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Statistical Reaction Analysis of Residue Desulfurization Based on Molecular Structures

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Heavy oils contain many kinds of organic compounds which have complex structures. Thus, it is difficult to determine these characteristics to develop suitable catalysts. Recently, due to the development of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), the detailed composition data of heavy oils can be obtained. In this research, the authors proposed a new method to analyse chemical reactions using the input/output composition data from FT-ICR-MS. In this method, representative chemical reactions were defined and assumed the series of reactions linearly. As a result, the conversion ratios of each chemical reaction can be simply obtained and statistically compared by molecular structures. The authors applied this method to a residue desulfurization in a petroleum refinery as a case study and compared the reaction ratios by molecular structures. From this analysis, the authors found that the molecular structure significantly affects the conversion ratio in desulfurization reaction and captured the characteristics of this reaction. Therefore, this analysis might be promising to analyse reactions for providing insights into catalysts and process design.

1. Introduction

The word 'petroleomics' was named by Marshall and Rogers (2004) and the precise analysing method of molecular elemental composition for petroleomics was developed by Marshall and Rogers (2008). In this concept, molecular structures contained in crude oils are compositionally analysed by using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) like genomics and proteomics (Rogers and Marshall, 2010). From this analysed data, researchers have managed to capture the detail components information of petroleum (Nagy et al., 2019) and the chemical and physical characteristics of compounds (Vanini et al., 2020). In the concept of petroleomics, new processes for petroleum refineries or petroleum chemical plants, or petroleum products might be designed according to the oil characteristics (Lozano et al., 2020). In fact, most of the molecular structures in crude oils can be analysed by FT-ICR-MS, and many researchers have started to develop reaction models based on these analysed molecular structures for understanding heavy oils' characteristics such as asphaltene which is insoluble in alkanes but soluble in aromatic solvents (Ancheyta et al., 2009) and organic compounds contained sulphur (Mitra-Kirtley and Mullins, 2010), for catalyst designs (Klein et al., 2006), for process designs and simulations for heavy oils upgrading (Ancheyta, 2013), and for catalytic reactors (Ancheyta, 2011) in refineries.
In petroleum refineries, all products must be hydroprocessed to reduce the boiling range of the feedstock or to remove impurities such as metals, sulphur, nitrogen, and high carbon-forming compounds. These processes are called residue refining, atmospheric distillation residue desulfurization (ARDS), vacuum distillation residue desulfurization (VRDS), and hydrogen desulfurization (HDS) (Gary et al., 2007). Japan Petroleum Energy Center (JPEC) has developed a new refining technology based on petroleomics for investigating reaction kinetics and mechanisms of ARDS and residue fluid catalytic cracking operations (Katano et al. 2020). In this investigation, the distributions of molecular structures in feed and product mixture of atmospheric distillation residue were initially illustrated and categorized using double bond equivalent values (DBE) and carbon numbers in components. From these data, molecular structures and reaction networks were then rebuilt and

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analysed. According to this investigation, more than 25 million molecules were needed to register into a database considering all molecules as petroleum informatics. Furthermore, it is too complex to analyse the overall reactions based on molecular structures even with many assumptions because there are too many reaction paths in ARDS and it is necessary to install all reaction kinetics information to them.
Therefore, the authors developed the simple stochastic reaction analysis method using petroleomics as a first step to capture reaction characteristics and to develop reaction mechanisms in ARDS in this research.

2. Assumptions

To analyze the reactions in the process, the authors made the assumptions for simplifying molecular data and reactions.

2.1 Component category based on molecular structures

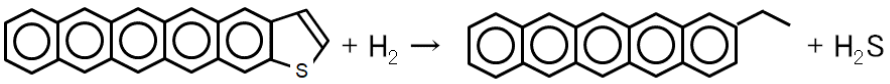
JPEC has created a molecular database and developed a new chemical structure description named Juxtaposed Attributes for Chemical-structure Description (JACD). In this JACD, core structure (3,623 types), side chain, and bridge chain information are described with their compositions in the oil to represent the molecular structure (Nakamura, 2017).
To reduce the number of structures for making the database simpler, the authors re-categorized molecular structure description with the following assumptions:

1. All components consist of carbon, hydrogen, sulphur, and nitrogen which represent 97.5 % of feed components.
2. A core contains only four types of ring structures including benzene, naphthene (cycloalkane), thiophene, and pyridine.
3. When a component contains sulphur, this molecular has a thiophene ring structure. When a component contains nitrogen, this molecular has a pyridine ring structure.
4. The maximum core number is two, so the component can be single core or double core followed by JACD.
5. The maximum number of naphthene rings in each core is three. When a component has more than four naphthene rings, it is assumed to have three naphthene rings.
6. The maximum number of thiophene rings in each component is two which represent 99.9 % of feed components. When a component has more than three sulphur atoms, it is assumed to have two thiophene rings.
7. The maximum number of pyridine rings in each component is one which represent 99.6 % of feed components. When a component has more than two nitrogen atoms, it is assumed to have a pyridine ring.
8. The maximum total number of benzene rings and naphthene rings is five for each core. When a core contains more than six rings (benzene + naphthene), it is assumed to have five benzene rings.
9. All rings connect straight lines.

By following the assumptions above, the authors re-categorized the components of feed/product streams of ARDS from the molecular structure data sets represented by JACD.

2.2 Reactions in ARDS

To analyze the chemical reactions in ARDS. The following three main reactions (desulfurization, denitrification, and hydrogenation) are considered. To explain the reactions, the core consisted of five benzene rings are used as examples in the following equations.



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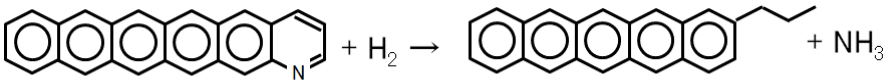

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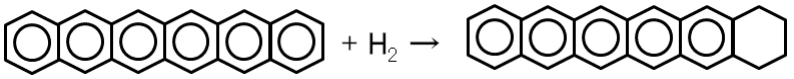
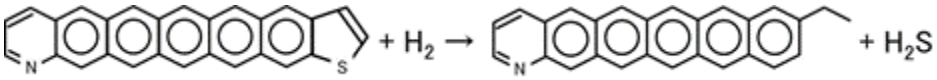


(3)

In addition, the following two additional assumptions related to the reaction procedures were set to analyze reactions from data.

10. Desulfurization and denitrification reactions occur before hydrogenation reactions.
11. Desulfurization reactions occur before denitrification reactions.

Using these two assumptions, the following series of reactions can be assumed when a component has both nitrogen and sulphur.



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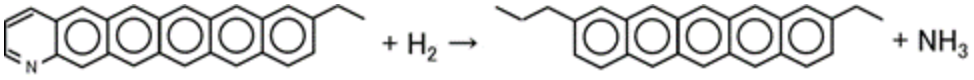

(5)

3. Design of the reaction model

The compositions of feed and product composition data sets of ARDS were expressed by vectors **x** and **y**. The vectors are coordinated by the molecular structures. ARDS is assumed to be a linear relation of the feed data as shown in Figure 1. The relation between **x** and **y** can be simply written by

$$\mathbf{y} = \mathbf{A}\mathbf{x} \tag{6}$$

where **A** represents the overall reaction matrix in ARDS.

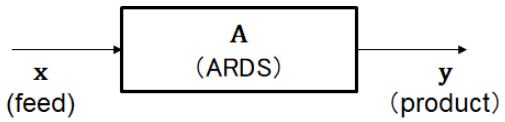

Figure 1: linear relation between feed and product data sets

Following the assumptions set in section 2.2, vectors **x** and **y** are coordinated as follows:

$$\mathbf{x} = [\mathbf{x_{CH}} \quad \mathbf{x_{S1}} \quad \mathbf{x_{S2}} \quad \mathbf{x_N} \quad \mathbf{x_{NS1}} \quad \mathbf{x_{NS2}}]^{\mathbf{T}}, \mathbf{y} = [\mathbf{y_{CH}} \quad \mathbf{y_{S1}} \quad \mathbf{y_{S2}} \quad \mathbf{y_N} \quad \mathbf{y_{NS1}} \quad \mathbf{y_{NS2}}]^{\mathbf{T}} \tag{7}$$

where vectors with subscript CH denote composition vectors that do not contain sulphur and nitrogen atoms. Subscript S1 denotes components that contain a sulphur atom, and S2 denotes components that contain two sulphur atoms. Subscript N denotes components that contain a nitrogen atom. Subscript NS1 and NS2 denote components that contain a nitrogen atom and one or two sulphur atoms respectively.
In this case, the reaction matrix can be written by the following formula:

$$\mathbf{A} = \begin{pmatrix} \mathbf{A}_{\mathrm{CH}} & \mathbf{A}_{\mathrm{CH}}(\mathbf{I}-\mathbf{A}_{\mathrm{S1}}) & \mathbf{A}_{\mathrm{CH}}(\mathbf{I}-\mathbf{A}_{\mathrm{S1}})(\mathbf{I}-\mathbf{A}_{\mathrm{S2}}) & \mathbf{A}_{\mathrm{CH}}(\mathbf{I}-\mathbf{A}_{\mathrm{N}}) \\ 0 & \mathbf{A}_{\mathrm{S1}} & \mathbf{A}_{\mathrm{S1}}(\mathbf{I}-\mathbf{A}_{\mathrm{S2}}) & 0 \\ 0 & 0 & \mathbf{A}_{\mathrm{S2}} & 0 \\ 0 & 0 & 0 & \mathbf{A}_{\mathrm{N}} \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\begin{pmatrix} \mathbf{A}_{\mathrm{CH}}(\mathbf{I}-\mathbf{A}_{\mathrm{N}})(\mathbf{I}-\mathbf{A}_{\mathrm{NS1}}) & \mathbf{A}_{\mathrm{CH}}(\mathbf{I}-\mathbf{A}_{\mathrm{N}})(\mathbf{I}-\mathbf{A}_{\mathrm{NS1}})(\mathbf{I}-\mathbf{A}_{\mathrm{NS2}}) \\ 0 & 0 \\ 0 & 0 \\ \mathbf{A}_{\mathrm{N}}(\mathbf{I}-\mathbf{A}_{\mathrm{NS1}}) & \mathbf{A}_{\mathrm{N}}(\mathbf{I}-\mathbf{A}_{\mathrm{NS1}})(\mathbf{I}-\mathbf{A}_{\mathrm{NS2}}) \\ \mathbf{A}_{\mathrm{NS1}} & \mathbf{A}_{\mathrm{NS1}}(\mathbf{I}-\mathbf{A}_{\mathrm{NS2}}) \\ 0 & \mathbf{A}_{\mathrm{NS2}} \end{pmatrix} \tag{8}$$

where $\mathbf{A_{CH}}$ represents hydrogenation, $\mathbf{A_{Si}}$ represents desulfurization, $\mathbf{A_N}$ represents denitrification, and $\mathbf{A_{NSi}}$ represents desulfurization when components have both sulphur and nitrogen atoms. The subscript *i* denotes the number of sulphur atoms.
Therefore, an appearance reaction ratio matrix **C** can be represented by the following equation.

$$\mathbf{C} = \mathbf{I} - \mathbf{A} \tag{6}$$

where **I** is the identity matrix.

4. Results of reaction analysis

By following the assumptions and reaction models described in sections 2 and 3. The reaction ratios of desulfurization and denitrification were analysed based on molecular structures.

4.1 Desulfurization reaction

The results of the reaction ratio of desulfurization reaction for components with a single core from S1 are shown in Figure 2. The x-axis of this figure shows the core structure represented by vector. The element of this vector is the number of benzene rings and the number of naphthene rings in the core. Sample 1 and sample 2 are the different types of crude oils. Considering the general characteristics of these samples, sample 2 is a heavier oil than sample 1. The reaction temperature in both cases is set at 370 °C.

Comparing these results, it is obviously understood that the lower reaction ratio of sample 2 than that of sample 1 is not caused by core structure. This is simply because sample 2 is a heavier oil.

Furthermore, the reaction ratio decreases with the increase of the total number of rings (benzene rings + naphthene rings). This phenomenon is consistent with heavier component reaction ratio decrease.

To confirm the relationship, collinearity coefficients between the reaction ratio and the total numbers of rings were checked as shown in Table 1. The collinearity coefficients are smaller than -0.85. This means that the increase in the total number of rings negatively affected the reaction ratio of desulfurization.

Looking at the same total number of rings, the reaction ratio increases with the increase of naphthene rings. In other words, two samples have the same peak at the core consisting of naphthene rings. Thus, it can be said that the reaction ratio of desulfurization depends on the molecular structures. To verify the relationship, collinearity coefficients between the reaction ratio and the increase of naphthene rings as shown in Table 2. It shows clearly that the increase of naphthene rings in the core has a positive impact on the reaction ratio of desulfurization.

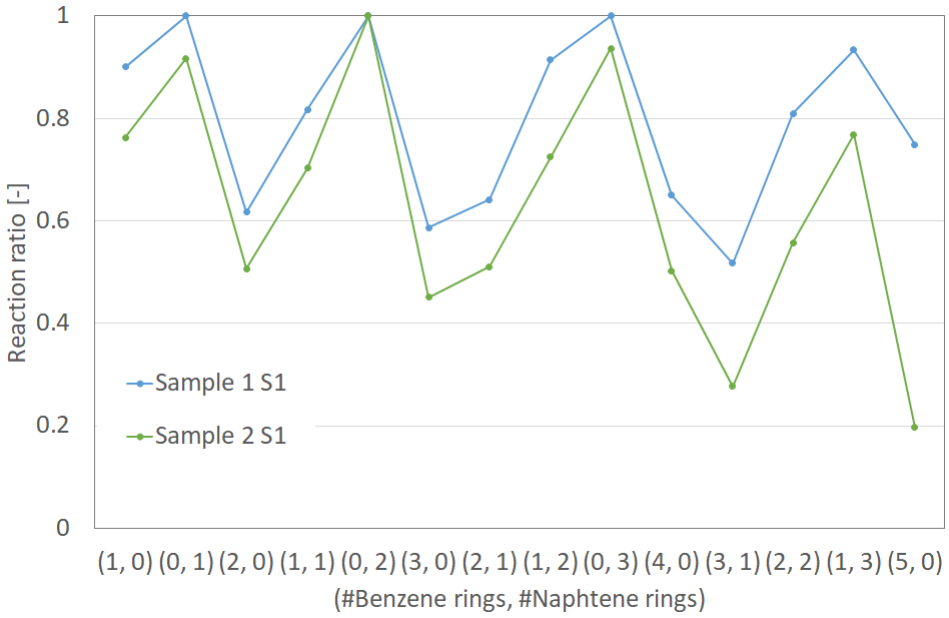

Figure 2: Relation of reaction ratio of desulfurization and molecular structures

Table 1: Average reaction ratios in each total numbers of rings

Total numbers of rings (=benzene + naphthene)	1	2	3	4	5	collinearity coefficient
Sample 1 (Ave. reaction ratio)	0.950	0.812	0.786	0.728	0.749	-0.878
Sample 2 (Ave. reaction ratio)	0.840	0.737	0.656	0.526	0.197	-0.952

Table 2: Relationship between reaction ratios and molecular structures (increase of naphthene rings)

Total numbers of rings (=benzene + naphthene)	1	2	3	4	5
Sample 1 (collinearity coefficient)	1	1.000	0.965	0.811	NA
Sample 2 (collinearity coefficient)	1	0.993	0.976	0.689	NA

4.2 Denitrification reaction

The results of the reaction ratio of the denitrification and desulfurization reaction for single core from N are shown in Figure 3. Unfortunately, the relationship between reaction ratio and molecular structures cannot be clearly observed. However, it is possible to say that the reaction ratio increases with the increase of the total number of rings (benzene rings + naphthene rings) as shown in Table 3. Furthermore, the core components might have an influence to the denitrification reaction. But at this moment, the authors did not find the previous results which show the detail reaction mechanism by the molecular structures.

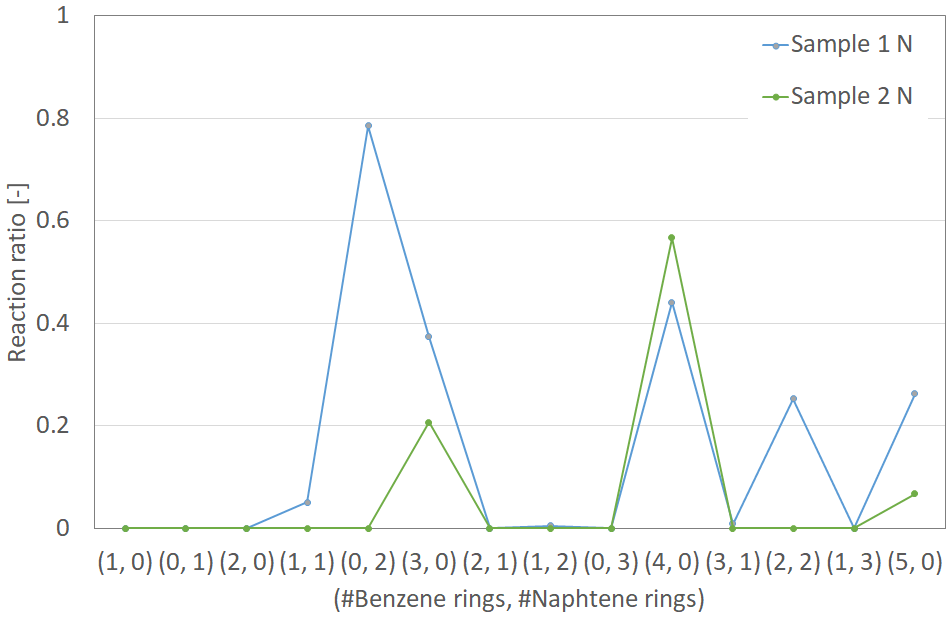

Figure 3: Relation of reaction ratio of denitrification and molecular structures

Table 3: Average reaction ratios in each total numbers of rings

Total numbers of rings (=benzene + naphthene)	1	2	3	4	5	collinearity coefficient
Sample 1 (Ave. reaction ratio)	0	0.279	0.095	0.176	0.263	0.571
Sample 2 (Ave. reaction ratio)	0	0	0.052	0.142	0.068	0.748

4.3 Discussion

Hagiwara et al. (2016) reported the detailed molecular structure-based modelling of residue desulfurization. In their research, they managed to analyse the reaction kinetics of the representative components with assumptions. Furthermore, they reported that more than 2,000 reaction paths must be considered depending on the molecular structures. Then, the product components will be estimated from their reaction model. On the other hand, the proposed method does not show the reaction kinetics based on molecular structures but statistically provides the reaction key molecular structures in the analysed ARDS. In fact, the insight that the reaction ratio of desulfurization increases with the increase of naphthene rings was firstly found by this analysis. Therefore, it has a possibility to integrate the proposed method into their modelling as an initial test. In addition,

the current results are reasonable to understand reaction characteristics and differences based on the molecular structure without complex calculations as compared with their modelling.

5. Conclusions

The detailed analysis of reaction mechanisms related to petroleum refinery is difficult and complex due to the vast number of components that exist in crude oils. Furthermore, several reactions are taking place at the same time in each process.

In this research, the simple reaction analysis method from the statistical data set based on molecular structures and petroleomics has been proposed. In this method, chemical reactions are represented by a linear model by assuming only four elemental reactions. To apply this method of analysis to ARDS, some characteristics dependant on the molecular structures are observed. These characteristics are somehow consistent with the previous results without any complex calculation and experiments. In addition, the proposed method provided the important insights to understand the reaction mechanism. With the reaction characteristics from this investigation, the detailed reaction kinetics and mechanism model will be developed as a future study. Moreover, the current simple analysis and developed model should be combined with the detailed conventional chemical reaction analysis method in ARDS after evaluating several oils data and capturing more characteristics. Therefore, the proposed method has a large possibility as an initial test to start detailed reaction mechanisms.

Acknowledgements

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