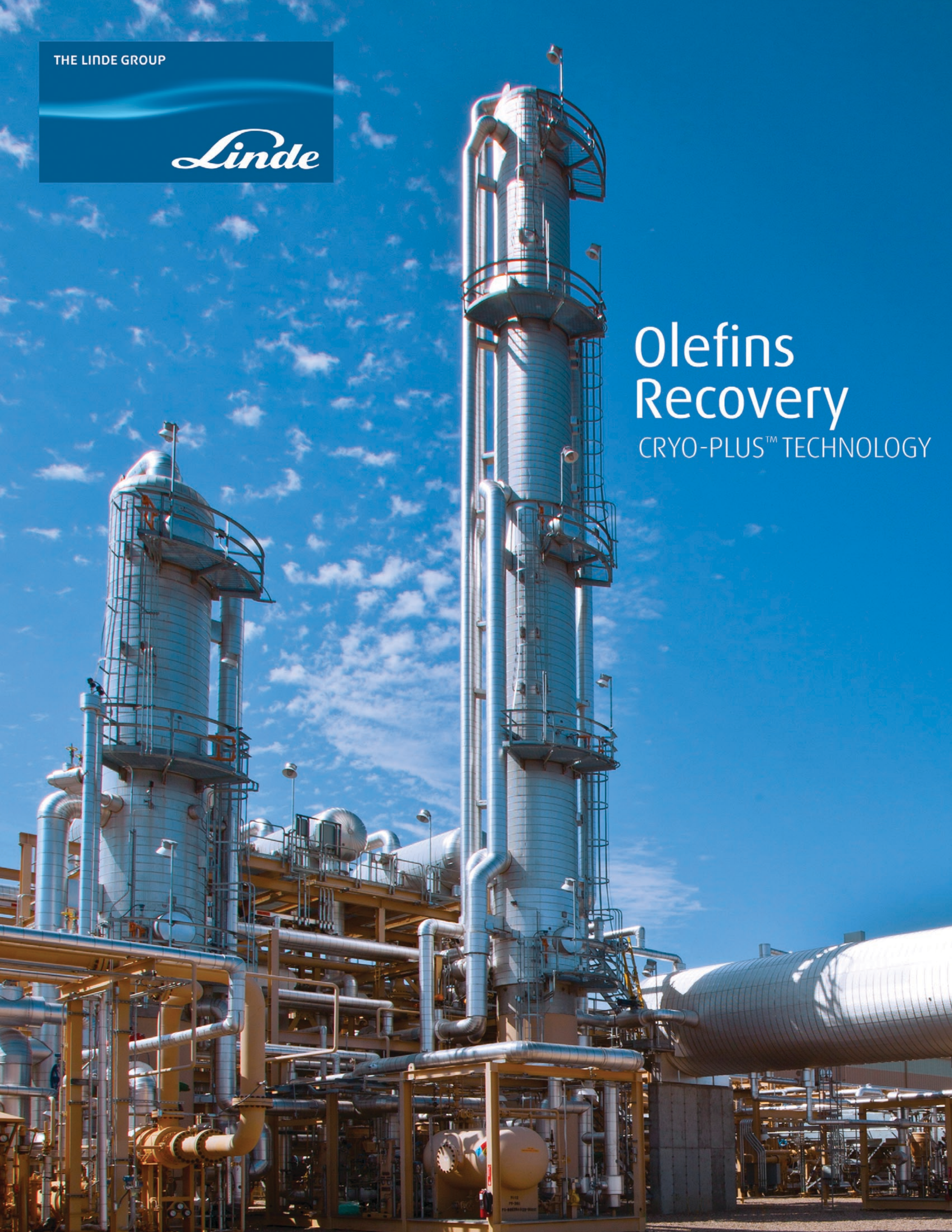
THE LINDE GROUP

Linde

Olefins Recovery

CRYO-PLUS™ TECHNOLOGY



REFINING & PETROCHEMICAL EXPERIENCE

Linde Process Plants, Inc. (LPP) has constructed more than twenty (20) CRYO-PLUS™ units since 1984.

Proprietary Technology

Higher Recovery with Less Energy

Designed to be used in low-pressure hydrogen-bearing off-gas applications, the patented CRYO-PLUS™ process recovers approximately 98% of the propylene and heavier components with less energy required than traditional liquid recovery processes.

Higher Product Yields

The resulting incremental recovery of the olefins such as propylene and butylene by the CRYO-PLUS™ process means that more feedstock is available for alkylation and polymerization. The result is an overall increase in production of high-octane, zero sulfur, gasoline.

Our Advanced Design for Ethylene Recovery

The CRYO-PLUS C2=™ technology was specifically designed to recover ethylene and heavier hydrocarbons from low-pressure hydrogen-bearing refinery off-gas streams. Our patented design has eliminated many of the problems associated with technologies that predate the CRYO-PLUS C2=™ technology.

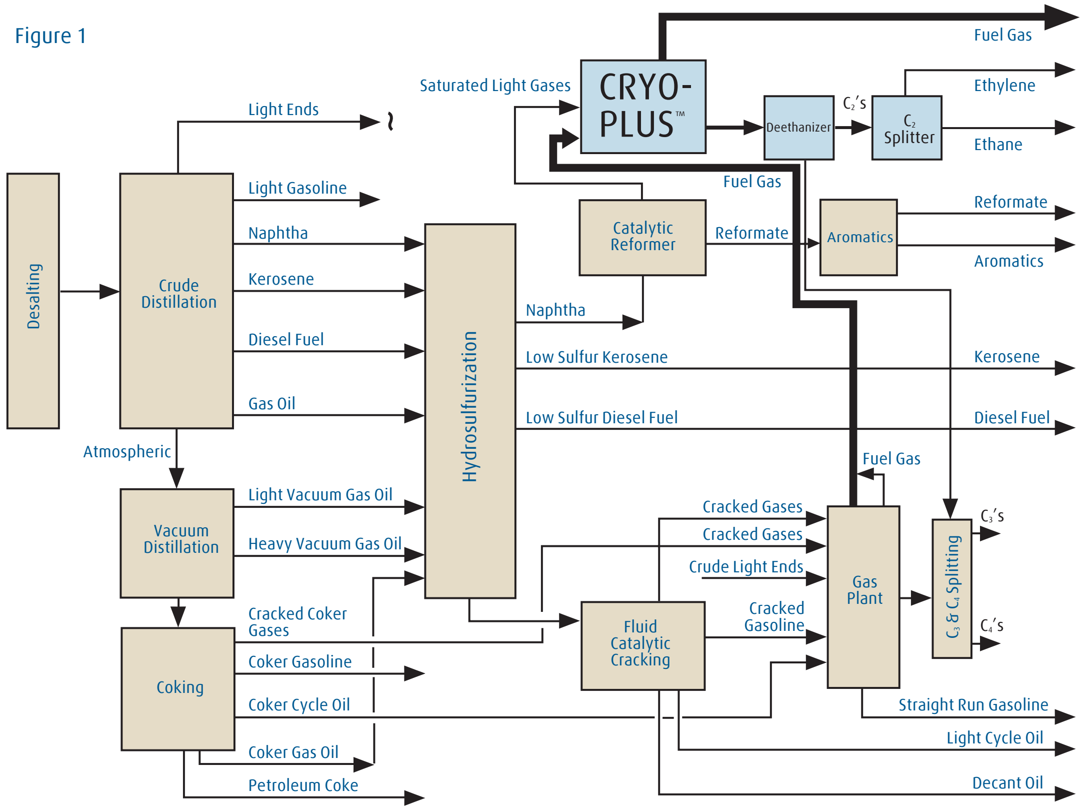
Refinery Configuration

Some of the principal crude oil conversion processes are fluid catalytic cracking and catalytic reforming. Both processes convert crude products (naphtha and gas oils) into high-octane unleaded gasoline blending components (reformate and FCC gasoline). Cracking and reforming processes produce large quantities of both saturated and unsaturated gases.

Excess Fuel Gas in Refineries

The additional gas that is produced overloads refinery gas recovery processes. As a result, large quantities of propylene and propane (C_3's), and butylenes and butanes (C_4's) are being lost to the fuel system. Many refineries produce more fuel gas than they use and flaring of the excess gas is all too frequently the result.


Figure 1



CRYO-PLUS™ in Typical Refinery Process

CRYO-PLUS™

CRYO-PLUS™ improves recovery of C_3+ components, thus allowing refiners to maintain a fuel gas balance while adding profits to the bottom line. At the same time, the incremental propylene, butylene and isobutane recovered become valuable feeds for polymerization or alkylation processes and result in even higher conversion of crude to high-octane gasoline.

CRYO-PLUS™

To date, LPP has installed over twenty (20) CRYO-PLUS™ Recovery Systems in North American refineries. The economic payout of these systems can be as low as one year. A majority of these systems were designed for recovery of propylene and heavier hydrocarbons, but a modified form of this technology, CRYO-PLUS C2=™ has been installed at several refineries for recovery of ethylene, ethane, C_2's and C_3+ hydrocarbons.

Where is CRYO-PLUS™ Used

The primary sources of fuel gas in a refinery are the fluid catalytic cracking unit (FCCU) and catalytic reforming unit (CRU), although coking and other cracking processes also produce large quantities of gas. Traditionally refineries utilize lean oil recovery systems to recover the C_3 and heavier components in the gas streams. Unfortunately, these lean oil systems recover less than 80% of the C_3's and much of the C_4's can slip through into the fuel gas. As long as the quantity of gas produced is relatively small, the low recovery efficiencies have little effect on the heating value of the fuel stream. However, as more gas is produced, the amount of C_3+ in the fuel gas becomes significant, even if the lean oil system recovery efficiency is maintained. Since the heating value of C_3's and C_4's is much greater than that of methane, an excess of fuel gas can often occur with a change in fuel gas combustion characteristics. Figure 1 is a block flow for a typical refinery processing scheme, which indicates where CRYO-PLUS™ is integrated within the operation.

CRYO-PLUS™ Benefits

The optimum C_3+ recovery is a function of the relative values of the recovered components, the fuel gas, utilities, and the required economic payout. CRYO-PLUS™ recovery for C_3's is typically 95% with essentially 100% recovery of the C4's and heavier components. Typical CRYO-PLUS™ feed and product compositions are indicated in Table 1A. The material balance is for a nominal 50 MMSCFD feed gas from an FCCU. For example assuming a refinery fuel gas value of $4.27/MMBTU, this gas as fuel has a value of approximately $10,306/hr. The CRYO-PLUS™ technology recovers approximately 3,609 BBL/Day of mixed C_3+ liquids. If the average value of the C_3+ liquids is $2.36/gallon, then the combined value of the C_3+ liquids plus the residue as fuel is over $22,626/hr. This differential results in a gross margin between the two operations of over $107,923,000 per year. These simplified calculations assume that the refinery consumes all the fuel. When flaring these excess fuels, these already impressive economics improve dramatically. (Substitute your own product values and see your impact.) The recovered liquid stream's composition is a reflection of the fuel gas streams that comprise the CRYO-PLUS™ feeds. However, cracked gas from the FCCU and coker typically comprise a major portion of the feed gas and as such, the liquid product from the CRYO-PLUS™ contains a substantial olefin fraction, and can often be fed to an alkylation unit where the propylene and butylene combine with isobutane in the alkylation process to produce high-octane C_7 and C_8 gasoline compounds. Alternatively, the C_3's and C_4's can be split by fractionation and each can be fed to a separate process for further upgrading or simply sold as chemical feedstock.

A subtle, but very real benefit of CRYO-PLUS™ derives from the change in the fuel gas composition after removing the C_3 and C_4 components. The higher heating value of the C_3's and C_4's results in a higher flame temperature within the furnace or boiler; this may result in higher NO_x emissions. Removal of C_3 and C_4 components from the fuel gas therefore achieves a measurable reduction in NO_x emissions. This incremental reduction may be enough to keep a refinery in compliance and avoid expensive NO_x reduction modifications for combustion processes. In addition, during cold weather, the water and C_3+ components in refinery fuel gas can condense in the fuel system and present a potential safety hazard if they reach a process furnace or boiler in the liquid state. The residual gas from a CRYO-PLUS™ is dry and has a hydrocarbon dew point of less than -100°F, thus eliminating the possibility of water or hydrocarbon condensation.

Table 1-A Typical Propylene Plus Recovery

Component	Feed Mol/Hr	Residue Gas Mol/Hr	Liquid Product Mol/Hr	Recovery %
H_2	1274.66	1274.66	0.00	
H_2S	0.00	0.00	0.00	
CO	37.97	37.97	0.00	
CO_2	0.00	0.00	0.00	
COS	0.00	0.00	0.00	
N_2	222.39	222.39	0.00	
O_2	5.42	5.42	0.00	
C_1	1789.94	1789.94	0.00	0.00
C_2=	596.65	596.65	0.00	0.00
C_2	884.12	888.13	0.19	0.02
C_3=	309.17	7.45	301.72	97.59
C_3	173.57	2.18	171.38	98.74
C_4=	43.39	0.00	43.39	100.00
IsoC_4	32.54	0.00	32.54	100.00
NC_4	27.12	0.00	27.12	100.00
C_5+	27.12	0.00	27.12	100.00
H_2O	66.64	0.00	0.00	
Totals				
Mol/Hr	5,489.68	4,820.60	603.44	
Lb/Hr	100,770.3	72,441.6	28,328.7	
MMSCFD	50.000	43.910	5.500	
BBL/day			3609	
MMBTU/hr	2,413	1,812	601	
Avg. Mol Wt	20.38	17.11	46.77	
BTU/SCF	1,172.1	990.5	2,622.9	

Table 1-B Typical Ethylene Plus Recovery

Component	Feed Mol/Hr	Residue Gas Mol/Hr	Liquid Product Mol/Hr	Recovery %
H_2	1274.66	1274.66	0.00	
H_2S	0.00	0.00	0.00	
CO	37.97	37.97	0.00	
CO_2	0.00	0.00	0.00	
COS	0.00	0.00	0.00	
N_2	222.39	222.39	0.00	
O_2	5.42	5.42	0.00	
C_1	1789.94	1789.94	0.18	0.01
C_2=	596.65	58.35	538.30	90.22
C_2	884.12	36.07	848.04	95.92
C_3=	309.17	0.99	308.18	99.68
C_3	173.57	0.40	173.17	99.77
C_4=	43.39	0.00	43.38	99.99
IsoC_4	32.54	0.00	32.54	100.00
NC_4	27.12	0.00	27.12	100.00
C_5+	27.12	0.00	27.12	100.00
H_2O	66.64	0.00	0.00	
Totals				
Mol/Hr	5,489.68	3,426.02	1,998.02	
Lb/Hr	100,770.3	31,492.5	69,277.9	
MMSCFD	50.000	31.204	18.198	
BBL/day			11,451	
MMBTU/hr	2,413	908	1,504	
Avg. Mol Wt	20.38	12.12	34.62	
BTU/SCF	1,172.1	698.6	1,984.1	

CRYO-PLUS C2=™

Ethylene is a primary hydrocarbon building block for many chemicals, plastics, and fabrics. Ethane is the feed of choice for ethylene production. Refinery cracking processes produce ethylene and ethane. In the refinery, these compounds only have fuel value. However, recovery of these C_2's as an ethylene product or as a petrochemical plant feedstock enhances their value and can result in a substantial increase in profitability of a refinery operation. In the U.S., many refineries are located near petrochemical complexes. Internationally, the refinery and petrochemical operations are often integrated. The CRYO-PLUS C2=™ process has been proven to be the most cost effective technology for recovery of C_2's from refinery fuel gas streams. Figure 1 indicates how the process is integrated and Table 1B reflects the relative feed and product compositions from a typical CRYO-PLUS C2=™ unit. A simple economic evaluation indicates the potential benefit of C_2+ recovery using the same feed as used for C_3+ recovery. The feed gas fuel value is again $10,306/hr, assuming $4.27/MMBTU. The C_2+ recovery results in almost 11,451 BBL/day of liquids. Assuming a value of $1.27/gallon for these liquids, the differential gross margin between the refinery with and without CRYO-PLUS C2=™ is over $166,679,000 per year.

How CRYO PLUS™ Processes Work

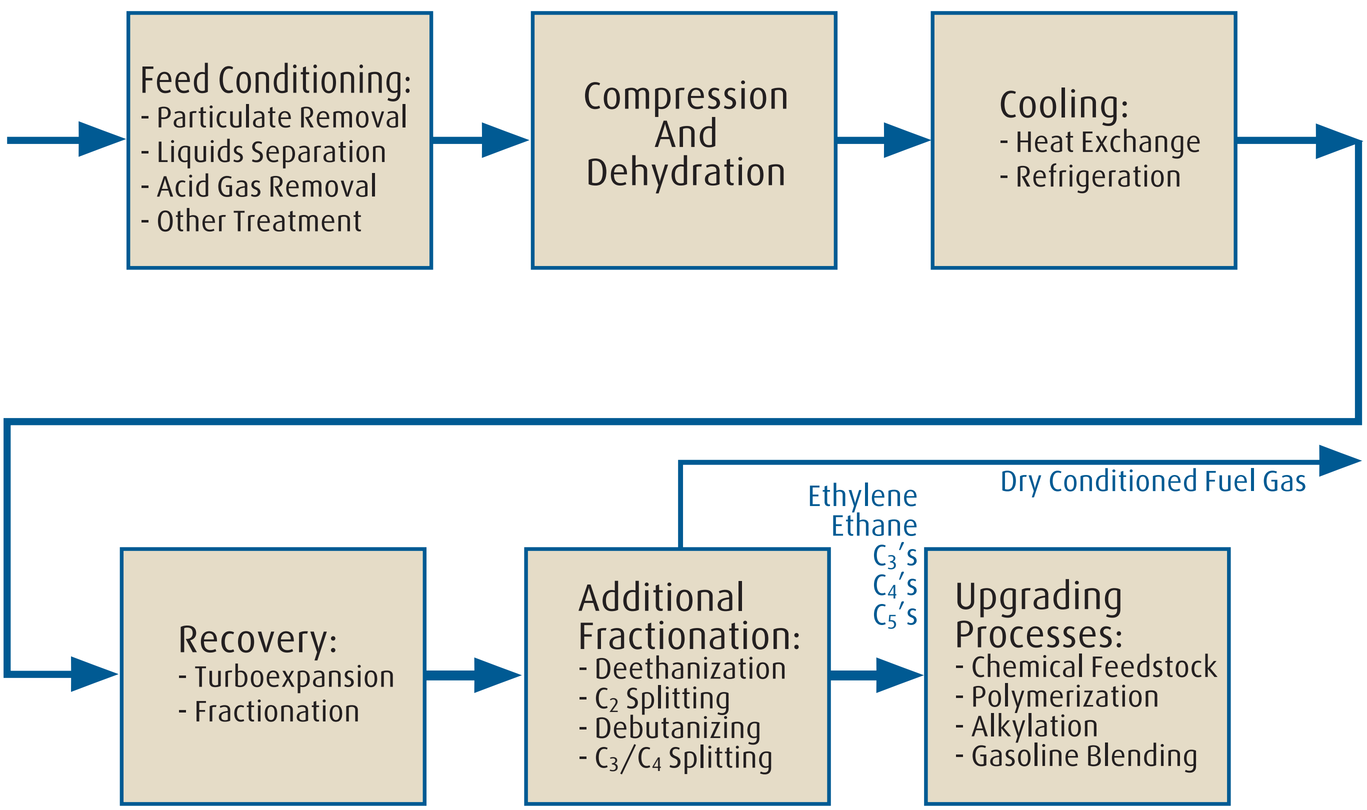
CRYO-PLUS™ and CRYO-PLUS C2=™ are cryogenic recovery technologies which utilize a turbo-expander to recover energy while cooling the feed gas. CRYO-PLUS™ technologies are unique in their ability to process low-pressure hydrogen bearing refinery fuel gas streams and obtain high recoveries with less compressor and/or refrigeration horsepower than conventional or competing cryogenic processes. A description of the unit operations follows. Figure 2 is a block flow of CRYO-PLUS™ processing.

Feed Conditioning

To protect the unit against upset conditions, feeds may first pass through a coalescing filter/separator designed to remove solid particles and liquid droplets that may carry over from upstream processes.

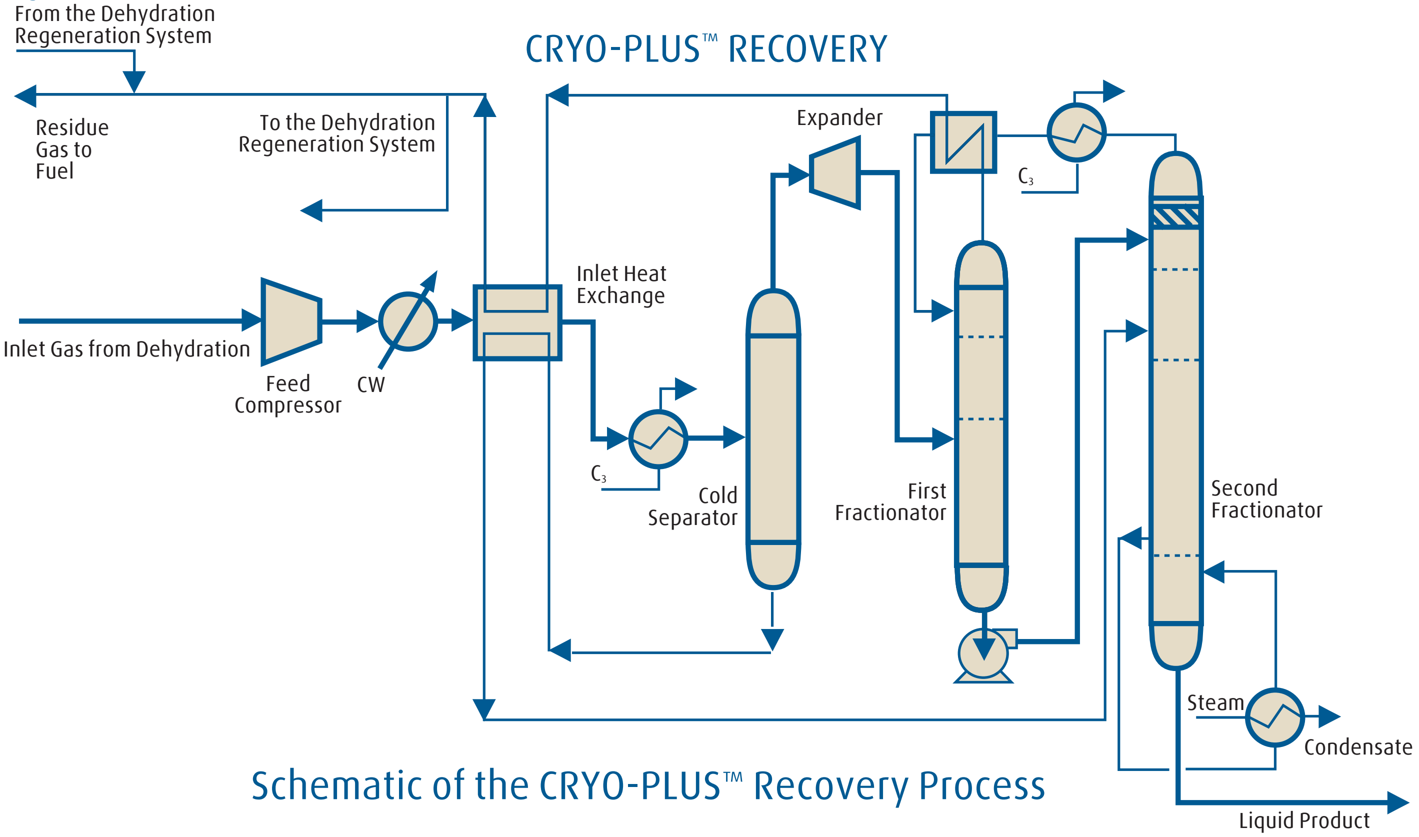
Although CRYO-PLUS™ can tolerate small quantities of H_2S and CO_2 these compounds are not desirable. The use of an amine treating unit for removal of acid gas components removes these compounds in an absorption process as a feed conditioning step

Figure 2



Block Flow Diagram of CRYO-PLUS™ Processing

Figure 3



Schematic of the CRYO-PLUS™ Recovery Process

REFINERY PLANTS

Plant Location	Off-Gas Feed	Product Recovered	Project Type	MMSCFD Size	Inlet H_2 Mol %
Alma, MI	FCC + CCR	C3+	EPF	16	51
Lake Charles, LA	FCC	C3+	EPC	40	18
Ponca City, OK	FCC	C3+	EPF	20	15
Tyler, TX	FCC + CCR + SAT	C3+	EPC	26	72
Port Allen, LA	FCC	C3+	EPF	6	21
Ponca City, OK	CCR	C3+	EPF	30	76
Gallup, NM	SAT	C3+	EPC	1	21
Memphis, TN	FCC + CCR	C3+	EPC	18	47
Denver, CO	FCC + CCR + SAT	C3+	EPC	16	55
Meraux, LA	FCC	C3+	EPF	13	21
Convent, LA	CCR Post - H2 Removal	C3+	EPC	9	5
Big Springs, TX	FCC	C3+	EPC	13	22
Belle Chasse, LA	FCC	C3+	EPF	45	24
Billings, MT	FCC + COKER + SAT	C3+	EPF	16	14
Houston, TX	FCC + COKER	C2+	EPC	66	17
Los Angeles, CA	FCC + CCR	C3+	E	63	9
Linden, NJ	FCC	C2+	EPC	48	23
Fort McMurray, Alberta	FCC	C2+/ C3+	E	107	12
Haifa, Israel	FCC	C2+	EPF	6	13
Port Arthur, TX	FCC	C3+	E	16	17

Feed Compression

The next step is to compress the feed streams unless it is already at elevated pressures. An air cooler or cooling water, cools the gas downstream of the compressor to remove the heat of compression. (Heat of compression can also be used as a heat source for fractionation as permitted by the process heat balance and temperature driving force.)

Dehydration

To avoid ice and hydrate formation in the cryogenic section of the process, the water content of the gas is reduced to an acceptable level through adsorption in molecular sieve desiccant beds. This is a batch process, where multiple (two or more) adsorption beds are used. One or more of the adsorption beds are being regenerated to restore their capacity while the other bed(s) are on-line and drying the feed gas. A recycle portion of the dry gas can be heated and used for regeneration of the beds to drive off the adsorbed water. Cooling of this stream condenses the removed water, before it recycles and combines with the feed gas. A portion of the residue gas may also be used for the regeneration on a once through basis. Downstream of the adsorption beds, the gas passes through a dust filter to remove any particulate carryover before subsequent processing.

Feed Cooling

After dehydration, the feed gas flows into the cold section of the process, where cooling by exchange of heat with the residue gas and cold separator liquids takes place using a brazed aluminum plate-fin heat exchanger. Although not always a requirement, the gas may be further cooled using external refrigeration before it goes to the cryogenic portion of the process.

Cold Separation

Following cooling, the feed gas is partially condensed and delivered to a vapor/liquid separator. The liquid then flows through the inlet exchanger to cool the feed gas before entering the deethanizer (or demethanizer for C_2 recovery) for fractionation. The vapor flows to the inlet of the expander/compressor. As the gas expands, it provides the work/energy for the compression. The expansion and removal of energy cools the gas further and causes additional condensation. The expander discharges into the first tower of a two-stage fractionation process. The configuration and the combination of fractionation and heat transfer between these two columns is the proprietary, patented technology that gives CRYO-PLUS™ its advantages (higher recovery at reduced horsepower) over competing technologies.

A residue gas and a deethanized (or demethanized for ethylene recovery) liquid product are produced from this two tower scheme. The residue gas is at or near the fuel system pressure. Following exchange with the feed gas in the inlet cooling step, it arrives at the fuel system as a dry, stable heating value fuel. The liquid product from the fractionation system is the recovered C_2+ or C_3+ liquid hydrocarbons. The liquid often undergoes additional processing, such as additional fractionation in downstream columns. For C_3+ recovery, the liquid stream is normally debutanized. The C_3's and C_4's may then be fed to an alkylation process, or split with the C_3's going to polymerization and only the C_4's going to alkylation feed. For C_2+ recovery, a deethanizer normally precedes the debutanizer. The overhead from the deethanizer, ethane, and ethylene can then be split as required by their final destination requirements.

Hydrogen Recovery

The feed gas for CRYO-PLUS™ typically originates from the fluid catalytic cracking unit (FCCU) coker and the catalytic reformer unit (CRU) and as such contains a significant quantity of hydrogen. If desired, the CRYO-PLUS™ process can produce hydrogen as a residue gas stream by some modifications to the flow scheme.

Customized Design

Most refineries have limited plot space. LPP specifically designs and fabricates unique modules to fit the available space. A growing number of petroleum and chemical corporations have come to recognize the benefits of modular fabrication over traditional field fabricated process systems. Besides the traditional focus on lower initial cost, modular fabrication results in many other operational and maintenance advantages. Modular fabrication results in streamlined project execution, a predictable schedule, low cost, and minimizes the risk of construction within an operating plant.

Modular Construction

The chemical and petrochemical industries recognize the challenges of conventional on-site construction. Modularization will minimize the on-site construction time and thereby reduce cost and schedule of the overall project.

Shorter Project Schedule

With field fabrication, workers are at the mercy of the environment. Schedule and quality often suffers under adverse weather conditions. LPP's skilled and stable work force performs their work in the controlled environment of one of the finest fabrication facilities in the US, maintaining schedule regardless of weather conditions with ISO-9001 quality.

Safer to Construct Away from Hazardous Processes

On-site construction alongside operational equipment carrying high-pressure hydrocarbons increases on-site construction risk. LPP performs fabrication in the safety of a controlled environment without the risk of plant upsets or construction worker's errors, and then transports the completed prefabricated and preassembled system to the jobsite, where a small crew quickly installs them, thus minimizing risk.

Less Downtime

The cost of downtime associated with construction can add significantly to the overall cost of construction. LPP is minimizing downtime by building units off-site.

About LPP

LPP is a company with over forty years' experience in refining, petrochemicals and natural gas processing. As a subsidiary of The Linde Group, we are a totally integrated technology, engineering, fabrication, and construction company.

Engineering

Engineers are available with all of the disciplines required to provide turnkey plant installations using proprietary technology or the client's design.

Fabrication

LPP is a leader in the field of engineering and fabrication of turnkey process systems. In addition to road and rail transportation, our fabrication facilities have access to the Port of Catoosa on the Arkansas River, which can transport prefabricated modules on oceangoing barges to global markets via the Port of New Orleans.

Technology

Either proprietary LPP or licensed technology is used.

With LPP's Experience and Resources You are Assured Success

Only Linde Process Plants, Inc. has the combination of proprietary technologies, proven experience, specialized skills, impressive record of accomplishment, and certified fabrication facilities to deliver major turnkey process plants to global markets successfully.

Processes Offered by LPP

- CRYO-PLUS™, Recovers C_3+
- CRYO-PLUS C2=™, Recovers C_2+
- Sulfur Recovery
- Natural Gas Processing
- Nitrogen Rejection
- Helium/Hydrogen Liquefiers

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