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Review of Recovery Methods for Acetic Acid from Industrial Waste Streams by Reactive Distillation

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Abstract

This paper addresses an industrially important problem of recovery of acetic acid from a wastewater streams via reactive distillation. The separation (or recovery) of organic residues from aqueous waste streams released from chemical and petrochemical industries is critical and indispensable from the points of view of pollution control and recovery of useful materials. The disposal of wastewaters containing most widely used industrial organic acids such as acetic acid, formic acid and propionic acid has been recognized as a significant expense to the industry and environment. In this paper, existing methods of physical separation of acetic acid from wastewater is presented. Available conventional techniques including fractional distillation, liquid extraction, adsorption, precipitation, ion exchange, etc. have been briefly reviewed emphasizing the major drawbacks of these methods. A new method – reactive distillation - for recovering acetic acids from dilute aqueous solutions is described and compared with the other conventional techniques. Reactive distillation is an efficient, economical, and environmental friendly method for separation of acetic acid from wastewater streams.

Keywords: *Clean technology, wastewater, pollution prevention, recovery of acetic acid, separation processes, reactive distillation, esterification*

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INTRODUCTION

In recent years wastes have been considered to be a serious worldwide environmental problem. These wastes must be treated to overcome the pollution issues. However, industrial wastes can contain a number of valuable organic components and recovery of these components is imperative economically [1]. The ever-growing ecological considerations and stringent laws are driving in whole world to a system of increased recovery, regenerations and reuse of industrial wastes. Moreover, the principle focus of recycling effort has been post-consumer products. Nevertheless, the recovery, regeneration and Reuses of industrial wastes are gaining momentum, and are going to be an established trend worldwide. Cleaner technologies include pollution prevention, waste minimization and cleaner production [2]. These technologies respond to a high-energy demand in emerging markets, a strong push for energy self-sufficiency and an emerging consensus on climate change by leveraging scientific breakthroughs and abundant private capital. The recovery of dilute acetic acid from wastewater streams is a foremost dilemma in the petrochemical and chemical industries [3].This includes the manufacture of cellulose esters, terphthalic acid, dimethyl terphthalate and reactions involving acetic anhydride. Acetic acid is commonly found in significant concentrations when one can make detailed characterization of industrial wastewater streams. The concentration of these acids can differ significantly. Among these processes, the process for the manufacture of cellulose acetate from acetylation of cellulose by acetic acid, acetic anhydride and sulfuric acid, is typically associated with a 35% w/w aqueous solution of acetic acid as a waste stream. Terphthalic acid process involves the concentration even up to 65% w/w if acetic acid in water [4]. The wood distillation

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contains much lower concentrations (1–8 % w/w) of acetic acid. [5]

The Need for Recovery of Acetic Acids

Advanced treatment of wastewater streams containing substantial amount of acetic acid and formic acid to meet future water quality standards has been recognized as a significant expense to the industry and environment. In addition to treatment requirements, the discharge of acetic acid containing waste water represents the loss of valuable resource [6]. Today acetic acid is one of the most important industrial organic acids and consumed worldwide, about half of it in USA. The global demand of acetic acid is around 6.5 million tonnes per year (Mt/a), of which approximately 1.5 Mt/a is met by recycling; the remainder is manufactured from petrochemical feed stocks or from biological sources. The largest single use of acetic acid is in the production of vinyl acetate monomer that is used for vinyl plastics, adhesives, textile finishes and latex paints and it is closely followed by acetic anhydride and ester production. This acetic anhydride is used for cellulose acetate and pharmaceuticals and plasticizers production. In the food industry acetic acid is used under the food additive code E260 as an acidity regulator. The esters of acetic acid are popular as solvents or artificial flavorings [5].

Techniques for Separation of Acetic Acid from Waste water

Organic acids, widely used in the food, pharmaceutical and chemical industries, are important chemicals. As a result of a thorough waste characterization program and preliminary evaluation of the costs that would be associated with secondary treatment, the work toward developing removal and recovery of waste stream components is started in 1974. The separation of acetic acids from wastewater has been important and essential from the points of view of pollution control and industrially for more than a century [7]. Several physical separation techniques such as liquid extraction, ultra filtration, reverse osmosis, electro-dialysis, direct distillation, liquid surfactant membrane extraction, anion exchange, precipitation and adsorption have been employed to remove acetic acids from aqueous solution. The following section gives a brief review for various methods used for recovery of acetic acid from wastewater streams.

Adsorption

Carboxylic acids may be recovered by adsorption on solid adsorbent. Carboxylic acid is separated by using a polymer adsorbent of pyridine skeletal structure and a cross-linked structure [4]. The polymer adsorbent showed good selectivity and high adsorption capacity for carboxylic acids even in the presence of inorganic salts [8]. The selected elutants were aliphatic alcohol, aliphatic ketones and carboxylic esters. But the costs associated with regeneration of commercial adsorbents make adsorption operation very expensive.

Precipitation

In the calcium precipitation process for the purification of lactic acid by precipitation, the separation and final purification stages account for up to 50% of the production costs and produces a large quantity of solid waste. So, traditional calcium precipitation method is simple and reliable but it is expensive and unfriendly to the environment as it consumes lime and sulphuric acid and also produces a large quantity of calcium sulphate sludge as solid waste [7].

Distillation

Water is the lower boiling component and relative volatility of water to acetic acid is very low. Although acetic acid and water do not form an azeotrope, it is necessary to have a large number of equilibrium stages and a very high reflux ratio to obtain glacial grade acid by simple distillation. As an alternative to fractionation, to reduce energy consumption, azeotropic dehydration can be employed with addition of another liquid. In this technique, the entrainer carries the water overhead in the distillation column with the mixture being phase separated after condensation and entrainer being returned to the column. It is effective only for high concentration of acids [7, 9].

Liquid-Liquid Extraction

For intermediate concentrations between 5 to 50%, liquid-liquid extraction is usually employed, typically followed by azeotropic distillation [7]. Pure solvents such as low

molecular weight esters, ethers, alcohols, ketones and hydrocarbons etc. are unable to give sufficient distribution coefficients for carboxylic acids. The solvent extract stream, containing the acid removed from waste stream and some dissolved water is sent to a distillation column where solvent and water is taken as overhead product [4, 7].

Membrane Processes

A potentially effective treatment of these waste solutions is to use membranes to remove and recover the organic contaminants. Established membrane processes that have been utilized for wastewater treatment include ultra filtration, reverse osmosis, electro-dialysis, and nanofilteration evaporation [3, 10]. The small size of the organics excludes the use of ultrafilteration and microfilteration, and the osmotic pressure limitation from high salt content makes reverse osmosis impractical. Attractive features of this membrane process include the ability to recover the acids in concentrated form for reuse or more economical disposal of waste, low pressure (ambient) operation, simple scale-up using commercial hollow fiber modules, and ease of *in-situ* regeneration of the polymeric liquid [5]. This process is not cost effective; even it has shown treatment feasibility for several types of aqueous waste streams.

In these processes, the problem of membrane fouling, this requires frequent cleaning of the dialyzer [11]. It gives a higher extent of acids separation but with increased power and energy consumption. The drawbacks are being of hindered implementation, mainly complexity of operation and swelling in liquid surfactant membrane and supported liquid membrane often suffers from membrane instability [12].

Reactive Distillation Technology for Recovery of Acetic Acid from Waste Streams

Reactive Distillation Process

With ever-growing environmental concerns, petrochemical and fine chemical industries face a ubiquitous issue in recovering dilute acetic acid from its aqueous solutions. Reactive distillation (RD) holds dominance over conventional physical separation methods such as distillation and extraction. Distillation is associated with the high costs involved in vaporizing the more volatile water that exists in high proportions and possesses a high latent heat of vaporization. Extraction is limited in view of the distribution of the components in the reacting system.

The execution of RD reduces capital and operating costs, and allows for a wider range of operating conditions [3, 5]. RD is receiving increasing attention and holds a huge potential for the recovery of acetic acid. RD is the combination of chemical reaction and distillative product separation in single piece of equipment, offers several dividends over conventional processes in which the reaction and the product separation are done in series, especially for reactions limited by equilibrium constraints [13]. Improved selectivity, increased conversion, better heat control, effective utilization of reaction heat, scope for difficult separations and the avoidance of azeotrope are a few of the advantages that RD offers [14]. As the products in RD are continuously separated from the reaction zone, no limiting chemical equilibrium can be established and thus the reaction velocity is maintained at a high rate, resulting in greater yields. Other benefits of RD can include the minimization of side reactions and the utilization of the heat of reaction for the mass transfer within the same column. Therefore the capital investment and operating costs are significantly lower with RD than for conventional processes. Examples for successful applications of RD have, among others, been reported for esterifications, etherifications, alkylations and isomerizations [13, 14]. Sulzer Chemtech has developed special structured catalytic packings for RD columns; see Figure 1 [13].

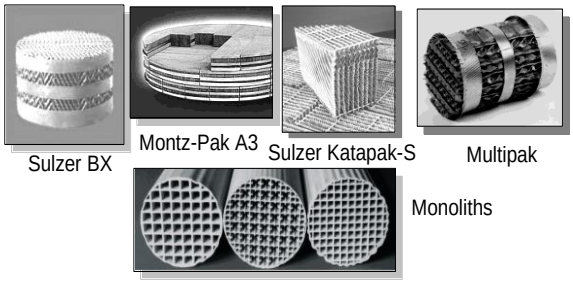

Fig.1: *RD Column Internals.*

RD is a potentially important method of separation for the recovery of dilute acetic acid from its aqueous streams. Moreover, a value added product in the form of Isoamyl acetate is produced during the recovery of acetic acid by esterification with Isoamyl alcohol. An additional column will be required for the complete separation of Isoamyl alcohol and Isoamyl acetate. The energy costs for the additional column would be minimized as the water content of the top organic product is kept to a minimal [15].

Continuous Fatty Acid Esterification Process

The following section describes the basic principles and suggests a possible process set-up for RD process. In this example, the esterification of acetic acid with Isoamyl alcohol is described.

In principle, RD column consists of three different sections; middle one reactive section, bottom one stripping section and top one rectifying section. The reaction and distillation (separation) takes place in middle section; i.e. reactive section. A peristaltic pump was being used to introduce feed to the column. Two peristaltic pumps were used for two feeds. A double-coiled condenser was used and it has been ensured that the condensation is complete**.** The experimental setup of a laboratory scale reactive distillation consists of 3 m tall distillation column of inside diameter 50 mm that operates at atmospheric pressure is used. The reboiler (2 lit) is heated with the help of a heating mantle (2KW).The non-reactive rectifying and stripping sections were packed with wire mesh packing.

The middle reactive zone is packed with structured packing embedded with TULSION^{R} –T- 63 MP *(courtesy Thermax India Ltd.),* ion exchange resins as a catalyst. The stripping section is 1 m tall, reactive section 1 m, and rectification section 1 m tall in height respectively. A proper insulation with external wall heating arrangement is provided to minimize the heat losses to the surrounding. The reaction mixture consisting of acetic acid, Isoamyl alcohol, Isoamyl acetate and water or an equilibrium mixture from the batch reactor is fed continuously to the column through a feed module. An electronically driven metering pump is used to transfer the liquid from the feed tank to the column. The boil-up rate is an important parameter in RD processes. As the reflux ratio is fixed, the boil-up is the only operating parameter that can be efficiently changed to obtain the better RD column performance. Hence it is possible to operate the column over a wide range of boil-up rates to study its effect. A wattmeter is used to measure the wattage power supplied to the heating mantle.

The process scheme for RD process on Laboratory scale is shown in Figure 2.

In the condenser, two immiscible phases are formed, an aqueous phase i.e. almost pure water and an organic phase containing water, amyl alcohol and amyl acetate. The feed is preheated before introducing it to the column. Phase separator with the condenser (Dean and stark arrangement) is used to provide reflux to the column and to continuously withdraw water formed during the reaction. Thermometer wells are provided at different locations in the column to measure these temperatures (Position 1- Position 8).

The conventional separation methods such as distillation and extraction suffer from several drawbacks and are very expensive in terms of time, energy and chemicals. RD is a method of separation that holds huge potential in the recovery of acetic acid from aqueous streams. Through the application of RD via the reaction of acetic acid with an aliphatic alcohol (e.g. Isoamyl alcohol), a useful ester in the form of e.g. Isoamyl acetate was produced [16]. The esters of acetic acid, namely, Isoamyl acetate, n-butyl acetate, n-hexyl acetate, have a wide range of industrial applications [3, 13].

Advantages of the Reactive Distillation Process

The combination of reaction and separation by distillation in one unit allows a continuous production, with reduced processing time. This leads to constant high product quality and at the same time simpler maintenance and process control, which is especially valuable for larger production capacities. Well-defined and narrow residence time at gentle conditions throughout the whole plant minimizes degradation of the fatty acids and fatty acid esters [13].

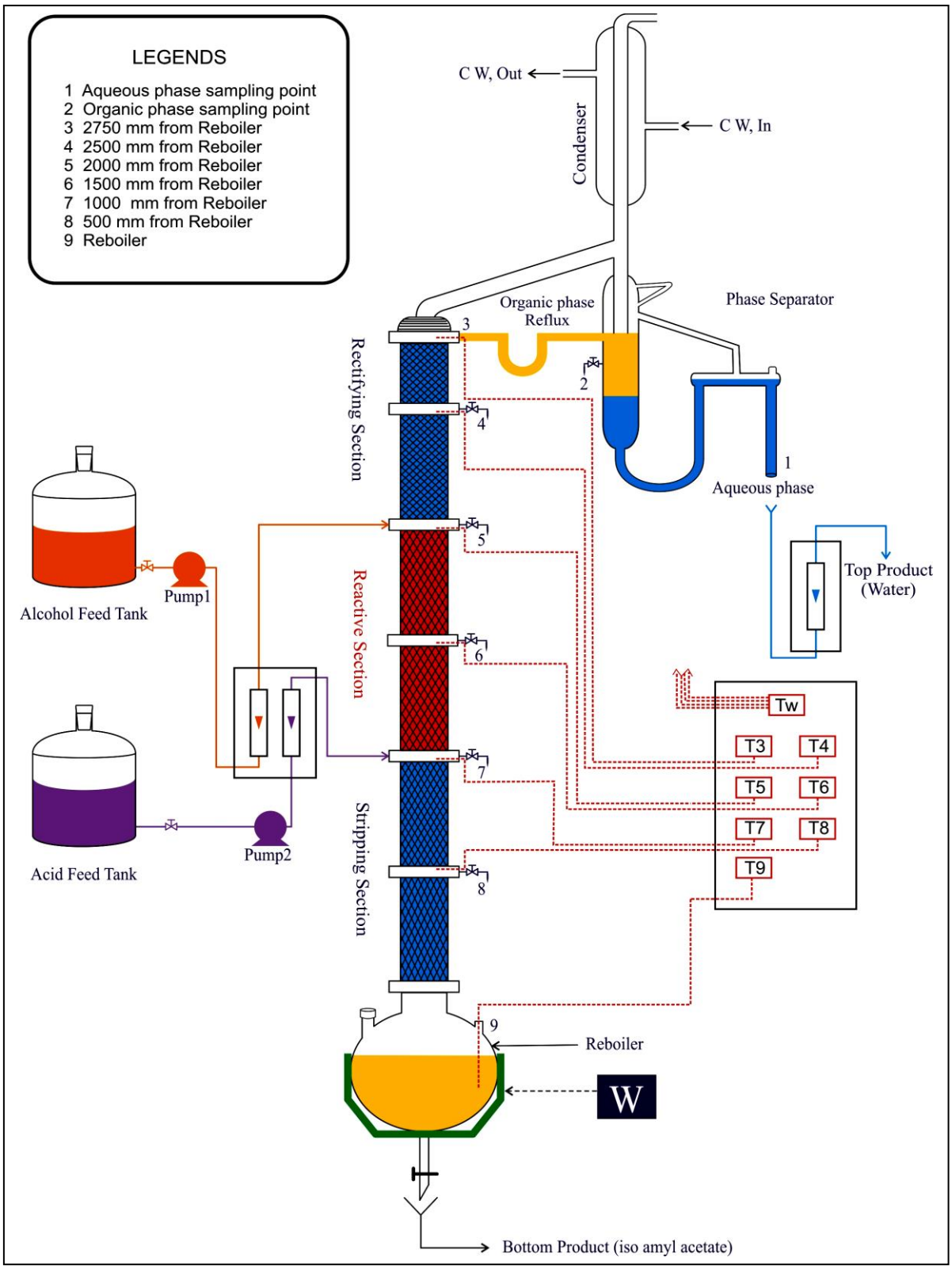

Fig.2: *Continuous RD Process on Laboratory Scale [16].*

No neutralization, separation or recycling of catalyst is necessary. There is no necessity of emptying and cleaning the equipment, reducing the waste streams to the absolute minimum. The energy consumption of the RD process is only half of the conventional batch one. Also the size of the plant could be drastically reduced [14].

CONCLUSION

It is important to have an efficient and sustainable technology for the separation/recovery of acetic acids from the wastewater stream in view of pollution control and recovery of useful components. Several conventional separation techniques discussed in this paper have been employed to remove carboxylic acids from aqueous solution. Some of these techniques are not environment friendly and others are not cost effective. RD process allows the operation to run continuously, economically leading to a consistently high product quality. RD has been proposed as a promising green technology for separation/recovery of acetic acids from wastewater.

Moreover, a value added product in the form of Isoamyl acetate is produced during recovery of acetic acid by esterification with Isoamyl alcohol. Finally we conclude that RD process is cleaner technology and front-runner in recovery/separation and production of chemicals on industrial scale.

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