Various Commercial Manufacturing Processes

The traditional method of manufacturing carbon disulfide by the high temperature reaction of charcoal and sulfur vapor has been largely replaced by the petrochemical process involving the catalytic reaction of natural gas (methane) and sulfur vapor. Since about 1950, the natural gas-sulfur process has practically outmoded the charcoal process in the United States. Other methods for carbon disulfide manufacture have been proposed, but they have not yet achieved significance.

Charcoal–Sulfur Process :

The reaction of charcoal and sulfur vapor at temperatures in the range 750-1000ºC has been used for many years for the manufacture of carbon disulfide. Two processes are used, the retort and electrothermal processes. Raw material requirements are same for both the processes. Sulfur of high quality and of low ash content is essential, especially in the retort method, where deposits of carbonaceous and inorganic material on the walls of the retort reduce the heat transfer with the resultant loss in disulfide production or cause failure of the retort due to the high external temperature necessary to maintain sufficient reaction heat. Hardwood charcoal of low ash content, less than 2%, is preferred as the carbon source. Consistent particle sizes are desirable to provide a uniform bed in the retort and to prevent bridging or undue packing. Particles of approximately 1-4 in. in diameter are the most suitable. For best yields of carbon disulfide, a charcoal that has been retorted under carefully controlled conditions is required. Retorting temperatures of 400-500ºC are used. Higher temperatures impair the reactivity of charcoal, whereas at lower temperatures carbonization is incomplete and selectivity for carbon disulfide production is reduced. Charcoal is generally precalcined at the plant to drive off moisture, which has been readsorbed in the porous structure and to reduce the amount of hydrogen and oxygen compounds. By this treatment, side reactions resulting in the formation of hydrogen sulfide and carbon oxysulfide are diminished, and greater efficiency is realized on charged sulfur.

Retort Process:

The first apparatus for making carbon disulfide in quantity was described in 1829 by C.Brunner. this apparatus was constructed of graphite and produced about 0.5 lb of carbon disulfide per hour. Externally heated earthenware or cast iron retorts were generally used in the earlier years. With the advent of the viscose rayon industry, production of carbon disulfide increased and the technical methods improved. In present day plants the reaction of charcoal and sulfur vapor is carried out in direct-fired retorts, which are generally constructed of cast iron, alloy steel or refractory firebrick. The retorts are set in furnaces and heated by gas or other suitable fuel. Thus, a carbon disulfide plant consists of different types of retorts, different methods of charging sulfur and charcoal, and different recovery methods. Retorts are generally of oval or cylindrical design, and are about 8-10 ft. long and 3-4 ft in diameter. Carbon disulfide production from an individual retort varies from 1000-7000 lbs. per day. Sulfur consumption is about 0.95 lb/lb of carbon disulfide produced. Because of the high temperature of the reaction and the corrosive nature of sulfur, the life of an individual retort is limited. Reports on the life of a retort vary from 40 days to over a year.

In the older plants the sulfur was fed to the retort batch wise in solid form, but in newer installations liquid sulfur is fed as required to each retort from a common melting tank. The products, carbon disulfide, hydrogen sulfide, sulfur vapor and sulfur oxysulfide, are distilled overhead through a condenser, where the sulfur and most of the carbon disulfide are condensed separately and withdrawn. In general practice, carbon disulfide is purified by distillation. In some cases refrigeration is used to condense the carbon disulfide more efficiently and the hydrogen sulfide is discarded by burning.

Electrothermal Process :

The first electric furnace for the manufacture of carbon disulfide was patented by E.R.Taylor in 1901. In this type of internally heated retort, the precalcined charcoal is introduced at the top of a vertical, resistance type electric furnace. Four carbon electrodes are located horizontally and symmetrically around the circular base or hearth of the furnace and extended towards the center so that the ends are about one foot apart. A resistance bed of charcoal or coke is distributed over the cylindrical space between the electrodes. The heat generated by the imposed electric current through this bed of resistor carbon is transferred to the main charcoal bed above. Reaction temperatures in the furnace are 800-1000ºC and thermal efficiency is around 35-40%.

Sulfur, generally in molten form, passes through an annular space adjacent to the outer wall of the furnace where it is vaporized instantly and reacts with the hot charcoal. The imposed voltage and rate of sulfur charge control production rates. Carbon disulfide and by products, such as hydrogen sulfide and other sulfur compounds, are withdrawn at the top of the furnace and enter a condenser where most of the carbon disulfide is recovered. Recovery and purification steps are similar to those used in the retort system. Other designs of the electric furnaces, both arc and resistance types have been proposed. The Taylor furnace is 16 ft. in diameter and about 40 feet high. It has been stated that the furnace will run for 8-12 months at a capacity of 14,000 lbs per day. The advantage of the electric furnace over externally fired retorts is that the source of heat is inside the walls of the furnace. This and the fact that most electric furnaces are brick lined or designed so that heat loss is minimized by charging the sulfur in an annular space near the outside wall, results in low outside wall temperatures; therefore corrosion of the outer metal shell is small.

Disadvantages of the electric furnace include its high consumption of electrical energy (approx. 1000kWh/ton of carbon disulfide formed), the difficulty of control and the extended length of time needed for shutdown and clean-outs.

Catalytic Methane-Sulfur Process:

The Hydrocarbon-Sulfur process which involves the catalytic reaction of methane (or natural gas) and sulfur vapor to form carbon disulfide has practically the charcoal-sulfur retort method in U.S. several plants, based on this process, have been installed outside the U.S., principally in Europe. The reaction may be shown as

$$CH_4 + 4\ S \rightarrow 2\ H_2S$$

Higher molecular weight hydrocarbons present in the natural gas react in a similar fashion,

$$C_3H8 + 10\ S \rightarrow 3\ CS_2 + 4\ H_2S$$

But they can also lead to other products, as described below. Thermodynamically the reaction is very favorable for carbon disulfide formation, and with the methane-sulfur system carbon disulfide yields of over 90-mole % per pass are realized over active catalysts such as silica gel. The reaction is endothermic and conversion increases with increasing temperature and / or residence time of the reactants in the catalyst zone. The process operates in the temperature range 500-700ºC. Space velocities, based on the hydrocarbon gas charge, are on the order of 100-400 volumes of gas per hr./unit volume of catalyst. Sulfur is usually charged in slightly higher than stoichiometric amount. The reaction proceeds without the formation of byproducts. The hydrogen sulfide formed maybe used as an end product or it may be reconverted to elemental sulfur, for recycle to the reaction system in a separate partial oxidation unit using the Claus process. In the Claus process, part of the hydrogen sulfide is burnt with air to form sulfur dioxide, and the sulfur dioxide then reacts with the remaining hydrogen sulfide, at about 300C in the presence of a catalyst, to form sulfur. The two stages of the hydrogen sulfide conversion maybe represented by the following equations:

$$2\ H_2S + 3\ O_2 \rightarrow 2\ SO_2 + 2\ H_2O$$

$$SO_2 + 2\ H_2S \rightarrow 3\ S + 2\ H_2O$$

Conversion to sulfur is about 95% based on the hydrogen sulfide charge. A flow sheet of the carbon disulfide reaction section is shown in the figure. Molten sulfur, which is maintained at about 130ºC, is transferred to a sulfur boiler where it is vaporized and heated to 575-650ºC to convert the sulfur vapor largely to the diatomic form. Methane, or natural gas from which higher molecular weight paraffin are substantially removed, is preheated to 550-650ºC and mixed with the sulfur vapor. The mixed stream, with or without further heating, is then passed downward through a fixed-bed catalytic reactor for the formation of carbon disulfide. There are several variations in the preheating of the reactant streams. At its normal boiling point (445ºC), sulfur vapor exists mainly as a polyatomic molecule (S_8). As the temperature is raised toward the reaction temperature of the process, the S_8 molecule decomposes endothermically into smaller molecular weight species (S_6 and S_2).

For e.g., the mole fractions of S_2, S_6 and S_8 molecular species of sulfur vapor, at a total pressure of 20 psig, are given in the table. This dissociation is also favored by the reaction in partial pressure of the sulfur vapor, which occurs during the mixing of the reaction streams or in the reactor as sulfur is consumed in the formation of carbon disulfide and hydrogen disulfide. To reduce the extent of endothermic dissociation of sulfur vapor in the catalyst bed, which would cause a large temperature drop across the adiabatic reactor, it is advantageous to maximize the dissociation before the reactants reach the catalyst. Mixing the sulfur vapor and preheated methane streams and passing the mixture through a super heater before it enters the reactor does this.

This procedure imposes a top limit to the amounts of the other hydrocarbons, such as propane or heavier in the methane feed. If present in large amounts, these higher molecular weight hydrocarbons, which are more reactive than methane under conditions, will react thermally with the sulfur in the super heater to produce polymerization and condensation products, with resultant loss of heat transfer and catalyst contamination. Sulfur dissociation prior to the reaction zone, is augmented also b superheating both in the sulfur boiler and methane pre heater. Another approach to temperature control involves the use of several catalytic reactors in series with reheating of gases between the different stages of reaction. In this method the reaction mixture of methane and sulfur vapor enters the first reactor at about 600ºC. Conditions in this reactor are adjusted to produce a conversion of 30-40% with a temperature drop of 70-100ºCacross the catalyst bed. The reactor effluent is then reheated to around 600ºC. Under similar conditions a single reactor would require a preheat temperature of about 675ºC.

Typical reaction conditions for the process are as follows: temperature, 570-620ºC; pressure, 20-30psig; vapor hour space velocity, 400-600. A modification of this process uses methane of high purity (99+) and operates at somewhat higher temperature. Sulfur is generally used in about 10% excess of the stoichiometric requirement to improve conversion of methane and to prevent the occurrence of side reactions. Carbon disulfide yields, based on methane are 90-95%. The reactor effluent is cooled about 130ºC and the unreacted sulfur is separated in a gas-sulfur separator and recycled to the process. Small amounts of sulfur dust, which remain entrained in the product gas stream, are removed in this gas-sulfur separator by scrubbing with liquid sulfur. The carbon disulfide is separated from hydrogen sulfide by preferential absorption in a suitable mineral oil solvent from which it is subsequently stripped and sent to a distillation section. The stripped carbon disulfide is separated from small amounts of impurities in two successive distillations with low boiling impurities being removed overhead in the first column. The bottoms material from this first column, which contains small amounts of higher boiling impurities, is distilled in a second column where the final high-purity carbon disulfide is recovered as distillate. Refrigerated, overhead condensers are preferably used on these distillation columns. The off-gas from the carbon disulfide absorber contains 90-95% hydrogen sulfide and passes to the sulfur recovery unit. Due to the corrosive nature of sulfur and hydrogen sulfide at high temperatures, stainless-steel alloys are employed the preheaters and reactor units. High chromium (25% chromium) and stabilized nickel chromium alloys are satisfactory. The purity of the methane or natural gas is an important factor in this process. Natural gas containing about 98% methane is desirable to prevent undesirable by-products due to the reaction of higher molecular weight hydrocarbons with sulfur. The content of propane and paraffin higher in molecular weight then propane should be below 1%.

The by-products formed when appreciable amounts of higher molecular weight hydrocarbons are present in the methane feed impair the smooth operation of the process. As mentioned above, these hydrocarbons, because of their high reactivity, react thermally with sulfur to some degree in the heating sections. Side reactions also occur in the catalyst bed, which tend to foul the catalyst and contaminate the unreacted sulfur. If the amount of contaminants is too large, the sulfur is unfit for recycle. To produce a suitable methane charge, a feed preparation system is used to enrich the methane content of the natural gas. This unit consists of an absorption and stripping section by which the heavier hydrocarbon components are removed by selective absorption in a mineral oil solvent.

Sulfur of commercial specifications is suitable as charge material. Because of the unique viscosity characteristics of sulfur (high viscosity in the range 150-330ºC, temperatures of the melter and charge lines are maintained at around 130ºC by steam jacketing. At this temperature the viscosity is low and the liquid sulfur maybe pumped readily.

Besides the silica gel catalyst of the process, various other catalytic compositions promote the reaction. These catalysts include alumina, silica-alumina, and bauxite. Silica-zirconia, and materials of these types promoted with metal oxides or sulfides from Groups V to VIII of the periodic table.

Miscellaneous:

The use of carbon oxysulfide as a reactant or intermediate in the preparation of carbon disulfide has frequently been investigated. Such studies have had two main purposes. First, many investigations have been concerned with the kinetics and equilibria in systems containing carbon, oxygen and sulfur.

Secondly, because carbon oxysulfide is formed as a product when many compounds containing carbon, oxygen and sulfur are reacted – i.e., carbon mono oxide and sulfur react at elevated temperatures to give nearly quantitative yields of carbon oxysulfides – it has been considered as an intermediate source for the production of carbon disulfide. The conversion of carbon oxysulfide to carbon disulfide is a high temperature reaction, since only 30% conversion is thermodynamically possible at 600ºC.

Choice of process:

Out of the four processes described in the previous pages, catalytic hydrocarbon process is preferable to the other processes. The process offers many advantages over the other process. Primarily in that it is a continuos process and utilizes a cheap and readily source of carbon in the form of methane or natural gas and it operates at much lower temperatures than those of the retort process. Corrosion difficulties are thus greatly reduced. As the process is a catalytic process, the reaction rate is very high and the conversion is also about 95%. The reaction proceeds without side reactions and upon separation from H_2S, pure CS_2 is obtained. This leads to a total savings labor and maintenance per ton of carbon disulfide produced. The process can be designed for high capacities of production as compared against the retort method. Another advantage of using the process is the generation of steam in the process, which can be utilized.

The process is well suited for developing countries which have well developed textile industries and therefore a large carbon disulfide demand, such as India.

Considering the above-mentioned factors, the catalytic methane-sulfur process is chosen for the production of carbon disulfide. The detailed flow sheet for the process is given in the next page.