Preliminary Study of the Heat Release From Esterification Process

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Abstract-- Esterification is one of the popular processes in chemical engineering. Various important products are produced from this reaction and their applications are varied. Esterification process can be classified as exothermic reaction where in every reaction; a few amount of heat will be released to the surrounding. Hence it is a quite simple reaction; the study on heat releases should not be exceptional. In this study, two different parameters (effect of different catalyst concentration and different operating temperature) are applied to determine the amount of heat release and the possibility of the reaction in creating runaway reaction. The study has selected an esterification reaction between acetic acid and methanol because of their well known reaction and it is a moderated exothermic process.

Index Term--- esterification reaction, exothermic reaction, runaway reaction

I. INTRODUCTION

Esterification of carboxylic acids with alcohol in the presence of acid catalyst has been the subject of investigation by many research workers. Both homogeneous and heterogeneous catalyst had been used for this purpose. Mineral acids can be given as the example of homogeneous catalyst and a cation-exchange resin in the acid form can serve as heterogeneous catalyst [1].

Esterification process involved the reaction of ethanol and acetic acid catalyzed by sulfuric acid were chosen in this work. The stoichiometry reaction of the process is as below:

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O}
\]

Ethanol reacts with acetic acid in producing ethyl acetate. This reaction is called a homogeneous liquid phase. Normally, in the absence of a catalyst, the reactions are very slow and require typically several days to attain the equilibrium [7]. Therefore, a catalyst was added to enhance the reaction. The catalyst could be heterogeneous or homogenous. In this reaction, sulfuric acid acted as a homogeneous catalyst. This catalyst is already known as an efficient mineral acid catalyst [7].

The reaction was selected because it is a well known reaction, simple and moderately exothermic [Heat or reaction, \(\Delta H = -0.0114\text{kJ/mol}\)] with no danger of decomposition reaction. Furthermore, this type of reaction also got the attention of other researchers in studying the possible runaway reaction on different chemical types [3][4][6].

The commercial production of ethyl acetate is mainly by two processes: the Tischenko reaction produces ethyl acetate by direct conversion of ethanol via acetaldehyde using an aluminum alkoxide catalyst and the production of ethyl acetate by direct esterification of ethanol with acetic acid and sulfuric acid catalyst. In this experiment, the direct synthesis of ethyl acetate was chosen. For a normal operation, the reactant concentration and catalyst concentration were set respectively to be 6M and 3M [2]. The reaction was carried out at room temperature with 5% catalyst volume and without cooling water.

Furthermore, the product from this reaction (i.e., ethyl acetate) is a very important solvent and is used in many products and industries [5]. It is used extensively as a solvent for high-resolution printing inks and laminating adhesives. It is also an important solvent in paints, resin coatings and varnishes and also used in the pharmaceutical industry as a process and purification solvent.

To the best of our knowledge, no researcher has reported the study on the heat release from esterification of acetic acid with ethanol in the presence of sulfuric acid. The information of heat release from esterification process can be used to detect the possibility of runaway reaction [3][4][6]. The function of temperature and concentration can be applied to investigate runaway phenomena [6].

This work was undertaken to study on the heat release from esterification of acetic acid with ethanol in the presence of sulfuric acid as a catalyst. The reaction was selected because it is a well-known reaction and is moderately exothermic reaction with no danger of decomposition reactions and for which accurate kinetic exist; the reaction exhibits second-order kinetics when no strong acid is present and a kind of autocatalytic behaviour when the acid is introduced.

II. EXPERIMENTAL SECTION

A Pilots-Plant Installation

The experiment was carried out in a pilot-plant batch reactor. The schematic diagram for the pilot-plant batch reactor is shown in Figure 1.
The pilot-plant batch reactor consists of reaction vessel, electric heating via heating mantle, variable speed stirrer, temperature indicator, cooling coil, feed vessel, gas feed pipe and solid discharge pipe. The maximum capacity of the reaction vessel is 20 liters.

9.5L of ethanol and 9.5L of ethyl acetate were charged to the reaction vessel via the feed vessel and charge port. The reaction vessel was fitted with a manually adjusted variable speed (0-800 rpm) stirrer enabling the degree of mixing to be varied. Heating was supplied by a heating mantle with manually adjusted power setting; the reaction temperature was indicated by a dial thermometer in the reaction vessel. The reaction vessel was also fitted with an internal cooling coil allowing the reaction mixture to be cooled. By varying the heating and cooling, exothermic reaction could be studied.

During the reaction process, any vapors produced passed up through the fractionating packed column to the condenser where they were condensed. Any non-condensable gases passed through the condenser to vent or to the vacuum system. Condensate from the condenser flowed back down to the reflux divider where it could be directed either to the top of the packed column or removed as product by adjusting the reflux valve.

During all the experiments, the process temperature and conductivity were recorded using a temperature indicator and conductivity meter. On the other hand, the concentration of product (ethyl acetate) was measured from the titration process.

B. Experiment Design

A set of three experiments were carried out in the pilot-scale chemical plant. The selected reaction was the catalyzed esterification between acetic acid and ethanol. In this experiment sulphuric acid is acted as a catalyst for the reaction. It is our interest to analyze the reaction because it is moderately exothermic reaction with no danger of side or decomposition reactions. In addition, this reaction has been extensively studied in the past.

The reactor was operated with three different catalyst concentrations and with three different temperatures. The parameters and operating conditions are listed in Table I.

![Fig. 1. Pilot-plant batch reactor](image)

**TABLE I**

<table>
<thead>
<tr>
<th>OPERATION CONDITON FOR THE ESTERIFICATION EXPERIMENT</th>
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<tbody>
<tr>
<td><strong>Experiment 1:</strong></td>
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<tr>
<td>Different catalyst concentration</td>
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<tr>
<td>Temperature: room temp</td>
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<tr>
<td>Acetic acid concentration: 6M</td>
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<tr>
<td>Ethanol concentration: 6M</td>
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<tr>
<td>Sulfuric acid concentration: 3M, 4M &amp; 5M</td>
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<td>Stirrer speed: 50 rpm</td>
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<td><strong>Experiment 2:</strong></td>
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<tr>
<td>Different operating temperature</td>
</tr>
<tr>
<td>Temperature: room temp, 40°C &amp; 50°C</td>
</tr>
<tr>
<td>Acetic acid concentration: 6M</td>
</tr>
<tr>
<td>Ethanol concentration: 6M</td>
</tr>
<tr>
<td>Sulfuric acid concentration: 3M</td>
</tr>
<tr>
<td>Stirrer speed: 50 rpm</td>
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C. Experimental Procedure

The esterification experiments have been carried out following the procedure summarized below:

**Experiment 1:**

(i) Ethanol (reactant B) was weighted and loaded into the reactor vessel using feed vessel.
(ii) Acetic acid (reactant A) was weighted and loaded into reactor vessel.
(iii) Sulfuric acid (catalyst) is added to the reactor vessel.
(iv) When the reaction had finished, the reactor contents were discharged.
(v) The experiment is repeated with different catalyst concentration.

Experiment 2:
(i) Ethanol (reactant B) was weighted and loaded into the reactor vessel using feed vessel.
(ii) Acetic acid (reactant A) was weighted and loaded into other reactor vessel.
(iii) Reactor vessel and other reactor vessel temperatures were set at the desired temperature.
(iv) Once both reactor vessel and other reactor vessel had reached the set-point temperature, acetic acid was added to the reactor from the feed vessel.
(v) Sulfuric acid (catalyst) is added to the reactor vessel.
(vi) The experiment is repeated with different temperature set-up.

III. RESULTS
Figure 2 and 3 represent the experimental results for both two experiments. In the first experiment, the differential temperature will increase gradually with time by increasing the catalyst concentration for the 3, 4 and 5 M until they reach the equilibrium at 70, 60 and 30 min respectively. The differential temperature then reaches other equilibrium stage at 130, 120 and 110 min. At this stage, the differential pressure constant at 57.14%, 64.29% and 75% respectively. The differential pressure were constant because of the reaction already reached the equilibrium. The running of the experiment after 200 min is believed will not change the differential temperature.

Compared to Figure 3, the differential pressure at this experiment is quite longer to reach the equilibrium stage. By increasing the operating temperature, the equilibrium stage is difficult to achieve. It shown at ambient, 40°C and 50°C, the equilibrium stage only reach after 70, 80 and 120 min respectively. It also shows that at every 10°C temperature increase, the differential pressure will increase between 43-50%. From this experiment, the temperature will increase 1.4-1.5 times from their operating temperature.

IV. CONCLUSION
The results show that the possibility more heat will be released from this reaction with higher catalyst concentration and higher operating temperature. It also shows that the possibility runaway reaction will occur. Dangerous process conditions which cannot be carried out in experimental set-ups were simulated by special developed simulators. The information from this experiment was applied to develop a fault detection system.

ACKNOWLEDGEMENT
The authors acknowledge Ministry of Science, Technology and Innovation Malaysia for the Science Fund Grant (03-01-05-SF0220) to support the present research work.

VI. REFERENCES

