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# PRODUCTION OF ACETALDEHYDE

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**Abstract:**

There are two methods for producing acetaldehyde by ethylene oxidation: the two-stage techniques established by Wacker-Chemie and the one-stage process developed by Farbwerke Hoechst. Acetaldehyde may be produced in a single step by direct oxidation of ethylene in the gaseous phase in the presence of palladium chloride and water. On a large scale, the procedure is typically carried out as follows: Ethylene is oxidised in a bubble column reactor containing an aqueous solution of CuCl2, CuCl, and PdCl2 with oxygen in a cyclic process at 400°C and 3 bar pressure (absolute pressure), The term "single-stage manufacture" refers to the oxidation of the ethylene yielding acetaldehyde and the reoxidation of the palladium chloride reduced in this process (reoxidation being affected by CuCl2 which is converted into CuCl, which in turn is reoxidized by oxygen) being carried out in one reactor.

The gas stream exiting the reactor, which contains steam, acetaldehyde, ethylene, and minor quantities of oxygen, carbon dioxide, acetic acid, crotonaldehyde, and chlorinated chemicals (such as methyl chloride, ethyl chloride, and chloro acetaldehyde), is cooled in a condenser to around 80° to 130° C. The condensate produced, which mostly consists of water and trace quantities of acetaldehyde and acetic acid, is often recycled back into the reactor. Small quantities of copper oxalate and high molecular by-products are also generated and stay persistent in the catalyst solution, whilst the volatile by-products, together with the acetaldehyde and unreacted starting chemicals, exit the reactor.

To prevent the buildup of these by-products, a tiny portion of the liquid phase is continually drained from the reactor. After that, the pressure is released, and the dissolved low-boiling chemicals such as acetaldehyde, ethylene, and carbon dioxide flash and are evacuated. The degassed solution is transferred to a regeneration vessel and heated to a temperature of approximately 165° to 180° C. The regenerated solution is recycled into the reactor. After being cooled in the condenser, the gas current exiting the reactor is typically cooled further through heat exchangers to around 30° to 80° C. The acetaldehyde is then cleaned out of the gas stream in a scrubber. After removing a portion of the residual gas (to minimise a buildup of carbon dioxide and inert gas) and adding new ethylene, the leftover gas is returned to the reactor.

The condensate from the heat exchangers and the aqueous acetaldehyde solution from the scrubbers are mixed in a collecting tank. This "crude aldehyde" combination is routed via a two-

stage distillation process. In this process, low-boiling chemicals (methyl chloride, ethyl chloride) and dissolved gases such as ethylene and carbon dioxide are produced as the overhead in a first stage by extractive distillation using water as an extraction agent. The bottom product is transported to the second distillation process, where pure acetaldehyde is produced as the overhead product. A side stream comprising mostly crotonaldehyde is removed. The high-boiling by-products (particularly acetic acid and chloro acetaldehyde) and water are taken from the bottom. The extracted combination is referred to as "waste water."

**Keywords:** Ethylene, EthylAlcohol,and Acetylene: SaturatedHydrocarbons:

## I.0 INTRODUCTION:

Ethanal is one of the earliest known aldehydes, having been created in 1774 by Swedish scientist Carl Wilhelm Scheele by the action of manganese dioxide and sulfuric acid on ethanol. Its structure was not fully known until 60 years later, when Justus von Liebig identified the composition of ethanal, explained its production from ethanol, and gave the chemical group the name aldehydes. Kutscherow discovered acetaldehyde by adding water to acetylene in 1881. Acetaldehyde was widely employed as an intermediary in the production of acetone from acetic acid during World War I. The shortest carbon chain aldehyde is ethanal (acetaldehyde). It has a core carbon atom with a double connection to an oxygen atom (the carbonyl group), a single link to a hydrogen atom, and a single bond to another carbon atom coupled to three hydrogen atoms (methyl group). Its chemical formula is $CH_3CHO$.

Acetaldehyde is a simple, naturally occurring organic molecule found in many ripe fruits, including apples, grapes, and citrus fruits (up to 230 ppm).It is formed during the fermentation of sugar to alcohol and is found naturally in butter, olives, frozen veggies, and cheese. It occurs after exposure to oxygen in wine and other alcoholic drinks (up to 140 ppm). It can even be detected in human blood as an intermediary in the metabolism of carbohydrates. Acetaldehyde is an authorised food ingredient that is used to enhance citrus flavours and smells. It may be found as a flavouring component in ice creams, candies, baked products, chocolates, rum, and wine.

Acetaldehyde may be found in oak and tobacco leaves, as well as the fruity scents of apple, raspberry, strawberry, pear, and pineapple. It may also be found in the distillation fluids of orris, cumin, chenopodium, essential oils of Magnolia grandiflora, rosemary, clary sage, daffodil, bitter orange, camphor angelica, fennel mustard, whiskey, rose wine, and rum.

Acetaldehyde occurs naturally in broccoli, coffee, grapefruit, grapes, lemons, mushrooms, onions, oranges, peaches, pears, pineapples, raspberries, and strawberries.It has been found in the essential oils of alfalfa, rosemary, balm, clary sage, daffodil, bitter orange, camphor, angelica, fennel, mustard, and peppermint. Acetaldehyde (systematically ethanal) is an organic chemical molecule having the formula $CH_3CHO$, which scientists sometimes abbreviate as MeCHO (Me =methyl).

It is one among the most significant aldehydes, occurring extensively in nature and being generated on a considerable scale industrially. Acetaldehyde occurs naturally in coffee and bread and is created by plants as part of their regular metabolism. It is also formed by the oxidation of ethylene and is often thought to be the source of hangovers after alcohol use by drinking spirits. Air, water, soil, or groundwater, as well as drink and smoke, are all potential routes of exposure.

## 2.0 PROPERTIES OF ACETALDEHDYE:

Physicalproperties:

Acetaldehyde is a colorless, mobile liquid with a powerful stifling stench that, in weak doses, is rather fruity and pleasant. Table 1 shows some of the physical features of acetaldehyde.

| **Properties** | **Values** |
|---|---|
| Physical State | colorless liquid |
| Formula weight g/mol | 44.053 |
| Melting point °C | -123.5 |
| Boiling point at 101.3 kPa (1 atm), °C | 20.16 |
| Specific Density | 0.8045 |
| Coefficientofexpansionper °C(0-30°C) | 0.00169 |
| Refractive index | 1.33113 |
| Vapordensity(air=1) | 1.52 |
| Absolute viscosity at 15 °CmPa.s b | 0.02456 |
| Specific heat at 0 °C,J/(g.K) | 2.18 |
| At 25 °C | 1.41 |
| Latent heat of fusion, kJ/mol | 3.24 |
| Latent heat of vaporization, kJ/mol | 25.71 |
| Heat of solution in water at 0 °C, kJ/mol | -8.2 |
| At 25 °C | -6.82 |

| | |
|---|---|
| Heatofcombustionofliquidat constant pressure, kJ /mol | 11867.9 |
| Heat of formation at 273 K, kJ/mol | -165.48 |
| Freeenergyof formation at 273K,kJ/mol | -136.4 |
| Critical temperature, °C | 181.5 |
| Critical pressure, MPa (atm) | 6.40(63.2) |
| Dipole moment, C-m (debyes ) | 9.04x 10 – 30 |
| Ionization potential, Ev | 10.5 |
| Dissociation constant at 0 °C, K | 0.7 x 10 – 14 |
| Flash point, closed cup, °C | -38 |
| Ignitiontemperatureinair,°C | 165 |

**Chemical Properties**:
Acetaldehyde is a highly reactive molecule that exhibits the usual aldehyde reactions; given appropriate circumstances, the oxygen or any hydrogen may be substituted. Acetaldehyde passes through a variety of condensation, addition, and polymerization processes.

## 3.0 METHODS OF MANUFACTURING OF ACETALDEHYDE

### 3.1 Oxidation of ethylene

The economics of the different procedures for producing acetaldehyde are heavily influenced by the price of the feedstock. Since 1960, the liquid-phase oxidation of ethylene has been the preferred method. Commercial production is still possible by the partial oxidation of ethyl alcohol, dehydrogenation of ethyl alcohol, and hydration of acetylene. Acetaldehyde is also generated as a by-product of the reactions of ethyl alcohol with acetic acid.There is two methods for producing acetaldehyde from ethylene oxidation: the two-stage process developed by Wacker-Chemie and the one-stage technique developed by Farbwerke Hoechst.It is known that acetaldehyde may be produced in a single step by direct oxidation of ethylene in the gaseous phase in the presence of palladium chloride and water (cf. Jira, Blau, Grimm; Hydrocarbon Processing, March 1976, pages 97 to 100).

On a large scale, the procedure is typically carried out as follows: Ethylene is oxidised in a bubble column reactor containing an aqueous solution of CuCl2, CuCl, and PdCl2 with oxygen in a cyclic process at 400°C and 3 bar pressure (absolute pressure), The term "single-stage manufacture" refers to the oxidation of the ethylene yielding acetaldehyde and the reoxidation of the palladium chloride reduced in this process (reoxidation being affected by CuCl2 which is converted into CuCl, which in turn is reoxidized by oxygen) being carried out in one reactor.

The gas stream exiting the reactor, which contains steam, acetaldehyde, ethylene, and minor quantities of oxygen, carbon dioxide, acetic acid, crotonaldehyde, and chlorinated chemicals (such as methyl chloride, ethyl chloride, and chloro acetaldehyde), is cooled in a condenser to around 80° to 130° C. The condensate produced, which mostly consists of water and trace quantities of acetaldehyde and acetic acid, is often recycled back into the reactor. Small quantities of copper oxalate and high molecular by-products are also generated and stay persistent in the catalyst solution, whilst the volatile by-products, together with the acetaldehyde and unreacted starting chemicals, depart the reactor. To prevent the build-up of these by-products, a tiny portion of the liquid phase is continually drained from the reactor. After that, the pressure is released, and the dissolved low-boiling chemicals such as acetaldehyde, ethylene, and carbon dioxide flash and are evacuated.

The degassed solution is transferred to a regeneration vessel and heated to a temperature of approximately 165° to 180° C. The regenerated solution is recycled into the reactor. After being cooled in the condenser, the gas current exiting the reactor is normally cooled further through heat exchangers to around 30° to 80° C. The acetaldehyde is then cleaned out of the gas stream in a scrubber. After removing a portion of the residual gas (to minimise a buildup of carbon dioxide and inert gas) and adding new ethylene, the leftover gas is returned to the reactor. The condensate from the heat exchangers and the aqueous acetaldehyde solution from the scrubbers are mixed in a collecting tank.

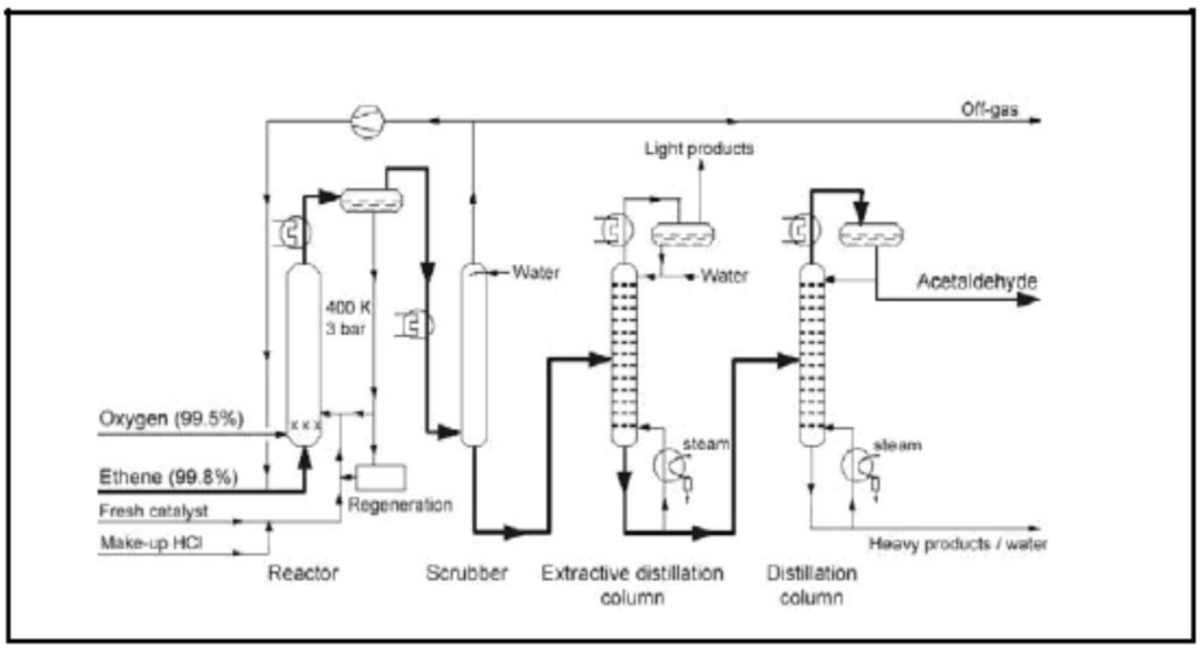
This "crude aldehyde" combination is then sent through a two-stage distillation process. In this process, low - boiling chemicals (methyl chloride, ethyl chloride) and dissolved gases such as ethylene and carbon dioxide are produced as the overhead in a first stage by extractive distillation using water as an extraction agent. The bottom product is transported to the second distillation process, where pure acetaldehyde is produced as the overhead product. A sidestream comprising mostly crotonaldehyde is removed. The high-boiling by-products (particularly acetic acid and chloro acetaldehyde) and water are taken from the bottom. The extracted combination is referred to as "waste water."

In the two-stage process, ethylene and oxygen (air) react in the liquid phase in two steps. In the first step, ethylene is nearly fully transformed to acetaldehyde in a titanium tube plug-flow reactor in a single pass. The reaction is carried out at 125 -130 0C using palladium and cupric chloride catalysts at 1.13 Mpa (150 psig). Acetaldehyde generated in the first reactor is removed from the reaction loop through adiabatic flashing in a tower. The flash stage also reduces 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 oxidised to the cupric state with air. The high-pressure off-gas from the oxidation reactor, predominantly nitrogen, is separated from the liquid-catalyst solution and washed to remove acetaldehyde before venting. In the catalyst regenerator, a tiny fraction of the catalyst stream is heated to remove unwanted copper oxalate.

The flasher overhead is fed into a distillation system, where water is removed for recycling to the reactor system and organic contaminants, including chlorinated aldehydes, are extracted from the purified acetaldehyde output. In the two-stage technique, the ethylene reaction and the oxidation reaction take place in separate reactors. However, the two - step variation of the process necessitates a catalyst circulation, which consumes a lot of energy and is technically less common than the single - stage variant.

This approach is technically straightforward, has a smooth response, and has a good selectivity. The process's excellent economics are owing to the availability of ethylene. It is extensively employed in many nations and is often recognised as the most cost-effective industrial process approach.

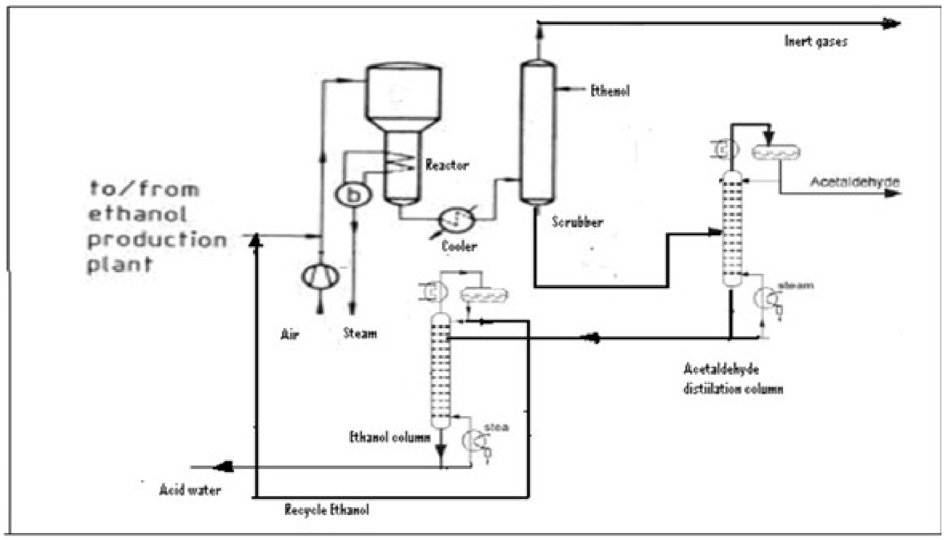



Productionofacetaldehydefromoxidationofethylene

## 3.2FROM ETHYL ALCOHOL

In the reactor, ethanol is combined with air and passed through a silver catalyst at 500-650 degrees Celsius. The high temperature gas (acetaldehyde and unconverted alcohol) from the oxidizer exit is cooled and condensed before being transferred to the scrubber to absorb acetaldehyde and unconverted ethanol. Nitrogen, hydrogen, methane, carbon monoxide, carbon dioxide gas, and other inert gases are expelled from the tower's top. After heating the diluted acetaldehyde solution at the bottom of the scrubber, which contains acetaldehyde, alcohol, acetic acid, and water, it is sent to the distillation tower, where the gas phase fraction from the tower top, which is 99% acetaldehyde, is partly collected and the majority is refluxed back.

The ethanol and water solution released from the bottom of the distillation tower is forced into the ethanol recovery tower, where ethanol is separated from butanol, ethyl acetate, and most of the water. These contaminants escape the bottom Stream and are transferred to trash treatment. The distillate is an 85 - wt.% ethanol solution that is recycled back into the feed.




**Acetaldehydeproduction from oxidationof Ethanol**

**3.3 FROMACETYLENE**:

A carefully built hydrator manages the following chemical steps to convert acetylene to acetaldehyde..

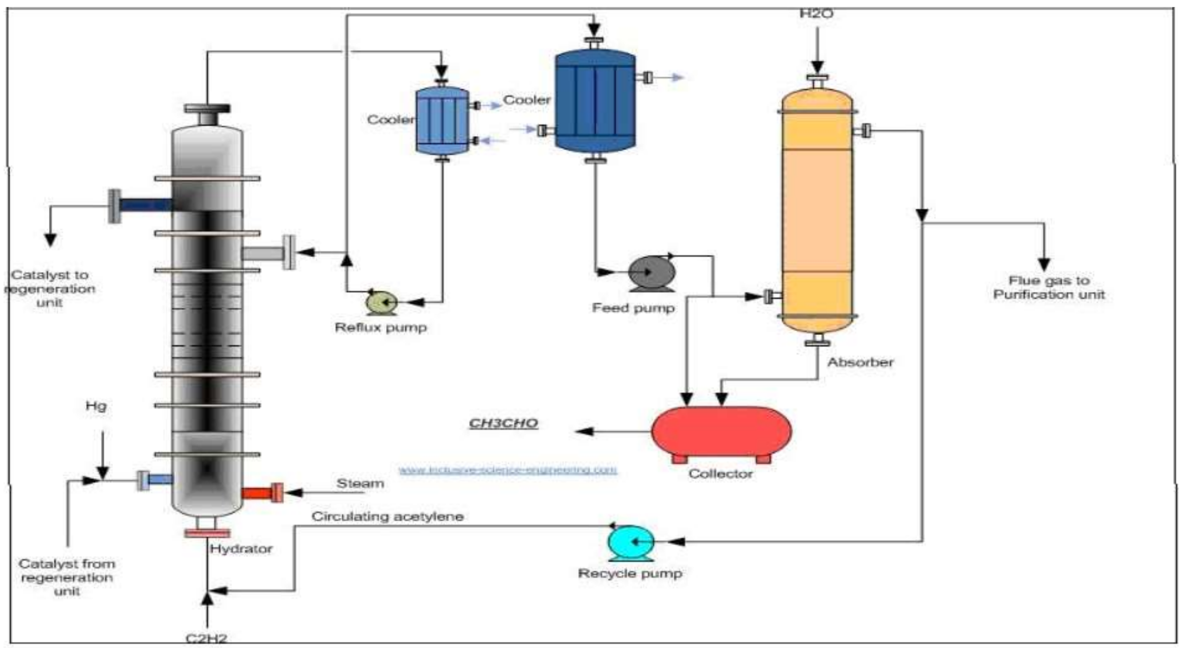
$$C_2H_2 + H_2O \rightarrow CH_3CHO + 151\ KCal$$

The hydrator operates at 1.5 to 2.5 atm pressure and temperatures ranging from 80 to 100oC. The liquid catalyst is supplied with acetylene on a continual basis. Steam, which is pumped at the bottom of the column, keeps the temperature stable. The hydrator is constructed of stainless steel or ferrosilicon. The hydrator's top stream is sent to a chiller. The water vapour is completely condensed and recycled. The second cooler uses the first cooler's output. Acetaldehyde and traces of water are condensed.

A water scrubber receives unreacted acetylene and non-condensable vapour. The water scrubber is set to function at 10oC. Acetaldehyde and water-soluble chemicals are washed away. The residual gases are either utilised as fuel or returned to the dehydrator. 19 The liquid catalyst is a sulfuric acid-dispersed solution of mercury (II) sulphate. Because acetaldehyde is a good reducing agent, it lowers Hg(II) to Hg(I), and then Hg(I) to Hg.

$$2Hg_2SO_4 + H_2O + CH_3CHO \rightarrow Hg_2SO_4 + H_2SO_4 + CH_3COOHHg_2SO_4 + H_2O + CH_3CHO \rightarrow 2Hg + H_2SO_4 + CH_3COOH$$

As a hydrator, fluidized bed equipment is employed. In addition to mercury, zinc oxide, magnesium oxide, and iron oxide are utilised. Calculations in general Onetonne of acetaldehyde require 680 kg of acetylene and 0.1 kilogramme of mercury. This method converts at a rate of 50-60% every pass. The procedure regenerates the catalyst.




**Production Of acetaldehyde by liquid phase reaction of acetylene**

3.4 FROM SATURATED HYDROCARBONS:

Acetaldehyde is produced as a byproduct of the vapor-phase oxidation of saturated hydrocarbons, such as butane or butane mixtures, with air or, in greater yield, oxygen. The primary products of butane oxidation are acetaldehyde, formaldehyde, methanol, acetone, and mixed solvents; additional aldehydes, alcohols, ketones, glycols, acetals, epoxides, and organic acids are generated in lower amounts. This is historically significant. Unlike the acetylene pathway, it has little possibility of becoming a large process. derived from synthesis Gas: In 1974, a rhodium-catalyzed technique for turning synthesis gas directly into acetaldehyde in a single step was discovered (84-85).

$$CO + H_2 = CH_3CHO + \text{other products}$$

At 3000 C and 2.0 Mpa, synthesis gas is passed through 5% rhodium on SiO2 (20 atm). The main co-products are acetaldehyde (24%), acetic acid (20%), and ethanol (16%). If there is a significant degree of coal gasification in the years 1980 and beyond, interest in using synthesis gas as a raw material for acetaldehyde manufacture will rise.

4.0 CONCLUSION:

Acetaldehyde is a colourless, mobile liquid with a powerful stifling stench that is slightly fruity and pleasant at weak quantities. Acetaldehyde is a simple, naturally occurring organic molecule found in many ripe fruits, including apples, grapes, and citrus fruits (up to 230ppm). It is formed during the fermentation of sugar to alcohol and is found naturally in butter, olives, frozen veggies, and cheese. It occurs after exposure to oxygen in wine and other alcoholic drinks.Acetaldehyde is made mostly from ethylene across the globe; however some is still made from ethanol and acetylene. As the industry continues to shift toward the more efficient and lower-overall-cost carbonylation-of-methanol method, global demand for acetaldehyde has continued to fall.During the period 2000-2014, the worldwide market for acetaldehyde is predicted to increase at a rate of 2-3% each year.Because ethylene, a key raw ingredient in the synthesis of acetaldehyde, is a petrochemical product, establishing a factory with a capacity of 150 tonnes per year in Gujarat is a safe move.We created a 150 TPA plant with a techno-economic feasibility study that includes need, demand, and supply analysis, as well as going through a mass, energy balance, and comprehensive equipment design process.The payback time (3 years) and rate of return indicate that the factory is an economically feasible and lucrative business to invest in, whether for an established organisation or a newcomer in the market.

## 5.0 ACKNOWLEDGEMENT:

I am thankful to my guide and god for giving me such a big opportunity in my life. I would also like to thank those who have directly or indirectly helped me in my work.

## 6.0 REFERENCES:

1. Ullmann’s, An ullmann's EncyclopediaofIndustrial Organic ChemistryEdition 7,Page no.87
2. https://en.wikipedia.org/wiki/Acetaldehyde
3. EncyclopediaofIndustrial OrganicChemistry Edition7,Pageno.99
4. Belloche,A.,Müller,H.S.P.,Menten,K.M.,Schilke,P.,&Comito,C.2013,A&A,559,A47[NASAADS][CrossRef][EDPSciences][GoogleScholar]
5. Bennett,C.J.,Osamura,Y.,Lebar,M.D.,&Kaiser,R.I.2005,ApJ,634,698[NASAADS][CrossRef][PubMed][Google Scholar]
6. Bisschop,S.E.,Fuchs,G.W.,vanDishoeck,E.F.,&Linnartz,H.2007,A&A,474,1061[NASAA

DS][CrossRef][EDPSciences][GoogleScholar]

7. Bisschop,S.E.,Jørgensen,J.K.,Bourke,T.L.,Bottinelli,S.,&vanDishoeck,E.F.2008,A&A,488, 959[NASAADS][CrossRef][EDPSciences][GoogleScholar]
8. Collings,M.P.,Anderson,M.A.,Chen,R.,etal.2004,MNRAS,354,1133[NASAADS][CrossRef][Google Scholar]
9. Dickens,J.E.,Irvine,W.M.,Ohishi,M.,etal.1997,inAm.Astron.Soc.Meet.Abstracts, BAAS, 29, 1245 [NASAADS][Google Scholar]
10. Fuchs,G.W.,Cuppen,H.M.,Ioppolo,S.,etal.2009,A&A,505,629[NASAADS][CrossRef][EDPSciences][Google Scholar]
11. Garrod,R.T.,&Herbst,E.2006,A&A,457,927[NASAADS][CrossRef][EDPSciences][Google Scholar]
12. Garrod,R.T.,Wakelam,V.,&Herbst,E.2007,A&A,467,1103[NASAADS][CrossRef][EDPSciences][Google Scholar]
13. Garrod,R.T.,Weaver,S.L.W.,&Herbst,E.2008,ApJ,682,283[NASAADS][CrossRef][Google Scholar]
14. "Production of Acetaldehyde", by Sushmitasharma(091431) VinayJaiswal(091434)Jaypee university of engineering and technology,A.B. Road,Raghogarh, Dist. Guna-473226,M.P.,INDIA2011-2012.