CHAPTER FOUR

Gasoline Manufacturing Processes

CATALYTIC REFORMING

Catalytic reforming of heavy naphtha is a key process in the production of gasoline. The major components of petroleum naphthas are paraffins, naphthenes, and aromatic hydrocarbons. The relative amount of these hydrocarbons depend on the origin of the crude oil. The aromatic content of the reforming feed is usually below 20% of the total hydrocarbons whereas the paraffins and naphthenes vary between 10 and 70% depending on the origin of the crude oil.

The aim of catalytic reforming is to transform, as much as possible, hydrocarbons with low octane to hydrocarbons with high octane. The chemical reactions that lead to these changes are guided by a catalyst under well-defined operating conditions.

From the octane view point, the best hydrocarbon fuels for an internal combustion engine are isoparaffinic and aromatic hydrocarbons. For example, the aromatic hydrocarbons from C_7 to C_{10} have research octane numbers (RON) of 118 to 171, whereas the corresponding cyclohexanes have octane numbers of 43 to 104. A similar comparison can be made between isoparaffins and normal paraffins.

The chemical reactions of catalytic reforming are grouped according to the respective hydrocarbon type.

REFORMING REACTIONS

Dehydrogenation

The naphthenic hydrocarbons are dehydrogenated to form aromatics (see Figure 4-1). The reaction is extremely fast, and the yields obtained

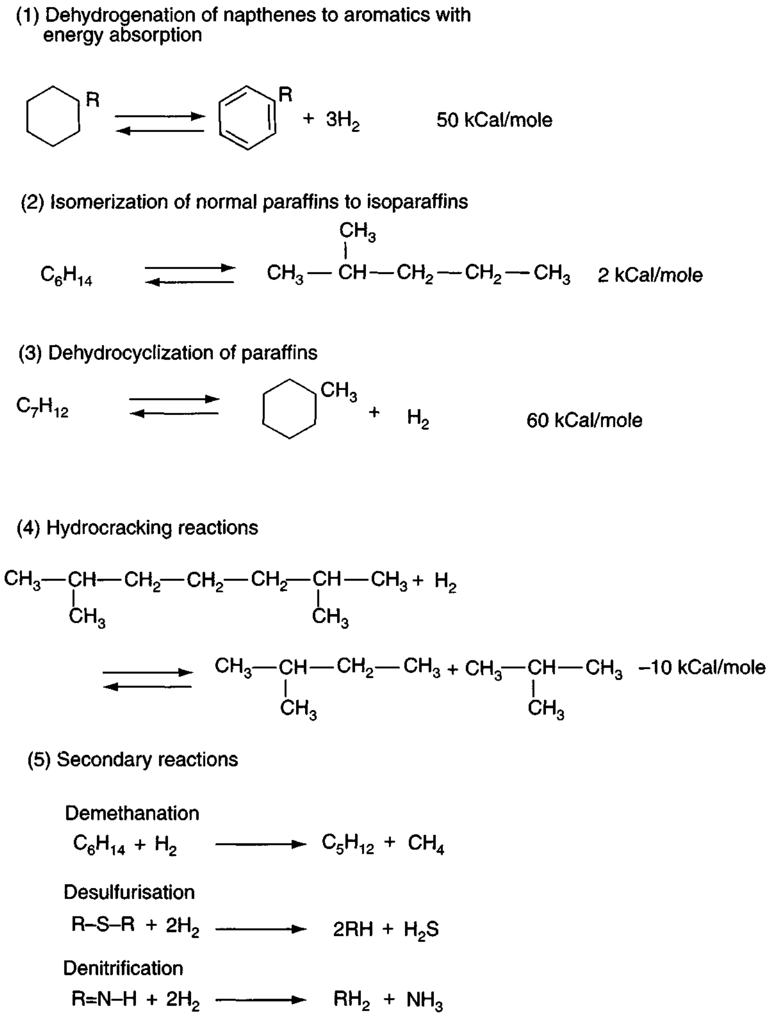

Figure 4-1. Reforming reactions.

are almost those predicted by thermodynamics. Also, the reaction is endothermic, ΔH 50 kCal/mole. Dehydrogenation reactions are very important, because they increase the octane number and the reactions produce hydrogen. The only disadvantage is their endothermicity. Due to the large heat absorption, the feed has to be reheated several times, requiring a number of furnaces and reactors.

Isomerisation

Isomerisation of paraffins is also a fast reaction. The reaction is almost thermoneutral, ΔH 2 kCal/mole. This reaction has a negligible effect on the final octane number.

Dehydrocyclization

The dehydrocyclization of paraffins is the key reaction for producing high-octane gasoline. It is highly endothermic, ΔH 60 kCal/mole. The yield of this reaction is limited by kinetics. The reaction rate is much slower than the naphthene dehydrogenation. Its contribution to increasing the octane number is extremely important because the change of a paraffin mixture to corresponding aromatics lead to increase in octane from 60 to 80. A lower rate of this reaction leads to more severe operating conditions and increase in coke formation.

Hydrocracking

Hydrocracking reactions (see Figure 4-1) are important in the reforming reactors. Unlike other reforming reactions, hydrocracking is exothermic with a heat release of 10 kCal/mole. Compared to hydrodecyclization, the reaction rate is small at low temperature and conversion rates. However, the rate increases with higher temperatures and increases in aromatic content when it becomes an important competitor of hydrodecyclization reactions. The reaction products appear in the reformate and in the gases. The presence of light components C_4 and C_5 gives important volatility properties to reformate. Also, hydrocracking decreases the liquid yield and increases the aromatic content due to a concentration effect.

FEED QUALITY

Typically, the feed to a cat reformer unit for gasoline production is a heavy straight-run naphtha with an initial boiling point (IBP) of 194°F and final boiling point (FBP) of 284°F. Benzene is an undesirable component in the gasoline because of environmental pollution concerns. It is therefore important to minimize or exclude any benzene precursors in the cat reformer feed by keeping the feed IBP higher than 180°F. The cat reformer feed is hydrotreated in a naphtha hydrotreater unit to remove any sulfur, nitrogen, and other impurities which can poison the reforming catalyst.

CATALYST

The catalyst used for cat reforming consists of a high-purity alumina base impregnated with platinum and metallic activators. The platinum content is approximately 0.35% by weight. The catalyst is generally in spheres of 2 mm diameter. In semi-regenerative-type units, the life cycle is about 1 year, after which catalyst is regenerated by burning off carbon.

SEMI-REGENERATIVE REFORMING UNIT

A simplified process flow diagram of a semi-regenerative reforming unit is shown in Figure 4-2. The unit consists of three reactors, containing a reforming catalyst, fired heaters, a hydrogen recycling system with a gas drier and product debutanizer.

Hydrotreated naphtha charge from the naphtha unifiner is combined with a hydrogen-rich recycling stream and passes through a low-pressure drop feed effluent heat exchanger, heater, then the first reactor in the series at about 900°F. As the reactions in the reactors are endothermic due to dehydrogenation of naphthenes to aromatics and dehydrocyclization of paraffins to aromatic carbons, the outlet temperature of the reactor effluent drops, and this stream is reheated and enters the second reactor. Similarly, the effluent of the second reactor is again heated before it enters the third reactor.

The reactor effluent from the last reactor is cooled in the feed reactor effluent heat exchanger, followed by air and water coolers. It is then separated into a liquid product and a hydrogen-rich gas. A part of the separated gas is recycled. The rest of hydrogen-rich gas is bled off to maintain system pressure.

The liquid product from the separator drum is stabilized in the debutanizer column, where lighter components such as C_1, C_2, C_3, and C_4 gases are removed as overhead product and used as refinery fuel. The condensed liquid from debutanizer overhead drum is returned to the column as reflux. The debutanizer bottom product, after heat exchange with debutanizer feed, is sent to reformate storage tanks.

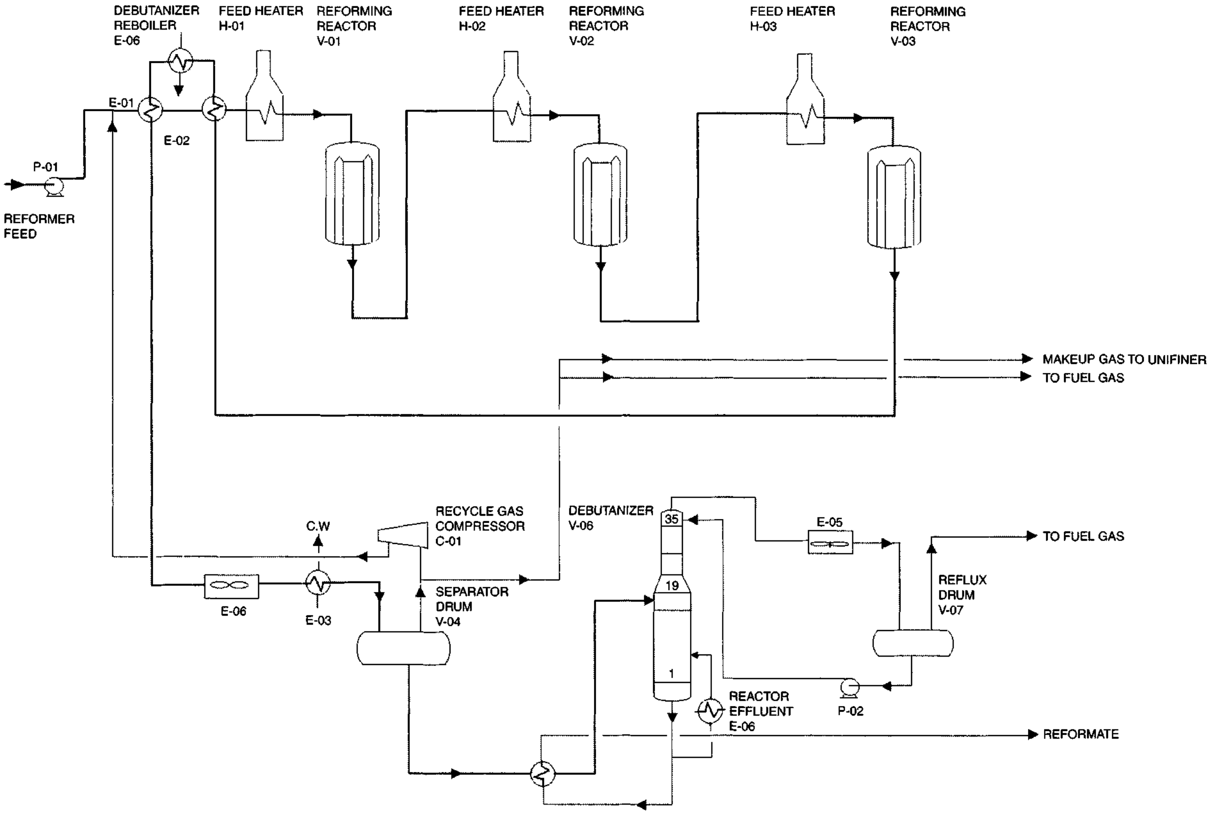

Figure 4-2. Catalytic reformer unit.

CONTINUOUS REGENERATION

Catalyst reforming technology is available in which fresh catalyst is added to the first reactor and moves through all the reactors. A part of the catalyst, about 5%, is continuously withdrawn and regenerated batchwise in a fixed-bed regenerator in the same manner as in semi-regenerative procedures. The regenerated catalyst is returned to the first reactor.

The advantage of the scheme is that the reforming operation can be conducted at higher temperatures and lower pressures, resulting in greater reformate yield, even at high severities. The activity of the catalyst remains constant throughout the run. No downtime for periodic regeneration of the catalyst is required as for semi-regenerative reformer units.

OPERATING CONDITIONS AND YIELDS

The typical operating conditions of a semi-regenerative cat reformer unit are shown in Table 4-1. The yields from the unit and properties of the reformate are shown in Tables 4-2 to 4-5.

FLUID CATALYTIC CRACKING

Fluid catalytic cracking (FCC) is an effective refinery process for conversion of heavy gas oils into gasoline blend components. Cracking

Table 4-1
Catalytic Reformer Operating Conditions

OPERATING VARIABLE	UNITS	
REACTOR WEIGHTED AVERAGE		
INLET TEMPERATURE, SOR	°F	934
INLET TEMPERATURE, EOR	°F	1013
SEPARATOR PRESSURE	psig	185.00
SEPARATOR TEMPERATURE	°F	130.00
RECYCLE RATIO		
MOLES H_2/MOLES FEED		4.5
SPACE VELOCITY (WHSV)		2.75

WHSV = LIQUID HOURLY SPACE VELOCITY ON WEIGHT BASIS.

Table 4-2
Reformer Feed and Product Properties

PROPERTY	UNITS	
FEED (HYDROTREATED HEAVY NAPHTHA, TBP 194–284°F)		
DISTILLATION		
IBP	°F	194
10%		203
30%		221
50%		239
70%		257
90%		275
EP		284
SULFUR	ppmw	0.5
NITROGEN	ppmw	0.5
AS	ppb	<1
PB	ppb	<1
CU	ppb	<1
WATER	ppm	<10
PONA		
P	VOL%	69
N		20
A		11
SPECIFIC GRAVITY		0.734
REFORMATE		
SPECIFIC GRAVITY		0.778
RON		96
ASTM DISTILLATION	°F	
IBP		140
30%		194
50%		230
70%		257
FBP		311
RVP	psi	3.4

IBP = INITIAL BOILING POINT; EP = END POINT; FBP = FINAL BOILING POINT; RVP = REID VAPOR PRESSURE.

is achieved at high temperatures in contact with powdered catalyst without the use of hydrogen. After separation of the catalyst, the hydrocarbons are separated into the desired products by fractionation. The main products of the FCC process are gasoline, distillate fuel oil, and olefinic C_3/C_4 liquefied petroleum gas (LPG). By-product coke, which is deposited on the catalyst during the reaction, is burned off in the regenerator. The heat

Table 4-3
Reformer Yields

COMPONENT	96 RON W/W
FEED	
HEAVY NAPHTHA	1.0000
TOTAL FEED	1.0000
PRODUCTS	
H_2	0.0193
C_1	0.0085
C_2	0.0138
C_3	0.0269
IC_4	0.0180
NC_4	0.0228
IC_5	0.0276
NC_5	0.0184
C_{6+}	0.8447
TOTAL PRODUCT	1.0000

Table 4-4
Cat Reformer Product Yields, W/W
(*Continuous Catalyst Regeneration Unit*)

	100 RON	102 RON
FEED		
HEAVY NAPHTHA	1.0000	1.0000
TOTAL FEED	1.0000	1.0000
PRODUCTS		
H_2	0.0310	0.0320
C_1	0.0120	0.0140
C_2	0.0200	0.0230
C_3	0.0290	0.0330
IC_4	0.0170	0.0190
NC_4	0.0230	0.0260
C_{5+}	0.8680	0.8530
TOTAL	1.0000	1.0000

liberated during the combustion of coke supplies the heat required to vaporize the feedstock and heat of reaction.

FCC gasoline historically has been the principal blend component for gasoline formulations. Distillate cut is a diesel boiling range material

Table 4-5
Cat Refomer Utility Consumption *(per Ton Feed)*

UTILITY	UNITS	SEMI-REGENERATIVE REFORMER	CONTINUOUS REFORMER
FUEL GAS	mmBtu	2.32	2.3200
STEAM	mmBtu	0.47	0.4700
POWER	kWhr	5.3	17.0000
COOLING WATER	MIG	0.7	1.2800

used as a diesel blend component after hydrotreating. Heavier cuts such as light cycle oil, heavy cycle oil, and clarified oils are used as fuel oil blend components and are excellent cutter stocks for vacuum resids. The olefinic LPG produced in the FCC process can be used in downstream alkylation and polymerization processes to yield more gasoline.

The feed to FCC unit (FCCU) is heavy diesel and vacuum gas oil from the crude distillation unit. The properties of a typical FCCU feed are shown in Table 4-12. Feed contaminants such as sulfur, nitrogen, and trace metals, such as nickel and vanadium, affect the yield and qualities of the product and also the catalyst consumption of the unit.

Higher sulfur in the feed is reflected in the products. While all cracked products contain some sulfur, sulfur distribution varies widely in the cracked product and cannot be controlled by operating parameters or catalyst design.

Nitrogen compounds temporarily deactivate the catalyst, resulting in lower conversion levels. This effect is reversible and can be controlled by operating at the highest possible reactor temperature.

However, the nickel and vanadium cause the most problems. Their effects on the cracking catalyst are quite different. Nickel increases the coke and gas yield, while vanadium is deactivator of zeolite catalyst, causing higher makeup catalyst addition rates.

CATALYST

FCC catalyst is a fine powder made up primarily of silica and alumina and containing acid sites that enable the catalyst to crack heavy hydrocarbons to gasoline and lighter products without formation of excessive amount of coke. Catalyst particles are of 50–60 microns in diameter. Earlier FCC catalysts were natural occurring clays, which suffered from low cracking activity and poor stability. Later synthetic silica/alumina catalysts containing 25% alumina were developed, which were more active and stable.

These were replaced with present day zeolite catalysts with greatly increased activity, stability, and improved selectivity. It has been realized for some time that better FCCU yield could be achieved with shorter contact time between the feedstock and the catalyst by using zeolite catalysts. With the earlier catalysts of low activity and long residence time, some of the gasoline formed cracked further in the catalyst bed to LPG resulting in lower gasoline yield. Development of zeolite catalyst made possible short contact time cracking in a riser, yielding in higher gasoline and lower coke.

The present day FCCU catalyst consists of basically three components: zeolites, active matrix, and a binder. It is possible to alter the process yield by adjusting the zeolite/matrix ratio. Optimizing the zeolite/active matrix ratio is done to achieve the best overall yield for a given unit, product slate, and feedstock. The use of zeolites in the FCCU has contributed most significantly to this advance. The coke yield decreases dramatically as the zeolite content of the catalyst increases.

The overall activity of the catalyst increases for a given zeolite content. The effect is more pronounced with an easier-to-crack paraffinic feed. With a paraffinic feed, a significant increase in conversion is observed with increasing zeolite content. Aromatic feed however is less susceptible to higher zeolite activity.

The large pore structure of the active matrix portion of the catalyst provides for easy access of large, heavy oil molecules, thereby providing their effective conversion. The matrix surface area is also a factor in strippability: The ability to strip hydrocarbons from the catalyst surface increases as pore diameter increases. With aromatic feeds, coke yield increases dramatically with increasing matrix contribution. The paraffinic feed shows a similar but less dramatic response. LPG yields are not significantly affected by matrix contribution, but dry gas yields for both paraffinic and aromatic feeds are directly related to matrix activity. Gasoline selectivity decreases with increasing conversion and increasing matrix activity.

Both FCCU design and catalyst improvements have combined to yield higher conversion/lower coke ratios over the years.

OPERATING CONDITIONS

The operating conditions for processing vacuum gas oil feed to maximize the production of light cat gasoline are shown in Tables 4-6 and 4-7.

Table 4-6
FCCU Reactor Operating Conditions

VARIABLE	UNITS	
FEED TEMPERATURE	°F	446
CATALYST/OIL RATIO		5.4
CATALYST CIRCULATION RATE*	tons/min	21.7
CATALYST MAKEUP RATE*	tons/day	2.5
RISER OUTLET TEMPERATURE	°F	991
DISPERSION STEAM	Wt% F. FEED	0.9
STRIPPING STEAM	tons/ton CATALYST	0.0213
REACTOR PRESSURE	psig	30
REGENERATOR PRESSURE	psig	33
REGENERATOR TEMPERATURE	°F	1341
FLUE GAS TEMPERATURE	°F	1355

* FOR UNIT FEED RATE OF 40 mbpsd.

Table 4-7
Regenerator Cyclone Operating Conditions

VARIABLE	UNIT	
GAS MOL WT		29.4
GAS VISCOSITY	C.P.	0.042
GAS DENSITY	lb/ft^3	0.071
REGENERATOR SUPERFICIAL VELOCITY	ft/sec	2.92
FIRST-STAGE CYCLONE INLET VELOCITY	ft/sec	0.16
SECOND-STAGE CYCLONE INLET VELOCITY	ft/sec	0.16

CP = Centipoise (viscosity units).

PRODUCT YIELDS

The yield of products in FCC depends on the feedstock quality, type of catalyst, and operating conditions. FCC units are usually operated to maximize the yield of gasoline; however, the process is versatile and can be operated to maximize middle distillate or LPG, both of which are at the expense of gasoline. The yields are shown in Table 4-8. Table 4-9 shows the composition of FCCU gases. Table 4-10 shows yields for a low-severity operation to maximize middle distillates. Table 4-11 shows the utility consumption for a FCCU unit. A summary of FCCU product qualities is presented in Table 4-12.

Table 4-8
FCCU Yields (Gasoline Operation)

STREAM	V/V	W/W
VGO	1.0000	1.0000
TOTAL FEED	1.0000	1.0000
PRODUCTS		
H_2S		0.0015
HYDROGEN		0.0006
METHANE		0.0165
ETHYLENE		0.0127
ETHANE		0.0139
PROPYLENE	0.0750	0.0434
PROPANE	0.0306	0.0173
BUTYLENES	0.0912	0.0617
ISOBUTANES	0.0617	0.0386
n-BUTANES	0.0208	0.0135
TOTAL GASES	0.2793	0.2197
LIGHT CAT NAPHTHA	0.4353	0.3419
HEAVY CAT NAPHTHA	0.1638	0.1561
DISTILLATE	0.1360	0.1410
LIGHT CYCLE GAS OIL	0.0196	0.0210
CLARIFIED OIL	0.0552	0.0656
COKE		0.0547
TOTAL		1.0000

Light Cat Naphtha

The light cat naphtha cut from FCCU has a high mercaptan sulfur content, about 120 ppm: therefore, further treatment of this cut is necessary to reduce the mercaption content to below 5 ppm by a Merox or equivalent process, before it can be blended into gasoline formulations. The light cat naphtha or FCCU light gasoline has a RON of 91–92 and MON (motor octane numbers) of approximately 80–81. Where gasoline specifications are not very stringent, light cat naphtha forms the major blend component of gasoline blends. However, if MON and other constraining specifications exist, other blend components, such as cat reformate, alkylate, or MTBE (methyl tertiary butyl ether), may be required in the blend to compensate for the low MON of light cat naphtha.

Table 4-9
FCCU Gases Composition

COMPONENT	DRY GAS	LPG
H_2O	0.60	
N_2	8.10	
CO	0.47	
CO_2	1.40	
H_2S	1.48	0.14
H_2	11.88	
C_1	38.62	
$C_2=$	16.97	
C_2	16.92	0.38
$C_3=$	2.02	29.29
C_3	0.60	11.24
IC_4		19.47
NC_4		6.55
$C_4=$		32.04
C_{4+}	0.94	
C_{5+}		0.89
TOTAL	100.00	100.00
MOL WT	21.6	51.20
NET HEATING VALUE, BTU/SCF	1008	2625.00

Heavy Cat Naphtha

Most heavy cat naphtha or gasoline is disposed of as a gasoline blend component at present. However, because of its high end point (375°F) and higher density (API 33.4 compared to 68.5 for light cat naphtha), future gasoline specs will find it increasingly difficult to include this material in gasoline blends and can pose serious disposal problems.

Distillate

The distillate cut, boiling in the diesel range has a very low cetane index of 28, compared to a typical value of 53 for straight-run diesels. Also, the untreated distillate cannot be blended into diesel blends because of the storage stability problems they may create. Blends with distillate from the FCCU must be hydrotreated before they are blended into finished diesels.

Table 4-10
FCCU Yields to Maximize Middle Distillate Operation

	W/W
STREAM	
VGO	1.0000
TOTAL FEED	1.0000
PRODUCTS	
H_2S	0.0014
HYDROGEN	0.0026
METHANE	0.0072
ETHYLENE	0.0030
ETHANE	0.0033
PROPYLENE	0.0220
PROPANE	0.0090
BUTYLENES	0.0346
ISOBUTANES	0.0199
n-BUTANES	0.0058
TOTAL GASES	0.1088
LIGHT CAT NAPHTHA	0.2765
HEAVY CAT NAPHTHA	0.1265
DISTILLATE	0.3566
LIGHT CYCLE GAS OIL	0.0533
CLARIFIED OIL	0.0344
COKE	0.0439
TOTAL	1.0000

Light-Cycle Gas Oil/Clarified Oil

These cuts are excellent cutter stocks for fuel oil blending because of its high aromatic content.

Table 4-11
Utility Consumption *(per Ton Feed)*

UTILITY	UNITS	CONSUMPTION
FUEL	mmBtu	0
STEAM	mmBtu	−0.093
POWER	kWhr	5.2
COOLING WATER	MIG*	2.92

*MIG = 1000 IMPERIAL GALLONS.

Table 4-12
FCCU Feed and Product Properties

PROPERTY	UNITS	FEED	LCN	HCN	DISTILLATE	LCO	CLARIFIED OIL
API		25.6	68.5	33.4	20	15.3	5
BROMINE NUMBER			66.5	16			
CETANE INDEX					27.9		
CON CARBON	%Wt	0.29					4.5
DISTILLATION	°F						
IBP			105	265	400	625	
10%			130	285	440	640	675
50%			180	330	525	655	815
90%			150	375	600	675	920
EP					640	725	
SPECIFIC GRAVITY		0.901	0.708	0.858	0.934	0.964	1.037
MERCAPTANS	ppmw		120	300			
SULFUR	%Wt	0.4	0.03	0.12	0.55	0.95	1.34
METALS	ppmw						0.1
NICKEL + VANADIUM	wppm	0.9					
NITROGEN	ppmw	880	13	45			
PONA ANALYSIS	% VOL						
PARAFFINS			37	19			
OLEFINS			35	10			
NAPHTHENES			13	12			
AROMATICS			15	59			
POUR POINT	°F				0	32	63
RON			91.6	92			
MON			80.4	80.5			
RVP	Psi		8.4	0.4			
VISCOSITY 122	Cst				2.9	9.5	110

RESID PROCESSING IN THE FCCU

It is possible to process resid feed in the FCCU in place of vacuum gas oil. The resid feed is no less crackable than vacuum gas oil. Paraffinic resid crack easily yields higher-valued products, while aromatic feeds is difficult to crack. Increasing the aromatic resid level in the feed increases coke and dry gas yields and decreases overall conversion and gasoline yield. However, the metals (nickel and vanadium) and Conradson (Con) carbon of the resid from most crudes make processing of resid in the FCCU unattractive.

With pure VGO feed, the coke yield is about 5% of the feed. If now resid is added to this feed, displacing some VGO, and the severity of FCCU operation maintained, the coke yield will increase, depending on the Con carbon content of the resid. About 40% of the Con carbon is converted to coke. Metals in the resid increase this quantity to almost 50%. As the coke yield increases, regenerator temperatures increase. At a 6% coke yield, the regenerator temperature increases to 1360°F and some form of catalyst cooling is required. At about 8% coke yield, it may be difficult to find an outlet for the steam generated from catalyst cooling, and this limits the quality of resid processed in the unit. Increasing, Ni and V in the feed due to resid injection increase the catalyst deactivation rate and hence the catalyst addition rate. Also, the conversion rate falls. Thus, resid processing in FCCU is economical with resid from crudes with very low metal and Con carbon contents, such as Bombay High, Brent, Murban, etc.

THE REFINERY FCCU UNIT

The VGO feed from storage or the vacuum distillation unit flows to feed surge drum V-107 and is heated to about 445°F (see Figure 4-3). The preheated feed is mixed with a small amount of dispersion steam and enters FCCU reactor V-101, where a stream of hot catalyst coming from regenerator V-102, at 1360°F, contacts the feed. The catalyst/oil ratio is about 5.4. The catalyst, oil, and steam mixture flows up through the reactor tube, where cracking reactions occur during its short residence at a temperature of approximately 990°F. At the end of the reactor, the cracked oil/catalyst mixture is separated by cyclones. The reactor effluent passes through one or more cyclones to separate any entrained catalyst particles; next any entrained hydrocarbons are stripped from the catalyst by medium pressure (MP) steam. The effluent flows out of the reactor to

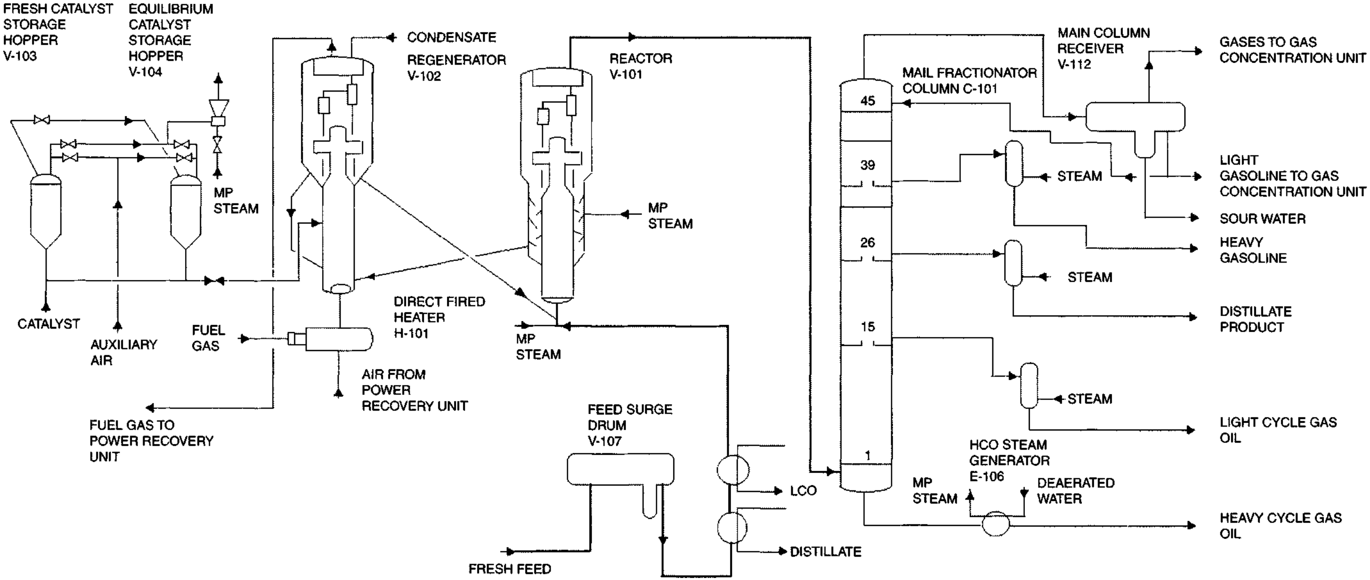

Figure 4-3. Fluid catalytic cracking unit. LCO = light cycle oil.

distillation column C-101, where the cracked effluent is separated into different products. About 5% of the feed is converted to carbon, which is deposited on the catalyst.

After steam stripping, the hot, separated catalyst is transported to FCCU regenerator V-102 by a stream of air. In the regenerator, the carbon deposited on the catalyst is burned off in a stream of hot air. Air for combustion is preheated to 435°F. Due to combustion of carbon, the catalyst temperature rises to about 1340°F, and the carbon on the catalyst is burned off. Flue gases pass through a number of cyclones to reduce particulate emission, produced from the attrition of the catalyst particles. The hot, regenerated catalyst flows back to FCCU reactor V-101 to continue the cycle. The hot flue gases, at 1340°F, generated by combustion of coke on the catalyst, are sent to a power recovery turbine. The power generated is used in an air blower to supply air to the regenerator.

Makeup catalyst is added to the regenerator to compensate for the loss of catalyst due to particle attrition and emitted to atmosphere.

The FCCU reactor effluent is sent to fractionation column C-101, very similar to a crude distillation column, with side strippers for the side cuts. The column has about 45 trays. The feed is introduced at the bottom of the column. The main cuts are;

- Vapors from the overhead reflux drum, which are sent to the gas concentration unit. The liquid, the light gasoline, is also sent to the gas concentration unit. Part of this stream provides the reflux to the fractionating column.
- Heavy gasoline.
- Distillate.
- Light cycle oil.
- Heavy cycle oil.

The broad cuts of heavy gasoline, distillate, and light cycle oil are drawn from the main column to their respective steam strippers, with six plates in each, and stripped light ends are returned to the column. The stripped side cuts are withdrawn as product.

THE FCCU GAS CONCENTRATION UNIT

The FCCU main fractionator column overhead receiver V-112 operates at about 20 psig and 104°F (see Figure 4-4). The vapors from this

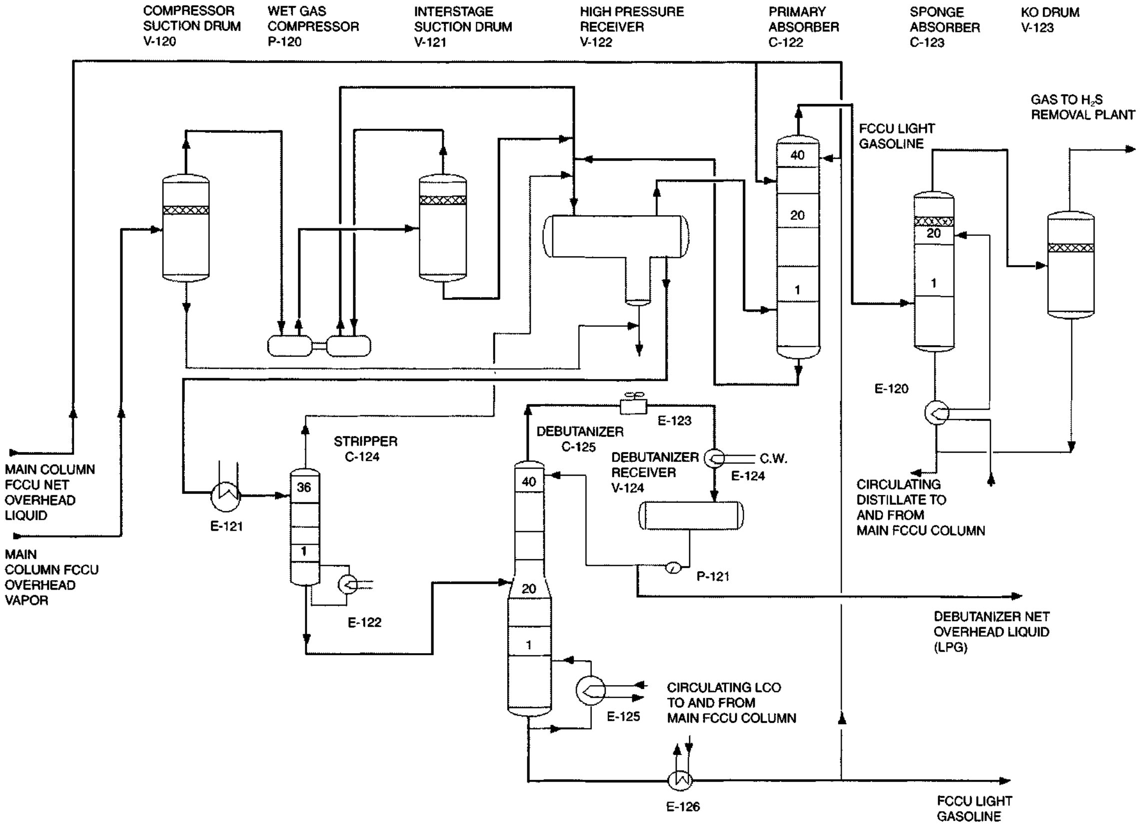

Figure 4-4. FCCU gas concentration unit. KO = knockout; C.W. = cooling water; LCO = light cycle oil.

drum are compressed in wet gas compressor P-120 to 205 psig. A part of the vapor condenses by compression and is collected in high-pressure receiver V-122.

The vapor from the high pressure receiver is fed to the bottom of primary absorber C-122, a column with 40 plates and operating at about 200 psig. The liquid separated in overhead drum V-112 of main FCCU column is used as the absorbent medium. The rich effluent containing the absorbed gas flows to high pressure receiver V-122.

The unabsorbed gases from C-122 flow to a second absorber C-123, the sponge absorber, a column with 20 plates and operating at 197 psig. The bottom stream from the sponge absorber goes back as reflux to the main FCCU fractionator column.

The liquid from high-pressure receiver V-122 goes to stripper C-124, with 35 plates, to strip off light ends. The stripper bottoms next go to debutanizer column C-125 with 40 plates, operating at 160 psig. Here, any LPG contained in the feed is separated as an overhead product, and the light gasoline stream is recovered as the bottom stream from the debutanizer column.

ALKYLATION

Alkylation is an important refining process for the production of alkylate, a high-octane gasoline blending component. Alkylate product is a mixture of branched hydrocarbons of gasoline boiling range. Alkylate has a motor octane (MON) of 90–95 and a research octane (RON) of 93–98. Because of its high octane and low vapor pressure, alkylate is considered an excellent blending component for gasoline.

Alkylates are produced by the reaction of isobutylene with isobutane in the presence of a catalyst (sulfuric acid) at low temperatures, as per the reactions shown in Figure 4-5. Propylene present in the feed in small concentration also reacts with isobutane to form isoheptane.

Under reaction conditions unfavorable to alkylate formation, propylene may also polymerize to form the undesirable product polypropylene. Amylenes can undergo a similar reaction to form alkylate, but since amylenes have a high octane number to start with, their conversion to alkylate is not as advantageous, as in the case of butylenes. Another side reaction that can negatively affect the formation of alkylate is ester formation by the reaction of olefin with sulfuric acid.

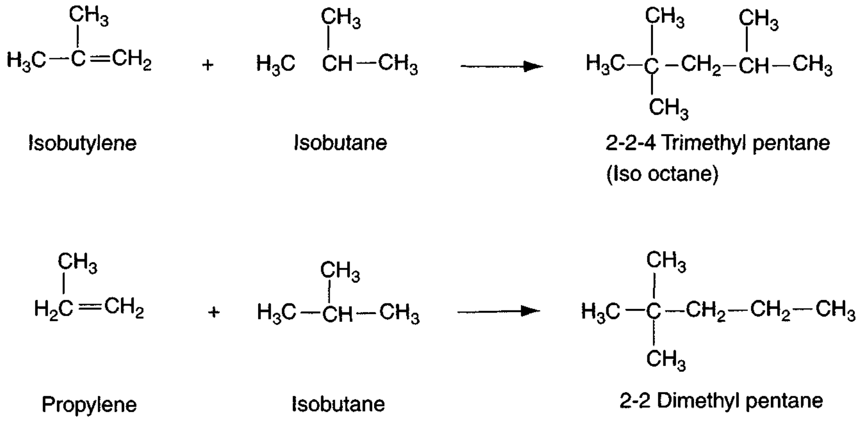

Figure 4-5. Alkylation reactions.

PROCESS VARIABLES

The process variables that influence the quality of alkylate product (octane, distillation, and density) and acid consumption rate are the olefin type, isobutene concentration, temperature, mixing, space velocity, and acid strength and composition. These are described next.

Olefin Type

The type of olefin in the alkylation feed, especially the ratio of butylene to propylene affects the product quality and acid consumption rate. In propylene alkylation, the octane is about 5 numbers lower and acid consumption about twice those of butylene alkylation. The heat of the reaction, isobutane consumption, and alkylate yield vary with olefin type.

Isobutane Concentration

In the alkylation reaction, a molecule of olefin reacts with a molecule of isobutane to form an alkylate molecule. This reaction occurs in the presence of a sulfuric acid catalyst. A side reaction that competes with the alkylation reaction is polymerization. In this reaction, two or more olefin molecules react with each other to form a polymer. Polymerization causes lower product octane and increased acid consumption.

Both alkylation and polymerization occur in the acid phase. Because olefins are extremely soluble in the acid phase and isobutene is only slightly soluble, a large excess of isobutene must be maintained within the reaction zone to ensure that enough isobutene is absorbed by the acid to react with the olefins.

Temperature

Minimizing the reaction temperature reduces polymerization rate relative to the alkylation rate, resulting in a higher octane number and lower acid consumption. The optimum temperature for sulfuric acid alkylation is 45–50°F. Temperatures below 40°F are avoided to prevent freezing the sulfuric acid. Also, very low temperatures retard settling rates in the acid settler and can result in acid carryover.

The temperature in the contactor depends on the olefin feed rate, which in turn determines the heat of the reaction generated. Removal of heat from the reactor is a function of compressor suction pressure. Lower suction pressure produce more vaporization of the contactor effluent stream within the tubes of the contactor, which in turn produces more cooling and a lower contactor temperature.

Mixing

Vigorous mixing of hydrocarbon and acid is very beneficial for the reaction. Increased mixing produces a finer dispersion of hydrocarbon droplets in the acid continuous phase emulsion, increasing the surface area for mass transfer of isobutane into the acid catalyst. This improves the product quality and reduces acid consumption.

Space Velocity

Because alkylation occurs almost instantaneously, the residence time of reactants is not a limiting parameter. The space velocity (*SV*) in this case may be defined as follows:

$$SV = \frac{\text{olefin in contactor (bbl/hr)}}{\text{acid in contactor (bbl)}}$$

The term is simply a measure of the concentration of olefins in the acid phase of the reactor. As the olefin space velocity increases, octane tends to decrease and acid consumption tends to increase.

Acid Strength and Composition

The minimum acid strength required to operate the system is 85–87 wt%, although this varies somewhat depending on the olefin type and spent acid composition. At acid strengths lower than this, polymerization becomes so predominant that the acid strength cannot be maintained and the plant is said to be in an *acid runaway* condition. To provide a sufficient safety margin, an acid strength of 89–90% H_2SO_4 is used. However, the composition of acid diluents, as well as acid strength, is important. Water lowers the acid catalytic activity three to five times faster than hydrocarbon diluents. Some water is necessary to ionize the acid. The optimum water content is approximately 0.5–1% by weight. Impurities present in the olefin feed stream either react with or are absorbed in the acid catalyst, causing a decrease in strength and a need for increased acid makeup.

ALKYLATION PROCESS

Feed Sources

The feed to alkylate unit is usually cracked LPG from the FCCU unit. The FCCU's LPG is fractionated into a C_3/C_4 splitter to remove propane and lighter components (see Figure 4-6). The bottom stream from the splitter is charged to MTBE unit, if the refinery has one, which along with its primary product produces a raffinate stream that contains isobutane and butylene in a ratio suitable for alkylate manufacture. The composition of the raffinate stream is roughly as follows:

COMPONENT	VOL%
ISOBUTANE	47.3
NORMAL BUTANE	11.4
ISOPENTANE	1.4
BUTYLENE	38.9
AMYLENES	0.8
BUTADIENE	0.2

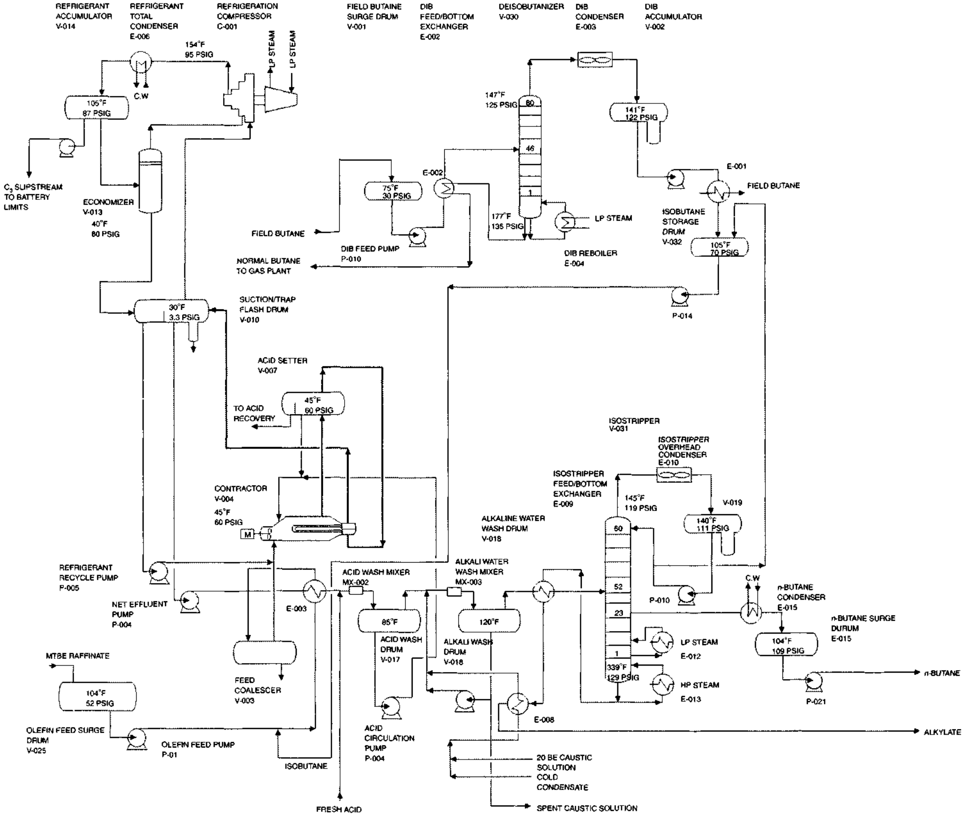

Figure 4-6. Alkylation process flow diagram.

If the refinery has no MTBE unit, the isobutane content of the FCCU gases may be insufficient to react to all the isobutylene in the feed and isobutane from external sources may be required.

Reaction Zone

The olefin feed is combined with the recycled isobutane stream before being charged to the reaction zone. The combined feed is at 104°F and saturated with dissolved water. The combined feed stream is cooled to 57°F by exchanging heat in E-003 with the contactor net effluent stream, which is then fed to alkylation reactor.

The alkylation reactor or contactors are horizontal pressure vessels containing a mixing impeller, an inner circulation tube, and a tube bundle to remove heat generated by the alkylation reaction.

Feed is injected into the suction side of the impeller inside the circulation tube. The impeller rapidly disperses the hydrocarbon feed in the acid catalyst to form an emulsion. The emulsion is circulated at high rates within the reactor. A portion of the emulsion is withdrawn from the reactor at the discharge side of the impeller and flows to acid settler V-007, where the acid and the hydrocarbon phases are allowed to separate. Being heavier, the acid settles to the bottom of the vessel and is returned to the suction side of the reactor impeller. Thus, the impeller acts as emulsion pump between the reactors and settlers.

The sulfuric acid present within the reaction zone serves as a catalyst to alkylation reactions. A certain amount of acid is consumed as a result of side reactions and feed contaminants. To maintain the desired spent acid strength, a small amount of fresh acid (98.5 wt% H_2SO_4) is continuously charged to the reactor and an equivalent amount of 90% H_2SO_4 spent acid is withdrawn from the aftersettler.

The fresh acid is drawn from acid wash drum V-017 in the effluent-treating section. The spent acid is sent to an acid aftersettler drum to recover hydrocarbons which are sent back to acid settlers. The spent acid goes down to an acid blow-down drum for degassing before being sent out of the battery limit for storage or disposal.

The acid-free hydrocarbon phase flows from the top of the acid settler through a back-pressure control valve into the tube side of the reactor tube bundle. The back-pressure control valve is set at about 64 psig to maintain the contents of the settler in liquid phase. As the hydrocarbon stream passes through the control valve, its pressure is reduced to

4.3 psig, flashing a portion of the stream's lighter components and cooling this stream to about 30°F. When the two-phase stream passes through the tube bundle, additional vapor is generated as a result of heat generated by alkylation reactions.

Refrigeration Section

After leaving the tube bundles, the contractor effluent stream flows into the suction trap side of the suction trap/flash drum V-010, where the liquid and vapor portions are separated. The suction trap/flash drum is a two-compartment vessel with a common vapor space. The net reactor effluent is accumulated on the suction trap side of a separation baffle and pumped to the effluent treating section. Cold refrigerant condensate from the refrigeration system is accumulated on the other side of the baffle. This refrigerant recycling stream consists mostly of isobutane and is returned to the reactor by refrigerant recycle pump P-005. The vapor portions of both streams are combined and flow to the suction side of refrigeration compressor C-001. The compressor increases the pressure of the refrigerant vapor to 95 psig. At this pressure, the compressor discharge stream is condensed by the refrigerant total condenser with cooling water at the ambient temperature.

The refrigerant condensate is collected in refrigerant accumulator drum V-014. A part of the refrigerant condensate is treated in a caustic wash followed by a coalescer to remove any traces of acidic components before being charged to an external C_3/C_4 splitter column.

This slipstream to the external C_3/C_4 splitter purges propane from the alkylation unit and prevents propane concentration from increasing within the unit. Most of isobutane present in the propane slipstream is recycled to the alkylation unit by way of C_3/C_4 splitter bottoms.

The remaining refrigerant condensate from the refrigerant accumulator drum flows to economizer drum V-013. As the condensate enters the economizer drum, it is flashed through a control valve to a pressure of 45 psig. At this pressure, a portion of the stream is vaporized. The economizer vapor flows to an intermediate stage of the compressor, while the cooled economizer liquid flows to the flash drum side of the suction trap/flash drum V-010, where further vaporization and cooling occurs.

Effluent Treatment

The liquid phase from the contactor tube bundle is collected on the suction trap side of suction trap/flash drum V-010. This stream contains traces of acid and neutral esters formed by the reaction of sulfuric acid with olefins. The esters are corrosive and must be removed to prevent corrosion in the downstream equipment. These esters are removed in the effluent treating section by washing the stream with fresh sulfuric acid followed by washing with a dilute alkaline water stream.

The net effluent from the suction trap is at 35°F. This stream is pumped through feed/effluent exchanger E-003 to heat it to 85°F. The net effluent stream is next contacted with fresh acid in acid mixer MX-002. The circulating acid is mixed with net effluent just ahead of the acid wash mixer. The hydrocarbon and acid phases are separated with the aid of electrostatic precipitator EP-01 in acid wash drum V-017. Some of the acid from this drum flows to the reaction section, while the remainder is recirculated. Fresh acid is pumped from storage at a continuous rate to maintain the acid level in this drum at 25%.

The treated hydrocarbon effluent flows from the top of acid wash drum V-017 to the alkaline water wash drum V-018 to neutralize any remaining esters as well as any entrained acid carried over from the acid wash. The alkaline water wash is operated at 120°F to thermally decompose the remaining esters.

Heat is added to the alkaline washwater by heat exchange with the isostripper bottoms stream. The circulating alkaline water is heated to 160°F before mixing with the hydrocarbon stream. The hydrocarbon/alkaline water mixture flows through alkaline water wash mixer MX-003 and then into the alkaline water wash drum, where the hydrocarbon and aqueous phases are separated by gravity settling.

Isobutane Stripper

The treated net contractor effluent is heated by heat exchange with isostripper bottom stream in exchanger E-009 to 165°F and fed to the isobutane stripper, where isbutane is stripped off from the alkylate product.

The overhead isobutane vapor is condensed in air cooler E-010 and collected in accumulator drum V-019. A portion of this liquid is refluxed back to the column, while the bulk of isobutane is recycled to the reaction section via isobutane storage drum V-032.

Normal butane is removed from the column as a vapor side draw from 22nd plate and sent outside the unit battery limit.

The isostripper bottom liquid is the alkylate product. The hot alkylate product is cooled by heat exchange with isostripper feed in E-009, circulating alkaline water heater in E-008, and finally in alkylate cooler E-014 before being sent to storage.

The operating conditions of an alkylation unit are shown in Table 4-13. Table 4-14 shows the effect of olefin type on alkylation. The process yields, utility consumption, and feed and product properties are shown in Tables 4-15 to 4-17.

ISOMERIZATION OF C_5/C_6 NORMAL PARAFFINS

GENERAL

Most gasoline formulations require inclusion of some light naphtha to meet the front-end distillation and octane specs. However, C_5/C_6 normal paraffins in this boiling range have low octane, which make them very

Table 4-13
Alkylation Unit Operating Conditions

OPERATING PARAMETERS	UNITS	
CONTACTOR/SETTLER		
Contactor Feed Temperature	°F	39
Contactor/Settler Temperature	°F	45
Settler Pressure	psig	60
Mixer speed	rpm	600
% Acid in the Contactors	LV%	50–60
Acid (H_2SO_4) Strength	Wt%	93–96
REFRIGERATION SECTION		
Compressor Suction Temperature	°F	30
Compressor Suction Pressure	psig	1.3
Compressor Discharge Temperature	°F	148
Compressor Discharge Pressure	psig	95
Economizer Vapor Temperature	°F	79
Economizer Vapor Pressure	psig	43
DEISOBUTANIZER		
Feed Temperature	°F	141
Feed Pressure	psig	119
Column Top Temperature	°F	147
Column Top Pressure	psig	125
Column Bottom Temperature	°F	177
Column Bottom Pressure	psig	135
Number of Plates		60

Table 4-14
Effect of Olefin Type on Alkylate Yield and Quality

PROCESS PARAMETER	UNITS	PROPYLENE	BUTYLENE	AMYLENE
TRUE ALKYLATE YIELD	bbl/bbl OLEFIN	1.77	1.72	1.58
REACTION ISOBUTANE	bbl/bbl OLEFIN	1.30	1.13	1.00
HEAT OF REACTION	Btu/lb OLEFIN	840	615	500
ALKYLATE RON		90	93	93
ALKYLATE MON		89	93	93
ACID CONSUMPTION	lb/bbl ALKYLATE	38	21	29

Table 4-15
Alkylation Process Yields

STREAM	YIELD WT%
FEED	
RAFFINATE EX MTBE PLANT	1.0000
PRODUCTS	
C_3 PURGE STREAM	0.0069
C_4 TO BOILERS	0.0596
ALKYLATE PRODUCT	0.9290
LOSS	0.0045
TOTAL	1.0000

Table 4-16
Alkylation Unit Utility Consumption
(per Ton Feed)

UTILITY	UNITS	
POWER	kWhr	64.085
STEAM	mmBtu	2.0402
COOLING WATER	MIG	12.065

difficult to include in the gasoline formulation. Branched chain C_5 and C_6 hydrocarbons have higher octane, making them more suitable for inclusion in gasoline (Table 4-18).

Table 4-17
Properties of Feed and Product

PROPERTY	UNITS	
FEED (MTBE RAFFINATE)		
COMPOSITION	Wt%	
PROPANE		0.06
I-BUTANE		45.53
N-BUTANE		11.36
I-PENTANE		1.52
N-PENTANE		0.03
$C_{4=}$		40.51
$C_{5=}$		0.76
1,3 BD		0.23
TOTAL		100.00
FEED TOTAL SULFUR	ppmw	20
TOTAL OXYGENATES	ppmw	800
ALKYLATE PRODUCT		
RON		96
MON		94
ASTM DISTILLATION		
IBP	°F	102
10%		160
30%		212
50%		223
70%		230
90%		258
EP		401

Table 4-18
Properties of Normal (*N*-) and Isoparaffins (*I*-)

HYDROCARBONS	BP, °F	RVP, psia	RON	MON
N-C_5	96.8	15	62	62
I-C_5	82.4	20	92	89.6
N-C_6	156.2	5	25	26
2-METHYL PENTANE	140	7	73	73
3-METHYL PENTANE	145.4	6	75	73
2–2 DIMETHYL BUTANE	122	10	92	93
2–3 DIMETHYL BUTANE	136.4	7	102	94

NOTE:
BP = BOILING POINT.
RVP = REID VAPORIZATION PRESSURE.

The isomerization process is designed for continuous catalytic isomerization of pentanes, hexanes, and their mixtures. The process is conducted in an atmosphere of hydrogen over a fixed bed of catalyst and at operating conditions that promote isomerization and minimize hydrocracking.

Ideally, the isomerization catalyst should convert the feed paraffins to the high-octane-number branched molecules—C_5 to isopentanes, C_6 to 2-3 dimethyl butane, and the like—however, the isomerization reaction is equilibrium limited with low temperatures favoring the formation of branched isomers. Under commercial conditions, the ratio of isoparaffin to normal paraffin in the reactor effluent is 3:1 and 9:1, respectively, for pentane and hexanes.

Dehydrocyclization is partially promoted and the reactor effluent contains less naphthenes than in the feed. The C_6 isomer equilibrium distribution is split approximately 45/55 between the higher-octane dimethyl butanes and lower-octane methyl pentanes. For typical C_5/C_6 feeds, the equilibrium limits the product research octane to approximately 83–85 clear on a one-pass basis.

Feed to the isomerization unit is a hydrotreated C_5/C_6 cut, free from sulfur, nitrogen, and water. The bulk of the straight-run C_7 cut is normally included in the cat reformer feed, due to its high content of aromatic precursors and because some of it cracks to C_3 and C_4 under isomerization unit operating conditions. The isomerization unit catalyst is otherwise unaffected by a high concentration of C_7 in the feed. Benzene, if present in the feed, is hydrogenated to cyclohexane, which is then isomerized to an equilibrium mixture of methyl cyclopentane, cyclohexane, and partially converted to isoparaffin. This represents an octane loss but liquid volume increase.

Feed to the isomerization unit needs to be hydrotreated to remove sulfur. Sulfur reduces the isomerization rate and therefore the octane number. Its effect, however, is temporary, and the catalyst resumes its normal activity once the feed sulfur concentration falls. Water is the only potential contaminant that can poison the catalyst and shorten its life.

The isomerization process normally has two reactors in a series flow configuration, each containing an equal volume of catalyst. Valves and piping are provided, which permit reversal of the process positions of the two reactors and isolation of either for catalyst replacement. Over time, the catalyst becomes deactivated by water. When the catalyst in the lead reactor is spent, the reactor is taken off-line for reloading. During the short period when the reactor is out of service, the second reactor is used to maintain continuous operation until the catalyst reloading is completed, allowing an almost 100% onstream factor.

Both isomerization and benzene hydrogenation are exothermic reactions, and the temperature increases across the reactor. Equilibrium requires that the reactor temperature be as low as the activity of the catalyst permits. Therefore, the effluent from the first reactor is cooled by heat exchange with cold incoming feed before entering the second reactor. Thus, the two-reactor system permits the imposition of an inverse temperature gradient. Most of the isomerization is accomplished at a high rate in the first reactor and under more favorable equilibrium conditions in the second reactor.

CATALYST

The catalyst used in the isomerization process have a zeolites base or are platinum-impregnated chlorinated alumina, although the latter are preferred. Due to their chlorinated nature, these are very sensitive to feed impurities, particularly water, elemental oxygen, sulfur, and nitrogen. The reactor operating temperature is 300–340°F. The reactor is operated at approximately 450 psig.

Organic chloride promoter (CCl_4) is continuously added with the feed (measured in parts per million) and converted to hydrogen chloride in the reactor. It is not necessary to provide separate equipment for recovery and reuse of hydrogen chloride. It is permitted to leave the unit by way of the stabilizer gas. The quantity of stabilizer gas is small due to minimum hydrocracking of the feed. The stabilizer gas is scrubbed for removal of hydrogen chloride before entering the refinery fuel system.

Single-pass isomerization of C_5/C_6 straight-run feed gives a product of 83–85 research octane clear. This can be increased to 92–93 by recycling unconverted C_5/C_6 back to the reactor.

The coking propensity of isomerization catalyst is low, thus there is no need for hydrogen recycling. The only hydrogen present is that required for saturation of aromatics and a small excess for adjustment to changes in feed composition.

HYDROCARBON CONTAMINANTS

The tendency of the catalyst to coke or sludge is minimal. The process therefore offers great flexibility with respect to the amount of hydrocarbons other than C_5/C_6. Sharp fractionation is not required to prevent C_6

cyclics and C_7 from entering the isomerization reactor. The effect of some of these hydrocarbons follows.

Olefins

The isomerization catalyst can tolerate up to 2% of C_5/C_6 olefins. Therefore, the feed from an FCCU or thermal cracker cannot be handled in an isomerization unit. Large quantities of olefins, if present in the feed, physically coat the catalyst following polymerization.

Cyclic Compounds

Cyclic compounds, if present in the feed, are adsorbed on the catalyst, reducing the active sites available for paraffin isomerization. Therefore, if the feed contains significant amounts of cyclic compounds, such as benzene, the catalyst inventory in the reactor has to be increased. Unsaturated cyclic hydrocarbons consume considerable quantities of hydrogen, resulting in exothermic reactions, which is undesirable from an isomerization equilibrium view point. Benzene is rapidly hydrogenated and converted to cyclohexanes. Cyclohexanes and other C_6 naphthenes are partially converted to C_6 paraffins.

C_7 Hydrocarbons

C_7 hydrocarbons crack readily to C_3 and C_4, and those that do not hydrocrack are isomerized to a mixture having a lower octane number than C_5 or C_6. C_7 naphthenes have an effect similar to C_6 naphthenes.

ISOMERIZATION PROCESS

Light naphtha feed is charged by charge pump P-101 to one of the two drier vessels, D-101 and 102, filled with molecular sieves, and designed to remove water to protect the catalyst (see Figure 4-7). The makeup hydrogen is compressed by makeup gas compressor C-101 to 500 psig. The gas then flows to gas driers D103 and D104, similar to those for liquid feedstock before it is combined with fresh feed. The feed is mixed with makeup hydrogen, heated through heat exchange with reactor effluent in E-101 and E-102 and a steam heater E-103, heated with medium pressure steam, and sent to the reactors. In normal operation, two reactors in series are employed.

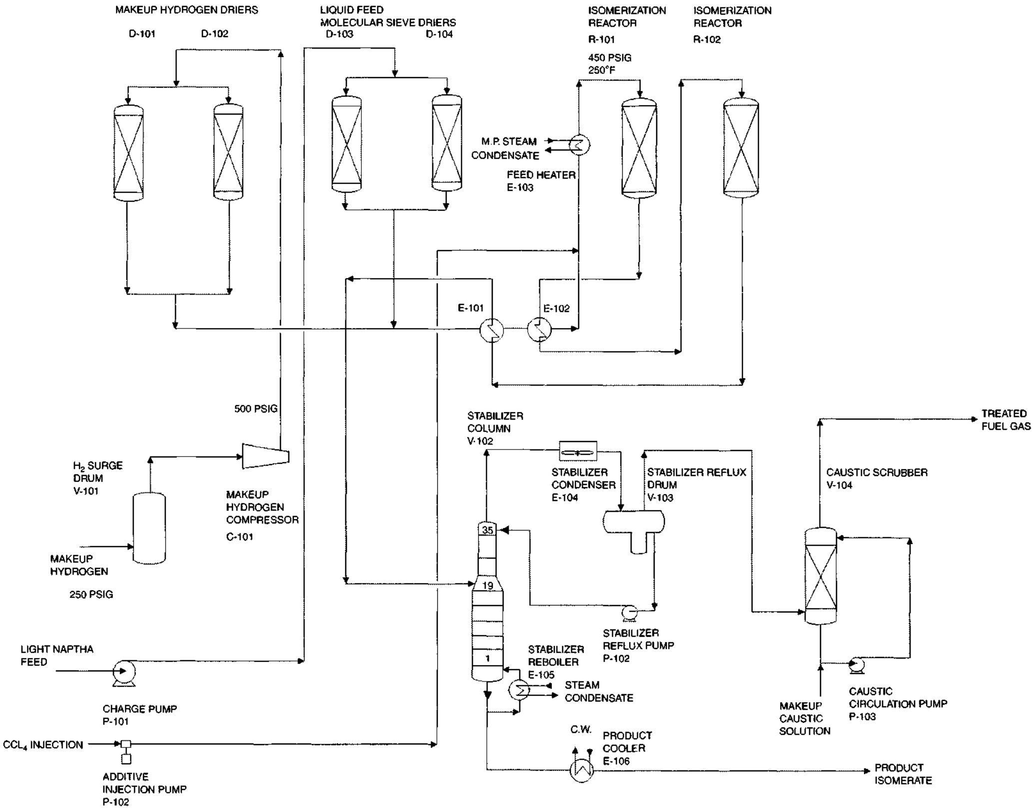

Figure 4-7. C_5/C_6 paraffins isomerization process. M.P. = medium pressure; C.W. = cooling water.

Table 4-19
C_5/C_6 Isomerization Operating Conditions

VARIABLE	UNITS	
REACTOR PRESSURE	psig	450
REACTOR INLET TEMP	°F	300–340
H_2/HC MOLE RATIO		0.05
LHSV	hr^{-1}	2

The reactor effluent is heat exchanged with fresh feed in E-101 and taken directly to product stabiliser column V-102. The column overhead vapor product flows to the off-gas caustic wash column. In this column, the off gas is washed with dilute caustic, circulated by a pump at the bottom of the column, to remove traces of chlorides before the gas flows to the fuel system. The stabilized, isomerized liquid product flows from the bottom of the column and is transferred to the gasoline blending system. Alternatively, the stabilizer bottom can be separated into normal and isoparaffin components to recycle low-octane normal paraffin. Product octanes in the range of 88–92 RON can be obtained by this method. Recycle of normal paraffins and, if possible, methyl pentanes is required to increase octane gain.

The efficiency of separation by distillation is limited, however, because normal C5 boils between i-C_5 (isopentane) and C_6 isomers, separation by a molecular sieve is more effective. The molecular sieve selectively adsorbs normal paraffins, due to their smaller pore diameter, while excluding the larger-branched molecules.

The operating conditions of an isomerization unit are shown in Table 4-19. The process yields, utility consumption, and feed and product properties are shown in Tables 4-20 to 4-22.

METHYL TERTIARY BUTYL ETHER

Methyl tertiary butyl ether (MTBE) is produced by the reaction of isobutene with methanol (see Figure 4-8). Its main use is as a gasoline blending component, due to its high octane level (RON = 115–135, MON = 98–100). Any hydrocarbon stream containing isobutene can be used for the production of MTBE. In refineries with a cat cracker unit, C_4 cut from cat cracking is the principal source of isobutene for

Table 4-20
Isomerization Unit Yields

STREAM	YIELD WT%
FEED	
LIGHT NAPHTHA FEED	1.0000
HYDROGEN	0.0040
TOTAL FEED	1.0040
PRODUCT	
ISOMERATE	0.9940
GASES	0.0100
TOTAL PRODUCT	1.0040

Table 4-21
Isomerization Unit Utility Consumption
(per Ton Feed)

UTILITY	UNITS	CONSUMPTION
ELECTRICITY	kWhr	7.22
MP STEAM	mmBtu	0.536
COOLING WATER	MIG	6.15

MTBE production. In petrochemical plants, C_4 cut from steam cracking after butadiene extraction can be used for MTBE manufacture.

CHEMICAL REACTIONS

Methanol reacts with isobutene to form MTBE. A number of secondary reactions can also occur, depending on the operating conditions and feed impurities (see Figure 4-9).

The etherification reaction is conducted in the presence of a catalyst that is cationic resin and strongly acidic. These resins are produced by sulfonation of a copolymer of polysryrene and divinyl benzene. These catalysts are very sensitive to impurities, which could destroy their acidic function, and high temperatures, which could remove the sulfonic bond. The activity of the catalyst allows operation below 195°F.

To obtain optimum yields, the reactor temperature is kept as low as possible to minimize side reactions and maximizing MTBE yield.

Table 4-22
Isomerisation Unit Feed and Product Properties
Feed (Light Natural Naphtha)

FEED COMPOSITION	WT FRACTION
ISOPENTANE	0.2431
N-PENTANE	0.3616
2,2 DIMETHYL BUTANE	0.0122
2,3 DIMETHYL BUTANE	0.0225
2,METHYL PENTANE	0.0970
3,METHYL PENTANE	0.0644
N-HEXANE	0.0225
METHYL CYCLOPENTANE	0.0592
CYCLOHEXANE	0.0695
BENZENE	0.0246
C7 AND HEAVIER	0.0234
TOTAL FEED	1.0000
FEED S.G	0.6502
FEED RVP, PSI	11.30

PRODUCT PROPERTIES
C4+ ISOMERATE

PROPERTY	UNITS	
RON		84.2
MON		81.6
SPECIFIC GRAVITY		0.6390
RVP	PSI	14.5

C5+ ISOMERATE

PROPERTY	UNITS	
RON		84
MON		81.3
SPECIFIC GRAVITY		0.641
RVP	psi	13.5
ASTM D-86 DISTILLATION		
IBP	°F	91.8
10%	°F	94.1
20%	°F	97.4
50%	°F	104.4
70%	°F	127.1
90%	°F	146.4
95%	°F	157.1
FBP	°F	184.4

TYPICAL MAXIMUM FEED CONTA-MINANT LEVEL (*FOR CHLORINATED ALUMINA CATALYSTS*)

CONTAMINANT	UNITS	
SULFUR	ppmw	1
NITROGEN	ppmw	1
WATER	ppmw	0.5
OXYGENATES	ppmw	0.5

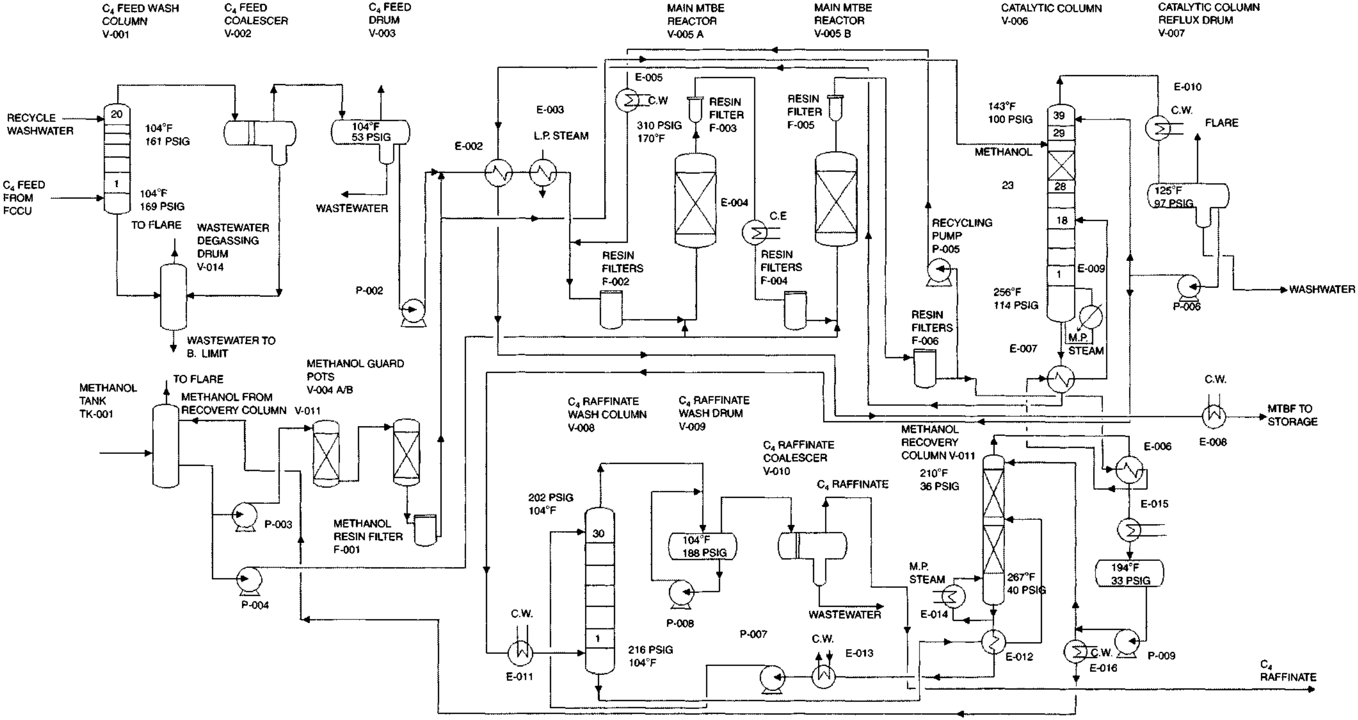

Figure 4-8. MTBE manufacture. L.P. = low pressure; M.P. = medium pressure; C.W. = cooling water.

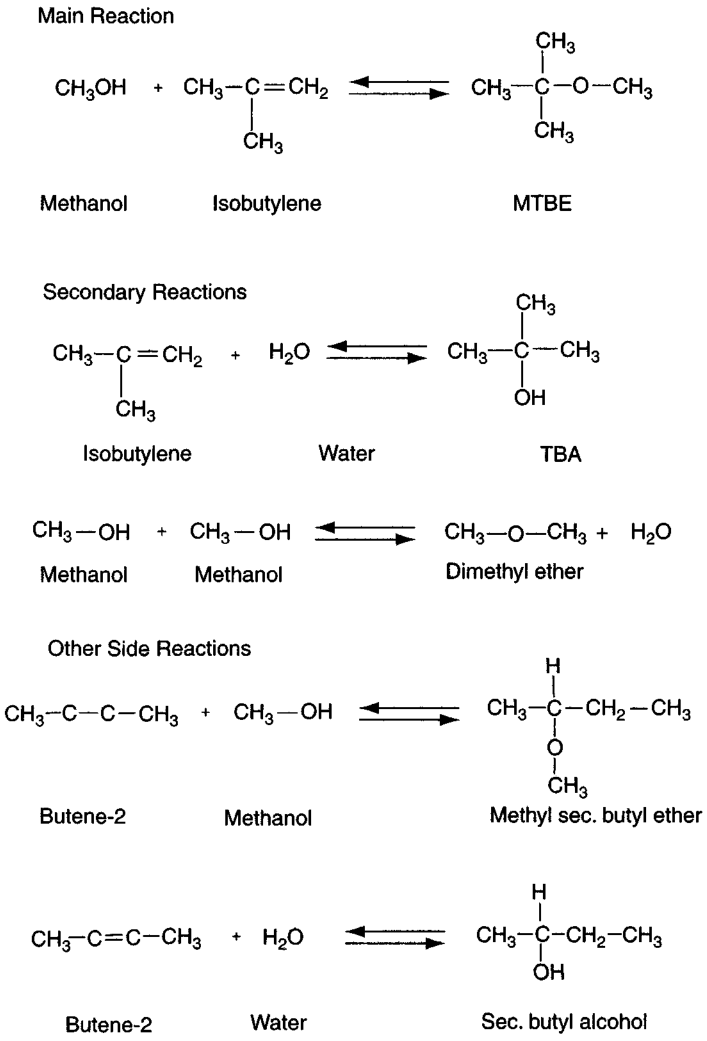

Figure 4-9. MBTE reactions.

Pressure has no effect on the reaction, but the pressure is chosen to keep the system in a liquid phase. The pressure of the catalyst column is adjusted to keep the temperature at a minimum level and optimum conversion rate to MTBE.

Conversion increases with higher methanol at a constant temperature. However, higher methanol results in increased processing costs to recover excess methanol, and an economic optimum has to be determined between increased conversion and increased production cost.

PROCESS DESCRIPTION

The MTBE process consists of the following sections: feed wash, main reaction, catalyst distillation, C_4 raffinate wash, and methanol washing and recovery.

The Feed Wash Section

C_4 feed washing is done in 20-tray sieve column V-001 to remove actonitrile in addition to other impurities; here, C_4 feed is washed with cold condensate. The tower is operated full of liquid with the water/hydrocarbon interface maintained above the top tray. Water effluent from V-001 is sent to V-014 for degassing. C_4 from the column top flows to C_4 coalescer drum V-002 and C_4 surge drum V-003.

The Reaction Section

The main reactors are vertical vessels, each having expandable bed of an ion-exchange-resin-type catalyst. Methanol makeup, mixed with methanol recycle, is pumped from TK-001 by pump P-003, through methanol guard pots V-004 to remove basic and cationic compounds.

The C_4 feed and a part of methanol respectively pumped through P-002 and P-003 under flow and flow ratio control are mixed with recycle before feeding the main reactors V-005 A/B. The two reactors are installed in series. The feed is heated with LP steam in feed preheaters E-002 and E-003. Interreactor cooler E-004 is used during EOR conditions of column catalyst to increase conversion.

The catalyst is fluidized by recycling a part of reactor effluent through P-005. The temperature of the reactor is controlled by cooling the recycled stream with cooling water in exchanger E-005, which removes the heat of reaction and heat added during preheat in E-003. Filters F-002/4/6 are installed at both reactor inlet and outlets to collect fine particles from the resins. The conversion in the reactors is up to 80%.

Cartridge filters with an acrylic wool fiber filter element are installed at the inlet of reactors to trap circulating resin particles of 75+ micron size. Similarly, strainers are placed at reactor outlets to trap circulating fine particles originating from the catalyst bed.

The Catalytic Distillation Section

Isobutylene final conversion is achieved in a catalytic column V-006, where the reaction and distillation are simultaneous. This column includes a fractionating tower yielding MTBE product at the bottom and unconverted C_4 raffinate/methanol azeotrope at top. Additional conversion is made possible by enhanced contact between reactants in a number of packed beds. In addition to packed beds, the column is equipped with approximately 40 trays for distillation.

The main reactor effluent is preheated in methanol recovery column condenser E-006, then in feed/bottom exchanger E-007 before entering column V-006. The methanol injection at the top of first resin bed is controlled by the methanol analyzer on the bottom of the column. Also, methanol is injected at other points to improve conversion. Bottom MTBE product is sent to storage after cooling via feed/bottom heat exchange in E-007, feed preheater E-002, and trim cooler E-008. The overhead of the column is condensed in cooling water condenser E-010. One part of the reflux drum V-007 liquid is sent to the column through P-006, and the other part to the methanol recovery section. C_4 distillate is sent to the fuel gas header.

The C_4 Raffinate Wash

The C_4 catalyst column distillate from distillate reflux drum V-007, after cooling in trim cooler E-011, is sent to wash column V-008 to remove the methanol. Washing is done with a countercurrent water stream pumped from the methanol recovery column through P-007. The C_4 overhead raffinate is freed from methanol by a second water wash, where water is recirculated by pump P-008, and freed from water in coalescer V-010 before being sent to the battery limit. Spent water is sent from V-009 to feed washing column V-001.

The Methanol Fractionation Section

V-008 bottom preheated in feed/bottom exchanger E-012 is sent to methanol recovery column V-011 under interface-level control. Bottom water product is recirculated to a second washing after cooling in feed/bottom exchanger E-012 and trim cooler E-013.

The overhead column vapors are condensed in E-006 with the catalytic column feed and in trim cooler E-015. One part of the reflux drum liquid is sent to the column through P-009, and the other part is sent to methanol tank V-051. The column is reboiled with medium pressure steam in thermo-syphon reboiler E-014.

PROCESS VARIABLES

Reactor Outlet Temperature

The optimum temperature for MTBE synthesis has been found to be approximately 175°F. Lower temperatures retard conversion to MTBE but minimize side reactions.

Table 4-23
MTBE Operating Conditions

OPERATING PARAMETER	UNIT	
REACTOR		
REACTOR TEMPERATURE	°F	175
REACTOR PRESSURE	psig	310
SPACE VELOCITY, LHSV	hr^{-1}	4.9
CATALYTIC COLUMN		
COLUMN TOP TEMPERATURE	°F	145
COLUMN TOP PRESSURE	psig	100
REFLUX DRUM TEMP.	°F	125
REFLUX DRUM PRESSURE	psig	97
COLUMN BOTTOM TEMPERATURE	°F	276
COLUMN BOTTOM PRESSURE	psig	114
NUMBER OF PLATES		40
C_4 FEED WASH COLUMN		
COLUMN TOP PRESSURE	psig	169
COLUMN TEMPERATURE	°F	104
NUMBER OF PLATES		20
RAFFINATE WASH COLUMN		
COLUMN TOP TEMPERATURE	°F	104
COLUMN TOP PRESSURE	psig	202
COLUMN BOTTOM TEMPERATURE	°F	104
COLUMN BOTTOM PRESSURE	psig	216
NUMBER OF PLATES		30
METHANOL RECOVERY COLUMN		
COLUMN TOP PRESSURE	psig	36
COLUMN TOP TEMPERATURE	°F	210
COLUMN BOTTOM TEMPERATURE	°F	287
COLUMN BOTTOM PRESSURE	psig	40

Reactor Pressure

The reactor pressure is chosen to keep the reactants in liquid state. The optimum pressure is approximately 310 psig. A lower pressure induces vaporization of the C_4 feed, a poor reaction rate, and heat transfer in the reactor.

Recycle Flow

The recycle flow is required to keep the bed in the expanded state. The expanded level of the bed is approximately 130% of the static level of the catalyst in the reactor. The superficial liquid velocity depends on the temperature and composition of the liquid and catalyst particle size, shape, and density.

The operating conditions of an MTBE unit are shown in Table 4-23. The process yields, utility consumption, and feed and product properties are shown in Tables 4-24 to 4-26.

Table 4-24
MTBE Process Yields

FEED	YIELD % WT
C_4/C_4 = MIX FEED	1.0000
METHANOL	0.0731
TOTAL FEED	1.0731
PRODUCT	
MTBE PRODUCT	0.2338
RAFFINATE	0.8393
TOTAL PRODUCT	1.0731

Table 4-25
MTBE Utility Consumption *(per Ton C_4 Feed)*

UTILITY	UNITS	CONSUMPTION
POWER	kWhr	5.978
STEAM	mmBtu	0.87
COOLING WATER	MIG*	0.509

*MIG = 1000 IMPERIAL GALLONS.

Table 4-26
MTBE Feedstock and Product Properties

	UNITS	C_4 FEED	METHANOL	MTBE	C_4 RAFFINATE
SPECIFIC GRAVITY		0.584	0.792	0.74	0.551
MOL WT		57.4	32	88	57.3
VAPOR PRESSURE	100°F, psia	62		9.6	
TOTAL SULFUR	ppmw	17			20
C_4 FEED COMPOSITION	MOL%				
PROPYLENE		0.010			
PROPANE		0.070			
BUTYLENES		47.730			
BUTANES		50.400			
PENTANES		1.590			
DIOLEFINS, ETC.		0.200			
MTBE COMPOSITION	Wt%				
MTBE WT%				98.9	
METHANOL				0.2	
DIMER				0.5	
TBA				0.3	
MTBE RON				114	