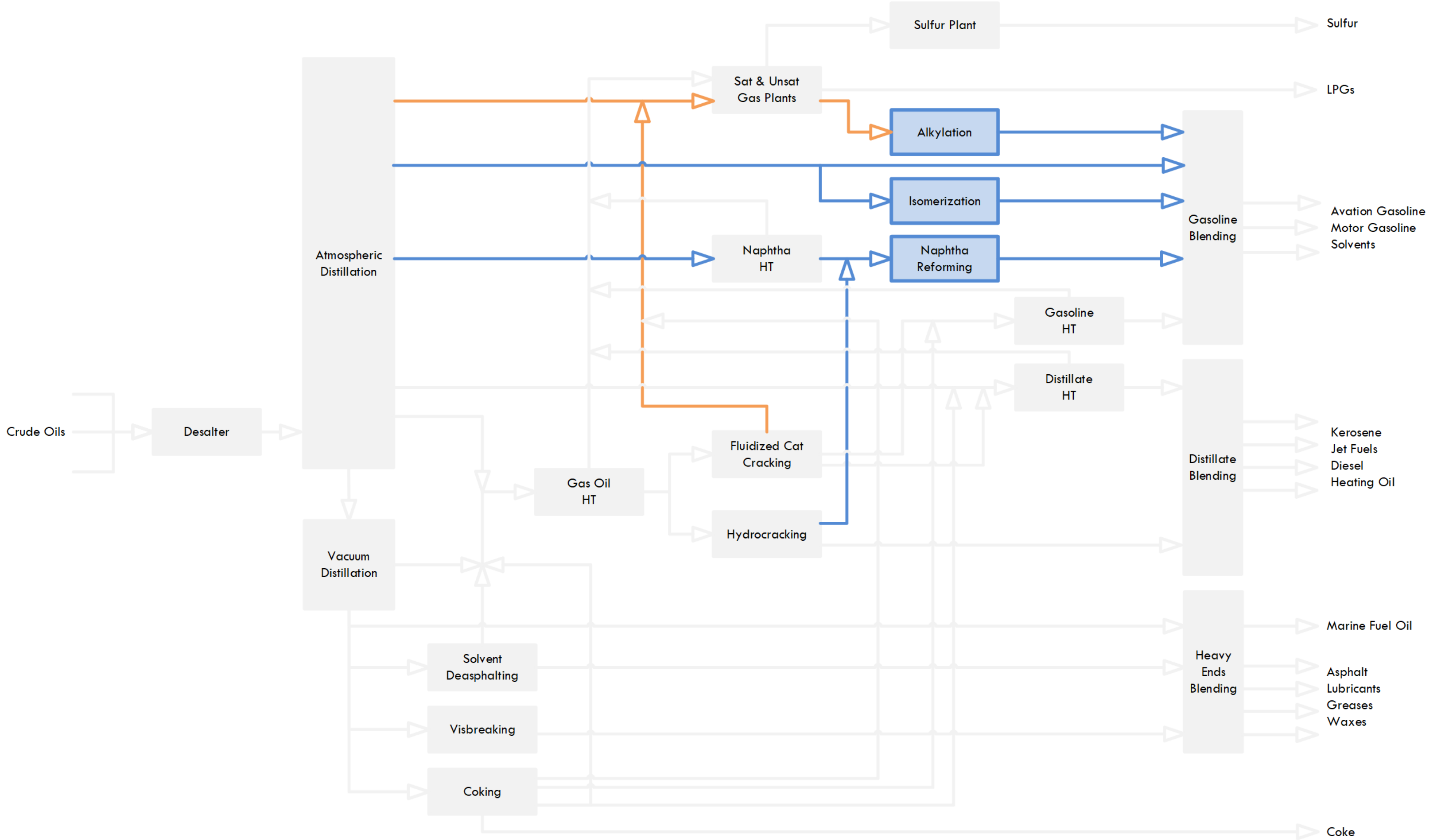
Gasoline Upgrading: Reforming, Isomerization, & Alkylation

Chapters 10 & 11

COLORADO SCHOOL OF MINES

Petroleum Refinery Block Flow Diagram



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Gasoline Upgrading

Purpose

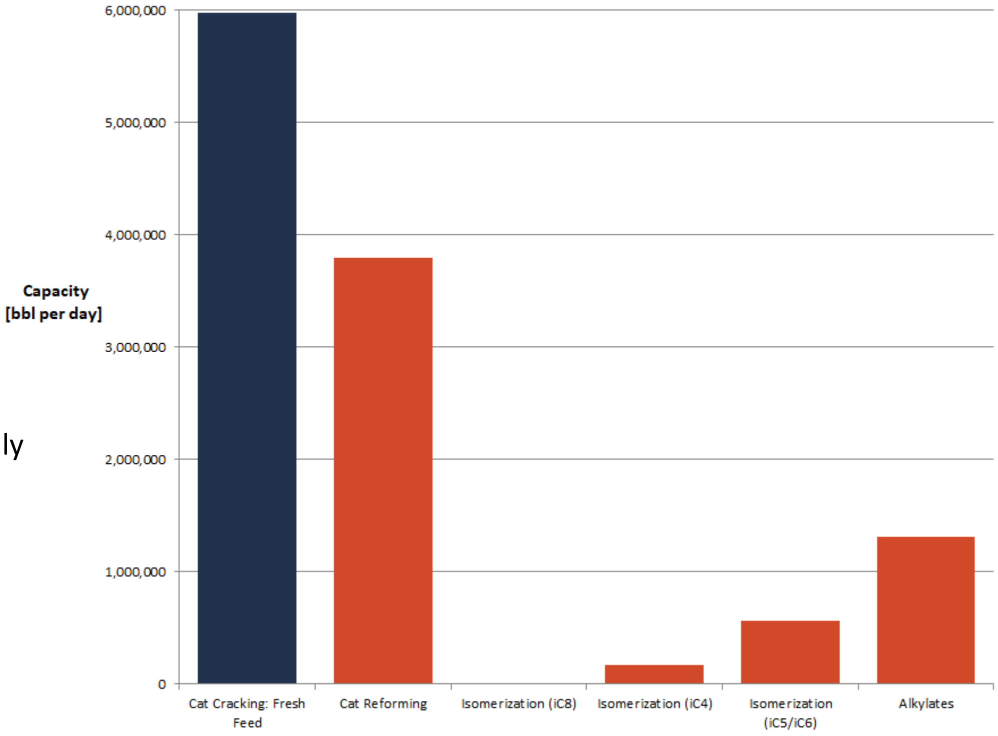
- Increase the quality of feed stocks of the same boiling range as gasoline

Characteristics

- Catalytic Reforming
  - Converts naphthenes to aromatics
  - Produces hydrogen
- Isomerization
  - Re-arranges straight chains to branched isomers
  - Very little change in boiling points
- Alkylation
  - Use olefins produced in other processes (primarily FCCU)
  - Produce isooctane
  - Liquid acid catalyst

Products

- Gasoline blend stocks of improved octane and/or volatility



EIA, Jan. 1, 2019 database, published June 2019
http://www.eia.gov/petroleum/refinerycapacity/

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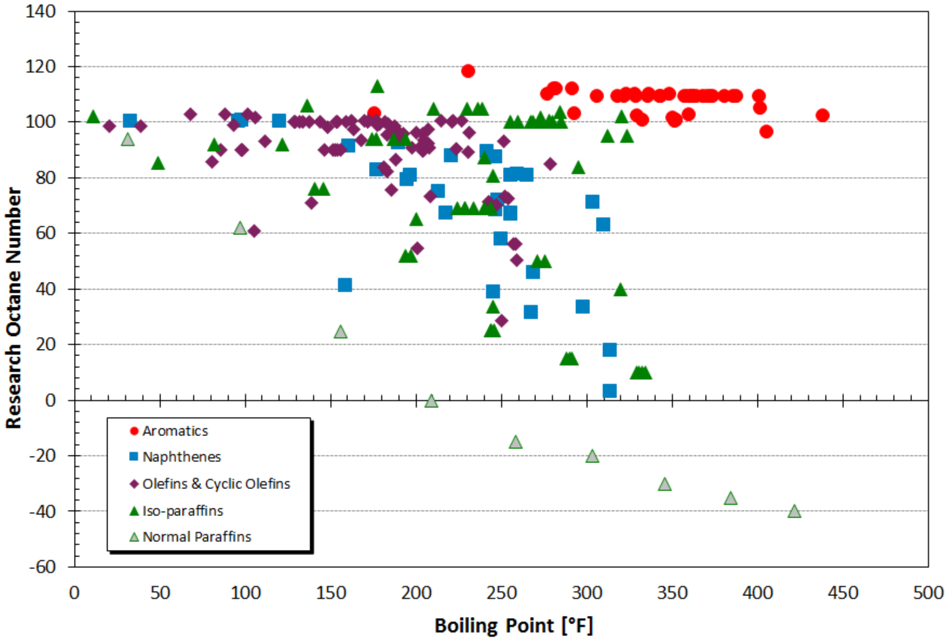
Dependency of Octane on Chemical Structure

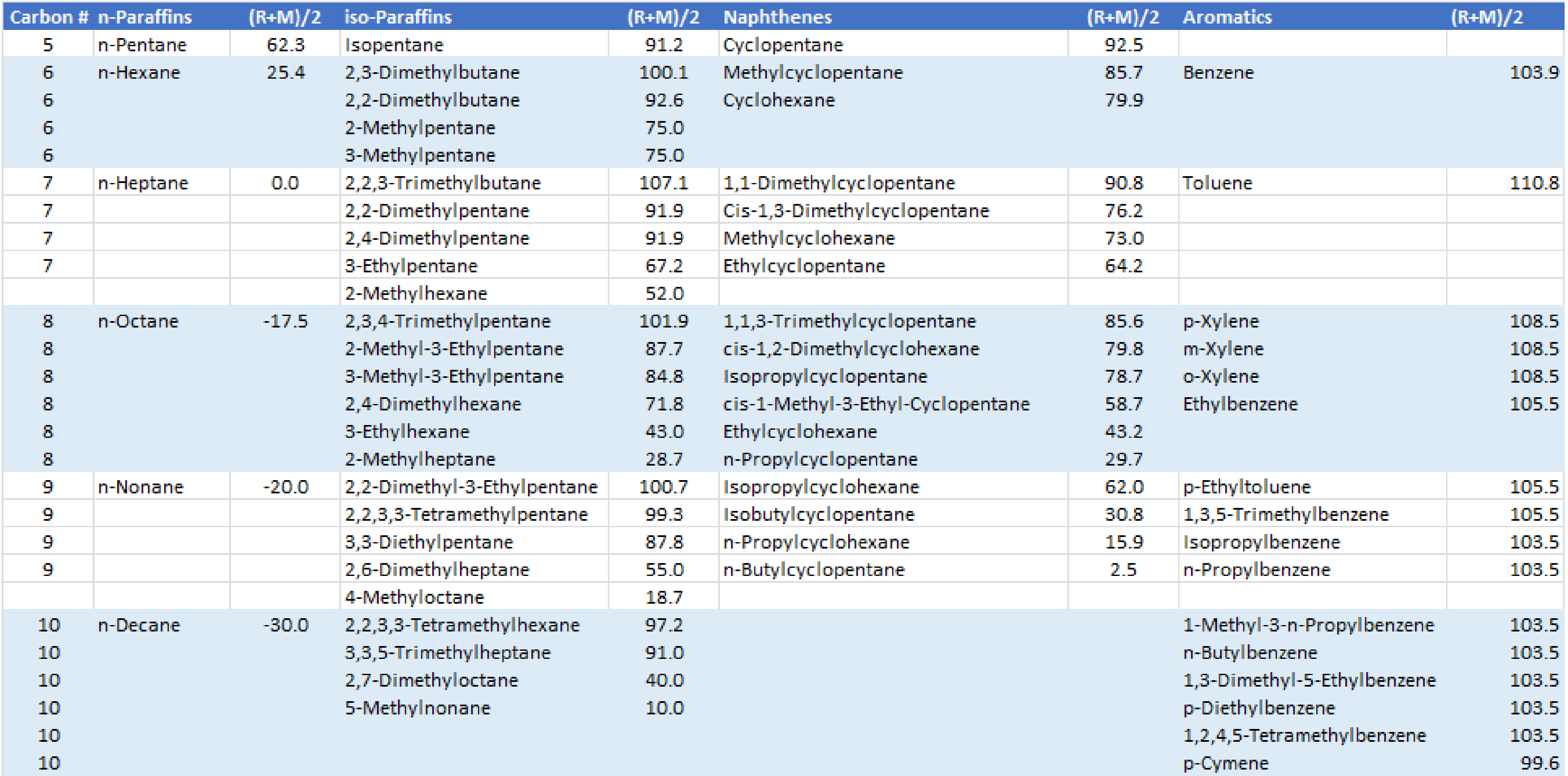
	RON	MON
Paraffins		
n-butane	94	89.6
isobutane	102	97.6
n-pentane	62	62.6
i-pentane	92	90.3
n-hexane	24.8	26
C6 monomethyls	76	73.9
2,2-dimethylbutane	91.8	93.4
2,3-dimethylbutane	105.8	94.3
n-heptane	0	0
C7 monomethyls	52	52
C7 dimethyls	93.76	90
2,2,3-trimethylbutane	112.8	101.32
n-octane	-15	-20
C8 monomethyls	25	32.3
C8 dimethyls	69	74.5
C8 trimethyls	105	98.8
n-nonane	-20	-20
C9 monomethyls	15	22.3
C9 dimethyls	50	60
C9 trimethyls	100	93
n-decane	-30	-30
C10 monomethyls	10	10
C10 dimethyls	40	40
C10 trimethyls	95	87
n-undecane	-35	-35
C11 monomethyl	5	5
C11 dimethyls	35	35
C11 trimethyls	90	82
n-dodecane	-40	-40
C12 monomethyl	5	5
C12 dimethyls	30	30
C12 trimethyls	85	80

	RON	MON
Naphthenes		
cyclopentane	100	84.9
cyclohexane	82.5	77.2
m-cyclopentane	91.3	80
C7 naphthenes	82	77
C8 naphthenes	55	50
C9 naphthenes	35	30
Aromatics		
benzene	102.7	105
toluene	118	103.5
C8 aromatics	112	105
C9 aromatics	110	101
C10 aromatics	109	98
C11 aromatics	105	94
C12 aromatics	102	90
Olefins/Cyclic Olefins		
n-butenes	98.7	82.1
n-pentenes	90	77.2
i-pentenes	103	82
cyclopentene	93.3	69.7
n-hexenes	90	80
i-hexenes	100	83
Total C6 cyclic olefins	95	80
total C7d	90	78
total C8d	90	77
Oxygenates		
MTBE	115.2	97.2
TAME	115	98
EtOH	108	92.9



"Development of a Detailed Gasoline Composition-Based Octane Model"
Prasenjeet Ghosh, Karlton J. Hickey, and Stephen B. Jaffe
Ind. Eng. Chem. Res. 2006, 45, 337-345

Dependency of Octane on Chemical Structure



Carbon #	n-Paraffins	(R+M)/2	iso-Paraffins	(R+M)/2	Naphthenes	(R+M)/2	Aromatics	(R+M)/2
5	n-Pentane	62.3	Isopentane	91.2	Cyclopentane	92.5		
6	n-Hexane	25.4	2,3-Dimethylbutane	100.1	Methylcyclopentane	85.7	Benzene	103.9
6			2,2-Dimethylbutane	92.6	Cyclohexane	79.9		
6			2-Methylpentane	75.0				
6			3-Methylpentane	75.0				
7	n-Heptane	0.0	2,2,3-Trimethylbutane	107.1	1,1-Dimethylcyclopentane	90.8	Toluene	110.8
7			2,2-Dimethylpentane	91.9	Cis-1,3-Dimethylcyclopentane	76.2		
7			2,4-Dimethylpentane	91.9	Methylcyclohexane	73.0		
7			3-Ethylpentane	67.2	Ethylcyclopentane	64.2		
			2-Methylhexane	52.0				
8	n-Octane	-17.5	2,3,4-Trimethylpentane	101.9	1,1,3-Trimethylcyclopentane	85.6	p-Xylene	108.5
8			2-Methyl-3-Ethylpentane	87.7	cis-1,2-Dimethylcyclohexane	79.8	m-Xylene	108.5
8			3-Methyl-3-Ethylpentane	84.8	Isopropylcyclopentane	78.7	o-Xylene	108.5
8			2,4-Dimethylhexane	71.8	cis-1-Methyl-3-Ethyl-Cyclopentane	58.7	Ethylbenzene	105.5
8			3-Ethylhexane	43.0	Ethylcyclohexane	43.2		
8			2-Methylheptane	28.7	n-Propylcyclopentane	29.7		
9	n-Nonane	-20.0	2,2-Dimethyl-3-Ethylpentane	100.7	Isopropylcyclohexane	62.0	p-Ethyltoluene	105.5
9			2,2,3,3-Tetramethylpentane	99.3	Isobutylcyclopentane	30.8	1,3,5-Trimethylbenzene	105.5
9			3,3-Diethylpentane	87.8	n-Propylcyclohexane	15.9	Isopropylbenzene	103.5
9			2,6-Dimethylheptane	55.0	n-Butylcyclopentane	2.5	n-Propylbenzene	103.5
			4-Methyloctane	18.7				
10	n-Decane	-30.0	2,2,3,3-Tetramethylhexane	97.2			1-Methyl-3-n-Propylbenzene	103.5
10			3,3,5-Trimethylheptane	91.0			n-Butylbenzene	103.5
10			2,7-Dimethyloctane	40.0			1,3-Dimethyl-5-Ethylbenzene	103.5
10			5-Methylnonane	10.0			p-Diethylbenzene	103.5
10							1,2,4,5-Tetramethylbenzene	103.5
10							p-Cymene	99.6

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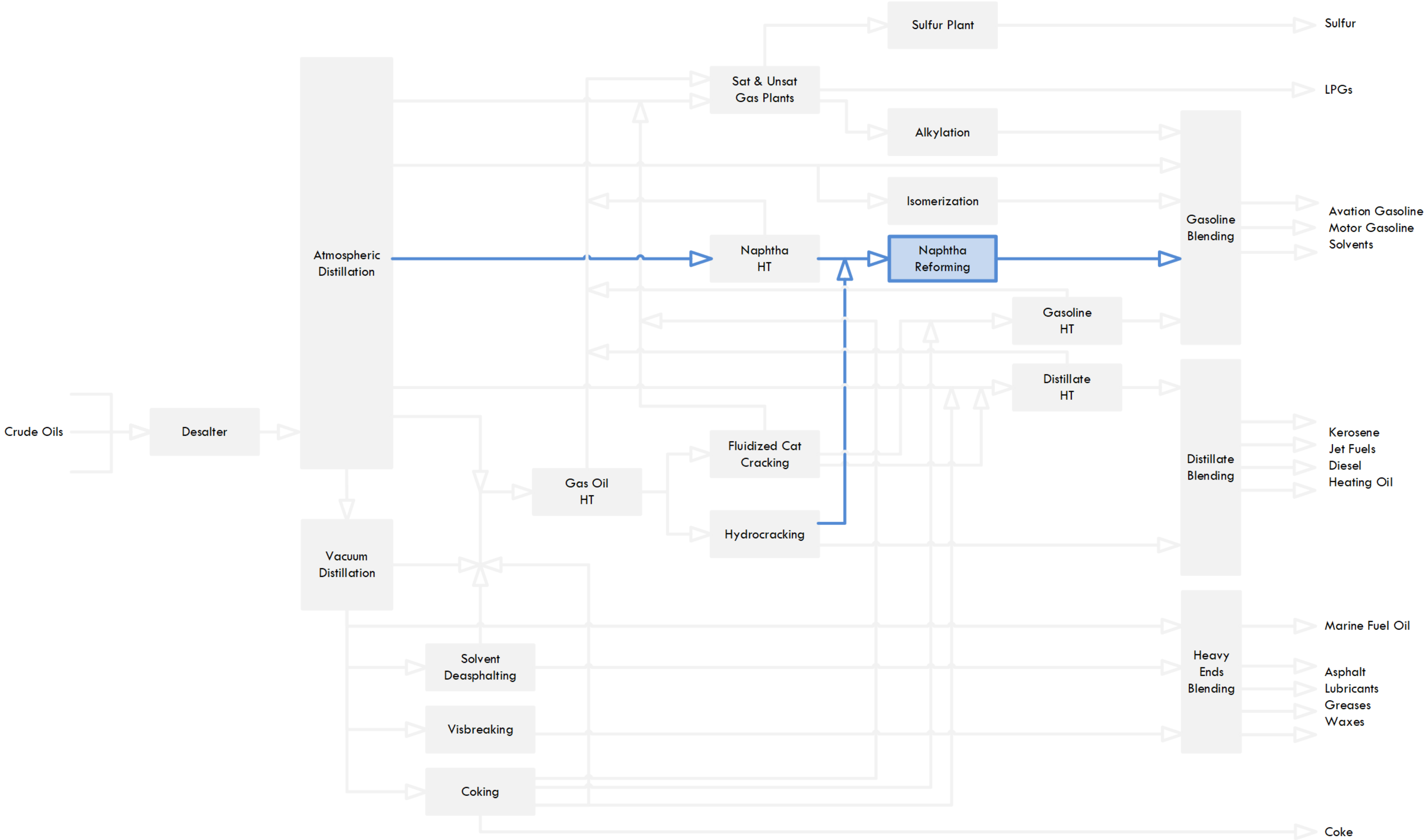
Naphtha Reforming



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Naphtha Reforming

Almost every refinery in the world has a reformer

Purpose to enhance aromatic content of naphtha

- Feed stocks to aromatics complex
- Improve the octane rating for gasoline

Many different commercial catalytic reforming processes

- Hydroforming
- Platforming
- Powerforming
- Ultraforming
- Thermofor catalytic reforming

Primary reactions

- Dehydrogenation
  - naphthenes → aromatics
- Isomerization
  - normal paraffins → branched isoparaffins
- Hydrogen as by-product
  - Ultimately used in hydrotreating
  - Catalytic reforming 2nd to FCC in commercial importance to refiners

Reformate desirable component for gasoline

- High octane number, low vapor pressure, very low sulfur levels, & low olefins concentration
- US regulations on levels of benzene, aromatics, & olefins
  - Air quality concerns

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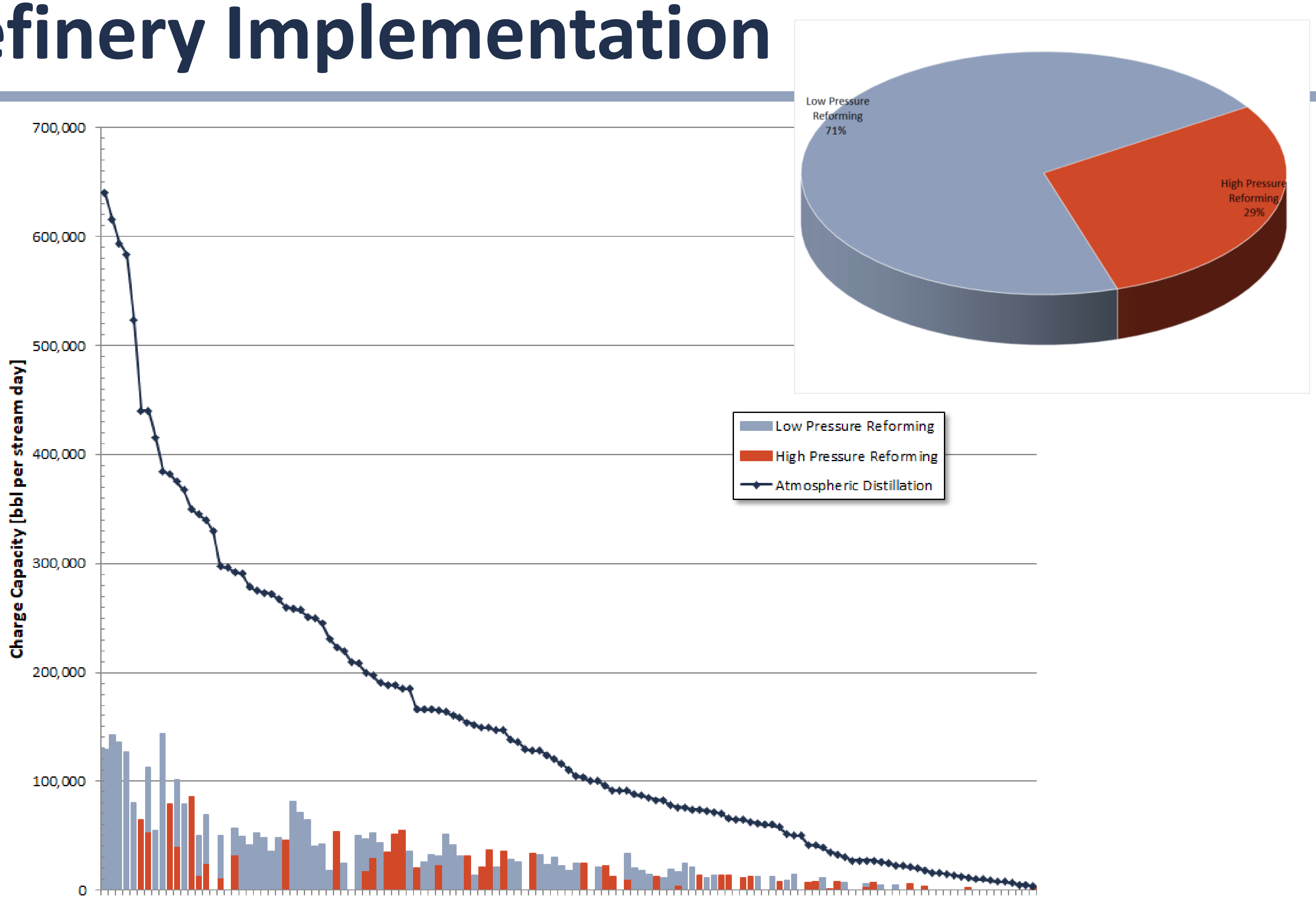
U.S. Refinery Implementation



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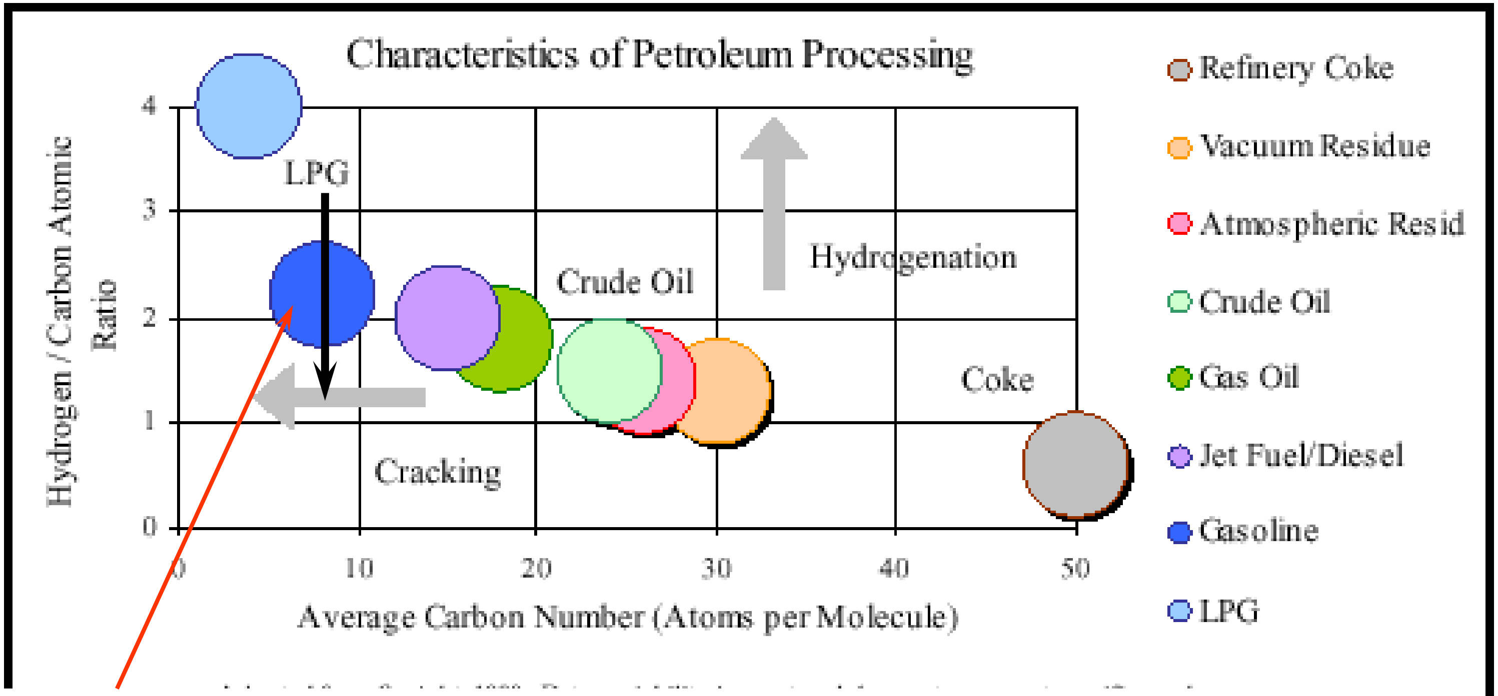
Characteristics of Petroleum Products



Reforming: drive off hydrogen for better gasoline properties w/o changing size

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Feedstocks & Products

Hydrotreated heavy naphtha feedstock

- Light straight run naphtha tends to crack to butanes & lighter
- Gas oil streams tend to hydrocrack & deposit coke on the reforming catalyst

Catalyst is noble metal (e.g. platinum) – very sensitive to sulfur & nitrogen

- Feed stocks hydrotreated for sulfur & nitrogen removal
- Control of chloride & water also important

Severity

- High severity used to maximize aromatics
  - Sent to BTX separation for aromatic feedstocks
- Low severity used for gasoline blend stocks

Produces the majority of the hydrogen used for hydrotreating

Reforming Chemistry

Uses a solid catalyst to convert naphthenes to the corresponding aromatics & isomerize paraffinic structures to isomeric forms

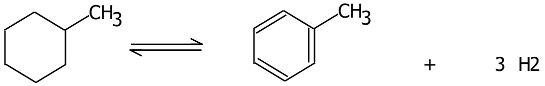
- Both reactions lead to a marked increase in octane number
- Both reactions lead to volume shrinkage

Correlations permit the use of a PONA analysis of the feed for prediction of yield and quality of the product

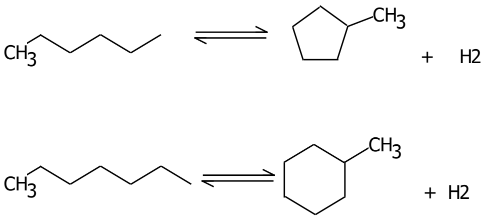
- Originally feed qualities measured in terms of Watson "K" Factor — a rough indication of amount of paraffins

Aromatics largely untouched by reactions

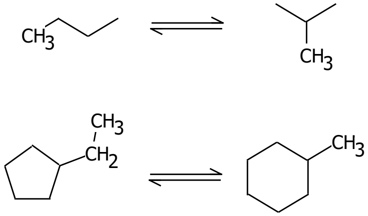
Dehydrogenation



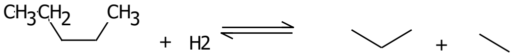
Dehydrocyclization



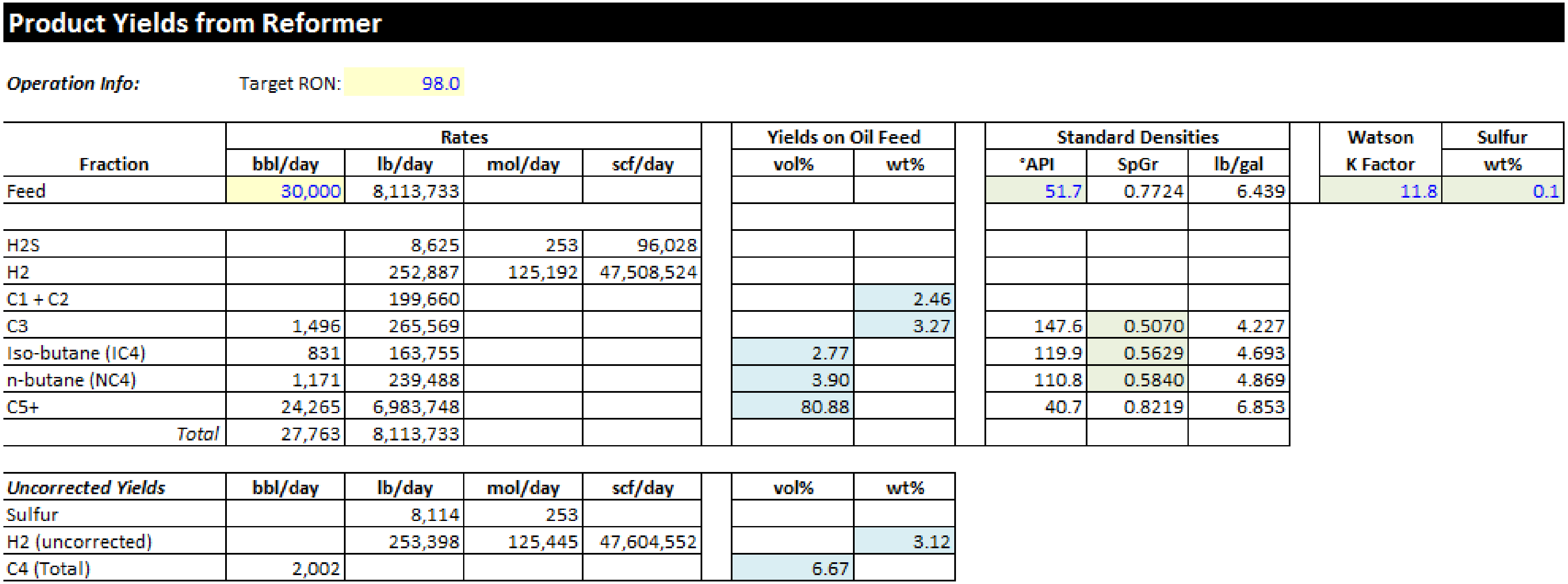
Isomerization



Hydrocracking



Reformer Yield Example



Product Yields from Reformer

Operation Info: Target RON: 98.0

	Rates				Yields on Oil Feed		Standard Densities			Watson	Sulfur
Fraction	**bbl/day**	**lb/day**	**mol/day**	**scf/day**	**vol%**	**wt%**	**°API**	**SpGr**	**lb/gal**	**K Factor**	**wt%**
Feed	30,000	8,113,733					51.7	0.7724	6.439	11.8	0.1
H2S		8,625	253	96,028							
H2		252,887	125,192	47,508,524							
C1 + C2		199,660				2.46					
C3	1,496	265,569				3.27	147.6	0.5070	4.227		
Iso-butane (IC4)	831	163,755			2.77		119.9	0.5629	4.693		
n-butane (NC4)	1,171	239,488			3.90		110.8	0.5840	4.869		
C5+	24,265	6,983,748			80.88		40.7	0.8219	6.853		
Total	27,763	8,113,733									

Uncorrected Yields	**bbl/day**	**lb/day**	**mol/day**	**scf/day**	**vol%**	**wt%**
Sulfur		8,114	253			
H2 (uncorrected)		253,398	125,445	47,604,552		3.12
C4 (Total)	2,002				6.67	

Reformer Yield Trends

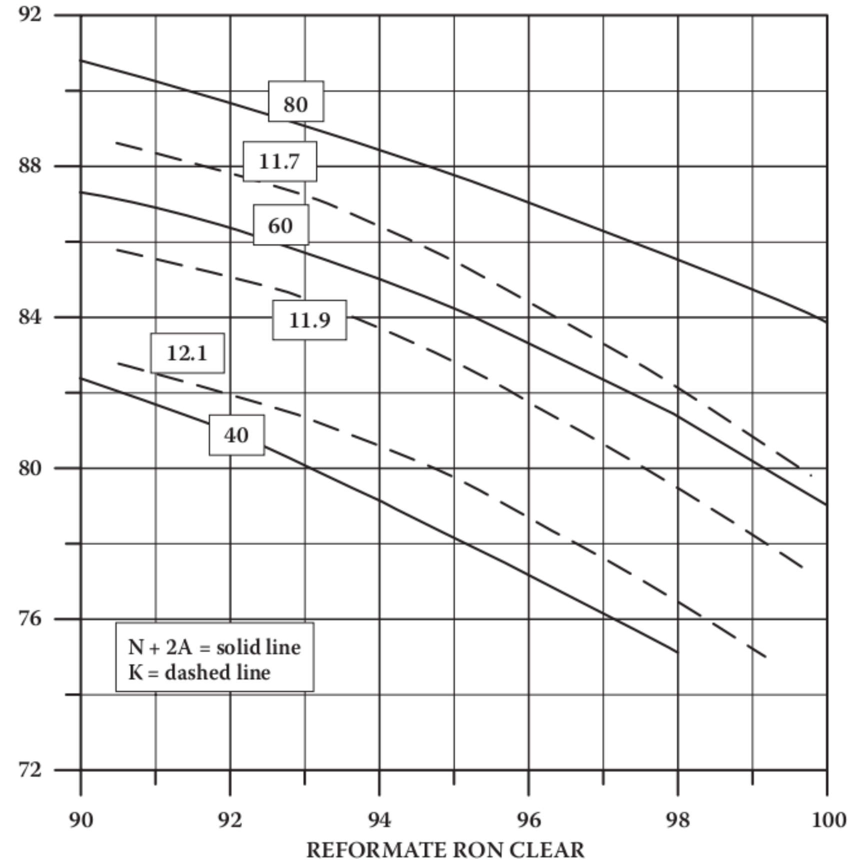


FIGURE 10.4 Catalytic reforming yield correlations.

Note: Y-axis is C5+ gasoline yield

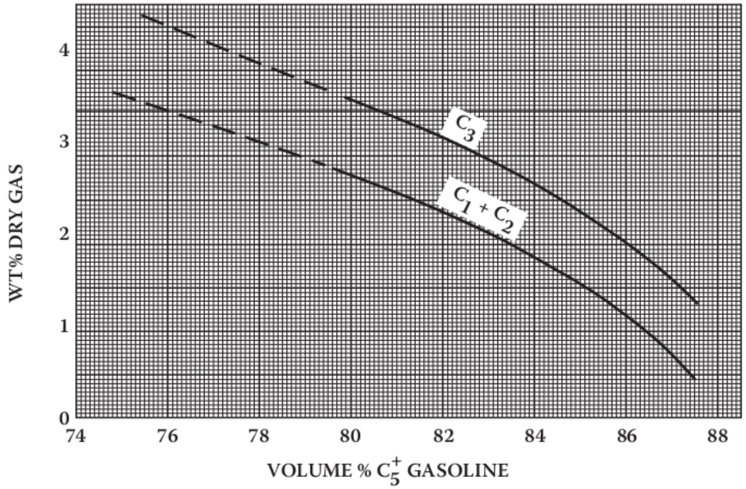


FIGURE 10.6 Catalytic reforming yield correlations.

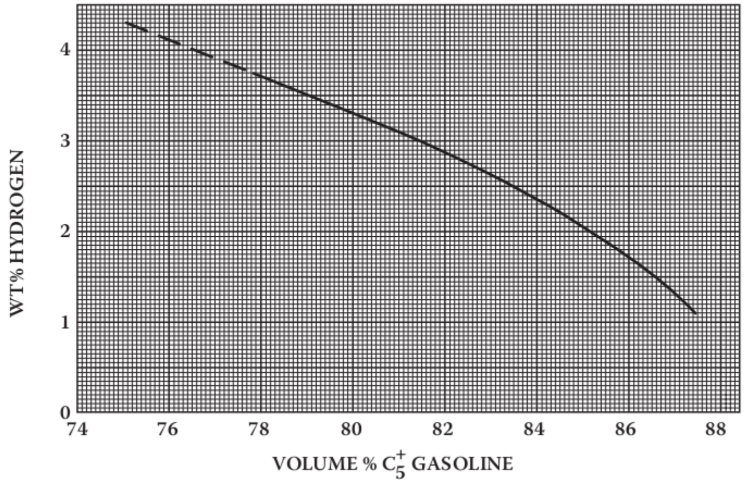
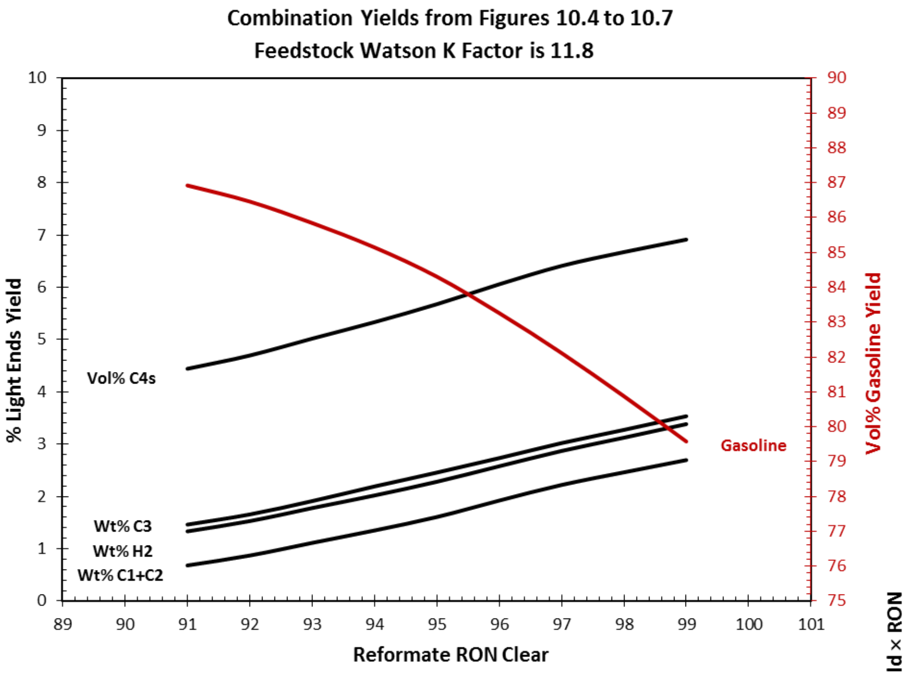
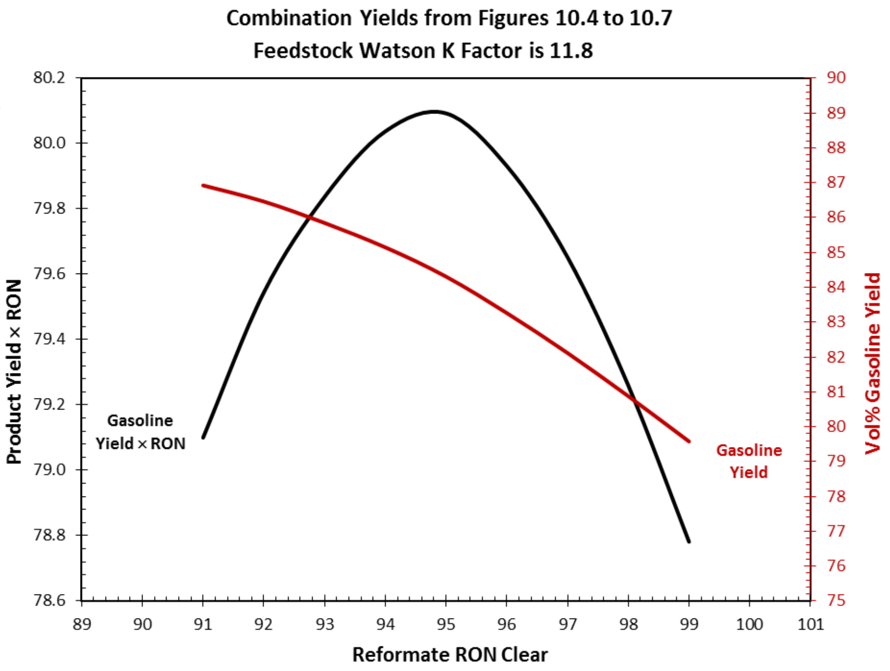


FIGURE 10.7 Catalytic reforming yield correlations.

Combined Production Trends





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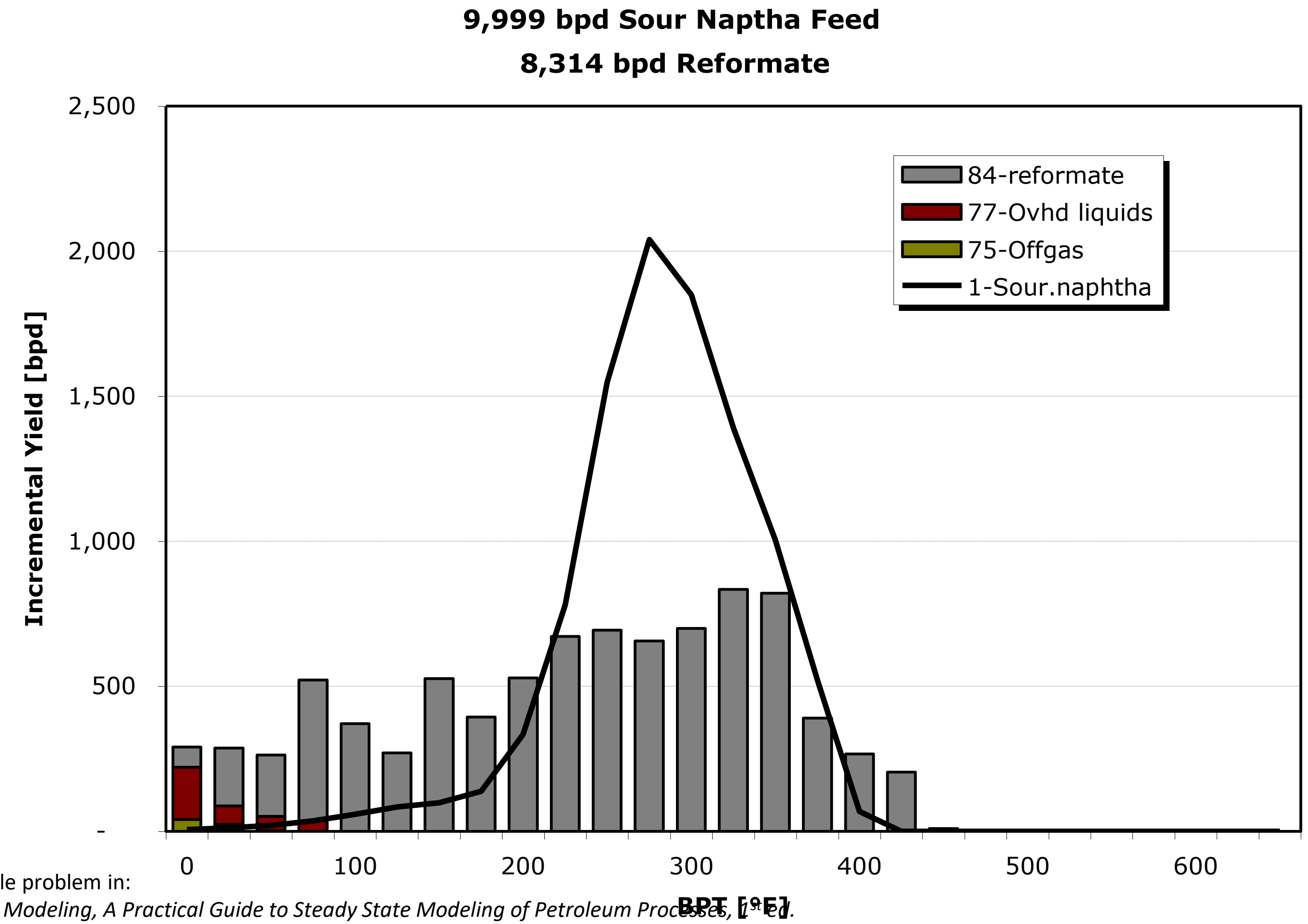
Boiling Point Ranges for Products


9,999 bpd Sour Naptha Feed

8,314 bpd Reformate

Based on example problem in:
Refinery Process Modeling, A Practical Guide to Steady State Modeling of Petroleum Processes, 1st ed.
Gerald Kaes, Athens Printing Company, 02004

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Effects of Process Variables

Primary control for changing conditions or qualities is reactor temperature

- Normally about 950°F at reactor inlet
- May be raised for declining catalyst activity or to compensate for lower quality feedstock
- Higher reactor temperature increases octane rating but reduces yield & run length

Design considerations for improvement in quality will include pressure, recycle ratio, reactor residence time, & catalyst activity

- Low reactor pressure increases yield & octane but increases coke make
- Increased hydrogen partial pressure due to hydrogen recycle (hydrogen to hydrocarbon ratio) suppresses coke formation, hydrogen yield & octane gain, but promotes hydrocracking
- Low space velocity favors aromatics formation but also promotes cracking by operating closer to equilibrium conditions
- Higher activity catalysts cost more but increases run lengths and/or yields

Specific Catalytic Reforming Processes

Hydroforming

- Early cyclic process used to produce toluene for TNT during World War II
- Molybdenum oxide on alumina catalyst
- Rapid coking of the catalyst, requiring a cyclic regeneration of reactors about every four hours
  - Timing mechanism used for lawn sprinkler systems used to switch from reforming to regeneration service
  - Reactor system included one extra "swing" reactor
    - Facilitate periodic removal & regeneration of a reactor

UOP Semi-Regenerative Platforming

- Low platinum
- Regeneration once a year
- Made naphtha octane improvement accessible to all refiners

UOP Continuous Regeneration of Reforming Catalyst

- Moving bed process
  - Continuously regenerating a portion of a moving bed of catalyst to remove coke & sustain activity
  - Operating pressures lowered to 50 psig
- Three reactors stacked one on top of the other
  - Gravity flow of the catalyst from top to bottom
  - Reactants pass radially through the catalyst to the inner conduit and then to the next bed
  - Mode of regeneration is proprietary – probably employs air or oxygen burning of the coke followed by reduction & acidification

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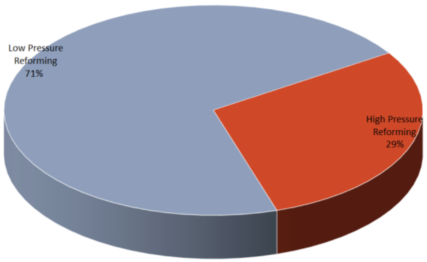
High Pressure Reforming – Semi-Regen



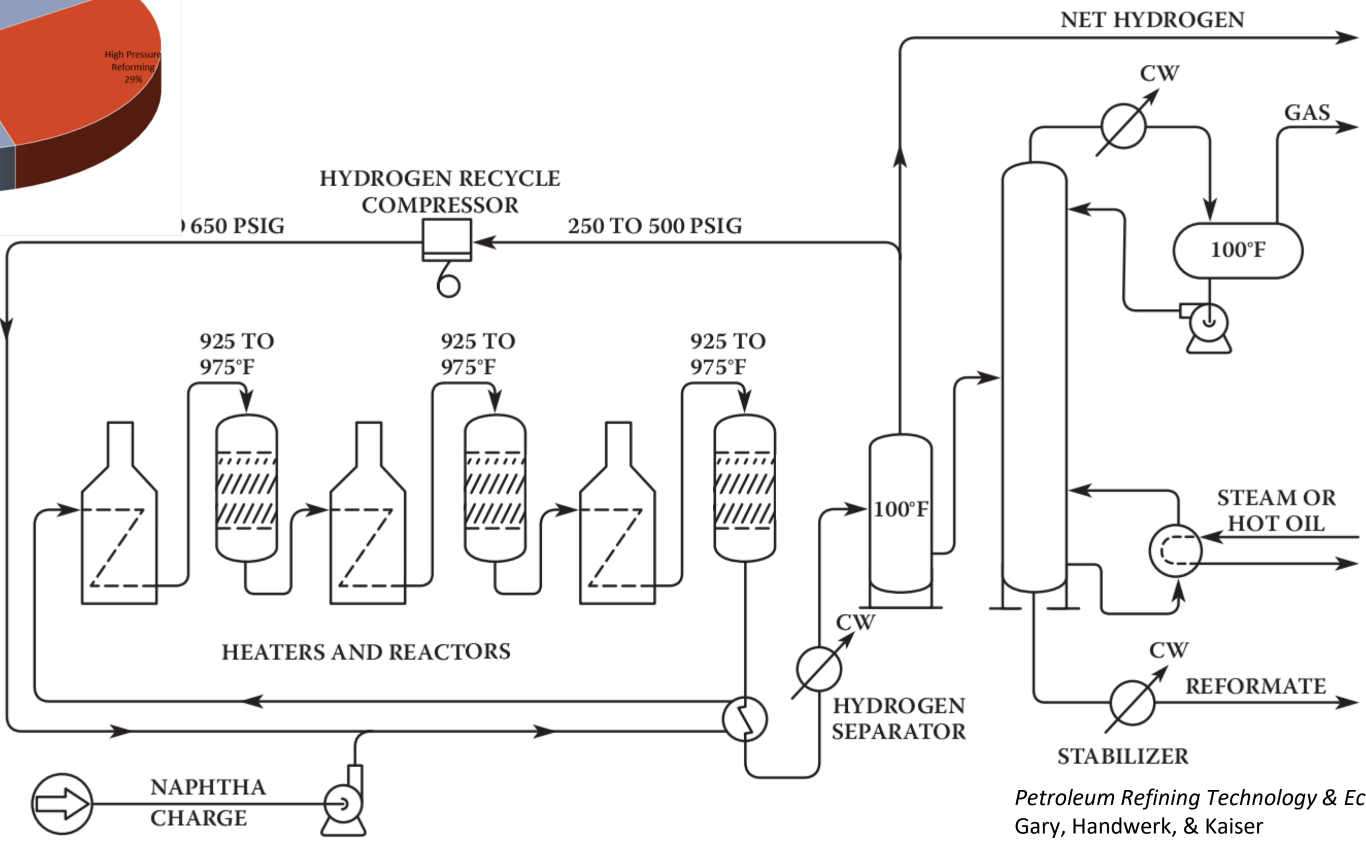


FIGURE 10.1 Catalytic reforming, semiregenerative process.

Petroleum Refining Technology & Economics, 5th ed.
Gary, Handwerk, & Kaiser
CRC Press, 2007

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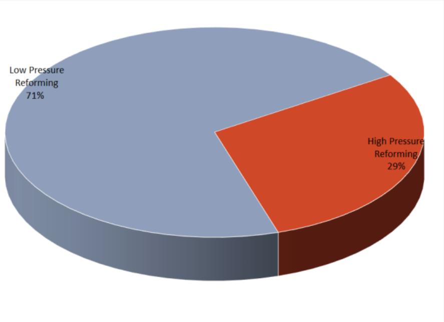
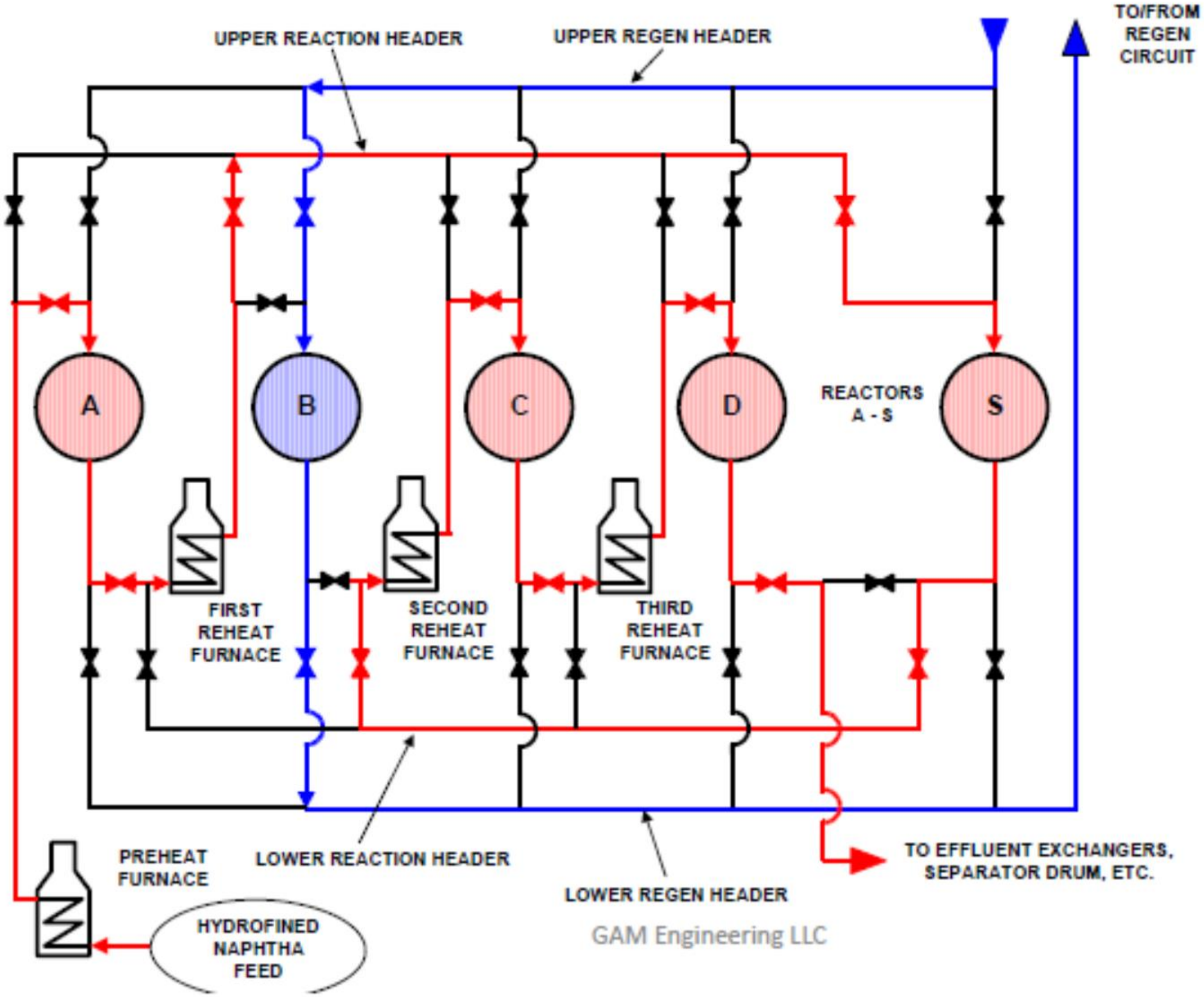
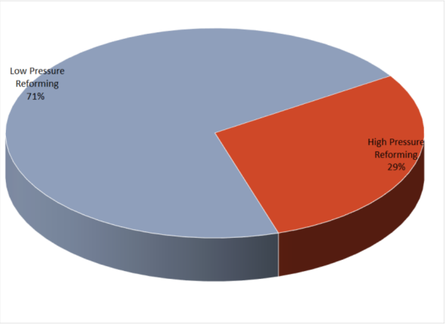
High Pressure Reforming – Semi-Regen

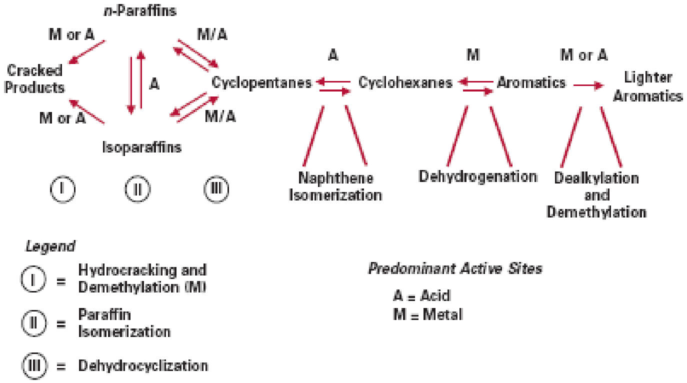


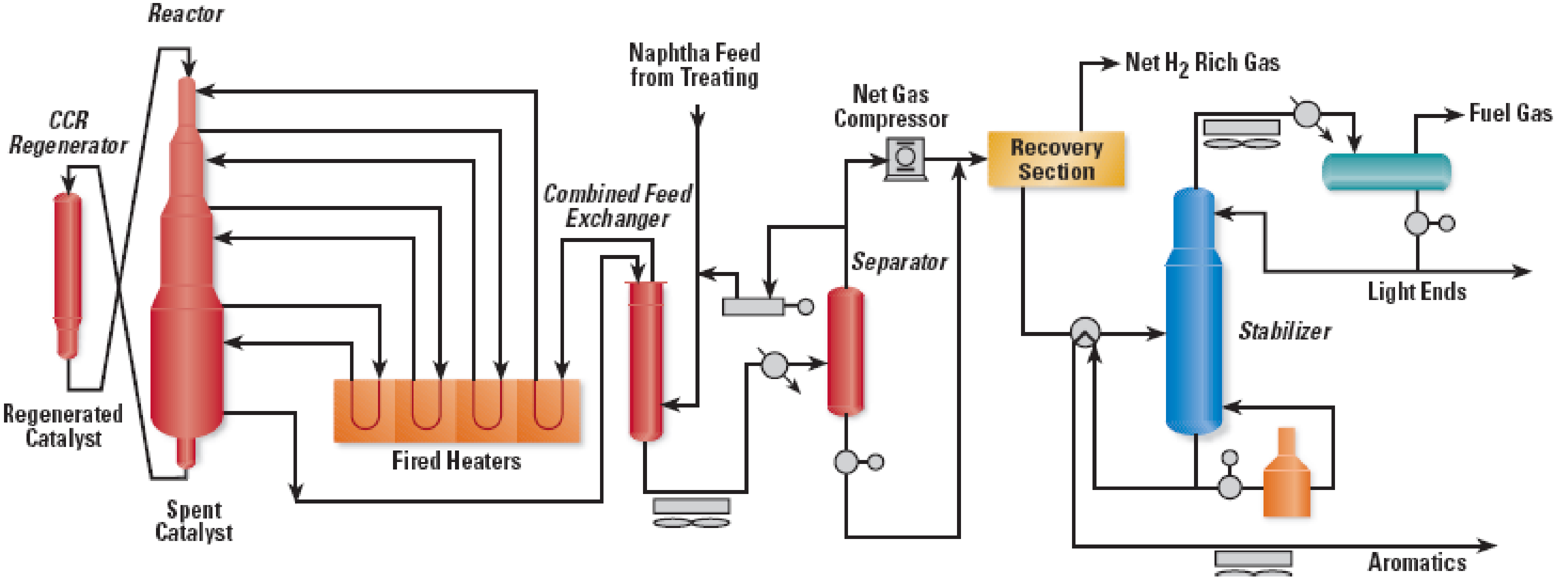


Catalytic Reforming for Aromatics Production
Topsoe Catalysis Forum
Munkerupgaard, Denmark August 27-28, 2015
Greg Marshall, GAM Engineering LLC

Low Pressure Reforming – UOP's CCR Platforming^{TM} Process







http://www.uop.com/objects/CCR%20Platforming.pdf

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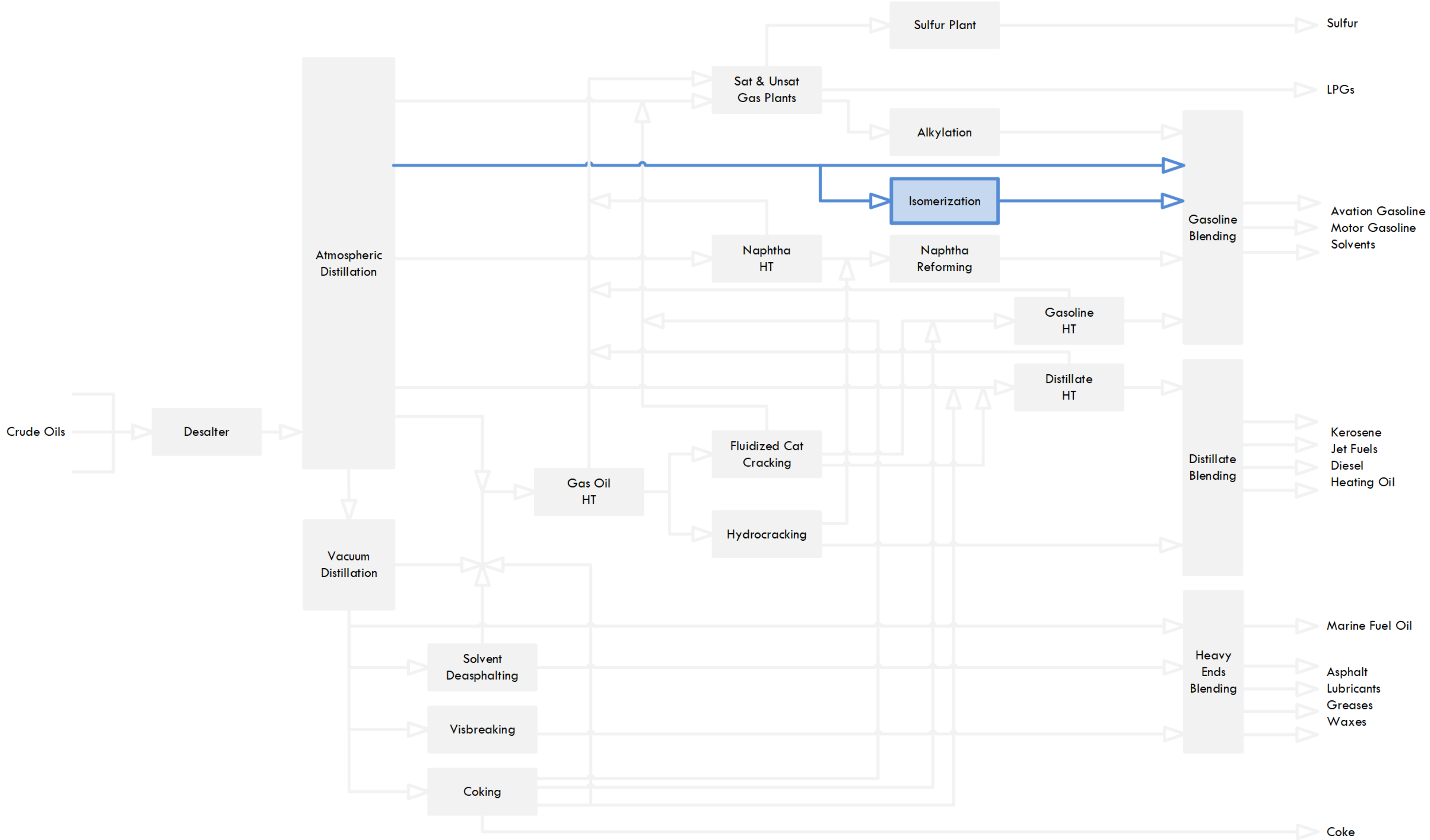
C_5/C_6 Isomerization



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C4 & C5/C6 Isomerization

C_4 isomerization

- Convert nC_4 to iC_4
- iC4 more desirable as alkylation feedstock

C_5/C_6 Isomerization

- Improve the octane rating of straight run gasoline
  - N-paraffins isomerized to branched isoparaffins
  - Will also convert any nC_4 to iC_4
- High RVP (about 17 psi) — limits its use in gasoline pool

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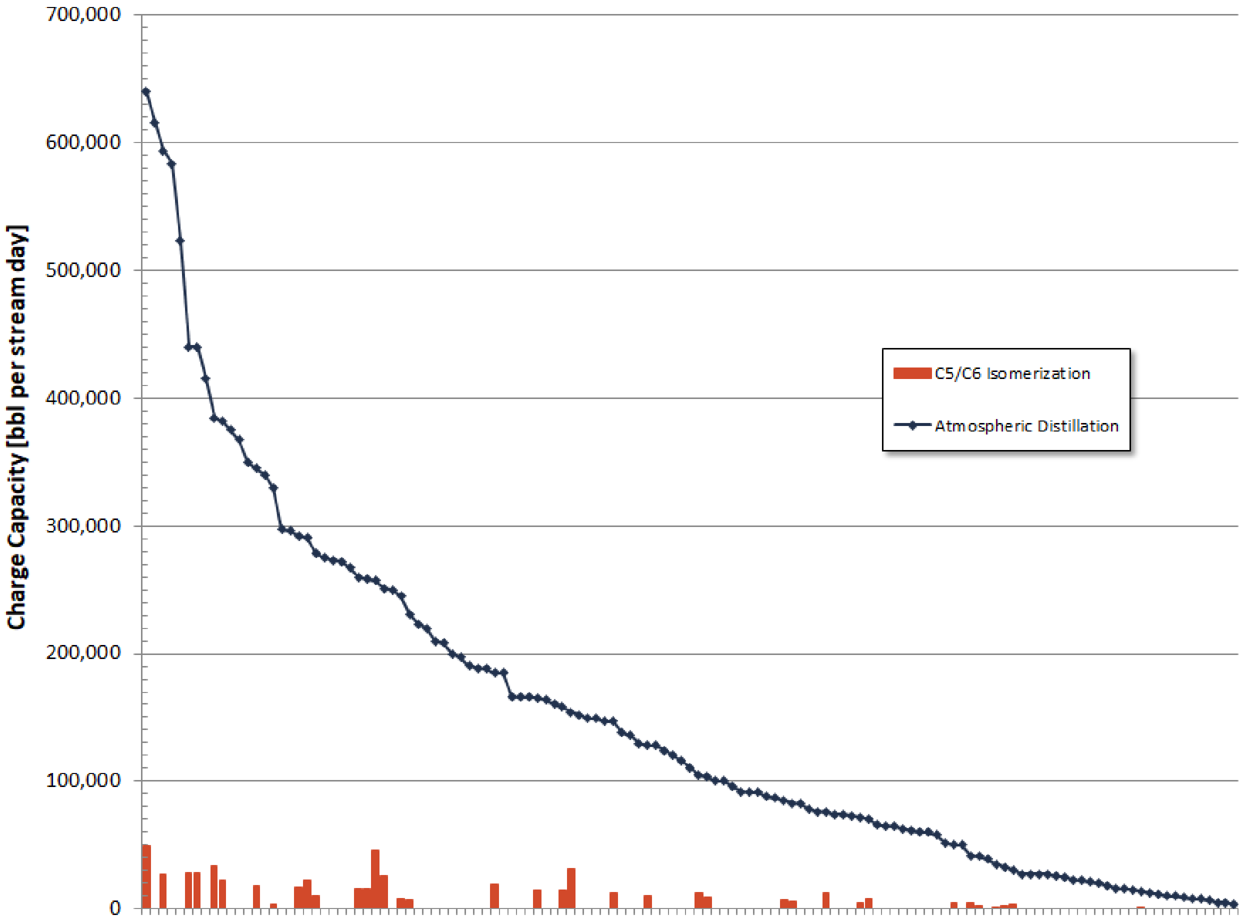
U.S. Refinery Implementation



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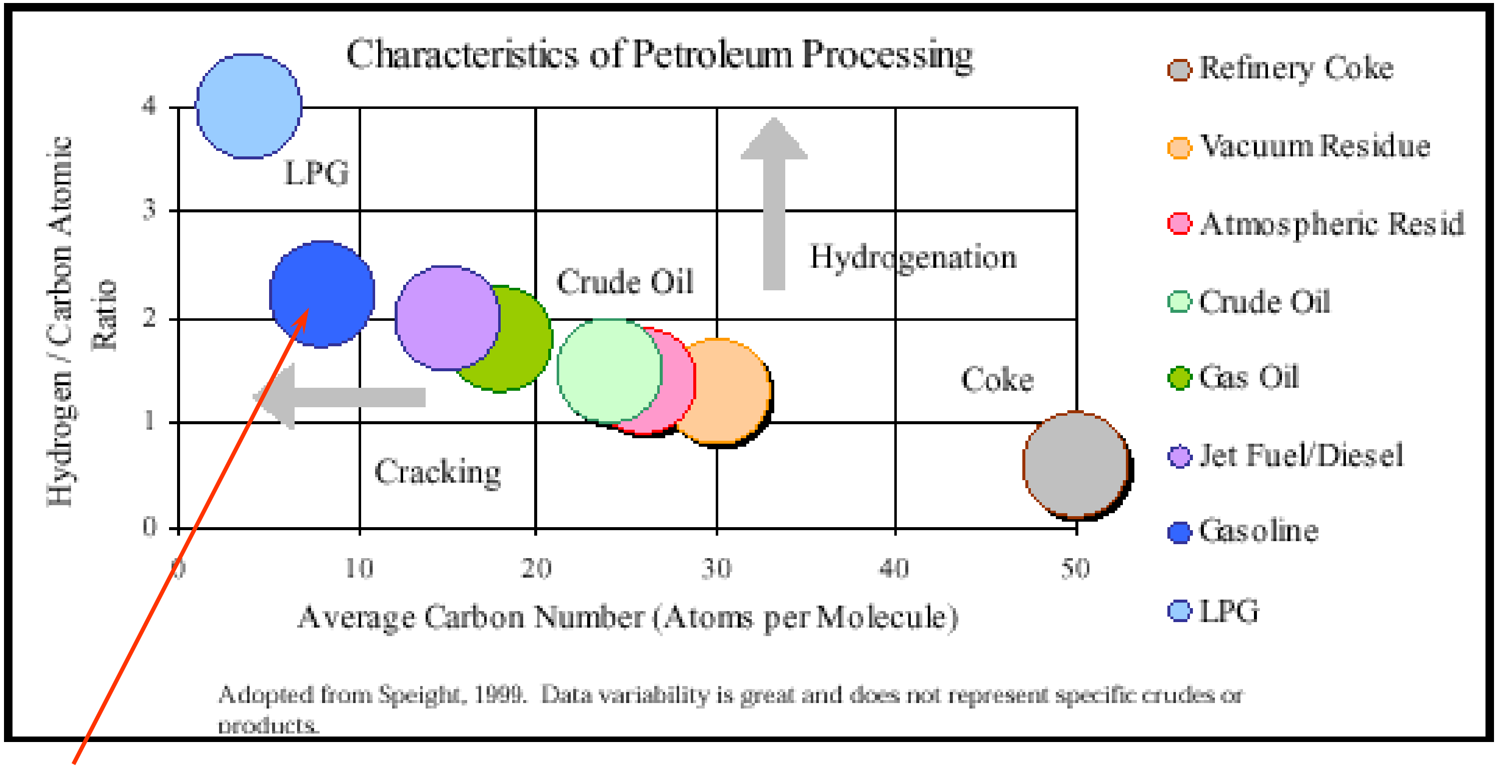
Characteristics of Petroleum Products



Adopted from Speight, 1999. Data variability is great and does not represent specific crudes or products.

Isomerization: rearrange molecules for better gasoline properties w/o changing size

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History of Isomerization

Aviation gasoline for World War II

- Butane isomerization was developed to create the needed isobutane feedstock
- Aluminum chloride catalyst
- Many of these units were shut down after the war

Tetra Ethyl Lead Phase-Out in 1970s

- Straight Run Gasoline (SRG) relied on TEL for octane improvement
- Research Octane Number (RON) of only 70
  - SRG mostly paraffinic pentanes & hexanes with some heptanes and octanes

Isomerization could provide needed octane boost

- Equivalent Isoparaffins have higher RON

C5/C6 Isomerization Processes

Vapor phase process

- Hydrogen used to suppress dehydrogenation & coking
- High yields & high selectivity to high-octane isomeric forms
- Provides moderate (but important) contribution to the gasoline pool

Catalyst types

- Chloride alumina catalyst
  - Organic chloride deposited on active metal sites
    - High temperature treatment with CCl_4
  - Chlorides sensitive to moisture – drying of feed & hydrogen make-up essential
- Acidic zeolite with noble metal catalyst
  - Platinum catalyst
  - Does not require activation by HCl

Pros

- Reforming conditions not appropriate for the paraffinic components in SRG
- Essentially zero benzene, aromatics, & olefins
- Very low sulfur levels

Cons

- High vapor pressure
- Moderate octane levels — (R+M)/2 only 85

C5/C6 Isomerization – Feedstocks & Products

Lightest naphtha feed stock (SRG) with pentanes, hexanes, & small amounts of heptanes

- Feed often debutanized — 'Debutanized Straight Run'

Sulfur & nitrogen must be removed since catalysts employ an 'acid site' for activity

- Merox
- Clay treating
- Hydrotreating

Common for Straight Run Gasoline & Naphtha to be hydrotreated as one stream & then separated

Products

- Isoparaffins & cycloparaffins
- Small amounts of light gasses from hydrocracking
- Unconverted feedstock

Increased severity increases octane but also increases yield of light ends

Yields depend on feedstock characteristics & product octane

- Poor quality feeds might yield 85% or less liquid product
- Good feeds might yield 97% liquid product

Isomerization Chemistry

Primary reaction is to convert normal paraffins to isomeric paraffins

Olefins may isomerize and shift the position of the double bond

- 1-butene could shift to a mixture of cis-2-butene & trans-2-butene

Cycloparaffins (naphthenes) may isomerize & break the ring forming an olefin

- Cyclobutane to butene

Effects of Process Variables

Low temperature, moderate hydrogen partial pressure, low space velocity promote long run lengths

Isomerization yields controlled by chemical equilibrium

- Removing isoparaffins from feedstock can shift the reactor equilibrium & increase the final product octane

Temperature primary process control variable

- Higher temperatures increase processing severity (including hydrocracking)

Other process variables

- Higher pressures increase catalyst life but increases undesirable hydrocracking reactions
- Increased hydrogen partial pressure promotes hydrocracking but prolongs catalyst life
- Space velocity balanced against capital cost, temperature, run length & yields

Process Improvement

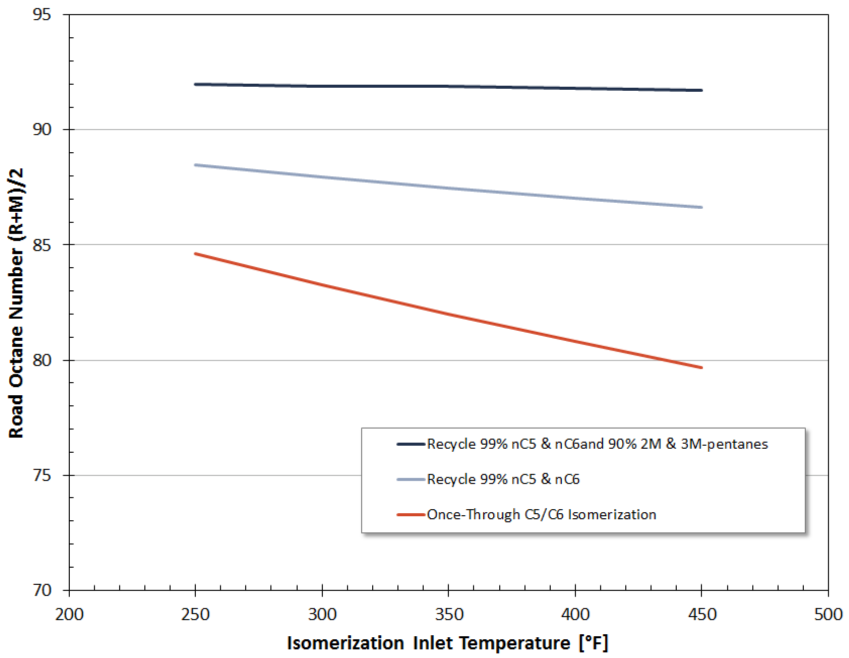
Removing isopentane from feed & bypass reactor

Use molecular sieves to remove & recycle normal-paraffins

- Separation carried out entirely in vapor phase — no reflux utilities but cyclic operation

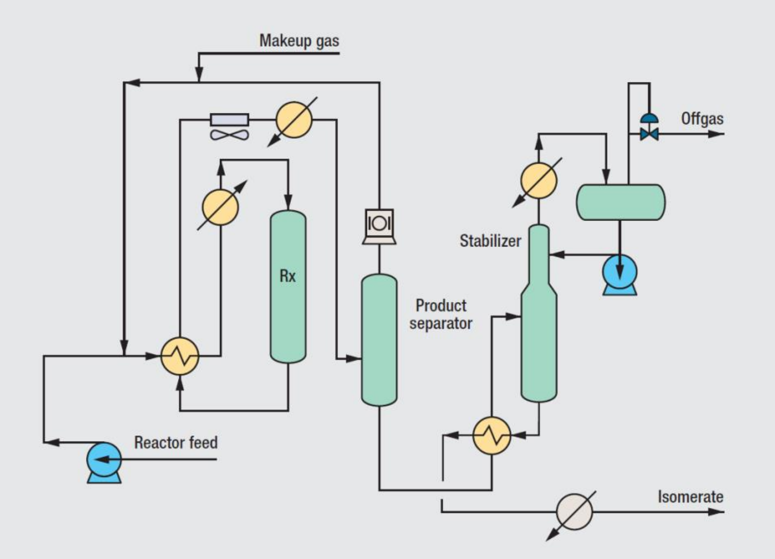
Side draw of n-hexane, 2-methylpentane, 3-methylpentane & recycle

- Octane approaching 92 RON
- Suitable for blending into premium at no octane penalty



Compound	Boiling Point [°F]	RON	MON	(R+M)/2
Neopentane	49.1	85.5	80.2	82.9
Isopentane	82.12	92.3	90.3	91.3
n-Pentane	96.92	61.7	62.6	62.2
2,2-Dimethylbutane	121.52	91.8	93.4	92.6
2,3-Dimethylbutane	136.38	100.3	94.3	97.3
2-Methylpentane	140.47	73.4	73.5	73.5
3-Methylpentane	145.91	74.5	74.3	74.4
n-Hexane	155.72	24.8	26.0	25.4

Isomerization Options

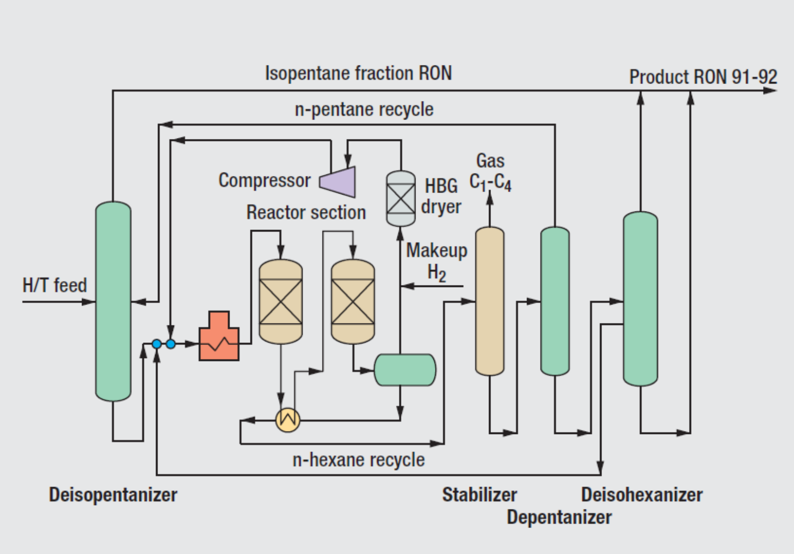


UOP's Par-Isom process

Nonchlorided-alumina catalyst – regenerable & tolerant to sulfur & water

Typical product octanes 81 – 87 depending on flow configuration & feedstock qualities

Typically 97 wt% yield of fresh feed



GTC Technology's Isomalk-2 process

Optimized for high conversion rate with close approach to thermal equilibrium

Produce up to 93 RON with full recycle

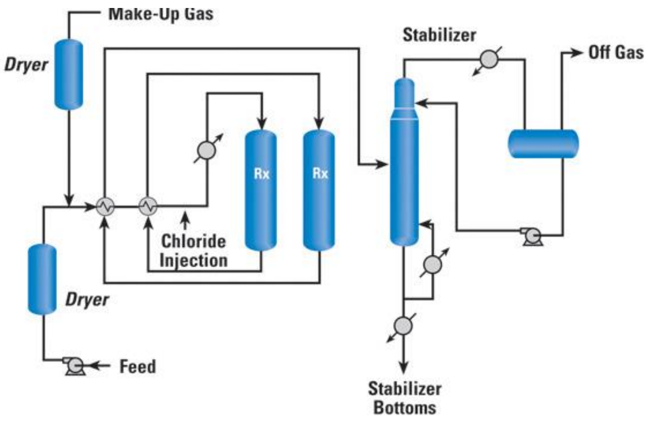
Operates 120ºC – 180ºC (250ºF – 350ºF)

Over 98% mass yield

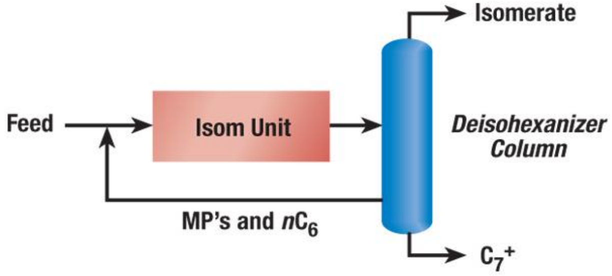
2011 Refining Processes Handbook
Hydrocarbon Processing, 2011

Updated: July 3, 2019

Increased Octane Through Separation & Recycle

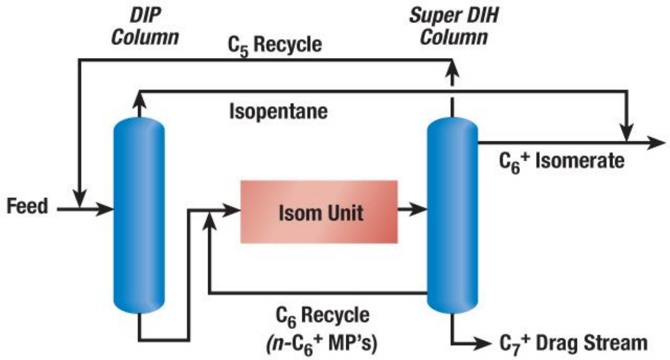


UOP Penex^{TM} – Hydrocarbon Once-Through
Limited by equilibrium – 80—84 RONC



Isomerization/DIH – Recycles unconverted low octane isomers
87—89 RONC

Compound	Boiling Point [°F]	RON	MON	(R+M)/2
Neopentane	49.1	85.5	80.2	82.9
Isopentane	82.12	92.3	90.3	91.3
n-Pentane	96.92	61.7	62.6	62.2
2,2-Dimethylbutane	121.52	91.8	93.4	92.6
2,3-Dimethylbutane	136.38	100.3	94.3	97.3
2-Methylpentane	140.47	73.4	73.5	73.5
3-Methylpentane	145.91	74.5	74.3	74.4
n-Hexane	155.72	24.8	26.0	25.4

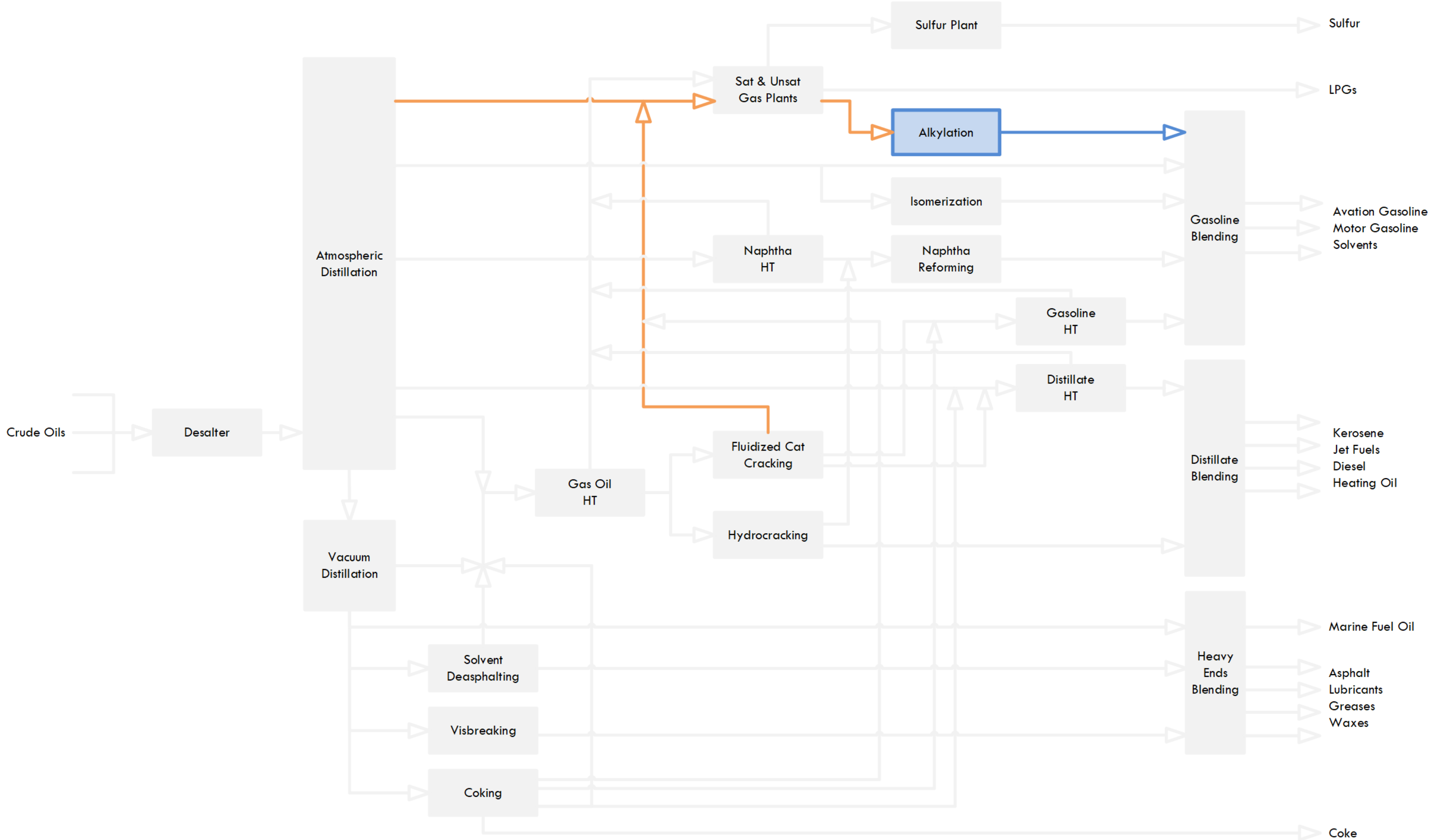


DIP/Isomerization/Super DIH 90-93 RONC

http://www.uop.com/processing-solutions/refining/gasoline/#naphtha-isomerization

Updated: July 3, 2019

Alkylation



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Alkylation & Polymerization

Processes to make gasoline components from materials that are too light to otherwise be in gasoline

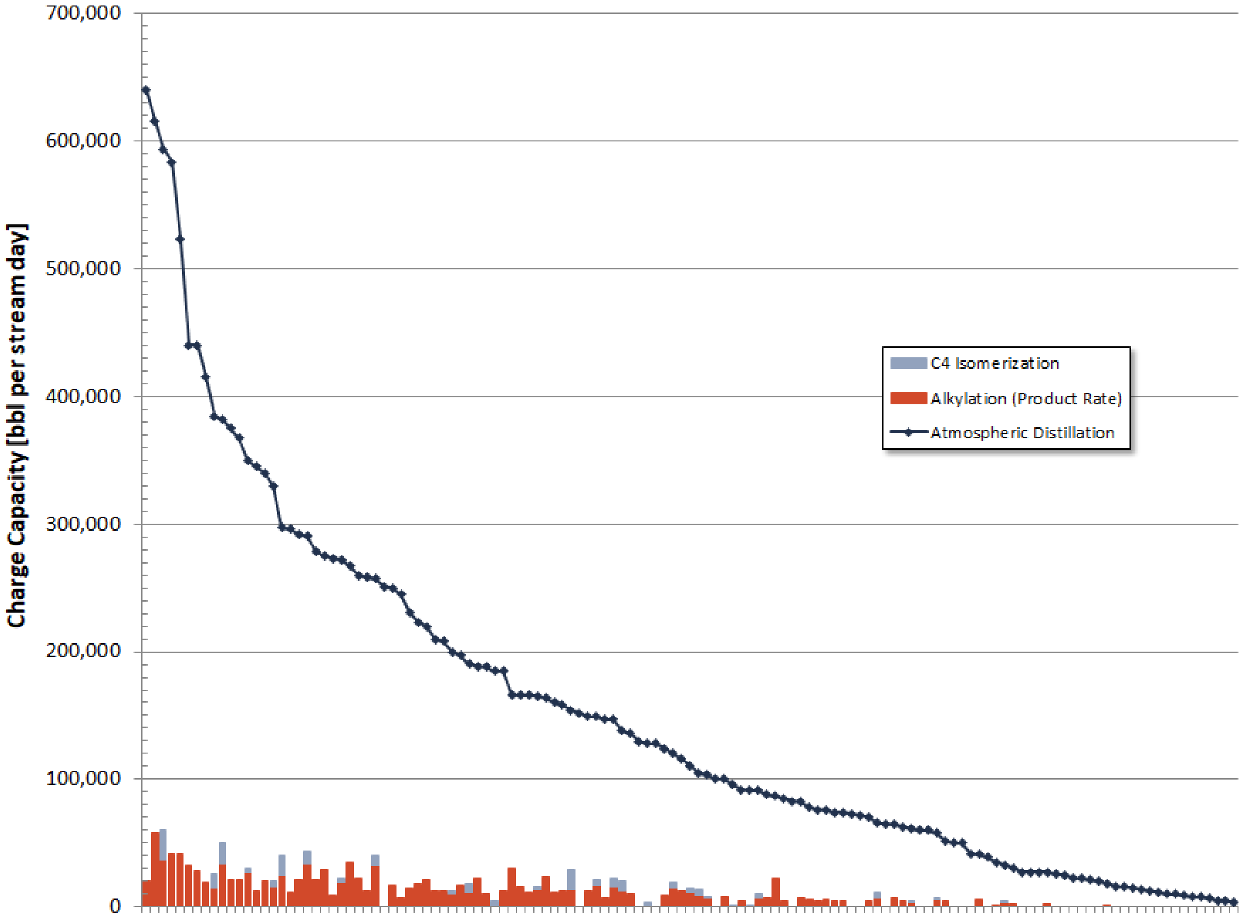
Alkylation

- Form a longer chain highly branched isoparaffin by reacting an alkyl group (almost exclusively isobutane) with a light olefin (predominately butylene)
- Produces high-octane gasoline

Polymerization

- Formation of very short chains
- Product is nearly all olefinic — high research octane but moderate motor octane number

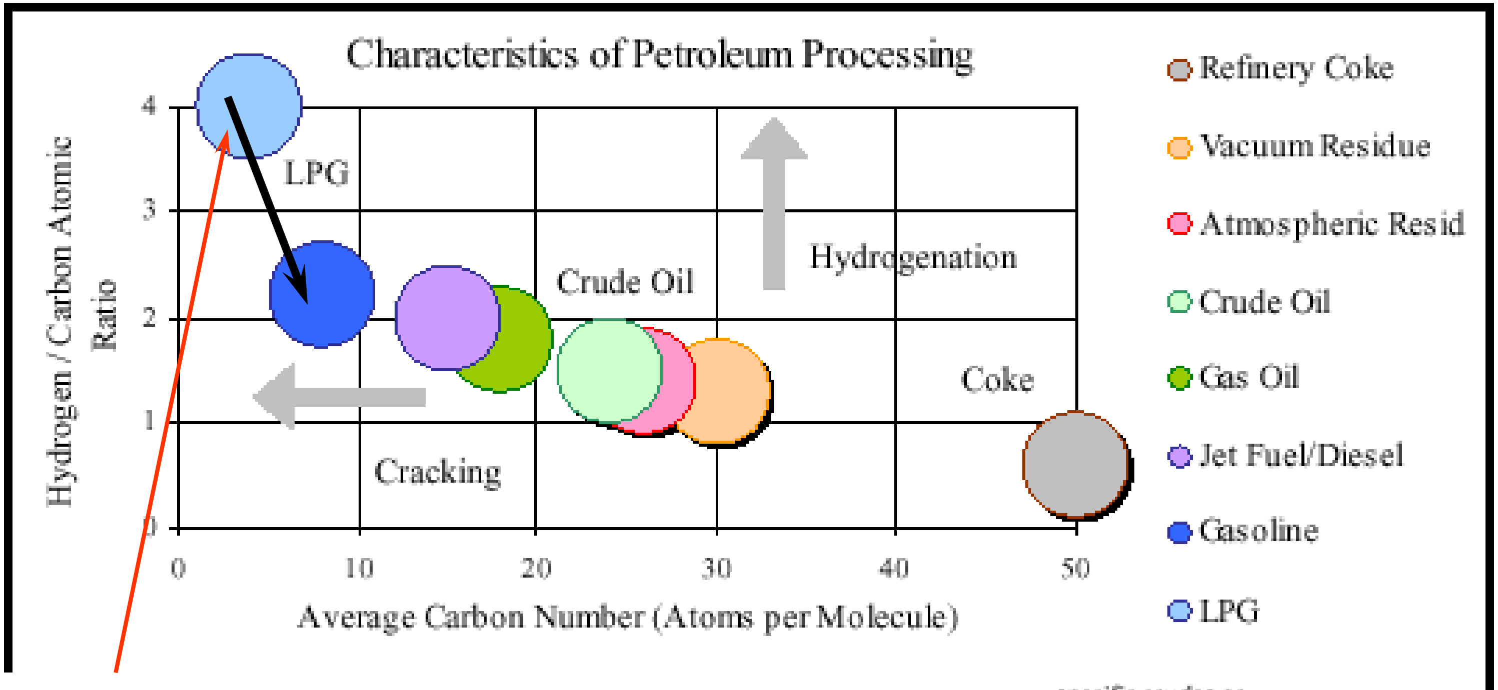
U.S. Refinery Implementation



EIA, Jan. 1, 2019 database, published June 2019
http://www.eia.gov/petroleum/refinerycapacity/

Updated: July 3, 2019

Characteristics of Petroleum Products



Alkylation: combine small molecules for gasoline with good properties

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Olefin Alkylation & Polymerization

1920s & 1930s other methods used to improve gasoline octane

- Tetra Ethyl Lead in Straight Run Gasoline
- Thermal reforming of naphtha
- Thermal polymerization of olefinic light ends to hexenes, heptenes, & octenes

In late 1930s & early 1940s, alkylation of olefins was developed to improve the octane of aviation gasoline

- Vladimir Ipatieff had discovered aluminum chloride catalysis in 1932

FCC significantly increased the production of light ends

- High concentration of the C3, C4, & C5 isomers, both olefinic & paraffinic
- Led to development of both catalytic polymerization & alkylation

Following end of the Korean conflict (1953) refiners investigated use of their catalytic polymerization and alkylation capacity for production of higher-octane motor fuels

- Chicken & egg — increasing octane production capacity & higher performance engines in automobiles led to the octane race in mid 1950s

Both polymerization & alkylation were adapted — *alkylation became the dominant process*

By the 1960s, polymerization units were being phased out & new plants utilized alkylation technology

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Sulfuric Acid vs. HF Alkylation

Sulfuric Acid Alkylation

Developed by consortium of major refiners & contractors

- Anglo-Iranian Oil, Humble Oil & Refining, Shell Development, Standard Oil Development, & the Texas Company
- First unit at Humble Baytown Refinery, 1938
- Many alkylation plants were built at the same time as the catalytic cracking units
- Operated during World War II for aviation gasoline production

Sulfuric acid alkylation required access to acid regeneration on a large scale

- Most located on deep water for barge transport of spent acid to regeneration at acid plants & return of fresh acid
- Economic handicap for inland Midwestern refineries

HF Acid Alkylation

Separately developed by Phillips Petroleum & UOP

- HF could be readily regenerated in alkylation plant facilities
- No need to transport catalyst in large quantities for regeneration

Feedstocks & Products

Olefinic stream from the catalytic cracker

- Butylene preferred olefin – produces highest octane number & yields
- isobutane & isopentane can be reacted with the olefin
  - Isopentane not usually used since it is a good gasoline blend stock

High octane number & low vapor pressure

Catalytic cracker feed contains significant sulfur

- Treating unit often precedes alkylation unit

Alkylate desirable component for high performance automotive fuels

- Very high octane index (R+M)/2 of 95
- Low vapor pressure
  - Vapor pressure is adjusted for final boiling point
  - IBP adjusted for addition of normal butane
- Low sulfur levels
- Essentially no olefins, benzene or aromatics

Feedstock Considerations

Olefin Feed

Butylene preferred

- Produces the highest isooctane levels
- Resulting Research Octane Numbers of 93-95 (with isobutane)
- RON and MON are about equal for alkylation
- Amounts of butylene consumed per alkylate produced is the lowest
- Side reactions are limited

Propylene worse

- Octane numbers are low (89-92 RON)
- Propylene & acid consumption are high

Pentene results are mixed

- Side reactions frequent

Isoparaffin Feed

Excess isobutane required — typical volume ratio of isobutane:olefin in the feed is 6-10

- Limited isobutane solubility in acid phase
- Olefins need to be surrounded by isobutane exposed to acid — if not, olefins will polymerize instead of alkylate

Newer plants have multi-injection & vigorous mixing systems

- Effect of isobutane is expressed in terms of concentration in the reaction zone
- Isobutane:olefin ratios maintained at 10,000:1

C4 Isomerization

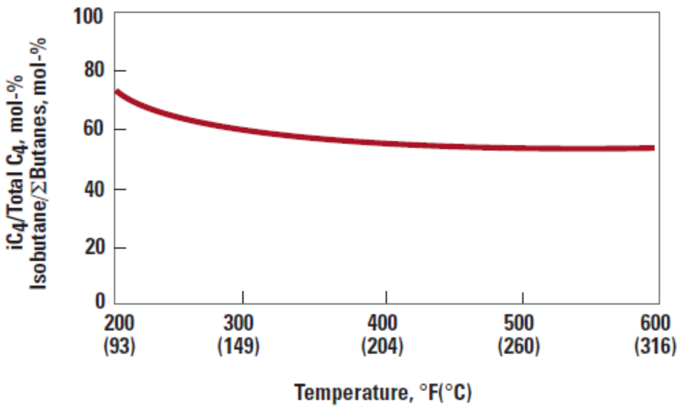
UOP's Butamer^{TM} process is a high-efficiency, cost effective means to meet isobutane demands by isomerizing nC_4 to iC_4

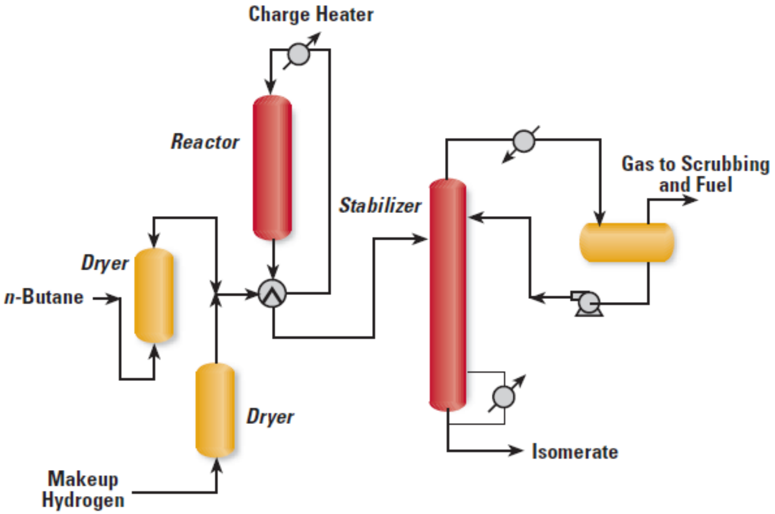
Equilibrium limited

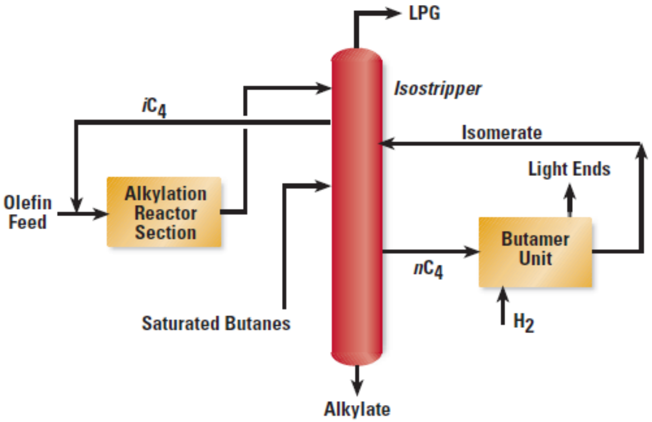
- Low temperature favors iC_4
- High-activity chlorided-alumina catalysts used

High selectivity to iC_4 by separating & recycling nC_4 to extinction

- Once-through lower capital cost







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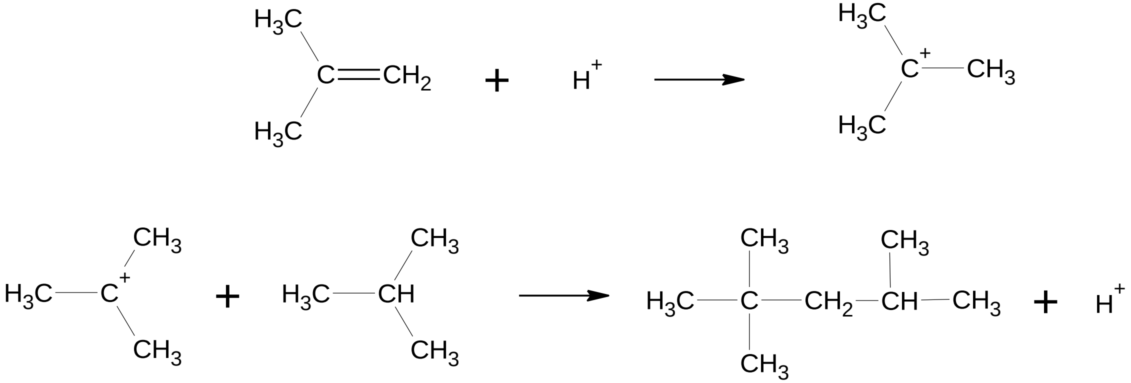
Process Chemistry Examples

Isobutylene & isobutane form 2,2,4-trimethylpentane (isooctane)



Propylene & isobutane form 2,2-dimethylpentane as primary product with 2,3 & 2,4-dimethylpentane as secondary products

Olefin	Paraffin	Product	RON
Isobutylene	Isobutane	Isooctane	100
Propylene	Isobutane	2,2-dimethylpentane	92.8
		2,3-dimethylpentane	91.1
		2,4-dimethylpentane	88.0

Alkylation Process Chemistry

Acid catalyzed alkylation combines isoparaffins & olefins to form alkylate, highly branched alkanes

- Usually only isobutane is used
- Isopentane can be a good gasoline blend stock for winter gasoline

Friedel-Crafts reaction — Lewis acid (HF or H2SO4) promotes carbonium ion on a tertiary isoparaffin that rapidly reacts with any double bond it encounters (propylene, butylenes, or pentylenes)

The reaction carried out in the liquid phase with an acid/reactant emulsion maintained at moderate temperatures

Propylene, butylene, & pentenes used — butylene preferred

- High octane isooctane alkylate produced
- Lower reactant consumption

Alkylation reactions have complex mechanisms & may produce many different varieties

Operating Variables & Their Effects

Capacity expressed in terms of **alkylate product**, not feed capacity

Most important variables

- Type of olefin
  - Propylene, butylene, or pentene
- Isobutane concentration – isobutane:olefin ratio
- Olefin injection & mixing
- Reaction temperature
- Catalyst type & strength

Critical measures for success

- Alkylate octane number
- Volume olefin & isobutane consumed per volume alkylate produced
  - Degree of undesirable side reactions
- Acid consumption

Isobutane/Olefin Injection & Mixing

More important in sulfuric acid systems

- Acid viscosity at operating temperatures

Provide optimal reaction conditions for the very fast reaction

- Inject olefin feedstock in incremental fashion to increase isobutane/olefin ratios
- Newer plants designed for multi-injection locations into an agitated emulsion to disperse olefin as rapidly as possible

Systems with single point injection can easily have an overload of olefin in the emulsion

- Leads to lower quality & higher acid consumption from esterification reactions

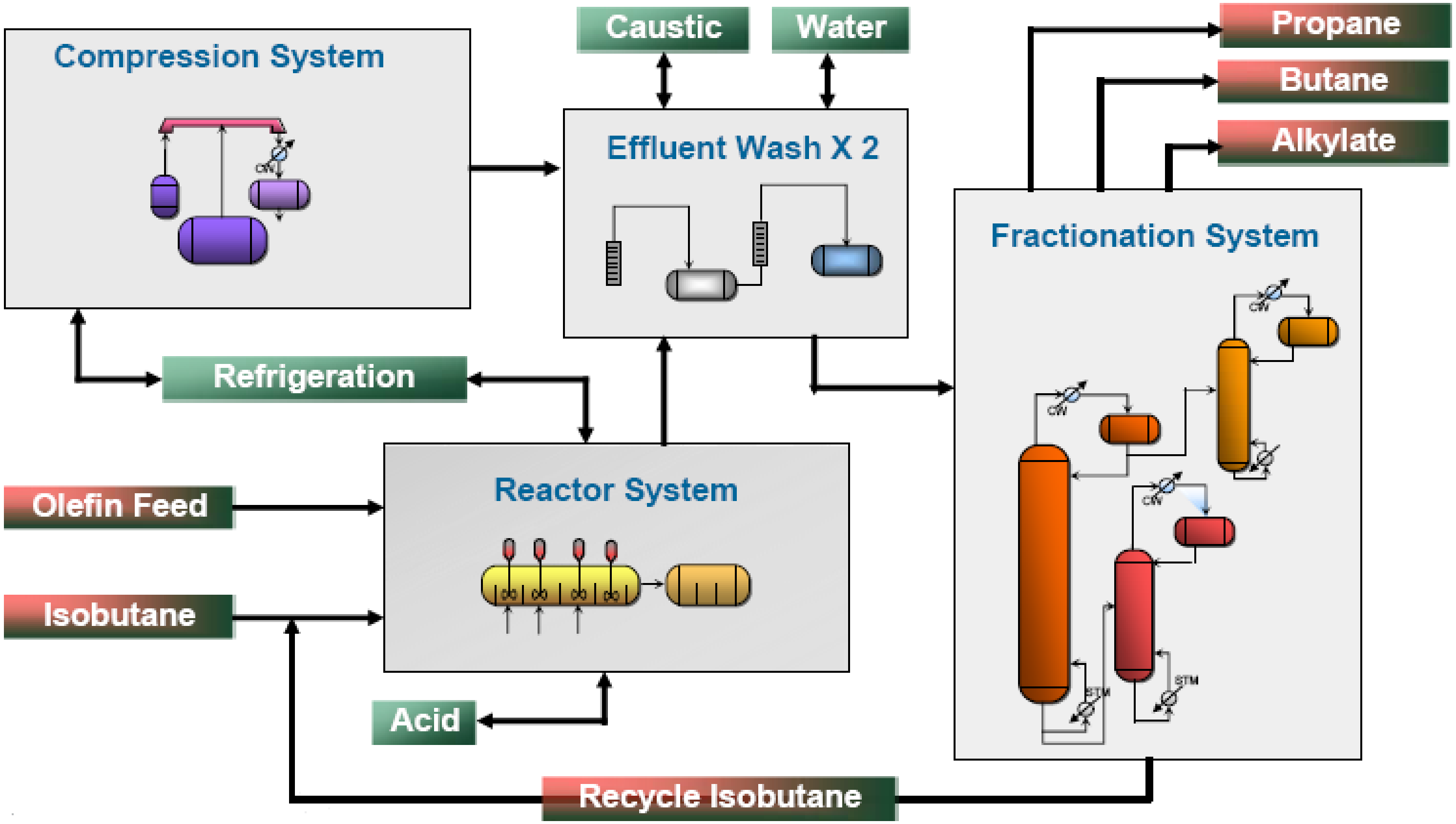
Process Considerations

	Sulfuric Acid	HF Acid
Reaction Temperature	Increasing temperatures reduces octane number	
	Sulfuric Acid systems at **45ºF** – chilled water, refrigeration, and/or autorefrigeration needed	HF systems at **95ºF** – cooling water sufficient
Acid Strength	Considered "spent" about 88 wt% sulfuric acid	Normally kept in range of 86 – 92 wt%. 84% is minimum
	Water lowers acid activity 3 – 5 times as fast as hydrocarbon diluents	HF with water lead to corrosion
Regeneration	Acid regeneration on a large scale – most located on deep water for barge transport of spent acid to regeneration at acid plant & return of fresh acid	HF regenerated on site by distillation – only small acid quantities for makeup need be transported
Other Considerations	Dominant process but…	Smaller footprint
	Requires extensive recuperation of spent acid	Urban community concerns to hazards of HF escape[1,2].

[1] "United Steelworkers Union Calls for Industry-wide Phase-out of Hydrogen Fluoride in Oil Refinery Alkylation Units," August 31, 2009 http://www.usw.org/media_center/releases_advisories?id=0207

[2] "Philadelphia refinery blast puts new spotlight on toxic chemical," June 21, 2019 https://www.hydrocarbonprocessing.com/news/2019/06/philadelphia-refinery-blast-puts-new-spotlight-on-toxic-chemical

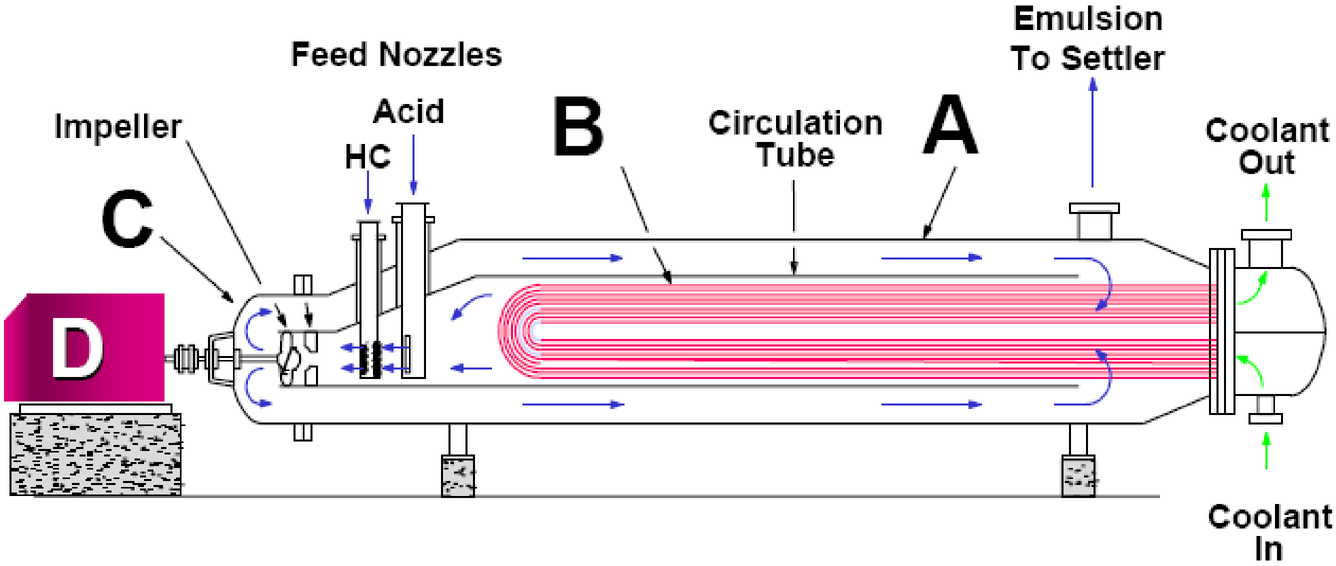
Autorefrigerated Reactor Sulfuric Acid Alkylation (EMRE)



Sulfuric Acid Alkylation Technology
Dr. Girish K. Chitnis, Mr. Ron D. McGihon, Mr. Aneesh Prasad and Mr. Christopher M. Dean
"Growing Importance of Alkylation" September 2009
http://www.exxonmobil.com/Apps/RefiningTechnologies/Files/Conference_2009_sulfuricalkylation_Sept.pdf

STRATCO® ContactorTM Reactor Sulfuric Acid Alkylation (DuPont)

A - Contactor Reactor Shell
B - Tube Bundle Assembly
C - Hydraulic Head Assembly
D - Motor, Turbine/Driver



STRATCO® Alkylation Technology Improvements
Kevin Bockwinkel
2007 NPRA Annual Meeting
http://www2.dupont.com/Sustainable_Solutions/en_US/assets/downloads/stratco/STRATCO_AlkylationTechnologyImprovements.pdf

HF Alkylation System

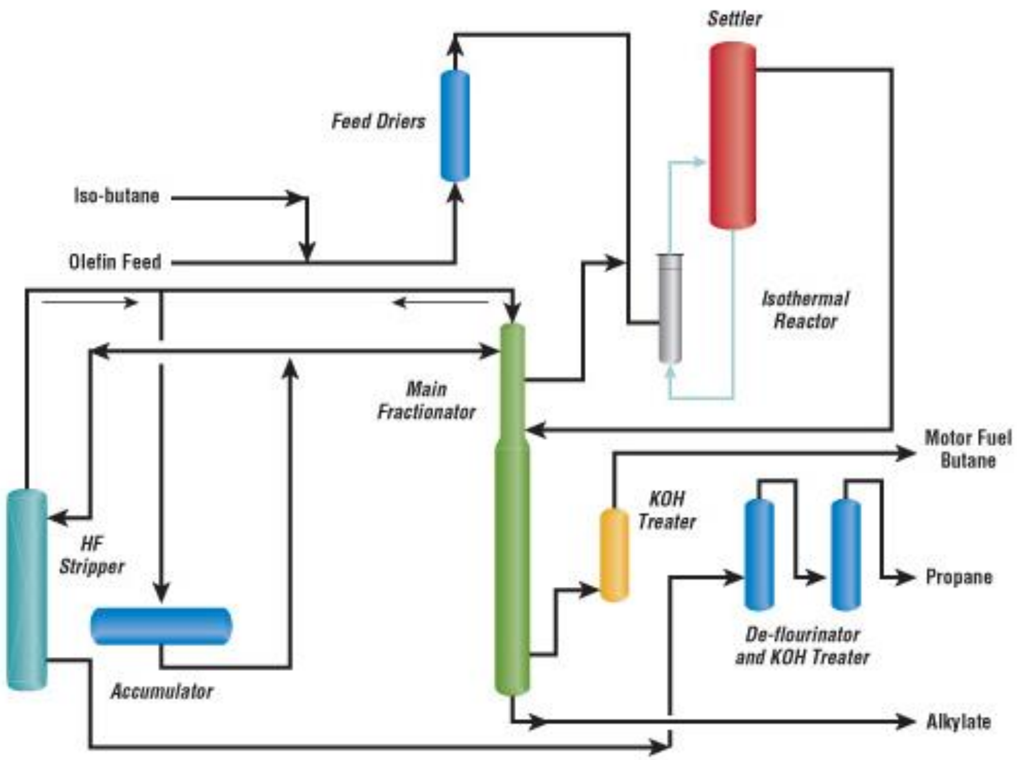
Differences to sulfuric acid systems

- Feed driers essential to minimize catalyst consumption
  - Water forms an azeotrope with HF leading to acid loss
- HF stripper required on depropanizer overhead to clean up propane for LPG
- HF regenerator operating on a slip stream from acid settler
  - Many acid soluble organic compounds decompose but some must be rejected as acid soluble oil
- Spent acid requires special neutralization
  - Convert HF to calcium fluoride & burnable waste
  - Overall acid loss should be less than one pound per barrel of acid produced

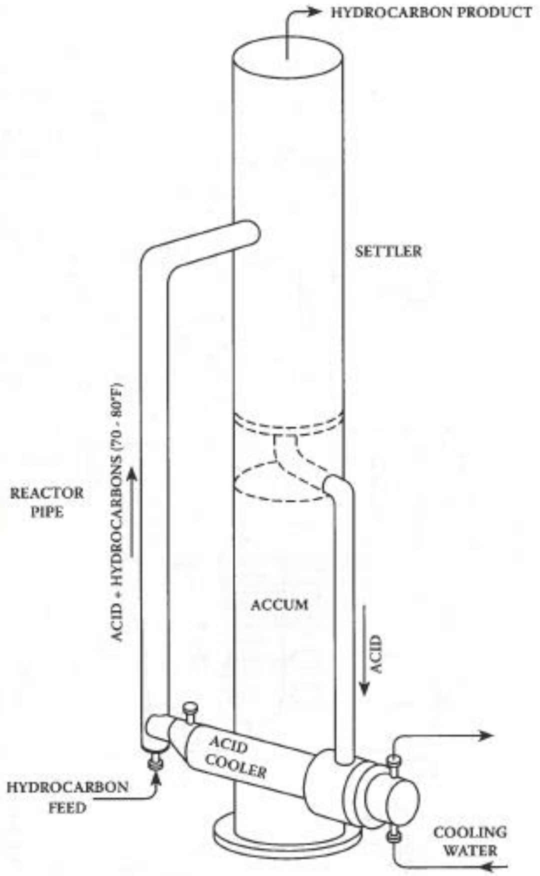
Elaborate HF venting, neutralization & recovery system

- Considered by the public to be a threat in terms of large releases of HF
- New designs minimize the inventory of HF in the unit far below earlier designs
  - Risk is minimized, not eliminated

UOP/Phillips Alkylation Process



http://www.uop.com/processing-solutions/refining/gasoline/#alkylation



Petroleum Refining Technology & Economics, 5th ed.
Gary, Handwerk, & Kaiser
CRC Press, 2007

Updated: July 3, 2019

Phillips Alkylation Process Mass Balance

Component	Olefin Feed	Saturated Butanes	Propane Yield	Motor-Fuel Butane Yield	Motor-Fuel Alylate Yield	Acid Oils
Ethane	0.49		0.49			
Propylene	21.04					
Propane	17.42	0.30	18.77			
Isobutane	191.81	13.48	0.34	3.13	0.19	
Butenes	169.10					
n-Butane	63.17	10.11		63.35	9.93	
Pentanes	4.90	0.42		3.67	1.65	
Alkylate					390.17	
Acid Oils						0.55
Total	467.93	24.31	19.60	70.15	401.94	0.55
Stream Totals		492.24				492.24
RVP [psi]					6.0	
Specific Gravity					0.70	
RON, clear					95.0	
MON, clear					93.5	
FBP [°C]					195	
FBP [°F]					383	

Summary

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Gasoline Upgrading Process Comparisons

	Pros	Cons
Reforming	• High octane • Low RVP • By-product hydrogen	• High aromatics (benzene)
Isomerization	• Better octane than LSR • Too light for reforming • Low aromatics & olefins • Very low sulfur levels	• Octane still relatively low • High RVP
Alkylation	• Good octane • Low RVP	• Requires light ends – issue if no FCCU • HF community concerns

Supplemental Slides

Updated: July 3, 2019

Reformer Installed Cost

Includes

- ISBL facilities to produce 102 RON reformate from sulfur-free HSR naphtha
- Product debutanizer
- All necessary controllers & instrumentation
- All ISBL facilities
- Heat exchange to accept feed & release products at ambient temperature

Excludes

- Cooling water, steam & power supply
- Feed & product storage
- Initial catalyst charge
- Royalty
- Feed fractionation or desulfurization

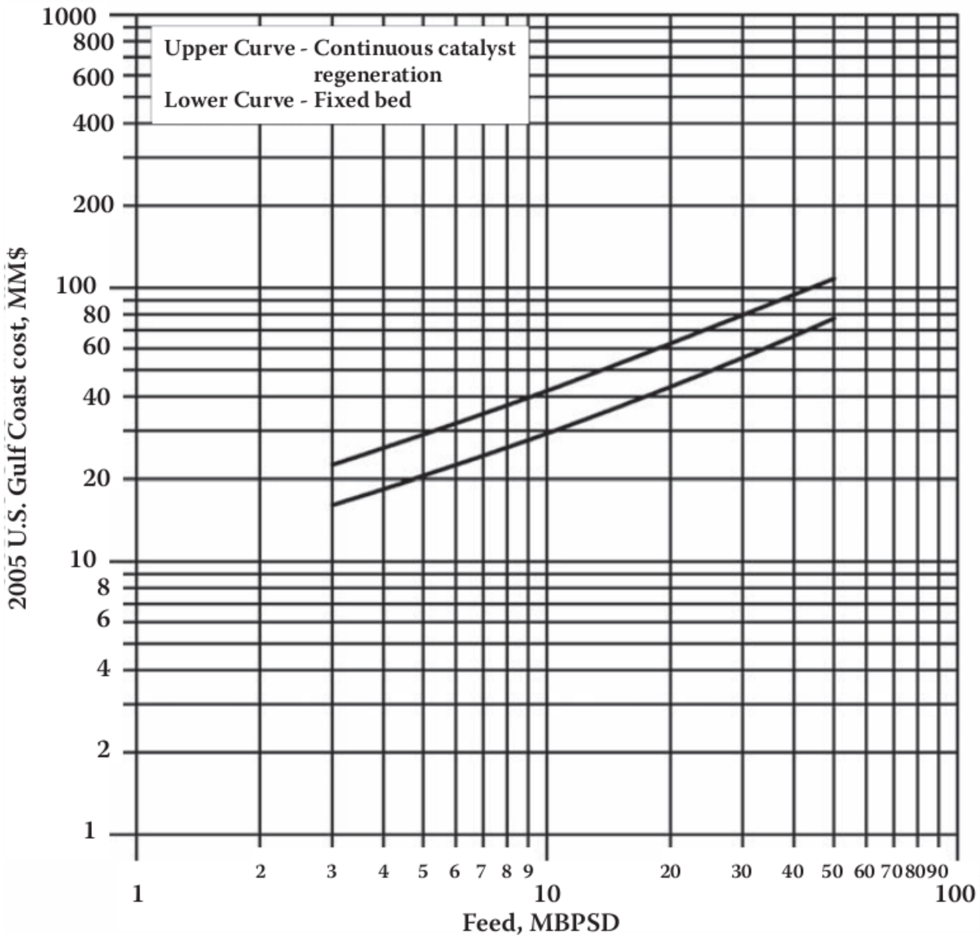


FIGURE 10.8 Catalytic reforming unit investment cost: 2005 U.S. Gulf Coast (see Table 10.2).

Petroleum Refining Technology & Economics, 5th ed.
Gary, Handwerk, & Kaiser
CRC Press, 2007

Isomerization Installed Cost

Includes

- Drying of feed & hydrogen makeup
- Complete preheat, reaction, & H2 circulation facilities
- Product stabilization
- Heat exchange to cool products to ambient temperature
- All necessary controllers & instrumentation
- Paid royalty

Excludes

- Hydrogen source
- Feed desulfurization
- Cooling water, steam & power supply
- Feed & product storage
- Initial catalyst charge

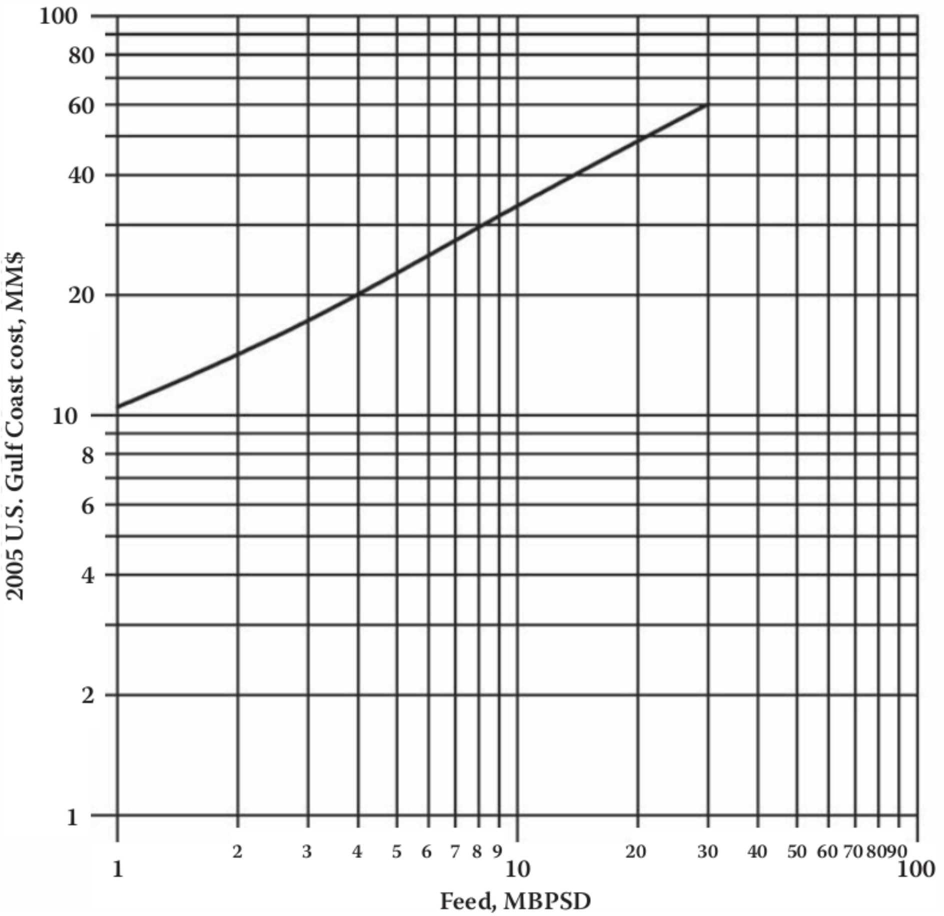


FIGURE 10.10 Paraffin isomerization units (platinum catalyst type) investment cost: 2005 U.S. Gulf Coast (see Table 10.3).

Petroleum Refining Technology & Economics, 5th ed.
Gary, Handwerk, & Kaiser
CRC Press, 2007

Alkylation Installed Cost

Includes

- Facilities to produce alkylate from feed with iC4 & C3 to C5 olefins
- All necessary controllers & instrumentation
- All ISBL facilities
- Feed treating (molecular sieve to remove moisture from feed)

Excludes

- Cooling water, steam & power supply
- Feed & product storage

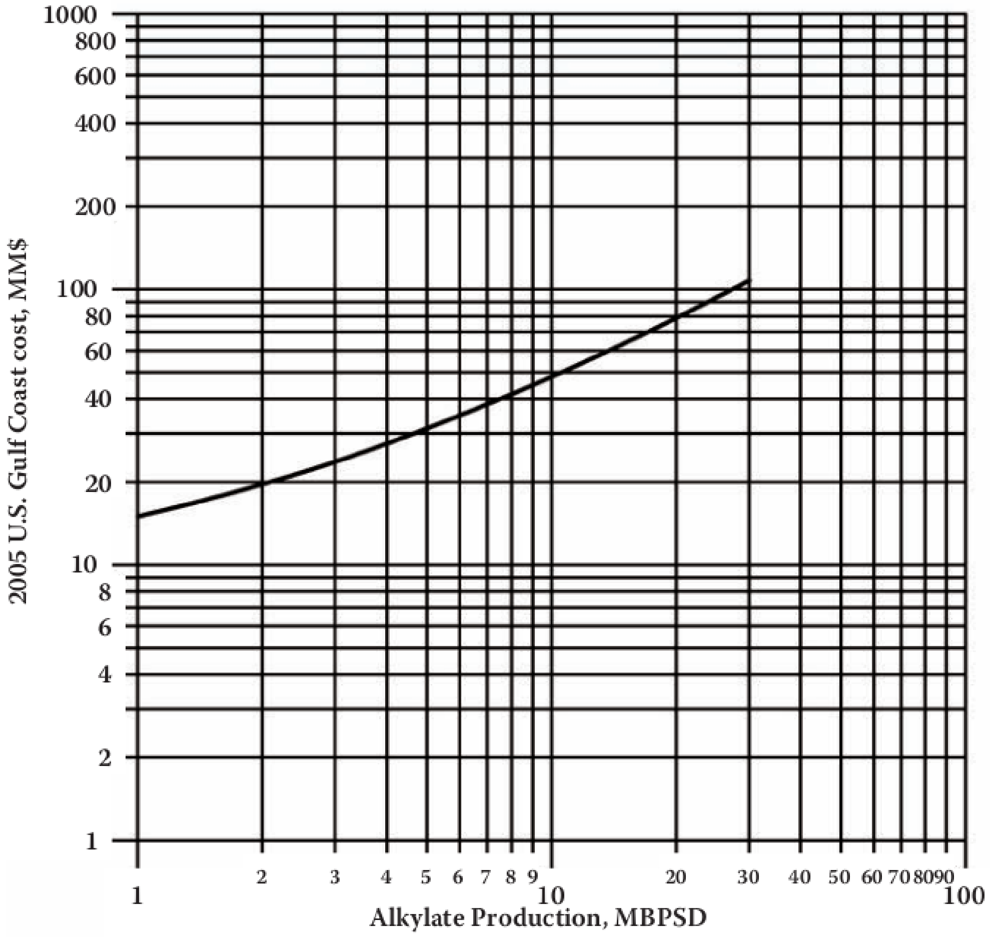


FIGURE 11.6 Alkylation unit investment cost: 2005 U.S. Gulf Coast (see Table 11.6).

Petroleum Refining Technology & Economics, 5th ed.
Gary, Handwerk, & Kaiser
CRC Press, 2007

Updated: July 3, 2019

Catalytic Reforming Technologies

Provider	Features
Axens (1)	Catalyst regenerated in-place at end of cycle. Operates in pressure range of 170 - 350 psig.
Axens (2)	Advanced Octanizing process, uses continuous catalyst regeneration allowing pressures as low as 50 psig.
UOP	CCR Platforming process. Radial-flow reactors arranged in vertical stack.

Isomerization Technologies

Provider	Features
Axens	Either once-through or Ipsorb Isom with normal paraffin recycle to extinction.
CDTECH	ISOMPLUS zeolite-based catalyst.
UOP (1)	Par-Isom process uses high-performance nonchlorided-alumina catalysts
UOP (2)	HOT (hydrogen-once-through) Penex process eliminates need of recycle-gas compressor. Fixed bed using high-activity chloride-promoted catalyst.
UOP (3)	HOT (hydrogen-once-through) Butamer process eliminates need of recycle-gas compressor. Two series reactors provide high on-stream efficiency.

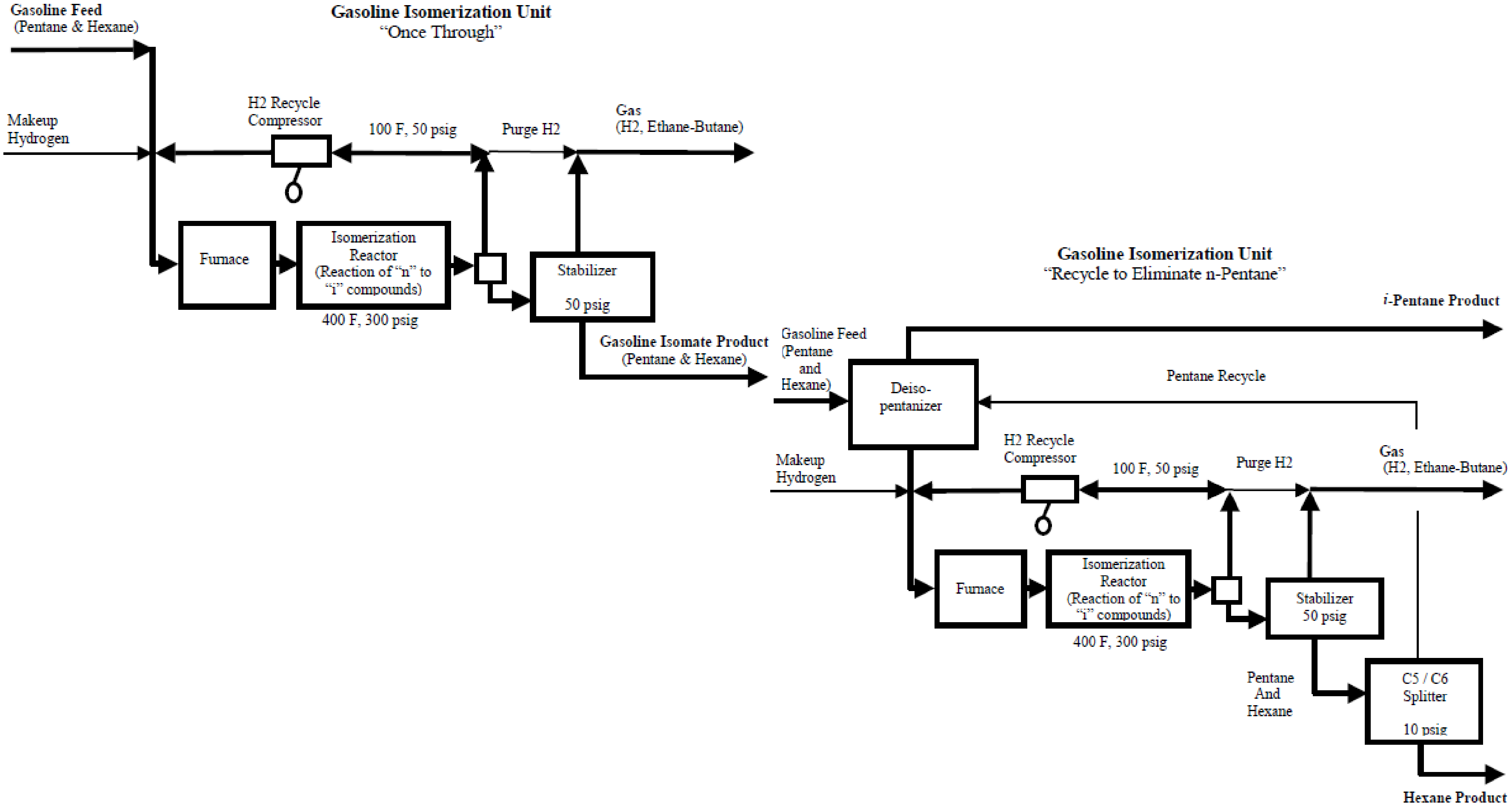
Alkylation Technologies

Provider	Features
CDTECH (1)	CDAlkyl low-temperature sulfuric acid alkylation.
CDTECH (2)	CDAlkylPlus low-temperature sulfuric acid alkylation coupled with olefin pretreatment step.
DuPont	Uses STRATCO Effluent Refrigeration Alkylation process using sulfuric acid
Lummus Technology	AlkylClean process using solid acid catalyst. Demonstration unit only.
Refining Hydrocarbon Technologies LLC	RHT-Alkylation process uses sulfuric acid. Eductor mixing device.
ExxonMobil Research & Engineering	Sulfuric acid alkylation using autorefrigerated reactor.
UOP (1)	Modified HF Alkylation to reduce aerosol formation.
UOP (2)	Indirect Alkylation (InAlk) uses solid catalyst. Olefins polymerize & higher molecular weight material hydrogenated.
KBR	K-SAAT Solid Acid Alkylation technology

Effects of Reforming Process Variables

Reaction	Pressure	Temperature
Isomerization of naphthenes	Indeterminate	Indeterminate
Dehydrocyclization of paraffins to naphthenes	Low pressure	High temperature
Dehydrogenation of naphthenes to aromatics	Low pressure	High temperature
Isomerization of normal paraffins to isoparaffins	Slight dependence	Slight dependence
Hydrocracking	High pressure	High temperature

Isomerization With & Without iC5 Removal



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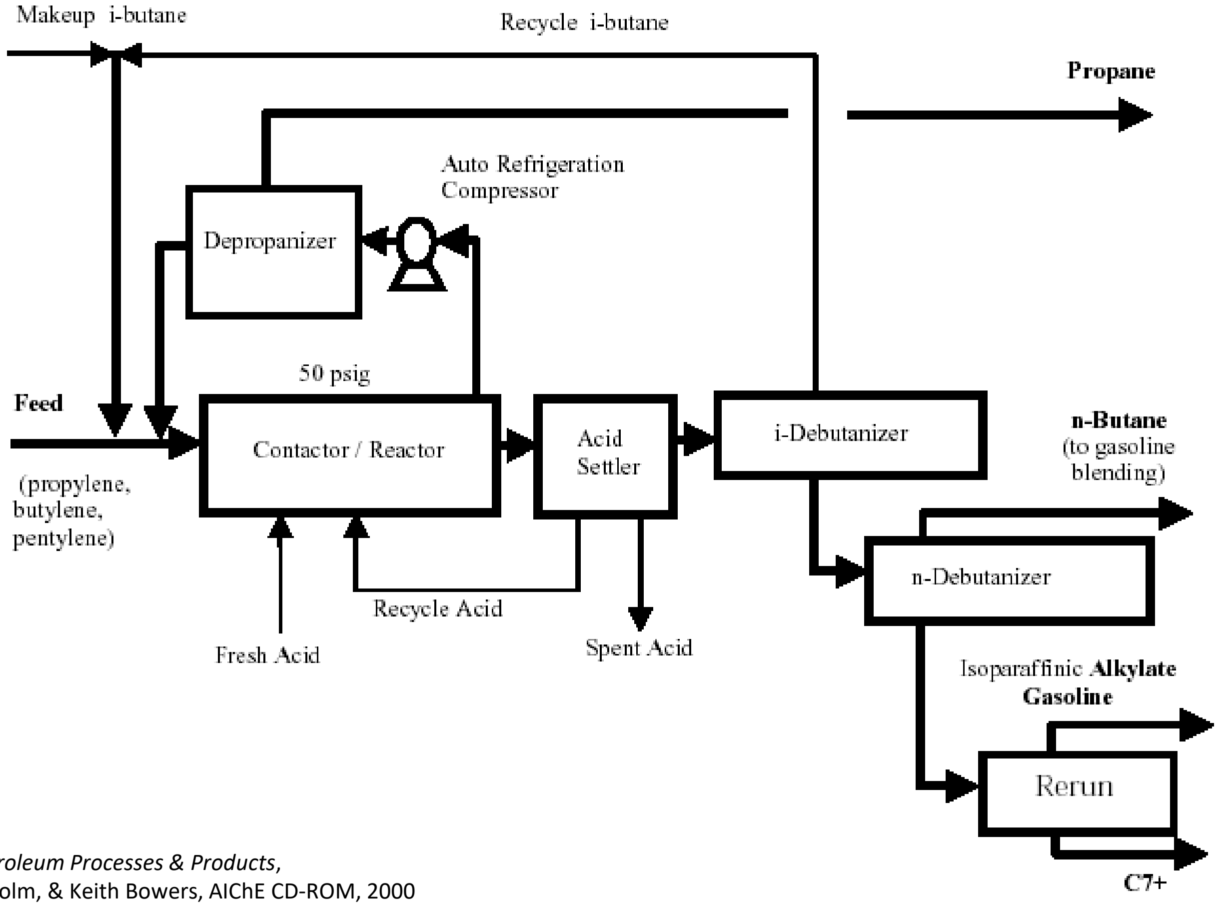
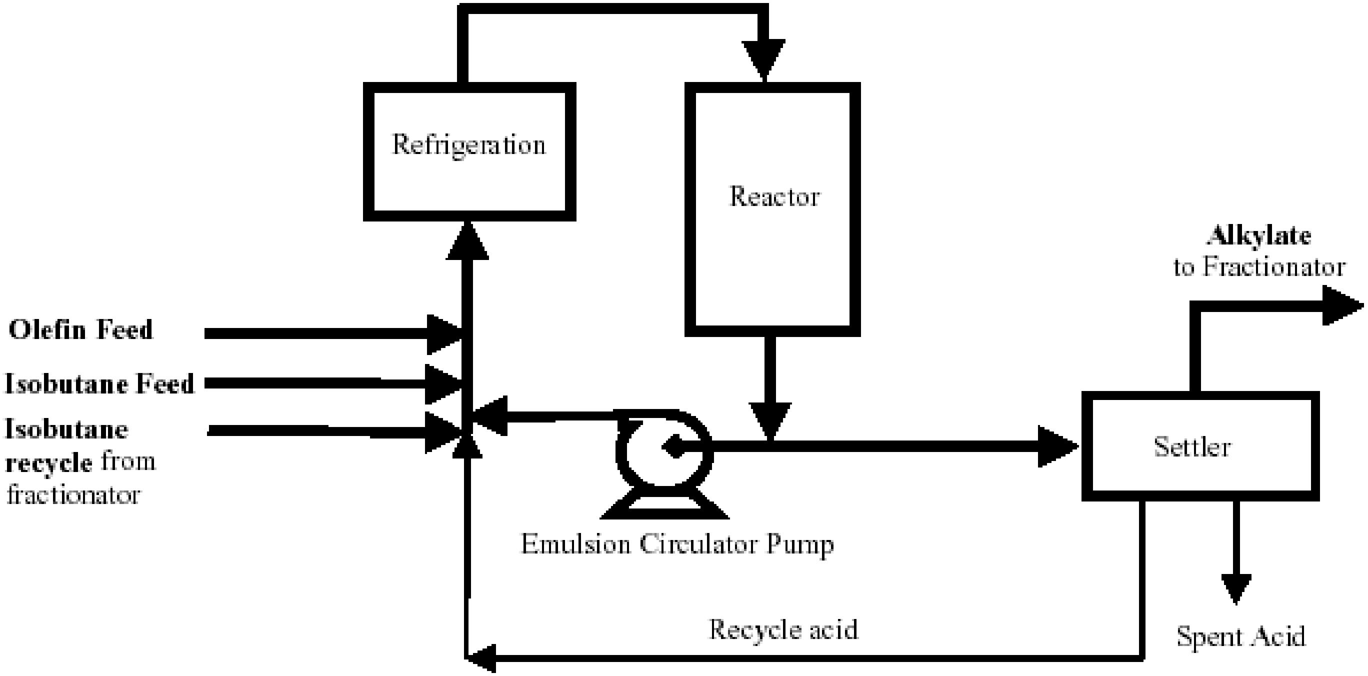
Sulfuric Acid Alkylation



Refining Overview – Petroleum Processes & Products,
by Freeman Self, Ed Ekholm, & Keith Bowers, AIChE CD-ROM, 2000

Time Tank Reactors



Refining Overview – Petroleum Processes & Products,
by Freeman Self, Ed Ekholm, & Keith Bowers, AIChE CD-ROM, 2000

HF Alkylation Process Effluent Management

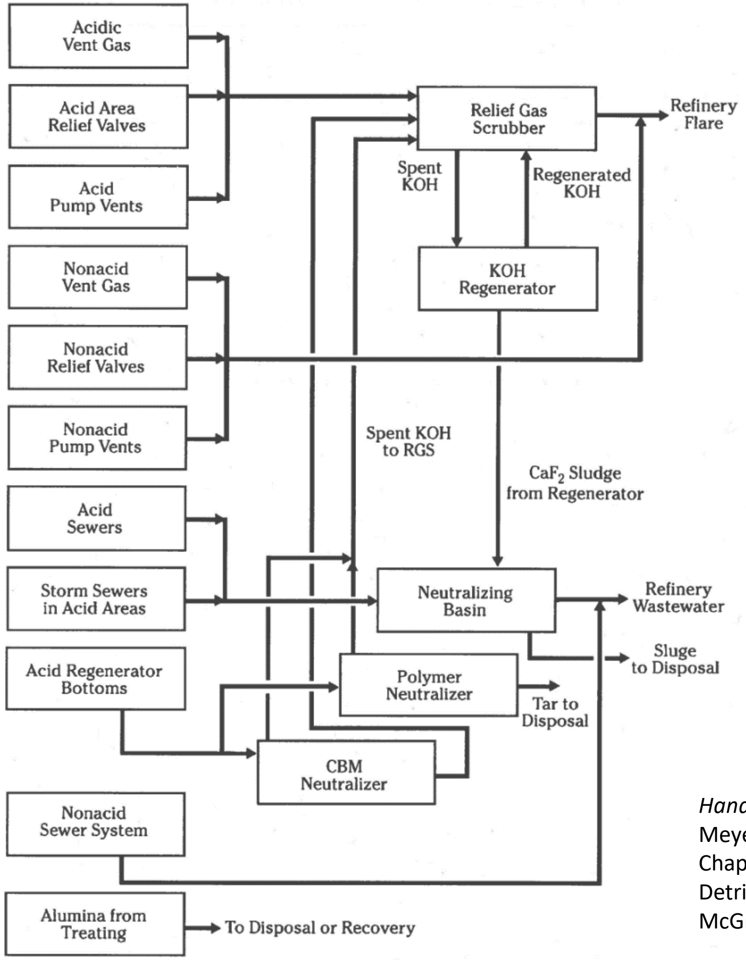


FIGURE 1.4.5 UOP HF Alkylation process effluent management.

Handbook of Petroleum Refining Processes, 3rd ed.
Meyers (ed.)
Chapter 1.4, "UOP HF Alkylation Technology"
Detrick, Himes, Meister, & Nowak
McGraw-Hill, 2004

Updated: July 3, 2019