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**DEVELOPMENT OF CATALYTIC CRACKING  
IN JAPAN**

**BY**

**N. NAKAHARA**

**PRESIDENT OF TOA KEMYO K.K.**

## ENCLOSURE (G)

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The study of catalytic cracking of kerosene and gas oil was first started by Ryonosuke KOBAYASHI and the late Haru KAJIMOTO under the direction of Prof. TANAKA of the Imperial Japanese University of TOKYO in 1934. In 1937, Ryonosuke KOBAYASHI, with the assistance of Yuzo KOGA (Ogura Oil Co.) and Tchei TAKAYAMA, (Nippon Soda Co.), continued research work but failed to make much headway as demand for aviation gasoline was not great at that time. In 1938, stimulated by report of the success of the Houdry Process, in U.S.A., KOBAYASHI and WATANABE succeeded in proving that 92 octane gasoline (0.1% lead added) was obtainable by this method. From this time on study of the process was very much encouraged, and KOBAYASHI was sent to America to study the process. Upon his return, more was learned about the progress of the Houdry Process and also the fact that U. O. P. was making headway in this work. The possibility of buying the license was discussed by the Army and Navy, and study of the process was more vigorously continued by Kobayashi Research Laboratory, Ogura Oil, Nippon Soda, the Army and Navy.

In 1939, with the opening of the Army Fuel Institute, Engineers of the Ogura Oil Co., (KOGA, ISHIMARU, ISHIKAWA), designed the first catalytic cracking pilot plant under the direction of Lieut. Col. AKASHI. This plant still exists in the Fuchu Army Fuel Institute. In the fall of 1939 Toa Fuel Co. sent NAKAHARA and KOGA to the U. S. A. to purchase the Houdry patents. Lieut. Col. YANAGI of the Army and Lieut. Comdr. FUJIMOTO of the Navy also went to the U. S. A., with HORIS of the Nippon Gasoline Co., to negotiate for purchase of U. O. P. patents. In the meantime, Toa Fuel Co. (TSUKUDA et al.), confirmed that 92 octane gasoline could be obtained by catalytic cracking. All negotiations for purchase of the patents failed since the Moral Embargo was declared in the U. S. A. about that time. The necessity for completing the process in Japan became imperative and design of commercial scale units began. As a result, the Army started construction of two units in MARIYU, the Navy two units in YOKKAICHI and one in Formosa, and Toa Fuel Co. one unit in NAKAYAMA. Of these, only one unit each was completed by the Army and Navy before termination of the war.

In 1941, orders were given to the oil companies by the War Dept. and Dept. of Commerce regarding the conversion of thermal cracking units. Nippon Oil converted their cracking units at KANSAI and YOKOHAMA to catalytic cracking, and these were in operation before the termination of war. (The Kansai unit was first to be converted and started operating in 1943). Showa Oil converted their Schwartz units to catalytic cracking and started operations before August, 1945. Nippon Soda continued studies at its subsidiary, Koa Oil, but the work was mostly centered on reforming and did not progress very far. One of the two catalytic cracking units in the Army Refinery started operation in the summer of 1943, and one of Navy's Yokkaichi plants also started about the same time. All the Army and Navy units had automatic circulation of gas, oil, air and steam, but the Nippon Oil unit had to be switched by hand. None of these units was equipped with the molten salt, or other method, of absorbing reaction heat.

The difference between the Toa Fuel Co. and Army and Navy units was that in the former the absorption of reaction heat at the time of regeneration of catalyst was effected by means of water vapor. As to the number of the reaction towers, the Army and Navy plants were equipped with three units per one apparatus, or a multiple thereof; i.e. reaction time was equal to regeneration time, while Toa Kenryo had four units or a multiple; i.e., the regeneration time was twice the reaction time. The interior construction of all the reaction towers was similar; i.e., a cylindrical reaction tower equipped with a certain number of perforated longitudinal pipes, some of which were used as oil vapor inlet pipes and others as oil vapor outlet pipes. The oil vapor inlet pipe was a single pipe for the Army and Navy, and a double pipe for Toa Kenryo. (Refer to Figure 1(C)).

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The results of Nippon Oil's test run are shown in Appendix I. The Army obtained a somewhat higher aviation gasoline yield, but the octane value was between 90-91 (0.164 Ethyl Fluid). This was caused mainly by the difference between the automatic and hand worked method of switching circulation, and also due to the fact that in the reaction tower, the holes of the oil vapor inlet nozzle were arranged in uniform pitch in the Nippon Oil design, while in Army design, the holes were arranged in non-uniform pitch with a smaller number towards the base of the reaction tower, thereby causing more uniform distribution of oil vapor in the reaction tower.

The Army installed a pilot plant at FUCHU for research work, and the following points were mainly studied: (1) design of the oil vapor inlet nozzle, (2) catalyst studies: a mixture of active acid clays obtained from the acid clays produced at NISHIKANBARA District, Niigata Prefecture, and in the neighborhood of ITOIGAWA, to which was added a small quantity of chromium oxide, showed good results. "Kanuma" earth, however, was better. In particular, activated "Kanuma" earth had a higher activity after regeneration than when fresh, and its activity was maintained for a longer time. (3) As to the reaction tower, it was clearly shown that over-heating at the time of regeneration could be prevented in a single cylindrical tower having no internal structure, instead of using a tower with cooling tubes, if five times or more of the theoretical quantity of air, required was fed in at the time of regeneration of the catalyst.

Catalytic cracking research studies were also made by the Nippon Oil and the Mitsubishi Oil Companies, but no significant results were reported. One example of Mitsubishi's research work is given in a report presented to the Army, (Refer to Appendix II). The Toa Nenryo Co. studied various catalytic cracking catalysts, the cracking of kerosenes and gas oils produced in the Southern Islands, and also reaction tower design. The data thereon are given in reports listed in Appendix I. The Navy carried on research work independently, details of which were not disclosed.

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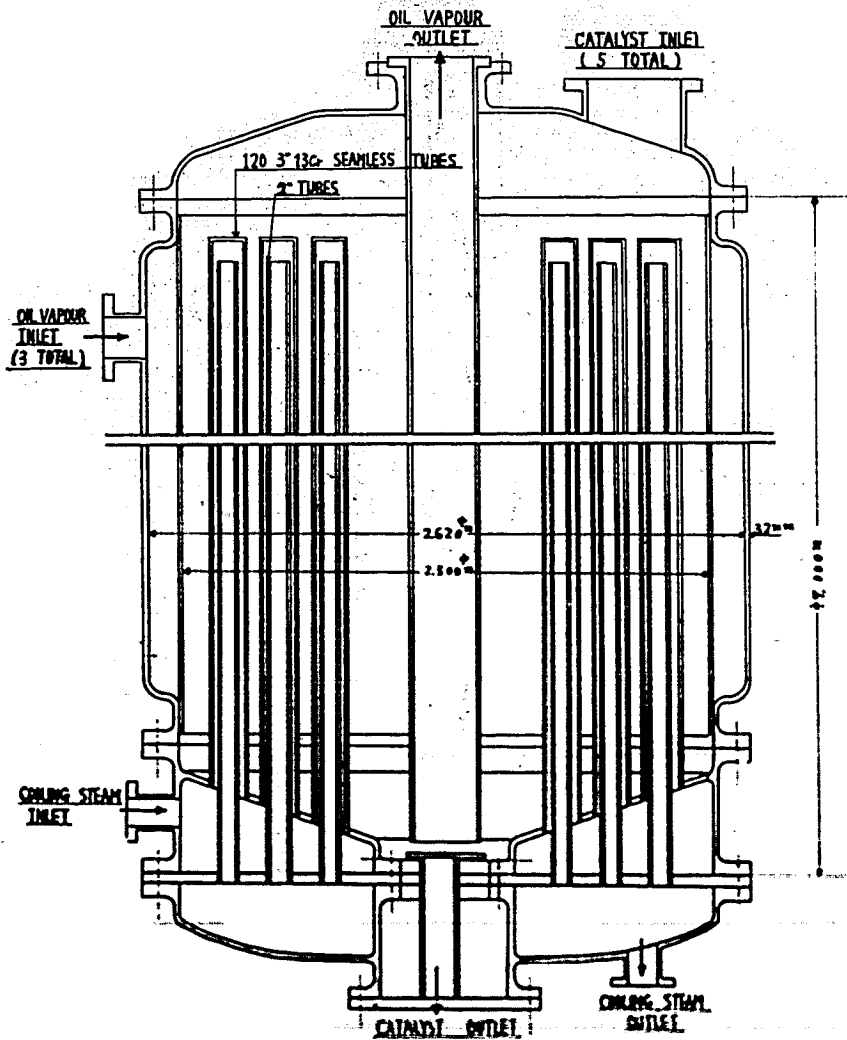


Figure 1 (C)

ROUGH SKETCH OF INNER CONSTRUCTION OF TIA NEARBY TYPE REACTION TOWER

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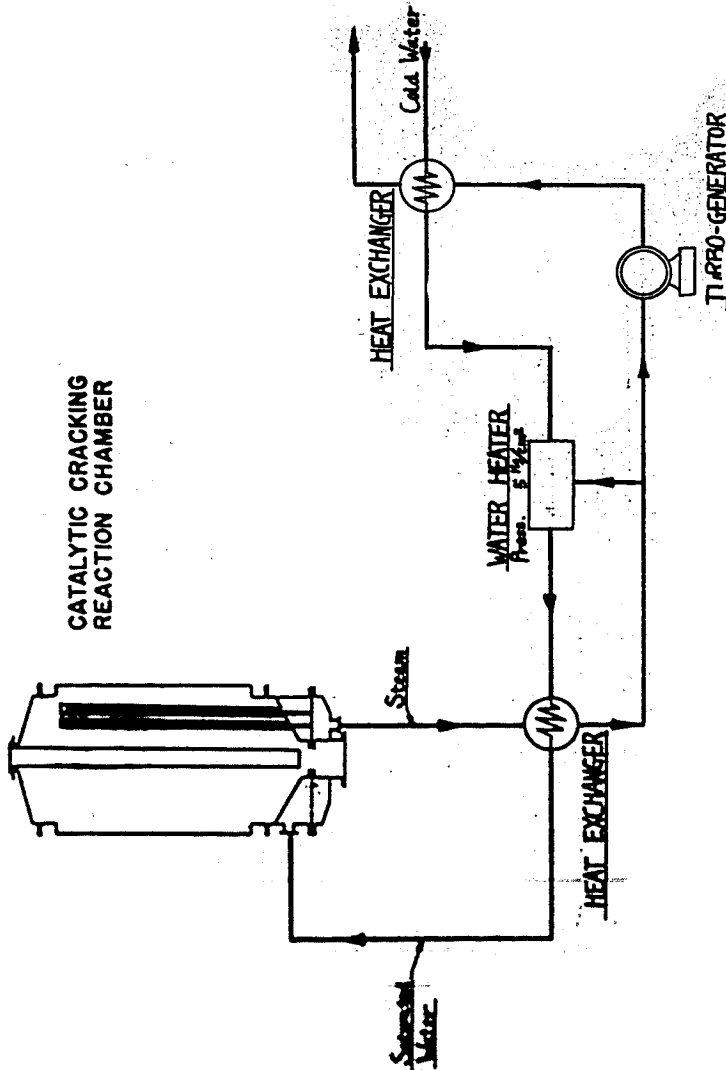


Figure 2 (C)  
FLOW CHART OF COOLING SYSTEM  
TUA NENYO TYPE REACTION CHAMBER

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## APPENDIX I

CATALYTIC CRACKING TESTS OF THE NIPPON OIL CO., LTD.  
28 Nov. 1945

I. The catalytic cracking of kerosene from Sumatra crude was studied on a laboratory scale at the Tsurumi and the Kansai Refineries of the Nippon Oil Co. and at the Tsurumi Refinery on an industrial scale. The Sumatra kerosene had the following inspection:

|                       |       |
|-----------------------|-------|
| Specific gravity..... | 0.828 |
| Distillation          |       |
| IBP.....              | 156°C |
| 10%.....              | 212°C |
| 97%.....              | 270°C |
| Sulphur.....          | 0.03% |
| Unsats.....           | 2%    |
| Aromatics.....        | 12%   |
| Naphthenes.....       | 0%    |
| Paraffins.....        | 86%   |

II. Tests of Japanese Active Acid Clays

The following reaction conditions were used in the tests of the various clays:

|                       |           |
|-----------------------|-----------|
| Vol. of Catalyst..... | 3.6 lit   |
| Oil preheat Temp..... | 460-470°C |
| Cracking Temp.....    | 400-450°C |
| Oil flow.....         | 60 cc/min |
| Space velocity.....   | 1.0       |

Test No.

| Clay                                | "A" from <sup>1</sup> Takeda<br>Clay Co. | "B" from <sup>2</sup> Takeda<br>Clay Co. | "D" from <sup>3</sup> Nippon<br>Clay Co. |
|-------------------------------------|--|--|--|
| <u>Clay Analysis</u>                |  |  |  |
| S. O <sub>2</sub> wt%               | 67.1                                     | 69.8                                     | 68.0                                     |
| Al <sub>2</sub> O <sub>3</sub>      | 19.3                                     | 17.3                                     | 14.1                                     |
| <u>Total Cracked Oil</u>            |  |  |  |
| Yield, %                            | 83.2                                     | 95.0                                     | 87.5                                     |
| S. G.                               | .821                                     | .822                                     | .823                                     |
| <u>Aviation Dist. (below 150°C)</u> |  |  |  |
| Yield, %                            | 10.0                                     | 13.3                                     | 17.3                                     |
| S. G.                               | .755                                     | .761                                     | .755                                     |
| <u>Octane No.</u>                   |  |  |  |
| Clear                               | 77.4                                     | 76.2                                     | 76.4                                     |
| 0.1% lead                           | 89.2                                     | 80.6                                     | 80.4                                     |



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III. Effect of Reaction Conditions

|                          | Test No. |      |      |      |      |      |      |
|--------------------------|----------|------|------|------|------|------|------|
|                          | 1        | 2    | 3    | 4    | 5    | 6    | 7    |
| Takeda Clay              | C        | C    | C    | C    | A+B  | A+B  | A+B  |
| Vol. of Clay, (lit)      | 19       | 19   | 19   | 19   | 19   | 19   | 19   |
| Run length, (hr)         | -        | -    | -    | -    | -    | -    | -    |
| Oil Rate, (cc/min)       | 300      | 250  | 250  | 250  | 240  | 240  | 240  |
| Preheat Temp., (°C)      | 500      | 450  | 440  | 480  | 480  | 450  | 440  |
| React. Temp. (°C)        | 450      | 460  | 460  | 450  | 450  | 450  | 450  |
| Space Velocity           | .95      | .79  | .79  | .79  | .79  | .79  | .79  |
| <u>Cracked Oil</u>       |          |      |      |      |      |      |      |
| Yield (%)                | 97.2     | 99.0 | 99.1 | 99.0 | 94.0 | 97.5 | 99.0 |
| S. G.                    | .821     | .822 | .824 | .826 | .820 | .824 | .818 |
| IBP (°C)                 | 74       | 62   | 67   | 66   | 64   | 52   | 51   |
| F.B.P. (°C)              | 287      | 289  | 280  | 285  | 285  | 287  | 283  |
| <u>Aviation Dist.</u>    |          |      |      |      |      |      |      |
| Yield on Cracked Oil (%) | 10.4     | 10.6 | 10.6 | 10.9 | 12.5 | 9.7  | 14.6 |
| S. G.                    | .766     | .768 | .760 | .763 | .755 | .759 | .745 |
| IBP (°C)                 | 42       | 44   | 40   | 58   | 46   | 48   | 41   |
| 50% pt (°C)              | 123      | 118  | 113  | 122  | 117  | 124  | 117  |
| 95% pt (°C)              | 154      | 148  | 147  | 153  | 151  | 153  | 147  |
| <u>Octane No.</u>        |          |      |      |      |      |      |      |
| Clear                    | 76       | 73   | 75   | 76   | 78   | 77   | 77   |
| 0.1% lead                | 81       | 88   | 89   | 88   | 90   | 90   | 90   |

IV. Treatment for Improving Octane Number

1. Acid Treatment. By treating the aviation gasoline with 2% of 80%  $H_2SO_4$  and 2% of 98%  $H_2SO_4$  aviation gasoline of 91-91.5 (with 0.1% lead) was obtained in yield of 80-82%.

2. Catalytic Treatment. By passing 60 cc/min of cracked oil boiling below 100°C over 3.6 L. of Takeda B or C clay catalyst at a reaction temperature of 330-350°C, an aviation fuel was produced with an octane number of 92.1-92.4 (with 0.1% lead).

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## APPENDIX II

LIST OF PAPERS OBTAINED DEALING WITH  
CATALYTIC CRACKING RESEARCH IN JAPAN

(ATIS No. 4647)

| <u>NavTechJap No.</u> | <u>Title (&amp; Co.)</u>  | <u>Date</u> |
|-----------------------|---|-------------|
| ND26-0032.1           | Result of Catalytic Cracking on Pilot Plant Scale. (Mitsubishi Oil Co.)                       | Oct., 1943. |
| 0032.2                | Catalytic Cracking of Gas Oil Fraction of Palembang Crude. (Toa Fuel Research Lab.)           | Apr., 1943. |
| 0032.3                | Report on the Test Run of Catalytic Cracking (Toa Fuel Ind. Co.)                              | July, 1943. |
| 0032.4                | Catalytic Cracking of Gas Oil from Kettleman Hill Crude (Toa Fuel Research Lab.)              | May, 1942.  |
| 0032.5                | Catalytic Cracking of Gas Oil from Mangunjaja Crude. (Toa Fuel Research Lab.)                 | Apr., 1943. |
| 0032.6                | Catalytic Cracking of Gas Oil from Djambi Crude. (Toa Fuel Research Lab.)                     | June, 1942. |
| 0032.7                | Catalytic Cracking of Gas Oil from Synthetic Oil by Fischer-Tropsch. (Toa Fuel Research Lab.) | June, 1942. |
| 0032.8                | Report on the Result of Test Run of the NNK Unit. (Nippon Oil Co.)                            | Nov., 1943. |
| 0032.9                | Studies on the Catalytic Cracking Reaction Tower. (Toa Fuel Research Lab.)                    |             |