Fluidized catalytic cracking process decarbonization

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Emissions of greenhouse gases (GHG) due to human activity have increased significantly since the industrial revolution, and carbon dioxide (CO_2) emitted by burning fossil-derived fuels is a key contributor. Decarbonizing the transportation and energy sectors is important to reduce GHG emissions that contribute to anthropogenic climate change. Governments worldwide have created emissions benchmarks, incentives and statutory requirements to lower the CO_2 footprint of these industries. Furthermore, carbon tax policies and carbon trading marketplaces are under development that will have large impacts and change the way these businesses conventionally run. If fossil-based liquid fuels continue to be used for transportation and energy generation, lowering the CO_2 footprint of the transportation sector will remain an important long-term issue.

The global oil refining industry is a significant contributor to CO_2 emissions, which are generated in several different ways:

- Directly from activities controlled by the refinery, such as combustion of fossil fuel to generate heat or power (Scope 1)
- Indirectly from activities outside the control of the refiner, such as purchased electrical power sourced from an external supplier (Scope 2)
- Indirectly from the extraction of the crude oil feed to the refinery and the use of the finished product sold by the refiner, such as gasoline combustion in automobiles (Scope 3).

Consequently, refiners are investigating approaches to reduce the CO_2 footprint of fuels production as well as the end use of the refined products. The objective is to ensure environmental sustainability, while at the same time, maintaining economic viability of operations while producing necessary commodities.

The focus of this article is to share the results of modeling various low-capital strategies that incrementally lower Scope 1 and Scope 2 CO_2 emissions. Practical changes to hardware and operations of the fluidized catalytic cracking unit (FCCU) will allow refiners to reduce the CO_2 footprint.

FCC DECARBONIZATION STUDY

The FCCU is a heavy oil conversion process that has historically been operated to maximize yields of gasoline-range material. The FCC process has been in commercial operation since the 1940s and is a critical step in converting low-value, high-boiling point, heavy hydrocarbon fractions into lighter, high-value products, such as liquefied petroleum gas (LPG), gasoline and diesel.

The FCCU is energy-intensive and creates 20%–30% of total Scope 1 and Scope 2 CO_2 emissions from a typical refinery. Coke combustion in the FCC catalyst regenerator and burning of the byproduct offgas in the refinery fuel gas system are key Scope 1 emissions sources. The reactor-regenerator operates symbiotically, and the energy required in the reactor to vaporize feed and promote endothermic catalytic cracking reactions is supplied by hot circulating catalyst from the regenerator. The catalyst surface and pores are covered with coke deposits, byproducts of the catalytic cracking reactions. At the riser termination point, catalyst and reactor product vapors are separated in the cyclone system before catalyst flows to the regenerator for combustion in the presence of air. The catalyst is heated up as coke deposits are combusted, and a single circulation cycle is completed as the hot catalyst is circulated to the riser again.

The base FCCU modeled in this study is the author's company's FCCU design[a] which processes approximately 50,000 bpd of conventional vacuum gasoil (VGO) feedstock with a 22° API gravity and is operated at a riser severity that promotes gasoline production. The major energy consumers and producers considered in this study are shown in **FIG. 1.** The largest contributor to CO_2 footprint is coke combustion in the regenerator, which directly generates CO_2 emitted from the flue gas stack. If the unit is equipped with a flue gas expander, kinetic energy in the flue gas stream is converted to electricity that can be used to power the air blower and export to the refinery electrical system if excess is available.

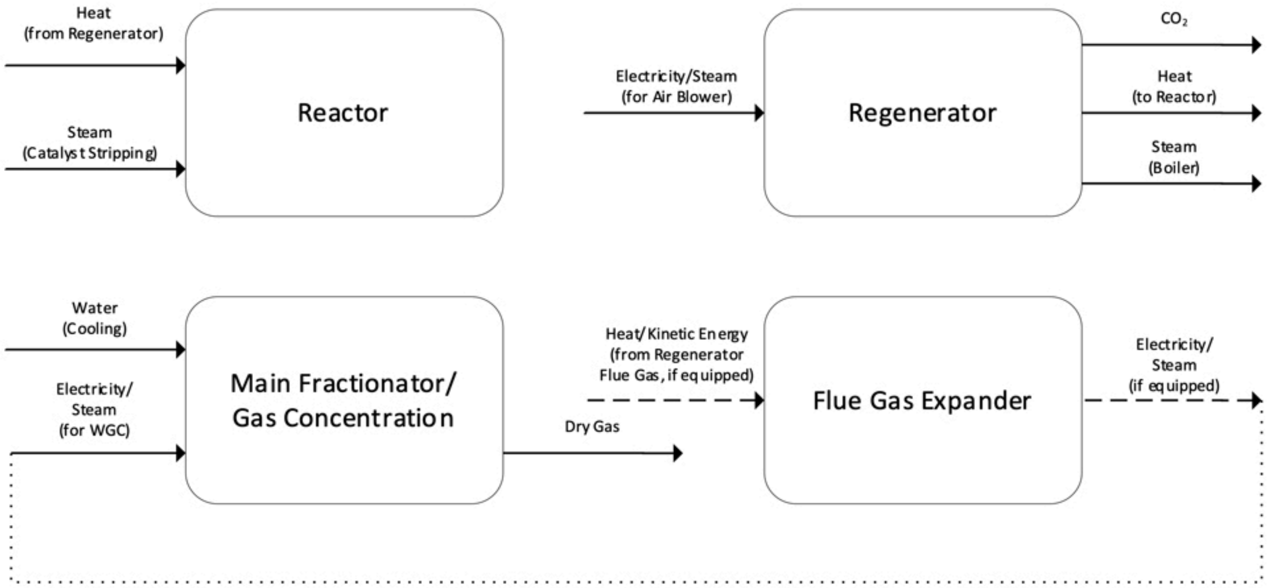


FIG. 1. Major FCCU unit energy consumers and producers.

All utilities consumed, generated and coke combusted have been normalized to units of CO_2 from equivalent methane combustion for ease of evaluation and comparison. Conventional natural gas generation was considered for all cases with shifting electricity and utility demands.

Nearly 70% of the FCCU's CO_2 footprint is a result of coke combustion in the regenerator. The remaining contributors (FIG. 2) were dry gas product combustion, steam consumption, electrical power consumption and energy used in circulating cooling water.

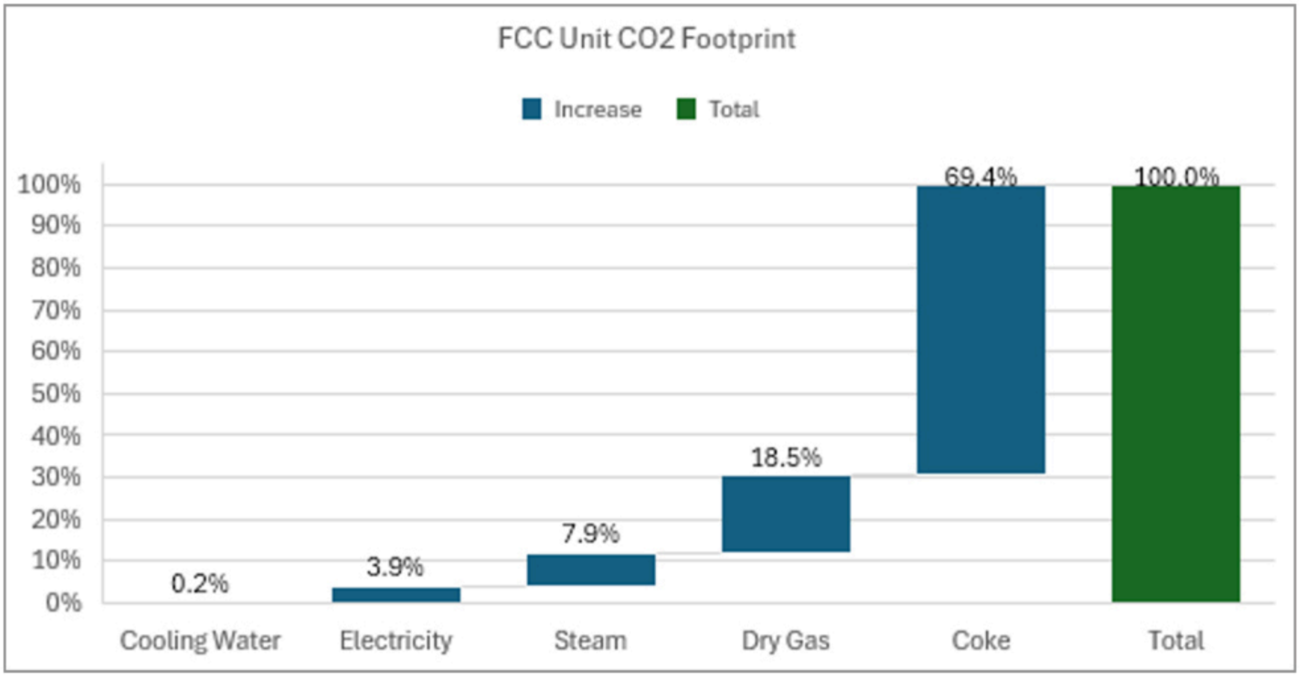


FIG. 2. FCC process contributors to CO_2 emissions.

FCCU decarbonization options. Decarbonizing the FCCU requires the implementation of strategies that are specific to the FCCU, as well as approaches that can be adopted throughout the entire refinery.

The solutions available include energy efficiency improvements, energy recovery equipment, reductions in carbon intensity of utilities, hardware technology that inherently produces less CO_2, and CO_2 carbon capture and storage (CCS), as seen in **FIG. 3.**

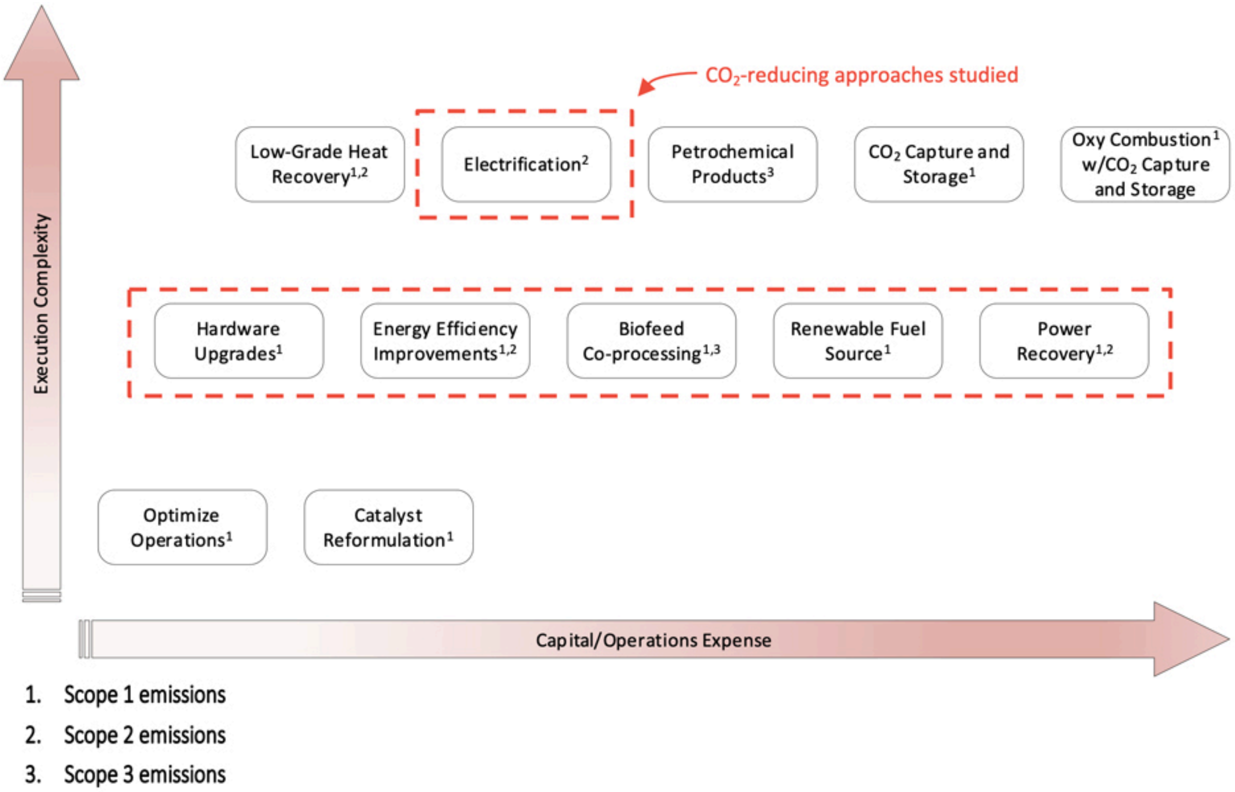


FIG. 3. Projected complexity and cost of various decarbonization approaches: Scope 1 emissions^{1}; Scope 2 emissions^{2}; and Scope 3 emissions^{3}.

The key is to ensure that the FCCU and the refinery remain economically viable while reducing their CO_2 footprint. This article is the first in a series of FCC decarbonization strategies, the focus of this first being on several low- and moderate-capital approaches.

Lowering the FCC and refinery CO_2 footprint offers a significant financial benefit in regions that enforce emissions limits. Considering the EU carbon trading market's approximate price of $80/metric t and a conservative projected value of $120/metric t in 2030, the value of lowering base FCCU emissions by 25% is more than $18 MM/yr, as shown in **FIG. 4.**

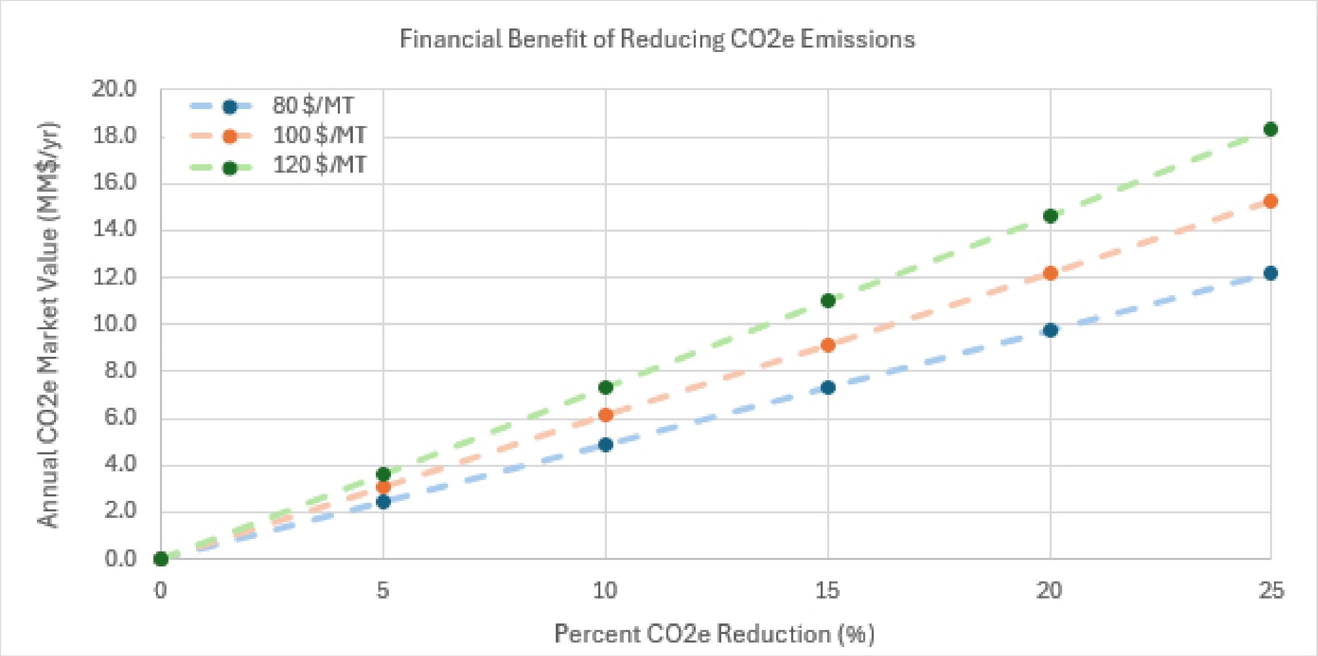


FIG. 4. Annual financial benefit of reduced CO_2 emissions in the base FCCU at current EU market prices and two escalated price sensitivity scenarios.

CONVERTER MODIFICATIONS

Flue gas expander power recovery. As the FCCU catalytically converts heavy hydrocarbon feedstock, coke byproducts deposit on catalyst. This coke is burned off the catalyst surface in the presence of air in the regeneration step, providing necessary heat to the reactor and sustaining the reactor-regenerator heat balance. The resultant waste flue gas is released into the atmosphere following treatment and heat recovery. Typically, waste heat recovery from the flue gas occurs through the generation of steam, but there is also a significant amount of potential energy that can be converted and captured in the form of kinetic energy. Normally, this valuable kinetic energy is lost by letting flue gas pressure down through a double-disc slide valve and orifice chamber.

FCCUs equipped with a power recovery train can capitalize on this available energy by directing a portion of the flue gas stream to an expander turbine, which generates sufficient power to drive the air blower. The expander can be directly coupled with the air blower or connected separately to an electrical power generator.

Considering the addition of a flue gas expander to a unit at a constant air blower rate, the energy intensity of the unit is lowered (**FIG. 5**). The expander will recover energy from the flue gas stream, which is used to power the blower. In the author's company's model[a], the steam consumption for powering the main air blower remained the same in both cases, and electricity generated by the expander was exported. This effectively lowered the overall FCCU CO_2 footprint by 7% compared to the Base Case.

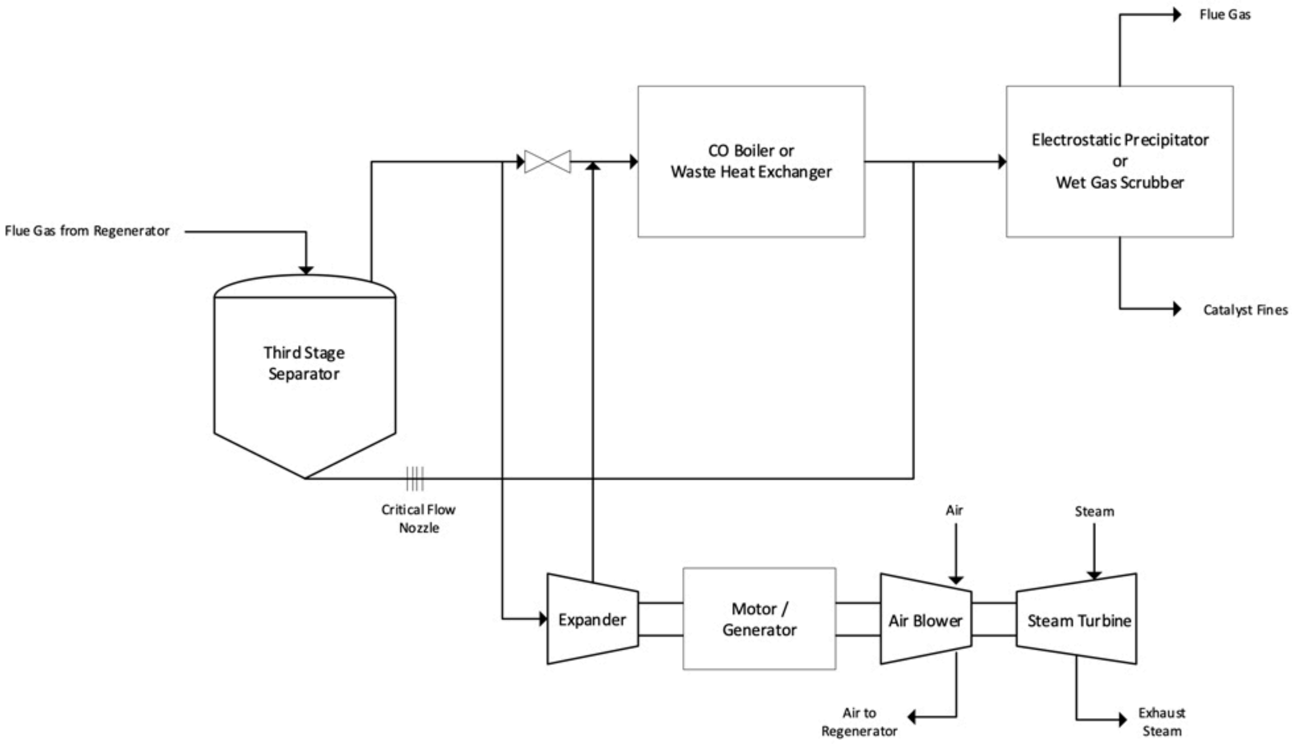


FIG. 5. Flue gas recovery system process flow diagram.

The equivalent CO_2 emissions, shown in **TABLE 1,** are lowered by recovering energy from the flue gas system and operating at the optimal reactor pressure, limited by the wet gas compressor.

TABLE 1. Equivalent CO_2 emissions

Case	Reactor pressure, psig	Regenerator pressure, psig	Equivalent CO_2, metric tpd	Reactor-regenerator CO_2 change, %	Main fractionator/vapor recovery unit (VRU) CO_2 change, %	Total FCCU CO_2 change, %
Base	25	30	2,139	--	--	--
Base w/expander	25	30	1,989	-9.3	--	-7

The flue gas expander is a well-understood and proven technology for improving energy efficiency and lowering CO_2 footprint.

Converter hardware. Improving or maintaining the profitability of the FCCU is always at the forefront of a refiner's goals. Increasing production of high-value products is a key pathway to better profitability, but this generally requires an increased riser outlet temperature and catalyst-to-oil ratio. This requires additional energy, results in more undesired low-value byproducts and increases CO_2 footprint. It is important to focus on improving operational efficiency by minimizing these factors when investigating options for producing more high-value products.

To improve higher value product yield disposition and operational efficiency, the author's company recommends installing its most modern hardware in both grassroots and revamp engineering designs. In addition to conventional benefits, the CO_2 footprint is lowered when considered on an LPG and gasoline yield basis: CO_2 equivalent (CO_2e)/(LPG + gasoline) x 100%.

The technologies evaluated in this section (**FIG. 6**) include a closed cyclone riser termination device[b], proprietary feed nozzles[c] and spent catalyst stripper packing[d].

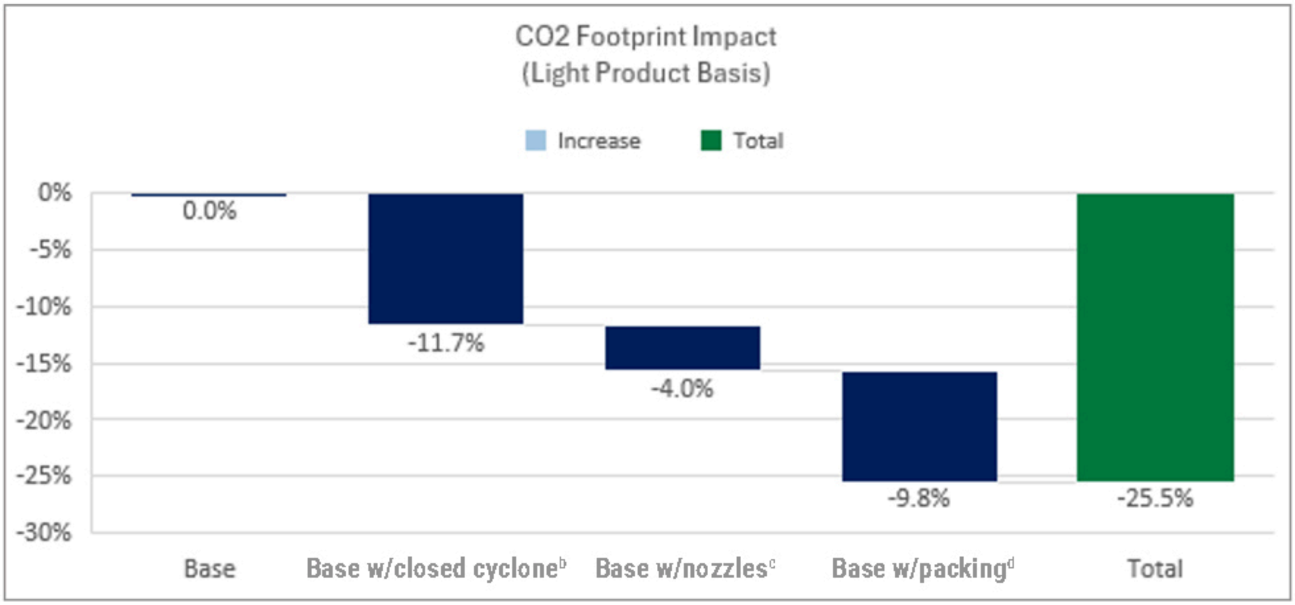


FIG. 6. CO_2 footprint with advanced converter hardware implementation.

The author's company's closed cyclone riser termination device[b] directly couples the riser outlet to the reactor cyclone system, forcing rapid separation of catalyst and hydrocarbons at the riser termination point. This reduces post-riser cracking and prevents vapor stagnation, thereby limiting low-value dry gas and coke production, and increased gasoline and light cycle oil (LCO) yields.

The company's proprietary feed nozzles[c] perform reliably and feature a single slot opening to minimize erosion, with teeth engineered to increase the wet surface area and enhance feed atomization. The feed injection system enables efficient performance through rapid vaporization with effective contact between oil and catalyst. The benefits include increased liquid product yields, reduced dry gas and coke yields, and alleviation of operational limitations such as the wet gas compressor capacity and air blower rate.

The company's spent catalyst stripper packing[d] increases the recovery of light, hydrogen (H_2)-rich hydrocarbons entrained in circulating spent catalyst and lowers the amount of steam required to do so. The immediate impact is lower delta coke and regenerator temperatures, which force higher catalyst circulation at a constant riser outlet temperature, leading to increased liquid yields and LPG selectivity.

The refining industry balances objectives to increase profitability, comply with government-mandated emissions targets, meet internal environment stewardship goals and deliver lower-carbon-emitting products to meet customer demands. These FCC hardware technologies can be adopted to increase profitability while lowering CO_2 emissions based on LPG and gasoline production. Modern technologies improve efficiency, enabling increased production of light products while reducing the CO_2 footprint of the FCCU.

Main fractionator and VRU heat integration. Superheated effluent vapor flows from the reactor overhead to the main fractionator and vapor recovery section for cooling, separation, and recovery of various fractions and components. Heat integration is a common feature of the main fractionator and VRU, with heat being recovered through various preheat exchangers, pumparounds, reboilers and steam generators. This study considers changes to equipment that lower the energy intensity and resultant CO_2 footprint. The main fractionator and VRU shown in FIG. 7 are a standard configuration and are used as the Base Case for comparison. As with every FCC process variable, adjusting a single parameter has adjacent impacts that must be considered prior to execution.

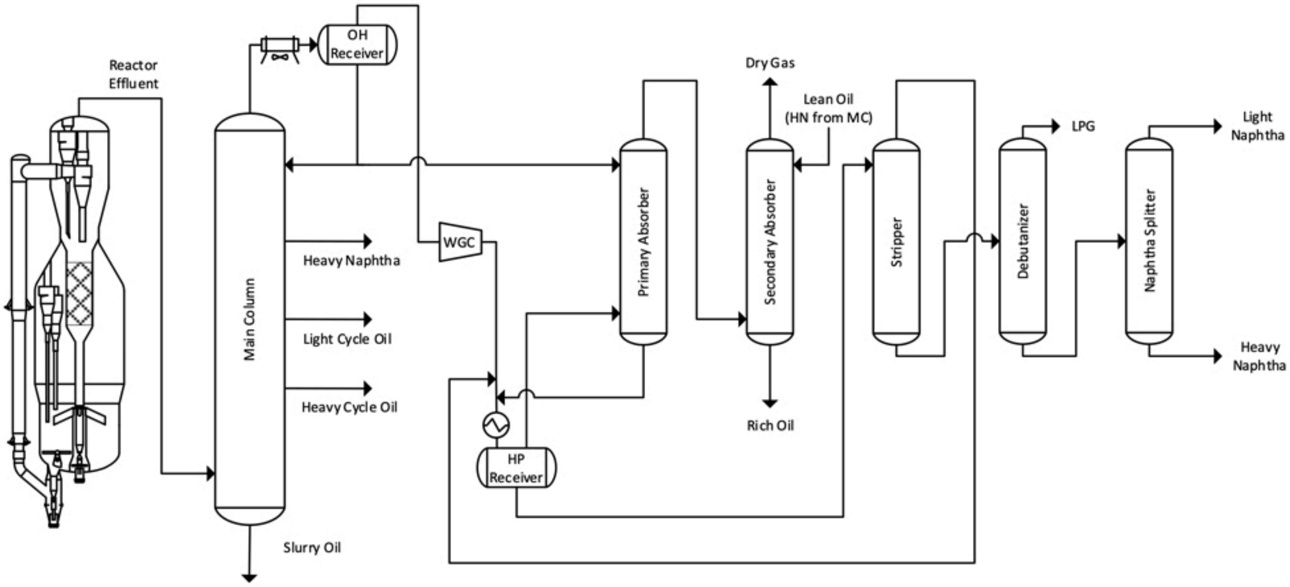


FIG. 7. Main column and vapor recovery section.

Electric wet gas compressor. This case substituted an electric-powered wet gas compressor (FIG. 8) for a steam turbine-driven compressor. The unit was equipped with a flue gas expander and steam generator. After installation of the electric compressor, steam was exported and the unit shifted from a net consumer to a producer of steam. Typical efficiencies were assumed both for generating electricity at a power plant to provide energy to the compressor as well as burning natural gas to generate steam. Compared to the Base Case, the CO_2 generated in the process of converting fuel to electricity increased, while CO_2 generated to supply the plant steam system decreased. The replacement of steam with electricity resulted in lower CO_2 emissions and a lower overall footprint of 1%.

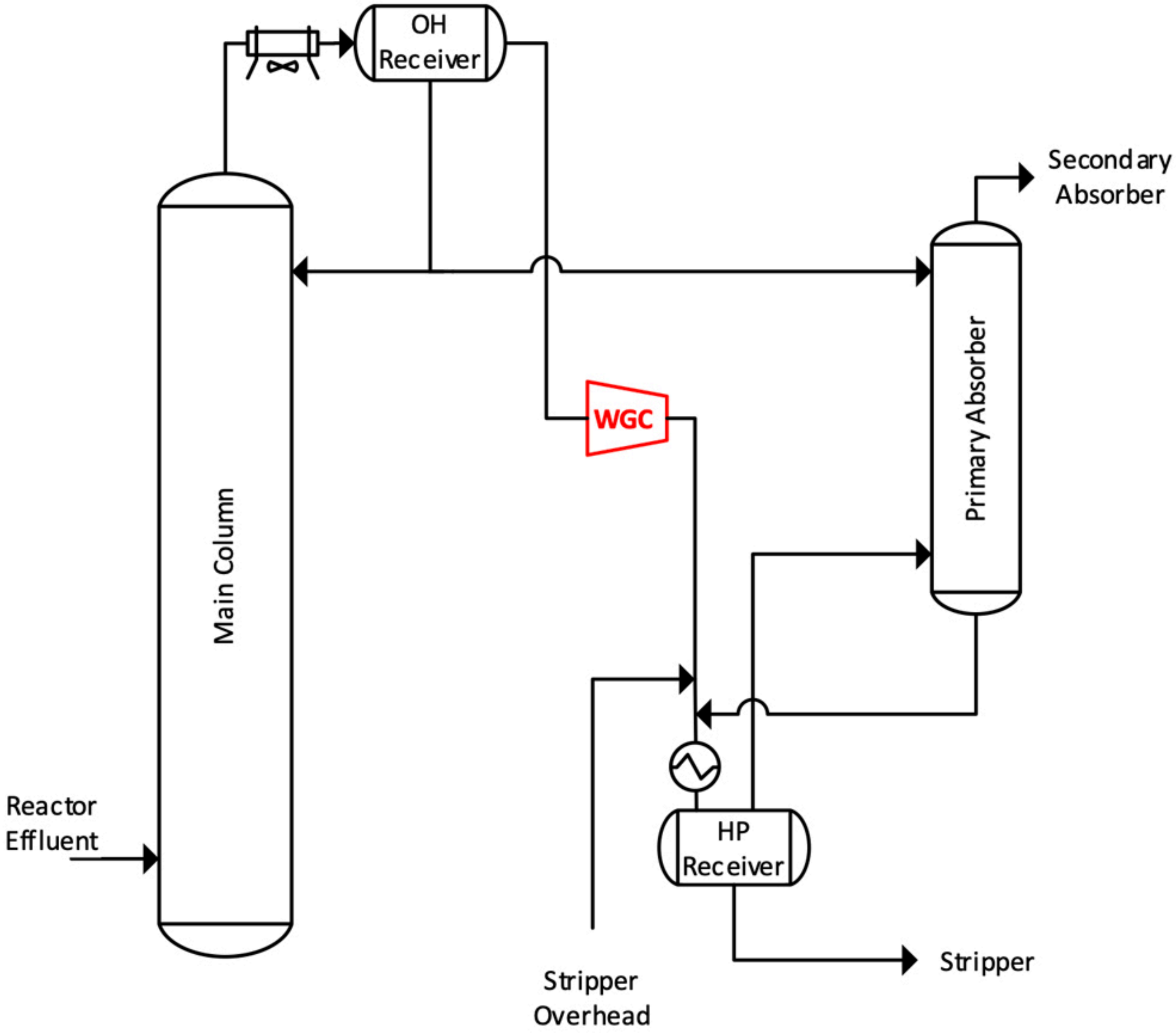


FIG. 8. Fractionation section with electric-powered wet gas compressor.

Lower lean oil rate to primary absorber. The primary absorber is fed a supplemental lean oil stream from the bottom of the debutanizer tower to absorb LPG from the dry gas. A chiller was added to lower this lean oil temperature by 36°F to increase its absorption efficiency, and a second absorber pumparound exchanger was added (**FIG. 9**).

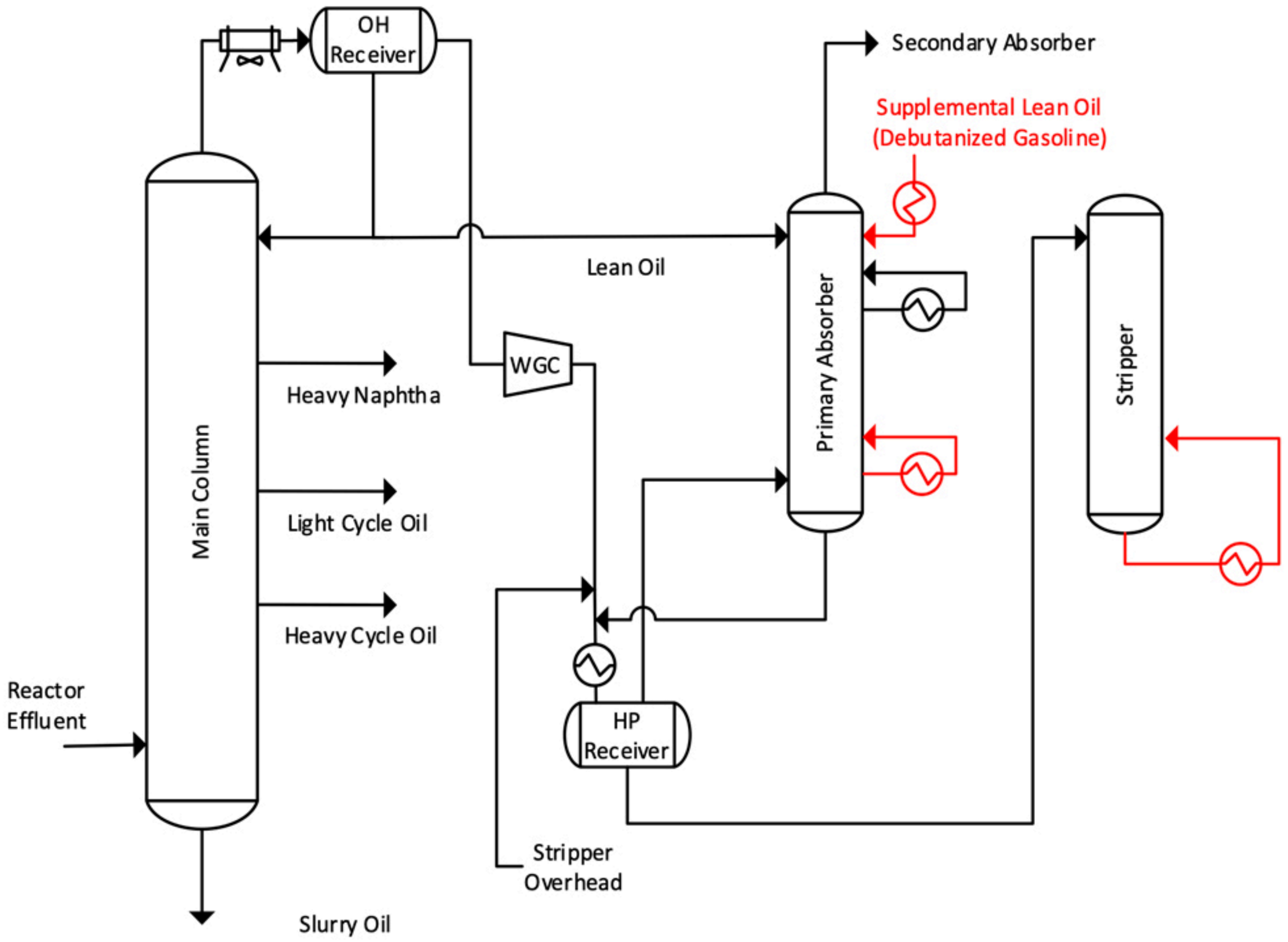


FIG. 9. Vapor recovery section pumparound modifications.

The combined duty of the two pumparounds, 3 MMBtu/hr, was lower than the single pumparound exchanger duty of 5.1 MMBtu/hr. This improved absorption efficiency of the lean oil, debutanized gasoline, resulted in a lower supplemental lean oil flowrate and lower stripper reboiler duty by 13.4 MMBtu/hr at the same C_3's recovery rate. The total changes in duty are shown in **TABLE 2.** The reduced utility requirements of this configuration lowered the CO_2 footprint by 1.9%.

TABLE 2. Heat exchanger duty shifts

Heat exchanger	Base Case, MMBtu/hr	Lean oil optimization, MMBtu/hr
Stripper reboiler	73.4	60.1
Debutanized gasoline fin fan	22.3	14.3
Debutanized gasoline cooling water	4.3	2.9
Debutanized gasoline chiller	–	2.8
Primary absorber upper pumparound	5.1	1.5
Primary absorber lower pumparound	–	1.5
Total	**105.1**	**83.1**

Incremental cooling water duty substituted for air cooler duty. This case partially substituted heat exchange duty from air coolers to cooling water exchangers. Water cooling is a more effective heat transfer service compared to air cooling, driven by the heat capacity of each medium. The approximate standard heat capacity of water is 1 Btu/lb-°F, and air is 0.24 Btu/lb-°F.

In this scenario, the process outlet temperature for each air cooler was set to 25°F above the air supply temperature. This standard value can be adjusted based on the limitations of the geographical location and existing equipment and facilities. All air cooler process outlet temperatures were increased—the affected equipment is highlighted in **FIG. 10.** The resultant duties shown in **TABLE 3** were shifted from air cooling to water cooling service. The increased cooling efficiency resulted in lower unit utility consumption and an overall CO_2 footprint reduction of 0.2%.

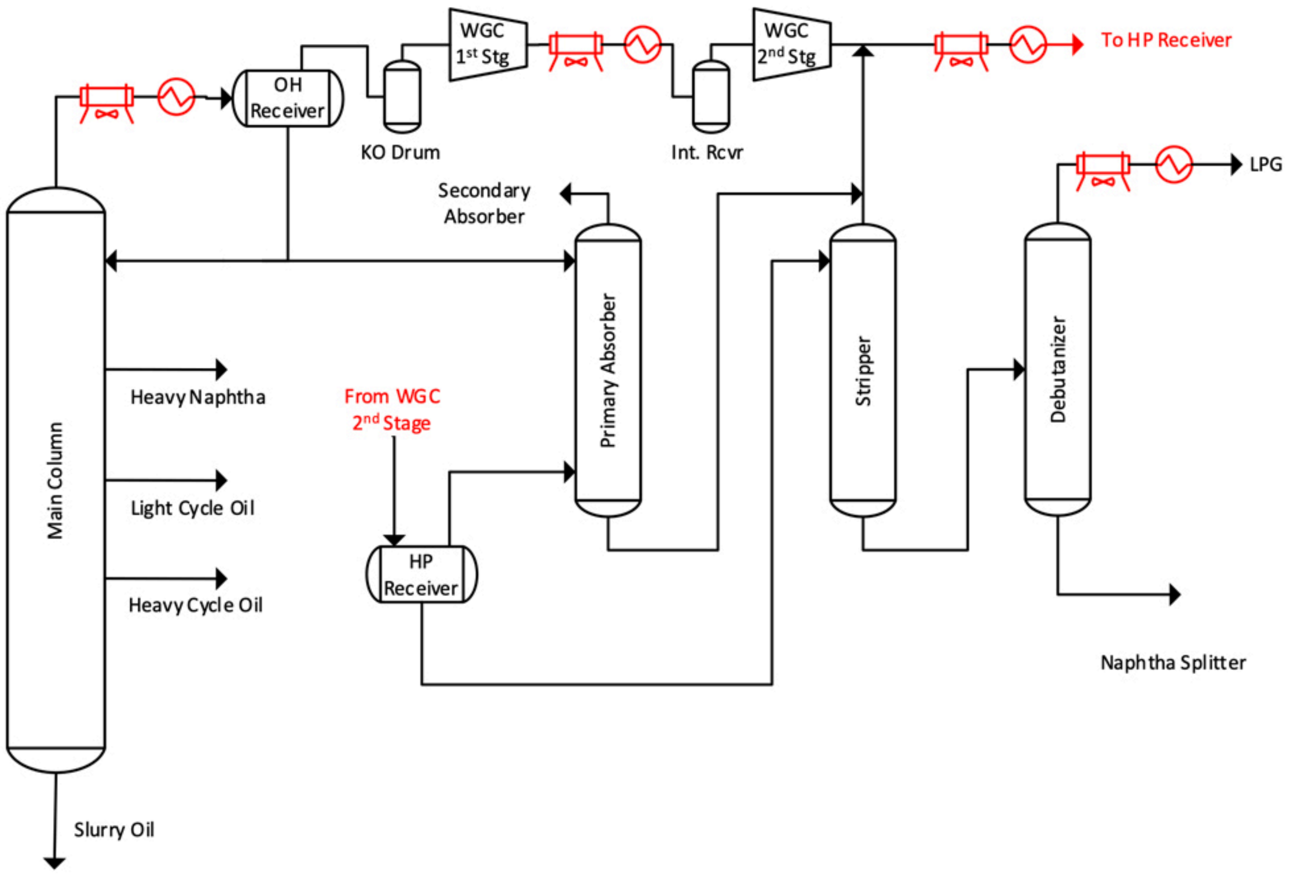


FIG. 10. Cooling water duty replaced air cooling duty.

TABLE 3. Duty shifted from air cooling to water cooling exchangers

	Main fractionator overhead condenser	Wet gas compressor interstage cooler	Wet gas compressor discharge cooler	Debutanizer overhead cooler
Duty, MMBtu/hr	13.8	2.1	1.9	31.1

Naphtha splitter steam reboiler. This case substituted the naphtha splitter steam reboiler (**FIG. 11**) for one that integrates with the main fractionation heavy cycle oil pumparound; removing the steam for one that integrates with the main fractionation heavy cycle oil pumparound, removing the steam required for supplying the 54.6-MMBtu/hr reboiler resulted in a lower CO_2 footprint of 5.3%.

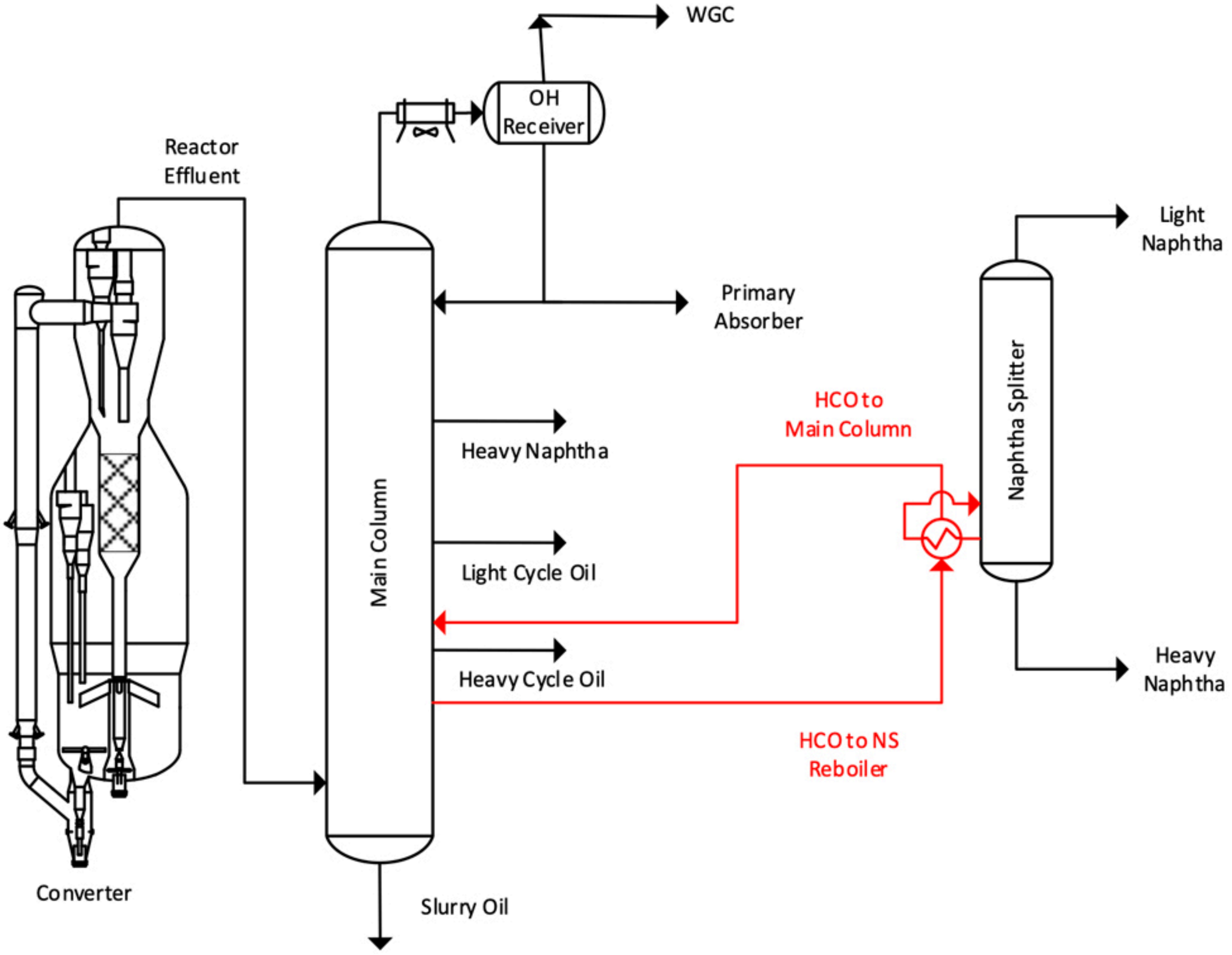


FIG. 11. Main column heat integration with naphtha splitter reboiler.

Flue gas expander. As discussed in the **Converter hardware** section above, the addition of a flue gas expander significantly increased the unit's energy recovery. The steam use of the unit was considered the same in both cases, and electricity was exported in the flue gas expander case. This equipment lowered the CO_2 footprint by 7% compared to the Base Case.

The FCCU CO_2 reductions from the application of the flue gas expander and the modifications discussed in this section are summarized in **FIG. 12.**

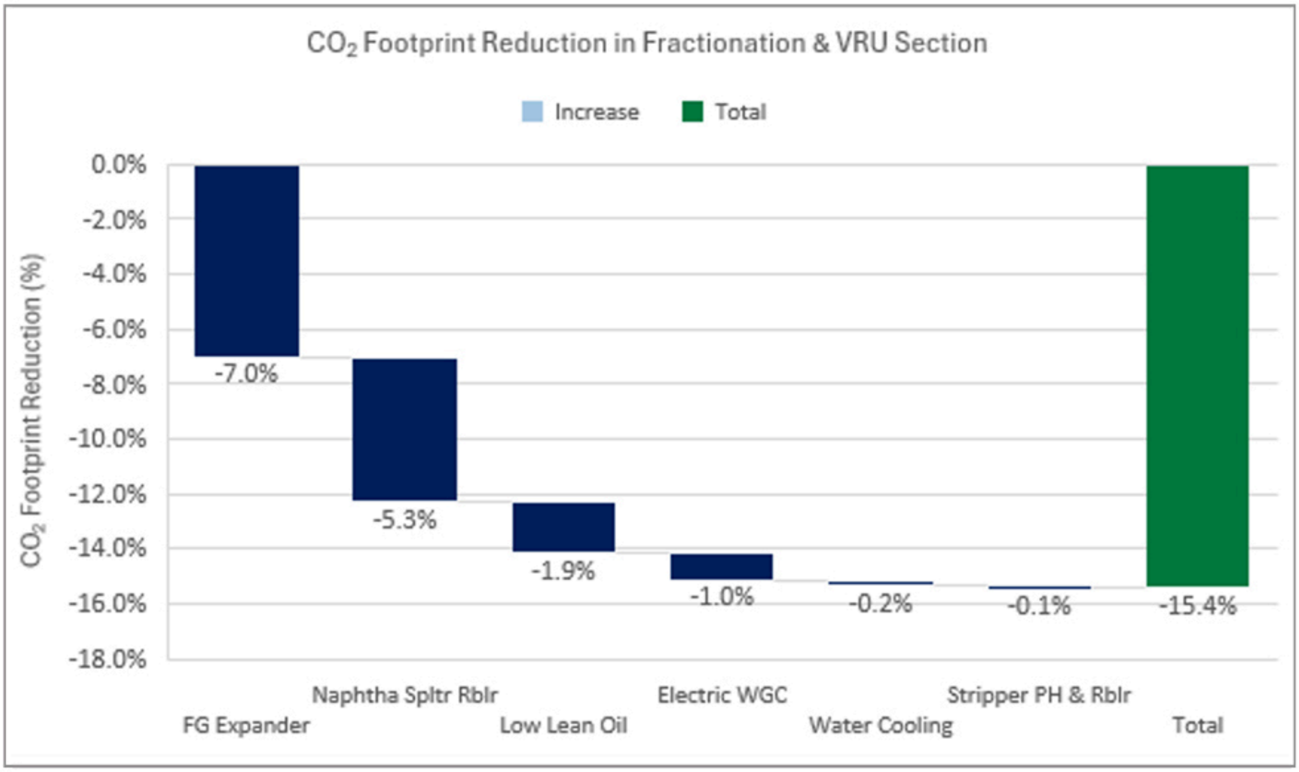


FIG. 12. CO_2 emissions reductions due to expander and main fractionator/VRU modifications.

The design of each FCCU main fractionator and vapor recovery section is unique; however, as shown in this section, there are opportunities to improve energy efficiency and reduce CO_2 footprint.

Co-processing. An effective strategy for lowering the FCCU CO_2 footprint is to co-process renewable biogenic liquids. Commonly, a portion of the FCCU VGO feedstock is displaced with renewable material such as vegetable oil, animal fat, palm oil, waste cooking oil or cellulosic sources such as pyrolysis oil. The author's company has performed several case studies for co-processing biogenic feedstocks of various types to fit within refinery strategies.

Biogenic feedstocks are generally categorized into 1st and 2nd Generations, each with unique properties and characteristics, as presented in **TABLE 4.**

TABLE 4. Biogenic feedstocks physical properties, origins and design considerations

	1st Generation	2nd Generation	Typical VGO
Specific gravity	0.9–1	1–1.5	0.9–0.95
Total acid number (TAN), mg/KOH-g	1–25	4–100	< 1
Impurities, ppm	> 5	> 25	< 5
Continuous catalytic reforming (CCR), wt%	0.05–0.5	10–35	0.2
Oxygen content, wt%	8–12	25–60	0–0.5
Origin/source	Vegetable oil, animal fat, palm oil, waste cooking oil	Cellulosic biomass	Crude oil
Design considerations	Can blend with VGO; similar yields as VGO; oxygen content ~10 wt%; lower impurity content; high TAN (metallurgy)	Relatively unstable; high oxygen content; low temperature injection; high viscosity; contains solids, free water; high impurities; high TAN (metallurgy)	Conventional technology

Renewable LPG and gasoline through co-processing palm oil. A study has been completed to compare the FCC yields of a standard VGO feedstock to co-processing with 10 wt% palm oil. The benefit of this approach is the production of LPG and gasoline with renewable components, and the resultant reduction of Scope 3 emissions (**TABLE 5**). Co-processing 10 wt% palm oil resulted in renewable content in LPG of 12 wt%, gasoline of 11 wt% and diesel 11 wt%.

TABLE 5. Ex-reactor yields results based on pilot plant yield data

	Ex-reactor yields (100% VGO)	Ex-reactor yields [90% VGO + 10% palm oil mill effluent (POME)]	Renewable content of products (90% VGO + 10% POME)
Product, wt%			
Dry gas, C_2-	2.68	2.5	3
C_3 LPG	13.02	12.39	5
C_4 LPG	18.66	18.02	7
Gasoline	40.74	41.07	11
LCO	13.6	13.72	11
Slurry	5.95	5.68	6
Coke	5.35	5.3	9
CO_2/CO/H_2O	0	0.1/0.24/0.99	100
Conversion	80.45	80.6	----

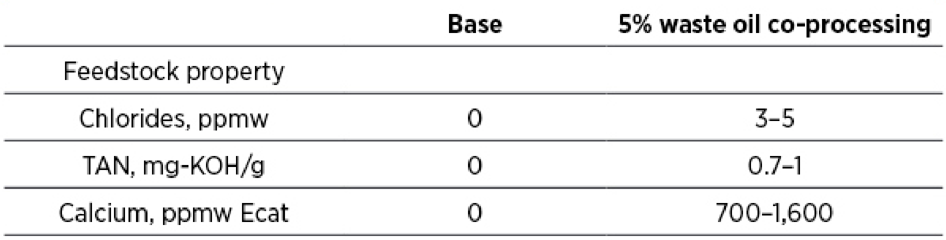
Notes: 1. Yield estimates based on pilot plant testing data 2. Constant operating conditions 3. Carbon coke content assumed to be 94 wt%
4. CO_2, CO and H_2O are kinetic products of palm oil

Co-processing renewable feedstocks is a solution for refiners exploring routes to reduce the CO_2 impact of their refined fuel products.

Renewable gasoline through co-processing lipidic waste oil. A study was completed for a refiner to enable co-processing of waste oils such as POME and cashew nut shell liquid in its FCCU, with the goal of achieving 5 wt% renewable gasoline content. A large volume of waste oil was available; however, naphthenic acid corrosion was a concern if mixing with the main FCC feed, due to high TAN, high feed sulfur and high feed preheat temperature. The impact of high metals and chloride concentrations were also a concern for equilibrium catalyst (Ecat) deactivation.

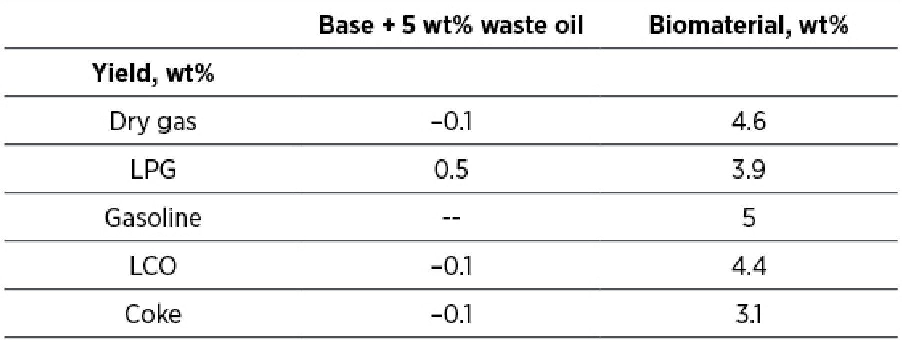
The solution was to co-process approximately 5 wt% waste oil, which resulted in 5 wt% renewable content in gasoline (**TABLES 6** and **7**). A dedicated proprietary feed nozzle[C] and biofeed line was recommended to allow operation at lower temperatures to limit the risk of naphthenic acid corrosion. The fresh catalyst addition rate was slightly higher to offset the impact of metals.

TABLE 6. Feedstock properties for co-processing with waste oil



	Base	5% waste oil co-processing
Feedstock property		
Chlorides, ppmw	0	3–5
TAN, mg-KOH/g	0	0.7–1
Calcium, ppmw Ecat	0	700–1,600

TABLE 7. Product yields for co-processing with waste oil



	Base + 5 wt% waste oil	Biomaterial, wt%
Yield, wt%		
Dry gas	–0.1	4.6
LPG	0.5	3.9
Gasoline	--	5
LCO	–0.1	4.4
Coke	–0.1	3.1

Co-processing renewable feeds can be challenging, but solutions are available that consider the unique characteristics of each type of renewable feedstock.

Plastic circularity in a petrochemical FCCU. A study was completed to evaluate processing feedstock as part of a circular plastic system. FCC LPG products are commonly used as feedstocks for petrochemical conversion units, and this study considered 5 vol%–10 vol% plastic-derived pyrolysis oil co-processing (**TABLE 8**).

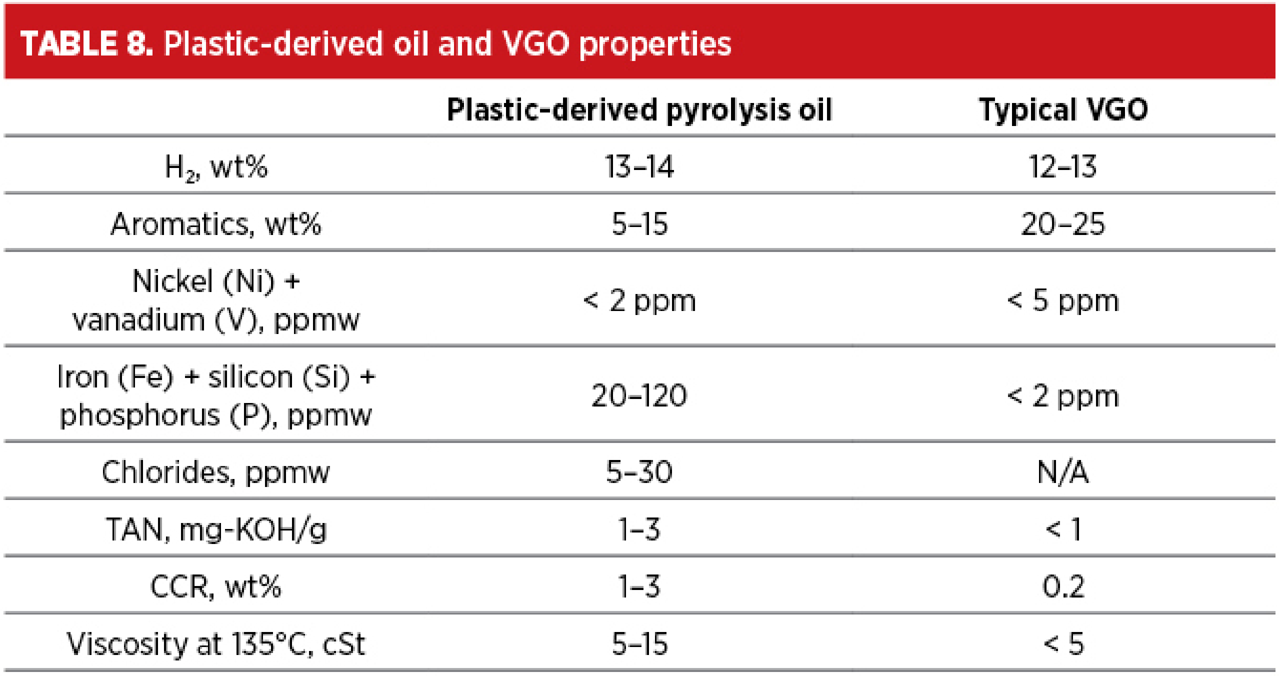


TABLE 8. Plastic-derived oil and VGO properties

	Plastic-derived pyrolysis oil	Typical VGO
H_2, wt%	13–14	12–13
Aromatics, wt%	5–15	20–25
Nickel (Ni) + vanadium (V), ppmw	< 2 ppm	< 5 ppm
Iron (Fe) + silicon (Si) + phosphorus (P), ppmw	20–120	< 2 ppm
Chlorides, ppmw	5–30	N/A
TAN, mg-KOH/g	1–3	< 1
CCR, wt%	1–3	0.2
Viscosity at 135°C, cSt	5–15	< 5

The benefits of processing plastic derived oils include:

- Product yields that approximate VGO
- Miscible in conventional FCCU feedstocks
- High H_2 content, readily crackable
- Aromatics < 15 wt%
    - Cracks to high-value products.

Commonly faced challenges include:

- High TAN, specialized alloys required
- High chlorides, main column ammonium chloride (NH_4Cl) deposition
- Variability in composition and contaminants
- Viscosity and pumpability at increased concentrations of plastic pyrolysis oils.

Takeaways. Incremental FCCU modifications introduced throughout this study lowered the CO_2 footprint. CO_2 emissions from the reactor-regenerator circuit were reduced 25.5% on an LPG and gasoline yield basis by adopting next-generation reactor and regenerator hardware, including a closed cyclone riser termination device[b], proprietary feed nozzles[c] and spent catalyst stripper packing[d].

To this point, these technologies have been developed and implemented for profit-improvement purposes to meet stringent corporate payback period requirements. The significant reduction in the CO_2 footprint adds an attractive incentive to reduce the environmental impact of the FCCU while increasing profitability.

The installation of a flue gas expander, along with changes to the main fractionator and vapor recovery section, lowered the CO_2 footprint of the unit 15.4%. Significant reductions in CO_2 emissions were realized through heat integration, wet gas compressor electrification, and heat and energy recovery equipment. Execution of the presented unit changes will vary based on the existing unit configuration, but the scenarios covered are generally applicable. It is critical to consider the impact of these changes throughout the entire reactor-regenerator circuit, fractionator and vapor recovery sections prior to implementation to ensure a holistic approach to equipment constraints, limitations and product yield impacts.

The author's company has been designing and licensing FCCUs since co-designing the first commercial unit in 1942 at the ExxonMobil plant in Baton Rouge, Louisiana (U.S.). The FCC process has undergone significant shifts to improve efficiency and target greater gasoline and LPG yields—aided by hardware and catalyst technology developments—and will continue to evolve to meet market demands. The company offers technological solutions for refiners to improve operational and energy efficiency while increasing yields of valuable products. **HP**

NOTES

a. KBR's Orthoflow™
b. KBR's Closed Cyclones™ riser termination device
c. KBR's specATOMAX-R™ feed nozzles
d. KBR's Spent Catalyst Stripper Packing™

ACKNOWLEDGEMENT

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