

ENGINEERING DESIGN SEMINAR

SEPTEMBER 6, 1994 – NOVEMBER 11, 1994

HYDROTREATING

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MAINTENANCE AND INSPECTION

UOP ENGINEERING DESIGN SEMINAR

HYDROTREATING

September 6, 1994 - November 11, 1994

(ver. 26)

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 Mike O'Brien

INTRODUCTION

Reactor Systems

Hydrotreating Basics

Reactor Systems

Stable Property	Fractionation System	Reactor System
Mass Balance	X	X
Molar Composition	X	
Heat Content	X	

Catalyst: A substance which causes a change, especially an increase in the rate of a chemical reaction, that is itself unchanged in the end.

Except for: Permanent Poisons
Temporary Poisons
Fouling
Physical Damage

Hydrotreating Basics

Hydrotreating

Catalytic – Fixed Bed

Reactions with Hydrogen

Stabilizes Products

Conversion of Unsaturation → Saturates

Olefins

Unstable diolefins

Removes Objectional Elements

Sulfur → Hydrogen Sulfide

Nitrogen → Ammonia

Oxygen → Water

Halides → Hydrogen Halide

Metals → Catalyst

Product Boiling Range ≈ Feed

Hydrocracking

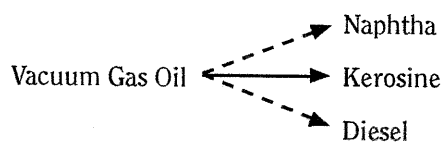
Catalytic

Reactions with Hydrogen

Hydrotreats Feed

Reduce Boiling Range

Naphtha → LPG



EDS-R00-2001

Uniform High Quality Products

Upgrades Products

UOP's Involved With Hydroprocessing in Mid-1930's

Hydrogenation of C₈ polymer (iso-octene) to iso-octanes for aviation fuel
on Co - Mo catalyst

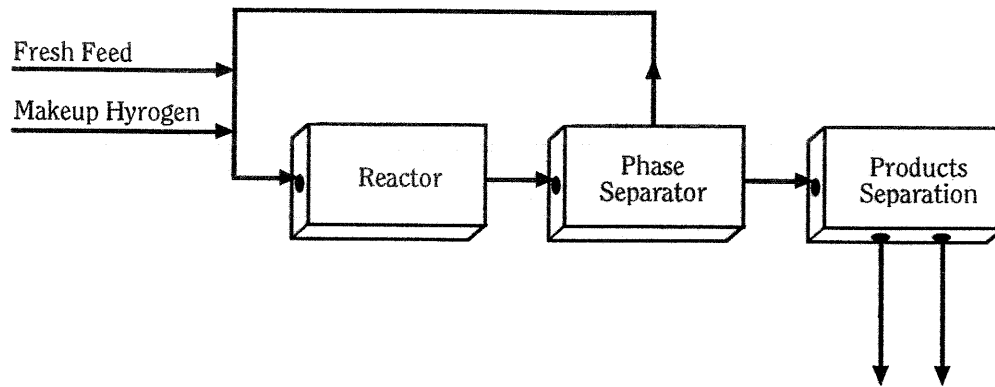
UOP's Commercialization of Platforming in 1949 Made Commercialization of
Hydrotreating Possible

By-Product Hydrogen Available At
Reasonable Purity
Reasonable Cost
Sufficient Quantities

**For barrels processed, hydrotreating is the most widely applied
process technology.**

Figure 1

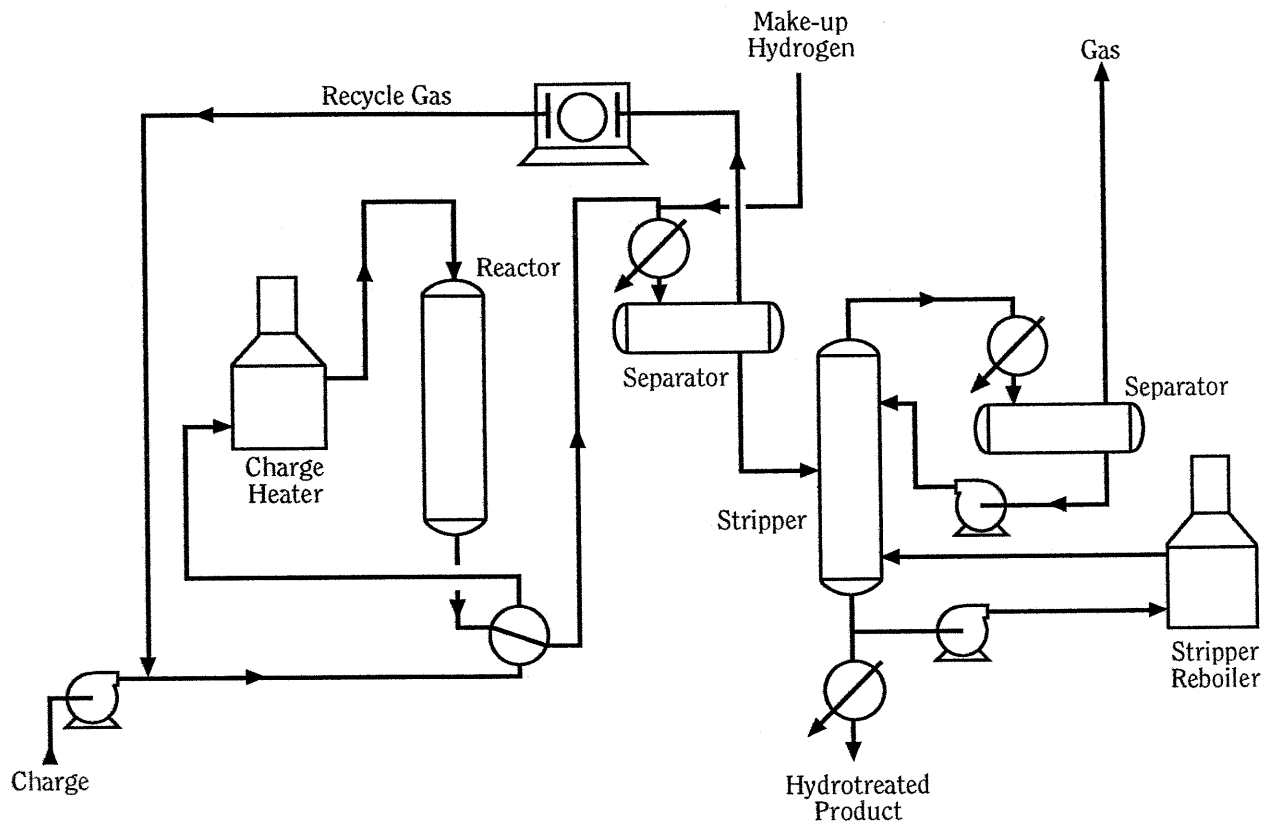
*Hydroprocessing
(The Basics)*



EDS-R00-2002

Figure 2

Naphtha Hydrotreating Process



EDS-R00-2003

CHEMISTRY OF HYDROTREATING

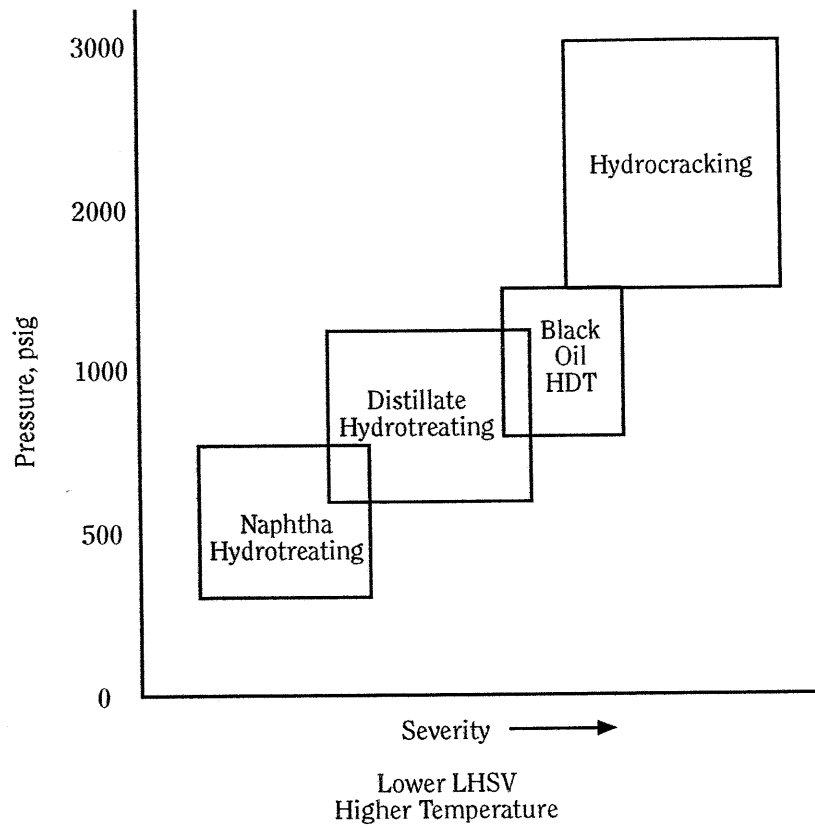
Hydrotreating Reactions

Hydrotreater Feed Stocks

Rates of Reactions

Figure 3

Chemistry of Hydroprocessing



EDS-R00-2004

Hydrotreating Reactions

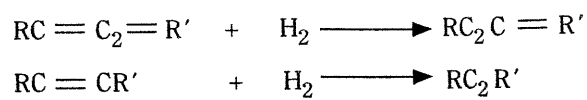
Hydrogenation (Olefin Saturation)

Reduced coking tendency of products

Improve color stability of cracked gas oils.

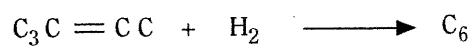
Reduce gum formation in gasolines (diolefin saturation.)

Hydrogenation (olefin saturation)



EDS-R00-2040

For example:



EDS-R00-2041

Desulfurization

Prevent poisoning of catalyst in downstream processing units.

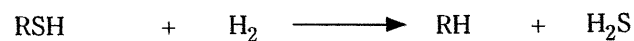
Improve blending quality of diesel fuels and fuel oils.

Lower sulfur content in catalytic cracker feed stocks to produce a lower sulfur product.

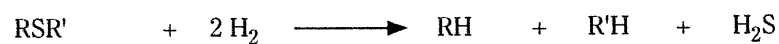
Improve the odor of products.

Reactions

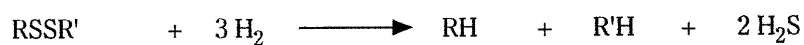
Mercaptans



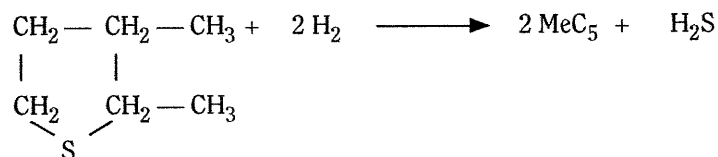
Sulfides



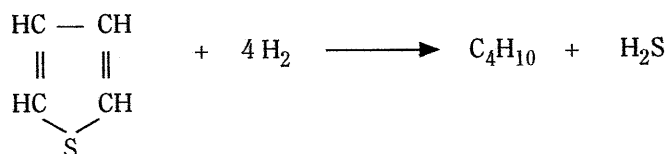
Disulfides



Cyclic Sulfides



Thiophenes



EDS-R00-2005

Denitrification

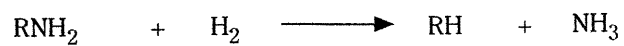
Prevent poisoning of platinum catalyst in Platforming® (catalytic reforming) units.

Removal from feed to catalytic cracking units to limit catalyst deactivation.

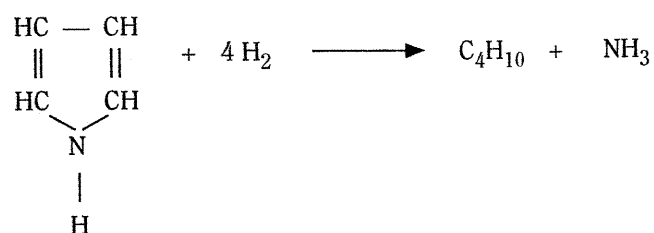
Protection of the isomerization catalyst.

Reactions

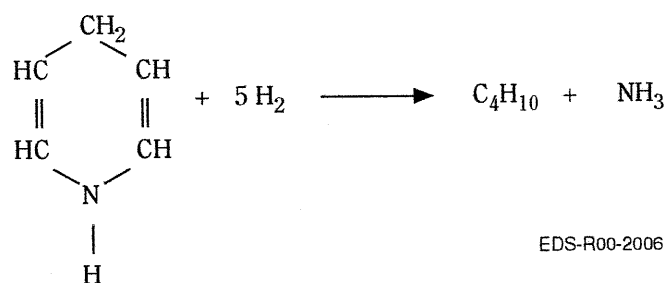
Amine



Pyrrole



Pyridine



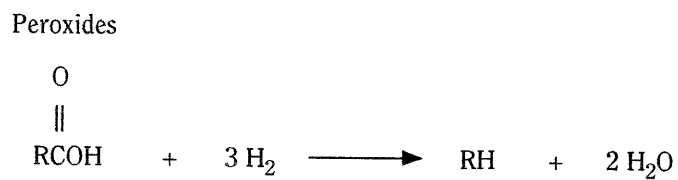
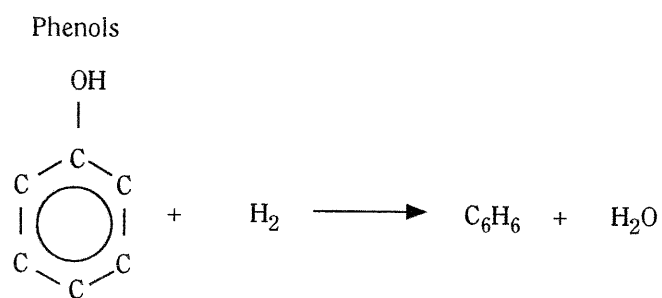
EDS-R00-2006

Deoxidation

Maintain the water balance within the platforming unit.

Reduce fouling tendency of products.

Reactions

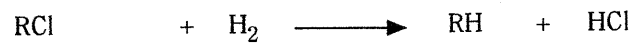


EDS-R00-2007

Dehalogenation

Reduce fouling tendency

Chlorides



EDS-R00-2042

Hydrogenation (Aromatics Saturation)

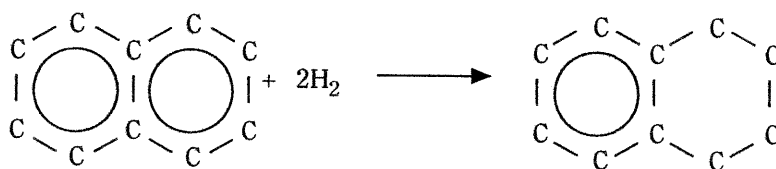
Lower aromatics content of product.

Improve smoke point

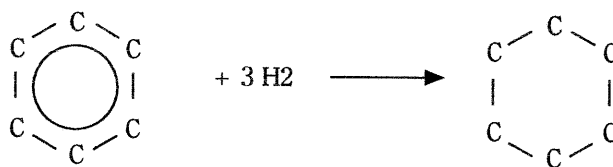
Reactions

Hydrogenation (Aromatics Saturation)

Polyaromatics



Monoaromatics



Hydrocracking



EDS-R00-2008

Feed Stock Types

Virgin Stocks (Straight Run)

Naphthas

Cetane Index improved

Distillates

Kerosine

Diesel

Gas Oils

Vacuum Gas Oil

Reduced Crude (650 °F +) : *remove impurities*

Vacuum Resid (1050 °F +) : *remove impurities
metal - Sulfur Nitrogen*

Cracked Feeds : *olefins / Aromatics
Reduce unsaturated compounds*

Thermal

Naphthas

Distillates

Catalytic Cracked (FCC)

Deasphalted Feeds

Synthetic Hydrocarbons

coal gas

Desulfurization Kinetics

First Order Reactions

Two Simultaneous First Order Reactions

"Easy" Sulfur : Mercaptan

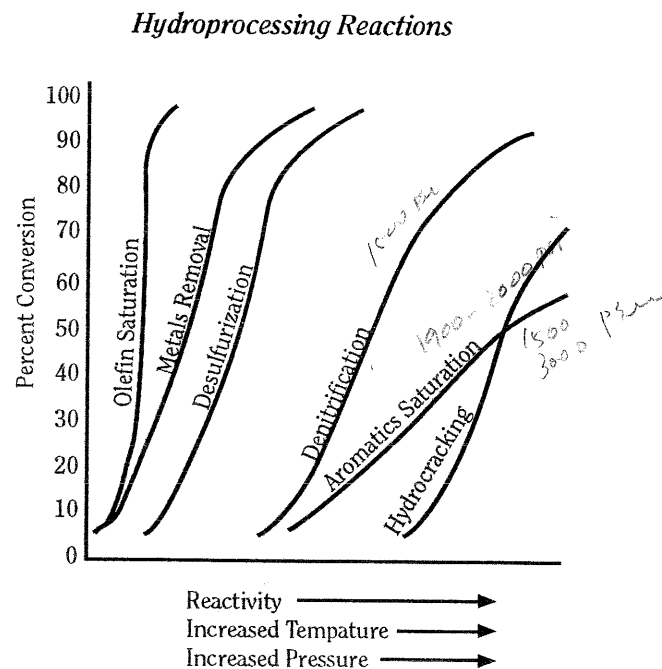
"Difficult" Sulfur : Long chain H.C. sulfur

Pseudo Second Order Reactions

Moderate desulfurization levels for distillates and lighter, first order kinetic expression adequately represents system

For high severity operations and for heavier oils (residua), either two simultaneous reactions or pseudo second order reaction can be used

Figure 4



EDS-R00-2009

Desulfurization Kinetics

Process	Relative Reaction Rate	Relative Heat of Reaction
Desulfurization	100	100
Olefin Saturation	80	500
Denitrification	20	10

Removal of oxygenates and chlorides occurs at approximately the same rate as denitrification.

CATALYST

Hydrotreating Catalysts

Activation of Catalyst

Deactivation of Catalyst

Regeneration or Disposal

Hydrotreating Catalyst

Initiates Oxidation-Reduction (Redox) Reaction

Transition Metal Catalyst on Alumina Base

Spherical or Extrudate

Dense Loaded : *most activated area*

Composition	Application
Co - Mo	Desulfurization Some nitrogen removal
Ni - Mo, or Co - Ni - Mo	Desulfurization Denitrification
Ni - W	Sever denitrification

Catalyst Activation

Purchase: a complex of metal and non-metal oxides

Conversion
of
metal oxides to metal sulfides
using H₂S vapor
at
elevated temperature and pressure

Operate: a complex of non-metal oxides and metal sulfides

Catalyst Deactivation

Temporary

Accumulation of coke on active sites on the catalyst

Chemical combination of nitrogen and sulfur with the catalyst

Solids deposited at the top of the bed

Permanent

Accumulation of metals and halides on the catalyst

Regeneration of Catalyst

Regeneration

No need to purchase new catalyst

No catalyst disposal cost

Unit out of service time

1 week to 18 weeks

Infrequently used procedures

Temporary equipment and piping

At some sites, ex-situ regeneration is available.

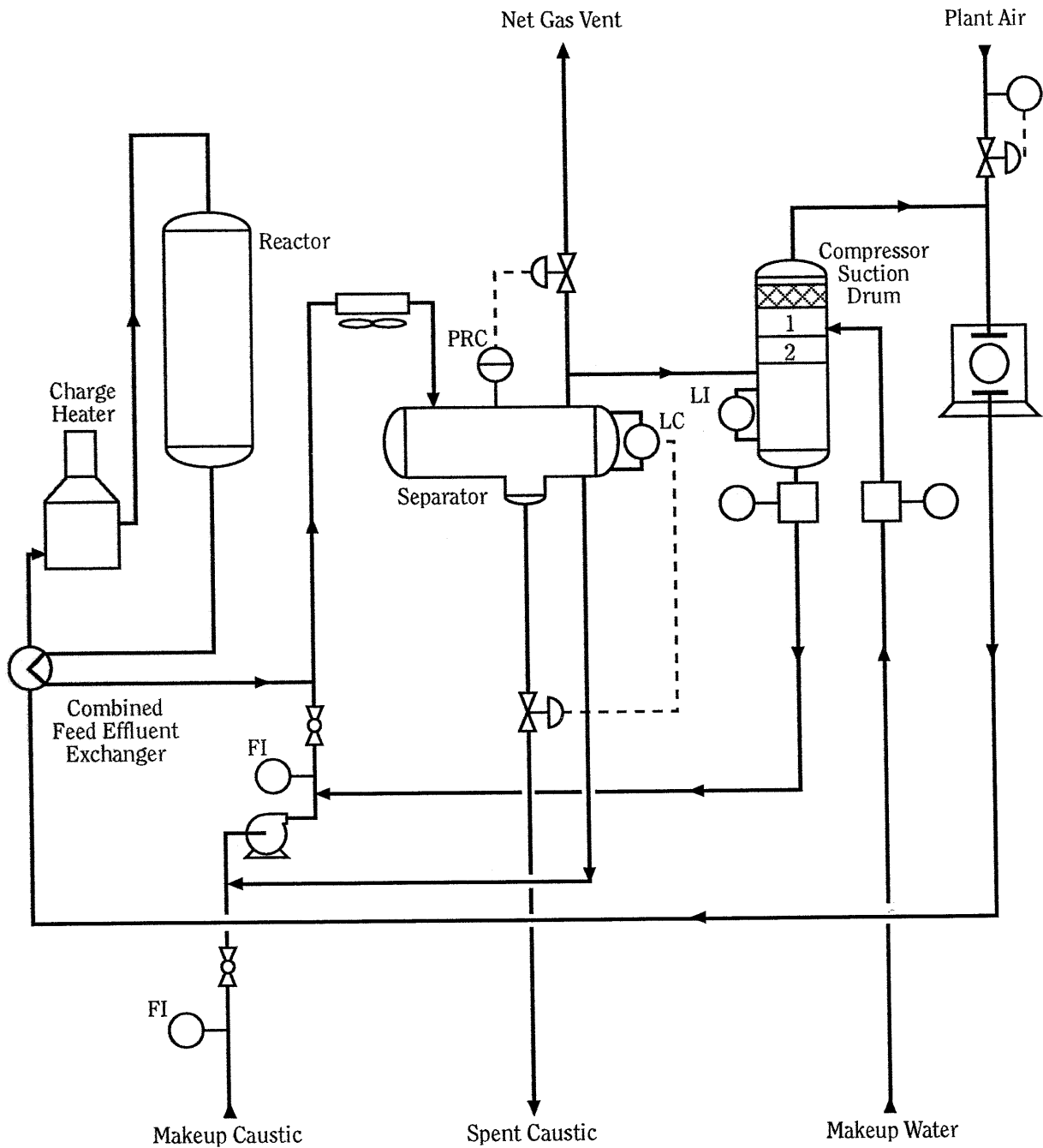
Disposal

Hazardous waste disposal

In some locations, catalyst can be taken to metals recovery site.

Figure 5

*Hydrotreating Unit
Inert Gas Regeneration Process Flow
(Typical)*



EDS-R00-2010

REACTOR CIRCUIT DESIGN

Process Definition

Yield Estimate

Material Balance

Reactor Yields Influenced By:

Feed Properties

Level of Desulfurization

Process Conditions

Desired Product Properties

Catalyst Type

Feed Properties

Characterization Of Feed Oil

Analysis

Correlations

Thermodynamic Properties

Definition Of Contaminant Levels

Feed/Product

Feed Stock Processability

Processing Conditions

Processing Scheme

Processing History Of Material

Feed Stock Definition

Crude Source or Derivation of Feed

Composition

API Gravity (Specific Gravity)

Distillation

ASTM

TBP

Contaminant Levels

Sulfur

Nitrogen

Bromine Number (Olefin Content)

Conradson Carbon

C₇ Insolubles (Asphaltenes)

Metals

Halogens

Non-Metals

Miscellaneous Properties

Viscosity

Pour Point

Color

Acidity

Aniline Point

Centane Number

Centane Index

Contaminant Sources

Oil Field Production (Secondary/Tertiary Recovery)

Water Flooding

Solvent Treating

Transport And Storage

Sea Water Contamination

Oxygen Exposure

Excessive Use of Inhibitor

Upstream Operations

Inadequate Desalting

Entrainment from Crude and Vacuum Operations

Asphaltenes

Metals

Excessive Use of Inhibitor

Rerun of Contaminated Slops

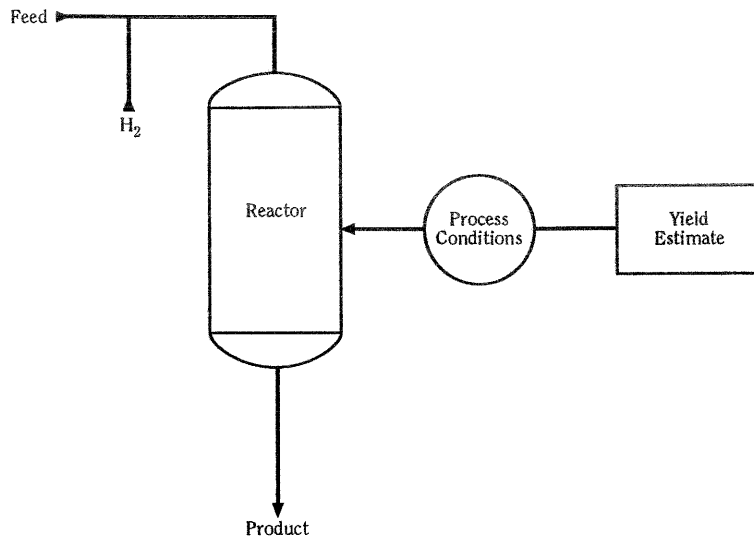
Characterization Of Product Oil

Product Specifications

Pilot Plant/Commercial Data

Correlations

Figure 6



EDS-R00-2012

Process Variables

Pressure (Hydrogen Partial Pressure)

250–3000 psig

Temperature

400–800 °F

*600 : Metal
550 : S*

LHSV (Space Velocity)

Linear Hour Space Velocity

0.5–10 hr⁻¹

Hydrogen-to-Feed Ratio (std ft³/bbl)

250–10,000

Typ. 80–90 %.

H₂ = 70 % . lower limit

Recycle Gas Purity

= depends on H₂ partial pressure

Catalysts

Effect Of Variables

Reaction rate is a function of hydrogen partial pressure. $= f(H_2)$

Increase $H_2 \rightarrow$ Increase reaction rate

Variables:

Pressure

Hydrogen-to-Fresh Feed Ratio

Recycle Gas Purity

Makeup Gas Purity

Temperature

Reaction Threshold	Operating Range	Maximum Operating
$<550^\circ\text{F}$	$550-750^\circ\text{F}$	$>750^\circ\text{F}$

Sulfur
removal.

GSO = Sulfur monosulfide

Space Velocity (LHSV)

Reaction Rate = Function of $(1/\text{LHSV})$

LHSV In Units Of h^{-1}

Lower LHSV $\rightarrow$ More Residence Time on Catalyst

Naphtha Hydrotreating Yield Estimate

Charge Stock

Source	Straight Run Light Arabian Crude
API	61.0
Specific Gravity	0.7351
Weight Percent Sulfur	0.0320
Total Nitrogen Weight ppm	<1.0

ASTM D-86	
IBP	178 °F
10 Percent	220
30 Percent	234
50 Percent	250
70 Percent	270
90 Percent	300
EP Percent	330

Product Requirements

Platformer Feedstock

Sulfur, weight ppm 0.5

Total Nitrogen, weight ppm 0.5

Weight Yield = Feed + Hydrogen Consumption

Product Distribution

NH₃

H₂S

C₁-C₅

C₆ Plus

Yield Estimate

Yield Distribution

Component	Weight Percent	Volume Percent
Raw Oil	100.00	100.00
Hydrogen	0.05	
NH ₃	Trace	
H ₂ S	0.03	
C ₁	Trace	
C ₂	0.01	
C ₃	0.01	0.01
C ₄	0.02	0.02
C ₅	0.02	0.02
C ₆ ⁺	99.96	100.06
Total	100.05	100.11

Product Specific Gravity

Component	Specific Gravity	^o API
C ₄	0.5787	
C ₅	0.6290	
C ₆ ⁺	0.7343	61.2

Material Balance

Feed Naphtha Characterization

$$VABP = \frac{10 \text{ pct} + 30 \text{ pct} + 50 \text{ pct} + 70 \text{ pct} + 90 \text{ pct}}{5} =$$

$$\frac{220 + 234 + 250 + 270 + 300}{5} = 254.8$$

$$\text{Engler Slope} = \frac{90 \text{ pct} - 10 \text{ pct}}{80} = \frac{300 - 220}{80} = 1.0$$

API = 61 10.725 lb/h per bbl/d

MABP = 250 → molecular weight = 112.5

CABP = 253 → UOP K = 12.14

Product C₆₊ Characterization

Assume ASTM D-86 of Product = Feed

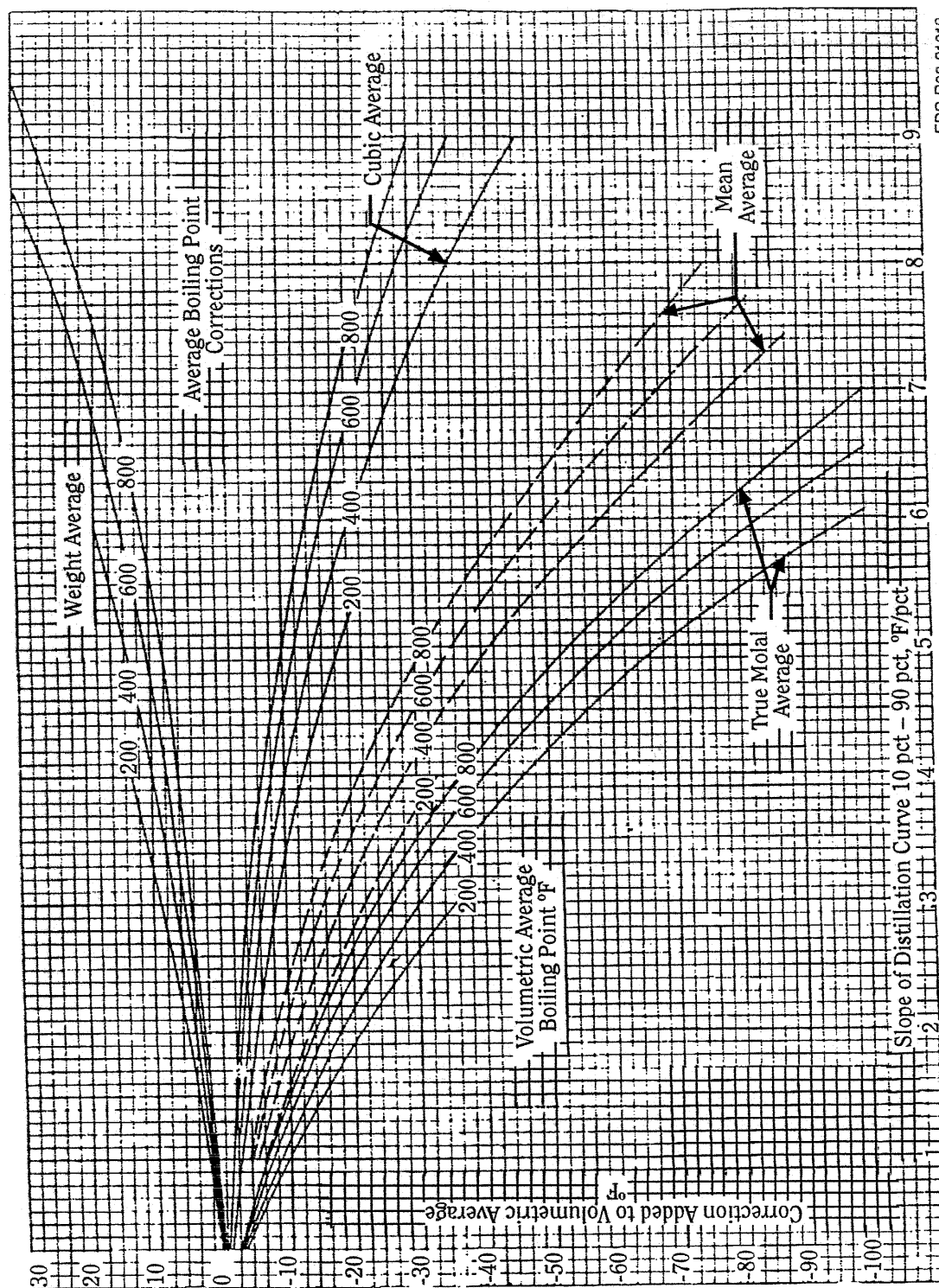
API = 61.2 10.714 lb/h per bbl/d

MABP = 250 → molecular weight = 112.0

CABP = 253 → UOP K = 12.15

RE - B1

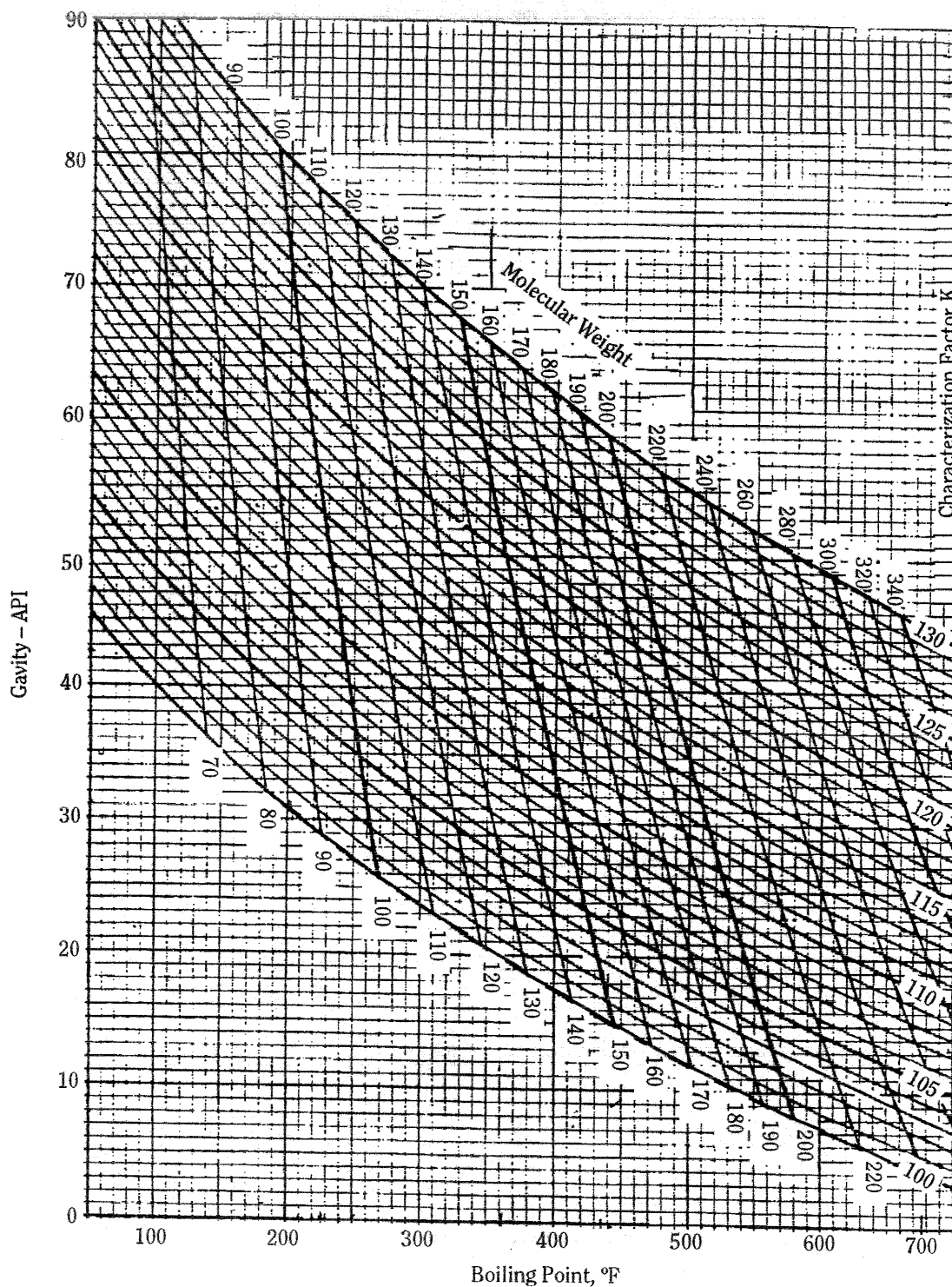
Figure 7



EDS-R00-21013

Figure 8

Characterization Factor K - Cubic-Average Boiling Point
Molecular Weight - Mean Average Boiling Point
(Low Range RE - B2)



EDS-R00-2014

Naphtha Yield Estimate

Process Conditions	
Pressure at Separator, psig	350
Minimum Reactor Temperature, °F	600
Maximum Reactor Temperature, °F	650
Fresh Feed Rate, bpsd	20000
LHSV on Fresh Feed, 1/h	8
H ₂ to Reactor Inlet on Fresh Feed, scfb	400
Maximum Allowable Reactor Delta T, °F	50
Minimum H ₂ in Recycle Gas, mol percent	70
Heat of Reaction on Fresh Feed, Btu/lb	6.5
Wash Water, volume percent on Fresh Feed	3

Makeup Hydrogen Composition	Mol Percent
Hydrogen	82.7
Methane	6.3
Ethane	4.7
Propane	3.1
Butanes	1.8
Pentanes	1.4

PROCESS DESIGN

MATERIAL BALANCE

Feed Mass Rates

$$\text{Raw Oil Rate} = 20000 \text{ bpsd} = (20000 \text{ bpsd}) \left(10.725 \frac{\text{lb/h}}{\text{bpsd}} \right) = 214500 \text{ lb/h}$$

$$\text{Hydrogen Consumption} = (214500)(0.0005) = 107.25 \text{ lb/h}$$

$$\text{Total in} = \text{Raw Oil} + \text{Hydrogen} = 214500 + 107.25 = 214607.25$$

Mass Conserved Across Reactor

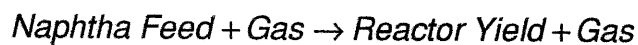
$$\text{In} = \text{Out} = 214607.25 \text{ lb/h}$$

Chemical Composition Changes Due to Reactions

Reactor Yields

Component	Weight Percent	lb/h	Molecular Weight	mol/h
H ₂ S	0.03	64.35	34.08	1.89
H ₂	-0.05	-107.25	2.02	-53.09
C ₁	-	-	-	-
C ₂	0.01	21.45	30.07	0.71
C ₃	0.01	21.45	44.10	0.49
C ₄	0.02	42.90	58.12	0.74
C ₅	0.02	42.90	72.15	0.59
C ₆ ⁺	99.96	214414.20	112.00	1914.41
Total	100.00	214500.00	-	1865.74

Mol Balance Across the Reactor



Once Through Hydrogen Scheme

$$H_2 \text{ to Reactor} = 400 \text{ std ft}^3/\text{bbl}$$

$$\frac{(400 \text{ std ft}^3/\text{bbl})(20000 \text{ bpd})}{(24 \text{ h/d})(379 \text{ std ft}^3/\text{mol})} = 879.5 \text{ mols/h of Hydrogen}$$

Makeup gas to reactor (assume 82.7 percent H₂ in makeup gas)

$$= \frac{879.5 \text{ mols/h}}{0.827}$$

$$= 1063.5 \text{ mols/h of Makeup Gas}$$

	Reactor Yield	Makeup Gas	Reactor Effluent	
Component	mol/h	mol/h	mol/h	mol fraction (z _i)
H ₂ S	1.89	0.00	1.89	0.001
H ₂	-53.09	879.50	826.41	0.282
C ₁	0.00	67.00	67.00	0.023
C ₂	0.71	49.99	50.69	0.017
C ₃	0.49	32.96	33.46	0.011
C ₄	0.74	19.14	19.88	0.007
C ₅	0.59	14.89	15.49	0.005
C ₆ ⁺	1914.41	0.00	1914.41	0.654
Total	1865.74	1063.48	2929.23	1.000

Separate the light ends, H₂S, and NH₃ from the treated naphtha.

Mol Balance:

$$E = V + L$$

Component Balance:

$$z_i E = y_i V + x_i L$$

Equilibrium:

$$K_i \equiv y_i / x_i$$

$$K_i = \text{Function}(P, T)$$

Weakly dependent on composition

Pressure set by yield estimate

Temperature set by yield estimate

where:

E = mol/h Total Effluent

V = mol/h Vapor Effluent

L = mol/h Liquid Effluent

z_i = mol fraction of i in Reactor Effluent

x_i = mol fraction of i in Liquid

y_i = mol fraction of i in Vapor

Select separator temperature.

Find K_i for given P, T

Then:

$$x_i = \frac{z_i E}{(K_i V) + L}$$

$$1 = \sum \frac{z_i E}{(K_i V) + L}$$

Estimate a vapor rate V (which determines liquid rate L).

Calculate x_i 's. If sum does not = 1, try new V .

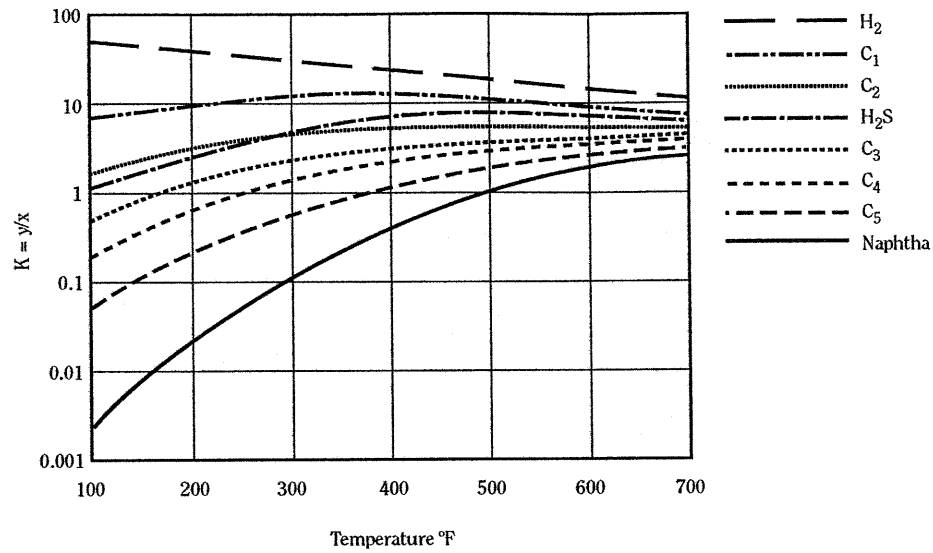
Reactor Effluent Rate (E) = 2930 mol/h

Assume Separator Vapor = ____ mol/h

Then Liquid Rate = ____ mol/h

Figure 9

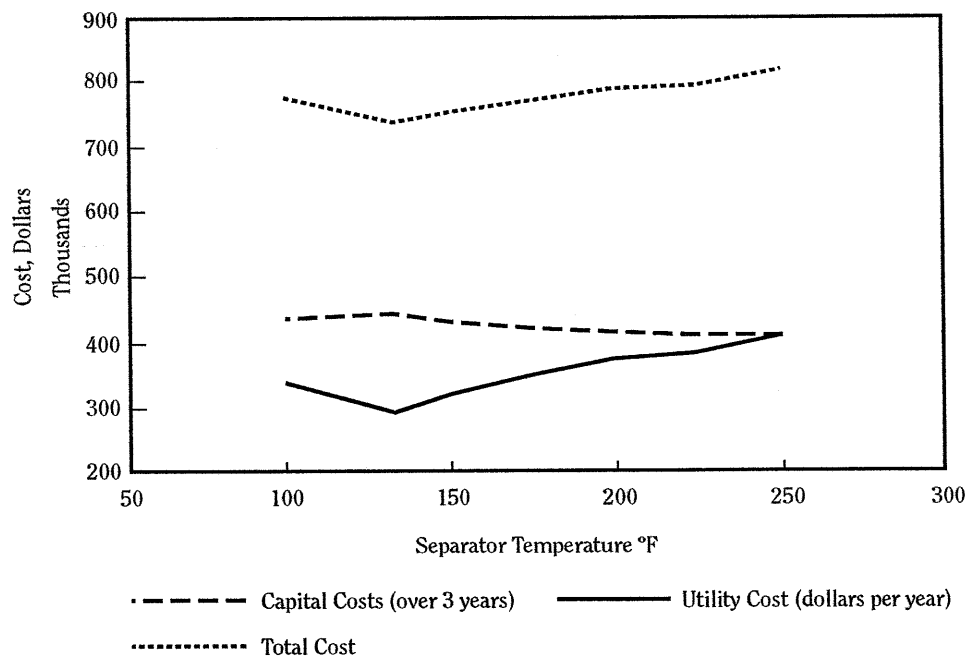
*Equilibrium K Values
(350 psig)*



EDS-R00-2015

Figure 10

Optimum Temperature



EDS-R00-2016

Trial 1

Component	z_i	$K_i @ 120^\circ\text{F}$	x_i	y_i
H ₂ S	$6.45 \cdot 10^{-4}$	1.370		
H ₂	0.282	50.000		
C ₁	0.023	7.810		
C ₂	0.017	1.960		
C ₃	0.011	0.650		
C ₄	$6.79 \cdot 10^{-3}$	0.247		
C ₅	$5.29 \cdot 10^{-3}$	0.079		
C ₆ ⁺	0.653	0.004		
Total	1.000			

$$x_i = \frac{z_i E}{(K_i V) + L} \text{ and } y_i = K_i x_i$$

Reactor Effluent Rate (E) = 2930 mol/h

Assume Separator Vapor (V) = 1000 mol/h

Then Liquid Rate (L) = 1930 mol/h

Trial 1

Component	z_i	K_i	x_i	y_i
H ₂ S	$6.45 \cdot 10^{-4}$	1.370	0.0006	0.0008
H ₂	0.282	50.000	0.0159	0.7961
C ₁	0.023	7.810	0.0069	0.0538
C ₂	0.017	1.960	0.0130	0.0256
C ₃	0.011	0.650	0.0126	0.0082
C ₄	$6.79 \cdot 10^{-3}$	0.247	0.0091	0.0023
C ₅	$5.29 \cdot 10^{-3}$	0.079	0.0077	0.0006
C ₆ ⁺	0.653	0.004	0.9900	0.0040
Total	1.000		1.0558	0.8914

$$x_i = \frac{z_i E}{(K_i V) + L} \text{ and } y_i = K_i x_i$$

Reactor Effluent Rate (E) = 2930 mol/h

Assume Separator Vapor (V) = 878 mol/h

Then Liquid Rate (L) = 2052 mol/h

Trial 2

Component	z_i	K_i	x_i	y_i
H ₂ S	6.45 10 ⁻⁴	1.370	0.0006	0.0008
H ₂	0.282	50.000	0.0180	0.9000
C ₁	0.023	7.810	0.0075	0.0586
C ₂	0.017	1.960	0.0132	0.0258
C ₃	0.011	0.650	0.0123	0.0080
C ₄	6.79 10 ⁻³	0.247	0.0088	0.0022
C ₅	5.29 10 ⁻³	0.079	0.0073	0.0006
C ₆ ⁺	0.653	0.004	0.9308	0.0037
Total	1.000		0.9985	0.9997

$$x_i = \frac{z_i E}{(K_i V) + L} \text{ and } y_i = K_i x_i$$

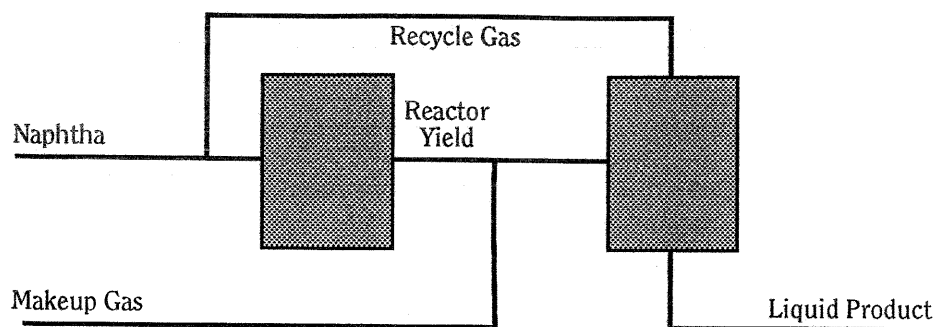
1064 mols/h of 82.7 percent hydrogen gas supplied.

878 mols/h of hydrogen rich gas (90 mol percent), but with 800 ppmv H₂S left

Consider recycle of gas from separator back to the reactor.

Figure 11

Material Balance Envelope



Mass In = Mass Out

Composition of Liquid Out = Reactor Yield + Makeup Gas

Liquid in Equilibrium with Recycle Gas (Bubble Point)
Rate of Recycle Gas can be set to any rate

EDS-R00-2017

For bubble point liquid:

$$\sum K_i x_i = 1.0$$

Assume make-up hydrogen = _____ mol/h

Trial 1

Component	Reactor Yield	Makeup Gas	Separator Liquid	x_i	K	$K_i x_i$
H ₂ S	1.89				1.370	
H ₂	-53.09				50.000	
C ₁	—				7.810	
C ₂	0.71				1.960	
C ₃	0.49				0.650	
C ₄	0.74				0.247	
C ₅	0.60				0.079	
C ₆ ⁺	1914.41				0.004	
Total	1865.75					

Assume makeup hydrogen = 80 mol/h

Trial 1

Component	Reactor Yield	Makeup Gas	Separator Liquid	x_i	K_i	$K_i x_i$
H ₂ S	1.89	0.00	1.89	$9.71 \cdot 10^{-4}$	1.370	0.0013
H ₂	-53.09	66.16	13.07	$6.72 \cdot 10^{-3}$	50.000	0.3360
C ₁	-	5.04	5.04	$2.59 \cdot 10^{-3}$	7.810	0.0202
C ₂	0.71	3.76	4.47	$2.30 \cdot 10^{-3}$	1.960	0.0045
C ₃	0.49	2.48	2.97	$1.53 \cdot 10^{-3}$	0.650	0.0010
C ₄	0.74	1.44	2.18	$1.12 \cdot 10^{-3}$	0.247	0.0003
C ₅	0.60	1.12	1.72	$8.84 \cdot 10^{-4}$	0.079	0.0001
C ₆ ⁺	1914.41	0.00	1914.41	0.9839	0.004	0.0039
Total	1865.75	80.00	1945.75	1.0000		0.3673

Assume makeup gas = 120 mol/h

Trial 2

Component	Reactor Yield	Makeup Gas	Separator Liquid	x_i	K_i	$K_i x_i$
H ₂ S	1.89	0.00	1.89	$9.52 \cdot 10^{-4}$	1.370	0.0013
H ₂	-53.09	99.24	46.15	0.0232	50.000	1.1600
C ₁	-	7.56	7.56	$3.81 \cdot 10^{-3}$	7.810	0.0298
C ₂	0.71	5.64	6.35	$3.20 \cdot 10^{-3}$	1.960	0.0063
C ₃	0.49	3.72	4.21	$2.12 \cdot 10^{-3}$	0.650	0.0014
C ₄	0.74	2.16	2.90	$1.46 \cdot 10^{-3}$	0.247	0.0004
C ₅	0.60	1.68	2.28	$1.15 \cdot 10^{-4}$	0.079	<0.0001
C ₆ ⁺	1914.41	0.00	1914.41	0.96407	0.004	0.0039
Total	1865.75	120.00	1985.75	0.99996		1.2032

For the next guess, interpolate:

$$\frac{X - 80}{120 - 80} = \frac{1.000 - 0.3673}{1.2032 - 0.3673}$$

or X = 110.27 mol/h of recycle gas

Assume makeup recycle gas = 110 mol/h

Trial 3

Component	Reactor Yield	Makeup Gas	Separator Liquid	x_i	K_i	$K_i x_i = y_i$
H ₂ S	1.89	0.00	1.89	$9.56 \cdot 10^{-4}$	1.370	0.0013
H ₂	-53.09	90.97	37.88	0.01917	50.000	0.9586
C ₁	—	6.93	6.93	$3.51 \cdot 10^{-3}$	7.810	0.0274
C ₂	0.71	5.17	5.88	$2.98 \cdot 10^{-3}$	1.960	0.0059
C ₃	0.49	3.41	3.90	$1.98 \cdot 10^{-3}$	0.650	0.0013
C ₄	0.74	1.98	2.72	$1.37 \cdot 10^{-3}$	0.247	0.0003
C ₅	0.60	1.54	2.14	$1.08 \cdot 10^{-3}$	0.079	0.0001
C ₆ ⁺	1914.41	0.00	1914.41	0.96846	0.004	0.0039
Total	1865.75	110.00	1975.75	0.99853		0.9988

The final column gives the composition of the recycle gas. The yield estimate specified a minimum H₂ concentration of 70 percent for these separator conditions. The H₂ concentration is 95.86 percent. If purity is a problem, it is usually due to the methane.

Lower separator temperature

Higher purity makeup gas

Vent some recycle gas from the system

Increase separator pressure to maintain same hydrogen partial pressure at lower purity

Recycle Gas Rate

H₂ to Reactor = 400 std ft³/bbl

$$\frac{(400 \text{ std ft}^3/\text{bbl})(20000 \text{ bpd})}{(24 \text{ h/d})(379 \text{ std ft}^3/\text{mol})}$$

$$= 879.5 \text{ mol/h Hydrogen}$$

$$\text{Recycle gas to reactor} = 879.5/0.9586$$

$$= 917 \text{ mols/h of Recycle Gas}$$

Component	Mol Fraction	mols/h	mol/wt	lb/h
H ₂ S	0.0013	1.19	34.08	40.63
H ₂	0.9586	879.50	2.02	1775.65
C ₁	0.0274	25.13	16.04	403.02
C ₂	0.0059	5.41	30.07	162.69
C ₃	0.0013	1.19	44.10	52.57
C ₄	0.0003	0.28	58.12	15.99
C ₅	0.0001	0.09	72.15	6.62
C ₆ ⁺	0.0039	3.58	112.0	400.55
Total	1.0	917.00		2857.72

$$\text{Recycle Gas Mol Wt} = 2857.72/917 = 312$$

Heat Balance

Process Requirements

Reaction Temperature

Start of Run (SOR) – Minimum Reactor Inlet

End of Run (EOR) – Maximum Reactor Outlet

UOP Designs for EOR and Evaluates Other Operations

Heat Of Reaction

Hydrotreating Reactions are Exothermic

Yield Estimate Gives the Heat of Reaction as Btu/lb Feed

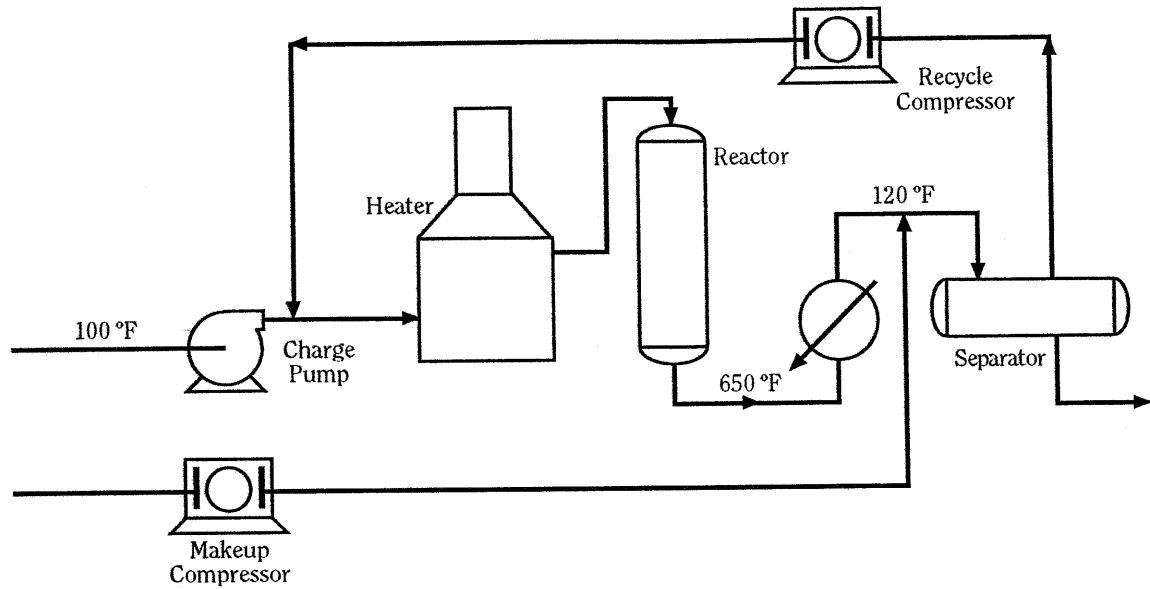
For this example, $\Delta H = 6.5$ Btu/lb fresh feed

Feed Rate = 20000 BPSD = 2145000 lb/h

Heat of Reaction = 2145000×6.5 Btu/lb = 13.94×10^6 Btu/h

Figure 12

Reactor – Thermal Requirements



EDS-R00-2018

Reactor – Thermal Requirements

Calculate reactor effluent conditions at EOR $T = 650^{\circ}\text{F}$

Component	Reactor Effluent mol/h	y_i	K_i at 650°F	y_i/K_i
H_2S	3.08	$1.11 \cdot 10^{-3}$	5.80	$1.914 \cdot 10^{-4}$
H_2	826.41	0.2970	12.10	0.0245
C_1	25.13	$9.03 \cdot 10^{-3}$	7.80	$1.158 \cdot 10^{-3}$
C_2	6.12	$2.20 \cdot 10^{-3}$	4.90	$4.490 \cdot 10^{-4}$
C_3	1.68	$6.04 \cdot 10^{-4}$	4.30	$1.405 \cdot 10^{-4}$
C_4	1.02	$3.67 \cdot 10^{-4}$	3.35	$1.096 \cdot 10^{-4}$
C_5	0.69	$2.48 \cdot 10^{-4}$	2.70	$9.185 \cdot 10^{-5}$
C_6^{+}	1917.99	0.6894	2.15	0.3207
Total	2782.12	1.0000		0.3473

If $\sum \frac{y_i}{K_i} < 1$ then all vapor

PROCESS DESIGN

Heat Balance

Reactor – Thermal Requirements

Calculate Reactor Effluent Conditions at EOR $T = 650^{\circ}\text{F}$

Component	Reactor Effluent mol/h	Molecular Weight	lb/h	Btu/lb 650 °F	Btu/h
H ₂ S	3.08	34.08	105	350	$0.037 \cdot 10^6$
H ₂	826.41	2.02	1669	2035	$3.396 \cdot 10^6$
C ₁	25.13	16.04	403	466	$0.188 \cdot 10^6$
C ₂	6.12	30.07	184	481	$0.089 \cdot 10^6$
C ₃	1.68	44.10	73	488	$0.036 \cdot 10^6$
C ₄	1.02	58.12	59	479	$0.028 \cdot 10^6$
C ₅	0.69	72.15	50	471	$0.024 \cdot 10^6$
C ₆ ⁺	1917.99	112.00	214815	448	$96.24 \cdot 10^6$
Total	2782.12		217358		$100.0 \cdot 10^6$

Reactor Inlet Temperature

$$\text{Heat of Reaction} = (214500 \text{ lb/h})(6.5 \text{ Btu/lb}) = 1.39 \cdot 10^6 \text{ Btu/h}$$

$$\text{Reactor Feed Enthalpy} = 100.0 - 1.39 \cdot 10^6 \text{ Btu/h} = 98.61 \cdot 10^6 \text{ Btu/h}$$

By trial-and-error, temperature of feed to reactor can be calculated.

Calculate reactor feed temperature when enthalpy = 98.16×10^6 Btu/hr

Component	Reactor Feed (lb/hr)	Btu/lb 600°F	10^6 Btu/h	Btu/lb 650°F	10^6 Btu/h
H ₂ S	41	336	0.014	350	0.014
H ₂	1777	1859	3.303	2035	3.616
C ₁	403	426	0.172	466	0.188
C ₂	163	444	0.072	481	0.078
C ₃	52	451	0.023	488	0.025
C ₄	15	442	0.007	479	0.007
C ₅	6	434	0.003	471	0.003
C ₆ ⁺	401	403	0.162	448	0.180
Feed	214500	403	86.44	448	96.24
Total	217358		90.20		100.35

Interpolate

$$\frac{T - 600}{650 - 600} = \frac{98.16 - 90.2}{100.35 - 90.2}$$

Reactor Feed Temperature = 639 °F

Calculate enthalpies of other stream where composition and temperature are known.

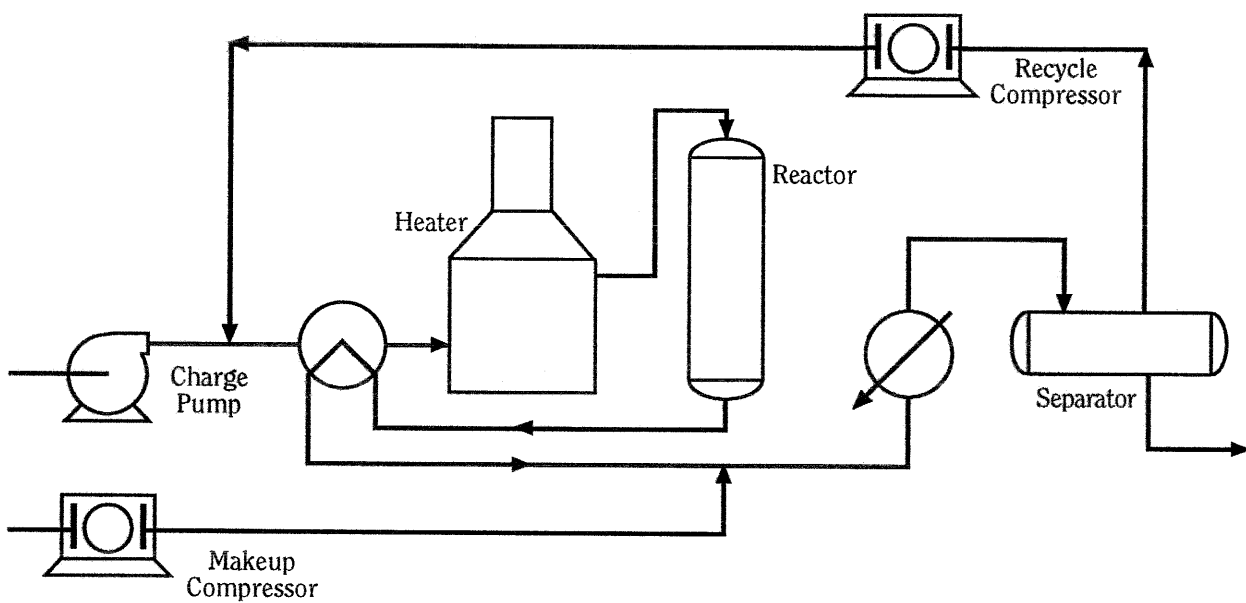
Efficiency – Waste Heat Recovery

Approximate Heating Duty Required: $98.16 - 4.23 - 0.61 = 93.32 \text{ } 10^6 \text{ Btu/hr}$

Approximate Cooling Duty Required: $100.35 + 0.13 - 6.24 - 0.61 = 93.63 \text{ } 10^6 \text{ Btu/hr}$

Figure 13

Efficiency – Waste Heat Recovery



EDS-R00-2020

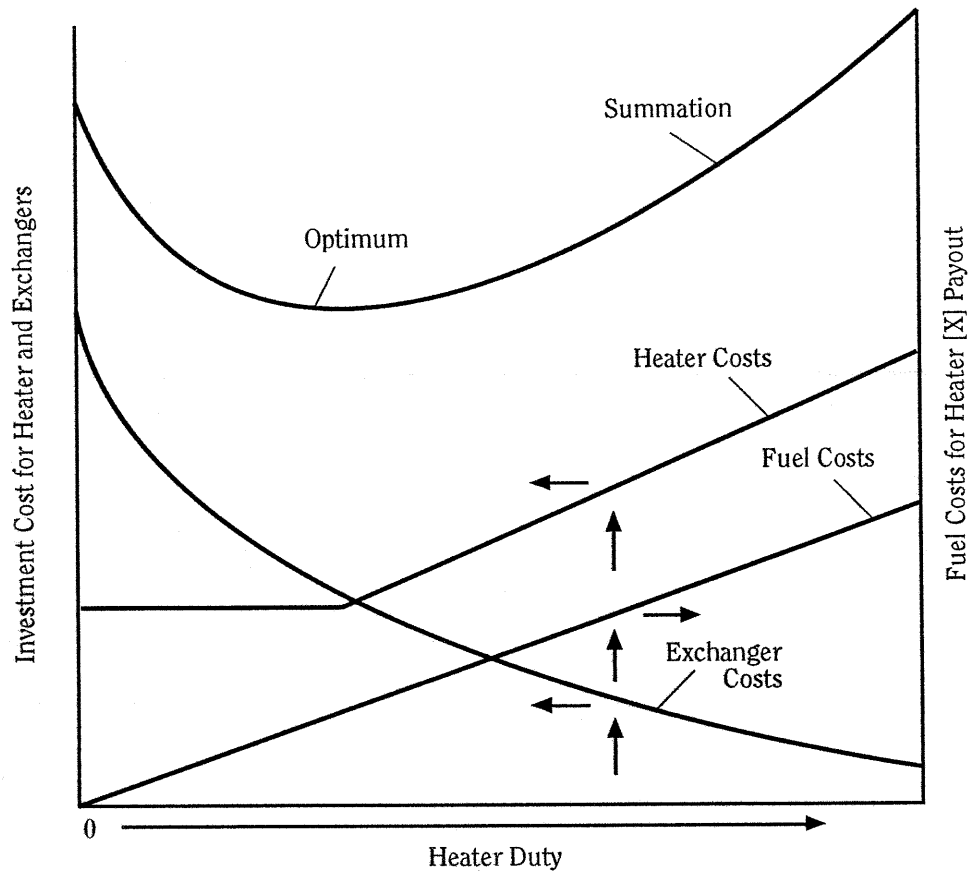
How much duty should the combined feed exchanger be desired for?

Economics

Operability

Figure 14

Excess Heat Utilization



EDS-R00-2021

What is the operational penalty of designing with a high combined feed exchanger (CFE) to fired heater ratio?

Small variations in conditions will cause large variations in heater duty as percent of design.

Typ: 5-7 ratio

Guidelines for Ratio of Duties (as percent of total heat units required)

Ratio	Upset	Feed H	CFE Duty	To Heater	To Reactor	Heater Duty	Percent Deviation
11:1	Normal Case	5	85	90	98	8	—
	Cold Feed	2	85	87	98	11	38
	Fouled CFE	5	81	86	98	12	50
	Less Heat of Reaction	5	85	90	100	10	25
	Hot Feed	8	85	93	98	5	-37
	Cleaned CFE	5	89	94	98	4	-50
	More Heat of Reaction	5	85	90	96	6	-25
4:1	Normal Case	5	74	79	98	19	—
	Cold Feed	2	74	76	98	22	16
	Fouled CFE	5	70	75	98	23	21
	Less Heat of Reaction	5	74	79	100	21	11
	Hot Feed	8	74	82	98	16	-16
	Cleaned CFE	5	78	83	98	15	-21
	More Heat of Reaction	5	74	79	96	17	-11

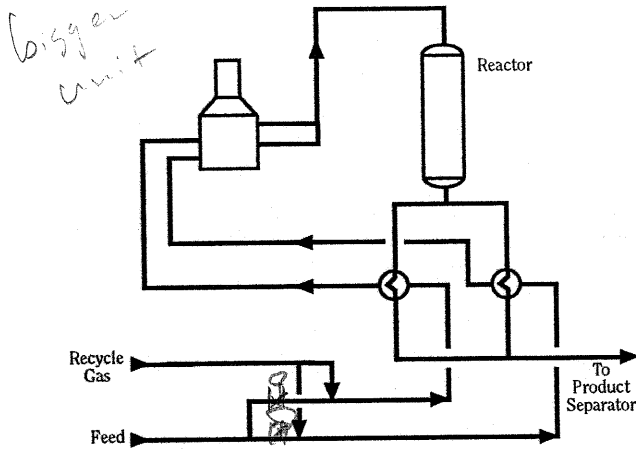
Heater/Exchange Schemes

Flow Scheme	Normal	Alternate 1	Alternate 2	Alternate 3
Thermal Efficiency	HIGH	LOW	MID	MID
Heater Protection	YES	NO	YES	YES
Circuit Pressure Drop	HIGH	LOW	MID	MID
Scaling Potential	YES	NO	YES	YES
Control Valve Count	HIGH	LOW	MID	HIGH
High Temperature CV	NO	NO	NO	YES
Heater Outlet Temperature	Same as reactor	HIGH	HIGH	Same as reactor
Start-up Capability	GOOD	POOR	MID	GOOD
Number of Exchangers	HIGH	LOW	MID	LOW
Plot Space	HIGH	LOW	MID	LOW
High Temperature Liquid	NO	YES	NO	NO

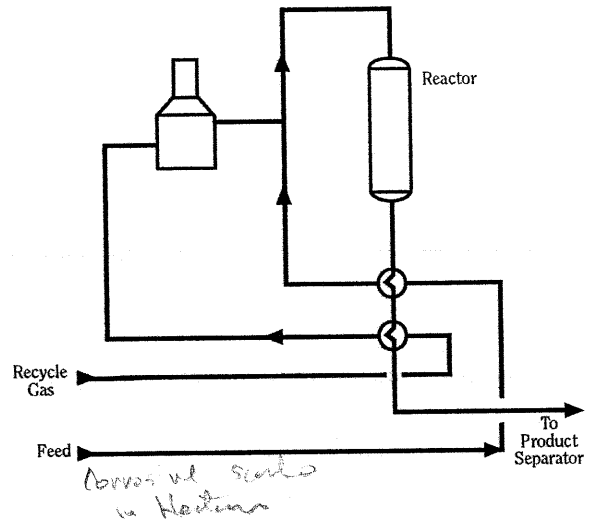
Figure 15

Heater / Exchanger Schemes

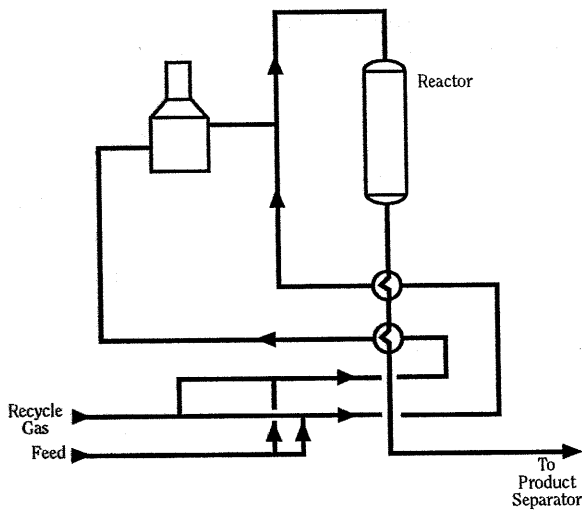
Normal Flow Scheme



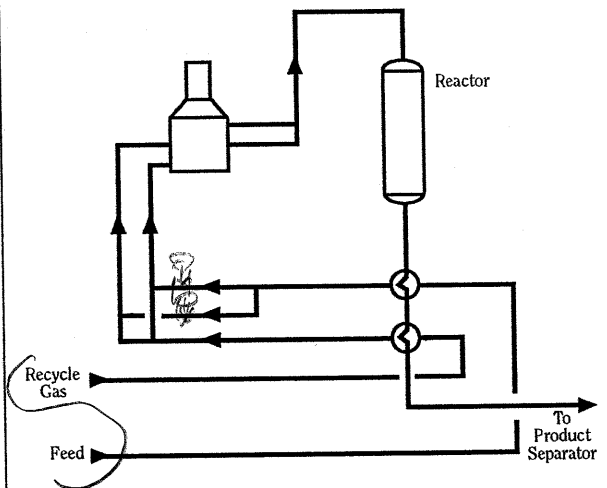
Alternate Scheme One



Alternate Scheme Two



Alternate Scheme Three



EDS-R00-2022

Heater/Exchange Schemes Conclusions

Normal flow scheme is best for most units.

Alternate scheme one is used for units where liquid feed properties would result in excessive corrosion in the heater tubes.

Alternate scheme two is used for units with high heat of reaction.

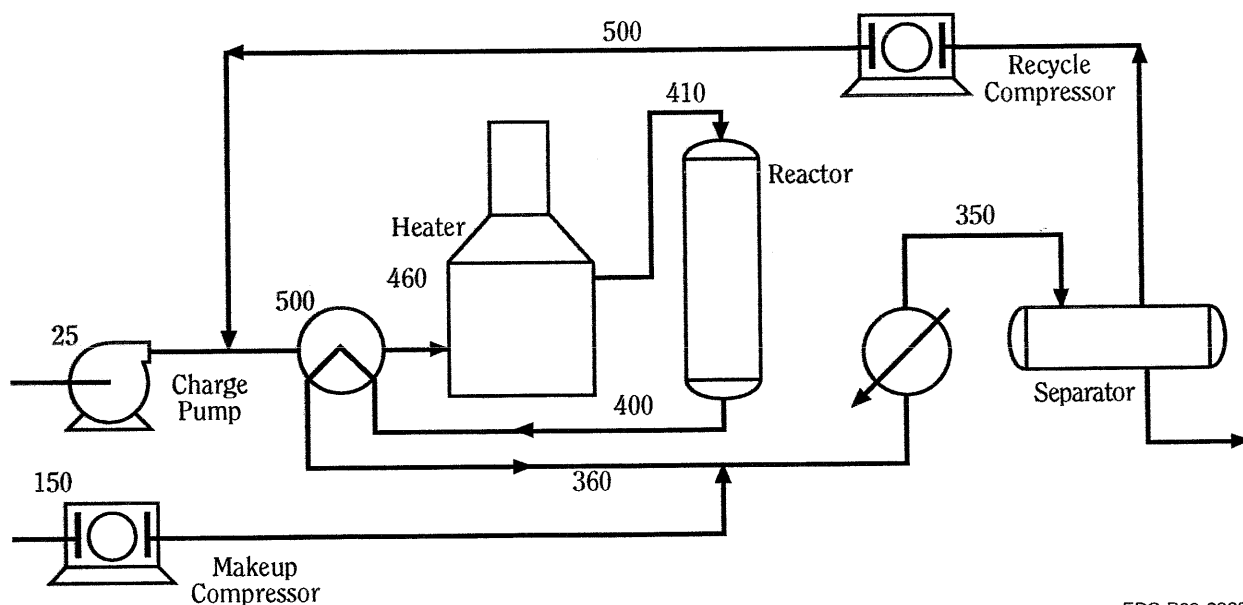
Alternate scheme three is used when available plot space prohibits multiple exchanger trains.

Hydraulics

Need to assign preliminary estimates of equipment, valve, line pressure drops for process design purposes.

At typical naphtha hydrotreating operating pressures, pressure differentials in reactor circuit have a minimal effect on phase equilibrium constants (K's) and enthalpy functions.

Figure 16



EDS-R00-2023

Typical Reactor Circuit Hydraulics For NHT		
	Δ Pressure	psig
Separator (Control Point)	—	350
Condenser	10	360
Exchange (Tube)	40	400
Reactor	10	410
Heater	50	460
Exchange (Shell)	40	500

Compressors

Adds energy to the system

Temperature of the gas rises on compression

Type of compressor to use:

Depends on compression ratio

Inlet volume at flowing conditions

Actual cubic feet per minute (A ft³/m)

$$V = \frac{zNRT}{P}$$

Suction		Recycle Gas Compressor	Makeup Gas Compressor
Temperature	°F	120.	100.
(Absolute)	°R	580.	560.
Pressure	psig	350.	150.0
(Absolute)	psia	364.7	164.7
Compressibility		1.00	1.00
mols/h	N	917.00	110.00
C _p /C _v		1.38	1.31
Volume	ft ³ /h	15648.00	4013.00
A ft ³ /m		261.00	67.00

For flows less than 1000 A ft³/m reciprocating compressors are used.

Estimate of the discharge temperature:

$$T_d = T_s \left(\frac{P_d}{P_s} \right)^{\frac{k-1}{k}}$$

where:

$$k = \frac{C_p}{C_v}$$

Recycle Compressor:

$$T_d = 580 \left(\frac{514.7}{364.7} \right)^{\frac{1.38-1}{1.38}} = 638^\circ R = 178^\circ F$$

Makeup Compressor:

$$T_d = 560 \left(\frac{399.7}{164.7} \right)^{\frac{1.31-1}{1.31}} = 691^\circ R = 231^\circ F$$

470° R
Operating Limit

Recycle Gas Enthalpy

Component	mols/h	mol/wt	lb/h	Btu/lb	10 ⁶ Btu/h
H ₂ S	1.19	34.08	40.63	221	0.01
H ₂	879.50	2.02	1775.65	380	0.67
C ₁	25.13	16.04	403.09	138	0.06
C ₂	5.41	30.07	162.68	190	0.03
C ₃	1.19	44.10	52.48	204	0.01
C ₄	0.28	58.12	16.27	190	<<
C ₅	0.09	72.15	6.49	190	<<
C ₆ ⁺	3.58	112.0	400.96	136	0.05
Total	917.00		2858.25		0.83

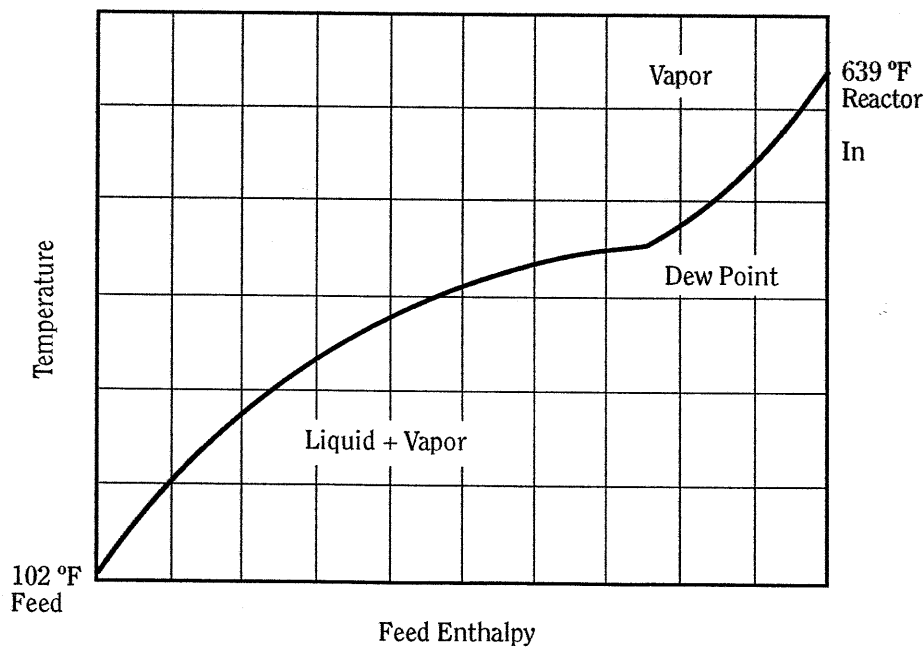
Similarly, the enthalpy of the makeup gas can be calculated (0.21 10⁶ Btu/h)

Combined Feed Exchanger (CFE) Design

6:1 Ratio

Figure 18

Combined Feed Exchanger (CFE) Design



EDS-R00-2038

Heat of vaporization of feed = 128 Btu/lb

After all the feed is vaporized, temperature rise is faster.

Feed enthalpy is known = $4.23 + 0.84 = 5.07 \times 10^6$ Btu/h.

Reactor feed temperature and enthalpy calculated previously.

$$\text{Dewpoint} = \sum \frac{y_i}{K_i} = 1$$

For mixed phase region, use previous equation to calculate vapor and liquid composition and amount.

$$x_i = \frac{z_i E}{(K_i V) + L}$$

Duty of heater and CFE combined = $98.16 - 5.07 = 93.09 \times 10^6$ Btu/h.

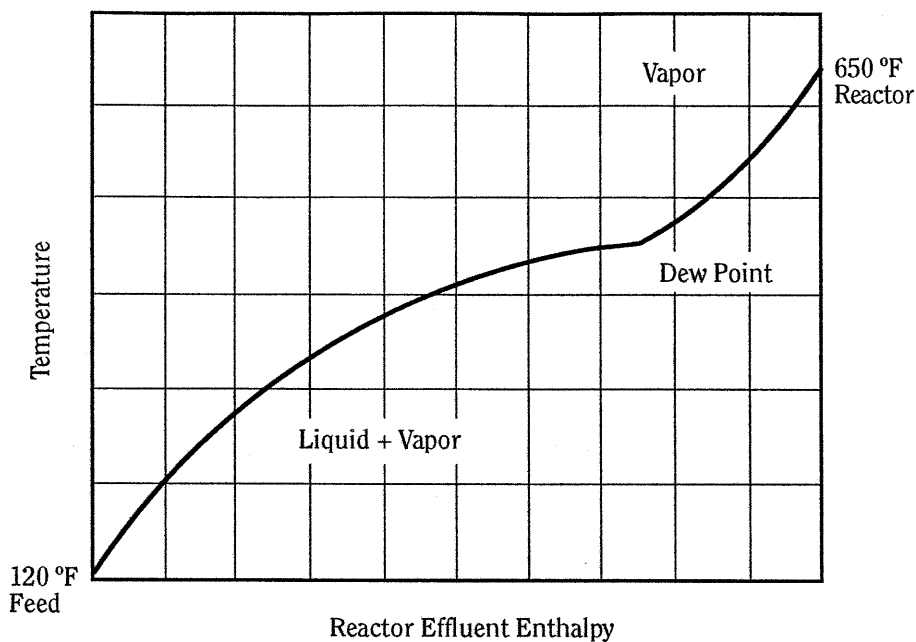
Choose a 6:1 ratio for CFE: Fired Heater

CFE Duty = 79.8×10^6 Btu/h.

Heater Duty = 13.29×10^6 Btu/h.

Figure 19

Combined Feed Exchanger (CFE) Design



EDS-R00-2039

Dew Point Calculations – Reactor Effluent

Component	mol wt	COMBINED FEED			REACTOR EFFLUENT		
		mols	lbs	y	mols	lbs	y
H ₂ S	34.08	1.19	41	0.0004	3.08	105	0.0011
H ₂	2.02	879.50	1777	0.3115	826.41	1669	0.2971
C ₁	16.04	25.13	403	0.0089	25.13	403	0.0090
C ₂	30.07	5.41	163	0.0019	6.12	184	0.0022
C ₃	44.10	1.19	52	0.0004	1.68	74	0.0006
C ₄	58.12	0.28	16	0.0001	1.02	59	0.0004
C ₅	72.15	0.09	6	0.0001	0.69	50	0.0002
C ₆ ⁺	112.00	3.58	401	0.0013	1917.99	214815	0.6894
Feed	112.50	1906.67	214500	0.6754	0	0	0.0000
Total		2823.04	217359	1.0000	2782.12	217539	1.0000

			V = 1300	V =
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Component	z_i	$K_i @ 400^\circ\text{F}$	x_i	y_i	x_i	y_i
H ₂ S	0.0011	7.00	0.0003	0.0020		
H ₂	0.2970	22.80	0.0266	0.6054		
C ₁	0.0090	13.00	0.0014	0.0178		
C ₂	0.0022	5.20	0.0007	0.0039		
C ₃	0.0006	3.20	0.0003	0.0010		
C ₄	0.0004	2.18	0.0002	0.0005		
C ₅	0.0002	1.22	0.0002	0.0003		
C ₆ ⁺	0.6894	0.37	0.9770	0.3615		
Feed	0.0000	0.37	0.0000	0.0000		
Total			1.0067	0.9923	1.0000	1.0000

Component	LIQUID =				VAPOR =			
	mols/h	lb/h	Btu/lb	10 ⁶ Btu/h	mols/h	lb/h	Btu/lb	10 ⁶ Btu/h
H ₂ S			204.7				280.9	
H ₂			204.7				1161.1	
C ₁			204.7				279.9	
C ₂			204.7				311.0	
C ₃			204.7				317.8	
C ₄			204.7				306.8	
C ₅			204.7				290.8	
C ₆ ⁺			204.7				309.1	
Feed			204.7				309.1	
Total								

Point for CFE Heat Curve: Reactor Effluent

$$T = 400^\circ\text{F}$$

$$H = \text{_____} 10^6 \text{ Btu/h}$$

Component	y_i	$K_i @ 500^\circ\text{F}$	y_i/K_i	$K_i @ 450^\circ\text{F}$	y_i/K_i	$K_i @ 463^\circ\text{F}$	y_i/K_i
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H ₂ S	0.0011	6.50	0.0002	7.60	0.0001	7.60	0.0001
H ₂	0.2971	17.50	0.0170	20.00	0.0149	19.32	0.0154
C ₁	0.0090	11.30	0.0008	12.20	0.0007	11.96	0.0008
C ₂	0.0022	5.40	0.0004	5.40	0.0004	5.40	0.0004
C ₃	0.0006	2.90	0.0002	3.60	0.0002	3.40	0.0002
C ₄	0.0004	2.75	0.0001	2.50	0.0002	2.56	0.0002
C ₅	0.0002	1.82	0.0001	1.52	0.0001	1.59	0.0001
C ₆ ⁺	0.6894	0.98	0.7035	0.62	1.1119	0.70	0.9847
Feed	0.0000	0.98	0.0000	0.62	0.0000	0.70	0.0000
Total	1.0000		0.7223		1.1285		1.0019

Component	lb/h	Btu/lb	10 ⁶ Btu/h
H ₂ S	105	297.5	0.03
H ₂	1669	1369.8	2.29
C ₁	403	322.5	0.13
C ₂	184	349.6	0.06
C ₃	74	356.6	0.03
C ₄	59	346.5	0.02
C ₅	50	334.8	0.02
C ₆ ⁺	214815	339.0	72.82
Feed	0	339.0	0.00
Total	217359		75.40

Point for CFE Heat Curve: Reactor Effluent

$$T = 463^{\circ}\text{F}$$

$$H = 75.40 \times 10^6 \text{ Btu/h}$$

Mixed Phase Calculations – Reactor Effluent

Component	z_i	$K_i @ 300^\circ\text{F}$	$V = 1000$		$V = 907$	
			x_i	y_i	x_i	y_i
H ₂ S	0.0011	4.70	0.0005	0.0022	0.0005	0.0024
H ₂	0.2970	29.60	0.0263	0.7795	0.0288	0.8517
C ₁	0.0090	11.90	0.0018	0.0219	0.0020	0.0236
C ₂	0.0022	4.45	0.0010	0.0044	0.0010	0.0046
C ₃	0.0006	2.18	0.0004	0.0009	0.0004	0.0010
C ₄	0.0004	1.39	0.0003	0.0004	0.0003	0.0005
C ₅	0.0002	0.60	0.0003	0.0002	0.0003	0.0002
C ₆ ⁺	0.6894	0.12	1.0083	0.1210	0.9667	0.1160
Feed	0.0000	0.12	0.0000	0.0000	0.0000	0.0000
Total			1.0389	0.9305	1.0000	1.0000

Component	LIQUID = 1875.12				VAPOR = 907			
	mols/h	lb/h	Btu/lb	10 ⁶ Btu/h	mols/h	lb/h	Btu/lb	10 ⁶ Btu/h
H ₂ S	0.94	32	183.9	0.01	2.14	73	253.0	0.02
H ₂	53.95	109	183.9	0.02	772.46	1560	816.0	1.27
C ₁	3.72	60	183.9	0.01	21.41	343	213.0	0.07
C ₂	1.94	58	183.9	0.01	4.18	126	251.0	0.03
C ₃	0.82	36	183.9	0.01	0.86	38	256.0	0.01
C ₄	0.61	35	183.9	0.01	0.41	24	238.0	0.01
C ₅	0.53	39	153.7	0.01	0.16	11	246.0	0.01
C ₆ ⁺	1812.77	203030	135.0	27.41	105.22	11785	259.0	3.05
Feed	0.00	0	135.0	0.00	0.00	0	259.0	0.00
Total	1875.00	203399		27.49	906.83	13960		4.47

Point for CFE Heat Curve: Reactor Effluent

$$T = 300^\circ\text{F}$$

$$H = 31.94 \times 10^6 \text{ Btu/h}$$

			$V = 1300$	$V = 1277$
--	--	--	------------	------------

Component	z_i	$K_i @ 400^\circ\text{F}$	x_i	y_i	x_i	y_i
H ₂ S	0.0011	7.00	0.0003	0.0020	0.0003	0.0021
H ₂	0.2971	22.80	0.0266	0.6054	0.0270	0.6153
C ₁	0.0090	13.00	0.0014	0.0178	0.0014	0.0180
C ₂	0.0022	5.20	0.0007	0.0039	0.0008	0.0039
C ₃	0.0006	3.20	0.0003	0.0010	0.0003	0.0010
C ₄	0.0004	2.18	0.0002	0.0005	0.0002	0.0005
C ₅	0.0002	1.22	0.0002	0.0003	0.0002	0.0003
C ₆ ⁺	0.6894	0.37	0.9770	0.3615	0.9699	0.3588
Feed	0.0000	0.37	0.0000	0.0000	0.0000	0.0000
Total			1.0067	0.9924	1.0001	0.9999

Component	LIQUID = 1505.12				VAPOR = 1227			
	mols/h	lb/h	Btu/lb	10 ⁶ Btu/h	mols/h	lb/h	Btu/lb	10 ⁶ Btu/h
H ₂ S	0.44	15	204.7	<<	2.64	90	280.9	0.03
H ₂	40.62	82	204.7	0.02	785.79	1587	1161.1	1.84
C ₁	2.09	34	204.7	0.01	23.04	370	279.9	0.10
C ₂	1.13	34	204.7	0.01	4.99	150	311.0	0.05
C ₃	0.45	20	204.7	<<	1.23	54	317.8	0.02
C ₄	0.36	21	204.7	<<	0.66	38	306.8	0.01
C ₅	0.34	24	204.7	0.01	0.35	25	290.8	0.01
C ₆ ⁺	1459.74	163491	204.7	33.47	458.25	51324	309.1	15.86
Feed	0.00	0	204.7	0.00	0.00	0	309.1	0.00
Total	1505.00	163721		33.51	1276.94	53638		17.92

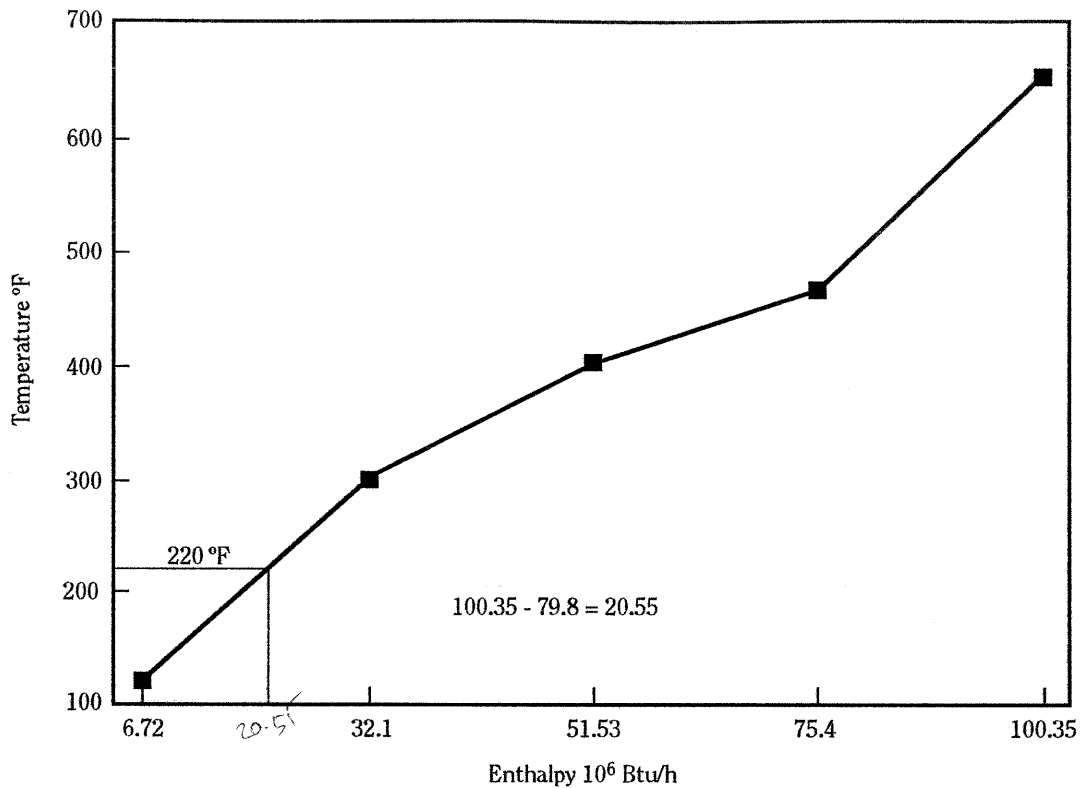
Point for CFE heat curve: Reactor Effluent

$$T = 400^\circ\text{F}$$

$$H = 51.43 \times 10^6 \text{ Btu/h}$$

Figure 20

Reactor Effluent Enthalpy



EDS-R00-2024

Dew Point Calculations – Combined Feed

Component	mol wt	COMBINED FEED			REACTOR EFFLUENT		
		mols	lbs	y	mols	lbs	y
H ₂ S	34.08	1.19	41	0.0004	3.08	105	0.0011
H ₂	2.02	879.50	1777	0.3115	826.41	1669	0.2971
C ₁	16.04	25.13	403	0.0089	25.13	403	0.0090
C ₂	30.07	5.41	163	0.0019	6.12	184	0.0022
C ₃	44.10	1.19	52	0.0004	1.68	74	0.0006
C ₄	58.12	0.28	16	0.0001	1.02	59	0.0004
C ₅	72.15	0.09	6	0.0001	0.69	50	0.0002
C ₆ ⁺	112.00	3.58	401	0.0013	1917.99	214815	0.6894
Feed	112.50	1906.67	214500	0.6754	0	0	0.0000
Total		2823.04	217359	1.0000	2782.12	217359	1.0000
Component	y _i	K _i @ 500°F	y _i /K _i	K _i @ 450°F	y _i /K _i	K _i @ 461°F	y _i /K _i

H ₂ S	0.0004	6.50	0.0001	7.60	0.0001	7.60	0.0001
H ₂	0.3115	17.50	0.0178	20.00	0.0156	19.42	0.0160
C ₁	0.0089	11.30	0.0008	12.20	0.0007	12.00	0.0007
C ₂	0.0019	5.40	0.0004	5.40	0.0004	5.40	0.0004
C ₃	0.0004	2.90	0.0001	3.60	0.0001	3.43	0.0001
C ₄	0.0001	2.75	<<	2.50	<<	2.55	<<
C ₅	0.0001	1.82	<<	1.52	<<	1.58	<<
C ₆ ⁺	0.0013	0.98	0.0013	0.62	0.0020	0.69	0.0018
Feed	0.6754	0.98	0.6892	0.62	1.0893	0.69	0.9850
Total	1.0000		0.7097		1.1082		1.0041

Component	lb/h	Btu/lb	10 ⁶ Btu/h
H ₂ S	41	297.5	0.01
H ₂	1777	1369.8	2.43
C ₁	403	322.5	0.13
C ₂	163	349.6	0.06
C ₃	52	356.6	0.02
C ₄	16	346.5	0.01
C ₅	6	334.8	<<
C ₆ ⁺	401	339.0	0.14
Feed	214500	339.0	72.72
Total	217359		75.51

Point for CFE heat curve: Combined Feed

$$T = 461^{\circ}\text{F}$$

$$H = 75.51 \text{ } 10^6 \text{ Btu/hr}$$

Note: We want to keep the feed all vapor if possible

Mixed Phase Calculations – Combined Feed

Component	z_i	$K_i @ 300$	$V = 950$		$V = 965$	
			x_i	y_i	x_i	y_i
H ₂ S	0.0004	4.70	0.0002	0.0009	0.0002	0.0009
H ₂	0.3115	29.60	0.0293	0.8680	0.0289	0.8557
C ₁	0.0089	11.90	0.0019	0.0227	0.0019	0.0224
C ₂	0.0019	4.45	0.0009	0.0039	0.0009	0.0039
C ₃	0.0004	2.18	0.0003	0.0007	0.0003	0.0007
C ₄	0.0001	1.39	0.0001	0.0001	0.0001	0.0001
C ₅	0.0001	0.60	<<	<<	<<	<<
C ₆ ⁺	0.0013	0.12	0.0018	0.0002	0.0018	0.0002
Feed	0.6754	0.12	0.9596	0.1151	0.9660	0.1159
Total			0.9941	1.0116	1.0001	0.9998

Component	LIQUID = 1858.04				VAPOR = 965			
	mols/h	lb/h	Btu/lb	10 ⁶ Btu/h	mols/h	lb/h	Btu/lb	10 ⁶ Btu/h
H ₂ S	0.35	12	183.9	<<	0.84	29	253.0	0.01
H ₂	53.72	109	183.9	0.02	825.78	1668	816.0	1.36
C ₁	3.50	56	183.9	0.01	21.63	347	213.0	0.07
C ₂	1.63	49	183.9	0.01	3.78	114	251.0	0.03
C ₃	0.56	25	183.9	0.01	0.63	28	256.0	0.01
C ₄	0.16	9	183.9	<<	0.12	7	238.0	<<
C ₅	0.07	5	153.7	<<	0.02	2	246.0	<<
C ₆ ⁺	3.37	377	135.0	0.05	0.21	24	259.0	0.01
Feed	1794.81	201916	135.0	27.26	111.86	12584	259.0	3.26
Total	1858.00	202558		27.35	964.87	14801		4.75

Point for CFE Heat Curve: Combined Feed

$$T = 300^{\circ}\text{F}$$

$$H = 32.10 \cdot 10^6 \text{ Btu/h}$$

Mixed Phase Calculations – Combined Feed

Component	z_i	$K_i @ 400^\circ\text{F}$	$V = 1300$		$V = 1357$	
			x_i	y_i	x_i	y_i
H ₂ S	0.0004	7.00	0.0001	0.0008	0.0001	0.0008
H ₂	0.3115	22.80	0.0282	0.6435	0.0271	0.6188
C ₁	0.0089	13.00	0.0014	0.0177	0.0013	0.0171
C ₂	0.0019	5.20	0.0007	0.0034	0.0006	0.0033
C ₃	0.0004	3.20	0.0002	0.0007	0.0002	0.0007
C ₄	0.0001	2.18	0.0001	0.0001	0.0001	0.0001
C ₅	0.0001	1.22	<<	<<	<<	<<
C ₆ ⁺	0.0013	0.37	0.0018	0.0007	0.0018	0.0007
Feed	0.6754	0.37	0.9514	0.3520	0.9688	0.3584
Total			0.9839	1.0189	1.0000	0.9999

Component	LIQUID = 1466.04				VAPOR = 1357			
	mols/h	lb/h	Btu/lb	10 ⁶ Btu/h	mols/h	lb/h	Btu/lb	10 ⁶ Btu/h
H ₂ S	0.16	5	204.7	<<	1.03	35	280.9	0.01
H ₂	39.79	80	204.7	0.02	839.71	1696	1161.1	1.97
C ₁	1.93	31	204.7	0.01	23.20	372	279.9	0.10
C ₂	0.93	28	204.7	0.01	4.48	135	311.0	0.04
C ₃	0.30	13	204.7	0.00	0.89	39	317.8	0.01
C ₄	0.09	5	204.7	0.00	0.19	11	306.8	0.01
C ₅	0.04	3	204.7	0.00	0.05	3	290.8	0.01
C ₆ ⁺	2.67	299	204.7	0.06	0.91	102	309.1	0.03
Feed	1420.26	159779	204.7	32.70	486.41	54721	309.1	16.91
Total	1466.00	160244		32.80	1356.87	57115		19.09

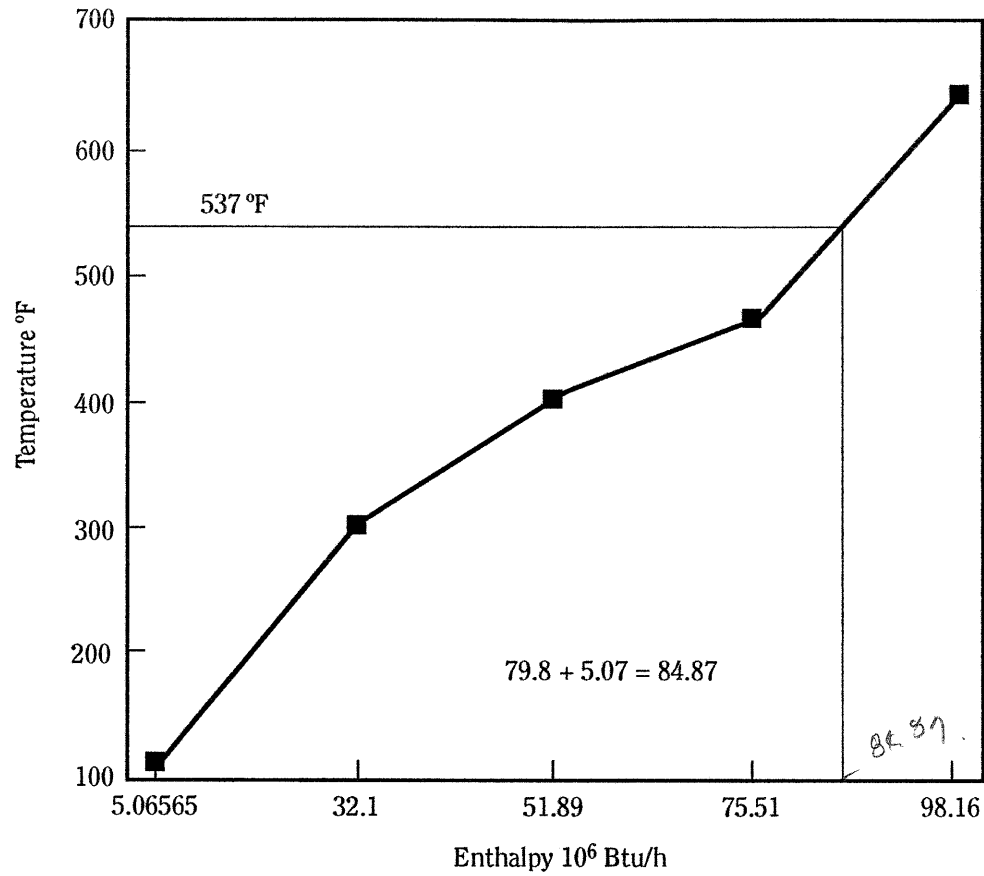
Point for CFE Heat Curve: Combined Feed

$$T = 400^\circ\text{F}$$

$$H = 51.89 \text{ } 10^6\text{Btu/h}$$

Figure 21

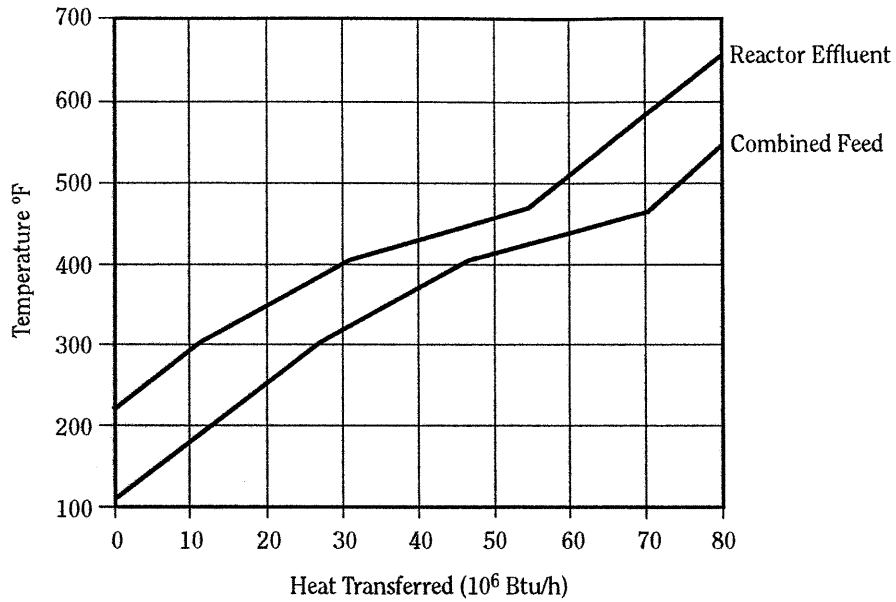
Combined Feed Enthalpy



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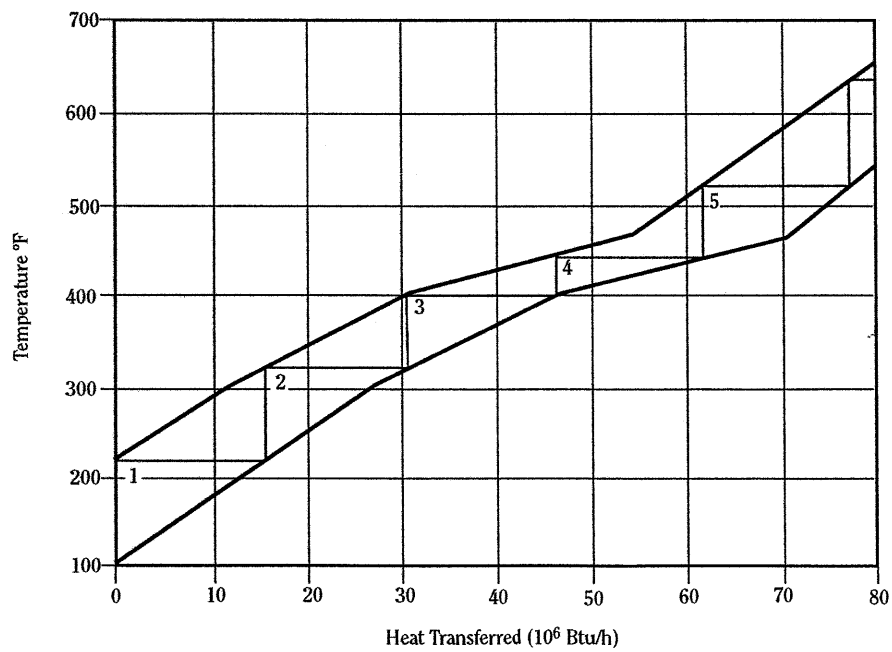
Figure 22

*Combined Feed Exchanger
Heat Release Curve*



EDS-R00-2026

Figure 23



EDS-R00-2027

Component	Feed	Recycle Gas	Combined Feed to Reactor	Reactor Yield	Reactor Effluent	Makeup Gas	Total to Separator	Separator Liquid	Separator Vapor
H ₂ S	0.0	1.19	1.19	1.89	3.08	0.00	3.08	1.89	1.19
H ₂	0.0	879.50	879.50	-53.09	826.41	90.97	917.38	37.88	879.50
C ₁	0.0	25.13	25.13	0.00	25.13	6.93	32.06	6.93	25.13
C ₂	0.0	5.41	5.41	0.71	6.12	5.17	11.29	5.88	5.41
C ₃	0.0	1.19	1.19	0.49	1.68	3.41	5.09	3.9	1.19
C ₄	0.0	0.28	0.28	0.74	1.02	1.98	3.00	2.72	0.28
C ₅	0.0	0.09	0.09	0.6	0.69	1.54	2.23	2.14	0.09
C ₆ ⁺	0.0	3.58	3.58	1914.41	1917.99	0.00	1917.99	1914.41	3.58
Feed	1906.67	0.00	1906.67	-1906.67	0.00	0.00	0.00	0.00	0.00
Total mol/h	1906.67	916.37	2823.04	-40.92	2782.12	110.00	2892.12	1975.75	916.37
lb/h	214500.00	2858.00	217358.00		217358.00				2858.00
°API	61.00								
mol wt	112.50	3.12	76.98		78.13				3.12
BPSD	20000.00								
10 ⁶ Std ft ³ /d			639		650	100		120	120
Temperature °F	100		98.16		100.35	0.13		6.28	0.61
10 ⁶ Btu/h	4.23								
Pressure, psig	25					150		350	350

Figure 24

UOP

HEAT RELEASE CURVES

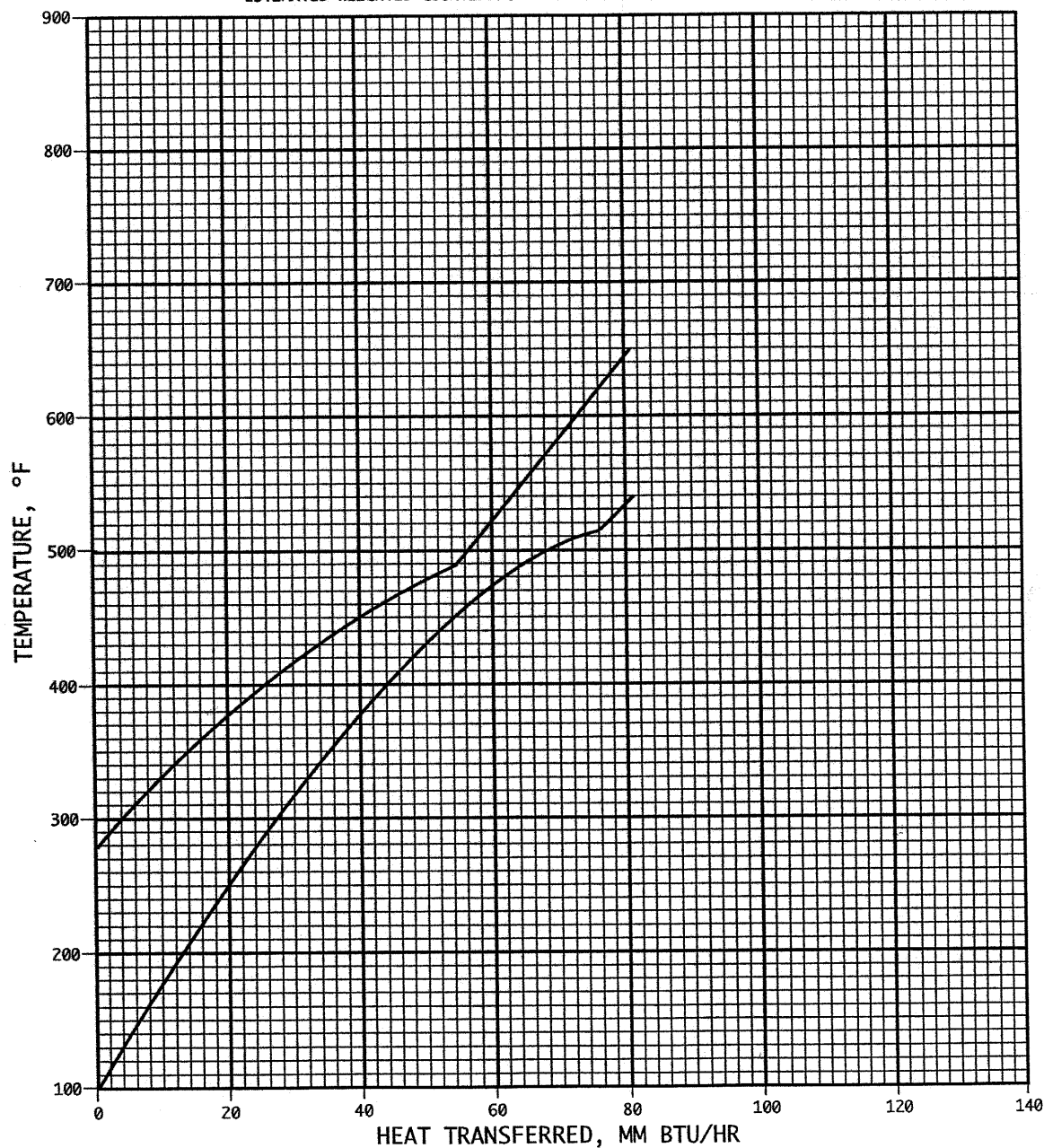
UOP HYDROTREATING PROCESS
SAMPLE PROGRAM
UOP NAPHTHA HYDROTREATING UNIT
BASE CASE

HOT STREAM, EFFLUENT FROM REACTOR
INLET TEMP 649.96°F, PRESS 501.66 PSIG
OUTLET TEMP 278.79°F, PRESS 469.66 PSIG
COLD STREAM, COMBINED FEED FROM COMBINED FEED MIXER
INLET TEMP 101.92°F, PRESS 578.97 PSIG
OUTLET TEMP 539.88°F, PRESS 546.97 PSIG

HOT SIDE DRY DEW POINT 489.22°F, PRESS 491.16 PSIG
COLD SIDE DRY DEW POINT 516.74°F, PRESS 548.80 PSIG

HEAT TRANSFERRED 81.00 MM BTU/HR

ESTIMATED WEIGHTED COUNTERFLOW MTD 79.88°F



EDS-R00-2028

Comp	Feed	Recycle gas	CF to Rx	Rx Yield	Rx Effl	Makeup gas	Mtl to Sep	Separator liquid	Separator vapor
H ₂ S	0.0	1.19	1.19	1.89	3.08	0.0	3.08	1.89	1.19
H ₂	0.0	879.5	879.5	-53.09	826.41	90.97	917.38	37.88	879.5
C1	0.0	25.13	25.13	0	25.13	6.93	32.06	6.93	25.13
C2	0.0	5.41	5.41	0.71	6.12	5.17	11.29	5.88	5.41
C3	0.0	1.19	1.19	0.49	1.68	3.41	5.09	3.9	1.19
C4	0.0	0.28	0.28	0.74	1.02	1.98	3.00	2.72	0.28
C5	0.0	0.09	0.09	0.6	0.69	1.54	2.23	2.14	0.09
C6+	0.0	3.58	3.58	1914.41	1917.99	0.0	1917.99	1914.41	3.58
FEED	1906.67	0.0	1906.67	-1906.67	0.0	0.0	0.0	0.0	0.0
Total	1906.67	916.37	2823.04	-40.92	2782.12	110.00	2892.12	1975.75	916.37
Lb/Hr	214500	2858	217358		217358	826	218184	215326	2858
API	61								
MW	112.5	3.12	76.98		78.13	7.51	75.44	108.98	3.12
BPSD	20000	---							
MMSCFD	---	8.34			25.31	1.00			
Temp °F	100		639		650	100		120	120
MMBTU/H	4.23		98.16		100.35	0.13		6.24	0.61
Press Psig	25					150		350	350

Figure 25

UOP

HEAT RELEASE CURVES

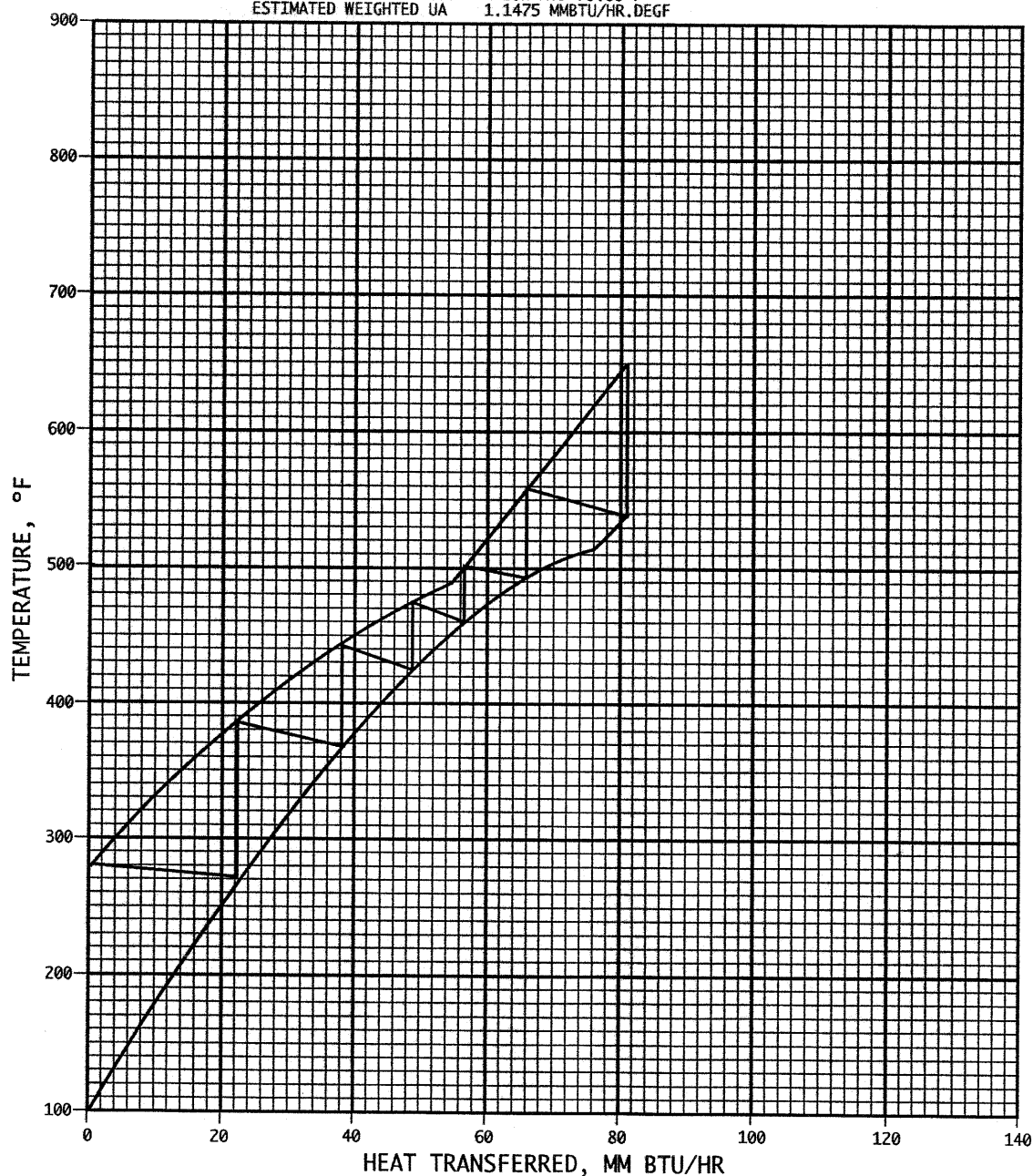
UOP HYDROTREATING PROCESS
SAMPLE PROGRAM
UOP NAPHTHA HYDROTREATING UNIT
BASE CASE

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OUTLET TEMP 278.79°F, PRESS 469.66 PSIG
COLD STREAM, COMBINED FEED FROM COMBINED FEED MIXER
INLET TEMP 101.92°F, PRESS 578.97 PSIG
OUTLET TEMP 539.88°F, PRESS 546.97 PSIG

HOT SIDE DRY DEW POINT 489.22°F, PRESS 491.16 PSIG
COLD SIDE DRY DEW POINT 516.74°F, PRESS 548.80 PSIG

HEAT TRANSFERRED 81.00 MM BTU/HR

ESTIMATED WEIGHTED COUNTERFLOW MTD 79.88°F
ESTIMATED WEIGHTED UA 1.1475 MMBTU/HR.DEGF



EDS-R00-2029

FRACTIONATION

Naphtha Hydrotreating

Kerosine Hydrotreating

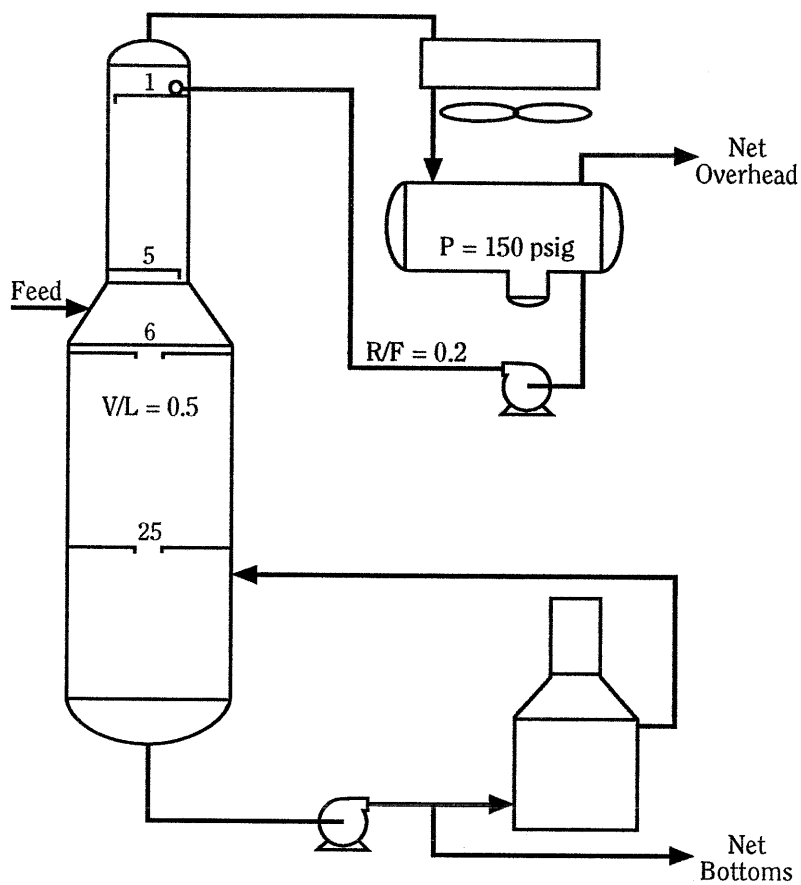
Distillate Hydrotreating

Heavy Oil Hydrotreating

Hydrocracking

Figure 26

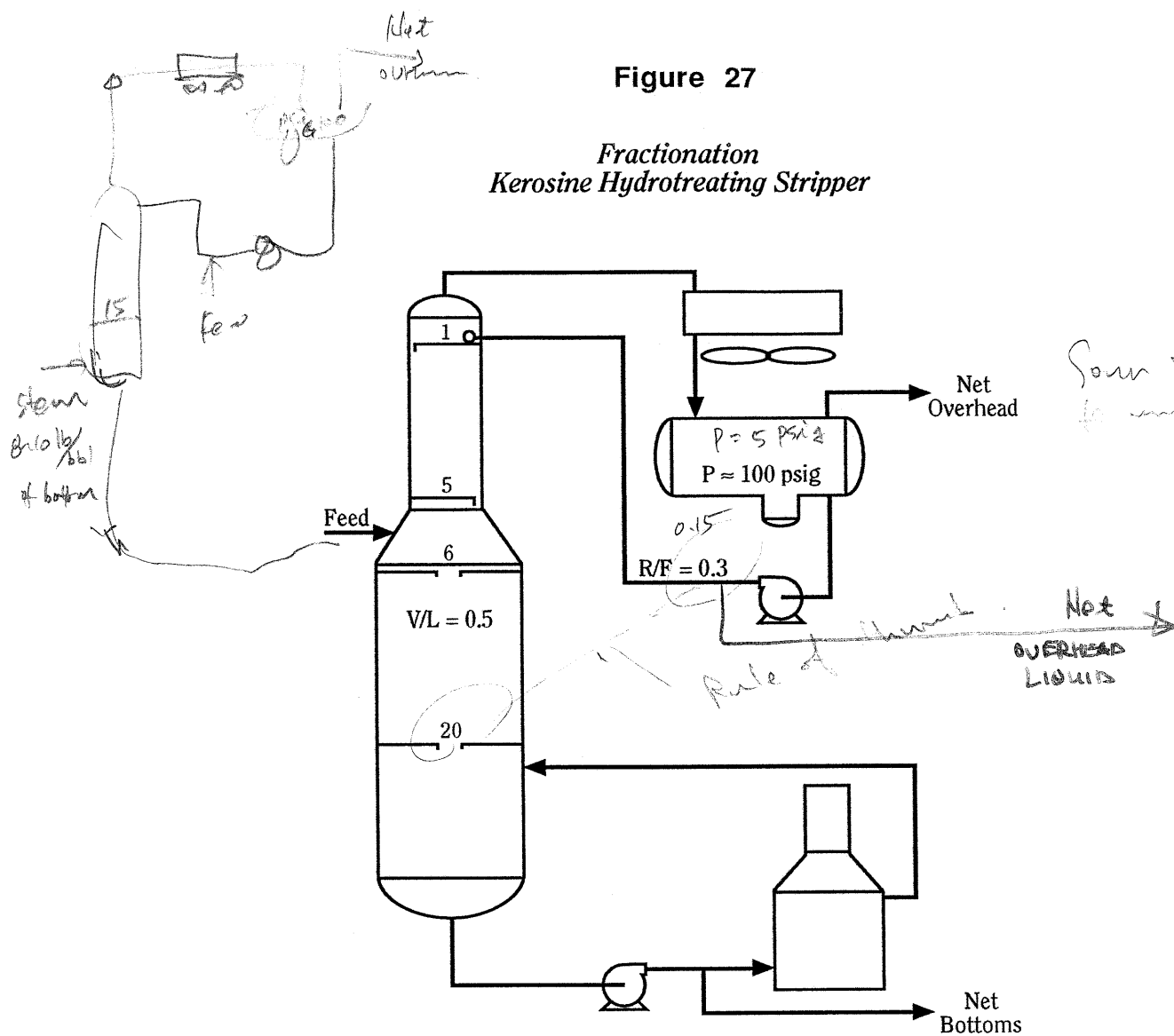
*Fractionation
Naphtha Hydrotreating Stripper*



*Some gas treating
FG*

*0.5 ppm
sulfur*

EDS-R00-2030

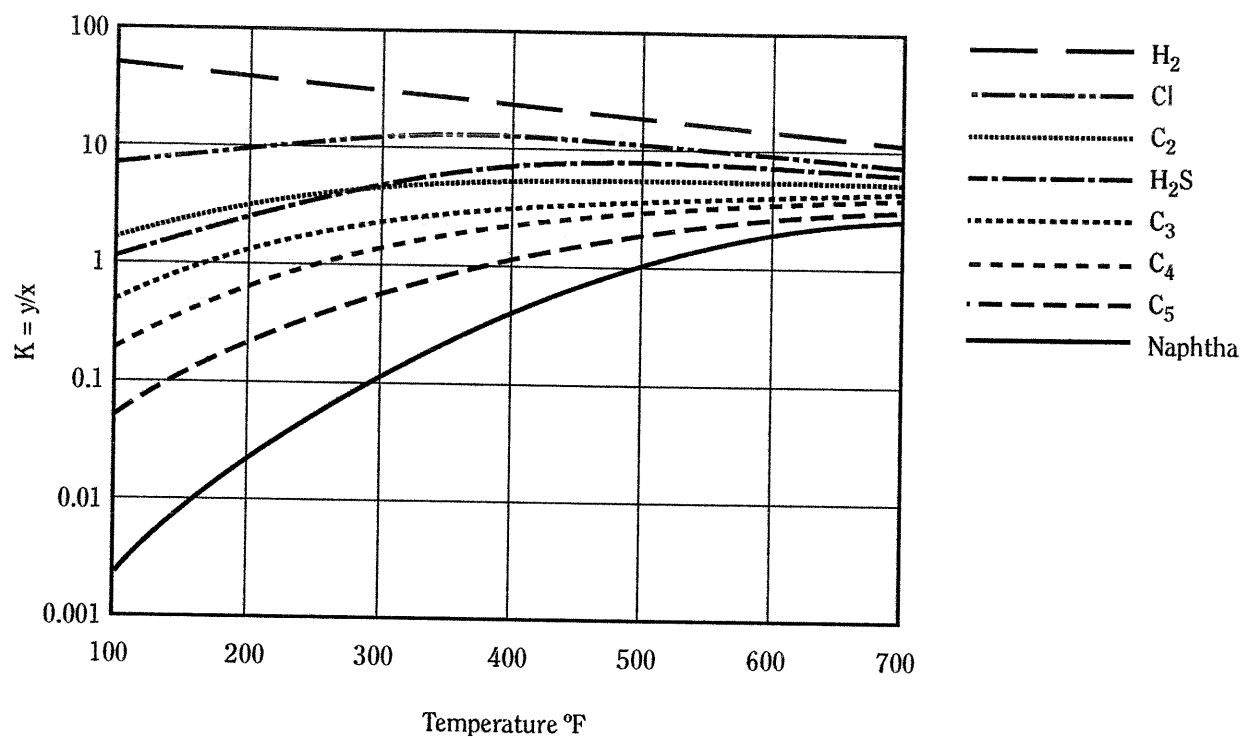


EDS-R00-2031

Stream stripper: only control of flash point

Figure 28

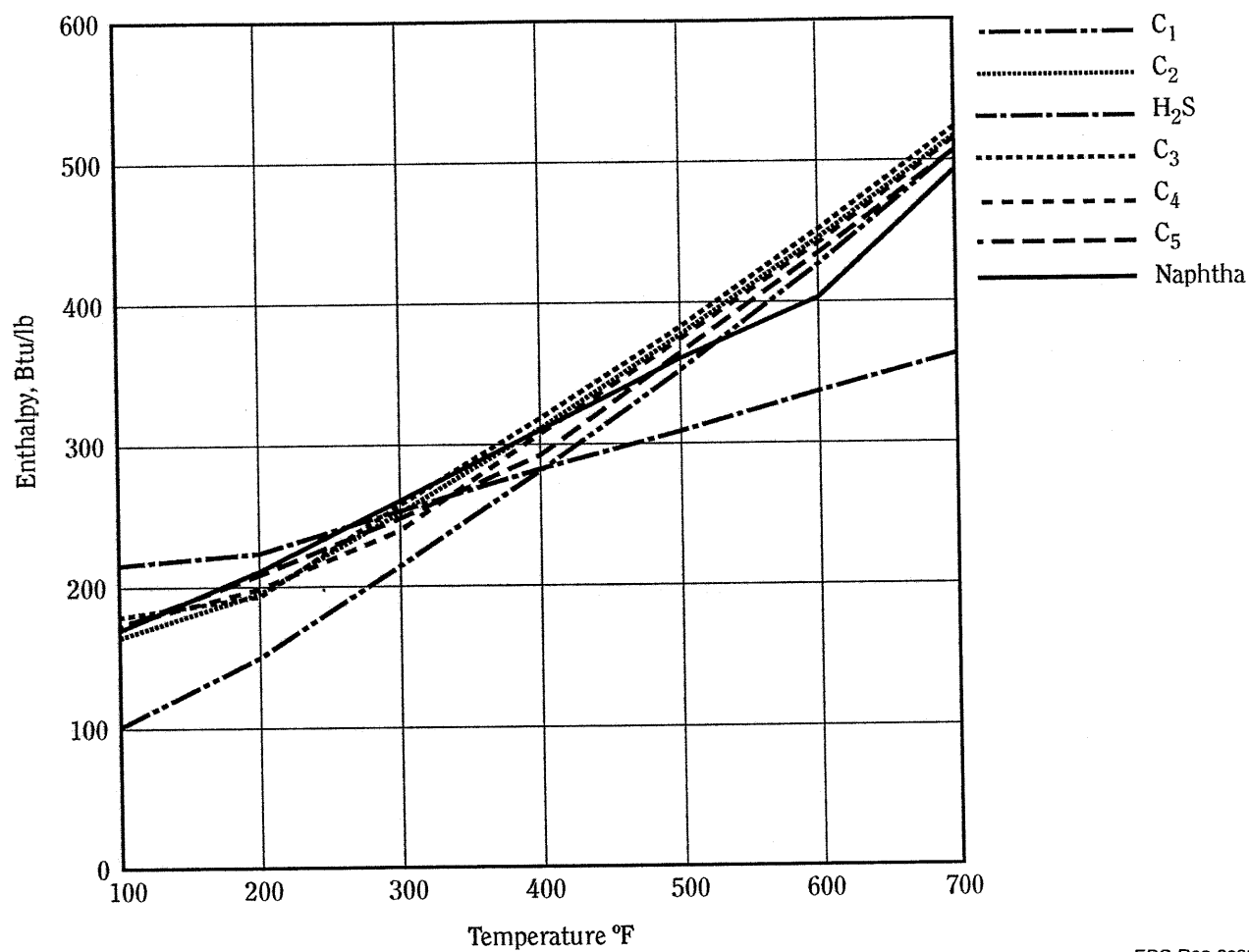
*Equilibrium K Values
(350 psig)*



EDS-R00-2032

Figure 29

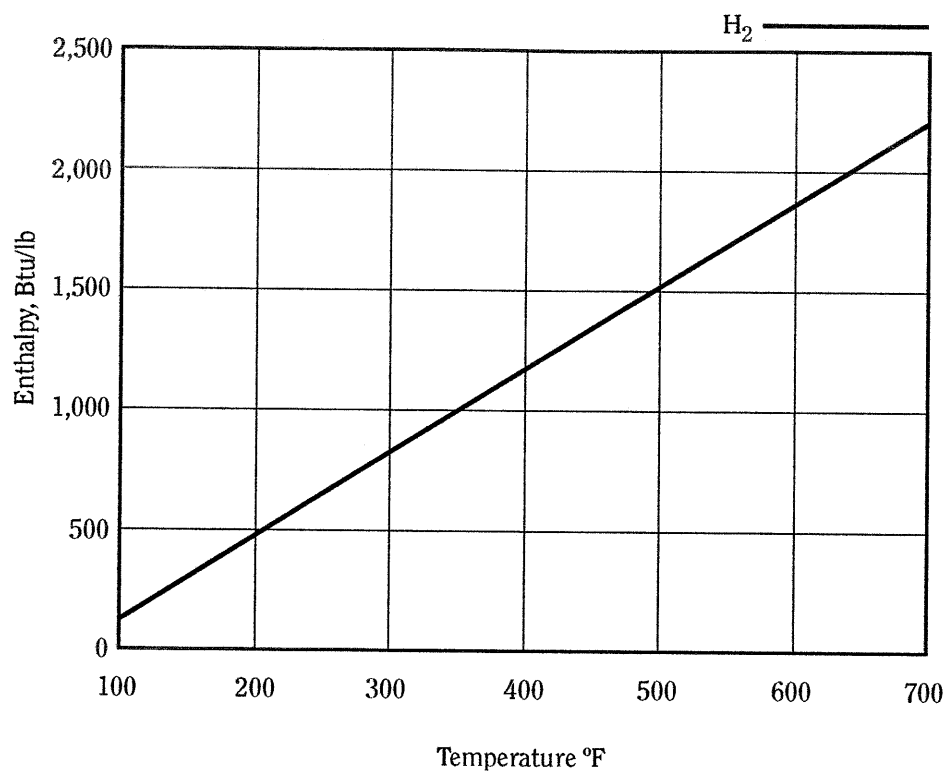
Vapor Enthalpy (Btu/lb)
(350 psig)



EDS-R00-2033

Figure 30

*Vapor Enthalpy (Btu/lb)
(350 psig)*

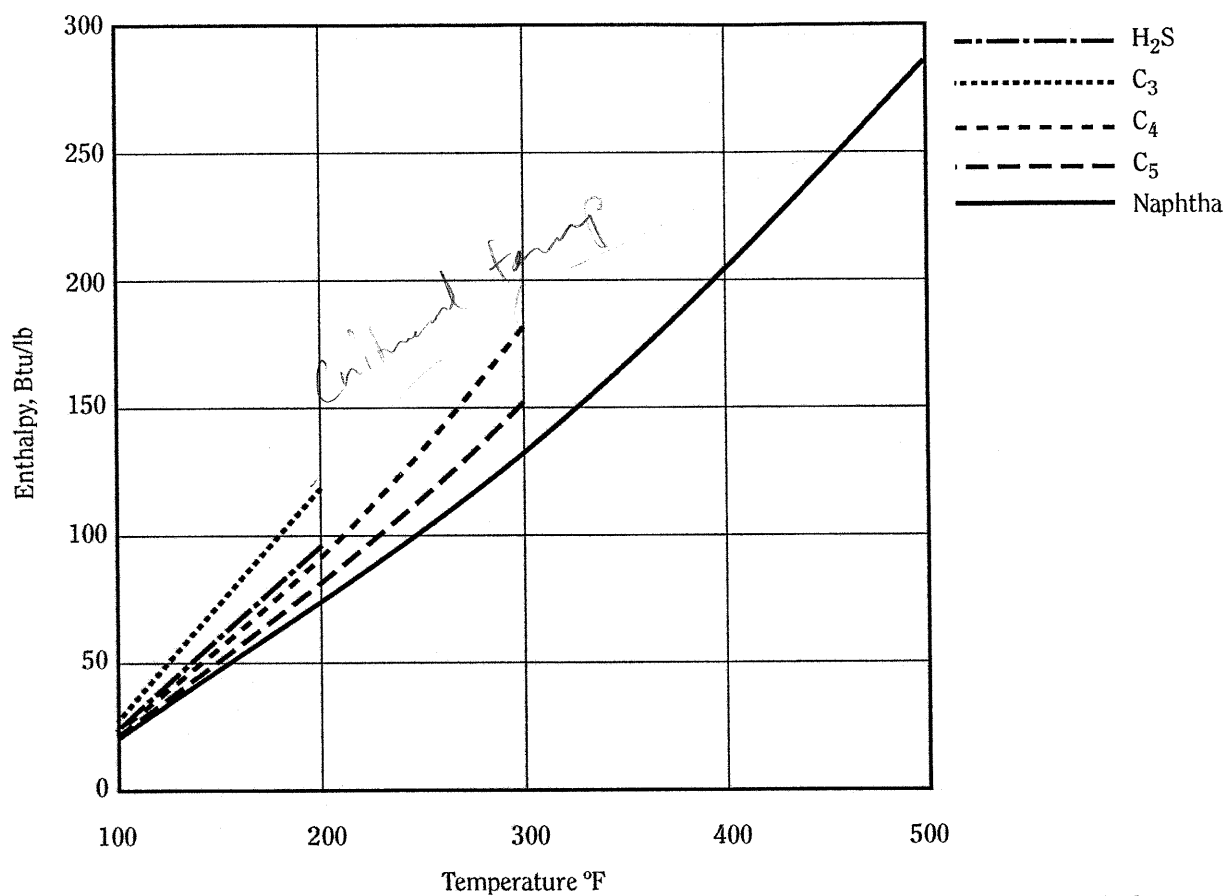


EDS-R00-2034

Temperature, °F	100	200	300	400	500	600	700
H ₂ S	215	224	253	281	308	336	364
H ₂	134	475	816	1161	1509	1859	2210
C ₁	101	150	213	280	351	426	506
C ₂	164	194	251	311	375	444	517
C ₃	179	193	256	318	382	451	524
C ₄	173	198	238	307	373	442	515
C ₅	172	208	246	291	364	434	507
C ₆ ⁺ Naphtha	169	211	259	309	359	403	493

Figure 31

Liquid Enthalpy (Btu/lb)
(350 psig)



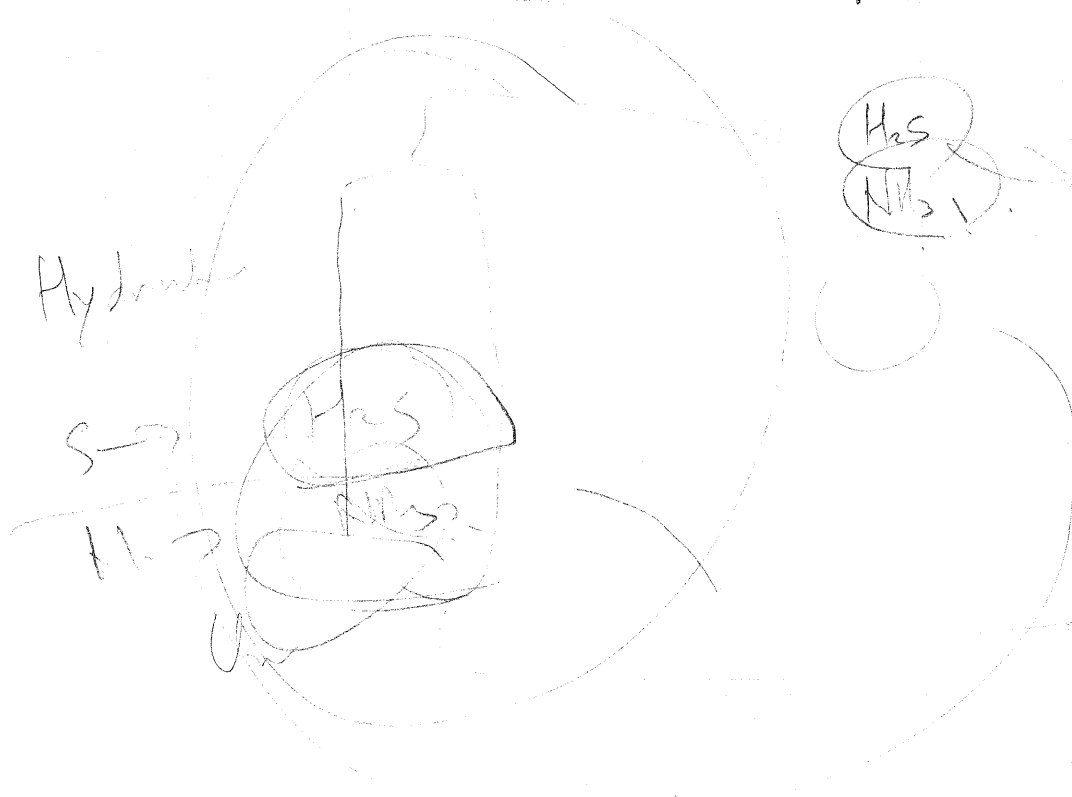
EDS-R00-2035

Temperature, °F	100	200	300	400
H ₂ S	21.4	95.7		
C ₃	26.7	119		
C ₄	23.3	90.7	184	
C ₅	21.5	81.6	154	
C ₆ ⁺ Naphtha	19.7	73.7	135	205

HYDROTREATING UNIT DESIGN

oct. 26

by Msc J. L. Bonucci
Mr. Mike O'Donn



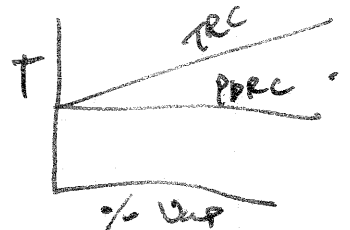
Steam stripper application

- H₂O Removal 15%
- H₂S Removal 30%
- H₂HC 80%.

Feed injection = for catalyst activity deactivation
15 ppm

Water wash : 3 vol % of feed rate
25 % of liquid.

Reboiler Control : $\frac{\% \text{ Vaporization}}{\Delta T} < 0.2$



ENGINEERING DESIGN SEMINAR

SEPTEMBER 6, 1994 – NOVEMBER 11, 1994

WASTE DISPOSAL

TABLE OF CONTENTS

Introduction

Sources of Waste / *water, solid wastes.*

U.S. Laws & Regulations

- Effluents Problem
- Video on Environmental Compliance

Collection System (Waste Waters)

- Hydraulics Problem

Treatment Systems

- Video on Hazardous Waste Treatment

Conclusion

INTRODUCTION

Waste Water & Solid Waste

Sources of Information

Industry Trends for Water/Solid Waste

Laws and Regulations: "More and Stricter"

Hazardous Waste and Toxic Pollutants

Waste Minimization

Pollution Prevention (e.g., Source Reduction)

Recycling (e.g., Oil Recovery)

Public Preserving Natural Resources

Increased Cost to Society

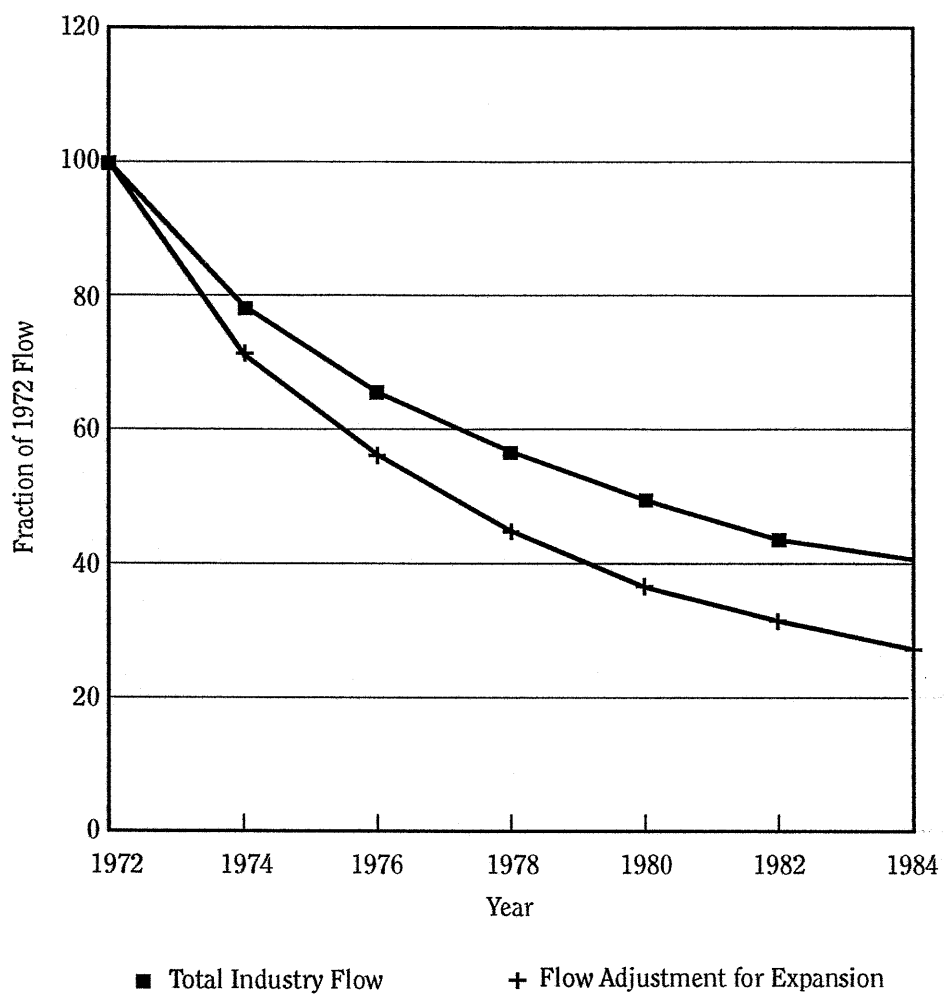
126 Environmental Protection Agency Priority Pollutants

Base-Neutral Extractable Organics	Volatile Organics	Pesticides/PCBs
Acenaphthene Acenaphthylene Anthracene Benzdine Benzo(a)anthracene Benzo(a)pyrene 3,4-Benzofluoranthene Benzo(ghi)perylene Benzo(k)fluoranthene bis(2-Chloroethoxy) methane bis(2-Chloroethyl) ether bis(2-Chlorisopropyl) ether bis(2-Ethylhexyl) phthalate 4-Bromophenyl phenyl ether Butyl benzyl phthalate 2-Chloronaphthalene 4-Chlorophenyl phenyl ether Chrysene Dibenzo(a,h)anthracene 1,2-Dichlorobenzene 1,3-Dichlorobenzene 1,4-Dichlorobenzene 3,3-Dichlorobenzidine Diethyl phthalate Dimethyl phthalate Di-n-butyl phthalate 2,4-dinitrotoluene 2,6-dinitrotoluene Di-n-octyl phthalate 1,2-diphenylhydrazine Fluoranthene Fluorene Hexachlorobenzene Hexachlorobutadiene Hexachlorocyclopentadiene Hexachloroethane Indeno(1,2,3-c,d)pyrene Isophorone Naphthalene Nitrobenzene N-Nitrosodimethylamine N-Nitrosodi-n-propylamine N-Nitrosodiphenylamine Phenanthrene Pyrene 1,2,4-Trichlorobenzene 2,3,7,8-Tetrachloro-dibenzo-p-dioxin	Acrolein Acrylonitrile Benzene Bromoform Carbon tetrachloride Chlorobenzene Chlorodibromomethane Chloroethane 2-Chloroethyl vinyl ether Chloroform Dichlorobromomethane 1,1-Dichloroethane 1,2-Dichloroethane 1,1-Dichloroethylene 1,2-Dichloropropane 1,3-Dichloropropylene Ethylbenzene Methyl bromide Methyl chloride Methylene chloride 1,1,2,2-Tetrachloroethane Tetrachloroethylene Toluene 1,2-trans-Dichloroethylene 1,1,1-Trichloroethane 1,1,2-Trichloroethane Trichloroethylene Vinyl chloride Acid Extractable Organics 2-chlorophenol 2,4-Dichlorophenol 2,4-Dimethylphenol 4,6-Dinitro-o-cresol 2,4-Dinitrophenol 2-Nitrophenol 4-Nitrophenol p-Chloro-m-cresol Pentachlorophenol Phenol 2,4,6-Trichlorophenol	Aldrin alpha-BHC beta-BHC gamma-BHC delta-BHC Chlordane 4,4'-DDT 4,4'-DDE 4,4"-DDD Dieldrin alpha-Endosulfan beta-Endosulfan Endosulfan sulfate Endrin Endrin aldehyde Heptachlor Heptachlor epoxide PCB-1242 PCB-1254 PCB-1221 PCB-1232 PCB-1248 PCB-1260 PCB-1016 Toxaphene Metals Antimony Arsenic Beryllium Cadmium Chromium Copper Lead Mercury Nickel Selenium Silver Thallium Zinc Miscellaneous Total cyanides Asbestos

Revised as per Federal Register, Vol. 50, No. 165, pp 34623-34624, August 26, 1985

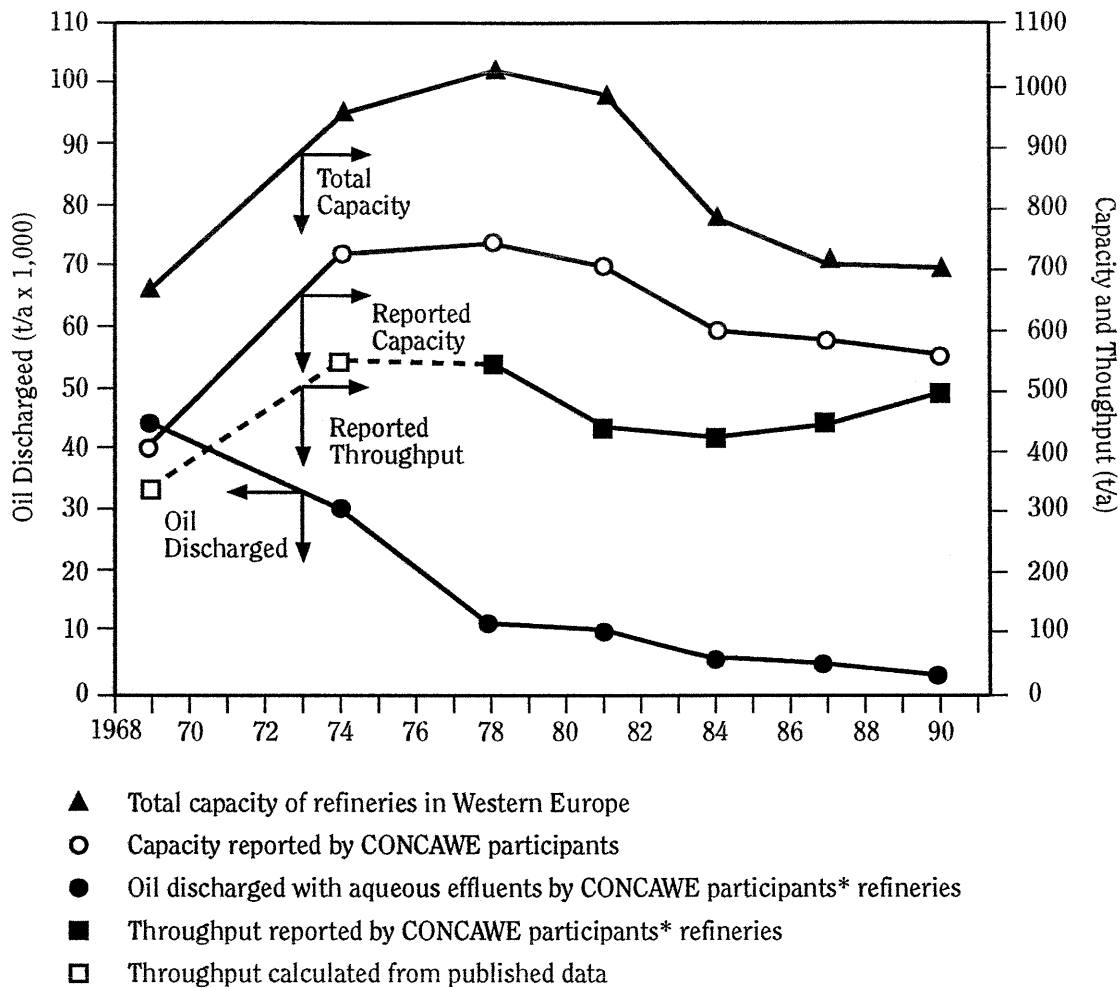
Figure 1

Historical Trend of USA Total Refining Industry Water Usage



EDS-R00-4001

Figure 2



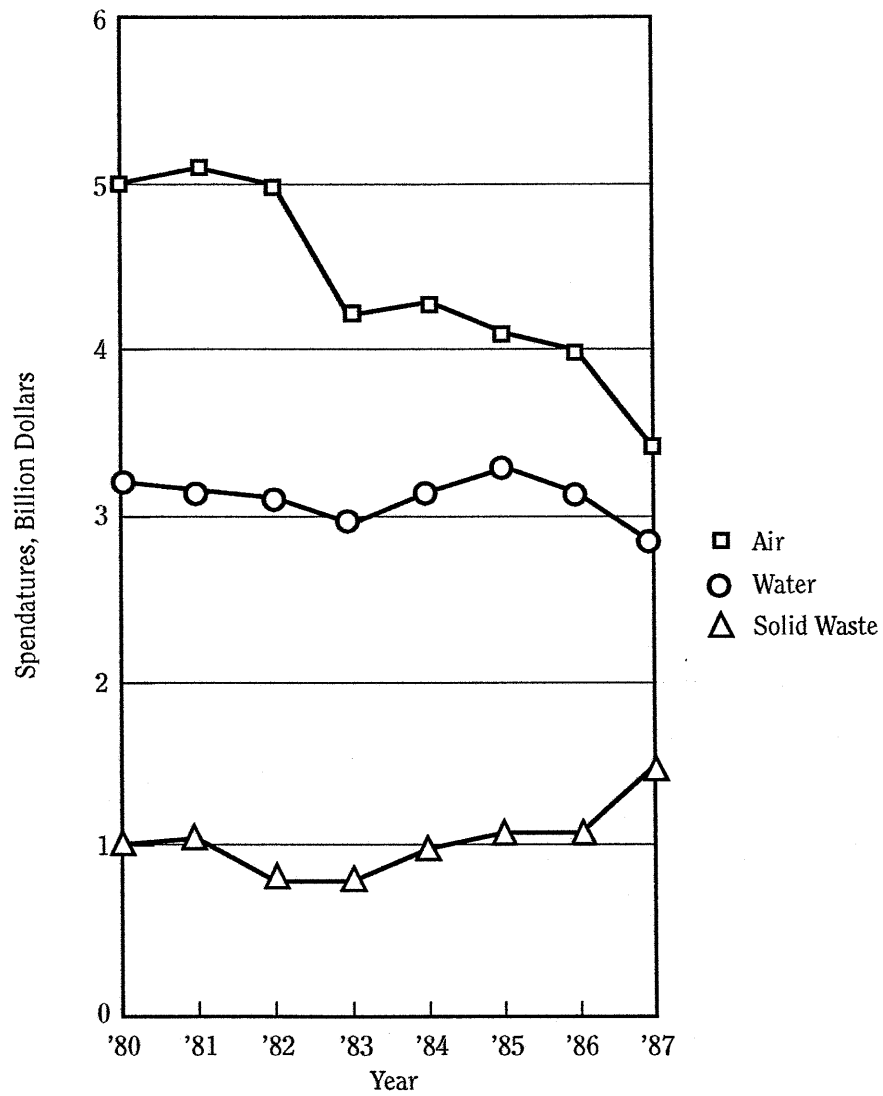
EDS-R00-4002

*From CONCAWE Report No. 1/92 "Trends in Oil Discharged with Aqueous Effluents from Oil Refineries in Western Europe - 1990 Survey"

Note: **CONCAWE** is the oil companies' international study group for conservation of clean air and water - Europe (established in 1963).

Figure 3

*U.S. Pollution Spending **

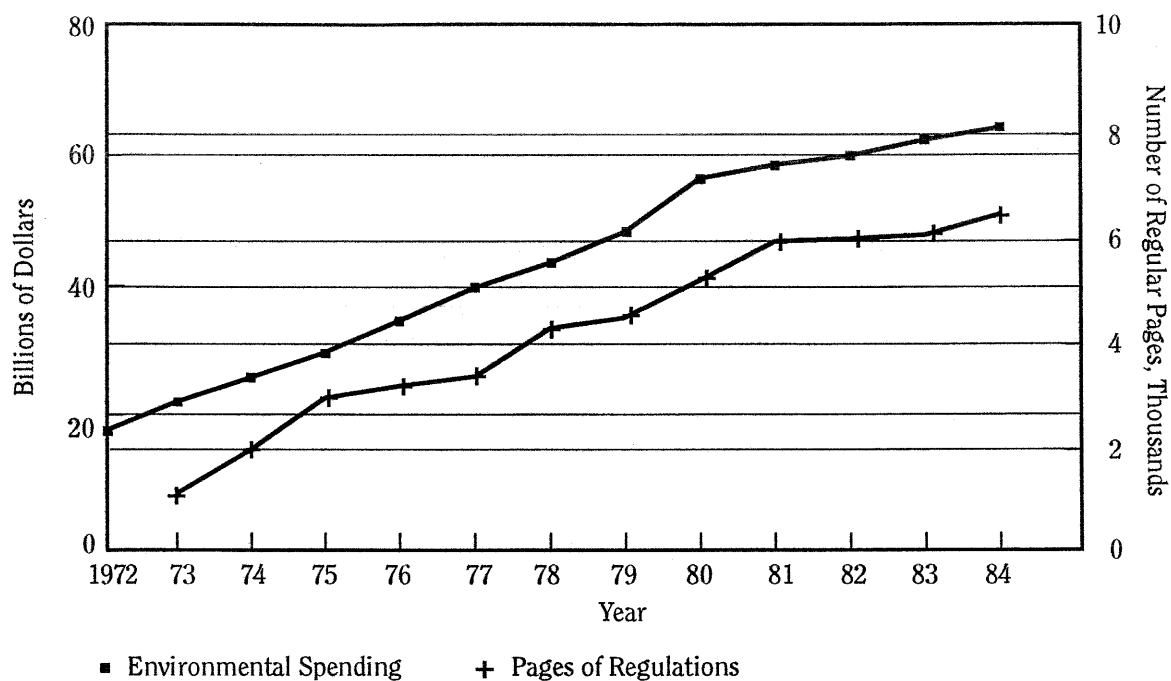


* Expenditures on new equipment

EDS-R00-4003

Figure 4

Environmental Spending versus Regulation



EDS-R00-4004

Update Note: Per the Bureau of National Affairs, Inc. , **\$81.8 Billion** was spent in the U. S. regulating the environment in 1990 (**Breakdown:** 42% Water, 33% Air, 25%Solid Waste).

SOURCES OF WASTE

General Waste

Wastewaters

Hazardous Waste

General Waste Generation in the Petroleum Refining Industry

Oily Sludges/Other Organic Wastes API Separator Sludge* DAF Float* Slop Oil Emulsion Solids* Leaded Tank Bottoms* Other Separator Sludges* Pond Sediments Nonleaded Tank Bottoms Waste Oils/Spent Solvents Other Oily Sludges/Organic Wastes NOS*,** Contaminated Soils/Solids Heat Exchanger Bundle Cleaning Sludge* Contaminated Soil/Solids Waste Coke/Carbon/Charcoal Waste Sulfur Other Contaminated Soils NOS Other Wastes Other Wastes NOS	Spent Catalysts Fluid Cracking Catalyst or Equivalent Hydroprocessing Catalyst Other Spent Catalyst NOS Aqueous Waste Biomass Oil Contaminated Waters (Not Washwater) High pH/Low pH Waters Spent Sulfite Solution Spent Stretford Solution Other Aqueous Wastes NOS Chemicals/Inorganic Wastes Spent Caustics Spent Acids Waste Amines Other Inorganic Wastes NOS
---	--

* RCRC listed hazardous wastes for the petroleum refining industry

** NOS – Not Otherwise Specified

Generation of Wastewaters in the Petroleum Refining Industry

Unit Operation	Function	Waste Generated
Desalting	Reduce inorganic salts and suspended solids in crude to prevent fouling of equipment; remove inorganic impurities that poison catalysts	Desalting sludge; desalter brine
Fractionation: vacuum, atmospheric flash, distillation	Separate constituents of crude oil	Wastewater from overhead accumulators; discharge from oil sampling lines; oil emulsions from condensers; barometric condenser water
Cracking: catalytic, visbreaking, thermal, hydrocracking	Convert heavy oil fractions into lighter oil fractions	Wastewater from overhead accumulators and steam strippers
Reforming	Convert naphthas to finished high-octane gasoline	Wastewater from overhead accumulators on stripping towers
Alkylation	Convert gaseous hydrocarbons to high-octane fuel	Wastewater from overhead accumulators in fractionation section; alkylation reactor; caustic wash
Hydrotreating	Saturate olefins and remove contaminants such as sulfur, nitrogen and oxygen compounds	Wastewater from overhead accumulators on fractionators and steam strippers; sour water stripper bottoms
Polymerization	Convert olefins to high-octane gasoline	Wastewater from caustic scrubbers and pretreatment washwater towers
Isomerization	Convert light gasoline materials into high-octane isomers for fuel	Wastewater from leaks and spills
Solvent refining and extraction of oil stocks	Obtain lube oil fractions and aromatics from feedstocks containing hydrocarbons and undesirable materials	Wastewater from bottom of fractionation towers
Dewaxing	Remove wax from lube oil stocks to produce products with low pour points and to recover wax for further processing	Wastewater from leaks and spills
Coking	Convert heavy oil fractions into lighter oil fractions and into solid petroleum coke	Cutting water blowdown; fractionation section overhead accumulator waters
Aromatic extraction	Recovery of benzene, toluene, and xylene from gasoline stocks	Wastewater from overhead accumulator on stripping towers and condensers
Deasphalting	Separate asphalts or resins from vacuum distillation residuals; recover paraffinic catalytic cracking stock from distillation residuals	Sour water from overhead condensers on steam strippers; spills
Drying and sweetening	Remove sulfur compounds; improve color, odor; oxidation stability; inhibitor response; remove water, carbon dioxide, and other impurities	Spent caustic; wastewater from water washing of treated product; regeneration of treating solution

Generation of Wastewaters in the Petroleum Refining Industry, Continued

Unit Operation	Function	Waste Generated
Grease manufacture	Produce wide range of lubricating greases	Wastewater from leaks and washing of batch process units
Lubricating oil finishing	Produce motor oils and lubricating greases	Wastewater from rinses and clay treatment; sludge from sampling; leaks
Hydrogen manufacture	Produce hydrogen needed for refining processes	Wastewater from desulfurization unit
Storage tanks	Storage of crude oil, intermediates, and final products	Settled water and sludge from tank bottoms and cleaning
Sulfur recovery	Removal of sulfur compounds from hydrocarbon streams and recovery of sulfur product	Spent caustics; spent amine solution; spent Stretford solution
Blending and packaging	Produce and package final products	Wastewater from tank wash; vessel cleaning water
Cooling water system	Heat exchanger operation	Blowdown from cooling tower systems; once-through cooling water
Surface and storm water collection	Treatment of storm and surface drainage	Wastewater from storm and surface drainage
Utilities	Steam and electricity generation	Boiler blowdown
Marine terminals	Load and unload marine vessels with crude oil and refined products	Ballast water
General wastewaters	Maintenance	Wash water; pump gland water; leaks and spills on every operation

Sources:

Jacobs Engineering Company, Assessment of Hazardous Waste Management, 1967 (Reference 3)
 Jones, H. R. Pollution Control (Reference 11)
 Gloyna and Ford, Characteristics and Pollutonal Problems (Reference 12)

Hazardous Waste

Definition

"A 'solid waste' that may pose a substantial present or potential hazard to human health or the environment when improperly stored, treated, transported, disposed or otherwise managed."

Figure 5



EDS-R00-4005

Identification

Listing	
From specific sources	"K" Wastes
From non-specific sources	"F" Wastes
From discarded commercial products and their residues (acute hazardous wastes)	"P" Wastes
From discarded commercial products and their residues (toxic hazardous wastes)	"U" Wastes
Characteristic Ignitibility Corrositivity Reactivity Toxicity	"D" Wastes
"Mixture" Rule	
"Derived From" Rule	

Listed Hazardous Wastes From Petroleum Refineries

Designation	Hazardous Waste Description
K048	Dissolved Air Flotation Float
K049	Slop Oil Emulsion Solids
K050	Heat Exchanger Bundle Cleaning Sludge
K051	API Separator Sludge
K052	Tank Bottoms (Leaded)
F037	Primary Sludge From Gravity Separation of Process Wastewaters and Oily Cooling Wastewaters
F038	Secondary Sludge From Physical and/or Chemical Separation of Process Wastewaters and Oily Cooling Wastewaters

UNITED STATES LAWS AND REGULATIONS

Recent United States Pollution Control Laws

1972 Federal Water Pollution Control Act ("Clean Water Act")

Achieve clean water for swimming, boating and protecting fish and wildlife by 1983

Amended 1977 and 1987 with focus on toxics and water quality

1976 Resource Conservation and Recovery Act (RCRA)

First hazardous waste program

"Cradle-to-grave" hazardous waste management

1980 Comprehensive Environmental Responsibility Compensation and Liability Act (CERCLA)

Hazardous substance releases from inactive sites

Ammended in 1986 with "SARA" ("Community right-to-know")

1990 Pollution Prevention Act

United States Federal Regulations

Water and Solid/Hazardous Waste

Clean Water Act Effluent Guidelines and Standards for Petroleum Refining National Pollutant Discharge Elimination System Permit Regulation <i>NPDES Permit</i>	40 CFR 419 40 CFR 122
Clean Air Act Standards of Performance for New Stationary Sources; VOC Emissions from Petroleum Refinery Wastewater Systems National Emission Standard for Benzene Waste Operations National Emission Standard for Hazardous Air Pollutants	40 CFR 60 Subpt. QQQ 40 CFR 61 Subpt. FF 40 CFR 63 Subpts. F–H
RCRA (Solid and Hazardous Waste) Identification and Listing of Hazardous Wastes Regulations for Owners and Operators of Permitted Hazardous Waste Facilities Regulations on Land Disposal Restrictions Technical Standards and Corrective Action Requirements for Owners and Operators of Underground Storage Tanks	40 CFR 261 40 CFR 264 40 CFR 268 40 CFR 280

Note: CFR = Code of Federal Regulations

Effluent Guidelines

Wastewater

Mass Limitations to Refiners

"Dilution is no solution to pollution"

Factors for Allowance

Size: Quantity of Raw Material (e.g., crude) Processed

Complexity of Processes

Topping
Cracking
Petrochemical
Lube
Integrated

Effluent Limitations

Wastewater

Pollutants Regulated in Refinery Wastewaters
Effluent Guidelines for Petroleum Refining Industry
BOD ₅ (5-Day Biological Oxygen Demand)
TSS (Total Suspended Solids)
COD (Chemical Oxygen Demand)
Oil and Grease
Phenolic Compounds
Ammonia as N
Sulfide
Total Chromium
Hexavalent Chromium
Priority (Toxic) Pollutants – (126)
Volatile Organic Compounds (VOC) – (28)
Organic Hazardous Air Pollutants (Including Benzene) – (75)
Any Pollutant Determined to Cause Local Water Body to Fail to Meet Water Quality Standards
All Pollutants in Permit

Pollutants Are **Generally** Permitted For:

Maximum Of Pollutant In One (1) Day

Average Of Daily Maximums Of Pollutants For 30 Consecutive Days

Long-Term Average

But Must Report Increases, i.e.,:

For Frequent, Routine Increases For:

5 Times Permitted Allowance

Toxic Pollutant > 100 Micrograms/Liter

For Infrequent, Non-Routine Increases For:

10 Times Permitted Allowance

Toxic Pollutant > 500 Micrograms/Liter

Stormwater

General Permit Requirement:

Create Stormwater Pollution Prevention Plan ("SWP3")

SWP3 Requirements

Form Pollution Prevention Team

Describe Potential Pollutant Sources

Use "Best Management Practices"

Comply With Plan (Inspections and Recordkeeping)

Typical Sampling Data

Oil and Grease, pH, BOD, COD, TSS, Total Phosphorous, Nitrate/Nitrite
Nitrogen, Total Kjeldahl Nitrogen, Any Pollutant in Permit

Hazardous Waste Treatment Standards

Treatment is prerequisite for land disposal.

Treatment based on:

Best demonstrated available technology = "BDAT"

Petroleum refinery BDAT

Non-wastewater: (> 1 percent TOC or TSS)

Fluid bed incineration with ash stabilizer

Solvent extraction

Wastewater: (< 1 percent TOC and TSS)

Organics – Incineration

Non-organics – Chemical precipitation
Vacuum filtration

Using United States Refinery Effluent Tables

Problem

Look up allowed mass/time for refinery. (Table 1b)

Determine complexity (process) and size factors.

$$\begin{aligned}
 & * \sum \left[\text{Process Weighting Factor} \left(\frac{\text{Refinery Unit Capacity}}{\text{Refinery Capacity}} \right) \right]_{\text{Unit}} \\
 & \quad \downarrow \quad \quad \quad \text{Table IV} \\
 & \text{Process Configuration Factor} \xrightarrow[\text{Type}]{\text{Facility}} \text{Process Factor} \\
 & \quad \quad \quad \text{Table II} \\
 & * \text{Refinery Size} \xrightarrow[\text{Type}]{\text{Facility}} \text{Size Factor} \\
 & \quad \quad \quad \text{Table I}
 \end{aligned}$$

Adjust allowed mass/time by process and size factors.

$$(\text{Mass/Time})(\text{Process Factor})(\text{Size Factor}) = \text{Final Allowed Mass/Time}$$

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WASTE DISPOSAL

EFFLUENT GUIDELINES PROBLEM

A U.S. REFINERY IS CATEGORIZED AS A LUBE FACILITY AND HAS A 125,000 BBL/DAY CAPACITY THROUGHPUT. THE FACILITY IS MADE UP OF THE FOLLOWING PROCESSES AS INDICATED BELOW WITH THEIR RESPECTIVE CAPACITIES:

<u>PROCESS</u>	<u>CAPACITY IN 1000 BBL/DAY</u>
CRUDE - ATMOSPHERIC	125
DESALTING	125
VACUUM	60
CRACKING - FCC	41
HYDROCRACKING	20
LUBES HYDROFINING	5.3
FURFURAL EXTRACTION	4.0
PHENOL EXTRACTION	4.0
ASPHALT	4.0

DETERMINE THE FOLLOWING ALLOWABLE EFFLUENTS FOR THIS REFINERY:

- MAXIMUM KG IN ONE DAY OF TOTAL SUSPENDED SOLIDS.
- MAXIMUM AVERAGE OF DAILY VALUES OF OIL & GREASE FOR 30 CONSECUTIVE DAYS.

Hint: First calculate total refinery configuration factor.

TABLE IA
EFFLUENT GUIDELINES
PETROLEUM REFINING POINT SOURCE CATEGORY
NEW SOURCE PERFORMANCE STANDARDS (NSPS) (NOTES 1,2)

Effluent Characteristics	Topping:		Cracking:	
	Maximum For Any One Day	Average of Daily Values for thirty Consecutive Days Shall Not Exceed	Maximum For any One Day	Average of Daily Values for Thirty Consecutive Days Shall Not Exceed
Metric Units: kilograms per thousand cubic meters of feedstock (kg/1,000m ³)				
BOD ₅	11.8	6.3	16.3	8.7
TSS ₅	8.3	4.9	11.3	7.2
COD (Note 3)	61.0	32.0	118.0	61.0
Oil and Grease	3.6	1.9	4.8	2.6
Phenolic Compounds	0.088	0.043	0.119	0.058
Ammonia as N	2.8	1.3	10.8	8.6
Sulfide	0.078	0.035	0.105	0.048
Total Chromium	0.18	0.105	0.24	0.14
Hexavalent Chromium	0.015	0.0068	0.02	0.0088

English Units: pounds per thousand barrels of feedstock (lb/1,000 bb1)

BOD ₅	4.2	2.2	5.8	3.1
TSS ₅	3.0	1.9	4.0	2.5
COD (Note 3)	21.7	11.2	41.5	21.0
Oil and Grease	1.3	0.7	1.7	0.93
Phenolic Compounds	0.031	0.016	0.042	0.02
Ammonia as N	1.0	0.45	6.6	3.0
Sulfide	0.027	0.012	0.037	0.017
Total Chromium	0.064	0.037	0.084	0.049
Hexavalent Chromium	0.0052	0.0025	0.0072	0.032

NOTES:

- (1) To obtain actual limitations all values in this table must be multiplied by a subcategory dependent variable, F; where F is the product of the process factor and the size factor and the crude throughput (in thousand barrels per day).
- (2) Once-through cooling water may be discharged with a total organic carbon (TOC) concentration not to exceed 5 mg/l.
- (3) In any case in which the applicant can demonstrate that the chloride ion concentration in the effluent exceeds 1000 mg/l (1000 PPM), the regional administrator may substitute TOC as a parameter in lieu of COD. Effluent limitations for TOC shall be based on effluent data from the plant correlating TOC to BOD₅. If in the judgement of the regional administrator, adequate correlation data are not available, the effluent limitations for TOC shall be established at a ratio of 2.2 to 1 to the applicable effluent limitation on BOD₅.

TABLE 1B
EFFLUENT GUIDELINES
PETROLEUM REFINING POINT SOURCE CATEGORY
NEW SOURCE PERFORMANCE STANDARDS (NSPS)

Effluent Characteristics	Petrochemical		Lube		Integrated	
	Maximum For Any One Day	Average of Daily Values for thirty Consecutive Days Shall Not Exceed	Maximum For any One Day	Average of Daily Values for Thirty Consecutive Days Shall Not Exceed	Maximum For any One Day	Values for Thirty Consecutive Days Shall Not Exceed
Metric Units: kilograms per thousand cubic meters of feedstock (kg/1,000m ³)						
BOD ₅	21.8	11.6	34.6	18.4	41.6	22.1
TSS ₅	14.9	9.5	23.4	14.9	28.1	17.9
COD	133.0	69.0	245.0	126.0	295.0	152.0
Oil and Grease	6.6	3.5	10.5	5.6	12.6	6.7
Phenolic Compounds	0.158	0.077	0.25	0.12	0.3	0.14
Ammonia as N	23.4	10.7	23.4	10.7	23.4	10.7
Sulfide	0.14	0.063	0.22	0.1	0.26	0.12
Total Chromium	0.32	0.19	0.52	0.31	0.64	0.37
Hexavalent Chromium	0.025	0.012	0.046	0.021	0.052	0.024
English Units: pounds per thousand barrels of feedstock (lb/1,000 bbl)						
BOD ₅	7.7	4.1	12.2	6.5	14.7	7.8
TSS ₅	5.2	3.3	8.3	5.3	9.9	6.3
COD	47.0	24.0	87.0	45.0	104.0	5.4
Oil and Grease	2.4	1.3	3.8	2.0	4.5	2.4
Phenolic Compounds	0.056	0.027	0.068	0.043	0.105	0.51
Ammonia as N	0.3	3.0	0.3	3.8	8.3	3.8
Sulfide	0.05	0.022	0.078	0.035	0.093	0.042
Total Chromium	0.116	0.068	0.18	0.105	0.22	0.13
Hexavalent Chromium	0.0096	0.0044	0.022	0.0072	0.019	0.0084

TABLE II
EFFLUENT GUIDELINES
PETROLEUM REFINING POINT SOURCE CATEGORY
NEW SOURCE PERFORMANCE STANDARDS (NSPS)

1,000 Barrels of Feedstock Per Stream - Day	Size Factors By Subcategory:				
	Topping:	Cracking:	Petrochemical:	Lube:	Integrated:
	Size Factor	Size Factor	Size Factor	Size Factor	Size Factor
Less than 24.9	1.02	.91	.73	.71	.73
25.0 to 49.9	1.06	.95	.76	.71	.73
50.0 to 74.9	1.16	1.04	.83	.74	.73
75.0 to 99.9	1.26	1.13	.91	.81	.73
100.0 to 124.9	1.38	1.23	.99	.88	.73
125.0 to 149.9	1.50	1.35	1.08	.97	.76
150.0 to 174.9	1.57	1.41	1.13	1.05	.83
175.0 to 199.9	1.57	1.41	1.13	1.14	.91
200.0 to 224.9	1.57	1.41	1.13	1.19	.99
225.0 or greater	1.57	1.41	1.13	1.19	1.04

TABLE IV
EFFLUENT GUIDELINES
PETROLEUM REFINING POINT SOURCE CATEGORY
BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE (BAT)
PROCESS CONFIGURATION - PROCESS BREAKDOWN

PROCESS CATEGORY	PROCESSES INCLUDED	WEIGHTING FACTOR
Crude	desalting atmospheric distillation vacuum distillation	1
Cracking and Coking	fluid catalytic cracking thermoform houdrifiow gas-oil cracking visbreaking fluid coking delayed coking	6
Lube	lube hydrofining white oil manufacturing propane - dewaxing, deasphalting duo sol, solvent dewaxing lube vac. tower, wax fract. centrifuging and chilling MEK dewaxing deoiling (wax) naphthenic lubes SO2 extraction wax pressing wax plant (with neutral separ.) furfural extraction clay contacting - percolation wax sweating acid treating phenol extraction	13
Asphalt	asphalt production asphalt oxidation asphalt emulsifying	12

TABLE III
EFFLUENT GUIDELINES
PETROLEUM REFINING POINT SOURCE CATEGORY
NEW SOURCE PERFORMANCE STANDARDS (NSPS)

Process Factors By Subcategory:					
	Topping:	Cracking:	Petrochemical:	Lube:	Integrated:
Process Configuration	Process Factor	Process Factor	Process Factor	Process Factor	Process Factor
Less than 2.49	0.62	0.58	0.73	0.81	0.75
2.5 to 3.49	0.67	0.63	0.73	0.81	0.75
3.5 to 4.49	0.80	0.74	0.73	0.81	0.75
4.5 to 5.49	0.95	0.88	0.80	0.81	0.75
5.5 to 5.99	1.07	1.00	0.91	0.81	0.75
6.0 to 6.49	1.17	1.09	0.99	0.81	0.75
6.5 to 6.99	1.27	1.19	1.08	0.88	0.82
7.0 to 7.49	1.39	1.29	1.17	0.88	0.82
7.5 to 7.99	1.51	1.41	1.28	1.00	0.92
8.0 to 8.49	1.64	1.53	1.39	1.09	1.00
8.5 to 8.99	1.79	1.67	1.51	1.19	1.10
9.0 to 9.49	1.95	1.82	1.65	1.29	1.20
9.5 to 9.99	2.12	1.89	1.72	1.41	1.30
10.0 to 10.49	2.31	1.89	1.72	1.53	1.42
10.5 to 10.99	2.51	1.89	1.72	1.67	1.54
11.0 to 11.49	2.73	1.89	1.72	1.82	1.68
11.5 to 11.99	2.98	1.89	1.72	1.98	1.83
12.0 to 12.49	3.24	1.89	1.72	2.15	1.99
12.5 to 12.99	3.53	1.89	1.72	2.34	2.17
13.0 to 13.49	3.84	1.89	1.72	2.44	2.26
13.5 to 13.99	4.18	1.89	1.72	2.44	2.26
14.0 or greater	4.36	1.89	1.72	2.44	2.26

COLLECTION SYSTEM (WASTEWATERS)

Definitions

Sewer Types

Sewer Pipe Material

Design Layout

Design Hydraulics

Hydraulics Problem

Definitions

Sewer

Junction Box

Catch Basin

Drain Funnel

Main Sewer Header

Lateral

Invert

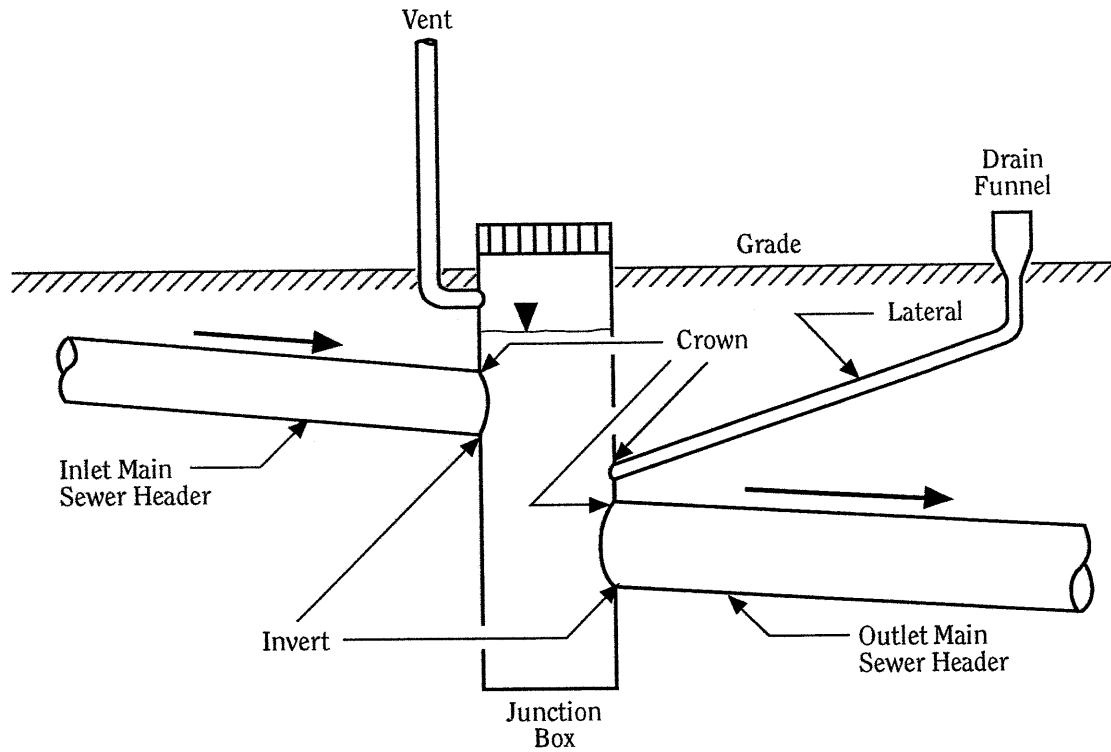
Crown

Control Device

See UOP Standard Spec. 8-17 "Sewers and Drainage".

Figure 6

Definition Graphics



EDS-ROO-4006

Sewer Types

Sewer Type	Source of Wastewater	Typical Destination
Sanitary	Lavatories, toilets, showers, kitchen facilities	Onsite septic system Onsite sanitary treatment plant
Process Area		
Separate Oily Process Water	Pumps, compressors, vessels, HC tanks, cooling tower blow-down	Oil-water separator
Oily Surface Water	Surface water run-off from rain, fire fighting, cleanup/washdown operations	Oil-water separator/Storm water pond
Combined Oily Water	Oily process plus oily surface water	Storm water pond
Clean Water	Roadways, parking lots, vacant land, building roofs and areas, outside tank dike areas, LPG storage/loading areas, water tank drains and overflows	Natural drainage Clean water reservoir
Chemical	Designated chemical waste requiring special handling	Underground storage tanks system or above-grade collection system
Acid	Surface drainage with contaminants, acid pumps, vessel drains, etc.	Neutralization pit

Sewer Pipe Material

Advantages/Disadvantages

Sewer Pipe Material	Advantages	Disadvantages
Carbon Steel	Availability Long laying lengths	Poor soil corrosive resistance Cost
Cast/Ductile Iron	High internal/external strength	Poor corrosive resistance to acid, some soils
Concrete	Cost Ease of strength that can be provided Wide size range	No acid/H ₂ S resistance (requires increased wall special concrete, coating/lining)
Clay	Good acid/alkali corrosive resistance Good resistance to scour	Brittle tendency Limited sizes/strength
Plastics (PVC)	Lightweight Good corrosive resistance	Availability Not very heat resistant

UOP ENGINEERING DESIGN SEMINAR
WASTE DISPOSAL

ANSWER TO EFFLUENT GUIDELINES PROBLEM

1. FIRST CALCULATE THE PROCESS CONFIGURATION FOR THE REFINERY:

PROCESS	PROCESS CAPACITY (1000 BBL/DAY)	CAPACITY OF PROCESS IN RELATION TO REFINERY THROUGHPUT	PROCESS WEIGHTING FACTOR	PROCESS CONFIGURATION FACTOR
CRUDE - ATM. VACUUM DESALTING	125 60 125	1.0 0.480 1.0		
		2.480	X	1
				= 2.48
CRACKING-FCC HYDROCRACKING	41 20	.328 .160		
		.488	X	6
				= 2.93
LUBES HYDROFINING FURFURAL EXTRACTION PHENOL EXTRACTION	5.30 4 4	.042 .032 .032		
		.106	X	13
				= 1.38
ASPHALT	4	.032	X	12
				= 0.38
PROCESS CONFIGURATION FACTOR			=	7.17

2.. SECOND, LOOK UP ALLOWABLE MASS LOADINGS IN THE TABLE FOR NEW SOURCE PERFORMANCE STANDARDS SINCE IT IS A NEW REFINERY. LOADS PER 1000 M3 FEEDSTOCK ARE:

- a) MAXIMUM KG/DAY OF SUSPENDED SOLIDS = 23.4 (TABLE IB)
b) MAXIMUM AVERAGE OF DAILY OIL & GREASE KG VALUES FOR 30 CONSECUTIVE DAYS = 5.6 "

3. THIRD, CALCULATE EFFLUENT VALUES USING APPROPRIATE FACTORS FROM EFFLUENT GUIDELINES FOR PETROLEUM REFINING POINT SOURCE CATEGORY, NEW SOURCE PERFORMANCE STANDARDS:

$$\text{M3 FEEDSTOCK} = 125,000 \text{ BBLs} \times (0.159 \text{ M3/BBL}) = 19,875 \text{ M3}$$

$$\begin{aligned} \text{a) MAX. TSS/ DAY} &= \text{EFFLUENT LIMITATION (TABLE IB)} \times \text{PROCESS SIZE FACTOR (TABLE II)} \times \text{PROCESS FACTOR (TABLE III)} \\ &= (23.4)(19.875) \times 0.97 \times 0.88 \\ &= \underline{397 \text{ KG/DAY}} \end{aligned}$$

$$\text{b) MAX. AVG. O&G/DAY (OVER 30 DAYS)} = (5.6)(19.875) \times 0.97 \times 0.88 = \underline{95 \text{ KG/DAY}}$$

Sewer Pipe Material Costs – (1991)

\$/ft

Pipe Material	Pipe Size 6 inches			Pipe Size 12 inches		
	Material	Installation*	Total	Material	Installation*	Total
PVX-SDR 35 (Bell/PE)	1.58	4.16	5.74	5.02	2.78	7.80
Vitrified Clay (Bell/PE)	2.97	5.62	8.59	10.24	5.90	16.14
Non-Reinforced Concrete	3.14	6.75	9.89	6.81	5.15	11.96
Ductile Iron (Mechanical Joint)	7.15	7.59	14.74	16.54	12.70	29.24
Cast Iron (Bell and Spigot)	7.23	9.54	16.77	29.57	15.20	44.77
Carbon Steel (Coat and wrap)	22.00	12.39	34.39	57.24	20.30	77.54
FRP (Epoxy resin)	14.30	12.99	27.29	54.24	19.10	73.34
*Installation includes: back-hoe digging a 2 feet wide by 3 feet deep trench (0 to 1 slope), making up and setting pipe, back-fill and compaction. For setting pipe in a sand bedding, add \$0.53/foot for 6 inches and \$1.23 for 12 inch sizes.						
All costs are in U. S. dollars – no extras are included for overhead and profit.						

Design Layout

Design Considerations

Topography

Wastewater Source/Destination Locations

Interferences (Especially Below-Grade)

Segregated or Combined Streams

Emission Control

Groundwater Protection

Typical Sewer Routing (Drawing C36399-D)

Typical Collection Components

Emission Control Summary

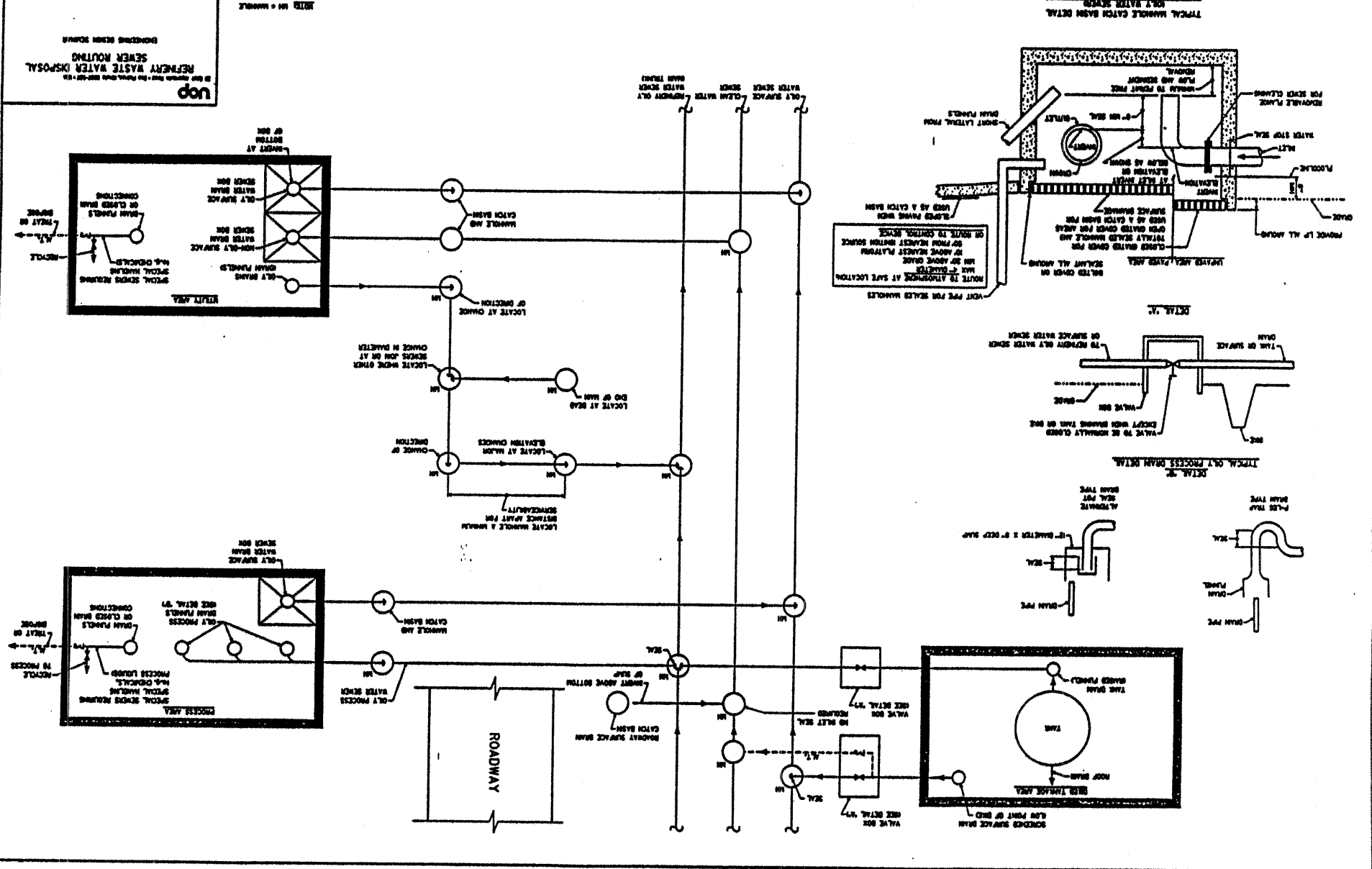
Groundwater Protection

Typical Collection Components

Individual Drains

Sewers

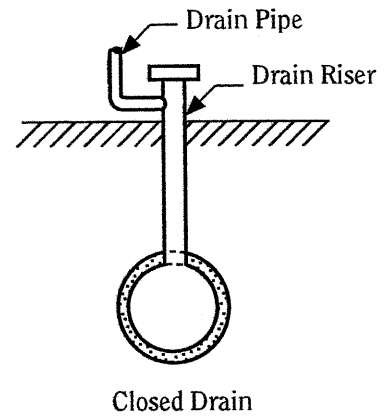
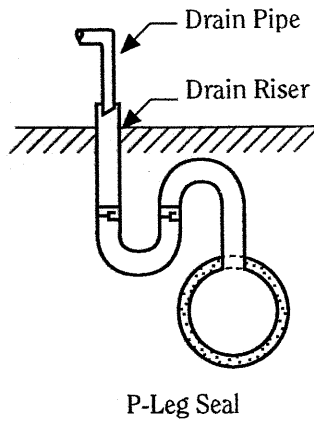
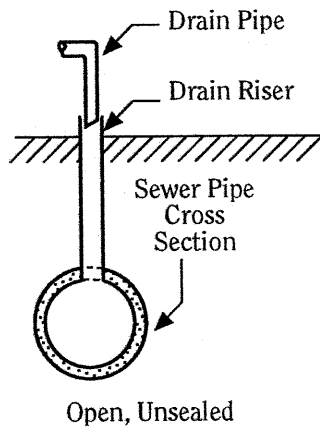
Junction Boxes (also manholes, catch basins)



Figure

Figure 8

Individual Drains



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