

A Comparative Study between Propane Dehydrogenation (PDH) Technologies and Plants in Saudi Arabia

Hisham A. Maddah*

Department of Chemical Engineering, King Abdulaziz University, Rabigh, Saudi Arabia

Email: hmaddah@kau.edu.sa

Abstract

Propane dehydrogenation (PDH) is a promising catalytic technology utilized for the conversion of propane into propylene which is involved in many petrochemical applications. A comparison between current PDH plants and technologies (CATOFIN and OLEFLEX) in Saudi Arabia was discussed to analyze propylene production capacity, reactor type/configuration, reaction catalyst, operating conditions, performance, advantages, disadvantages and other design specifications/considerations of PDH technologies. CATOFIN and OLEFLEX chemical processes have been critically reviewed and explained for better understanding. CATOFIN uses chromium-oxide catalysts in horizontal fixed-bed parallel reactors, while OLEFLEX uses platinum catalysts in vertical moving-bed series reactors. There are four PDH plants in Saudi Arabia: NATPET and Al-Waha (CATOFIN plants), APC and SPC (OLEFLEX plants); with a propylene production capacity of 420, 450, 455 and 455 KTA, respectively. Both technologies have a similar operating temperature of > 600 °C, operating pressure of ~ 1 bar; and propylene selectivity of $\sim 90\%$. Propane/propylene conversions in CATOFIN and OLEFLEX are $\sim 50\%$ and $\sim 40\%$, respectively.

Keywords: Propane dehydrogenation; CATOFIN; OLEFLEX; Propylene; PDH.

1. Introduction

Propane is a three-carbon alkane which is either in gas or compressed liquid state and usually produced from oil processing in petroleum refineries or from natural gas plants. Propane is utilized as a fuel source in engines, barbecues, portable stoves, heating, and cooling. Further processing of propane yield to more valuable products like propylene and polypropylene (PP) [1].

* Corresponding author.

Propylene is usually extracted and produced from propane-rich liquid petroleum gas (LPG) streams in gas plants. Propylene also comes from other sources like propane byproduct from such refinery operations as hydro-cracking and fluidized catalytic cracking (FCC) [2]. Propylene is one of the most common building blocks in petrochemicals and growth in propylene production is primarily driven by the industry demand for polypropylene. The expected growth rate of polypropylene is 5% per year [2].

Polypropylene plastic is one of the most desired products in many industrial applications and is used in such everyday products as packaging materials and outdoor clothing. Production of PP requires converting propane to propylene in the first place [3–5]. However, the production of propylene from steam crackers is expected to fall because steam crackers are mostly utilized for the production of ethylene. Also, even though FCC contribution to the production of propylene has been increasing enormously in the last few decades, FCC provides only 29% of the propylene supply to the market. Thus, alternative routes such as Propane Dehydrogenation (PDH) and metathesis have to be considered to make up for the propylene shortage [6].

PDH is a promising catalytic technology which has been used for a long time to convert propane into propylene for petrochemical applications, Figure 1. In other words, PDH technology is capable of producing a high purity polymer grade of propylene from a propane rich stream. Dehydrogenation of a hydrocarbon feed consists of two steps: (1) dehydrogenating the hydrocarbon feed, (2) removal of the hydrogen that is being formed by a specific dehydrogenation reaction [3–5].

PDH reaction, as shown in Eq. (1), is normally carried at high temperature with a relatively low pressure and in the presence of either a Platinum (Pt) or a Chromium (Cr) catalyst to achieve a reasonable conversion of propane into propylene. The reaction is highly endothermic since reactants absorb energy from its surroundings in the form of heat; and because any endothermic reaction needs a specific amount of heat to be spontaneous, the enthalpy (ΔH) at constant pressure and the internal energy (ΔU) at constant volume must be positive [4]–[6].

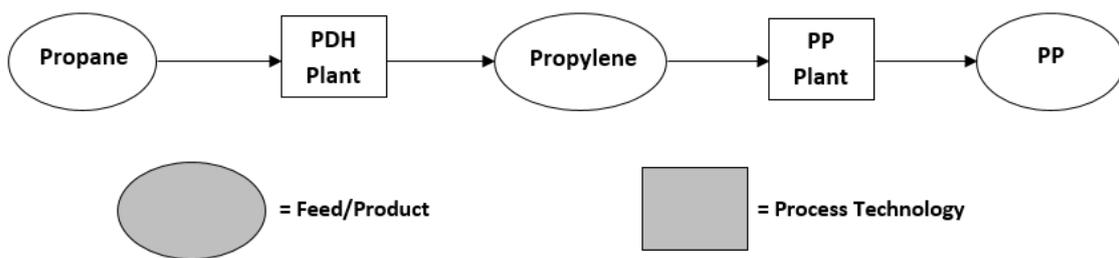
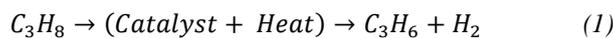


Figure 1: Process flow diagram of polypropylene (PP) production through propane dehydrogenation (PDH)



There are five available commercial PDH technologies: (1) CATOFIN (fixed-bed) from ABB Lummus Global, (2) OLEFLEX (moving-bed) from UOP, (3) Fluidized bed dehydrogenation from Snamprogetti, (4) PDH from Linde-BASF-Statoil and (5) Steam active reforming (STAR) from Krupp Udhe. Each technology has its own advantages and disadvantages. Differences arise in the utilized catalyst, technology process, operating

conditions (temperature and pressure) and performance. CATOFIN and OLEFLEX are the only commercial proven PDH technologies [7]; hence, this paper focus on understanding the chemical processes behind CATOFIN and OLEFLEX technologies for the production of propylene from propane streams. A comparison between current PDH plants and technologies (CATOFIN and OLEFLEX) in Saudi Arabia was discussed to analyze propylene production capacity, reactor type/configuration, reaction catalyst, operating conditions, performance, advantages, disadvantages and other design specifications/considerations of PDH technologies.

2. PDH Technologies/Plants in Saudi Arabia

Currently, there are a total of four PDH plants in the Kingdom of Saudi Arabia. Al-Waha and NATPET companies are using OLEFLEX-UOP technology; where SPC and APC companies are using CATOFIN-ABB Lummus as summarized in Table 1. CATOFIN and OLEFLEX technical details were studied with respect to the previously mentioned plants in the Kingdom of Saudi Arabia. Studied technical data included dehydrogenation process temperature, pressure, catalyst, conversion, yield, selectivity, reactor, and refrigeration system. Moreover, project costs, utility requirements, Di-Methyl Di-Sulfide (DMDS) consumption and production capacity for each company were discussed [8].

2.1 CATOFIN (fixed-bed) from ABB Lummus Global

CATOFIN dehydrogenation technology is a reliable and commercially proven process for the production of propylene from propane. The CATOFIN process uses fixed-bed catalyst reactors to achieve an appropriate conversion and selectivity with less energy consumption. The CATOFIN process can be operated at optimum reactor pressure and temperature to maximize propane conversion with high propylene yield. Propane to propylene selectivity is nearly greater than 86 mol %. Selected features and advantages of CATOFIN technology for propylene production are shown in Table 2. Typical feedstocks and products ratios in CATOFIN processes are shown in Table 3 [9]. CATOFIN does not require high capital and/or operating costs which as a result reduce propylene production cost to a low-cost value of approximately 57.20 \$/lb of the product. In the United States, a capital cost of about \$ 416.3 million is estimated for a CATOFIN plant with a production capacity of 500,000 metric tons per year (MTA) of polymer-grade propylene [9]. CATOFIN consists of multiple parallel adiabatic fixed-bed reactors that contain a $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst. Dehydrogenation of propane and regeneration of catalyst are the most critical parameters in designing CATOFIN PDH plants. Normally, dehydrogenation and regeneration steps are carried out simultaneously every ten minutes with short periods of purging and evacuation operations in-between, Figure 2. However, the dehydrogenation reaction is endothermic and requires a high temperature which produces a significant amount of coke. Coke deposition results in a decrease in bed temperature and loss of catalyst activity (coke formation and chromium reduction). Reactivation of the catalyst is achieved by blowing hot air on the catalyst bed to burn the formed coke and recover the bed temperature under oxidizing conditions. Average catalyst lifetime is two to three years and catalyst activity gradually decreases over time. As discussed earlier, CATOFIN facility is capable of producing high-purity grade propylene from propane rich streams through the following steps: dehydrogenation of propane to make propylene, compression of reactor effluent, recovery and purification of the product [14,15].

Table 1: Available PDH plants and their technologies in the Kingdom of Saudi Arabia

PDH Plant (Technology)	Company Logo	Company Profile	Place	Production Capacity* (KT/Year)
Al-Waha [10] (OLEFLEX)		Al-Waha Petrochemical Co. has constructed a polypropylene plant based on Lyondell Basell's technology. Al-Waha was formed in 2006 as a joint between Sahara Petrochemicals Company (75%) and Lyondell Basell (25%).	Jubail	450
NATPET [11] (OLEFLEX)		The National Petrochemical Industrial Co. (NATPET) has built a polypropylene plant which produces polypropylene product mix of homopolymers, random and heterophasic copolymers for various applications.	Yanbu	420
SPC [12] (CATOFIN)		Saudi Polyolefin Co. (SPC) has two integrated factories namely, propylene factory and polypropylene (PP) factory.	Jubail	455
APC [13] (CATOFIN)		Advanced Petrochemical Company (APC) was established as a joint stock company in 2005 to develop an integrated PDH and Polypropylene complex comprising an area of 650,000 m ² and PP production of 450 KT/Year.	Jubail	455

*Production capacity in kilotonne per year (KT/Year = KTA) and is reported for propylene production.

Table 2: Selected CATOFIN features and their advantages [9]

CATOFIN Feature	Advantage
High conversion and high catalyst selectivity	Lower investment and operating costs
High single train capacity	Feasible for economical scale
No hydrogen recirculation or dilution steam	Lower investment and operating costs
Adiabatic fixed bed reactors	Reliable and robust operation
No catalyst losses	Environmental-friendly design

The CATOFIN process converts propane to propylene over a fixed-bed chromium-alumina catalyst ($\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$; alumina pellets with 18 – 20% weight chromium). The unconverted propane is recycled to optimize process conversion and achieve a maximum net product of propylene. Operating conditions for the process are manipulated until an appropriate relationship between selectivity, conversion, and energy consumption are observed. Simultaneously, side reactions take place and result in the formation of undesired

light and heavy hydrocarbons as well as deposition of coke on the catalyst. The endothermic reaction takes place in multiple fixed-bed reactors that operate on a cyclic basis with a continuous process as illustrated in Figures 3 and 4. In one complete cycle, hydrocarbon vapors are dehydrogenated and the reactor is then purged with steam and blown with air to reheat the catalyst and burn off the deposited coke (less than 0.1 wt. % of catalyst) as a consequence of the reaction cycle. A single endothermic reaction cycle is followed by various evacuation/reduction processes prior to the beginning of the next cycle [8] [15].

Table 3: Typical feedstocks and products ratios in CATOFIN [9]

Typical Feedstocks		Typical Products	
Propane	95 mol % min	Propylene	99.5 mol % min
Ethane	2.5 mol % max	Propane	0.5 mol % max
Butane	2.5 mol % max	Ethylene + Ethane	100 mol ppm max
Sulfur	10 wt. ppm max	MAPD*	10 mol ppm max
		Carbon Oxides	5 mol ppm max

*MAPD: 1-(Methylamino)-2,3-Propanediol

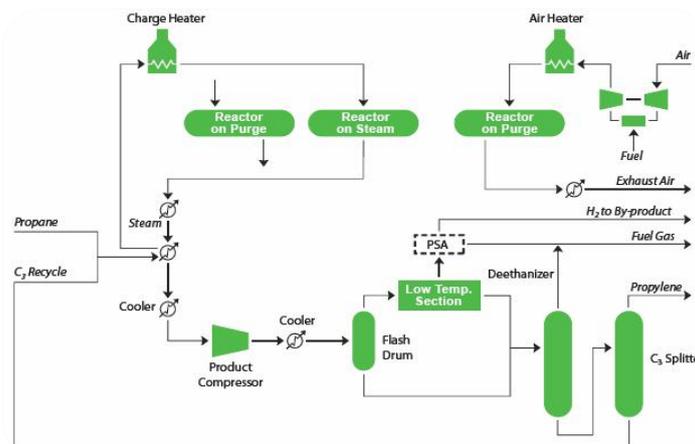


Figure 2: CATOFIN process flow diagram (PFD) [9]

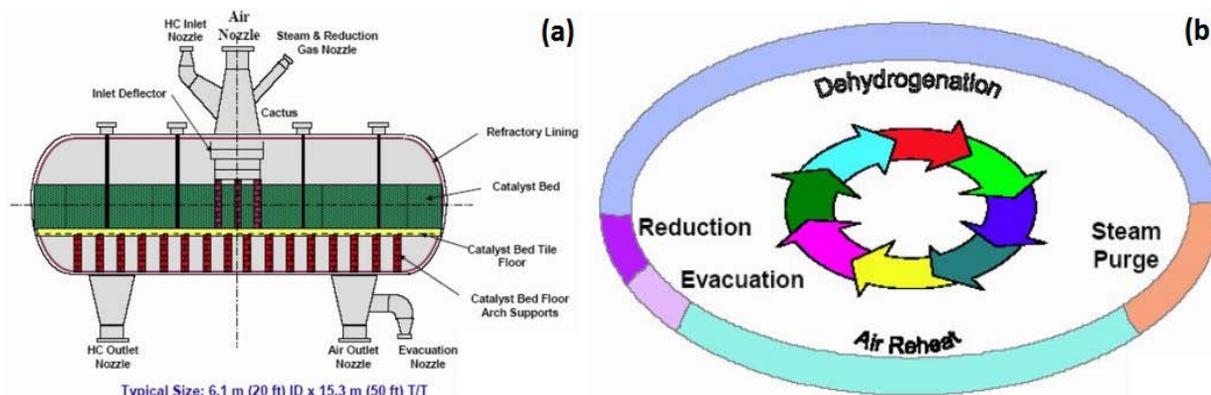


Figure 3: CATOFIN reactor: (a) A cross-section schematic (b) Operation cycle [8]

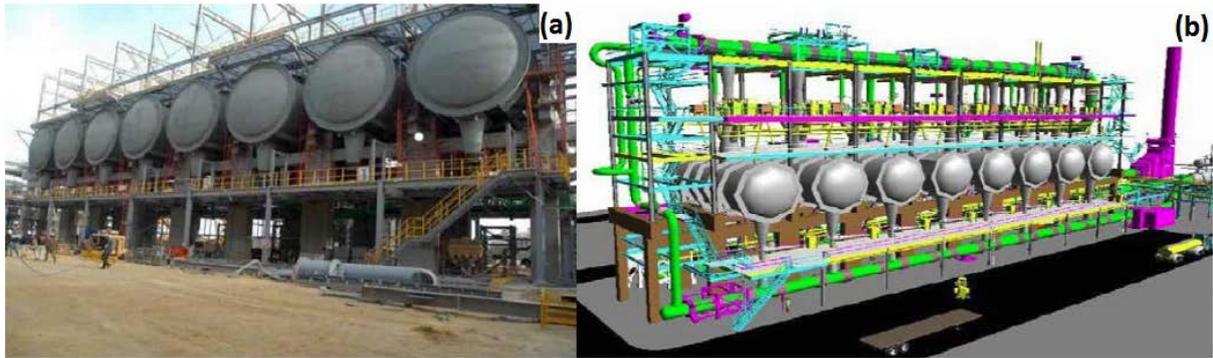


Figure 4: CATOFIN 8-reactors: (a) In APC plant (Jubail) [13], (b) 3D layout installation [8]

2.1.1 Advantages of CATOFIN Technology [8]

- Low feedstock consumption: less than 1.2 ton-propane/ton-propylene (1.18 ton/ton).
- Low operating pressure (near vacuum) for higher conversion of 0.3 ~ 1.0 bar absolute.
- Low reactor inlet temperature ($T \leq 600$ °C) for the higher selectivity of ~ 89 wt. %.
- High tolerance for feed impurities: olefins (~ 3 wt. %) and total C4 (~ 7 wt. %) is acceptable.
- Low compression energy that reduces compressor investment cost.
- A small amount of coke formation (less than 0.1 wt. % of catalyst).
- Complete coke burn-off is possible by in-situ regeneration cycle.
- Separate catalyst regeneration facility is not required.
- High sulfur (DMDS) injection is not required.
- Low catalyst cost due to using non-precious metal.

2.1.2 PDH (CATOFIN) Plants in Saudi Arabia

Saudi Polyolefin Company (SPC): TASNEE Company (SPC is a subsidiary company; TASNEE owns 75% of SPC whereas Lyondell Basell owns 25%) is one of the leading private companies who invests in Saudi petrochemical industry and petrochemical business. TASNEE has grown to be the second largest petrochemical company among the top 100 Saudi companies. TASNEE Petrochemical complex is constructed in Jubail Industrial City which consists of two giant projects: PDH factory with a production capacity of 455 KTA and PP factory with a production capacity of 450 KTA; and production goes back to early 2004 [12].

Advanced Petrochemical Company (APC): Advanced Petrochemical Company was established as a joint stock company in the Kingdom of Saudi Arabia on 27th Shaban 1426H (Corresponding to 1 October 2005) to develop an integrated PDH and PP complex in Jubail Industrial City comprising an area of 650,000 m². APC complex produces 450,000 tons per annum (450 KTA) of polypropylene. The company utilizes CATOFIN technologies provided by ABB Lummus and Novolen Technology Holdings (NTH) to produce propane derivatives that are marketed both locally and globally. CATOFIN-ABB Lummus technology converts propane gas into propylene with a capacity of 455 KTA. Propane is received from Saudi Aramco (Gas & Oil Company) through pipelines and sent to eight fixed-bed reactors which operate in sequence and reactors' product is purified in order to

obtain a high purity propylene of 99.5%. Further, produced propylene may be liquefied and sent to PP plant for polymerization. In the PP plant of APC Company, NOVOLEN technology is used to produce 450 KTA of polypropylene in two production lines. The first line produces both homopolymer and random copolymer grades with a total capacity of 180 KTA. The second line produces homo-polymer grades with a capacity of 270 KTA [13].

Table 4 shows a comparative analysis of discussed CATOFIN PDH plants (SPC and APC) in Saudi Arabia [8].

Table 4: CATOFIN PDH plants in the Kingdom of Saudi Arabia and their capacities [8]

Project/Licensee	Location/Country	Capacity (KTA)*	Startup	Remark
SPC	Al-Jubail, KSA	455	2004	PDH + PP Integration
NPPC*	Al-Jubail, KSA	455	2007	PDH + PP Integration

*NPPC was the former name of APC Company, KTA refers to kilotons per annum and/or kilotonne per year (KT/Year = KTA)

2.1.3 CATOFIN Chemical Process

CATOFIN dehydrogenation is a continuous process that is carried out in cyclic-multiple reactors (four horizontal reactors connected in parallel) with a controlled sequence of reaction and reheat/regeneration. The process starts with the endothermic reaction, as discussed in Eq. (1), followed by steam purging, evacuation, catalyst air-regeneration and another evacuation. Specifically, the fresh feed of high pure propane (98%), including the recycled feed from C_3 splitter bottoms, is preheated and vaporized by exchanging heat with hot process streams. Hot feed is then sent to a charge heater for further heating to reach the reaction temperature of 540 ~ 760 °C. Sales gas are utilized to fuel charge heaters. When the required feed temperature is maintained, reactor section inlet valves open allowing propane to enter into the cyclic-multiple fixed-bed catalytic reactor where dehydrogenation reaction occurs subsequently [8,9,16].

Propane enters the first reactor to be converted to propylene within 7 ~ 15 minutes. Two parallel reactors carry out the conversion process (reaction) to increase the weight percent of propylene and achieve a propylene conversion of 45 ~ 50%. Reactor effluent (propane/propylene = C_3/C_3'') is cooled through feed-effluent heat exchangers which also increase the feed temperature. Propane/propylene product is furtherly cooled in a trim cooler unit before being compressed (7 ~ 20 atm), dried and cooled again to enter a flash drum which separates light products (tail gas, light gas, H_2 , C_1) at the distillate and liquid products (C_2 & C_3/C_3'') at the bottom [8,9,16].

Distillate products are sent to a low-temperature recovery section to reject light ends where a pressure swing adsorption (PSA) unit receives and process light gases to produce a hydrogen-rich gas (99.9%), fuel gas and $CO/CO_2/C_2$ as by-products. Both bottom-liquid streams of the low-temperature recovery section (C_4 and oil) and the flash drum (C_2 & C_3/C_3'') are combined and passed through a deoiler unit to separate heavy materials while remaining products are sent to a deethanizer unit to extract C_2 as a fuel gas at the distillate. Deethanizer bottom-

stream (C_3/C_3'') passes through a two-column C_3 splitter unit to obtain the desired final product (propylene = C_3'') at the distillate. The unconverted propane/propylene mixture at the C_3 splitter bottom is recycled and heated to go over the whole conversion process again [8,9,16].

Removal of deposited carbon on the catalyst is achieved by placing spent catalysts in a heater and injecting fuel/air, through a gas turbine, into the heater. Hot air 800 ~ 1000 °C reactivates spent catalysts to be furtherly used in the purge reactor. Hot-air-carbonaceous contaminants are discarded by passing the air through a heat exchanger, knowing that recovered catalysts get attached to the reactor-side (fixed-bed). The entire reactor operation is computer controlled and requires no operator input [8,9,16]. More specific process and operating conditions data regarding CATOFIN-ABB Lummus plants in Saudi Arabia are shown in Table 5 [17].

Table 5: Process & conditions for CATOFIN-ABB Lummus Plants in the Kingdom of Saudi Arabia [17]

Parameter	Unit	Value/Description
Process Type	N/A	Semi-continuous
Reference plant	N/A	SPC & APC (in Jubail)
Total PDH plants in operation	N/A	Three (3)
Average plant size	m × m	205 × 175
Catalyst type	N/A	Chromium-based
Catalyst quantity	MT	688
Catalyst life	years	2
Average propane consumption	MT/MT	1.23
Reactor inlet temperature	°C	610
Conversion per pass	%	45
Propylene selectivity	%	88
Propylene yield per pass	%	39.6
CO2 emissions	N/A	High
Reactor pressure	atm	Sub-atmosphere
Ethylene refrigeration system	N/A	Required
Project cost	MM US\$	210
Electricity	kW	60.1
Fuel	MW	2.56
DM (De-Mineralized) water	MT	1.1
Cooling water	m ³	78.2
Nitrogen	m ³	21.2
DMDS consumption	Kg/day	58

*MT: Metric ton = 1000 kg ; MM: Million

2.2 OLEFLEX (moving-bed) from UOP

UOP OLEFLEX is a continuous catalytic dehydrogenation process technology utilized for the production of light olefins from their corresponding paraffin; and specifically used to convert propane (feedstock) into propylene. The OLEFLEX process uses a platinum-based catalyst (DeH-14) to promote the dehydrogenation reaction that is shown in Eq. (1). DeH-14 catalyst maintains high activity and allows for high productivity and selectivity which is characterized by lower platinum costs than previously used catalysts [2]. Besides propane dehydrogenation, OLEFLEX unit can be used for dehydrogenation of isobutane, normal butane, or isopentane feedstock separately or as mixtures. OLEFLEX technology was commercialized in 1990, and by 2002 more than 1,250,000 MTA of propylene was produced from various OLEFLEX units located in different places in the world. Feedstock and products of a typical OLEFLEX unit are shown in Figure 5 [4,18].

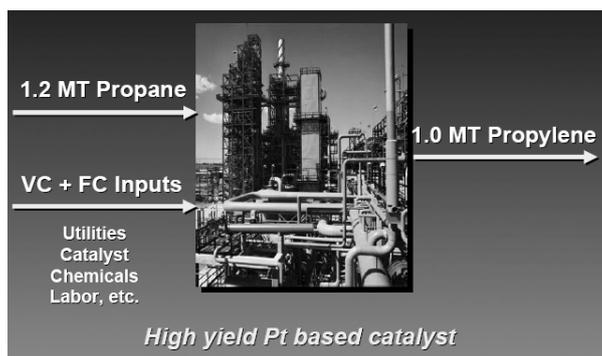


Figure 5: OLEFLEX technology mass balance (feedstock and products) [4]

OLEFLEX utilizes proprietary platinum on alumina catalyst with three generations of catalysts that have been developed since the first catalyst (DeH-12) in 1996; the last catalyst generation (DeH-14) was developed in 2002. OLEFLEX technology includes four series adiabatic reactors which facilitate the endothermic dehydrogenation reaction. Inter heaters are included just right after each reactor to maintain the desired reaction temperature. A continuous catalyst regeneration (CCR) system is applied to continuously regenerate spent catalysts and maintain high conversion and selectivity. CCR allows the unit to process continuously without a required shut down for catalyst reactivation. Propane dehydrogenation via OLEFLEX produces pure propylene with no co-products unless hydrogen recovery is desired. UOP OLEFLEX system equipment includes PSA units, CCR, UOP lock hopper control, distillation trays, high-flux tubes and process instrumentation controls (PIC). OLEFLEX technology can be integrated with other plant processes to reduce production expenses of the desired product [8,2].

UOP OLEFLEX process, as shown in Figure 6, consists of three main units [8]:

- Dehydrogenation reactor unit: Includes four radial-flow reactors, charge and inter-stage heaters and a reactor feed-effluent heat exchanger.
- Product recovery unit: Cryogenic system separates (H₂) from hydrocarbon and recycle unconverted propane by the following steps;
 - a) Net gas from OLEFLEX is recovered at 85 ~ 93 mol % hydrogen purity (recycled H₂).

- b) Separator liquid is sent to a selective hydrogenation unit called Hüls SHP to eliminate di-olefins and acetylenes.
 - c) SHP liquid is sent to a Deethanizer to eliminate light hydrocarbon products and bottom-product (heavy) is injected into a propane-propylene (P-P) splitter to produce polymer-grade propylene product.
 - d) Unconverted propane is recycled to the reactor section.
- Continuous catalyst regeneration (CCR) unit: Operates in a continuous mode to burn formed coke off catalyst and returns catalyst to its fresh activity.

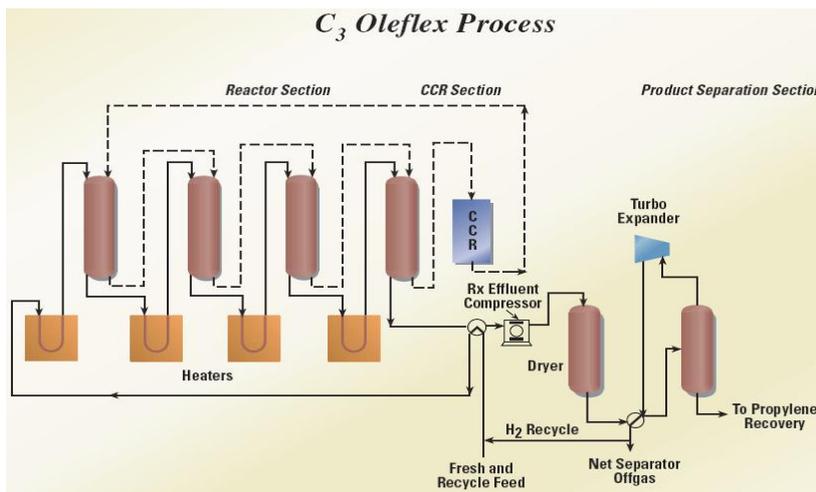


Figure 6: OLEFLEX process flow diagram (PFD) [2]

2.2.1 Advantages of OLEFLEX Technology

OLEFLEX technology has numerous features and advantages, including but not limited to, OLEFLEX is a new route for high-quality propylene supply for downstream use which allows for the control of propylene and polypropylene costs in the future by the continuous on-stream production of propylene; OLEFLEX is potentially capable of being integrated with other downstream technologies [2]. OLEFLEX provides the lowest cash cost of production and highest return on investment when compared to other PDH technologies due to these reasons: low operating costs enabled by low feedstock consumption and low energy usage, low capital costs because of having a continuous process with highly active, stable catalysts and ability to change catalysts without interrupting propylene production [19].

2.2.2 PDH (OLEFLEX) Plants in Saudi Arabia

Al-Waha Company: Al-Waha was established in September 2006 as a limited liability joint venture company between Sahara and Lyondell Basell with a 75% and 25% shareholding, respectively. The share capital of Al-Waha is SR 1,547.6 million. Al-Waha was established to construct, own and operate a petrochemical complex that produces 467,000 tons of propylene as the primary feedstock for the production of 450,000 tons of polypropylene. Polypropylene products are sold in both regional and international markets. Al-Waha plant is located in Jubail Industrial City in the eastern region of Saudi Arabia and commenced commercial operations on

1 April 2011. The plant is one of the projects of SAHARA Petrochemicals Company which was established on 7th April 2004 with a paid up capital of SR 1.5 billion and later increased to be SR 2.9 billion. SAHARA Petrochemicals is a Saudi joint stock company participates in the formation of some limited liability companies in Jubail Industrial City, as joint ventures with foreign partners who enjoy distinguished experiences and latest advanced technologies to produce and market primary materials like propylene, polypropylene, and polyethylene [10].

National Petrochemical Industrial Company (NATPET): NATPET Company has built a 400,000 MT/Year polypropylene plant in Yanbu Industrial City on the west coast of Saudi Arabia. The constructed plant produces a mix of polypropylene products including homopolymers, random and heterophasic Copolymers that are suitable for various applications. *NATPET* has acquired state of the art Spheripol process to produce polypropylene from Lyondell Basell (the world leader in polypropylene technology). *NATPET* will be targeting customers in different parts of the globe with the focus on Saudi Arabia, GCC, Turkey and Middle East markets. NATPET is geared to ensure maximum customer satisfaction through a complete offering package including product quality, competitive terms, and conditions, on-time delivery, technical support, a wide range of grade mix premium products, outstanding after sales services and continuous development [11,20].

Table 6 shows a comparison analysis discussed OLEFLEX PDH plants (Al-Waha and NATPET) in Saudi Arabia [8].

Table 6: OLEFLEX PDH plants in the Kingdom of Saudi Arabia and their capacities [8]

Project/Licensee	Location/Country	Capacity (KTA)*	Startup	Remark
Al-Waha	Jubail, KSA	450	2009	PDH + PP Integration
Alujain	Yanbu, KSA	400	2007	PDH + PP Integration

*Alujain was the former name of NATPET Company, KTA refers to kilotons per annum and/or kilotonne per year (KT/Year = KTA)

2.2.3 OLEFLEX Chemical Process

OLEFLEX consists of three main sections: the reactor section, the catalyst regeneration section and product separation section. Fresh and recycled propane are fed into a depropanizer tower for pretreatment purposes. Purified propane is mixed with small amounts of recycled hydrogen-rich gas and then passed by a heat exchanger that raise feed (propane) temperature when it comes in contact with 4th-reactor product (hot). Combined feed enters the 1st-heater which furtherly and rapidly increases feed temperature to the spontaneous endothermic reaction temperature 630 ~ 650 °C. Propane moves through the four reactors in series (with a moving-bed catalyst) where 1st-reactor product is heated again in a 2nd-heater to maintain reaction temperature for the feed and prior entering the 2nd-reactor. The same procedure is repeated for the last two stages (4 stages in total) to have a maximum propane/propylene conversion of 35 ~ 40% [2,16].

Obviously, dehydrogenation reactor section consists of a single train with four separate reaction stages (radial

flow fixed-bed catalytic reactor) in series with a heater prior to each stage. A small amount of catalyst is continuously removed from the bottom of the 4th-reactor while an equivalent amount of a regenerated catalyst is added to the top of the 1st-reactor [2,16].

Spent catalyst is sent to a CCR unit to be regenerated. Catalyst regeneration is necessary because coke formation reduces propylene conversion and hydrogen recycling; catalyst lifetime is about three years. Regeneration catalyst system is designed to burn the coke off the catalyst, redistribute platinum, remove excess moisture and return the catalyst its fresh state. Typically, the regeneration cycle takes around five to ten days to be done completely [2,16]. Propylene/propane product is cooled, compressed, dried from excess moisture and contaminants and sent to a low-temperature separation system where a propylene-rich product (liquid phase) is separated from light products (gas phase). The liquid stream is mainly composed of propylene and unreacted propane where the gas stream is approximately 90% hydrogen with methane and ethane. The liquid stream is pumped to a selective hydrogenation unit (Hüls SHP) to eliminate undesired di-olefins and acetylenes, to be < 5 wt. % ppm, and then sent to a two-column deethanizer system to remove hydrogen and light ends. The treated liquid stream enters a C₃ splitter unit to separate propylene/propane product into polymer-grade propylene and propane that is recycled. It is worth to mention that the reactor/product separation section and regeneration section are totally independent where catalytic dehydrogenation process operates continuously regardless of catalyst regeneration progress [2,16]. OLEFLEX reactor and catalyst regenerator design considerations and process and operating conditions information for OLEFLEX-UOP plants in the Kingdom of Saudi Arabia are shown in Table 7 and Table 8, respectively.

Table 7: Process/design considerations for OLEFLEX reactor and catalyst regenerator [8]

Reactor	Catalyst Regenerator
<p>Components:</p> <ul style="list-style-type: none"> • Four (4) radial flow reactors; • Catalytic reaction is independent of CCR; • Catalyst heater and interstage heaters; • Catalyst reduction and moving system. <p>Operating conditions:</p> <ul style="list-style-type: none"> • Temperature: 630 ~ 650 °C ; Pressure: 1.1 ~ 2.1 bar <p>Design considerations:</p> <ul style="list-style-type: none"> • Interstage heaters are required (endothermic reaction); • The thermal cracking reaction is limited by the maximum temperature; pressure becomes the dominant variable. 	<p>Regeneration:</p> <ul style="list-style-type: none"> • Burning off coke from catalyst; • Oxidation & chlorination; • Pt redistribution; • Drying of the catalyst; • Reduction of the catalyst.

Table 8: Process and conditions for OLEFLEX-UOP Plants in the Kingdom of Saudi Arabia [17]

Parameter	Unit	Value/Description
Process Type	N/A	Continuous
Reference plant	N/A	NATPET & Al-Waha
Total PDH plants in operation	N/A	Five (5)
Plant size	m × m	188 × 92
Catalyst type	N/A	Platinum-based
Catalyst quantity	MT	119
Catalyst life	years	3
Average Propane consumption	MT/MT	1.23
Reactor inlet temperature	°C	648
Conversion per pass	%	36.4
Propylene Selectivity	%	85
Propylene Yield per pass	%	31
CO ₂ emissions	N/A	Low
Reactor pressure	atm	Above atmosphere
Ethylene refrigeration system	N/A	Not required
Project cost	MM US\$	174
Electricity	kW	95.7
Fuel	MW	0.76
DM (De-Mineralized) water	MT	0.17
Cooling water	m ³	81.3
Nitrogen	m ³	4.49
DMDS consumption	Kg/day	816

*MT: Metric ton = 1000 kg ; MM: Million

3. Summary

A comparison between studied PDH technologies (CATOFIN vs. OLEFLEX) is established in Table 9 which shows information related to reactor type and configuration, catalyst, operating conditions, performance, advantages, and disadvantages. Also, current and available PDH plants in the Kingdom of Saudi Arabia are summarized and compared in Table 10.

Table 9: A comparison between PDH technologies (CATOFIN vs. OLEFLEX)* [8]

	CATOFIN by LUMMUS	OLEFLEX by UOP
Reactor System	Horizontal, Fixed Beds in Parallel (8)	Vertical, Catalyst Moving Beds in Series(4)
Catalyst /Catalyst life	Chromium oxide / > 3 years Spent Catalysts dump-out & land filling	Platinum / 5 years Spent Catalysts dump-out & Pt recovery
Catalyst Regen. Cat. Regen. Cycle Time	In-situ, Cyclic regeneration 10~20 minutes	CCR (Continuous Cat. Regen.) 7 days
RX. Operation Cond.	600 C, 0.3~1.0 bara	630~650 C, 1.2~2.0 bara
. Conversion(%) . Selectivity (%)	45~50% 80~90%	35~40% 80~90%
Advantages	. No separate CCR Facility req'd . No H ₂ recycle gas . Higher conversion due to Vac. Cond . Lower C ₃ consumption . Lower catalyst cost	. Safe & reliability in operation . Longer catalysts life . High on-stream operation
Disadvantages	. Frequent reactor change operation by cycle operation(~12 min.)	. Complicated Reactor Internals design . Higher Capex. and Opex.
Commercial Plant	4 + 3 plants (max. capa: 500, 000 MTA)	8 + 1 plants (max. capa: 450,000 MTA)

*Commercial plants are the currently available operating PDH plants in the world.

Table 10: PDH plants (CATOFIN and OLEFLEX) in the Kingdom of Saudi Arabia* [8]

Project. Licensee	Location	Startup	Capa.(kta)	Process	EPC Contractor	Remark
SPC (Saudi Polyolefin Co)	Saudi, Al-Jubail	2004	455	Catofin	Samsung	PDH + PP
NPPC (National Polyolefin Co.)	Saudi, Al-Jubail	2007	455	Catofin	Samsung	PDH + PP
Alujain (NatPet)	Saudi, Yanbu	2008	420	Oleflex		PDH + PP
Al-waha	Saudi, Al-Jubail	2009	450	Oleflex	Daelim /Tecnimont	PDH + PP (TCM)

*Currently, NPPC is APC; and Alujain is NATPET

4. Conclusion

CATOFIN and OLEFLEX technologies have been discussed and compared between available PDH plants in Saudi Arabia. Both technologies require a high temperature of > 600 °C and a low pressure of ~ 1 bar. CATOFIN uses chromium-oxide catalysts in horizontal fixed-bed parallel reactors, while OLEFLEX uses platinum catalysts in vertical moving-bed series reactors. There are four PDH plants in Saudi Arabia: NATPET and Al-Waha (CATOFIN), APC and SPC (OLEFLEX); with a propylene capacity of ~ 450 KTA. Propane/propylene conversions in CATOFIN and OLEFLEX are $\sim 50\%$ and $\sim 40\%$, respectively.

Acknowledgments

The author wishes to express his gratitude towards Saudi Aramco Company for providing access to their feasibility reports. Also, I would like to acknowledge the Saudi Arabian Cultural Mission (SACM) and King Abdulaziz University (KAU) for their continuous support and encouragement to accomplish this work.

References

- [1] B.-Z. Wan and H. Min Chu, "Reaction Kinetics of Propane Dehydrogenation over Partially Reduced Zinc Oxide supported on Silicalite," J. Chem. Soc. Faraday Trans, vol. 88, no. 19, pp. 2943–2947, 1992.
- [2] UOP-LLC, "Oleflex Process for Propylene Production," Process Technology and Equipment, pp. 1–2, 2004.
- [3] A. Stahl et al., "Process for the dehydrogenation of a hydrocarbon feedstock," U.S. Patent No. 6,326,523, 2001.
- [4] B. Glover, "Light Olefin Technologies," in UOP LLC; Journées Annuelles du Pétrole, 2007.
- [5] H. A. Maddah, "Polypropylene as a Promising Plastic: A Review," Am. J. Polym. Sci., vol. 6, no. 1, pp. 1–11, 2016.

- [6] Chemicals-technology, "Tarragona Propane Dehydrogenation Project." [Online]. Available: <http://www.chemicals-technology.com/projects/tarragona-propane-dehydrogenation>.
- [7] Al-Zamil Company, "Propylene Sources Sheet in Propane-Propylene Based Industries in Saudi Arabia (Propylene by Propane Dehydrogenation) - Feasibility Study," 2001.
- [8] GS Engineering/Construction, Ed., "Propylene Technology by PDH & Metathesis," 2008.
- [9] Lummus-Technology-CB&I-Company, "CATOFIN Dehydrogenation," Chicago, pp. 1–2, 2009.
- [10] Sahara-PCC, "Propylene and Polypropylene Plant," 2004. [Online]. Available: <http://saharapcc.com>.
- [11] National-Petrochemical-Industrial-Co., "OLEFLEX and Polypropylene Plant," 1999. [Online]. Available: <http://www.natpet.com/>.
- [12] Tasnee, "CATOFIN PDH Plant," 1985.
- [13] Advanced-Petrochemical-Company, "CATOFIN PDH Plant," 2005. [Online]. Available: <https://advancedpetrochem.com>.
- [14] W. Won, K. S. Lee, S. Lee, and C. Jung, "Repetitive control and online optimization of Catofin propane process," in IFAC Proceedings Volumes (IFAC-PapersOnline), 2009, vol. 7, no. PART 1, pp. 273–278.
- [15] Clariant, "CATOFIN Dehydrogenation," 1995. [Online]. Available: <https://www.clariant.com>.
- [16] Al-Zamil-&-Brothers-Company, "Pre-Feasibility Study for PDH/ACN/PP Complex," vol. Volume I, 2004.
- [17] Saudi-Aramco, "Kingdom of Saudi Arabia PDH Projects," 2009.
- [18] R. A. Meyers, Handbook of petroleum refining processes. McGraw-Hill, 2004.
- [19] M. Banach, "On-Purpose Propylene from Propane," Honeywell UOP, 2017.
- [20] NATPET, "Propylene and Polypropylene Expansion Project - Feasibility Study," 2007.