



Commercialization of the World's First Oleflex Unit*

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Purposive propylene production via catalytic dehydrogenation of propane on a commercial scale unit was attempted for the first time in early 1990 when the UOP-designed first Oleflex unit went on stream at NPC, Thailand. Prior to that time, propylene was simply a by-product of other processes, i.e. naphtha-based steam cracker and fluid catalytic cracker. The situation in Thailand at that time, with no naphtha-based steam cracker and only a small catalytic cracker in the country, called for a purposive propylene production route to satisfy the demand for propylene. The UOP propane dehydrogenation process was therefore chosen and the Thai Oleflex Unit became the first commercial scale propane dehydrogenation unit. Some problems were encountered during the initial stage of operation. With the joint effort between the UOP support team and NPC technical staff, the problems were resolved to the satisfaction of the owner. The solutions applied included changes and modifications of certain hardware, modification to certain operating conditions, and a change to new versions of catalyst with better performance. In addition, UOP's commitment to improve the stability and selectivity of the Oleflex catalyst resulted in the availability of several new versions of catalyst over the years and NPC has enjoyed the benefits of these improvements. Over some 10 years of operation with over 3,200 days on-stream, NPC has operated on four versions of Oleflex catalyst and has noted improvement of each new version over the previous ones. Five batches of catalyst have been loaded on the unit. Regrettably, in spite of the technical success in operating the unit, the many changes in the economic picture and climate of the country and the region have resulted in the decline of the profitability of the unit. Although the return is well below the expectation, it is still economical to keep the unit in operation. The paper describes the various operating experiences and the performance data of the unit, including the catalyst performance. The catalyst life in general significantly exceeded expectation. The economic performance of the unit over the year is also included.

Key words : commercialization, the World First Oleflex Unit

Propylene has been and still is an important by-product of steam cracking and catalytic cracking operations. In general, propylene demand can be met from these two sources of supply, thanks to the increasing capacity of the two processes. Propylene price for chemical industry use usually follows its value as alkylate feedstock, which is an alternative outlet of propylene in the oil industry. The price of gasoline thus has an important influence on the propylene price in the market. As a result, the propylene price has been kept low most of the time, especially in the United States.

For locations which are short of propylene, such as in the Far East, purposive propylene production via catalytic dehydrogenation of propane can become a viable alternative, subject to the existing economic conditions. This was the case for Thailand in 1985. The discovery of natural gas in the Gulf of Thailand provided the country with ethane and propane (E/P) while the demand for ethylene and propylene was rapidly increasing. A gas-based olefin plant was thus

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planned for the production of 315,000 tons per annum (tpa) of ethylene and 105,000 tpa of propylene. Although an E/P cracker could have been chosen, inadequate availability of propane ruled out this alternative. The propane dehydrogenation route giving a very high propylene yield was the only way to use the valuable propane for producing propylene. Two propane dehydrogenation processes were available for licensing at that time, both with no commercial plant experience. UOP Oleflex process was selected by NPC, and plant construction was completed at the end of 1989. The start-up of the NPC's oleflex in early 1990 marked the first operation of a commercial scale propane dehydrogenation unit in the world.

The Operating Experience

It is quite normal that, in operating a new process with a new design, one has to go through a learning curve to get to the desired target, solving any teething problems along the way. Corrections and modifications are usually unavoidable. This was particularly the case for NPC, which had no previous experience from other plants on which to rely.

The chemical equation for propane dehydrogenation to propylene looks quite simple. However, to put it to work is no simple matter. The severe thermodynamic equilibrium limitation of the reaction pushes the required operat-

ing temperature to a high level coupled with the need for an active and selective catalyst. The high severity of the operation gives rise to several undesirable side reactions, both thermal and catalytic, leading to several forms of coke deposited on catalyst and equipment. Understanding these side reactions is of paramount importance for the success of the process. To take care of the coked catalyst, continuous regeneration is required. The Oleflex unit thus consists of four radial flow moving bed reactors together with the UOP CCR system (Fig. 1). The process set-up is very similar to the world famous UOP CCR Platforming process. However, the high-severity environment (reactor inlet temperatures 650 °C and 1 kg/cm²g reactor outlet pressure) required gave rise to several new unique problems of their own, encompassing mechanical, metallurgical, process and operational aspects.

Fortunately UOP is well equipped with a pool of highly knowledgeable experts well versed in all aspects of the technology, supported by modern research facilities. The UOP support team for the Oleflex operation was of first class quality, particularly in the problem solving area. They worked hand in hand with NPC Technical and Engineering staff and jointly came up with the required solutions in a speedy manner, thanks to the support of both UOP and NPC management as well as the construction contractor,

without which the correction work could not be as effective.

Table 1 lists the major operational highlights of NPC's Oleflex. Several incidents occurred during the first year of operation, requiring immediate correction. Later modifications are for process improvements carried out at properly planned periods. Several lessons have been learned through these experiences. The more important ones will be discussed below.

1. Void blowing January 16, 1990 was the date of the initial start-up of the Oleflex unit and on-grade propylene was produced on January 19. However on Feb. 16, 1990 while the feed rate was 96 per cent of design, the temperature drop across Reactor 2 suddenly decreased and it was not possible to transfer catalyst from Reactor 1 to Reactor 2. Pressure drop across Reactor 3 increased sharply, necessitating unit shut-down. Inspection revealed a reactor screen defect allowing passage of catalyst into the feed inlet area during shutdown. At each re-start the feed pushed back the catalyst chips against the screen partially blinding the screen cumulatively. With less open area for the feed flow, the feed velocity through the catalyst area increased to a point that a void was created in the catalyst bed, blocking the flow of the catalyst. The high velocity attrited and turned catalyst into chips and fines and transported them to the next reactor. Figure 2 shows the catalyst flow through the internal parts

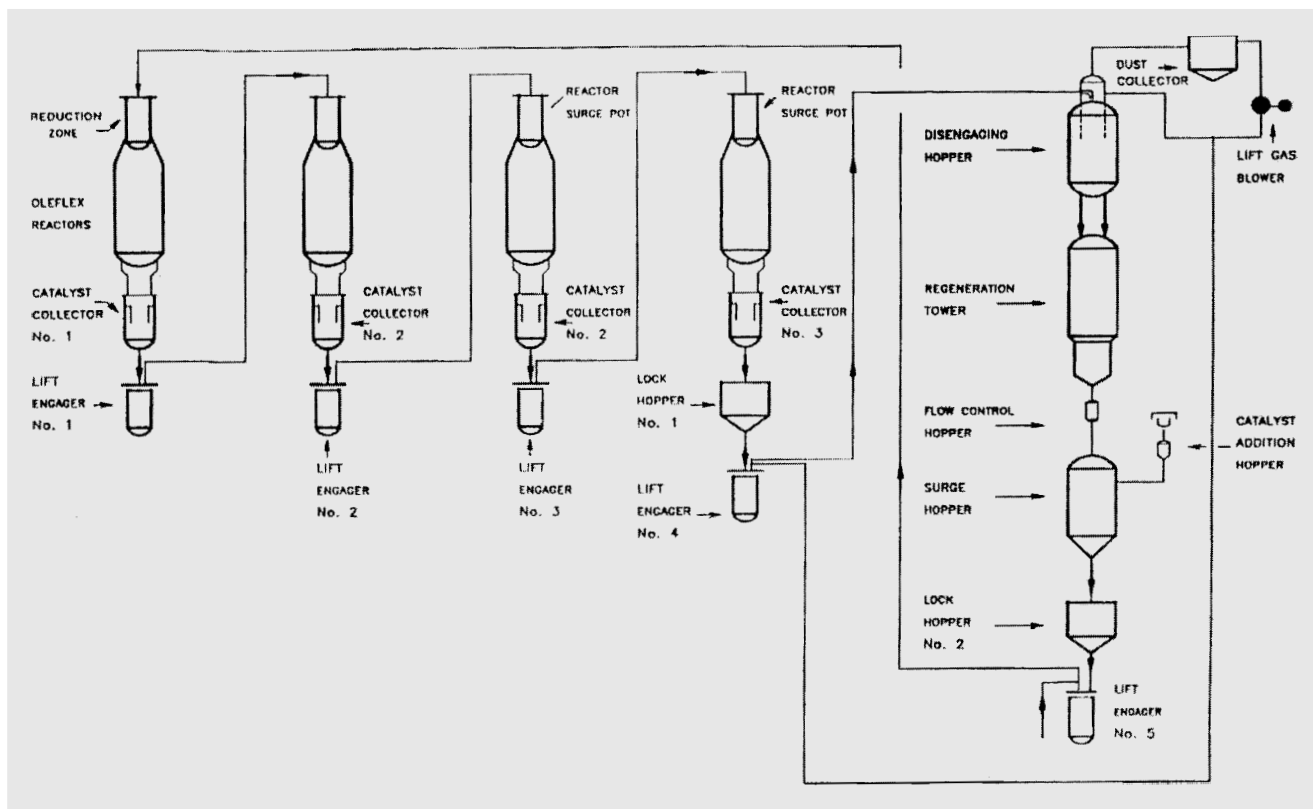


Fig. 1
Oleflex catalyst regeneration section

Table 1 Operational highligh

January 1990	Initial start-up with 1 st batch of DEH-6
February 1990	Void blowing
June 1990	Loss of sulfur injection-coking problem (clean and repair screens)
December 1990	Catalyst deactivation by CO (apply PSA-H ₂ in April 1991)
April 1991	Catalyst change on the fly to DEH-6 2 nd batch
February 1992	Switch to DEH-8 catalyst, install electric heater at surge pot and change screen material to SS 347
May 1993	Replace HCFE
February 1994	Add Rx effluent cooler and replace cold box
January 1995	Catalyst change on the fly to DEH-10
August 1996	Catalyst collector cracked by PTA (material change to 347 in 1997)
April 1998	Change catalyst to DEH-12 after a major turnaround
January 2002	Lastest major turnaround DEH-12 kept in operation

of the reactor. Reactor 3 screen was severely blocked causing excessive pressure drop. The screen defect was probably caused by unknown impact to the spot. After the screen was repaired and the damaged part replaced, the unit was brought back on line. Reactor pressure drop recorders and alarms were installed on all reactors for early detection of impending problems.

2. Coking problems

a) Soot Coke Formation-Loss of Sulfur Injection

Following the Void Blowing problems, the unit was repaired and put back in operation on May 17, 1990. While the unit

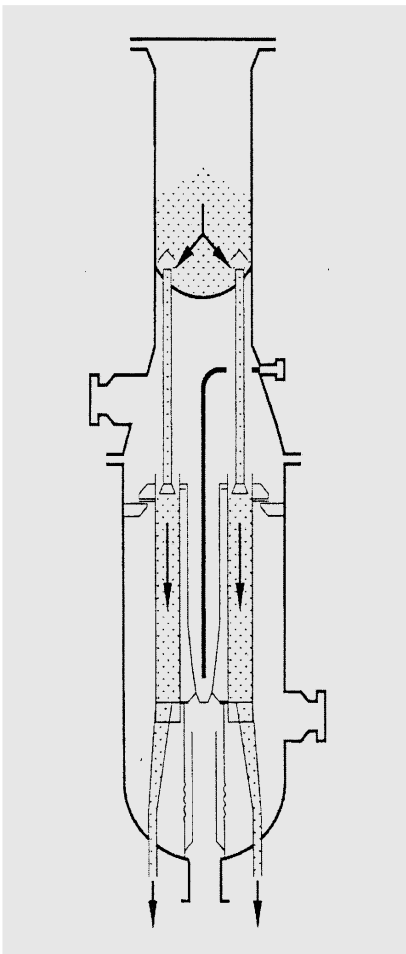


Fig. 2
Catalyst flow

was adjusted to the design level on June 3, 1990 sulfur injection into the feed was interrupted on two separate occasions as a result of blockage of the injection line. The unit remained in operation without sulfur for some four hours each time during the injection line clearing operation. The reactor pressure drop increase was noted and later soot coke was found in catalyst samples. The pressure drop increase was highest in Reactor 3 which finally reached the void blowing zone. The unit was shut

down July 12 for inspection and screen cleaning. Sulfur injection is intended to prevent exposure of the metal surface to Olefin molecules at high temperature by providing iron sulfide film on the surface. Olefin will react with free or open iron molecules, pulling iron out from the wall. Additional olefins continue to add on this coke particle which eventually drops off in rod form. Sulfur injection is therefore extremely important. To ensure uninterrupted sulfur injection a double injection system was installed with a spare. Alternative injection point and low flow alarm were also added.

b) Thermal Coke and Coke Precursors.

In spite of the tight control of the sulfur injection and the disappearance of soot coke in catalyst samples, problems with the reactor pressure drop increase continued, albeit at a much lower rate. It was noted that the presence of even a small amount of C_4 's in the feed also caused a pressure drop increase due to thermal coke and Heavies formation. Olefins also behave the same way as coke precursors. Stricter control of C_4 's and Heavies in feed was thus implemented. Later on the MA-PD converter unit treating the propane recycle stream was switched to complete hydrogenation operation to eliminate any olefins in feed. Positive results were obtained. Notwithstanding the above-mentioned fouling of the reactor screens by coke and Heavies

persisting, more measures are required if a long on-stream time is to be achieved.

3. Metallurgical problems

a) Carburization and Corrosion

During the screen-cleaning shut down in 1990, metallurgical inspection of the entire system was carried out. Carburization and corrosive attack were discovered in several areas, particularly within the reaction zones. The high temperature environment coupled with the severe coke deposition on the metal surface induced these problems. The corrosion was mostly of the under-deposits type. To withstand the reactor environment better, it was believed that the screen material should be changed from SS 304 to SS 347. This was effected in 1992.

b) Thermal Stress and Thermal Cycling

The temperature profile inside the reactor developed thermal stress on metal during operation. With the aid of a computer program, it was discovered that the reactor basket was not strong enough to withstand the thermal stress developed. More stiffening rods were added to strengthen the basket. In addition, it was discovered that the thermal cycling resulting from the transfer of relatively cold catalyst through the hot reactor contributed significantly to the stress problem, particularly at high catalyst circulation rate. Catalyst heat-up zones to increase catalyst temperature before



entering reactor internals were added by installing an electric heater at the surge pot in 1992. In addition, a system for trickle mode operation of the catalyst circulation was provided to limit the catalyst circulation rate during the start-up after a quick shut-down, such as a compressor trip. This is to prevent a hoop stress problem.

4. Polythionic acid attack

Stainless steel is susceptible to polythionic attack. The standard procedure is to neutralize the equipment to remove the acidic sulfide prior to opening to the atmosphere. In the case of equipment heavily fouled by coke deposit as was the case of Oleflex reactor, the standard procedure was not effective since the neutralization solution could not get under the deposit. An additional step had to be added, i.e. hydrogen stripping of the reactor system prior to the neutralization.

5. Impact of Heavies on heat exchangers

Although the amount of Heavies formed in the C₃-Oleflex was much less than the C₄-ones, it was enough to cause problems in the downstream heat exchangers and coolers. For the hot combined feed heat exchangers, coke penetrated the small opening between the tubes and the tubesheet, eventually causing tube leaks. They had to be replaced by new ones with tubes welded to the tube sheet on both sides of the sheet. As for the Reactor Effluent Coolers, fouling by Heavies limited the effective heat exchanger duty.

More cooler surface had to be added.

Catalyst Performance and Development

1. Catalyst deactivation by carbon monoxide (CO) The phenomenon of catalyst deactivation was discovered only a few months after a steady operation of the unit, i.e. December 1990. The catalyst did not readily respond to the process; variable changes and catalyst poisoning was suspected. A rush research program in the UOP lab finally established that the presence of CO in the hydrogen recycle stream used for reducing the metal oxides at the catalyst reduction step was responsible for poisoning the metal function of the catalyst. The presence of CO at the level found in hydrogen recycle gas will not cause any problem in other parts of the reactor system. Arrangement to supply PSA hydrogen to the reduction zone was made during the first quarter of 1991 and the CO-damaged catalyst was subsequently replaced by a new DEH-6 batch in April 1991.

2. DEH-8 Development The new DEH-6 batch, however, did not live up to expectation. The catalyst performance was inadequate and catalyst activity decline was noted in successive months of operation. UOP accelerated their catalyst development program and a reformulated catalyst, DEH-6B, became available early 1992. The catalyst was renamed DEH-8 which

was to become the standard catalyst for all Oleflex units. NPC loaded DEH-8 catalyst into its unit in April 1992. DEH-8 was proven to be a stable catalyst. The catalyst activity decline with time was much slower that had been the case with the other catalysts.

3. DEH-10 development

UOP research, in the meantime, gained more understanding of the platinum/attenuator interaction and the deactivation mechanism. New formulations of catalyst were developed, aiming at the reduction of platinum content as well as those of modifier and attenuator. The low platinum content not only makes the catalyst cheaper, but also reduces the Heavies formation. The first in the series of the new catalysts was DEH-10. At the time of the announcement of the DEH-10 catalyst, the performance of DEH-8 in NPC unit was still satisfactory. NPC, however, studied and followed the progress of DEH-10 used in other units. At the end of 1994 the performance of DEH-8 dropped off rather sharply and DEH-10 was loaded on the fly replacing DEH-8 in January 1995. Normally the operating conditions of the unit at the beginning of run and the end of run are practically the same. The selectivity decline determines the acceptable limit of the catalyst life.

4. DEH-12 development

Further improvement in catalyst formulation resulted in the availability of DEH-12 catalyst with further reduction in platinum and at-



tenuator contents. The development was primarily aimed at the reduction of Heavies formation as well as the increase of on-stream time. The new catalyst was discussed at the 1997 Oleflex conference. Again the performance of the DEH-10 catalyst in the unit was still satisfactory. The switch-over to DEH-12 at NPC was carried out in April 1998 with satisfactory results.

Figures 3, 4, 5 show the performance of DEH-8, DEH-10, and DEH-12 catalyst on the NPC unit. The slower selectivity decline of the newer catalyst version contributed significantly to the longer catalyst life and the improved economics of the operation. The cycle length is not limited by the cata-

lyst activity but by the maximum allowable reactor pressure drop. The current DEH-12 batch has been in service for some three years and it is still in good condition. It is expected that this batch can last 1-2 years longer than had previously been the case.

5. DEH-14 catalyst DEH-14 is the latest version of the newly improved catalyst. UOP revealed this new catalyst at the 2001 Oleflex conference. With the lower attenuator level, the performance targets for DEH-14 are :

- Equivalent initial activity
- Equivalent selectivity
- Higher coking stability
- Higher long-term stability

NPC will have to study the

benefit of the new catalyst for the next catalyst replacement operation. Table 2 summarizes the catalyst composition comparison. UOP will continue to come up with newer catalyst versions.

The Economic Performance of the Unit

In justifying the construction of the Propane Dehydrogenation Unit, the offtaker, which is a polypropylene producer, agreed to pay for the propylene on a cost-plus basis. The total production cost was passed on to the offtaker plus 15 per cent return on investment. This was acceptable in the beginning since the market price of propylene was high and the government put 20 per cent duty on

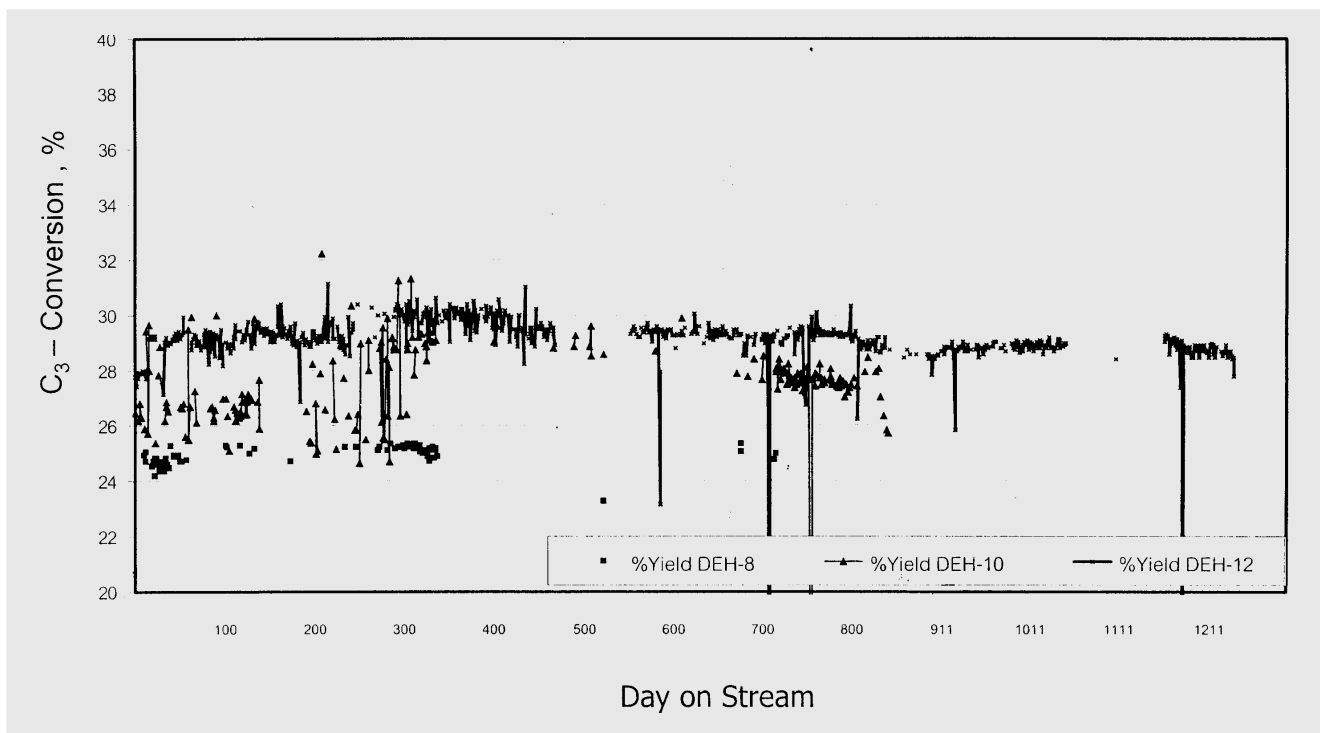


Fig. 3

C₃ propylene yield comparison (%wt.)

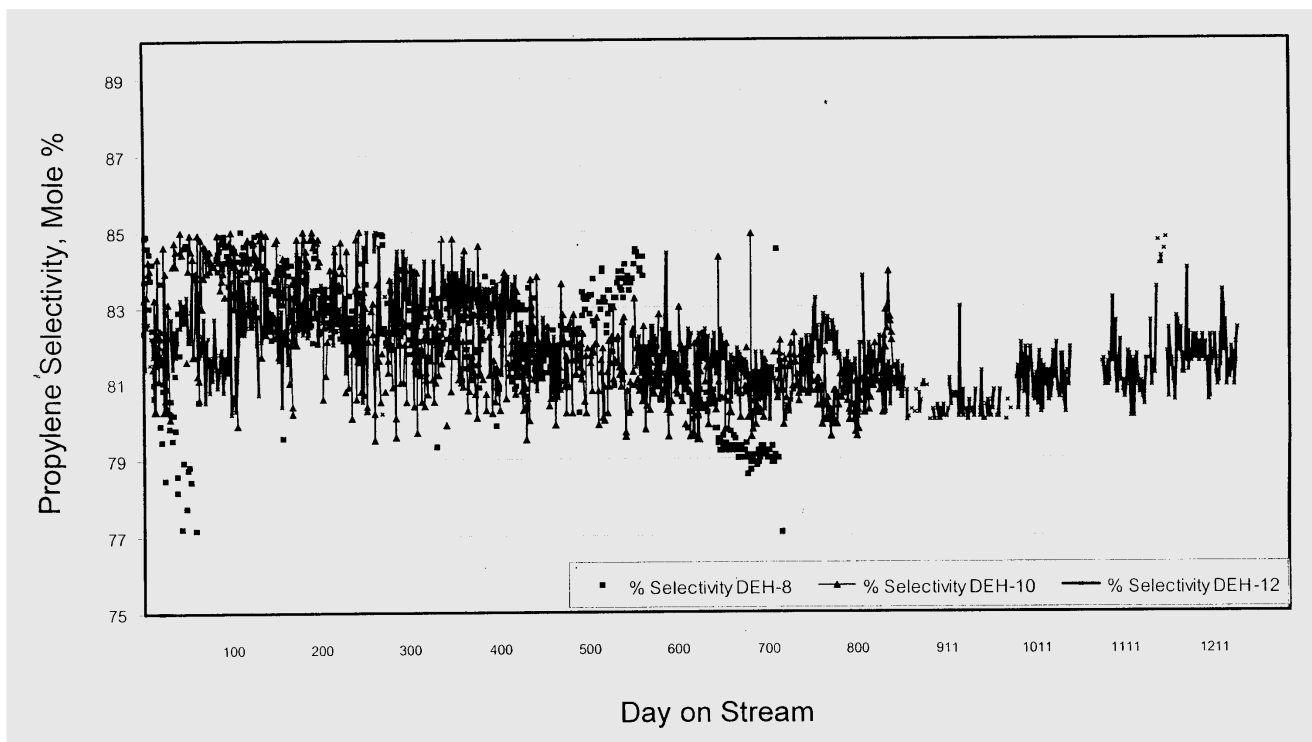


Fig. 4
Propylene selectivity comparison (%wt.)

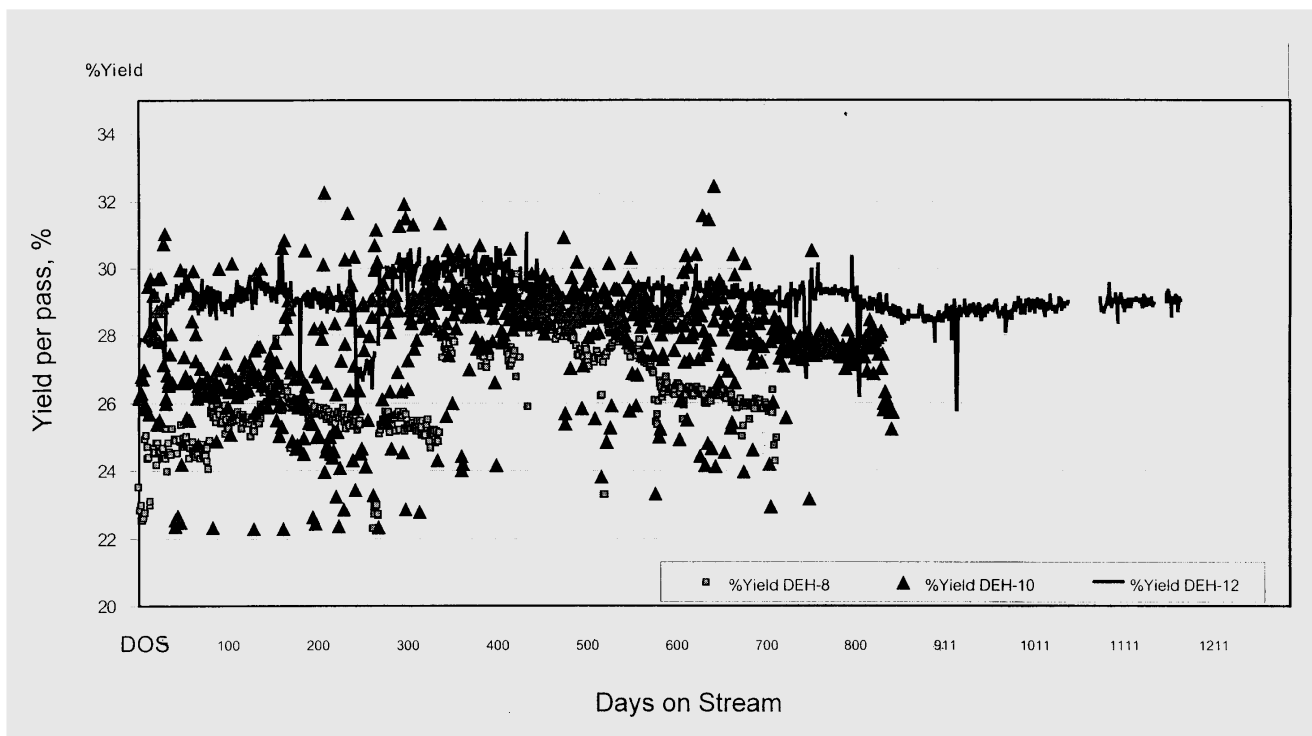


Fig. 5
Propylene yield per pass comparison





Table 2 UOP oleflex catalyst development

	Deh-8	DeH-10	DeH-12	DeH-14
Pt wt%	0.75	0.60	0.45	0.45
Modifier wt%	Base	0.3*Base	0.3*Base	-
Attenuator wt%	Base	Base	0.7*Base	lower than DeH-12

(*UOP do not specify level)

the propylene import. The inefficiency of the initial operation was therefore absorbed by the offtaker who was not at all happy with the deal. When the market price of propylene came down, the cost-plus formula was no longer acceptable and NPC had to agree to a selling price relating to the market prices. As a result, propylene selling price has been coming down. In addition, the duty protection on propylene was lifted. NPC has no leverage and has to compete openly with other producers.

As shown in Figure 6, propylene selling price trends downward while propane feedstock price remains relatively stable, thanks to the co-operation of our feed supplier, PTT, which is also a major share holder. As may be noted the propylene-propane price differential averages at \$277 /ton with the minimum being \$100 /ton. At this level, the total cost can be covered adequately with the exception of the minimum price differential period. Figure 7 shows the relative breakdown of the various costs.

Conclusion

Development of the Oleflex process required a great deal of efforts and only through the commitment and perserverance of UOP could successful operation be achieved. Technology transfer is also very important in commercializing the process and UOP have great success in this aspect, gaining trust from clients. Im-

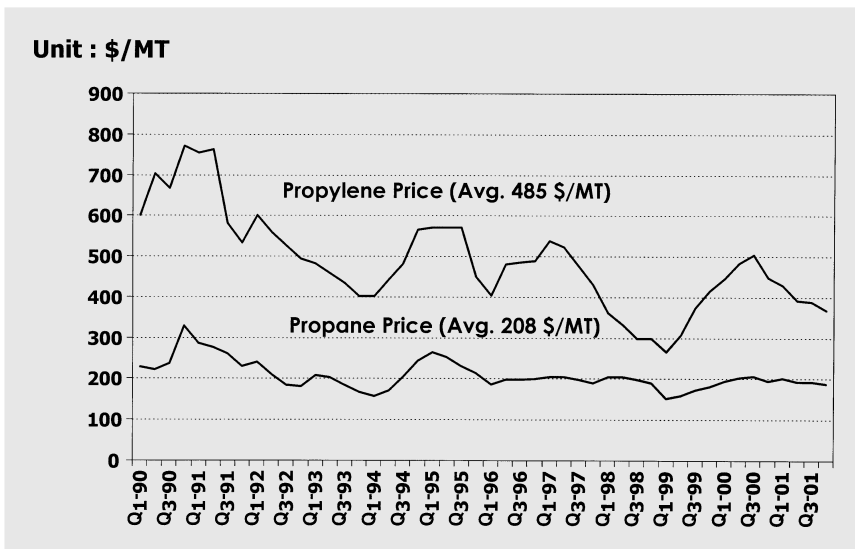


Fig 6
NDC propylene and propane price 1990-2001

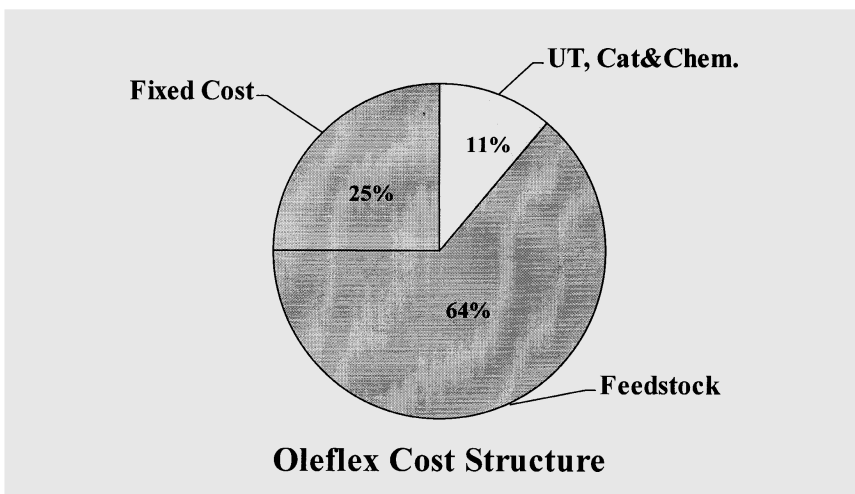


Fig 7
Economic performance (cost of production) 2001



provement of the process is still going on to optimize the operation. The industry will certainly gain the benefits and advances in science will move forwards.

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บทคัดย่อ

การนำโอเลเฟล็กซ์หน่วยแรกของโลกเข้าใช้งานในเชิงพาณิชย์
ปราโมทย์ ไชยเวช

ภาควิชาเคมี สำนักวิทยาศาสตร์ ราชบัณฑิตยสถาน

การผลิตโพรพิลีนจากโพรเพนโดยวิธีคาตาลิติกดีไฮโดรจีเนชันในเชิงพาณิชย์ได้เริ่มขึ้นเป็นครั้งแรกในประเทศไทยเมื่อต้นปี พ.ศ. ๒๕๓๓ ที่บริษัท ปิโตรเคมีแห่งชาติ จำกัด (มหาชน) โดยใช้หน่วยโอเลเฟล็กซ์หน่วยแรกที่ได้รับการออกแบบโดยบริษัท ยูโอพี. ก่อนหน้านั้นโพรพิลีนเป็นเพียงผลพลอยได้จากกระบวนการอื่น, กล่าวคือ กระบวนการเนฟธาแครกเกอร์และกระบวนการฟลูอิดคาตาลิติกแครกเกอร์. โดยที่ขณะนั้นประเทศไทยยังไม่มีเนฟธาแครกเกอร์ และมีหน่วยฟลูอิดคาตาลิติกแครกเกอร์ขนาดเล็กอยู่เท่านั้น. เมื่อมีความต้องการโพรพิลีน จึงต้องหาวิธีใหม่ที่ผลิตโพรพิลีนโดยตรง โดยเลือกใช้วิธีดีไฮโดรจีเนตโพรเพนของบริษัทยูโอพี. หน่วยโอเลเฟล็กซ์ของไทยจึงเป็นหน่วยดีไฮโดรจีเนตโพรเพนเชิงพาณิชย์แห่งแรก. เมื่อเริ่มเดินเครื่องได้ประสบปัญหาต่างๆ, หน่วยงานทางเทคนิคของยูโอพีและของบริษัทปิโตรเคมีแห่งชาติ ได้ร่วมกันแก้ปัญหาจนได้ผลเป็นที่น่าพอใจ. การแก้ปัญหาต้องใช้วิธีเปลี่ยนและแก้ไขอุปกรณ์ต่างๆ, แก้ไขวิธีการและสภาวะการเดินเครื่อง, และเปลี่ยนใช้คาตาลิสต์แบบใหม่ๆ ที่ทำงานได้ดีขึ้น. การที่ยูโอพีได้สัญญาว่าจะมุ่งมั่นในการแก้ไขคาตาลิสต์ของหน่วยโอเลเฟล็กซ์ให้มีความคงทนและมีประสิทธิภาพสูงขึ้น ทำให้มีคาตาลิสต์ประเภทใหม่ ๆ ออกมาเรื่อยๆ และบริษัทปิโตรเคมีฯ ได้รับผลประโยชน์จากการนี้ตลอดมา. ในการเดินเครื่องมาเป็นระยะเวลากว่าสิบปี ใช้เวลาในการผลิตกว่า ๓,๒๐๐ วัน บริษัทปิโตรเคมีฯ ได้เปลี่ยนคาตาลิสต์ไป ๔ สูตร ซึ่งสูตรใหม่ได้ผลดีกว่าสูตรเดิมทุกครั้งที่ทำกาเปลี่ยน, โดยทั้งสิ้นได้เปลี่ยนคาตาลิสต์ไป ๕ ครั้ง. เป็นที่น่าเสียดายที่ แม้จะได้รับความสำเร็จต่างๆ ในด้านเทคนิค ผลกำไรจากการผลิตกลับลดลง. ทั้งนี้เพราะสภาพทางเศรษฐกิจของประเทศและของภูมิภาคได้เปลี่ยนแปลงไปหลายประการ แม้ผลประโยชน์จะน้อยกว่าที่คาดหวังไว้มาก แต่ก็ยังคุ้มทุนเพียงพอที่จะผลิตต่อไป. ในบทความนี้ได้กล่าวถึงประสบการณ์ต่างๆ, ข้อมูลผลการปฏิบัติการ รวมทั้งประสิทธิภาพของคาตาลิสต์. โดยทั่วไปอายุของคาตาลิสต์จะยืนยาวกว่าที่คาดการณ์ไว้ ผลการประกอบการทางเศรษฐศาสตร์ในช่วงปีต่างๆ ก็รวมอยู่ด้วย.

คำสำคัญ : โอเลเฟล็กซ์, เชิงพาณิชย์