Paving the Way to Low-Carbon Propylene from the FCC Unit

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Abstract:

Many countries are adopting policies and regulations to drive toward carbon neutrality. This is expected to have a huge impact on the oil & gas industry in the mid- and long-term. It will be vital for refiners to understand how to navigate this journey, and to adapt their processes to maximize profits. For example, high carbon emissions taxation together with increased energy costs will put refining margins under pressure in regions like Europe, while coming regulations will likely impact energy producers from other continents targeting exports to the EU.

Through the shifting paradigm, the demand for petrochemical products is expected to remain strong through to 2050 and beyond, which demonstrates the resilience of light olefins and chemicals products. Therefore, refineries with petrochemicals integration will be more competitive than others in the face of declining demand for liquid products such as gasoline and diesel. In addition to shifting refinery product outputs, refiners may be required to reduce the carbon intensity of their products. One way that refiners can align with this goal is to adapt the FCC to become an increasingly large producer of light olefins, which not only meets the increasing market need, but can be done in a cost competitively way and with lower carbon intensity than other technologies.

Production of petrochemicals requires monomer sources, and among all the potential sources for these petrochemicals, catalytic processes require the lowest energy input. This makes propylene from catalytic processes less carbon intensive than thermal counterparts. Several analyses show that light olefins production from the FCC unit has the most favorable cost position (vs thermal and other catalytic routes). Further, via catalytic approaches, light olefins from the FCC can be produced without increasing Scope I emissions and since the production of light olefins is at the expense of transportation fuels from the FCC, this approach also decreases Scope III emissions.

Grace has built holistic strategies to help refiners to minimize CO_2 emissions while boosting profitability further through optimization of yields. In this paper, Grace explains in detail what potential strategies can be actioned for maximum light olefins production at minimum operating carbon intensity, how long-term partnerships deliver value in building integral solutions, and the newest technology advances that will help FCC units to achieve the maximum profitability producing Low Carbon Propylene.

INTRODUCTION

Propylene plays a critical role in the petrochemical industry. Approximately 70% of propylene produced is used in the manufacture of polypropylene, a widely used polymer in durable goods and packaging among other uses. The demand for propylene is projected to increase by 36% through 2030 (or 4% annualized). [1] One challenge associated with meeting the increased demand for propylene is the CO_2 emitted during its production. The production of propylene and ethylene is estimated to generate 250 – 300 million Metric Tons (MTs) of CO_2 per year. Since the annual demand for propylene and ethylene combined is approximately 295 million MTs per year, the production of C_2= and C_3= therefore generates on average approximately 1 MT of CO_2 per MT of C_2= or C_3=. [2]

Jurisdictions are continuing to implement CO_2 taxation or increase the magnitude of their CO_2 tax with the aim to reduce emissions. Countries in the Asia Pacific are implementing new carbon taxes, like Singapore

[3]. The carbon tax in Europe has recently reached values of ~€100/MT. [4] Against this backdrop, petrochemical feedstock producers will be challenged to reduce the carbon intensity of their production processes. These actions to produce petrochemicals and fuels with lower carbon intensity are driving shifting behavior demonstrated in the figure below.

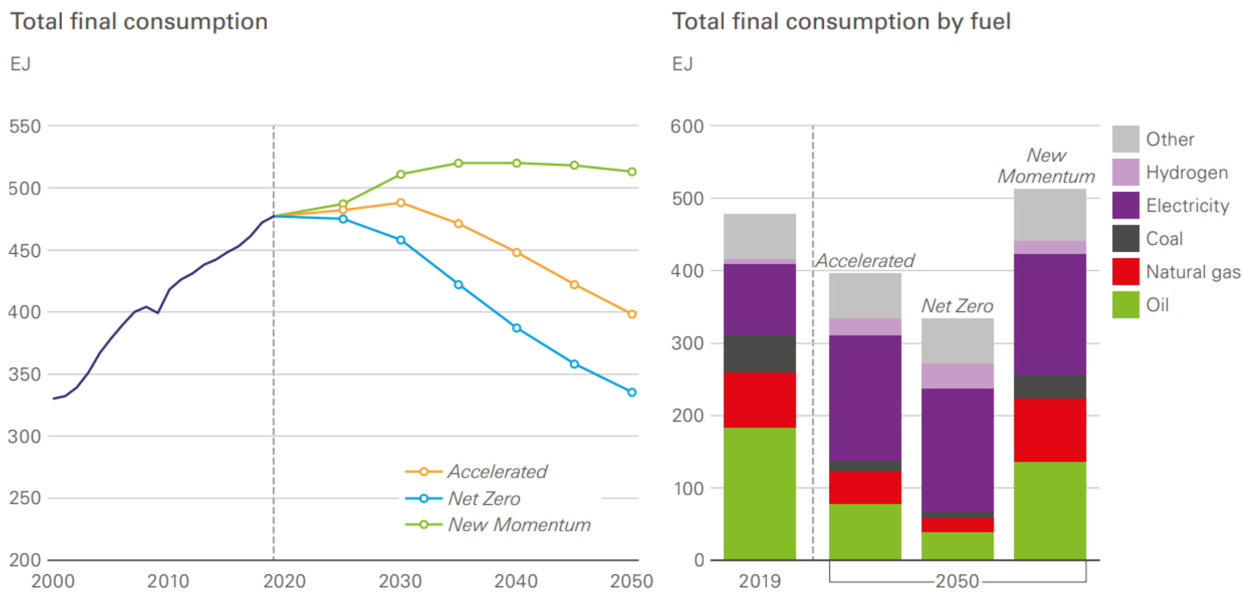

Figure 1. Energy consumption outlook, BP Energy Outlook 2023

Propylene is made via different processes, the three most important are steam cracking, Fluid Catalytic Cracking (FCC), and Propane Dehydrogenation (PDH). This article compares the carbon emissions of these processes and further examines the carbon intensity of propylene from the FCC Unit (FCCU). ZSM-5 technology is discussed including its unique ability to increase the yield of propylene from the FCC without increasing CO_2 emissions. Finally, a Life Cycle Analysis for producing propylene from the FCC is presented, showing how Scope III emissions change when a refinery shifts operation between transportation fuels and propylene mode.

Carbon Intensity of Different Processes

The process to produce propylene (and ethylene) involves either cracking of larger molecules (naphtha, VGO, resid, ethane, propane, butane) in the case of steam cracking and FCC or dehydrogenation of propane in the case of PDH. These reactions are endothermic and require significant amounts of energy. Table 1 shows ranges for the carbon intensity of different processes. Note that in both steam cracking and FCC, propylene is one of several products yielded, so the emissions are expressed as MT of CO_2 per MT of total product produced.

	CO_2/ Product (MT/MT)	RXN Temperature, °C
Refinery/FCC [5]	0.3 – 0.4	550
PDH [6]	1.2 - 1.7	630
Steam Cracker [7]	1.0 – 1.8	840

Table 1. CO_2 emissions generated per unit of product produced and typical reaction temperature for several processes.

Table 1 shows that the refinery-based propylene has the lowest carbon intensity. The main reason for this is that enabled by catalytic activity, the FCCU typically operates at the lowest temperature among the different technologies. Unlike steam cracking, FCC is enabled by catalytic technology and therefore is a more energy efficient process. Further, when compared to PDH, FCC is not equilibrium-limited: while the dehydrogenation of propane takes place in the presence of a catalyst in PDH, the reverse reaction is also possible and higher reaction temperatures are required to drive the equilibrium towards propylene. [8] As a result, the FCC has the lowest reaction temperature. CO_2 emissions generated in propylene production processes stem from heating feedstocks to the required reaction temperatures: the higher the temperature the larger the energy requirement and CO_2 emissions generated. Some of this energy is provided by burning coke produced in these processes (in the case of the FCCU most of the energy is supplied this way, more on this below).

The implication of Table 1 is striking: if lowering emissions were the sole metric in determining the preferred method for producing propylene, it would be preferred to source propylene from the refinery. In practice, it is not so simple since the refinery and the FCCU are traditionally geared towards producing fuels.

In addition to its position as the lowest carbon intensity source of propylene it is also important to recognize that the refinery (which includes FCC) also is advantageous as the lowest cash cost option among alternative technologies. Figure 2 shows the results of an analysis conducted by Grace to estimate the cash and capital cost to produce propylene using various technologies. This analysis takes into account feed and operating costs while also considering capital cost for incremental PDH capacity.

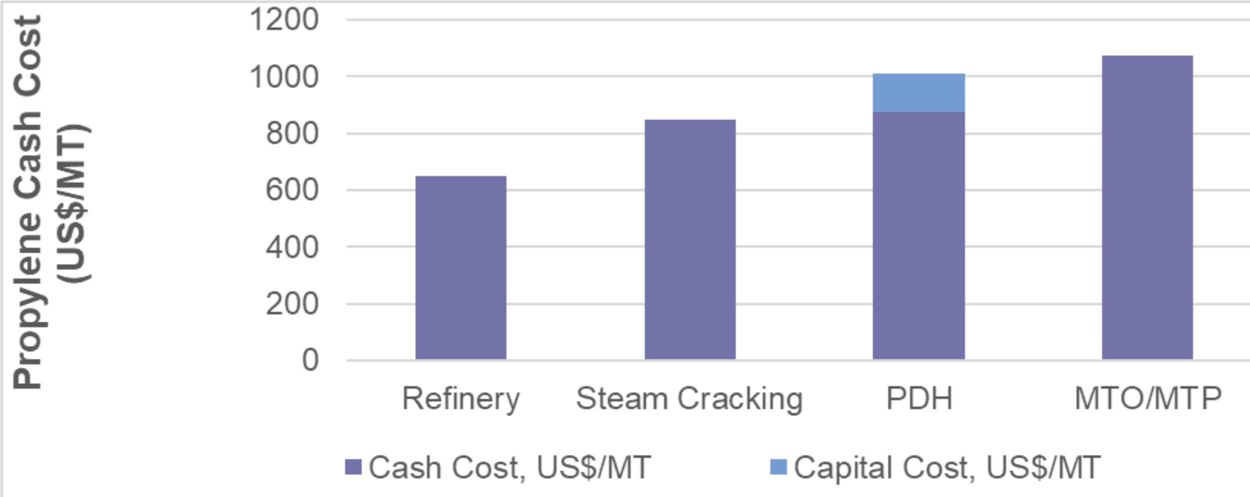

Figure 2. Cash and capital cost position for propylene with various technologies

FCC Chemistry: Coke Generation and Propylene Production

The FCCU requires the production and combustion of coke to generate the heat required to vaporize the feedstock and drive the endothermic cracking reactions taking place in the riser. The combustion of this coke in the FCCU accounts for approximately 15 - 20% of the CO_2 emissions from the refinery. [9] [10] The coke produced in the FCCU stems from several contributors: (i) hydrogen redistribution reactions in the catalytic cracking, (ii) cracking of heavy feed components, (iii) poor feed vaporization, (iv) dehydrogenation reactions catalyzed by contaminant metals in the feed, and (v) unstripped hydrocarbons entrained in the catalyst leaving the reactor.

The coke yield directly contributes to the Scope I, or direct, CO_2 emissions from the FCCU. Factors that increase the coke yield, for example operating at higher reaction temperature, will increase emissions from the FCCU. Reducing FCCU severity (reducing riser temperature), reducing Catalyst-to-Oil ratio (C/O) (for example by increasing feed temperature, reducing catalyst cooler duty, etc.), or reducing slurry or Light Cycle Oil (LCO) recycle rates will all reduce CO_2 emissions from the FCCU, accomplishing the objective of reduced Scope I CO_2 emissions. However, these moves typically lead to reduced conversion and increased slurry from the FCCU. While it may be desirable to operate the FCCU at lower direct emissions by decreasing coke yield, this is generally not economically attractive.

The yield of propylene from the FCCU can be increased by (i) increasing reaction temperature, (ii) increasing C/O, (iii) decreasing the hydrocarbon partial pressure (introducing additional steam into the process), (iv) improving feed quality, (v) reformulating the catalyst to drive propylene yield higher, and (vi) the use of ZSM-5 technology. Options (i) thru (iii) will either increase coke yield or require additional energy thereby increasing emissions from the process whereas ZSM-5 technology usage has a neutral effect on CO_2 emissions (the catalyst itself can be reformulated to minimize changes in coke yields). The effect of changing operation variables and impact on CO_2 emission and propylene production is shown in Table 2 below.

Operational Move	Effect on Propylene Production	Effect on CO_2 Emissions
Increase ZSM-5 Additive Rate	↑	↔
Reduce Riser Severity	↓	↓
Reduce C/O (higher Feed T, etc.)	↓	↓
Reduce Gasoline/LCO Recycle	↓	↓

Table 2. Summary of the effect of different FCCU variables on CO_2 emissions and propylene yield.

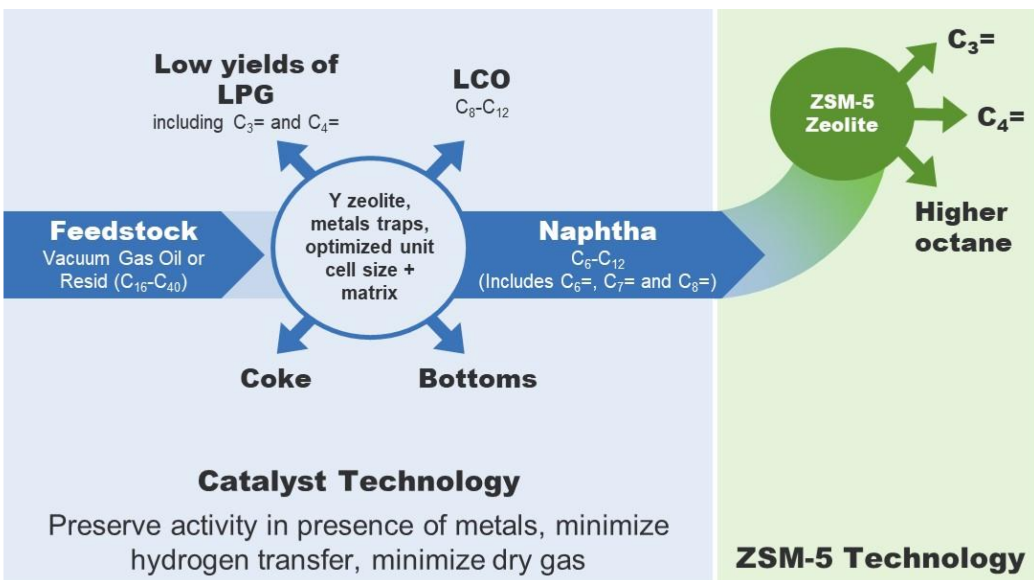

Figure 3. Schematic indicating the roles of Y-zeolite based catalyst and ZSM-5 technology in the generation of propylene and butylene.

ZSM-5 technology is key to increasing C_3= yield from the FCC. This shape selective zeolite cracks gasoline range molecules predominantly into LPG olefins. [11] In general, to maximize propylene and FCC gasoline RON, the preferred base catalyst generates and preserves the maximum yield of gasoline range olefins so that these can be further cracked by the ZSM-5 technology into propylene. The concept is well illustrated in Figure 3, showing the catalytic approach to maximize LPG olefins from the FCC.

Use of ZSM-5 has two key advantages over operational handles to increase the yield of propylene from the FCC: (i) it has no effects on the coke yield in the FCC, therefore it has a negligible effect on process CO_2 emissions, and (ii) it has an outsized impact on propylene yields relative to changing operational handles. This last point is exemplified by the data in Figure 4: for this comparison between a base catalyst with and without a high activity ZSM-5 additive, the propylene yield is observed to increase ~ 2 wt% on fresh feed basis (ff) when the riser temperature is increased by ~20°C whereas use of only 2 wt% ZSM-5 additive increases the C3= yield by nearly this amount at *constant temperature*.

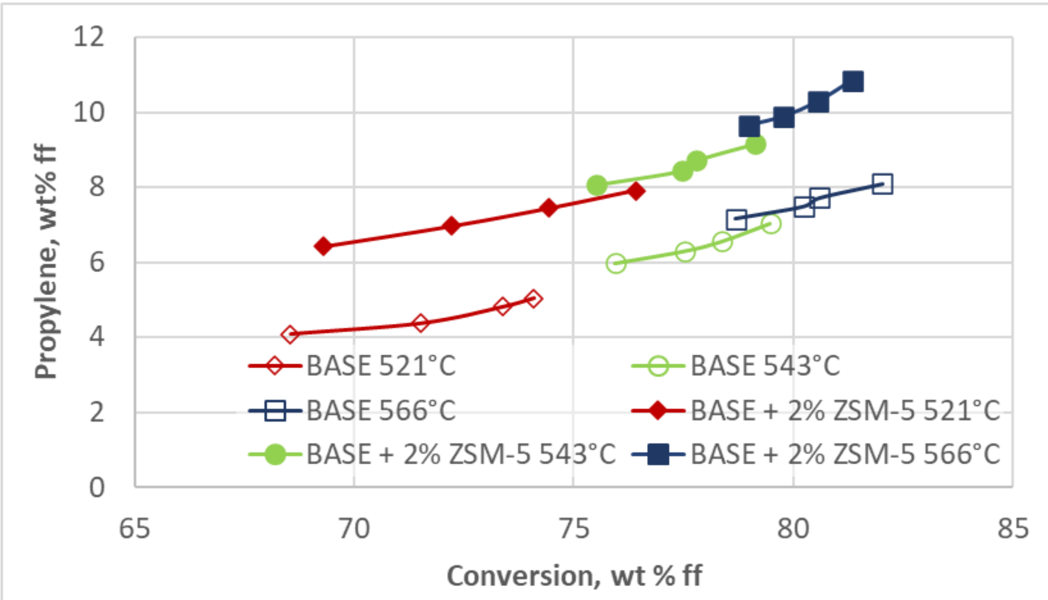

Figure 4. Davison Circulating Riser (DCR™) data comparing propylene yields between a base catalyst (open symbols) and the same base catalyst + 2 wt% of a high activity ZSM-5 additive (filled symbols) at various temperatures between 521 and 565°C.

Generally, operational shifts that reduce CO_2 emissions from the FCCU, accomplishing the objective of reduced Scope I CO_2 emissions, also reduce the production of LPG olefins from the FCCU. To regain the lost LPG olefins from these operating moves, ZSM-5 additive rates could then be increased until the desired LPG production rates are met. Figure 5 depicts a commercial example where the adaptability of the FCC was exploited to reduce Riser Outlet Temperature (ROT) while recovering the valuable C_3= yield by using ZSM-5 technology. [12] As shown in Figure 5, the ROT in this commercial example was reduced by ~25°C, which resulted in a decrease in Scope I emissions of approximately 35,000 MT of CO_2/year while maintaining the same propylene yield. This example highlights the flexibility of the FCCU to achieve different yield and CO_2 emission profiles.

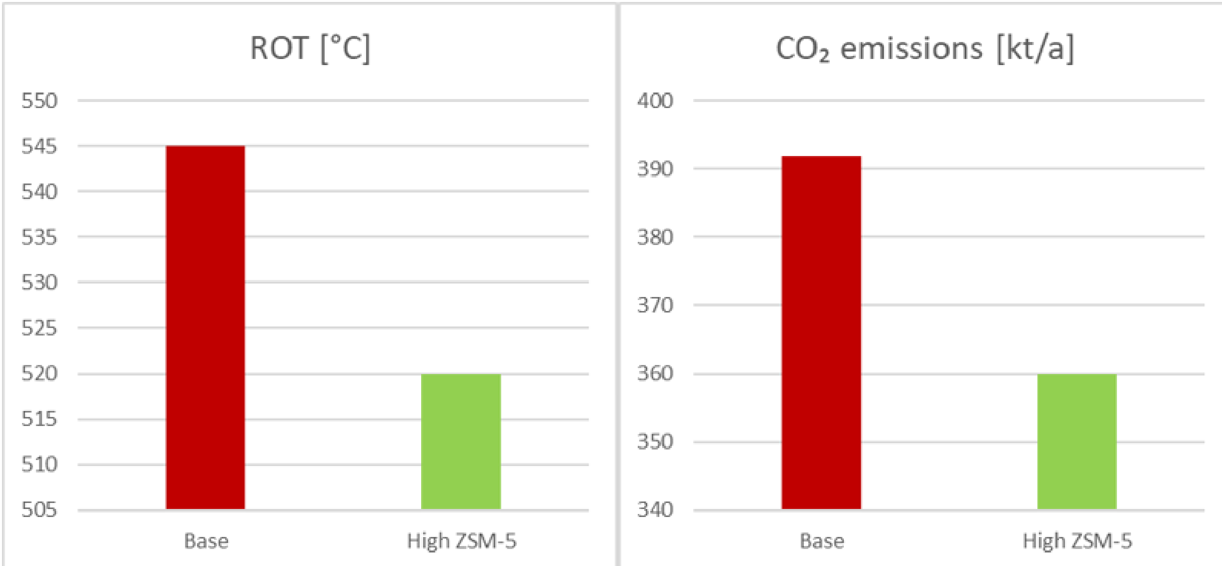

Figure 5. Commercial FCC unit data comparing standard operation at high ROT (red) with a case for low ROT, high ZSM-5 technology case (green). Adapted from [12].

ZSM-5 additives are available from many suppliers but *range widely in activity*. Applications targeting the highest propylene yields benefit greatly from ZSM-5 additives with corresponding activity levels. Higher activity ZSM-5 additives require lower additive usage, minimizing the dilution of base catalyst activity. This affords the refiner with flexibility to employ catalysts with low hydrogen transfer, boosting C_3= yield even further.

W. R. Grace has a long track record in ZSM-5 innovation: the high activity additives currently in our portfolio include OlefinsUltra® MZ technology and the latest ZAVANTI™ additive, intended for the applications with the highest C_3= yields. [13] [14]

Life Cycle Assessment (LCA): Comparison of Scope III Emissions Between an FCCU producing fuels and one producing propylene using ZSM-5

Grace recently conducted a LCA to better understand how the use of ZSM-5 additive affects Scope III CO_2 emissions from the FCCU: a calculator was developed to quantify the change in emissions that results when an FCCU focused on gasoline production uses ZSM-5 technology to produce propylene. This comparison is made at constant operating conditions.

Several assumptions were made in this LCA, including:

- The carbon intensity of FCC catalyst and ZSM-5 additive manufacturing is the same and when additive is used, the addition rate of the catalyst decreases by the amount of additive used.
- Propylene generated by the FCC is routed to petrochemical plants for production of polypropylene. The assumption used in this LCA for emissions generated during polymerization of propylene is based on the work of Alsabri, et al. [15] Also we assume there is capacity in the FCCU propylene purification train to handle additional propylene produced.
- In addition to generating propylene, the use of ZSM-5 generates other LPG olefins (C_4=s) and saturates as well as a small amount of ethylene. We assume all of these components are combusted as fuels since C_4=s are alkylated and added into the gasoline blending pool, and propane, C_4

saturates and ethylene are burned as fuel. The assumption used in the LCA for emissions generated in the combustion of fuels is 8.887 kilograms of CO_2 per gallon of fuel consumed. [16]

- Globally, 19% of all plastics were incinerated in 2019, so it is assumed that eventually the plastics derived from ZSM-5 usage are incinerated at this rate. [17] Estimated emissions rate of ~3 kg CO_{2e} per kg of plastic incinerated is assumed for this LCA, in line with the estimates of others. [18]

Utilizing ZSM-5 in the FCCU has the following primary effects on Scope III CO_2 emissions:

- More CO_2 generated from increased rates in petrochemical plants to produce polypropylene
- More CO_2 generated from combustion of propane, C_4s and C_2=
- More CO_2 generated from plastics incineration
- Less CO_2 generated from combustion of FCC gasoline in vehicles: this is a result of gasoline being converted by ZSM-5 into propylene and other lighter molecules

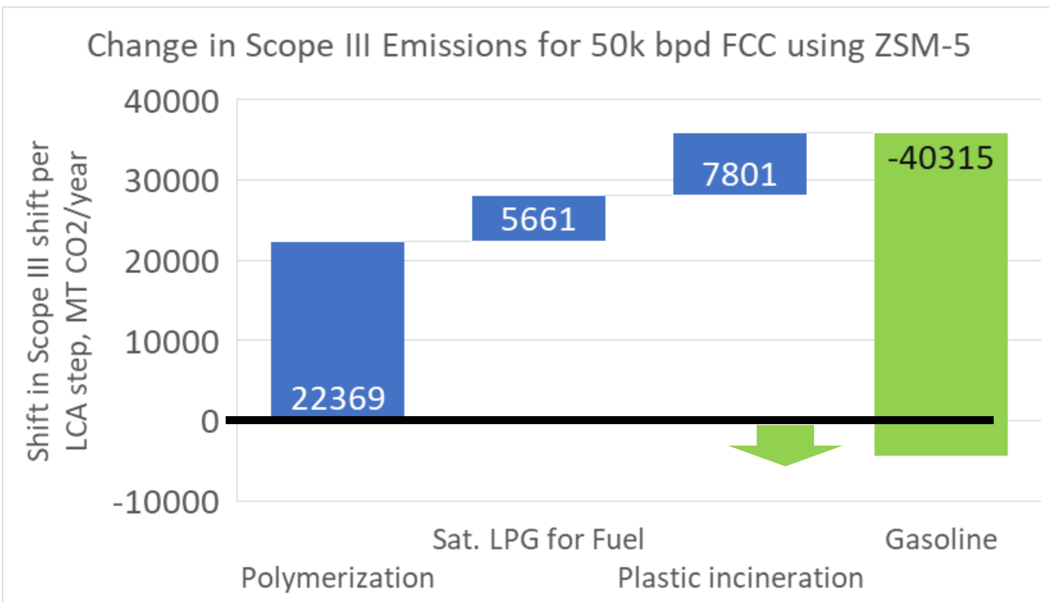

Figure 6. Results of LCA for changes in Scope III emissions from an FCCU when enough ZSM-5 is used to reduce gasoline by 1 wt%ff (assumed throughput of the FCCU is 50 kbpd). The green arrow indicates that the net effect of ZSM-5 usage is to decrease Scope III emissions.

The results from the LCA indicate that for a 50 kbpd FCCU, the use of ZSM-5 additive to convert 1 wt%ff of gasoline-range material translates into a 4,500 MT/year reduction in Scope III CO_2 emissions (this is roughly equivalent to the emissions produced by 1,000 passenger vehicles in a year). [16] These effects are summarized in Figure 6.

Outlook and Conclusion

Propylene from the FCCU features the lowest carbon intensity among the main propylene production routes. The FCCU also has the most favorable cost position for propylene. [13] While the FCCU can yield significant propylene, it has traditionally targeted maximum gasoline. This is not surprising when considering the historical growth in transportation fuel demand. However, once transportation fuel demand peaks, Grace predicts more FCCUs will shift their focus towards propylene. The improved cost position, lower carbon intensity, and growth in demand for propylene will provide tailwinds to refiners that adopt a propylene strategy to maximize profitability in the long term.

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