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Review Article

Environmental and Safety Considerations for Olefins Conversion Unit

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Abstract *- The olefins conversion process, like any other process, involves a certain amount of risk. As this unit operates with highly volatile and flammable liquids and gases, additional safety precautions must be taken. All personnel connected with the operation and maintenance of this unit should have a clear understanding of the hazards involved and the possible results of careless operation or careless use of tools in the plant area. All vessels and equipment have been designed for handling the liquid and gases at temperatures and pressure, which may exist in the unit's normal operation. Safety and depressurizing valves have been provided to relieve excessive pressure. Lines or vessels containing liquids should not be "blocked in" with no means of relieving pressure which might be generated due to an increase in temperature.*

Keywords *- Leaks, Catalyst Handling and Dumping, Pressure relief, Fire protection, Extreme temperature.*

1. Introduction

Olefins Conversion Technology (OCT) employs metathesis and isomerization chemistry to produce propylene from reacting ethylene with C4 and C5 olefins. This is the only commercially demonstrated route to propylene using metathesis chemistry. The source of the C4 and C5 olefins can be steam cracking, refinery processes, MTO or ethylene dimerization. Polymer-grade propylene is readily produced in a simple catalytic fixed bed reactor without the use of super fractionators since no paraffins are formed in the metathesis or isomerization reactions. In addition, the metathesis reactions are mildly exothermic. There is no energy input into the reaction step, making OCT the only route to propylene that does not require energy input in the reaction step. This reduces operating costs and greenhouse gas emissions.

Further, since OCT has a selectivity to propylene of over 95%, very few by-products are produced, which offers superior operating economics and low capital investment. OCT is the most selective route to propylene of all demonstrated routes. Worldwide, there are 49 OCT units either in operation or under design, producing over nine million metric tons of propylene—more than 10% of worldwide capacity. Unit capacity ranges from 60 kta of polymer-grade propylene to 800 kta of propylene.

The OCT process can handle a wide range of feedstock compositions, making the unit flexible to take advantage of many lower-value feedstocks. The ethylene stream can vary from dilute ethylene, typically from an FCC, to polymer-grade ethylene. The C4 stream has similar flexibility because butanes pass through the system as inerts. After pre-treatment, raw pyrolysis gasoline from the ethylene plant or C5 s from the refinery can be directly processed in the olefins conversion unit. Another important characteristic of the process is product purification: the system does not require the superfractionator usually associated with propylene purification. Both C2 and C4 feeds generally have only minor quantities of propane, and since the reaction system does not generate any propane, propane/ propylene separation is not required. The propylene produced contains only the propane contained in the ethylene or C4 feed. This means that the propylene purity usually exceeds the polymergrade level produced by the majority of steam crackers without any superfractionators. When integrated with a grassroots steam cracker, the by-product flexibility of the cracker is greatly enhanced. With high propylene value and demand, the OCT unit can be operated to increase the propylene-to-ethylene ratio to above 1.0. Importing an external C4 and C5 stream can further increase the ratio should the propylene value fall; the steam cracker can produce as much as 115% of its nameplate ethylene capacity while exporting either a mixed C4 stream or a C4 stream where the butadiene has been hydrogenated to butenes. The operation can thereby be optimized depending on the relative values of ethylene, propylene, butene, and mixed C4 s and C5 s. This product flexibility ensures profitable operation as by-product values shift over the 30+ year life-cycle of the facility.

Ethylene feed plus recycled ethylene are mixed with the C4 /C5 feed plus butenes/pentenes recycled and heated prior to entering the fixed-bed metathesis reactor. The catalyst promotes the reaction of ethylene and butene-2 to form propylene, ethylene and pentenes to propylene and butenes and simultaneously isomerizes butene-1 to butene-2. A small amount of coke is formed on the catalyst, so the beds are periodically regenerated using nitrogen-diluted air. The ethylene-to-olefins feed ratio to the reactor is optimized to maintain high olefin conversion in the 60 to 80% range and propylene selectivity greater than 92%. The reactor product is cooled and fractionated to remove ethylene for recycling. A small portion of this recycle stream is purged to remove methane, ethane, and other light impurities from the process. The ethylene column bottoms are fed to the propylene column, where butenes/pentenes are separated for recycling to the reactor. Some are purged to remove unreacted butenes, isobutenes, butanes, unreacted pentenes, isopentenes, pentanes and heavies from the process. The propylene column overhead is a high-purity, polymer-grade propylene product. This process description is for a stand-alone OCT unit that can be added to any refining/petrochemical complex.

The utility requirements—which include cooling water, steam, electricity, fuel gas, nitrogen, and air—are typically integrated with the existing complex. CDIsis® can isomerize the isobutene to normal butene. Isobutene was often utilized for MTBE production, which was a gasoline additive to enhance octane value. However, due to recent environmental requirements, the production of MTBE is phasing out, and alternative utilization of isobutene is requested. Based on these backgrounds, CDIsis® technology was developed by Lummus to convert isobutene to normal butenes. CDIsis® technology can maximize the utilization of isobutene in mixed C4 feedstock via the OCT process. Integration of CDIsis® technology with the OCT process allows an economical and cost-effective solution to enhance propylene production.

Skeletal Isomerization Reaction of isobutylene to 1-butene and 2-butene in reaction 1 as below

$$CH3 - C - CH3 = CH2 \leftrightarrow CH2 = CH - CH2 - CH3 \;\; CH3 - CH = CH - CH3 \quad (1)$$

Available C4's from steam cracker is being reduced due to the increasing demand for butadiene and the decreasing amount of liquid feed cracking. C5's OCT process is developed by Lummus Technology to make up for the shortage of propylene production and extend the feedstock for propylene production. The reaction schemes of C5's OCT process are very similar to that of butenes OCT, consisting of isomerization and metathesis reaction. C5's OCT is being regarded as a new propylene-boosting technology to compensate for the shortage of C4s feed. Reaction scheme in C5 OCT in reaction 2 and propylene metathesis in reaction 3 below

$$CH2 = CH2 \;\; CH2 = CH2 + CH3CH = CHCH2CH3 \rightarrow CH2 = CHCH3 \;\; CH2 = CHCH3 \;\; CH2 = CHCH3 \quad (2)$$

$$C4H8 + C2H4 \rightarrow 2\; C3H6 \quad (3)$$

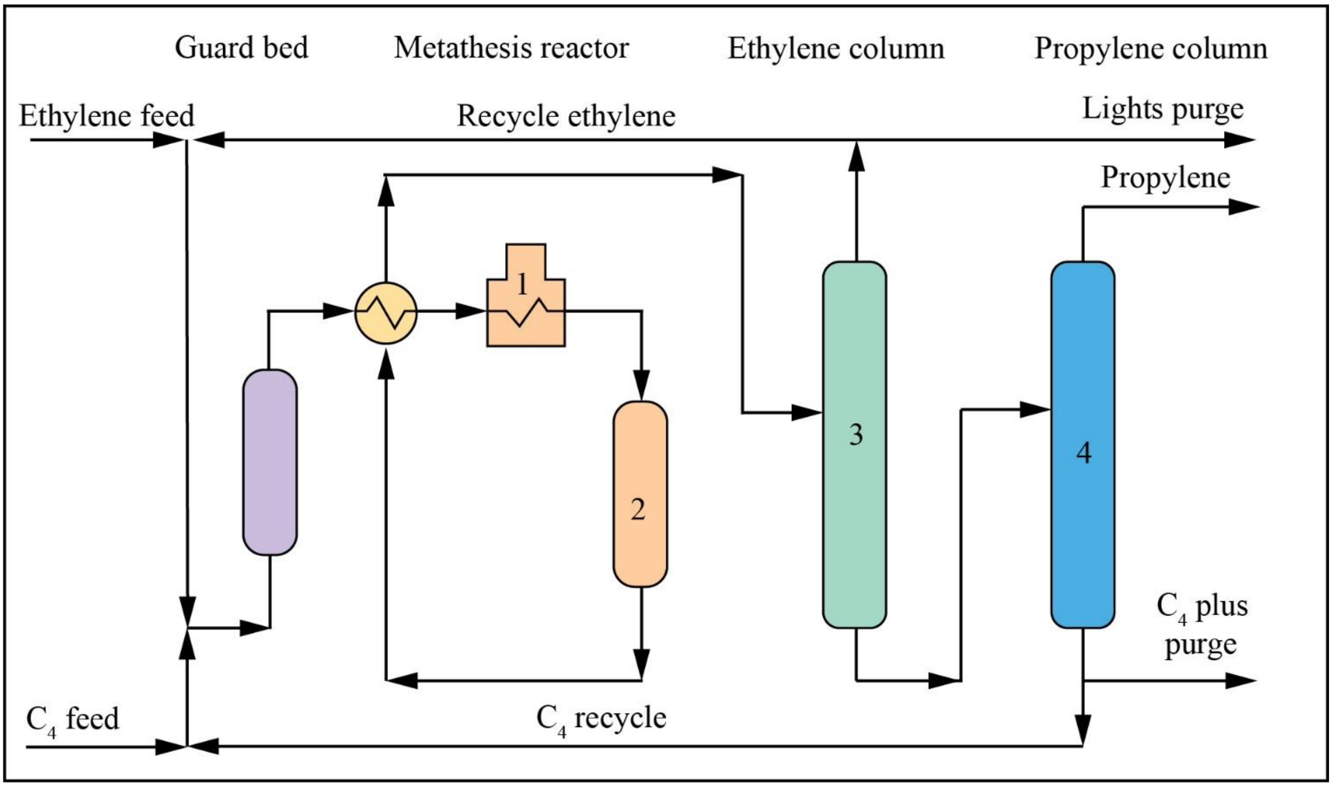

Fig. 4 Olefins Conversion unit process flow scheme

2. Related Topic

2.1. Opening Lines and Equipments

Lines or equipment containing liquids that will auto-refrigerate if the pressure is lowered should generally be kept at pressure until the liquid is removed before depressuring them. Releasing of hydrocarbon vapors in the air in large amounts should be avoided due to health and fire hazards. When it is necessary to release gas into the atmosphere, especially at ground level, it should be done slowly under a blanket of steam to dilute and disperse the gases so that there is no undue hazard to personnel.

2.2. Opening Large Vessels

When large vessels such as towers or drums are to be opened, the following precautions should be taken:

- All liquid is to be removed, and the system purged with steam and flooded with water until free of hydrocarbon vapors and other toxic and flammable materials.
- After complete maintenance and before the vessels are returned to service, the air must be displaced with steam or purged with inert gas. Each piece of equipment can be freed of hydrocarbon either by steaming or by evacuating and purging with nitrogen.

2.3. Leaks

In case a leak develops in a line or equipment carrying flammable or volatile liquids or gases, the leak should be stopped as rapidly as possible by isolating, deinventorying, and depressuring. Steam and water spray may be used to assist in leak dispersion until repairs can be made or pressure can be reduced as long as this action does not unnecessarily expose personnel to potential harm.

2.4. Catalyst and Chemical Handling

Most chemicals are potentially hazardous and can endanger personnel and property if improperly handled. It is, therefore, imperative that all of the hazardous characteristics of any chemical be fully understood before attempting to handle it. Noxious effects from the adsorbent and catalyst used may also occur during loading and unloading operations.

2.4.1. Chemicals

Acetylene, Butadiene, Butane, Butene, Carbon Dioxide, Carbon Monoxide, DME, Ethane Ethyene, Hexene, Hydrogen, Isobutane, Isobutene, Methane, Methylacetylene, Octene, Pentene, Propadiene, Propane, and Propylene.

2.4.2. Absorbents

C4 Feed Treaters, Metals Treater, DP Reactor Feed Treaters, Nitrogen Treater

2.4.3. Catalyst

DP Reactors (Magnesium Oxide (MgO) /Tungsten Oxide (WO3))

2.5. Adsorbent and Catalyst Dumping

- The adsorbent in the C4 Feed Treaters and adsorbent in the DP Reactor Feed Treaters and Nitrogen Treaters present a low health risk by inhalation. Dry procedures should be used for cleaning up since the adsorbents will generate heat when in contact with water. Dusting should be avoided.
- The Metals Treater is also a low health risk by inhalation. Minimize exposure to air as the product is liable to self-heating in contact with air without an energy supply. Dusting should be avoided. Disposed material should be collected in mild steel or stainless steel containers.
- Dumping DP Reactor catalysts, Engelhard Magnesium Oxide (MgO) and Engelhard Tungsten Oxide (WO3) is a hazardous operation. The dust from the catalyst contains heavy metals and should not be inhaled. Proper ventilation of the work area and proper respiratory protection must be utilized. Clean up of dust by vacuum cleaners or by washing down is needed after the operation is complete. Disposal of wash down should be handled in an environmentally approved manner.

2.6. Pressure Relief and Flare Systems

- Steam is discharged into the atmosphere by the safety valves on the Deethylenizer Reboiler and Depropylenizer Reboiler. They discharge at a safe location.

2.7. Fire Protection System

The following equipments are provided in order to tackle any fire in the plant: Fire-Water Supply, Storage, Pumping and Distribution, Monitors and Hydrants, Fixed Spray Systems, Fire Water Curtains, Sprinkler Systems, Foam and Dry Chemical Systems, Portable Extinguishers, Flammable Gas Detectors, Mobile Equipment, Fire Detection and Alarm Systems, Gaseous Fire Extinguishing Agent Systems.

2.8. Extreme Temperature

The plant has a wide range of operating temperatures, up to 1200°C in the fire heaters (firebox) to approximately -46°C in the Deethylenizer condenser. The operators must be aware that low temperatures have almost the same effect on human skin as high temperatures. They produce painful and slow-healing blisters. In addition, the human skin, because of its moisture content, freezes and adheres tightly to any very cold surface with which it comes in contact. Very painful injury can result. All equipment is designed for operating temperatures, and a safety factor is applied. However, the operators must take care that the equipment is not exposed to extreme temperatures for which it is not designed. The equipment in plant sections containing light hydrocarbons is constructed of materials suitable for the expected normal operating temperatures, with sufficient margin to account for normally expected upsets. Use of pressurizing gases such as nitrogen or fuel gas should never be used to drain liquids from the equipment as they can

3. Benefits

OCT can be readily integrated with a steam cracker. When integrated with a naphtha cracker, the maximum propylene-to-ethylene ratio can be increased from 0.6 to 1.2, essentially doubling the amount of propylene produced. Both the C4 and C5 raffinate streams are increased in value from feed or gasoline blending value to polymer-grade propylene value. In addition, the ethylene plus propylene yields are increased by as much as two and one half times relative to recycle cracking of the raffinates. When integrated with an ethane cracker, which as a stand-alone unit produces very little propylene, OCT combined with ethylene dimerization can be used to produce any desired quantity of PG propylene, making it the only route of ethane feed to propylene product.

OCT can also utilize the C4 and C5 raffinate from various refinery processing schemes or the C4 and C5 raffinate from MTO units. When integrated with refinery streams, ethylene can be recovered from refinery off-gas streams and used as feed for the OCT. Doing so will upgrade the recovered ethylene from fuel value to PG propylene value and the C4/C5 raffinate from alkylate or gasoline blending value to propylene value. When integrated with an MTO unit, ethylene plus propylene production increases by up to 15%. Mild operating conditions lead to a design that is essentially all carbon steel material. Utility consumption is very low and limited to the product recovery utility consumers. The high selectivity limits feed consumption and by-product quantities. The non-noble metal catalyst offers long cycle times between regeneration and long life, comprising less than 1% of the operating costs. These features combine to offer the lowest capital costs for PG propylene production and the highest return on investments.

4. Conclusion

All the precautions and recommendations in the related topic are helpful to avoid issues for hazardous scenarios around the unit or personnel. It is critical to have process hazard analysis prior to modified design executions and new designs as that help to protect the unit depending on the level of risk.

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