Esterification : continuous noncatalytic production of lower acetates
by John A Runberg

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering at Montana State College
Montana State University

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The use of increased temperature obtained by rectifying at super-atmospheric pressure was investigated as a means of carrying out the continuous non-catalytic esterification of the lower alcohols with acetic acid.

The non-catalytic esterification rate at the boiling point at 60 psig pressure was determined for ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, n-amyl, and sec-amyl alcohols with acetic acid.

The ternary azeotrope composition at 60 psig pressure was determined for each acetate system and a continuous non-catalytic esterification carried out for each ester.

It was found that continuous non-catalytic esterification could be successfully carried out at 60 psig pressure for each ester studied except methyl acetate which formed no ternary azeotrope and tert-butyl and tert-amyl acetates which formed at too slow a rate.

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Bozeman, Montana
August 1950

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ABSTRACT

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I INTRODUCTION

In the commercial preparation of esters from the lower alcohols and organic acids the esterification reaction is invariably carried out in the presence of a catalyst. The esterification is usually accomplished by heating to the boiling point a mixture of alcohol, organic acid, and catalyst. The ester is usually separated by rectification as fast as it is formed. In the absence of a catalyst, except in the case of a high boiling alcohol with a high boiling acid, esterification cannot be effected by boiling at atmospheric pressure in a reasonable time without some other means of speeding up the reaction. The esterification rates expressed as percent conversion per hour of the lower alcohols with acetic acid at their atmospheric boiling points, are given in Table III. Esterification in the absence of a catalyst would have some distinct advantages. In general practice hydrochloric and sulfuric acids are the most commonly used catalysts, the latter in most commercial plants because of its cheapness. Both acids are corrosive on metals and sulfuric acid may cause dehydration of an alcohol if used in too great an amount or at too high a temperature. (2)

It is well known that the rate of noncatalytic esterification increases rapidly with temperature, doubling with each 15-25°C. rise in temperature. The esterification rates at 155°C. (4) are compared to the rates at the atmospheric boiling point in Table III. The rates at 155°C. are from the work of Menschutkin (4). He sealed equal mol portions of alcohols and acetic acid in glass tubes and heated them to 155°C. for one

hour. The unreacted acid was then titrated and the per cent esterification calculated. If the reaction can be effected at a sufficiently high temperature, a satisfactory rate can be obtained in the absence of any catalyst. A suitable temperature may be obtained by carrying out the esterification in a rectification column operated under sufficient pressure to give the desired boiling temperature.

The ester is usually removed from the reaction mixture in the form of a ternary constant boiling mixture. The ternary consists of alcohol, ester, and water. In order to carry out the reaction continuously, the feed must contain in addition to a mol of alcohol per mol of acid, one or more of the components of the ternary in order that no component build up as excess in the still pot.

The research necessary before any continuous esterification can be carried out by the proposed method involves the determination of a temperature and pressure at which the esterification rate is sufficiently high, and the determination of the composition of the lowest boiling ternary azeotrope at that pressure.

It was the purpose of this work to determine: 1 - the non-catalytic esterification rate at the boiling temperature corresponding to 60 psig pressure of methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-amyl, iso-amyl, and tert-amyl alcohols with acetic acid: 2 - the composition of the corresponding ternary azeotrope formed for each of these at the temperature and pressure used in 1; and

3 - make up a charge in the correct proportions and operate the esterification process continuously for each of the systems named above at the pressure selected.

II EQUIPMENT, PROCEDURES AND MATERIALS

A. EQUIPMENT

The equipment used in this investigation consisted of a pressurized esterification unit, shown in Figure 1; a glass precision column, and a total reflux system.

The pressurized esterification unit consisted of a copper precision column similar to a glass laboratory column. The inside diameter of the column was 1 1/4-inches and a section 52-inches long was packed with 1/4-inch glass-helices. The still pot was constructed from a stainless steel oxygen tank with a capacity of about 1800 ml. silver soldered to the copper column. The copper column was jacketed by 48 mm. glass tubing inside 64 mm. glass tubing with a heating coil spiraling the length of the inside tube. Power was supplied to the heating element through an autotransformer. The condenser section consisted of a water jacket constructed of an 11-inch section of two-inch standard iron pipe and a cold finger 12-inches long constructed of 1/2-inch copper tubing (1). The flow of water through the cold finger was controlled by using a laboratory bellows pump supplied from a constant head source. The reflux ratio obtained in the cold finger type condensing head could not be measured but was estimated to be in the range of from 5-1 to 10-1.

Connected to the still pot and also capable of being pressurized was a copper feed tank with a capacity of about 5000 ml. A pressurized receiver constructed of 1 1/2-inch standard iron pipe completed the unit making it possible to run the system continuously while under pressure.

The unit was kept under the desired pressure by means of an air compressor and a DeVilbiss Pressure Regulator. A 110-volt 550-watt heater controlled by an autotransformer supplied the heat to the still pot.

A glass precision column, one-inch in diameter with a 36-inch section packed with 1/4-inch glass-helices and equipped with a Corad type condensing head was used to make atmospheric separations.

The equipment used to determine the esterification rate at atmospheric pressure consisted of a 250 ml. Erlenmeyer flask, a pyrex glass Liebig condenser, a 110-volt 550-watt heater controlled by an autotransformer, an ice bath, and a 50 ml. buret.

B. PROCEDURES

TERNARY AZEOTROPE COMPOSITION UNDER 60 PSIG PRESSURE: As a first approximation it was assumed that the ternary azeotrope composition under 60 psig pressure would be the same as at atmospheric pressure. From the atmospheric ternary composition data, Table I (3), the proportions of alcohol and acid, and water if necessary, required to form the ternary azeotrope were calculated. About 1000 ml. of this mixture was then charged to the unit and boiled under 60 psig pressure at total reflux for one hour. Product was then taken off at a high reflux ratio until the temperature in the still pot began to climb indicating exhaustion of the ternary azeotrope.

The product was then redistilled in the glass precision column under atmospheric pressure. The atmospheric ternary azeotrope would come off first and continue to come off until one of the constituents of the ternary was exhausted from the charge. The next higher boiling azeotrope, always a binary, would then come off until one or both of its constituents were exhausted. Any material remaining would be one of the three original constituents of the ternary. By determining the amount and composition of each fraction the composition of the ternary obtained under 60 psig pressure could then be calculated.

This procedure was then repeated using the ternary azeotrope composition determined above as a basis for the proper feed composition. The 60 psig ternary azeotrope thus obtained was analyzed as above. If the ternary azeotrope obtained from the second determination was approximately the same

as that from the first determination it was assumed to be the correct 60 psig ternary azeotrope, if not another determination was made.

ESTERIFICATION RATE UNDER 60 PSIG PRESSURE: The proper feed charge for continuous operation was calculated from the final 60 psig ternary azeotrope composition. A large batch of feed was prepared and the unit was operated continuously for 30 to 40 hours. The unit was operated at decreasing reflux ratios to determine how fast product could be removed without resulting in a temperature rise in the head. The product taken off each hour was weighed and by keeping the amount of charge in the still pot approximately constant the per cent of charge removed per hour could be calculated. An estimate of the rate of esterification under operating conditions was thus obtained. This may not be the maximum esterification rate under the operating conditions because the capacity of the column may have been reached before the rate of take-off equaled the rate of esterification.

The 30 to 40 hour run also served as a check on the feed composition. If there was a build-up of any component in the still pot it indicated that the feed composition was incorrect.

In the case of ethyl, n-propyl, and iso-propyl alcohols, the feed was of one phase and could be admitted to the still pot continuously by adjusting the valve on the feed tank. In the case of the higher alcohols the feed was two phases and was added in small batches so that the operation was approximately continuous.

ESTERIFICATION RATE AT ATMOSPHERIC PRESSURE: To determine the rate of esterification at the boiling point under atmospheric pressure equal mol portions of alcohol and acetic acid were placed in an Erlenmeyer flask and boiled at total reflux using a pyrex glass Liebig concenser set in a vertical position. After boiling for one hour the flask was placed in an ice bath and the unreacted acid was titrated with a standard solution of sodium hydroxide using phenolphthalein as the indicator. The per cent of esterification could then be calculated.

C. MATERIALS

The acetic acid used in this investigation was c.p. grade obtained from Merck and Company Inc.

The alcohols used were c.p. grade obtained from Sharples, Eimer and Amend, and Eastman Kodak.

III SAMPLE CALCULATIONS

Calculations of feed charge on the basis of the atmospheric pressure ternary, ternary composition at 60 psig pressure, and feed charge based on the ternary at 60 psig pressure for n-amyl acetate are presented as typical for all acetates produced.

A. Calculation of feed charge on the basis of the atmospheric ternary:

	Ester	Alcohol	Water
Weight per cent	10.5	33.3	56.2
Mol weight	130.2	88.15	18
Mols	.0806	.378	3.12
Mols	1	4.68	38.7

Feed Charge

	Mols	Grams
Acid	1	60
Alcohol	4.68 + 1	500
Water	38.7 - 1	678

B. Calculation of ternary composition under 60 psig pressure: Analysis of the ternary product under 60 psig pressure was 44.7% atmospheric ternary (10.5% ester, 33.3% alcohol, and 56.2% water), 40.3% binary (46% alcohol and 54% water), and 15% water.

	Ester	Alcohol	Water
Atm. ternary	4.7	14.9	25.1
A-W binary	0	18.6	21.7
Water	0	0	15.0
60 psig ternary	4.7	33.5	61.8

C. Calculation of feed charge on basis of 60 psig ternary:

	Ester	Alcohol	Water
Weight per cent	4.7	33.5	61.8
Mol weight	130.2	88.15	18
Mols	.0361	.380	3.43
Mols	1	10.52	95

Feed Charge

	Mols	Grams
Acid	1	60
Alcohol	10.52 * 1	1015
Water	95 - 1	1690

IV RESULTS

It was deceided to operate the unit under a pressure of 60 psig since this would give a substantial temperature rise compared to the atmospheric boiling points and was about the maximum pressure at which the equipment used could be operated.

The literature indicates that there is no ternary azeotrope formed by methyl alcohol, methyl acetate, and water and also indicates that the lowest boiling binary azeotrope is composed of methyl alcohol and methyl acetate. Therefore, the esterification method proposed could not be operated continuously since there would be no method of carrying off the water formed in the esterification reaction. On the chance that there might be a ternary azeotrope at a pressure of 60 psig, a mixture of acetic acid and methyl alcohol based on the alcohol-ester binary azeotrope was fed to the unit. The product was analyzed and, as at atmospheric pressure, the lowest boiling azeotrope was the alcohol ester binary.

The esterification of ethyl alcohol with acetic acid under a pressure of 60 psig resulted in a ternary azeotrope boiling at 120°C. and consisting of 36.7 per cent alcohol, 56.6 per cent ethyl acetate, and 6.7 per cent water. Thus, the ternary azeotrope would remove only 58 per cent of the water formed by the esterification reaction. To make the operation continuous it was necessary to add enough anhydrous ethyl acetate and extra ethyl alcohol to the feed to form the ternary azeotrope with the remaining 42 per cent water. The feed composition for continuous operation is given in Table IV. During a long run based on this feed

composition 4291 grams were fed to the unit. Product was removed at a rate as high as 27.3 per cent of the still pot charge per hour without any build up of any component or any temperature rise. Analysis listed in Tables I, II, and III are in weight per cent.

The esterification of n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, n-amyl, and sec-amyl alcohols with acetic acid under 60 psig pressure resulted in ternary azeotropes of the compositions give in Table II. In each case the ternary azeotrope would remove all the water formed by the esterification reaction, and in order that the product from the still correspond with the ternary azeotrope composition, an excess of alcohol and water had to be added to the feed. Long runs were made for each esterification with feed at the composition given in Table IV and in each case product was removed at the maximum rate indicated in Table III.

In the case of both tert-butyl and tert-amyl alcohols with acetic acid the esterification rate was so slow that a reflux ratio high enough to keep the temperature constant could not be maintained. When a small amount of product was withdrawn the head temperature would immediately begin to rise.

The rates of esterification at the atmospheric boiling points given in Table III were calculated from experimental data.

V SUMMARY

The following summary may be drawn from the results found in this investigation:

1. Esterification of the lower alcohols by acetic acid, with the exception of methyl alcohol, may be carried out continuously in the absence of a catalyst in a rectification column under pressure.
2. In all cases the ternary azeotrope composition at 60 psig pressure is different from that at atmospheric pressure.
3. In all cases the per cent ester in the ternary azeotrope is less at 60 psig pressure than at atmospheric pressure.

VI LITERATURE CITED

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VII APPENDIX

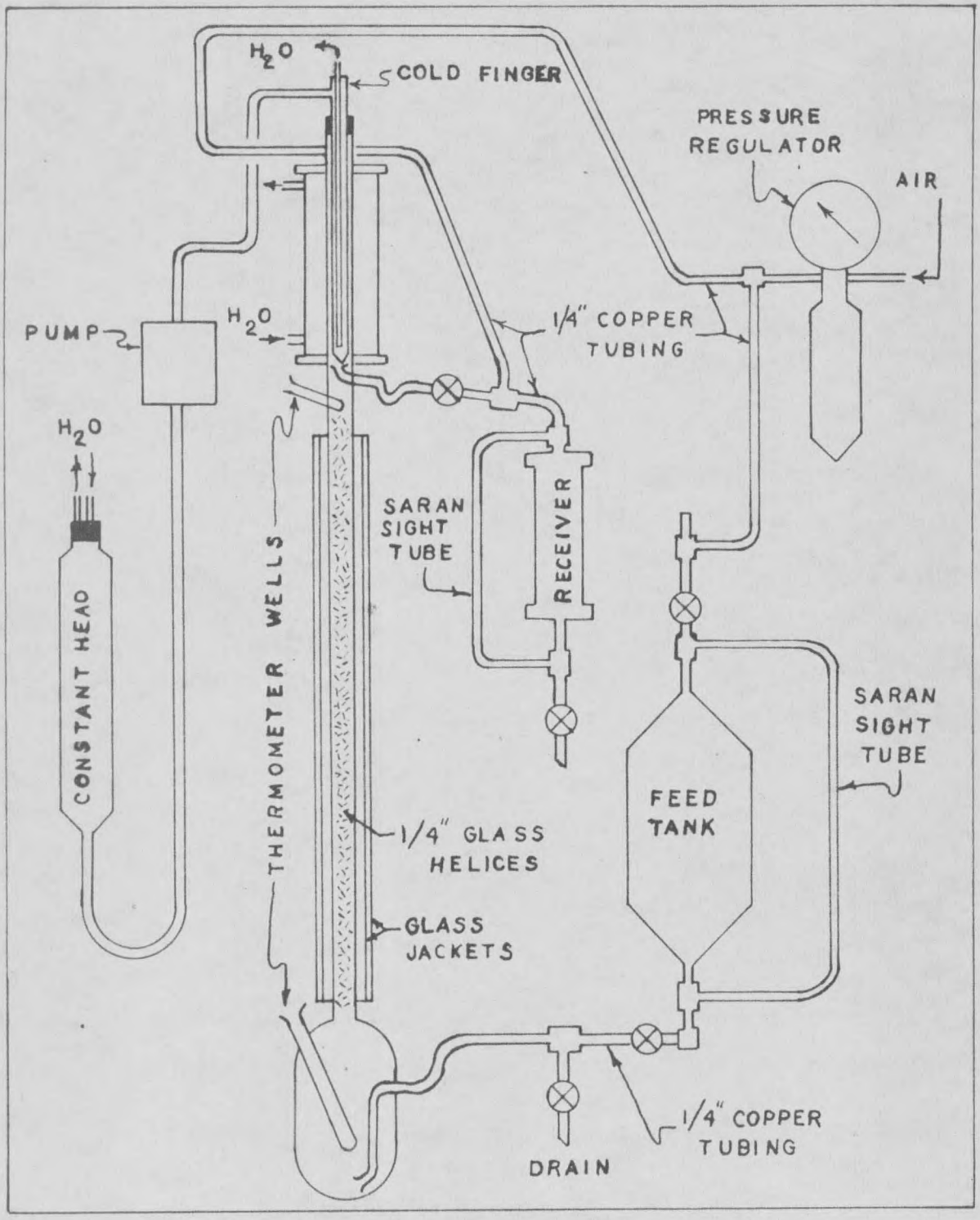

Figure 1 Schematic Diagram of Equipment

Table I

ATMOSPHERIC AZEOTROPE COMPOSITIONS

Ester		E-W Binaries		A-W		E-A		Ternary			
	B.P. °C.	B.P. °C.	% W	B.P. °C.	% W	B.P. °C.	% A	B.P. °C.	% E	% A	% W
Methyl Acetate	57.1	56.5	3.5			54.0	18.5	No ternary			
Ethyl Acetate	77.1	70.45	8.6	78.15	4.4	71.8	30.6	70.3	83.2	9.0	7.8
n-Propyl Acetate	101.6	82.4	12.5	87.7	28.3	94.2	40	82.2	59.5	19.5	21.0
iso-Propyl Acetate	91.0	77.4	6.2	80.4	12.1	81.3	60	76.2	63.7	26.2	10.1
n-Butyl Acetate	125.1	90.2	26.7	92.4	38.0	117.2	47	89.4	35.3	27.4	37.3
iso-Butyl Acetate	116.3	87.5	19.5	89.9	33.0	87.4	16.6	86.8	46.5	23.1	30.4
sec-Butyl Acetate	112	86.6	19.4	88.5	32.0	99.6	13.7	86.0	32	45	23
tert-Butyl Acetate	96	no date		79.9	11.8	no data		no data			
n-Amyl Acetate	148	95.2	41	95.9	54	no azeo.		94.8	10.5	33.3	56.2
iso-Amyl Acetate	139	93.8	36.2	95.2	49.6	no azeo.		93.6	24	31.2	44.8
tert-Amyl Acetate	no data										

E- Ester A- Alcohol W- Water

Table II

60 PSIG TERNARY AZEOTROPES

Ester	B.P. °C.	%Alcohol	%Ester	%Water
Methyl Acetate		No ternary		
Ethyl Acetate	120	36.7	55.6	6.7
n-Propyl Acetate	127	57.9	23.0	19.1
iso-Propyl Acetate	122	60.8	28.0	11.2
n-Butyl Acetate	135	47.1	15.2	37.8
iso-Butyl Acetate	133	41.6	26.9	31.5
sec-Butyl Acetate	133	63.4	6.4	30.2
tert-Butyl Acetate		No data		
n-Amyl Acetate	142	33.5	4.7	61.8
iso-Amyl Acetate	140	39.9	13.2	46.9
tert-Amyl Acetate		No data		

Table III

ESTERIFICATION RATES

Ester	Atmospheric Temp. °C.	Rate Rate	155°C. Rate	60 PSIG Temp. °C.	Rate Rate
Methyl Acetate	62	10.90	55.60		
Ethyl Acetate	77	8.73	46.95	133	27.3
n-Propyl Acetate	95	9.70	46.92	140	28.6
iso-Propyl Acetate	82	2.20	26.53	136	23.0
n-Butyl Acetate	101	14.25	46.85	145	26.0
iso-Butyl Acetate	98	11.75	44.36	143	20.4
sec-Butyl Acetate	97	4.30	22.59	144	10.2
tert-Butyl Acetate	87	0.22	1.43		
n-Amyl Acetate	104	13.00		150	19.7
iso-Amyl Acetate	103	11.35		148	17.8
tert-Amyl Acetate	95	None			

Table IV

FEED COMPOSITION FOR CONTINUOUS OPERATION

Ester	%Acid	%Alcohol	%Water	%Ester
Methyl Acetate	Continuous operation not possible			
Ethyl Acetate	22.4	53.8	0	23.8
iso-Propyl Acetate	16.7	77.6	5.7	0
n-Propyl Acetate	13.5	71.5	15.0	0
n-Butyl Acetate	7.9	56.7	35.4	0
iso-Butyl Acetate	13.9	58.7	27.4	0
sec-Butyl Acetate	3.3	67.4	29.3	0
tert-Butyl Acetate	--	--	--	-
n-Amyl Acetate	2.2	36.7	61.1	0
iso-Amyl Acetate	6.1	49.0	44.9	0
tert-Amyl Acetate	--	--	--	-