

# Original Article: Processes Review of Propylene Production by Catalytic Cracking of C<sub>4</sub>-C<sub>8</sub> Olefins

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## ABSTRACT

Propylene is the second most widely product in the world after ethylene. The amount of propylene produced by steam cracking processes as the first source of ethylene and propylene production is limited. New methods of propylene production (dehydrogenation of propane, conversion of methanol to olefins, conversion of methanol to propylene, etc.) can supply some of its growing demands. The intermediate conversion processes of olefins can meet part of the market demand by converting some of the lighter or heavier olefins from thermal cracking furnaces and by increasing the amount of propylene product. In this paper, we study the technology and economics of several catalytic cracking processes of C<sub>4</sub> to C<sub>8</sub> carbon olefins. The processes investigated in this report for the catalytic conversion of the by-product of heavier olefins to propylene include Omega, OCP, Superflex, Propylur, and MOI processes.

## Introduction

Propylene along with ethylene is one of the widely used chemical products. The most usage of propylene is in the production of polypropylene [1-3]. Propylene is also used to produce intermediate products such as propylene oxide, acrylonitrile, cumene, acrylic acid, and propyl alcohol. Almost 80% of produced propylene is obtained from the thermal cracking of light hydrocarbons and/or refinery processes of fluidized bed catalytic cracking. Although these resources produce a large amount of required propylene, it should be considered that ethylene is the main product of

cracking furnaces with steam [4-6]. The processes of fluidized bed catalytic cracking are also the priority of petrol and diesel fuel production. The majority of ethylene and propylene is obtained by ethylene furnaces with light hydrocarbon fuels such as ethane, propane, butane, gas condensates, and light naphtha. Light fuels produce more ethylene and heavier fuels produce propylene and heavier compounds. Usually, propylene is considered a furnaces side product, however, the main product is ethylene [5-7].

Another important source of propylene is refinery processes of fluidized bed catalytic

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cracking which are considered a catalytic cracking process side product [8-10].

The amount of obtained propylene from fluidized bed catalytic cracking can be adjusted by alteration in operating conditions and process main products economics involved petrol and diesel fuel as well [11].

Currently, 50% of global propylene production is from steam cracking processes and 29% is from FCC refinery units. In recent years, new technologies of propylene production is considered [12-14]. By using new processes of propylene production in recent decades, the amount of propylene production from 5% in 2006 increased to 22% in 2016 and it is predicted that it will be increased by 28% in 2022.

It is expected that propylene demand will be increased between 2016-2026 at a 3.9% approximate rate [15-17]. It is predicted that production capacity during these years has increased by 3.5% and production operation rate with a slight growth remains around 80-85%.

Polypropylene has dominated the most propylene usage which is predicted that during 2016-2026 encounters with 4.3%.

Propylene prices dropped during 2015-2018, and again due to demand growth, the price increased and reached 1200 \$/ton. Also, C4 raffinate as a feed of olefin catalytic cracking processes with a price less than 800 \$/ton can produce an appropriate value added for olefin to propylene catalytic cracking processes [18].

### Olefins Conversion Processes

Olefins stream conversion processes and olefins compound enriched streams are mainly used as an in-process conversion process. However, every single process can be used to produce propylene from light olefin streams such as ethylene, or heavier streams such as butylene or olefins with five carbons or heavier compounds.

These processes are often considered as a small part of a larger ethylene unit [19].

The leading motivation to develop olefins conversion processes is demand alteration for different olefins such as ethylene, propylene, and butylene and consequently, product price alteration in the market. It is predicted that in the future, propylene demand growth more than ethylene. On the other hand, propylene production by using thermal cracking methods is expected to decrease because lighter feeds are increasing compared with naphtha feeds. Even with liquid feeds and light naphtha increasing, the portion of propylene to ethylene would have a limited increase [20].

Intermediate olefin conversion processes have presented some methods for easy conversion of low-valued olefin compounds to propylene. There is a wide range of light and heavier olefins conversion processes. Some of these processes which can be marketable are ethylene and butylene metathesis, olefin catalytic cracking, and direct conversion of ethylene to propylene. Unlike the steam cracking process, all other processes are catalytic [21].

### Olefins Catalytic Cracking

One of the Olefins intermediate conversion processes involves C4+ olefins catalytic cracking to produce propylene. Generally, a zeolite catalyst ZSM-S is used for olefins catalytic cracking processes. 5,6,7,8,9. The catalyst is designed with high selectivity to propylene and held the production of lighter olefins as same as heavier olefins C5+ in the minimum level. In comparison with naphtha or paraffin hydrocarbons common thermal cracking, the olefin cracking process has various important advantages. The most important advantage of olefin catalytic cracking processes is the high proportion of propylene production to ethylene in comparison with thermal cracking processes. Olefins cracking process presented by Asahi Kasei company has a portion of propylene to the

produced ethylene close to 4, whereas the common steam cracking processes are presented a portion of propylene to the produced ethylene of about 0.65 to 0.7.

Catalytic processes' heat of reaction is significantly less than thermal processes. Therefore, using single-stage adiabatic reactors in these processes is an important economical advantage. Finally, the catalytic process reaction temperature is about 500-600 C, which is meaningfully less than the thermal process reaction temperature (800-850 C) [22].

This article has investigated five different C4 and C5 olefin catalytic cracking industrial processes for producing propylene. The first process is Omega presented by Asahi Kasei to produce propylene using C4 olefin streams catalytic conversion [23-25]. The second process is based on recent inventions of Total/Fine and UOP. This process produces propylene by C4-C8 olefins catalytic conversion. LyondellBasell has developed the third process which name is Superflex and it has been marketed by KBR. Using a fluidized bed reactor, this process converts different feeds such as C4, C5, naphtha, benzene, toluene, xylene, and so on to lighter olefins. Another process namely Propylur has been presented by Lurgi/Linde which converts C4 and C5 olefins to ethylene and propylene by catalytic cracking in a fixed bed reactor. The fifth process is the MOI process which has been developed by ExxonMobil. This process can convert various feeds such as cracked C4, light pyrolysis gasoline, and fluidized bed catalytic cracking light naphtha to propylene [26].

#### **Asahi Kasei company Omega process**

Asahi Kasei company has developed and industrialized a process to produce propylene from olefin-enriched hydrocarbon streams. Asahi had an old technology namely the alpha process to produce aromatics from non-olefin enriched streams. The omega process has been developed by using a sustainable catalyst with

high selectivity and the technical knowledge of the alpha process to produce propylene. The first industrial unit of this process with 50000 ton/y started to produce in 2006 in Okayama Japan. This unit has been purchased by Sayno petrochemical company [27-29]. The reactor system involves two adiabatic fixed-bed reactors. One of the reactors is in service and the other one is regenerating the catalyst. The reaction temperature depends on the composition of the feeds and it is between 530 to 600C and the pressure is between 1 to 5atm. The used catalyst is a zeolite with high stability and selectivity to produce propylene. During the reaction, the catalyst is deactivated and it needs to regenerate by using a controlled oxygen stream for burning catalyst surface cokes. Catalyst regeneration is done at 500C [30-32]. The reactor outlet stream is sent to a depropanizer tower to separate C3+ compounds from C4+.

C3 and lighter compounds can be sent to a C3 separation unit or deethanizer column to separate the propylene product. C2 and lighter compounds are returned to the furnace. C4+ compounds can be also returned to the thermal cracking furnaces or the reactor. These compounds can be also used as an alpha process feed [33].

The advantages of the Omega process compared to the common technologies of olefins production are at least 3% less energy consumption, a significant decrease in carbon dioxide emission, and propylene high selectivity. The ratio of propylene to ethylene (P/E) in naphtha common processes is about 0.65. This ratio in the Omega process is 1:4, while with the integration of this process with naphtha cracking processes, the propylene to ethylene ratio increase to 0.8 [34].

#### **Propylur process**

This process is exclusively presented by Linde to use in steam cracking processes. The propylur

process is low pressure with a stable temperature, and the adiabatic and catalytic process converts C4-C7 olefins to propylene with ethylene and C5+ production [35-37]. The driving force of this process is adjusting the propylene-to-ethylene ratio. Hence, the demand for propylene has been a lot, this process is used to increase propylene production and eliminate the side products of the ethylene production unit. The propylur process can be applied in refineries or any other resource of C4+ olefins such as MTBE. This process can be also applied to producing C4/C5 olefins in an FCC unit [38]. In the Lurgi company propylur process a steam-resistant zeolite catalyst is used. The used catalyst in the reactor is a ZSM-5 type which has an atomic proportion of about 50. The catalyst is performed in regular cycles of reaction and generation with the air because a high-performance catalyst is always available to the feed [39].

### Superflex process

Superflex is a process technology to produce light olefins/propylene from low-cost feed streams such as light gasoline caused by refinery FCC process (like olefin unit) and mixes C4 and C5 streams. The catalytic process converts these feeds with high selectivity using ZSM-5 special catalyst. This process is based on a fluidized bed catalytic reactor which can be integrated with an olefin unit and will be flexible with many process streams that are available in olefin units. This technology can be also used in petroleum refineries which improves the low-valued process streams and it increases propylene production. In both applications, the potential of low-valued material conversion to pure products exists with well economic benefits. This technology can be used simultaneously with other processes to produce propylene with highly economical benefits. The first global Superflex unit was constructed for Sasol in South Africa by KBR. According to the Sasol project

(Turbo project), about 250000 ton/y propylene were produced with extra ethylene. This is the first Superflex company in South Africa. 11 Superflex process feed is hydrocarbons between C4 to C8. Generally, the large amount of olefin in the feed increases ethylene and propylene production. Also, paraffin and naphtha in the reactor are cracked with a conversion percent less than olefins. Olefin presence in feed leads to an increase in the saturated hydrocarbon conversion percent. 12 The feed does not need to separate, because all olefin and paraffin isomers participate in propylene production. The feed stream can also involve aromatics, naphtha, and inert compounds such as nitrogen but the amount of benzene must not be more than 30 wt% of total feed. In more than 40 wt% of benzene concentration, alkylation is important and the light olefins yield is decreased. 11

Special modified catalyst ZSM-5 with silica to aluminum (Si/Al) ratio, of 20 to 60 is used in the Superflex process. 13,14,15,16

### OCP process

The OCP process is developed for using C4-C8 olefins from different resources such as steam cracking furnaces, refineries, and methanol to olefin conversion units (MTO). OCP catalyst can also convert heavier olefins such as C5 and light catalytic naphtha (LCN). Therefore, non-reacted C5 olefin compounds can also with non-reacted C4 returned to improve the propylene production yield. The possibility of using a C5 olefin stream considering the low value of this feed in this range, is considered a significant advantage. 4

The OCP process is used a zeolite-based catalyst with an aluminum silicate catalyst structure. The ratio of silicon to aluminum in the catalyst is significantly important. Generally, to achieve the desired efficiency, the proportion of silicon to aluminum should be at least more than 180. The reactions of hydrogen transfer depend on the

power and density of the catalyst acid sites. These reactions cause coke formation during the olefins conversion and as a result, the stability of the catalyst decreases during the time. Moreover, these reactions tend to produce saturated compounds such as paraffin, intermediate non-stable DN compounds, aromatics, and cyclic olefins that none of them are suitable for cracking to the light olefins. The high portion of silicon/aluminum in the catalyst structure decreases the catalyst acidity and consequently, the stability of the catalyst increases. With an olefin-based feed (30-5-wt%) can be reached an olefin stable conversion to propylene with a high yield. 17

### **Mobil olefin conversion process (MOI)**

The Mobil olefin conversion process is a branch of technologies based on Mobil methanol such as methanol to gasoline (MTG), methanol to olefin (MTO), and olefins to gasoline/distillate. In these processes, small olefins in an oligomerization reactions series and cracking under relatively high pressures and low temperatures convert to larger olefins. MOI process has been based on understanding the olefins conversion thermodynamics. MOI process has been based on fluid catalytic cracking technology (FCC) by using a zeolite catalyst.18

The zeolite catalyst (e.g. ZSM-5 and MCM-22) adjusted for propylene and ethylene selectivity improvement is the heart of the MOI process. In effective zeolite catalysts, silica to aluminum molar ratio is at least 1:25 and it can convert 10-30 wt% of C5-C12 in a one-pass fluidized bed operation.19

### **Result and Discussion**

Table 1 presents a comparison of five olefin catalytic cracking which is mentioned in this report. Four of them are industrialized and only

the MOI process remains in the engineering phase. MOI process and Superflex are in fluidized bed reactors and the others are in fixed bed reactors. Most of the time processes are done in atmospheric pressure and temperature around 500C. Each process uses a special zeolite catalyst with Si/Al ratio for olefins cracking. Generally, feed diolefin content, the amount of butadiene and acetylene in feed, and also the amount of isobutylene in feed should be controlled to prevent coke formation and catalyst deactivation. Feed diolefin content can increase in the propylur process up to 1.5 wt% and in the Omega process up to 2.5 wt%. Among investigated processes, the MOI and Superflex processes can convert various feeds, and especially in the Superflex process naphtha and paraffin compounds crack in the reactor with a lower percentage compared with olefins. Also, the feed can involve aromatic compounds, but the amount of benzene should not be more than 30 wt% of the total feed. Although the propylene to produced ethylene ratio in common light olefins production processes (steam cracking furnaces) is 0.6 to 0.65, this ratio can increase in catalytic cracking processes from 1:2 in MOI and Superflex processes to 1:4 in other processes. By integrating the steam cracking process with the catalytic cracking process, the propylene to produced ethylene ratio increases up to 0.8 and in some cases (propylur process) it increases up to 1.0. The newest olefins catalytic cracking process is the OCP process, coupled with the methanol to olefins (MTO) process in 2009. The first industrial unit with 295000 ton/y was constructed in China. The propylene to produced ethylene ratio in this process (MTO/UOP) can increase between 1.25 to 1.8.

**Table 1.** Comparison of olefins catalytic cracking processes

Processes	Omega	OCP	Superflex	Propylur	MOI
License	Asahi Kasei	Total /UOP	KBR/ LyondellBasell	Lurgi/Linde	ExxonMobil
Commercial Plant					
Capacity (MT/Y)	50,000	295,000*	240,000	---	---
Started (Year)	2006	2013	2006	2003	---
Location	Okayama, Japan	Nanjing, China	South Africa	BP's Worringen/ Germany	---
Reactor	Adiabatic Fixed-bed	Fixed-bed	Fluidized-bed	Adiabatic Fixed-bed	Fluidized- bed
Temperature (°C)	530-600	500-600	500-700	500	400-600
Pressure (atm)	1-5	1-5	1-2	1-2	1-2
Feedstock					
	C4 Raffinate	Light Catalytic Naphtha (LCN)	FCC Naphtha or C4s	C4 Raffinate-I	Cracked C4s
		C5 fraction of LCN	Cracked Naphtha	Raffinate-II	Light PYolysis Gasoline
		C4 Raffinate- II	BTX	PYolysis Gasoline	FCC Light Naphtha
			MTBE Raffinate		
			C5 Olefins from Gasoline		
di-Olefin Content	<2.5%	<0.1%	---	<1.5%	---
Catalyst	Ag/Na/ZSM-5	MFI	H-ZSM-5	ZSM-5	MCM-22
Si/Al	800-2000	280-1000	20-60	~50	20-40
Modified by			1wt% Phosphorous		
Raw Material Consumption (per lb propylene)	2.16 lb	2.49 lb	3.03 lb	1.91 lb	3.80 lb
Propylene Yield (wt%)	46	40	33-48	50-60	14-26
P/E	4:1	4:1	2:1	4:1	2:1
P/E, (integrated with Naphtha Cracker/MTO)	0.8	1.25-1.8	0.8	1.0	0.75
*MTO/UOP process					

### Economical comparison of olefins catalytic cracking processes

In this report, the production costs of each catalytic cracking process are considered for different industrial unit capacities. Considering

data and economic estimations are achieved for different processes are related for various years, (from 1999 for MOI process, 2001 for propylur process, 2008 for Superflex until 2017 for Omega and OCP processes. By updating the information using PEP Cost Index. August 2020

20 The comparison is possible. The updated total fixed capital cost (TFC) until August 2020 is presented in Table 2 for catalytic cracking processes. Considering units' different

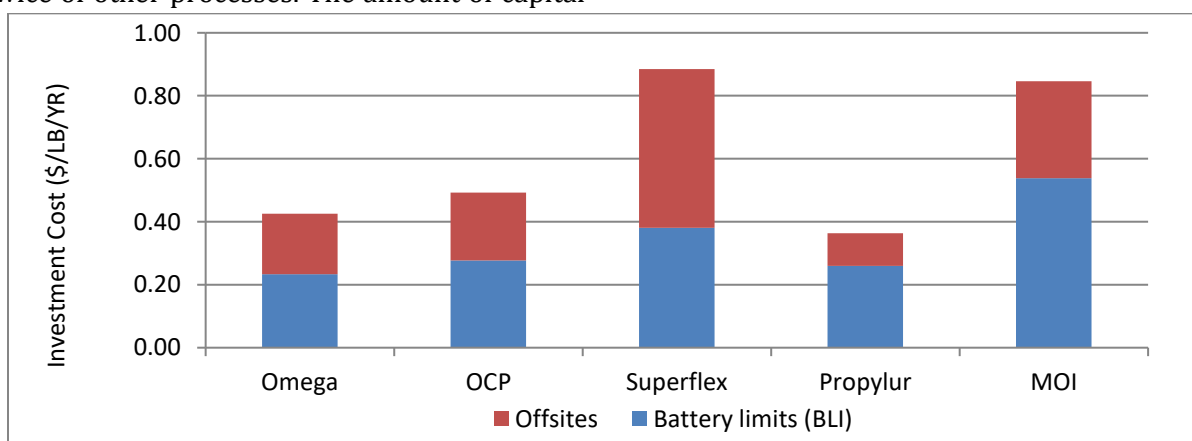
capacities, the required capital cost for 1lb/y propylene production is calculated to better comparison of TFCs is possible.

**Table 2.** Comparison of total fixed capital of olefin catalytic cracking processes

Processes	Omega	OCP	Superflex	Propylur	MOI
Capacity (Million LB/Y)	110.00	110.00	513.00	326	448
Cost Index (Y)	Q1 2017	Q1 2017	2008	2001	1999
Investment (\$Millions)					
Battery limits (BLI)	23.50	27.90	125.80	43.20	122.00
Offsites	19.30	21.60	166.50	17.10	70.00
Total Fixed Capital (TFC)	42.80	49.50	292.30	60.30	192.00
Cost Index Update (Y)[20]	Q2 2020	Q2 2020	Q2 2020	Q2 2020	Q2 2020
Investment (\$Millions)					
Battery limits (BLI)	25.70	30.51	195.46	84.79	241.02
Offsites	21.11	23.62	258.69	33.56	138.29
Total Fixed Capital (TFC)	46.81	54.13	454.15	118.36	379.32
Investment (\$/LB/Y)[20]					
Battery limits (BLI)	0.23	0.28	0.38	0.26	0.54
Offsites	0.19	0.21	0.50	0.10	0.31
Total Fixed Capital (TFC)	0.43	0.49	0.89	0.36	0.85

The amount of capital cost for 1lb/y propylene production in MOI and Superflex processes is the most so that the required capital cost is about twice of other processes. The amount of capital

cost for the propylur process is the least among the investigated processes. For a better understanding, figure 1 is considered.



**Figure 1.** Total fixed capital - Olefins catalytic cracking processes

Capacity: 1lb/y (propylene)

The battery limits capital costs for propylur, Omega, and OCP processes are approximately

the same. The low propylur process total capital cost in the offsite section is related to being low in this process's costs. The information in Table 3 shows that propylur process offsite costs have decreased because of unpreicting low temperature cooling services. The Superflex and MOI processes have a high capital cost of

equipment compared with other processes, and they are because of their fluidized bed reactors and unit's required compressors. On the other hand, the Superflex process has a high offsite cost which is related to the unit's cooling services.

**Table 3.** Total investment- Olefins catalytic cracking processes- Capacity: 1000lb/y (propylene)

	Omega	OCP	Superflex	Propylur	MOI
Battery Limits Equipment					
Reactors	0.6	0.7	23.3	16.3	16.8
Columns	4.5	6.2	21.6	16.6	2.1
Vessels	1.7	2.4	6.5	1.2	15.7
Heat Exchangers	4.6	5.8	22.2	29.0	11.2
Furnaces	4.1	4.5	7.8	4.8	21.0
Compressors	18.7	19.5	25.1	11.1	71.5
Pumps	1.6	2.6	1.7	0.6	1.1
Miscellaneous Equipment			3.2		
Total	35.8	41.7	111.4	79.6	139.4
Direct Installation Costs	81.8	98.6	129.6	78.2	141.1
Indirect Costs	52.6	61.4	36.2	57.3	110.7
Unscheduled Equipment, 10%	17.0	20.2	27.7	10.8	39.1
Battery Limits, Installed	187.3	221.8	304.9	225.9	430.3
Contingency, 25%	46.8	55.5	76.2	33.9	107.6
Battery Limits Investment	234.1	277.3	381.1	259.8	537.9
Off-Sites, Installed					
Clarified water	6.6	6.6	6.9	2.0	4.4
Cooling Water	9.1	14.4	36.7	0.5	22.4
Prosses Water	3.4	3.4	4.0	1.0	2.8
Boiler Feed Water	11.6	11.6	12.6	6.7	7.5
Steam	26.7	26.7	58.9	35.8	30.1
Refrigeration	49.2	56.6	252.2		
Tankage	17.6	18.3	1.8		26.7
Utilities and Storage	124.1	137.5	373.3	46.0	93.8
General Service Facilities	17.9	20.7	12.6	30.6	126.4



Waste Treatment	11.7	13.9	17.5	13.0	26.9
Total	153.7	172.1	403.4	89.6	247.1
Contingency, 25%	38.4	43.0	100.8	13.4	61.8
Off-Sites Investment	192.2	215.1	504.2	103.0	308.9
Total Fixed Capital	426.2	492.4	885.3	362.9	846.8

### Required utilities for olefin catalytic cracking processes

The required utilities for 1lb/y propylene production for investigated processes in this report are summarized in Table 4. The cooling water consumption in Superflex and MOI processes is much more than the other processes. Also, the Superflex process needs -140F cooling in the separation section because

of having low propylene to produced ethylene ratio and also polymer grade ethylene production. The propylur process has the least cooling water consumption but, by contrast, it has the most steam and electricity consumption among the investigated processes. High electricity consumption is related to the process's electrical heaters.

**Table 4.** Utilities summary- Olefins catalytic cracking processes- Capacity: 1lb/y (propylene)

Processes		Omega	OCP	Superflex	Propylur	MOI
Utilities	Unit	Consumption per LB	Consumption per LB	Consumption per LB	Consumption per LB	Consumption per LB
Cooling Water	GAL	6.2	11.7	28.9	0.257	32.6
Steam, 150 PSIG	BL	0.948	1.8	4.15	6.29	3.02
Steam, 600 PSIG	BL	--	--	--	--	0.216
Electricity	KWH	0.0685	0.0766	0.147	0.238	0.136
Natural Gas	BTU	1420	1640	2520	1090	1200
Fuel Oil	BTU	--	--	--	--	3600
Refrigeration, -45F	TON-HR	0.00638	0.00609	--	--	--
Refrigeration, 20F	TON-HR	0.0415	0.0573	--	--	--
Refrigeration, -140F	TON-HR	--	--	0.00476	--	--
Refrigeration, -40F	TON-HR	--	--	0.177	--	--
Refrigeration, 50F	TON-HR	--	--	0.013	--	--

### Environmental footprints of olefin catalytic cracking processes

In recent years, in addition to economic factors, process environmental footprints in confronting

carbon emissions and water consumption is being significantly important. Carbon footprint involves direct and indirect process carbon dioxide emissions. The direct carbon dioxide emission is caused by different process streams such as boilers and heaters which use natural gas. The indirect carbon dioxide emission is caused by electricity consumption which is occurred in electricity generators. The water

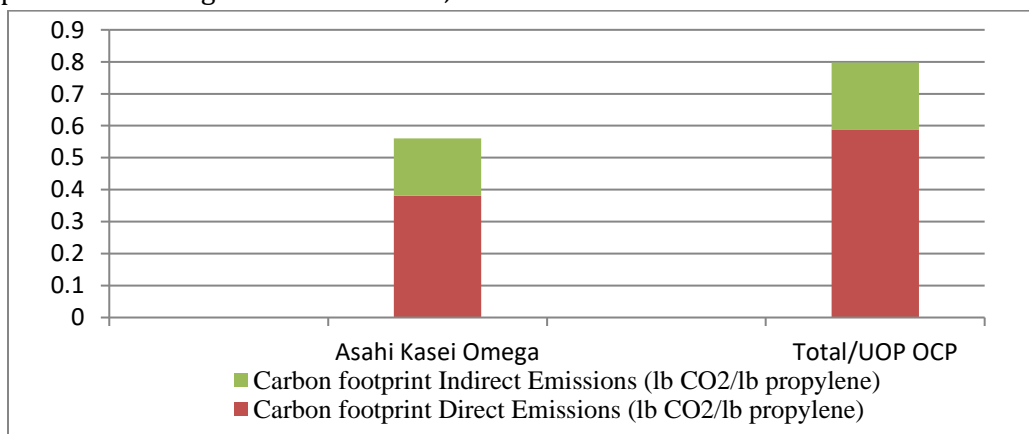
footprints involve water loss in cooling towers and steam consumption. Also indirectly involves the consumption of required cooling water for utility equipment such as coolers. In table 5 environmental parameters of two samples from olefins catalytic cracking new processes are compared. Unfortunately, there were no presentable older environmental data.

**Table 5.** Environmental footprints of Olefins catalytic cracking processes

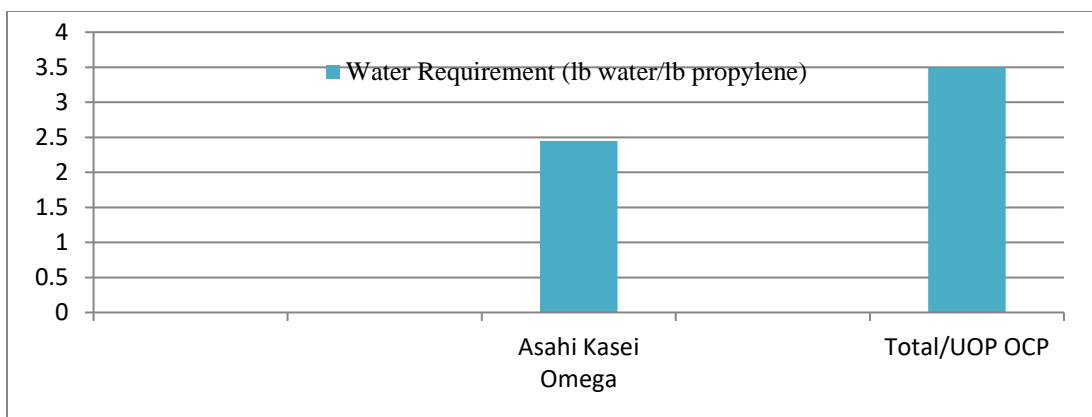
Processes	Asahi Kasei Omega	Total/UOP OCP
Carbon footprint		
Direct Emissions (lb CO <sub>2</sub> /lb propylene)	0.381	0.588
Indirect Emissions (lb CO <sub>2</sub> /lb propylene)	0.179	0.210
Total Emissions (lb CO <sub>2</sub> /lb propylene)	0.560	0.798
Water Requirement (lb water/lb propylene)	2.45	3.49

Figure 2 and Figure 3 show the consumption of carbon dioxide emissions and water consumption for OCP and Omega processes. Carbon emissions and water footprint mainly relate to the unit's utilities consumption. The direct carbon emission from the OCP process is more than the Omega process because of more consumption of natural gas and steam. Also, this

process has more indirect carbon emissions because of high electricity consumption. Considering the water footprint, the Omega process has less cooling water and steam consumption, while water loss in the OCP process is relatively more.



**Figure 2.** Carbon emissions of Olefins catalytic cracking processes



**Figure 3.** The water footprint of Olefins catalytic cracking processes

### Conclusion

Despite being unavailability of environmental data related to the other processes, it can be guessed that the Superflex process has the most consumption of utilities in the cooling water section, natural gas, steam, electricity, and cooling. As a result, it has the most carbon dioxide emission and water loss among the investigated processes. The MOI process utilities consumption is also considerable and the carbon dioxide emission is high. The amount of water loss in this process is competitive with the Superflex process. One of the advantages of the propylur process is very low cooling water consumption and as a result, the water loss in this process is low.

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