APPENDIX M

SUMMARY OF MAJOR TYPES OF
CaRFG2 REFINERY MODIFICATIONS

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Summary of Major Types of CaRFG2 Refinery Modifications:

Alkylation Units

A process unit that combines small-molecule hydrocarbon gases produced in the FCCU with a branched chain hydrocarbon called isobutane, producing a material called alkylate, which is blended into gasoline to raise the octane rating. Alkylate is a high octane, low vapor pressure gasoline blending component that essentially contains no olefins, aromatics, or sulfur. This plant improves the ultimate gasoline-making ability of the FCC plant. Therefore, many California refineries built new or modified existing units to increase alkylate production to blend and to produce greater amounts of CaRFG2.

Alkylate is produced by combining C3, C4, and C5 components with isobutane (nC4). The process of alkylation is the reverse of cracking. Olefins (such as butenes and propenes) and isobutane are used as feedstocks and combined to produce alkylate. This process enables refiners to utilize lighter components that otherwise could not be blended into gasoline due to their high vapor pressures. Feed to alkylation unit can include pentanes from light cracked gasoline treaters, isobutanes from butane isomerization unit, and C3/C4 streams from delayed coking units.

Isomerization Units – C4/C5/C6

A refinery that has an alkylation plant is not likely to have exactly enough is-butane to match the proplylene and butylene (olefin) feeds. The refiner usually has two choices – buy iso-butane or make it in a butane isomerization (BI) plant.

Isomerization is the rearrangement of straight chain hydrocarbon molecules to form branched chain products or to convert normal paraffins to their isomer. This means that the unit rearranges molecular structure of hydrocarbons, changing straight-chain hydrocarbons into branched-chain hydrocarbons of a higher octane rating. The primary benefit of isomerization is to provide octane enhancement. The available catalysts used for isomerization contain platinum on various bases.

This unit will convert n-butane (a straight chain C4 molecule) to iso-butane (a branched molecule). The butane isomerization unit is an intermediate step in the formation of alkylate, because the unit produces isobutane from feed to the new alkylation unit. Feed includes normal butanes from alkylation units.

The feed to the BI plant is normal butane or mixed butanes (iso and normal), which are sometimes called field grade butanes if they come from a gas processing plant. The butanes should not have any trace of olefins that would deactivate the catalyst.

These types of units will also convert low octane pentane (C5) and hexane (C6) molecules to high octane isopentane (nC5) and isohexane (nC6). Pentanes and hexanes are difficult to reform and are isomerized using aluminum chloride or precious metal catalysts to form gasoline blending components of fairly high octane value. This unit will also destroy benzene.

TAME Units

These units were designed to produce TAME (Tertiary Amyl Methyl Ether), an oxygenated compound which could be blended into gasoline to help meet the new reformulated gasoline oxygenate specification. The TAME plan can also reduce the olefin content and vapor pressure required for reformulated gasoline. TAME is made by reacting isoamylenes with methanol, very similar to MTBE which is formed by reacting

isobutenes with methanol. The TAME and MTBE units were built to reduce the amount of MTBE that must be imported to supplement gasoline octane and oxygenate requirements.

MTBE Units

Methyl Tertiary Butyl Ether, or MTBE, is a blending additive that increases the oxygen content of gasoline to comply with both federal and California oxygenate requirements. The ingredients for MTBE are iso-butylene and methanol. The feed consists of iso-butylene, fresh methanol, and recycle methanol. Almost 90% of the iso-butylene converts to MTBE in the MTBE plant reactor.

Some refineries built these units to have on-site production of oxygenates rather than to import oxygenates or to use this on-site production to supplement their oxygenate imports and to comply with the federal oxygenate requirement.

Hydrogen Plants

These plants are designed to produce additional hydrogen that is needed for isomerization, hydrotreating, and saturating units. Hydrogen is formed in the steam methane reformer (SMR) furnace by reacting hydrocarbons with steam in the presence of a catalyst. The SMR furnace can be equipped with low NO_x burners and SCR to reduce NO_x emissions.

Hydrotreaters

Hydrotreating is used to improve the quality of gasoline, jet fuel, and diesel fuel components. Sulfur and nitrogen compounds are removed, and olefins are saturated by adding hydrogen at high pressure in the presence of a catalyst. Hydrotreating catalyst is similar to the catalyst described under reforming, but usually contains nickel, molybdenum, and/or platinum. These units are designed to remove sulfur and other contaminants from a hydrocarbon (petroleum) with heat and pressure in the presence of a catalyst.
Distillate Hydrotreater:
This unit will process streams from a delayed coking unit and Flexicoker and crude distillation units. This unit will remove sulfur and nitrogen compounds from jet fuel, diesel fuel, and feed to the catalytic cracking unit. Gasoline Hydrotreater - Heavy Cracked: This unit will treat heavy cracked gasoline to meet the new sulfur and olefin specifications for reformulated fuels. The hydrotreating process uses hydrogen, in the presence of a metal oxide catalyst, to remove sulfur and nitrogen. Olefins (unsaturated hydrocarbons) will also be converted to paraffins.

Butamer Plant

A facility that can be built to provide additional isobutane required for the Alkylation Plant. Butane (C4) treating facilities are usually built to remove impurities from the FCC Plant butane (C4) streams that are fed to the existing Alkylation and MTBE plants to improve the yield and quality of alkylate and MTBE.

Storage Tanks

Storage for gasoline, oxygenate, alkylate, or other fuel blending materials.

Fluid Catalytic Cracking Units (FCCU)

Cracking is the breaking down of higher molecular weight hydrocarbons to lighter components by the application of heat. Cracking in the presence of a suitable catalyst produces an improvement in yield and quality over simple thermal cracking.

These units are designed to split large hydrocarbon molecules into smaller hydrocarbon molecules with the assistance of a catalyst. The FCC Plant can be the largest gasoline component producer in the refinery. It also produces feedstocks for other refinery plants, such as the alkylation, MTBE, and TAME

plants. This is a process of cracking heavy gas oil feeds and large molecules into smaller molecules in the gasoline and surrounding ranges with heat and pressure in a powdery catalyst that flows like a fluid.

Catalytic Reforming Unit (CRU)

Reforming is a process to convert naptha fractions to products of higher octane value. Catalytic reforming is applied to various straight-run and cracked naptha fractions and consists primarily of dehydrogenation of napthenes to aromatics. This process uses heat, pressure, and a catalysts to change base gasoline components into a high-octane gasoline component called reformate. The reforming catalyst material consists of small solid cylindrical structures composed of an inert based, generally alumina, and a metal, platinum.

Hydrocracking Units

Hydrocracking is the process of "cracking" long hydrocarbon molecules with high pressure under a high-hydrogen content atmosphere. This process includes mixing gas oils or residue (heavier) hydrocarbons with hydrogen under high pressure and temperature and in the presence of a catalyst to produce light oils. Catalytic cracking is designed more for (light) hydrocarbons whereas hydrocracking addresses the (heavier) hydrocarbons so that more gasoline and diesel fuels can be produced by breaking up larger chain hydrocarbons at a refinery.