Prospect of Petroleomics as a Tool for Changing Refining Technologies

Keita Katano, Yuuki Takahashi, Koichi Sato, Koji Tsuji, Toshiaki Hayasaka, Tsutomu Nakamura, Yoshiyuki Toyooka, and Kazuhiro Inamura *

Japan Petroleum Energy Center (JPEC), 11-1 Shibakoen 2-chome, Minato-ku, Tokyo 105-0011, JAPAN

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Japan Petroleum Energy Center (JPEC) and partners have been developing “Petroleomics” as a new refining technology since 2011. Petroleomics can be a technology to achieve the ultimate method based on molecular reaction models with molecular level analyses of heavy oil. After the fundamental stage taking five years, our petroleum informatics database includes more than 25 million chemical structures of heavy oil components constructed with the aid of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). Subsequently, reaction modeling studies were applied to residue hydrodesulfurization (RDS) and the aggregation model for asphaltenes to sediments, both of which are particularly important subjects in heavy oil upgrading. Our Petroleomics project is now in the application stage to attempt three major investigations: a molecular database of crude oils including unconventional oils, total optimization of RDS and residue fluid catalytic cracking (RFCC) operations with reaction modeling, and the mechanism of asphaltene aggregation responsible for fouling and plugging in some heavy oil upgrading processes. Further progress in Petroleomics is expected to achieve practical applications in refineries, such as advanced performance diagnosis, operational optimization, and catalyst and process development.

Keywords
Petroleomics, Heavy oil, Molecular database, Reaction modeling, Asphaltene aggregation

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* To whom correspondence should be addressed.
* E-mail: ka-inamura@pecj.or.jp

1. Introduction

Modern analytical methods have allowed considerable progress in the field of refining technology. Conventional gas chromatography (GC) can provide both qualitative and quantitative information about almost all chemical species contained in gasoline (naphtha). GC methods identified the most refractory sulfur compound in gas oil (diesel) as 4,6-dimethyldibenzothiophene using a selective sulfur detector, sulfur chemiluminescence detector (SCD) in the early 2000s, and two-dimensional gas chromatography (2D-GC or GC × GC) provided details on the chemical species distributions at the molecular level in the range from lighter paraffin to complex naphthenic tri-aromatics. These analytical techniques have helped to achieve improvements in both regulations and refining processes for clean fuels, such as lower benzene content in gasoline and ultra-low sulfur content in gasoline and diesel. However, heavy oils, such as vacuum gas oil (VGO) and vacuum residue (VR), had not been investigated at the molecular level until quite recently, mainly because of their complexities. Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) as ultrahigh resolution MS was first applied to petroleum analysis in 1994, and has been extensively used at the National High Magnetic Field Laboratory (NHMFL) to investigate heavy oils, leading to a new methodology for petroleum called “Petroleomics”.

Almost all crude oil was imported into Japan, especially from the Middle East (total 87.3 %, 39.4 % from Saudi Arabia and 24.8 % from United Arab Emirates in 2017), so efficient utilization of petroleum has been the most crucial issue in the oil industry. In particular, noble use of petroleum has been the top target, especially at Japan Petroleum Energy Center (JPEC), requiring the technological enhancement of heavy oil upgrading. The conventional approach for process studies, for example RDS unit, has considered heavy oils as simplified lumping models and overall reaction rates for several major reactions, such as hydrodemetallization (HDM) and hydrodesulfurization (HDS), simply because limited information was available on heavy oil components at the molecular level.

The Petroleomics approach based on molecular level feed and product information and statistical analysis can investigate the heavy oil upgrading process using molecular kinetics models, with the potential for molec-
As a fundamental stage, the study from FY2011 to FY2015 began to build an oil component database at the molecular level based on structural analyses with FT-ICR MS to introduce the informatics approach to petroleum by combining structural and physical properties.

2. Analytical Procedures
2.1. Sample Preparation

Direct measurement with FT-ICR MS of crude oil samples easily causes under/overestimates of heavy oil components due to their different ionization efficiencies. Therefore, heavy oil should be separated into several fractions based on the chemical structures of the sample. The extended SARA (saturate, aromatic, resin and asphaltene) fractionation method is routinely used at JPEC before FT-ICR MS measurements as shown in Fig. 2, where heavy oil samples, such as atmospheric residue (AR) or vacuum residue (VR), were separated into seven fractions by column chromatography: saturates (Sa), one-, two-, three- or higher ring aromatics (1A, 2A, 3A*), polar and polyaromatic resins (Po, PA), and asphaltenes (AS)

\[
\text{DBE} = c - h/2 + n/2 + 1
\]

for elemental formulas of \( C_{c}H_{h}N_{n}O_{o}S_{s} \). In Fig. 4, the range of carbon number remarkably decreased in the order of 1A, PA, AS, indicating that petroleum molecules contained in 1A have longer alkyl side chains than PA and AS. The range of DBE values of 1A, PA, AS were 3-16, 12-33, and 4-38, respectively. The distribution of AS was aligned on the line of planar aromatic limit, and the trend was clearer than for PA. This suggests that AS contains highly condensed (poly-cyclic) aromatic species with shorter alkyl side chains than PA. The DBE versus carbon number plot is one of the most important visualization methods to obtain deep insight into such FT-ICR MS data.
2. 1. 3. Core Structure Estimation Using Collision Induced Dissociation (CID)

In the measurements with collision induced dissociation (CID), ions passing the quadrupole mass analyzer (Q1) were sent into the collision cell. The Q1 was opened and all parent ions were subjected to CID, because mass isolation of each ion is not practical for highly complex mixture such as heavy oil sample. Under this condition, parent ions decompose into constituent core structures, with each core structure consisting of a combination of aromatic, naphthenic and hetero-atom rings, as fragment ions.

Figure 5 shows the distributions of 1A, PA, and AS fractions from a VR sample before and after CID. The distributions of VR-1A before and after CID were located almost in the same range of DBE. Therefore, VR-1A contains single-core molecules as the main component. In contrast, the distributions of PA and AS showed remarkable shift in the lower DBE direction. In particular, the high DBE range of VR-AS (DBE: 26-38) needs at least two cores to explain the structure. It is suggested that VR-PA and VR-AS contain both single- and multi-core molecules. This information can be utilized to reconstruct residue molecules as input. Figure 6 shows the concept of the structure estimation method with CID. More detailed explanation is given in our publication elsewhere⑩.

2. 1. 4. Data Analysis

MS peak detection, internal calibration and assignment of elemental formulas were performed with Composer software (Sierra Analytics, Inc.), and other procedures are detailed elsewhere⑪,15. The chemical structure of each oil molecule can be defined by a combination of core structures, bridge and side chains, where the order of combination of each component is not considered and so all derivatives (isomers) are treated as the same component.

2. 2. Petro-informatics Database

A comprehensive database for petroleum molecules was constructed containing information about the known chemical structure and physical properties. Definition of the chemical structure allows calculation
of some bulk properties. Physicochemical properties such as boiling and melting points are obtained using the group contribution method. Other thermochemical properties such as formation energy and heat capacity are obtained from quantum chemistry calculations. Extensive efforts to construct the database for all petroleum molecules are ongoing, and the number of registered molecules has exceeded 25 million.

2.3. Molecular-based Reaction Modeling for RDS and Asphaltene Aggregation

RDS was selected for the first application of the Petro-Informatics Database as a platform for reaction modeling. Reaction behavior of involved cores was investigated using the chemical structure description data of cores during the RDS reaction. As a result, 1233 types of cores were selected as dominant species accounting for over 95 mol% of the feed and products, and reaction networks for these cores were proposed consisting of 2107 reaction pathways. For example, reaction pathways of two ring cores with S and N are shown in Fig. 7. The second application was the asphaltene aggregation modeling as described in the next section.

3. Application to Practical Uses of Petroleomics in Refineries

The second stage of the Petroleomics project began in FY2016. Based on the technologies developed in the fundamental stage, application and utilization technologies are being developed for practical uses of Petroleomics in refineries, where our developed technologies may be useful for performance diagnoses, as well as operational optimization, and new catalyst and process development, as shown in Fig. 8. Some of main subjects in progress are explained as follows.

3.1. Crude Oil Database with Petroleomics

Lighter crude oils are preferred in Japan with average 36.0° API gravity (S: 1.45 wt%), and a feasibility study for processing heavier crude oils, such as unconventional oils (oil sands) and heavy oils, will be essential, so we initiated to create a crude oil database with Petroleomics. A total of 12 selected crude oils have been processed up to 2018 and are listed in Fig. 9. Carbon number versus DBE plots as heavy component distribution diagrams are shown in Fig. 10 for three atmospheric residues (AR, cut at 360 °C). AR of Crude-B contained more components with higher DBE values at carbon number around 35 than AR of Crude-A, indicating more polycyclic aromatic hydrocarbons (PAHs) with 6-10 aromatic rings and fewer side chains. In contrast, AR of Crude-C contained components widely distributed from PAH to 1-3 ring aromatics with many side chains. Crude-B and Crude-C contained much higher amounts of nitrogen-containing components than AR of Crude-A. HDS and HDN reactivities of these ARs are now being investigated based on their compositions.
reactor from the feed to the desulfurized AR (DSAR) products. The study of molecular-based reaction modeling is now being expanded to the RFCC process as illustrated in Fig. 11, in which fundamental reactions in RFCC are considered.17)

Figure 12 shows comparative diagrams for 22 types of core components found in the RFCC feed and products, in which these cores account for 98% of all cores in RFCC products. One and two ring aromatic cores are the majority in the products, which are formed through aromatization of paraffins, dehydrogenation and ring-opening reactions. In contrast, PAH cores with more than four aromatic rings undergo very little change in quantity except for some cores with a naphthenic ring, indicating that catalytic cracking only occurs at the hydrogenated naphthenic ring. Figure 13 shows comparative diagrams for different numbers of rings (aromatic + naphthenic) in the RFCC feed and products. One- and two-ring cores increased in the RFCC product, whereas more than three-ring cores decreased.

Two possible reactions could account for the decreases in quantity of three- and higher ring core, ring opening
by cracking of the naphthenic ring, decreasing the number of rings, or aromatization and coke-formation by dehydrogenation. Being applied in the same procedure as for the RDS reactions, most molecular components in DSAR as a feed for RFCC and their products were analyzed. The reaction networks of one- to six-ring cores for RFCC were obtained as shown in Fig. 14. By fitting reaction rates to experimental data, the following reaction trends were obtained; ring opening is in the order of three-ring > four-ring > five-ring, and ring opening rate was higher for cores with more naphthenic rings among aromatic + naphthenic cores with the same number of rings (aromatic + naphthenic). Our reaction network modeling of RFCC is now being expanded to both coking reactions and aliphatic chain reactions.

3.3. Mechanism of Asphaltene Aggregation

The aggregation model for asphaltenes (AS) to sediments, which are the primary causes of fouling and plugging, was developed as the Multi-Component Aggregation Model (MCAM). The model consists of the Hansen solubility parameter (HSP) and has been developed by a joint research group between Kansai University, National Institute of Advanced Industrial Science and Technology (AIST) and JPEC. All molecular-based heavy oil components in AS can be attributed to a specific HSP value from its compositional data. Figure 15 shows the HSP of AS extracted from VR of Canadian oil sand bitumen (CaAs) in a 3D diagram as an example. The radius of the sphere is called the interaction radius $R_0$. Quantitative evaluation of the solubility can be determined using the $R_a$ value, meaning the distance of the HSPs for both substances.

$$R_a = \left[4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 \right]^{1/2}$$

Quantitative evaluation of solubility can be represented...
by the $R_a$ value. With a small difference in HSP between solute and solvent ($R_a < R_0$), the solute is likely to be soluble in the solvent. Thus, the degree of solubility can be determined by relative energy difference (RED = $R_a/R_0$). HSPs and solubility score of CaAs in some organic solvents are listed in Table 1. Bromobenzene was determined as the best solvent for CaAs.

Distribution of specific components between soluble, aggregate and precipitate phases can now be determined by the degree of AS aggregation ($D_{agg}$) as a function of the HSP values of the component and liquid phase, concentrations and temperature. In addition, HSP values have been precisely determined for a series of synthetic AS model compounds using experimental solubility testing.

The developed AS aggregation model is now being applied for some refinery tasks, such as the degree of sediment estimated from the feed compositions in some heavy oil upgrading processes, and crude oil stability after mixing (miscibility) in a storage tank. A successful example is a case study of precipitates (sediment) estimation in the heat exchanger located after the ebullated-bed resid hydrocracking unit, as shown in Fig. 16.

![Diagram](image-url)

**Fig. 16** Precipitates Estimated for the Resid Hydrocracker by MCAM

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**Table 1** Hansen Solubility Parameters and Solubility Score of CaAs in Some Organic Solvents

| Solvent   | $\delta_d$ ([J/cm$^3$]$^{1/2}$) | $\delta_p$ ([J/cm$^3$]$^{1/2}$) | $\delta_h$ ([J/cm$^3$]$^{1/2}$) | $\delta_t$ ([J/cm$^3$]$^{1/2}$) | $R_a$ ([J/cm$^3$]$^{1/2}$) | RED $R_a/R_0$ | Score |
|-----------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|-----------------------------|----------------|-------|
| As (CA)   | 19.1                            | 4.2                             | 4.4                             | 20.1                            | 6.1                         |                |       |
| Bromobenzene | 19.2                          | 5.5                             | 4.1                             | 20.4                            | 1.3                         | 0.22           | 1     |
| Toluene   | 18.0                            | 1.4                             | 2.0                             | 18.2                            | 4.3                         | 0.70           | 1     |
| Benzene   | 18.4                            | 0.0                             | 2.0                             | 18.5                            | 5.0                         | 0.83           | 1     |
| THF       | 16.8                            | 5.7                             | 8.0                             | 19.5                            | 6.0                         | 1.0            | 1     |
| Cyclohexane | 16.8                          | 0.0                             | 0.2                             | 16.8                            | 7.5                         | 1.2            | 0     |
| Acetone   | 15.5                            | 10.4                            | 7.0                             | 19.9                            | 9.9                         | 1.6            | 0     |
| Pentane   | 14.5                            | 0.0                             | 0.0                             | 14.5                            | 11.0                        | 1.8            | 0     |
| Ethanol   | 15.8                            | 8.8                             | 19.4                            | 26.5                            | 17.0                        | 2.8            | 0     |
4. Conclusion

Our Petroleomics project is reviewed from the fundamental stage started in FY2011 to the ongoing application stage. The crude oil database based on Petroleomics is expanding in terms of both quality and quantity and is expected to become invaluable as a shared resource for dramatic progress in operational reliabilities and productivities in refineries.

Acknowledgment

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要 目

石油精製技術を変革するツールとしてのベトロリオミクスの展望

片野 恵太, 高橋 祐樹, 佐藤 浩一, 篠 浩二, 早坂 俊明, 中村 勉, 豊岡 義行, 稲村 和浩

(一財)石油エネルギー技術センター, 105-0001 東京都港区芝公園2-11-4住友不動産芝公園タワー

(一財)石油エネルギー技術センター（JPEC）は2011年度より「ベトロリオミクス」と称する新しい石油精製技術の体系化にチャレンジしている。当技術は、重質油成分を分子レベルで解析し反応モデルを構築する究極的手法と言える。最初の5年間で、フーリエ変換イオンサイクロトロン共鳴質量分析計（FT-ICR MS）を用い重質油の構成成分として2500万のデータベースを構え、残油直接脱硫（RDS）装置での分子反応や重質油処理中でのアスファルテン（AS）凝集解析予測モデルへの応用を提案してきた。最近では、これらを基盤技術として発展させ、非在来型原油を中心とした原油の分子レベルでのデータベース化、RDSと残油流動接触分解（RFCC）装置の最適効率運転を目指した分子反応モデリング、さらに残油アップグレーディング装置におけるAS凝聚解析予測など、実用レベルの技術への展開を図っている。