

# Progress Report on the Joint Study for Catalytic Polymerization Unit Improvement in QP Refinery

During fiscal 2013, JCCP implemented the “Joint Study for Catalytic Polymerization Unit Improvement in QP Refinery” with the Mesaieed Refinery, operated by Qatar’s national oil company Qatar Petroleum, and made a proposal for improvement based on the results of the study.

## 1. Background

Qatar is an oil-producing country in the Middle East region with a population of approximately 1.7 million. It exports LNG, crude oil and oil products, and has proven reserves of some 25.9 billion barrels of crude oil, estimated to have a reserves-to-production ratio of around 45 years. Of the roughly 1,569,000 barrels of crude oil that the country produces per day, approximately 28%, or 440,000 barrels/day, is exported to Japan, making Qatar the third-largest supplier of crude oil to Japan, after UAE. With respect to natural gas, Qatar boasts the world’s largest proven reserve. Having production facilities with the capacity to produce more than 93 million tons/year of natural gas, the country has also established deep ties with engineering companies in Japan.

QP’s Mesaieed Refinery consists of three principal

systems: Refinery 1, Refinery 2, and a condensate refinery. The group of crude oil distillation units that comprise the 10,000b/d Refinery 1 were built in 1974, and those comprising Refinery 2 were additionally built in 1984 with a 70,000b/d capacity, along with new downstream facilities. Thereafter, import/export facilities were installed in 1989, and a group of condensate distillation units (condensate refinery) were built in 2001. Moreover, accompanying these facilities, various additions have been made over the years to achieve high efficiency.

To contribute to the Mesaieed Refinery’s initiatives for further development, JCCP has implemented a series of technical cooperation projects with the refinery as its counterpart since fiscal 2004. They have included studies on flare gas reduction technology, studies on LPG recovery efficiency improvement, support for countermeasures against corrosion/fouling, and studies on operational improvement of naphtha hydrodesulfurization units in refineries, among others. Based on the relationship of trust that has evolved continuously through such projects, JCCP has once again agreed to implement the project described below in fiscal 2013, in response a request from QP.



*Presentation at the final debriefing meeting*



*Participants of the final debriefing meeting*

## 2. Overview

- 1) Implementation period: April 2013 – March 2014
- 2) Overseas counterpart: Qatar Petroleum (QP)
- 3) Participating company: Cosmo Engineering Co., Ltd.
- 4) Objective: Operational improvement of the catalytic polymerization unit at the refinery

At QP, gasoline base material and product LPG are produced from light olefins that are generated in the residue fluid catalytic cracking (RFCC) unit. However, the production of LPG with product specifications requires a larger amount of auxiliary feedstock hydrogen for hydrogenation than initially planned. As matters stand, an excessive amount of LPG accompanies the off-gas from the hydrogenation unit that is used in the refinery as fuel gas, and is compromising product LPG yield. Furthermore, the high vapor pressure of product LPG is also posing a problem with their safe and stable storage, and there has thus been a need for operational improvement toward achieving greater LPG yield. In response to this need, JCCP implemented a countermeasure assistance project for operational improvement of the catalytic polymerization unit at QP's Mesaieed Refinery, based on the experience and technologies for operational improvement accumulated by Japan's oil industry. Through this project, JCCP has not only contributed to increasing operational efficiency at the Mesaieed Refinery, but is confident that it has adequately transferred Japan's oil refining technologies and know-how related to operational improvement to Qatar Petroleum.

## 3. Summary

As a result of a survey and examination of operational status conducted jointly with QP, it was found that the catalytic polymerization unit at the Mesaieed Refinery has the following issues.

- (1) To achieve LPG with product specifications in the catalytic polymerization unit, a far larger amount of auxiliary feedstock hydrogen than the design amount was consumed for hydrogenation in the hydrogenation unit.
- (2) The reaction temperature that was set to increase olefin conversion rate in the hydrogenation unit had a smaller margin than the polymerization reaction-causing temperature, so there was concern

regarding the risk of the polymerization reaction deactivating the hydrogenation catalyst.

- (3) Among the auxiliary feedstock hydrogen for hydrogenation mentioned in (1) above, the large amount of hydrogen discharged from the top of the product LPG separator was accompanied by LPG, thereby undermining product LPG yield.
- (4) Exhaust gas was drawn out from the top of the product LPG separator in order to maintain safe LPG vapor pressure in the storage tank, and this also contributed to undermining LPG yield.

The following proposals were made in regard to the above problems.

- (1) Judging by the result of analysis of the hydrogenation catalyst extracted from the hydrogenation unit, the decline in catalyst activity is thought to be caused mainly by catalyst poisoning by chloride compounds.
- (2) It is most likely that the chloride compounds are derived from by-product hydrogen from a continuous regeneration-type catalytic reformer that is the source of hydrogen for hydrogenation, but further efforts should be made to identifying the source of the chloride compounds by implementing an analysis of the feedstock LPG system and hydrogenation system.
- (3) The analysis result mentioned in (1) above also includes sulfur compounds. Although they are not as strongly poisonous to catalysts as chloride compounds, the source of sulfur compounds should also be identified from the perspective of the lifecycle of high-cost hydrogenation catalysts.
- (4) At present, chlorine removal is performed after mixing feedstock LPG and hydrogen for hydrogenation, but there is concern that organic chloride compounds are generated from catalytic action on the chlorine removal adsorbent. Since adsorption treatment by adsorbents becomes difficult once organic chloride compounds are generated, an inquiry should be made with a Chlorine Guard absorbent manufacturer and conversion made to a chlorine adsorbent that does not synthesize organic chlorine.
- (5) As hydrogen-rich gas from a continuous regeneration-type catalytic reformer is also probably used as the source of hydrogen for units such as naphtha, kerosene and diesel oil hydrotreaters, consideration should also be given to

the removal of chloride compounds on the reformer side.

- (6) Even if the activity of hydrogenation catalysts is restored and the amount of hydrogen for hydrogenation is decreased, it would probably still be necessary to maintain a certain amount of hydrogen venting from the top of the product LPG separator to control the product LPG vapor pressure, so any drop in LPG yield caused by the LPG accompanying the vented hydrogen is likely inevitable.
- (7) To curb the drop in LPG yield as mentioned in (6) above, the installation of a fractionating column is recommended in place of a product separation tank.
- (8) In addition to the present vapor-phase hydrogenation, there is also liquid-phase hydrogenation, which has become more prevalent in recent years. From various aspects, the adoption of liquid-phase hydrogenation should also be considered as an option.



*Debriefing session with QP*

A final report was prepared based on the above survey and examination results, and a final debriefing meeting was held with the attendance of members from various departments of the Mesaieed Refinery. The fact that active discussions took place among members from different departments during the presentation could also be interpreted as an indication that the content of the proposals was highly beneficial to QP.

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