VALUE-UP of SECONDARY RESIDUES

in PETROCHEMICAL COMPLEX

Steam Reforming using Internally Circulating Fluidized-Bed Gasifier (ICFG)

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by
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EBARA CORPORATION, JAPAN
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1. Petrochemical Complex in Japan

### Oil and Energy Balance

*<for 2002 Fiscal Year>*

<table>
<thead>
<tr>
<th>Source</th>
<th>Quantity</th>
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<tbody>
<tr>
<td>Crude Oil Production</td>
<td>755,889 kl</td>
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<tr>
<td>Crude Oil Import</td>
<td>241,897,627 kl</td>
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<tr>
<td>Naphtha Import</td>
<td>30,215,827 kl</td>
</tr>
<tr>
<td>LPG Import</td>
<td>13,923,839 t</td>
</tr>
<tr>
<td>LNG Import</td>
<td>53,878,000 t</td>
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</table>

<table>
<thead>
<tr>
<th>Plant</th>
<th>Production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery Plant</td>
<td>Light Oil</td>
</tr>
<tr>
<td>Petrochemical Plant</td>
<td>Heavy Oil</td>
</tr>
<tr>
<td>Fuel Company</td>
<td>Other Oil</td>
</tr>
<tr>
<td>Power Company</td>
<td>Light Oil : Gasoline, Naphtha, Jet Fuel, Kerosene, Diesel Fuel Oil</td>
</tr>
<tr>
<td>Gas Company</td>
<td>Heavy Oil : A Grade, B Grade, C Grade</td>
</tr>
<tr>
<td></td>
<td>Other Oil : Lube Oil, Asphalt, Paraffine</td>
</tr>
</tbody>
</table>

- Naphtha : Import (30MMt) > Production (19MMt)
- LPG : Import (14MMt) > Production 5MMt

Data Source : "Petroleum Association of Japan"
1. Petrochemical Complex in Japan

**Demand of Oil Products**

- **Light Oil**
- **Heavy Oil**
- **Fuel Oil Total**

**Graph:**

- Fiscal Year 1980
- Fiscal Year 1990
- Fiscal Year 2000
- Fiscal Year 2001

**Data:****

- Light Oil Demand Increase
- Heavy Oil Demand Decrease

**Solution Required:**

- Load-Down Crisis of Refinery Plant
  (Heavy Oil = Consecutive By-product)

**Refinery Plant in Japan**
- Number of Refinery Plant: 35
- Topper Total Capacity: 500bbl/d

**Law and Regulation**

- Sulfur Content → Gasoline and Diesel Fuel
- Particle Matter → Diesel Vehicle

**Data Source:**
"Petroleum Association of Japan"
## 1. Petrochemical Complex in Japan

### Petrochemical Complex and Ethylene Plant

<table>
<thead>
<tr>
<th>Location of Complex</th>
<th>Ethylene Producer</th>
<th>Ethylene Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kashima</td>
<td>Mitsubishi Chemicals</td>
<td>828,000 T/Y</td>
</tr>
<tr>
<td>Chiba</td>
<td>Sumitomo Chemicals</td>
<td>380,000 T/Y</td>
</tr>
<tr>
<td></td>
<td>Idemitsu Kosan</td>
<td>374,000 T/Y</td>
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<tr>
<td></td>
<td>Mitui Chemicals</td>
<td>553,000 T/Y</td>
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<tr>
<td></td>
<td>Maruzen Petrochemical</td>
<td>480,000 T/Y</td>
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<tr>
<td></td>
<td>Maruzen Petrochemical</td>
<td>690,000 T/Y</td>
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<tr>
<td>Kawasaki</td>
<td>Tonen Chemicals</td>
<td>478,000 T/Y</td>
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<tr>
<td></td>
<td>Nippon Petrochemicals</td>
<td>404,000 T/Y</td>
</tr>
<tr>
<td>Yokkaichi</td>
<td>Tosoh</td>
<td>493,000 T/Y</td>
</tr>
<tr>
<td>Senboku</td>
<td>Mitsui Chemicals</td>
<td>455,000 T/Y</td>
</tr>
<tr>
<td>Mizushima</td>
<td>Ashahi Kasei</td>
<td>443,000 T/Y</td>
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<td></td>
<td>Mitsubishi Chemicals</td>
<td>450,000 T/Y</td>
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<tr>
<td></td>
<td>Idemitsu Kosan</td>
<td>623,000 T/Y</td>
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<tr>
<td></td>
<td>Showa Denko</td>
<td>581,000 T/Y</td>
</tr>
<tr>
<td><strong>(Total)</strong></td>
<td></td>
<td><strong>7,232,000 T/Y</strong></td>
</tr>
</tbody>
</table>

Almost All Feedstock = Naphtha

Cracking Heavy Oil = Cousecutive By-product

Ethylene 7,232 × 10^3 t/y

→ 767 × 10^3 t/y Cracking Heavy

Current Trend = Gas Oil Cracking instead of Naphtha Cracking

Substantial Increase in Cracking Heavy

Cracking Heavy = Less Market

Petrochemical Complex Residue

Value-Up is Required

Data Source: "Japan Petrochemical Industry Association"
1. Petrochemical Complex in Japan

Scenario for Value-Up

How to sustain Petrochemical Complex

Correlation of Ethylene and Refinery Plant

Petrochemical Complex Secondary Residues
- Cracking Heavy Oil from Ethylene Plant
- Vacuum Residue from Refinery Plant
- Industry Waste
- Others

VALUE-UP "BOX"

Social Demand
Law and Regulation
Current Trend

Hydrogen for Hydrocracking and Hydrodesulfurization in Refinery Plant

Gas for Oil Substitute Production such as DME, GTL and Methanol

Hydrogen for Future Hydrogen Society (Fuel Cell, Gas Engine and Gas Turbine)

Consumption Reduction in Naphtha as Feedstock for Hydrogen Production

Short Term Value-Up Measure

Reduction in Crude Oil Import

Middle and Long Term Value-Up Measure
2. Internally Circulating Fluidized-Bed Gasifier

Progress in EBARA Fluidized-Bed Technology 1/2

TIF (145 plants)  
Unshredding, Large sized

ICFB (22 plants)  
To Gasification

Ash Melting

Gasification

Technology

PICFB  
Pressurization Technology

Product Gas  Combustion Gas

Gasification Chamber  Combustion Chamber

Fluid Media + Char + Catalyst

ICFG  
GTC2004 (Washington, DC)
2. Internally Circulating Fluidized-Bed Gasifier

Progress in EBARA Fluidized-Bed Technology 2/2

SDP: Sterile Disposal Plant
TIF: Twin Interchanging Fluidized-bed
ICFB: Internally Circulating Fluidized-bed Boiler
PICFB: Pressurized ICFB
TIFG: TIF Gasifier
PTIFG: Pressurized TIFG
ICFG: Internally Circulating Fluidized-bed Gasifier
PICFG: Pressurized ICFG

▼: Commercialization Phase

Pilot Plant I
Internally Circulating Fluidized-bed Gasifier (ICFG)

Test plant II (for municipal waste) is subsidized by Ministry of Education, Culture, Sports, Science and Technology

For Chemical Recycling of High Calorie Waste Subsidized by METI / NEDO

Gasification & Ash Melting Technology: TIFG (Self-hot-ash-melting)

Pressurized Twin Internally Gasifier PTIFG

ICFB for Coal Use: Multi-fuel type, small dispersed-siting type, suitable for small scale power plant

SDP: Sterile Disposal Plant
TIF: Twin Interchanging Fluidized-bed
ICFB: Internally Circulating Fluidized-bed Boiler
PICFB: Pressurized ICFB
TIFG: TIF Gasifier
PTIFG: Pressurized TIFG
ICFG: Internally Circulating Fluidized-bed Gasifier
PICFG: Pressurized ICFG

Project subsidized by Agency of Natural Resources and Energy of the former Ministry of International Trade and Industry (now Ministry of Economy, Trade and Industry), for promotion of coal production and utilization technology

Development
Internally Circulating Fluidized-bed Boiler (For high-heat-value waste)

Unshredded Revolving Type Fluidized Bed Incinerator: TIF (For municipal and industrial waste)

Revolving Type Fluidized Bed Incinerator: SDP (For small scale, industrial waste use)

For Chemical Recycling of High Calorie Waste Subsidized by METI / NEDO

Gasification & Ash Melting Technology: TIFG (Self-hot-ash-melting)

Pressurized Twin Internally Gasifier PTIFG

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Development
Internally Circulating Fluidized-bed Boiler (For high-heat-value waste)

Unshredded Revolving Type Fluidized Bed Incinerator: TIF (For municipal and industrial waste)

Revolving Type Fluidized Bed Incinerator: SDP (For small scale, industrial waste use)
2. Internally Circulating Fluidized-Bed Gasifier

Mechanism and Function 1/2

- Consisting of Gasification Chamber (reducing zone) and Combustion Chamber (oxidizing zone), isolated by common Bed Material (river sand) working also as the Seal.
- Bed Material is fluidized by Steam in Gasification Chamber and by Air in Combustion Chamber respectively.
- Fluidization of Bed Material is so controlled by Steam and Air, as to maintain optimum temperatures in two Chambers. No need for a complicated Bed Material Recycling Device.
- Multi-Nozzles are provided for Feedstock Supply. Solid, Liquid and Gas Phases Feedstocks are acceptable in any combination.
- Simple structure
  No need for any special consumables
2. Internally Circulating Fluidized-Bed Gasifier

Mechanism and Function 2/2

- Feedstock In → Contacted with BM → Thermally Cracked
  → Gas and Lighter to GC Outlet → Tar and Char deposited on BM
  → BM transferred to CC → Tar and Char combusted by Air in CC
  → BM Heated up → BM transferred back to GC
  → Combustion Heat for Thermal Cracking

- BM self cleaned
- No Pretreatment of Feedstock
- Simple and Effective Heat Transfer Function
- Carbon Rejection → applicable to High C/H Feedstock
- Higher Calorific Value of GC Outlet Raw Product Gas
- No Consecutive By-product, such as Coke and Pitch
- Co-Gasification Effect

BM: Bed Material
GC: Gasification Chamber
CC: Combustion Chamber
3. ICFG Gasification Performance

ICFG Pilot Plant 1/2

↑ Pilot Plant I
3 MWth
(6.2 t-cracking heavy/d)

↑ Pilot Plant II
2 MWth
(4.1 t-cracking heavy/d)
3. ICFG Gasification Performance

ICFG Pilot Plant 2/2

- Feedstock
- Water
- Air
- Product gas
- Combustion gas
- Ash

Elevator
Conveyor
Drier
Bunker
Yard

- Pipe conveyor
- Cyclone
- Sub feeder
- Main feeder
- Ash feeder
- Steam
- Incombustibles

- Combustion gas cooler
- Air heater
- Bag filter
- I.D.F.
- Catalyst filling up tower
- Stack

- Water
- Gasifier
- Combustion
- Gas cooler
- Bag filter
- Ash mixer
- Ash

- Gas turbine
- Gas compressor
- Gas engine

GTC2004 (Washington, DC)
3. ICFG Gasification Performance

Calculated Performance

Relationship between heat value of feedstock and cool gas efficiency (calculation only)

Relationship between heat value of feedstock and heat value of product gas (calculation only)
3. ICFG Gasification Performance

Performance by Pilot Plant

Relationship between (H+O)/C and Gas Yield for Solid Feedstock

Relationship between FC and Char Yield for Solid Feedstock
3. ICFG Gasification Performance

ICFG Laboratory Equipment 1/2

Schematic Diagram of Equipment

- Scrubber
- Tar sampler
- Catalyst fixed bed gasification zone
- Oil feeder
- Nitrogen (for feedstock dispersion)
- BM feeder
- BM
- Fluidized-bed pyrolysis zone
- Fluid pre-heater zone
- Spent BM
- GC
- CO/CO2/O2 meter
- Oxygen
- Quencher
- GC
- BM feedrer
- Fluidization media (Steam, Nitrogen, Air)

BM: bed material
3. ICFG Gasification Performance

ICFG Laboratory Equipment 2/2
3. ICFG Gasification Performance

Performance by Laboratory Equipment

Feedstock: Cracking heavy (supplied by Maruzen Petrochemical)
Ultimate analysis: C 90.9%, H 8.1%, N <0.01%, O 0.8%

Relationship between bed temperature and yield

Effect of bed temperature: constant increase in gas yield and coke yield, constant decrease in oil yield
3. ICFG Gasification Performance

Performance by Laboratory Equipment

Distillation curves of feedstock vs generated oils

Pyrolytically generated oils have distillation curves lighter fraction than feedstock.
3. ICFG Gasification Performance

Performance by Laboratory Equipment

3/4

Distillation curves of feedstock and oils obtained

250～450℃ fraction increased in bed temperature around 500℃ (932℃)
250℃+ fraction significantly decreased in bed temperature around 800℃ (1,472℃)

Increase in Polymerized Component
Rejection of Above
Become Lower C/H

Percentage of vaporized oil (wt%carbon; 100% means amount feedstock feed)
3. ICFG Gasification Performance

Performance by Laboratory Equipment

4/4

Relationship between bed temperature and yields

Effect of bed temperature: Coking of aromatics in feedstock
4. Application Models to Petrochemical Complex

Process Configuration

- Ethylene Cracking
- Steam
- Oxygen
- Air
- ICFG Gasification Chamber
- THR Steam Reformer
- Heat Recovery
- Scrubber
- Compressor
- Product Gas
- Carbon Recovery
- Waste Water Treatment
- Waste Water
- ICFG Combustion Chamber
- Heat Recovery
- Combustion Gas

THR: Total Hydrogen Recycle

THR Catalyst
1) Developed by Toyo Engineering Corporation.
2) Catalyst for Steam Reforming of Topped Bottom Oil and Vacuum Residue.
3) | Career | T-12 | T-48 |
   | 12CaO-7Al₂O₃ | 12CaO-7Al₂O₃ |
4) Characteristics
   - Carbon Anti-Deposition
   - Activity under High Temperature
   - Activity under Sulfur and Heavy Metals

Development and Demonstration
1) R & D of Catalyst: Initiated in 1966
2) Demonstration
   - Plant size: 14t/d
   - Feedstock: Vacuum Residue
   - Period: 1985 ~ 1986
   - Operating Temperature: 960 ~ 1,030°C

Literature
1) Tomita, Processing of the 11th World Petroleum Congress, 4, 407 (1983)
2) Tomita, Processing of the 7th International Congress on Catalysis, Part B, 804 (1980)
4. Application Models to Petrochemical Complex

Correlation of Ethylene Plant and Refinery Plant

Feedstock Naphtha → Conventional Steam Reforming

(Current Process)

Feedstock Cracking Heavy → ICFG-THR Steam Reforming

(ICFG/THR Process)

CO Shift → Purification

Hydrogen Gas for Refinery use (Hydrocracking) (Hydrodesulfurization)

Note: Existing equipments and facilities are utilized at maximum extent possible.

Naphtha Feedstock for H₂ Production

Naphtha is Salable

Reduction in Naphtha Consumption

Crude Oil Import Reduction

Naphtha Import Reduction

Cracking Heavy is Consecutive Byproduct

Need Market at Higher Price Level

Substitution of Naphtha by Cracking Heavy

Substitution of Naphtha by Cracking

Cracking Heavy Oil Heat History High C/H Value Aromatics

Feedstock for Conventional Steam Reforming is not acceptable

Steam Reforming by ICFG/THR Process
4. Application Models to Petrochemical Complex

Correlation in Petrochemical Complex 1/3

"A" Petrochemical Complex in Japan

Present

- Pipe line rack is available
- A2 Plant produces H2 from Naphtha, via Steam Reforming Process.
- A3 Plant produces H2 from Naphtha, via Steam Reforming Process.
- A4 Plant produces CO from LPG, via Partial Oxidation Process.
- A5 Plant produces CO from Naphtha, via Partial Oxidation Process.

Future Alternative

- A1 will produce Synthesis Gas from Ethylene Cracking Heavy as Feedstock, via ICFG/THR Steam Reforming Process.
- Synthesis Gases are transported through Pipe Lines to A2, A3, A4 and A5. And the gases are purified to H2 and CO.
"B" Petrochemical Complex in Japan

- B2 Ethylene Plant
- B4 Industrial Waste
- B1 Chemical Plant
- B3 Oil Refinery Plant
- B5 Municipal Waste
- ICFG/THR Gasifier

Recycling of Secondary Materials is Current Practice
B1 Chemical Plant needs a Cheaper Synthesis Gas

ICFG has a function to process Multiple Feedstocks. Some of Waste contain Oxygen component. The oxygen activates radical reaction.
4. Application Models to Petrochemical Complex

Other Correlation Ways 3/3

“C” Petrochemical Complex and Vicinity

- C2 Oil Refinery
  - (H₂)
  - (Lighter Oil)
  - Heavy Residue Upgrading
  - (Syn.Gas)

- C3 Ethylene Plant
  - (Syn.Gas)

- C4 Enterprises
  - (Electric Power)

“D” Industrial Area and Surroundings

- Petrochemical Complex
  - Heavy Residues
  - Industrial Waste

- Power Company
  - Fuel Oil
  - Coal

- Gasifier Co-Gasifier Upgrading
  - Gas Oil
  - Fuel Hydrogen
  - Industrial Waste
  - Municipal Waste

- Neighboring Areas
  - Municipal Communities

ICFG is dream tool for Gasifier, Co-Gasifier and Upgrading

Still in pilot but would be commercial soon!
5. Development Program

Development Schedule

"Value-Up of Secondary Residues in Petrochemical Complex" will keep developing as per the following schedule:

<table>
<thead>
<tr>
<th>Fiscal Year</th>
<th>2004</th>
<th>2005</th>
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<tbody>
<tr>
<td>Process Development</td>
<td></td>
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</tr>
<tr>
<td>1) Laboratory Test</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2) Pilot Plant Test</td>
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<tr>
<td>3) Feasibility Study</td>
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<tr>
<td>Project Development</td>
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<tr>
<td>1) Application Models</td>
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</tr>
<tr>
<td>2) Project Planning</td>
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<td></td>
</tr>
<tr>
<td>Commercialization</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) 100t/d Plant</td>
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<td></td>
</tr>
<tr>
<td>2) Commercial Plant</td>
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</tbody>
</table>

Themes:
- Gasification of Petrochemical Complex Residues
- Upgrading of Oil Residues in Refinery Plant

Developers:
- Maruzen Petrochemical CO. , Ltd
- EBARA Corporation
- Toyo Engineering Corporation

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See you at GTC 2005!

Thank you for attention.

The above program called "VALUE-UP of SECONDARY RESIDUES in PETROCHEMICAL COMPLEX" is supported by Japan's Ministry Economy, Trade and Industry through New Energy and Industrial Technology Development Organization "NEDO", and is subsidized under the Project of Strategic Development for Energy Conservation Technology.