Ethylene glycol

Summary

Ethylene Glycol is a much sought after organic compound belonging to the diols family. It is colourless, odourless and is miscible in water and most organic compounds. It was first synthesized by a French chemist, Charles Wurtz, in 1859. Even though it did not gain commercial importance at the time, during World War I, the Germans used ethylene glycol as a substitute for glycerol in explosives (ethy). During and following World War II, ethylene glycol was extensively used as an anti-freeze for engines and machinery in general. This led to an increase in production of ethylene glycol. By the early 1970s, demand for ethylene glycol rose dramatically as it used in the manufacture of polyester fibre, with a further rise in levels of consumption spurred on due to phasing out of glass bottles in favour of PET bottles. In the year 2007, there were 99 ethylene glycol plants globally and the total amount of ethylene glycol produced that year was estimated to be roughly 17. 8 million tons (icis). The demand for ethylene glycol, MEG in particular is expected to rise due higher demand from industries in China.

In comparison to existing ethylene glycol plants, the plant design that is discussed in this report would be attractive to a producer of ethylene glycol on a small to medium scale, catering to a local market. The plant discussed in this report aims to produce 10, 500 tonnes of MEG and 4, 500 tonnes of DEG, and commercially viable amounts of TEG and TetEG every year. This plant will be in operation for 8000 hours per year. For this production target to be realised it is necessary to have a ethylene oxide flow rate of 1493. 56 kg/h to be fed into the reactor.

A crude ethylene glycol mixture is produced by the hydrolysis of ethylene oxide with excess water in a tubular type reactor operating at 1950C and a pressure of 21. 44 bar. In the reactor all the ethylene oxide is converted into the four types of ethylene glycols, with the formation of MEG being the most favored. For every 1 mole of ethylene oxide in the feed stream there are 6 moles of water and 0. 269 moles of recycled MEG. This ratio is strictly maintained so as to optimize ethylene glycol conversion to MEG, the most favored product and DEG, the second most favored product. The resulting mixture of water and glycols is then fed to a flash drum operating at atmospheric pressure, where almost one third of the water in the product stream is removed along with some MEG. The removed water and MEG is recycled and sent back to a holding vessel. After the flash drum the water-glycol mixture undergoes a series of distillation cycles so as to separate out the components of the ethylene glycols and rid them of water. The first distillation column, T-01 operates 2000C and 1 atm. During this distillation process nearly 99% of all remaining water is removed and recycled. The highly concentrated ethylene glycol mixture is them pumped to a second distillation column, T-02 operating at 2350C and 0. 8 atm, (vacuum). Here 99% of all MEG entering the column is removed and a significant amount of MEG is recycled. However most of the MEG is sent to storage at a rate of 1312. 86 kg/h. The remaining mixture of glycols enter distillation column, T-03, where all DEG is removed and sent to storage at a rate of 562. 50 kg/h. The fourth and final distillation column operating at 2600C and 0. 8 bar removes nearly 99% of available TetEG. The remaining glycol mixture contains TetEG, is extracted using a tar sill. This process produces 2. 58 kg/h of waste largely made up of TetEG. Since the reactions within the reactor produce a lot of heat, water is pumped into the reactor at a rate of 965. 5373 kg/h, resulting in the formation of steam at a pressure of 6 bar. Due to the hydrolysis of ethylene oxide in water, some water is lost in the reaction and as well as in storage of the ethylene glycol products. To keep this process running at its optimum, a fresh water feed of 489. 50 kg/h is added to the process.

Literature Survey

Even though Charles Wurtz had derived ethylene glycol by the hydrolysis of ethylene glycol diacetate in the year 1859, its commercial importance wasn't realized until during World War 1, during which the Germans had started an industrial process to produce ethylene glycol to substitute for glycerol in explosives. And only in 1930 did the production of ethylene glycol via industrial chemistry really take off, since it was used as anti-freeze for machinery. The demand for anti-freeze shot up markedly during and after World War 2. As more motor vehicles and machinery were built and sold during the years following World War 2, demand for ethylene glycol grew along with production. Between the late 1960's and earl 1970's there was a renewed and greater demand for ethylene glycol, due to the manufacture of polyesters fibers. From then onwards to the early 1990's production of ethylene glycol fluctuated. The demand for ethylene glycol would go on to increase throughout the 1990's and 2000's due to the increase in the amount of plastic, especially PET bottles being manufactured. The increase in demand was further boosted by the rapid growth of Asian economies, namely India and China. China accounts for nearly a third of the global MEG demand. Global production of ethylene glycol in 2007 was estimated at 17.

8m tones (PCI). According to the Merchant Research & Consulting Ltd. rising demand from polyester fiber and PET resin markets means that one to two world-scale EG plants are needed every year. The cost of ethylene oxide feedstock is also expected to increase due to demand in the ethylene glycol sector as well as demand for other ethylene oxide derivatives. New plants are being built in the Middle East to produce low-cost feedstocks, which are expected to cater to the American and Asian markets.

Presently, the commercial applications of ethylene glycol are numerous and range from the traditional use as an anti-freeze to more hi-tech uses such as the manufacture of capacitors. Some of the applications are polyester resins for fiber, PET containers, and film applications; all-weather automotive antifreeze and coolants, defrosting and deicing aircraft; heat-transfer solutions for coolants for gas compressors, heating, ventilating, and air-conditioning systems; water-based formulations such as adhesives, latex paints, and asphalt emulsions; manufacture of capacitors; and unsaturated polyester resins (ethy).

MEG is the most widely sought after of the commercially available ethylene glycols, and in the year 2007 it accounted for 90% of all ethylene glycol produced (icis). In the year 2007, nearly 82% of all MEG produced was bought by companies in the polyester manufacturing business. The demand for polyester stems from the Asian region, China in particular, where it is used in the textile industry, and this has led to a 5-6% increase in production of MEG per year. Demand for polyethylene terephthalate (PET) bottle resin has been growing strongly globally since the beverage business phasing out the use of glass bottles and replacing with the more durable PET bottles.

Demand for MEG for the manufacture of anti-freeze was at 12%, and demand is expected to decrease slightly over the years largely due recycling and substitution by propylene glycol-based antifreeze.

Apart from its use in the manufacture of polyurethanes, DEG is also used in the treatment of corks, glue, paper and cellophane. DEG along with TEG is used in the dehydration of natural gas, an area where demand for DEG and TEG is set to rise over the years. DEG and TEG have excellent hygroscopic properties and along with their low volatility are best suited for applications such as dehydration of natural gas and as a dehumidifier in air conditioning systems.

According to research and industry analysts, PCI, there were 72 MEG producing companies in 2007 operating 99 plants spread across 31 countries. Of these, the top 10 producers account for close to 50% of global ethylene glycol capacity. The top producers were Dow and Nan Ya Plastics Corp with 1. 75 million tons each while Jubail United Petrochemical Co was the third largest with 1. 5 million tons. Other major producers include Shell, a South Korean company Honam, Equate, Reliance (India), Sabic (Saudi Arabia), ExxonMobil, Equistar, Old World Industries.

Late last year prices of MEG were trading at $860-875/ton CFR, cost and freight included in Asian trade. By the beginning of the year with news that plants in Saudi Arabia will be shutting down for maintenance and increasing stockpiles in Chinese ports, led to a bullish rally during trade, sending the price of MEG to $970-980/ton. Towards the end of February, with the beginning of the Chinese New Year holidays, a period of relaxed trade, and with the Saudi Arabian plants coming back online, the price of MEG showed signs of returning to pre January levels (icis).

However in the short to medium term prices of MEG are expected drop due to new more efficient plants being built which would result in slightly more MEG being produced that demand. Therefore this possibility of over abundant supply may drive MEG prices slightly lower than $860-875/ton (PCI).

Ethylene glycol used to be manufactured by the hydrolysis of ethylene oxide (EO) which was produced via ethylene chlorohydrin but this method has been superseded by a direct oxidation route.

The EO is first produced by the oxidation of ethylene in the presence of oxygen or air and a silver oxide catalyst. A crude ethylene glycol mixture is then produced by the hydrolysis of EO with water under pressure. The water-glycol mixture is fed to evaporators where the water is recovered and recycled. Fractional distillation under vacuum is used to separate the monoethylene glycol from the diethylene and triethylene glycols.

Mitsubishi Chemical has developed a catalytic process that employs a phosphorous-based catalyst for converting ethylene oxide to monoethylene glycol (MEG) with little by-product formation. Shell has subsequently acquired exclusive rights to the Mitsubishi Chemical process and licenses a combined EO/MEG technology as an integrated Omega (only mono-ethylene glycol advanced) process package.

The Omega process is claimed to have a MEG selectivity of over 99%, compared to 90% for conventional, non-catalytic processes. It is claimed to have lower capital costs due to the elimination of purification and handling equipment for by-products. Operating costs are also reduced as it uses much less water lowering utility and water treatment costs.

The first plant to use the Omega process is Lotte Daesan’s 400, 000 tonne/year unit at Daesan, Korea, started up in May 2008. Shell plans to use the process in a 750, 000 tonne/year plant in Singapore, due for start-up in 2010.

Researchers have looked at other EG processes such as the reaction of ethylene and carbon dioxide to give ethylene carbonate followed by hydrolysis, and the direct oxidation of ethylene to glycol acetate anhydride which can be hydrolysed to ethylene glycol and acetic acid.