Development of Petroleomics Technology

Japan Petroleum Energy Center
Chikanori Nakaoka
1. Background and Requirement of Japanese Oil Industry
2. A new technology “Petroleomics” as a solution
3. Constituent Technologies of “Petroleomics”
4. Leaders of “Petroleomics” in the world
5. Development of “Petroleomics” in JPEC
   5.1. Method for Detailed composition analysis
   5.2. Topics in Detailed composition analysis
   5.3. Promotion system by Collaboration
6. Summary
1. Background and Requirement of Japanese Oil Industry

Background of Japanese Oil Industry

- Decrease of domestic demand for heavy fuel oil
- Treatment of heavy and/or unconventional crude
- Promotion of bottomless of refineries

Requirement for Development

Advanced Upgrading + Without huge investment

Solution

Establishment of “Petroleomics” as technical fundamental

Contribute for the improvement of:
- Global energy security
- Global environmental issues

Make the effectiveness of petroleum usage up to ultimate level

Apply the technology to domestic refineries

Development of advanced upgrading technology with Petroleomics

“Petroleomics” is the principle that it should be possible to correlate (and ultimately predict) their properties and behavior from sufficiently complete characterization of the organic composition of petroleum and its relatives and products.

*PNAS 2008, 105/47, 18090-18095.*
Conventional approach cannot make a solution for the requirement in the near future.

A new technology “Petroleomics” can give us the way of ultimate approach from molecule-based reaction modeling with molecule-based analyses on heavy oil.

**Conventional**

- **Crude Oil** → **Process** (Simple operation) → **Products** → **Residue**

- **Requirement-1**
  - Heavy fraction increases from heavier feedstock

- **Requirement-2**
  - More conversion of heavy fraction

- **Difficulty is** …
  - Residue increase
  - Shorter operation period
  - Difficult Sulfur removal

**New Approach**

- **Crude Oil** → **Process** (Molecule-based Reaction Modeling) → **Heavy Fraction** → **Products**

- **Enhancement of Conversion Selectivity**

- **Reduction**

- **Residue**

- **Detailed Analysis**

- **Molecular Structure**

- **the best control in process/operation**
3. Constituent Technologies of “Petroleomics”

(1) Detailed composition analysis

(2) Molecule-based kinetic modeling

(3) Petro-informatics

Petroleum feed oil is processed into various products through detailed composition analysis, molecule-based kinetic modeling, and petro-informatics. The output includes chemicals, fuels, and materials, which are managed through petro-informatics supply systems.
### 4. Leaders of “Petroleomics” in the world

**Petro-informatics**

**Kim Gr. (Korea)**
- Informatics
  - Statistics analysis
  - Crude data base

**JPEC Gr. (Japan)**
- Comprehensive approach
  - Pre-separation for MS
  - Focus on downstream

**Tanaka(Idemitsu) Gr. (Japan)**
- Comprehensive approach
  - Analysis + Modeling + Informatics

**Russell Gr. (US)**
- IM-MS

**Marshall Gr. (US)**
- Detailed analysis
  - FT-ICR-MS development
  - Many collaborations

**Klein Gr. (US)**
- Kinetic modeling
  - KMT development
  - Many collaborations

**Martin Gr. (Canada)**
- LC × LC

**Gray Gr. (Canada)**
- Asphaltene chemistry

**Molecule-based kinetic modeling**

**Detailed composition analysis**

**JPEC integrates whole technologies of “Petroleomics”**
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5. Development of “Petroleomics” in JPEC

Composition of Petroleum Products

<table>
<thead>
<tr>
<th>bp, ℃</th>
<th>naphtha</th>
<th>kerosene</th>
<th>VGO</th>
<th>VR</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>350</td>
<td>540</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- paraffins
- naphthenes
- benzenes
- benzothiophenes
- naphthalenes
- dibenzothiophenes
- phenanthrenes
- pyrenes
- crysene
- benzopyrenes
- ashpaltenes

Then, “Molecule-based Modeling”? How to realize “Molecule-based Analysis”??
5.1. Method for Detailed composition analysis

(1) Concept for detailed compositional analysis of heavy oils

Complexity of the major portions of heavy oils could be organized with hetero-elements, HC types, and molecular weight.

Combination of pre-separation and MS analysis.
5.1. Method for Detailed composition analysis

(2) Pre-separation

The new fractionation method: the Separation along the Aromatic Ring Numbers (SARNs)

Heavy oils

Solvent Extraction

Asphaltenes

Maltenes

Column Chromatography

Saturates 1-rings 2-rings 3-rings + Polars Poly Aromatics

Liquid Chromatography

3-rings 4-rings (peri) 4-rings (cata) 5-rings +
5.1. Method for Detailed composition analysis

(3) Fourier transform ion cyclotron resonance mass spectrometry

Working since Jan. 2012

world-wide top level resolution

FT-ICR-MS solariX 12T (by Bruker Daltonics)
Petroleomics require to distinguish the fourth decimal place! …to know how many S,N,C,H contained in molecule.

⇒ For this purpose, the resolution of FT-ICR-MS is necessary.
5.2. Topics in Detailed composition analysis (1)

【Example-1】
Analysis of **Heavy Basic Nitrogen Compounds**

[Why?] may deactivate the ARDS catalyst activity?
may spoil the ARDS catalyst life?

[Mission] to identify the compounds and their quantities
⇒ This information may help development of catalyst/process...

Deactivation Factors

1. Metal Deposition
2. Coke Formation
   ②-1 Residual carbon
   ②-2 Poly-aromatics
   ②-3 Basic Nitrogen

②-3 Basic Nitrogen
5.2.(1) Samples and Preparation for MS analysis

**Samples**

(1) Atmospheric Residue (AR)
(2) Product Oil A, B, and C; hydro-treated oil of AR

**Pre-separation**

Heavy oils

- Solvent Extraction
  - Asphaltenes
  - Maltenes

Column Chromatography

- Saturates
- 1-rings
- 2-rings
- 3-rings + Polars

Liquid Chromatography

- 3-rings
- 4-rings (peri)
- 4-rings (cata)
- 5-rings + Poly Aromatics

Basic Nitrogen Compounds
5.2.(1) Analysis results by FT-ICR-MS

Selected assignments: N [H]

Basic Nitrogen compounds in Polar Resin

Polar Resin (whole)

Intensity

Molecular Weight

Internal Reference

214.2029
580.5501
922.0090
1080.8023
1221.9956
1370.3339

ESI_Pos_seisei3_Po_b_25_1000_(TM)_64_000005
Assigned Spectrum

Intensity

Molecular Weight

5.2. Analysis results by FT-ICR-MS

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Assigned Spectrum
Further analysis on MS data --- concerning structure of molecule

**DBE (Double Bond Equivalent) - Indicator of Ring structure**

$$DBE = (N_{\text{carbon}} + 1) + \left( \frac{N_{\text{nitrogen}}}{2} \right) - \left( \frac{N_{\text{hydrogen}}}{2} \right) - \left( \frac{N_{\text{halogen}}}{2} \right)$$

(Example)

- **DBE = 1**
  - Naphthenic Ring:
  - H/C balance of 1 Double Bond

- **DBE = 4**
  - Aromatic Ring:
  - H/C balance of 4 Double Bonds

- **DBE = 7**

- **DBE = 10**
5.2.(1) Detailed composition analysis by DBE-plot

Basic Nitrogen compounds in Polar Resin

DBE plot shows Distribution and population of the basic nitrogen compounds

...but not so good for quantity comparison

【DBE=7】
(ex) Alkyl Quinoline

【DBE=4】
(ex) Alkyl Pyridine

horizontal Section
...the same DBE value
By the information from FT-ICR-MS data followed with pre-separation, we can estimate the amount of polar resin and basic nitrogen compounds. ⇒ Such information may help us to develop a new catalyst/process/...
5.2. Topics in Detailed composition analysis (2)

【Example-2】
Analysis of Composition Change during Hydro-cracking

Composition of Vacuum Residue — 3-rings+ Aromatics(3A+) Fraction —

3A+ Fraction (12.7 wt% of Vacuum Residue)

DBE=10 : minimum level of 3-rings Aromatics

DBE vs. Carbon Number
According to the cracking, Carbon Number Decreased (Alkyl side chain dissociated) Aromatic rings saturated
5.3. Promotion system by Collaboration

**ATRI of JPEC**
- Director
- Manager
- Leader
  - Analysis Gr.
  - Modeling Gr.
  - Researchers
  - Researchers

**H. O. of JPEC**
- Director
- Senior chief researcher
- Chief researcher

**Labs in Companies**
- Improvements of heavy oil upgrading technologies
  - Idemitsu Kosan
  - Kobe Steel
  - Chiyoda Corp.
  - JX Energy
  - Cosmo Oil

- New process developments
  - Kobe Steel
  - Chiyoda Corp.

**Fundamental Study & Tech. Establishment**

**Feedback & Feedforward**

**Application Study & Development**

※**ATRI : Advanced Technology & Research Institute**
6. Summary

1. “Petroleomics” is Molecular-based approach, and will give a new solution for Petroleum upgrading.

2. JPEC started “Petroleomics” study by employing the latest adequate technologies.

3. FT-ICR-MS following detailed pre-separation showed the possibility of heavy fraction analysis in residue.
   --- Heavy basic nitrogen compounds are analyzed.
   --- Such information may help us to develop a new catalyst/process/ ....

4. “Petroleomics” study can be sophisticated by cooperation with the relating companies’ research.
Thank you for your attention

http://www.pecj.or.jp/english/index_e.html