



Continuous noncatalytic esterification of lower formates
by Ih-Cheo Yang

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

It was found that the rate of esterification of lower alcohols (n-propyl, n-butyl, iso-butyl, n-amyl, iso-amyl alcohol) with formic acid is increased by the raising of temperature.

The use of increased temperature obtained by rectifying at 60 psig pressure was investigated as a means of carrying out the continuous non-catalytic esterification of n-propyl, n-butyl, iso-butyl, n-amyl, and iso-amyl alcohol with formic acid.

The non-catalytic esterification rates at the atmospheric pressure and at 60 psig pressure were determined for n-propyl, n-butyl, iso-butyl, n-amyl and iso-amyl alcohol with formic acid. The ternary azeotropic composition at 60 psig pressure was determined for each formate system and a continuous non-catalytic esterification carried out for each ester.

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Submitted to the Graduate Faculty
in
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ABSTRACT

It was found that the rate of esterification of lower alcohols (n-propyl, n-butyl, iso-butyl, n-amyl, iso-amyl alcohol) with formic acid is increased by the raising of temperature.

The use of increased temperature obtained by rectifying at 60 psig pressure was investigated as a means of carrying out the continuous non-catalytic esterification of n-propyl, n-butyl, iso-butyl, n-amyl, and iso-amyl alcohol with formic acid.

The non-catalytic esterification rates at the atmospheric pressure and at 60 psig pressure were determined for n-propyl, n-butyl, iso-butyl, n-amyl and iso-amyl alcohol with formic acid. The ternary azeotropic composition at 60 psig pressure was determined for each formate system and a continuous non-catalytic esterification carried out for each ester.

I. INTRODUCTION

The most important factors causing an increased rate of esterification are catalyst and rise in temperature.

Catalysts, such as hydrochloric and sulfuric acids are used in commercial preparations of esters because of their relative low cost. The raw materials are organic acid, lower alcohol in excess, and a little sulfuric acid. They are mixed, conducted through heat exchangers and passed through an esterification column at atmospheric pressure. The overhead from this column is the ternary azeotrope and consists of alcohol, ester and water.

The rate of chemical reaction increases rapidly with increased temperature. The empirical Arrhenius Equation:

$$\frac{d \ln k}{dT} = \frac{A}{RT^2}$$

is the relation between the specific reaction velocity constant K and temperature. T is the absolute temperature, R is the gas law constant, and A is the energy of activation. 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.

In order to carry out the reaction continuously, the ester must be removed from the reaction mixture in the form of a ternary constant boiling mixture. The ternary consists of alcohol, ester and water, and the feed charge is calculated from the composition of this ternary. The

feed charge must be of such a composition that no component will build up as excess in the still pot. Before the continuous esterification is carried out, it is necessary to determine a temperature and pressure at which the esterification rate is sufficiently high, as well as 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 (expressed as per cent conversion per hour) at the boiling point under atmospheric pressure of n-propyl, n-butyl, iso-butyl, n-amyl, and iso-amyl alcohol with formic acid.
- (2) the non-catalytic esterification rate at the boiling temperature corresponding to 60 psig pressure of each of the alcohols named above.
- (3) the composition of the ternary azeotrope formed in each case at the temperature corresponding to 60 psig pressure.
- (4) the proper charge for each of the systems named above, correct for 60 psig pressure, and to operate the esterification process continuously at this 60 psig pressure.

II. PROCESSES

A. Determination of the esterification rate at atmospheric pressure.

1. Equipment:

The equipment consisted of 250 ml. Erlenmeyer flask, a Pyrex glass Liebig condenser, a 110-volt, 500 watt heater controlled by an autotransformer, an ice bath, and a 50 ml. buret.

2. Materials:

The formic acid used was 98-100% pure, obtained from General Chemical Division, Allied Chemical & Dye Corporation. (The calculation in this investigation is based on 99% pure). The n-propyl, n-butyl, n-amyl, iso-butyl, and iso-amyl alcohols used were c.p. grade, obtained from Sharples, Eimer and Amend, and Eastman Kodak Co.

3. Procedure:

Equal mol portions of alcohol and formic acid were placed in an Erlenmeyer flask and boiled under atmospheric pressure at total reflux by using a Pyrex glass Liebig condenser. After one hour boiling, 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 percent of esterification could then be calculated.

B. Preparation of 60 psig pressure ternary and analysis of its composition.

1. Equipment:

(a) The 60 psig pressure esterification unit is shown in Fig.

1. The unit consisted of a copper precision column $1\frac{1}{4}$ inches in

diameter by 52 inches long. The column was packed with $\frac{1}{4}$ inch glass helices. The still pot which was silver soldered to the copper column, was constructed from a stainless steel oxygen tank with a capacity of about 1800 ml. 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 $\frac{1}{2}$ -inch copper tubing (1). The flow of water through the cold finger was controlled by using a laboratory bellows pump. The condenser motor was supplied from a constant head source. The reflux ratio obtained in the cold finger was estimated to be in the range of 5-1 to 10-1.

Connected to the still pot was a copper feed tank with a capacity of about five liters, and a receiver constructed of $1\frac{1}{2}$ inch standard iron pipe. Both the feedback and receiver were kept under the same operating pressure as the column.

The desired pressure was obtained by means of an air compressor and a DeVilbiss Pressure Regulator. Two 110-volt 550 watt heaters controlled by auto-transformers supplied the heat to the still pot and the column.

(b) For the purpose of analysis:

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

2. Procedure:

It was first 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, the proportions of alcohol, acid and water (if necessary) required to form the ternary azeotrope were calculated. For example:

Atmospheric ternary of iso-butyl formate consists of the following:

	Isobutyl formate	Isobutyl alcohol	Water
Wt. %	76	6.7	17.3
Mols wt.	102.13	74.12	18
Mols	0.7425	0.0904	0.9605
Mols	1	0.122	1.295

Feed Charge

	Mols	Grams
Formic acid	1	46
Isobutyl alcohol	1 + 0.122	83.2
Water	1.295-1	5.3

About 100 gm. 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.

This product was then redistilled in the glass precision column under atmospheric pressure. The atmospheric ternary azeotrope came off first and continued to come off until one of the constituents was exhausted, when the temperature of the flask be-

gan to climb. The next higher boiling azeotrope, always a binary, then came off until one or both of its constituents were exhausted, when the temperature of the flask again began to climb. The composition of the ternary obtained under 60 psig pressure could then be calculated.

For example: Analysis of the isobutyl formate ternary under 60 psig pressure was 63.3% atmospheric ternary, (76% isobutyl formate, 6.7% isobutyl alcohol, 17.3% water), 21.9% binary (67% isobutyl alcohol, 33% water) and 14.8% water.

	Isobutyl formate	Isobutyl alcohol	Water
Atm. ternary	$63.3 \times 76 = 48.1$	$63.3 \times 6.7 = 4.2$	$63.3 \times 17.3 = 11.0$
Alcohol-water binary	0	$21.9 \times 67 = 14.7$	$21.9 \times 33 = 7.2$
Water	0)	14.8
Therefore 60PSIG TERNARY =	48.1	18.9	33.0

C. Estimation of the esterification rate under 60 psig pressure

Procedure:

The proper feed charge was calculated from the final 60 psig ternary azeotrope composition. For example, 60 psig isobutyl ternary consists of 48.1% isobutyl formate, 18.9% isobutyl alcohol, and 33.0% water.

	Isobutyl formate	Isobutyl alcohol	Water
wt. %	48.1	18.9	33
Mol. wt.	102.13	74.12	18
Mols	0.470	0.255	1.835
Mols	1.	0.542	3.91

Feed Charge

	Mols	Grams
Formic acid	1	46
Isobutyl alcohol 1 + 0.542		114.4
Water	3.91 - 1	52.4

According to the feed charge ratio, about 100-150 gms. of this mixture (based on $\frac{1}{2}$ mol of formic acid) was then charged to the unit and boiled under 60 psig. pressure at total reflux for one hour. The head was changed from total reflux to zero reflux until the temperature in the still pot began to climb, indicating exhaustion of the ternary azeotrope (about 12-15 min.) The weight of the ternary and the esterification rate under 60 psig pressure were calculated. For example, from the feed charge ratio shown above, feed 23 gms. formic acid, 57.2 gms. isobutyl alcohol and 26.2 gms. water to the unit. The weight of the ternary obtained from the above method is 55 gms. From analysis, the composition of isobutyl formate in 60 psig ternary is 48.1%. So the isobutyl formate formed is $55 \times 0.481 = 26.4$ gms.



$$\begin{array}{ccc} 46 & : & 102 \\ x & : & 26.4 \end{array}$$

∴ $x = 11.9$ gms. of HCOOH used to form 26.4 gms.

Isobutyl formate. Therefore, the esterification rate under 60 psig pressure = $\frac{11.9}{23} \times 100 = 51.8\%$

The procedure can be repeated several times to get the mean value.

III. RESULTS

A pressure of 60 psig, which would give a substantial temperature rise compared to the atmospheric boiling point, was about the maximum pressure at which the equipment used could be operated. The continuous non-catalytic esterification of n-propyl, n-butyl, isobutyl, n-amyl, and isoamyl alcohols with formic acid could be successfully operated in this unit.

The esterification rate at atmospheric pressure and 60 psig pressure of n-propyl, n-butyl, isobutyl, n-amyl, and isoamyl alcohols with formic acid given in Table II were calculated from experimental data.

The compositions of 60 psig pressure azeotrope ternaries were analyzed and calculated as given in Table III.

For continuous operation, the feed charges were calculated according to the compositions of 60 psig pressure ternary. The feed charge compositions are given in Table IV. The product was removed at the rate as high as the esterification rate, under 60 psig. pressure.

IV. SUMMARY OF RESULTS

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

1. The esterification rate under 60 psig pressure is much higher than that at atmospheric pressure.
2. Esterification of n-propyl, n-butyl, isobutyl, n-amyl, isoamyl alcohols by formic acid may be carried out continuously in the absence of a catalyst in a rectification column under 60 psig pressure.

3. The 60 psig pressure ternary composition is different from that at atmospheric pressure in all cases.
4. The per cent of ester in the ternary azeotrope is less at 60 psig pressure than at atmospheric pressure in all cases.

V. DISCUSSION

From Arrhenius equation $\ln \frac{K_2}{K_1} = \frac{A}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$ we can calculate the energy of activation from experimental data. For n-propyl formate $A = 7410$ cal/g. mol; n-butyl formate, $A = 6890$ cal/g. mol; isobutyl formate $A = 5880$ cal./g. mol; n-amyl formate $A = 2500$ cal/g. mol; Isoamyl formate $A = 1720$ cal/g. mol.

From Arrhenius equation the reaction rate constant can also be found. For example, to find the reaction rate of isobutyl formate at 155°C. From experimental data, $K_1 = 51.6$ at 138°C.

$$\therefore \ln \frac{K_2}{51.6} = \frac{5880}{1.986} \left(\frac{1}{273} - \frac{1}{155} \right)$$

$$\therefore K_2 = 67.8\% \text{ at } 155^\circ\text{C.}$$

From literature, $K = 61.69\%$ at 155°C. (2)

VI. LITERATURE CITED

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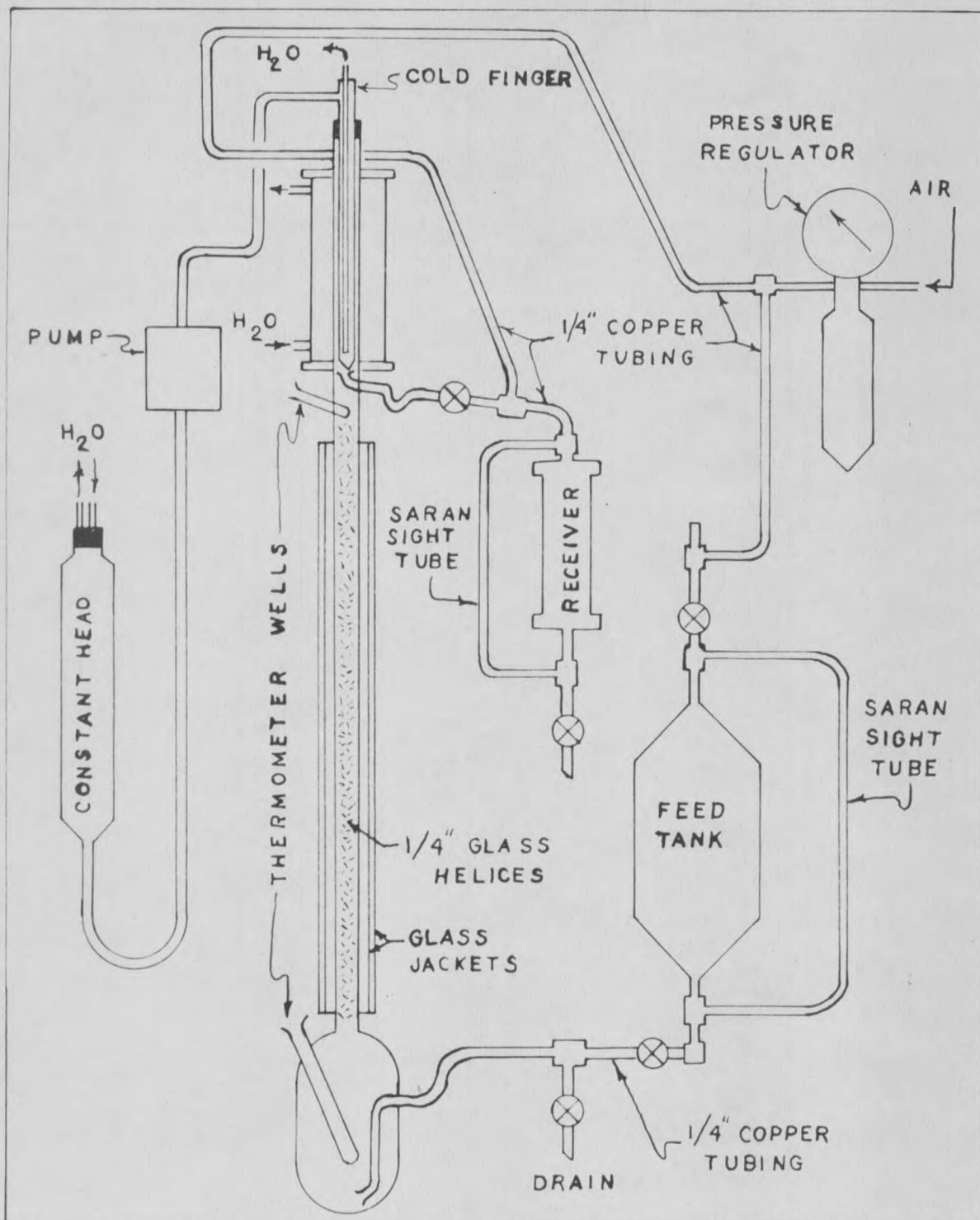


Figure 1 Schematic Diagram of Equipment

TABLE I - ATMOSPHERIC AZEOTROPE COMPOSITIONS (3)

	A	E	Binary E-W		Binary A-W		Binary E-A		B.P. °C	wt.% E	wt.% A	wt.% W
	B.P. °C	B.P. °C	B.P. °C	wt. % W	B.P. °C	wt. % W	B.P. °C	wt. % A				
Ethyl Formate	78.3	54.1	--	--	78.15	4.4	No Azeo.			No data		
n-Propyl Formate	79.2	81	71.6	2.3	87.7	28.3	80.6	9.8	70.8	82	5	13
Isopropyl Formate	82.5	71	No data		80.4	12.1	No data			No data		
n-Butyl Formate	117.7	106.9	83.8	15	92.4	38	105.8	23.7	83.6	68.7	10	21.3
Isobutyl Formate	107.9	98.5	80.4	7.8	89.9	33	97.8	20.6	80.2	76	6.7	17.3
n-Amyl Formate	137.8	132	91.6	23.4	95.9	54	130.4	43	91.4	41.2	21.2	37.6
Isoamyl Formate	131.6	123.3	90.2	21.	95.2	49.6	123.6	26	89.8	48	19.6	32.4

E - Ester

A - Alcohol

W - Water

TABLE II - ESTERIFICATION RATES

Ester	Atmospheric Rate		60 psig Rate	
	Temp. °C	Rate	Temp. °C	Rate
n-Propyl Formate	90	11.0	134	26.3
n-Butyl Formate	104.5	28.9	144	31.6
Isobutyl Formate	98	24.6	138	51.6
n-Amyl Formate	108	13.9	144.5	18.6
Isoamyl Formate	106	21.0	143	23.3

(From literature the esterification rate of Isobutyl Formate at 155°C. is 61.69%) (2)

TABLE III - 60 PSIG TERNARY AZEOTROPES

Ester	B.P.°C	wt. % Alcohol	wt. % Ester	wt. % Water
n-Propyl Formate	134	30.7	32.4	36.9
n-Butyl Formate	144	27.3	39.0	33.7
Isobutyl Formate	138	18.9	48.1	33.0
n-Amyl Formate	144.5	20.2	24.5	55.3
Isoamyl Formate	143	27.6	18.3	54.1

TABLE IV. - FEED COMPOSITION FOR CONTINUOUS OPERATION

Ester	wt. % Acid	wt. % Alcohol	wt. % Water
n-Propyl Formate	17.0	52.9	30.1
n-Butyl Formate	17.5	55.7	26.8
Isobutyl Formate	21.6	53.9	24.5
n-Amyl Formate	9.6	39.5	50.9
Isoamyl Formate	7.3	40.7	52.0

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