Ethyl acetate properties

Ethyl acetate is the most popular ester from ethanol and acetic acid. It is manufactured on a large scale for use as a solvent. Ethyl acetate is a moderately polar solvent that has the advantages of being volatile, relatively non-toxic, and non-hygroscopic. Ethyl Acetate is an organic compound which also known as, ethyl ethanoate, commonly abbreviated EtOAc or EA. Below is the table of Ethyl Acetate general data and physical properties:

FORMULA

CH3COOCH2CH3

MOLECULAR WEIGHT

88. 10

MELTING POINT

-83. 6°C

BOILING POINT

77. 15°C

INDEX OF REFRACTION nd20

1. 372

DENSITY d20

0. 902 g/mL

SPECIFIC HEAT (20°C)

0. 459 kcal/kg.°C

LATENT HEAT (bp)

88 kcal/kg

VISCOSITY (20°C)

0. 455 cP

EA SOLUBILITY IN WATER (20°C)

7. 7 wt.%

WATER SOLUBILITY IN EA (20°C)

3. 3 wt.%

Table 1. 1 : Physical Properties of Ethyl Acetate

Ethyl acetate can dissolve up to 3% water and has a solubility of 8% in water at room temperature. At elevated temperature its solubility in water is higher. It is unstable in the presence of strong aqueous bases and acids.

Ethyl Acetate can be manufactured by several types of process such as esterification, Tishchenko’s reaction and Advanced Acetates by Direct Addition (AVADA) technology. In 1985 it was approximately 400000 tones in tons were produced yearly in Japan, North America, and Europe combined. The commercial Ethyl Acetate is a clear, colorless, sweet smell odor and has a minimum purity of 99. 8%, with water and ethanol not exceeding 0. 03%.

Historical Review of Ethylbenzene Processes

Ethyl Acetate is primarily produced by direct esterification of ethyl alcohol (e. g ethanol) with acetic acid, a process which involves mixing acetic acid with excess of ethyl alcohol and adding a small amount of sulphuric acid. This mixture contains about 65% of ester (EA). Then the EA is separated and purified by distillation in order to achieve commercial specification. This process considers as exothermic and safe where the heat of reaction is -0. 0114kJ/mol with no danger of decomposition.

Other methods that often use in manufacturing ethyl acetate are based on Tishchenko's reaction. This reaction is by combining two equivalents of acetaldehyde in the presence of an alkoxide base as catalyst. This way is a commercial method of producing ethyl acetate. Due to the observation and experiment by Tishchenko, the result shown that the obtainable yield of ethyl acetate by adding aluminum ethoxide to acetaldehyde at -20oC is 61%.

In addition, new and interesting process of manufacturing ethyl acetate is Advanced Acetates by Direct Addition (AVADA) technology. This reaction used the reaction of ethylene, acetic acid and water with the presence of heteropoly acid (HPA) catalyst. It then will undergo reaction at vapor phase before being fed into the separation section where the major product and by-product being separated. This process can produce ethyl acetate at 99% concentration.

The Uses of Ethyl Acetate

Ethyl acetate is used as solvent in a wide range application especially in industries. It is one of the most popular solvent that used in surface coating and thinners manufacture such as nitrocellulose lacquers, varnishes and

thinners. It exhibits high dilution ratios with both aromatic and aliphatic diluents and is the least toxic of industrial organic solvents.

Pharmaceuticals also required ethyl acetate as an extraction solvent for the concentration and purification of antibiotics. Manufacturing of various drugs also used ethyl acetate as an intermediate. High purity product can be used as a viscosity reducer for resins used in photoresist formulations in the electronics industry. Besides that, ethyl acetate acts as a solvent in the preparation of synthetic fruit essences, flavors and perfumes.

On the other hand, the extensive amounts of ethyl acetate are used in the manufacture of flexible packaging and in the manufacture of polyester films and BOPP films. It is also used in the treatment of aluminium foils. Ethyl acetate is used as solvent to dissolve the resin, control the viscosity and modify the drying rate in inks for flexographic and rotogravure printing.

Based on ICIS article that has been updated April 2008, the global demand is predicted to grow at 3-4%/year because of strong demand for surface coatings and as a replacement for restricted solvents. China and Southeast Asia are largest demand while Western Europe is developed markets. Southeast Asia and China are expected to become the most popular for ethyl acetate production and consumption. The Southeast Asian paints and coatings market is expected to grow at 5-6%/year.

Japan’s Daicel Industries is converting an acetic acid plant in Otake, Hiroshima to produce ethyl acetate by using bio-ethanol as the raw material. It will have a capacity of 50, 000 tonnes/year with production expected to start in spring 2009.

The global demand growth for US is about 2%/year to 2009. According to ICIS Chemical Business (ICB), US demand increased from 88, 500 tonnes in 2005 to 95, 300 tonnes in 2009. Around 60% of ethyl acetate is consumed in US as a solvent in a variety of coating formulations. These coatings are used for wood furniture and fixtures, agricultural, construction and mining equipment, containers and closures, auto refinishing, and maintenance and marine applications.

Around 20% of the ethyl acetate is used as solvent-based architectural coatings for both exterior and interior use. This sector has been growing at approximately 6%/year. However, in industrial coatings the usage of ethyl acetate is decline because of environmental constraints has largely been completed and future growth in the US is estimated to be a healthier 2. 5%/year up to 2009.

OEM (original equipment manufacturer) solvent-based coatings have been declining slowly in the US. The OEM sector, however, is the largest and represents 58% of ethyl acetate’s coatings use demand. The remaining sector, specialty coatings, which includes marine coatings, has held steady.

The European market is reported to be balanced with big supply and steady demand. However, future demand is expected to be flat and or even contract slightly as consumption by local paints and inks sectors shrinks as production moves eastwards.

In the UK, INEOS has acquired BP’s ethyl acetate business including a 250, 000 tonnes/year plant in Hull. Future consolidation is seen as possible in Europe as ethylene-based producers struggle to compete against more

competitive ethanol-based production. Europe could also become more reliant on imports.

PROCESS BACKGROUND

Esterification

Esterification is a chemical reaction process between alcohol and carboxylic acid in the presence of catalyst that formed ester. This mixture converts to ester about 65% at room temperature. The commonly concentrated sulphuric acid is acting as a esterification catalyst to enhance the reaction. The sulphuric acid removes water to help shift the equilibrium towards forming more ester product. Water is a by- product and must be removed in order to get the equilibrium in the desired direction. This process is a simple process, well known reaction, and moderately exothermic where the heat or reaction, H is -0. 0114kJ/mol with no danger of decomposition reaction. The optimum temperature for this reaction is in the range of 363 K – 400 K while the optimum pressure is in the range of 20 bar – 40 bar.

Ethanoic Acid + Ethanol Ethyl Acetate + Water

CH3COOH + C2H5OH CH3C02C2H5

The reaction between acetic acid and ethanol to produce ethyl acetate in the presence of concentrated sulphuric acid. This process is released a few amount of heat to the surrounding and classified as exothermic reaction. This reaction is called a homogeneous liquid phase. Water is formed in the reaction is removed continuously to ensure maximum conversion of acetic acid.

The catalyst can be heteregenous and homogeneous. There are two categories of catalyst that can be used in this reaction, mineral acid catalyst and para toluene sulphonic acid or ion exchange resins can serve as heterogenous catalyst.

Process Description

Ethanol and acetic acid together with crude ethyl acetate is fed into the reactor in the presence of concentrated sulphuric acid to produce ester and water. Then, the products are fed into the distillation column (DC1) to separate water and ester (ethyl acetate). The bottom product of DC1 is water and the overhead product is ethyl acetate. This part are taken by dehydration and azeotropic distillation of ethyl acetate and water. The overhead product is passed to the decanter to separate the organic phase and aquase phase. The upper layer known as organic phase while lower layer known as aqueous phase. partially of organic phase is fed into the reactor and another potion of organic phased is passed into the second distillation column (DC2). The second column is a purify process where to give the pure ethyl acetate (bottom product). The top product is a mixture that consists of ethyl acetate, water and ethanol. this mixture is separated after cooling process and the light phase is fed back to DC2 and the rest is transferred to the second decanter where its process is same as the first decanter to separate the organic and aqueous phase.

Pipeline is used to combine the aqueous phase from the both decanters and distilled in the third column to give waste water at the bottom product and again ester, water and alcohol. This stream is recycled into the reaction column.

Raw Material

Ethanol:

Ethanol is one of the material that is being used in the esterification process. it is also known as ethyl alcohol. ethanol is a volatile, flammable and colorless liquid. Ethanol can be obtain by fermentation of plants. Ethanol is relatively non-toxic and dissolve in water. It is a renewable energy source and it has less harmfull effects on the environment. However, ethanol will also give an impacts to the environment. The use of ethanol is a problem for conventional air pollutants. Ethanol used will increase the emission of chemicals that lead to the production of ozone.

Ethanoic acid:

One of the raw material needed to complete the reaction. Ethanoic Acid is one of the simplest carboxylic acid. it is a colourless liquid with an unpleasant pungent odour. ethanoic acid is produced by the oxidation of ethanol. Ethanoic acid is highly corrosive to the metals and it is also potentially harmful to our health.

Sulphuric acid (catalyst):

Sulphuric acid is chosed as homogeneous catalyst in this reaction. this catalyst is very effective mineral acid catalyst. however, this sulphuric acid is strongly corrosive and leaves sulfate residues. besides that, it is also generates large amount of heat.

Tishchenko's Reaction

Tishchenko's reaction is a reaction that need the presence of an alkoxide base while two equivalents of acetaldehyde is combining. This way is becoming commercial method of producing ethyl acetate in Europe since acetaldehyde become important intermediate on the basis of acetylene. Due to Tishchenko, the obtainable yield of ethyl acetate by adding aluminum ethoxide to acetaldehyde at -20°C is 61%. The reaction is expressed by,

[catalyst; alkoxide base (e. g Aluminum Ethoxide)]

2CH3CHO CH3COOCH2CH3

(Acetaldehyde) (Ethyl Acetate)

Figure 1. 3: Tishchenko's process

Process Description

For the process of Tishchenko's reaction, acetaldehydes will be introduced to the catalyst solution continuously. The catalyst is first need to be prepared by dissolving granular Aluminium in an ethanol-ethyl acetate mixture in the presence of aluminium chloride and small amount of zinc chloride. This catalyst (basicly Aluminum Ethoxide) is prepare uncontinuosly.

In reactor, while acetaldehyde contact with the prepared catalyst, the ratio of the reaction partner must be adjust in order to obtain 98% transformation of acetaldehyde in one passage. A further 1. 5% transformation is achieved in stirring vessels. Consecutively to make sure the reaction temperature is kept to 0°C, brine with normally -20°C will be used as the cooler. This

reaction takes approximately 1 hour to completely mix before being transfer to residue separation.

Next, separator is needed to remove the residue that contain in the mixture. The distillable products are removed by evaporation. For the economic issue, the residue is treated with water to regain ethanol. For the residual slurry, it can either be given to biological degradation plant or it can be burned together with other organic waste products.

Subsequently, the distillable products need to be purifying in so that it can achieve commercial purity which is approximately 99. 8%. Therefore, distillation column is used. For the 1st series of distillation column, light end are separated and this steam is further distilled to take non-converted acetaldehyde, which is returned to reactor. Then ethanol that contain ethyl acetate is separated for reuse in catalyst preparation.

The bottom of 1st column give the high quality or grade of ethyl acetate that only will obtain at the head of the next column due to the need of separation of high boiling condensation products in mixture with ethyl acetate which will be remove at the bottom. In addition, further small column is needed to recover another part of pure ethyl acetate to isolate acetaldehyde diethyl acetal. Hence, after purification is done the recover product can used as an important intermediate or hydrolyzed in an acid medium to give reusable acetaldehyde and ethanol.

Raw Material

Acetaldehyde

It is also known as ethanal. Acetaldehyde is one of the most important aldehyde and is being produced in a large scale industrially. This substance can be produced by the oxidation of ethylene. Although it is not a costly substance and it is very easy to get, acetaldehyde is a very toxic substance. It can give harm to living organisms and toxic substance is not an environmental friendly. It is an air pollutant resulting from combustion.

Advanced Acetates By Direct Addition (Avada)

In AVADA process, ethyl acetate is produced by reacting ethylene with acetic acid and water in the presence of heteropoly acid catalyst. The amount of water being used is in range from 1-10 mole% based on the total ethylene and acetic acid. The presence of water can reduce the amount of unwanted by-product that formed by the reaction. The mole ratio of ethylene to acetic acid in the feed stream is in range of 6. 0 to 12. 2, while for ethylene to water, the mole ratio is between 8. 0 to 17. 0 and the mole ratio of acetic acid to water is from 1. 25 to 1. 40.

Heteropoly acid

CH2 = CH2 + CH3C02H CH3C02CH2CH3

(ethylene) (acetic acid) Water (ethyl acetate)

The reaction is preferably carried out at a temperature in the range from 160°C to 195°C while the preferably pressure is between 1200 kPa to 1500 kPa.

The catalyst used must consist at least one heteropoly acid salt of a metal such as litium, cuprum, and magnesium which supported on a carrier. The

heteropoly acid used is phosphotungstic acid while the carrier is silica. Heteropoly acids usually have a high molecular weight in the range of 700 – 8500 and include dimeric complexes. They have high solubility in polar solvents such as water or other oxygenated solvents. In order to achieve optimum performance, the carrier should free from metals or elements which can affect the catalytic activity of the system. To prepare the carrier, firstly the heteropoly acid is dissolved in distilled water, demineralised water, alcohols or other non-aqueous solution. Then the carrier is soaked in the acid solution for several hours with periodic manual stirring. After that it is filtered using Buchner funnel to remove any excess acid. The wet catalyst is then placed in an oven at elevated temperature for several hours to dry. Lastly it is allowed to cool to ambient temperature in desiccators. Now this supported catalyst is ready to be used in esterification process.

BASIC FLOW DIAGRAM OF ETHYL ACETATE PRODUCTION BY AVADA

The basic flow diagram of the unit is shown in the above figure. The unit consist of feed section, reaction section, and product and by-product separation section.

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The fresh feed which contain ethylene, acetic acid and water are fed into the vaporiser. Vaporiser is used to change the liquid phase feed into vapour phase as the reaction is preferably carried out in the vapour phase. It also

includes a recycle system for both unreacted feeds and all the major by-products.

The combined feed vapour stream is fed to a reactor train comprising of four fixed bed reactors in which each reactor already filled with catalyst. The reactants are passed over the catalyst suitably at a GHSV (Gas Hourly Space Velocity) of 300 to 2000 per hour. The first three reactors are fitted with acid/water injection to the exit streams. This is to facilitate independent control of reactor inlet temperatures and to maintain the desired ethylene to acid ratio. The fourth reactor functions as finishing reactor where the final conversion of ethylene and acetic acid to ethyl acetate is achieved. There are four by-product formed from the reaction which are 2-butanone, acetaldehyde, ethanol and diethyl ether.

The crude product stream exiting the last reactor is cooled before entering the flash drum where the separation of non-condensable (gas) and condensable (liquid) phases occurs.

The recovered gas is recycled back to the vaporiser while the liquid stream enters the product separation and purification system. In this system, series of distillation columns designed to recover and purify the final product. It is also to recover the unreacted acetic acid, water, ethanol and light ends streams for recycling back to the vaporiser.

Advantages and Disadvantages of AVADA

The AVADA process is superior to other additional processes in terms of environmental protection. This is because AVADA uses a solid acid catalyst. Therefore, there are fewer requirements for the treatment and disposal of

aqueous effluent compared to traditional esterification reaction that produces as much water as ethyl acetate. Since AVADA process eliminates the intermediate esterification steps and the need for ethanol, it save about 20% on energy cost compare to conventional routes. The AVADA process produces high purity (more than 99%) which reduces the production of by-products. Undesirable by products such as 2-butanone and acetaldehyde may be controlled by careful adjustment of feed composition and reaction temperatures while maintaining acceptable ethyl acetate yields. The production of c4 unsaturated hydrocarbons is significantly reduced. Therefore, the catalyst lifetime can be extended. The disadvantages of AVADA process is rapid catalyst deactivation thus disturbing the quality of the product. However, this problem can be solved using a bed porous silica beads with the heteropolyacid impregnated in the pores.

PROCESS SELECTION

There are three methods found in the production of ethyl acetate which are Tishchenko, Esterification and Advanced Acetates by Direct Addition (AVADA). By considering all of the advantages and disadvantages of each process, the Acetates by Direct Addition (AVADA) was chosen as the best alternative to produce ethyl acetate. The main reason AVADA was chosen are because the catalyst used is environmental friendly.

TICHSHENKO’S

ESTERIFICATION

ADVANCED ACETATE BY DIRECT ADDICTION (AVADA)

RAW MATERIAL

Acetaldehyde

Ethanol

Acetic acid

Ethylene

Acetic acid

Water

CATALYST

Alkoxide base (e. g aluminium ethoxide)

Produced large amount of aluminium residue which is not easily separated

Produce large amount of wastewater

Acid catalyst (e. g Sulphuric acid)

Very corrosive

Produce sulphate residue

Heteropolyacid (e. g phosphotungstic acid)

The catalyst lifetime can be extended

Using solid catalyst- waste free and less requirement for treatment

OPERATING CONDITION

0°C

1 hour reaction

90 0C – 127°C

20 bar – 40 bar

160°C – 195°C

1200 kPa – 1500kPa

PURITY

Crude ethyl 61 % purity

Crude ethyl 55 % purity

Crude ethyl 99 % purity

NUMBER OF EQUIPMENT USE

5 equipments (distillation column, feed surge drum, reactor, separator, mixer)

3 equipments (reactor , decanter, distillation column)

5 equipments (vaporizer, reactor, flash drum, distillation column, compressor)

REACTION

2Acetaldehyde Ethyl Acetate

ethanol + ethanoic acid ethyl acetate

Ethylene + acetic acid

Ethyl acetate

AVAILABILITY OF RAW MATERIAL

Produce in large scale in Europe due to the importance of acetaldehyde as intermediate on the basis ofacetylene

Easy to get in china

Table 1. 2: Comparison between all processes

PROCESS	ADVANTAGES	DISADVANTAGES
AVADA (Advanced Acetates By Direct Addition)	Undesirable by products such as 2-butanone and acetaldehyde may be controlled by careful adjustment of feed composition and reaction temperatures while maintaining acceptable ethyl acetate yields.	The production of c4unsaturated hydrocarbons is significantly reduced. The catalyst lifetime may be significantly extended.

The process economics are improved by a reduced requirement to operate process purge streams to reduce the recycle of undesirable by-products and by the ability to de-bottleneck the product purification system.

Very high purity (> 99%).

Avoid environmental hazards by using heteropolyacids (environmentally friendly).

More energy efficiency – save ~20% on energy costs.

Using solid catalyst – waste free and less requirement for treatment and disposal of aqueous effluent.

Rapid catalyst deactivation thus disturbing the quality of the product.

Esterification

Well known reaction.

Moderately exothermic reactions with no danger of decomposition of reactions.

The reaction also exhibit second order ractions when no strong acid is present and a kind of autocatalytic behaviour when the acid is introducespurification system.

Acidic feedstocks

Concentrated sulphuric acid is a harmful chemical reagent.

Generates large amount of heat.

Tishchenko’s Reaction

The raw materials are produced in large quantities.

The price of the raw material is not very costly.

It is an alternative way due to expensive price of ethanol.

Produce large amount of aluminium residue which is not easily separated due to the use of aluminium ethoxide as a catalyst .

The use of the catalyst can create a large amount of wastewaters and thus extra cost is needed to treat the waste.

The raw material, acetaldehyde is a very toxic substance.

Table 1. 3 : Advantages and disadvantages of each processes