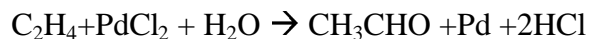


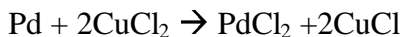
MANUFACTURING PROCESSES AND SELECTION

The economics of the various processes for the manufacture of acetaldehyde are strongly dependent on the price of the feedstock used. Since 1960, the liquid-phase oxidation of ethylene has been the process of choice. However, there is still commercial production by the partial oxidation of ethyl alcohol, dehydrogenation of ethyl alcohol and the hydration of acetylene. Acetaldehyde is also formed as a co product with ethyl alcohol and acetic acid.

3.1 Oxidation of Ethylene: Wacker – Chemie and Farbwerke Hoechst, developed the direct liquid phase oxidation of ethylene in 1957 – 1959. The catalyst is an aqueous solution of PdCl₂ and CuCl₂. In 1894, F.C. Phillips observed the reaction of ethylene with an aqueous palladium chloride solution to form acetaldehyde.



The metallic palladium is reoxidized to PdCl₂ with CuCl₂ and the cuprous chloride formed is reoxidized with oxygen or air.



The net result is a process in which ethylene is oxidized continuously through a series of oxidation – reduction reactions.



Studies of the reaction mechanism of the catalytic oxidation have suggested that a cis – hydroxyethylene – palladium π complex is formed initially, followed by an intramolecular exchange of hydrogen and palladium to give a gem – hydroxyethyl palladium species which leads to acetaldehyde and metallic palladium.

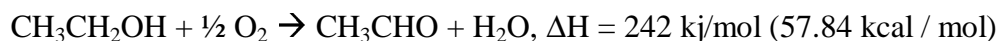
There are two variations for the production of acetaldehyde by the oxidation of ethylene; the two – stage process developed by Wacker – Chemie and the one – stage process developed by Farbwerke Hoechst. In the two – stage process ethylene and oxygen (air) react in the liquid phase in two stages. In the first stage ethylene is almost completely converted to acetaldehyde in one pass in a tubular plug-flow reactor made of

titanium. The reaction is conducted at 125-130⁰C and 1.13 Mpa (150 psig) palladium and cupric chloride catalysts. Acetaldehyde produced in the first reactor is removed from the reaction loop by adiabatic flashing in a tower. The flash step also removes the heat of reaction. The catalyst solution is recycled from the flash – tower base to the second stage (or oxidation) reactor where the cuprous salt is oxidized to the cupric state with air. The high pressure off – gas from the oxidation reactor, mostly nitrogen, is separated from the liquid – catalyst solution and scrubbed to remove acetaldehyde before venting. A small portion of the catalyst stream is heated in the catalyst regenerator to destroy undesirable copper oxalate. The flasher overhead is fed to a distillation system where water is removed for recycle to the reactor system and organic impurities, including chlorinated aldehydes, are separated from the purified acetaldehyde product.

In the one-stage process ethylene, oxygen, and recycle gas are directed to a vertical reactor for contact with the catalyst solution under slight pressure. The water evaporated during the reaction absorbs the heat evolved, and make – up water is fed as necessary to maintain the catalytic solution concentration. The gases are water – scrubbed and the resulting acetaldehyde solution is fed to a distillation column. The tail – gas from the scrubber is recycled to the reactor. Inerts are eliminated from the recycle gas in a bled – stream which flows to an auxiliary reactor for additional ethylene conversion. This oxidation process for olefins has been exploited commercially principally for the production of acetaldehyde, but the reaction can also be applied to the production of acetone from propylene and methyl ethyl ketone from butanes. Careful control of the potential of the catalyst with the oxygen stream induced commercially by a variation of this reaction.

3.2 From Ethyl Alcohol:

3.2.1 Acetaldehyde is produced commercially by the catalytic oxidation of ethyl alcohol. Passing alcohol vapors and preheated air over a silver catalyst at 480⁰C carries out the oxidation.



With a multitubular reactor, conversions of 74-82% per pass can be obtained while generating steam to be used elsewhere in the process.

3.2.2 Acetaldehyde also, produced commercially by the dehydrogenation of ethyl alcohol.

Reaction:



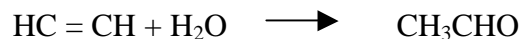
Catalyst: Cu -Co-Cr₂O₃

Temperature: 280 – 350⁰ C.

Process description: The raw material i.e., ethanol is vaporized and the vapors, so generated, are heated in a heat exchanger to the reaction temperature by hot product stream. The product stream is cooled to –10⁰ C and in doing it, all unreacted ethanol and acetaldehyde are condensed. The out going gaseous stream, containing hydrogen mainly, is scrubbed with dilute alcohol (alcohol + water) to remove uncondensed products and the undissolved gas. The remaining pure hydrogen (98%) is burnt in stack.

Figure 2, shows the flow sheet of the process in which ethanol is vaporized in vaporizer and heated to the reactor temperature in heat exchanger. The heated vapors are passed through the converter. The product stream is first cooled in heat exchanger and then in condensers using water and liquid ammonia. This condenses most of the unreacted ethanol and the acetaldehyde formed in reactor. The escaping gas, which is almost pure hydrogen, is scrubbed by ethanol to remove all the traces of the product. The liquid stream consisting of mainly ethanol and acetaldehyde, is distilled in distillation column to get acetaldehyde.

3.3 From Acetylene: Acetaldehyde has been produced commercially by the hydration of acetylene since 1916. However, the development of the process for the direct oxidation of ethylene in the 1960s has almost completely replaced the acetylene – based processes and in 1976 there was only small volume production in a few European countries. In the older processes, acetylene of high purity is passed under a pressure of 103.4 kPa (15 psi) into a vertical reactor containing a mercury catalyst dissolved in 18-25% sulfuric acid at 70-90⁰C.



Fresh catalyst is fed to the reactor periodically; the catalyst may be added in the mercurous form but it has been shown that the catalytic species is a mercuric ion complex (100). The excess acetylene sweeps out the dissolved acetaldehyde which is condensed by water and refrigerated brine and scrubbed with water; the crude acetaldehyde is purified by distillation and the unreacted acetylene is recycled. The catalytic mercuric ion is reduced to catalytically inactive mercurous sulfate and metallic mercury; this sludge, consisting of reduced catalyst and tars, is drained from the reactor at intervals and resulfated. Adding ferric or other salts to the reaction solution can reduce the rate of catalyst depletion. The ferric ion reoxidizes mercurous to the mercuric ion while it is reduced to the ferrous state; consequently, the quantity of sludge, which must be recovered, is reduced (81,101). In one variation, acetylene is completely hydrated with water in a single operation at 68-73⁰C using the mercuric iron salt catalyst. The acetaldehyde is partially removed by vacuum distillation and the mother liquor recycled to the reactor. The aldehyde vapors are cooled to about 35⁰C, compressed to 253 kPa (2.5 atm), and condensed. It is claimed that this combination of vacuum and pressure operations substantially reduces heating and refrigeration costs.

Acetaldehyde may also be made from methyl vinyl ether and ethylidene diacetate, both of which can be made from acetylene. Methyl vinyl ether is made by the addition of methanol to acetylene at 1.62 Mpa (16 atm) in a vertical reactor containing a 20% methanolic solution of potassium hydroxide. Hydrolysis of the ether with dilute sulfuric acid yields acetaldehyde and methanol which are separated by distillation; the methanol is recycled to the reactor. Acetylene and acetic acid form ethylidene diacetate in the presence of mercuric oxide and sulfuric acid at 60-80⁰C and atmospheric pressure. After separation, the ethylidene diacetate is decomposed to acetaldehyde and acetic anhydride by heating to 150⁰C in the presence of a zinc chloride catalyst (81). Acetaldehyde has been made from methyl vinyl ether and ethylidene diacetate in the past, but neither process is used today.

3.4 From Saturated Hydrocarbons: Acetaldehyde is formed as a co product in the vapor – phase oxidation of saturated hydrocarbons, such as butane or mixtures containing butane, with air or, in higher yield, oxygen. Oxidation of butane yields acetaldehyde, formaldehyde, methanol, acetone, and mixed solvents as major products; other aldehydes, alcohols, ketones, glycols, acetals, epoxides, and organic acids are formed in smaller concentrations. This is of historic interest. Unlike the acetylene route, it has almost no chance to be used as a major process.

From synthesis Gas: A rhodium-catalyzed process capable of converting synthesis gas directly into acetaldehyde in a single step was reported in 1974 (84-85).



The process comprises passing synthesis gas over 5% rhodium on SiO₂ at 300⁰C and 2.0 Mpa (20 atm). The principal co products are acetaldehyde, 24% acetic acid, 20%; and ethanol, 16%. In the years 1980 and beyond, if there will be a substantial degree of coal gasification, the interest in the use of synthesis gas as a raw material for acetaldehyde production will increase.

3.5 Specifications, Analytical, and Test Methods:

Commercial acetaldehyde has the following typical specifications: assay, 99% min; color, water-white; acidity, 0.5% max (acetic acid); specific gravity, 0.790 at 20⁰C; bp, 20.8 at 101.3 kPa (1 atm). Acetaldehyde is shipped in steel drums and tank cars bearing the ICC red label. IN the liquid state, it is noncorrosive to most metals; however, it oxidizes readily, particularly in the vapor state, to acetic acid. Precautions to be observed in the handling of acetaldehyde have been published by the manufacturing chemists association.

Analytical methods based on many of the reactions common to aldehydes have been developed for the determination of acetaldehyde. In the absence of other aldehydes, it can be detected by the formation of a mirror from an alkaline silver nitrate solution (Tollens' reagent) and by the reduction of Fehling's solution. It can be determined quantitatively by fuchsin-sulfur dioxide solution (Schiff's reagent) or by the reaction with sodium bisulfite, the excess bisulfite being estimated iodometrically. Acetaldehyde

present in mixtures with other carbonyl compounds, organic acids, etc. can be determined by paper chromatography of 2,4 – dinitrophenylhydrazones polarographic analysis either of the untreated mixture or of the semicarbazones, the color reaction with thymol blue on silica gel (detector tube method) mercurimetric oxidation, argentometric titration, microscopic and spectrophotometric methods, and gas – liquid chromatographic analysis. With the advent of gas – liquid chromatographic techniques, this method has superseded most chemical tests for routine analysis.

Acetaldehyde can be isolated and identified by the crystalline compounds of characteristic melting points formed with hydrazine's, semicarbazides, etc.; these derivatives of aldehydes can be separated by paper and column chromatography. Acetaldehyde has been separated quantitatively from other carbonyl compounds on an ion exchange resin in the bisulfite form; the aldehyde is eluted from the column with a solution of sodium chloride. In larger quantities, it may be isolated by passing the vapor into ether and saturating the ether with dry ammonia; the product, acetaldehyde – ammonia, crystallizes from the ether solution. The reactions of acetaldehyde with bisulfite, hydrazine's, oximes, semicarbazones, and 5,5–dimethyl – 1,3 cyclohexanedione (dimedone) have been used to isolate acetaldehyde from solutions.

3.6 PROCESS SELECTION:

Here, ethyl alcohol dehydrogenation is selected for the production of acetaldehyde. Because, in this process, hydrogen is taken out as a by-product which can be used elsewhere or which can be used to generate heat. In dehydrogenation process more conversion-taking place compared to other processes. The dehydrogenation catalyst has a life of several years but requires periodic reactivation. In dehydrogenation process, number of products are less, so separation of acetaldehyde from other product is not a difficult problem.