

Generation, Management and Optimization of Thermal Cracking Reaction Network for Hydrocarbons by Bond-Electron Matrix

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In this paper, an object oriented method is developed for generation, optimization and management of a hydrocarbon (C_xH_y) pyrolysis reaction network using a Bond-Electron (BE) matrix. A computer program was developed using C++ language. This program can provide and generate a pyrolysis reaction network for a wide range of hydrocarbons, including alkanes, olefins, diolefins, cyclic and aromatic compounds, using the linear notation structure of the reactant species. Furthermore, the reaction patterns and pruning methods are considered and a new method is presented for identification of reactants and products. The structural identification of species contained in the network allows one to approximate the species and reactions thermochemical properties by group contribution or semiempirical quantum chemistry methods. The reaction network generated by this method can be used directly for simulation of thermal cracking reactions or as input for thermal cracking simulators such as REACT, CHEMKIN and KINALC.

INTRODUCTION

The thermal cracking of hydrocarbons occurs through a complex reaction network involving many components. When the feed is a complex mixture, the number of components and reactions in the network becomes enormous and writing them down can be tedious and prone to error. Hence, in recent years, different research groups have independently worked on the generation of thermal cracking or low-temperature hydrocarbon combustion reactions.

Representation of molecules and reactions based on the graph theory is a suitable case for the generation of a cracking reaction network. A graph, V, E , is an ordered pair, where V is a finite, nonempty set whose elements are termed vertices and E is a set of an unordered pair of distinct vertices of V . Based on graph theory, the image of a graph can be achieved by representing each vertex in V by a point in the

plane and each edge in E by a line joining the points representing the vertices with which it is incident [1].

The basic representation of a molecule is graphical. Based on the graph theory, the geometrical figure of a molecule can be described by several matrix forms, such as adjacency matrix, connectivity matrix, etc. Matrix representation of a molecule must include two important specifications that consist of bond order and type of atoms. The adjacency matrix for a molecule (with n atoms) is an n by n matrix, with element 0 or 1, depending upon atomic connectivity. In this matrix form, the number of covalence bonds between atoms are not specified and it might be possible that two different molecules have the same matrix form. Another way for describing the chemical structure of a molecule is the use of the connectivity matrix. Elements of this matrix are 0, 1, 2 or 3, depending upon the type of bond order of atoms. The connectivity or adjacency matrices cannot specify electronic states of atoms in the molecules. The bond and Electron matrix is a transformed type of connectivity matrix. In this matrix form, the method of numbering the matrix elements is similar to the connectivity matrix but the main diagonal elements show the number of free electrons of chemical component atoms.

Based on graph theory, if A_1 and A_2 , are the

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adjacency matrices of two graphs, G_1 and G_2 , then G_1 is isomorphic to G_2 if a permutation of the rows and columns of A_1 can be found to transform A_1 into A_2 . In general, all $n!$ possible permutations, where n is the number of vertices of G_1 (and G_2), can be found for comparison of two graphs [1]. This condition increases the complexity of reactions and component identification in the network generating procedure. Due to this problem, several research groups have reported some algorithms for identifying two isomorph graphs [2-5].

For simulating cracking processes, in addition to the representation and identification of a molecule, which is contained in the network, some other information is required. This information can be used in the form of a help vector, together with the matrix form of a molecule. Considering the matrix type, various methods are suggested for the generation of a cracking reaction network in different cracking processes [3,6-10].

GENERATION OF REACTION NETWORK FOR HYDROCARBONS THERMAL CRACKING

Five stages are considered for generation of a thermal cracking reaction network. These stages can be summarized as follows [11]:

1. Characterization of hydrocarbons by some useful notation,
2. Representation of a graph by a matrix,
3. Selection of some appropriate rule for showing the reactions pattern,
4. Specification of components and resulting reactions,
5. Generation of thermochemical properties of components and reactions.

These stages are applied sequentially for generating and representing the reaction network. A brief introduction of each stage is given as follows.

First Stage

Before constructing a basic structure for representing molecular connectivity, one of the most important

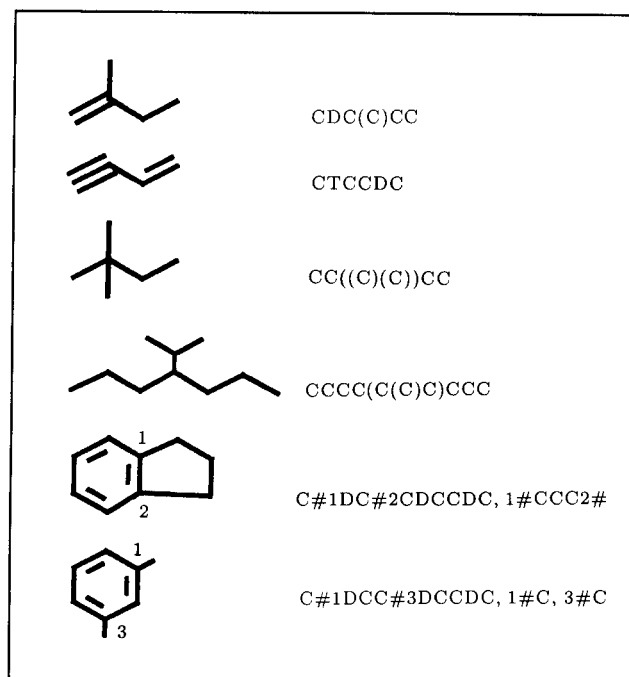


Figure 1. Some examples for linear notation.

problems is the conversion of a conventional notation of a chemical component into a matrix form. In this work, a linear notation [5,12] has been selected for representing different chemical species. In the linear notation approach, each atom of a molecule can be shown by its atomic name and its bond type with other neighboring atoms, which are abbreviated to *D* for double bond, *T* for triple bond and # for cyclic component. Some examples of the linear notation of chemical species are shown in Figure 1.

Second Stage

Several matrix forms have been proposed for representing chemical components. Taking into account the advantages and disadvantages of these matrix forms, which are represented in Table 1, BE matrix is revealed to be more efficient than the other matrix forms. All species matrices used for chemical species are sparse because of the small, fixed valences of atoms. Furthermore, the designing of computer programs using the matrix forms of a graph will lose some computer

Table 1. Advantages and disadvantages of various graph's matrix types.

Properties	Adjacency	C-C Boolean	Connectivity	BE
Bond-order	No	No	Yes	Yes
Electronic state	No	No	No	Yes
Non-similarity for isomorph graphs	No	No	No	No
Non-similarity for non isomorph graphs	No	-	Yes	Yes

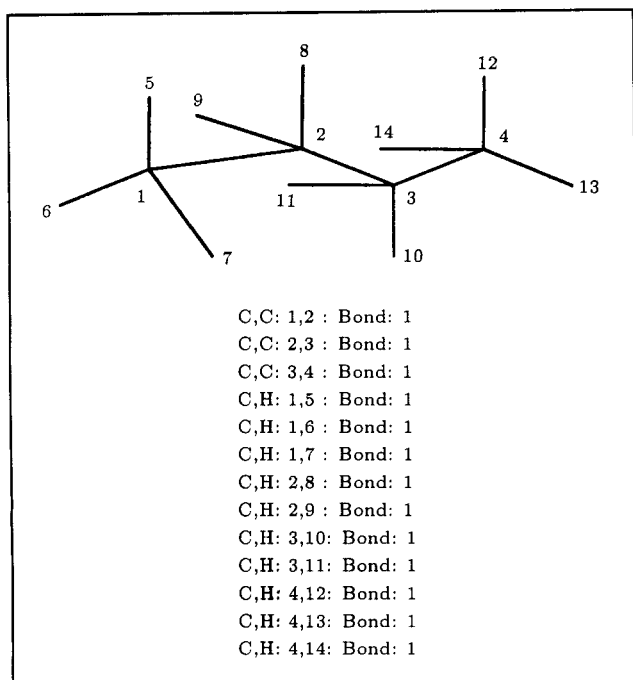


Figure 2. Specification of BE list of butane.

memory. The more efficient adjacency structure of a graph is a set of lists [13], one for each vertex. The list for a vertex v contains all vertices which are connected to it. Therefore, the representation of chemical species by a BE list is more efficient than the matrix form. Constructing a BE list for any chemical components initially requires a basic structure for storing atomic connectivity. This structure can store the following properties for each pair of atoms in a molecule [11]:

- Atom-to-atom bond type,
- Atom-to-atom location number,
- Atom-to-atom characteristic notation.

An example of a BE list of butane is shown in Figure 2.

Third Stage

For representing and generating a reaction network, the main reactions considered are described as follows:

- Fission: Breaking of C-C or C-H bonds,
- H-abstraction: Abstraction of hydrogen atoms from all types of carbon,
- Radical addition: Addition of a radical to the double or triple bond position,
- Recombination: Addition of a radical to another radical from a free electron position,
- β -scission: Breaking of a C-C or C-H bond from the β position of carbon radical,

- Isomerization: Intermolecular migration of the free electron on carbon,
- Disproportionation: Addition of a radical to another radical or molecule and production of a new radical and a new molecule.

Fourth Stage

Taking into account the above reactions, one can proceed with generation of the product species. A complex reaction network can contain so many species and reactions. Identification of these species and reactions in the network is one of the main problems in representing such networks. In this work, a unique specification number (SPN), based on the BE matrix, was defined for identification of any chemical species. This specification number is obtained by combining some parameters as follows:

$$\text{SPN} = N_c, S_{be}, M_{be}, N_{cy}, N_r, \quad (1)$$

in which:

$$C_i = \sum_{\substack{j=1 \\ i \neq j}}^{N_c} BE_j, \quad (2)$$

$$S_{be} = \sum_{i=1}^{N_c} C_i, \quad (3)$$

$$M_{be} = \prod_{i=1}^{N_c} C_i, \quad (4)$$

- N_{cy} : 1 for cyclic component, otherwise 0,
 N_r : Summation of hydrogen in location of radical atom,
 N_c : Carbon number,
 BE: BE matrix elements.

Specification numbers for some chemical species are shown in Table 2. The isomorphism algorithm,

Table 2. Specification number for some chemical species.

Component	Specification Number
Propane	342
<i>n</i> -butane	464
Iso-butane	463
Ethylene	244
Propylene	366
1-butene	4812
2-butene	489
Benzene	6187291
Ethyl-benzene	62219441
Orto-xylene	62212961
Meta-xylene	62212961
Para-xylene	62212961

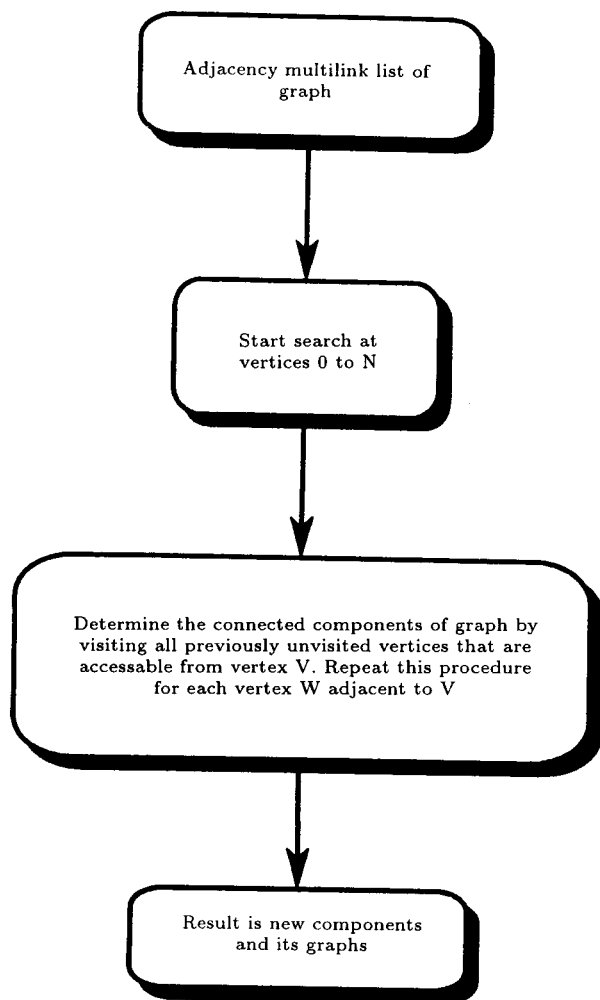


Figure 3. Connectivity algorithm.

which is used in this work, is much simpler than the Hopcroft and Tarjan algorithm [4]. The connectivity algorithm that is used for separating the reaction product from the produced components graph list is shown in Figure 3 and the isomorphism algorithm is shown in Figure 4.

Fifth Stage

After the generation and specification of reactions, the thermochemical properties of species and reactions can be obtained using semiempirical quantum chemistry methods [14-17], semiempirical relations [6] and/or stored database information [18-25].

RESULTS AND DISCUSSION

The logic of the algorithm for the generation of reaction mechanisms is outlined in Figure 5. In the proposed method, each molecule is defined as an object which has some properties such as a BE list. Also, reactions are represented as some form of operator overloading [13] on the objects. This method provides a suitable form

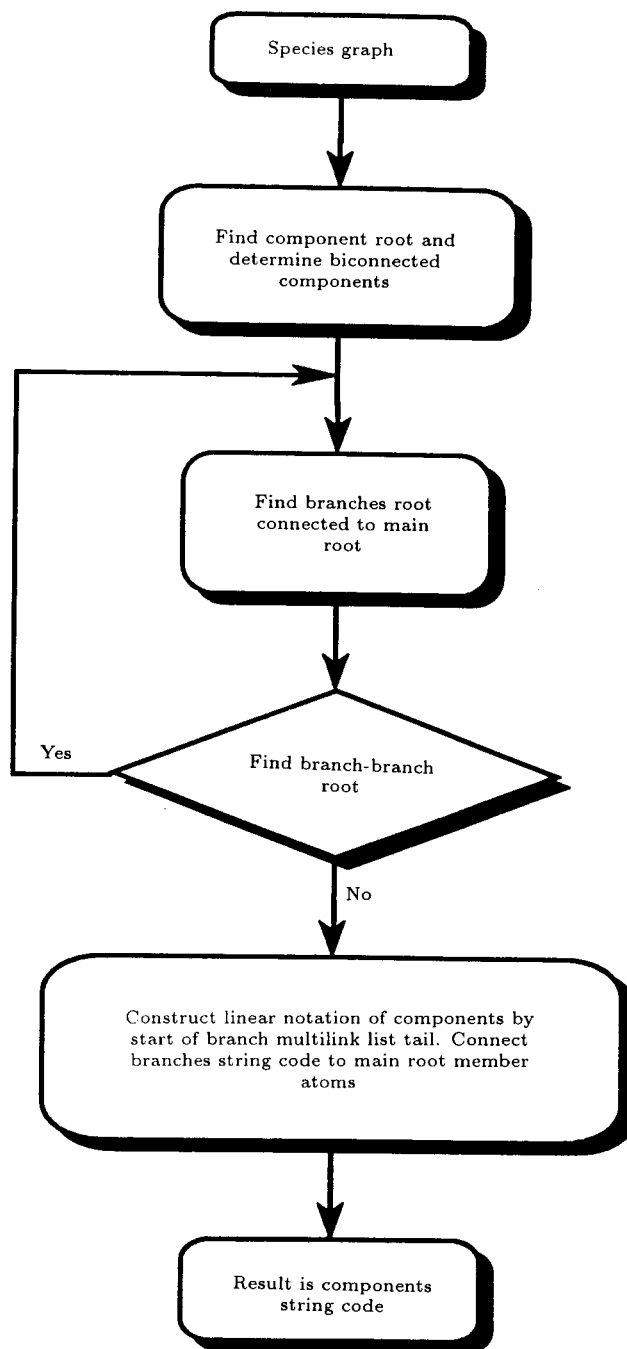


Figure 4. Isomorphism algorithm.

of reaction pattern. The most important step of the algorithm for the generation of thermal cracking reactions is identification of species and reactions in the reaction network. If incorrect species and reactions are selected in the identification step, the complexity of the reaction network will be increased and the final generated network will include some redundant species and reactions. For these reasons, in this work, a new method for identification of species and reactions is presented, based on a specification number. This real number is produced, based on the one-

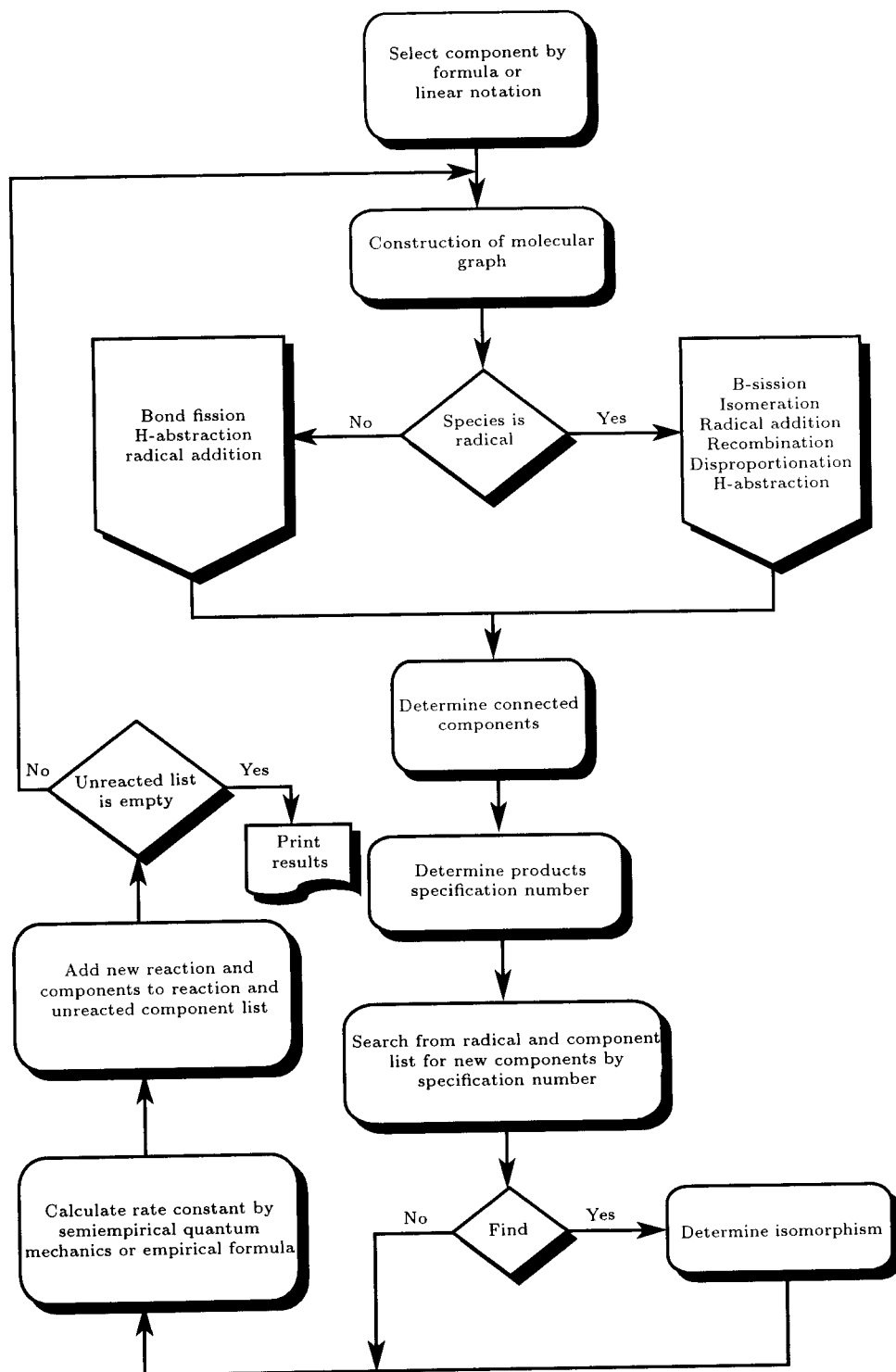


Figure 5. Overall algorithm of the reaction network generation for hydrocarbon cracking (for more detail see [6]).

dimensional structure of the chemical species and is a unique number for any chemical species (except two-isomorph molecules). Based on SPN, the reaction and component properties can be computed in the reaction network. It should be emphasized that a major advantage of the software developed in this work is that the characteristic notation of the reaction network, as

well as the SPN notation of the reaction network, are produced simultaneously. The designed compiler can also compile the SPN notation of each reaction. From the output of the compiler, the component properties can be extracted from the database. The designed database is based on the DIPPR databank and the component properties in the database are arranged by

SPN. The produced reaction network, which includes all the reactions and component properties, can be used by an available modeling and simulation software.

Also, in this research, a new simplified method is described for general identification of hydrocarbon components (C_xH_y), for comparison between two-isomorph graphs, based on linear notation of chemical species.

In the modeling of complex reaction systems, it is often desirable to limit, or prune, the generated specific reactions. In this work, a pruning technique is developed, based on the generic reactions, the reactants and the products. A set of seven generic reaction types, which are used to generate the reaction network by the designed reaction generator, can be summarized as follows:

- Fission of a hydrocarbon to form one or two radicals,
- Hydrogen abstraction from a hydrocarbon to form a radical,
- Addition of two radicals to form a larger hydrocarbon,
- Addition of an olefin and a radical to form a larger radical,
- Addition of two radicals to form an olefin or cyclic hydrocarbon and a radical,
- β -scission of a radical to form an olefin and a smaller radical,
- 1,4 or 1,5 hydrogen migration or shift.

Pruning methods are efficient ways of managing and reducing a reaction network. For example, in thermal cracking reactions under high temperature and low-pressure conditions, successive β -scissions of large radicals result in a product distribution characterized

by multistep decomposition. Under such conditions, only smaller radicals, methyl radicals and hydrogen atoms participate in hydrogen abstraction reactions. On the other hand, under low temperature and high pressure conditions, the product distribution is represented by a single step decomposition, in which larger radicals produced from the decomposition of parent radicals participate in hydrogen abstraction reactions. Radical addition reactions are also favored under such conditions. The pruning parameters used in this work are based on the carbon number. These are optional parameters to limit the number of reactions and are specified for a specific feed molecule. For example, in the case of a feed containing C_3 and C_4 hydrocarbons (Table 3), a pruning parameter of 3 for hydrogen abstraction reactions allows for hydrogen abstraction reactions involving radicals of up to 3 carbons, or a pruning parameter of 7 for recombination reactions allows for recombination of radicals resulting in a product containing, at most 7 carbons. A pruning parameter of 6 for radical addition reactions would limit the addition of radicals to olefins, giving a larger radical of, at most, 6 carbons. A pruning parameter of 5 for β -scission would limit β -scission reactions to radicals with, at most, 5 carbons. In the case of C_3 and C_4 feeds, this would exclude the decomposition of larger radicals formed as secondary products. It should be emphasized that the pruning parameters are specified based on the type of feed. For example, the pruning parameters outlined in Table 3 apply to feeds with 3 or 4 carbons and should be adjusted for feeds with higher carbon numbers. These pruning methods are advantageous, since the number of thermal cracking reactions for hydrocarbons could, otherwise, increase to thousands.

Another feature of the computer program de-

Table 3. Number of thermal cracking reactions network for some species.

Specifications	Propane	Butane	Iso-Butane	Mixture
Molecule	112	112	112	112
Radical	141	141	141	141
Fission (4)*	39	39	38	39
β -scission (5)	80	83	82(5)	81
H-abstraction (3)	1821	1821	1821	1821
Radical addition (6)	380	370	366	372
Isomeration (4)	34	34	34	34
Recombination (7)	682	682	682	682
Disproportionation (5,6)	50	52	52	52
Total	3086	3081	3075	3081

* Pruning parameter

veloped in this work, is the generation of a reaction network, along with the thermochemical properties of species that are contained in the network as input for chemical reaction simulator software such as KINALC, CHEMKIN and REACT [26-28].

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