary vector which is a $3 \times N$ array is introduced to store these details of the species. The first row of this auxiliary vector contains only one valid element in row 1 and column 1 which reflects the type of the species: the value of the element will be 0 if the species is paraffinic or olefinic; the value of this element records the position of carbon atom with positive charge if the species is a carbenium ion. The rest of the elements in this row are set 0. The second row stores the series of each carbon atom of the species which is equal to the sum of each column of the $N \times N$ matrix from column 1 to column N . The possible values of the sum of each column could be 1, 2, 3 and 4 which represent the primary, secondary, tertiary, and quaternary carbon atoms, respectively. The third row stores the nature of each carbon atom of the species and the specific number is shown in Table 1.

Examples of the chemical formulas and their digital representation of paraffin, olefin and carbenium ion with eight carbon atoms are displayed in Fig. 3(a), (b) and (c), respectively. The value of each element in the matrix is determined by how the carbon chain skeleton is numbered. A species can be numbered in several random ways, which will result in more than one matrix for the same species.

3.2. Standardized numbering rules

It will take too much time in computer aided species discrimination and elementary steps expression if the species could not have a uniquely digital representation. To solve this problem, some standardized and uniform numbering rules need to be designed, shown as following:

- (1) Identify the type of species numbered such as paraffins, olefins and carbenium ions;
- (2) Traverse the matrix representing the species and confirm the longest carbon chain as the main chain;
- (3) The numbering starts from the primary carbon at one side of the main chain;

- (4) If the species being standardized is paraffinic, just make sure the minimization of the sum of the numbering of carbon atoms which have branched chains;
- (5) If the species is olefinic, minimization of the sum of numbering of carbon atoms which have double bonds is guaranteed preferentially, and then make sure minimization of the sum of the numbering of carbon atoms which have branched chains;
- (6) If the species is a carbenium ion, numbering of carbon atom with a positive charge is in minimization preferentially, and then guarantee minimization of the sum of the numbering of carbon atoms which have branched chains.

Based on the above standardized numbering rules, chemical formulas of the paraffin, olefin and carbenium ion species could be numbered uniquely, e.g., standardized numbering of C8 species shown in Fig. 4.

3.3. Digital representation of the elementary steps

3.3.1. (De)protonation

Protonation is a reaction that an olefin molecule in adsorbed state captures a proton to produce a carbenium ion on acid sites of the catalysts. For example, a 4,5-dimethyl-2-hexene protonates turning into a 4,5-dimethyl-2-hexane carbenium ion or a 4,5-dimethyl-3-hexane carbenium ion (shown in Fig. 5). The double bond of 4,5-dimethyl-2-hexene is between carbon atom 2 and carbon atom 3, so the position of the positive charge could be carbon atom 2 or carbon atom 3 (here we only show the former in Fig. 5). Compared to reactant matrix, the value of the first element of row $N + 1$ (the first row of the auxiliary vector) in product matrix should be changed from 0 to 2 or 3. The values of the second and third elements in row $N + 3$ (the third row of the auxiliary vector) in product matrix should be changed from 0 to 1. The values of the other elements remain unchanged owing to the unchanged carbon chain skeleton structure of the reactant and product in the protonation reaction. Deprotonation is the reverse process of protonation.

3.3.2. Hydride-shift

Hydride-shift(HS) is a reaction in which the positive charge of a carbenium ion migrates from one carbon atom to another one through route 1–2 or 1–3[13], in which the route 1–2 refers to the migration of the positive charge from the original carbon atom to its α -position and the route 1–3 means that to its β position. Take 2,3-dimethyl-2-hexane carbenium ion as an example. The possible HS products are 2,3-dimethyl-3-hexane carbenium ion and 2,3-dimethyl-4-hexane carbenium ion. The matrix variation about HS of 2,3-dimethyl-2-hexane carbenium ion is shown in Fig. 6. The carbon chain skeleton structures of reactant and product remain unchanged, but just mark the position of positive charge.

3.3.3. Methyl-shift

Methyl-shift (MS) is a type of isomerization, in which the number of branched chains is not changed but the positions changed. The 3,5-dimethyl-2-hexane carbenium ion is used as an example to exhibit MS reaction in Fig. 7. The detailed processes implemented by computer are shown as follows. Here, the carbon atom with the positive charge is numbered r . First of all, traverse the reactant matrix and find the α -position carbon atom i adjacent to the carbon atom r . Secondly, find the carbon atom j ($j \neq r$) adjacent to the carbon atom i . Carbon atom j is referred to as the β -position carbon atom of carbon atom r . Moreover, carbon atom j must be primary carbon atom. During the MS reaction, the values of elements of matrix m_{ji} and m_{ij} will be set as to $m_{ji} = m_{ij} = 0$ and the values of elements of matrix m_{rj} and m_{jr} will be set as $m_{rj} = m_{jr} = 1$.

Table 1

Code number of the nature of each carbon atom

Code number	The nature of the carbon atom
0	Unsaturated aliphatic carbon atom
1	Saturated aliphatic carbon atom

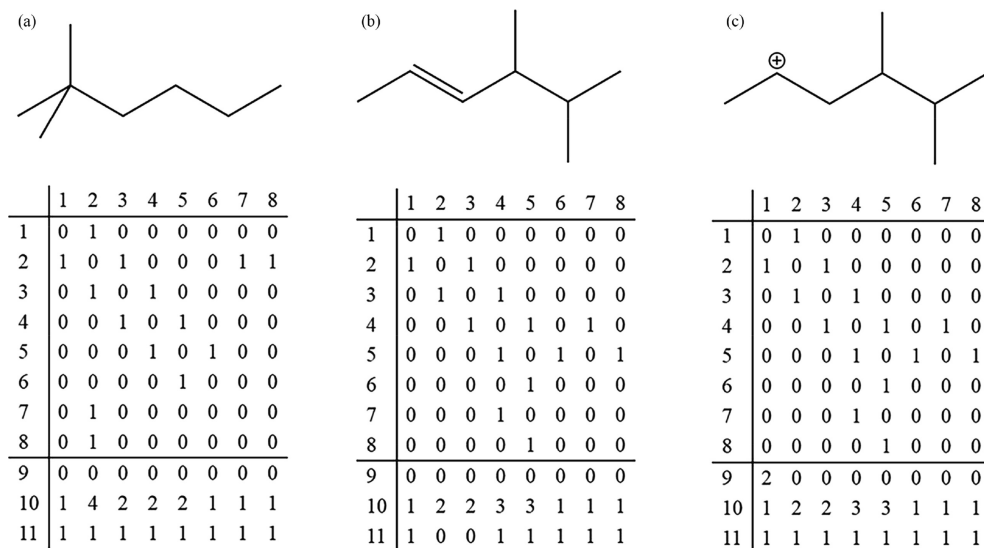


Fig. 3. Chemical formulas and the digital representations of paraffin (a), olefin (b) and carbenium ion (c).

The numbering of carbon atom with positive charge is changed from r to i . The sum of each column of the product matrix from row 1 to row N will be recalculated to check the series of each carbon atom in the product. The nature of each carbon atom will not be changed during the MS reaction.

3.3.4. PCP-branching

Protonated cyclopropane branching (PCP-branching) is an isomerization reaction which changes the branching degree of the species. PCP-branching plays a significant role in converting n -paraffins into mono-branched paraffins and then going further into multi-branched paraffins. Compared with HS and MS, PCP-branching is slower and could not be set as an equilibrium step in kinetic modeling [18]. The total carbon number of a carbenium ion must be greater than 4 for PCP-branching occurring. PCP-branching can be considered as a combination of two steps, cyclization and cleavage. For instance, 2-methyl-2-heptane carbenium ion goes through a PCP-branching reaction. It undergoes an intermediate cyclopropane carbenium ion, subsequently some bond of the cyclopropane carbenium ion breaks in terms of two different ways, as shown in Fig. 8. Assuming the carbon atom r is with a positive charge, a carbon atom i adjacent to the carbon atom r , another carbon atom j ($j \neq r$) adjacent to the carbon atom i and carbon atom r forms cyclopropane, then two different cleavages (α -cleavage and β -cleavage) may occur. The α -cleavage refers to bond cleavage between carbon atom r and carbon atom i , while the β -cleavage refers to the cleavage between carbon atom r and carbon atom j .

3.3.5. β -scission

In hydrocracking of FTS wax, the long-chain paraffins are cracked into short-chain paraffins by β -scission reaction. The total carbon number of a reactant carbenium ion should be greater than 6 for β -scission reaction occurring. In addition, the β -position of the carbon

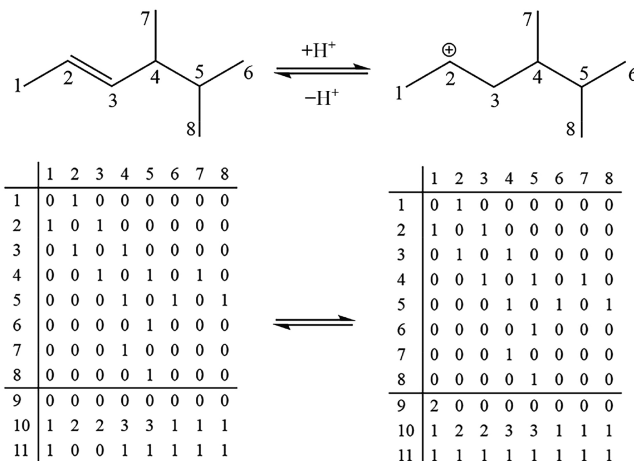


Fig. 5. Protonation of 4,5-dimethyl-2-hexene to form 4,5-dimethyl-2-hexane carbenium ion.

atom with a positive charge would better be a tertiary or quaternary carbon atom to avoid producing unstable primary carbenium ion or methyl carbenium ion. A β -scission reaction of 4,4-dimethyl-2-hexane carbenium ion is displayed in Fig. 9. Assuming a carbon atom r is with positive charge, its α -position is carbon atom i and β -position is carbon atom j . The positive charge will transfer from carbon atom r to carbon atom j and a double bond will form between carbon atom r and carbon atom i during the β -scission reaction.

4. Scheme of the Reaction Network Generation of FTS Wax Hydrocracking

A huge amount of new olefins and carbenium ions will be formed during the reaction network generation on acid active sites

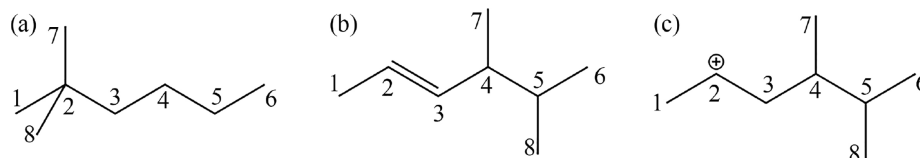


Fig. 4. Standardized numbering of the chemical formulas of paraffin (a), olefin (b) and carbenium ion (c).

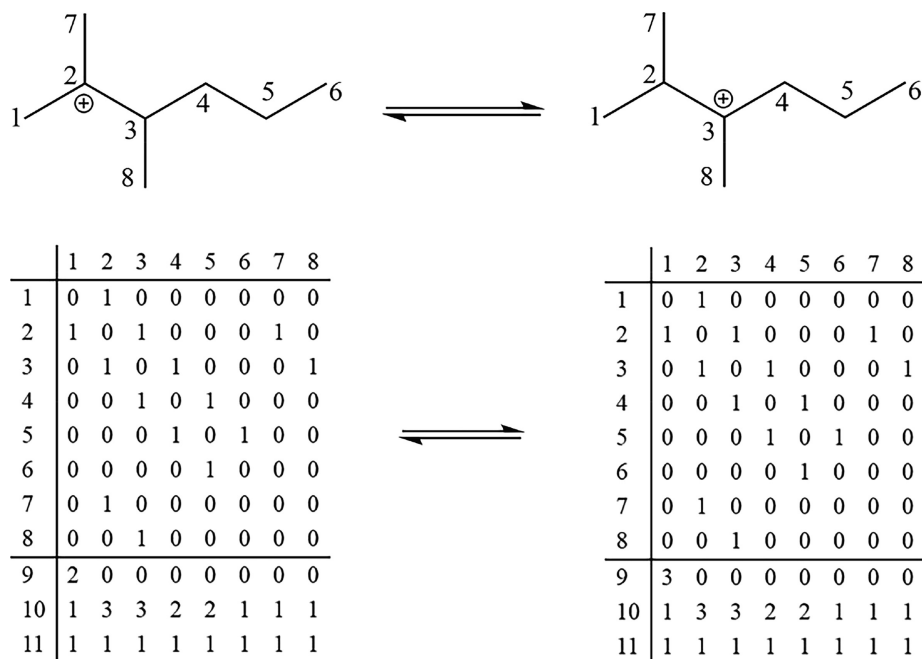


Fig. 6. HS of 2,3-dimethyl-2-hexane carbenium ion to form 2,3-dimethyl-3-hexane carbenium ion.

of the catalyst. They are stored respectively by dynamic memory allocation in the form of linear lists. During the generating process, the computer constantly traverses and identifies the matrixes of the species formed, and compares them with the species stored in the corresponding linear list to judge whether the products formed are new species or not. The new species will be stored in corresponding linear list and undergo the possible elementary steps as reactants, otherwise they will be eliminated. The program will cycle continuously until there is no new species being detected. The linear list of dynamic memory allocation greatly reduces the running time and improves the efficiency in reaction network generation. Furthermore, some useful information for kinetic equation derivation of FTS wax hydrocracking could be recorded simultaneously. A detailed reaction network generating scheme is exhibited in Fig. 10.

Although the dynamic memory allocation is used during the generation of the reaction network, the amount of memory used for storing the matrixes increases dramatically with increasing carbon number of the reactants. To avoid the huge memory consumption in the reaction network generation of FTS wax hydrocracking, a new characteristic vector with nine elements is designed to correlate all the key information of the $(3 + N) \times N$ matrix. The nine elements in the new characteristic vector are $a, b, c, d, e, f, g, h, i$, respectively. The meaning of each element is explained as follows:

- a —the total carbon number of a species;
- b —the number of the carbon atoms of the longest chain;
- c —the number of the branched chain of a species;
- d —the type of a species: if the species is an olefin, $d = 0$; if the species is a paraffin, $d = 1$; if the species is a carbenium ion; d represents the position of positive charge in the standardized numbering species;
- e —the position of the first branched chain in the standardized numbering species;
- f —the position of the second branched chain in the standardized numbering species;
- g —the position of the third branched chain in the standardized numbering species;

- h —the numbering of the first carbon atom which has a double bond in the standardized numbering species;
- i —the numbering of the second carbon atom which has a double bond in the standardized numbering species;

The transformation between the new characteristic vector and the corresponding matrix and the function of the new characteristic vector in the reaction network generation is explained in Fig. 11. The characteristic vector of the species stored in the linear list is taken out and transformed automatically into the corresponding matrix, then the matrix goes through reactions to produce product matrix. After a standardized numbering step, the matrix of the product is automatically transformed into the corresponding characteristic vector. The characteristic vector of the new product is identified and judged to determine whether it should be stored or not. In addition, the use of the characteristic vector will remark-

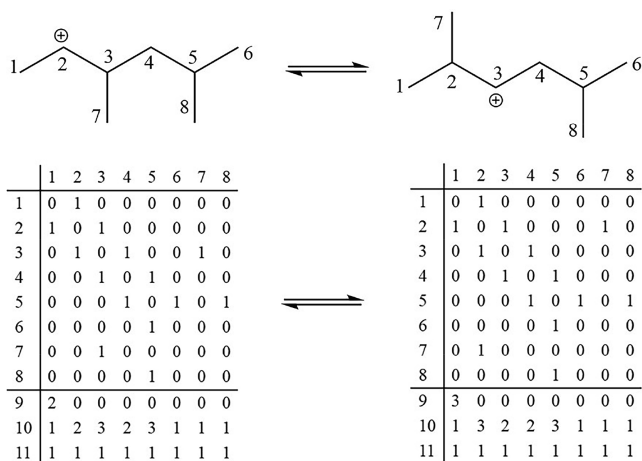


Fig. 7. Converting 3,5-dimethyl-2-hexane carbenium ion into 2,5-dimethyl-3-hexane carbenium ion by MS reaction.

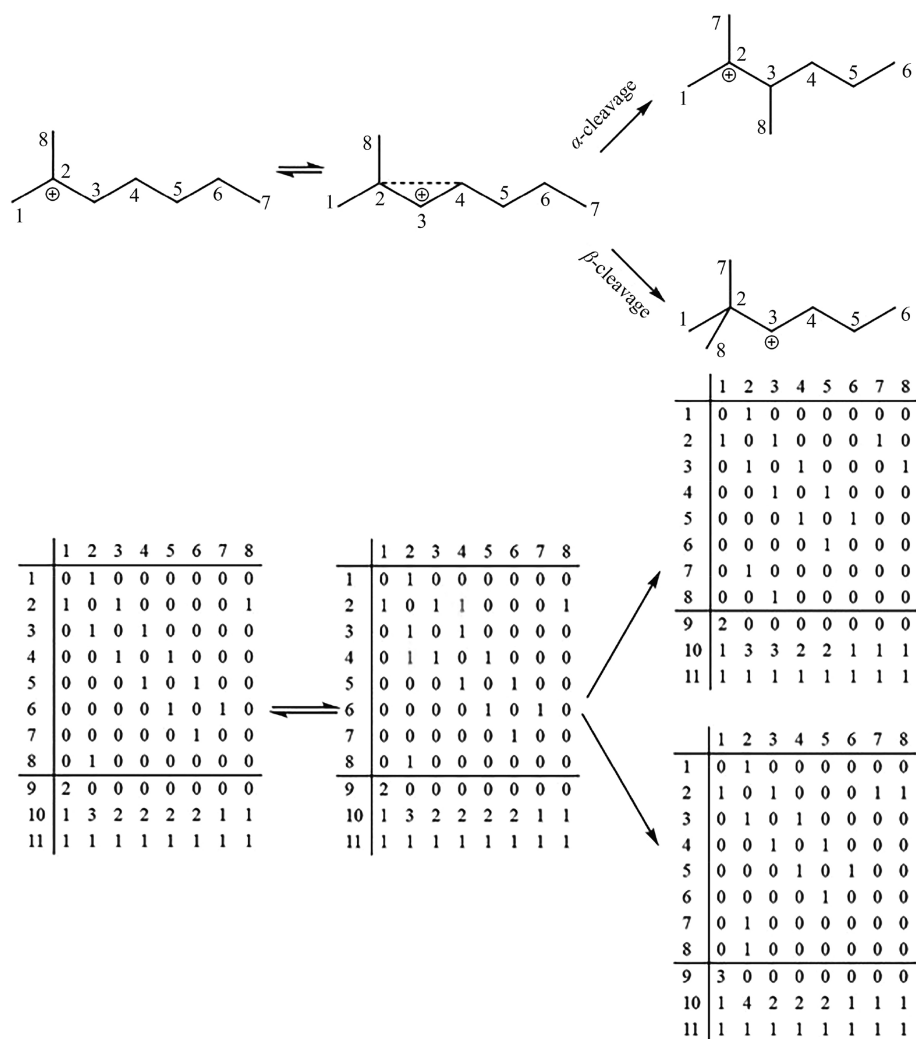
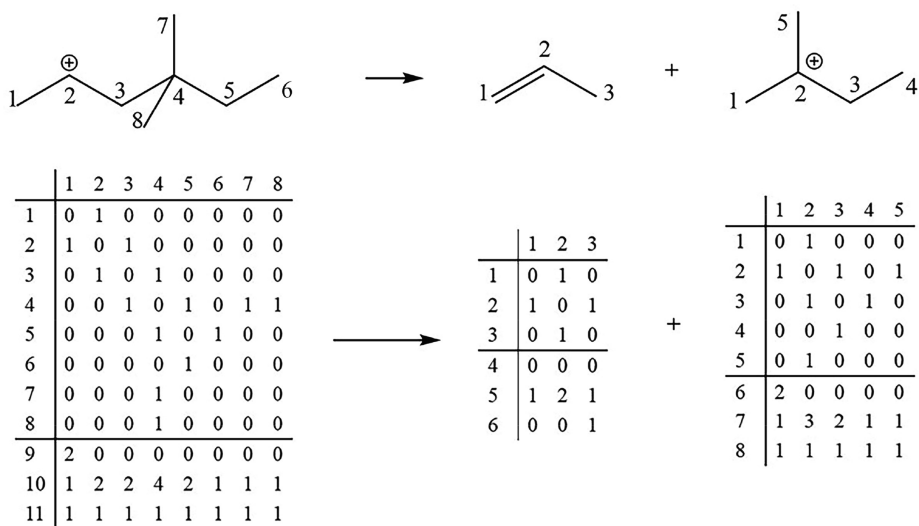


Fig. 8. The PCP-branching process of 2-methyl-2-heptane carbenium ion.

Fig. 9. β -scission process of 4,4-dimethyl-2-hexane carbenium ion.

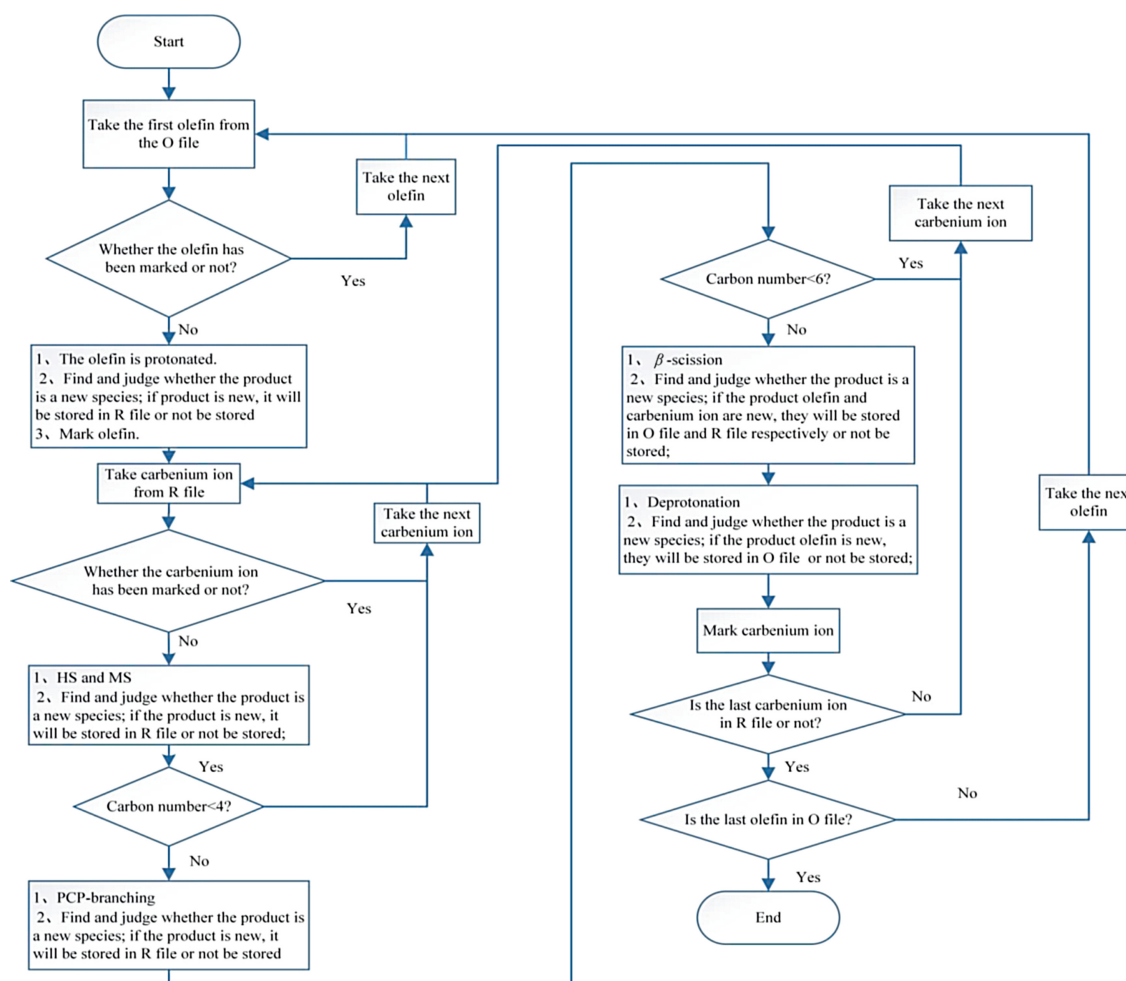


Fig. 10. The detailed reaction network generation scheme for FTS wax hydrocracking.

ably decrease the computing time in the process of species discrimination.

5. Results and Discussion

Considering the reality that some isomers of linear long-carbon-chain hydrocarbons could hardly be separated and quantified in GC&MS analysis (as shown in Fig. 1), some post-lumped approach could be adopted in detailed mechanism kinetic modeling. According to the GC analysis results of the products in FTS wax hydrocracking, paraffins with given carbon number can be classified into normal paraffins, mono-branched paraffins, di-branched paraffins and tri-branched paraffins with several typical molecular formulas. Some molecules which are in very low selectivity or even cannot be found in the products could be eliminated from the elementary steps, thus further simplifying the reaction network. The numbers of elementary steps and intermediates produced in the reaction network generation with FTS wax chain length are shown in Fig. 12. It can be seen from the results that with the increase of carbon number, the number of possible elementary steps and intermediates expand exponentially. Some more specific numbers in FTS wax with C55 hydrocracking are presented in Table 2. By using the current reaction network programming method, the hydrocracking reaction network of some higher carbon number FTS wax components, e.g., carbon atom up to C70, could also be generated smoothly and efficiently.

6. Conclusions

Kinetic modeling of FTS wax hydrocracking at elementary step level requires detailed reaction networks. A $(3 + N) \times N$ matrix which combines a Boolean adjacency matrix and an auxiliary vector is developed digitally to represent the hydrocarbon molecules and carbenium ions and generate the reaction networks by a com-

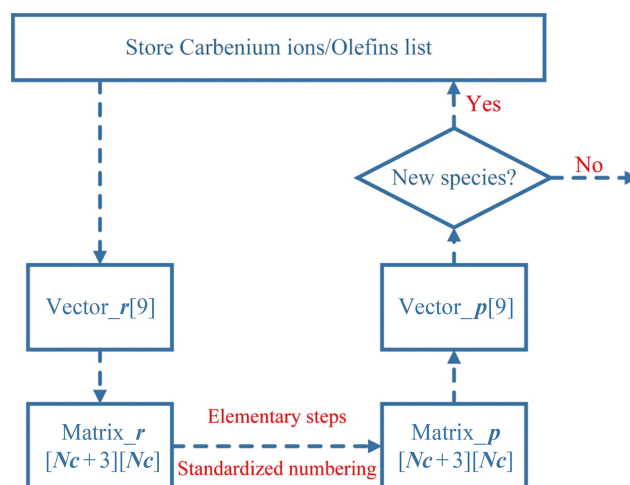


Fig. 11. The function of the characteristic vector in reaction network generation.

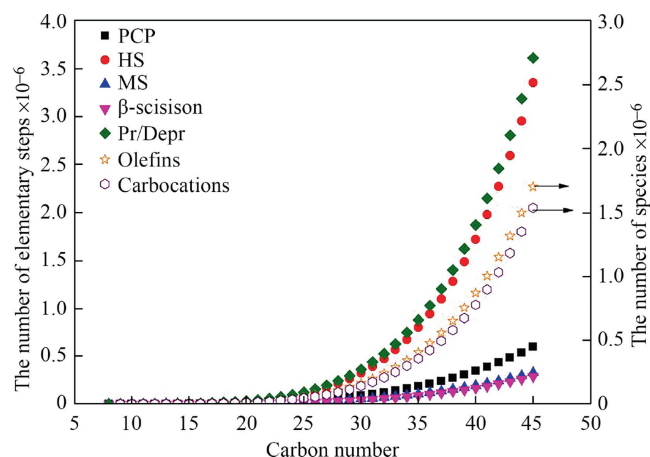


Fig. 12. The chart of changing trend of the number of elementary steps and the number of species in the reaction network with the carbon chain length.

Table 2

Results for reaction network of hydrocracking of C55 *n*-paraffin

The elementary steps/species	The number of elementary steps/species
(De) Protonation	10,882,385
Hydride-shift	10,249,807
Methyl-shift	794,761
PCP-branching	1,473,584
β -scission	715,887
Olefins	5,739,217
Carbenium ions	5,279,609

puter. A group of standardized numbering rules are designed to maintain the unique of the species involved. Dynamic memory allocation for species is used to improve the efficiency of reaction network generation. Automatic transformation between a characteristic vector with nine elements and a matrix representing the species greatly reduces the consumption of computer memory and provides a method for generating reaction networks of the FTS wax hydrocracking with carbon atom numbers up to 70 efficiently.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] V. Calemme, S. Peratello, S. Pavoni, G. Clerici, C. Perego, Hydroconversion of a mixture of long chain *n*-paraffins to middle distillate: Effect of the operating parameters and products properties, *Stud. Surf. Sci. Catal.* 136 (2001) 307–312.
- [2] R.Y. Yang, L.P. Zhou, J.H. Gao, X. Hao, B.S. Wu, Y. Yang, Y.W. Li, Effects of experimental operations on the Fischer-Tropsch product distribution, *Catal. Today* 298 (2017) 77–88.
- [3] V. Calemme, S. Corraera, C. Perego, P. Pollesel, L. Pellegrini, Hydroconversion of Fischer-Tropsch waxes: Assessment of the operating conditions effect by factorial design experiments, *Catal. Today* 106 (1–4) (2005) 282–287.
- [4] V. Calemme, C. Gambaro, W.O. Parker Jr, R. Carbone Jr, R. Giardino Jr, P. Sciorletti Jr, Middle distillates from hydrocracking of FT waxes: Composition, characteristics and emission properties, *Catal. Today* 149 (1–2) (2010) 40–46.
- [5] F.A.N. Fernandes, U.M. Teles, Modeling and optimization of Fischer-Tropsch products hydrocracking, *Fuel Process. Technol.* 88 (2) (2007) 207–214.
- [6] C. Gambaro, V. Calemme, D. Molinari, J. Denayer, Hydrocracking of Fischer-Tropsch waxes: Kinetic modeling via LHHW approach, *AIChE J.* 57 (3) (2011) 711–723.
- [7] T.M. Moustafa, G.F. Froment, Kinetic modeling of coke formation and deactivation in the catalytic cracking of vacuum gas oil, *Ind. Eng. Chem. Res.* 42 (1) (2003) 14–25.
- [8] H. Kumar, G.F. Froment, Mechanistic kinetic modeling of the hydrocracking of complex feedstocks, such as vacuum gas oils, *Ind. Eng. Chem. Res.* 46 (18) (2007) 5881–5897.
- [9] T. Zhang, C. Leyva, G.F. Froment, J. Martinis, Vacuum gas oil hydrocracking on NiMo/USY zeolite catalysts. Experimental study and kinetic modeling, *Ind. Eng. Chem. Res.* 54 (3) (2015) 858–868.
- [10] G.F. Froment, Single event kinetic modeling of complex catalytic processes, *Catal. Rev.-Sci. Eng.* 47 (1) (2005) 83–124.
- [11] P.J. Clymans, G.F. Froment, Computer-generation of reaction paths and rate equations in the thermal cracking of normal and branched paraffins, *Comput. Chem. Eng.* 8 (2) (1984) 137–142.
- [12] M.A. Baltanas, G.F. Froment, Computer generation of reaction networks and calculation of product distributions in the hydroisomerization and hydrocracking of paraffins on Pt-containing bifunctional catalysts, *Comput. Chem. Eng.* 9 (1) (1985) 71–81.
- [13] E. Vynckier, G.F. Froment, Modeling of the kinetics of complex processes based upon elementary steps, in: *Kinetic and Thermodynamic Lumping of Multicomponent Mixtures*, Elsevier, Amsterdam, 1991, pp. 131–161.
- [14] T.Y. Park, G.F. Froment, Kinetic modeling of the methanol to olefins process. 1. Model formulation, *Ind. Eng. Chem. Res.* 40 (20) (2001) 4172–4186.
- [15] T.Y. Park, G.F. Froment, Kinetic modeling of the methanol to olefins process. 2. Experimental results, model discrimination, and parameter estimation, *Ind. Eng. Chem. Res.* 40 (20) (2001) 4187–4196.
- [16] D. Guillaume, Network generation of oligomerization reactions: Principles, *Ind. Eng. Chem. Res.* 45 (13) (2006) 4554–4557.
- [17] F. Jin, G.F. Froment, Automatic generation of reaction network for complex process, *Comput. Appl. Chem.* 30 (1) (2013) 1–7.
- [18] H. Kumar, G.F. Froment, A generalized mechanistic kinetic model for the hydroisomerization and hydrocracking of long-chain paraffins, *Ind. Eng. Chem. Res.* 46 (12) (2007) 4075–4090.