

Figure 11. Thermal Conductivity of Unvented Latex against Per Cent Conversion

Temp., ° C.	Symbol
28.1	○
38.6	△

where t = temperature in ° C. The data of Smith (13), based on the work of Bridgman (5) and Daniloff (6) agree with this expression within 5.1% at 30° C. but lie about 55% higher at 75° C. The present calibration data on ethanol lie from 7.9 to 8.3% above this equation throughout the temperature range of 28° to 48° C.

The data of Bates, Hazzard, and Palmer on methanol are represented by the equation:

$$K_t = 0.00054 - 0.00000150 t \text{ cal./sec., cm., } ^\circ \text{ C.}$$

Smith's data on methanol agree with this equation exactly at 30° C. but lie about 14% higher at 75° C. In the present work, the value obtained for methanol at 33.3° C. was about 7% below the equation. Therefore the present apparatus gives results

that agree within about $\pm 7\%$ with the data of Bates *et al.* The latter are probably the best available at present, judging from their completeness and the reproducibility reported.

Data on Latex. The thermal conductivity of stripped latex and three samples of vented latex between 51.0 and 75.5% conversion over a temperature range of 28° to 48° C. have been obtained and are shown in Table II and Figure 10. The conductivity of the 51.0% sample is constant over the given temperature range within the experimental error; for the 69.9 and 75.5% conversion samples, the conductivity increases about 10% over this temperature range. In Figure 11, the thermal conductivity of unvented latex is plotted against per cent conversion for three temperatures. Conductivity increases about 50% at all temperatures between the conversions of 50 and 75.5%.

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BUTADIENE FROM ETHYL ALCOHOL

Improved Production Processes

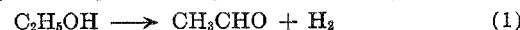
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The American process for production of butadiene from ethyl alcohol, as developed by the Carbide and Carbon Chemicals Corporation, was operated with a 2.75 to 1 molar ratio of ethyl alcohol to acetaldehyde feed for optimal yields of butadiene. Two improved methods utilizing different over-all feed ratios have been devised; these give higher yields than do the conventional plant operations. First, it has been demonstrated that injecting an auxiliary side stream, rich in acetaldehyde, into the catalyst bed at or above the midsection, where the aldehyde is rapidly depleted, leads to yields of 64 to 68 mole % and conversions of 35 to 37 mole % per pass. These results compare with 63 and 34 mole %, respectively, for calibration runs without the side stream. An increased total throughput, hence increased production, is also realized. The second novel method of operation comprises an auxiliary feed of ethyl alcohol added at or below the midpoint of the catalyst section; this affords consistent yields of about 76 mole %.

Preliminary work on a two-step process with ethyl alcohol-acetaldehyde feeds has been found promising but further study is required. Carbon deposition is not prohibitive in these procedures.

PRODUCTION of butadiene from ethyl alcohol, as developed by the Carbide and Carbon Chemicals Corporation (7), is a two-step process represented by the following equations:



The investigations of the present project were concentrated on the second step of this process because the first step gave a yield of 92% acetaldehyde whereas the best over-all yield of butadiene from the two steps was 65% of theoretical. The outlook was hopeful for improvement in view of the fact that an increase of only 1% in the yield of butadiene would represent an enormous saving in both time and money in the emergency rubber program.

The major efforts of the program were assigned to the betterment of the catalyst employed in the second step. Two or more successive reactions are involved in this step and the method of plant operation was a limiting factor for obtaining optimal conditions for these several reactions. Some attention therefore was devoted to devising new methods of operating this second step. The present paper records only the studies relevant to methods of operation—studies initiated with the idea of controlled variation of the ratio of reactants in the butadiene reactors. Because of the early termination of the project, this work was not carried to an entirely conclusive end, but the results are reported here to demonstrate improvements obtainable in the event that future requirements will justify further refinements in the process. A logical continuation of this work would involve establishing optimal partial pressures of reactants as well as the optimal ratio which should be maintained in various portions of the catalyst bed.

COMMERCIAL PROCESS

Early in this work it was confirmed that two or more successive reactions occur during the formation of butadiene from acetaldehyde and ethyl alcohol according to the proposal of Quattlebaum *et al.* (5). The optimal plant operating conditions for carrying out these successive reactions in one reactor as established by Carbide and Carbon Chemicals Corporation were as follows:

Temperature	325–350° C.
Pressure	Essentially atmospheric
Feed Rate	0.4 to 0.5 vol. liquid feed per vol. of catalyst per hour (liquid hourly space velocity)
Feed Ratio ^a	2.75 moles ethyl alcohol per mole acetaldehyde

^a Feed ratios refer to moles of ethyl alcohol per moles of acetaldehyde.

The optimal feed rate is believed to be 0.6 liquid hourly space velocity (2) instead of the above rate.

In the standard commercial process (7) for producing butadiene from ethyl alcohol the initial step comprises the passing of the ethyl alcohol vapors over a suitable catalyst to produce acetaldehyde. Ethyl alcohol and acetaldehyde are then mixed in 2.75 to 1 to 3 to 1 mole ratio, the vapors of this mixture passing over a suitable catalyst (about 2% tantalum pentoxide on silica gel) at 325° to 350° C. and 0.4 to 0.5 space velocity to produce butadiene in about 62 to 63 mole % yield based on total ethyl alcohol feed. Regeneration by burning off in situ at 400° C. is necessary at intervals of 100 to 120 hours. With fresh or new catalyst, mole conversions of 28 to 30% are obtained per pass; after prolonged operation conversions of about half this amount are realized. A molar ratio of ethyl alcohol to acetaldehyde of 2.75 to 1 to 3 to 1 gives the optimal initial feed composition. Somewhat higher ratios of ethyl alcohol to acetaldehyde may give rise to slightly higher yields but lower conversions per pass. Higher concentrations of acetaldehyde lead to higher conversions but shorter periods of operation between catalyst regenerations because of excessive carbon deposition on the catalyst. (Standard laboratory runs with fresh catalyst showed about the same over-all yield as the commercial plant but the laboratory mole per cent conversion per pass was higher—about 33% against 28 to 30%.)

Variations in plant reactor composition thus were limited to those resultant from a fixed initial feed. Restricted conditions of temperature and feed rate likewise had been established for optimal yields in the current plants. The problem of improving yield and/or conversion seemed to be one of finding new methods or systems of operation which permitted controlled variation of reaction compositions in various sections of the catalyst bed. A study of variation of catalyst and temperature in the fore and after parts of the reaction system was begun but not completed.

OPERATING METHODS INVESTIGATED

The methods investigated are based on the need of controlling the ratio of reactants in the reactors as well as in the feed. A

TABLE I. COMPARISON OF OPERATION PROCEDURES
(Temperatures 350° C.; commercial tantalum-silica catalyst; initial feed ratio 2.75)

Procedure	Average Feed Rate, L.H.S.V. ^a	Over-all Ethyl Alcohol to Aldehyde Molar Feed Ratio	Conversion to C ₄ H ₆ , Mole %	Yield of Butadiene, Mole %
Standard conventional operation	0.40	2.75	34	63
1 ^b	0.40	1.76	31	66
2A	0.58	2.12	37	68
2B	0.59	4.07	28	76
3	0.40	2.10	38	67
Ethyl alcohol (92%) feed	0.40	..	Nil	..
Acetaldehyde feed	0.40	..	Nil	..

^a Liquid hourly space velocity.

^b Auxiliary acetaldehyde feed added at four points.

factor usually ignored in discussions of optimal conditions for plant operation was the gradual change in feed ratio throughout the 17.5-foot length of catalyst bed. An entering feed ratio of 2.75 to 1 might be accompanied by an effluent having an 8 to 1 ratio of ethyl alcohol to aldehyde. Therefore any assumption implying one optimal concentration of ethyl alcohol and acetaldehyde throughout the reaction chamber appeared highly improbable; it would be fortuitous if the same operating conditions, the same concentrations of reactants, and the same catalyst were optimal for the several reactions involved.

Three variations in operating methods were included in this study:

1. Multiple-point addition of an auxiliary feed
2. Spot addition of an auxiliary feed: (A) enriched acetaldehyde feed as a side stream; and (B) high ethanol feed as a side stream
3. Two-stage process with ethanol-acetaldehyde feeds

The data for the third operating method show promise but this phase of the work was not carried to a conclusive point.

A comparison of these operating procedures under the commercial optimal conditions (other than reactant ratios) is set forth briefly in Table I. Data for conventional operations and for ethyl alcohol alone and acetaldehyde alone as feeds are included for comparison.

From the standpoint of yield of butadiene the best procedure appears to be that in which alcohol is added as a side stream

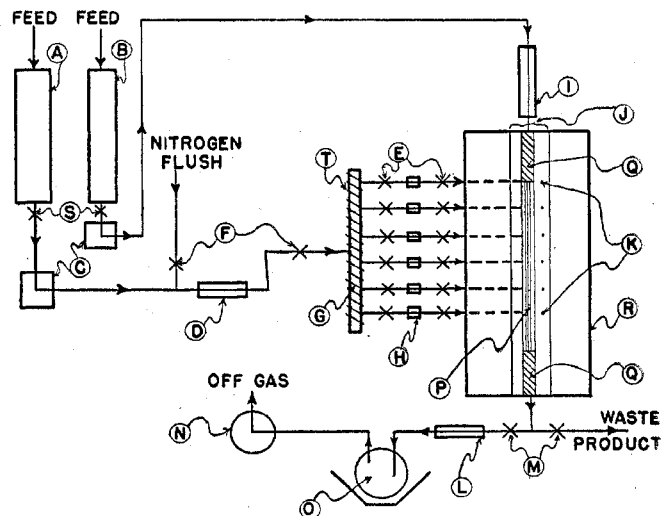


Figure 1. Multiple-Point Injection Test Unit

A = feeder 1:1 mixture; B = feeder 2.75:1 mixture; C = Corson bellows pump; D = feed preheater (steam); E = needle valves; F = valves; G = manifold; H = orifice housing; I = feed preheater (steam); J = furnace block; K = thermocouples; L = water condenser; M = valves; N = wet test meter; O = receiver flask; P = 300 cc. of catalyst; Q = inert packing; R = furnace shell and insulation; S = stopcocks; T = heating element

(method 2B) at or below the midpoint of the catalyst bed. A combination thereof with the operation (method 2A) in which acetaldehyde-rich feed is added above the midpoint might show further improvement, but available time did not permit an assessment of this combination. Further work on the two-stage procedure (method 3) is desirable to establish optimal catalyst and conditions for the initial crotonaldehyde condensation in view of the high conversions obtained.

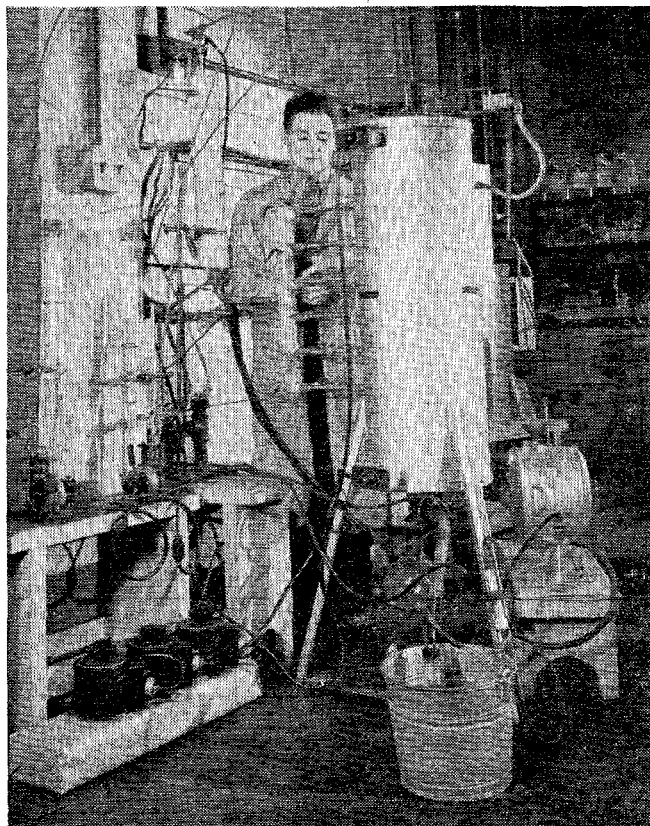


Figure 2. Laboratory Unit with Multiple-Point Feed System

Equipment. The reactor and assembly evolved for flexible operations are illustrated by a flow diagram, Figure 1, and photograph, Figure 2.

The reaction chamber comprised an insulated electrically-heated 3-inch stainless steel block, 36 inches long with a 1-inch hole drilled centrally. A series of six 0.625-inch holes at 4-inch intervals were connected with side arms equipped with needle valves for control of auxiliary feed flows. (The catalyst bed comprised a zone 24 × 1 inch inside diameter.) Seven thermocouples and auxiliary devices for recording and controlling catalyst-bed temperatures were provided. Temperature was controlled so as to have a spread of only a few degrees along the entire length of the catalyst section of the furnace block.

The top flange plate closure was connected to a feed steam preheater with standard fittings. The bottom plate was joined in like manner to a water condenser followed by a product-collection system. The side stream or auxiliary feed entered first a steam preheater and then an electrically-heated manifold (maintained at about 165° C.). Feeds were pumped from buret reservoirs by means of bellows-type pumps (1). Other details of the assembly and equipment are clearly shown in Figures 1 and 2.

Operating Procedure. The reactor was charged as follows: 50 cc. of an inert packing (Carborundum) was followed with 300 cc. of 8- to 12-mesh catalyst; finally 65 cc. of the same inert

packing was added to serve as the preheat section. The catalyst was flushed with nitrogen while bringing up and adjusting the temperature to 350° C.

After charging the feed reservoirs with the desired feeds the nitrogen flush was discontinued and the bellows pumps were started. Operation for 1 hour constituted the prerun during which final adjustments in temperature and feed rates were made. The effluent was shunted to the waste-product receiver. Also, during this interval, the product receiver flask was attached to the condenser and packed in dry ice. Just prior to completion of the prerun the feed reservoirs were refilled. Immediately at the end of the prerun the flow to the product receiver was started; at the same time the entry to the waste-product receiver was closed.

At the end of the 4-hour run the product flask was weighed and stored in a dry-ice chamber to await analysis. The net weight of the product divided by the weight of the total feed gave the liquid weight recovery; the amount of gas was of the order of 1 liter per 100 grams of feed. At the beginning of the project the same charge of catalyst was employed in a series of runs employing only a nitrogen-flushing period between runs. Contrary to previous information this practice was found inadequate for maintaining consistent catalytic activity. To obtain consistently comparable data fresh catalyst was necessary in each run.

Analytical Procedure. The analytical procedure consisted of an initial distillation through an 18-plate packed column and collection of the following fractions: initial boiling point to 13° C.; 13° to 30° C.; and 30° to 95° C. These fractions were analyzed as follows: the first fraction for butadiene and acetaldehyde; the second fraction for acetaldehyde; and the third fraction for ethyl alcohol acetaldehyde, and acetal. Butadiene was determined on an aldehyde-free gas sample by the Koppers-Hineckley maleic anhydride method (8); acetaldehyde and acetal were determined by an hydroxylamine-hydrochloride method; and ethyl alcohol was found by phthalic anhydride esterification according to a modification of a method of Elving *et al.* (9).

Materials. Acetaldehyde (Niacet Chemical Company) of at least 99% purity and ethyl alcohol (Commercial Solvents Corporation) of 92 weight % were employed in preparing the ethyl alcohol-acetaldehyde feed mixtures. Crotonaldehyde, from Carbide and Carbon Chemicals Corporation, was fractionated to about 99% purity. Commercial tantala-silica catalyst was used as received from the Koppers, Kobuta, Pa., butadiene plant (mostly 3 to 10 mesh). Commercial silica gel catalyst was obtained from the Davison Chemical Company. Alkaline-set silica gel was prepared by the group on catalyst preparation (8).

Calculation of Results. The yield values were calculated as follows:

$$\text{Conversion, mole \%} = \frac{\text{moles of } C_4H_6 \text{ formed} \times 200}{\text{moles of feed } (C_2H_5OH + CH_3CHO)}$$

$$\text{Yield (or efficiency), mole \%} = \frac{\text{moles of } C_4H_6 \text{ formed} \times 200}{\text{moles } C_2H_5OH \text{ consumed} + \frac{\text{moles } CH_3CHO \text{ consumed}}{0.92}}$$

$$\text{Acetaldehyde (or ethyl alcohol) efficiency, mole \%} = \frac{\text{moles } C_4H_6 \text{ formed} \times 100}{\text{moles } CH_3CHO \text{ (or } C_2H_5OH) \text{ consumed}}$$

The moles of acetaldehyde consumed were divided by 0.92 because the commercial dehydrogenation of ethyl alcohol gave about 92% yields of acetaldehyde. The yield data in this paper therefore refer to an over-all efficiency of the process based on ethyl alcohol in conformity with plant practice. For conversion, this factor 0.92 is not employed, again because of the plant practice.

Reproducibility of Results. Preceding this study 16 duplicate experiments were made on fresh commercial catalyst as received, at 350° C., 2.75 to 1 feed ratio, 0.4 liquid hourly space velocity, and 8-hour duration. Knowledge of reproducibility is essential to avoid misinterpretations of inherent vagaries of the intricate sequence of the steps of the operation and reaction.

	Mean	Standard Deviation
Over-all efficiency, %	63.6	1.6
Conversion, %	35.6	2.5
Ethyl alcohol efficiency	55.1	2.1
Acetaldehyde efficiency	82.7	4.2

MULTIPLE-POINT ADDITION OF AUXILIARY FEED

During normal plant operation the acetaldehyde concentration decreases throughout the catalyst section of each plant reactor while the alcohol to aldehyde ratio increases. To determine whether a sustained 2.75 to 1 or lower feed ratio is actually optimal, runs were made with and without the addition of auxiliary acetaldehyde simultaneously through the lower five jets (Table II). Improvement in ultimate yield, but not conversion, was obtained as a result of multiple-point addition with jets 2 to 5, but not with jets 2 to 6. Although it is probable that these results could be improved by use of fresh or regenerated catalyst for each run, considerations of the mechanical and economic factors involved in providing multiple-point addition to each of the many tubes in a commercial jacketed reactor led to investigation of simpler methods of operation employing spot-addition of an auxiliary feed. In all subsequent work fresh catalyst was used in each run to obviate any question of comparability of data.

SPOT-ADDITION OF AN AUXILIARY FEED

Enriched Acetaldehyde Feed as Side Stream. In a series of five 8-hour standardization runs using commercial tantala-silica catalyst at the optimal plant conditions (350° C. with 2.75 to 1

TABLE II. PROCEDURE 1—MULTIPLE-POINT ADDITION OF ALDEHYDE FEED

Commercial tantala-silica catalyst^a; 350° C.; 0.4 average liquid hourly space velocity; and material balance 99 to 100%

Type of Operation	No. of Runs	Over-all Molar Feed Ratio ^b	Conversion per Pass, Mole %	Yield, Av. Mole %
1 ^c (jets 2-6)	3	1.89:1	26	58
1 ^c (jets 2-5)	1	1.76:1	31	66
Standard ^d	3	2.75:1	34	63

^a Regeneration of catalyst was not effected between runs.

^b Over-all feed ratio as used throughout this paper is not descriptive of ratio of reactants at any point in the reaction zone but applies only to the mole ratio of total reactants (ethyl alcohol:acetaldehyde) fed during the test via top and jet feed streams.

^c Feed to top 2.75 to 1; multiple-point addition of 1 to 1 feed at jets indicated.

^d Feed to top of catalyst bed 2.75 to 1; no auxiliary feed.

TABLE III. PROCEDURE 2A—SPOT-ADDITION OF AUXILIARY FEED

(Commercial tantala-silica catalyst; median temperature 350° C.; 2.75 to 1 feed to top; 1 to 1 feed to jet indicated, about 20% of total feed; 4-hour runs preceded by 1-hour prerin; material balances 99 to 100%; average liquid hourly space velocity about 0.58)

1:1 Feed to Jet No.	No. of Runs	Av. Over-All Mole Ratio EtOH:AcH	Conversion, Mole %	Yield, Av. Mole %	Ethyl Alcohol Efficiency, %	Aldehyde Efficiency, %
1	1	2.07:1	35	62	52	83
2	5	2.18:1	35	64	58	80
3	4	2.17:1	36	66	59	81
4	6	2.12:1	37	68	61	82
5	4	2.12:1	34	67	60	80
6	5	2.18:1	31	62	53	79
^a	3	2.75:1	34	63	55	83
^b	1	3.43:1	28	60	47	80

^a Standardization runs (with no jet feed) at 0.40 liquid hourly space velocity.

^b Ethyl alcohol instead of acetaldehyde: ethyl alcohol feed to jet 2 (0.40 liquid hourly space velocity).

TABLE IV. PROCEDURE 2B—EFFECT OF INCREASED ETHYL ALCOHOL CONCENTRATION

(Commercial tantala-silica catalyst; 350° C.; 2.75 to 1 feed to top; 92 wt. % ethyl alcohol to jet indicated; material balance 98.1 to 100%; and average liquid hourly space velocity about 0.57)

Ethyl Alcohol to Jet No.	No. of Runs	Over-All Ratio EtOH:AcH	Jet Feed as Vol. % of Total Feed	Conversion, Av. Mole %	Yield, Mole %	Ethyl Alcohol Efficiency, %	Aldehyde Efficiency, %
2 ^a	1	3.43:1	16.3	28	60	47	90
3	2	2.84:1	24.0	23	60	50	83
4	4	4.07:1	27.4	28	76	66	94
5	2	4.00:1	26.7	28	70	62	86
6	2	3.96:1	25.9	26	66	59	85
^b	3	2.75	0	34	63	55	83

^a Liquid hourly space velocity was 0.40.

^b Standardization runs at 0.40 liquid hourly space velocity with no jet feed.

TABLE V. PROCEDURE 2B—EFFECT OF INCREASED ETHYL ALCOHOL CONCENTRATION

(Standard tantala-silica catalyst; 350° C.; 2:1 feed to top; 92 wt. % ethyl alcohol to jet indicated; material balance 99 to 100%; and av. over-all feed ratio 2.9:1)

Jet for Auxiliary Feed	No. of Runs	Av. Liquid Hourly Space Velocity	Av. Jet Feed as Vol. % of Total Feed	Conversion, Av. Mole %	Yield, Av. Mole %	Ethyl Alcohol Efficiency, %	Aldehyde Efficiency, %
3	2	0.48	25.3	28	67	62	80
4	2	0.56	24.2	31	66	61	79
5	2	0.57	25.1	33	69	67	77
6	2	0.58	25.1	31	63	59	74
^a	2	0.40	0	40	60	59	69

^a Calibration run with 2:1 feed and no side stream.

feed at 0.4 liquid hourly space velocity) the average mole ratio of ethyl alcohol to acetaldehyde varied from 2.75 to 1 (in feed to the top of the catalyst bed) to 7.83 to 1 (in the exit product). Investigation of spot-addition was initiated to establish the portions of the reaction zone where higher acetaldehyde concentrations are beneficial—that is, where auxiliary acetaldehyde should be added.

A stream of feed enriched in acetaldehyde (1 to 1 mole ratio of ethyl alcohol to acetaldehyde) was passed into the catalyst bed at various side entrances. The data are shown in Table III along with the findings in standard runs and in one run with ethyl alcohol side stream (the latter demonstrated the adverse effect of a high feed ratio in the forepart of the reactor). Yields and conversions were both enhanced by addition of acetaldehyde in the forepart of the system; ethyl alcohol efficiencies were likewise improved.

High Ethyl Alcohol Feed as Side Stream. Following the investigation of spot-addition of feeds enriched with acetaldehyde, the effect of increasing the ethyl alcohol concentration at various parts of the catalyst bed was studied. A series of runs was made in which 2.75 to 1 feed was led to the top of the catalyst bed with a side stream of 92 weight % of ethyl alcohol entering at each side arm in turn. The results are presented in Table IV. Although the over-all liquid hourly space velocity was different from the standard runs owing to the side streams, it has been concluded that the effect of this difference was minor, first because of results from other studies (2), and secondly because this liquid hourly space velocity was not a weighted value to correct for the fact that the side stream did not transverse the whole catalyst bed.

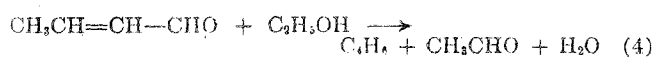
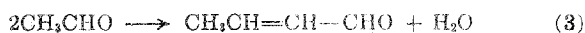
Highest yields as well as highest aldehyde and ethyl alcohol efficiencies were obtained with the ethyl alcohol side stream entering at or below the middle of the catalyst bed. It is apparent that with this method of operation conversions were markedly lower than when using a 1 to 1 feed as the auxiliary feed stream (or when operating in the standard manner passing 2.75 to 1 feed to the top without auxiliary feed). Actual production rate, however, was still high as a result of the high average over-all liquid hourly space velocity.

With the object of maintaining the high yields without incurring this decrease in conversion, runs were made in which additional ethyl alcohol was fed at intermediate points but a 2 to 1 feed was substituted for the 2.75 to 1 feed previously employed. The results of these runs shown in Table V are to be compared with data for 2.75 to 1 feed in Table IV. The 2 to 1 feed raised the conversion level but lowered the yield and aldehyde efficiency in comparison with 2.75 to 1 feed. Longer operations, preferably in a pilot plant, would be necessary to establish the rate of carbon deposition and length of operating cycle for 2 to 1 feed relative to standard operations (the efficacy of 2 to 1 instead of 2.75 to 1 feed in this type of operation would depend on considerations of operable cycle length and urgency of increasing production rate with a sacrifice in over-all yield).

Operation with the addition of an auxiliary feed stream, as defined above, might be carried out commercially with only relatively slight alteration of existing equipment. Two of the present reactors might be connected in series, auxiliary ethyl alcohol being added to the effluent product from the first reactor to make the feed entering the second.

DISCUSSION OF RESULTS

Reaction Mechanism. From Tables III, IV, and V it is clear that high conversions and yields are favored by methods of operation in which relatively high aldehyde concentrations obtain in the forepart of the catalyst bed with relatively high ethyl alcohol concentrations in the lower section. This conclusion is in accord with the mechanism represented by the equation proposed by Quattlebaum *et al.* (4, 5):



In view of findings from a study on the mechanism of this reaction (4, 5) Equations 3 and 4 appear to be well verified successive reactions of the process. Reaction 4 itself may involve two or more reactions. If aldol is formed it must be rapidly dehydrated to crotonaldehyde because crotonaldehyde, but not aldol, has been identified in the reaction products. (In other work (4) it was demonstrated that free crotyl alcohol is not a major intermediate, but that a catalyst complex involving crotonaldehyde and/or crotyl alcohol is a possible intermediate.)

Ethyl Alcohol or Acetaldehyde Alone as Feed. To determine the action of commercial tantalum-silica catalyst on ethyl alcohol at 350° C., runs were made in which 92 weight % ethyl alcohol was passed over the catalyst at 0.4 liquid hourly space velocity. About 0.5% acetaldehyde with no more than a trace of butadiene was produced and only slightly more noncondensable gas resulted than when passing 2.75 to 1 feed. Weight recoveries were good but ethyl alcohol in the liquid products amounts to only 82% of the amount fed. (Part of the alcohol consumed was attributed to ether formation.) This demonstrates a definite loss of ethyl alcohol to by-products independent of the butadiene reaction.

Likewise acetaldehyde alone was passed over the same catalyst at 325° C. and 0.4 liquid hourly space velocity; no butadiene was formed—only aldehyde condensation products (crotonaldehyde, higher aldehydes, etc.) and unreacted acetaldehyde were recovered. Crotonaldehyde was identified via 2,4-dinitrophenylhydrazone. There resulted about 63% recovery of acetaldehyde and a 15% conversion to crotonaldehyde. Apparently an equilibrium well toward the acetaldehyde side of the crotonaldehyde formation is approached in the absence of ethyl alcohol.

Ethyl Alcohol-Crotonaldehyde Feed. To test reaction 4 of the postulated mechanism, runs were made in which ethyl alcohol-crotonaldehyde mixtures were passed over the commercial tantalum-silica catalyst at 350° C. Good yields were obtained, as shown in Table VI. It appears from these data that

TABLE VI. BUTADIENE FROM ETHYL ALCOHOL-CROTONALDEHYDE

(Four-hour runs; standard tantalum-silica catalyst; 350° C.; 0.4 liquid hourly space velocity; material balance 99 to 100%)

Run	Mole Feed Ratio, Alcohol:Aldehyde	Conversion of Total Feed to C ₄ H ₆ , Mole %	Yield ^a , Mole%	Moles C ₄ H ₆ per Mole C ₄ H ₈ O Consumed
1	2.0	36	50	0.80
2	2.45	45	56	1.10
3	6.0	48	70	1.80

$$^a \text{Yield \%} = \frac{\text{moles C}_4\text{H}_6 \times 100}{\text{moles C}_1 \text{ feed consumed} + \text{moles C}_2 \text{ feed consumed}/2}$$

crotonaldehyde is a logical intermediate in the ethyl alcohol process. The high conversions indicate rapid reaction of crotonaldehyde with ethyl alcohol; probably the crotonaldehyde formation is the slower rate-controlling step of the process. Relative efficiencies of acetaldehyde and ethyl alcohol as effected by feed ratio throw further light on the interpretation.

Feed Ratio and Efficiencies. The effect on efficiencies of the individual reactants, due to variation of the initial feed ratio (when no adjustment of subsequent ratios of reactants is made) is shown in Table VII.

TABLE VII. EFFICIENCIES OF REACTANTS

(Four-hour runs; 350° C.; 0.40 liquid hourly space velocity; standard tantalum-silica catalyst)

Initial Feed Ratio	Initial Partial Pressure, Atm.		Conversion, Mole %	Yield, Mole %	% Efficiency	
	Acet-aldehyde	Ethyl Alcohol			Ethyl Alcohol	Acet-aldehyde
3.5:1	0.189	0.66	28	59	45	92
3:1	0.213	0.643	30	62	51	90
2.75:1	0.228	0.628	34	64	55	83
2.5:1	0.245	0.612	35	67	61	80
2:1	0.290	0.58	40	60	59	69
1.75:1	0.315	0.555	37	62	64	65
0.5:1	0.40	0.20	36	48	69	40

The trend toward increasing efficiency of acetaldehyde utilization and decreasing efficiency of ethyl alcohol utilization with increasing ethyl alcohol to acetaldehyde ratio in the initial feed is readily apparent.

Conclusions. There is thus no single optimal feed ratio for simultaneously maintaining optimal ethyl alcohol and acetaldehyde efficiencies. A compromise must be struck to attain optimal over-all yields. The data obtained by spot-addition of either reactant at varying points of the reaction system indicate that the optimal ratio in the forezone is different from that in the latter part of the reactor. The so-called optimal feed ratio in the standard process is fictitious and meaningless as far as the ratio of partial pressures of reactants throughout the reaction system is concerned. The inlet ratio of 2.75 to 1 has changed progressively to 8 to 1 at the outlet, and actual partial pressures of the reactants have fallen to relatively low values because of dilution by products of both the main and side reactions. Evidence obtained by diluting the feed with water (4) indicates that too low partial pressures of reactants decreases the over-all efficiency or yield, meaning that the ratio of formation of products to by-products is lowered. The predominating reaction in the forepart of the reaction zone leads to depletion of acetaldehyde which can be profitably countered by adding aldehyde-rich feed where a higher optimal partial pressure appears to exist. (The standard initial mole fraction of acetaldehyde of 0.223 decreases to 0.08 at the midpoint.) The effect of dilution can be minimized by addition of either or both reactants. Increasing the ethyl alcohol partial pressure, hence ethyl alcohol to aldehyde ratio, in the hind part of the reaction zone is interpreted as serving two purposes: more nearly completely reducing the crotonaldehyde to butadiene; and more efficiently effecting this reduction by offsetting the continual de-

crease in partial pressure of the ethyl alcohol while at the same time decreasing the contact time. The first point is possibly of lesser importance; the partial pressure of crotonaldehyde in effluent from standard runs is about 0.006 to 0.007 atmosphere whereas with added ethyl alcohol near the midpoint of the reaction zone the corresponding partial pressure is 0.003 atmosphere.

At this point it seemed expedient to postpone further study of optimal partial pressures in various parts of a one-step reaction system until optimal conditions of each individual reaction had been established.

TWO-STAGE PROCESS

First Stage. To investigate the role of tantalum-silica gel in the condensation of acetaldehyde to crotonaldehyde, acetaldehyde without ethyl alcohol was passed over the commercial tantalum-silica catalyst, over a commercial silica gel, and over alkaline-set gel prepared in this laboratory (8). The yields of crotonaldehyde in these exploratory runs are set forth in Table VIII. The silica gel appeared advantageous in these runs; the alkaline-set gel was the best.

TABLE VIII. EFFECT OF CATALYST ON ACETALDEHYDE
(Three-hour runs; 0.4 liquid hourly space velocity)

Temp., ° C.	Catalyst	% Conversion to:	
		Crotonaldehyde	By-products
280	Standard tantalum-silica	12	15
325	Standard tantalum-silica	15	22
375	Standard tantalum-silica	20	30
280	Silica gel (commercial)	22	13
280	Silica gel (alkaline-set)	30	15
350	Silica gel (commercial)	26	16

Second Stage. In an investigation of the second step of this process, effluent from a run with 1 to 1 feed over the commercial tantalum-silica catalyst (this first stage employed approximately 0.4 liquid hourly space velocity at varying temperatures) was stripped of any butadiene and diluted with 92 weight % ethyl alcohol to make an over-all feed of 2 to 1 or 3 to 1 ratio. This resultant feed then was passed over more of the tantalum-silica catalyst at 350° C. at 0.5 liquid hourly space velocity in the second stage. Data for three exploratory runs are presented in Table IX for comparison with the usual standard runs at 350° C.; for 230° C. the yield is good (67% against 60% for one-stage process).

TABLE IX. COMMERCIAL TANTALUM-SILICA CATALYST—TWO-STAGE OPERATION

(Second stage, 350° C. and 0.4 liquid hourly space velocity; first stage, 0.4 liquid hourly space velocity; and 1 to 1 feed ratio)

Temp. for 1st Stage, ° C.	Over-All Feed Ratio	Conversion, Mole %	Ultimate Yield, %	Ethyl	Acet-
				Alcohol Efficiency, %	aldehyde Efficiency, %
205	3:1	30	62	63	67
230	2:1	38	67	74	66
275	3:1	22	60	58	64
Normal One-Stage Operations					
	3:1	30	62	51	90
	2:1	40	60	59	69

Since at 205° and 230° C. in the first stage both a high conversion and yield were realized, it was attempted to accomplish the two stages more efficiently in one reactor (with tantalum-silica catalyst and 2.75 to 1 feed) by employing a temperature gradient: 230° C. at the inlet and 370° C. at the outlet. However, the yields were the same as obtained conventionally with 350° C. throughout the reactor.

As alkaline-set silica gel appeared better than the tantalum-silica catalyst at 230° C. for the first step (crotonaldehyde formation, Table VIII) the two-stage operation (Table IX) was repeated with this type of silica gel at 230° C. for the first stage.

TABLE X. PROCEDURE 3—TWO-STAGE OPERATION

(Over-all feed ratio 2 to 1. First stage: 1 to 1 feed; 230° C.; 0.45 liquid hourly space velocity. Second stage: 350° C.; 0.4 liquid hourly space velocity; 2% tantalum-silica catalyst)

Operation	Catalyst in First Stage	Con- version, Av. Mole %	Yield, Av. Mole %	Ethyl Alcohol Efficiency, Av. %	Acet- aldehyde Efficiency, Av. %
Two-stage	SiO ₂ gel (alkaline-set)	36	65	59	79
Two-stage	2% Ta ₂ O ₅ -SiO ₂	38	67	74	66
One-stage (2:1 feed)	40	60	59	69

The effluent was stripped of C₄ hydrocarbons plus lighter material and then diluted with 92 weight % ethyl alcohol to give an over-all feed of 2 to 1 ratio for use in the second stage with the commercial tantalum-silica catalyst at 350° C. In four runs made, butadiene, in trace quantity, was found in the first stage product of only one run. This finding was in marked contrast to results for the commercial tantalum-silica catalyst in the low temperature first-stage operation (Table IX). Average results of these runs are given in Table X in comparison with tantalum-silica catalyst in two-stage operations and standard operations for 2 to 1 feed ratio.

These results are considered encouraging in view of the following facts: the first-stage operation was carried out at the not necessarily optimal temperature of 230° C.; practically no search was made for a better catalyst for formation of crotonaldehyde; and the 2 to 1 over-all feed ratio is not expected to be the optimal feed ratio (Table VII). The reversal of order of efficiency of the ethyl alcohol and acetaldehyde consumptions by use of silica gel catalyst is worthy of further study.

The extent of carbonization of the standard catalyst when passing 1 to 1 feed at approximately 0.4 liquid hourly space velocity at a temperature of 230° to 240° C. was not found prohibitive. In a test comprising a 40-hour period of continuous operation the silica gel catalyst was still white in contrast to the darker color of the commercial catalyst after 40 hours in conventional operation. However, burn-off of the silica gel did indicate about one third more high molecular weight material than with the commercial catalyst (2.2% against 1.6% apparent carbon).

Further work on a two-stage process was curtailed because of a change in the program.

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