SELECTED PROFITABLE CHEMICAL INDUSTRIES

SiRi

61st Publication on Small Scale Industries

SELECTED PROFITABLE CHEMICAL INDUSTRIES

Most practicable book which will help as a guide to young entrepreneurs, manufacturers of various chemicals. The book contains complete manufacturing processes, uses and applications, market position and cost estimations with profitability analysis, of more than 125 profitable chemicals. Thus it is very helpful to new entrepreneurs as well as manufacturers of any one of the chemical described in the book. The book also includes the addresses of plant, machinery and raw materials suppliers and manufacturers.

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Price [illegible] : [illegible] 75.00
Overseas : $ 20 or £ 10

SMALL INDUSTRY RESEARCH INSTITUTE (Regd.)

World Renowned Institute for Industrial Publications

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Published by :

Small Industry Research Institute
4/43, Roop Nagar, Delhi-110007. Phone : 220885

Edition 1981-82

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Printed at : J.N. Prtnts 251/8, Padam Nagar Delhi-7 *12/80/12*

Preface

Indian Chemical Industry has developed in the last two decades and proved one of the most successful industry in India. Most of the industrially important chemicals are being manufactured in the country today but there is still gap between demand and production. And so there is still very good scope for the manufacture of a number of new chemicals or setting up new capacities for the production. Setting up such chemical industries, huge amount of foreign exchange can be saved and thus one can help to the country. In this book, an attempt has been made to give the project profiles of such selected chemicals which are either imported or manufactured indigenously, are in short supply. Selection of such chemicals have been made with thorough market survey of whole India with the help of Government and Private bodies. To give impetus to the development of selected chemicals, complete manufacturing processes, uses and applications, market positions, cost estimations with profitability analysis have been described. Apart from this addresses of manufacturers and suppliers of plant, machinery and raw materials are also included in this book.

The plant economics given in the product profiles is in nature of preliminary guideline for the selection of an item for manufacture. All this information is very essential in selecting an industry and would help a great deal in setting up the plant too. It is hoped, this book will help to small scale industrialists, prospective entrepreneurs and technocrats for developing their products. We are sure that setting up of these units in the small scale and a few in the medium scale will go a long way in filling the gap between demand and production. We thank all individuals, private agencies and government bodies connected with this work for their excellent co-operation and help which they extended for the completion of this book.

AUTHOR

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Acetaldehyde

Acetaldehyde from Acetylene

Material and Energy Requirements

Basis : 1 ton of Acetaldehyde	
Acetylene	1,240 lbs.
Catalysts (Sulphuric Acid and Mercurous Sulphate)	small
Electricity	120 Kwhr.
Steam	7,500 lbs.

Plant and Machinery

Reactor
Scrubber
Columns
Catalyst Recovery Plant
Absorption Column
Motors and Pumps
Storage and Mixing Tanks
Preheaters

Process

Acetaldehyde may be manufactured by the hydration of acetylene in the presence of a mercurous sulphate. Catalyst acetone of high purity (95%) is passed under a pressure of 15 psi into a reactor containing mercurous sulphate dissolved in 18 to 25 percent sulphuric acid solution. The heat reaction maintains the contents of the reactor at 70 to 100°C. During the reaction the mercurous sulphate is reduced to metallic mercury that settles to the bottom of the reactor as sludge. A portion of sludge is withdrawn every 15 minute and make up catalyst is added intermittently at a rate that insures a complete change of catalyst every 8 hours. The sludge is sent to a catalyst recovery system for reconversion to mercurous sulphate. Vapours of acetaldehyde, water and unreacted acetylene are led from the reactor to a series of scrubbing towers and passed counter current to water to dissolve the acetaldehyde. A weak acetaldehyde solution leaves the bottom of the scrubber, and stripped acetylene gas leaves the top. The acetaldehyde solution is pumped to a column for concentration. Vapours leaving the top of the column may vary from 80-99% acetaldehyde, depending upon column efficiency. Crotonaldehyde is the by-product of the distillation. Scrubbed acetylene is recycled to the reactor.

Reaction

$$CH \equiv CH + H_2O \xrightarrow[95\%\ \text{yield}]{} CH_3CHO$$

Uses

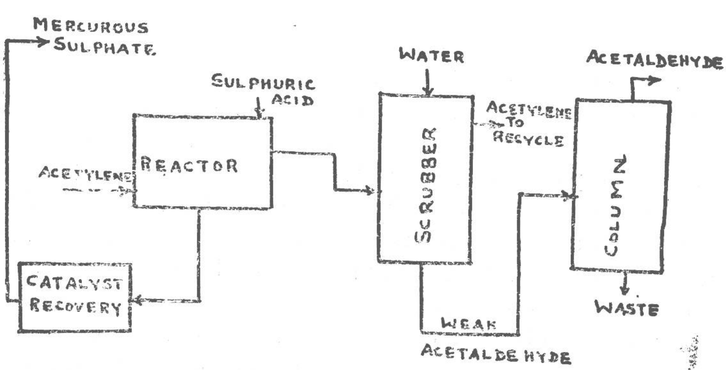
In the manufacture of Acetic Acid and Acetic Anhydride, *n*-Butanol, Ethyl Hexanol Pentaerythritol etc.

Properties

Colourless, fuming, flammable liquid with a pungent, furity odour.

Soluble in all proportion with water, alcohol, ether and benzene at room temperature.

Flash Point (open cup)		40°F
Ignition temperature		365°F
Vapour density		1.52
Explosive limit	lower	4
	upper	57
Maximum allowable concentration		200



FLOW DIAGRAM FOR MANUFACTURE OF ACETALDEHYDE FROM ACETYLENE

COST ESTIMATION

Details of Plant and Machineries

	Nos.	Rupees
Reactors	2	28,000
Scrubbers	2	25,000
Mixing and Storage Tanks	2	18,000
Columns	2	25,000
Pumps and Motors	4	12,000
Boiler	1	25,000
Heat Exchanger	1	35,000
		1,68,000
Piping work with valves		25,000
Installation and Electrification		15,000
	Total	2,08,000

Manpower Requirement

	Nos.	Rupees
Engineers	2	2,000
Chemists	2	2,400
Supervisors	2	1,000
Skilled workers	10	3,000
Unskilled workers	15	3,750
Labourers	20	2,400
Accountant	1	700
Clerks/Typists	2	700
Peon and Chowkidar	2	350
	Total	16,300

Utilities and Overheads

		Rupees
Power and Water		5,000
Fuel Gas		6,000
Office Expenses		5,000
Packaging of Material		5,000
Conveyance, Advertising and Publicity		6,000
	Total	27,000

Land and Building

Total area 2000 square metres on rent Rs. 5,000

Profitability per month *Rupees*

(*a*) *Expenses*

Raw Material	95,000
Staff Salary	16,300
Utilities and Overhead	27,000
Rent for land and building	5,000
Interest @ 12% per annum on fixed investment	2,080
Depreciation on Plant and Machinery at 10% per annum	1,680
Total	1,47,060

(*b*) *Profit and Loss Account*

Total cost of producing 30 tonnes of Acetaldehyde=Rs. 1,47,060
Return from 30 tonnes of Acetaldehyde @ Rs. 8000 per tonne $=30\times8000=$Rs. 2,40,000

Net Profit on account of producing 30 tonnes of Acetaldehyde =Rs. 2,40,000—1,47,060=Rs. 92,940

Acetaldehyde from Ethanol by vapour phase oxidation or Dehydrogenation

Reaction

$$CH_3CH_2OH \longrightarrow CH_3CHO+H_2$$

or

$$CH_3CH_2OH+\tfrac{1}{2}O_2 \xrightarrow[\text{(85—95\% yield)}]{} CH_3CHO+H_2O$$

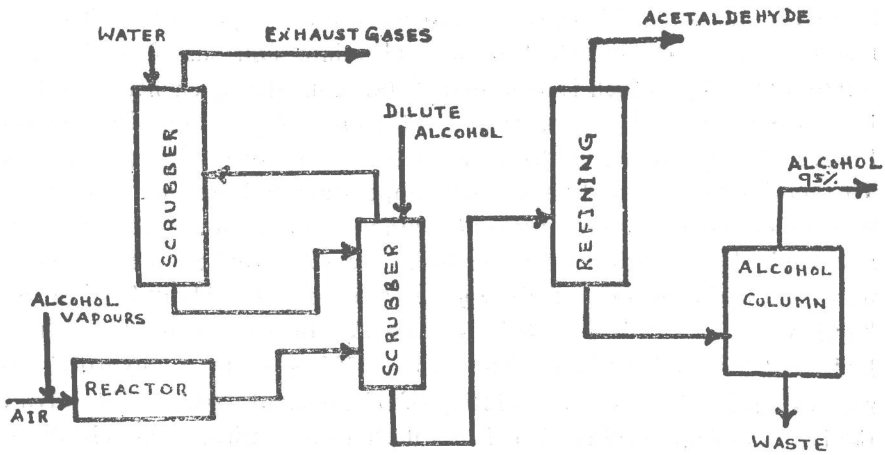
Material Requirement

Basis : 1 M.T. of Acetaldehyde
Ethanol (100%) 1150 kgs.

Process

Ethanol vapours (50—95%) and preheated air are mixed in such proportions that the exothermic heat of oxidation just exceeds the absorbed heat of dehydrogenation, in which case the reaction will proceed without the external application of heat. The vapours pass through a reactor containing a silver gauze catalyst. Reactor temperature depends on the air/ethanol/steam ratio and the velocity of the gases over the catalyst, and may vary from 375—550°C. Exit gases from the convertor, containing ethanol and acetaldehyde, are led to a scrubbing column where cold, dilute ethanol cools the gases and dissolves both ethanol and acetaldehyde. The stripped gases leaving the top of the scrubber are scrubbed again with water and released to the atmosphere. The dilute alcohol-acetaldehyde solution from the bottom of the scrubbing column is rectified in a refining column to produce 99% acetaldehyde as overhead. The dilute alcohol solution leaving the bottom of the column is concentrated in the conventional manner. Conversion per pass generally ranges from 25—35%.

When a straight dehydrogenation process, the usual procedure, is being carried out, a chromium activated copper catalyst may be used. The temperature of the reaction is maintained by external heating at 260—290°C. A condenser is usually installed just ahead of the scrubber. Conversion of alcohol per pass ranges from 30 to 50%.



FLOW DIAGRAM OF ACETALDEHYDE FROM ETHANOL BY VAPOUR OXIDATION

Acetaldehyde from Butane by vapour phase oxidation

Reaction

$$C_4H_{10} + O_2(\text{air}) \longrightarrow \begin{matrix} CH_3CHO \\ HCHO \\ CH_3OH \end{matrix} + \begin{Bmatrix} \text{Alcohols} \\ \text{Ketones} \\ \text{Glycols} \\ \text{Methylal} \\ \text{Other aldehydes} \\ \text{Organic acids} \end{Bmatrix} + \begin{Bmatrix} CO_2 \\ CO \\ N_2 \end{Bmatrix}$$

Material Requirement

Basis : 1 M.T. Acetaldehyde.

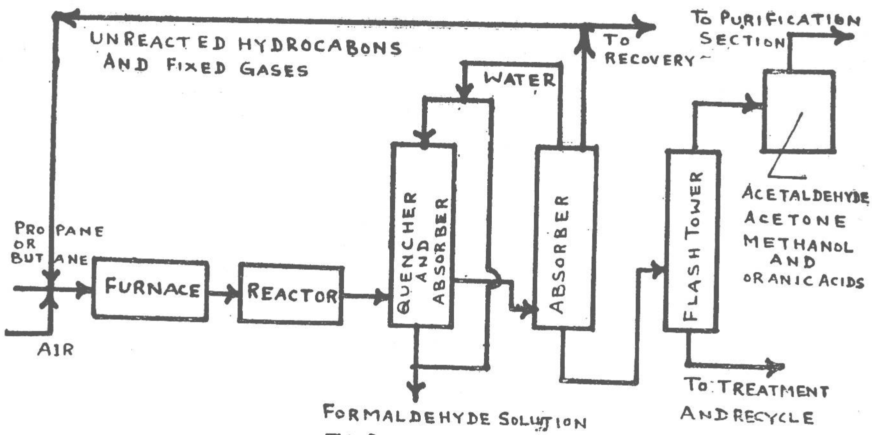
Formaldehyde	1110 kg.
Methanol	645 kg.
Mixed solvents	388 kg.
Acetone	130 kg.
Butane	5530 litres
Air	2530 m³

Process

Both propane and butane may be oxidized non-catalytically with oxygen or air to yield a complex mixture of simple organic compounds, which may be separated by fractionation. Butane and propane (1 part by volume) is mixed with 2 volumes of compressed air and 7 volumes of recycle gases (unreacted hydrocarbon, carbon monoxide, carbon dioxide, nitrogen) and delivered to a tube furnace at 100 psi, where mixture is heated to 375°C. The gases then pass to an empty steel tube, where hydrocarbon is oxidised. Because of the heat of the reaction, the temperature increases to 455°C. A section packed with ceramic shapes is located at the outlet side of the reactor to decompose peroxides. The hot reaction gases are quenched by a cold dilute aqueous fromaldehyde solution (12-14%) which is recirculated through the quencher scrubber. Part of the solution is drawn off and sent to recovery section of the plant. Fresh make up water is added continually to the recirculating solution. The scrubber is operated under such temperature and pressure conditions that other organics go overhead without absorption. This gaseous mixture is then absorbed by water in a second scrubber, which allows unreacted hydrocarbons of fixed gases to be vented. About 75% of this humidified stream is recycled through the furnace along with fresh hydrocarbons feed and air. The other 25% goes to a hydrocarbon recovery unit. The aqueous solution of oxygenated compounds leaving the bottom of the scrubber is fed to a flash tower, whence the chemicals go overhead to the purification section of the plant. The very dilute acidic bottoms are cooled, neutralized with caustic and recycled to the water absorber.

The purification section of the plant is a complex and highly specialised one, utilizing three phase distillation in conjunction with straight extraction. The chemical mixture entering the purification section contains about 40 components worth recovery.

When *n*-butane is the raw material, the chief product of the reaction are acetaldehyde (31 kg./100 kg. butane), formaldehyde (33 kg.) and methanol (20 kg.). Other major products are acetone (4 kg.) and mixed solvents (12 kg.) yields from propane are similar qualitatively, but isobutane yields acetone (2 kg./1 kg. isobutane) in greatest quantity. In addition to the specific products mentioned, recoverable amount of *n*-propyl alcohol, isobutyl and *n*-butyl alcohols, methyl ethyl ketone, and oxides of ethylene, propylene and butylene are present, one plant using the process separates formaldehyde, acetaldehyde, methanol, and acetone from the reactor effluent, and then hydrogenates the remaining mixture of aldehydes and olefins to alcohols and paraffins before further attempting recovery operations.



FLOW DIAGRAM OF ACETALDEHYDE FROM BUTANE BY VAPOUR PHASE OXIDATION

Process conditions can be varied considerably, so that by choice of raw material, reaction conditions, and recovery methods different ratios of the product components may be obtained. For instance, in one modification in which steam is used as a reaction-gas diluent, 100 kg. of butane yields 15.2 kg. of formaldehyde, 19.6 kg. acetaldehyde, 19 kg. of methanol, 7 kg. acetone, 1 kg. *l*-propanol, 0.5 kg. butanol, and 11.4 kg. mixed organic acids.

In another modification, air is added to the hydrocarbon steam in two stages. Improved yields of oxygenated compounds are said to result from this procedure.

Economic Aspects

The importance of acetaldehyde lies in its use as an intermediate in the manufacture of other organic chemicals, for example Acetic Acid, Acetic Anhydride, Pentaerythritol, Butanol, Chloral, 2-Ethylhexanol and Metaldehyde. Its natural manufacturers therefore are the producers of such chemicals or those manufacturing other chemicals from ethylene. Over 80% of the acetaldehyde made is used in the same plant in which it is produced.

Previously most of the acetaldehyde was produced by oxidation of dehydrogenation of ethanol. Over 80% is now produced by direct oxidation of ethylene. Acetaldehyde is also produced by oxidation of light hydrocarbons and as a byproduct of the vinyl acetate process. The acetylene method is now obsolete.

Acetic acid and acetic anhydride account for approximately 50% of acetaldehyde production, making these chemicals major outlets for acetaldehyde. Acetaldehyde consumption in the future will be effected by the use of alternative processes to produce acetic acid and acetic anhydride (the methanol carbon monoxide route or *via* hydrocarbon oxidation) and *n*-butanol and 2-ethylhexanol (from propylene by the oxo-process).

Acetaldehyde (CH_3CHO) *from Ethylene by direct oxidation*

Reaction

$$C_2H_4+\frac{1}{2}O_2 \xrightarrow[PdCl_2]{CuCl_2} CH_3CHO$$

(95% yield)

Material and Utility Requirements

Basis : 1 ton Acetaldehyde.

Ethylene	670 kg.
Oxygen	$290m^3$
Hydrochloric acid and catalyst	Small quantity
Cooling water	$300m^3$
Demineralized water	$3m^3$
Steam	1600 kg.
Electricity	210 kwh.

High purity ethylene (99.7%) and oxygen (99%), both under 100 psi are fed into the bottom of a vertical reactor containing a catalyst solution of undisclosed concentration.

The catalyst solution is essentially a water solution of cupric chloride ($CuCl_2$) and a small amount of palladium chloride ($PdCl_2$). The reactions taking place (at a pressure slightly above atmospheric) can be written :

$$C_2H_4+PdCl_2+H_2O \longrightarrow CH_3CHO+Pd+2HCl$$
$$Pd+2CuCl_2 \longrightarrow PdCl_2+2CuCl$$
$$2CuCl+\frac{1}{2}O_2+2HCl \longrightarrow 2CuCl_2+H_2O$$

During the reaction palladium chloride is reduced to elemental palladium. This palladium is oxidised to palladium chloride by cupric chloride. The cupric chloride thus formed is reoxidized to cupric state by oxygen fed to the system.