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**TECHNOLOGY ADVANCES IMPROVE LIQUID
RECOVERY FROM REFINERY OFF-GASES**

by

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**TECHNOLOGY ADVANCES IMPROVE LIQUID RECOVERY
from
REFINERY OFF-GASES**

By:
Ron D. Key – The Pro-Quip Corporation
Zaheer I. Malik – The Pro-Quip Corporation

Over the last several years, refineries have faced increasing challenges to:

- Increase the octane number of gasoline
- Reduce the benzene content of gasoline
- Reduce the amount of process off-gases that are flared
- Remain profitable with increasing pressures on margins

The “Cryo-Plus” and “Cryo-Plus C₂” processes have been specifically designed to recover valuable hydrocarbon liquids from hydrogen-bearing refinery off-gases. These off-gases are produced by such units as Fluid Catalytic Crackers, Catalytic Reformers, Cokers, Crude Units and Hydrotreaters. The Cryo-Plus and Cryo-Plus C₂ Liquid Recovery Processes use proven gas processing technology and have now been installed in sixteen (16) refineries.

CRYO-PLUS

Background:

The Cryo-Plus process was expressly designed to recover propylene and heavier components from refinery off-gas streams. The propylene recovered is often used as a feed stock to a polypropylene or cumene unit. The isobutane recovered is an excellent feed stock for the alkylation unit. The butenes recovered can also be used in other chemical or refining units. The pentane plus fraction is further fractionated and isomerized and/or blended with the gasoline product.

Prior to the invention of the Cryo-Plus process, a circulating lean oil process was used to absorb propylene and heavier components from refinery off-gases. The absorption process, while providing a reasonably good recovery of propylene and heavier components, is energy intensive and requires several pieces of operating equipment. Additional pieces of equipment usually

imply an increased quantity of control loops and additional plot space. Refineries have well established plot plans in populated areas. Additional plot space is not easily obtained nor is this additional plot space inexpensive.

Process Description

The Cryo-Plus process is based upon proven gas processing technology specifically adapted for refinery off-gas streams. Depending on the available feed pressure, the gases are either compressed or directly fed to the dehydration system. The dehydration system uses 3A molecular sieve. The 3A molecular sieve has smaller pore diameter and thus adsorbs fewer hydrocarbons than 4A molecular sieve generally used in natural gas dehydration applications. In addition, the 3A molecular sieve allows for a lower regeneration temperature. A lower regeneration temperature is desirable to eliminate the possibility of the cracking or polymerization of the higher molecular weight (C_4^+) olefinic compounds in the refinery off-gas feed stream.

Figure One depicts the Cryo-Plus process. Inlet gas is cooled and partially condensed by heat exchange with propane and/or propylene refrigerant, residue (fuel) gas, cold separator liquids, and possibly a side reboiler. In the cold separator, the initial phase separation occurs. The condensed liquids are fed through a heat exchanger cooling the inlet gas and then to a deethanizer. The vapors from the cold separator are expanded through a turbo-expander. The turbo-expander recovers energy to be used for inlet or residue gas compression. The turbo-expansion of the vapor also liquefies 8 to 15 percent (weight) of the cold separator vapors. The two-phase expander outlet stream enters the light-ends fractionating column (LEFC). The separated vapors flow upward through the LEFC and are contacted with condensed overhead liquids from the deethanizer. The LEFC bottoms liquids are pumped through a heat exchanger or directly to the deethanizer as the process design requires. The deethanizer fractionates the ethane and lighter components from the propylene and heavier components. The ethane/ethylene-rich overhead from the deethanizer is typically chilled via propane and/or propylene refrigeration producing the first liquid portion of the reflux stream. Further cross

exchange with the LEFC vapors provides additional condensation. This two-phase stream is then flashed into the LEFC entering on the top tray. After chilling, a significant quantity of the ethane/ethylene has been condensed. When introduced into the top of the LEFC, this ethane/ethylene vaporizes providing latent heat condensation of the propylene and heavier components. The trays in the LEFC provides some additional fractionation and heat exchange thus facilitating the separation. The vaporized ethane/ethylene flows upward through the LEFC combining with the hydrogen, nitrogen and methane contained in the inlet gas to ultimately become the residue (fuel) gas for the refinery.

The liquids produced in the LEFC flow downward and combine with the expander outlet liquids. These liquids flow to the LEFC bottoms pump and then are pumped to the deethanizer. The deethanizer may be a reboiled absorber or a refluxed, reboiled column.

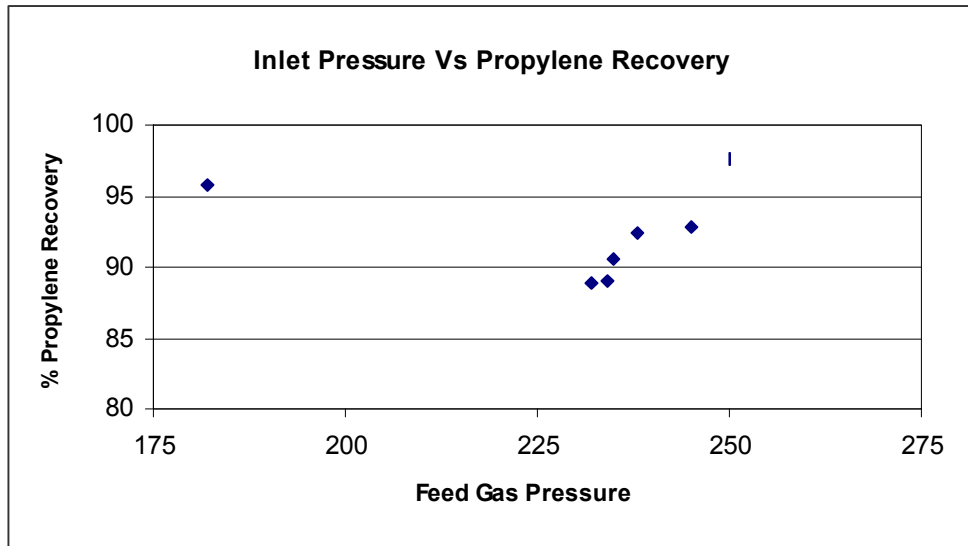
Table A presents a typical material balance for a Cryo-Plus Unit.

Flexibility

The strength of the Cryo-Plus Process is its ability to operate under varying flow rates, feed compositions, and pressures. Refinery feed streams are, if anything, variable. Usually, Cryo-Plus units see feed streams from multiple units. As units are brought on-line, taken off-line, and in the case of Cokers, operate in a cyclical manner, the Cryo-Plus technology has proven to have the flexibility to ride through these variations. One U.S. Gulf Coast Refiner feeds a Cryo-Plus Unit from two (2) fluid catalytic cracking units. Both of the FCC's supply approximately equal feed volumes to the Cryo Plus Unit. Unfortunately, another occurrence in the refinery caused one of the FCC Units to shutdown without prior warning. The Cryo-Plus Unit control system adjusted and the unit continued running after a step function change from 100% to 50% of flow rate.

The level of propylene recovery is dependent on the feed gas composition, refrigeration level, and inlet pressure. Typically Cryo-Plus units utilize external mechanical refrigeration. The

external refrigeration provides flexibility for varying composition and flow rate. A graph of inlet pressure versus propylene recovery from operating plants is shown in Figure 2. As is evident from the graph, recovery remains high over a wide range of inlet pressures.



Improved Fuel Gas

Another benefit of the Cryo-Plus process is the improvement of the refinery fuel gas stream. The Cryo-Plus process removes in excess of 90% of the propylene in the feed gas stream and essentially 100% of all heavier products thus producing a fuel gas that contains nitrogen, hydrogen, carbon monoxide, methane, ethylene and ethane. Refiners report the reduced dew point of the fuel gas improves winter operations significantly. In addition, the fuel gas is much dryer than the water saturated fuel gas the refiner had previously burned prior to the installation of the Cryo-Plus Unit. Thus, safety issues and operating difficulties associated with both free water and hydrocarbon condensate are eliminated with the installation of a Cryo-Plus Unit.

By recovering the heavier hydrocarbons, the refinery achieves a better fuel gas balance. The off-gases gas were traditionally placed into the fuel gas header, consumed by users as required, and the excess flared. By using a Cryo-Plus unit, the quantity of gas flared has been significantly reduced or eliminated, thus, the total emissions of the refinery are greatly reduced.

Downstream Hydrogen Recovery

Refiners are becoming more and more deficit in hydrogen. New reformulated gasoline regulations, and more severe sulfur removal regulations are causing the consumption of hydrogen in such new units as Aromatic Saturators, Polishing Distillate Hydrotreaters and Gasoline Hydrotreaters. Refiners are looking at alternate, lower cost sources for hydrogen. The residue gas from a Cryo-Plus Unit provides an excellent source of opportunity for hydrogen recovery. Depending on the feed stock, it is not unusual to see residue gases ranging from 35 to 90% (mol) hydrogen. These gases can be compressed and separated into hydrogen and hydrocarbons via many processes including pressure swing adsorption (PSA), membrane separation technology, and cryogenic separation. Also, this gas is an excellent feedstock to a traditional steam/methane reforming hydrogen production plant. The recovery of hydrogen has shown, in other studies, to be competitive with the production of hydrogen via traditional techniques such as steam/methane reforming.

Case Studies

Table B provides a summary of the results of three (3) of the Cryo-Plus Units that were installed in U.S. refineries. In all cases, the refinery is now in fuel gas balance, is recovering additional liquids for use in product upgrading and have enjoyed a payout ranging from less than one year to less than two years.

CRYO-PLUS C₂⁼

Background

Ethylene is a primary feed stock for many chemical processes. Traditionally, ethane has been cracked to ethylene in a furnace. While a Cryo-Plus C₂⁼ process cannot replace a world-class ethylene facility, it can recover ethylene from off-gas streams at a lower cost than the production of ethylene from a traditional cracking furnace. Thus, the use of Cryo-Plus C₂⁼ technology in refinery ethylene recovery and in the ethane recycle loop of a traditional ethylene production facility has merit.

The Cryo-Plus C₂⁼ process builds on the fifteen (15) success stories of the Cryo-Plus process and takes the technology to the next level of recovery. This patented technology generally allows for ethylene recoveries in excess of 90% for most refinery off-gas streams technology as indicated in Table “C”. The Cryo-Plus C₂⁼ is very similar to the Cryo-Plus process with specific modifications to enhance ethylene recovery. The refinery off-gases are compressed to a higher pressure to facilitate ethylene/ethane liquification and recovery. These gases are recovered in a demethanizer. The LEFC technology is used in the Cryo-Plus C₂⁼ process to provide a separation between ethylene and methane. In the Cryo-Plus C₂⁼ process, the LEFC uses liquid methane to condense ethylene and ethane. Calculations and field data show the Cryo-Plus C₂⁼ process selectively sacrifices ethane to recover the more valuable ethylene.

Case Study

In 1995, a U.S. Gulf Coast refiner approached Pro-Quip with the possibility of collecting off-gases from several refineries in the area and processing these gases to recover ethylene and ethane for use in an olefins production plant. The refiner had utilized cryogenic technology in another facility and was well aware of its benefits.

The Cryo-Plus C₂⁼ design utilizes higher pressure in the front end cooling/condensation portion of the facility as opposed to a more traditional low pressure approach that often requires cascade refrigeration. Consequently, there was some concern regarding the prediction of the vapor-liquid phase equilibrium in the high pressure cold separator due to the influence of the hydrogen and other refinery components in the feed gases. Pro-Quip commissioned an independent laboratory to synthesize a gas that mimicked the gas anticipated to be the feed stock. The laboratory then simulated the performance of the cold separator by chilling the gases at the appropriate pressure and temperature, collecting and analyzing liquid and vapor samples and measuring the liquid volume production over a given amount of time. The process simulation predictions and laboratory results yielded a very credible agreement. With the proven accuracy of the

correlation, the refiner was confident the Cryo-Plus C₂⁼ technology could be successfully applied for ethylene recovery and satisfy the olefins production plant requirements.

The olefins plant produces a polymer grade ethylene stream. Therefore, treating of the gases were required upstream of the Cryo-Plus C₂⁼ process to remove arsine, acetylene, butadienes, COS and of course, moisture. After treating and compression, the gas was delivered to the Cryo-Plus C₂⁼ facility at approximately 750 psig. The process scheme used for the Cryo-Plus C₂⁼ plant is similar to that shown in Figure 3.

The engineering and design began in March 1996 with mechanical completion achieved by June 4, 1997. A performance test was conducted on August 22, 1997. Table D shows the performance test results including the calculated recovery level and also the actual recovery level obtained.

ACKNOWLEDGEMENTS

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REFERENCES:

1. Buck, Loren L., Separating Hydrocarbon Gases, U.S. Patent No. 4,617,039, October 14, 1986.
2. Buck, Loren L. and Key, Ronald D., Process for C₂ Recovery, U.S. Patent No. 4,895,584, January 30, 1990.

Figure 1
SCHEMATIC OF THE CRYO-PLUS® RECOVERY PROCESS
 U.S. Patent No. 4,617,039

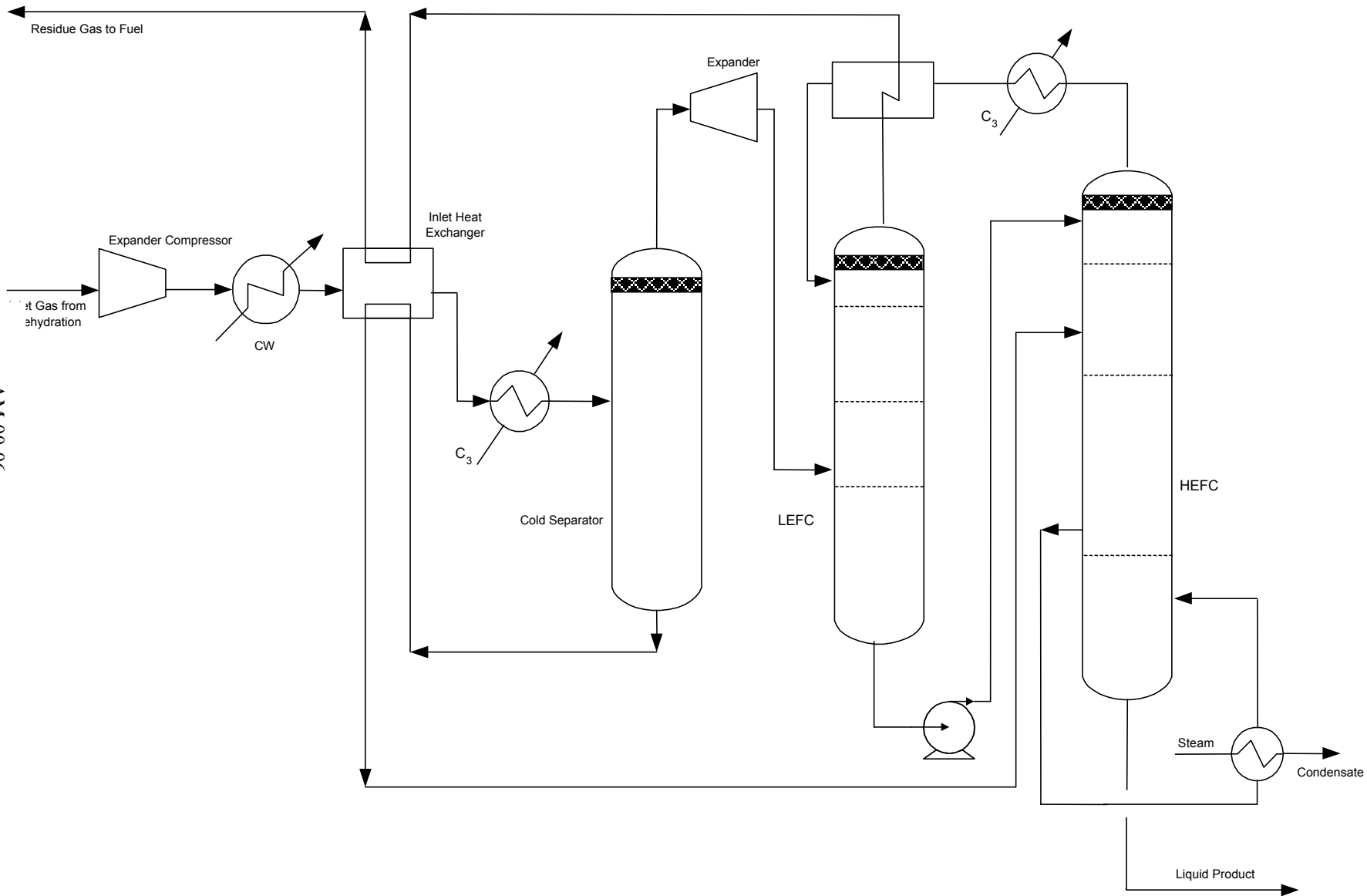


Table A
TYPICAL PROPYLENE PLUS RECOVERY

Component	Feed Mol/Hr	Residue Gas Mol/Hr	Liquid Product Mol/Hr	Recovery %
H ₂	1,274.66	1,274.66	0.00	
H ₂ S	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	1,789.94	1,789.94	0.00	0.00
C ₂ =	596.65	596.65	0.00	0.00
C ₂	884.12	883.13	0.99	0.02
C ₃ =	309.17	7.45	301.72	97.59
C ₃	173.57	2.18	171.39	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 ₂ O	66.64	0.00	0.00	
Totals				
Mol/Hr	5,490.70	4,819.79	603.46	
Lb/Hr	111,885	82,463	28,222	
SCFD	50,000,000	43,905,965	---	
BBL/day	---	---	3,574	
Mol. Wt.	20.38	17.11	46.77	
BTU/SCF	1,056.45	899.03	---	

Table B
CRYO-PLUS[®] CASE STUDIES

	Case Study I	Case Study II	Case Study III
Refinery	US Upper Midwest 42,000 BPD	US Gulf Coast 164,000 BPD	US Central Plains 134,000 BPD
Problem	<ul style="list-style-type: none"> Fuel system imbalance Total 16 MMSCFD with significant portion flared 	<ul style="list-style-type: none"> Fuel system imbalance 40 MMSCFD flared or exported to a local chemical plant Gasoline blending agents for octane improvement required 	<ul style="list-style-type: none"> Fuel system imbalance in summer Gasoline blending agents for octane improvement required
Solution	<ul style="list-style-type: none"> Engineering analysis performed by Pro-Quip Contract awarded to Pro-Quip Period from order to startup: nine months The Cryo-Plus unit was designed to extract approximately 90% of the C₃'s and essentially 100% of the C₄'s 	<ul style="list-style-type: none"> Engineering analysis performed by Pro-Quip Contract awarded to Pro-Quip Period from order to startup: eleven months 	<ul style="list-style-type: none"> Engineering analysis performed by Pro-Quip Contract awarded to Pro-Quip Period from order to startup: nine months The Cryo-Plus unit was designed to extract approximately 87% of the C₃'s and essentially 100% of the C₄'s
Benefits	<ul style="list-style-type: none"> The refinery is now in fuel gas balance 550 BBP of liquid hydrocarbons recovered Additional alkylate for gasoline upgrading produced 	<ul style="list-style-type: none"> The refinery is now in fuel gas balance and has a high quality fuel stream that can be marketed as pipeline quality gas instead of being sold to the chemical plant 1,750 BPD of liquid hydrocarbons recovered Additional alkylate for gasoline upgrading produced 	<ul style="list-style-type: none"> The refinery is now in fuel gas balance 1,225 BPD of liquid hydrocarbons recovered Additional alkylate for gasoline upgrading produced
Payout	<ul style="list-style-type: none"> Less than a year 	<ul style="list-style-type: none"> Much less than a year 	<ul style="list-style-type: none"> Less than two years

Table C
TYPICAL ETHYLENE PLUS RECOVERY

Component	Feed Mol/Hr	Residue Gas Mol/Hr	Liquid Product Mol/Hr	Recovery %
H ₂	1,274.66	1,274.66	0.00	
H ₂ S	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	1,789.94	1,789.76	0.18	0.01
C ₂ =	596.65	58.35	538.30	90.22
C ₂	884.12	36.07	848.05	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	0.01	43.38	99.98
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 ₂ O	66.64	0.00	0.00	
Totals				
Mol/Hr	5,490.70	3,426.02	1,998.04	
Lb/Hr	111,885	41,530	69,155	
SCFD	50,000,000	31,204,159	---	
BBL/day	---	---	11,650	
Mol. Wt.	20.38	12.12	34.62	
BTU/SCF	1,056.45	623.81	---	

Figure 3
SCHEMATIC OF THE CRYO-PLUS[®]C₂ RECOVERY PROCESS
 U.S. Patent No. 4,895,584

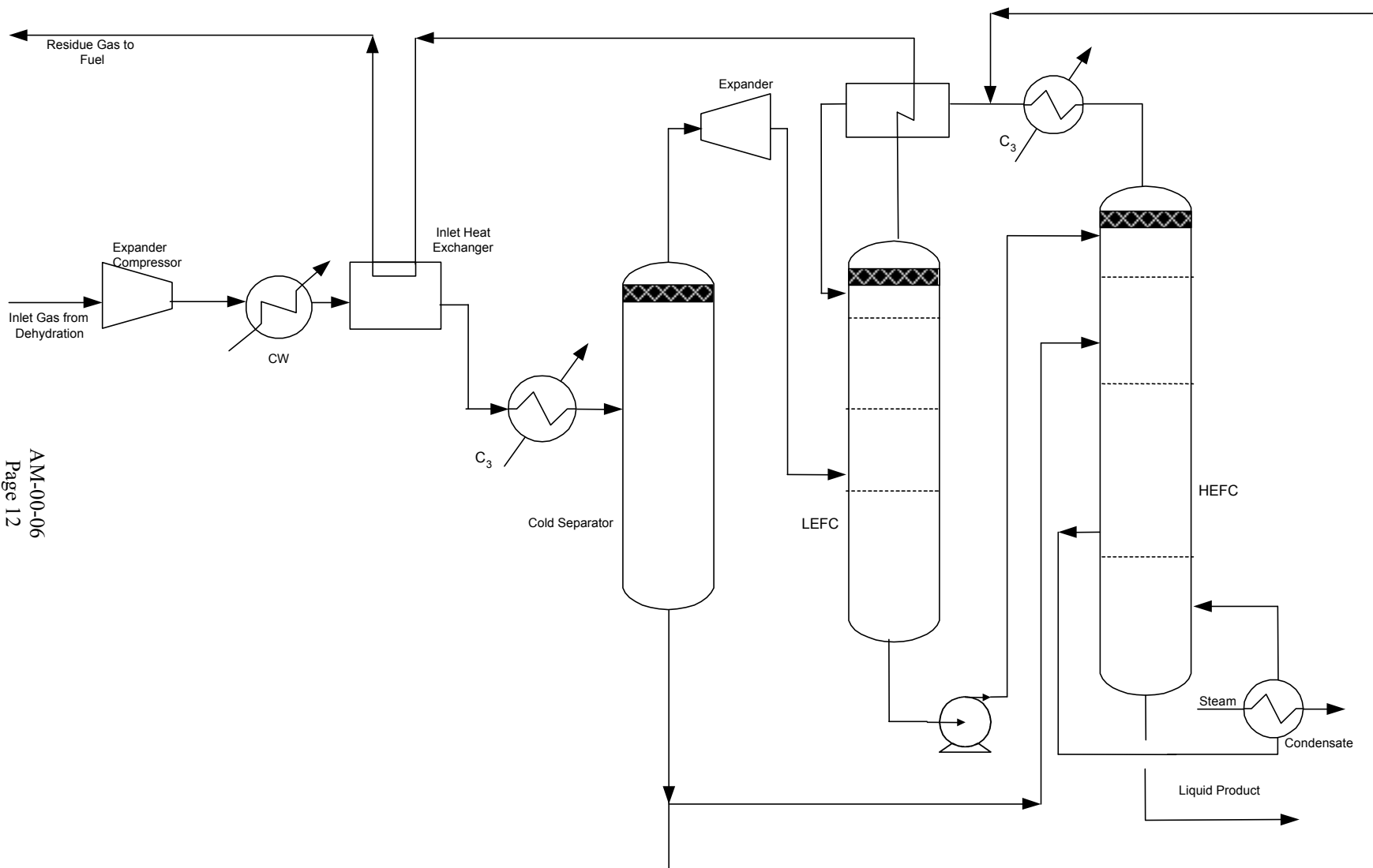


Table D
U.S. GULF COAST CRYO-PLUS C₂⁻ PERFORMANCE TEST RESULTS

Component	Feed Mol/Hr	Residue Gas Mol/Hr	Liquid Product Mol/Hr	Actual Recovery (%)	Calculated Recovery (%)
H2	0.00	0.00	0.00	0.00	0.00
H2S	1,000.53	1,000.53	0.00	0.00	0.00
CO	25.57	25.57	0.00	0.00	0.00
CO2	4.65	4.65	0.00	0.00	0.00
COS	0.00	0.00	0.00	0.00	0.00
N2	237.06	237.06	0.00	0.00	0.00
O2	0.00	0.00	0.00	0.00	0.00
C1	2,656.46	2,656.46	0.00	0.00	0.00
C2=	522.34	69.84	452.51	86.63	86.01
C2	982.52	49.32	933.20	94.98	93.98
C3=	148.16	0.71	147.45	99.52	99.49
C3	115.62	0.50	115.13	99.57	99.64
C4=	44.74	0.00	44.74	100.00	99.99
ISO C4	18.01	0.00	18.01	100.00	99.99
NC4	12.78	0.00	12.78	100.00	99.99
C5+	40.67	0.00	40.67	100.00	100.00
TOTALS					
Mol/Hr	5,809.11	4,044.64	1,764.49	---	---
Lb/Hr	114,956	55,689	59,267	---	---
SCFD	52,909,394	36,838,466	---	---	---
Bbl/Day	---	---	9,275	---	---
Mol. Wt.	19.79	13.77	33.59	---	---
Btu/SCF	1,139	793	---	---	---