Molecular-level reaction network in delayed coking process based on structure-oriented lumping

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Abstract

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1

Abstract Based on the structure-oriented lumping method, a molecular-level reaction kinetic model of the delayed coking process, which adopted 24 structural increments to construct the feed molecular matrix containing 2,944 molecules, was established with a reaction network containing 74,581 reactions using MAT-LAB. The reliability of the model was verified by experimental results. According to the discriminant rules of structural increments, 173 structural vectors in gasoline and 1,132 structural vectors in diesel were classified into different group compositions, respectively. The model could track the reaction path of any specific molecule in the complex thermal cracking reaction network. The influences of operation conditions such as recycle ratio on the product distribution could be discovered through the calculation of the molecular-level model, which is helpful for the process optimization and precise regulation of product composition for the delayed coking plants.

KEYWORDS structure-oriented lumping, reaction kinetics, thermal cracking, reaction network

1 INTRODUCTION

Due to the heavier tendency of crude oil,[1,2] delayed coking based on deep thermal cracking reaction is receiving more and more attention as one of the most important processing technology for heavy oils.[3] Free radical chain reaction theory is widely used to explain the mechanism of thermal cracking reaction, includes chain initiation, chain growth and chain termination.[4,5] The chain initiation due to the breaking of the C-C bond is usually the control step of the reaction. The chain growth mainly includes the substitution reaction, decomposition reaction, addition reaction and displacement reaction of free radicals. The chain termination refers to the combination of unpaired electrons of free radicals to form stable molecules, which stops the chain reaction.

The analysis and characterization method of heavy oil is far from mature due to the extreme complexity of petroleum composition.[6] The application of supercritical fluid extraction and fractionation (SFEF) technology[7-9] and Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry technology made breakthroughs in understanding the complex molecular structure of petroleum.[10-13] At the same time, the rapidly-developing computing technology greatly promoted the development of petroleum processing models from the traditional multi-lumping models[14-17] based on fractions to the molecular-level reaction kinetic models. Representative modeling method for molecular-level reaction kinetic models of refining processes included the structure-oriented lumping (SOL) method,[18-20] the modified molecular-type homologous serious (MTHS) representation,[21] and Bond-Electron matrix with Monte Carlo simulation and atomic topology.[22-25]

SOL method has been proved to be effective for heavy oil processing models. ExxonMobil has developed molecular composition fine tuning algorithm, molecular property calculation method, and constructed some molecular-level models of petroleum processing processes based on SOL method. These models could predict the product properties, such as octane number, cetane number, etc.. They have been successfully applied in their refineries. Tian developed a molecular composition matrix calculation model for petroleum,[26] and built a kinetic model for steam cracking which could calculate the contents of 132 molecules with reaction conditions.[27] Liu and Chen established the molecular-level model for the fluid catalytic cracking process at the molecular level.[28] The model introduced feedback of the heat effects to improve the calculation accuracy.

In this paper, the delayed coking reaction kinetic model was built based on the free radical chain reaction mechanism and the SOL method to describe the reaction path of reactant molecules and the generation path of product molecules in the reaction network. The information from the structural vectors in the products especially gasoline and diesel provides reference for the precise control of the delayed coking process at the molecular level.

2 CONSTRUCTING THE MOLECULAR COMPOSITION MATRIX OF RESIDUE OILS

2.1 Characterization of residue oils

The characterization method for residue oils established in this paper is shown in Figure 1.
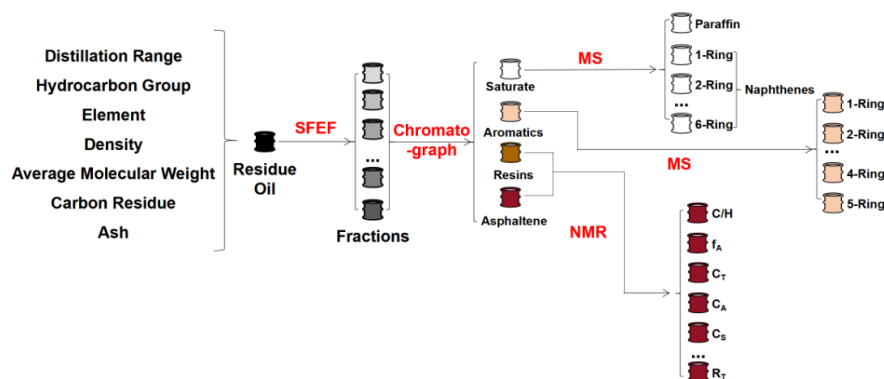
Abbreviations: MS, mass spectrometry; NMR, nuclear magnetic resonance; C/H, ratio of carbon to hydrogen;

f_A, fraction of aromatic carbon; C_T, total carbon number; C_A, aromatic carbon number;

C_S, saturated carbon number; R_T, total number of rings

FIGURE 1 Characterization flowchart of residue oils

The macroscopic properties such as distillation range, density, average molecular weight, etc. of the residue oils were obtained using the corresponding analytical instruments. The residue oil was separated into narrow fractions using supercritical fluid extraction and fractionation (SFEF) technology. Each narrow fraction was separated using Al_2O_3 column chromatography to obtain sub-fractions of saturates, aromatics, resins, and asphaltenes.[29] The saturates and aromatics were analyzed to get the ring numbers of naphthenes and aromatics. The resins and asphaltenes were analyzed using the element analyzer, analog distillation instrument, time-of-flight MS, NMR to get the average structure parameters according to the Brown-Ladner method.[30,31] Taking a feed oil of the delayed coking plant from PetroChina as an example, partial characterization results of the residue oil obtained by the aforementioned methods are shown in Table S1, Table S2, Table S3 and Figure S1 in the Supporting Information.

2.2 Molecular composition matrix based on structure-oriented lumping

24 structural increments representing hydrocarbon and heteroatom are selected to describe the molecular composition of the residue oils. The chemical structural formulas of 24 structural increments are shown in Table 1.

TABLE 1 The chemical structural formulas of 24 structural increments

Increments	A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me
Structures												
Increments	IH	AA	NS	RS	AN	NN	RN	NO	RO	KO	Ni	V
Structures	H_2										Ni	V

The structure of each molecule in residue oil can be represented by a row vector containing 24 structural increments. Each element in the vector represents the number of corresponding structural increments in the molecule. Table 2 lists the structure vectors of two typical residue molecules.

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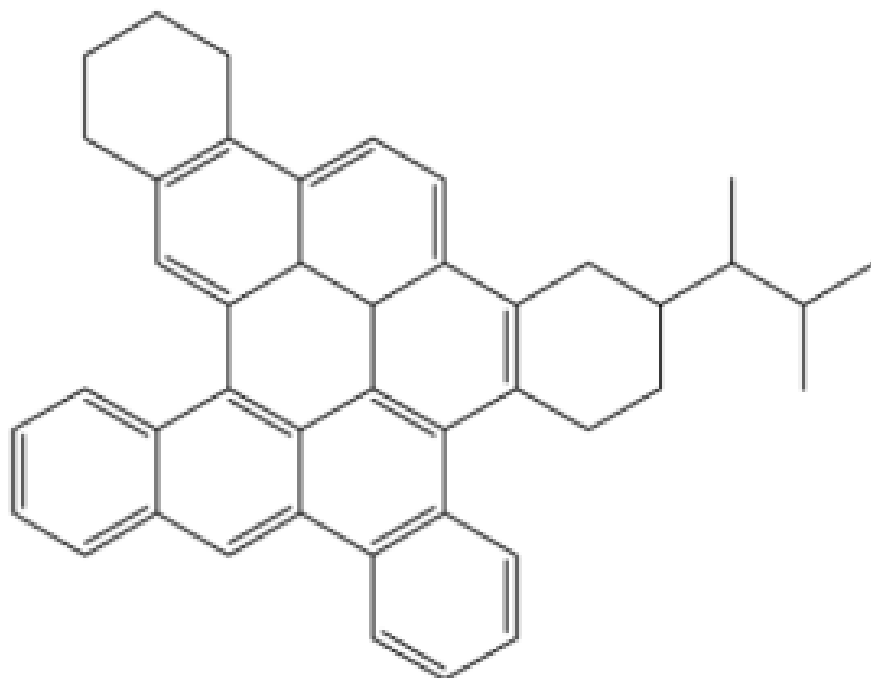
Typical molecule 1:
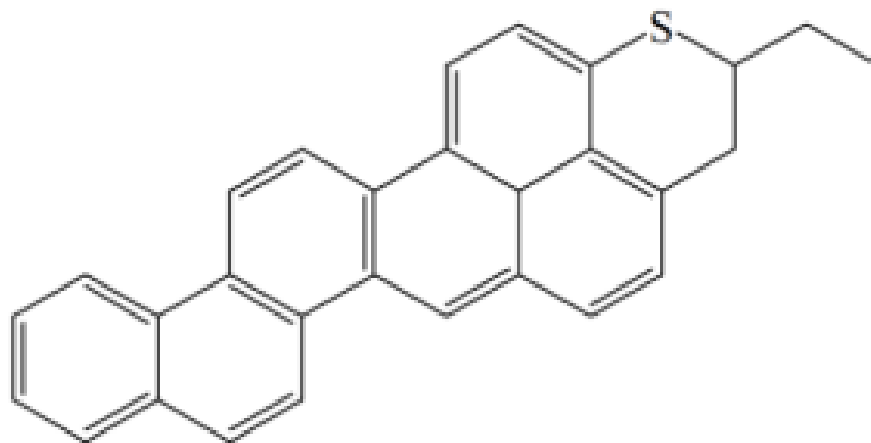
Typical molecule 2:

TABLE 2 Structural vectors of two typical residue molecules

Structural increments	A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN
Molecule 1	1	5	2	0	0	2	0	0	0	5	2	0	0	0	0	0	0	0
Molecule 2	1	4	1	0	0	1	0	0	0	2	0	0	0	0	1	0	0	0

2.3 Constructing the molecular composition matrix of oils

According to the composition characteristics of the oils in the delayed coking process, the molecular com-

4

position matrix consisted 2944 rows×25 columns was constructed using the generating algorithm in our previous work.[32] The first 2944 rows×24 columns represented 2944 structural vectors. Each structural vector corresponds to one or several molecules with same structural increments. The last column containing 2944 elements represented the contents of the corresponding molecules in the oil. The molecular composition matrix of the delayed coking feed oil used is this paper is shown in Table S5 in the Supporting Information.

The calculated values of the distillation range, the contents of SARA, the number of aromatic rings, the number of naphthenic rings, and the element contents are in great agreement with the measured values (the measured properties of the residue oil and the calculated values according to the molecular composition matrix were presented in Figure S2 and Table S4 in the Supporting Information). It means that the molecular composition matrix constructed by the above method could describe the molecular composition of the residue oil well.

3 CONSTRUCTION AND VERIFICATION OF MOLECULAR-LEVEL REACTION KINETIC MODEL

3.1 Construction of the reaction kinetic model based on structure-oriented lumping

According to the free radical chain reaction mechanism of delayed coking process, 19 reaction rules were formed. Each rule included two parts: reactant selection rule and product generation rule. Typical reaction rules are shown in Table 3. The symbol "" means "and"; the symbol "" means "or".

TABLE 3 Typical reaction rules for delayed coking process

Reaction type	Reaction rule
Paraffins, Carbon chain breaking	Reactant selection rules: Product 1 generation rules: ,, Product 2 generation rules: ,
Olefins, Carbon chain breaking	Reactant selection rules: Product 1 generation rules: ,, Product 2 generation rules: ,
Naphthenes, Side chain breaking	Reactant selection rules: Product 1 generation rules: ,,Rest were all 0 Product 2 generat
Aromatics, Side chain breaking	Reactant selection rules: Product 1 generation rules: ,,Rest were all 0 Product 2 generat
Naphthenes, Ring opening	Reactant selection rules: Product generation rules: ,,
Cycloalkyl, Ring opening	Reactant selection rules: Product generation rules: ,,
Dehydrogenation -olefination	Reactant selection rules: Product 1 generation rules: ,Rest were all 0 Product 2 generati
Dehydrogenation -aromatization	Reactant selection rules: Product 1 generation rules: ,Rest were all 0,Product 1×2 Prod

All the reaction rules were compiled into program codes in Matlab software. The molecules in the molecular composition matrix of feed oil could be identified by the suitable reactant selection rules, and the molecular composition matrix of product was generated by the corresponding reaction rules. The reaction rate constants used to calculate the reaction network can be gained from the follows equation.[33,34]

where, k_B is the Boltzmann constant, J/K;

h is the Planck constant, 6.626×10^{-34} J·S;

T is the temperature , K;

R is the ideal gas constant, R=8.314 J·mol^{-1}·K^{-1};

ΔS_m is the entropy changes before and after reaction, J·mol^{-1}·K^{-1};

ΔE is the reaction energy barrier, kcal/mol

Some typical reaction rate constants k for delayed coking process at the reaction temperature of 495 are shown in the Table 4.

TABLE 4 Typical reaction rate constants for delayed coking process

Reaction type	k / s^{-1}

5

Paraffins, Carbon chain breaking	2.02×10^{-3}
Olefins, Carbon chain breaking	1.83×10^{-3}
Naphthenes, Side chain breaking	8.95×10^{-4}
Aromatics, Side chain breaking	8.30×10^{-4}
Naphthenes, Ring opening	1.15×10^{-4}
Cycloalkyl, Ring opening	3.27×10^{-5}
Dehydrogenation-olefination	1.29×10^{-4}
Dehydrogenation-aromatization	6.93×10^{-5}

The whole reaction time t of delayed coking process was divided into n intervals. Each interval was Δt_i (i =1-n). In the reaction time Δt_1 , the molecular composition matrix of feed oil and reaction temperature T were input, and the reaction network was established based on the reaction rules of the SOL method. Combining with the reaction rate constants, the reaction kinetics differential equations were constructed, and then solved using the improved *Runge-Kutta* method to get the product molecular composition matrix of Δt_1 , which was the feed molecular composition matrix of the reaction time Δt_2 . At the same time, the total reaction heat in the reaction time Δt_1 was calculated and converted into the temperature difference ΔT_1 to obtain the reaction temperature $\Delta t_2 = T + \Delta T_1$ for the next reaction interval. Then the coking process of the reaction time Δt_2 was calculated. The calculation was repeated until the reaction time reached t . The calculation diagram of the delayed coking model was shown in Figure 2.
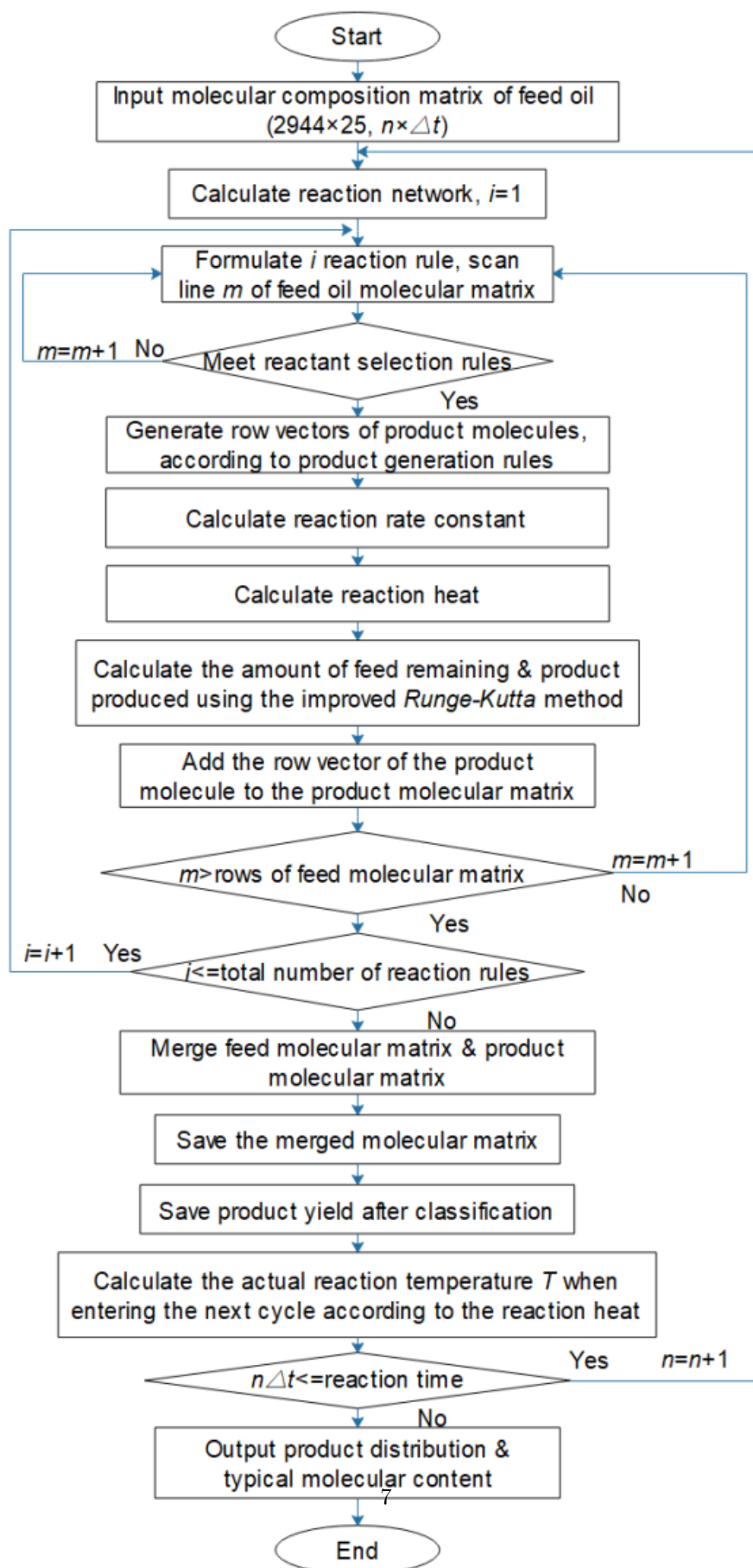
```
                              ┌──────────────┐
                              │    Start     │
                              └──────────────┘
                                     │
           ┌─────────────────────────────────────────────────┐
           │  Input molecular composition matrix of feed oil  │
           │              (2944×25, n×△t)                     │
           └─────────────────────────────────────────────────┘
                                     │
              ┌────────────────────────────────────────┐
              │   Calculate reaction network, i=1       │
              └────────────────────────────────────────┘
                                     │
              ┌────────────────────────────────────────┐
              │   Formulate i reaction rule, scan       │
              │   line m of feed oil molecular matrix   │
              └────────────────────────────────────────┘
                                     │
    m=m+1  No        ◇ Meet reactant selection rules ◇
                                     │ Yes
              ┌────────────────────────────────────────┐
              │ Generate row vectors of product molecules, │
              │  according to product generation rules  │
              └────────────────────────────────────────┘
                                     │
              ┌────────────────────────────────────────┐
              │     Calculate reaction rate constant    │
              └────────────────────────────────────────┘
                                     │
              ┌────────────────────────────────────────┐
              │        Calculate reaction heat          │
              └────────────────────────────────────────┘
                                     │
              ┌────────────────────────────────────────┐
              │ Calculate the amount of feed remaining & product │
              │ produced using the improved Runge-Kutta method   │
              └────────────────────────────────────────┘
                                     │
              ┌────────────────────────────────────────┐
              │  Add the row vector of the product      │
              │  molecule to the product molecular matrix │
              └────────────────────────────────────────┘
                                     │
            ◇ m>rows of feed molecular matrix ◇      m=m+1
                                     │ Yes              No
   i=i+1  Yes  ◇ i<=total number of reaction rules ◇
                                     │ No
              ┌────────────────────────────────────────┐
              │  Merge feed molecular matrix & product  │
              │          molecular matrix               │
              └────────────────────────────────────────┘
                                     │
              ┌────────────────────────────────────────┐
              │      Save the merged molecular matrix   │
              └────────────────────────────────────────┘
                                     │
              ┌────────────────────────────────────────┐
              │    Save product yield after classification │
              └────────────────────────────────────────┘
                                     │
              ┌────────────────────────────────────────┐
              │ Calculate the actual reaction temperature T when │
              │ entering the next cycle according to the reaction heat │
              └────────────────────────────────────────┘
                                     │
            ◇ n△t<=reaction time ◇    Yes    n=n+1
                                     │ No
              ┌────────────────────────────────────────┐
              │   Output product distribution &         │
              │    typical molecular content            │
              └────────────────────────────────────────┘
                                     │
                              ┌──────────────┐
                              │     End      │
                              └──────────────┘
```

7

**FIGURE 2** Calculation diagram of delayed coking SOL model

3.2 Verification of SOL reaction kinetic model

3.2.1 Delayed coking experiments

The flowchart of delayed coking experimental plant is shown in Figure 3. The volume of coking reactor is 4L. The operation parameters are listed in Table 5.

TABLE 5 Operation parameters of the delayed coking experimental plant

Conditions	Values	Conditions	Values
Feeding flowrate, g/h	1000	Pressure, MPa	0.15
Stripping time, h	3	Recycle ratio	0-0.7
Temperature,	470-505	Water flowrate, g/h	20
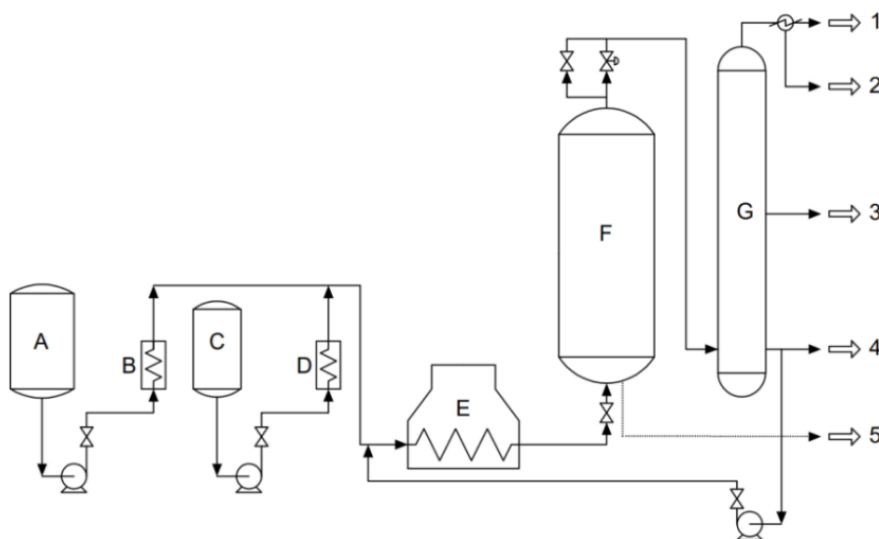
A Feed oil tank; B Feed oil preheater; C Water tank; D Water preheater;

E Heating furnace; F Coke reactor; G Distillation tower;

1 Gas; 2 Gasoline; 3 Diesel; 4 Gas oil; 5 Coke

FIGURE 3 Flow chart of the experimental plant for delayed coking

3.2.2 Verification of product yields of delayed coking products

The model calculated yields and the experimental yields of the delayed coking products at the reaction temperatures of 470-505 are shown in Figure 4.
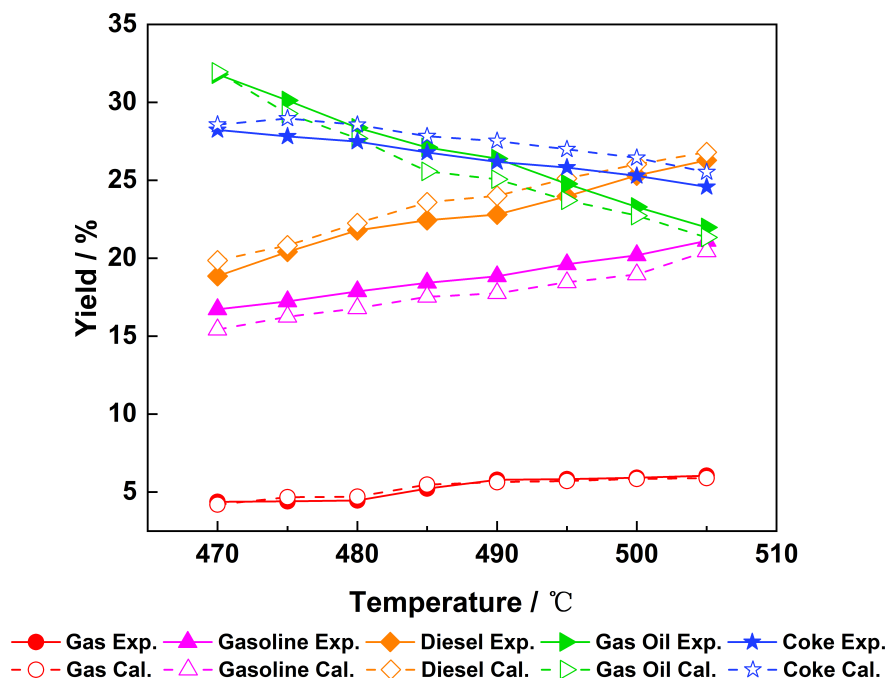
FIGURE 4 The model calculated and the experimental yields of the delayed coking products

The calculated yields of the gas, gasoline, diesel, gas oil, and coke by the delayed coking SOL reaction kinetic model were relatively close to the experiment results. The deviations were less than 1.5%.

TABLE 6 The calculated and experiment contents of typical molecules

	Typical molecule	475	475	485	485	495	495	505	505
	(wt%)	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
Coking gas	Methane	36.09	35.28	39.65	37.87	43.62	42.87	45.65	44.72
	Ethylene	6.76	6.37	7.05	6.73	7.63	7.28	9.16	8.74
	Isobutane	1.41	1.67	1.30	1.48	1.21	1.49	1.07	1.37
	Hydrogen	8.44	9.13	8.65	9.29	9.42	10.02	9.73	10.38
	Hydrogen sulfide	3.48	3.68	3.93	4.19	4.17	4.32	4.37	4.63
Coking gasoline	N-hexane	3.32	3.19	4.03	3.83	2.86	2.64	4.15	3.28
	Isoheptane	0.49	0.48	0.60	0.51	0.56	0.55	0.57	0.61
	2-Octene	0.47	0.51	0.41	0.43	0.43	0.48	0.47	0.51
	Methylcyclohexane	0.15	0.22	1.13	1.09	1.19	1.02	0.99	0.96
	O-xylene	0.73	0.66	0.72	0.98	0.96	0.73	0.94	1.01
Coking diesel	Pentadecane	1.81	1.92	1.84	1.96	2.03	2.11	2.05	2.17
	Tetradecadiene	0.29	0.27	0.28	0.26	0.31	0.30	0.37	0.36
	Trimethylphenanthrene	0.05	0.04	0.04	0.05	0.04	0.05	0.04	0.05

The model calculated and experimental contents of typical molecules are shown in Table 6. The deviations were less than 2.0%. The delayed coking reaction kinetic model based on the SOL method was reliable and could predict the product distribution at the molecular level.

4 MOLECULAR-LEVEL REACTION NETWORK IN DELAYED COKING PROCESS

The reaction kinetic model based on the free radical chain reaction mechanism and the SOL method provides

a novel method to study the complex reaction network and molecular reaction paths in the delayed coking process.

4.1 Calculation of the molecular distribution of product

The molecular composition matrix of delayed coking product containing 9,505 structural vectors was obtained through the calculation of the molecular-level reaction kinetic model at the reaction temperature of 495 and the recycle ratio of 0.5. Each structural vector represented one molecule or several molecules with the same structural characteristics. The product molecular composition matrix provided product information of delayed coking at the molecular level. In order to make clear statistics of the product distribution, molecules with the same number of carbons and the same number of Double Bond Equivalent (DBE) were added up.

The DBE-Carbon Number graphs at different residence times in Figure 5 show the change of product distribution as the reaction proceeded. In order to distinguish different group compositions in the graphs, it is stipulated that DBE of olefin = real DBE-0.50, DBE of naphthene = real DBE-0.25, DBE of aromatics = real DBE+0.25.
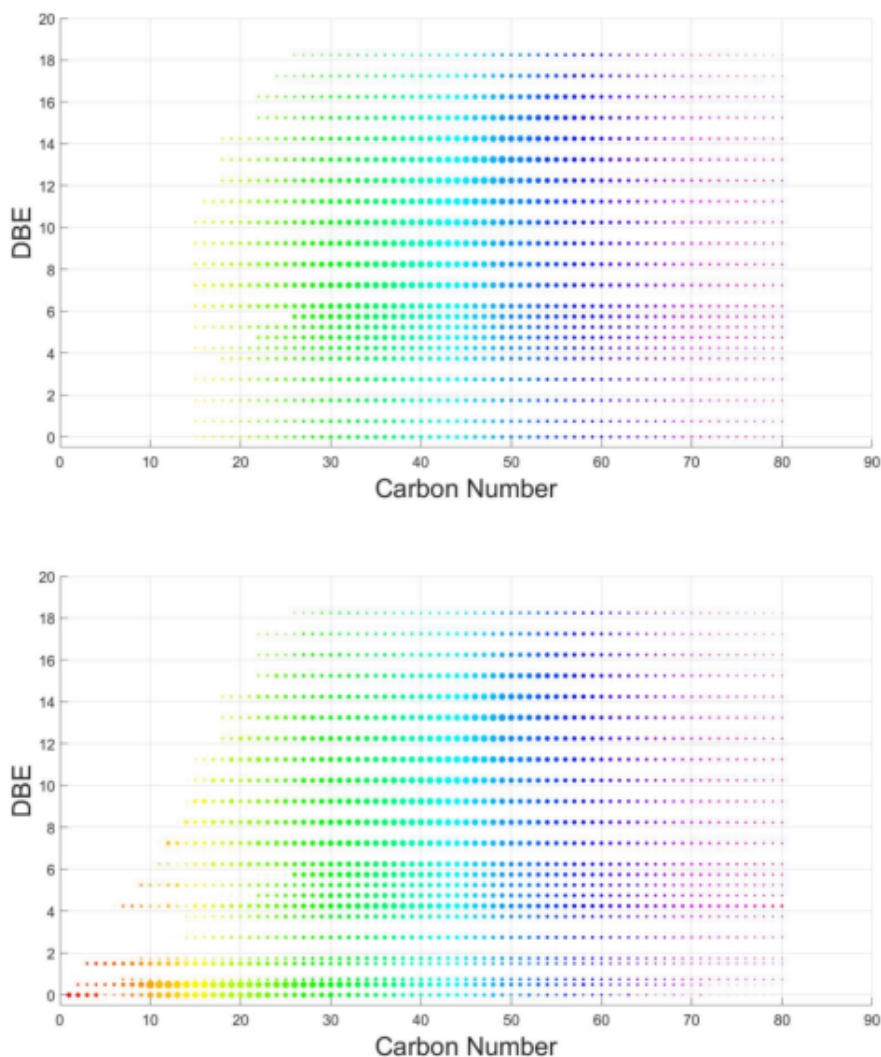
(a) Feed oil (b) RT =0.2
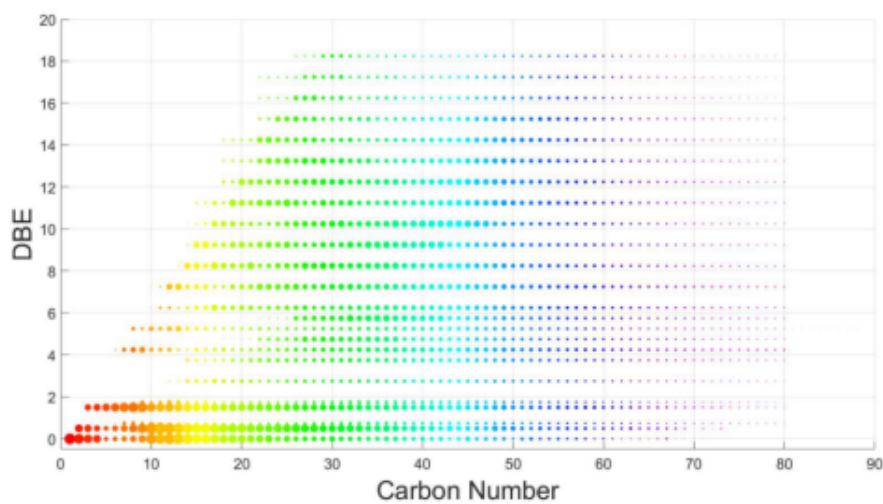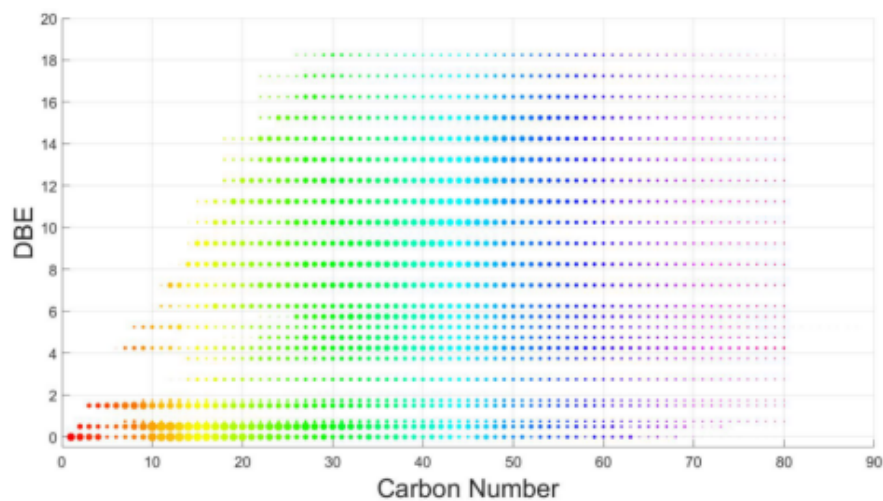
(c) RT = 0.4 (d) RT = 0.6
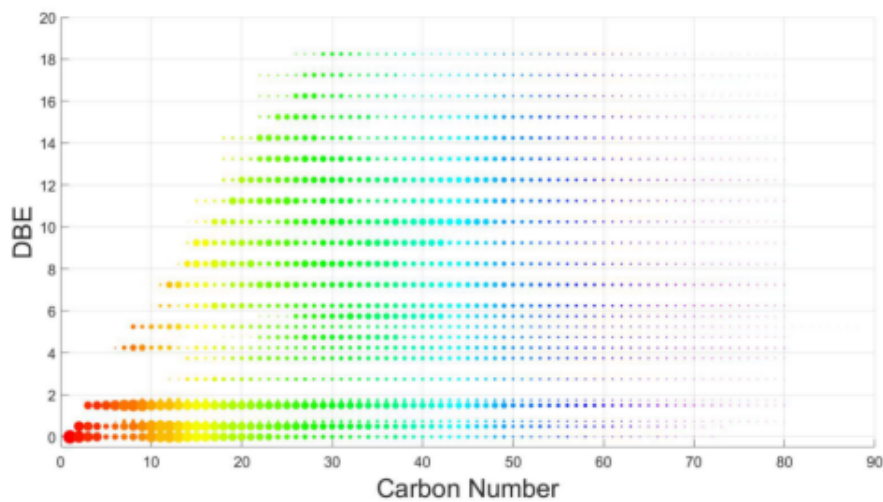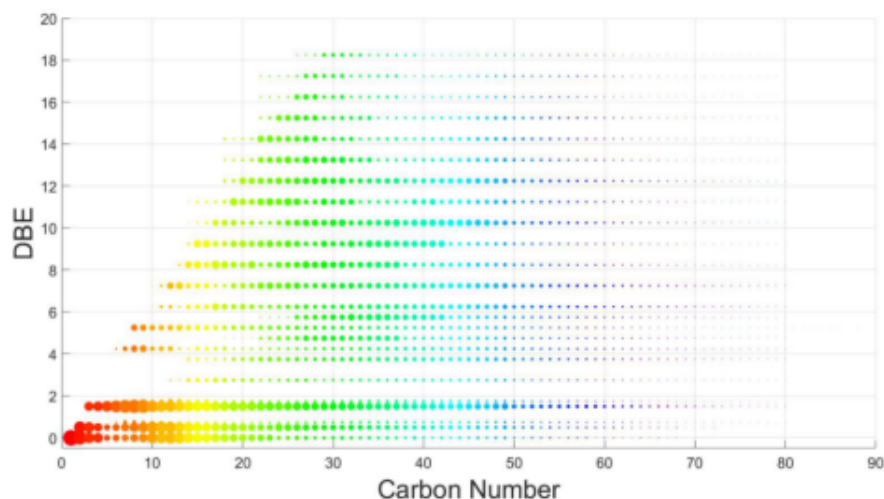
(e) RT = 0.8 (f) RT = 1.0

RT: Relative residence time

FIGURE 5 Product distributions at different relative residence times

The feed oil of delayed coking has no olefin molecules, which were intermediate products of thermal cracking reactions. As the reaction proceeded, the contents of paraffin, olefin, naphthene and aromatics with low carbon numbers increased. The model can present the molecular distribution at different residence times and give the reaction path of each molecule in the reaction system according to the reaction rules, which contributes to disclose the changes in the molecular contents between the reactants and products in the reaction system.

4.2 Influences of operation conditions on product distribution at molecular level

4.2.1 Influences of operation conditions on product yields at molecular level

The molecular composition matrix of product calculated by the SOL molecular level model contained 9,505 structural vectors, each of which represented one or several molecules. The structural vectors (molecules) in products were divided into five categories: gas, gasoline, diesel, gas oil, and coke based on the classification rules shown as follows:

Gas: Carbon Number[?]4;

Gasoline: Carbon Number[?]5 & Boiling Point[?]200;

Diesel: Carbon Number[?]23 & Boiling Point¿200 & Boiling Point[?]350;

Coke: Carbon Number[?]24 & Boiling Point¿450 or Content of Carbon[?]90%;

Gas oil: the rest.

The division of products based on the SOL model was much more accurate than the traditional multi-lumping model.

With the recycle ratio of 0.1-0.9 and the reaction temperature of 495, the molecular composition matrix of the delayed coking feed oil calculated in Section 2.3 was input into the delayed coking SOL model. The product yields based on the calculated product molecular matrix are shown in Figure 6.
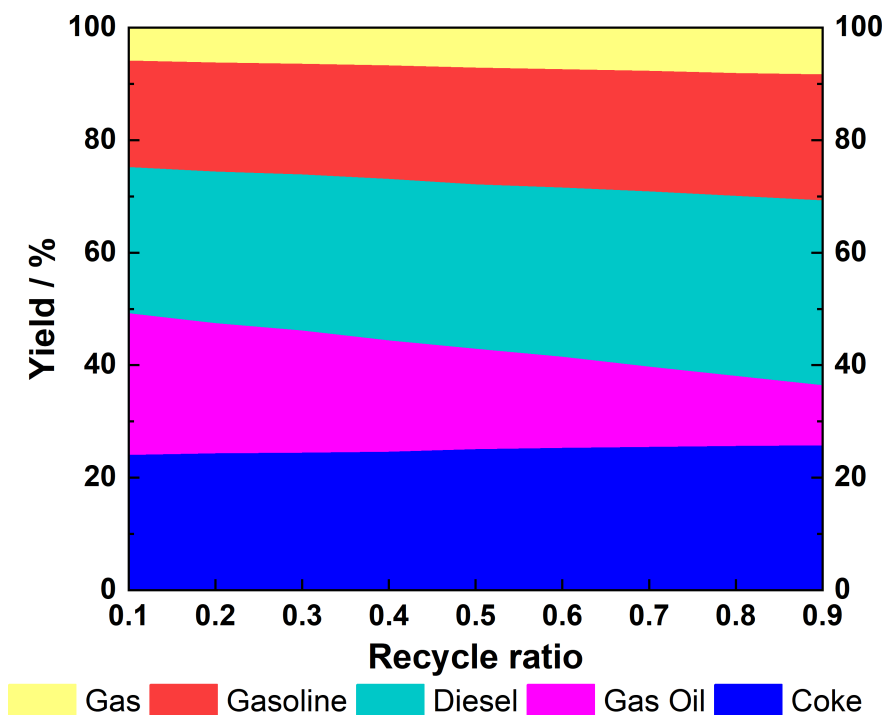
12

FIGURE 6 Influences of the recycle ratio on delayed coking product yields

The yields of gas, gasoline, diesel, and coke increased by 0.30%, 0.43%, 0.86%, and 0.22%, while the yield of gas oil decreased by 1.81% with the recycle ratio increment of 0.10. The increase of the recycle ratio means that more gas oil was recycled, so the yield of gas oil reduced.

4.2.2 Influences of recycle ratio on group composition of gasoline

TABLE 7 Discriminant rules of group composition in coking products

Group composition	Discriminant rules
Normal Paraffins	
Isoparaffins	
Olefins	
Naphthenes	
Aromatics	

According to the discriminant rule shown in Table 7, molecules in gasoline and diesel were classified into normal paraffin, isoparaffin, olefin, naphthene and aromatics. The number of structural vectors contained in gasoline, diesel and their group composition are shown in Table 8.

TABLE 8 Number of structural vectors in gasoline and diesel and their group composition

| Products	Normal paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics	Totally
Gasoline	9	23	24	40	77	173
Diesel	12	36	96	318	670	1132

At the reaction temperature of 495 and the recycle ratio of 0.5, the molecular composition matrix of gasoline

13

product calculated by the SOL reaction kinetic model is shown in the Table 9 (Details in Table S6).

TABLE 9 Molecular composition matrix of gasoline product

Molecule	A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN	NN	RN	N
1	0	0	0	0	0	0	0	0	0	4	1	0	1	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0	0	5	1	0	1	0	0	0	0	0	0	0
3	0	0	0	0	0	0	0	0	0	5	2	0	1	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	6	1	0	1	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0	0	6	2	0	1	0	0	0	0	0	0	0
...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
169	1	0	0	0	0	0	0	0	0	6	0	2	0	0	0	0	0	0	0	0
170	1	0	0	0	0	0	0	0	0	6	1	0	0	0	0	0	0	0	0	0
171	1	0	0	0	0	1	0	0	0	2	0	1	0	0	0	0	0	0	0	0
172	1	0	0	0	0	0	0	0	0	6	1	1	0	0	0	0	0	0	0	0
173	1	1	0	0	0	0	0	0	0	2	0	1	0	0	0	0	0	0	0	0

The distribution of the group compositions in gasoline can be obtained from the molecular composition matrix of gasoline.
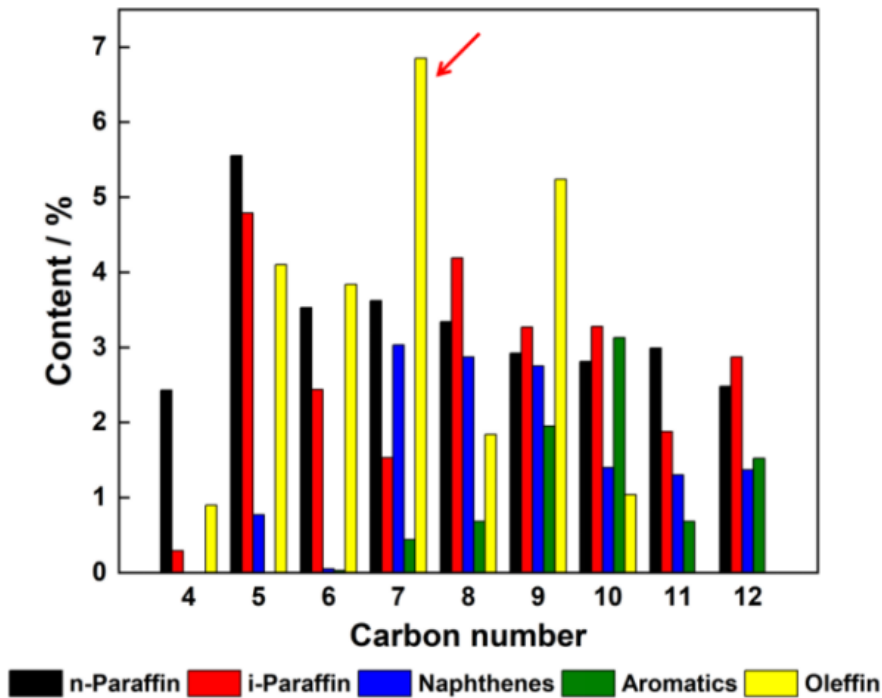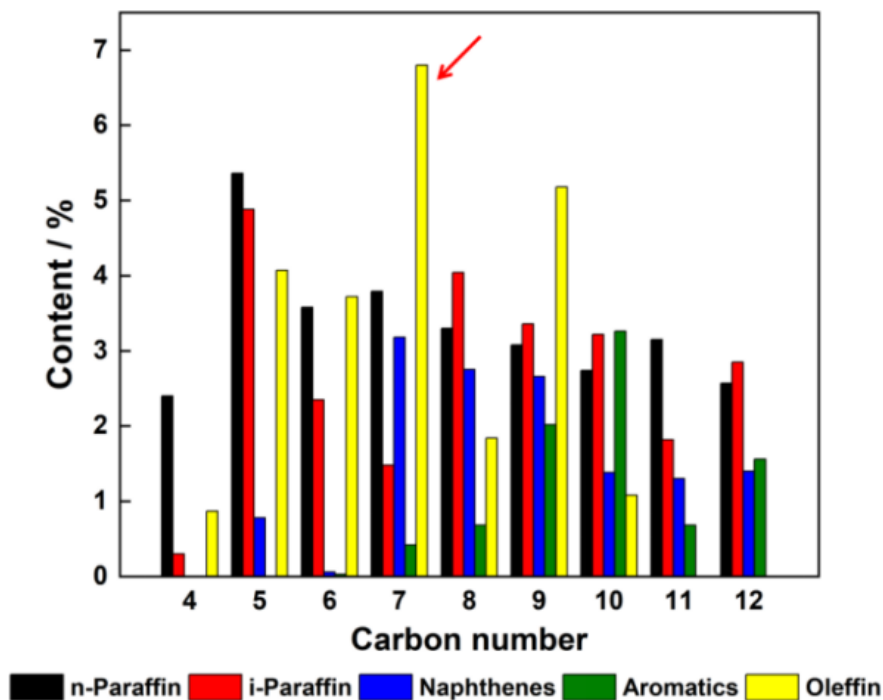
FIGURE 7 Experimental gasoline group composition **FIGURE 8** Calculated gasoline group composition

Figures 7 and 8 show the experimental and calculated group compositions of gasoline, respectively. The calculated group compositions are very close to the experimental values. The maximum deviation is less than 0.95%.

The group composition of gasoline calculated by the SOL model with different recycle ratios are shown in Figure 9.
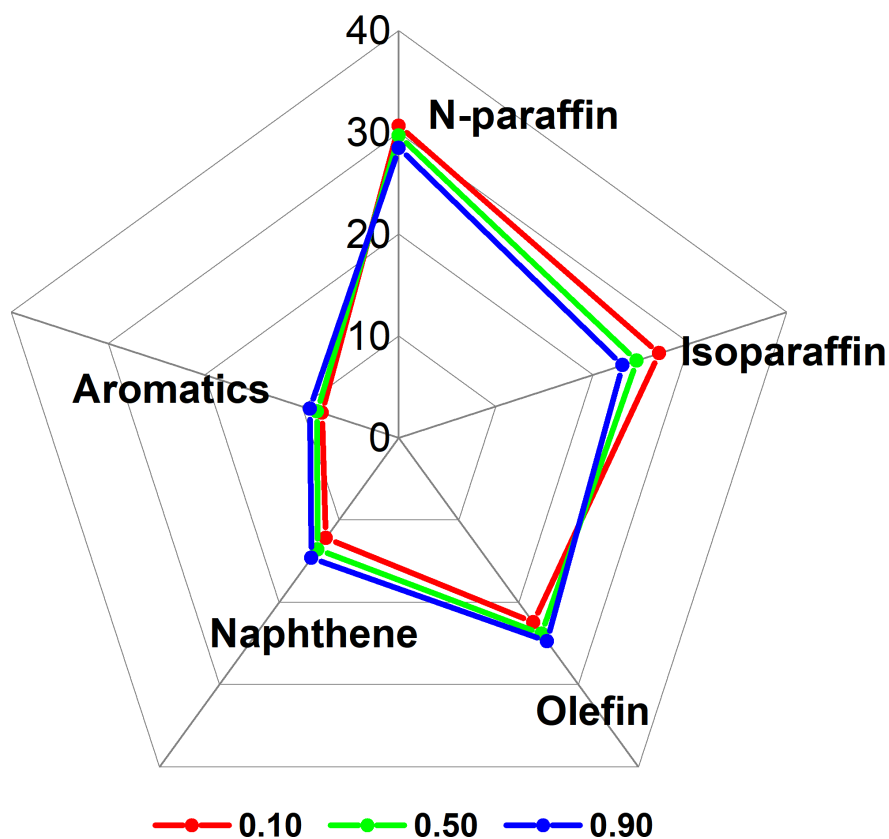
FIGURE 9 Influences of recycle ratio on group composition of gasoline

The contents of normal paraffin and isoparaffin were the highest in coking gasoline, followed by olefin, naphthene and aromatics. The content of normal paraffin and isoparaffin decreased by 0.27% and 0.47%, and the content of olefin, naphthene and aromatics increased by 0.28%, 0.30%, and 0.15% with the recycle ratio increment of 0.10.

4.2.3 Molecular level reaction network in delayed coking process

A certain proportion of coking gas oil is recycled to the feed oil. Group composition of coking gas oil (Detail structural matrix in Table S7) was calculated according to the discriminant rules in Table 7.
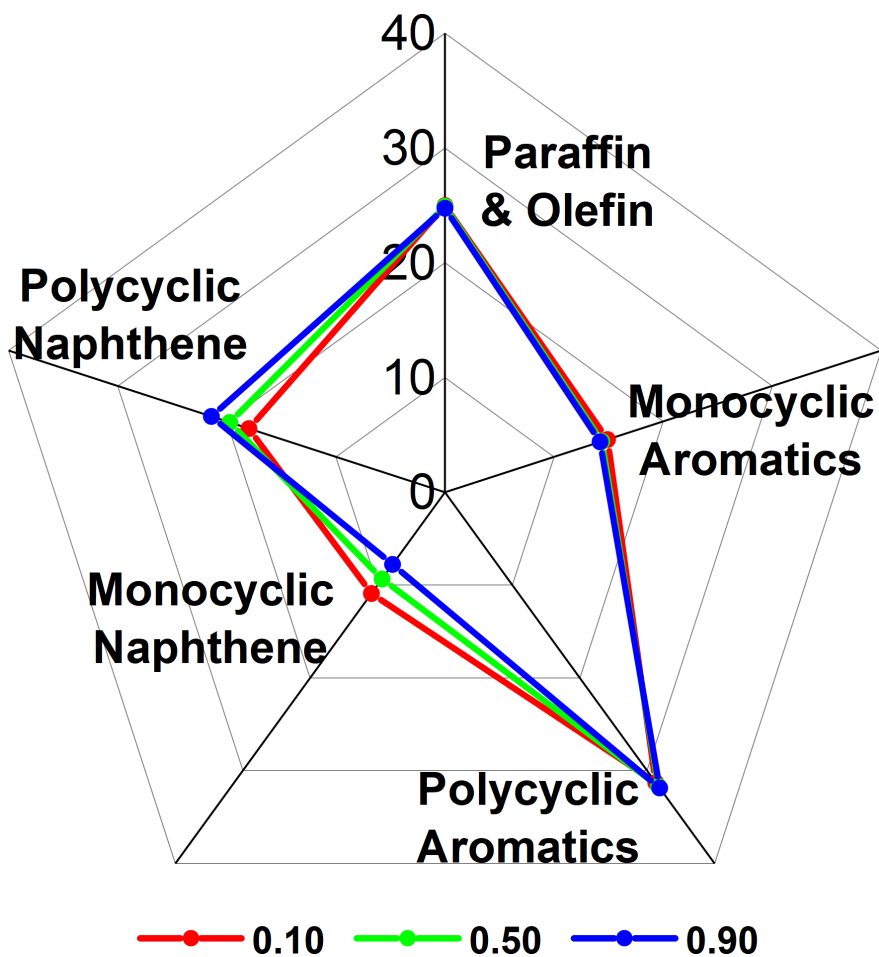
FIGURE 10 Influences of recycle ratio on group composition of gas oil

The polycyclic aromatics content in coking gas oil was the highest as shown in Figure 10. So we take the molecules with Carbon Number=40 and DBE=12 in gas oil as examples to illustrate the molecule reaction path. According to the molecular composition matrix of feed oil, four typical molecular structures shown in Figure 11 are represented by Carbon Number=40 and DBE=12. The structural vectors are shown in Table 10.
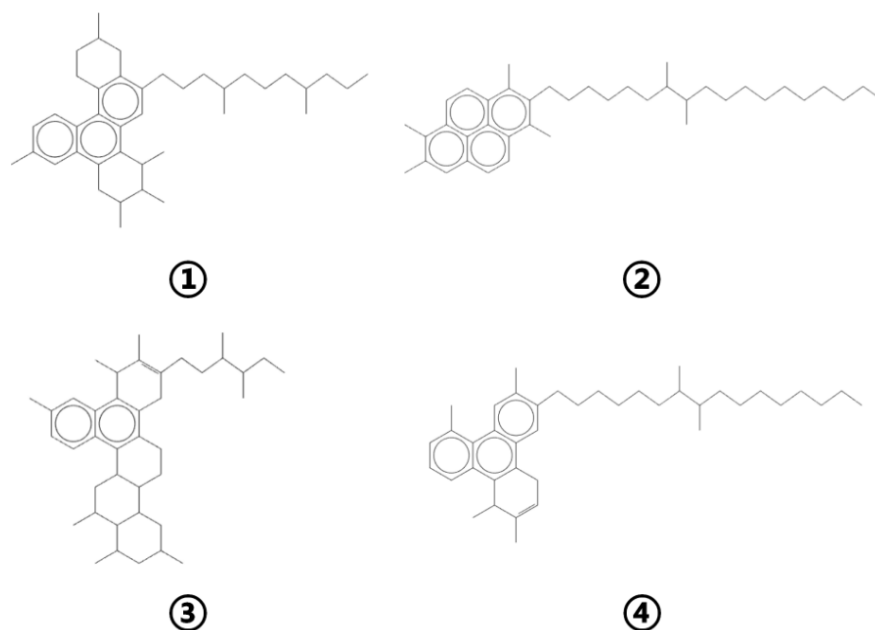
FIGURE 11 Four molecular structures represented by Carbon Number=40 and DBE=12

TABLE 10 Structural vectors of the four molecules represented by Carbon Number=40 and DBE=12

Reactant molecule	A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN
1	1	2	0	0	0	2	0	0	0	18	2	5	0	0	0	0	0
2	1	2	1	0	0	0	0	0	0	24	2	4	0	0	0	0	0
3	1	1	0	0	0	4	0	0	0	14	2	6	-1	0	0	0	0
4	1	2	0	0	0	1	0	0	0	22	2	4	-1	0	0	0	0

According to the free radical chain reaction mechanism, polycyclic aromatics with long side chains mainly undergo side chain breaking, dehydrogenation-olefination, dehydrogenation-aromatization and ring opening reactions in the delayed coking system. The reaction paths of the reactant molecules with Carbon Number=40 and DBE=12 predicted by the model are shown in Figure 12.
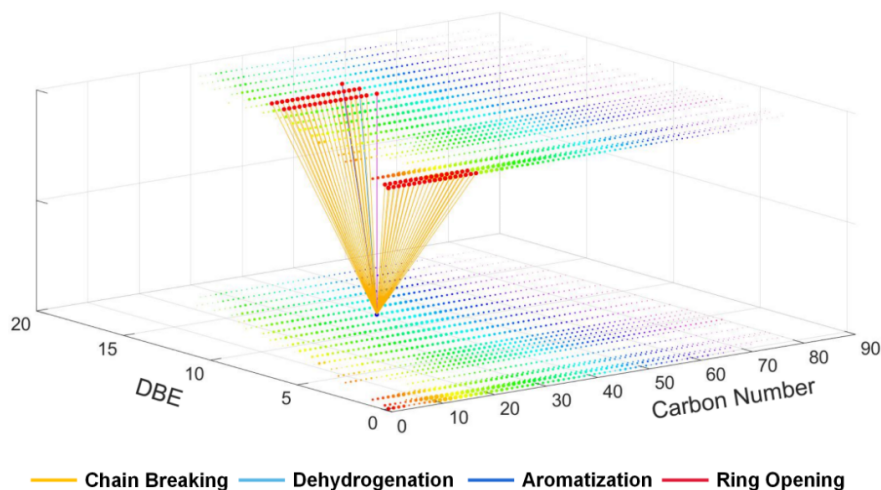
18

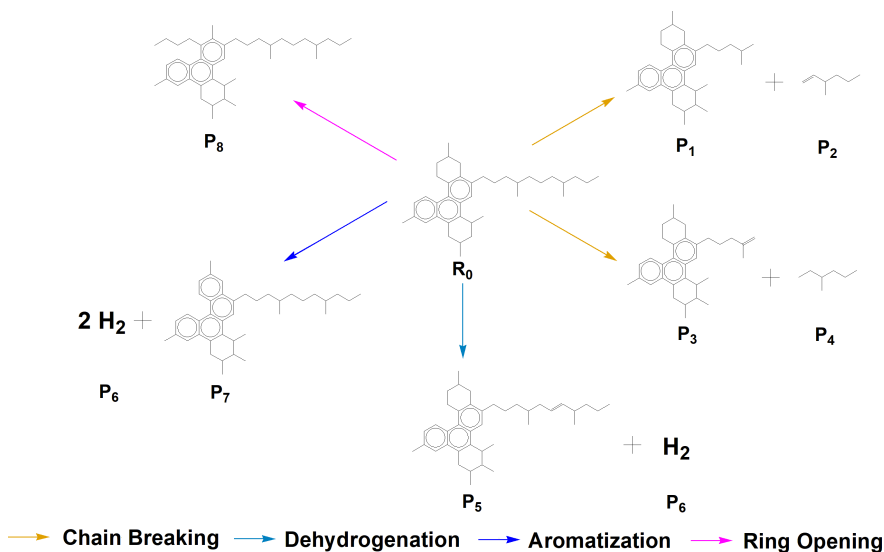**FIGURE 12** Reaction paths of the molecules with Carbon Number=40, DBE=12

FIGURE 13 Reaction network of reactant 1

Figure 13 shows the reaction network of reactant 1 formed by the SOL model. Four molecules with different structures carry out 111 reactions in total, and produce 139 product molecules. The structural vectors of product molecules are shown in Table 11 (Details in Table S8).

TABLE 11 Structural vectors of product molecules

Product molecule	A6	A4	A2	N6	N5	N4	N3	N2	N1	R	br	me	IH	AA	NS	RS	AN
1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0
2	0	0	0	0	0	0	0	0	0	1	0	0	1	0	0	0	0
3	0	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	2	0	0	1	0	0	0	0
5	0	0	0	0	0	0	0	0	0	3	0	0	0	0	0	0	0

19

...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
135	1	2	0	0	0	3	0	0	0	14	2	6	-1	0	0	0	0
136	1	3	0	0	0	0	0	0	0	22	2	4	-1	0	0	0	0
137	1	2	0	0	0	1	0	0	0	22	2	5	-1	0	0	0	0
138	1	1	0	0	0	3	0	0	0	18	2	6	-2	0	0	0	0
139	1	2	0	0	0	0	0	0	0	26	2	4	-2	0	0	0	0

As shown in Table 11 and Figure 12, the chain breaking reactions dominate in the reaction network of the reactant molecules with Carbon Number=40 and DBE=12. About 75% molecules in gas oil are cyclic hydrocarbons with side chains and can undergo chain breaking reactions to produce short chain paraffin and olefin, as well as naphthene and aromatics.

5 CONCLUSIONS

The delayed coking reaction kinetic model established based on the free radical chain reaction mechanism and SOL method showed good reliability on molecular distribution of coking product. The model could track the reaction path of any specific molecule in the complex thermal cracking reaction network. 173 structure vectors in gasoline and 1,132 structure vectors in diesel were obtained by the calculation of the SOL molecular-level model. And these gasoline and diesel structural vectors were classified into isoparaffins, normal paraffins, olefins, naphthenes and aromatics according to the discriminant rules. The influences of operation conditions such as recycle ratio on the product distribution could be discovered through the calculation of the molecular-level model, which is helpful for the process optimization and precise regulation of product composition for the delayed coking plants.

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