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Propane Dehydrogenation in a Modified Porous Membrane Reactor for Producing Propylene with Chemical and Polymer Grades

Azis Trianto
Yazid Bindar
Noezran
Department of Chemical Engineering
Institut Teknologi Bandung
Jl. Ganesa 10 Bandung 40132 Indonesia
Email: trianto@che.itb.ac.id

Propane dehydrogenation is a promising route for producing propylene to replace traditional cracking methods. A membrane reactor offers a possibility to produce not only chemical grade but also polymer grade of propylene. The purpose of the present study is to evaluate the performance of a Modified Porous Membrane Reactor (MPMR) in producing these two propylene grades simultaneously. The study involves evaluations based on thermodynamics and process flow sheeting. The performance of this reactor is compared to that of conventional reactor. At first, the thermodynamics is conducted using minimum Gibb's Energy approach. Then the process flow sheeting evaluation is built using the HYSYS simulator. The effect of inert gas (steam) concentration in both sweep and feed sides is investigated. The thermodynamics study results optimum temperature and inert gas concentration to obtain these two grades of propylene simultaneously. The propylene with polymer grade above 99% is produced from the sweep side outlet. The propylene with chemical grade is produced from the feed side outlet. The simultaneous production of these two grades of propylene has benefit in vanishing propane–propylene splitter.

Keywords: Membrane reactor, porous membrane, propane dehydrogenation, propylene production, *and* process simulation.

INTRODUCTION

The increasing value of polypropylene as a versatile polymer is one of the major influences to the change of propylene price, since the polypropylene productions use over half of the global propylene consumptions (Welrauch 1999). International Chemical Information Conference (ICIC) forecasts the rise on propylene demand and production capacity for regional and international markets until 2003 as given in the Table 1 (2001).

Global and national projections for propylene production give the increased in production quantity. There are several routes of propylene production. One of these routes is catalytic dehydrogenation of propane. This process has been commercialized by UOP as UOP Oleflex Process. This process produces propylene with polymer grade or chemical grade. This catalytic dehydrogenation of propane process has several problems with the major problem encountered in separation duty of propylene rectifying column,

Table 1. Propylene Demand and Production Capacity (ICIC 2001)

	Percentage of Increase	
	Demand	Production Capacity
World	4.6	3.3
Asia	5.9	4.5
North America	4.1	2.5
ASEAN	12.0	8.9
Western Europe	3.1	2.7
China	9.5	6.4
India	29.3	27.1
South Korea	4.9	1.8

or better known as propane-propylene splitter column. Propylene with high purity production needs large separation duty. Furthermore, since the boiling point of propane and propylene is very close, the column must have a lot of stages.

Various methods have been proposed to solve the problem propane-propylene splitter (Cheng 2001, Cheng 2001, Cottrell 2001). However, they could not reduce the propane-propylene separation duty significantly. This gives opportunity for other methods with various approaches.

Propane dehydrogenation is an endothermic and equilibrium reaction. High conversion for this type of reaction can be achieved with high operating temperature and low hydrogen partial pressure. If hydrogen as reaction product is separated as fast as possible inside the reactor continually, the partial pressure of hydrogen will decrease and larger conversion will be achieved.

A membrane can be used to separate hydrogen because of its chemical properties or its small pore size. Reactor that uses the membrane wall inside is called as membrane reactor. In a membrane reactor, hydrogen diffuses through the wall from the catalyst zone. Wood introduces this method in 1968 to improve the yield of cyclohexane dehydrogenation (Wood 1968). Thenceforth, many efforts have been done to further develop the membrane reactor technology. The motivation of those efforts is to achieve high conversion with modification of various parameters.

Trianto and Kokugan in 1999 gave a new modification of the membrane reactor with high performance for dehydrogenation reaction. They called the reactor as Modified Porous Membrane Reactor (MPMR) (Trianto 1999, Trianto 2001). MPMR is sa new configuration of membrane reactor where the reaction took places in both sides of membrane reactor, i.e. the sweep side and the feed side. The difference between the Conventional Porous Membrane Reactor (CPMR) and MPMR is schematically described in Fig. 1. This MPMR can give higher conversion than CPMR due to the reactant permeation or reactant loss problem that occurs in CPMR (Trianto 2001, Kokugan 2001).

This present assessment suggests that MPMR is able produce propylene from propane by dehydrogenation reaction with polymer and chemical grades simultaneously. The schematic description of the suggested process system is in Figure 2. This assessment also evaluates the performance of a model MPMR process system and compares it to a model of UOP Oleflex process system.

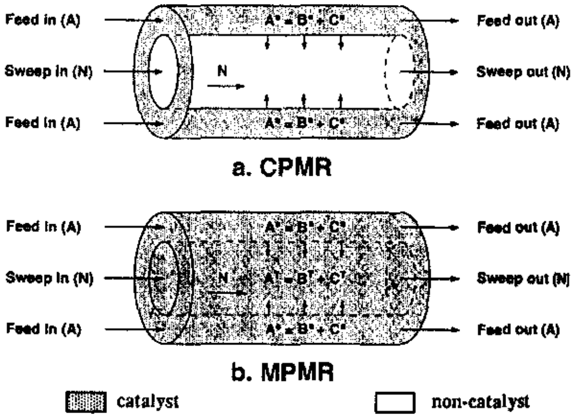

Figure 1. CMPR and MPMR Diagram

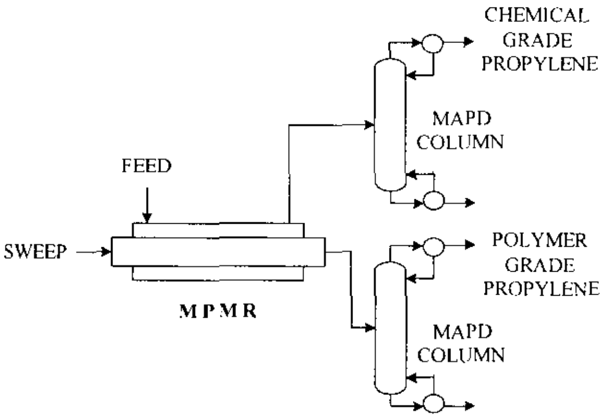

Figure 2. MPMR Process System

METHOD OF EVALUATION

The present assessment performs evaluation in two phases. The first phase is thermodynamics evaluation of propane dehydrogenation. The results of this evaluation is an optimum operating condition such as operating temperature at atmospheric condition and inert concentration which give the highest conversion. The second step is evaluation of several scenarios of process systems. These process systems are built based on thermodynamics evaluation results. The evaluation of these scenarios will result an optimum scenario for the production of propylene with high purity and minimum consumption of feed energy.

Thermodynamic evaluation of propane dehydrogenation is carried out using minimizing method of Gibb's energy change due to temperature change. The pressure is constant and is held at atmospheric condition. The relation can be written as:

$$\frac{d\left(\Delta G^o / RT\right)}{dT} = \frac{-\Delta H^o}{RT^2} \qquad (1)$$

Reaction equilibrium constant K correlates with temperature and Gibb's energy as described in:

$$\frac{\Delta G^o}{RT} = -\ln K \qquad (2)$$

The change of reaction equilibrium constant affects the change of reaction conversion. Therefore, the evaluation investigates the relation between the change of reaction conversion and the change of temperature. Thermodynamic evaluation is conducted at temperature range of 0°C-1000°C. Thermodynamic evaluation is also made to investigate the effect of inert concentration, i.e. steam in this study, to the reaction conversion and propylene production. The evaluation uses ratios of steam/propane at 0, 1, 5, 10, and 50.

Two scenarios of process systems were built based on the thermodynamic evaluation results. First scenario is a process system that produces propylene using the MPMR. Performance of this process system scenario is compared with the second scenario, i.e. a process system that produces propylene using a model of UOP Oleflex Process. The evaluation of these scenarios is tested at product basis of 100 kmole/hr polymer grade propylene and 1000 kmole/ hr chemical grade propylene. Both scenarios use pure propane as reactant and steam as inert for reactor feed. The operating temperature and steam concentration for both scenarios is defined from thermodynamics evaluation results. The effect of hydrogen separation inside MPMR is neglected.

The comparison between both scenarios is conducted for various operating variables such as: consumption of propane, consumption of steam, consumption of energy, and hydrogen production. For all evaluations carried out in this study, the products of propane dehydrogenation are assumed to be propylene, propadiene, methyl acetylene, and hydrogen.

RESULTS AND DISCUSSION

The thermodynamic evaluation at isothermal condition shows that level of propane conversion increases as the temperature increases. However, there is an optimum temperature at which propylene production reaches a maximum. Figure 3 shows propane dehydrogenation conversion, propylene production, methyl acetylene production, and propadiene production as a function of temperature. As shown in Figure 3, the optimum temperature for propylene production is obtained at temperature around 800 °C. Due to this reason, temperature of 800 °C is selected as the operating condition for the second phase evaluation.

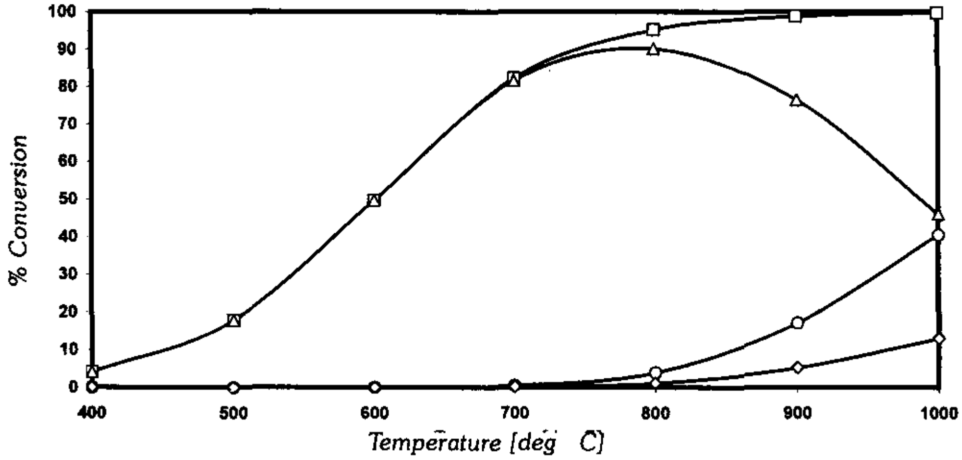

Figure 3. Effect of Temperature on Propane Conversion, Propylene, Methyl Acetylene, and Propadiene Productions

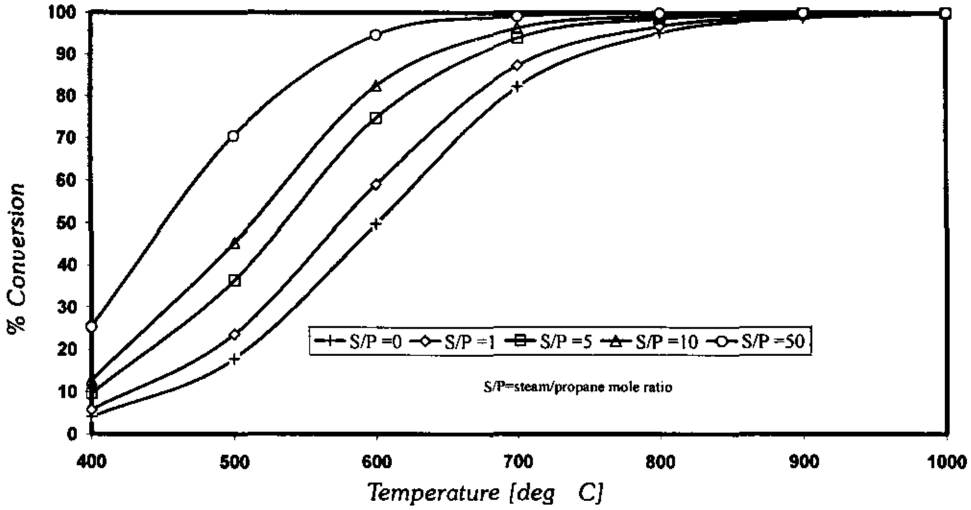

Figure 4. Effect of Steam/Propane Mole Ration on Propane Conversion

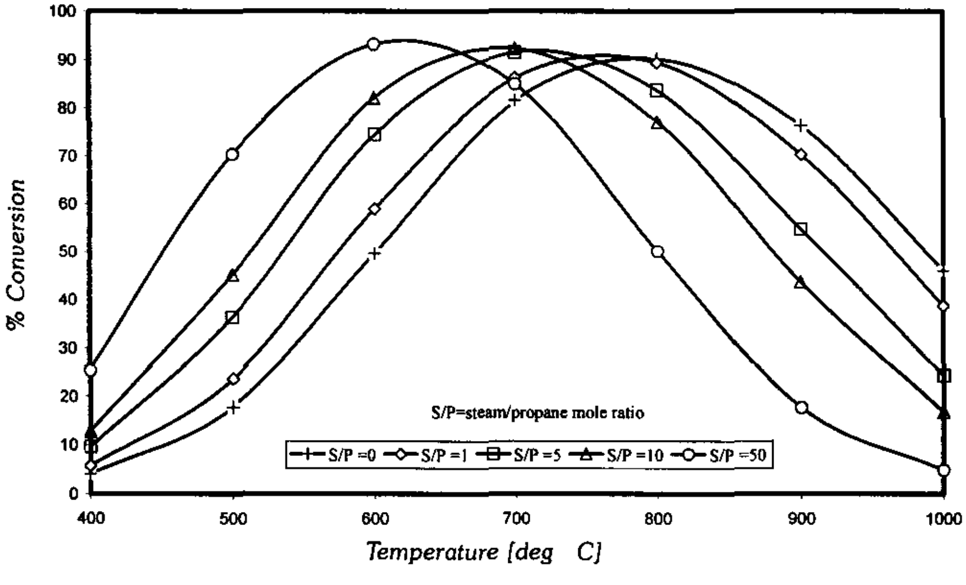

Figure 5. Effect of Steam/Propane Mole Ratio on Propylene Production

Table 2. Value of Comparison Variables for Production Polymer Grade Propylene

Variables	MPMR-Sweep (Polymer Grade)	UOP (Polymer Grade)
Feed Consumption		
Propane (kg/hr)	6875	4900
H_2O (kg/hr)	126390	-
Feed Preheating Energy Consumption (kJ/hr)	1.3×10^7	8.0×10^5
Reactor Energy Consumption (kJ/hr)	2.0×10^7	1.3×10^7
H_2O Separation Energy Consumption (kJ/hr)	-	-
H_2 Production (kg/hr)	425	215
H_2 Separation Energy Consumption (kJ/hr)	3.9×10^6	3.5×10^6
MAPD Separation Energy Consumption (kJ/hr)	7.0×10^5	-
MAPD Column Stages	57	-
Propane-Propylene Splitter Energy Consumption (kJ/hr)	-	1.5×10^7
Propane-Propylene Splitter Stages	-	183

Table 3. Value of Comparison Variables for Production Chemical Grade Propylene

Variables	MPMR-Sweep (Polymer Grade)	UOP (Polymer Grade)
Feed Consumption		
Propane (kg/hr)	48526	49266
H_2O (kg/hr)	26168	-
Feed Preheating Energy Consumption (kJ/hr)	1.3×10^7	1.0×10^7
Reactor Energy Consumption (kJ/hr)	1.3×10^8	1.3×10^8
H_2O Separation Energy Consumption (kJ/hr)	-	-
H_2 Production (kg/hr)	2194	2124
H_2 Separation Energy Consumption (kJ/hr)	3.7×10^7	3.6×10^7
MAPD Separation Energy Consumption (kJ/hr)	1.8×10^7	-
MAPD Column Stages	50	-
Propane-Propylene Splitter Energy Consumption (kJ/hr)	-	7.4×10^7
Propane-Propylene Splitter Stages	-	156

Figure 4 shows the effect of steam to propane ratio towards the propane conversion. The result shows that high level of propane conversion can be achieved at lower temperature at high steam/propane mole ratio. This can be understood since propane dehydrogenation is a decomposition reaction, so the presence of inert will shift the reaction to the product side.

Figure 5 shows effect of steam/propane mole ratio towards the propylene production. It can also be seen in this figure that high level of propylene production can be achieved at lower temperature using large steam/propane ratio. However, propylene production decreases at a certain point of temperature at each steam/propane ratio as the side reactions that produce methyl acetylene and propadiene begin to occur.

Temperature of 800°C and atmospheric pressure will be used as the operating conditions at certain ratio of steam/propane for second phase evaluation. The reason for selecting operating temperature has been described previously. Meanwhile the sweep/feed mole ratio in MPMR (see Figure 2) is fixed to be 6.73. In this case sweep is steam, while feed is propane. The selection of such value is based *on several considerations such as optimum steam consumption, high level of propane conversion, high level of propylene production, and minimum productions of methyl acetylene and propadiene (MAPD).*

Both scenarios, MPMR scenario and UOP scenario, are configured to produce both of propylene with polymer and chemical grade simultaneously. The configuration of the MPMR is modeled as split plug flow reactor; the first reactor represents the sweep side of MPMR for producing polymer grade propylene and the second one represents the feed side of MPMR for producing chemical grade propylene. The scenario of UOP process system is modeled the same as that of MPMR. The schematic description of both scenarios is shown in Figures 6 and 7. The difference between both scenarios is feed component. Feed components for MPMR scenario (feed) are propane and steam, while feed component for UOP scenario is propane only.

The reactant permeation or propane permeation from feed side through membrane wall represents propane feed to the sweep side of MPMR. The fraction of propane permeation is assumed to be 0.12 of the total propane feed, while its value for steam permeation is assumed to be 0.17. These values were based on experimental results using Vycor glass membrane (Silalahi 2003).

The evaluation of those process system scenarios were conducted using HYSYS ver. 2.4.1 process simulator. Tables 2 and 3 show the comparison of variables.

CONCLUSIONS

A study on propane dehydrogenation for producing propylene with polymer and chemical grades simultaneously in Modified Membrane Porous Reactor has been carried out. It is observed that the reaction can be conducted thermodynamically at atmospheric pressure, at 800°C with a certain steam/propane ratio. Propylene with polymer grade is produced at the

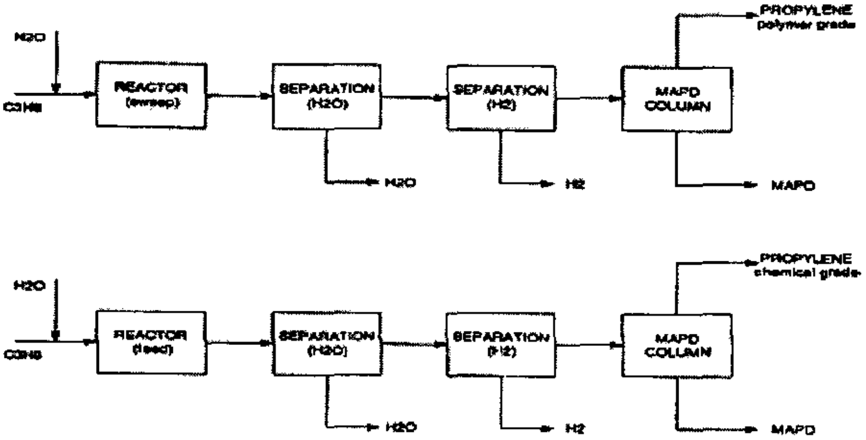

Figure 6. MPMR Process System Scenario

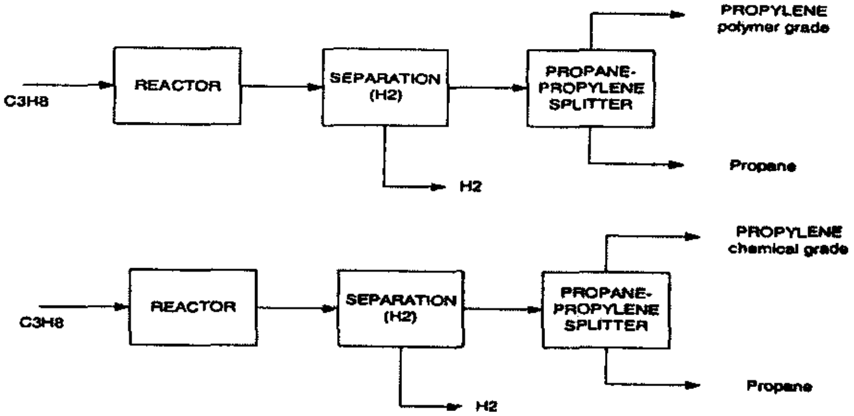

Figure 7. UOP Process System Scenario

sweep side outlet and propylene with chemical grade is produced at the feed side outlet of the MPMR. As shown above, for producing both propylene grades, the MPMR process system feed consumption is larger than UOP process system. MPMR process system produces hydrogen greater than UOP Process system. For producing polymer grade propylene, the energy consumption MPMR process system is larger than UOP, but in producing chemical grade propylene, MPMR uses less energy than UOP. Therefore, the overall energy consumption used by MPMR for producing polymer and chemical grades of propylene simultaneously is less than the UOP process system. MPMR process system does not use propane–propylene splitter, because both of reactor products have small quantity of unconverted propane, which meets both of the commercial product specifications, 0.05% wt. for polymer grade propylene and 0.5% wt for chemical grade propylene. MPMR only requires MAPD column for methyl acetylene and propadiene separation that need less stages than propane–propylene splitter.

NOMENCLATURE

DG^o	standard Gibb's energy change, $J\ mole^{-1}$
DH^o	standard enthalpy change, $J\ mole^{-1}$
K	reaction equilibrium constant
R	ideal gas constant, $8.314\ J\ mol^{-1}\ K^{-1}$
T	temperature, K

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