Propylene

HIGHLIGHTS

Processes and technology status – Propylene is mainly a byproduct of two processes the steam cracking and fluid catalytic cracking (FCC). Due to high and increasing demand of propylene, the mentioned byproducts are not enough for the market and on purpose production technologies are developed as well such as propane dehydrogenation (PDH) [1]. Other main on purpose processes for propylene production are methanol to olefin (MTO), methanol to propylene (MTP), metathesis and Superflex technology [2]. Moreover, bio- and CO_2-routs are green technologies for propylene production which are under development.

Cost – Various production routes impose different costs. Furthermore, feedstock costs play an important role on the propylene production specially in the case of PDH technology. Further details on costs are available in this fact sheet for the main propylene production routes. For instant, price of PDH route is equal to 596.35 €$_{2007}$ /ton[1] of propylene [3].

Potential and barriers – Opportunities in front of propylene production are increase in propylene production and development of new feedstock resources such as shale gas in Europe. Weaknesses of propylene production plants are high feedstock and energy costs, high labor costs, high environmental and legislative cost. Moreover, threats ahead are imports of petrochemical derivatives, declining petrochemical production, closure of refineries and steam crackers [4].

Propylene – Propylene (C_3H_6) is one of the most important building blocks for the entire chemical industry and the raw material for plastic polypropylene, which is a common component mainly used in the automotive and textile industries, for plastic films for packaging and many other products [5].

The primary worldwide process for production of light olefins such as propylene is steam cracking, known also as

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[1] 817 USD$_{2007}$/ton of propylene. The values are converted from mean USD values to € in the reference year of 2007, based on 1 €$_{2007}$ = 1.37 USD$_{2007}$ [57]

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thermal pyrolysis or thermal cracking[2]. The conventional propylene productions are byproduct streams from two chemical processes. The first one is the byproduct from the steam cracking of liquid feedstocks such as naphtha as well as gas oil and condensates to produce ethylene [6], [7]. Naphtha is a mixture of hydrocarbons. 70 % of the Propylene was produced via steam cracking in 2007 [3]. The second source is byproduct from off-gases produced in fluid catalytic cracking (FCC) units in refineries. However, refinery propylene needs to be purified for chemical and polymer use [7].

The remainder of propylene is produced using on-purpose technologies such as propane dehydrogenation (PDH), methanol to propylene and olefin metathesis [8] that plays an increasingly key role in closing the global shortage in traditional propylene supplies [1], [6]. Moreover, propylene price was increasing faster in comparison to the propane price historically that makes producers even more eager to invest on propylene production [9]. Different feedstocks and related technologies for production of propylene are briefly illustrated in figure 1. In addition, naphtha with ethane which comes from shale gas as the feedstock for ethylene production leads to essentially eliminate propylene as co-production from ethylene plants. This switch is expected to create a substantial gap in propylene supply while the demand is expected to grow [10].

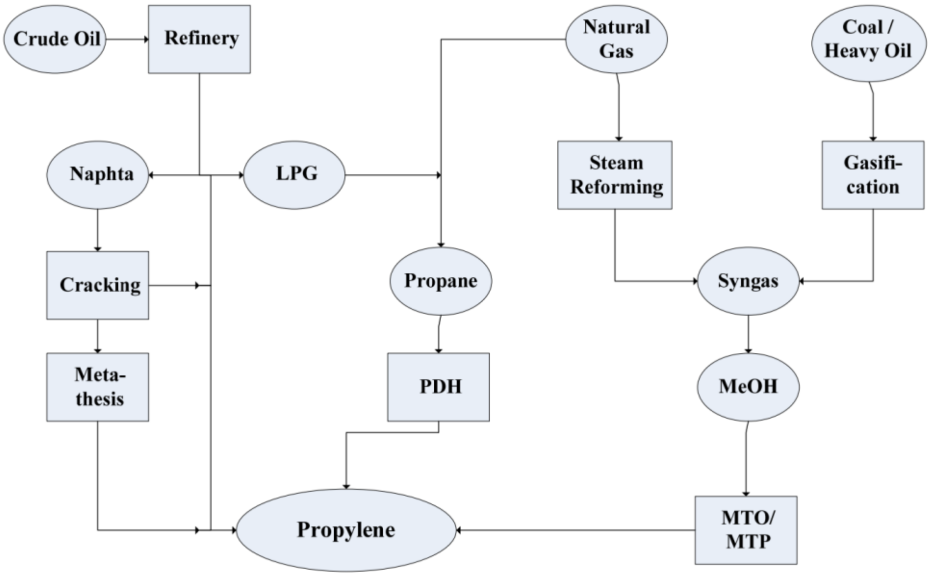

Figure 1. Propylene value chain [10]

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[2] Steam cracking is a complex process, producing more than one product and accepting a variety of hydrocarbons as feedstock, ranging from natural gas liquids (ethane, propane, butane) to petroleum liquids (naphtha, distillate fuel oil).

Propylene is traded commercially in three grades: polymer grade (PG) 99.5% or higher purity, chemical grade (CG) 90–96% purity, and refinery grade (RG) 50–70% purity [11]. At steam cracker, produced propylene has the chemical grade of 92-96% and remainder is propane. This grade can be upgraded to polymer grade which is 99.5%, using a C_3 splitter. The refinery production has the polymer grade of 70%, the remainder being propane [12].

Process overview – As explained in previous session, there exist traditional and on-purpose methodologies for production of propylene.

On the supply side of the balance, propylene is a by-product of ethylene plants and refineries. Currently, about 61% of propylene is produced in ethylene plants, 34% in petroleum refineries and less than 3% in on-purpose propylene-only production plants [13]. The supply percentage of propylene in 2007 are reported as figure 2 showing 63.3% from steam cracker, 27.9% from FCC unit, 4% from refinery splitters, 2.6% from PDH process, 1.9% from metathesis and 0.3% from other routs [14].

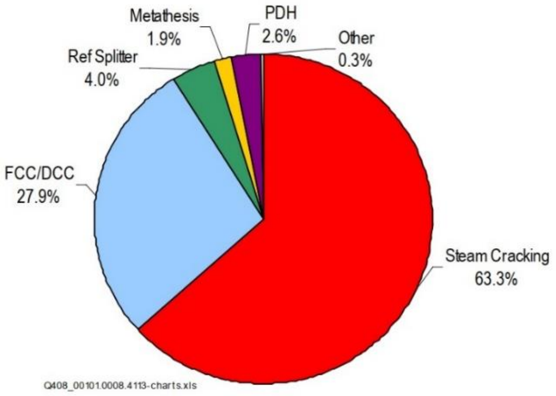


Figure 2. Global propylene capacity in 2007 [14]

CO_2 emission - Life cycle GHG emissions of propylene production via different routes shows that GHG emissions from petroleum-based propylene production is less than that of the coal-based propylene production. Moreover, catalytic cracking (CC), stream cracking (SC) pathways lead to 1.60 and 2.06 ton CO_{2}eq/ton propylene, respectively [15]. Light hydrocarbons have the highest benefit due to the decrease of GHG emissions and primary energy demand (PED). In addition, extraction stages play more contribution to the reduction of GHGs; hence, reducing GHGs from extraction is more effective than other stages [15].

Production of propylene in Belgium

Propylene is being produced in Belgium at three different refineries/petrochemicals namely the Total located in Antwerp, BASF in Antwerp and Borealis in Kallo. The overall produced propylene in Belgium was 1805000 tons/year by 2013 [16].

Propylene as by-products

1-1- By-product of steam cracker

1-1-1- Conventional steam cracking

The production of light olefins is mainly achieved by thermal steam cracking of light naphtha at temperatures above 1073 K; however, this approach requires large amounts of energy because of the high reaction temperature, which leads to increased carbon dioxide emissions, and the propylene to ethylene product ratio cannot be controlled [17]. The propylene ethylene production through steam cracking includes a series of parallel cracking furnaces having the feed. Then, quenching and compressing occurs followed by separation units. The sepse units are namely, a demethaniser, deethaniser, depropaniser, debutanizer, and depentaniser alongside a propylene and ethylene fractionator to further separate ethane and propane from ethylene and propylene. Other products from these units are hydrogen, butadiene, benzene, C_4 and C_5 fractions, which have also partly use in the oil refinery. The produced hydrogen is more valuable to the refinery plant than to the ethylene plant. Moreover, a portion of hydrogen can be transferred to the oil refinery, as well [6].

The cracking reaction is carried out in cracking furnaces as shown in figure 3 [3]. The steam cracking process suffers from coke formation and it significantly contributes to the emission of CO_2 into the atmosphere [18].

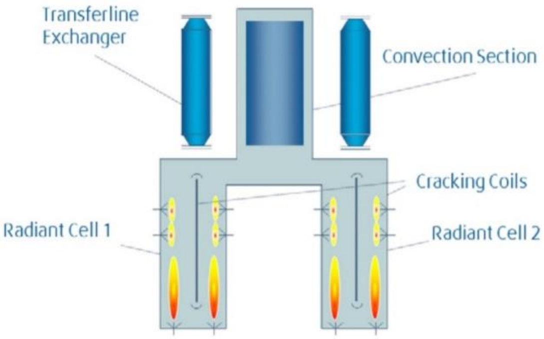
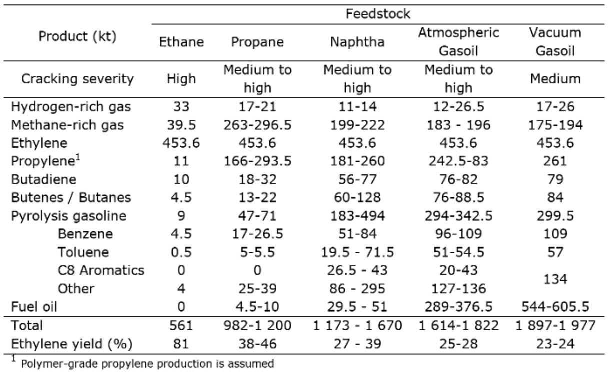


Figure 3. Cracking furnace [3]

Propylene yields at steam cracking vary between 1.5–18%, depending mainly on the feedstock and operating conditions [6]. The rate of propylene output as a byproduct of ethylene production process which is cracking of naphtha and other liquids such as gas oil and condensates, can be increased. By altering the cracking severity and the feedstock, the propylene to ethylene ratio can vary from 0.4:1 to 0.75:1. Moreover, smaller amounts of propylene can be obtained from cracking propane and butane [8].

From feedstock point of view, steam cracking production can be Ethane based, Gas oil based or Naphtha based. Typical product streams of steam cracker for the different feedstocks are shown in Table 1 [19].

Table 1. Typical product yields for different feedstocks in a plant with ethylene capacity 453.6 kt/y [19].

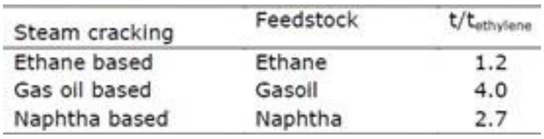


Product (kt)	Feedstock				
	Ethane	Propane	Naphtha	Atmospheric Gasoil	Vacuum Gasoil
Cracking severity	High	Medium to high	Medium to high	Medium to high	Medium
Hydrogen-rich gas	33	17-21	11-14	12-26.5	17-26
Methane-rich gas	39.5	263-296.5	199-222	183 - 196	175-194
Ethylene	453.6	453.6	453.6	453.6	453.6
Propylene[1]	11	166-293.5	181-260	242.5-83	261
Butadiene	10	18-32	56-77	76-82	79
Butenes / Butanes	4.5	13-22	60-128	76-88.5	84
Pyrolysis gasoline	9	47-71	183-494	294-342.5	299.5
Benzene	4.5	17-26.5	51-84	96-109	109
Toluene	0.5	5-5.5	19.5 - 71.5	51-54.5	57
C8 Aromatics	0	0	26.5 - 43	20-43	134
Other	4	25-39	86 - 295	127-136	
Fuel oil	0	4.5-10	29.5 - 51	289-376.5	544-605.5
Total	561	982-1 200	1 173 - 1 670	1 614-1 822	1 897-1 977
Ethylene yield (%)	81	38-46	27 - 39	25-28	23-24

[1] Polymer-grade propylene production is assumed

The feedstock consumption for steam cracking are listed in table 2 based on the ethylene production [19]. The required feedstock for the naphtha-based steam cracker is reported to be 2.7 $t/t_{Ethylene}$ [19]. Moreover, yields of the propylene at steam cracker per ton of ethylene is 0.53 $t_{Propylene}/t_{Ethylene}$ [6]. Therefore, steam cracker naphtha input fo propylene production is equal to 5.09 $t_{Naphtha}/ t_{Propylene}$.

Table 2. Feedstock consumption for steam cracking production [19].

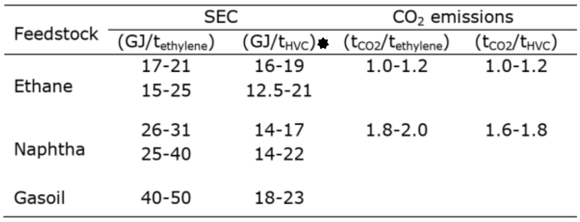


Steam cracking	Feedstock	$t/t_{ethylene}$
Ethane based	Ethane	1.2
Gas oil based	Gasoil	4.0
Naphtha based	Naphtha	2.7

The process energy use in the case of steam cracking is the sum of the theoretical thermodynamic energy requirement (the minimum energy input requirement for converting feedstock to desired product in an endothermic reaction) together with any energy losses. Losses can occur because of fouling, coking or other reasons.

An overview of the specific energy consumptions (SEC) for steam cracking in the case of ethane and naphtha is included in Table 3 [19].

Table 3. Overview of energy use and CO_2 emissions of ethane and naphtha steam cracking [19]



Feedstock	SEC		CO_2 emissions	
	$(GJ/t_{ethylene})$	(GJ/t_{HVC})*	$(t_{CO2}/t_{ethylene})$	(t_{CO2}/t_{HVC})
Ethane	17-21	16-19	1.0-1.2	1.0-1.2
	15-25	12.5-21		
Naphtha	26-31	14-17	1.8-2.0	1.6-1.8
	25-40	14-22		
Gasoil	40-50	18-23		

* HVC represents high value chemicals

Energy for the compression and separation is provided by steam, almost all of which is produced in the heat exchangers after the pyrolysis. Typically, there is no net steam import or export. A small amount of electricity, about 1 $GJ/t_{ethylene}$, is provided from external sources [19].

Considering the lower calorific value of naphtha which is equal to 44.9 [MJ/kg] [20], total energy consumption for naphtha-based steam cracking is around 121.23 $GJ/t_{ethylene}$ or 239.93 $GJ/ t_{propylene}$ [19], [21].

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The utility consumption of catalytic crackers per ton of product is estimated to be 120-2000 MJ of fuel, 2-60 kWh of electricity and 50-20 m^3 of cooling water, while concerning the steam the process consumes about 30-90 kg and produces 40-60 kg [19].

1-1-2- Electrification of steam cracking

Electrification can reduce CO_2 emission from steam cracker up to 90%. BASF expects the development of the first electrically heated cracking furnace by 2025 [22].
Utilization of coil surrounding tubes for heat generation, however, it is at infant stages and not commercialized yet [22]. Typically, ethylene yields are increased by raising the cracking temperature and reducing the residence time. The metallurgy of the cracking coils is the limiting factor in increasing the cracking temperature [22]. New designs for reduction of coke formation will decrease process related CO_2 emission [22]. Steam cracking of hydrocarbons is, and will likely remain, the leading technology for light olefin production for the coming decades [22]. Furthermore, the new reaction system known as the Roto Dynamic Reactor (RDR) supplied by an electric motor to reduce both pressure drop and residence time, and thereby achieve better selectivity leading to lower specific energy consumption [22].

1-2- By-product of FCC

Fluid catalytic cracking (FCC) is one of the major conversion technologies in the oil refinery industry. FCC currently produces the majority of the world’s gasoline, as well as an important fraction of propylene for the polymer industry [23]. A large proportion of propylene demand in Europe can be satisfied by steam cracking, but the rest is supplied from extraction from refinery Fluidized Catalytic Cracker (FCC) off gas [19] as shown in figure 4.

Indeed, catalytic cracking has been shown to be a useful mean of reducing the reaction temperature needed to crack naphtha and increase the propylene to ethylene product ratio [17]. Total’s Antwerp complex is located in the port area of Antwerp, Belgium, and comprises a refinery, the Fina Antwerp Olefins plant and a polyethylene plant. The complex produces a variety of petroleum products, including fuel oil, gasoline, LPG, chemicals, diesel and jet fuel, including ethylene, propylene, C_4 fractions and aromatics such as benzene, toluene, xylene and styrene [24].

The propylene production distribution in 2009 is reported to be 70% from steam cracking at 52 million tons, 25% from FCC conversion at 19 million tons and 5% from other methods [25]. New catalysts are now available that increase propylene output from the FCCs such as furrieries and various zeolites with different pore structures [7]. FCC which uses hydrocarbons to produce C_3H_6, at moderate pressure and high temperatures, over zeolites, such as, ZSM-5, often modified with metals to increase selectivity to C_3H_6. It is considered greener than steam cracking due to lower energy demand and decreased CO_2 emissions [26]. Specialized catalysts that contain ZSM-5 zeolite[3] combined with increased operating severity lead to higher liquefied petroleum gas (LPG)[4] olefin yield, mainly propylene, in a FCC unit at the expense of gasoline [27].

Emission at FCC unit is related to the coke generation on catalyst which contributes to average 19% of $CO_{2,eq}$, for worldwide operations as it is released in 2000 [28]. FCC involves up to 20 % less resources consumption and emissions compared to steam cracking [19]. FCC is producing gasoline as well as propylene, with a ratio of about 15.3:1 Other links for FCC and since gasoline production is not part of the chemical industry, only the emissions and consumptions attributed to propylene should be taken into consideration. The process consumes 1.7 kWh/$t_{propylene}$ electricity, 0.95 GJ/$t_{propylene}$ fuel for thermal needs and 0.08 t/$t_{propylene}$ medium pressure steam [19].

Feedstock consumption of FCC is 26.3 ton of distillate fuel oil per ton products. The amount corresponding to propylene is 1.61 t/$t_{propylene}$, calculated by mass allocation between gasoline and propylene. The emission factor used for direct emissions is 0.21 t_{CO2}/$t_{Propylene}$ [19]. The optimum cash cost of propylene production from an FCC unit is an intricate balance of capital, throughput, operating severity and overall product values [30]. Refiners optimize their FCC unit by maximizing converted barrels (throughput), minimizing their operating and capital costs, and producing a flexible product slate. Main problem with pushing the limits of propylene production from an FCC unit is that all of these optimization factors are negatively impacted.

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[3] ZSM-5 is an aluminosilicate zeolite belonging to the pentasil family of zeolites. Its chemical formula is NanAlnSi96–nO192·16H2O (0<n<27).

[4] Liquefied petroleum gas is composed of 98% C_3 and C_4 [58], a mixture of 48% propane, 50% butane, and 2% pentane.

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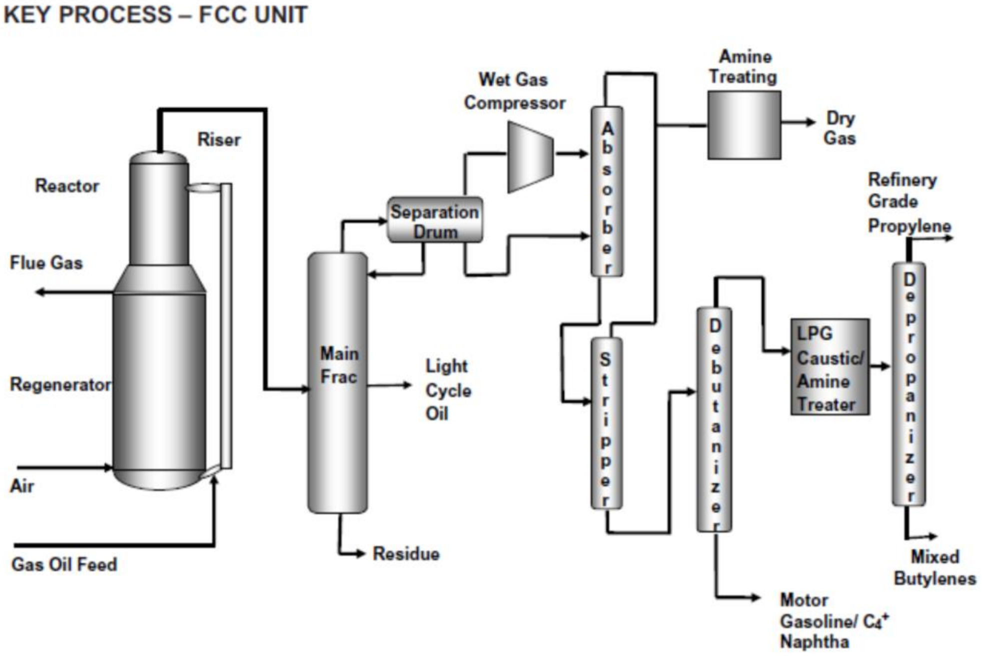

Figure 4. Fluid Catalytic Cracking BFD [29]

The operating conditions needed to maximize propylene yield as a weight percentage of fresh feed require significantly larger equipment per barrel processed, resulting in a higher capital cost. Moving the operation from gasoline to propylene mode derates the operating capacity by approximately 50 %. In other words, if a unit is designed for a gasoline mode throughput of 50 000 bpd, to maximize severity to propylene mode operation in the same equipment the feed rate would need to be reduced to approximately 25 000 bpd [30]. The operating costs associated with maximum propylene production are higher than for gasoline mode operation [30].

Refiners may increase propylene yields from 4-6 wt% up to a maximum of approximately 12 wt%, assuming these refiners possess sufficient light gas handling capacities. Generally, this is accomplished through upgrading the Wet Gas Compressor plus increasing the distillation capacity of the FCC product recovery section. Even minor capacity increases will generally require investments in excess of 20.820 MM€$_{2021}$[5] [31].

The second option will be to retrofit the unit to a high severity operation at a cost of 125

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[5] The value ($25 million) is converted to € based on 1 €$_{2021,\ march}$ = 1,2 \$$_{2021,\ march}$ [57]

– 166.7 MM€$_{2021}$[6] [31]. The total capital cost for FCC unit construction is 342.34[7] MM€$_{2015}$ [32].

1-3- propylene from shale gas feedstock

Dow Chemical Company announced in October 2016 that it developed a fluidized catalytic dehydrogenation (FCDh) technology to produce propylene from shale gas feedstock. It is operated in a circulating fluid bed based on Fluid Catalytic Cracking (FCC) technology [33].

Shale gas typically has more Natural Gas Liquids (NGLs) and introduces new clean feedstock in the form of ethane, propane, butanes and higher hydrocarbons in the market [34].

2- On-purpose propylene production processes

The share of on purpose propylene production was 22% of total demand in 2018 to close the supply/demand gap and is expected to grow up to 32% by 2027 [1], [6].

2-1- Propane dehydrogenation (PDH)

The dehydrogenation of light hydrocarbons involves the breaking of two carbon–hydrogen bonds with the simultaneous formation of a hydrogen and carbon-carbon double bond selectively [11].

PDH reaction, as shown in Eq. (1), is normally carried out 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 [35].

$$C_3H_8 \rightarrow (Catalyst + \ Heat) \rightarrow C_3H_6 + H_2 \quad \text{Eq. (1)}$$

Propane dehydrogenation reaction is reversible and highly endothermic (ΔH_{298K} = +124 kJ/mol) [36].

The reaction of propane to propylene is endothermic in nature. Hence, firing of heaters are required to heat the process gas to roughly 600 °C to maintain catalyst activity and increase conversion. A suitable catalyst for paraffin dehydrogenation is the one that favors C–H over C–C bond [11].

PDH can occur via two routes of Oleflex process and CATOFIN process. Both processes work a high temperatures and low pressures. The CATOFIN technology uses an adiabatic fixed-bed reactor [11] while Oleflex process uses fluidized bed reactor with higher performance [1]. UOP's Oleflex

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[6] The value \$150 – \$200 million) is converted to € based on 1 €$_{2021, march}$ = 1,2 \$$_{2021, march}$ [57]

[7] The values are converted from \$ to € based on 1 €$_{2015}$ = 1,11 \$$_{2015}$ [57], MM refers to million

process is used in 16 of the 23 operating PDH units in the world. Since this technology is the target of Belgian plants as well, this study focus on Oleflex pathway of PDH.

Propylene production rate is reported to be 1MT/ 1.2 MT propane feedstock for a typical OLEFLEX unit with platinum based catalyst ($1MT_{Propylene}$ / $1.2\ MT_{Propane}$) [35].

2-1-1- The Oleflex process

The Oleflex process of Universal Oil Products (UOP) used a series of moving bed reactors with inter stage heating. UOP Oleflex dehydrogenation process has three sections: reactor section, product recovery section, and catalyst regeneration section as shown in figure 5 The reactor section consists of three or more radial-flow (moving bed) reactors, charge heater for hydrocarbon feed preheating, inter-stage heaters, and a feed-effluent gas-gas exchanger. In the product recovery section, the reactor effluents are cooled, compressed, and sent to the cryogenic system for hydrogen (of ~90 mole% purity) and hydrocarbon separation/recovery. Liquid hydrocarbons were sent to selective hydrogenation to eliminate diolefins and acetylenes and then to de-ethanizer and propane-propylene splitter. The process is mostly commercialized for the production of PG propylene. The continuous catalyst regeneration (CCR) section burns coke over the catalyst and returns the regenerated catalyst to the reactor. [11]. Key benefits of the process are lower capital expenditure, lower operating expenditure, better economy of scale, higher plant productivity and dependability, smaller environmental footprint, and UOP’s project execution, technical services, and continuous innovation [1]. In series of reactors with a moving-bed catalyst, maximum propane/propylene conversion is 35 - 40% [35].

2-2- Energy requirements of PDH process

The dehydrogenation of propane and isobutane to corresponding olefin reactions has an activation energy of ~121–143 kJ/mol and can be presented as following [11]:

$$C_3H_8 \leftrightarrow C_3H_6 + H_2$$
$$i{-}C_4H_{10} \leftrightarrow i{-}C_4H_8 + H_2$$

Reactions are reversible, prone to volume expansion and highly endothermic; therefore, higher temperatures and lower pressure (under vacuum) favor forward reactions. The most important aspect of light alkane dehydrogenation is the energy requirement for the endothermic reaction [11].

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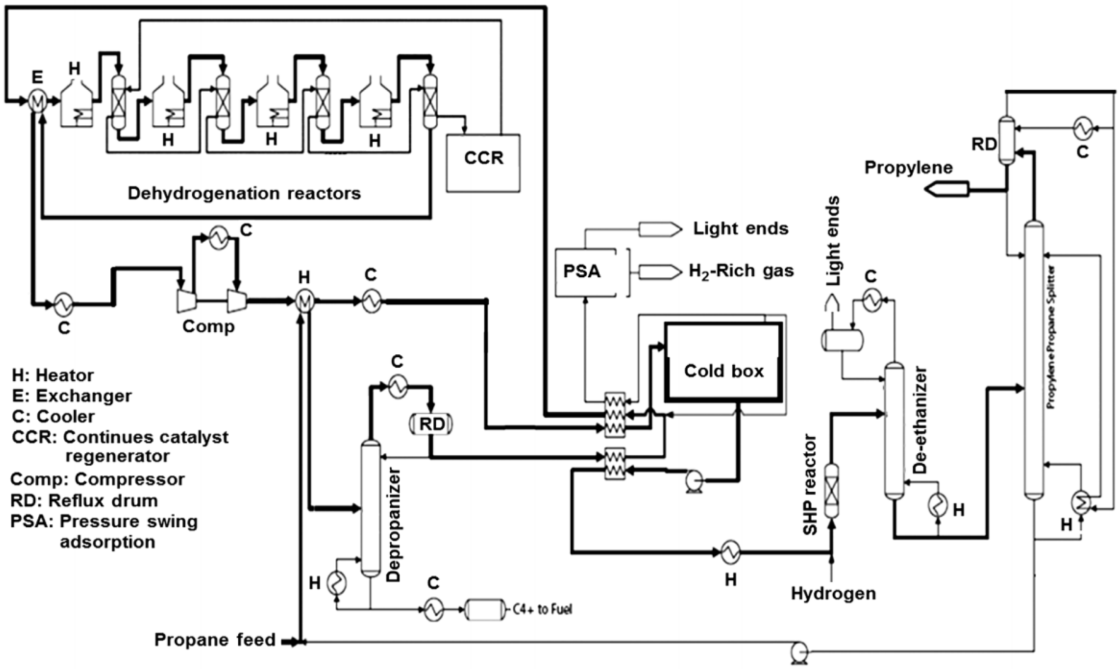

Figure 5. UOP Oleflex propane dehydrogenation process

Heat input to the reactor is one of the main technological challenges, which differentiates commercial reactor designs and processes from each other in addition to the catalyst. On the contrary, high temperature promotes side reactions and coke formation and deactivates catalyst [11]. The reactor section, compression and cooling section, and the product separation section are the big energy consumers in the process [34].

Total energy requirements of a conventional PDH plant is reported to be around 0.145 kW for 1 kmol/h of feed [37] which is equal to 11.84 GJ/$t_{Propane}$.

The utilities used in the process include cooling water, low pressure (LP) steam, natural gas for firing in the heaters, and purchased electricity [34]. Main utilities vales for the base case without waste heat recovery are as following:

1. LP Steam: 237.4 MW
2. Natural Gas: 159.3 MW [8]
3. Cooling water: 358 MW [34].

2-3- Electricity requirements of PDH

Electricity requirements of PDH plants are mainly for running of pumps and compressors and refrigerant condenser. Reactor Effluent Compressors consumes 95% of total electricity input [34]. Required

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[8] 1 MWh = 6.9217540840251·10-8 Mt LNG [34] = 0.069217541 t LNG

electricity is equal to 35.6 MW [34] (onsite electricity generation is not included). Moreover, the electricity consumption constitutes about 24% of the utility costs [34]. The electricity requirements of PDH process is equal to 2502 kJ/kg$_{\text{Propylene}}$ (1.843 kWh/t$_{\text{Propylene}}$) and total energy requirements including steam, cooling and natural gas combustion is 10351.37 kJ (10.35 (GJ/t$_{\text{Propylene}}$)) [21].

Based on the provided data for SPC PDH plant (the OLEFLEX process) with a propylene capacity of 455 KTA (kilotons per annum), located in Kingdom of Saudi Arabia [35], and considering 8760 working hours per year, the required electricity is 1.843 kWh/ton$_{\text{Propylene}}$[9].

2-4- Cost analysis of PDH

Overall, the financial benefits can add up to $20 million/y lower net cost of production, an additional $80 million of net present value and an additional 3% return on investment compared to other PDH technologies [1]. Initial investment cost of PDH plant is 574.86[10] €$_{2015}$/t [38].

In the new configuration, propylene production was rebalanced between the FCC and the PDH. FCC propylene yield was lowered to 10wt%, which resulted in a propylene cash cost of production equivalent to the PDH. Adjusting the propylene balance saves 118.64 €$_{2018}$/MT[11], because the PDH cash cost of production is lower than that of the FCC [39].

2-5- CO_2 emission of PDH

Three major greenhouse gas emission sources have been identified in the PDH process [34]:

1. Natural gas combustion
2. Electricity consumption
3. Burning/flaring of waste streams

Emission Factors for Natural Gas Combustion for CO_2: 1.92[12] (t_{CO2}/t_{NG}[13]) [34]. For a plant with 30 year [38] life, the CO_2 emission coefficient is reported to be 0.81 (t_{CO2}/t) [38].

Emission factors for electricity generation based on the mean values of electricity consumption categorized based on sub-regional grids within United States are as following: 156.898 kg/MWhr CO_2, 60.704 kg/GWhr Methane and 8.768 kg/GWhr

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[9] 95.7 (kWh/description) electricity
[10] 1 €$_{2015}$ = 1,11 $$_{2015}$ [57]
[11] 1 €$_{2018}$ = 1,18 $$_{2018}$ [57]
[12] 120,000 lb/scf, 1 Pound per cubic foot is approximately equal to 16.01846337 kilograms per cubic meter.
[13] NG = Natural gas

N_2O.[14] (156.898 kg/MWhr CO_2, 0.0607 kg/MWhr Methane and 0.0088 kg/MWhr N_2O).

2-6- PDH in Belgium

Borealis is producing propylene by conversion of propane at the dehydrogenation unit located in Kallo (Antwerp). The rate of product was 480,000 tons per year in 2003 [40]. The plan of Borealis for building of a new Honeywell UOP's Oleflex™ technology based PDH plant at Kallo site (Antwerp, Belgium) is postponed. Instead, the producer decided to reorganize the schedule of work on the ethylene production via ethane cracker by investing 3 bn €$_{2021}$ on the project [41].

2-7- New approaches on energy saving and CO_2 reduction in PDH:

2-7-1- Membrane reactor concept

PDH is energy intensive (due to its highly endothermic nature). Also, the downstream separation of the equilibrium propylene/propane mixture requires even more energy than the reaction step, due to the small volatility difference. The separation is currently achieved in cryogenic or high-pressure distillation columns with more than 100 trays. The membrane reactor concept has been proposed for equilibrium-limited reactions like PDH wherein the performance can be intensified by selective permeation of one or more of the products (hydrogen and propylene) through membranes, thereby shifting the equilibrium to the product side. Among several different types of membrane reactor configurations, the packed bed membrane reactor (PBMR) which is composed of consists of a packed bed of catalyst similar to a conventional packed bed has been most widely recognized [37]. Figure 6 depicts the role of membrane at PBMR process.

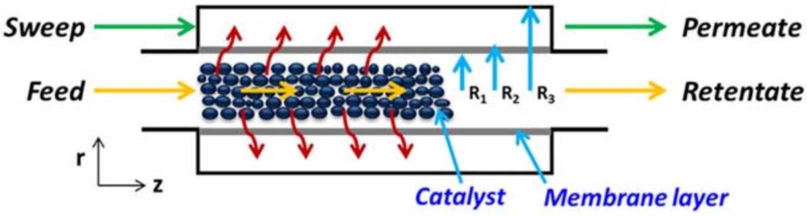

Figure 6. Schematic of a PDH PBMR (The red arrows denote permeation through the membrane surrounding the packed bed. R_1, R_2, and R_3 denote the membrane inner radius, membrane outer radius, and radius of the shell side respectively) [37]

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[14] 345.9 (lb/MWhr) CO_2, 133.83 (lb/GWhr) Methane and 19.33 (lb/GWhr) N_2O.

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2-7-2- Selective hydrogen combustion

Rui Hu et. al. has proposed, simulated, and optimized a co-fed process combining PDH- Oleflex process with selective hydrogen combustion (SHC). The co-fed process uses adiabatic moving bed radial flow reactors as PDH reactors and adiabatic fixed bed reactors as SHC reactors. Their results show higher propylene yield of 6.0-46.1% and saving 2.86-7.24 × 10^6 kJ per ton of propylene under different operating conditions. This advantages are due to consumption of some hydrogen in the process which shifts the reaction equilibrium towards propylene. Moreover, the combusted hydrogen occurs between several PDH reactors and provides a considerable portion of required heat [36]. Co-feeding streams, such as H_2, and CO_2 can have a positive effect on coke elimination. In addition to H_2, co-feeding CO_2 is an attractive method, where CO_2 acts as a soft oxidant, and can reduce the amount of coke formed at elevated temperature on the catalysts via the reverse Boudouard reaction, thereby increasing conversion and maintaining the stability of the catalysts [33]. There are significant roles of CO_2, including removal of coke deposition, re-oxidation of the reduced metal oxides [33].

2-7-3- Coupling exothermic reactions

Coupling exothermic reactions such as CO_2 hydrogenation, ammonia synthesis, olefin refinement and hydrogen storage with the endothermic non-oxidative PDH can promote the transformation of propane. Appropriate reaction temperature and the matching of individual active sites are the key issues [33].

2-7-4- Emission reduction techniques:

CO_2 capture and storage is capable of achieving 90% reduction of produced CO_2 emissions and thus is considered to be the most effective control method [42]. Some processes produce significant quantities of hydrogen, which produces no CO_2 emissions when burned. Thus, use of a completely carbon-free fuel such as 100% hydrogen, has the potential of reducing CO_2 emissions by 100% [42].

3- Methanol to olefins (MTO) and methanol to propylene (MTP)

3-1- MTO and MTP in Belgium

With propylene demand growing faster than ethylene, combined with the building of more ethane crackers (which produce no propylene) rather than naphtha crackers, on-purpose technologies are being employed increasingly to make propylene.

Together with TOTAL, UOP constructed a demonstration unit in Feluy, Belgium, can process roughly 10 ton methanol feed per day [43] and showed significantly more propylene than ethylene production [8], [44]. However, the commercial scale construction of this plant is postponed to 2025. The combined MTO/OCP process has two separate reaction systems, i.e., a fluidized bed MTO system and a fixed bed C_4^+ cracking system [15]. An increasing gap of propylene production that has to be filled by other propylene sources. Lurgi's new MTP process directly aims to fill that gap [45]. The methanol feed is sent to an adiabatically operated dimethyl-ether (DME) pre-reactor where methanol is converted to DME and water using a high-activity high-selectivity catalyst such as aluminum oxide catalyst. The reaction is exothermic [10].

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

$$(\Delta G = -12{,}1 kcal.mol^{-1}, 25°C)$$

The methanol/water/DME stream is routed to the first MTP reactor where also the steam is added. The product mixture is then cooled and the product gas, organic liquid and water are separated [45]. The MTP process operates at slightly elevated pressure (1.3-1.6 bar), moderate steam addition (0.5-1.0 kg per kg of methanol) and low reactor inlet temperatures (400-450°C) [45]. For a feed rate of 5000 t of methanol per day, approx. 519,000 t of propylene are produced per year. By-products include fuel gas and LPG as well as liquid gasoline and process water [45]. Researchers have succeeded in introducing a new binder that improves catalytic properties of ZSM-5 for the MTP reaction [46]. Since the propylene purification demands a very large reboiler duty, the implementation of a heat pump is suitable. Typically, ratios reboiler duty to compressor power over 10 may be obtained. In this case, a heat pump can be implemented for propylene purification for driving a 6 MW side reboiler, located few trays above the bottom. The heat pump requires about 0.6 MW power and can cover 75% from the overall hot utility, the rest being ensured by LP steam [47]. By on-site electricity production, and installation of Rankine cycle, no extra electricity is required for MTP process [21]. Total energy requirements of MTP based on propylene production is reported to be 2.502 $GJ/t_{propylene}$. However, total energy requirements including steam, cooling and natural gas combustion is equal to 13119 $kJ/kg_{propylene}$ (13.12 ($GJ/t_{propylene}$) [21].

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[15] C_4^+ are hydrocarbons with 4 carbons and more.

3-2- Significant Differences between MTO and MTP

The first difference between the two processes is the desired product. Whereas MTO claims ethylene as well as propylene as desired product, MTP is designed to produce mainly propylene and a smaller amount of gasoline [10].

According to the process itself, the second main difference between the processes is the type of reactor. The MTO uses a fluidized-bed reactor, which is favorable with respect to the exothermic reaction so that the released heat can be removed faster. Moreover, the spent catalyst can be regenerated easily by continuously removing a part of the catalyst from the reactor and reroute it back after regeneration. However, the fluidized-bed implies the presence of a stable catalyst, which had to be developed for these special conditions. On the other hand, MTP uses a fixed-bed reactor. The difficulty with respect to the heat of reaction is overcome by using multiple catalyst beds and introduction of fresh reactants after each bed. A fixed-bed reactor is easier to scale-up, has lower investment costs and provides higher product selectivity due to the uniform resistant time of the reactants [10].

An important difference between the two processes is the feedstock. Whereas MTO can use crude methanol[16], the methanol for MTP has to be purified prior to the reaction. This results in additional investment costs for MTP compared to MTO [10].

Methanol is an intermediate for the coal-to-olefins (CTO) process as well. To produce the methanol intermediate for the CTO process, coal gasification produces syngas (carbon monoxide), which is then converted to methanol by traditional technologies [48].

Both MTO and methanol-to-propylene (MTP) technologies use specialized catalysts to promote the conversion of methanol into olefins. Put simply, MTO technology uses a fluidized bed reactor to convert methanol into ethylene, propylene and water, while MTP technology uses an initial reactor to convert methanol into dimethyl ether (DME), and then parallel fixed bed reactors to convert DME into propylene, gasoline and water [48]. Figure 7 depicts detailed blog flow diagram (BFD) of MTO and MTP processes respectively

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[16] Some impurities in crude methanol from natural gas are higher alcohols, methyl-formate and di-isopropyl ether [59].

and illustrates the difference of reactor types in more details. When methanol prices are very low (~ 300 $\$_{2015}$/ton), the return on investment (ROI) is quite attractive (40%–65%) for both processes.

MTO and MTP process costa depends highly on methanol price. realistic price range for methanol is between 400–500 $\$_{2015}$per ton. When the product selling prices are relatively low (e.g., 1200 $\$_{2015}$/ton for MTO and 1130 $\$_{2015}$/ton for MTP) the ROI for a methanol price of 400 $\$_{2015}$/ton is about 10% which is barely acceptable. At a methanol price of 600 $\$_{2015}$/ton, both processes are economically infeasible [10]. Figure 8 compares costs of propylene production through different technologies [21]. Hence, the cost of PDH plant is 1.053 €$_{2020}$/kg$_{\text{Propylene}}$, MTP$_{\text{NG}}$ is 1.56 €$_{2020}$/kg$_{\text{Propylene}}$, Naphtha is 1.23 €$_{2020}$/kg$_{\text{Propylene}}$[17].

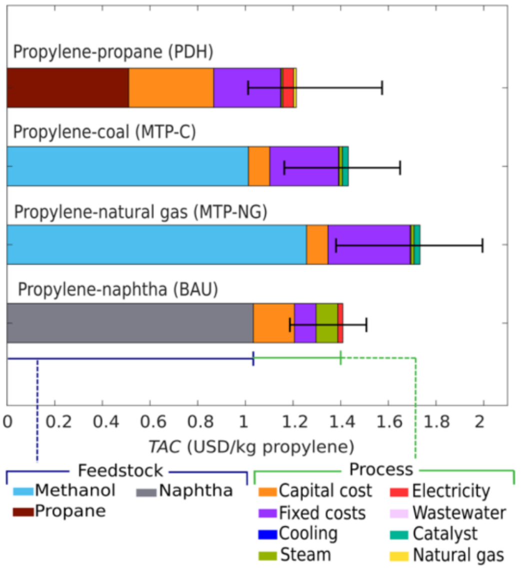
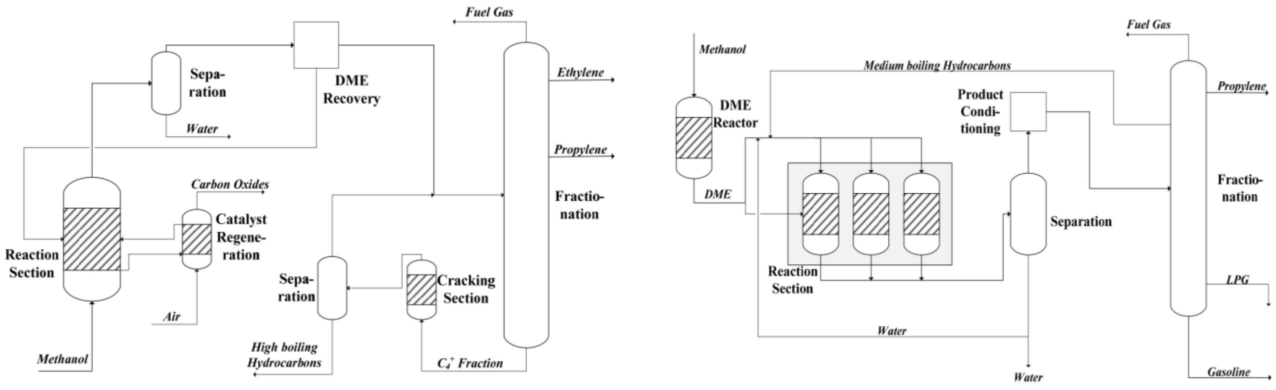


Figure 8. Total annualized cost (TAC) for each process alternative [21]



(a)

(b)

Figure 7. Process flow diagram a) methanol-to-olefins (MTO) process b) methanol-to-propylene (MTP) process [10]. (DME is dimethyl ether, CH_3OCH_3, simplified to C_2H_6O).

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[17] 1.2 USD$_{2020}$/kg$_{\text{Propylene}}$, MTP$_{\text{NG}}$ is 1.78 USD$_{2020}$/kg$_{\text{Propylene}}$, Naphtha is 1.4 USD$_{2020}$/kg$_{\text{Propylene}}$. The values are converted from $ to € based on 1 €$_{2020}$ = 1,14 $$_{2020}$ [57]

3-3- CO_2 emission of MTO and MTP processes

For the MTO and MTP processes, the CO_2 emission is reported as 13.4 and 12.7 ton/ton product respectively [10]. Concerning the total annual emission, the MTP process emits about 12% more than the MTO process, but the product types and flows are different. Therefore, another perspective is to consider the normalized emissions per ton of product or ton of propylene. Here, the MTP process produces less emissions both per ton of total product (−3%) and per ton of propylene (−30%). The latter result is skewed in favor of the MTP process because the primary product is propylene. These differences along with the possibility for carbon capture and sequestration should be further pursued if there is interest or regulation pertaining to the carbon footprint of the process [10].

MTO plant is attractive due to less GHG emission compared to a naphtha cracker. MTO unit emits approximately 1 t of CO_2 less per ton of light olefins produced. Most of the CO_2 in the gas-to-olefins (GTO) chain is linked to the methanol production. Therefore, an alternative is a segregated GTO concept. This concept is based on methanol production in a location with low natural gas prices compared to western Europe and transport of methanol in dedicated, large vessels to an MTO plant located in Europe [49].

4- Metathesis of ethylene and butylene

The term "metathesis" is derived from the Greek meta (change) and tithemi (place). It refers to the changing of positions of the "R" groups around a pair of double bonds [50]. Metathesis reactions are chemical reactions in which two hydrocarbons (alkanes, alkenes or alkynes) are converted to two new hydrocarbons by the exchange of carbon–carbon single, double or triple bonds. These are usually catalyzed by a metal catalyst [51]. Supported rhenium oxide-based catalyst is known to be active for olefin metathesis at low temperatures (i.e., 25 °C), whereas, molybdenum oxide- or tungsten oxide-based catalysts require much higher reaction temperatures (100–500 °C). Moreover, high propylene yield (88%) was obtained under mild reaction conditions using the unconventional feed of ethylene and 2-pentene over SiO_2–Al_2O_3 supported Re_2O_7-based catalysts [52].

Olefins metathesis is an energy-neutral reaction that is enabled by a proprietary catalyst system. By applying this reaction, a portion of the propylene product is derived without the high-energy input otherwise required by the thermal cracking route. For a fixed production rate of ethylene and propylene, energy consumption is thereby reduced with a similar level of reduction in the greenhouse gases produced. Investment is lowered by 5% and the operating margin is improved, due to lower feedstock consumption and the production of a higher-value by-product slate, including a 50% increase in benzene and a 30% decrease in pyrolysis gasoline [53].

The second metathesis reaction is the reaction of butenes alone to produce a mixture of ethylene, propylene and hexene[18]. By using the metathesis reaction, butene replaces the ethylene, reducing the feedstock costs by more than half. In addition to the production of hexene, ethylene and propylene are also produced catalytically with no energy input into the reaction. This permits a further reduction in energy consumption and greenhouse gas emissions, since a portion of the ethylene and propylene are produced by 'energy neutral' metathesis [53].

5- Superflex Technology

Superflex is a fluidized catalytic cracking technology that converts olefinic streams from petrochemical or refinery sources to significant amounts of propylene and ethylene. Superflex uses a fluid riser-type reactor, quite similar to an FCC reactor, to convert hydrocarbon feeds, typically in the C_4-C_8 carbon range, to predominately propylene. Generally, the higher the olefin content of the feed, the higher the propylene yield [54].

In addition to propylene, the major by-products are ethylene and a highly aromatic gasoline stream. It has been proven that typical overall yields as a function of feedstock type. Overall, ultimate propylene plus ethylene yields between 50 and 70% can be achieved with olefinic feedstocks and the recycle to extinction of unconverted C_4/C_5 from the reactor. A simplified flowsheet for the Superflex process is shown in Figure 9 Superflex technology will continue to play a strategic role in meeting future propylene demands in a cost-effective manner. Both refiners and ethylene plant owners will benefit from the conversion of low-value or problematic internal streams to high-value light olefins. Because of the robust and flexible nature of the technology, Superflex will enable the

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[18] Hexene is a high value comonomer used in the production of polyethylene.

producer to convert a wide variety of low-cost feeds into higher margin propylene and ethylene [54].

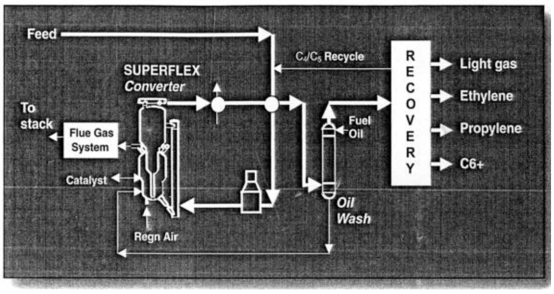

Figure 9. Simplified Superflex flow scheme [54]

6- Bio-propylene

Corn, vegetable oils and other biomass products have been effectively used as feedstocks for the production of bio-propylene, via processes such as gasification, metathesis, dehydrogenation, fermentation, and cracking [26]. Bio-propylene could be obtained from biological resources by butylene dehydration of bio-isobutanol obtained from glucose following the general scheme reported in Figure 10 Bio-propylene has not yet been commercialized [55].

The most promising route to obtain propylene is probably through methanol, further processed to obtain propylene monomer via Lurgi's methanol-to-propylene (MTP) process or UOP's methanol-to-olefins process using the same industrial plants as for petrochemical methanol [55].

7- CO_2-based polypropylene

Producing plastic from captured CO_2 via Power-to-X (PtX) route could prove to decarbonize the feedstock, provide climate change mitigation, and create new business based on sustainability. CO_2-based polypropylene is a net carbon sink at -0.64 kg CO_2 equivalents (CO_2.e) per kg of the polymer and generates 2.27 kg CO_2.eq less emissions than petrochemical polypropylene. Electrolysis of water is identified as the GHG hotspot of this product system due to its high electricity consumption, which is currently a hurdle for power-to-X technology. CO_2-based polypropylene can act as a carbon sink in long-term applications [56]. Figure 11 depicts the CO_2-based propylene via methanol-to-olefins route which is followed by polymerization to produce polypropylene.

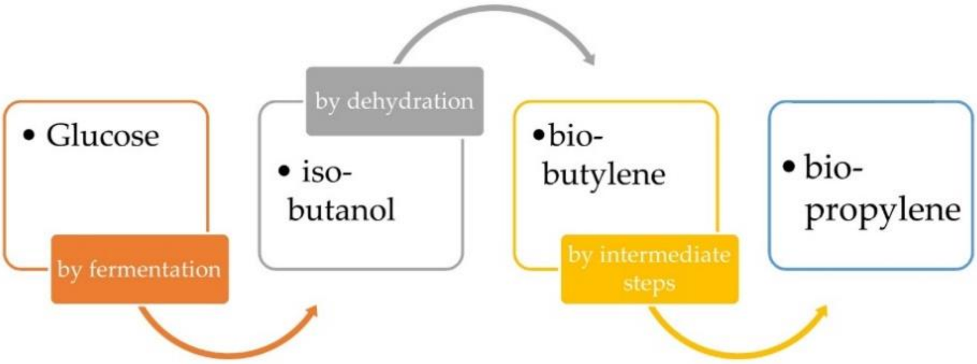

Figure 10. General scheme for Bio-Propylene

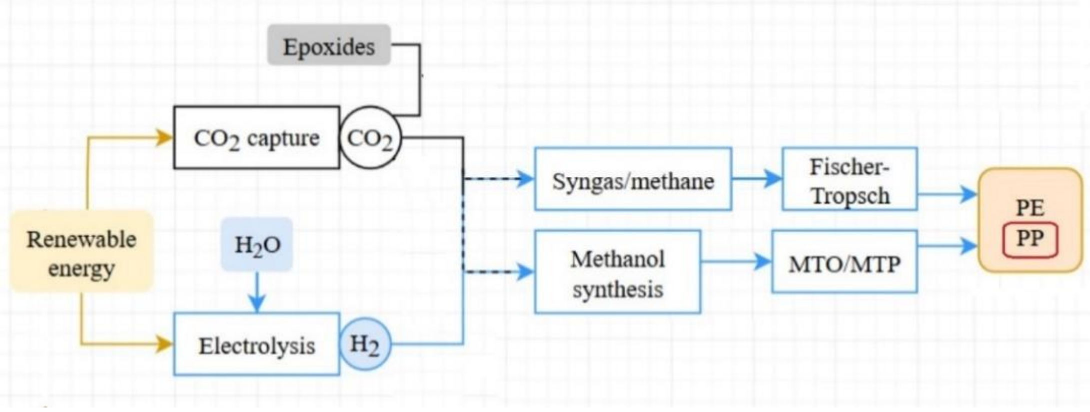

Figure 11. Pathways to convert CO_2 into polymers. PE, polyethylene; PP, polypropylene [56].

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8- Table of summary

Table 4. Summary table, key propylene data

Main production methods	Global supply percentage in 2007	Feedstocks	Propylene yield
By-product from **steam cracker**	63.3 %	Liquid feedstocks e.g. naphtha, LPGs, gas oil	1.5–18 %
By-product from FCC	27.9%	Distillate fuel oil	25 - 40 % (with ZSM-5 catalyst)
PDH	2.6%	Light hydrocarbons - propane	35-40 % [35]
MTP	- **	Purified crude methanol	50% [46]
Energy requirements based on the type of feedstock	**Electricity**		**Total energy consumption**
Steam cracker (Naphtha-based)	44 (kWh/$t_{ethylene}$)		120 (GJ/$t_{ethylene}$) [19]
FCC	1.7 kWh/$t_{propylene}$		0.95 GJ/$t_{propylene}$ fuel (and 0.08 t/$t_{propylene}$ medium pressure steam)
PDH	1.843 kWh/$t_{propylene}$		10.35 (GJ/$t_{propylene}$) [21]
MTP	NO ***		13.12 (GJ/$t_{propylene}$) [21]
Costs			
Steam cracker	1230 (€$_{2020}$ /$ton_{propylene}$) [21]		
FCC	- ****		
PDH route	574.86 (€$_{2015}$ /$ton_{propylene}$) [38], 1053 (€$_{2020}$ /$ton_{propylene}$) [21]		
MTP	1560 (€$_{2020}$ /$ton_{propylene}$) [21]10.35 (GJ/$t_{propylene}$)		

* Demand was growing faster than production in recent years and on-purpose production methodologies are required to fill the gap. Hence, the exact supply percentages via various propylene production methodologies are not available.

** New technology (MTO/MTP applications are gaining momentum and will fill the demand gap).

*** On-site electricity production is included which results in "No extra electricity demand" [21].

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**** There is not cost data available for FCC unit based on the propylene production. Total capital cost for FCC unit construction is[19] 342.34 MM€$_{2015}$ [32]

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[19] The values are converted from $ to € based on 1 €$_{2015}$ = 1,11 $$_{2015}$, MM refers to million

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