



"The Key to Residue Upgrading"

Advanced **EUREKA** Process



CHIYODA
CORPORATION

FDC

Introduction

The Eureka process is a commercially proven thermal cracking process to produce valuable cracked oil and aromatic petroleum pitch from heavy residual materials. The etymological meaning of "EUREKA" is "I've found it" -

Archimedes' exclamation when he discovered the principle of buoyancy. The first commercial plant was constructed in Fuji Oil Refinery Complex in Japan and commenced operation in 1976.

The unit has been operated successfully for more than 30 years since then. Accumulated successful operational experiences and continuous engineering developments have resulted in further significant improvements to the process. Two years of continuous operation by controlling

coking have been achieved and more sophisticated and robust design improvements have been implemented using up-to-date technologies such as computational fluid dynamics(CFD) and finite element analysis(FEA). In addition, an energy saving device has been introduced.

Outstanding Environmentally Friendly Process

- Continuous operation in a closed system
- Environmentally clean and healthy plant yard
- Accomplishment of stringent legislative requirements

Molten Pitch & Pitch Flaker

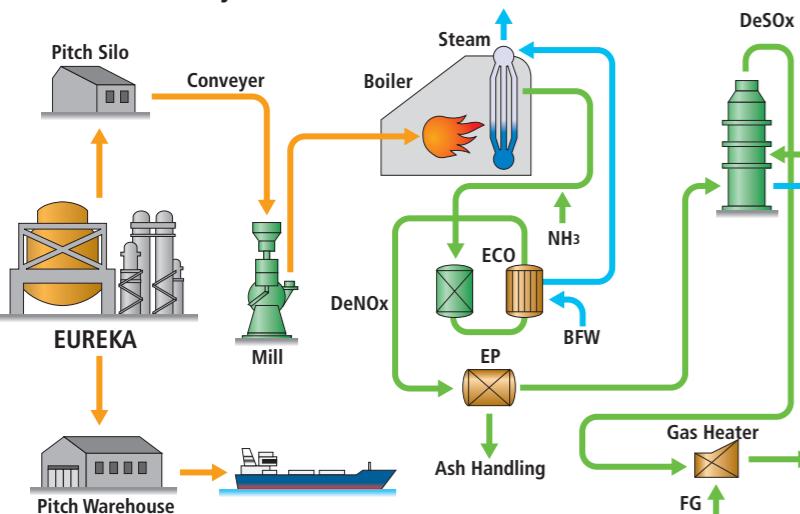


ADVANCED EUREKA PROCESS

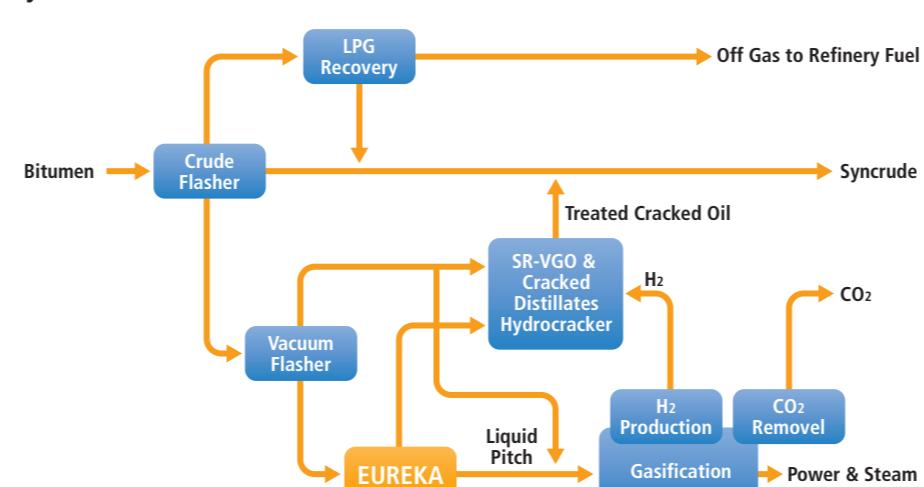
Unique Pitch Utilization

- Binder for metallurgical coke
- Boiler fuel as solid
- Feedstock to gasification as liquid

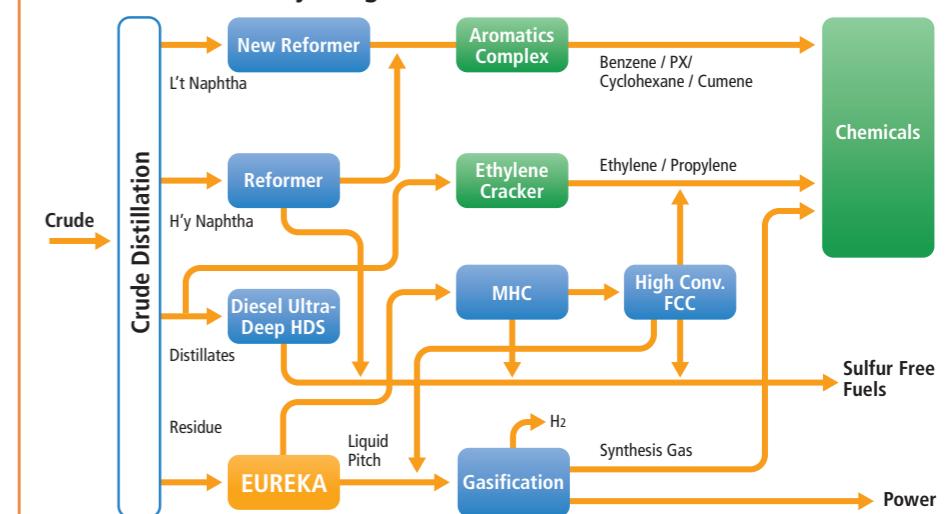
Pitch Combustion System



Syncrude Production Scheme in Combination with Gasification



Chemical and Refinery Integration in Combination with Gasification



Process Description

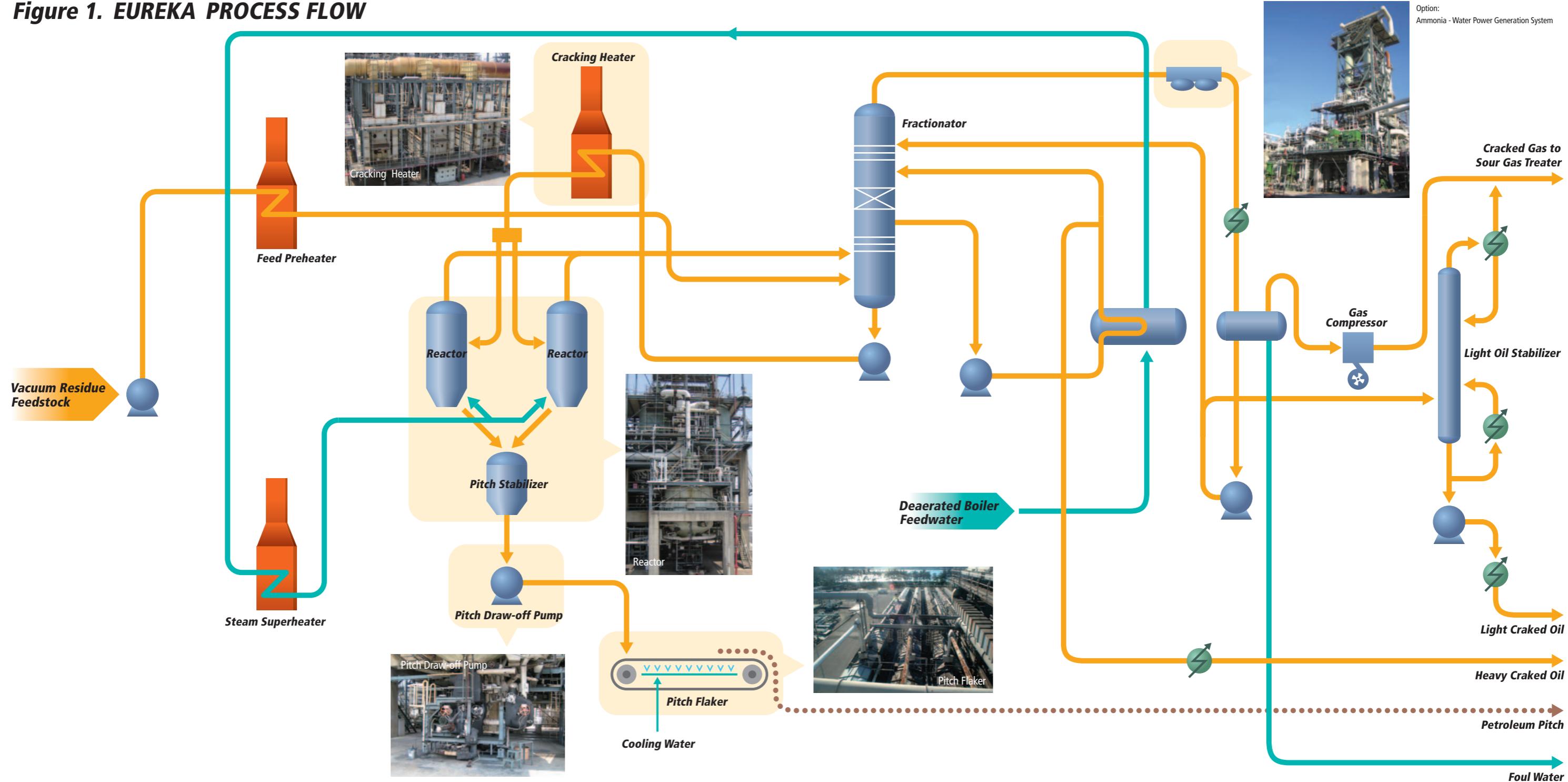
The Eureka plant, using heavy vacuum residue, employs process technology for thermal cracking, cracked oil fractionation, and pitch cooling and flaking. Figure 1 is a simplified Eureka process flow diagram. The feedstock from storage tank is first preheated at the feed preheater, led to the cracking heater via the bottom section of the fractionator and heated to about 490°C.

The effluent from the cracking heater flows into one of the two reactors through an automatically operated switch valve. Thus the reaction in the reactor is carried out semi-batch-wise under operating conditions of 50 – 80kPa(g) and 400°C – 430°C. In the reactor the thermally cracked low-molecular-weight hydrocarbons are stripped by steam and sent to the fractionator.

A simultaneous radical condensation reaction causes the remnant to finally form a petroleum pitch. At the end of the reaction, the pitch remaining in the reactor is quenched then allowed to flow down to the pitch stabilizer. The molten pitch is continuously pumped out from the pitch stabilizer and sent to the pitch flaker where it is cooled and solidified into flakes.

The cracked vapor is fractionated in the fractionator into heavy cracked oil and light cracked oil. A large amount of heat from the reactor is recovered in the form of steam. Cracked gas is compressed and then routed to a sour gas treater. Steam condensate is sent to the foul water treatment facilities.

Figure 1. EUREKA PROCESS FLOW



Performance

Feedstock

Heavy petroleum residue with high asphaltene content is preferably used as a feedstock. Typical properties of the feedstock are shown in Table 1.

Table 1 Typical Feedstock Properties

| Feedstock | Vacuum residue of Middle East crude mixture |
|----------------------------------|---|
| API | 5.4 |
| Specific gravity 15/4°C | 1.033 |
| Conradson carbon residue content | 22.5 wt% |
| Sulfur content | 4.0 wt% |
| Nitrogen content | 0.25 wt% |
| Asphaltene content | 8.0 wt% |

Products

1. Large Yield of Cracked Oils

Products yields from this feedstock are shown in Table 2. The yield of cracked oils is greater than those from other residue thermal cracking processes.

Table 2 Typical Product Yield

| | |
|---|----------|
| H ₂ S gas | 0.7 wt% |
| C ₄ -Cracked gas | 3.6 wt% |
| C ₅ /240°C Cracked light oil | 19.2 wt% |
| 240/540°C Cracked heavy oil | 42.5 wt% |
| Petroleum pitch | 34.0 wt% |

2. Production of Valuable Petroleum Pitch

The most characteristic feature of the Eureka Process is that the thermally cracked remnant is a pitch of an aromatic nature in a molten state during the process and is stable as a solid. Typical pitch properties are shown in Table 3. In the various scenarios described below, there are numerous possibilities for utilization of the pitch.

1) As a binder for metallurgical coke

Steel companies in Japan have been using this pitch to save expensive coking coal since 1976.

2) As a boiler fuel

Single burning of pulverized pitch has been commercialized at the refinery's 130 T/H utility boiler since April 1983. For boiler fuel the typical pitch properties, compared with those of petroleum cokes are listed in Table 4.

3) As a gasifier feedstock

As a gasifier feedstock, the pulverized pitch has already been tested in a commercial plant. The liquid charge is an alternative for more attractive utilization.

Table 3 Typical Properties of Product Pitch

| | |
|-----------------------------|---------|
| Softening point * | 225°C |
| Volatile matter | 40 wt% |
| Solvent insoluble n-Heptane | 76 wt% |
| Benzene | 50 wt% |
| Quinoline | 15 wt% |
| Sulfur content | 5.9 wt% |

* By Ring & Ball method

Table 4 Comparison of Properties of Solid Fuel

| | Eureka | Delayed Coking | Fluid Coking |
|-----------------------------------|---------------|----------------|---------------|
| Volatile matter, wt% | 40 - 50 | 6 - 14 | 4 - 10 |
| Heating value, Kcal/Kg | 8,800 - 9,200 | 7,800 - 8,600 | 7,700 - 8,000 |
| Hardgrove index | 150 - 170 | 50 - 100 | 15 - 20 |
| Fuel Ratio * | < 2 | 5 - 10 | 10 - 20 |
| Req'd fineness, % (200 mesh pass) | Base | More | More |

* Fixed carbon / Volatile matter

3. Product Oil is Easy to Upgrade

The product cracked oil contains only very small amounts of metals, carbon residues and asphaltenes. So it is possible to produce a large amount of low sulfur fuel oil or light distillates from the petroleum residual feedstock by providing downstream hydrodesulfurization, catalytic cracking or hydrocracking. Typical product oil properties are shown in Table 5.

Table 5 Typical Product Oil Properties

| Property | Unit | CLO | CHO |
|----------------|--------|-------|-------|
| ° API | | 47.3 | 20.2 |
| Sulfur | wt% | 1.26 | 2.70 |
| Nitrogen | wt ppm | 260 | 1980 |
| ASTM Dist. IBP | °C | 43 | 218 |
| 95% | °C | 322 | 520 |
| EP | °C | 333 | 549 |
| Br. No. | g/100g | 55 | 18 |
| Diene value | g/100g | 4 | 2 |
| Asphaltene | wt ppm | 25 | 80 |
| Ni | wt ppm | < 0.2 | < 0.2 |
| V | wt ppm | < 0.2 | < 0.2 |

Advances in Technology

Improving Operability and Maintainability (Two Years of Continuous Operation)

Through more than 30 years operation in Fuji Oil Refinery, many challenging improvements to operability and maintainability have been performed. During two years of continuous operation a high availability of around 97% (including planned shutdowns) has been achieved.

Saving Energy and Resources

1. Ammonia-Water Power Generation System

For the purpose of energy saving in the process, the refined Rankin Cycle using ammonia-water was applied in 2005 in Fuji Oil Refinery.

The lower level heat of Eureka fractionator overhead stream (around 110°C), which was originally wasted by cooling with air fin cooler, is now recovered as electric power, by introduction of the system where the design capacity of power generated is 4,000 KW, thus electric power consumption in the Eureka process is almost balanced.

2. Waste Water Recycling System

From the viewpoint of saving resources and global application of the Eureka process, the reduction of waste water is regarded as one of the key issues and therefore a Waste Water Recycling System is being developed. This system consists of the combination of stripping and distillation columns and the steam recovered from the distillation column can be recycled to the reactor through the steam superheater.

The system is not yet applied in the actual unit but will be ready for commercial use with some further development.

Table 6 Utilities Requirement

| | Current | Remarks |
|-----------------------------|--------------|------------|
| Electricity (Kwh / Kl-Feed) | 19.3 | Balance *1 |
| Fuel (GJ / Kl-Feed) | 1.44 | Balance *2 |
| BFW (ton / Kl-Feed) | 0.35 | 0.07 *3 |
| Steam (Kg / Kl-Feed) | -26 (export) | — |

*1 When being applied Ammonia-Water Power Generation System.

*2 When being utilized C4 Cracked Gas generated.

*3 When being applied Waste Water Recycling System.

Enhancing Reliable Design

1. Analysis of bubbling type reactor

The coking issue in the reactor top section and overhead line is caused by the entrained coke precursor in the reactor vapor. For resolving this issue, the liquid droplet behavior in the reactor was analyzed using Computational Fluid Dynamics (CFD).

As the result of this investigation, the amount of steam injected and the layout of steam injection nozzles were optimized so that the control of coking can be limited by suppressing the amount of entrainment.

The new reactors applied with this design concept were installed in 2007 in Fuji Oil Refinery and the performance is under observation.

2. Analysis of thermal stress on reactor support type

The reactor was exposed to conditions of thermal stress because the temperature of the reactor increased from 350°C to 430°C every 3 hrs.

In spite of these circumstances, the Eureka reactors have, up to now, coped extremely well except only for some limited repairs required around the saddles, which originally supported the reactors on the structure. Finite element analysis has now been performed to determine a more robust design for the supports.

Reactors with new type of support were installed in 2007.

3. Analysis of cracking heater

The cracking heater is one of the critical equipment in the Eureka process. From an operability and maintainability point of view a sufficient run length between decoking has to be achieved. To estimate the fouling rate in the tubes, a tubular fouling model was established.

Currently, by using CFD, heat distribution in the cracking heater can be analyzed.

By changing burner distributions and firing states, equalization of heat flux and surface temperature of heating tube can be achieved.

In combination with the coking simulator and firing analysis by CFD the local formation of coke can be prevented.



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