

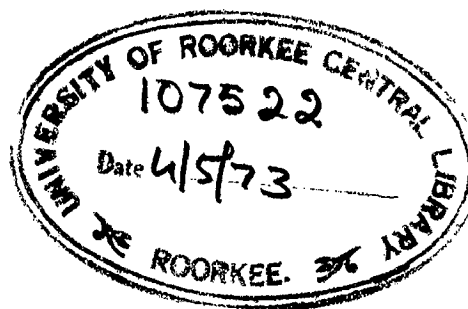
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DEVELOPMENT OF IMPROVED CATALYST FOR CATALYSIS OF ETHYLALCOHOL-ACETALDEHYDE TO BUTADIENE

A Dissertation
submitted in partial fulfilment
of the requirements for the award of the degree
of
MASTER OF ENGINEERING
in
PLANT AND EQUIPMENT DESIGN

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DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF ROORKEE
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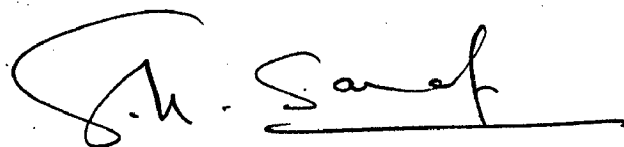
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CERTIFICATE

Certified that the dissertation entitled "DEVELOPMENT OF IMPROVED CATALYST FOR CATALYSIS OF ETHYLALCOHOL-ACETALDEHYDE TO BUTADIENE" which is being submitted by Shri Mahesh Chandra S/O Shri Radhey Lal in partial fulfilment for the award of Degree of Master of Engineering in Chemical Engineering (Plant and Equipment Design) of the University of Roorkee, Roorkee, is a record of his own work carried out by him under my supervision and guidance. The matter embodied in this dissertation has not been submitted for award of any degree or diploma.

This is further to certify that he has worked for a period eight months from January 1972 to August 1972 for preparing his dissertation at this University.



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CHAPTER II N T R O D U C T I O N

Rubber consumption is an index of industrial growth of a nation. Rapid industrialization during the last decade resulted in an increased demand of rubber products in our country. Natural rubber resources are too meager to meet the total demand. In 1970-71 the production of natural rubber was nearly 92,200 tons while the total consumption was 1,34,000 tons⁽¹⁸⁾. It is estimated that total requirement of rubber by the end of Fourth Five Year Plan will be approximately 2,38,000 tons while the production of natural rubber is expected to be only 1,20,000 tons.

In order to close the widening gap between production of natural rubber and the total demand for rubber products as well as to conserve available land resources for production of food and other cash crops, the Synthetics and Chemicals Ltd. have built and commissioned in 1963 at Bareilly a synthetic rubber plant to produce 30,000 tons of styrene-butadiene rubber per year using alcohol as raw material. This plant is unique of its kind in the world as it combines at one place facilities for large scale production of butadiene and styrene, the two important raw materials needed for the production of styrene-butadiene rubber.

When this project was in planning stage the availability of petroleum hydrocarbons as industrial feed-stocks was very much restricted while alcohol was abundantly available at low price as a by-product from sugar industry in U.P. and Bihar. Simplicity of alcohol based process also promised a better economy. *other processes*

Butadiene plant of Synthetics and Chemicals Ltd. when operated at full capacity consumes nearly 66,000 gallons of alcohol to produce 80 tons of butadiene per day. In addition, National Organic Chemical Industries Ltd., Thana is currently supplying nearly 7000 tons per year of by-product butadiene obtained during naptha cracking. Availability of alcohol in recent years has become a serious problem and the plant is trying to conserve as much alcohol as possible by process improvements to give better ultimate ethyl alcohol selectivity to butadiene.

In commercial operation tantalum oxide on silica gel (2 percent Ta_2O_5 -98 percent SiO_2) is used for catalysis of ethyl alcohol-acetaldehyde to butadiene. Normal plant operation gives 28 to 30 percent conversion with an ultimate yield in this step of 70 percent. The ultimate selectivity from ethanol reduces to nearly 65 percent since the efficiency of ethyl alcohol conversion to acetaldehyde is only 92 percent. Thus a significant fraction of total alcohol consumed in the plant is converted to undesirable by-products.

The purpose of this dissertation is to develop a catalyst which can be a suitable substitute to the imported tantala-silica catalyst. In addition, work is also carried out to develop a promoted tantala-silica catalyst based on imported commercial catalyst which can give a better performance both in conversion and ultimate yield. Shortage of alcohol in India may necessitate its import and, therefore, a slight improvement in the ultimate yield in catalysis ethylalcohol-acetaldehyde to butadiene by using a suitable promoted tantala-silica catalyst has a special significance.

This work is mainly devoted to promote imported tantala-silica catalyst with cupric oxide or zirconium oxide as promoter. Some tantalum oxide-silica gel catalysts are also prepared and tested using indigenous silica gel.

The line of action pursued to develop promoted catalyst has shown promise and few more test runs are needed to arrive at final conclusions regarding the effectiveness of cupric oxide or zirconium oxide as promoters for tantala-silica catalyst and the optimum promoter compositions. The indigenously prepared tantalum oxide-silica catalyst has also shown good results and some more development work is necessary for commercial adaptation.

CHAPTER II

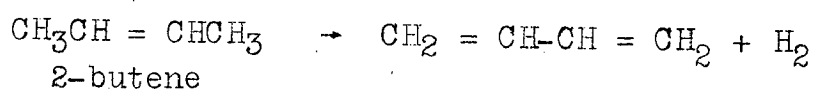
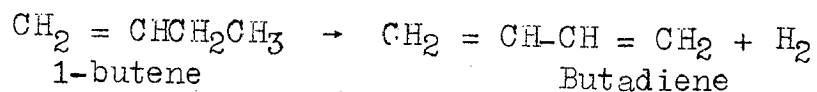
LITERATURE REVIEW

Butadiene does not occur as such in nature. It is, however, present in varying quantities in the products obtained from high temperature petroleum processes.

2.1 Methods of Manufacture

Some of the important methods reported in literature for the manufacture of butadiene are given below:

2.1.1 Catalytic Dehydrogenation of Butenes - The process involves the catalytic dehydrogenation of 1-butene and 2-butene at 630-700°C and at low butene partial pressure. The reaction proceeds quite readily and selectively



The catalyst used for the reaction is calcium nickle phosphate stabilized with 2 percent chromium oxide.

2.1.2 Dehydrogenation of n-Butane - Two processes for producing butadiene from n-butane are in commercial operation

(i) Houdry process - 95 percent or better n-C₄ feed stock is dehydrogenated at 620°C in one step to a mixture of butenes and butadiene. The butadiene is separated and unreacted butane together with butene is mixed with fresh feed and recycled. Activated alumina impregnated with 18-20 percent chromic oxide is used as catalyst.

(ii) Phillips Process - This process consists of two steps:

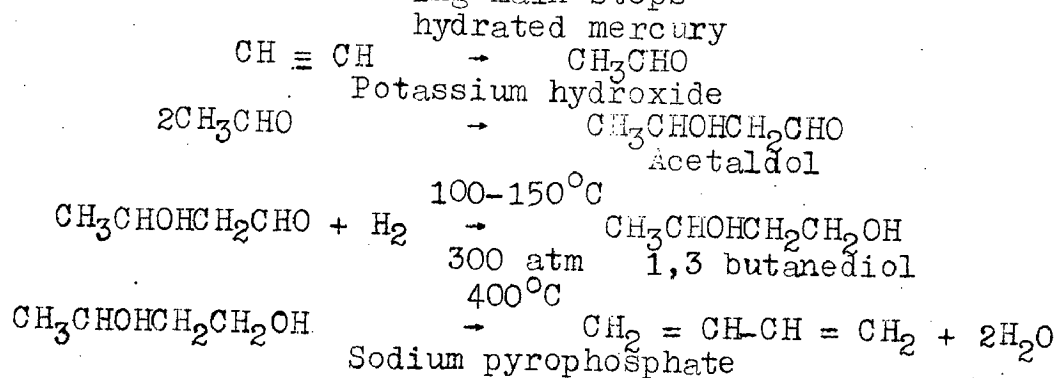
- (i) Dehydrogenation of n-butane to butene
- (ii) Dehydrogenation of mixed butenes to butadiene.

The butane dehydrogenation is carried out isothermally at 600-620°C., 1-20 psig and at a space velocity of about 700 using alumina-chromiona catalyst. The second step in this process is essentially same as described earlier.

2.1.3 Thermal Cracking of Petroleum Distillates - The preferred feed stock for thermal cracking operation range from naphtha with an end point of 200-230°C to light gas oil with an end point of 430°C.

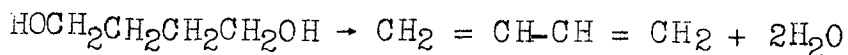
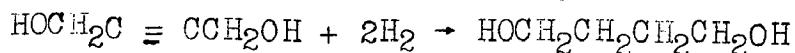
For optimum yield of butadiene and other light olefins and diolefins the cracking reaction has to be carried out at temperatures above 725°C with short residence time keeping hydrocarbon partial pressure very low to avoid undesirable side reactions.

2.1.4 Aldol Condensation Process - The process uses acetylene and involves following main steps

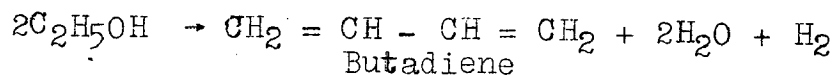


2.1.5 Process Using Acetylene and Formaldehyde -

Acetylene and formaldehyde is reacted to give 2-butyne -1,4 diol over copper acetylide catalyst, which is then hydrogenated to 1,4 - butanediol and subsequently dehydrated to butadiene. The overall yield based on acetylene consumption is 70 percent.



2.1.6 Process Using Ethyl Alcohol - There are two methods for the conversion of ethanol to butadiene: One step process and two step process. In one step process the dehydrogenation and dehydration reactions occur in same reactor and the overall reaction can be written as



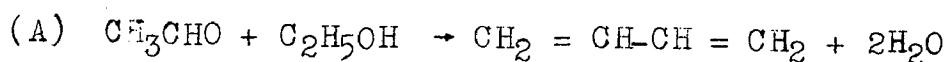
Yield and selectivity of one step process are poor as compared to two step process where dehydrogenation and dehydration are carried out separately with different catalyst. Ethanol (92-95 percent grade) is vaporized and passed over a dehydrogenation catalyst at 260-290°C to produce acetaldehyde. Acetaldehyde yield is 90-94 percent with 30-50 percent conversion per pass. In second step excess alcohol is mixed with acetaldehyde in molar ratio of 3:1 and fed as liquid to a fixed bed convertor containing tantala-silica catalyst. Pressure is essentially atmospheric, the temperature is 325-350°C and the liquid hourly space velocity is 0.4 to 0.6. A conversion of 28-30 percent based on acetaldehyde is obtained per pass with ultimate selectivity in this step of 75 percent.

2.2 Reaction Mechanism of Two step Process from Alcohol:

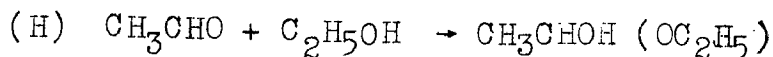
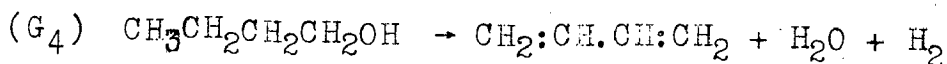
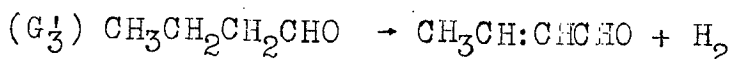
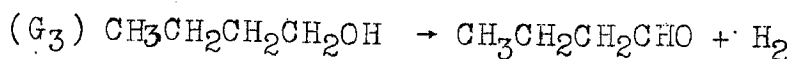
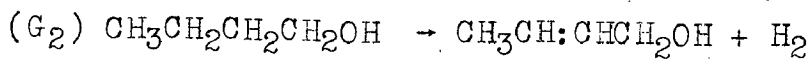
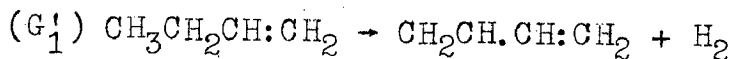
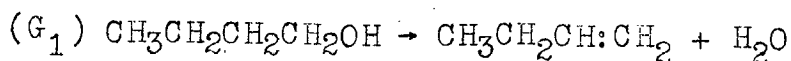
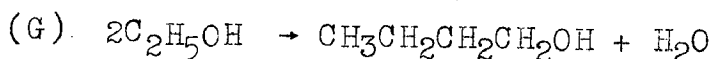
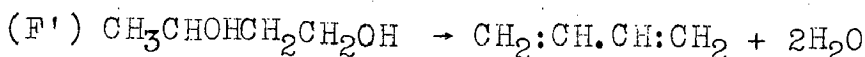
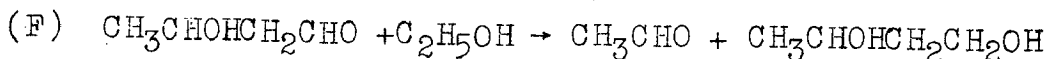
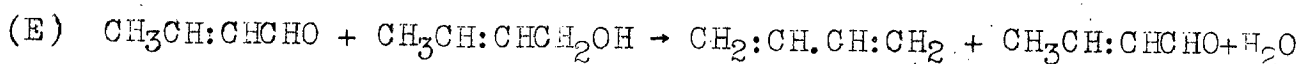
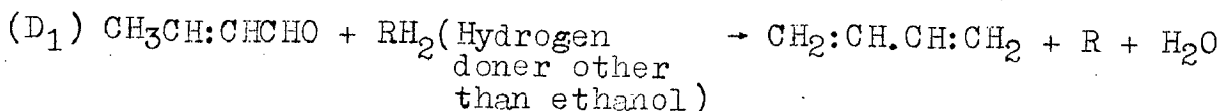
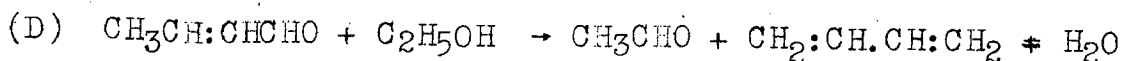
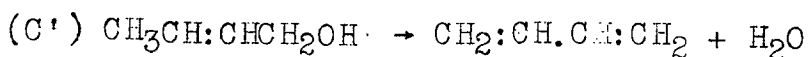
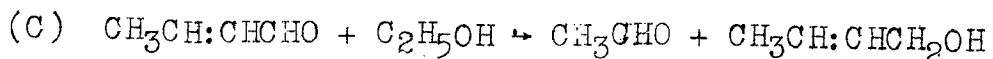
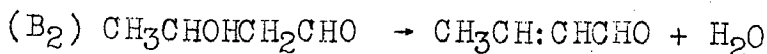
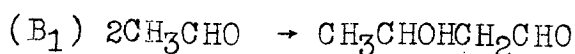
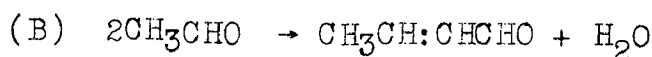
2.2.1 Main Reaction - Many hypothetical reaction mechanism are suggested for the formation of butadiene. Reaction mechanism involving the formation and deoxygenation of crotonaldehyde (reactions B, B₁, B₂, D) suggested by Jones and Cowrkers⁽⁴⁾

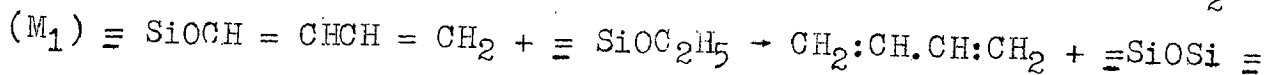
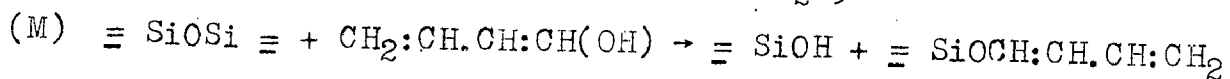
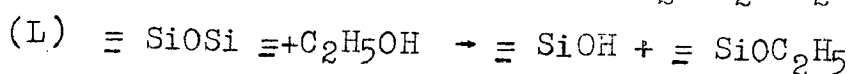
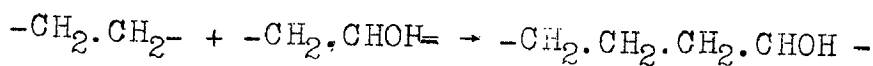
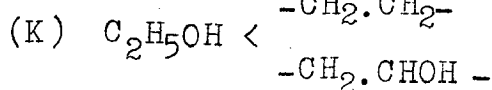
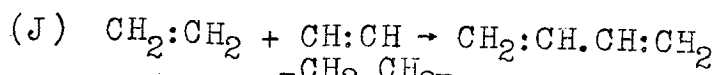
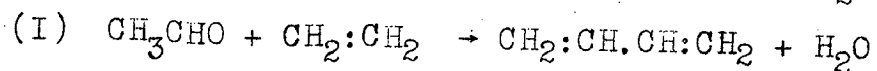
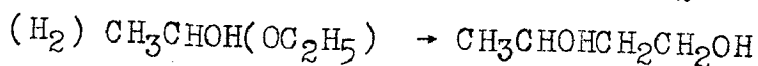
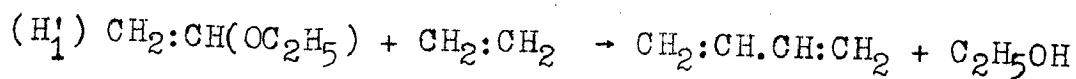
and Quattlebaum and Coworkers⁽¹⁾ based on their study of two step process.

The overall reaction is



and the probable reactions leading to the formation of butadiene are:





The bilateral mechanism (K) has little supporting evidence while for this mechanism Lebedev and Coworkers (as reported in Jones et al⁽⁴⁾) suggested that $-\text{CH}_2-\text{CH}_2-$ and $-\text{CH}_2-\text{CHOH}-$ radicals are first formed and then these combines to give butadiene. According to Quattlebaum et al⁽¹⁾, it would lead one to predict larger quantities of ethylene and butylene than actually formed and ignores acetaldehyde, which is a normal dehydrogenation product of ethanol.

n-Butanol (Reaction G) does not produce butadiene under process conditions as reported by Jones et al (4) and this eliminates the possibility of n-butaraldehyde as reaction intermediate. Furthermore, vinyl ether-ethylene feed gives negligible butadiene yield, thus reaction H can be omitted. It has also been observed that when acetaldehyde-ethylene and acetaldehyde-acetylene are used as feed mixtures (reaction I), it resulted in negligible butadiene yield and therefore reaction mechanism I can also be rejected.

Ethanol-butaraldehyde feed mixture resulted in butadiene but it is suspected that butadiene was formed from acetaldehyde obtained as a result of reaction of butaraldehyde with ethanol and not directly from butaraldehyde. 1,3-Butanediol, proposed by Ostromislensky (reported in Jones et al⁴) as intermediate, gave 12 percent per pass yield of butadiene, whereas ethanol and acetaldehyde gave about 30 percent yield. Thus 1,3 Butanediol (reaction F) can not be an intermediate product in formation of butadiene.

Detailed analysis of the experimental results lead Quattlebaum⁽¹⁾ to conclude that from the stand point of reaction mechanism the important facts are:

- (i) crotonaldehyde readily formed, when acetaldehyde is passed over tantalum oxide promoted catalyst,
- (ii) crotonaldehyde is not present in significant quantity in products when ethanol and acetaldehyde are converted to butadiene over some catalyst,
- (iii) crotonaldehyde is readily converted to butadiene by ethanol over same catalyst.

The extensive experimental studies on the mechanism of second step, that is, catalysis of ethanol-acetaldehyde to produce butadiene, lead Jones and Coworkers⁽⁴⁾ to conclude

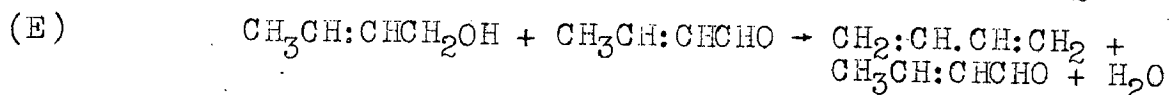
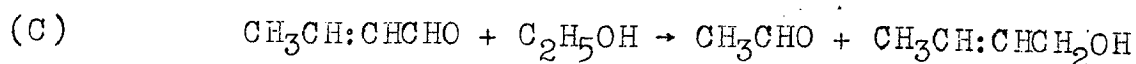
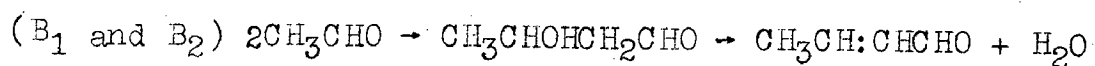
- (i) The final reaction which produces butadiene is the deoxygenation of crotonaldehyde by ethanol.
- (ii) A mixture of crotyl alcohol with a minor amount of crotonaldehyde is ideal for production of butadiene under the condition of ethanol-butadiene process.
- (iii) Feed mixtures capable of producing acetaldehyde in situ produce butadiene when processed over Tantalum-Silica gel catalyst.
- (iv) The primary function of the silica component of the commercial catalyst is to catalyze the condensation of acetaldehyde, whereas the function of the tantalum promoter is to catalyze the deoxygenation of crotonaldehyde by ethanol.

It seems therefore certain that the crotonaldehyde plays a key role in the synthesis of butadiene. The kinetic study also indicates⁽⁴⁾ that the rate controlling process at atmospheric pressure operation is a second order condensation of acetaldehyde. It looks probable that the acetaldehyde is condensed to a short lived transitory intermediate acetaldol which is then dehydrated to crotonaldehyde. It has also been established⁽¹⁾ that the crotonaldehyde is responsible for the formation of butadiene. Ethanol acts as a hydrogen donor and undergoes oxidation to acetaldehyde. Crotyl alcohol is the most likely transitory reaction intermediate but dehydration of crotyl alcohol to butadiene is definitely not a rate controlling step. Jones and Coworkers⁽⁴⁾ reported that both crotonaldehyde and crotyl alcohol were present in the crude catalyzate, acetaldol was not detected.

Recently Bhattacharya and Coworkers^(8,9) carried out a detailed investigation to study the influence of likely reaction intermediates on the overall conversion of ethanol to butadiene. However, these studies were carried out on catalysts other than tantalum-silica gel and findings of these workers are not of much help in establishing the mechanism of catalysis of ethanol-acetaldehyde to produce butadiene using tantalum-silica gel catalyst.

The work of earlier investigators^(1,2,4) has established that the rate controlling reactions in the catalysis of ethanol-acetaldehyde to produce butadiene over tantalum-silica gel catalyst are: (i) condensation of acetaldehyde to crotonaldehyde and (ii) deoxygenation of crotonaldehyde by ethanol to

produce butadiene. The first step in the reaction sequence is catalyzed by silica component and the second step by tantalum component of commercial catalyst. It is, however, possible that acetaldehyde may first condense to form a short lived intermediate acetaldol at the catalyst surface which may dehydrate rapidly to crotonaldehyde. The deoxygenation of crotonaldehyde by ethanol is more likely to proceed via crotyl alcohol as ^{some} crotyl alcohol is invariably present in reaction products. The most likely reaction sequence seems to be



The preference for reaction E, over direct dehydration of crotyl alcohol (reaction G₂) for butadiene formation is evident from the fact that tantalum-silica catalyst gave better butadiene yield when used with a mixture of crotyl alcohol-crotonaldehyde feed rather than crotyl alcohol alone.

2.2.2 Side Reactions - In the reaction of acetaldehyde and ethanol over tantalum oxide promoted silica gel catalyst, approximately one third of all material reacting is converted to products other than butadiene. The notable by-products found (2,3,16) are ethylene, propylene, butylene, ethyl ether, acetic acid, ethyl acetal, ethyl acetate, methyl ethyl ether, crotonaldehyde, crotyl alcohol, butyl alcohol, butaraldehyde, butanol, methyl ethyl ketones pentadienes, pentenes, hexaldehyde, hexadiene and hexanes. The other byproducts which are isolated but consumes less than 0.2 percent of total alcohol are Hexanol, viny cyclo-hexane, ethyl vinyl ether, propane,

oxides of carbon (CO, CO₂), Butyl acetate, ethane, Butane and Methane.

2.3 Thermodynamic Analysis of Reaction Equilibria:

Bhattacharya and Coworker⁽⁹⁾ have carried out thermodynamic feasibility studies of the individual steps in the suggested mechanism by evaluating free energy change and reaction equilibrium constant values at different temperatures. Some of the physico-chemical data required for such calculations was not available in published literature. This was estimated by applying group contribution method to stereochemical models. Such models were developed for acetaldo, crotonaldehyde, ethanol and butadiene. Table 2.1 gives free energy change and reaction equilibrium constant values at different temperatures for some important reactions leading to the formation of butadiene. It can be seen from equilibrium data that acetaldo concentration at reaction temperature of approximately 375°C will be negligible small but its existence as a short lived reaction intermediate in the formation of crotonaldehyde over a bifunctional catalyst can not be ruled out.

2.4 Catalysts:

The two step american process, in which dehydrogenation of ethyl alcohol to acetaldehyde and catalysis of acetaldehyde - ethyl alcohol to butadiene, is based on the earlier work of Ostromislensky (as reported by Quattlebaum et al⁽¹⁾). The research was initiated to investigate the variables affecting the conversion and ultimate yield to butadiene in the second step. Commercially this second step comprises of

TABLE 2-1
CALCULATED THERMODYNAMIC DATA

	Free energy change, F(Kcal/gm mole)		Reaction Equilibrium constant, K_p (atm unit)		Standard Heat of Reaction, H 298 Kcal/gm mole
	298°	733°	298°	733°	
(i) $C_2H_5OH \rightarrow CH_3CHO + H_2$	-	-1.1	-	2.39	12.1
(ii) $2CH_3CHO \rightarrow CH_3CHOHC_2H_5CHO$	2.6	12.8	1.12×10^{-2}	5.27×10^{-5}	-6.0
(iii) $CH_3CHOHC_2H_5CHO \rightarrow$ $CH_3CH = C_2H_5CHO + H_2O$	1.7	-20.9	5.6	1.028×10^7	9.2
(iv) $CH_3CH = CHCHO + C_2H_5OH \rightarrow$ $CH_2 = CH - CH = CH_2 + CH_3CHO + H_2O$	1.7	-7.3	5.6×10^2	2.8×10^2	9.0
(v) $CH_3CH = CHCHO + H_2 \rightarrow$ $CH_2 = CH - CH = CH_2 + H_2O$	-	-5.1	-	0.52×10^2	-4.2

processing a mixture of 69 weight percent ethanol, 24 weight percent acetaldehyde and 7 weight percent water over a suitable catalyst at a temperature range 325 to 400°C, a liquid hourly space velocity from 0.4 to 0.6 and atmospheric pressure. Corson and Coworkers^(5,6) carried out an extensive investigation to find a suitable catalyst composition, method of preparation and operating conditions for catalysis of acetaldehyde-ethyl alcohol to butadiene. Over 600 catalysts were tested by these workers and 40 different elements spread over the entire periodic table were involved in the investigation. List of important catalysts with ultimate yield and conversion is given in Appendix B. Catalyst activity was found to be maximal in oxides of element of group II to VI. The oxides of elements included in the diagonal band drawn through magnesium to uranium in periodic table are most specific. Combinations of silica gel with oxides of certain transitional element of group IV and V were most active except oxides of six elements viz antimony, cadmium, chromium, tin, titanium and zinc. Following is a brief summary of their findings.

(i) GROUP-1 (Li, Na, K, Cu, Ag) - The use of various combinations resulted in a maximum yield of butadiene to a value less than 20 percent.

(ii) GROUP-2 (Be, Mg, Ca, Ba, Zn, Cd). Each of these elements were tested in several combinations. The catalysts Beryllia-silica, magnesia-silica and magnesium carbonate-silica showed some promise. A series of 16 magnesia-silica catalysts with magnesia content from 3 to 70 percent were tested. The maximum attainable conversion per pass was 28 percent and ultimate yield was 55 percent at 375°C.

(iii) GROUP-3 (B, Al, Th) - No effective catalyst was obtained from this group.

(iv) GROUP-4 (Si, Ti, Zr, Sn, Hf, Pb, Th) - Major emphasis in this group was given to silica, titania, zirconia and hafnia because of their better performance.

(i) Titania-Silica - Numerous titania silica combinations were tested. The best of these (1.0 TiO₂-99.0 SiO₂) was prepared by impregnating silica gel with titanium chloride. This catalyst showed 18 percent per pass and 52 percent ultimate yield.

(ii) Zirconia-Silica - Numerous Zirconia-silica combinations were tested with regards to variables of composition and preparation. These were prepared by zirconyl nitrate impregnation on commercial silica gel and zirconia content was varied from 0.7 to 100 percent. The maximum attainable conversion per pass was 37 percent and ultimate yield was 55 percent.

(iii) Hafnia-Silica - 2 percent HfO₂ - 98 percent SiO₂ was found to be one of the best catalyst tested. It was prepared either by hafnium nitrate impregnation or in some cases by impregnating oxalic acid solution of hafnia on silica gel. Test run extending over 12 hours at 300°C, 0.4 to 0.6 liquid hourly space velocity and ethanol to acetaldehyde mole ratio of 2.5 in feed gave 31 mole percent per pass and 64 mole percent ultimate yield.

(v) GROUP-5 (V, Cb, Ta, P, Sb, Bi) - Test runs on vanadium oxide-silica, columbian oxide-silica, antimony oxide-silica and bismuthoxide-silica showed that these catalyst compositions have very low activity for butadiene synthesis. On the other hand tantalum-silica catalysts showed good activity and selectivity.

The effect of tantalum content on catalyst performance is discussed later in section 2.6. It has been observed that 2 percent tantalum oxide - 98 percent silica is optimum and this catalyst composition is used in commercial operation.

(vi) GROUP-6 (Cr, W, U, Mo, S) Tungsten trioxide-alumina, tungsten trioxide-silica catalysts were found to be in-effective. Uranium oxide-silica catalysts showed medium activity less than 55 percent ultimate yield at 350°C.

(vii) GROUP-7 (Mn, Cl, F) Manganese oxide-silica catalysts showed poor activity. Certain halide containing catalysts possessed some catalyst activity; Aluminium fluoride was best among these with 40 to 47 percent ultimate yield.

(viii) GROUP-8 (Ni, Ci, Fe) No satisfactory catalyst was obtained from this group. Catalysts showed poor activity less than 40 percent ultimate yield.

2.5 Ternary Catalysts - Various ternary catalysts were prepared and tested by Corson and coworkers⁽⁵⁾ to observe beneficial effect, if any, on butadiene synthesis. Tantalum oxide-silica gel were essential components with a third component used as a promoter. The promoter tested were CuO, ZrO₂, MgO and Ag₂O with tantalum content, varying in the range of 1.5 to 2.3 percent.

CuO-Ta₂O₅-SiO₂ catalyst - The commercial tantalasilica catalysts were promoted with CuO. Catalysts with 0.001, 0.01, 0.5, 1.1, 3, 10 percent CuO were tested and it was found that 1.1 percent copper is most suitable giving an ultimate yield of 63 percent and conversion 40 percent.

MgO-Ta₂O₅-SiO₂ catalyst - Several catalysts were prepared and tested. But it was concluded that performance of MgO promoted catalysts was no better than that of commercial tantalum-silica catalyst.

ZrO₂-Ta₂O₅-SiO₂ catalyst - Several catalyst compositions were tested. These ZrO₂ promoted tantalum-silica catalysts gave good results. The most suitable among these were 2.3 Ta₂O₅-0.2 ZrO₂-96.5 SiO₂ and 1.7 Ta₂O₅-1.8 ZrO₂ - 96.5 SiO₂.

The best catalyst compositions giving about minimum 30 percent per pass yield and 60 percent ultimate yield are given in Appendix B.

2.6 Effect of variables on the catalyst activity -

Available literature presents the effect of different variables in terms of overall efficiency, acetaldehyde efficiency, alcohol efficiency and butadiene yield. The variables affecting the system can be classified as follows:

(i) Primary variables

- a. Feed rate
- b. Ethanol-to-acetaldehyde ratio in feed
- c. Operating temperature
- d. Operating pressure
- e. Tantalum content of catalyst
- f. Catalyst age
- g. Catalyst particle size
- h. Catalyst bed thickness
- i. Impurities in feed

(ii) Secondary variables

Single or Multiple point addition of auxiliary feed.

Some of the above mentioned variables have significant influence on the system while others effect only marginally.

A brief summary outlining the influence of each of the above mentioned variable on the reactor performance is presented below.

2.6.1 Feed Rate - For a given quantity of catalyst, change in feed rate changes the space velocity and the butadiene production rate is accordingly affected. Increase in feed rate decreases contact time resulting in low conversion of reactants. Unconverted reactants are separated from reaction products and are recycled back to the reactor. The cost of separation is therefore increased. As the feed rate is decreased butadiene yield increases, reaches a maximum and then starts decreasing with further decrease in feed rate as undesirable side reactions involving primary reaction products become more and more significant. This is a typical behaviour to be expected when butadiene is an intermediate product of a series reaction. Optimum butadiene production rate is obtained at a liquid hourly space velocity defined as volume of feed as liquid/(hr)(volume of catalyst), of 0.6. However, the optimum value depends upon other variables, such as, catalyst age, operating temperature and ethanol to acetaldehyde ratio.

2.6.2 Ethanol-to-Acetaldehyde Ratio in Feed -

The molal ratio of ethanol-to-acetaldehyde in converter feed is very critical both for butadiene yield and overall efficiency. Maximum efficiency is obtained by using the ethanol-to-acetaldehyde mole ratio in the range of 2.7 to 2.8. However, the optimum value of this ratio can vary in the range of 2 to 3 depending upon the operating temperatures.

2.6.3 Operating Temperature - Reaction temperature affects both the main and undesirable side reactions. Dehydration reaction is generally favoured at higher temperature. The acetaldehyde efficiency is found to increase from 50 percent at 300°C to 95 percent at 375°C. The ethanol efficiency is found to increase at first as temperature is raised from 300°C, reaches a maximum and then starts decreasing at temperatures above 350°C. This may indicate that the rate constant of undesirable side reactions involving ethanol increases with increase in temperature at a faster rate than that of main reaction resulting in the production of butadiene. For a catalyst of average activity and an ethanol-to-acetaldehyde mole ratio of 2.75 optimum temperature is found to be 350°C.

2.6.4 Operating Pressure - Initial increase in pressure above atmospheric has resulted in some increase in butadiene production rate as a result of higher reactant concentrations but higher pressure favours the formation of undesirable byproducts. This may decrease the efficiency at higher pressure. The reported optimum pressure is 5 psig.

2.6.5 Tantala Content of Catalyst - The optimum tantala content is found to be two weight percent. At a lower operating temperature of 300°C beneficial effect of increase in tantala content to as high a value as ten weight percent were observed, but the highest conversion achieved at 300°C with ten weight percent tantala was still lower than that obtained at 350°C with two weight percent tantala.

2.6.6 Catalyst Age - Catalyst age is found to affect the conversion but not the efficiency. Average conversion of 28 percent during the first month of operation was found to decrease in a commercial plant to, as low as 20 percent after about four months of operation.

2.6.7 Catalyst Particle Size - At a given liquid hourly space velocity and temperature some decrease in conversion is observed for catalyst particle size exceeding 4 mesh. For catalyst particle size less than 4 mesh, intraparticle mass transfer limitations are in general insignificant and no adverse effect on conversion is observed.

2.6.8 Catalyst Bed Thickness - For a given liquid hourly space velocity, performance is not effected by catalyst bed thickness provided it is above ten inches. For very shallow beds, less than ten inches thick, marked decrease in conversion was observed probably due to the severe channelling in the flow.

2.6.9 Impurities in the Feed - Some byproducts are always formed along with butadiene in a commercial plant. Unreacted ethanol and acetaldehyde is seperated by distillation and recycled. Because of practical limitations on seperation efficiency achieved by distillation, an appreciable amount of reaction byproducts are also recycled. Some of these materials, such as, water and ether, only act as diluents while others, such as, olefins and higher molecular weight oxygenated compounds, decrease catalyst activity and adversely affects butadiene efficiency.

2.6.10 Secondary Variables - It has been reported that if an auxilliary feed rich in acetaldehyde is injected into the catalyst bed at or above mid-section where acetaldehyde concentration is low due to rapid depletion, higher butadiene yield and efficiency are obtained. Furthermore, higher butadiene efficiency is also reported when an auxillary feed rich in ethanol was injected to catalyst bed below the mid-point. However, no firm conclusion can be arrived at in view of limited experimental data.

2.7 Recent Fluidized - and Fixed-bed Investigations with Catalysts other than Tantalum.

All the earlier investigations were carried out using catalyst in fixed bed. Bhattacharya and Coworkers^(7,8) have extended this work to fluidized bed and investigated the performance of non-tantalum catalysts.

The fluidized bed studies are generally carried out to achieve more uniform temperature within the reactor. However for two step process the endothermic heat reaction of second step is of the order 7.0 Kcal/mole of butadiene. In view of the low heat of reaction the use of fluidized bed will have little advantage over fixed bed as far as uniformity of temperature is concerned.

Single and binary catalyst tested by these works are Al_2O_3 ; ZrO_2 ; ThO_2 ; $\text{ZrO}_2\text{-SiO}_2(2:98)$; $\text{ZrO}_2\text{-SiO}_2(3:97)$; $\text{MgO-SiO}_2(70:30)$; $\text{Al}_2\text{O}_3\text{-ZrO}_2(50:50)$; $\text{Al}_2\text{O}_3\text{-ThO}_2(50:50)$ and $\text{Al}_2\text{O}_3\text{-ZnO}(60:40)$. The performance of these catalysts was evaluated under fixed and fluidized bed conditions. The temperature range used for investigations was from 300 to 400 and ethanol to aldehyde mole ratio in the feed was always maintained close to 2.75 to 1.0.

The results reported by Bhattacharya and Coworkers are given in Table B-3, Appendix B. These investigators reported higher process yield for fluidized-bed operation than that for fixed-bed operation even when the value of liquid hourly space velocity was higher for fluidized-bed operation as compared to that of fixed-bed operation. In a well mixed fluidized-bed reactor this does not seem probable unless reaction is autocatalytic and further confirmation of

this behaviour is necessary. These results are not discussed further because the catalyst compositions used by Bhattacharya and Coworkers are non-tantalum based and they are not used in present investigations.

2.8 Silica Gel Support -

Silica is an active component in catalysis of ethanol-acetaldehyde mixture to butadiene because silica gel catalyses the condensation of acetaldehyde to crotonaldehyde, the first reaction in reaction mechanism. In addition this can provide large active surface for reaction to take place.

It was realised that properties of silica gel such as surface area, pore size and pore distribution depends upon numerous preparation variables.

Silica gel when used alone has some catalytic activity for production of butadiene⁽⁵⁾ (4 percent per pass, 23 percent ultimate) which was first attributed due to the presence of trace impurities in feed. But latter investigations with a relatively very pure sample also showed approximately the same catalytic activity. It is now believed that crotonaldehyde can be converted to butadiene on silica surface but at a much slower rate with poorer selectivity.

CHAPTER III

CATALYST PREPARATION

3.1 Introduction

Butadiene is commercially produced by passing a mixture of ethanol and acetaldehyde over a tantalum-silica gel catalyst at 330°C and essentially at atmospheric pressure. The commercial catalyst consists of two active components; tantalum oxide and silica gel. The tantalum oxide content in catalyst varies between 1.75 to 2.25 weight percent.

The object of present work is to prepare tantalum oxide-silica catalyst first and then to promote this catalyst with third component to give better conversion and/or ultimate yield. Cupric oxide and Zirconium oxide are tried as promoter. Earlier workers⁽⁵⁾ have indicated the usefulness of these components.

The present work is essentially divided into two parts:

- (i) Preparation of tantalum oxide-silica gel catalyst.
- (ii) Preparation of promoted catalyst using imported commercial tantalum oxide-silica gel catalyst with CuO or ZrO₂ as promoter.

3.2 Preparation of Tantalum Oxide-Silica Gel Catalyst

2 percent tantalum, 98 percent silica is most widely used catalyst in commercial operations to produce butadiene by two step process. This catalyst is prepared by impregnating tantalum oxide on silica gel. The catalyst

preparation method was essentially the same as reported by Quattlebaum et al⁽¹⁾ consisted of the following steps:

- (i) Preparation of solution for impregnation.
- (ii) Impregnation.
- (iii) Drying

Following is a brief description of various steps based on the reported work of Quattlebaum et al⁽¹⁾ and Corson and Coworkers⁽⁵⁾.

(i) Preparation of Solution for Impregnation -

Potassium tantalum fluoride, K_2TaF_7 , was used as the source to supply tantalum oxide. Potassium tantalum fluoride is only slightly soluble in water and effective dissolution of this salt was attained by dissolving it in sufficient quantity of distilled water. The approximate solution concentration of the salt in water was kept at 0.5 percent.

The solution of potassium tantalum fluoride was prepared by dissolving necessary quantity of salt in distilled water. Polythene container was used for dissolution with continuous stirring for sufficient time using a teflon stirrer.

Aqueous ammonia solution was used for precipitating tantalum oxide from the solution of potassium tantalum fluoride. The theoretical amount of ammonium hydroxide required as per the reaction stoichiometry is 5 moles per mole of potassium tantalum fluoride, but at least twice as much was provided. Suitable precipitation conditions were employed to give amorphous, nearly colloidal precipitate. When precipitate settled completely, the supernatant liquid was decanted and discarded.

conc?
detail

Wet precipitate was then washed by slurring with 5 to 20 volume of water for several hours. The extent, to which precipitate was freed from absorbed soluble ions, was estimated by the conductivity of successive filterates. *Why?* Washing was done using Demineralized hot water and continued until the conductivity of filterate fell below 10^{-4} mho with the removal of alkaline salts. Normally fibre washings were sufficient.

The precipitate was then dissolved in oxalic acid and tantalum oxide-oxalic acid complex on decomposition gave tantalum oxide. *How?*

Three parts by weight of oxalic acid was added per part of tantalum oxide to wet slurry and the solution was heated to evaporate water to bring the concentration of solution to desired value.

(ii) Impregnation -

Wetted silica gel was impregnated with tantalum oxide-oxalic acid complex by immersing the gel in solution. *Why?*

The method of impregnation used was to soak ~~the~~ water saturated silica gel in impregnating solution for sufficient time so that diffusion resulted in homogenous impregnation. *Conc.* Mild boiling is generally necessary to keep the concentration of solution throughout uniform. Sufficient time was allowed for diffusion to complete while keeping the concentration of tantalum-oxalic acid complex to a low value. This gave a more uniform distribution of tantalum oxide inside the pores of silica gel on decomposition.

After completing the impregnation, excess solution was drained and reused for second impregnation after adding make up solution to bring tantalum content to a desired value.

(iii) Drying -

The catalyst, after impregnation, is dried in air oven in controlled atmosphere. The drying procedure used is a very exacting one and was followed very carefully to avoid fractioning of silica gel. The catalyst was first dried at temperature below 100°C for sufficient time in controlled atmosphere and subsequently at higher temperature. The usual schedule for high temperature drying was to raise the temperature from that of room to 300 or 350°C during 4 to 6 hours and maintain the maximal temperature for 1 or more hours.

3.3 Promoting Commercial Catalyst with CuO

Many samples promoted with CuO were prepared using imported commercial tantalum oxide-silica gel catalyst by varying the cupric nitrate concentration in solution and time of impregnation. The results are shown in Table 3-1.

TABLE 3-1

Cupric nitrate concentration in solution as per cent CuO equivalent.	Percent concentration of CuO on catalyst			
	Hours of Impregnation			
	4	5	6	8
2	0.432	0.548	-	0.600
2.3	0.685	0.930	0.952	-
3	0.725	0.945	0.960	0.964
4	1.028	1.240	1.290	1.310
5	1.418	1.710	-	2.260
6	1.92	2.080	2.333	-

The effect of time of impregnation and CuO concentration in solution was analyzed and suitable procedure was established to prepare CuO promoted tantala silica catalysts containing CuO in the range of 0.2 to 1.6 percent.

3.3.1 Preparation of CuO Promoted Tantala-Silica Catalyst

The imported commercial catalyst was saturated with steam following a carefully controlled saturation to avoid cracking of catalyst. The catalyst was placed on a copper screen (iron screen was not used to avoid Fe contamination) above a beaker containing distilled water. The distilled water was evaporated till complete saturation of catalyst was achieved. The wetted catalyst was stored in a container under minimum quantity of water.

Cupric nitrate ($\text{Cu}(\text{NO}_2)_2 \cdot 3\text{H}_2\text{O}$) solution was prepared by dissolving necessary quantity of cupric nitrate AnalaR grade in measured quantity of distilled water. Water saturated tantalum oxide-silica gel catalyst was placed in cupric nitrate solution and gently boiled on hot plate. In some cases *Conc?* constant temperature bath was also used for impregnation instead of hot plate. To prevent the loss of water by evaporation, the beaker was covered with clock-glass filled with water.

The catalyst was separated from the solution after impregnation. The wet catalyst was **dried** in copper trays in an oven for one and a half hours under saturated humidity condition at 75°C . The saturated humidity condition is attained by raising temperature initially to 95°C .

While keeping water in open trays and then lower the temperature slowly to 75°C. After one and a half hours drying at 75°C, the temperature was slowly and gradually raised to 125°C over a period of 30 minutes and drying was continued for one more hour. The total drying period was three hours.

The cupric nitrate was then decomposed to CuO on the catalyst. The drying temperature of 125°C was sufficiently low not to give any appreciable decomposition of cupric nitrate. The rate of decomposition increased with temperature and decomposition was quite rapid at 275°C.

Dried catalyst was placed in a muffle furnace *extent* maintained at 150°C. The temperature was slowly raised to *of decomposition* 275°C in a period of one hour and held there for next two *of Cd(NO₃)₂* hours. Proper air circulation was maintained with the help of an air blower to keep temperature as uniform as possible in the furnace. The temperature was then rapidly increased to 350°C and maintained there for one more hour.

The catalyst was subsequently cooled and screened to remove fines produced during wetting impregnation, drying and decomposition. In spite of very carefully controlled *conditions* operating/*some* fines were always produced.

3.3.2 Preparation of Used Catalyst Promoted with CuO

Few samples of spent catalyst were promoted with CuO. 18000 hours used catalyst from the plant was selected for the present work. The catalyst was screened to remove fines below 8 mesh. Oversize catalyst was wetted and stored in water as described in earlier section.

Impregnation of used catalyst was carried out with an aim to achieve about 1.1 percent CuO. 4 percent CuO equivalent solution of $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was prepared by dissolving 121.50 gms of 'AnalaR' grade cupric nitrate in 1000 ml of distilled water. The wet catalyst was placed in this solution and heated gently on a hot plate for 4-1/4 hours. The beaker was covered with a clock-glass filled with water to maintain inside volume nearly constant. After 4-1/4 hours of impregnation the catalyst was separated from the solution.

The wet promoted catalyst was dried and decomposed under careful conditions as described earlier in section 3.3.1.

3.3.3 Preparation of Used Regenerated Catalyst Promoted with CuO

18000 hours used catalyst was promoted with CuO after regeneration. Two samples were regenerated in laboratory and one regenerated sample was supplied by M/S Synthetics and Chemicals Ltd.

3.3.3.1 Regeneration of First Catalyst

First catalyst sample was regenerated at 500°C . 1000 gms of spent catalyst was put in copper dishes and placed in muffle furnace. The temperature of furnace was raised to 500°C in 2 hours. The air was intermittently circulated in muffle with the help of ^{an} air blower and temperature maintained closely at 500°C for 12 hours. The regenerated catalyst was removed, cooled and screened to remove fines.

3.3.3.2 Regeneration of Second Catalyst -

The second catalyst was also regenerated exactly as described above except that the temperature was maintained at 550°C for regeneration.

3.3.3.3 Preparation of Promoted Regenerated Catalyst -

Three regenerated used catalyst samples were promoted with approximately 1.1 percent CuO following the procedure as described in section 3.3.2.

3.4 Preparation of Commercial Catalyst Promoted with ZrO₂

Few samples were also prepared by promoting zirconium oxide on commercial catalyst (2 percent tantalum- 98 percent silica) and ZrO₂ content was kept in the range of 0.2 to 1.8 percent.

Zirconium nitrate was used for impregnation. The solution for impregnation was prepared by dissolving 220 gms of zirconium nitrate in 800 ml of distilled water with some nitric acid to keep solution concentration equivalent to 10 percent ZrO₂. Water saturated catalyst was placed in that solution and beaker was gently heated in a water bath at 65°C. Low temperature was employed to prevent decomposition of zirconium nitrate. Impregnation temperature was kept constant for four hours and beaker was covered with clock-glass filled with water to maintain the solution volume constant.

After four hours of impregnation the catalyst was separated from solution. The spent solution was filtered and used for impregnation of other catalysts. The catalyst was put in clock-glasses and kept in an air oven. The atmosphere of

air oven was under saturated humidity condition at 60°C. The drying at this temperature was continued for two hours. The temperature of the oven was then slowly raised to 175°C and was maintained for next six hours for complete decomposition of zirconium nitrate to zirconium oxide.

show confirmed

The decomposed catalyst was screened to remove fines formed during wetting, impregnation and decomposition.

CHAPTER IVCATALYST TESTING

As a standard procedure catalyst is analysed for mesh size and tantalum oxide, volatile matter, oxalic acid, cupric oxide and zirconium oxide content before using it in a pilot-plant reactor for performance analysis. The performance analysis was carried out at the Synthetics and Chemicals Ltd., Bareilly.

4.1 Screen Analysis - Catalyst after drying and decomposition is screen analysed. Three screens 4,6 and 8 mesh (B.S.S.) were used for screening. The catalyst retained by 4,6 and 8 meshes is used for performance evaluation while catalyst passing through 8 mesh is rejected.

4.2 Chemical Analysis of Catalyst - For chemical analysis a representative sample of catalyst is taken and ground to very fine size.

4.2.1 Volatile Matter - About 5 grams of the ground sample is accurately weighed in a platinum crucible. The covered platinum crucible is heated in muffle furnace at 950°C for one hour. It is then cooled and weighed.

Volatile matter (percent by weight)

$$= \frac{\text{Loss in weight}}{\text{Weight of sample}} \times 100$$

4.2.2 Oxalic Acid - 5 to 10 grams of accurately weighed sample is digested with dilute sulphuric acid at about 80°C. This solution is titrated with standard potassium permagnet and oxalic acid is then calculated.

4.2.3 Tantalum Oxide - Tantalum oxide in catalyst is determined as total solid after removing silica.

The ground sample is heated in muffle furnace to 950°C and at this temperature for two hours more. This removes all traces of water, oxalic acid and volatile matter. The sample is then cooled in a desiccator.

Accurately weighed quantity of this sample is taken in a platinum crucible and silica is removed by using hydrofluoric acid. The total residue after silica removal is weighed as tantalum oxide and tantalum oxide content of the catalyst is calculated. It is not possible to report procedural details because it is a proprietary information of the Synthetics and Chemicals Ltd., Bareilly.

4.2.4 Cupric Oxide - 15 grams of catalyst is weighed accurately and leached with concentrated nitric acid. During leaching all cupric oxide is re-converted to cupric nitrate. The cupric nitrate solution in nitric acid is separated and remaining catalyst is washed with distilled water five to six times to remove all traces of cupric nitrate. After washings, the catalyst sample still appeared slightly bluish indicating presence of some cupric nitrate. To remove the last traces, the catalyst is dried and crushed to very fine size. It is now leached again with nitric acid.

*How to
check
complete
leaching*

The entire solution is now analysed for copper using sodium thiosulfate solution. The entire solution obtained during leaching and washing is divided into four to six equal parts and each part is separately analysed to achieve better accuracy using the standard procedure⁽¹⁷⁾ as given below:

The solution is heated and 1.0 gram of urea ~~AnalaR~~ *iron inter-*
 grade is added. The solution is boiled and boiling is conti- *ference*
 nued for one minute. This removes all nitrous acid or oxide *ammonia*
 of nitrogen which may be present. The solution is cooled *the acetic*
 and 3 grams of potassium iodide AnalaR grade dissolved in *acid*
 10 cc of distilled water is added. This is immediately titrated against standard 0.1 N sodium thiosulfate solution. 2 cc of starch solution is added when brown colour of iodine decreased in intensity sodium thiosulfate is added continuously until blue colour of solution became faint. Then 20 cc of 10 percent aqueous ammonium thiocyanate solution is added and titration is completed without any delay until the disappearance of blue colour completes.

The copper is calculated as

1 cc N $\text{Na}_2\text{S}_2\text{O}_3 \equiv 0.06354$ gram copper

cupric oxide content of catalyst is calculated by assuming that all copper present is in the form of cupric oxide.

4.2.5 Zirconium oxide - 50 grams catalyst impregnated with ZrO_2 is leached with concentrated nitric acid at 80-90°C.

The nitric acid containing zirconium nitrate (zirconium oxide is converted to zirconium nitrate by the action of nitric acid)

is separated and catalyst is washed carefully with hot distilled water for four to five times. The entire solution is then concentrate to about 20 ml. This is now transferred to a tared platinum crucible. The crucible is placed in muffle furnace. The temperature of muffle furnace is slowly raised from room to 950°C and maintained at 950°C for one hour. The remaining total solid is weighed as zirconium oxide and percentage of zirconium oxide on catalyst is calculated.

*complete
extraction
of ZrO₂
by the furnace
of Fe, Al*

4.3 Performance Analysis of Catalyst -

The performance analysis of the catalyst was carried out at the Development laboratory of Synthetics and Chemicals Ltd., Bareilly.

Ethanol and acetaldehyde feed mixture having a mole ratio of approximately 2.75 to 1 is charged to the feeding pipette. The flow through pipette is carefully controlled to obtain liquid hourly space velocity close to 0.6. The feed mixture from pipette goes to a preheater.

The preheater is a mild steel tube heated externally with electric heating coils. The temperature is controlled at 200°C with the help of a temperature controller. The liquid feed mixture is converted to vapors and these vapors are carried to the reactor. The temperature of the tube carrying the feed vapors is kept between 150 to 200°C to prevent condensation.

The reactor is made of a stainless steel tube having inside diameter as 1 inch and length 38 inch.

The feed enters at top and leaves at bottom. Reactor is externally heated using electric heating coils. The temperature is measured at the top and bottom of catalyst bed and controlled carefully at 330°C with the help of a temperature controller. The heated section is insulated to prevent heat loss.

The reactor has three zones; preheating at the top, reaction in the middle and cooling at bottom. The preheating and cooling zones are filled with glass raschig rings and reaction zone with catalyst. The catalyst after charging, is heated following a carefully controlled procedure with a continuous flow of hot air for a total period of about 88 hours before starting the test run. The highest temperature to which catalyst is raised during heating sequence is 350°C . The feed vapors entering from the top are preheated in preheating zone to 330°C before contacting the catalyst. The product vapors are cooled in a cooler made of a helical tube immersed in cold water. The temperature of cold water is kept at 2 to 3°C . Ethyl alcohol, acetaldehyde, ether, water and ethyl acetate are condensed in tube and collected in a flask. The uncondensed vapors pass into another flask kept under dry ice (solid CO_2 at -78°C) to condense butadiene, propylene, ethylene and Butylene. The uncondensed vapors contain some acetaldehyde and is removed by scrubbing with hydroxylamine hydrochloride solution. The gases after the scrubber are collected under water. The liquid fractions from flasks are analysed by chromatography. To check accuracy of results these fractions are also chemically analysed. Hydroxylamine hydrochloride is chemically analysed to give the quantity of acetaldehyde

removed during scrubbing. The gases collected under water are measured and analysed for composition using Orsat Analyser

G.C.
Koppers - Hinkley
& Orsat

CHAPTER VEXPERIMENTAL RESULTS AND DISCUSSION OF
CATALYST PERFORMANCE5.1 Experimental Results

Experimental results are presented in Tables D-1 to D-5 in Appendix D. These experiments are conducted at the Development Laboratory of the Synthetics and Chemical Ltd., Bareilly. A stainless-steel reactor of 1 inch diameter and 38 inch long is used for test runs. The catalysts are tested for intermittent and 120 hours continuous run. Temperature in the reactor is kept approximately at 330°C, liquid hourly space velocity is maintained at about 0.6, and ethanol to acetaldehyde mole ratio is kept at 2.75 to 1. All runs are carried out essentially at atmospheric pressure. 300 milliliter of catalyst is used for performance evaluation.

Measurements are made for feed composition, feed rate, reactor temperature, ethanol and acetaldehyde consumed, butadiene and by products formed in a specified period of time. From these measurements the following quantities are calculated: ethyl alcohol to acetaldehyde mole ratio in feed, accountability of feed to products, alcohol and acetaldehyde selectivities and ultimate selectivity of ethyl alcohol to butadiene. Defining relationships used for calculations are as follows.

Accountability of feed to products

$$= \frac{\text{Total weight of products}}{\text{Total weight of feed}} \times 100$$

Butadiene Production Rate, g/l/hr

$$= \frac{\text{Rate of butadiene produced}}{\text{Volume of catalyst}}$$

Per pass yield of Butadiene, mole percent

$$= \frac{\text{Moles of Butadiene Produced}}{\text{Total moles of ethyl alcohol and acetaldehyde in the feed.}} \times 100$$

Ethyl alcohol selectivity, mole percent

$$= \frac{\text{Moles of Butadiene Produced}}{\text{Moles of Ethyl alcohol consumed}} \times 100$$

Acetaldehyde selectivity, mole percent

$$= \frac{\text{Moles of Butadiene Produced}}{\text{Moles of Acetaldehyde consumed}} \times 100$$

Ultimate selectivity from ethyl alcohol, mole percent

$$= \frac{\text{Moles of Butadiene produced}}{\text{Moles of ethyl alcohol consumed} + \text{Moles of acetaldehyde consumed}/0.92} \times 200$$

The factor 0.92 accounts for the efficiency of ethyl alcohol conversion to acetaldehyde.

5.2 List of Catalysts Prepared

Catalysts were prepared by promoting tantala-silica imported fresh catalyst with cupric oxide and zirconium oxide. Some cupric oxide promoted samples were also prepared from 18000 hours plant used catalyst. Few fresh tantala-silica catalysts were also prepared using silica gel supplied by Jai Chemicals, Faridabad. Few freshly prepared tantala-silica catalysts using Jai Chemicals' silica gel were also promoted with cupric oxide.

A complete of lists of catalysts prepared is given in Table 5.1. It is to be noted that only some of the catalysts were used for performance evaluation because each test run normally require more than six days of continuous operation and involves tedious and time consuming analysis.

TABLE 5.1
LIST OF CATALYSES PREPARED

<u>Catalyst No.</u>	<u>Catalyst Description</u>	<u>CuO %</u>	<u>ZrO₂ %</u>	<u>Ta₂O₅ %</u>	<u>Remark</u>
C-1	Fresh imported	1.22	-	1.2	Tested
C-1A	Fresh imported	0.05	-	1.15	Tested
C-2	Fresh imported	0.24	-	1.02	Not Tested
C-3	Fresh imported	0.43	-	1.02	Not Tested
C-4	Fresh imported	0.60	-	1.40	Tested
C-5	Fresh imported	1.03	-	1.45	Tested
C-6	Fresh imported	1.10	-	1.15	Not Tested
C-7	Fresh imported	1.38	-	0.97	Not Tested
C-8	18000 hours used	nd*	-	0.937	Not Tested
C-9	18000 hours used Regenerated at 550 ^o C	1.08	-	1.50	Tested
C-10	18000 hours used Regenerated at 500 ^o C	1.08	-	1.32	Not Tested
C-11	18000 hours used Regenerated at 500 ^o C	1.12	-	1.03	Not Tested
C-12	Fresh imported	0.84	-	1.674	Not Tested
C-13	Fresh imported	0.76	-	1.368	Not Tested
C-14	Fresh imported	0.61	-	1.53	Not Tested
Zr-1	Fresh imported	-	nd	nd	Tested
Zr-2	Fresh imported	-	nd	nd	Not Tested
TF-1*	Prepared from Jai silica gel	-	-	nd	Tested
TF-Cu-1**	Prepared from Jai silica gel.	1.45	-	nd*	Not Tested
TF-Cu-2	Prepared from Jai silica gel.	2.01	-	3.01	

*nd - not determined

** Prepared by first impregnating silica gel with cupric nitrate solution, decomposed and then impregnated by tantalum oxalate solution

5.3 Discussion of Catalyst Performance

As discussed earlier, the tantalum content is quite critical to obtain high ultimate selectivity from ethanol. Tantalum content has a marked influence on ethyl alcohol and acetaldehyde selectivities.

5.3.1 Before discussing the chemical behaviour of catalyst it is, therefore, necessary to know its tantalum content.

5.3.1 Leaching of Ta₂O₅ - The tantalum oxide content of the imported commercial catalyst used at Bareilly, varies from 1.75 to 1.96 weight percent. Normally the tantalum oxide content/catalyst is supplied in tantalum oxalate form and is decomposed to tantalum oxide in the reactor. On wetting the imported fresh catalyst and storing in water to keep the silica gel saturated with water to prevent cracking during impregnation, it was observed that the colour of supernatant water is milky. Originally this colour was attributed due to the presence of fine silica particles formed due to cracking of silica gel but later it was found that some tantalum oxalate was leached from catalyst during wetting, storing and impregnation. Water containing tantalum oxalate also has a milky appearance. This was later conformed by tantalum analysis of promoted catalyst. The tantalum oxide content of fresh catalyst was substantially higher than that of the promoted catalysts prepared from them as can be noted from Table 5.2.

1.75
-
2.25

However, the tantalum loss due to leaching could not be completely prevented.

It may be necessary to compensate for the tantalum loss during the preparation of promoted catalysts either by having a higher tantalum content initially to start with or to impregnate the promoted catalyst again with tantalum oxalate under controlled conditions. One of the catalyst was prepared by impregnating the silica gel (supplied by Jai Chemicals) first with cupric nitrate and then with tantalum oxalate after decomposing the cupric nitrate to cupric oxide.

5.3.2 Production Rate - The production rate is directly proportional to per pass yield and analysis given below for production rate equally holds true for per pass yield. The production rate of all catalysts decreases with cycle time. The rate of decrease in production rate is very slow and more or less at a uniform rate for imported commercial catalyst (curve 1 fig.5.1). The initial production rate of butadien during intermittent runs (Run No.1,4,5,7,8; Table D-1, Appendix D) with CuO promoted catalyst C-1 (1.22 percent CuO-1.2 percent Ta_2O_5) has been 30 to 50 percent higher than that obtained for imported commercial tantala-silica catalyst containing 1.78 percent Ta_2O_5 . The production rate for promoted catalyst C-1 decreases very sharply with operating hours as can be observed from 120 hours continuous runs. The final production rate for the promoted catalyst C-1 at the end of 120 hours operation is only 48 percent of the initial value while in case of commercial catalyst this value is about 70 percent of the original value.

TABLE 5.2

COMPARISON OF COMPOSITION OF FRESH AND
CUPRIC OXIDE PROMOTED CATALYSTS

Promoted Catalyst			Fresh catalyst composition and condition	
Catalyst No.	CuO %	Ta ₂ O ₅ %	Ta ₂ O ₅ %	
C-1	1.22	1.2	1.96	Undecomposed
C-2	0.24	1.02	1.96	Undecomposed
C-3	0.43	1.02	1.96	Undecomposed
C-4	0.60	1.40	1.96	Undecomposed
C-5	1.03	1.45	1.96	Undecomposed
C-6	1.10	1.15	1.96	Undecomposed
C-7	1.38	0.97	1.96	Undecomposed
C-8	nd	0.937	1.50	18000 hours used catalyst
C-9	1.08	1.50	1.50	18000 hours used Regenerated at 550
C-10	1.08	1.30	1.50	18000 hours used Regenerated at 500
C-11	1.12	1.03	1.50	18000 hours used Regenerated at 550
C-12	0.84	1.674	1.78	Decomposed
C-13 ¹	0.76	1.368	1.78	Decomposed
C-14	0.61	1.53	1.78	Decomposed

Since tantalum oxalate is soluble in water it was considered desirable to decompose tantalum oxalate to tantalum oxide before impregnation with promotor component. The catalyst samples C-12, C-13, C-14 were prepared after decomposing the fresh catalyst. This reduced the tantalum loss due to leaching at the time of wetting, storing and impregnation as can be seen from data given in Table 5.2.

Curve No.	Catalyst	Catalyst Composition
1	As imported	1.78 % Ta ₂ O ₅ *
2	C-1	1.8 % Ta ₂ O ₅ -1.20% CuO*
3	C-1 (Reconstituted)	Same as above
4	C-1	1.45 % Ta ₂ O ₅ -1.03 % CuO*
5	TF-1**	3.10% Ta ₂ O ₅ -SiO ₂ +
6	TF-Cu-1**	Ta ₂ O ₅ -CuO-SiO ₂ +

* Balance SiO₂
 ** Jai Chemical silica gel
 + Not analysed

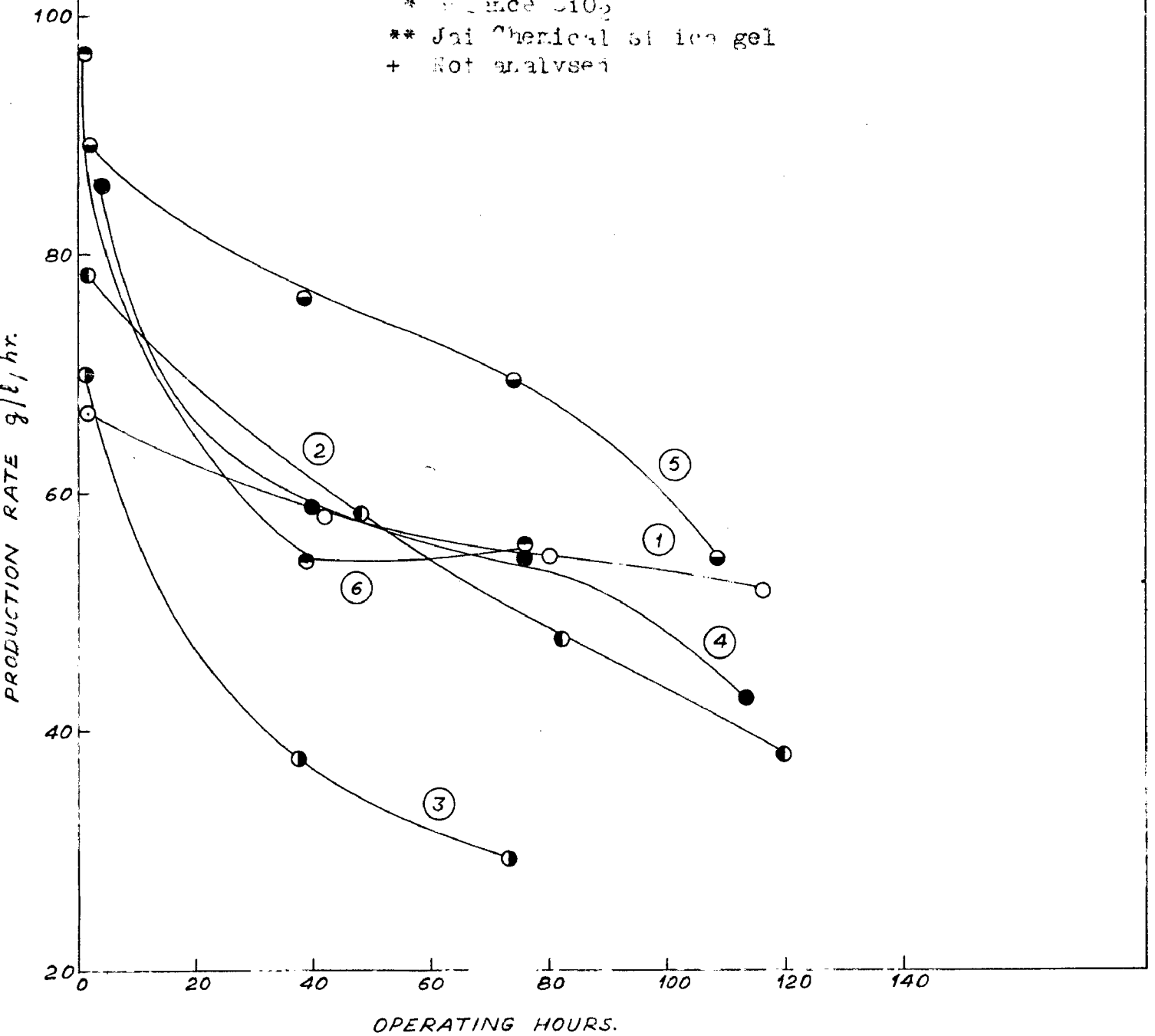


FIG. 5.1 EFFECT OF OPERATING HOURS ON PRODUCTION RATE

Composition of curve 1 and 2, fig. 5.1, indicate that the initial production rate for the promoted catalyst C-1 is nearly 17.4 percent higher than the initial rate for the commercial catalyst but production rate at the end of 120 operating hours is nearly 21.6 percent less. However, the time averaged production rate for 120 hours is nearly the same.

Curve 3 shows the variation in production with operating hours for catalyst C-1 after regeneration comparison of curve 2 and 3 indicate that not only the initial activity is low after regeneration (nearly 10 percent lower) but deactivation rate is also faster (nearly 40 percent lower).

Curve 4 shows the production rate for another promoted catalyst containing 1.45 percent Ta_2O_5 and 1.03 percent CuO prepared from fresh imported catalyst. Nature of the curve is essentially same as that of curve 2 however the time averaged production rate is nearly 5 percent higher than the imported commercial catalyst.

Curve 5 shows the production rate for the catalyst TF-1 prepared from silica gel supplied by Jai Chemicals. Tantalum content is not determined. It shows higher production rate than imported fresh catalyst for the entire 120 operating hours and time averaged production rate is nearly 26 percent higher than imported fresh catalyst.

This catalyst also shows a faster deactivation rate than the commercial catalyst.

Curve 6 shows the performance of cupric oxide promoted catalyst TF-C-1 prepared from catalyst TF-1. The initial activity of catalyst TF-C-1 is nearly 10 percent higher than that of catalyst TF-1 and is nearly 70 percent higher than that of imported commercial catalyst. However, it shows a very steep decline in activity initially similar to that shown by catalyst C-1 regenerated (curve 3).

Table 5.1 gives a list of other, catalysts tested. The performance data for some of these is given in Table D-1 to D-5, Appendix D. The performance of these catalysts, except that of 18000 hours used regenerated at 550°C catalyst C-9, was much poorer and is not discussed further.

From the above discussion it seems that both Ta₂O₅ and CuO content are important to get higher production rate. It is necessary that CuO content is maintained at a level of 1.1 to 1.2 percent while Ta₂O₅ content should exceed 1.2 percent and preferred range is 1.8 - 2.0 percent. The problem of rapid catalyst deactivation of promoted catalyst can only be solved partly by improvements in catalyst preparation techniques. Suitable adjustment in operating conditions, such as, temperature, ethyl alcohol to acetaldehyde mole ratio and duration of operating cycle, may be required to get optimal performance.

5.3.3 Ethylalcohol Selectivity -

The effect of operating hours on ethyl alcohol selectivity is plotted in figure 5.2. The ethyl alcohol selectivity increases with cycle time in all cases except for catalyst TF-Cu-1 (curve 6). The extremely low value obtained for 40 operating hours may be attributed to measurement or analysis error as the accountability value calculate for this run is unusually high (113.74 percent). Curve 1 shown the ethyl alcohol selectivity with operating hours for the imported catalyst. Selectivity increases with time but rate of increase is not rapid and the value for 120 operating hours is only 32 percent more than the initial value.

Curve 2 shows the ethyl alcohol selectivity for cupric oxide promoted catalyst C-1 with operating hours and indicates rapid initial increase in selectivity. The selectivity value for 82 operating hours is more than two times the initial value at 2 operating hours. The selectivity value shows a maxima at 82 hours and then decreases with further increase in operating hours. The initial selectivity value for catalyst C-1 is nearly 30 percent less while at about 80 operating hours it is 30 percent more than these of imported commercial catalyst. The selectivity values at 120 operating hours differ only marginally.

Curve 3 shows the ethyl alcohol selectivity for catalyst C-1 after regeneration. The test run was carried out for a total of 73 operating hours. Curve 3 is similar to curve 2 except that the values are 13 to 15 percent lower.

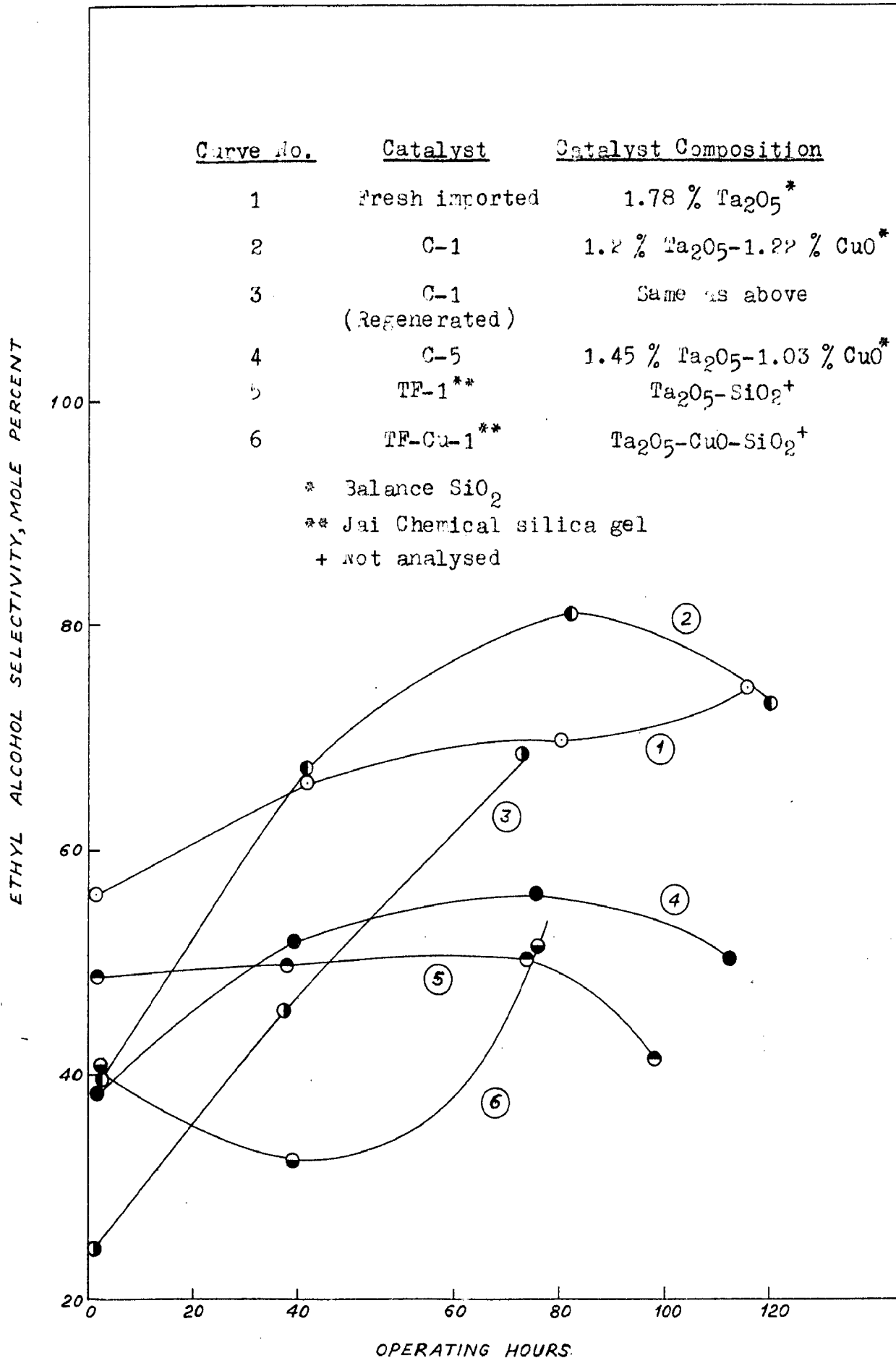


FIG.5.2 EFFECT OF OPERATING HOURS ON ETHYL ALCOHOL SELEC

Curve 4 shows the ethyl alcohol selectivity for cupric oxide promoted catalyst C-5. The trend is same as that for catalyst C-1 but the rate of increase for first 80 hours is not rapid. For first 80 operating hours ethyl alcohol selectivity for catalyst C-5 remains 14 to 18 per cent lower than that for fresh catalyst.

Curve 5 shows the ethyl alcohol selectivity for tantalum oxid-silica catalyst prepared from silica gel supplied by Jai Chemicals. For first 80 hours selectivity value remained at about 48.6 to 50.4 per cent and then allowed a 16 percent decrease at 120 operating hours. The selectivity values for this catalyst are ~~xxx~~ always less than that for imported commercial catalyst and the difference increases from nearly 8 percent to 33 percent with increase in cycle time.

Curve 6 shows the ethyl alcohol selectivity for cupric oxide promoted catalyst TF-Cu-1 prepared from catalyst TF-1. ~~xxxxxxxxx catalyst TF-Cu-1~~ For the catalyst TF-Cu-1 the value at 39 operating hours is disregarded because of poor overall accountability than the values indicate an increase with time. The initial value is about 8 percent lower than that for catalyst TF-1 but the values for two catalyst are nearly the same at about 80 operating hours.

The lower ethyl alcohol selectivity exhibited by cupric oxide promoted catalyst is due to the activity which copper catalysts exhibit for dehydrogenation of ethyl alcohol to acetaldehyde.

5.3.4 Acetaldehyde Selectivity - The effect of operating hours on acetaldehyde selectivity is plotted in figure 5.3. The acetaldehyde selectivity shows a marginal decrease with cycle time except for imported commercial catalyst. The cupric oxide promoted catalysts show a rapid decrease in aldehyde selectivity for first 40 hours of operation.

Curve 1 shows the acetaldehyde selectivity with operating hours for the imported catalyst. Selectivity decreases slowly with time resulting in a selectivity value after 120 operating hours only 10 percent lower than the initial value.

Curve 2 shows the acetaldehyde selectivity for cupric oxide promoted catalyst C-1 with operating hours and indicates rapid initial decrease in selectivity. The selectivity value at 40 operating hours is only 64 percent of the initial value. The change in selectivity between 40 and 82 operating hours is only marginal and rises steeply thereafter. The initial selectivity value for catalyst C-1 is about 146, nearly 90 percent higher than that of imported commercial catalyst, and clearly indicates acetaldehyde formation from ethanol as indicated earlier while discussing the effect of CuO on alcohol selectivity. It seems that some of the most active CuO sites producing acetaldehyde gets deactivated quickly resulting in the decline in acetaldehyde efficiency but after some time the rate of formation of acetaldehyde seems to stabilize. This may be responsible for increase in acetaldehyde activity during the later part of operating cycle, that is, 80 to 120 hours.

Curve No.	Catalyst	Catalyst Composition
1	Fresh imported	1.78 % Ta ₂ O ₅ ^{**}
2	C-1	1.2 % Ta ₂ O ₅ -1.22%CuO*
3	C-1 (degenerated)	Same as above
4	C-5	1.45 % Ta ₂ O ₅ -1.03 % CuO*
5	TF-1 ^{**}	Ta ₂ O ₅ -SiO ₂ ⁺
6	TF-Cu-1 ^{**}	Ta ₂ O ₅ -CuO-SiO ₂ ⁺

* balance SiO₂

** Jai Chemical silic. gel

+ Not analysed

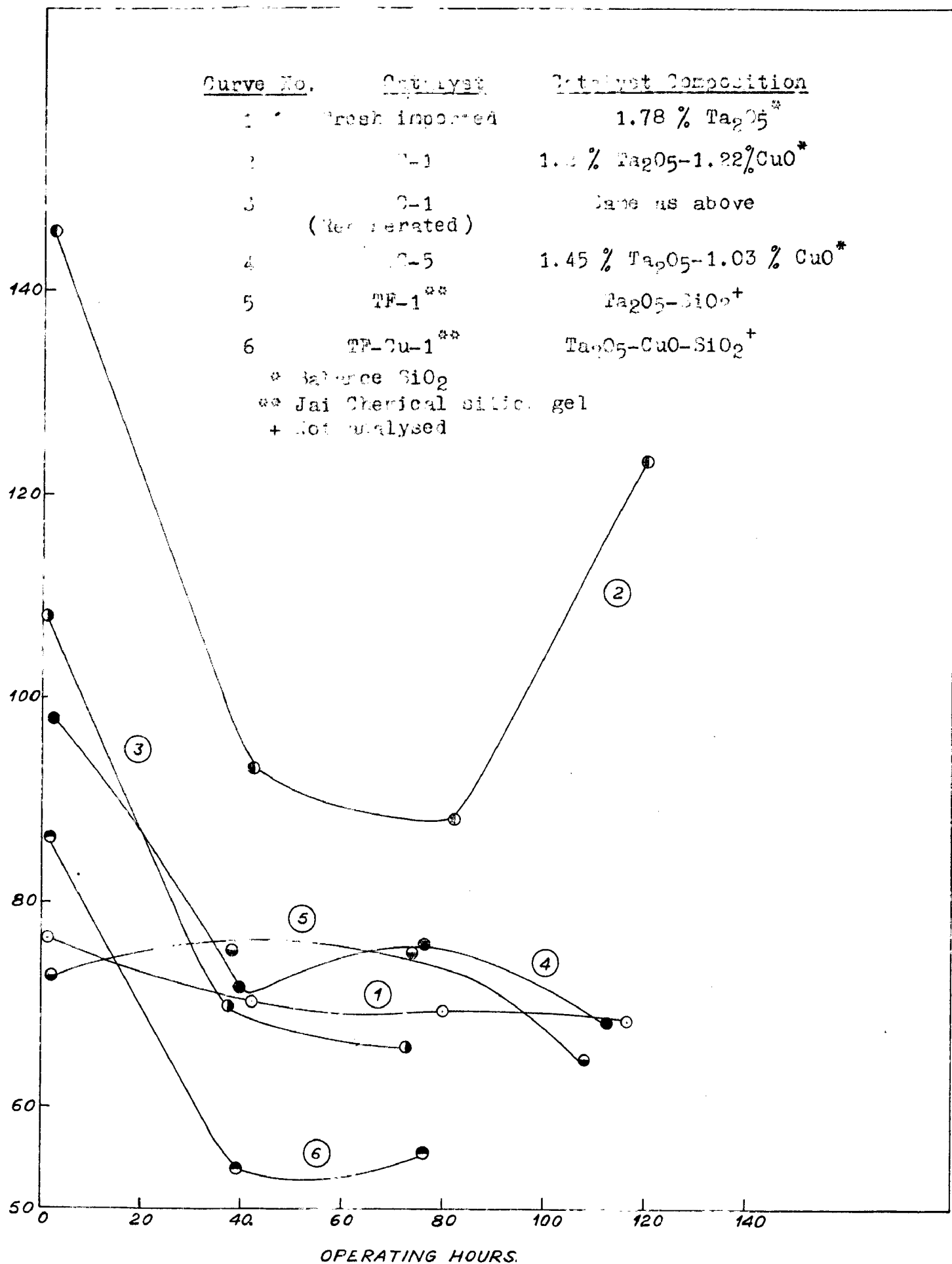


FIG. 5.3 EFFECT OF OPERATING HOURS ON ACETALDEHYDE SELECTIVITY

Curve 3 shows the acetaldehyde selectivity for catalyst C-1 after regeneration. The test run was carried out for a total of 73 hours. Curve 3 has same trend as curve 2 except that the values are about 25 percent lower indicating irreversible deactivation of some catalytic sites responsible for acetaldehyde formation.

Curve 4 shows the acetaldehyde selectivity for cupric oxide promoted catalyst C-5. The initial value is about quite high, about 24 percent higher than the value for imported commercial catalyst, and its behaviour is quite similar to that of catalyst C-1 after regeneration for first one-third of the cycle. In the latter part of the cycle the acetaldehyde selectivity values only change marginally.

Curve 5 shows the acetaldehyde selectivity for tabtalum oxide-silica catalyst prepared from silica gel supplied by Jai Chemicals. The initial value of acetaldehyde selectivity is only marginally lower than that of imported commercial catalyst. The selectivity first increases reaches a maxima after about 40 hours and then starts decreasing. The selectivity value at the end of 120 hours is only 11 percent less than the initial value. The time averaged acetaldehyde selectivity is nearly the same as that of imported commercial catalyst.

Curve 6 shows the acetaldehyde selectivity for cupric oxide promoted catalyst, TF-Cu-1, prepared from catalyst TF-1. The value at 39 operating hours can be disregarded because of poor accountability. The initial

value is about 12-13 percent higher than TF-1 but decreases rapidly with operating time showing a behaviour similar to catalysts C-1 and C-1 regenerated.

The higher acetaldehyde selectivities exhibited by cupric oxide promoted catalyst is due to the known activity of copper based catalyst for the dehydrogenation of ethyl alcohol to acetaldehyde. It also looks probable that this activity stabilizes after rapid initial deactivation of more active sites.

5.3.5 Ultimate Selectivity

Fig. 5.4 shows the effect of operating hours on ultimate selectivity. It is directly related to ethyl alcohol and acetaldehyde selectivities as can be seen from the relation given below:

$$\frac{1}{\text{Ultimate selectivity}} = 2 \left(\frac{1}{0.92 \times \text{aldehyde selectivity}} + \frac{1}{\text{alcohol selectivity}} \right)$$

To get high values of ultimate selectivity both aldehyde and alcohol selectivity values must be high. Catalyst C-1 (curve 2) gives significantly higher value than that for imported commercial catalyst for most of the operating cycle. All other catalysts have resulted in lower ultimate selectivity values. The time averaged selectivity of cupric oxide promoted catalyst C-1 is nearly 18 percent higher and that of catalyst C-5 is nearly 13 percent lower than that of imported commercial catalyst.

<u>Curve No.</u>	<u>Catalyst</u>	<u>Catalyst Composition</u>
1	Fresh imported	1.78 % Ta ₂ O ₅ *
2	C-1	1.2 % Ta ₂ O ₅ -1.22 % CuO*
3	C-1 (Regenerated)	Same as above
4	C-5	1.45 % Ta ₂ O ₅ -1.03 % CuO*
5	TF-1**	Ta ₂ O ₅ -SiO ₂ †
6	TF-Cu-1**	Ta ₂ O ₅ -CuO-SiO ₂ †

* Balance SiO₂

** Jai Chemical silica gel

† Not analysed

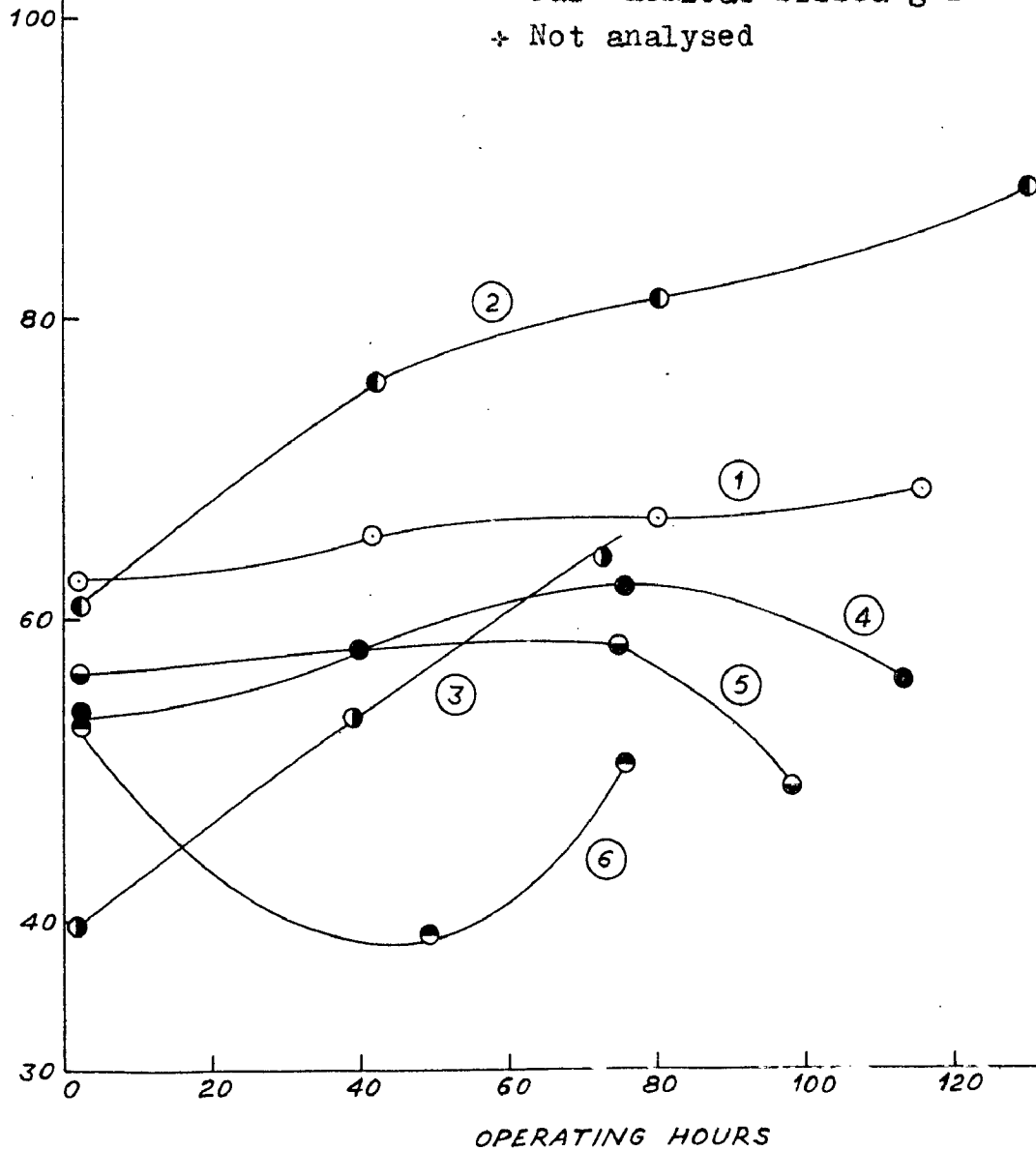


FIG. 5.4 EFFECT OF OPERATING HOURS ON ULTIMATE SELECTIVITY

5.3.6 By-products - The products obtained for catalyst C-1 are given in table D-2 Appendix D. The following trend for by-products is noted for catalyst C-1 after comparing with the by-products of fresh catalyst:

1. In comparison to butadiene produced the conversion of reactants to (butanes + butenes) is quite high initially (approx. 32 percent of butadiene) but stabilizes to about 10 percent of butadiene after 40 hours of operation.
2. In comparison to butadiene produced the conversion to ethylene monotonically increases from an initial value of approx. 5 percent to about 16 percent of butadiene with increase in cycle time.
3. In comparison to butadiene produced hydrogen production rate shows a rapid decrease (1.9 percent to 0.6 percent of butadiene at 2 and 42 hours of operation) and then a slight increase (0.75 percent of butadiene at 120 hours) with increase in cycle time.
4. Ether formation was quite low and no definite trend was observed.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. Tantalum oxide-silica gel catalyst can be prepared using indigenous silica gel to match the performance of imported commercial catalyst.

efficiency?

2. The use of cupric oxide as promotor to commercial silica-catalyst has distinct advantages over the imported catalyst both in terms of production rate and ultimate selectivity. This is largely due to the fact that copper based catalyst has dehydrogenating activity to produce acetaldehyde from ethyl alcohol at temperature range of 250° to 400°C. The following are the important observations for oxide promoted imported commercial catalyst.

repeatability

- (i) Rapid decline in catalyst activity with increase in cycle time.
- (ii) Increase in ultimate selectivity with increase in cycle time.
- (iii) Alcohol selectivity increases and acetaldehyde selectivity decreases with increase in cycle time upto 80 hours of operation and then trend is reversed. Changes are quite rapid during first 40 hours of operation.
- (iv) From the performance data collected so far it seems that promoted catalyst should contain 1.1 to 1.2 percent cupric oxide and a minimum of 1.2 percent tantalum oxide preferably in the range of 1.7 to 2.0 percent.

explains how.

Recommendations

1. The test on some more cupric oxide promoted catalysts in the composition range and indicated above is required to ascertain the most optimal composition.
2. Preliminarily indications are that the distribution of silica, Ta_2O_5 and CuO sites has an important influence on the catalyst performance.
3. After establishing the suitable catalyst composition, most optimal operating conditions may have to be determined by direct search technique.

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APPENDICES

APPENDIX APROPERTIES OF BUTADIENE(14)

1,3-butadiene is a colourless gas, slightly soluble in water, some what more soluble in methanol and ethanol, but readily soluble in acetone, ether, benzene, carbon-tetrachloride, chloroform, amyl acetate, furfural. It forms azeotropes with ammonia, methylamine acetaldehyde, n-butane. Its physical properties are summarized in table A-1.

TABLE A-1
Physical Properties of Butadiene

Molecular weight	54.09
Boiling point at 760 mm Hg	-4.413°C.
Freezing point at 760 mm Hg	-108.915°C
Critical temperature	152°C
Critical pressure	42.7 atm
Critical density	0.245 gm/ml
Density 20°C	0.6211 gm/ml
25°C	0.6149 gm/ml
Heat of formation at 25°C	
gas	26.33 Kcal/mole
liquid	21.21 Kcal/mole
Free energy of formation at 25°C	36.01

Butadiene exhibits an intense absorption in the near ultra violet region of 215-225 millimicron.

APPENDIX BSUCCESSFUL CATALYST COMPOSITIONS AND THEIR PERFORMANCE(5)

Typical successful catalyst compositions and their performance characteristics are listed in table B-1 based on their position in periodic table. Reported values of per pass yield and ultimate yield are the average values obtained during 8 hours run with ethanol-to-acetaldehyde mole ratio in feed as 2.75:1 and liquid hourly space velocity as 0.4. The compositions which gave per pass and ultimate yield values more than 30 and 60 mole percent are marked by asterick.

TABLE B-1Successful Catalyst Compositions and their Performance .

Catalyst composition, weight percent.	Temperature, °C.	Per pass yield, mole percent	Ultimate yield, mole percent
<u>GROUP - 1</u>			
1.0 K ₂ O - 99.0 Al ₂ O ₃	350	14	17
2.0 LiO ₂ - 98.0 SiO ₂	350	4	7
<u>GROUP - 2</u>			
15.1 BeO - 84.9 SiO ₂	350	7	29
21.0 MgO - 79.0 SiO ₂	375	23	54
49.3 MgO - 0.3 MgCl ₂ - 50.4 SiO ₂	350	25	50
60.0 MgCO ₃ - 40.0 Al ₂ O ₃	400	11	30
90.0 MgCO ₃ - 10.0 SiO ₂	400	25	49
2.0 ZnO - 98.0 Al ₂ O ₃	400	14	20
10.0 CdO - 90.0 SiO ₂	350	10	25

Catalyst composition weight percent	Temperature °C.	Per pass yield, mole percent	Ultimate yield, mole percent
<u>GROUP - 3</u>			
Al ₂ O ₃	350	21	29
AlF ₃	375	14	47
Fuller's earth	350	15	28
2.0 Ce ₂ O ₃ - 98.0 SiO ₂	350	12	27
2.3 Nd ₂ O ₃ - 97.7 SiO ₂	350	13	27
<u>GROUP - 4</u>			
SiO ₂	350	4	32
TiO ₂	350	8	20
ZrO ₂	400	8	9
SnO ₂	350	1	2
*2.3 ZrO ₂ - 97.7 SiO ₂	300	33	61
*2.0 HfO ₂ - 98.0 SiO ₂	300	31	64
1.0 TiO ₂ - 99.0 SiO ₂	350	18	52
2.0 SnO ₂ - 98.0 SiO ₂	400	9	20
2.0 ZrO ₂ - 5.0 ThO ₂ - 93.0 SiO ₂	350	32	55
<u>GROUP - 5</u>			
Ta ₂ O ₅	300	24	45
1.0 Ta ₂ O ₅ - 99.0 SiO ₂	350	27	60
1.2 Ta ₂ O ₅ - 98.8 SiO ₂	350	34	68
*2.0 Ta ₂ O ₅ - 1.1 CuO - 96.6 SiO ₂	350	40	60
*2.3 Ta ₂ O ₅ - 0.2 ZrO ₂ - 97.5 SiO ₂	300	32	62
5.7 Ta ₂ O ₅ - 94.3 Al ₂ O ₃	350	18	30
1.0 Nb ₂ O ₅ - 99.0 SiO ₂	350	15	39
5.0 V ₂ O ₅ - 95.0 SiO ₂	350	6	10
*2.0 Ta ₂ O ₅ - 98.0 SiO ₂	300	29	62
*2.3 Ta ₂ O ₅ - 97.7 SiO ₂	400	34	69

Catalyst composition weight percent	Temperature °C.	Per pass yield, mole percent	Ultimate yield, mole percent
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GROUP - 6

Cr ₂ O ₃	400	15	40
WO ₃	350	2	3
10.0 WO ₃ - 90.0 Al ₂ O ₃	300	11	15
12.0 Cr ₂ O ₃ - 88.0 Al ₂ O ₃	425	15	21
5.0 Cr ₂ O ₃ - 8.0 MgO - 87.0 SiO ₂	400	20	38
2.0 MoO ₃ - 98.0 SiO ₂	350	2	5
2.0 U ₃ O ₈ - 98.0 SiO ₂	350	17	22
5.0 U ₃ O ₈ - 8.0 MgO - 87.0 SiO ₂	350	20	34
1.0 U ₃ O ₈ - 2.0 Ta ₂ O ₅ - 97.0 SiO ₂	350	31	35
10.0 U ₃ O ₈ - 90.0 Floridin	375	18	30

GROUP - 7

9.2 MnO ₂ - 90.8 SiO ₂	400	23	37
MnCl ₂ - Florite	350	10	20
AlF ₃	350	13	40
15.0 NiS - 85.0 SiO ₂	350	18	30
15.0 Fe ₂ O ₃ - 85.0 SiO ₂	350	6	35

Best Catalyst Compositions and their Performance (5)

Best catalyst compositions and their performance characteristics are listed in table B-2. The reported values of per pass and ultimate yield are the average value with ethanol-to-acetaldehyde mole ratio in feed as 2.75:1 and liquid hourly space velocity as 0.4.

TABLE B-2
Best Catalyst Compositions and their Performance

Catalyst composition, weight percent	Hours of test.	Temperature °C	Per pass yield, mole percent	Ultimate yield, mole percent
1.1 Ta ₂ O ₅ - 98.9 SiO ₂	36	350	35-25	62-50
1.2 Ta ₂ O ₅ - 98.8 SiO ₂	8	350	44	63
1.3 Ta ₂ O ₅ - 98.7 SiO ₂	8	350	35	63
1.5 Ta ₂ O ₅ - 98.5 SiO ₂	8	350	33	65
1.7 Ta ₂ O ₅ - 98.3 SiO ₂	48	300	25	60
1.8 Ta ₂ O ₅ - 98.2 SiO ₂	8	350	32	62
1.9 Ta ₂ O ₅ - 98.1 SiO ₂	48	350	34	62
2.0 Ta ₂ O ₅ - 98.0 SiO ₂	48	300	29	62
2.1 Ta ₂ O ₅ - 97.9 SiO ₂	48	300	24	61
2.3 Ta ₂ O ₅ - 97.7 SiO ₂	8	400	34	69
2.4 Ta ₂ O ₅ - 97.6 SiO ₂	8	350	31	65
2.6 Ta ₂ O ₅ - 97.4 SiO ₂	48	350	39	60
2.8 Ta ₂ O ₅ - 97.2 SiO ₂	8	350	38	64
2.3 ZrO ₂ - 97.7 SiO ₂	8	300	33	61
2.7 ZrO ₂ - 97.3 SiO ₂	48	300	30	58
2.8 ZrO ₂ - 97.2 SiO ₂	8	300	30	64
2.9 ZrO ₂ - 97.1 SiO ₂	8	300	27	60

Catalyst composition, weight percent	Hours of test.	Tempe- rature °C	Per pass yield, mole percent	Ultimate yield, mole percent
2.0 HfO ₂ - 98.0 SiO ₂	24	300	29	64
0.001 CuO - 2.0 Ta ₂ O ₅ - 98.0 SiO ₂	8	350	36	60
1.1 CuO - 2.0 Ta ₂ O ₅ - 96.9 SiO ₂	12	350	40	63
0.1 ZrO ₂ - 1.7 Ta ₂ O ₅ - 98.2 SiO ₂	48	300	22	63-57
0.2 ZrO ₂ - 2.3 Ta ₂ O ₅ - 97.5 SiO ₂	48	300	29	64
0.2 ZrO ₂ - 1.1 Ta ₂ O ₅ - 98.7 SiO ₂	8	350	18	62
1.8 ZrO ₂ - 1.7 Ta ₂ O ₅ - 96.5 SiO ₂	48	350	29	64
1.0 MgO - 2.0 Ta ₂ O ₅ - 97.0 SiO ₂	8	350	38	62
2.0 MgO - 2.0 Ta ₂ O ₅ - 96.0 SiO ₂	48	350	32	60-58
8.0 MgO - 2.0 Ta ₂ O ₅ - 90.0 SiO ₂	48	350	31	60
0.5 Ag ₂ O - 2.0 Ta ₂ O ₅ - 97.5 SiO ₂	.8	350	37	60

TABLE B-3
 Comparison of fixed-bed and fluidized-bed operation
 (Ethanol to acetaldehyde mole ratio 2.75:1)

Catalyst	Fluidized Bed			Fixed Bed			
	Temp., °C	Feed rate, ml/hr/ml	Process yield, percent	Temp., °C	Feed rate, ml/hr/ml	Process yield, percent	Ultimate yield, percent
1. Al ₂ O ₃	350	1.10	37.3	350	0.4	21.0	30.0
2. ThO ₂	375	1.10	35.7	-	-	-	-
3. ZrO ₂	400	1.00	30.5	400	0.4	8.0	9.0
4. ZrO ₂ :SiO ₂ (2:98)	300	0.66	37.3	300	0.4	32.0	54.0
5. ZrO ₂ :SiO ₂ (3:97)	350	0.66	32.3	350	0.4	30.8	49.0
6. MgO:SiO ₂ (70:30)	400	0.66	35.3	400	0.4	23.0	45.0
7. Al ₂ O ₃ :ZrO ₂ (50:50)	375	1.00	33.5	300	0.6	8.0	-
8. Al ₂ O ₃ :ThO ₂ (50:50)	375	1.00	31.0	-	-	-	-
9. Al ₂ O ₃ :ZrO (60:40)	375	1.00	43.8	-	-	-	-

APPENDIX C

Chemical Formulae of Some Important Compounds Formed During Butadiene Synthesis.

Acetaldehyde	CH_3CHO
Acetylene	$\text{CH}\equiv\text{CH}$
Acetal-dol	$\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2-\text{CHO}$
Acetic acid	CH_3COOH
Butadiene (1,3-)	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
1-Butene	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$
2-Butene	$\text{CH}_3\text{CH}=\text{CHCH}_3$
n-Butane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
1,2-Butadiene	$\text{CH}_2=\text{C}=\text{CHCH}_3$
Butaraldehyde	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CHO}$
Butalene Glycol (1,3-Butanediol)	$\text{CH}_3-\text{CH}(\text{OH})=\text{CH}_2-\text{CH}_2\text{OH}$
Crotonaldehyde	$\text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$
Crotyl alcohol	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2(\text{OH})$
Ethanol	$\text{CH}_3-\text{CH}_2(\text{OH})$
Ethyl acetate	$\text{CH}_3-\text{COO}-\text{CH}_2-\text{CH}_3$
Ethyl ether	$\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$
Ethylene	$\text{CH}_2=\text{CH}_2$
Ethyl acetal	$\text{CH}_3-\text{CH}(-\text{O}-\text{CH}_2-\text{CH}_3)_2$
Propylene	$\text{CH}_3\text{CH}=\text{CH}_2$
Propane	$\text{CH}_3\text{CH}_2\text{CH}_3$
Vinyl ether	$\text{CH}_3-\text{CH}(\text{OH})(\text{OC}_2\text{H}_5)$
Water	H_2O

APPENDIX D

Experimental results are presented in tables D-1 to D-5. These experiments are conducted at the Development laboratory of the Synthetics and Chemicals Ltd., Bareilly. The description of pilot plant is given in Section 4.3.

Imported fresh catalysts, cupric oxidized promoted catalyst and freshly prepared tantala-silica catalyst on Jai Chemicals are used for performance evaluation. Table D-1 represents the performance analyses of catalyst C-1 on intermittent feed basis and continuous 120 hours cycle. The composition of product for catalyst C-1 is given in Table D-2. Table D-3 and D-4 gives the performance analysis of various CuO promoted catalyst and the performance analysis of freshly/^{prepared} tantala-silica and cupric oxide promoted tantala-silica catalyst on Jai Chemical silica gel are given in Table D-5.

TABLE D-1

Catalyst Performance Test Runs
(Carried out at Synthetics and Chemicals Ltd., Bareilly)

Catalyst description	Imported fresh catalyst promoted with CuO. (1.2 Ta ₂ O ₅ -1.22 CuO, 97.58 silica gel)									
	Run No	1	4	5	7*	8*	9	9	9	
Operating hours				Intermittent feed basis			2	42	82	120
<u>Operating conditions</u>										
Reactor temperature, °C	331	350	350	350	330	330	330	330	330	330
Total feed, gm.	374.2	352.8	375.6	410.5	336.3	366.6	357.4	370.7	361.4	361.4
Ethyl alcohol in feed, gm.	254.5	225.1	224.8	275.2	226.8	240.0	233.0	239.8	230.2	230.2
Acetaldehyde in feed, gm	78.4	76.2	76.5	77.2	67.3	72.0	75.1	78.4	69.4	69.4
Alcohol to acetaldehyde feed mole ratio	3.01	2.82	2.81	3.41	3.21	3.19	2.97	2.92	3.17	3.17
Space velocity LHSV	0.61	0.59	0.61	0.69	0.56	0.61	0.58	0.60	0.59	0.59
Accountability of feed to products.	97.89	98.09	97.76	100.97	102.83	97.23	98.24	98.85	97.20	97.20
<u>Experimental data</u>										
Butadiene formed, gm.	71.9	65.4	72.0	62.6	52.7	56.9	42.3	34.7	27.7	27.7
Acetaldehyde used, gm.	47.2	43.1	42.7	41.9	48.2	31.8	37.0	32.0	18.3	18.3
Ethyl alcohol used, gm.	147.4	147.7	116.6	164.4	112.3	123.3	53.6	36.5	32.4	32.4
<u>Mole percent results</u>										
Single pass yield	35.14	36.56	40.24	29.95	30.29	30.75	23.15	18.36	15.60	15.60
Ethyl alcohol selectivity	40.01	37.72	52.59	32.41	39.95	39.32	67.27	81.02	72.96	72.96
Acetaldehyde selectivity	119.88	123.78	137.32	121.67	88.97	145.96	93.16	88.21	123.46	123.46
Ultimate selectivity from ethanol.	58.73	56.67	74.27	50.26	53.69	60.83	75.38	81.08	88.85	88.85
<u>Production rate g/l/hr</u>	95.74	90.21	99.31	86.30	72.67	78.40	58.40	47.84	38.27	38.27

Run 2 and 6 spoiled due to leakage in sample collection assembly,
Run 3 spoiled due to breakage of fractionating head.

*After one regeneration in reactor at 410°C.

TABLE D-2

Product Composition for Various Runs Tested in Table D-1
(Carried out at Synthetics and Chemicals Ltd., Bareilly)

Catalyst description Imported fresh catalyst promoted with CuO.
(1.2 Ta₂O₅-1.22 CuO-97.58 SiO₂)

Run No.	1	4	5	7	8	9	9	9	9	9
Operating hours	Intermittent feed basis									
Components										
Ethyl alcohol	29.16	22.36	29.45	26.72	33.12	32.83	51.09	55.45	56.32	
Acetaldehyde	8.52	9.58	9.21	8.52	11.80	11.31	10.84	12.65	14.56	
Ethyl ether*	2.35	2.36	2.44	1.64	2.43	2.40	2.09	2.90	2.59	
Ethyl acetate	1.43	0.84	0.0	0.96	1.05	1.20	0.90	nil	nil	
Butadiene	18.25	18.90	19.61	15.09	15.23	16.0	12.06	9.46	7.9	
CIS-butene-2	0.99	1.26	0.71	1.31	0.91	0.95	0.13	0.10	0.12	
Trans-butene-2	1.19	1.40	1.01	1.91	1.25	1.30	0.25	0.18	0.21	
Butene-1	2.24	1.69	1.41	3.70	2.22	2.25	0.39	0.16	0.15	
n-butane	0.03	0.04	0.04	0.03	0.02	0.04	nil	0.003	0.003	
iso-butane	1.16	1.61	1.13	1.67	0.87	0.585	0.53	0.35	0.37	
Propylene	0.11	0.10	0.05	0.11	0.05	0.12	0.07	0.01	0.007	
Ethylene	3.23	1.78	1.53	1.68	1.27	0.79	0.83	0.87	1.29	
Hydrogen	-	0.427	0.31	0.43	0.40	0.3	0.07	0.06	0.06	
Water + unidentified HBF	30.64	37.64	33.10	36.24	29.44	29.924	29.745	17.773	16.433	

*Ethyl ether in feed stream was 2.53 percent, 2.67 percent, 3.22 percent, 3.08 percent, 2.30 percent in runs no. 1, 4, 5, 7 and 8 respectively. In feed stream of run no. 9 ethyl ether was 2.43 percent, 2.43 percent, 2.60 percent, 2.45 percent at 2, 42, 82 and 120 hours respectively.

TABLE D-3

Catalyst Performance Test Runs
(Carried out at Synthetics and Chemicals Ltd., Bareilly)

Catalyst description	Imported fresh catalyst promoted with CuO. (1.05Ta ₂ O ₅ -1.22 CuO-97.86SiO ₂) Regenerated at 410°C.				(1.05Ta ₂ O ₅ -1.09CuO-97.86SiO ₂) Regenerated at 410°C			
	1	1	73	25	2 ⁺	3	M-26A	M-26B
Run No.	1	37	330	330	330	330	329	331
Operating hours	1				hrs	67 hrs.	1.5	46.5
Operating conditions, °C				40	minute	25 minute		
Reactor temperature, °C	330	330	330	330	330	330	329	331
Total feed, g	348.7	337.6	336.0	365.6	365.6	356.7	189.3	194.6
Ethyl alcohol in feed, g	227.2	219.3	226.1	235.2	235.2	228.5	120.3	124.3
Acetaldehyde in feed, g	77.2	79.6	74.8	77.5	77.5	80.5	40.8	42.7
Alcohol to acetaldehyde feed mole ratio.	2.82	2.63	2.89	2.9	2.9	2.71	2.82	2.78
Space velocity LHSV	0.61	0.59	0.58	0.6	0.6	0.59	0.60	0.60
Accountability of feed to products, percent	93.05	100.4	99.04	96.2	96.2	98.04	101.4	96.4
Experimental Data								
Butadiene formed, g	47.5	25.4	19.9	3.06	3.06	1.52	19.4	15.7
Acetaldehyde used, g	35.8	29.7	24.7	2.61	2.61	11.82	15.8	20.7
Ethylalcohol used, g	163.8	37.5	23.1	46.34	46.34	2.26	63.3	30.3
Mole percent results								
Single pass yield,	26.30	14.33	11.14	1.65	1.65	0.82	20.33	15.83
Ethyl alcohol selectivity	24.71	45.83	68.51	5.66	5.66	57.14	26.16	44.19
Acetaldehyde selectivity,	108.24	69.71	65.59	-	-	10.41	90.64	61.89
Ultimate selectivity from ethanol	39.61*	53.46	64.17	10.64	10.64	16.42	39.82	49.77
Production rate g/l/hr	70.23	37.60	29.41	4.21	4.21	2.09	53.63	43.33

*The low ultimate selectivity from ethanol could possibly be due to poor feed to product accountability.

+ Run No.1 abandoned after half an hour due to excessive formation of gases.

TABLE D-4

Catalyst Performance Test Runs
(Carried out at Synthetics and Chemicals Ltd., Bareilly)

Catalyst description
Fresh imported catalyst promoted
with CuO.
(1.45 Ta₂O₅-1.03 CuO-97.52 SiO₂)

(1.40 Ta₂O₅-0.60 CuO-98.0 SiO₂)

Run Number	I-27A	I-27B	I-27C	I-27D	30B*	30C
Operating hours	1.75	39.50	75.50	113.00	14	52
Operating conditions						
Reactor temperature, °C	330	330	330	330	329	330.5
Total feed, g	367.5	355.1	386.6	380.4	346.3	372.1
Ethyl alcohol in feed, g	256.7	243.6	268.2	266.1	245.3	260.9
Acetaldehyde in feed, g	82.7	82.10	84.30	82.20	73.1	82.1
Alcohol to acetaldehyde feed mole ratio.	3.0	2.84	2.90	3.1	3.21	3.04
Space velocity LHSV	0.60	0.58	0.61	0.60	0.55	0.60
Accountability of feed to products, percent.	91.30	96.50	98.99	97.20	92.0	92.8
Experimental Data						
Butadiene formed, g	63.0	42.3	36.8	30.9	9.8	2.4
Acetaldehyde used, g	52.4	48.1	42.7	37.1	0.1	23.5
Ethyl alcohol used, g	140.8	69.6	60.7	52.6	60.9	17.6
Mole percent results						
Single pass yield	31.30	21.90	19.0	15.0	5.20	1.18
Ethyl alcohol selectivity	38.10	51.70	55.80	50.1	13.74	8.74
Acetaldehyde selectivity	97.90	71.50	75.80	68.0	5336.07 [†]	14.39
Ultimate selectivity from ethanol	53.50	57.90	62.0	55.7	27.41	10.53
Production rate g/l/hr	86.8	58.90	54.80	42.7	13.55	3.32

*Run No. 30A spoiled due to choking at the precooler outlet.

†The extremely high acetaldehyde selectivity was due to the fact that only 0.1 gram acetaldehyde was used up.

TABLE D-5

Catalyst Performance Test Runs
(Carried out at Synthetics and Chemicals Ltd., Bareilly)

Catalyst description	Freshly prepared catalysts using Slica Gel from Jai Chemicals.			
	TagO ₅ -	SiO ₂ -	CuO-	SiO ₂ -
Run No.	L-30A	L-30B	L-30C	L-30D
<u>Operating Hours</u>	2	38	74	108
<u>Operating conditions</u>				
Reactor temperature, °C	332	331	331	329
Total feed, g	353.1	375.5	370.0	328.0
Ethyl alcohol in feed, g	235.9	253.9	249.8	247.6
Alcohol to acetaldehyde feed mole ratio.	2.63	2.84	2.80	2.86
Space velocity LHSV	0.57	0.59	0.60	0.59
Accountability of feed to products, percent.	97.52	100.06	98.35	96.03
<u>Experimental Data</u>				
Butadiene formed, g	64.76	55.40	50.49	39.60
Acetaldehyde used, g	72.56	59.90	54.77	49.90
Ethyl alcohol used, g	113.58	95.63	85.38	81.45
<u>Mole percent results</u>				
Single pass yield	33.88	27.48	25.37	20.19
Ethyl alcohol selectivity	48.56	49.33	50.35	41.43
Acetaldehyde selectivity	72.71	75.25	75.11	64.62
Ultimate selectivity from ethyl alcohol.	56.28	57.61	58.27	48.83
<u>Production rate g/l/hr</u>	89.33	76.40	69.65	54.64
	L-31A	L-31B	L-31C	L-31D
	2	39	76	76
	329.5	330.0	330.0	330.0
	368.0	376.8	378.1	378.1
	247.7	260.4	256.3	256.3
	2.75	3.09	2.96	2.96
	0.60	0.61	0.61	0.61
	99.34	113.74	59.27	59.27
	71.1	42.1	43.2	43.2
	67.3	63.3	63.6	63.6
	149.3	110.7	71.5	71.5
	35.85	20.69	21.12	21.12
	40.55	32.41	51.55	51.55
	86.67	54.19	55.35	55.35
	53.63	39.28	51.21	51.21
	98.01	58.11	59.61	59.61