Synthesis of Acrolein from Glycerol Using FePO$_4$ Catalyst in Liquid Phase Dehydration

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Abstract. Acrolein is currently produced using propylene from crude oil while its price and scarcity are increasing. A renewable material such as glycerol is an attractive alternative for acrolein production. It can be obtained from crude palm oil (CPO) and is a byproduct of biodiesel production. Besides being able to compete economically, glycerol is an environmentally friendly material. The purpose of this study is to synthesize acrolein from glycerol using FePO$_4$ catalyst in liquid phase dehydration. The catalyst was prepared by three different methods: hydrothermal (catalyst A), deposition at Fe/P = 1.15 (catalyst B), and deposition at Fe/P = 1.20 (catalyst C). The experimental reaction temperature was varied at 220, 240 and 260 °C under constant atmospheric pressure. The results showed that catalyst C provided the best yield (91%), followed by catalyst A (90%) and catalyst B (82%). The increasing reaction temperature showed a tendency to increase the yield of acrolein, while the presence of oxygen reduced the yield of acrolein and allowed the reaction to produce more side products such as glycerol propanal, acetaldehyde, and propionate. Catalyst reuse without any regeneration resulted in a yield profile of acrolein that continued to decline.

Keywords: *acrolein; dehydration; glycerol; CPO; FePO$_4$ catalyst.*

1   Introduction

Acrolein is an intermediate product in the production of acrylic acid, an important monomer in the polymer industry. The global acrylic acid industry is still dominated by the United States and Western Europe, although currently the production of acrylic acid grows mainly in Asia and the Middle East. Acrylic acid is a primary material in the manufacture of superabsorbent polymers. Up to now acrylic acid is produced from petroleum through propylene oxidation in the vapor phase with a capacity of 4.2 million tons/year. There are two steps in the production process:

1. Oxidation of propylene to acrolein: there is a minor product of acrylic acid as a mixed oxide catalyst of Bi/Mo. Acrolein selectivity achieves 85% while propylene conversion achieves 95%.

2. Oxidation of acrolein to acrylic acid: the oxidation reaction is conducted in a single reaction step and requires separation and recycling of the acrolein.

Environmental issues such as global warming and the depletion of world oil reserves result in the need for an alternative for raw materials that are renewable and more environmentally friendly. Many researches on renewable raw materials to synthesize different chemicals are currently undertaken. In this work, glycerol was used for producing acrolein, which is a very attractive choice since glycerol can be obtained from crude palm oil (CPO) and is a by-product of biodiesel production. Additionally, glycerol can be obtained in large quantities as well as easily stored and transported.

Synthesis of acrylic acid from glycerol is carried out in two stages, i.e. dehydration and oxidation. It can be held in vapor phase or liquid phase as follows:
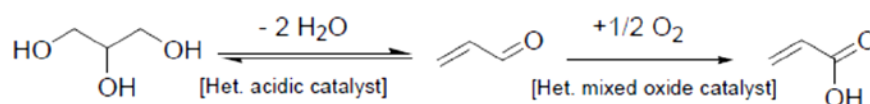
The first reaction is an endothermic dehydration of glycerol to acrolein by using an acid catalyst. Researchers from Arkema have demonstrated that a glycerol dehydration process using iron (III) phosphate catalyst in the vapor phase produces an acrolein yield of 80% and can result in a yield of up to 85% using the same catalyst when it has been modified [1-3]. The second reaction is an exothermic reaction of acrolein to acrylic acid using alumina oxide-VW-Mo-Cu-O catalyst.

Other researchers have reported various catalysts for glycerol dehydration. Silicotungstic acid supported on silica with mesopores of 10 nm showed the highest catalytic activity with an acrolein selectivity of >85 mol% under ambient pressure at 275 °C [4]. Ning reported that activated carbon (AC)-supported silicotungstic acid can be used as glycerol dehydration catalyst. The properties of the catalyst were closely related to silicotungstic acid dispersion and the relative quantities of strong acid sites [5]. Cesium 12-tungstophosphate, also possessing strong Brønsted acid sites, is an active catalyst for the dehydration of glycerol to acrolein in the gas-phase process under 1 bar pressure at 275 °C [6]. Nanocrystalline HZSM-5 catalysts with high Si/Al molar ratio (ca. 65) were used for gas phase dehydration of aqueous glycerol catalyst [7].

2   Research Methods

In the synthesis of acrolein in this work, glycerol dehydration was done by

using a batch reactor and iron (III) phosphate and potassium sulphate as catalysts under 1 bar pressure at a temperature of 190-260 °C. The reaction was carried out with atmospheric oxygen gas and reduction of the oxygen concentration using the nitrogen flow in the liquid phase. The experimantal equipment is shown in Figure 1.
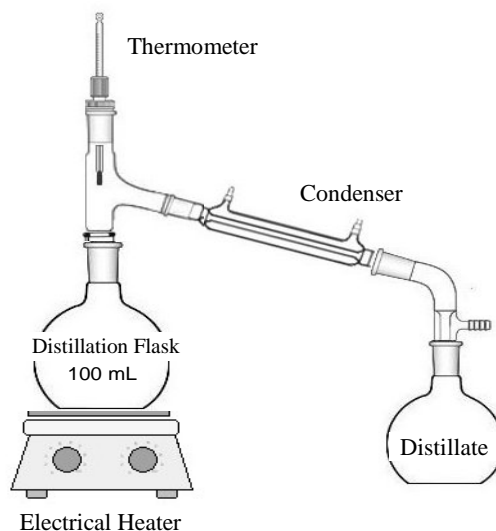

Figure 1 Set-up of research tools.

The reactor consisted of a 100 mL reaction flask equipped with a condenser, which was designed large enough to cool the reaction product, i.e. a length of 25 cm and a diameter of 4 cm. The material of the reactor was stainless steel and the operating conditions were adjusted to the reaction conditions.

Iron phosphate catalyst was made with three different methods. The first was hydrothermal synthesis, the result of which was Catalyst A. Equimolar $FeCl_3.6H_2O$ mixture (0.17 mol) and H_3PO_4 (85%) were mixed and dissolved in 200 mL of stirred water. The solution was then refluxed for 14 hours. The resulting yellow solid was dried overnight in an oven at a temperature of 80 °C and calcined at 400 °C for 4 hours.

The second method was deposition concentration the result of which was Catalyst B. $Fe(NO_3)_3.9H_2O$ of 12.29 g was dissolved in 500 mL of water and mixed with 4.03 g H_3PO_4 at P/Fe ratio = 1.15. The mixture was stirred at a temperature of 80 °C and evaporated. The solid obtained was further dried in an oven overnight at 80 °C and then calcined at 500 °C for 6 hours.

The third method produced Catalyst C, in which iron phosphate catalyst with a P/Fe ratio of 1.2 was prepared by diluting 33.2 g Fe(NO$_3$)$_3$.9H$_2$O and 11.5 g NH$_4$H$_2$PO$_4$ into water. The solution was stirred for 12 hours at room temperature, then evaporated until a solid formed. The solid was dried in an oven overnight at 80 °C and finally calcined at 550 °C for 4 hours.

All catalysts were analyzed using a BET Surface Area Analyzer Nova® 3200 to determine surface area, average diameter and total volume using the isothermal nitrogen adsorption method (BET).

Reactions were performed in the liquid phase using a 100 mL reaction flask and a condenser. Cooling water was used to provide an input temperature of around 20 °C. Analysis of the experimental results was done using GC-FID and GC-MS with the same column type, DB5, and equipped with a helium carrier gas at operation temperatures of 40-300 °C. Each peak shown in GC-FID and GC-MS was then identified.

3   Result and Analysis

In this study, the iron phosphate (FePO$_4$) catalysts as described above and the product in grain form were smoothed using a mortar. The catalyst products had a different color, as shown in Figure 2. Before calcination the FePO$_4$ catalysts had a brownish-yellow color, but after calcination the three methods produced three different colors. This color may be attributed to different raw materials and hence the purity of the FePO$_4$ allows a different reaction with air when calcined.
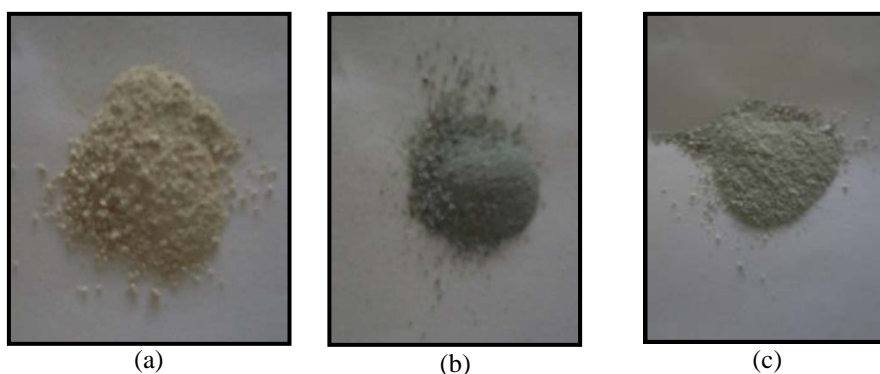

(a)   (b)   (c)

Figure 2 FePO$_4$ catalyst results using method A(a), B(b), and C(c).

Further characterization of the catalyst was performed using BET for surface area and SEM for surface structure. The characteristics of the BET test results are shown in Table 1.

Tabel 1   Surface Area, Average Diameter and Total Volume of Catalysts

Catalyst	Surface Area (m^2/g)	Average diameter (Å)	Total volume (cc/g)
A	5.4	182	0.047
B	2.2	171	0.095
C	10.2	185	0.025

$FePO_4$ has a particle size of 100-500 nm with a low surface area, below 30 m^2/g. Catalyst C had the highest surface area (10.2 m^2/g), then catalyst A (5.4 m^2/g) and catalyst B had the lowest (2.2 m^2/g). Iron phosphate catalyst has a lower surface area compared to other types of catalysts, such as zeolites and mixed oxide catalysts, so to increase the surface area of the catalyst it is necessary to use a buffer that has a large surface area, such as Al_2O_3.

Figure 3 shows the surface image of the iron phosphate catalysts using SEM. Iron phosphate particles have a particle size ranging from 100 nm to 500 nm.
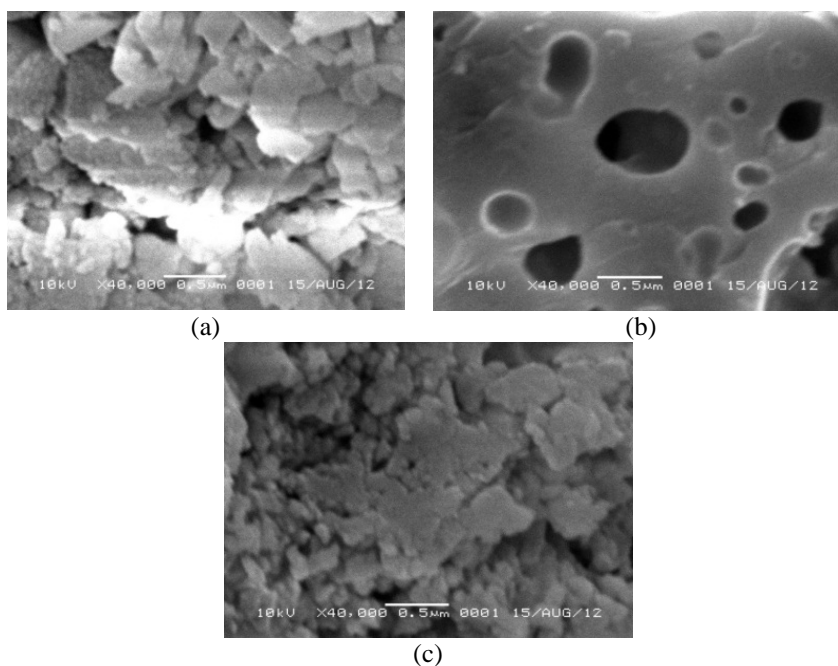

(a)

(b)

(c)

Figure 3   SEM photo with scale 40000X (a) A, (b) B, (c) C.
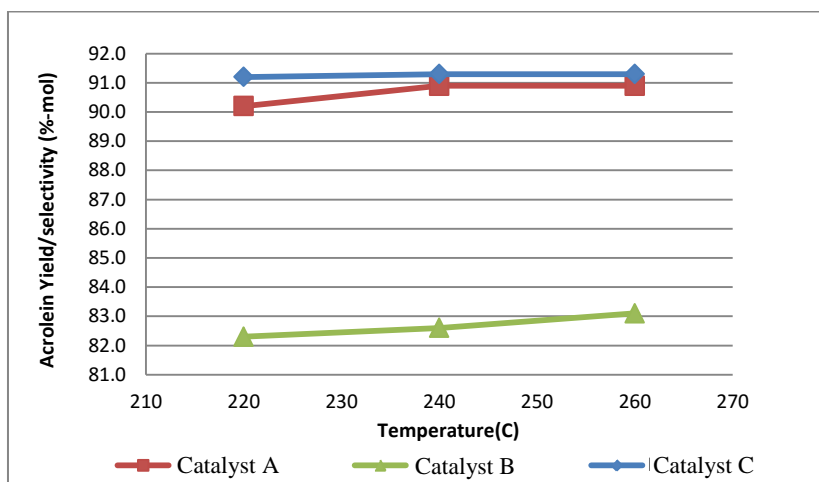
Figure 4   Yield and selectivity of acrolein on FePO$_4$ catalyst by method A, B and C.

The effects of temperature change on the yield of acrolein are shown in Figure 4. There was no residual glycerol observed on the flask, so the conversion was 100%. If the reaction conversion reaches 100%, the yield value is identical to the selectivity value. The increasing reaction temperature showed a tendency to increase the yield and selectivity of acrolein. FePO$_4$ catalyst can convert glycerol to acrolein in the liquid phase at 220-260 °C. Catalyst C gave the highest yield ($\pm$ 91%), followed by catalyst A ($\pm$ 90%), whereas catalyst B gave the lowest yield (an average of $\pm$ 82%).

To study the effect of oxygen presence in the reaction, catalyst B was subjected to a nitrogen treatment at temperature 240 °C. The result is shown in Figure 5. In the first treatment, the reaction was carried out under atmospheric air condition, while in the second treatment it was carried out under nitrogen flowing along the glycerol in order to reduce the oxygen content when the reaction was carried out.

The yield of acrolein using catalyst B performed under atmospheric air condition was smaller (82.3%) than that under nitrogen purging (91%). The oxygen presence allows the reaction to produce more side products, such as glycerol propanal, acetaldehyde and propionate.

FePO$_4$ catalyst was used in the reaction and then reused up to four times. The characteristics are shown in Figure 6.
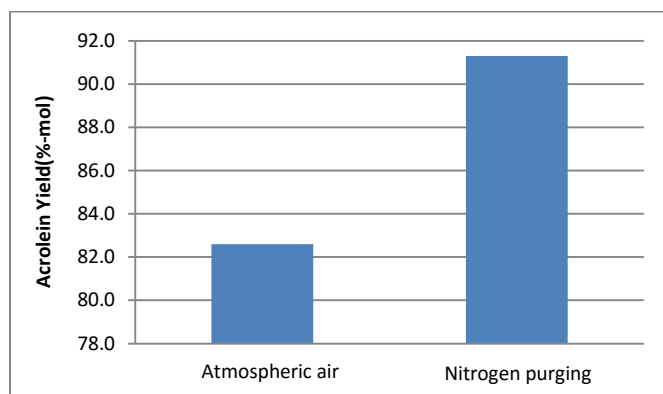
Figure 5 Yield of acrolein using catalyst B with 20% oxygen and after nitrogen purging.
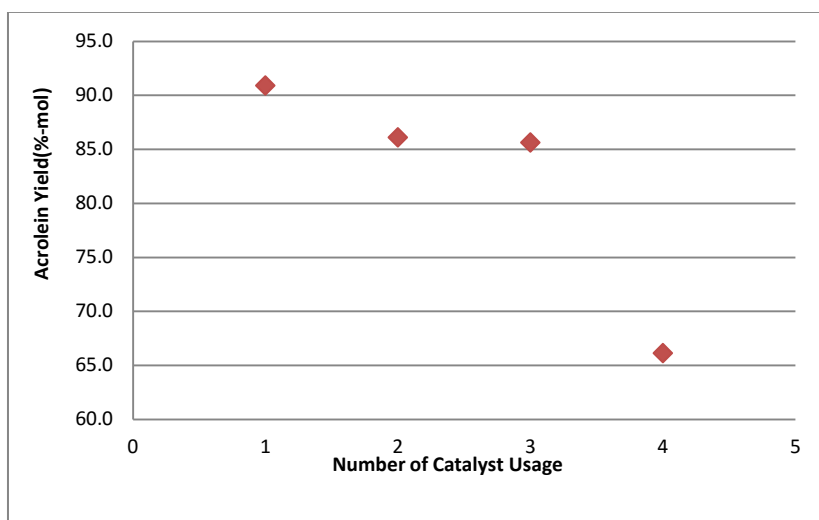

Figure 6 Profile of catalyst reuse for the yield of acrolein.

Based on Figure 6, catalyst reuse without any regeneration results in a yield profile of acrolein that continues to decline. During the first use of the catalyst, the yield of acrolein was 91%, the second use of the catalyst resulted in a yield of 86%, which was not much different from that of the third use, i.e. 85%. The fourth use resulted in a yield of 66%.

The decline in acrolein yield means an increase of byproducts. Figure 7 shows the yield of products and byproducts for catalyst A at three different temperatures.
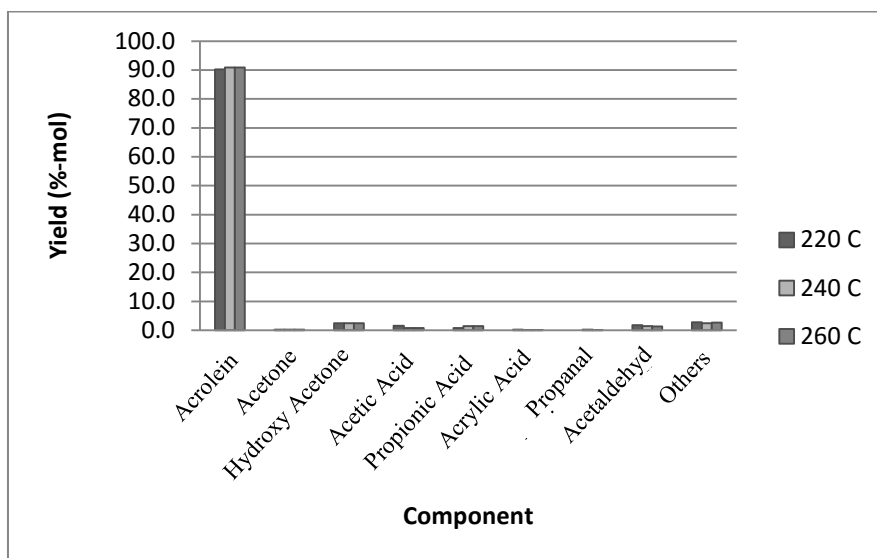
Figure 7 Yield of acrolein and glycerol dehydration byproducts of catalyst A.

4   Conclusion

Acrolein can be synthesized from glycerol through the liquid phase at temperature 220-260 °C using FePO$_4$ catalyst. The best yield was obtained with FePO$_4$ catalyst, synthesized with the method of deposition concentration (catalyst C), i.e. 91.3%. SEM analysis showed that catalyst C had the largest surface area (10.2 m^2/g), then catalyst A (5.4 m^2/g), and then catalyst B (2.2 m^2/g). The higher the reaction temperature, the faster the reaction and the higher the acrolein selectivity. Reduction of the oxygen concentration in the dehydration reaction of glycerol to acrolein by using catalyst B showed a significant increase in acrolein yield. Meanwhile, reuse of catalyst without regeneration was shown to be effective up to three times.

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