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Original Paper

Diesel molecular composition and blending modeling based on SU-BEM framework

Yue-Ming Guan [a, b, 1], Dong Guan [a, 1], Cheng Zhang [b], Sheng-Hua Yuan [b], Guang-Qing Cai [a], Lin-Zhou Zhang [a, *]

[a] State Key Laboratory of Heavy Oil Processing, Petroleum Molecular Engineering Center (PMEC), China University of Petroleum, Beijing, 102249, China
[b] SINOPEC Dalian Research Institute of Petroleum and Petrochemicals, SINOPEC, Dalian, 116045, Liaoning, China

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ABSTRACT

Diesel molecular compositional model has important application for diesel quality prediction, blending, and molecular-level process model development. In this paper, different types of diesel molecular compositional and blending models were constructed based on the SU-BEM framework. More than 1500 representative molecules were selected to form the molecular structure library. The probability density functions (PDFs) combination was determined by experimental data and experience. A quadratic optimization strategy combining genetic algorithm with local optimization algorithm was adopted to improve the accuracy of the compositional model. The model results show good agreement with the experimental data. The diesel blending model was constructed at the molecular-level based on the above diesel compositional models. The properties of the blending model accord with the experimental regulations. It is proved that the compositional models and blending model constructed have high accuracy and strong prediction capability, and are applicable to the industrial process.

1. Introduction

Diesel is an important petroleum product, which can be used as fuel and the feedstock of high-value chemical products. The molecular composition of diesel is the decisive factor for its quality and further processing scheme (Liu et al., 2011). An accurate diesel compositional model is important for industrial design and production. The molecular composition of diesel can be obtained by molecular-level characterization methods roughly, such as gas chromatography-mass spectrometry (GC-MS). In addition, the carbon number distribution can be obtained by gas chromatography-flame ionization detector (GC-FID) (Beens et al., 2000; Qian et al., 2002). In recent years, the development of two-dimensional gas chromatography (GC × GC) makes it possible to obtain the molecular information of diesel, but it's costly (Alvarez-Majmutov et al. 2014, 2015). Since the low cost, high efficiency, and accuracy, the molecular composition reconstruction method is adopted widely to construct diesel molecular compositional models using the existing analytical equipment in the laboratory or refinery (Neurock et al. 1990, 1993; Broadbelt et al. 1994a, 1994b).

The commonly used characterization methods of diesel in the industry include ASTM D86 distillation, GC-MS, element analysis (Zhang et al., 2014a). Each analytical method gives limited information on diesel composition. The molecular composition reconstruction method can integrate all of the information to build a reasonable molecular compositional model. Since the 1990s, researchers have gradually developed the molecular composition reconstruction method of petroleum fractions, different methods were developed. Quann and Jaffe (Quann and Jaffe, 1992; R.J.Quann and Jaffe, 1996) proposed the structure-oriented lumping (SOL) method to simplify a large number of molecular structures of petroleum molecules. The splicing of limited molecular structure fragments is used to express petroleum molecules. Combined with the group contribution method, the properties of feedstocks or products were successfully predicted. Using this method, Jaffe et al., (2005) developed a compositional model of residue. Tian and Liu et al. (Tian et al. 2010, 2012a, 2012b; Liu et al., 2017) constructed the molecular compositional models of petroleum fractions. At the same time, Klein's research group devoted to developing a more

* Corresponding author.
E-mail address: lzz@cup.edu.cn (L.-Z. Zhang).
[1] The first two authors contribute equally to this work.

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detailed molecular compositional model, using the bond-electron matrix (BEM). The probability density function (PDF) was used to constrain molecular distributions, greatly reducing the number of variables to be solved (Neurock et al., 1990; Petti et al., 1994; Campbell and Klein, 1997). On this basis, Zhang et al., (2014a) constructed the compositional model of residue. Hudebine et al. (Hudebine and Verstraet, 2004; Hudebine et al., 2009) developed the maximum information entropy method to construct the molecular compositional model of petroleum fractions. Besides, Peng et al. (Peng, 1999) developed the molecular type homologous series (MTHS) matrix method. Aye et al. (Aye and Zhang, 2005) used this method to construct petroleum molecular compositional models. Our group proposed the structural unit and bond-electron matrix (SU-BEM) method and established the compositional models of petroleum fractions (Feng et al., 2019; Chen et al. 2019, 2020).

The fuel oil blending model is an important application of the petroleum fraction compositional model. The molecular blending model of diesel can be constructed by mixing the compositional models. In the past, a lot of modeling work focused on gasoline blending, because of the complexity of the gasoline blending process (Jia and Ierapetritou, 2003; Moro and Pinto, 2004; Cerdá et al., 2016). Diesel blending is relatively easy, and it is often based on experience (Devarajan et al., 2020). The establishment of a diesel blending model helps to improve the blending efficiency and accuracy and enhance the income. In the past, diesel blending models were developed mostly based on a virtual component or lumped models (Neiro et al., 2014). However, the molecular-level compositional model is more suitable for the actual production process.

In this paper, based on the SU-BEM framework, we constructed molecular composition models of different types of diesel using conventional characterization data. And developed a molecular-level diesel blending method to complete the diesel blending model with the objective of cost minimization. The established diesel compositional model provides basic input data for the development of subsequent process models and is expected to be applied to engineering design and the actual industrial production process.

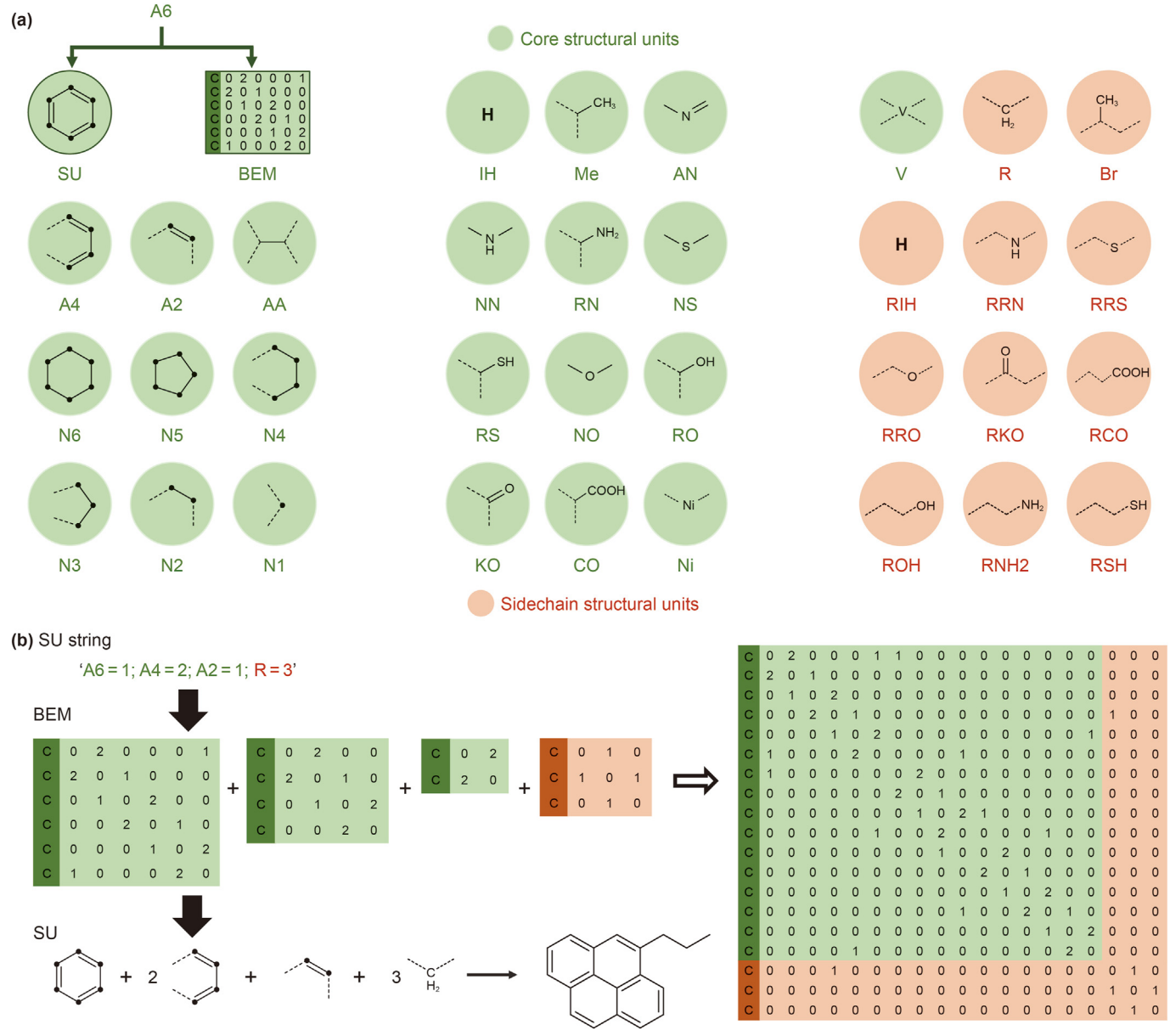

Fig. 1. The SU-BEM framework. **(a)** Chemical structure of structural units. **(b)** Examples of molecule construction by assembling the structural units.

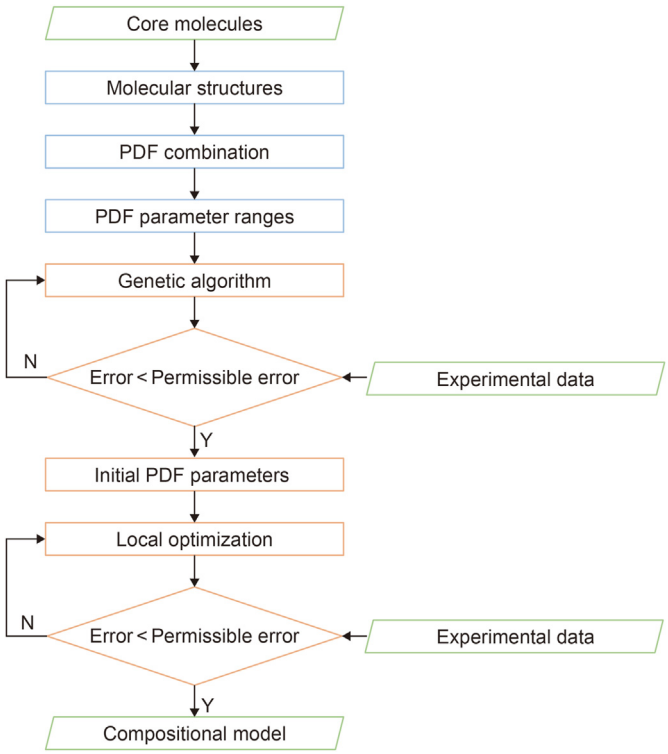

Fig. 2. Overall modeling framework.

2. Modeling

2.1. SU-BEM framework

The SU-BEM framework is a multi-scale digital representation method for petroleum molecules. The structure unit (SU) and the BEM method are combined to contain multi-scale information, such as molecular, functional group, and atomic topology information (Chen et al. 2019, 2020; Feng et al., 2019). The concept of SU is derived from the SOL method, and the specific structure units are shown in Fig. 1 (a). A total of 34 SUs was defined, including 23 core SUs used to form the ring core of petroleum molecule and its related heteroatom structure, and 11 sidechains SUs used to express the sidechain structure. According to the specific needs, the number of SU can be further increased. Fig. 1 (b) lists the typical molecular expression, in which "A6 = 1; A4 = 2; A2 = 1; R = 3;" represents that the molecule is composed of 1 A6 unit, 2 A4 units, 1 A2 unit, and 3 R units. In the SU-BEM framework, the defined SUs will be automatically converted into BEM for the development of underlying storage and subsequent process units. This method provides a basic molecular-level digital expression method for the petroleum molecule.

2.2. Compositional model construction

The molecular compositional model of petroleum includes the information of molecular structure, molecular fraction, single molecular properties, and bulk properties, in which the molecular structure and molecular fraction are the basis. The previous work showed that the method of preset molecular structure library and optimizing molecular fractions has high accuracy. The molecular fraction is calculated by PDF, so the actual optimization variables are PDF parameters. Because of the complexity of the model, a global optimization algorithm, such as the genetic algorithm, is often used. To further improve the accuracy of the solution, we adopted the quadratic optimization strategy. Firstly, the genetic algorithm is used to obtain the initial optimal solution, and the solution is then used as the initial value for the local optimization algorithm to obtain a more accurate solution. The overall modeling framework is shown in Fig. 2.

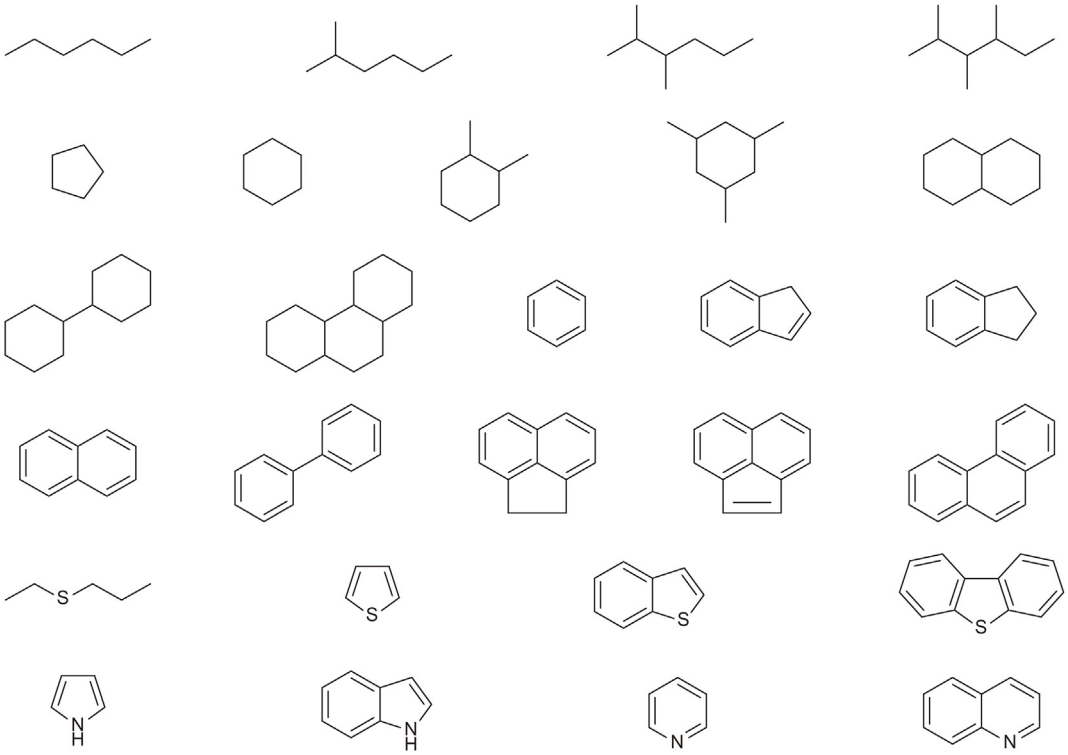

Fig. 3. Typical core molecules.

Table 1
Summary of core molecules.

Molecule type	Number of molecule cores	Aromatic ring number	Naphthene ring number
Paraffins	4	0	0
Naphthenes	30	0	1–3
Aromatics	52	1–3	1–2
Sulfur-containing species	11	0–2	0–3
Nitrogen-containing species	10	0–2	1–2
Total	107		

2.2.1. Core molecules

Determine the core molecular structures is the first step of molecular compositional modeling. Based on the method of preset molecular structure library, the selection of core molecules affects the accuracy of the model directly. In this paper, the previous molecular characterization results and conclusions were used to determine the core molecules (Zhang et al. 2012, 2013, 2014b), including paraffins, aromatics, naphthenes, sulfur-containing species, and nitrogen-containing species. The structures of typical core molecules are shown in Fig. 3, and the statistical information is shown in Table 1.

After the core molecules were determined, the molecular structure library was identified by expanding the sidechain length of the core molecules. According to the general distillation range of diesel, the boiling point range of 300–720 K, and the carbon number range of C_5–C_{27} were used as constraints for homolog series extension. Thus, the final molecule number of the diesel molecular structure library is 1591. For detailed information of the molecular compositional model, see the supporting information。

2.2.2. PDF sets

Based on the petroleum continuum theory, it is reasonable to use an appropriate PDF combination to constrain the molecular distribution of petroleum fractions. The PDF used in this paper are gamma PDF and histogram PDF, as shown in Eqs. (1) and (2).

$$f(\boldsymbol{x}) = \frac{(\boldsymbol{x}-\gamma)^{\alpha-1}\mathrm{e}^{-(\boldsymbol{x}-\gamma)/\beta}}{\Gamma(\alpha)\beta^{\alpha}} \tag{1}$$

$$f(\boldsymbol{x}) = X_i \tag{2}$$

The gamma PDF has three adjustable parameters: α、β、γ. In the histogram function, X_i is the value of each property, and the number of parameters is i (Zhang et al., 2014a; Feng et al., 2019).

To ensure the accuracy of the distillation curve of the compositional model, gamma PDF was used to constrain the boiling point distribution of all molecules in the first. On this basis, all molecules were divided into paraffins, naphthenes, and aromatics by histogram PDF, and then the distribution of carbon number, sidechain number, naphthene ring number, aromatic ring number, and heteroatom number were constrained to ensure the accuracy of molecular composition and element weight fraction predicted value. The specific PDF combination is shown in Fig. 4, with 34 parameters to be optimized.

2.2.3. Optimization

After the molecular structure library is determined, the PDF parameters need to be optimized to obtain the molecular fractions. The quadratic optimization strategy was used to minimize the error between the predicted value and the experimental data. The objective function is shown in equation (3).

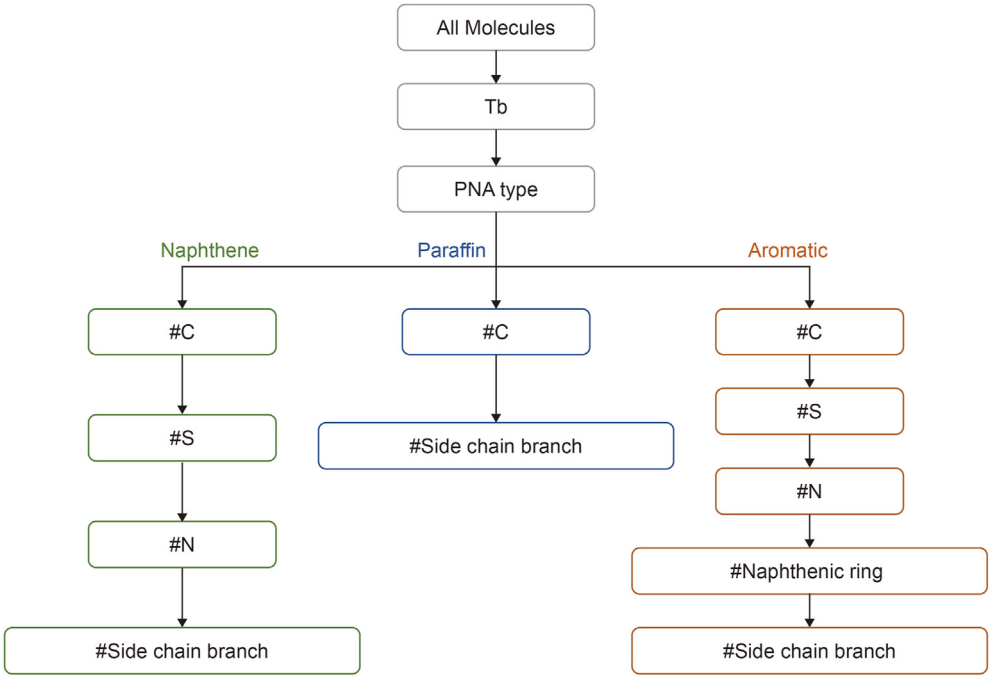

Fig. 4. PDF combination.

Table 2
Experimental and predicted bulk properties of straight-run diesel.

Measurement name	Analytical data	Calculated value
20 °C Density, g/cm^3	0.8262	0.8224
Carbon, wt%	85.9035	85.5613
Hydrogen, wt%	13.1880	13.5271
Sulfur, wt%	0.9060	0.9060
Nitrogen, wt%	0.0024	0.0064
P, wt%	0.512	0.509
1N, wt%	0.144	0.140
2N, wt%	0.062	0.056
3N, wt%	0.008	0.005
1A, wt%	0.197	0.193
2A, wt%	0.072	0.065
3A, wt%	0.005	0.001
Freezing point, K	241.15	270.69
Aniline point, K	340.65	351.16

Table 3
Experimental and predicted bulk properties of hydrogenated diesel.

Measurement name	Analytical data	Calculated value
20 °C Density, g/cm^3	0.8193	0.8145
Sulfur, wt%	0.0003	0.0003
P, wt%	0.517	0.516
1N, wt%	0.272	0.269
2N, wt%	0.126	0.127
3N, wt%	0.031	0.016
1A, wt%	0.047	0.047
2A, wt%	0.006	0.002
3A, wt%	0.001	0.000001
Freezing point, K	249.15	279.25
Pour point, K	252.15	253.77
Refractive index, 20 °C	1.45	1.46

$$obj = \sum \delta \left| y_{\exp} - y_{\text{pred}} \right| \tag{3}$$

Where, y_{exp} is the experimental data, y_{pred} is the predicted value and δ is the weight factor. The weight factor values are related to the reliability of the experimental data. The more accurate the experimental data is, the larger the value of δ will be set. And affecting the optimization direction of the optimal solution. In this paper, the genetic algorithm (GA) was used to find the feasible solution with a small error, which was used as the initial value for a local optimization to find the final solution. The GA doesn't need the initial value, only needs to give the feasible range of the parameters. Therefore, the genetic algorithm can search for the feasible solution with a relatively small error in the feasible region. On this basis, the local optimization algorithm can further search the local optimal solution with higher accuracy. The local optimization algorithm used in this paper is sequential quadratic programming (SQP). SQP is suitable to solve nonlinear optimization problems, by transforming the original problem into a series of quadratic programming subproblems.

2.3. Molecular blending modeling of diesel

The molecular diesel blending model is useful to improve the blending accuracy and feedstock applicability. The goal of the blending is to maximize revenue or minimize cost. Constraints are divided into quality constraints such as sulfur elemental fraction, supply constraints, and output constraints. Because of the nonlinear characteristics of most of the diesel properties, the diesel blending process is a typical nonlinear optimization problem.

This paper takes cost minimization as the objective function, as shown in equation (4).

$$obj = \sum P_i m_i \tag{4}$$

Among them, P_i is the price of diesel i, m_i is the blending quantity of diesel i. The constraint equations are shown in equations (5)–(7).

$$j_{ki} m_i \le J_k \tag{5}$$

$$0 \le m_i \le Q_i \tag{6}$$

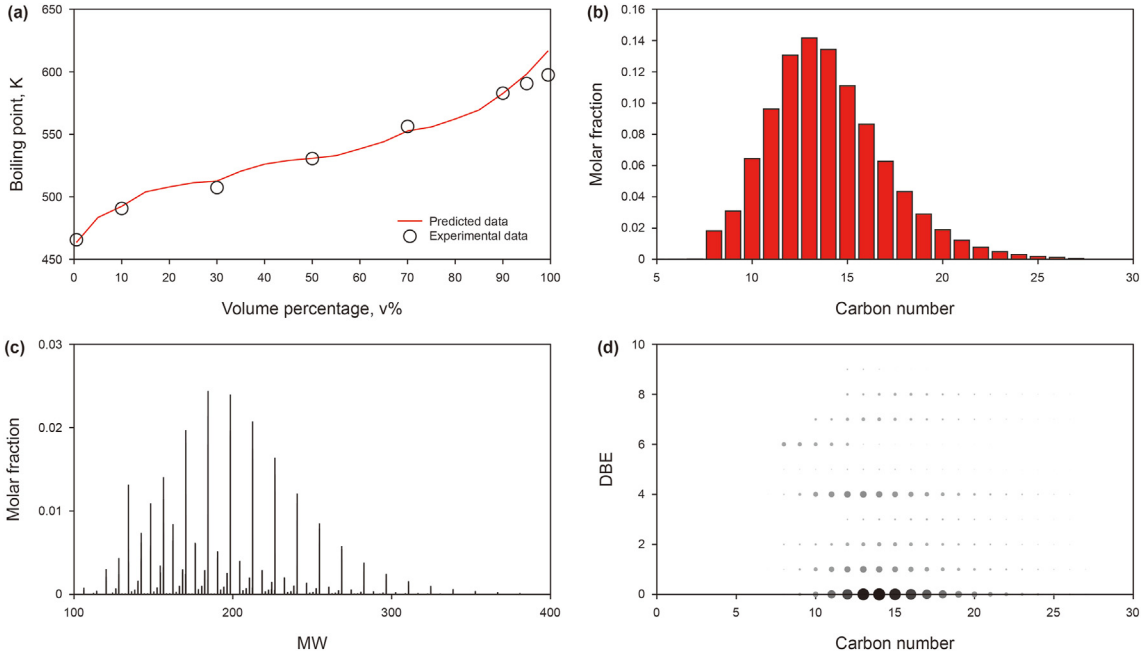

Fig. 5. Boiling point (**a**), carbon number (**b**), and molecular weight (**c**) distributions of the compositional model for straight-run diesel. DBE vs carbon number distribution of compositional model (**d**).

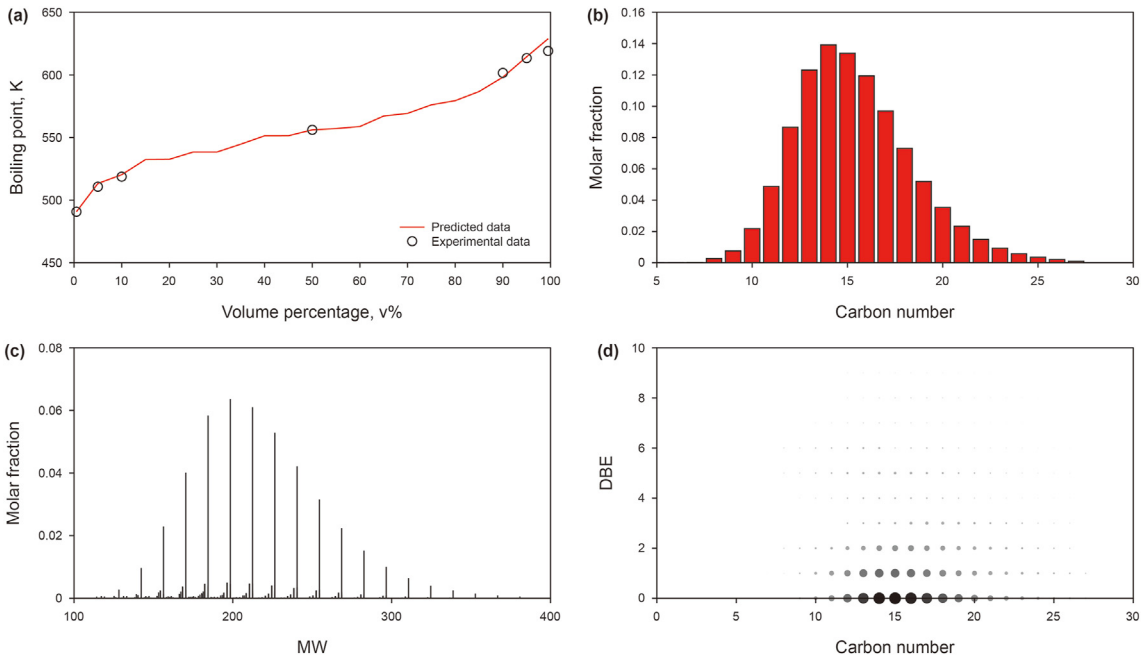

Fig. 6. Boiling point **(a)**, carbon number **(b)**, and molecular weight **(c)** distributions of the compositional model for hydrogenated diesel. DBE vs carbon number distribution of compositional model **(d)**.

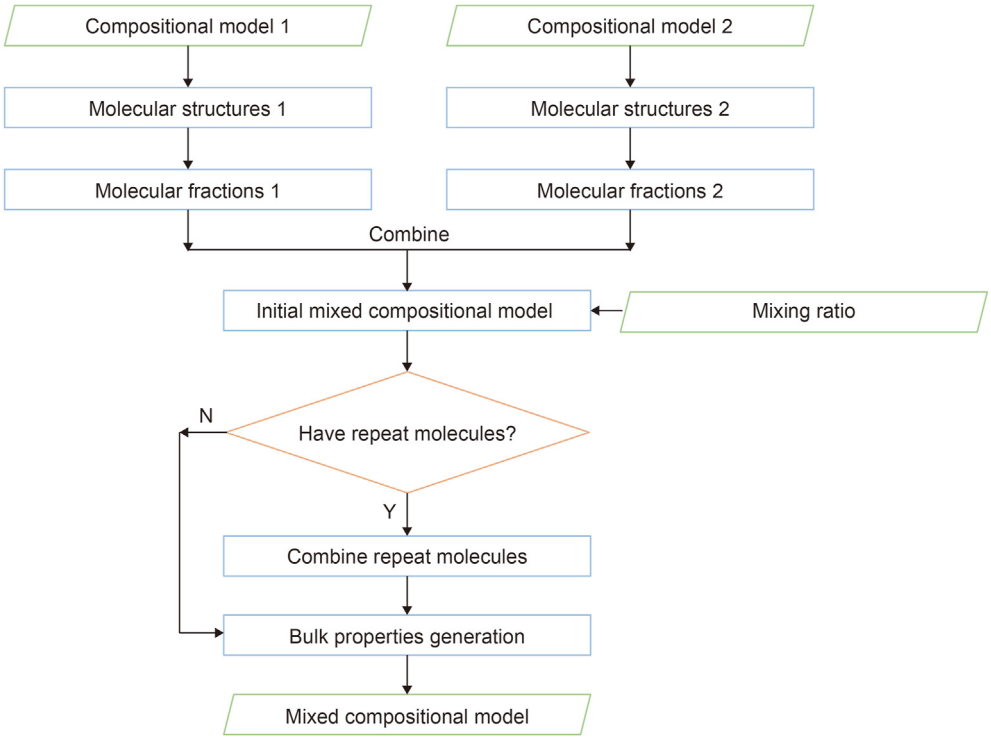

Fig. 7. Modeling framework of molecular diesel mixing model.

$$C = C_{need} \tag{7}$$

Where, C is the property of blended diesel products, C_{need} is the required property of product blended diesel. SQP algorithm is used in the optimization process.

3. Results and discussion

We selected different kinds of diesel analysis data to build a diesel compositional model and discusses the accuracy of the models. On this basis, the diesel blending model is constructed to test the predicted ability and application potential of the model.

Table 4
Experimental and predicted bulk properties of pure diesels.

Measurement name	Calculated value	Constraint index
20 °C Density, g/cm^3	0.8162	
Sulfur, wt%	0.2000	≤0.2
P, wt%	0.516	
1N, wt%	0.244	
2N, wt%	0.112	
3N, wt%	0.026	
1A, wt%	0.080	
2A, wt%	0.021	
3A, wt%	0.002	
Cetane number	54.4	≥50

3.1. Compositional model of straight-run diesel

According to the above modeling framework, the compositional model of straight-run diesel is constructed, the results are shown in Table 2. From the comparison between the predicted value and the analytical data, the overall error is small. Thus, the model has high predicted accuracy in density, element fraction, and molecular composition. Because of the difficulty of prediction of freezing point and aniline point, the predicted value of the model has some deviation. From the data of GC-MS analysis, the saturated hydrocarbon content of straight-run diesel, and the S, N elemental fraction is high. The predicted values also agree well with this regulation.

The comparison of distillation curves is shown in Fig. 5(a), and the predicted values of the model are in good agreement with the experimental data. Fig. 5(b)(c) (d) shows the carbon number distribution, molecular weight distribution and DBE vs carbon number distribution of the model, the distributions are reasonable. Therefore, the typical straight-run diesel compositional model constructed in this paper is in good agreement with the experimental data and reasonable.

3.2. Compositional model of hydrogenated diesel

Based on the straight-run diesel compositional model, the hydrogenated diesel compositional model is further established, and the results are shown in Table 3. The model results show good agreement with the experimental data. Similarly, there is a certain deviation of the freezing point. Compared with straight-run diesel, the content of aromatics and S, N elemental fraction of hydrogenated diesel is low.

The comparison of distillation curves is shown in Fig. 6(a), and the predicted values of the model are in good agreement with the experimental data. Fig. 6 (b)(c)(d) shows the carbon number distribution, molecular weight distribution, and DBE vs carbon number distribution of the hydrogenated diesel compositional model, which conforms to the experimental regulation. The compositional model of typical hydrogenated diesel constructed in this paper is in good agreement with the experimental results, and the molecular distribution is reasonable.

3.3. Molecular blending model

Based on the above straight-run diesel and hydrogenated diesel, the optimal blending ratio of diesel can be identified by minimizing the cost. The basis of the molecular-level blending model is the diesel mixing model, as shown in Fig. 7. Given the diesel proportion, the molecular compositional model should be combined according to the mixing proportion for the first time. After that, the same molecule should be combined. Finally, the bulk properties should be calculated according to the molecular fractions and single-molecule properties after mixing. On this basis, the proportion of different types of diesel is optimized to achieve the goal of cost minimization.

Assuming that the cost of straight-run and hydrogenated diesel is 3000 yuan/ton and 7000 yuan/ton, the output of straight-run and hydrogenated diesel are 2500 kg/h and 2000 kg/h, the demand for blended diesel is 2500 kg/h, the cetane number of the blended diesel is not less than 50, and the sulfur elemental fraction is no more than 0.2 wt%, the proportion of different types of diesel is optimized. The final blending ratio is straight-run diesel: hydrogenated diesel = 551:1949. The properties of blended diesel are shown in Table 4. The distillation curve and carbon number distribution of blended diesel and pure types of diesel are shown in Fig. 8. The carbon number distribution and distillation curve of blended diesel are between the pure types of diesel, which proves that the diesel blending model and compositional model in this paper have strong prediction ability. It can be seen that the production cost of straight-run diesel is low, but the sulfur elemental fraction is relatively high, and the cetane number is relatively low. Therefore, to meet the quality requirements, hydrogenated diesel accounts for a large proportion of blended diesel.

With the decrease of elemental fraction, the blending proportion of straight-run diesel will increase, and the blending amount of straight-run diesel will reach a peak value due to cetane number restriction, as shown in Fig. 9.

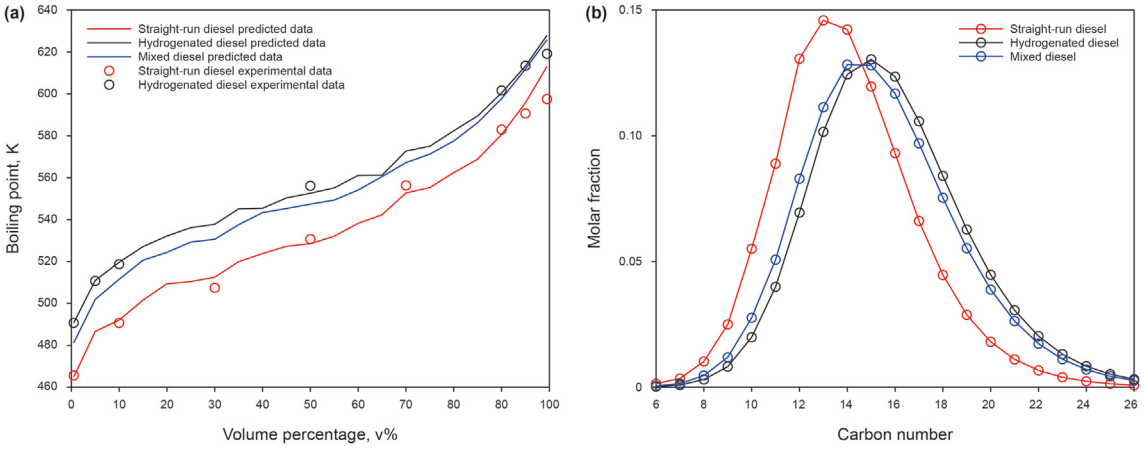

Fig. 8. Boiling point **(a)**, and carbon number **(b)** of the compositional model and experimental for pure types of diesels and blended diesel.

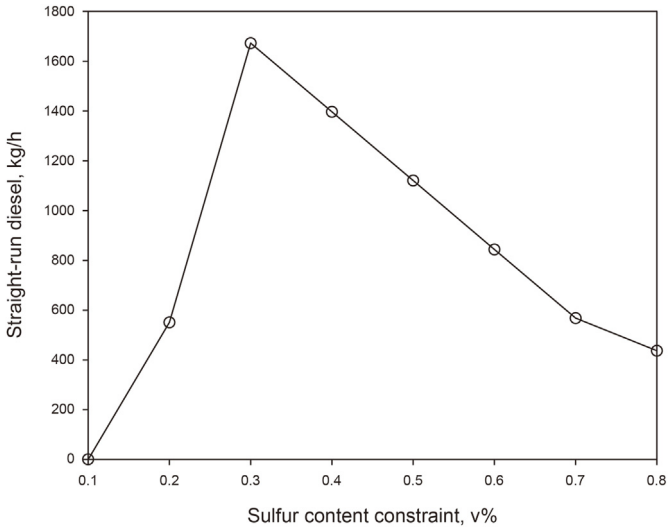

Fig. 9. The curve of straight-run diesel blending ratio with sulfur content constraint.

In summary, the diesel compositional model constructed in this paper has high accuracy and good prediction capability, which provides reliable basic input data for the development of subsequent process models, and is expected to be applied to industrial design and actual diesel blending process.

4. Conclusion

In this paper, based on the SU-BEM framework, a diesel molecular compositional model with 1591 representative molecules was constructed by using conventional diesel analysis data, and a diesel molecular-level blending model was developed. The predicted values of straight-run diesel and hydrogenated diesel are in good agreement with the experimental data. On this basis, the prediction of blended diesel properties is in line with the expectation. The above results show that the diesel molecular compositional and blending model constructed in this paper has high accuracy and prediction capability, and has high application value.

Acknowledgments

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