Extension of Solvent Treatment Method Developed by SATREPS Program to ASEAN Region

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Japan-Thailand SATREPS Project

Development of clean and efficient utilization of low rank coals and biomass by solvent treatment

Dec. 20, 2013 – Dec. 19, 2018

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Purposes of the SATREPS Project

1. To establish a technology converting low rank coals and/or biomass wastes using a new method called “Degradative Solvent Extraction”, which was developed by Kyoto University group, to raw material independent small molecular weight components called “Soluble” and Residue.

2. To develop technologies for utilizing Soluble and Residue effectively.
   eg. Preparation of value added materials such as carbon fiber, clean fuel, chemicals, etc. Effective methods to combust/gasify Residue

3. To assist the development of human resources and research capabilities in Thailand by conducting joint research.

➢ The technologies developed under cooperative researches will contribute to reduce the emission of global warming gases as well as environmental pollutants.

➢ The technologies developed will be disseminated to ASEAN countries which need such technologies.
What is the “Degradative Solvent Extraction”? 
**Proposed method**

In non-polar solvent

Brown coal molecule

Hydrogen bonding

Heated up to 150 °C

Heated up to 350 °C

Cooled

Non-evaporative dewatering

CO₂, H₂O

**Conventional heat-treatment**

In inert gas

Brown coal molecule

Hydrogen bonding

Heated up to 150 °C

Evaporative dewatering

Heated up to 350 °C

CO₂, H₂O

Cooled

Significant enlargement of the coal molecules

Upgrading without cross-linking reactions.
Apparatus and procedure

**Experimental conditions**

- **Coal**: 14 g-d.a.f. (Charged as received)
- **1-MN**: 300 mL
- **Temperature**: 350°C
- **Holding time**: 0, 1, 2, 3 h
- **Final pressure**: 2.3, 6.8, 15.7 MPa

**Apparatus and procedure**

- Autoclave 350 mL
- TC
- Pressure gauge
- Impeller
- Furnace
- Valve
- Reservoir 350 mL
- N₂
- Gas
- LY Coal
- Stainless Steel Filter 0.5 μm

**Soluble**
The extracted fraction which was soluble in the solvent even at room temperature

**Deposit**
The extracted fraction which precipitated as solid at room temperature
Apparatus used

- Autoclave
- Valve
- Reservoir

150 cm
Raw materials used

- Brown coal (Loy Yang)
- Rice straw
- Leucaena
Core technology is “Degradative Solvent Extraction”

- **Solvent treatment**
  - Dewatering · Upgrading
  - 350°C · 2 MPa

- **Soluble**
  - C base yield
  - Coal: ~30%
  - Biomass: ~70%

- **Deposit**
  - Coal: ~15%
  - Biomass: < 10%

- **Residue**
  - Coal: ~50%
  - Biomass: < 20%

**Raw material independent property**
- **Soluble and Deposit**
  - High HHV: C ≒ 82%, H ≒ 9%, O ≒ 9%
  - Low MW: 100-500, peak at ca. 300
  - 80% are volatile components
  - Melts below 100°C
  - Free from water and ash

- **Residue**
  - C ≒ 76%, H ≒ 5.5%, O ≒ 15.5%
  - Melts below 250°C
  - Free from water
  - Low ash content: < 1.4%

- **High reactivity to combustion**
- **Concentrated mineral components**

- **Coal**:
  - ~30%

- **Biomass**:
  - ~70%

- **Water**
  - ✓ High water content
  - ✓ Low heating value: C < 70%, O > 25%
  - ✓ High self-ignition tendency when dewatered

The method dewateres and upgrades various low grade carbonaceous resources, producing high quality extract in high yield under mild conditions.

- Almost no heating value loss through the treatment
- Soluble and Deposit have raw material independent properties
**Output 1**: Upgrading of low rank coals and biomass by solvent treatment
**Output 2**: Production of new bio-fuel from biomass wastes and effective upgrading
**Output 3**: Production of high-grade carbon materials from the Solubles
**Output 4**: Combustion/gasification of upgraded fuels/residues
Cooperative Structure of our project

Japan

**Head Investigator:** Kouichi Miura  
**Research fund:** 178 million yen from JST

**Kyoto University:** Miura Gr.  
Kouichi Miura, Specially App. Prof.  
Hideaki Ohgaki, Prof.  
Ryuichi Ashida, Assist. Prof.  
Motoaki Kawase, Prof.  
Taro Sonobe, Research Administrator  
Janewit Wannapeera, Dr.  
Trairat Muangthong-on, PhD cand.

**Akita University:** Sugawara Gr.  
Katsuyasu Sugawara, Prof.  
Takahiro, Kato, Assis. Prof.  
Kenji Murakami, Prof.

**CRIEPI:** Makino Gr.  
Hisao Makino, Dr.  
Kenji Tanno, Dr.  
Satoshi Umemoto, Dr.  
Atsushi Ikeda, Mr.  
Shiro Kajitani, Dr.

**Kobe Steel Co. Ltd:** Okuyama Gr.  
Noriyuki Okuyama, Dr.  
Takuya Yoshida, Dr.  
Shigeru Kinoshia, Mr.  
Koji Sakai, Mr.

Thailand

**Head Investigator:** Bundit Fungtammasan  
**Research fund:** 300 million yen from ODA

**JGSEE/KMUTT:** Bundit Gr.  
Assoc.Prof. Bundit Fungtammasan  
Assoc.Prof. Sirintornthep Tawprayoon  
Assoc.Prof. Nakorn Worasuwanarak  
Assoc.Prof. Suneeatk Fukuda  
Dr. Supachita Krerkkaiwan  
Ms. Sasithorn Buranatvedhy  
Mr. Supachai Jadsadjerm  
Mr.Jaggapan Sanduang  
Ms.Thitima Sornpitak  
Mr.Kaweewong Wongaiyara

**PTT-RTI, PTT Public Company Ltd:** Arunratt Gr.  
Arunratt Wuttimongkolchai, Ms.  
Suttipong Tunyapisesak, Mr.  
Suchada Butnark, Dr.  
Anurak Winitson, Dr.  
Suriya Portangjitlikit, Mr.  
Kornthape Prasirtsiriphum, Mr.

Four research groups from Japan and two research groups from Thailand are involved in this project.

More than 30 researchers from academy and industry contribute to this project.
## Planned Schedule of Research and Development

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<th>Activity</th>
<th>Schedule (from 2014 to 2018)</th>
<th>Group in charge</th>
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</thead>
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<tr>
<td>1.1 Production of Solubles from low rank coals and biomass using a batch autoclave</td>
<td></td>
<td>KU, JGSEE</td>
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<tr>
<td>1.2 To optimize the production of Solubles from low rank coals and biomass</td>
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<td>KU, JGSEE</td>
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<tr>
<td>1.3 To characterize the properties of Solubles and Residues from low rank coals and biomass</td>
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<td>KU, JGSEE</td>
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<td>1.4 To design and construct the semi-continuous extraction process (1 kg/h)</td>
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<td>KS, PTT</td>
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<tr>
<td>1.5 Production of Solubles from low rank coals and biomass using the semi-continuous extraction process</td>
<td></td>
<td>KS, PTT</td>
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<tr>
<td>1.6 Conceptual process design for constructing a pilot plant of 10 ton/day</td>
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<td>KS, PTT</td>
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<td><strong>Task 2. Production of new liquid biofuels from solubles</strong></td>
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<tr>
<td>2.1 Optimization of production of liquid biofuels using batch reactor (5 L)</td>
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<td>KU, JGSEE, PTT</td>
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<tr>
<td>2.2 Upgrading liquid products to liquid biofuels by hydrotreatment</td>
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<td>AU, PTT</td>
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<td>2.3 Combustion test in gas turbine engine</td>
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<td>CRIEPI, KS, PTT</td>
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<td>2.4 Cost estimation, feasibility study and scale-up plant (in case of technical soundness)</td>
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<td>KS, PTT</td>
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<tr>
<td><strong>Task 3. Production of high-grade carbonaceous materials from Solubles</strong></td>
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<tr>
<td>3.1 Characterization of Solubles as a raw material for high performance carbon materials</td>
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<td>KU, JGSEE</td>
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<tr>
<td>3.2 Design and construct a small apparatus producing carbon fiber/carbon black</td>
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<td>KU, JGSEE</td>
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<tr>
<td>3.3 Production of carbon fiber from Solubles</td>
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<td>KU, JGSEE</td>
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<tr>
<td>3.4 Design and construct a small continuous spinning apparatus (0.1 kg/h)</td>
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<td>3.5 Production of carbon fiber using a small continuous spinning apparatus</td>
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<td>KU, JGSEE, PTT</td>
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<tr>
<td>3.6 Conceptual process design for a pilot plant</td>
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<td>KU, JGSEE</td>
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<td><strong>Task 4: Combustion/gasification of upgraded fuels/residues</strong></td>
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<td>4.1 Fundamental Examination of combustion/gasification behaviors of upgraded fuels/residues in TG</td>
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<td>4.2 Examination of combustion/gasification behaviors of upgraded fuels/residues in Entrained bed reactor</td>
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<td>4.3 Examination of combustion behaviors of upgraded fuels/residues in Fluidized bed reactor</td>
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</table>
Preparation of carbon fiber from Soluble – Task 3 -

-20% of light fraction was removed by heat treatment

-20% of Soluble can be utilized as oil without treatment

Spinning using a mono-hole continuous spinner at -200°C

Oxidation treatment in air at -300°C

Heat treatment at -800°C
Continuous spinning of the modified Soluble

Modified Soluble is heated to 285°C

Pitch fiber coming out from the mono-hole

Pitch fibers collected

Rotating drum (16 cm φ) (rotating at 600 – 1000 rpm)

Fig. Mono-hole spinning machine
Carbon fibers: J-RS Soluble

- SEM images of carbon fibers (400x)

**Oil pitch**
- Fibers dia. 51.7-54.7 μm

**Air 300 °C, 85 min**
- Fibers dia. 11.4-16.7 μm

**N₂, 300 °C, 60 min**
- Fibers dia. 6.6-13.8 μm

**Air 330 °C, 30 min**
- Fibers dia. 12.1-16.8 μm
Carbon fibers: J-RS Soluble

- SEM cross-sectional images of carbon fibers (3000x)
  
  - Only one hollow was observed from the fibers prepared from Soluble treated by the N₂ purge.
  
  - Several hollows were observed from the fibers prepared from Soluble treated by the air oxidation.
## History of exchange

<table>
<thead>
<tr>
<th>Year</th>
<th>Number of dispatch researchers</th>
<th>Number x Day (man-day)</th>
<th>Number of accepted researchers</th>
<th>Number x Day (man-day)</th>
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<td>2015</td>
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<td>123</td>
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<td>2016</td>
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<tr>
<td>Total</td>
<td>96</td>
<td>812</td>
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<td>592</td>
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</tbody>
</table>
Visit Kyoto University (July. 17 – Aug. 3, 2014)

Training of solvent extraction and carbon fiber preparation
Akita University (June, July, 2014)

Training of solvent desulfurization experiments
Visit CRIEPI

(June. 15-17, 2015)

Training of DTF operation
The Thai members had an opportunity to see the continuous HPC production facility
Solvent Extraction Plant tour at Kobe Steel (April, 2015)