PART I

SYNTHESIS OF METHYL, ETHYL AND n-PROPYL VINYL ETHERS IN THE VAPOUR PHASE

SECTION I
I N T R O D U C T I O N

Chapter 1

Manufacture of Raw Materials.

Vinyl Ethers have come to occupy a very important position, amongst the various vinyl derivatives, which are now exploited industrially. Various methods for synthesis of alkyl vinyl ethers were known before 1930, but none was found to be commercially feasible. During the last world war when Germany was experiencing acute shortage of raw materials for plastic industries, extensive research programme was launched particularly by I.G.Farbenindustrie under the leadership of J.W.Reppe' to utilise acetylene, which was available in abundant quantities, as a raw material for the production of plastic monomers. This research led to the discovery of new and novel methods of the production of vinyl ethers by direct reaction of acetylene and alcohols under pressure.

The vinylation of alcohols, was conducted in batches in large autoclaves and the different alkyl vinyl ethers which were obtained found ready uses in various fields of adhesives, lacquers artificial resins, leather dressings, oil additives and organic intermediates for further synthesis.

Manufacture of Acetylene

The most important consideration for the manufacture of acetylene derivative is, cheap and abundant supply of acetylene gas. Manufacture of acetylene is therefore a logical fore-runner of the manufacture of vinyl derivatives on large scale.

There are three methods for the manufacture of acetylene, of which carbide process is best known and widely exploited. Calcium carbide is generated in large electrical furnaces by fusing together coke and lime stone, heat being supplied by means of an electric arc. Molten carbide is formed at very high temperatures, which is tapped and grannulated[1]. Carbide reacts with water producing acetylene and slaked lime which might be used again.

$$CaO + 3C \xrightarrow{2000^\circ C} CaC_2 + CO + 111 \text{ kg.-cal.}$$

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2 - 29.9 \text{ kg.-cal}$$

The main cost of this process is due to electric energy, other raw materials being cheap and of abundant supply. 10 to 11 units of electricity are consumed to produce 1 kg. of acetylene and 25-50 kgm electrode is used up for the manufacture of 1 ton of carbide. The advantage of this process is that, concentrated and relatively high purity acetylene is obtained. Traces of phosphine, and other gaseous impurities are removed easily by water scrubbing alone. Improved types of gas generators used at present, ensure complete decomposition of carbide and dry lime containing 6-7 per cent moisture is obtained as by-product[2].

The second method is the arc process, not so widely followed as the previous one, utilising waste hydrocarbon gases or natural gas. After removal of impurities, these by-product gases (mainly CH_4 and C_2H_6) are compressed to 0.4 atmospheres gauge and passed through an electric arc. The arc transforms 7000 kw energy into heat, producing a temperature of 3000°C. The gas coming out of the arc furnace, at a temperature of 1600-2000°C, is chilled with water spray. 4200 cu.m. of gas are produced per hour from each reactor, fed with 2800 cu.m. of Hydrocarbon gases. The main reactions that take place are shown below.

$$2\,CH_4 \longrightarrow C_2H_2 + 3\,H_2$$

$$CH_4 \longrightarrow C + 2\,H_2$$

The conversion to acetylene is 50 per cent per pass; about 50 per cent energy is lost in cooler. The compositions described in Reports are given overleaf.

TABLE - 1

	Coal Hydrogenation by-product gas.		Natural gas.	
	Feed	Product	Feed	Product
CO_2	0.2	0.0	0.3	0.0
C_2H_2	2.7	16.2	1.5	13.3
Olefins	3.2	3.6	1.4	0.9
O_2	0.2	0.2	0.3	0.2
CO	1.4	1.0	3.0	2.9
H_2	10.9	50.5	2.5	46.0
$CH_4 + C_2H_6$	74.5	25.1	80.2	27.8
N_2	6.9	3.4	10.8	8.9
	100.0	100.0	100.0	100.0

The exit gas contains 13-16 per cent acetylene, which again contains 10 percent diacetylene, methyl acetylene and other homologues. Diacetylene is a very objectionable impurity as it poisons acetaldehyde conversion catalyst. Hence, in modern processes, this dilute gas is first concentrated and purified by dissolving in water under 18-19 atmospheric pressure and then sent to acetaldehyde converters. Acetylene containing more than 12 per cent diacetylene is extremely dangerous and a little shock or spark is sufficient to start explosion. These impurities are separated by scrubbing with oil or by low temperature -- fractionation[3,4,5].

To produce 1 kgm of crude acetylene the power requirement is 8.9 kwh. However the subsequent purification and concentration processes consume a lot of power, the total requirement being 12.7 to 14.7 kwh per kgm of pure acetylene. The Arc process is a serious competitor to carbide process not only because of utilisation of by-product gases but also because it produces appreciable amounts of highly valued acetylene homologues.

Acetylene may also be prepared by Sachsse process from natural gas or methane by thermal cracking. Heat energy is supplied by partial combustion of methane itself[6,7].

$$2\ CH_4 \longrightarrow C_2H_2 + 3\ H_2 + 91\ \text{kg-cal.}$$

It has been found that the gaseous product consists of the following components :-

C_2H_2	...	8-9%
CO_2	...	3-4%
CO	...	24-26%
H_2	...	54-56%
CH_4	...	4-6%
O_2	...	0-0.4%

In actual operations, both oxygen and methane are pre-heated separately to 500°C, mixed and burned in a burner. Mixture ratio (800 m^3/hr CH_4 and 400 m^3/hr O_2) burner design,-

and rate of burning, are very critical[1]. Out-going gases at 1400°C are quenched to prevent further cracking. Conversion is 31 per cent per pass. The dilute acetylene obtained, was used directly for acetone synthesis[8]. Concentrated acetylene (70 percent) can however be produced by pressure water wash.

Another process known as Wulff process[9], a thermal method, has been developed in U.S.A. utilising natural & by-product gases. It differs from Sachsse process in its way of producing heat. A regenerative furnace, with carborundum tiles, is heated to 1200-1400°C by burning off-gases from the process (CO, H_2 etc.). A typical operating cycle is 65 seconds firing, 40 seconds cracking and 15 seconds purging. This process does not produce carbon black and employs low pressure steam to dilute the cracking stock. The energy cost of this process has been claimed to be lower than calcium carbide or electric arc processes.

<u>Total Acetylene Production for Chemical Industries</u>[10,11,12]
Metric tons

	Germany		England, U.S.A. & France
	1942	1943	1941-44
Carbide process	237,000	24,000 per month	300,000
Arc process and Sachsse process	58,000	3,000 per month	

Price of acetylene :

13 dollars - per 1000 cu.ft.

Production of acetylene in India uptil now has been negligible compared to the productions in other countries, the only source being imported carbide. Only recently, two factories have gone into production of carbide in a moderate scale. At present the consumption of acetylene is solely due to applications in welding and heating. With the expansion of heavy chemical industries during the 2nd five year plan period, production of acetylene is sure to rise.

It is also of interest to compare the various amounts of acetylene used up per month for the major chemical products, in Germany during the year, 1943-44 for which the data are available, as follows :-

Product			Monthly consumption in metric tons (1943)
Acetaldehyde		...	20,000
Acetone		...	485
Buna rubbers (Reppe' process)		-	1,760
Ethylene (by hydrogenation)		-	2,890
Vinyl Monomers	Vinyl chloride		1,080
	Vinyl acetate		480
	Vinyl ethers		150
Chlorinated products		...	850

Vinyl ether, which was a laboratory curiosity upto that period had just made its appearance and it is interesting to note that 5 tons/day of acetylene was consumed for production for different types of vinyl ethers alone.

Manufacture of Alcohols

The other raw materials consumed for ether production are various alcohols i.e. methanol, ethanol, propanol, butanol etc. Main processes for the manufacture of alcohols, shall be briefly surveyed.

Methanol, the first member of the series, used to be manufactured by wood distillation, which has completely been superceded by total synthesis. The alcohol fraction obtained from wood distillation, named wood - naptha, contained other impurities like acetone, acetic acid, and acetates which had to be carefully purified. Whereas methanol as obtained from synthesis gas is pure and anhydrous[9]; the reaction takes place under high pressure as follows :-

$$CO + 2 H_2 \longrightarrow CH_3 OH - 21.68 \text{ kg-cal}$$

The total world production[13] of methyl alcohol exceeded 138 million gallons in the year 1950-51. The production cost is also much less for the synthetic process. 4.8 million gallon of wood alcohol was produced in U.S.A. in 1941, at a cost 17 cents per gallon from wood distillation alone.

Present price fluctuates between 30-40 cents/gallons (1950) for synthetic product.

Ethyl alcohol is also produced synthetically though major quantity is still produced by fermentation process; the raw materials for fermentation are starchy materials, waste sugars, molasses or sugars obtained from wood hydrolysis; the cost per U.S.gallon was 50 cents in 1941. Synthol (Fischer Tropsch) or Ethylene hydration processes are also strong competitors of fermentation process and in future it might be superceded by cheaper synthetic processes[14,15,16]. Total production was 300 million gallons in U.S. in 1941 of which 210 million gallons from molasses.

Unfortunately the Indian production of ethyl alcohol is insignificant, compared to world production and leaves a great gap to be spanned. The phenomenal growth of sugar industry in the last two decades, has made available large quantities of molasses (a waste product of sugar industry) which is the basic material of fermentation in India. In round figures, 1.5 million tons of sugar produced per annum, (1950-52) make about 0.4 million tons of molasses available. Assuming an average rate of 57.7 gallons of alcohol obtainable per ton of molasses, this country is in a position to manufacture 25 million gallons of ethyl alcohol[17].

At present, however, only 9.36 million gallons (1950) of alcohol are being produced, the plants running at 30 per cent of their production level. The cost is very high compared to other countries but with incentives for higher production in the next 5 years plan and greater demand, the plants can go into full production with large reduction in alcohol price.

Present price of alcohol in India ... approx. Rs. 3/- per gal.

Present price of alcohol in U.S. ... approx. 1.05 dollars per gallon[17,18].

The following are the major fields of use of ethyl alcohol :-

i) Manufacture of ether, chloroform and ethyl chloride - for use as solvent and anaesthetic.

ii) Manufacture of ethyl acetate and acetone as solvent for synthetic paints.

iii) Manufacture of industrial thinners for varnishes and lacquers.

iv) Manufacture of base for plastic powders and monomers.

v) Manufacture of cosmetics and pharmaceuticals.

vi) Extraction of natural products

Propyl alcohol is manufactured synthetically by hydration of propylene and other processes[19,20]. Iso-propyl alcohol and ether are very important industrial commodities now produced in large quantities. Butyl alcohol together with acetone are mainly obtained by fermentation, in large vats. Amyl alcohols (isomeric mixture) are obtained from fractional distillation of fusel oil, a by-product of fermentation industry. Excepting fusel oil fractionation, manufacture of higher aliphatic alcohols has not started industrially in India