Process Chemistry

Introduction

Trace contaminants normally found in commercial C_3 - C_5 hydrocarbons, such as, water, hydrogen sulfide, mercaptans, oxygenates, and unsaturated hydrocarbons are removed using hydrogenation, fractionation, and molecular sieve sweetening technologies, thus offering a cleaner, more consistent and stable hydrocarbon.

Problems associated with contaminants

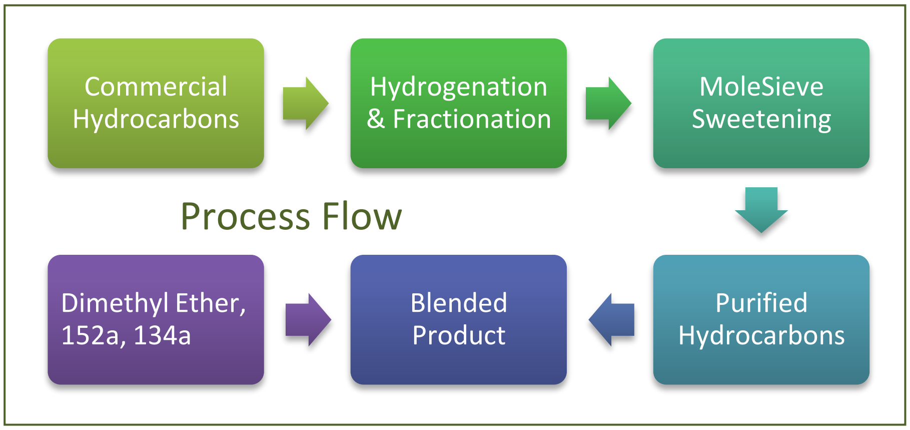
Water - corrosion, reactivity

Hydrogen Sulfide, Mercaptans - odor, discoloration, reactivity

Oxygenates, including peroxides - odor, reactivity

Unsaturated Hydrocarbons – reactivity

The following is a simplified block flow diagram for the manufacture of these products:



Hydrogenation & Fractionation

Fractionation is designed to separate various fractions of the product stream into their constituent parts. Diversified CPC Intl. operates two fractionation systems, HPA (High Purity Alkanes), and HPO (High Purity Olefins). The HPA fractionation system is a two-tower system designed to separate various fractions of the saturated hydrocarbon stream fed to the system. The equipment has been designed with the flexibility to process various raw material streams to produce 99.5% minimum and better purity hydrocarbon gases. The HPO fractionation system is a three tower system designed to produce 99.99% minimum and better purity gases.

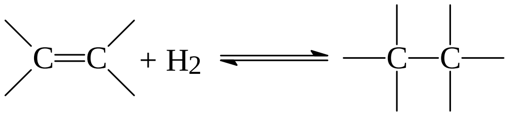
Hydrogenation removes objectionable materials by selectively reacting sulfur and oxygen containing compounds with hydrogen and by saturating olefinic hydrocarbons.

The chemistry of the hydro treating process is essentially that of a selective hydrogenation in the presence of excess hydrogen over a catalyst at elevated temperatures and pressure. Olefin saturation is promoted by the catalyst to a low equilibrium level that depends upon excess hydrogen concentrations and temperature. LP Gas is heated, processed top to bottom over a fixed bed vapor phase catalyst and cooled before molecular sieve sweetening occurs.

Due to the severe reducing atmosphere, the hydrogenation reaction also converts all sulfur species to hydrogen sulfide, and all oxygenates, including tertiary Butyl Hydroperoxide to water.

Both hydrogen sulfide and water are easily removed during the molecular sieve processes.

Hydrogenation Chemical Equations



Eq. 1. Conversion of Olefins to Saturated Hydrocarbons

$$RSH + H_2 \rightleftharpoons H_2S + RH$$

Eq. 2. Conversion of Sulfur Compounds

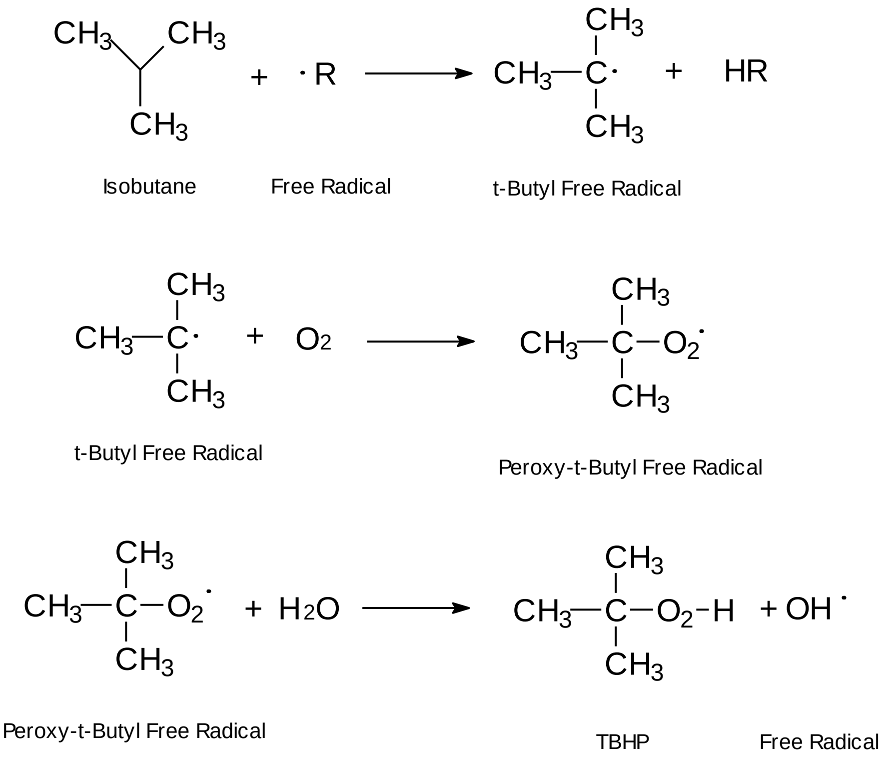
$$ROH + H_2 \rightleftharpoons H_2O + RH$$

Eq. 3. Conversion of Oxygenated Hydrocarbons

Tertiary Butyl Hydroperoxide (TBHP) and tertiary Butyl alcohol (TBA) can slowly form in bulk tanks or cylinders containing isobutane. When TBHP concentrations increase to about 1 to 5 ppm, its characteristic bleach odor can be detected. It has been proved to accrete slowly in these tanks, but the rate of growth increases with temperature, and rising oxygen (air), isobutylene, and moisture contents.

TBHP is formed by the reaction of isobutane or isobutylene, a free radical (•OH, •Cl, etc.), oxygen, and moisture. The hydroxyl radical, •OH, is present in the atmosphere and may be introduced into bulk containers through hoses during liquid transfer.

The chlorine radical, •Cl, may be present in containers that previously contained chlorinated hydrocarbons, such as Freon 12. It is also postulated that the rust covered interior of containers serves as a catalyst, forming traces of hydrogen peroxide and ephemeral hydrogen, •H.

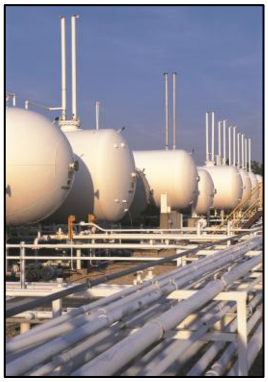


As with all free radical additions, this reaction is self-propagating and is only terminated when free radicals combine with each other or are removed from the reaction mixture.

TBHP forms most rapidly in containers when there is relatively little liquid present. This provides a larger reaction surface above the liquid level, as well as less dilution. Higher concentrations of TBHP are found in containers contaminated with isobutylene, since the hydroxyl radical preferentially attacks the double bond. Higher concentrations are also found in containers that are infrequently used or refilled. Finally, the production rate of TBHP is greater in warm summer weather than during other seasons of the year.

Traces of tertiary Butyl Alcohol (TBA) may be found in storage containers contaminated with TBHP, since TBHP may be hydrolyzed by water or other alcohols.

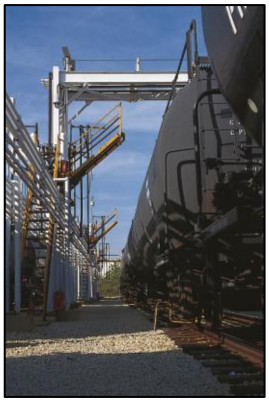
Molecular Sieve Sweetening



Molecular sieves have been used by the gas processing for many years. They are used to dry and purify (remove odor, sweeten) hydrocarbon feed stocks.

Molecular sieves are a complex of elements and compounds such as aluminum, silicon, oxygen, and sodium or similar elements combined together to form a stable ceramic crystalline structure containing precisely controlled openings or pores. They work because, like magnets, molecular sieves attract certain types of molecules.

Trace contaminants normally found in commercial grade hydrocarbons, such as water, hydrogen sulfide, mercaptans, oxygenates, and unsaturated hydrocarbons have positive and negative electrical poles. These polar molecules are attracted to molecular sieves. In contrast, nonpolar molecules, those of ethane and propane for example, are much more weakly attracted. Material is sweetened by processing the product bottom to top over a liquid phase fixed bed of molecular sieve.



At ambient temperatures, molecular sieves have a high capacity for the strongly attracted compounds like water, hydrogen sulfide, mercaptans, etc. At high temperatures, however, the capacity is much lower. For this reason, when molecular sieves become saturated (spent) the adsorbed compounds can be driven off at elevated temperatures using a purified gas stream. This process is called regeneration. Regeneration is accomplished by passing heated gas top to bottom over a vapor phase fixed bed of spent molecular sieve.

After heating, the molecular sieve is cooled down before returning the sieve to service.

Molecular sieve sweetening has limited capacity for the removal of unsaturated hydrocarbons. To insure the consistency, stability, and purity of the product, hydrogenation is required.

Blending

Once purified, our products can be blended to meet customer specifications. Products are blended directly into Tank Cars, Tank Trucks, or Cylinders utilizing a specialized system of piping, manifolds, meters, and controls.

Quality Assurance

Quality assurance is critical to the manufacture, production, and storage of our products. Critical parameters to ensure the purity, chemical stability, and suitability of our products include:

- Composition
- Unsaturated hydrocarbons
- Total sulfur
- Moisture
- Vapor pressure

Receiving, In-Process, and Final Inspections are performed to verify conformance to requirements.