Table I. Liquid-Vapor Equilibrium Data for Meso-Butylene Glycol–Water Mixture

	Butylene Glycol					Butylene Glycol			
Temp., ° C.	Weight % in:		Mole % in:		Temp., ° C.	Weight % in:		Mole % in:	
	Liquid	Vapor	Liquid	Vapor		Liquid	Vapor	Liquid	Vapor
Pressure = 750 ± 5 Mm.					Pressure = 127 ± 5 Mm.				
100.0	0.231	0.0244	0.0462	0.00486	58.4	0.423	0.0142	0.0847	0.00280
	0.530	0.0535	0.106	0.0107		0.700	0.0244	0.141	0.00486
	1.06	0.112	0.214	0.0224	58.5	1.34	0.0430	0.271	0.00859
	2.00	0.226	0.406	0.0453		4.58	0.153	0.950	0.0307
	4.28	0.470	0.886	0.0944		5.05	0.160	1.05	0.0321
	6.90	0.733	1.46	0.147		14.7	0.500	3.33	0.100
	8.84	0.920	1.90	0.185	59.0	15.8	0.460	3.62	0.0924
100.5	10.8	1.09	2.36	0.220		30.1	0.900	7.93	0.181
	15.2	1.45	3.46	0.293	60.4	40.6	1.60	12.02	0.324
101.0	27.6	2.68	7.08	0.548		58.7	2.92	22.1	0.598
101.8	40.7	3.40	12.1	0.699	63.0	69.0	3.16	30.8	0.648
	50.7	4.57	17.1	0.948		69.7	3.56	31.5	0.733
103.0	58.2	5.95	21.8	1.25	64.0	73.7	4.10	35.9	0.848
	69.4	7.66	31.2	1.63	71.0	85.5	8.20	54.1	1.76
105.0	70.0	7.00	31.8	1.48	74.0	91.6	15.2	68.6	3.46
106.0	73.7	8.40	35.9	1.80	81.0	93.3	19.0	73.6	4.48
109.3	87.6	11.8	58.6	2.61	92.0	93.6	40.9	74.5	12.2
113.4	90.3	16.8	65.1	3.88	106.2	96.2	63.4	83.5	25.7
117.0	92.9	22.5	72.4	5.49	118.0	98.6	79.3	93.4	43.4
134.8	95.7	45.7	81.7	14.4					
158.5	98.8	76.1	94.3	38.9					
Pressure = 30 Lb./Sq. In. Gage					Pressure = 65 Lb./Sq. In. Gage				
138.0	1.46	0.308	0.295	0.0617	154.5	0.291	0.0715	0.0583	0.0143
	2.66	0.585	0.543	0.117		0.670	0.176	0.135	0.0352
	5.05	1.10	1.10	0.222		2.67	0.692	0.545	0.139
	10.50	2.19	2.28	0.446		4.10	1.03	0.847	0.208
	12.3	2.60	2.73	0.531		6.87	1.73	1.45	0.351
	15.1	2.82	3.43	0.577		8.37	2.03	1.79	0.412
	16.9	3.26	3.89	0.669		8.58	2.21	1.84	0.449
	19.5	3.62	4.61	0.745	156.0	13.5	3.44	3.03	0.707
	21.4	4.01	5.16	0.828		13.5	3.27	3.06	0.671
136.0	24.8	4.61	6.19	0.957		16.8	3.90	3.88	0.805
	37.5	6.40	10.7	1.35		19.1	4.34	4.51	0.899
	40.2	7.20	11.9	1.53		19.3	4.57	4.56	0.948
	41.0	7.10	12.2	1.51	156.5	20.2	4.49	4.82	0.931
	50.0	8.60	16.7	1.85		25.0	5.28	6.25	1.10
138.0	61.1	10.6	23.9	2.32		27.8	5.47	7.15	1.14
139.5	66.2	11.9	28.1	2.63		29.7	5.95	7.82	1.24
149.7	68.5	12.8	30.3	2.85		33.9	7.80	9.30	1.66
151.6	73.5	14.6	35.7	3.31		40.4	8.90	11.9	1.92
155.0	76.7	16.2	39.7	3.72		44.7	9.70	13.9	2.10
					157.8	44.9	10.0	14.0	2.17
						50.3	10.4	16.8	2.27
					159.6	60.8	11.8	23.7	2.61
					160.2	64.0	12.6	26.2	2.80
					170.5	66.3	12.9	28.2	2.88
					172.2	72.0	15.0	34.0	3.41

is believed that the data are consistent and that the moderate scattering of the points in Figures 2 and 3 is not unreasonable.

Figure 3 can be used to obtain equilibrium values for aqueous solutions containing up to 35 mole % butylene glycol at pressures varying from 2.45 to 80 pounds per square inch absolute. The equilibrium values so obtained are sufficiently accurate for use in making engineering calculations.

ACKNOWLEDGMENT

The pressure equilibrium still was made available for this work through the courtesy of the Vulcan Copper and Supply Company. The authors acknowledge assistance of the Analytical and Physical Chemical Division of this laboratory in making some of the analyses.

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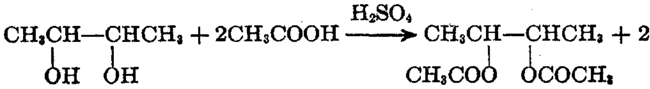
CONTINUOUS PROCESS for ACETYLATION of 2,3-BUTYLENE GLYCOL

THE development of a commercially feasible process for the production of 1,3-butadiene from 2,3-butylene glycol depended largely on the adaptation of each step to continuous operation. It has been shown (*4*) that the pyrolysis of the glycol diacetate is a more efficient route to butadiene than the direct catalytic dehydration of the glycol. The pyrolysis operation, the separation and purification of the butadiene, and the recovery and rectification of the acetic acid and by-products (*6*) were all readily adaptable to continuous processing equipment. The conversion of the glycol to its diacetate by continuous methods, however, required a more detailed investigation. Continuous esterification processes now in commercial operation are confined almost wholly to the manufacture of esters which can be removed from the reaction mixture by distillation. Since 2,3-butylene glycol diacetate has a boiling point of 193° C. and its water azeotrope (boiling point, 99.5° C.) is not readily separable from acetic acid, its manufacture was not adaptable to these systems (*3*).

ESTERIFICATION REACTIONS

The mineral-acid-catalyzed acetylation of 2,3-butylene glycol may be illustrated by the following equation:



$$\underset{\mathrm{OH}}{\mathrm{CH_3CH}}-\underset{\mathrm{OH}}{\mathrm{CHCH_3}} + 2\mathrm{CH_3COOH} \xrightarrow{\mathrm{H_2SO_4}} \underset{\mathrm{CH_3COO}}{\mathrm{CH_3CH}}-\underset{\mathrm{OCOCH_3}}{\mathrm{CHCH_3}} + 2\mathrm{H_2O} \qquad (1)$$

This reaction probably proceeds in two steps with the intermediate formation of the glycol monoacetate which is found to be present in the acetylation mixture in an amount inversely proportional to the degree of completion of the reaction.

In addition to the main acetylation reaction, several side reactions may also occur. A small amount of methyl ethyl ketone is always produced, and prolonged heating of the esterification mixture results in the formation of some butadiene and tarry decom-

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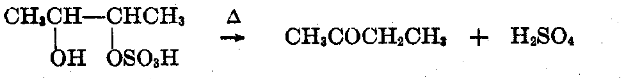
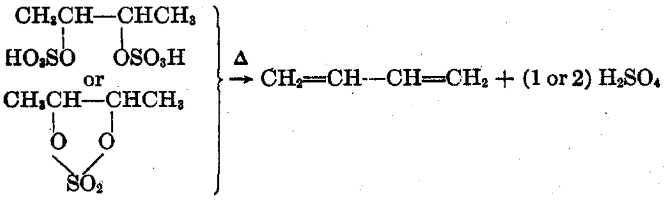
A practical continuous process for 2,3-butylene glycol diacetate consists in feeding the glycol, along with a catalytic amount of sulfuric acid, into the top of a reaction column while introducing a continuous stream of glacial acetic acid into the base of the column. Temperatures of 140-150° C. are maintained in the zone between the feeds. The column distillate, consisting of acetic acid, water, and traces of methyl ethyl ketone, is dehydrated in an auxiliary column, and the acetic acid returned to the esterification feed. The base product from the reaction column consists of glycol diacetate, acetic acid, and sulfuric acid esters of glycol. This mixture is separated by vacuum fractional distillation, the acetic acid and sulfuric acid esters being returned to the esterification column as feed and catalyst, respectively. The glycol diacetate so produced is of high quality and suitable for conversion to butadiene by pyrolysis. 2,3-Butylene glycol diacetate is produced in 97% yield; 3% of the glycol is converted to methyl ethyl ketone, and the excess acetic acid is recovered quantitatively. This procedure has been found applicable to the production of other high-boiling acetates.

position products. These by-products probably result from the thermal decomposition of the sulfuric acid esters, formed by the reaction of the acid catalyst and the glycol, and may be explained by the following equations:



$$\underset{OH}{CH_3CH}-\underset{OSO_3H}{CHCH_3} \xrightarrow{\Delta} CH_3COCH_2CH_3 + H_2SO_4 \qquad (2)$$



$$\left.\begin{array}{c} \underset{HO_3SO}{CH_3CH}-\underset{OSO_3H}{CHCH_3} \\ \text{or} \\ \underset{\underset{SO_2}{O \quad O}}{CH_3CH-CHCH_3} \end{array}\right\} \xrightarrow{\Delta} CH_2{=}CH-CH{=}CH_2 + (1 \text{ or } 2)\, H_2SO_4 \qquad (3)$$

Both of these side reactions occur to a certain extent under all conditions, but are minimized by conducting the esterification as a continuous rather than a batch operation. Under controlled conditions the conversion to methyl ethyl ketone does not exceed 3%, and the formation of butadiene can be almost completely prevented. The latter occurs only when the reaction mixture is subjected to prolonged heating or when the temperature is raised to 170° C. or above. This reaction is always accompanied by the formation of charred and tarry decomposition products and does not represent a satisfactory method of producing butadiene. The production of butadiene during the esterification is particularly undesirable because it is difficult to collect and purify, its formation represents an inefficient utilization of the glycol, and the accompanying decomposition products complicate the purification of the esterification products.

BATCH INVESTIGATIONS

The acetylation of 2,3-butylene glycol by batch processing methods was studied on both the laboratory and pilot-plant scale. The results of these studies were later used as a guide in developing the continuous process. Laboratory investigations showed that the reaction between the glycol and acetic acid proceeded rapidly to equilibrium (established at about 45% conversion to the glycol acetate) when heated in the presence of the usual esterification catalysts. Continuous removal, by an entrainer system, of the water formed during the reaction served to carry the reaction to about 90% completion within 4 to 5 hours. Effecting the last 7–10% of the reaction required 2 to 3 hours at the temperature of the refluxing reaction mixture.

Of the various catalysts studied, sulfuric acid and *p*-toluene sulfonic acid were the most effective in low concentrations. Sulfuric acid was chosen since it gave a satisfactory reaction rate at concentrations of 1–1.5% of the weight of the glycol, whereas 3% of *p*-toluene sulfonic acid was required. The availability and low cost of the sulfuric acid were also taken into consideration.

While the esterification reaction proceeded slightly faster at high ratios of acetic acid to glycol, completely satisfactory results were obtained on a batch scale by operating at a ratio of 2.5 moles of acetic acid to 1 mole of glycol.

Entrainers were evaluated on the basis of their water-carrying capacity and on their efficiency, in so far as loss of acetic acid in the removed water was concerned. Benzene and toluene removed water satisfactorily, but their use entailed some loss of acetic acid since both also form azeotropes with the acid. Isopropyl ether and petroleum ether were eliminated on the basis of their low-water carrying capacities. Isopropyl acetate, *n*-propyl acetate, and *n*-butyl acetate gave the most promising results. Of these, isopropyl acetate was selected for the batch investigations. Its azeotrope carries sufficient water to balance the rate of water formation and its separation from acetic acid is readily accomplished. *n*-Butyl acetate was not satisfactory for batch work since the rate of water production during the latter stages of the reaction was not sufficiently high to maintain the azeotropic composition with a fixed amount of entrainer. As a result, acetic acid became the lowest-boiling component of the system and was removed as distillate to a considerable extent. *n*-Propyl acetate was not available in sufficient quantity for this work. Preliminary investigations indicated, however, that it would be satisfactory.

LABORATORY PROCEDURE. The reaction flask was charged with 1 molar part of glycol, 2.5 molar parts of acetic acid, 0.016 molar part of sulfuric acid, and 0.5 part by weight of isopropyl acetate per part of glycol. The flask was equipped with a thermometer well and a packed fractionating column. The top of the column was connected to a condenser and decanter system. The decanter was adjusted so that the top, or entrainer layer, was continuously returned to the column as reflux, and the bottom, or water layer, was collected in a graduated receiver. The reaction mixture was heated to a vigorous boil, and the progress of the reaction was followed by noting the rate of water production. In the laboratory studies 6 to 8 hours were required to complete the reaction of a 10-gram-molar charge, as indicated by the cessation of water production. In every case the reaction was about 90% complete in the first 4 to 5 hours, and the remaining 2 to 3 hours were required to complete the reaction. During this latter period some darkening of the reaction mixture and some butadiene formation were noted. The temperature of the reaction mixture gradually increased during the course of the run from about 110° to 140° C.

At the end of a run the sulfuric acid catalyst was neutralized by the addition of an equivalent amount of crystalline sodium acetate. The precipitated sodium sulfate was removed by filtration, and the filtrate was fractionally distilled. The isopropyl acetate–acetic acid mixtures were analyzed and re-

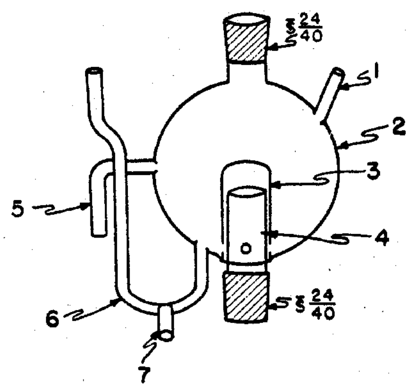


Figure 1. Unit or Plate of Laboratory Continuous Esterification Column

1. 10-mm. tube for thermometer insert
2. 250-ml. Pyrex flask
3. Cap sealed to outside of vapor inlet, having 3 vapor outlet holes near base
4. Vapor inlet from plate below
5. 10-mm. tube drain line
6. 10-mm. tube liquid inlet line
7. Capillary sampling tube

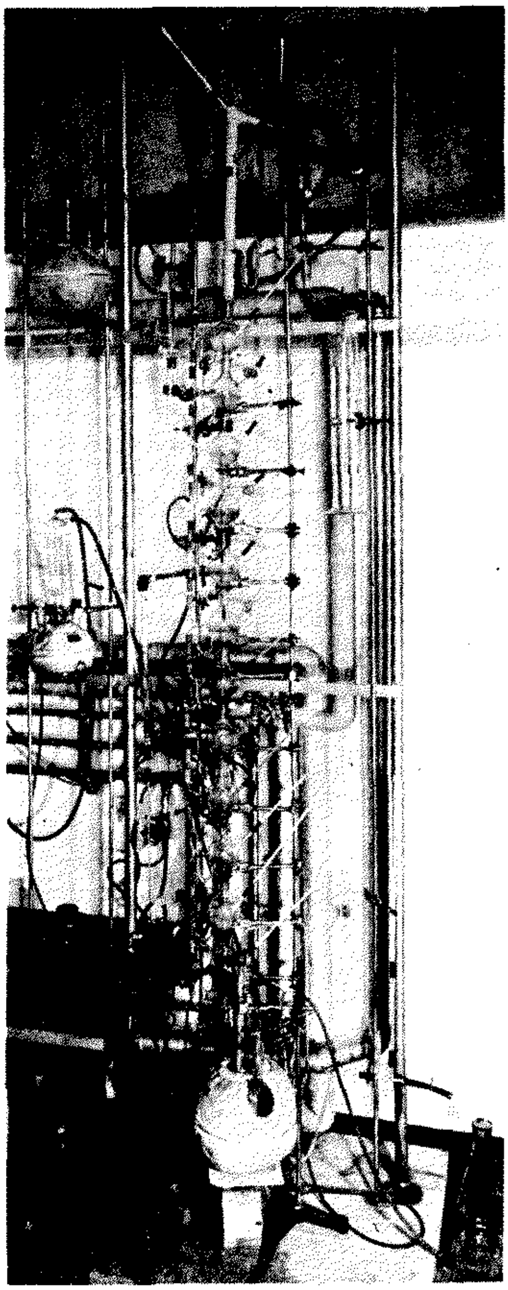


Figure 2. Laboratory Esterification Column

used in subsequent charges. The fraction distilling at 190–193° C. under atmospheric pressure was analyzed for purity as diacetate. In most instances this fraction was 98–99% pure, the other 1 to 2% being the glycol monoacetate.

In a series of laboratory runs the yield of diacetate averaged 97% of theoretical; the acetic acid recovery was quantitative, but some isopropyl acetate loss was encountered due to its partial hydrolysis and the removal of the isopropyl alcohol, with the water, from the system.

Pilot-Plant Procedure. On the basis of conditions developed in the laboratory studies, diacetate, for use in pilot-plant pyrolysis studies, was produced in a 150-gallon enamel-lined jacketed kettle equipped with a circulating-oil heating system. The column used on this kettle was constructed of copper and packed with stoneware Raschig rings. The vapors from this column were condensed and run to a glass decanter from which the entrainer was returned to the column, and the water was collected in a container mounted on a scale. Charges of 1.5 to 2.0 pound-moles of glycol were esterified in this equipment. The rate of heat transfer in the kettle was quite slow, and 24 to 30 hours were required to complete the reaction. Even after water production ceased, the reaction mixture still contained the equivalent of 4 to 5% of glycol monoacetate. In order to produce a diacetate of satisfactory quality for pilot-plant pyrolysis, it was necessary to complete the reaction with acetic anhydride. This was done after the catalyst had been neutralized and the charge filtered. The filtered charge was analyzed and the percentage of monoacetate calculated. Acetic anhydride, sufficient to react with all of the monoacetate and any water present, was added to the charge in a 50-gallon enamel-lined batch still. The charge was heated to 140° C. for an hour and then fractionally distilled under reduced pressure. The diacetate was collected after the acetic acid content of the distillate was less than 1%. The distilled diacetate produced by this method had a purity of 99.5–100%. All foreshots were charged back into subsequent charges or refractionated. Approximately 1500 pounds of high-quality diacetate was produced by this procedure, and yields of 96–97% were obtained consistently. Acetic acid recoveries were again quantitative, but the breakdown of isopropyl acetate exceeded expectations. The long time required for the pilot-plant runs and the lack of facilities for restripping the water produced resulted in considerable hydrolysis of the entrainer.

CONTINUOUS PROCESS STUDIES

During the batch investigations it was shown that the reaction proceeded to the extent of about 90% at a reasonably rapid rate, but complete esterification, as measured by water removal, required a disproportionate length of time. It seemed probable, therefore, that a study of time and temperature factors might result in the establishment of more favorable reaction conditions which would be applicable to continuous processing methods.

Apparatus. A bubble-cap column, or an interconnected series of reaction vessels provided with a means of controlling flow rates

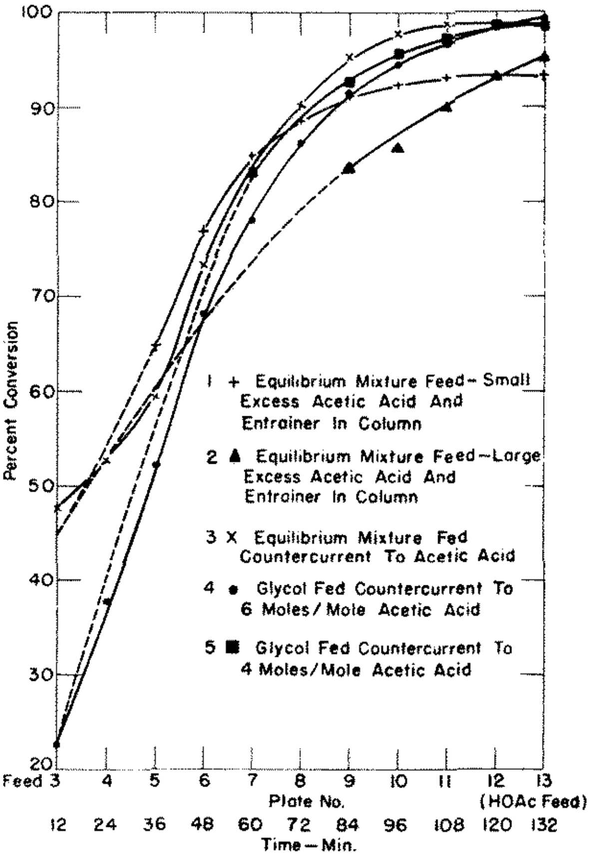


Figure 3. Conversion-Time Data for Continuous Esterification of 2,3-Butylene Glycol

and temperatures during the various stages of the reaction, appeared to be the most desirable types of apparatus for these studies. A column of heat-resistant glass was constructed of an interconnected series of units or plates as illustrated in Figure 1. These plates were joined through ₸ 24/40 joints, and the drain and inlet lines were connected via short lengths of glass and rubber tubing. Each plate was equipped with a sampling line attached to the liquid-inlet line so that samples could be withdrawn during operation and the contents of each plate drained for analysis at the end of a run. Each plate was heated by a small ring burner fitted around the vapor inlet connection from the plate below. The column, made up of twelve such plates, is shown in Figure 2. Under operating conditions each of these plates held 100 cc. of liquid. By using ten plates in the reaction zone, the liquid-holding capacity was 1000 cc., and the flow rate and residence time were readily calculated. In all cases two or three plates were installed above the glycol feed plate to effect some fractionation of distilling vapors. The base of the column was connected to either a large boiling flask (Figure 2), containing a catalyst neutralizing agent, or to a small flask equipped with a continuous drain line.

Table I. Esterification Data

Sample Source	Average Temp. of Boiling Liquid, ° C.	Composition, %: H_2O	Estimated H_2SO_4	Free HOAc	Combined HOAc	Glycol monoacetate	Glycol diacetate	% Complete
		Acetic Acid–Glycol Molar Ratio, 6 to 1						
Distillate	107	19.55	0.00	78.22	0.56	...	0.81	..
Plate 1[a]	108.5	8.36	0.00	90.53	0.44	...	0.64	..
Plate 2	....	8.16	0.00	89.93	0.24	...	0.35	..
Plate 3 (glyco feed)	116.5	8.00	0.75	62.72	8.04	17.69	(14.74 glycol)	22.50
Plate 4	...	5.46	0.75	72.67	7.87	17.32	(3.8 glycol)	37.83
Plate 5	124	4.03	0.75	71.39	11.20	26.95	1.53	52.23
Plate 6	....	2.25	0.75	55.00	23.32	23.99	18.01	68.14
Plate 7	146	1.43	0.75	36.91	36.70	22.53	38.37	78.19
Plate 8	....	0.69	0.75	24.15	47.43	16.50	57.91	86.35
Plate 9	152	0.38	0.75	19.02	52.60	10.44	69.41	91.73
Plate 10	151.5	0.33	0.75	20.65	52.40	6.65	71.62	94.55
Plate 11	150	0.23	0.75	22.93	51.55	3.87	72.22	96.70
Plate 12 (HOAc feed)	135	0.13	0.75	34.48	44.23	1.44	63.20	98.54
Product (pot)	162	0.00	0.77	12.08	60.35	1.14	86.78	99.15
		Acetic Acid–Glycol Molar Ratio, 4 to 1						
Distillate	101	27.29	...	67.96	2.00	...	2.90	(1.85 MEK)
Plate 1[a]	103	Not sampled						
Plate 3 (glycol feed)	116							
Plate 5	130							
Plate 7	145	0.62	1.15	16.94	50.71	22.70	58.58	83.10
Plate 8	....	0.41	1.15	17.67	52.81	12.28	68.49	90.44
Plate 9	147	0.40	1.15	18.94	52.66	8.92	70.50	92.85
Plate 10	147	0.30	1.15	20.35	52.69	5.21	72.99	95.69
Plate 11	148	0.16	1.15	21.36	52.53	3.35	73.98	97.18
Plate 12 (HOAc feed)	133				Not sampled			
Plate 13	....	0.18	1.15	42.24	38.65	1.10	55.33	98.68
Product (pot)	153	0.00	0.73	23.09	52.19	1.47	74.72	98.74
Vacuum dist. of product	115 (20 mm.)	0.00	0.00	26.35	50.78	0.00	73.65	100.00

[a] Plates numbered from top down (Figure 2).

Entrainer System. For the initial experimental work the plates in the reaction zone were charged with an amount of acetic acid equal to the molar excess used in batch operations. After this acetic acid had been brought to a boil, isopropyl acetate was charged to the top sections of the column. A feed, consisting of the stoichiometric amounts of glycol and acetic acid together with the sulfuric acid catalyst, was heated for about one hour to establish equilibrium, and then introduced near the top of the column. The feed rate was regulated to give a definite residence time in the column, usually 2 or 3 hours. Boiling was maintained in each plate and the distillate, consisting of the water–isopropyl acetate azeotrope, was condensed and run to a decanter, and the entrainer was returned to the top of the column. The water from the decanter was collected in a graduate to serve as an estimation of the reaction rate. The mixture obtained from the base of the column was either removed continuously or collected in a base receiver containing sufficient sodium acetate to neutralize the sulfuric acid catalyst. Feed rates, temperatures, and rate of water production were checked at regular intervals, and samples were periodically drawn from the various plates of the column to determine the course of the reaction. After standardizing the operating procedure by a series of trial runs, several longer runs were conducted in which the feed rate was varied to determine the residence time necessary for maximum conversion.

In all cases in which an entrainer was used in the system, the conversion to diacetate did not exceed 94% (Figure 3, curves 1 and 2). Residence times of 2 and 3 hours gave almost identical results. During these runs the temperatures of the boiling liquids in the center plates of the column were only a few degrees above the boiling point of acetic acid. Only the bottom plates were at a higher temperature. Analyses showed that these plates had lost acetic acid by fractionation. Attempts were then made to maintain a higher percentage of acetic acid in the column, but again the fractionation which occurred and the high reflux ratio resulting from the recycled entrainer kept the column temperatures too low for rapid reaction.

Countercurrent Reactor System. Atwood (*1*) had shown that a high degree of conversion was possible by continuously distilling a mixture of water and acetic acid from the reaction mixture while adding glacial acetic acid to the reaction vessel. From these data it appeared that a continuous system could be developed in which an excess of acetic acid was used to remove the water from the zone of reaction and at the same time provide the additional driving force to carry the acetylation to completion.

To test this procedure the column was converted to a countercurrent reactor in which a distillate of dilute acetic acid was removed at the top, and a continuous stream of glacial acetic acid was introduced near the base. The glycol-catalyst mixture was fed to the third plate from the top, the two plates above serving to fractionate the acetic acid–water mixture partially. By feeding a glycol–acetic acid equilibrium mixture countercurrently to acetic acid and by maintaining a ratio of 6 moles of acetic acid per mole of glycol, it was possible to raise the temperatures in the lower half of the zone between the feeds to 140–145° C. This resulted in a 98% conversion of glycol to diacetate, at a residence time of 2 hours. On further experimentation it was found that a feed of glycol and sulfuric acid introduced countercurrently to the acetic acid gave results equally as good as those obtained with the equilibrium mixture (Figure 3, curves 3, 4, and 5). The maintenance of a temperature range of 140–150° C. in the lower two thirds of the reaction zone resulted in 99% completion of the reaction. It was found that the same degree of completion could be attained in a 2-hour residence time with 4 moles of acetic acid per mole of glycol instead of the 6 previously used, provided the temperatures in the reaction zone were held in the 140–150° C. range. The data on several of these runs, showing the degree of reaction in the various plates of the column, are given in Table I and illustrated in Figure 3 (curves 4 and 5).

A material balance on several runs showed excellent yields and recoveries even though some acetic acid was lost due to slight leaks which developed in the apparatus during the operations.

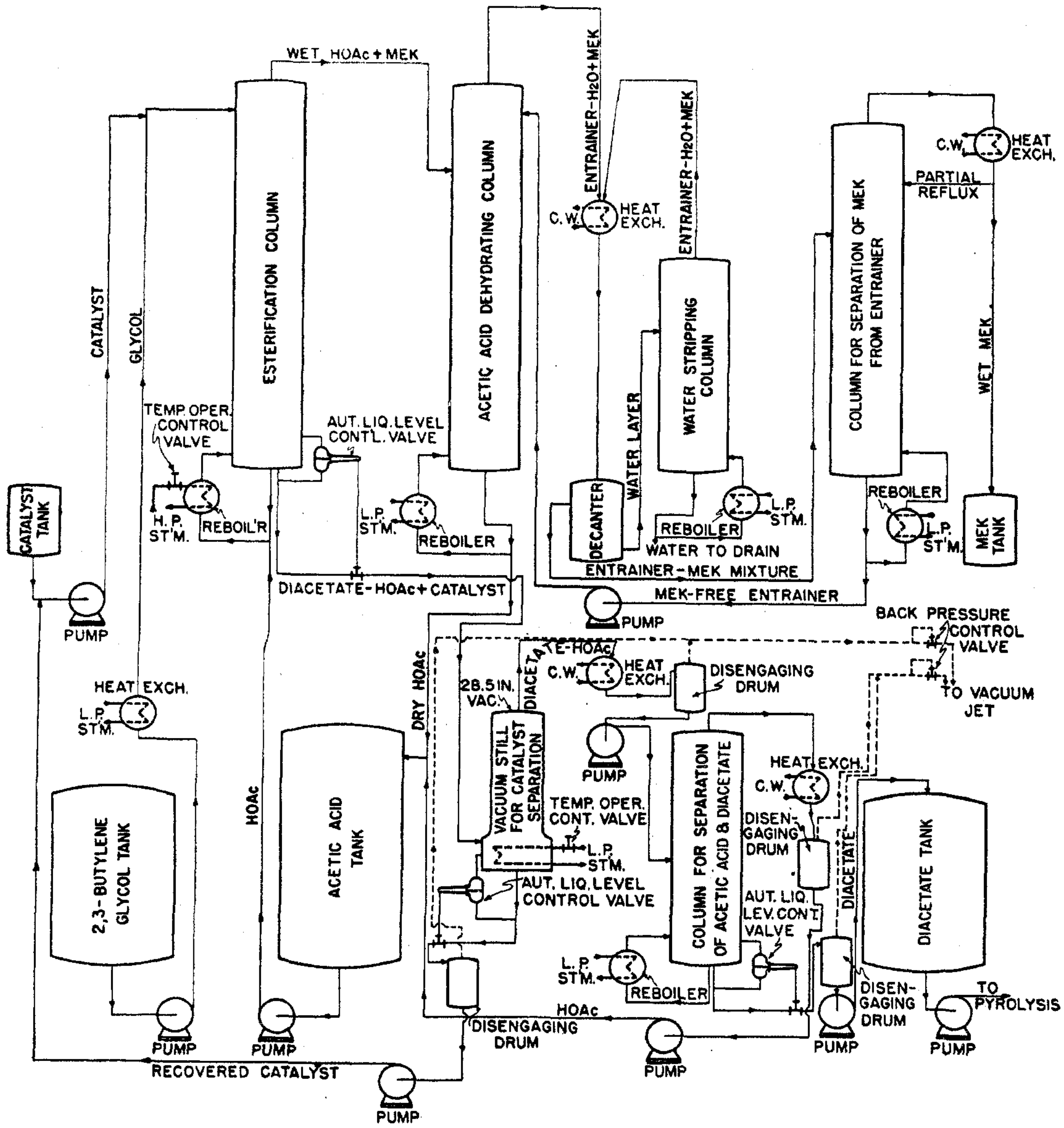


Figure 4. Flow Diagram of Proposed Continuous Process for the Acetylation of 2,3-Butylene Glycol

The average of these results shows 97% conversion of the glycol to acetates and a 3% conversion of glycol to methyl ethyl ketone. The acetate fraction consisted of 99% diacetate and 1% monoacetate. The over-all acetic acid recovery, as free and combined, was 98%. The acetic acid losses were mechanical and could be prevented in plant operation. No butadiene was produced.

RECOVERY OF ACETIC ACID. The acetic acid–water mixture collected as distillate contained 68% acetic acid, 27% water, 2% methyl ethyl ketone, and 3% glycol diacetate. This mixture was dehydrated in a batch still by adding isopropyl acetate and distilling the water-entrainer azeotrope to a continuous decanter which returned the entrainer layer to the packed column. After the water was removed, the anhydrous mixture was distilled. The isopropyl acetate fraction contained the methyl ethyl ketone. The glycol diacetate, which was evidently distilled with the dilute acetic acid from the esterification column as its water azeotrope, remained in the anhydrous acetic acid. Since it was retained in the dehydrated acetic acid from the dehydrating column and returned to the esterification column, no loss was incurred.

Dehydration of the esterification-column distillate by an entrainer system can be readily accomplished by the continuous methods used in the commercial dehydration of acetic acid (*5*). The presence of methyl ethyl ketone in this distillate necessitates an additional operation to prevent accumulation of the ketone in the entrainer. Using *n*-butyl acetate as entrainer, the separation of methyl ethyl ketone is effected by stripping its water azeotrope (boiling point 73.4° C.) from the entrainer layer before the butyl acetate is returned to the dehydration column.

PURIFICATION OF PRODUCT. The mixture which was continuously removed from the bottom of the esterification column consisted of 75% glycol diacetate, 23% acetic acid, 1% glycol monoacetate, and 1% sulfuric acid, combined in the form of glycol esters. Two methods of diacetate isolation were investigated. One involved the neutralization of sulfuric acid with sodium acetate, followed by filtration and fractional distillation. Under these conditions some solids always remained dissolved in the filtrate and accumulated in the still. This would be particularly troublesome in a continuous system. In addition, any glycol monoacetate present in the original mixture or liberated by neutralization of the sulfuric acid esters was left in the diacetate, and its presence was undesirable in the subsequent pyrolysis step (*4*). A second method consisted in a continuous vacuum distillation of the unneutralized product. By operating at a sufficiently reduced pressure so that the diacetate boiled at a temperature lower than that at which the sulfuric acid esters decomposed, it was possible to remove practically all of the diacetate–acetic acid mixture by distillation. The residual mixture of diacetate and the sulfuric acid esters can be recycled as the esterification catalyst, since several experiments have shown that this material functions fully as well as fresh sulfuric acid. This method has the following advantages over the neutralization method: It requires no filtration equipment; there are no dissolved solids to foul the distillation equipment; when the esterification is carried to a high degree of completion, the distillate contains practically no glycol monoacetate. Fractionation readily separates the acetic acid from the diacetate, or the mixture may be used directly for pyrolysis (*4*). Recycling of the catalyst residue also serves to prevent the loss of incompletely acetylated glycol. The distillation method does, however, require a vacuum of at least 28 inches to accomplish the separation of diacetate from the sulfuric acid esters without loss due to charring.

This continuous esterification process was applied to the preparation of ethylene glycol diacetate, methyl Cellosolve acetate, diethylene glycol diacetate, and glycerol triacetate. Excellent results were obtained in every case, and application of the method to the manufacture of a wide variety of industrially important acetates is indicated. A modification of the method has recently been applied to the manufacture of 2,3-butylene glycol diacetate in a column of commercial design by the staff of Joseph E. Seagram & Sons, Inc., who cooperated with this laboratory throughout the butylene glycol–butadiene investigation (*2*). It was found possible to reach and maintain the desired temperature in the reaction zone by supplying heat only to the column calandria. When a sufficiently high concentration of diacetate was produced in the reaction zone and when the temperature necessary for rapid esterification was maintained, a glycol to diacetate conversion of 98–99% resulted during a 2-hour residence time in the column.

Figure 4 is a flow diagram of the proposed process for acetylation of 2,3-butylene glycol, developed cooperatively with the Seagram organization.

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CONVERSION of 2,3-BUTYLENE GLYCOL to 1,3-BUTADIENE by PYROLYSIS of DIACETATE

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The conversion of 2,3-butylene glycol to butadiene by pyrolysis of its diacetate has been studied over a wide range of temperatures and contact times. Yields of 82% of butadiene (purity, 99%) were obtained on one-pass pyrolyses in the temperature range 575° to 600° C. An additional 5% was secured by isolation and pyrolysis of the intermediates left in the pyrolysis liquors. Acetic acid recoveries of 99% were obtained under optimum conditions. Methyl vinyl carbinyl and crotyl acetates were identified as the intermediates of the reaction. The main by-products were methyl ethyl ketone, methyl ethyl ketone enol-acetate (2-acetoxy-2-butene), and methyl acetyl acetone.

ONE of the important problems chosen for study at the inception of this laboratory in 1940 was the development of a commercial process for the production of 2,3-butylene glycol by fermentation of carbohydrate materials (*21*). It was understood that when sufficiently high yields of 2,3-butylene glycol were obtained to make the process of commercial interest and when the chemical was available, the development of a process for 1,3-butadiene would be undertaken. Work was actively started in January, 1942, at which time the importance of producing butadiene had become a major problem of national defense.

The possibility of direct catalytic dehydration by the methods in commercial use in Germany for converting 1,3-butylene glycol to 1,3-butadiene (*5*) was given first consideration as the basis of a process. A study of approximately seventy dehydration catalysts under a variety of conditions indicated that this route was impractical. Highest one-pass yields of butadiene reached 20% of theory, the main product in every case being methyl ethyl ketone, which did not yield butadiene under any of the conditions tried. The predominate tendency to form ketones under dehydration conditions is characteristic of compounds having hydroxyl groups on adjacent carbon atoms:

$$\underset{\text{2,3-Butylene glycol (I)}}{CH_3CHOHCHOHCH_3} \xrightarrow[\text{dehydration}]{\text{catalytic}} \underset{\text{Methyl ethyl ketone (II)}}{CH_3CH_2COCH_3}$$

Van Pelt and Wibaut (*14*) studied the behavior of a number of acetates under pyrolysis conditions and found that the olefins or

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