

**CATALYST DEACTIVATION STUDY OF THE
ESTERIFICATION OF DILUTE ACRYLIC ACID
WITH DIFFERENT CONCENTRATION
CATALYZED BY ION EXCHANGE RESIN**

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CATALYST DEACTIVATION STUDY OF THE ESTERIFICATION OF DILUTE ACRYLIC ACID WITH DIFFERENT CONCENTRATION CATALYZED BY ION EXCHANGE RESIN

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Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

**Faculty of Chemical & Natural Resources Engineering
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JUNE 2015

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SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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Dedication

To my supportive family, supervisor, Dr Chin Sim Yee and friends, thank you for your support and encouraged me in order to complete this thesis.

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ABSTRACT

Acid-catalysed esterification of acrylic acid with 2-ethylhexanol is the principal method for the manufacture of 2-ethylhexyl acrylate. 2-ethylhexyl acrylate is a clear, water-white liquid with a sweet odor and is readily miscible with most organic solvents, but has negligible solubility in water. In chemical industry, 2-ethylhexyl acrylate is primarily used as a reactive building block to produce polymer coating, adhesives and sealants and it can be polymerized itself. In addition, improving the water resistance, weather ability and sunlight resistance of final product can be made in presence of acrylic acid. Industrial waste water generally can be described as the water or liquid carries waste from industrial or commercial processes. The spent water (wastewater) may contain a large variety of organic compound such as acrylic acid, formaldehyde, acetic acid and more but acrylic acid dominate the amount in polymer industrial wastewater that could harm the aquatic organisms. Currently, incineration treatment method is neither environmental friendly and nor economical. So, reactive distillation in esterification process has potential to recover the acrylic acid in the industrial waste water. In this study, the esterification of dilute acrylic acid with 2-ethyl hexanol that catalyzed by ion exchange resin have been carried out. The objective of the present study was to investigate the deactivation of Amberlyst 15 in the esterification of dilute acrylic acid. Homogeneous catalyst have some limitations such as catalyst recovery problem, disposal of toxic wastes formed during reactions, separation of the products, and loss of catalysts that can cause the solid acid catalyst will be chosen in this study. The esterification process have been conducted in presence of Amberlyst 15 as a catalyst and Phenothiazine as polymerization inhibitor under certain conditions. The range of water content in the dilute acrylic acid have been varied and as well as the presence of inhibitor. The catalyst activity have been characterized to examine the morphology for fresh and used catalyst after the reaction. Another testing was to determine the catalyst compositions, to check the functional group of catalyst and to determine the measurement for its surface area. From the result, catalyst deactivation happened as increase in water content for diluted AA in the reaction mixture. The present study show that more water content needed to dilute AA solution and more polymerization inhibitor to prevent the polyacrylic acid formation in the reactions.

Key words: dilute acrylic acid, ion exchange resin, esterification, catalyst deactivation

ABSTRAK

Pengesteran asid-pemangkin asid akrilik dengan 2-ethylhexanol adalah kaedah utama dalam pembuatan 2-ethylhexyl akrilat. 2-ethylhexyl akrilat adalah cecair putih yang jelas dengan bau yang enak dan mudah larut bercampur dengan kebanyakan pelarut organik tetapi diabaikan kelarutan dalam air. Dalam industri kimia, 2-ethylhexyl akrilat terutamanya digunakan sebagai blok bangunan reaktif untuk menghasilkan salutan polimer, pelekat dan pengedap dan boleh dipolimerkan sendiri. Di samping itu, meningkatkan rintangan air, keupayaan cuaca dan rintangan cahaya matahari produk akhir boleh dibuat dalam kehadiran asid akrilik. Air sisa industri secara amnya boleh digambarkan sebagai air atau cecair membawa bahan buangan dari proses perindustrian atau perdagangan. Air yang digunakan (air sisa) boleh mengandungi pelbagai jenis sebatian organik seperti asid akrilik, formaldehid, asid asetik dan lebih tetapi asid akrilik menguasai jumlah dalam air sisa industri polimer yang boleh membahayakan organisma akuatik. Pada masa ini, kaedah rawatan pembakaran tidak mesra alam sekitar dan ekonomi. Jadi, penyulingan reaktif dalam proses pengesteran mempunyai potensi untuk pulih asid akrilik di dalam air sisa perindustrian. Dalam kajian ini, pengesteran asid akrilik cair dengan hexanol 2-etil yang dimangkin oleh resin pertukaran ion telah dijalankan. Objektif kajian ini adalah untuk menyiasat penyahaktifan Amberlyst 15 dalam pengesteran asid akrilik cair. Pemangkin homogen mempunyai beberapa batasan seperti masalah pemulihan pemangkin, pelupusan sisa toksik terbentuk semasa tindak balas, pengasingan produk, dan kehilangan pemangkin yang boleh menyebabkan asid pemangkin pepejal akan dipilih dalam kajian ini. Proses pengesteran telah dijalankan di hadapan Amberlyst 15 sebagai pemangkin dan Phenothiazine sebagai pempolimeran perencat di bawah syarat-syarat tertentu. Julat kandungan air dalam asid cair akrilik telah diubah dan juga kehadiran perencat. The activiy pemangkin telah dicirikan untuk memeriksa morfologi untuk pemangkin segar dan digunakan selepas tindak balas. Ujian lain adalah untuk menentukan komposisi pemangkin, untuk memeriksa kumpulan berfungsi bagi pemangkin dan menentukan ukuran bagi kawasan permukaannya. Dari keputusan, pemangkin penyahaktifan berlaku pertambahan kandungan air untuk AA dicairkan dalam campuran tindak balas. Pertunjukan Kajian ini bahawa kandungan air lebih diperlukan untuk mencairkan penyelesaian AA dan lebih pempolimeran perencat untuk mencegah pembentukan asid Akrilik dalam tindak balas.

Kata Kunci: asid akrilik cair, damar pertukaran ion, pengesteran, ketidakaktifan pemangkin

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LIST OF ABBREVIATIONS

BET -Brunauer – Ememett – Teller

FTIR- Fourier Transform Infrared Spectoscopy

SEM- Scanning Electron Microscopy

1 INTRODUCTION

1.1 Motivation and statement of problem

Industrial waste water generally can be described as the water or liquid carries waste from industrial or commercial processes, as well known as domestic wastewater. Any process or activity from industry, trade or business and animal operations as feedlots, poultry house or dairies may attributed to these wastes water that contain embrace a wide range of potential contaminant and concentrations (Inc. and Of, 2014; App.leg.wa.gov, 2014).

During mid 18th century, water pollution was located in small areas due to slow development until it comes to 21th century when industrial revolution proposed the development of the internal combustion engine and petroleum fuelled explosion of the chemical industry (SHI, n.d., 2014). The spent water (wastewater) may contain a large variety of organic compound such as acrylic acid, formaldehyde, acetic acid and more but acrylic acid dominate the amount in polymer industrial waste water in range 4-15 wt. % which leading to the range of chemical oxygen demand of approximately 30-60 g/l that could harm the aquatic organisms (Gong et al., 2009; Ahmad et al., 2014).

Acrylic acid (AA) is an important component for the production of acrylate ester with the reaction of alcohol such as methyl acrylate, butyl acrylate and 2-ethyl hexylacrylate. Acrylate ester is a monomer of the acrylate polymer which is applied in the industry of paints, papers, textiles and leather finishes, adhesive and plastics. Currently, the existing method used to treatment the waste water containing acrylic acid is incineration treatment method which is neither environmental friendly and nor economical. Incinerator ashes produce contaminated, unburned chemicals and new chemicals during the burning process. It is buried in landfill or dumped to the environment creating more toxic waste that poses a significant threat to public health and the environment instead of making waste dissappear (Scribd.com, 2014; Natracare.com, 2014).

Reactive distillation in esterification process is one of method to recover the acrylic acid in the industrial waste water. According to Saha, (2000), reactive distillation column that combines both reaction and separation processes have shown its potential to recover the carboxylic acid from wastewater. Esterification reactions is limited by

reaction equilibrium since it has its own limitation by reversible reaction. Catalysts accelerate the reaction to achieve the equilibrium state. Without the presence of catalyst, the esterification reaction will proceed extremely slow since this reaction is an equilibrium reaction and it is required in order to accelerate the reaction to achieve the equilibrium state. In this study, acrylic acid will react with 2-ethyl hexanol in the presence of ion exchange resin in order to produce 2-ethyl hexylacrylate and water. The purpose of having 2-ethyl hexanol is the widely production of 2-ethyl hexylacrylate in polyester manufacturing industry process that comes from reaction between acrylic acid and 2-ethyl hexanol.

1.2 Problem statement

The synthesis of acrylate ester such as 2-ethylhexyl acrylate through esterification process catalysed by homogeneous acid catalysts such as sulfuric acid has been reported in the literature and it is commercially practiced in chemical industry. Homogeneous catalysts are preferred in the conventional esterification reaction due to its higher catalytic activity and cheaper price. However, the use of strong acid in homogeneous system give negative effect towards the reaction since it can cause corrosion, pollution of environment and catalyst recovery problem. Numerous heterogeneous catalysts such as Amberlyst 15, Amberlyst 131, Dowex 50Wx-400 and Phosphotungstic acid could overcome the shortcomings of homogeneous catalysts while maintaining the activity to catalyse the esterification reaction using pure carboxylic acid. To date, the activity of these heterogeneous catalysts in the esterification of the dilute acrylic acid (the model waste water) with alcohol has not been reported in the literature. These solid catalysts might facing the problem of leaching in the dilute system (Komo'n et al., 2013). In the present study, Amberlyst 15 is used to catalyse the esterification of dilute acrylic acid with 2-ethyl hexanol. The cause of the catalyst deactivation is ascertained. 2 ethyl hexanol is the widely used in the production of 2-ethyl hexylacrylate for polyester manufacturing industry.

1.3 Objective

The objective of the present study is to investigate the deactivation of Amberlyst 15 in the esterification of dilute acrylic acid with 2-ethyl hexanol.

1.4 Scope of this research

The following are the scope of this research:

- a) Amberlyst 15 is tested in the esterification of dilute AA and 2EH at different concentrations of dilute AA (range is varied from 10-90 wt.%) and with/without the presence of inhibitor, Phenothiazine.
- b) The fresh and used catalysts are characterized for their morphology chemical compositions, functional groups and surface area. These characteristics are correlated to the catalyst performance during the esterification reaction.

c) Polymerization of inhibitor such as Phenothiazine is added in the process in order to know the main reason that contribute to the catalyst activity in esterification of acrylic acid.

1.5 Significance of study

The present study identifies the main reason of the deactivation of Amberlyst 15 occurred during the esterification of dilute AA with alcohol. A suitable method to prevent the deactivation can subsequently be suggested. A suitable heterogeneous catalyst without severe deactivation is hope to be used for the recovery of AA from the waste water, hence reducing the environmental problems.

1.6 Organizations of thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 consists of the reviews on literature related to the catalyst used for the esterification of acrylic acid with 2-ethyl hexanol. This review can be structured into three major sections. The first section is about esterification of acrylic acid with 2-ethyl hexanol, the second section is about catalyst used in the esterification of acrylic acid and 2-ethyl hexanol and the last section is about the important operating parameters for the esterification reaction.

Chapter 3 provides a general overview regarding the materials and methods used in the present research project. There are three major parts in this chapter which consists of the description of the materials used, the experimental procedure and the product and catalyst analysis.

Chapter 4 discusses the preliminary work of the present study. The results obtained from the experimental work of esterification of acrylic acid with 2-ethyl hexanol are discussed. Conclusions with recommendations are given at the end of this chapter.

2 LITERATURE REVIEW

2.1 Overview

This chapter consists of the reviews on literature related to the catalyst used for the esterification of pure and dilute acrylic acid with alcohol. The reviews can be organized into four main sections. Firstly, treatment method for the waste water containing acrylic acid is discussed. Secondly, the review on esterification of dilute carboxylic acid with alcohol is introduced. Thirdly, catalyst used in the esterification of acrylic acid with alcohol is discussed. Lastly, the importance of operating parameters used in the esterification reaction is presented.

2.2 Treatment method for the waste water containing acrylic acid

Acrylic acid is primarily used in production of esters, resins and polyacrylates from acrylate ester such as butyl acrylate, ethyl acrylate and 2-ethylhexyl acrylate. Acrylic acid may be released in wastewater and polymerizes readily in the presence of oxygen (Npi.gov.au, 2014). This acid known to be toxic to anaerobic bacteria when it presence in waste water and it is typically incinerated. The waste water containing high concentrations of acrylic acid need to be diluted for anaerobic treatment due to its toxicity (Allison et al., 2011).

Waste water containing acrylic acid with concentration in the range of 30 – 100 g/L and several other toxicant compounds comprises of high total organic content and chemical oxygen demand which may harm the aquatic organism (Ahmad et al., 2014). Incineration, the existing method used to treat this kind of waste water is neither economic feasible nor environmental friendly.

In point of view of pollution control toward the environment, the separation of organic residues from aqueous waste streams released from industries is important. The disposal of waste waters containing industrial organic acids such as acrylic acid, acetic acid, formic acid and propionic acid has been recognized which might contribute to environment pollution factor. Fractional distillation, liquid extraction, adsorption, precipitation, ion exchange and more being as conventional method proposed in

industry in order to reduce the global pollution issues (Kumar and Babu, 2008). Normally, most industry proposed common treatment process such as biological degradation or chemical oxidation and removal of this compound using adsorption process. Adsorption process can be considered as one of attractive method in order to remove the carboxylic acid from the waste water stream by using a polymer adsorbent which is good in selectivity and high adsorption capacity for carboxylic acids separation even in the presence of inorganic salts. Another popular method is pervaporation process that used for waste water containing carboxylic treatment. These methods have their own limitations such as high operating cost and applicable only to the waste water with certain carboxylic acid concentrations (Kumar et al., 2008; Maachi et al., 2001).

Alternatively, esterification reaction in reactive distillation column could be one of the promising methods used to recover acrylic acid from waste water. Reactive distillation (RD) is combination of chemical reaction and product separation that occur simultaneously in the same column especially for reversible reaction with presence of heterogeneous catalyst that is low capital investment and operating cost. Moreover, this method offers improved in selectivity, increased conversion, better heat control, minimization of side reactions and scope for difficult separations. Therefore the capital investment and operating costs are significantly lower with RD than for conventional processes (Patil and Kulkarni, 2014). In Saha (2000) which in their studied of recovery of dilute acetic acid through esterification in a reactive distillation column, 30% aqueous solution of acetic acid can be recovered by esterification with n-butanol and iso-amyl alcohol reactive distillation column using macroporous Indion 130 cation exchange resin as a catalyst bed, confined in stainless steel wire mesh tea bags. However, this reaction was limited to equilibrium reaction. The best result was obtained when the column was operated in counter-current mode.

2.3 Catalyst used in the esterification of acrylic acid with alcohol

Esterification process is in a liquid- phase process where the equilibrium of the reaction will limit the conversion of the reactants and basically, this reaction proceeds very slow in the absence of the catalyst. Hence, a catalyst is required in order to increase the reaction rate of the esterification reaction (Slawomir Ostrowski et al, 2011). Commonly, there are two major types of catalyst used in production of acrylic ester by esterification of acrylic acid and alcohol which are acidic homogeneous and

heterogeneous catalyst. Figure 2-1: Illustration of the trailing vortex behind the impeller blade by Van't Riet and Smith (1975).

2.3.1 Homogeneous catalyst

Esterification of acrylic acid with alcohol has commercialized using liquid catalysts such as sulfuric acid, hydrofluoric acid, and para-toluenesulfonic acid but these are toxic, corrosive and hard to remove from the reaction solution (Chen et al., 1999). Moreover, homogeneous catalysts have some limitations which include catalyst recovery problem, toxic waste disposal, product separation and loss of catalysts that can cause the solid acid catalyst which more demanding that can overcome those drawbacks of homogeneous catalyst (Moreno et al., 2011).

Effects of water on homogenous acid catalyzed esterification have been reported by different researchers and for instance, esterification was carried out using homogenous para-toluene sulfonic acid (p-TSA) with initial 15vol% water that shown the conversion of palmitic acids was decreased by around 40% after 4 h of reaction. It shown that the increasing amount of water added during the initial reaction will give effect to the decreasing rate of reaction. It can cause to deactivating effect of water on catalyst such as the decreasing of acid strength and loss of catalyst accessibility. The decreasing of acid strength is due to the water solvation which leads to a decrease in the concentration of protonated carboxylic acid, thus inhibiting the formation of esters (Liu et al., 2006; Aafaqi et al., 2004).

A comparison of heterogeneous versus homogeneous acid catalysis for the esterification reaction between acetic acid and methanol has been made. The reaction was carried out at 60oC and the homogeneous catalyst used was sulphuric acid while the heterogeneous catalyst used was Nafion/silica nanocomposite catalyst (SAC-13). The catalytic activity was compared which clearly shown that the sulphuric acid have higher catalytic activity compared to SAC-13. Sulphuric acid catalyst greatly inhibited by the initial water addition (Edgar Lotero et al, 2006).

According to Chen et al. in 1999, they had done some research regarding esterification of acrylic acid and 1-butanol catalyzed by homogeneous catalyst using para-toluenesulfonic acid (PTS) and Sulphuric acid (H₂SO₄) at temperature of 353K. After the experiment, the result shows that acid strength contained in PTS was much higher than H₂SO₄ based on rate constants and negative value of acidity function, -H₀. As -H₀ function decreased, the acid strength increased and the rate constant increased.

However, they also compared the homogeneous catalyst with heterogeneous such as Tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) which show the result that acid strength of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was 10 and 14 times larger than PTS and H_2SO_4 . Thus, the rate constant of heterogeneous catalyst much higher than homogenous catalyst as the reaction rate increases when the acid strength increased.

In this situation, an alternative of solid catalysts has received increasing attention in the past years in order to replace the liquid acid catalyst during the conventional esterification reaction. It is believed that, solid acid catalyst is more desirable due to its less toxic properties and easily to be recovered and separated from the product and also more environmental friendly since it does not corrode the reaction vessel. However, the solid catalysts in the esterification reaction of acids with alcohols must be active in the presence of water in the esterification of dilute carboxylic acid or water formed during the course of the reaction. Generally, the solid acids are less or even not active in water, and only few materials have been found to be water-tolerant (Komon et al., 2013).

2.3.2 Heterogeneous catalyst

The use of solid acid catalyst is more beneficial since it's eliminate corrosion, increase selectivity towards the esters, recovery the catalyst and more which can overcome the shortcomings of homogeneous catalyst. Various types of solid acid catalysts have been developed. These include zeolites, heteropolyacids, oxides and phosphates and organic-inorganic composites (Komon et al., 2013; Toshio Okuhara, 2002).

Sulfonated ion exchange resin can be classified into two main classes that widely used which are polystyrene or divinylbenzene matrix such as Amberlyst and Dowex and the other based on perfluorinated sulfonic acid resins like Nafion and Aciplex. For instance in some studied, homogeneous catalyst consisting of sulphuric acid, phosphoric acid, tungstosilicic acid and germanium tungsten acid as liquid acid catalyst while for solid acid catalyst type, solid oxides (zeolites and cesium salt of phosphotungstic acid) and organic resins (Amberlyst 15, Nafion-H, Amberlyst-200C) are used. The reaction between acrylic acid and 1-butanol was carried out at 80. As a result of comparison between the catalysts, liquid acid catalyst has yielded higher conversion as compared to solid acid catalyst types due to the leaching occurred in the solid catalyst during the

reaction. However, liquid acid catalyst is strongly inhibited by water that is produced during reactions in terms of water sensitivity, hence solid acid catalyst is more water resistance (Chen et al., 1999).

Esterification of acrylic acid and propylene glycol was studied using Amberlyst-15, Amberlyst-36 and cesium salt of phosphorous tungstic acid as the heterogeneous catalysts. The reaction was carried out in presence of 0.3 wt% of inhibitor, Phenothiazine as polymerization inhibitor at 353K with the acrylic acid: propylene glycol of 1:1. The catalyst loadings of Amberlyst-15, Amberlyst-36 and cesium salt of phosphorous tungstic acid were 5.54 wt.%, 5.57 wt.% and 4.73 wt.% respectively. The results showed that Amberlyst-36 accelerated the reaction rate the most but its product selectivity was considerably lower than Amberlyst-15 at the 45% conversion. On the other hand, the activity of cesium salt of phosphorous tungstic acid was the lowest as compared to the others, yielding a 4% conversion, in spite of its highest selectivity (100%).

Based on Chen et al. in 1999, they said tolerance of water is often important for the solid acids for the use in esterification because water is formed as a product. In Kimura et al., (1997) research of esterification of acrylic acid, the activities of liquid acid catalysts such as H_2SO_4 and p-toluenesulfonic acid, per unit acid amount were less than that of an acidic cesium salt of 12-tungstophosphoric acid ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$) even though activities per catalyst weight of the liquid acids were higher than $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$. Generally, solid acids catalyst will lose their catalytic activity in water but the strong acidity of solid acid catalyst is a reason for the high activity. Thus, the surface of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ has a hydrophobic nature and this hydrophobicity is responsible for the high catalytic activity of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$.

In previous study about the esterification of dilute acrylic acid using 2-ethyl hexanol which catalyzed by Amberlyst 15 was studied with various concentration of acrylic acid (10-100%) as model industrial waste water. Experiment was set ups in reactive distillation of esterification with total reflux and continuously water removal. As a result, esterification reaction was carried out with continuous water removal is much better than other since the yield of reaction of acrylic acid concentration ranged from 30 to 80 wt.% was increased. However, there was no change of the yield when acrylic acid concentrations ranged from 10 to 20 wt.% due to the catalyst fouled by poly-acrylic acid deposited. After the experiment, it shown that acrylic acid has potential to recover from waste water using esterification in reactive distillation column.

They found that concentration of dilute acrylic acid waste water should be increased or adopt more inhibitor to avoid poly-acrylic acid formation (Ahmad et al., 2014).

2.4 Important operating parameters for the esterification of acrylic acid

Esterification of acrylic acid could produce acrylic esters that consisting a double bond and functional carboxyl group. Water molecules are produced as the by-product during the reaction. Esterification of acrylic acid with 2-ethyl hexanol is commercially important in chemical industry and since the product generated which is 2-ethylhexyl acrylate that widely used in production of primarily for manufacturing homopolymers and copolymers (Momentive.com, 2014).

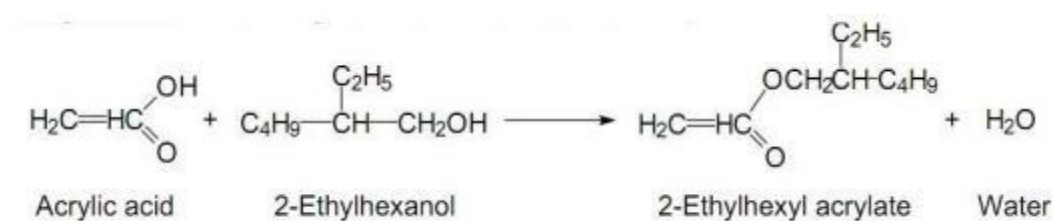


Figure 2-1: structure chemical reaction of esterification of carboxylic acid

Basically, ratio of 1:1 mixture of alcohol and carboxylic acid will yield an equilibrium mixture that is about 70% ester. This means that if ester were isolated from this mixture, at best a 70% yield would be obtained but this cannot be acceptable. Based on Le Chatelier's principle stated that a change in one of the variables that describe a system at equilibrium produces a shift in the position of the equilibrium that counteracts the effect of this change. For example, if a ratio of 3:1 or 1:3 of alcohol:carboxylic acid are used, the equilibrium would be move towards ester product and for unhindered systems would result in a 90% yield. Another product is water that normally being removed by another experimental set-up. Eventually, a 100% yield of ester can be obtained when the final amount of water is removed as the reaction has gone to completion. Thus, this method is called as esterification method (Esters, 2014; Chemed.chem.purdue.edu, 2014).

This esterification method is called Fischer esterification which esters are obtained by refluxing the parent carboxylic acid with the appropriate alcohol with an acid catalyst. The equilibrium can be driven to completion by using an excess of either the

alcohol or the carboxylic acid, or by removing the water as it forms. This is shown by the mechanism of carboxylic acid having reaction with alcohol (Mhhe.com, 2014).

2.4.1 Water content in the reactants

The resistance of solid catalysts to water poisoning is an important characteristic in determining their applicability for commercial esterification processes and the effect of water on acid-catalyzed esterification was studied using initial reaction kinetics with varying amounts of initially water added. The catalytic activity was significantly inhibited with increasing water concentration in the reaction mixture. Chen et al.(1999) have shown that when esterification of acrylic acid and 1-butanol was carried out using Nafion-H in the presence of an initial water concentration of 4.3 M, the conversion of acrylic acid after 4 h decreases from 60% without the addition of water to 30.6% at 80 °C.

The study of Ahmad et al. (2014) has shown that the presence of 10 wt.% of water did not inhibit the activity of the catalyst. The activity of the catalyst was significantly decreased when the initial water concentration is more than 10 wt. %. Deactivation of catalyst occurred due to severity of catalyst fouling that from deposition of substantial amount of poly-acrylic acid especially when amount of initial water concentration increase.

2.4.2 Presence of polymerization inhibitor

Acrylic acid polymerizes easily when exposed to heat, light or metals, and so a polymerization inhibitor is added to commercial acrylic acid to prevent the strong exothermic polymerization. The hydroquinone or hydroquinone monomethyl ether are compounds which are known as antioxidants and, specifically, as monomer stabilizers. They have been used as shelf stabilizers for acrylic monomers (Polymerization inhibitors for acrylic acids and esters, 2014). It is added in the esterification process of acrylic acid as an inhibitor to prevent its spontaneous polymerization that may due to its tendency to polymerize in shipping and storage (Li and Schork, 2006). Compound is difficult to stabilize if they have high number of short chains and high density of acrylates that resulting to high tendency of spontaneously.

By referring to Komoń et al., (2013), undesirable free-radical polymerization of acrylic acid and its ester can occur in the reaction condition. Therefore, polymerization inhibitors must be added in order to study the effect of the polymerization inhibitors. According to Niesbach et al., (2012) in their studied of esterification of acrylic acid in reactive distillation column, polymerization inhibitor which are hydroquinone monomethyl ether (MEHQ) and phenothiazine that needed in esterification reaction in order to avoid polymerization of acrylic acid occur. In the experiment, polymerization reaction happened when acrylic acid was preheated first. So, 1000 ppm phenothiazine was added to the acrylic acid feed tank to minimize the amount of acrylic acid polymer formed. The inhibitor solution at the top of the column contained 2.0 wt % phenothiazine and 2.0 wt % hydroquinone monomethyl ether as reactive distillation column was used in this process.

2.4.3 Effect of molar ratio

The concentration of alcohol had an influence on the reaction rate and on the conversion. Theoretically, conversion of acid will increase with increasing the initial molar ratio of alcohol to acid. Molar ratio of reactant used in the esterification process plays an important role for the percent conversion of reactants towards products, which is ester. Effect of molar ratio on esterification of carboxylic acid with alcohol was studied in previous study. For instance, variation amount of molar ratio has being studied by Singh et al. (2013) in esterification of butyric acid with ethanol. They varied amount of ethanol while the acrylic acid fixed. As a result, the equilibrium conversion of acid increased from 31% to 81% on varying ethanol to butyric acid ratio from 1 : 1 to 1 : 15 with catalyst loading of 73.2 kg/m³ at temperature 348 K.

In the kinetic study of catalyzed and uncatalyzed esterification reaction of acetic acid and methanol, the effect of molar ratio of reactants was studied. The different molar ratio were used such as 1:1, 1:2 and 1:3 of acetic acid and methanol at 55, 10% wt. catalyst and 1000 rpm speed. From the results obtained, it shows that the molar ratio of 1:3 has the highest fractional conversion (54%) compared to the other molar ratio (Iasir.net, 2013).

The effect of alcohol to acid molar ratio on conversion of acrylic acid was illustrated by Karakuş et al. (2014) where the alcohol to acid molar ratio changing from 1, 2, and 3. The increase of molar ratio of isobutyl alcohol to acrylic acid from 1 to 3

has increased the conversion of acrylic acid to 5.9%. Since lower the alcohol concentrations make the reaction equilibrium shifted toward the reactant side with increasing the ratio more acid reacts because of the excess of alcohol. Increase in the molar ratio from 2 to 3 leads to more increase in conversion. According to Komoń et al., (2013) when studied the esterification of acrylic acid and 2-ethyl hexan-1-ol, molar ratio of acid to alcohol was varied with 7:1, 5:1, 3:1, 1:1, 1:3, 1:5, and 1:7. As a result, conversion of acid increased when amount of alcohol increased. It can be summarized that conversion of acid itself will increase as the amount of alcohol used increase.

2.4.4 Effect of temperature

Temperature of reaction can be one of the factors to increase the conversion of products as rate of reaction also increase. A higher temperature is required in esterification reaction in order to obtain a high conversion of products. In Karakuş et al. (2014), effect of reaction temperature was studied by varied the temperature by at 338K, 348K and 358 K in the esterification of acrylic acid reaction. As the result, conversion of acrylic acid increased when the temperature increased. High temperature gives rise to more frequent and successful collisions for higher conversion of reactants to ester products. As known from the literature, the esterification rate decreased as degree of branching of alcohol increased due to the steric hindrance.

Another study proved the increase in temperature give high conversion of acid is in esterification of butyric acid and ethanol over Amberlyst 15 by Singh et al. (2013). The reaction is carried out with the temperature of 328K, 338K, 343K and 348K. With an increase in reaction temperature, the initial reaction rate or the conversion of the butyric acid is found to increase substantially. Thus, it shows that the higher temperature yields the greater conversion of the acid at fixed contact time.

At the end of the review of all the parameters, a summary table can be included for the range of parameters used for the esterification of acrylic acid.

Table 2-1: A summary table for the range of parameters used for the esterification of acrylic acid

Reaction (ref)	Water content in reactants	Presence of polymerization inhibitor	Temperature	Alcohol to AA Molar Ratio	Reaction performance
Esterification of acrylic acid and 2-ethyl hexanol catalyzed by Amberlyst 15 (Ahmad et al., 2014)	10wt.% of water doesn't inhibit the activity of catalyst and activity of catalyst decreased when initial water concentration is more than 10wt.%.	-	-	-	Activity of catalyst: decrease, initial water concentration: increase
Esterification of acrylic acid and 1-butanol catalyzed by Nafion-H (Chen et al., 1999)	4.3 M of initial water, the conversion of AA after 4h decrease 60% without the addition	-	-	-	Initial water concentration : increase, conversion of AA: increase

	of water to 30.6%				
Esterification of acrylic acid with 2-ethylhexan-1-ol (Komoń et al., 2013)	-	undesirable free-radical polymerization of acrylic acid and its ester can occur in the reaction condition	-	7:1, 5:1, 3:1, 1:1, 1:3, 1:5, and 1:7 as molar ratio of alcohol:acid used and as result, conversion of AA increased as amount of 2EH increased	molar ratio of alcohol:acid : increased Conversion of acid: increase
Esterification of butyric acid with ethanol (Singh et al. , 2013)	-	-	Varied temperature of 328K, 338K, 343K and 348K. With an increase in reaction temperature, the initial reaction rate or the conversion of the butyric acid is increase	Equilibrium conversion of acid increased from 31% to 81% on varying ethanol to butyric acid ratio from 1 : 1 to 1 : 15	molar ratio of alcohol:acid : increased Conversion of acid: increase
Esterification reaction of acetic acid and methanol	-	-	-	1:1, 1:2 and 1:3 of acetic acid and methanol were used.	molar ratio of alcohol:acid : increase Conversion of acid:

(Iasir.net, 2013).				Molar ratio of 1:3 has the highest fractional conversion (54%)	increase
Esterification of isobutyl alcohol and acrylic acid (Karakuş et al., 2014)	-	-	Varied the temperature by at 338K, 348K and 358 K. Thus, conversion of AA increased when the temperature increased	Alcohol to acid molar ratio changing from 1, 2, and 3. Molar ratio of isobutyl alcohol:AA increased from 1 to 3 has increased the conversion of AA to 5.9%.	<ul style="list-style-type: none"> • Temperature: increase, conversion of acrylic acid : increase • Molar ratio alcohol: acid: increase, Conversion of AA: increase
Esterification of acrylic acid in reactive distillation column, (Niesbach et al., 2012)		hydroquinone monomethyl ether (MEHQ) and phenothiazine added in the tank			To avoid polymerization occurred when acrylic acid was preheated, inhibitors were added.

*note: AA= acrylic acid; 2-EH= 2-ethyl hexanol

In this study, ratio of 1:3 of acrylic acid and 2-ethyl hexanol will be fixed throughout the study with absence of heterogeneous catalyst which is Amberlyst 15. The reactions will be studied with/without the presence of polymerization inhibitor, Phenothiazine and variation of water content.

3 MATERIALS AND METHOD

3.1 Overview

This chapter describes about the materials and methods used to conduct the present research study. The three parts in this chapter consisting the description of materials experimental procedures and product analysis.

3.2 Materials

3.2.1 Materials of esterification

Acrylic Acid (99%), 2-Ethyl Hexanol (99.6%), and Polymerization Inhibitor, Phenothiazine were purchased. Acrylic Acid and 2-Ethyl Hexanol as the reactant were mixed in the presence of water. Phenothiazine was used to inhibit the acrylic acid polymerization. Amberlyst 15(dry) as the strongly ion exchange resin that have 4.7 meq H⁺/g by dry weight was used as catalyst. All the materials used in the present study are summarized in Table.

Table 3-1: Chemicals used in esterification reaction

NO	NAME OF CHEMICALS	TYPES	BRANDS	PURITY	PURPOSE
1	Amberlyst 15	Solid	SIGMA ALDRICH	99%	Catalyst
2	Acrylic Acid	Liquid	SIGMA ALDRICH	99%	Reactant (Carboxylic acid)
4	2-Ethyl Hexanol	Liquid	SIGMA ALDRICH	99.6%	Reactant (Alcohol)
5	Phenothiazine	Solid	SIGMA ALDRICH	99%	Polymerization inhibitor

3.2.2 Materials of product analysis

Hexane GC grade ($\geq 98.5\%$) will be purchased and used as a solvent for the product analysis using gas chromatography to identify the chemical composition of the sample.

3.3 Experimental Procedures for Esterification Reaction

The preparation of reaction mixture from dilute acrylic acid and 2-ethyl hexanol were carried out following the method described in Ahmad et al., (2014). 6.4 ml sample of acrylic acid (AA) and 43.6 ml of 2-ethyl hexanol(2-EH) with the molar ratio of AA: 2 EH of 1:3 were prepared first. The amount of water with respect to acrylic acid were varied to form the dilute acrylic acid with the range of 10-90 wt% of water. The esterification was conducted in a three neck flask equipped with condenser, temperature controller and temperature probe. 2-EH charged into the flask and heated to desired temperature separately. The acrylic acid and the water were added until the temperature maintained and start the reaction. The catalyst was loaded after the temperature maintained. The reaction mixture stirred using magnetic stirrer. 5wt% of MEHQ which respect to acrylic acid as polymerization inhibitor and 10 wt% of Amberlyst 15 were added to the mixture. The mixture stirred at 500rpm and heated. The reaction temperature was controlled at 80°C. The condenser was attached to the vessel to reflux water. The experiment was run for 6 hours and the sample was collected for every 1 hour. The experiment was repeated without using polymerization inhibitor. All the other parameters remained the same.

3.4 Product analysis

3.4.1 2-Ethyl hexylacrylate sample analysis

The sample was collected every 1 hour and analyzed using gas chromatography (GC) equipped with a flame ionization detector (FID) and DB-200 column in order to detect the composition of acrylic acid, 2-ethyl hexanol and 2-ethyl hexylacrylate in the sample. The calibration curve was generated by GC and after getting the result, the yield and conversion of product will be calculated using equation below:

$$\text{yield}(\%), Y = \frac{C_{2EHA}}{C_{AA0}} \times 100\%$$
$$\text{conversion}(\%), X = \frac{C_{AA0} - C_{AA}}{C_{AA0}} \times 100\%$$

Where ;

C_{2EHA} = concentration of 2-ethylhexyl acrylate

C_{AA0} = initial concentration of acrylic acid

C_{AA} = final concentration of acrylic acid

3.4.2 Amberlyst 15 sample analysis

In order to examine the morphology of Amberlyst 15, scanning electron microscopy (SEM) was used for fresh and used catalyst after the reaction. Another testing were fourier transform infrared spectroscopy (FTIR) had been used to check the functional group of catalyst and nitrogen physisorption analyzer also had been used to catalyst surface area (Ahmad et al., 2014). The working principle of each instrument for characterization of the catalyst can be shown as below:

3.4.2.1 Scanning Electron Microscopy (SEM)

In analysing the morphology of the catalyst, scanning electron microscope method was used (Carl Zeiss EVO50). The catalyst was dried at 100 °C for 6 hours times and stored in desiccators in order to eliminate the moisture. Then by using a carbon conductive pad, the samples were mounted on a metal stub and the silver metals acts as conductor were placed at both sides the sample. Lastly, under vacuum state and in an argon atmosphere, the samples were coated with gold and were observed.

3.4.2.2 Fourier Transform Infrared (FTIR)

In order to check the functional group of the catalyst, FTIR have been used in this study. FTIR operates based on light refelxtion that might produce the wavelengths. Different wavelength from the light source penetrated the sample and on the other side of the sample and a detector which detects light that was transmitted through the sample. Based on the result obtained from the FTIR, usually the results obtain was in peak diagram and each peak on the infrared spectrum indicated to a chemical bond.

3.4.2.3 Measurement of Surface Area

Micrometetics ASAP 2020 surface analyzer was used in determining the surface area, pore volume, and also average pore diameter that were known as nitrogen adsorption and desorption isotherms process. At temperature ramping at two stages the samples were degassed and then the samples were analysed by using nitrogen gas at temperature of 191.15°C. In determining the surface area, Brunauer-Emmet-Teller application was used.

4 RESULTS AND DISCUSSION

4.1 Overview

This chapter discusses about the results obtained from experimental work of esterification of acrylic acid and 2-ethyl hexanol catalysed by Amberlyst 15.

4.2 Esterification of Acrylic Acid with 2 Ethyl Hexanol

The esterification of the AA aqueous solution containing the range of water (10-90wt.%) with 2EH was catalysed by 10 wt.% of Amberlyst 15 (weight of catalyst/weight of AA) without/with the presence of Phenothiazine inhibitor. The reaction was carried out in a batch reactor filled with 50 mL reaction mixture at 80. The molar ratio of AA to 2EH of 1:3.

Figure 4-1 and 4-2 are the standard curves for acrylic acid and 2-ethylhexyl acrylate. Figure 4-3 and figure 4-3 show the conversion and yield profile through 8 hours esterification reaction without the presence of inhibitor while figure 4-5 and figure 4-6 are the conversion and yield profile for 8 hours esterification reaction with the presence of inhibitor. Based on the profiles below, it show that the conversion decrease as the percentage of water content increase in the reaction for both reaction with and without inhibitor. It same goes to the amount of yield as the water content increase. A significant drop is observed when the reaction at 50% of water content and onwards for both reaction that is due to the poor accessibility of reactants to acid sites. The amount of water increase can contributed to the absorption of the reactants to acid sites (Haas, 2005). The interaction between Amberlyst 15 to the water is stronger than 2-Ethyl Hexanol.

Moreover, the amount of conversions for the reactions in the presence of polymerization inhibitor are much higher than the reaction without inhibitor. The presence of inhibitor in the reaction controlled the polymerization of acrylic acid that may contribute to high yield also. However, the yield of the reaction is much lower than the conversion that is due to polymerization of acrylic acid occurred during the reaction. According to Ahmad et al. (2014), the conversion of the reaction increased as well as the yield of 2-ethyl hexylacrylate increased over the time until it achieved equilibrium point after 5 hours. These results are different from this experiment since the reaction

didn't achieve any equilibrium point due to the temperature set point which should be above than 80°C in order to achieve equilibrium point.

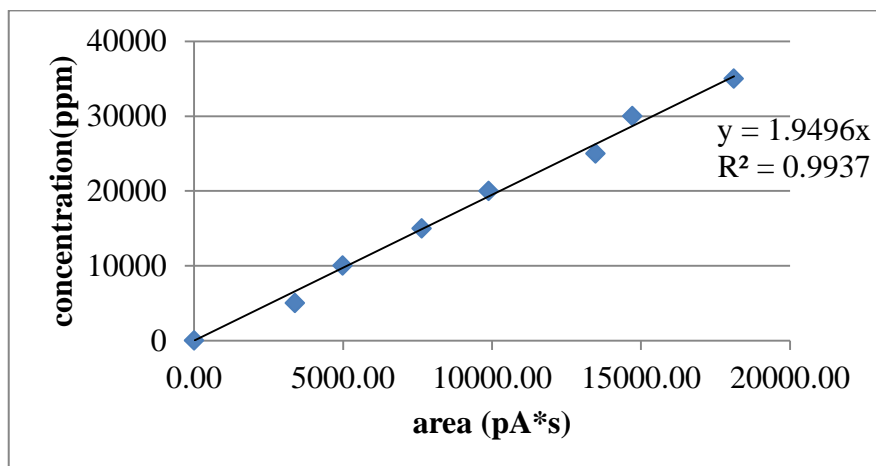


Figure 4-1: Standard curve of AA under 298K

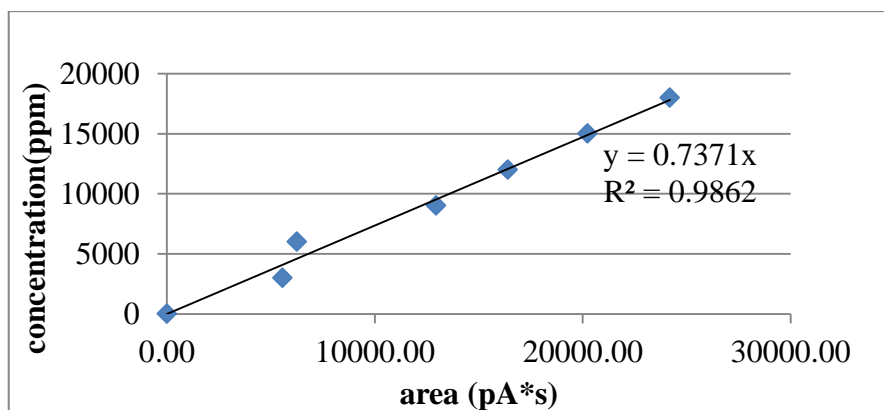


Figure 4-2: Standard curve of 2EH under 298K

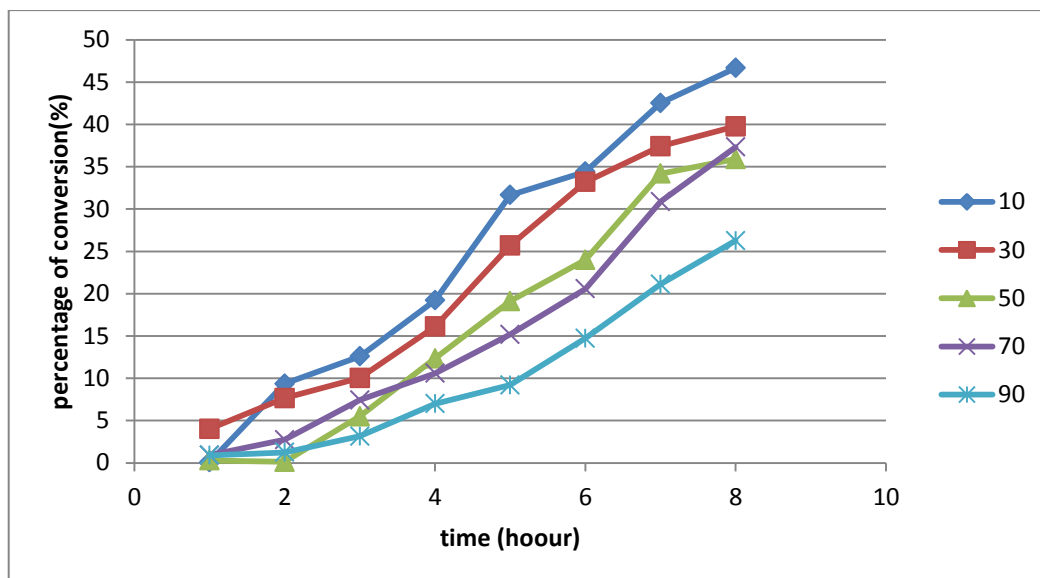


Figure 4-3: 2EHA conversion profile of the esterification of AA aqueous solution containing 10-90 wt% of water with 2EH at the temperature of 80°C, AA to 2EH ratio of 1 to 3 stirring speed of 600 rpm without inhibitor

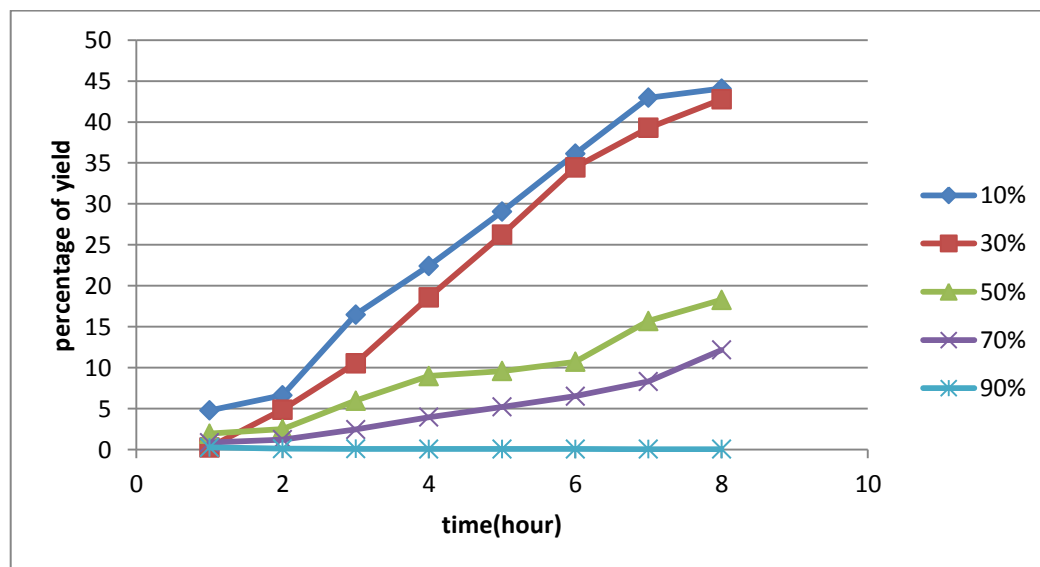


Figure 4-4: 2EHA yield profile of the esterification of AA aqueous solution containing 10-90wt% of water with 2EH at the temperature of 80°C, AA to 2EH ratio of 1 to 3 stirring speed of 600 without inhibitor

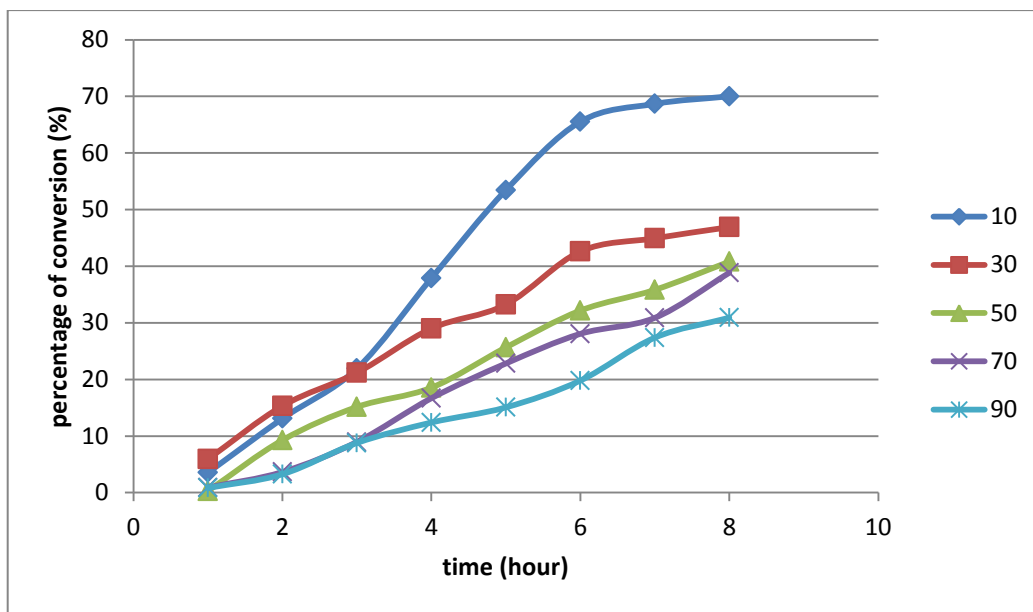


Figure 4-5: 2EHA conversion profile of the esterification of AA aqueous solution containing 10-90 wt% of water with 2EH at the temperature of 80°C, AA to 2EH ratio of 1 to 3 stirring speed of 600 rpm with inhibitor

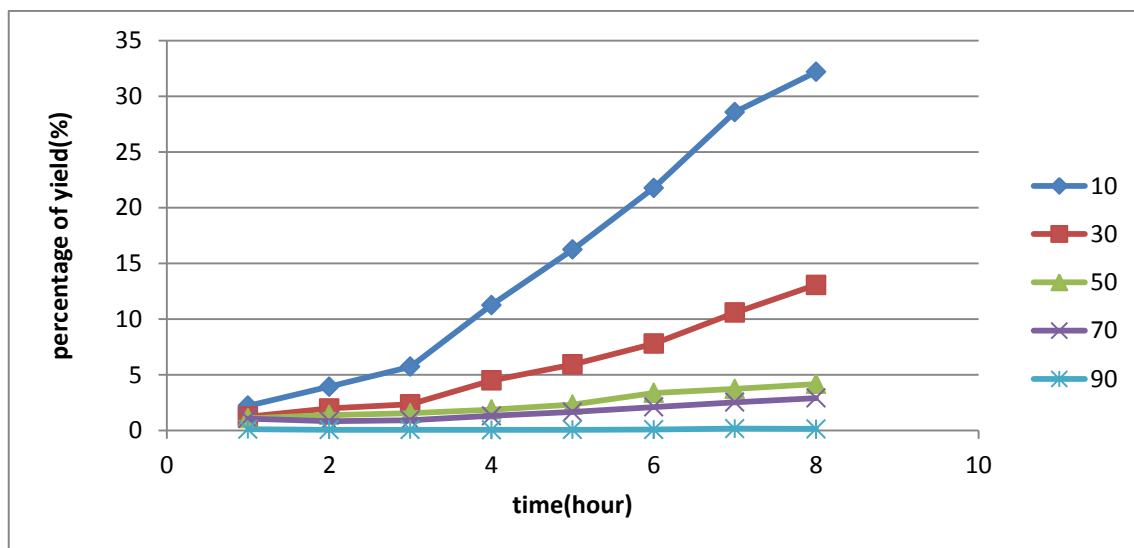


Figure 4-6: 2EHA yield profile of the esterification of AA aqueous solution containing 10-90 wt% of water with 2EH at the temperature of 80°C, AA to 2EH ratio of 1 to 3 stirring speed of 600 rpm with inhibitor

4.3 Catalyst characterizatio

In the catalyst characterizations, several testing had been used in order to examine the morphology of Amberlyst 15, scanning electron microscopy (SEM) was used for fresh and used catalyst after the reaction. Another testing were fourier transform infrared spectroscopy (FTIR) used to check the functional group of catalyst and nitrogen physisorption analyzer (BET) also used to catalyst surface area (Ahmad et al., 2014).

4.3.1 Scanning Electron Microscope (SEM)

The SEM micrographs of the fresh Amberlyst 15 outer surface under magnification of 20 are shown in Figure 6-1 while the SEM micrographs of the Amberlyst 15 outer surface under the magnification of 5000 are shown in Figure 6-2 in the appendix A. Based on Figure 6-1, it can be seen that some of the used catalysts have white deposits and the thin line cracks on the outer surface of catalysts. The thin line cracks enable the penetration of the reactants for the chemical reactions (Ahmad et al., 2014). Some of the cracks on the used catalysts for the reaction without inhibitor are covered by the white deposits, which are the polymer formed through the polymerisation of AA. The white deposits are not found on the fresh catalyst surface and are lesser on the used catalyst for the reaction with inhibitor. The polymerisation inhibitor present could stabilize the AA and prevent its polymerization that can cause reducing in catalyst activity (Anon, 2015). Comparing with the other used catalysts in the reaction with different AA concentration, more deposits are discovered on the catalyst used in the reaction with 90% of water. The presence of the significant amount of water has enhanced the polymerisation of AA.

Based on Figure 6-2, the smooth surface can be clearly seen on fresh catalyst. The fresh catalyst didn't go through any of reactions. So, it have smooth surface like other gel resins. The cracks are smaller in the used catalysts in the reactions without inhibitor since part of it is covered by the polymer formed.

4.3.2 Nitrogen Physisorption Measurement

Nitrogen physisorption measurement was carried out to determine the surface area of fresh and used Amberlyst 15. The surface area was calculated using Brunauer, Emmett and Teller (BET) method. Based on the table above, the fresh Amberlyst 15 was compared to the used Amberlyst 15 with different water content which are 10% of water content, 50% of water content and 90% of water content for without inhibitor and 50% of water content for with inhibitor.

The result show that the surface area increased as the amount of water content increased and for without inhibitor is higher than used catalyst with inhibitor at 50% of water content that tends for catalyst to be swollen. For 90% of water without inhibitor, the surface area for catalyst smaller than 50% of water. The surface area should bigger when increasing in water because the catalyst tends to swell in the reaction. However, the surface area can be small because macroporous space can be blocked due to so much swollen. All the isotherm of nitrogen physisorption measurement for fresh and used catalyst are at Appendix B

Table 4-1: Comparison of the nitrogen physisorption result of the fresh of Amberlyst 15 with different water content with and without inhibitor of Amberlyst 15

Properties	Fresh Catalyst	Used Catalyst			
		10% of H ₂ O (without inhibitor)	50% of H ₂ O (without inhibitor)	90% of H ₂ O (without inhibitor)	50% of H ₂ O (with inhibitor)
BET surface area (m ² /g)	37.208	45.342	48.788	39.0154	44.4812

4.3.3 Fourier Transform Infrared (FTIR)

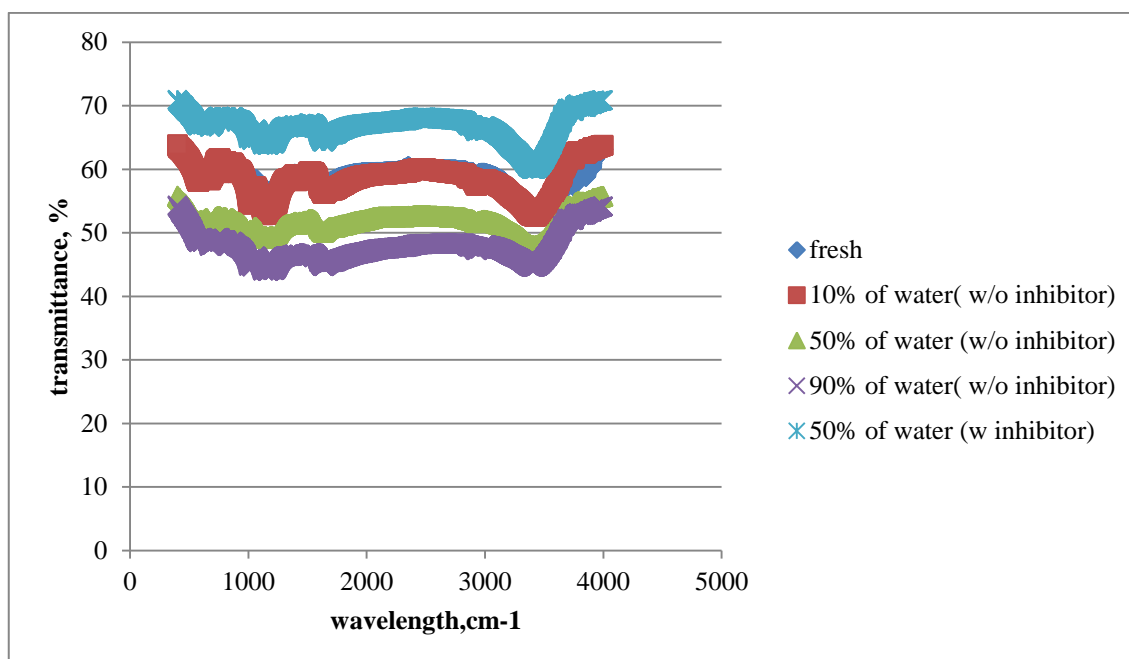


Figure 4-7: FTIR Spectrum for Amberlyst 15 with fresh and different water content in the presence of polymerization inhibitor

Figure 4-7 illustrates the spectra of FTIR analysis for fresh and used of Amberlyst 15 with different water content in the presence of Phenothiazine as polymerization inhibitor. Table 4 2 show that wavelength of Lewis acid and Bronsted acid for fresh and used Amberlyst 15 with different water content in presence of polymerization inhibitor. As the amount of water content increase, the number of wavelength of seems lower than fresh catalyst for without inhibitor and same goes to with inhibitor reaction for Bronsted acid. For Lewis acid, wavelength for used catalyst is higher than fresh catalyst.

Table 4-2: Wavelength of Lewis acid and Bronsted acid for fresh and used Amberlyst 15 with different water content in presence of polymerization inhibitor

	Lewis acid (cm ⁻¹)	Bronsted acid (cm ⁻¹)
fresh	1166.97	1642.94
10% of water (w/o inhibitor)	1168.96	1637.37
50% of water (w/o inhibitor)	1167.65	1633.33
90% of water (w/o inhibitor)	1166.2	1639.5
50% of water (w inhibitor)	1167.32	1632.99

5 CONCLUSION

The catalyst deactivation of Amberlyst 15 catalyzed by esterification of 2-ethyl hexanol(2-EH) and acrylic acid(AA) with different concentration was carried out in this study. The esterification process was continued using the presence of polymerization inhibitor with different percentage of water content. Based on the result obtained, catalyst deactivation happened due to high surface area, increase in functional group and high water tolerance. The present study show that more water content needed to dilute AA solution and more polymerization inhibitor to prevent the poly-acrylic acid formation in the reactions.

6 RECOMMENDATION

In order to improve the experimental studies in the coming semester, both AA aqueous solution and 2EH should be heated up simulataneously to the set point temperature before mixing and adding catalyst to avoid temperature fluctuation. The temperature should be set above than 80. The connection of the neck of the flask must be wrapped properly with layer of wool plus aluminium foil to reduce the heat loss to the surrounding. Besides, the condenser should be more slanted to ensure the water produced can be removed properly and sampling preparations for analysis should be more careful to avoid any handling error that might effect during analysis process.

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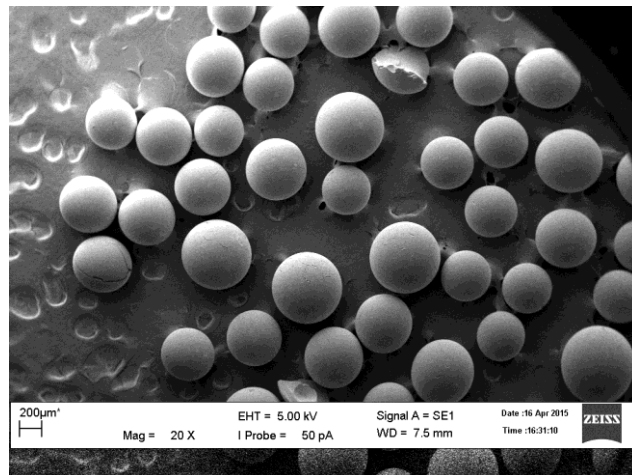
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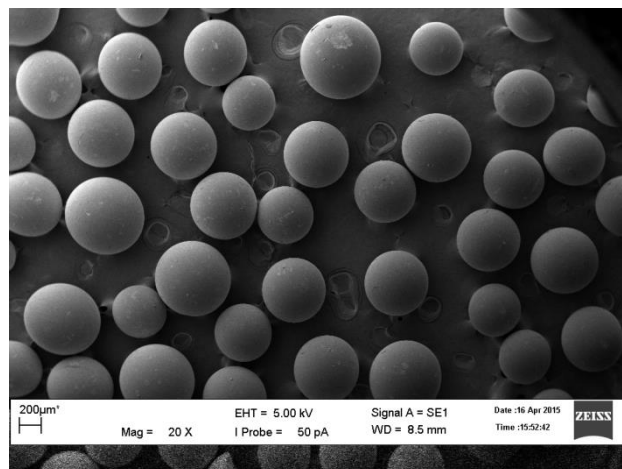
APPENDICES

6.1 Appendix A

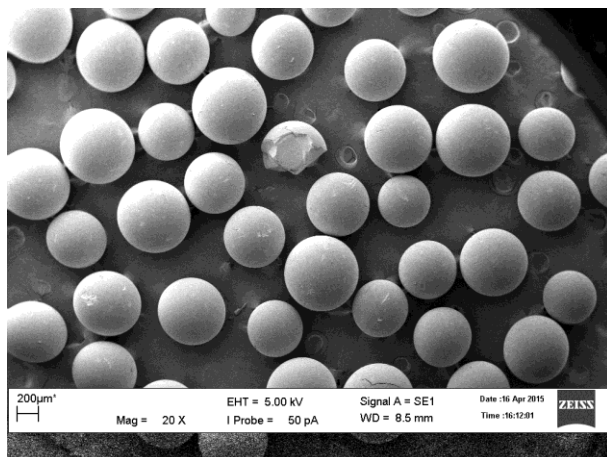
Scanning Electron Microscope (SEM)



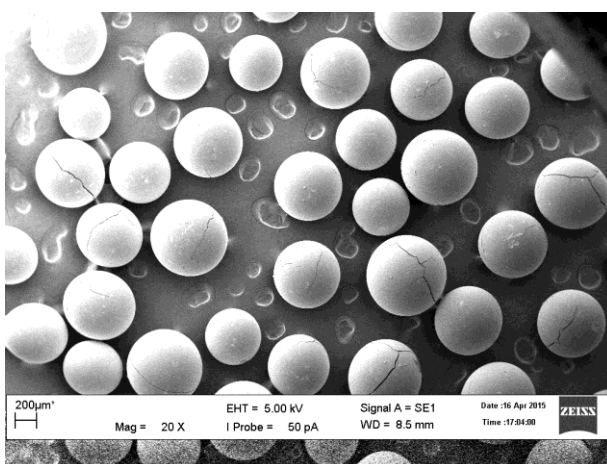
(a)



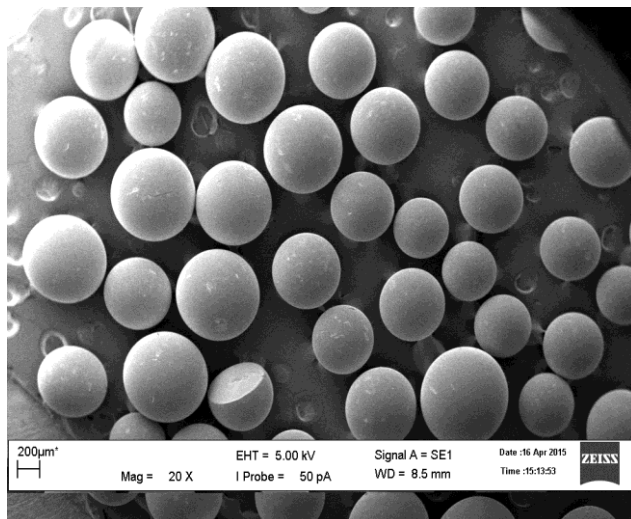
(b)



(c)

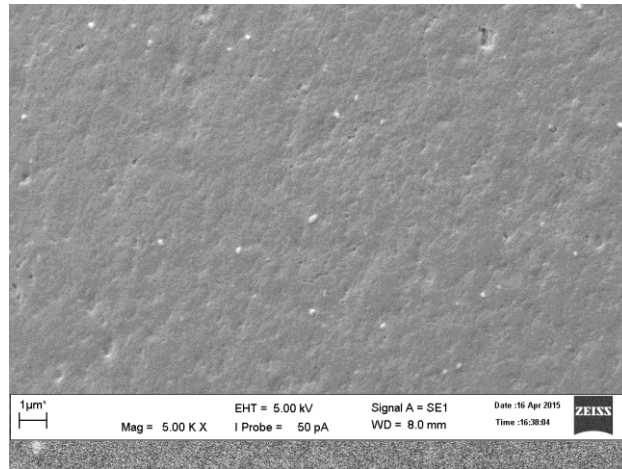


(d)

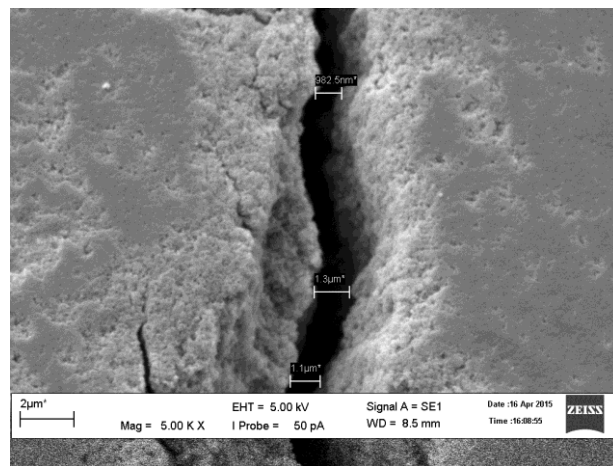


(e)

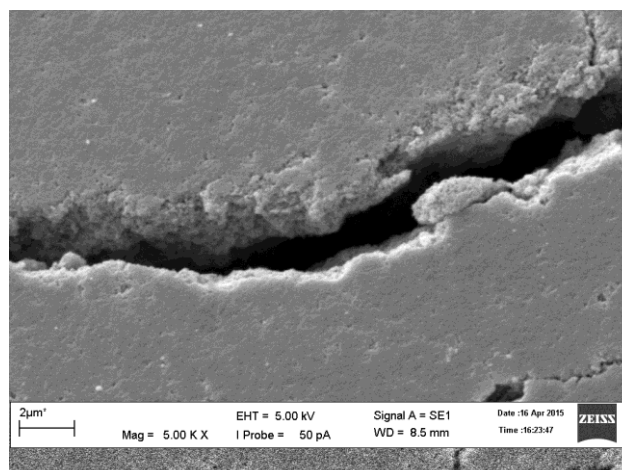
Figure 6-1: SEM micrographs of outer surface of Amberlyst 15 under magnification 20x with condition of; (a) fresh catalyst, (b) 10% of water content (without inhibitor), (c) 50% of water content (without inhibitor), (d) 50% of water content (with inhibitor) and (e) 90% of water (without inhibitor)



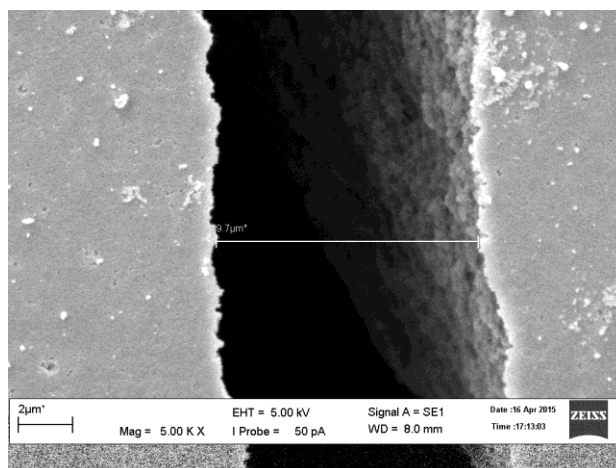
(a)



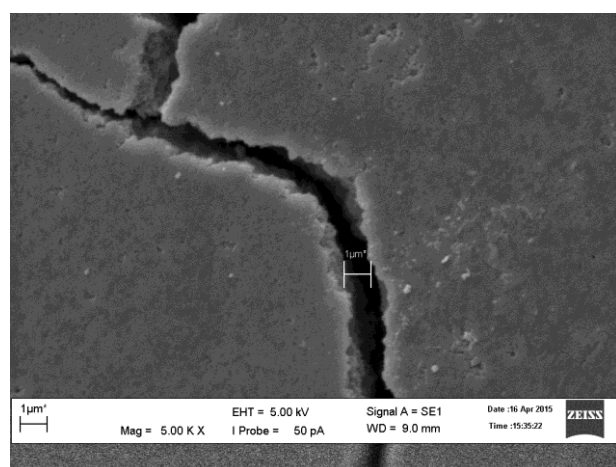
(b)



(c)



(d)



(e)

Figure 6-2: SEM micrographs of outer surface of Amberlyst 15 under magnification 5000x with condition of; (a) fresh catalyst, (b) 10% of water content (without inhibitor), (c) 50% of water content (without inhibitor), (d) 50% of water content (with inhibitor) and (e) 90% of water (without inhibitor).

6.2 Appendix B

Nitrogen Physisorption Measurement

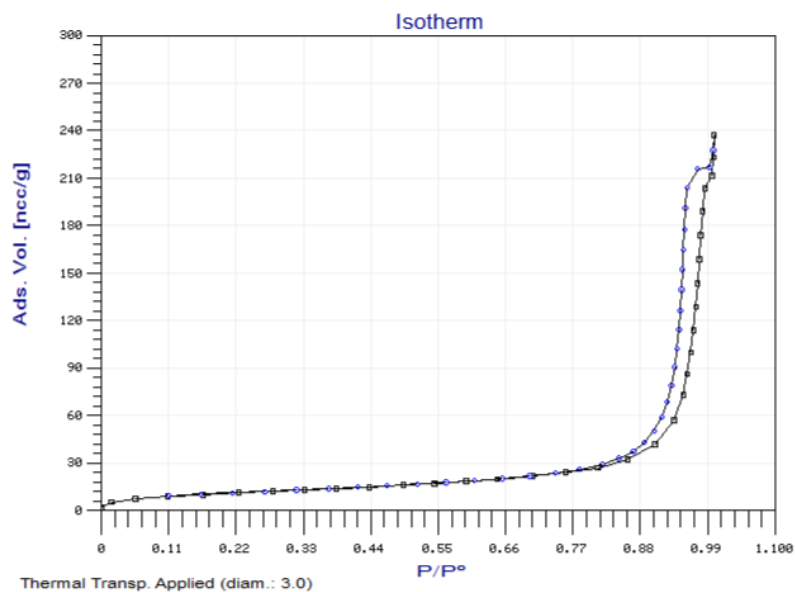


Figure 6-3: Nitrogen adsorption/desorption isotherm at -195.7°C for the fresh Amberlyst 15

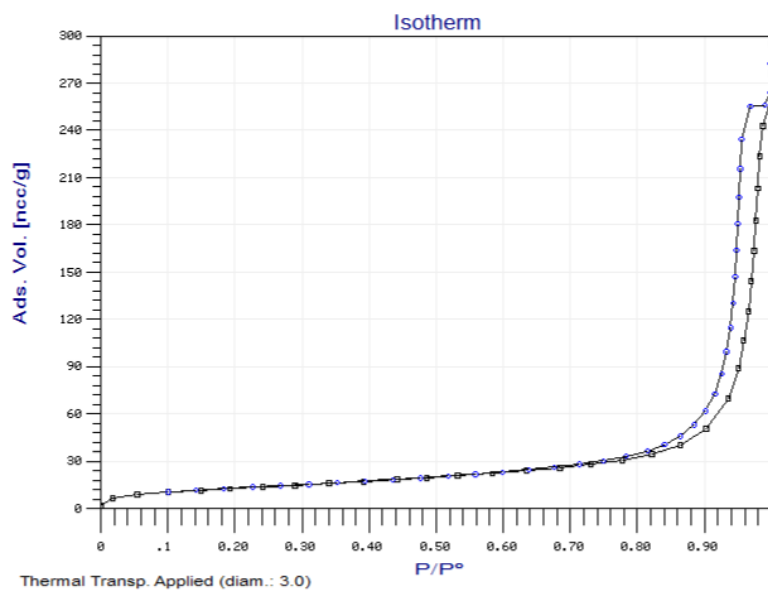


Figure 6-4: Nitrogen adsorption/desorption isotherm at -195.7°C for Amberlyst 15 at 10% of water content without inhibitor

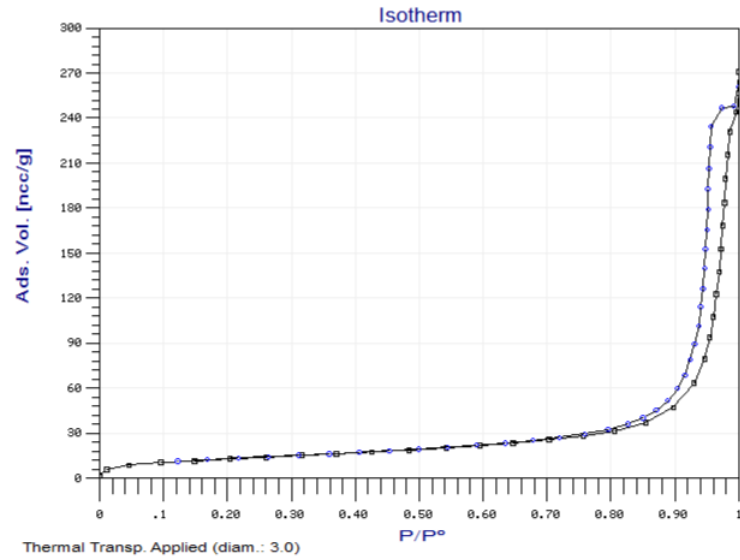


Figure 6-5: Nitrogen adsorption/desorption isotherm at -195.7°C for Amberlyst 15 at 50% of water content with inhibitor

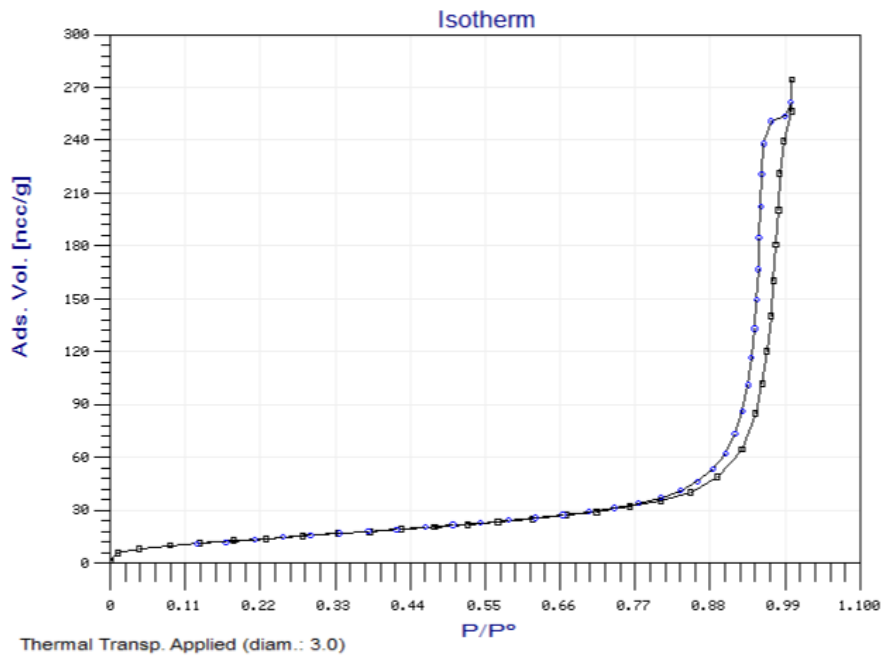


Figure 6-6: Nitrogen adsorption/desorption isotherm at -195.7°C for Amberlyst 15 at 50% of water content without inhibitor

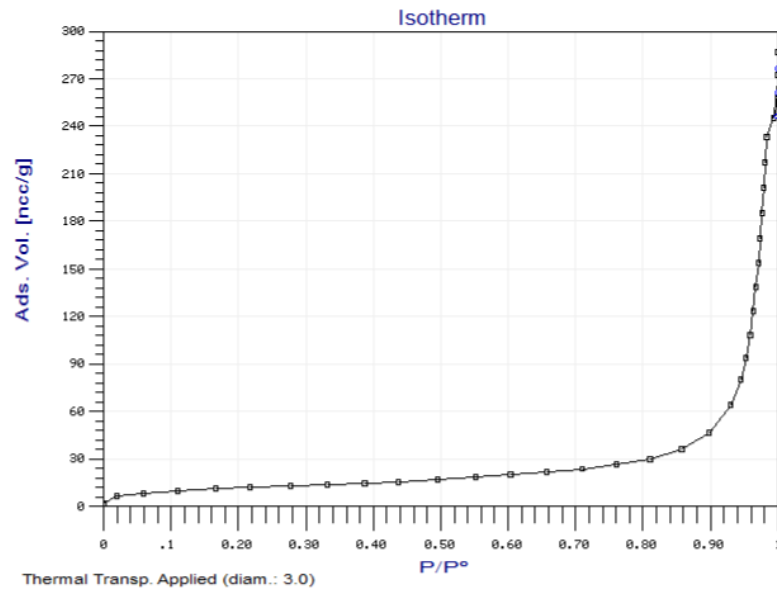


Figure 6-7: Nitrogen adsorption/desorption isotherm at -195.7°C for Amberlyst 15 at 90% of water content without inhibitor