

CHAPTER - I

GENERAL INTRODUCTION

A. Introduction :

1,3 butadiene, $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$, a diolefine with conjugated double bond, is highly reactive and has a remarkable power of polymerization and condensation.

This monomer is the most important starting material for the manufacture of synthetic rubber. Thermal polymerization of butadiene was first carried out independently by both Lebedev¹ and Harris².

Synthetic rubber was first prepared commercially in Germany during World War I, when the British blockade cut off Germany from all tropical rubber growing countries. At this time dimethyl butadiene was polymerized to give "Methyl Rubber". The work on synthetic rubber manufacture and also butadiene production was continued even after the War. The sustained efforts of I.G.Farbenindustrie led to the large scale production of butadiene from acetylene (via acetaldo and 1,3 butylene glycol³) which eventually paved the way to the manufacture of various types of synthetic rubbers, the Bunas.

The second period of development of butadiene rubbers

started along with World War II. In Germany the production of Buna-S, the general purpose rubber, was greatly increased. In Germany in the same period, Dr. Walter Reppe, discovered an improved method of butadiene synthesis from acetylene (discussed later). Concurrently in the United States, a large synthetic rubber industry was developed. The general-purpose rubber was known as GR-S (Government Rubber Styrene) and was manufactured in largest volume.

From the very beginning of the synthetic rubber era, butadiene has been used as the chief raw material in this field. So much has been the importance of this monomer that at present the butadiene rubbers are classified in seventeen groups, almost all of which have got high demand in the market. Of the large number of butadiene rubbers, the Buna-S (polybutadiene), GR-S (butadiene+ Styrene), and Hycar or Buna N (butadiene + acrylonitrile) worth special mention for their manifold applications.

Table -- 1

Production and Consumption of Natural and Synthetic Rubber in U. S. A.

Year	P R O D U C T I O N				C O N S U M P T I O N					
	Natural	S y n t h e t i c		Natural	S y n t h e t i c		GR-S	N-Type		
		Neoprene	Butyl		Neoprene	Butyl				
1958	67,591	872,565	97,806	54,113	32,431	70,183	730,196	69,694	53,432	26,590
1959	72,502	1,134,379	124,815	82,704	43,588	71,745	886,275	84,955	65,454	34,368
1960	58,666	1,172,006	134,442	100,684	38,405	50,898	900,495	81,055	62,345	30,875
1961 upto Nov.	37,377	1,116,732	118,546	90,786	41,125	42,695	888,148	80,332	61,226	34,400

All quantities in long tons.

Reference : Rubber Age, March, 1962.

The Table 1 shows the production and consumption of natural and other types of synthetic rubber in America, the largest rubber producer as well as consumer.

Table - 2

Consumption of natural and synthetic rubber in
India.

Year	Consumption	
	Natural	Synthetic
1955	27,000	106
1956	29,000	2,400
1957	31,765	3,032
1958	34,756	3,253
1959	38,664	4,342
1960	45,218	6,457
1961	48,250	9,331

All quantities in long tons.

Reference : Rubber News (India), January, 1962.

Indian condition

In India, the rubber manufacturing industry started in 1920 and consolidated its position during 1935-39. The rubber industry in India is now well established since the Second World War. India is perhaps the only country in the world to-day where rubber industry is largely fed with indigeneous natural rubber.

Rubber plays an important part in the industrial expansion of a country. Considering the rapid pace with which India is progressing to-wards industrialization, it has been estimated that by 1975, the rubber consumption may go upto 80,000 tons/year. The Government of India has sanctioned a scheme of replanting 70,000 acres of land with high yielding rubber plant species and also bringing more land under rubber plantation. On the completion of scheme, it is expected that in 1975, the total natural rubber production will reach 52,000 tons.

India was hardly using any synthetic rubbers a decade back. The consumption of synthetic rubber at present is 16% of the total rubber consumption, butadiene-styrene being the most popular. The other types of synthetic rubber e.g. neoprenes and acrylonitrile are also consumed to a small extent. In view of the importance of butadiene for the growth of synthetic rubber industry, butadiene plant having an annual production capacity of 30,000 tons has been erected at Bareilly, U.P. which will start functioning from 1963. Another plant of 20,000 tons a year capacity will be constructed in

Assam during the Third Five Year Plan period which will put our country amongst the leading synthetic rubber producing countries.

The economic and efficient production of butadiene is by far the most important step to successful implementation of Indian Synthetic Rubber programme. A number of processes are at present employed for production of butadiene on a commercial scale : Pyrolysis of hydrocarbons, for example, in the steam cracking process for producing ethylene ; catalytic dehydrogenation of butene and butane fractions of petroleum refinery gases ; syntheses based on acetylene as a feed stock ; dehydrogenation and dehydration of ethanol. These processes have recently been reviewed by Appleton⁴ and Bennett⁵. The economic utilization of the first and second sources presumes the necessity of a thriving petroleum industry and hence, the countries enjoying an abundant supply of natural petroleum can exploit the first two methods. Production of butadiene from acetylene either by the three-stage or four-stage process involves complicated operations.

Though the petroleum industry is gradually developing in this country, still one cannot be absolutely sure about its future since the reserve of the raw petroleum in this country is yet to be assessed. Hence the use of ethanol (whose supply is fairly assured) as a starting material for butadiene is all but natural. The methods for the production of butadiene from ethanol and also their relative usefulness will be discussed later on.

Other uses of butadiene :

Recently butadiene 1, 3 has found important uses in the preparation of the following industrial commodities over and above the synthetic rubber :-

- (i) Fire resistant plastics and resins⁶.
- (ii) Non-inflamable lubricating and transformer oils⁷.
- (iii) Additives in drying oils⁸.
- (iv) Metal wood, rubber glass or rubber-metal adhesives⁸.

B. Different Methods for the Production of Butadiene :

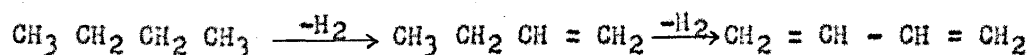
Butadiene was first prepared by Berthelot⁹ in 1867, by passing a mixture of acetylene and ethylene through a red hot iron tube. Since then various methods have been used to produce butadiene 1,3 from various types of organic compounds, almost all of them being of academic interest. The processes which have been exploited in commercial scale are but few and they have been recently reviewed by Appleton⁴ and Bennett⁵. The methods can be broadly classified as follows, depending on the starting material used :

- (i) Hydrocarbons of paraffin and monoolefine groups ;
(e.g. butene-butane fraction from petroleum refinery gases).
- (ii) Syntheses based on acetylene as feed stock.
- (iii) Dehydrogenation and dehydration of ethanol.

(i) Hydrocarbons of paraffin and monoolefine groups :-

A wide variety of diolefines can be produced from petroleum hydrocarbons by pyrolytic or chemical transformations. In the United States of America and in Russia, the petroleum hydrocarbons have been fully utilized for the commercial production of butadiene, since those countries abound in mineral oil supply. The refining and cracking of petroleum oil result in the production of saturated and unsaturated hydrocarbons ; of these, the cut from C₄ and C₆ is subjected to dehydrogenation, either in one-step or in two-steps to obtain butadiene.

n-Butane is one of the hydrocarbons found in the cut, which on stage wise or straight dehydrogenation, yields butadiene according to following equation :-



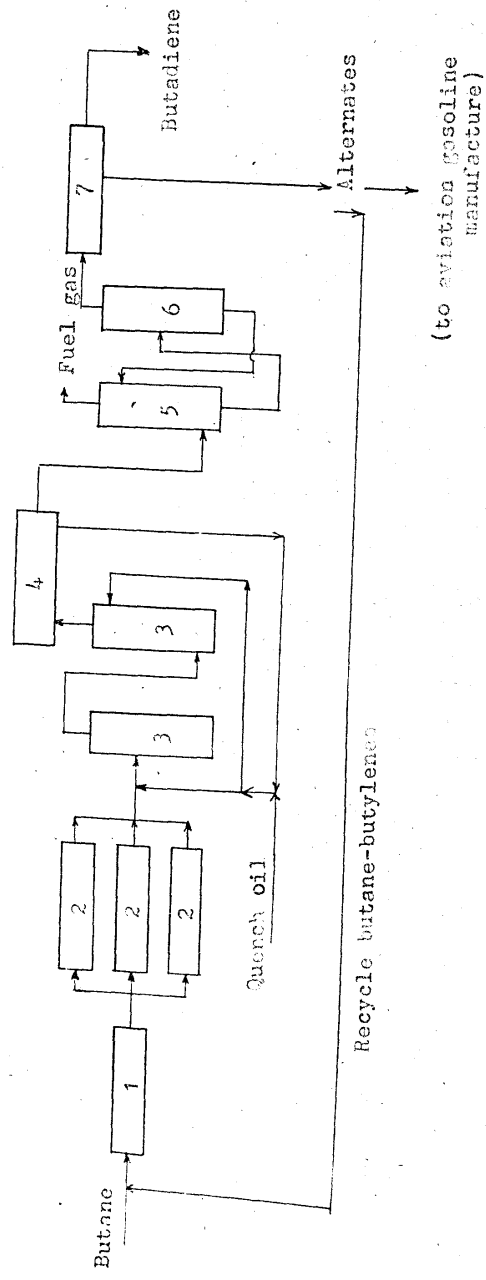
n-Butane

Butene - 1

Butadiene 1,3

A general review on n-butane dehydrogenation has been presented by Watson and coworkers¹⁰ in 1944.

Numerous publications and patents, are available in this field, which deal with the nature of the catalysts as well as their regeneration and also discusses the effect of different operational variables on this conversion. The same process can be employed with



- 1 - Preheater
- 2 - Reactor
- 3 - Quench tower
- 4 - Knock out drum
- 5 - Absorber
- 6 - Stripper
- 7 - Extraction system

FIGURE 1 - FLOW SHEET FOR THE PRODUCTION OF BUTADIENE FROM DEHYDROGENATION OF BUTANE.

slight modification when butane-butene mixture is used instead of butene alone.

The catalysts include the alloys and the oxides of chromium, molybdenum, tungsten, etc. supported on silica, kieselguhr, alumina, magnesia or clays like bentonite¹¹.

Crude butadiene is purified by absorption with cuprous salt solution or by extractive distillation with furfural.

A flow sheet of the process is given in Figure 1.

Catalytic dehydrogenation of cyclohexane is considered to be a simple route to butadiene when a small quantity of pure butadiene is needed¹².

(ii) Syntheses based on acetylene as feed stock :-

There are two industrial methods for the production of butadiene from acetylene :

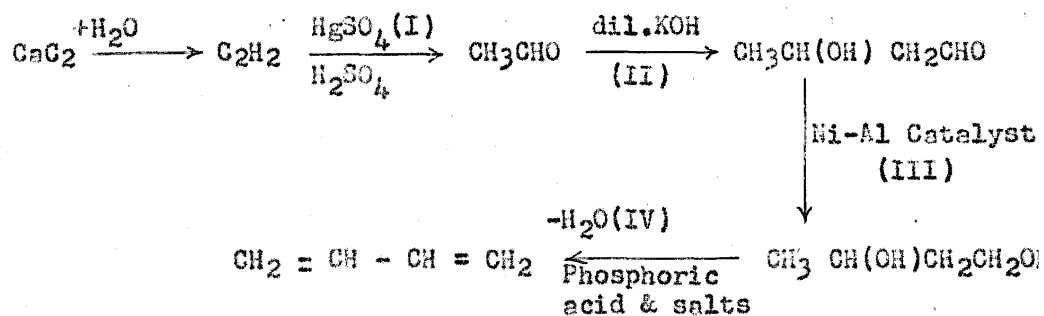
- (1) Butadiene by Aldol process.
- (2) Butadiene by Reppe process.

(1) Butadiene by Aldol process :

The aldol or "four step" process^{13,14,8} was the favoured method of producing butadiene in Germany before and during World War II. Acetylene produced from calcium carbide has been an important source of butadiene in countries where coke and lime are

available in plenty.

The reaction steps of the four-stage process is as follows :



The method of purification of butadiene is same as described before.

(2) Butadiene by Reppe's Process : (3 Stage process)

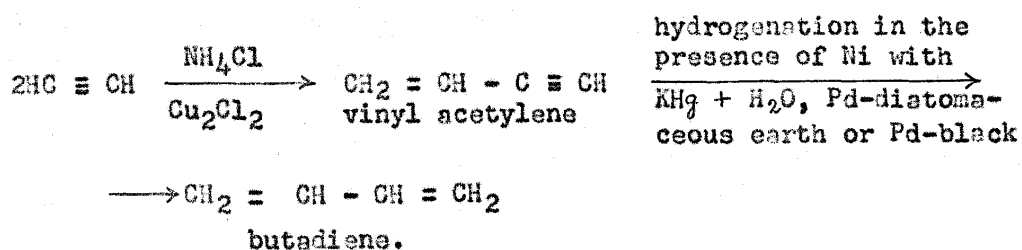
Another process for preparing butadiene from acetylene was developed by Reppe^{3,15} in Germany in the period just before and early in World War II. Acetylene and formaldehyde, in the presence of copper acetylide, react to form 2-butyne 1,4, diol ; the latter is reduced catalytically with hydrogen to 1,4-butane-diol, and the diol is dehydrated catalytically to yield butadiene. In the dehydration tetrahydrofuran is usually an intermediate. The yields are high and so is the purity.

This three stage process was followed by I. G. Farben industrie during the World War II.

Besides the above processes, two other reaction schemes can as well be followed for the production of butadiene :

Butadiene can also be prepared from acetylene through diacetylene ($\text{HC} \equiv \text{C} - \text{C} \equiv \text{H}$) as the intermediate. Diacetylene can be obtained by passing acetylene into an ammoniacal cuprous chloride solution. Diacetylene thus formed was converted to butadiene¹⁶.

The other scheme is that acetylene can be dimerized to vinyl acetylene¹⁷ which is then selectively hydrogenated to butadiene^{18, 19, 20}.



(iii) Dehydrogenation and dehydration of ethanol :

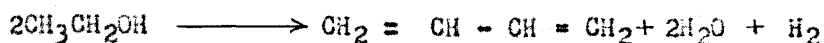
The first significant report regarding the preparation of butadiene from ethanol as raw material was made in 1915 by Ostromislensky²¹.

There are two commercial methods for the conversion of ethanol to butadiene :

- (a) One-step process
- (b) Two-step process

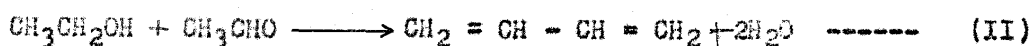
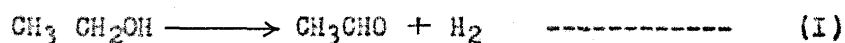
The one-step process, followed in Russia²², aims at the conversion of ethanol to butadiene by passing ethanol vapours over

a suitable catalyst at higher temperatures



A study of ^{the} equation indicates that the catalysts for this conversion should have both dehydrogenating and dehydrating capacity. This process is also known as Lebedev process.

The two-step process or Ostromislensky's process, followed in the U.S.A., involves in the following reactions, carried out in two separate catalytic units :



In the two-step process, ethanol and acetaldehyde are fed over a dehydrating type of catalyst to produce butadiene, the acetaldehyde being supplied by dehydrogenation of ethanol.

While discussing the relative merits of these two processes it must be mentioned that the one-step process is evidently simpler in operation and technology, a factor of considerable importance, though the purity and yield of butadiene are less. It requires, however, the selection of dual function catalysts which will effect a compromise between the two different types of reaction under the same operating conditions. In contrast it is claimed^{23, 24, 25} that the two-stage process gives higher conversion and ensures purer product.

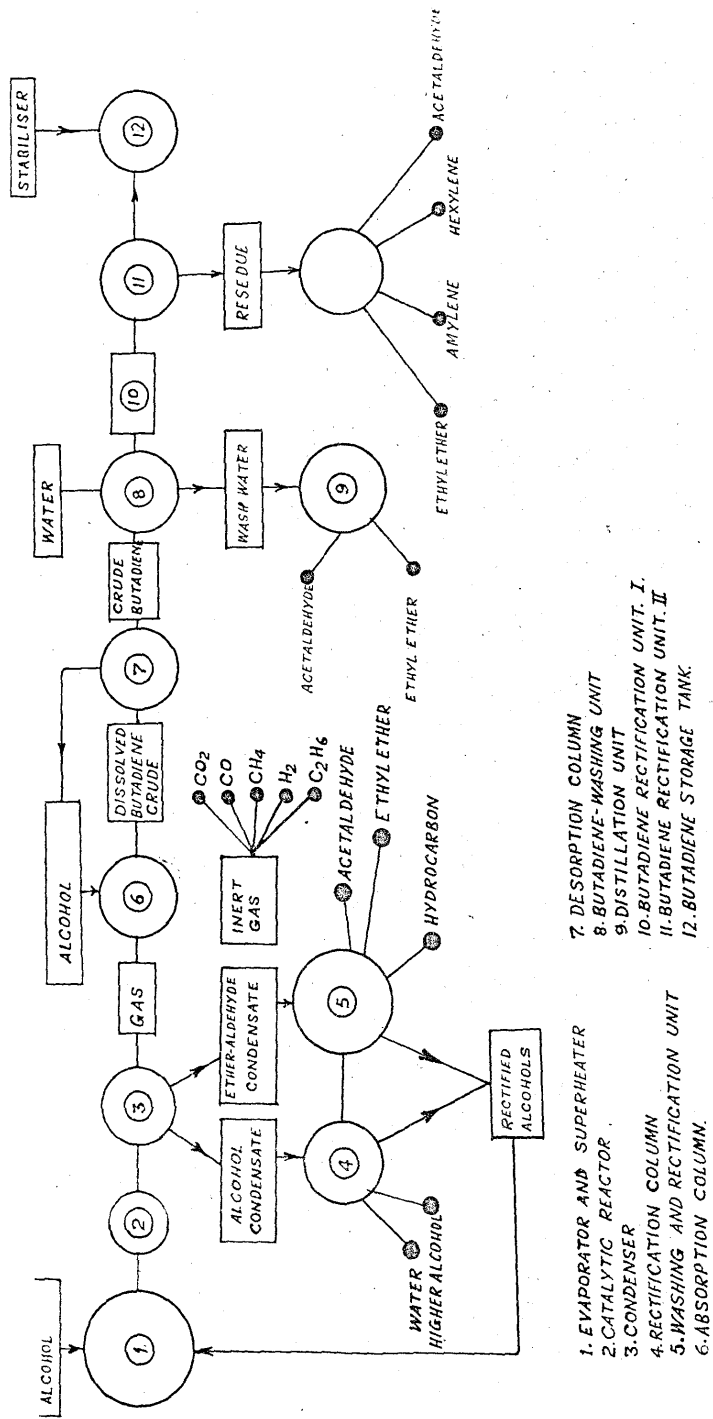


FIGURE-2. MANUFACTURE OF BUTADIENE FROM ALCOHOL (ONE-STEP PROCESS)

(a) One-step process :

A flow sheet of the one-step process is presented in Figure 2. Stagewise separation of the by-products is also indicated in the flow sheet²².

In this process, preheated ethanol vapour is passed through the reactor containing a catalyst suitable for simultaneous dehydrogenation and dehydration. The effluent gas is led through a two stage condenser. From the condensate, unconverted ethanol is recovered, purified and returned to the catalytic reactor.

Butadiene along with a number of C₄ hydrocarbons (containing butene-2 also) is extracted from the uncondensed gas by ethanol. The unabsorbed gas consists of hydrogen and ethylene.

The absorbed vapors are desorbed from ethanol by heating in stages when butene-2 (with some butadiene) comes out at 30-35°C and the major portion is expelled at 100-130°C. The final desorption takes place at 140-150°C for 15-30 minutes.

Crude butadiene is then washed with water to remove the major portions of acetaldehyde and ether. It is then cooled to -20°C by cold brine solution. The crude butadiene contains only 82% of fractions boiling below 4°C. This fraction contains butene-2 also.

This mixture is rectified in a coke packed column, generally

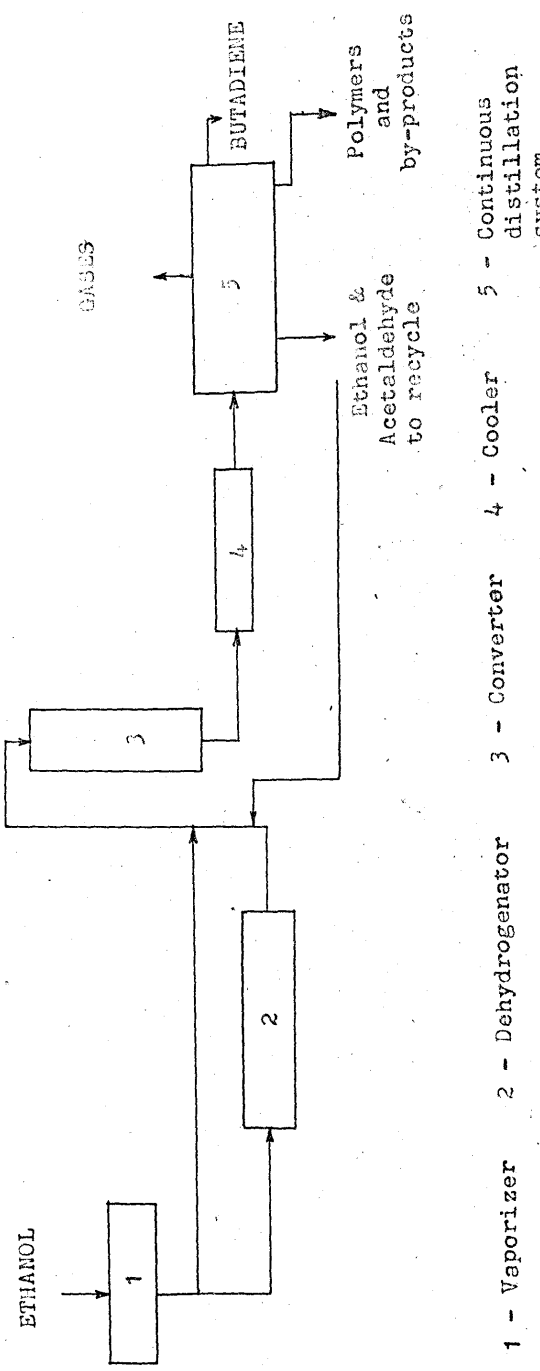
operated at atmospheric pressure. To remove last traces of acetaldehyde the effluent gases from the partial condenser is washed with 50% alkali solution and then subjected to final rectification. The final rectification is carried at -20° to $+2^{\circ}\text{C}$. Brine solution is used as coolant. Permanent gases, dissolved in butadiene, are separated in the rectification unit and perged to the atmosphere continually.

The rectified butadiene of polymerization grade is stored in spherical steel vessels at moderately low temperature (32°F) and slight pressure (3 psig). Polymerization during storage may be prevented by adding small quantities of stablizers (less than 1%) like, hydroquinone, tricresol, amines, etc. These inhibitors may be washed away from butadiene before actual polymer preparation, by simply washing with dilute hydrochloric acid or water.

(b) Two-step process :

This process was commercially utilized in America by the Carbide and Carbon Chemicals in 1941, when a butadiene plant of 20,000 tons per year capacity was erected²³. Three other commercial plants were also operated at 200% of rated capacity to meet the early emergency requirements for synthetic rubber²⁴. A flow sheet of the process followed by the Carbide and Carbon Chemicals is shown in Figure 3.

The dehydrogenation of ethanol is an old established



1 - Vaporizer 2 - Denhydrogenator 3 - Converter 4 - Cooler 5 - Continuous distillation system

FIGURE 3 : TWO-STEP PROCESS FOR THE PRODUCTION OF BUTADIENE FROM ETHANOL

process which can be conducted with good chemical efficiency under suitable conditions²⁶. The catalyst is copper on inert support, promoted with few percent of chromium oxide. In a temperature range of 250° - 300°C, single pass yields of 30 to 40 percent of acetaldehyde from ethanol can be obtained with a chemical efficiency of 92 percent or higher.

A mixture of ethanol and acetaldehyde vapours was then passed through a converter at a temperature of 360° - 375°C. The preferred molar ratio of ethanol to acetaldehyde in the feed mixture is 3 to 1. Tantalum-silica catalyst^{8,15} containing 2% tantalum pentoxide is reported to be a very good catalyst.

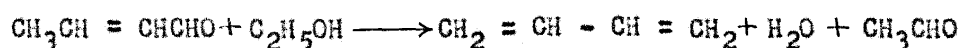
The converters are large heat exchangers fitted with 3" tubes of 20 ft. long. For heating and cooling the butadiene converters, a circulating, liquid Dowtherm system is generally selected.

The product from butadiene converter is then condensed partially, to make a rough separation between butadiene, butylenes and other fixed gases and the easily condensable mixture of ethanol, acetaldehyde etc. The uncondensed gases are then scrubbed. The scrubbing liquid from the butadiene removal scrubber is combined with butadiene condensate and delivered to a continuous distillation column. Ethanol, acetaldehyde etc. are recovered here as the high boiling fraction and fed back to the converter. The distillate is then passed into an absorption unit for removal of 4 carbon impurities and fixed gases, 'Chlorex' ($\beta\beta'$ dichloroethyl ether) being the

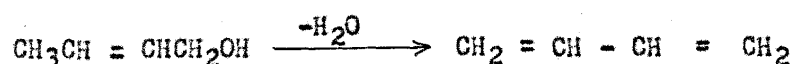
selective solvent. Butadiene is then finally purified by distillation.

Miscellaneous methods :

The methods for preparing conjugated diolefine hydrocarbons are numerous. A few oxygenated organic compounds, other than ethanol, have also been utilized as the possible sources of butadiene. The most important among these is crotonaldehyde, an intermediate of the two previously described processes for the conversion of ethanol to butadiene. Crotonaldehyde on reacting with ethanol²⁵ gives butadiene as follows :



Crotonyl alcohol²⁷ gives butadiene on dehydration with catalysts like Al_2O_3 , SiO_2 , MgSO_4 etc.



Butadiene has also been obtained during the pyrolysis of ethyl vinyl ether³.

n-Butanol and n-butane produce butadiene via n-butyl chloride by heating the latter with concentrated hydrochloric acid and anhydrous zinc chloride²⁸. Cyclobutanol vapour when passed over Al_2O_3 at 300-350°C yields 93 percent of butadiene²⁹.

According to Leyer³⁰, vinyl chloride, vinyl sulphide or

vinyl oxide when heated at 100-400°C in contact with heavy metals produce butadiene.

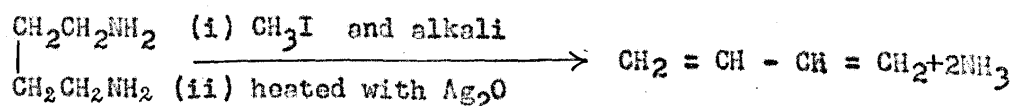
Direct thermal decomposition^{of} dichlorobutane with steam, and with or without catalysts, at temperatures of 450-700°C, produces butadiene^{31,32,33}.

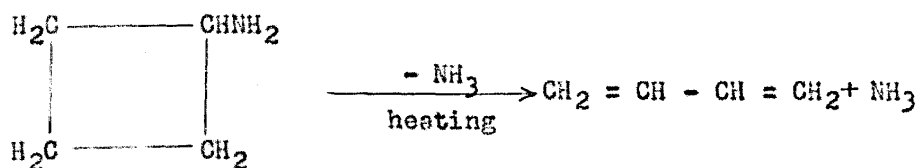
The Badische Fabrik³⁴ produced butadiene by heating the vapours of 2,3 dibromobutane at 340°-360°C in presence of barium chloride or lime.

A recent U.S. Patent³⁵ claims that the oxygenated products from Fischer-Tropsch reactor, when passed over a suitable catalyst like MgO-SiO₂ at 420°C, yields butadiene. In another patent³⁶ it has been claimed that petroleum fractions as well as ethanol can be converted to butadiene when energized by repeated exposure of electron beam at 50°-180°C, metallic oxides being used as the contact agent.

Some Japanese workers³⁷ reported that the shale oil distillate vapours when passed over heated nickel wire at 500-800°C gave 20% of butadiene.

Tetramethylene diamine³⁸ and aminocyclobutane³⁹, under suitable conditions give butadiene as follows :





4-methyl 1,3 dioxane⁴⁰, prepared by acid condensation of C_3H_6 with CH_2O (3-5% of H_2SO_4 , 105-150°C at 35-45 atm.), can be converted to butadiene by passing over calcium and other phosphates, yield being 75%.

Butadiene to ^{the} extent of 25% was obtained when technical hexanetriol⁴¹ was led over dehydrating catalyst Al_2O_3 or Boron phosphate at 300-500°C.

But these methods are not yet developed so as to be utilized industrially.

C. Scope of the Present Work :

The one-step process for the catalytic conversion of ethanol to butadiene has long been a commercial success in the East European countries ; but the operational details and especially the nature and composition of the catalyst used have been carefully guarded by patents. Corson, Jones, Welling, Hinckley and Stahly²⁴ in course of their investigation on the two-step process evinced some interest for the single stage process also. But due to war time emergency, their effort in this field could not be very systematic. Recently Bhattacharyya and Ganguly⁴²⁻⁴⁴ have made an exhaustive and valuable study on the one-step catalytic conversion of ethanol to

butadiene in the fixed bed. While mainly concerned with the fixed bed operation, they tried a few experiments in fluidized catalyst bed⁴⁵ and met with phenomenal success.

Considering the intrinsic characteristics of the fluidized bed in so far as the heat and mass transfer is concerned, one may logically anticipate that the endothermic reactions involved in both the processes might be more efficiently carried out under isothermal conditions in a fluidized catalyst bed having uniform temperature distribution throughout. These reactions have quite high values of equilibrium constant at the desired temperature range and hence the phenomenon of back mixing or diffusion, inherently associated with fluidization operation, will not hinder the desired reaction to any appreciable extent.

In view of the above considerations the present author has made an extensive investigation on the catalytic conversion of ethanol to butadiene in the fluidized catalyst bed, both by the one-step and two-step methods. The catalytic activity of various oxide systems (single or binary) which were reported to be promising by the previous workers, has been tested for in a fluidized catalytic reactor under a wide range of operating conditions. The influence of temperature, liquid feed rate, catalyst bed height etc. on the process conversion of ethanol to butadiene was studied. The effect of addition of water to ethanol was also studied in the former case ;

and for the two-step conversion, the effect of the feed composition (i.e. the mole ratio of ethanol to acetaldehyde) on the yield of butadiene has been thoroughly studied. For the smooth operation of a fluid bed reactor, a thorough idea regarding the fluidization characteristics of the solid used is all but essential. Hence, in the present investigation porosity, shape factor, minimum voidage etc. of the most active catalyst system have been determined by the conventional method suggested by Max Leva et. al.⁴⁶

The author, with the idea of forwarding and establishing his own views, has taken the liberty to use the pertinent results and observations reported by different workers in this field.