



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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Abstract:

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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PRODUCTION OF LOWER ACETATES

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JOHN A. RUNBERG

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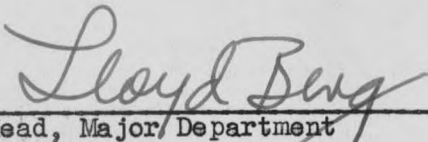
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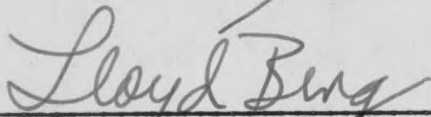
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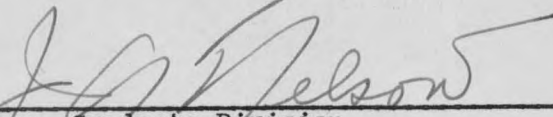
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ABSTRACT

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.

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

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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.

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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.

