

A method to clean industrial water via esterification: A review

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Abstract

Aqueous solutions of various acids are produced as by-products in reactions involving many important processes, such as in the production of esters and other industrial products. Thus, the recovery of the acid is a large problem which cannot be solved because of economical reasons. Even, the conventional separation methods such as distillation and extraction suffer from several drawbacks. Distillation is generally uneconomic because of the high costs involved in vaporizing water that is the most volatile compound and is present in very large proportion but possesses a large latent heat of vaporization. Extraction is limited by phase separation and distribution of the components involved in the reacting system. In this technology, water containing acid is simply purified by means of an esterification. Acid reacts with an alcohol in the presence of an acid catalyst to give the corresponding ester. The large amount of water is present at the beginning of the reaction, and thus, have the ability to shift the reaction equilibrium towards the ester (to the right) and not towards the reagent (thermodynamically favourite). Different acid catalysts have been used in both homogeneous (sulphuric acid) and heterogeneous phase (polymeric resins and sulphated zirconia) to improve the process rate towards the equilibrium efficiency.

Keywords: Water, Esterification, Acid, Alcohol, Catalyst

1. Introduction:

Treatment of water containing dilute acids is one of the ordinary problems at the industrial scale such as in the production of esters, terephthalic acid, Wacker process, destructive distillation of wood and various other industrial processes. Although many process i.e. extraction, activated sludge, distillations etc. are there to treat this contaminated water, but, these traditional methods are not efficient and are expensive to apply at industrial level. Distillation is usually unprofitable as it involves high costs in vaporizing water, which is the most volatile compound and is present in very large proportion but possesses a large latent heat of vaporization. And in the case of extraction process, it is complicated to perform phase separation and

distribution of the components produced during reaction in the reacting system. Due to these reasons, acids are unable to be removed from the dilute solutions. Esterification is one of the processes which have applied by a few of researchers to treat acid containing water to convert into valuable product as well as clean water [1, 2, 3].

1.1. Esterification:

Esterification is the chemical process for producing esters, compounds with chemical structure $R-COOR'$, where R and R' can either be alkyl or aryl groups. The esterification process has a broad spectrum of uses from the preparation of highly specialized esters in the chemical laboratory to the production

of millions of tons of commercial ester products that found uses in pharmaceutical, perfumery, food industries and in the preparation of biodiesel [4]. Generally, it is the equilibrium process in which the one reagent should be present in excess quantity to shift the equilibrium towards the desired product.

1.2. Use of Heterogeneous catalysts:

Traditionally, the products (ester and water) were prepared by merely mixing carboxylic acids with alcohols in the presence of various strong homogeneous catalysts i.e. p-toluensulphonic acid, sulphuric acid, hydrochloric acid etc. But, as the homogeneous catalysts suffers through major drawbacks such as low yields, harsh reaction conditions, use of hazardous materials, long reaction times [5], no separation of reaction products & catalyst; reactor corrosion problems and environmental inconveniences [6, 7]; heterogeneous catalysts are preferred over them. So, the use of product esters as biorenewable chemicals and as “green” solvents has encouraged the study of esterification reactions using heterogeneous catalysts such as ion exchange resins, modified zirconia and Nafion/silica nanocomposite SAC- 13 and many others, that overcomes the disadvantages of homogeneous catalysts [7, 8].

2. Water cleaning via Esterification:

By this technology, water containing acids are simply purified by means of an esterification and side by esters can be formed. The acid present in the solution reacts with offered alcohol in the presence of an acid catalyst to give the corresponding ester. Some of the researchers have purified water using this principle of esterification by different technologies and catalysts. Saha [1] purified a stream of contaminated water containing 30 % of acetic acid by an esterification

reaction. This reaction was performed by reactive distillation column of acetic acid with *n*-butanol/*iso*-amyl alcohol that is a reversible reaction using macro porous ion-exchange resin i.e. Indion 130, as a catalyst bed that is confined in a stainless steel wire mesh containing as tea bags. Various parameters, e.g. total feed flow rate, reflux ratio, length of catalytic section, effect of recycle of water and mole ratio of the reactants, location of feed points were investigated. By this, 51 % conversion of acetic acid was achieved during the reaction. It was found that by using reactive distillation column, recovery of acetic acid in the reaction was improved. It was observed that 58 % conversion was achieved at the mole ratio (acetic acid: *n*-butanol) of 1:2. In the reaction of acetic acid with *iso*-amyl alcohol, 51 % of the conversion of acetic acid was achieved at the same mole ratio (acetic acid to *iso*-amyl alcohol) of 1:2.

Further, Bianchi [2] investigated the vaporization of acetic acid (6%, w/w) at very low concentration by reacting with *n*-butanol and 2-ethyl-1-hexanol. The esterification of much diluted solution of acetic acid with alcohol was found to be reversible in nature. Therefore, the reaction equilibrium is to be shifted towards the ester and the reaction was found to be thermodynamically favourite, because of the presence of large amount of water. Both homogeneous (sulphuric acid) and heterogeneous phase (polymeric resins and sulphated zirconia) were tested to optimize the process efficiency of the catalyst for maximum conversion. Two types of experimental procedures were performed: (a) runs at complete evaporation condensation and; (b) runs with distillation and reaction product removal. In this second configuration, a complete removal of acetic acid was achieved as compared to first. The complete

conversion of acetic acid was achieved after 55 h of the reaction. The use of this method resulted into the removal of the reaction product (the ester), alcohol and the water. This is due to the presence of two azeotropic mixtures (alcohol/water, water/ester) that has a lower boiling point as compared to both pure alcohol and ester. Due to this reason, the distillation column was coupled with an azeotropic head that separates the organic phase from the aqueous one. Further, Yagy [3] developed a direct esterification of aqueous acetic acid with ethanol (molar ratio = 1:1) using polystyrene-supported or homogeneous sulfonic acids as a catalyst for the recovery of acetic acid from wastewater. Toluene was added to increase the

3.

onclusion:

Esterification is one of the suitable methods to separate water from the acids present in the water. It is cost effective and can be easily adopted at industrial scale. The reaction is equilibrium limited. The peculiarity of the method is the presence of large amount of water at the beginning of the reaction, and

4. References:

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equilibrium yield, which had a high ability to extract ethyl acetate from the aqueous phase. This methodology can be applied to general aqueous reactions for the conversion of acetic acid using hydrophilic substrates. The effect of the addition of inorganic salts (i.e. LiCl, NaCl, KCl and various other salts) on the ester yields was studied, and CaCl₂ was found to be the most effective salt in improving the equilibrium yield as compared to all other salts. It was found that even low amount of catalyst has efficiently accelerated the reaction. For the recovery of organic compounds from wastewater, although the highest yield (90%) is obtained in the reaction.

thus, the ability to shift the reaction equilibrium towards the ester and not towards the reagent (thermodynamically favorite). Various heterogeneous catalysts can be used to achieve the maximum yield of ester and water as the products.

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