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## ETHYL ACETATE: PROPERTIES, PRODUCTION PROCESSES AND APPLICATIONS - A REVIEW

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### ABSTRACT

Ethyl acetate is an important organic solvent widely used in the chemical industry. This review article attempts to provide an updated compilation of research studies reported on ethyl acetate production by using various methods/techniques/ processes and its parameters, which affect their productivity. The perspectives potential applications of ethyl acetate are also presented.

**Keywords:** Ethyl acetate, Esterification, Ethanol, Acetic acid.

### 1. INTRODUCTION

Ethyl acetate is the organic compound (an oxygenated solvent) with the formula  $\text{CH}_3\text{COOC}_2\text{H}_5$  and having a molecular weight of 88.10. This colourless liquid has a characteristic, pungent smell like certain glues or nail polish removers, in which it is used. Ethyl acetate is the 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. It is a weak hydrogen bond acceptor, and is not a donor due to the lack of an acidic proton. Ethyl acetate can dissolve up to 3% water and has a solubility of 8% in water at room temperature. It is unstable in the presence of strong aqueous bases and acids. It is soluble in most organic solvents, such as alcohol, acetone, ether and chloroform. It has been also used as solvent in many chemical processes for replacing aromatic

compounds which generated serious damage to the environment and human beings. With the increasing number of research groups worldwide thereby regularly increasing number of publications, covering many areas such as properties, production process and applications of ethyl acetate, we thought it worth to present comprehensive review article which covers the important work of all the research group across the world.

### 1. PRODUCTION OF ETHYL ACETATE

Industrial production of ethyl acetate is mainly classified into three processes, The first one is a classical Fischer esterification process<sup>1</sup> of ethanol with acetic acid in presence of acid catalyst. This process needs acid catalyst<sup>2</sup> such as sulphuric acid, hydrochloride acid, p-toluene sulfonic acid etc. This mixture converts to the ester in about 65% yield at room temperature.

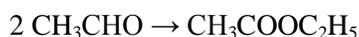


The reaction can be accelerated by acid catalysis and the equilibrium can be shifted to the right by removal of water. Mechanism of esterification reaction has been discussed by P. Sykes.<sup>3</sup>

The system is strongly non-ideal due to the presence of ethanol, acetic acid and water. The separation of pure components is very difficult due to the existence of five normal azeotropes, namely, ethanol–water; water–acetic acid, ethyl acetate–ethanol, ethyl acetate–water, and ethanol–ethyl acetate–water. I. Sujuki et al.<sup>4</sup> also determined the phase equilibrium for the system taking the reaction into account (they fitted 16 coefficients in modified Margules equations, for calculating the VLE-model of this mixture).

The normal boiling point of ethyl acetate, ethanol, water and acetic acid is 77.1, 78.4, 100 and 118.1 in °C respectively. The order of volatility is ethyl acetate, ethanol, water and acetic acid. Ethanol and water do not differ greatly in volatility, making it difficult to move ethanol up the column. The minimum-boiling binary homogeneous azeotropes are formed by ethanol–water at 78.2°C With 10.57mol% water and by ethyl acetate–ethanol at 71.8°C with 46 mol% ethanol. A minimum-boiling binary heterogeneous azeotrope<sup>5</sup> is formed by ethyl acetate–water at 70.4°C with 24mol% water, and a ternary, minimum-boiling azeotrope is formed by ethanol–ethyl acetate–water at 70.3°C with 12.4mol% ethanol and 60.1 mol% ethyl acetate.

The second one is Tishchenko Reaction<sup>6</sup> of acetaldehyde using aluminium triethoxide as a catalyst. In Germany and Japan, most ethyl acetate is produced via the Tishchenko process.



This method has been proposed by two different routes; (i) dehydrogenative process, which uses copper or palladium based catalyst and (ii) the oxidative one, which employs, PdO supported catalysts.

The former one produces, besides ethyl acetate, hydrogen and also, other by-products which make the acetate purification expensive. In the case of oxidation process, the purification is straightforward and the catalysts are very stable.

The third one, which has been recently commercialized, is addition of acetic acid to ethylene using clay and heteropoly acid<sup>7</sup> as a catalyst.

$\text{CH}_2=\text{CH}_2 + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5$   
The processes, however, have some disadvantages; both the conventional esterification and addition of acetic acid to ethylene need stock tanks and apparatus for several feed stocks. Moreover, they use acetic acid that causes apparatus corrosion. Although Teshchenko Reaction uses only one feed and it is a non-corrosive material, it is difficult to handle acetaldehyde because is not available outside of petrochemical industrial area. In such circumstances, an improved process of ethyl acetate production is strongly desired.

Several new technologies have been commercialised. BP's new *Avada* process<sup>8</sup> employed in a new plant at Hull, UK, uses ethylene and acetic acid with solid acid catalyst. Davy Process Technology (formerly Kvaerner) has licensed its ethanol-based process to Sasol; in this process ethanol is dehydrogenated to acetaldehyde, which further reacts to form ethyl acetate. Chinese National Petroleum has developed a one-step ethanol process where ethanol is partially oxidised to acetic acid and then esterified with excess ethanol to give ethyl acetate.

In esterification reactions the function of the catalysts is to donate protons for the autoprotolysis of the carboxylic acid. For this purpose, either inorganic acids, such as  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HI}$  or  $\text{Cl-SO}_3\text{OH}$  or organic acids such as p-toluene sulfonic acid have been used.<sup>9</sup> In spite of their lower cost, the interest for homogeneous catalysts in chemical industry has decreased because of their miscibility with reaction medium, which gives rise to problems such their separation or the corrosion of devices in contact with the acid. As a result there is an increasing attention for various process/techniques to obtain ethyl acetate.

## 2. DEVELOPMENTS IN THE PRODUCTION PROCESS

Generally, two types of catalysts have been used for the production of ethyl acetate,

- a) Homogeneous acid catalysts (eg. mineral acids like  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , alkyl sulfonic acid, aromatic sulfonic acid, methane sulfonic acid, benzene sulfonic acid, p-toluene sulfonic acid).
- b) Heterogeneous acid catalysts (eg. strong acid ion-exchange, Rohm Q-16, Hoss A-16).

Effect of different catalysts concentration, different operative temperature is applied to determine the amount of heat release and the possibility of the reaction in creating runaway reaction.

Esterification of ethanol with acetic acid on silica-alumina, alumina-boria, sodium-poisoned silica-alumina, and alumina has been investigated by the pulse technique and compared with ethanol dehydration.<sup>10</sup> The catalysts could be classified into two groups according to their catalytic behaviour; silica-alumina, alumina-boria, and sodium-poisoned silica-alumina belong to one group and alumina to another. Concerning the

silica-alumina group, it was recognized from a LFER (Linear Free Energy Relationship) approach and from poisoning with organic bases that the esterification proceeded on even weaker acid sites than other acid-catalyzed reactions such as dealkylation and dehydration. From simple kinetics based on a Langmuir-Hinshelwood mechanism, distinct differences were found between the two groups in that acetic acid adsorbed more tightly than ethanol on alumina and the reverse on the silica-alumina group, and that the activity ratios of esterification to dehydration were much larger on the silica-alumina group than on alumina. These characteristic behaviours of ethanol and acetic acid on silica-alumina and alumina were satisfactorily interpreted by the assumption that the active sites for esterification were protonic acid sites on the silica-alumina group, but Lewis acid sites on alumina. On the basis of these findings, an esterification mechanism was also proposed by authors.<sup>10</sup>

Y. Iwasawa et al.<sup>11</sup> prepared niobium catalysts for the formation of ethyl acetate from ethanol and acetic acid. The niobium catalysts involving single, pair, and monolayer Nb-sites have been prepared by the reaction between surface OH groups of  $\text{SiO}_2$  and  $\text{Nb}(\eta^3\text{-C}_3\text{H}_5)_4$ ,  $[\text{Nb}(\eta^5\text{-C}_5\text{H}_5)\text{H}-\mu(\eta^5, \eta^1\text{-C}_5\text{H}_4)]_2$ , and  $\text{Nb}(\text{OC}_2\text{H}_5)_5$ , respectively. The obtained Nb sites were found to be attached to the surface through oxygen atoms, showing Nb--Si bondings besides Nb---O bonds as proved by extended X-ray absorption fine structure (EXAFS). The Nb monomers on  $\text{SiO}_2$  were active for ethanol dehydrogenation which proceeds on Nb=O bonds with basic character, while the Nb dimers showed dehydration activity to form ethene and diethyl ether, based on acidic character. The Nb monolayers on

SiO<sub>2</sub> produced ethyl acetate from ethanol. The monolayer catalyst also showed a high activity for the formation of ethyl acetate from ethanol and acetic acid. The Nb atoms were suggested to be nearly uniformly supported in a monolayer-growth mode, where the Nb sites showed the Lewis acidic properties available for the catalytic esterification.

The synthesis of ethyl, n-butyl, isopentyl and benzyl acetates, ethyl and n-butyl benzoates and dioctylphthalates was achieved by using a H-ZSM-5 and two HY zeolites as catalysts under conditions similar to the classical case with sulfuric acid catalyst.<sup>12</sup> A high yield of acetates was obtained with essentially 100% selectivity.

M. Morbidelli et al.<sup>13</sup> mentioned that the characteristics of ion-exchange resins provide the basis for many processes of practical interest involving both sorption separations and catalytic reactions. The optimal design and operation of these processes require a proper understanding of the equilibrium behaviour of multicomponent liquid mixtures in contact with cross-linked polymeric resins, in terms of both the amount and composition of the sorbed mixture. For this, a model which describes the equilibrium between a polymer phase, described through the extended Flory-Huggins theory, and a liquid phase, which does not contain the polymer, has been developed. This has then been coupled with a kinetic model describing the catalytic reaction inside the resin particles. The model has been validated through an appropriate experimental analysis involving both equilibrium partitioning and reactive experiments, for the case of a highly cross-linked sulfonated resin in the presence of various mixtures of the components involved in the esterification of ethanol with

acetic acid. Authors also mentioned that the ability of the resin not only to catalyze the esterification reaction but also to shift the corresponding equilibrium conversion, due to its swelling capability. This approach is believed to apply to a wide class of reactions catalyzed by polymeric resins, and it is suitable for the optimal design of the corresponding process.

A report on selective oxidation of water-containing ethanol in the presence of excess ethanol provides a one-step preparation of ethyl acetate have been reported by J-R Chang et al.<sup>14</sup> Acetic acid is formed from the oxidation of ethanol catalyzed by a supported Pd catalyst and is further catalytically esterifies to ethyl acetate by the protons dissociated from acetic acid. The difference of the catalytic performance between hydrophilic and hydrophobic Pd catalysts was investigated by a continuous fixed-bed reactor run at 95°C, 35.4 atm, and an air/ethanol molar ratio of 2.37. They have studied that, after the induction period, the conversion of ethanol catalyzed by a styrene-divinylbenzene copolymer (SDB)-supported Pd catalyst is more than 20 times that catalyzed by a  $\gamma$ -alumina-supported Pd catalyst at a weight hourly space velocity (WHSV) of 2.4 h<sup>-1</sup>. However, it may be caused by weak metal-support interactions and the formation of palladium(II) acetate during the reaction.

A one step synthesis of ethyl acetate from a feed mixture of ethene, oxygen and water using a supported Pd and silicotungstic acid catalyst was demonstrated.<sup>15</sup> At about 180°C and 25% ethane conversion, ethyl acetate could be produced with up to 46% selectivity together with 34% acetic acid and ethanol that could be recycled. The catalyst was believed to be bifunctional with Pd providing the oxidation function and the

silicotungstic acid providing the acidic function.

The esterification of acetic acid with ethanol catalysed by an acidic ion-exchange resin (Amberlyst-15) was carried out in a batch reactor at temperatures between 50°C and 80°C at various starting compositions ranging from stoichiometric regime to the dilute regions have been reported by S. I Kirbaslar et al.<sup>16</sup> The resultant kinetic model fitted the experimental data well. The activation energy was found to be 104129 kJ.kmol<sup>-1</sup> for the formation of ethyl acetate. The ethyl acetate production was also carried out in a packed bed reactive distillation column operated in batch and continuous modes. The effects of the variables such as the reflux ratio, vapour rate and feed flow rate on ethyl acetate production were studied experimentally. A packed bed reactive distillation column operated in continuous mode gave the highest ethyl acetate composition, far surpassing the chemical equilibrium at operating conditions.

Sorption of acetic acid from ethyl acetate and ethanol (95%) has been investigated using polymeric ion-exchange resins<sup>17</sup> with a view for being possibly applied to the removal of acetic acid impurities from organic solvents. The resins have tertiary or quaternary amino functional groups on a styrene-divinyl benzene copolymer matrix. The equilibrium adsorption studies show very selective adsorption with a high loading capacity for acetic acid. The uptake of the acid from the organic solutions is by sorption reinforced by specific interaction with the functional groups on the polymer matrix. The specific interaction takes place by a hydrogen bonded complex formation between the acidic proton and the lone pair of electrons on the amino group. An

efficient application of ion-exchange resins is indicated in purification by ethyl acetate by selective sorption of acetic acid.

Pervaporation-aided esterification of acetic acid with ethanol was investigated at 70°C using zeolite T membranes by K-ichi Okamoto.<sup>18</sup> Almost complete conversion was reached within 8 h when initial molar ratios of alcohol to acetic acid were 1.5 and 2. The reaction time courses were well described by a simple model based on the assumptions that the reaction obeyed second-order kinetics and the permeation flux of each component was proportional to its concentration. They have also studied the influence of operating parameters on variation in conversion with reaction time was investigated by means of the simulation using the model.

Esterification reactions are conventionally carried out using homogeneous acids, such as sulphuric acid.<sup>19</sup> Especially in view of catalyst separation, the use of heterogeneous catalysts is now heavily pursued. A. Blik et al.<sup>20</sup> have assessed the potential of MCM-41 as a solid esterification catalyst and tested this in esterification of acetic acid and ethanol as a model reaction. Whereas the mechanism for the homogeneously catalysed esterification is long known, this does not hold for the esterification over heterogeneous catalysts. Using transient and steady state experiments, temperature-programmed desorption (TPD), and isotopic labelling experiments, the esterification mechanism over MCM-41 (Si/Al=16) is studied. Gas-phase esterification of acetic acid with ethanol over MCM-41 (Si/Al=16) is shown to proceed via a Langmuir-Hinshelwood-type mechanism, involving a protonated acetic acid intermediate.

Direct synthesis of ethyl acetate from ethanol over a Cu-Zn-Zr-Al-O catalyst was

investigated under pressured conditions between 200°C and 270°C by I. Kanichiro et al.<sup>21</sup> Both the selectivity to ethyl acetate and the space-time yield of ethyl acetate increase with increasing reaction pressure, whereas ethanol conversion decreases. The highest space-time yield of ethyl acetate is attained at a reaction pressure of about 0.8 MPa with maximum selectivity of 93 wt%. During the process, ethanol is first dehydrogenated to acetaldehyde and is then coupled with another ethanol molecule to form hemiacetal, which is further dehydrogenated to ethyl acetate. The concentration of by-products such as 1-butanol and butanone, which form after the aldol addition of acetaldehyde, decreases with increasing reaction pressure. Since the equilibrium of the dehydrogenation of ethanol to acetaldehyde shifts to an ethanol-rich composition at high pressure, the decrease in the partial pressure of acetaldehyde explains the suppression of the by-products formed through acetaldehyde.

Esterification reactions are typically limited by thermodynamic equilibrium, and face challenges with product purification. Commercially, it was carried out using either large excess of one of the reactants, or by removing through reactive distillation one of the products. As a result reactive distillation, which favourably shifts equilibrium through the removal of one of products, is becoming more common in plant-scale production. It is, however, an energy-demanding operation and is not recommended when dealing with temperature-sensitive chemicals or biocatalysts. The aforementioned difficulties have motivated efforts for the development of other coupled reactive/separation processes. Pervaporation membrane reactors (PVMR), in particular, are distillation. T. T.

Tsotsissa et al.<sup>22</sup> have developed to describe PVMR behaviour. The simulation results of the model have been validated with experimentally observed pervaporation membrane reactor conversions. The model is used to describe a number of alternative PVMR configurations and analyze the reactors that effect and optimize their performance.

The reactive distillation system for the production of ethyl acetate via esterification of acetic acid with ethanol using sulphuric acid as homogeneous catalyst have been reported by Y. T. Tang et al.<sup>23</sup> A suitable NRTL (non-random two-liquid) model parameter set for calculating of liquid activity coefficients has been established with excellent prediction of the compositions and temperatures for the four azeotropes in this system. In the VLE (vapour liquid equilibrium) calculations, vapor association of acetic acid due to dimerization has also been considered. A reactive distillation column with an overhead decanter can be designed to achieve over 93 wt% of ethyl acetate composition at organic phase top product stream while the bottom product stream is designed to be rich in acetic acid so that it can be recycled and mixed with fresh acid make-up stream to serve as acid feed to the reactive distillation column. Since the purity of the optimum top organic product is still not good enough for the ethyl acetate product specification in industry, an additional column is designed to purify the ethyl acetate product of the reactive distillation column to over 99.5 wt%. The top draw of the second column will be recycled back to the decanter. In summary, they have developed, the overall optimum design of this ethyl acetate reactive distillation system includes two columns

(including the reactive distillation column and the second column), one decanter, and two recycle streams. The optimum operating condition of the overall system will also be studied by authors to minimize the total operating cost of the overall system while meeting product specifications.

Most of the commercial processes for ethyl acetate productions are *via* liquid-phase esterification. Owing to the thermodynamic limitations, the overall yields of ethyl acetate are confined to 67% with equimolar reactant feeds of acetic acid and ethanol. An efficient two-phase reaction of ethyl acetate production in modified ZSM-5 zeolites has been reported by K-C Wu and Y-W Chen.<sup>24</sup> The reactions were conducted at 90–127 °C, with molar ratio of ethanol/acetic acid=1.5 and with LHSV=1 h<sup>-1</sup>. One of the critical parameters in this novel ethyl acetate synthesis process is the reaction (esterification) temperature. It was kept between the liquid- and gas-phase operation regimes at which some parts of the reacting composition were vaporized. The major consideration is based on the equilibrium constants in the gas-phase reaction, which are higher than those in the liquid phase. The initial reaction stage in the liquid phase has the advantage of smaller reactor size and more efficient contacting with the catalysts. As the equilibrium had been achieved in the final gas phase, a higher conversion of ethanol was obtained due to the equilibrium constant constraints. Consequently, both the equilibrium conversion constraint for the liquid-phase regime and the larger reactor volume requirement for the gas-phase reaction have been overcome. They have studied that the one-pass ethanol conversion was successfully improved from 67 to 85 mol%. In addition, the solid acid catalysts used in this novel process have low

impact to the environment and cause no corrosion to the reactor wall. These catalysts had continued performance for 2200 h. Evaluation also shows that half of the process water and one-third of the consumption of purification steam can be saved.

Vapor-liquid equilibrium for the quaternary reactive system, ethyl acetate + ethanol + water + acetic acid and constituent binary system ethyl acetate + ethanol, ethyl acetate + acetic acid and water + acetic acid has been determined at 101.3 kPa by J. Tojo et al.<sup>25</sup> UNIQUAC equation was used to correlate the experimental phase equilibrium data of the quaternary system. Experimental binary data were correlated using Wilson, NRTL and UNIQUAC equations.

The esterification of acetic acid by ethanol in presence of modified catalysis-phosphomolybdic acid (PMA) supported on silica gel (1–30 wt %) have been reported.<sup>26</sup> The catalysts were characterized by thermogravimetry (TG), differential thermal analysis (DTA), X-ray diffraction, FT-IR spectroscopy and N<sub>2</sub> adsorption measurements. The surface acidity and basicity of the catalysts were determined by adsorption of pyridine and the dehydration–dehydrogenation of 2-propanol. The gas-phase esterification of acetic acid by ethanol was carried out in a conventional flow bed reactor. The results clearly revealed that among the PMA loading, the use of 10 wt% catalysts showed maximum yield of ethyl acetate. This catalyst also improved on addition of Na or K-hydroxide. These results were correlated with the structure and the acid–base properties of the prepared catalysts.

SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZnO, SnO<sub>2</sub> and WO<sub>3</sub>-ZrO<sub>2</sub> (29%, w/w WO<sub>3</sub>) supported Pd catalysts (1%, w/w Pd) for the direct transformation

of ethanol to ethyl acetate under medium pressure conditions (1 MPa pressure) have been studied by P. R. de la Piscina et al.<sup>27</sup>

The synthesis of ethyl acetate was investigated using a heterogeneous catalyst-Commercial acid resin, Amberlyst 15 (Rohm and Haas) and a pervaporation unit - Commercial hydrophilic composite membrane, PERVAP 1000 and 1001 Le Carbone Lorraine<sup>28</sup>. Shifting the reaction equilibrium by selective water removal increased the ethyl acetate productivity. The effects of catalyst mass, reaction temperature, and initial reactants ratio were studied. The kinetic parameters, such as activation energy and apparent reaction order, were determined. The water production and removal rates obtained in reaction and pervaporation experiments, respectively, were used in a computational code to simulate the behaviour of the coupled system. The highest conversion was observed when an initial ethanol/acetic acid molar ratio of 9:1 was used. At this condition, the water production was reduced turning the water removal process more selective, increasing the acetic acid conversion from 51.0% to 63.9%.

Sulfonated polystyrene grafted silica gel particles<sup>29</sup> were synthesized for use as an acid catalyst in the liquid phase esterification of acetic acid with ethanol at 40-80°C. The synthesis of the grafted silica gel particles consists of three steps: polymerization, grafting, and sulfonation. The synthesized catalyst is non-cross-linked, non-swelling, and mechanically as well as chemically stable. It contains 29% covalently-bound sulfonated polystyrene chains that give an acid capacity of 0.99 mmol g<sup>-1</sup>. The kinetics of the grafted silica gel is as rapid as that of a commercial ion-exchange resin. Since the acid capacity

of the grafted silica gel is only 25% of the ion-exchange resin, the catalytic activity of acid groups in the grafted silica gel is higher than in the resin.

On the other hand, kinetic studies on the liquid phase esterification of C<sub>3</sub> and C<sub>4</sub> alcohols on acetic acid were carried out over zeolites<sup>30</sup> H $\beta$ , HY and HZSM5. Zeolite H $\beta$  was found to be the most active for the esterification reaction of ethanol and acetic acid. The acidity of zeolite determines the extent of the esterification reaction. The esterification reaction was found to follow the Eley-Rideal pathway. Acetic acid is activated by adsorption on the zeolite acid site, which then reacts with the alcohol in the bulk to form the corresponding acetate.

The reaction kinetics of the esterification of acetic acid with ethanol, catalyzed both homogeneously by the acetic acid, and heterogeneously by Amberlyst 15, has been investigated by A. Dominguez et al.<sup>31</sup> The reactions were carried out at several temperatures between 30-80°C and at various starting reactant compositions. Homogeneous and heterogeneous reactions have been described using the models proposed by T. Popken et al.<sup>32</sup> These models use activities instead of mole fractions. Activity coefficient has been calculated using ASOG<sup>33</sup> and UNIFAC<sup>34</sup> methods. A packed bed reactive distillation column filled with Amberlyst 15 has been employed to obtain ethyl acetate. The influence of feed compositions and reflux ratio has also been analysed.

An additional example, the aerobic oxidation of aqueous ethanol to produce acetic acid and ethyl acetate was studied using heterogeneous gold catalysts.<sup>35</sup> Comparing the performance of Au/MgAl<sub>2</sub>O<sub>4</sub> and Au/TiO<sub>2</sub> showed that these two catalysts exhibited similar performance in the

reaction. By proper selection of the reaction conditions, yields of 90–95% of acetic acid could be achieved at moderate temperatures and pressures. Based on author findings, a reaction pathway for the catalytic oxidation of ethanol *via* acetaldehyde to acetic acid is proposed, and the rate-determining step (RDS) in the mechanism is found to be the (possibly oxygen-assisted) dehydrogenation of ethanol to produce acetaldehyde. It also is concluded that most of the CO<sub>2</sub> formed as a by-product in the reaction results from the absorbed intermediate in the dehydrogenation of ethanol to produce acetaldehyde. By varying the amount of water in the reaction mixture, the possibilities for producing ethyl acetate by the aerobic oxidation of ethanol is also studied.

On the other hand, inert membrane reactors have been a subject of interest during the last decade, the two main applications consist of distributing a reactant to increase selectivity and remove a product to enhance conversion in equilibrium-limited reactions. Two different zeolite membranes, mordenite and zeolite A have been tested in the esterification of acetic acid with ethanol in a continuous membrane reactor packed with catalyst Amberlyst™ 15 by R. Mallada et al.<sup>36</sup> Both membranes are capable of shifting the equilibrium in less than 1 day of experiment. Mordenite membranes showed a great resistance to acidic reaction medium, with conversions of about 90% maintained for 5 days of experiment, with very high separation factors water/ethanol and water/acetic acid.

Mixed matrix membranes of sodium alginate (NaAlg) were prepared<sup>37</sup> by solution casting by incorporating 2.5, 5, 7.5 and 10 wt. % of zeolite beta particles for the production of ethyl acetate. The membranes

thus prepared were crosslinked with glutaraldehyde and tested for the pervaporation (PV) dehydration of ethanol and acetic acid at 30–60 °C. The aluminum-rich zeolite beta, with its hydrophilic nature as well as molecular sieving effect and its favorable interaction with hydrophilic NaAlg, was responsible to enhance the PV dehydration of acetic acid and ethanol in terms of separation factor, flux, pervaporation separation index (PSI) and enrichment factor ( $\beta$ ). Thermodynamic model for sorption process was investigated typically for water + ethanol mixtures based on Flory–Huggins theory to explain the PV performance. Based on these results, permeance and driving force mechanisms were also elucidated. Extraction or dissolution of zeolite beta from mixed matrix membranes is confirmed by equilibrium sorption. Arrhenius parameters for the process of permeation were calculated using these data at different temperatures to investigate their effects on the nature of the mixed matrix membrane. The plots of  $\ln J_p$  vs.  $1/T$  were constructed and found to follow the linear trends in the studied range of 30–60 °C for both the feed mixtures, indicating that flux followed the Arrhenius trend. PV experiments were also carried out for 5 and 10 wt. % incorporated NaAlg mixed matrix membranes at 70 °C to verify the suitability of the membranes at the esterification temperature. PV-aided catalytic esterification of acetic acid with ethanol was studied at 70 °C, which led to a considerable increase in ethyl acetate conversion with a reduction in reaction time as compared to the blank reaction due to continuous removal of water permeating through the barrier membrane.

Supported niobium pentoxide catalysts<sup>38</sup> are active for a variety of acid and redox

catalyzed reactions such as dehydration, hydrogenation and esterification. In this regards, niobium pentoxide has been supported on silica–alumina using two methods: grafting in  $\text{CH}_2\text{Cl}_2$  or ethanol solution with  $\text{NbCl}_5$  precursor, and impregnating in aqueous solution with ammonium niobium oxalate. These catalysts were used to characterize by various methods such as XRD, TG/DTG/DTA, FTIR, DRIFTS, FT-Raman, and calorimetric titration with pyridine. Calcination of the materials at  $800\text{ }^\circ\text{C}$  produced crystalline  $\text{Nb}_2\text{O}_5$  (T-phase) for the samples prepared by grafting, while a mixture of T- and H-phases are formed by aqueous impregnation, indicating the higher stability of the former materials. On the other hand, partial neutralization of hydroxyl groups occurred on the support surface by grafting process, and the neutralization reaction is practically complete at 25 wt. % of  $\text{Nb}_2\text{O}_5$  by impregnation. The catalysts with about 10 wt. % of  $\text{Nb}_2\text{O}_5$  prepared by aqueous impregnation reached the monolayer, while by grafting it predominates bulk  $\text{Nb}_2\text{O}_5$ , as demonstrated by FT-Raman. These catalysts also showed the highest acidity, when calcined at  $300\text{ }^\circ\text{C}$ . Based on these results, liquid phase esterification reactions of acetic acid were carried out with different alcohols (ethanol, *n*-butanol, and *iso*-pentanol). The yields were about the same, independent of the preparation method for 10 wt. %  $\text{Nb}_2\text{O}_5$  catalysts. The conversions using molar ratio 2:1 (acid: alcohol) after 8 h showed good results (83, 87, and 91%, respectively) and 100% selectivity for all esters.

The production of high-purity ethyl acetate using reactive distillation (RD) is studied experimentally in a pilot-scale plant. The objectives are twofold: (1) to realize the type-II RD process<sup>39</sup> for ethyl acetate

production with a pilot plant, a complex two-column configuration with liquid phase split, (2) to study the initial charges to the column holdups and a start-up procedure for continuous production.<sup>39</sup>

H-P Huang et al.<sup>40</sup> prepared a pilot-scale plant consists of one RD column (10 reactive trays plus structured packing for separation) and a downstream stripper with a decanter in between the two columns are equipped with temperature, flow, and level measurements and a Delta-V process control computer. The industrial grade alcohol (89 mol% ethanol, 11 mol%  $\text{H}_2\text{O}$ ) and acid (96.75 mol% acetic acid and 3.25 mol%  $\text{H}_2\text{O}$ ) are used as reactants. A product that contains more than 99 mol% ethyl acetate and less than 100 ppm acetic acid is required as specifications. The results from six experimental runs show that, with proper initial charges in the inventory holdups and a systematic start-up procedure, high-purity acetate can be produced in a straightforward manner.

Reduction of energy demand is a challenge that must be faced in coming years and process integration in chemical industry is pointed out as a feasible alternative to achieve more efficient processes. Pervaporation membrane reactors are the systems in which the separation and reaction are carried out simultaneously in order to increase conversions by removing one or more of the products formed during equilibrium reactions.<sup>41</sup>

C. P. Borges et al.<sup>42</sup> using acetic acid and ethanol as a model system, pervaporation-assisted heterogeneous catalytic esterification was investigated to increase ester conversion in mild operational conditions. The pervaporation-assisted esterifications were carried out using Amberlyst 15 and 35 (Rohm & Haas) as

catalyst and hydrophilic Pervap 1000 membrane (Sulzer) in a bench scale pervaporation apparatus. A catalytic membrane was also developed by coating the Pervap membrane with a thin superficial layer of tiny catalyst particles in poly (vinyl alcohol) solution. Reaction and separation were conducted in two separated steps and in a single one, by means of a catalytic membrane. For the former, the membrane-assisted reactor, it was observed that the ratio of membrane area to reaction volume is an important parameter to get equilibrium displacement. For the catalytic membrane there was an increase up to 60% in ethyl acetate conversion at 60 °C. These results indicate the potentiality of the coupled process, since catalyst concentration can be easily increased, leading to higher ester production rates.

A. Hasanoglu et al.<sup>43</sup> have been studied the esterification reaction of acetic acid and ethanol to produce ethyl acetate and water was investigated using a batch pervaporation Polydimethylsiloxane (PDMS) membrane reactor. The experiments were carried out in the temperature range of 50-70°C. The ratios of ethanol concentration to acetic acid concentration were chosen as 1 and 1.5. Amberlyst 15 and sulfuric acid were used as the catalysts. In this way, conversions were increased by continuous removal of ethyl acetate from the reaction media. Conversions are found to increase with an increase in both molar ratios of reactants and temperature. Temperature has a strong influence on the performance of the pervaporation membrane reactor because it acts on both the esterification kinetics and pervaporation.

Solid super acid catalysts including  $\text{SO}_4^{2-}/\text{ZrO}_2$  (SZ), rare earth (RE) oxide-promoted SZ and RE oxides together with

alumina-promoted SZ performances in the esterification reaction of ethanol and acetic acid were investigated by X. L. Zhou et al.<sup>44</sup> The textural property, crystalline phase and surface acidity of the catalysts were characterized by using nitrogen adsorption-desorption isotherms, XRD and FT-IR spectroscopy of pyridine adsorption techniques, respectively. Effects of the reaction time and catalyst reuse cycle as well as catalyst regeneration on the catalytic behaviours were also studied. Experimental results showed that  $\text{Yb}_2\text{O}_3\text{-Al}_2\text{O}_3$  promoted SZ (designated as SZAY) catalyst exhibited an optimal esterification performance; the Lewis acid sites with moderate and super strong strength could mainly be responsible for the esterification reaction; and doping both  $\text{Yb}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  on SZ not only boosted the esterification activity but also alleviated catalyst deactivation resulted from the surface sulfur loss by solvation.

On the other hand, the separation of ethyl acetate and ethanol is important but difficult due to their close boiling points and formation of an azeotropic mixture. The separation of the azeotropic mixture of ethyl acetate and ethanol using the hydrophilic ionic liquids (ILs) 1-alkyl-3-methylimidazolium chloride (alkyl = butyl, hexyl, and octyl) ( $[\text{C}_n\text{mim}]\text{Cl}$ ,  $n = 4, 6, 8$ ) and 1-allyl-3-methylimidazolium chloride and bromide ( $[\text{Amim}]\text{Cl}$  and  $[\text{Amim}]\text{Br}$ ) has been investigated by Ji Chen et al.<sup>45</sup> Triangle phase diagrams of five ILs with ethyl acetate and ethanol were constructed, and the biphasic regions were found as follows:  $[\text{Amim}]\text{Cl} > [\text{Amim}]\text{Br} > [\text{C}_4\text{mim}]\text{Cl} > [\text{C}_6\text{mim}]\text{Cl} > [\text{C}_8\text{mim}]\text{Cl}$ . The results showed that the hydrophilic ILs  $[\text{C}_n\text{mim}]\text{Cl}$  ( $n = 4, 6, 8$ ),  $[\text{Amim}]\text{Br}$ , and  $[\text{Amim}]\text{Cl}$  could remove ethanol effectively from the azeotropic mixture of ethyl acetate and

ethanol. Moreover, it was found that [Amim]Cl had the highest extraction efficiency, and the purity of ethyl acetate could reach 99.27 wt. % after extraction twice. These hydrophilic ILs are easily synthesized and purified, are economically feasible, and caused no erosion to the equipment, which usually happened for ILs containing F. ILs could be recycled by simple distillation. The separating process can reduce the energy consumption greatly, and the total process is green and environmentally benign.

The ethyl acetate synthesis by the oxidative route using a renewable raw material-PdO/SiO<sub>2</sub> catalyst can be considered as a very promising new process reported by L. G. Appel et al.<sup>46</sup> These catalysts were characterized by XPS, UV-vis, XRD, chemical analysis and BET. These catalysts were tested under different experimental conditions using a conventional system with a fixed bed reactor at atmospheric pressure. It was inferred that the ethyl acetate synthesis occurs via ethanol oxidation followed by the condensation reaction of acetaldehyde and ethanol or ethoxide species. Author also suggested that the rate limiting step of the synthesis change according to the rate of ethanol consumption. For low rates, the limiting step is the ethanol oxidation to acetaldehyde, and for the high ones, it is the condensation reaction. It was verified that the catalysts preparation conditions modify the PdO distribution on the support and its particle sizes, therefore, changing the ethanol consumption rate, and consequently, the selectivities to acetaldehyde, ethyl acetate, acetic acid and CO<sub>2</sub>.

The dynamics and shock-control in a reactive distillation column (RDC) for the trans-esterification of ethanol and acetic acid

was studied and simulated by M. Tajdari et al.<sup>47</sup> The dynamic behaviour of the process was experimentally analyzed. The reactants were conducted in a fifteen stages RDC in a single feed stream. An appropriate strategy was chosen and performed for column start up to achieve the steady state condition. The temperature, pressure, mass flow rates (TPF) and mole fractions effects in feed were considered in the column until a new steady state condition was obtained. For top flow of the column, the simulated results were compared with the experimental data. It concluded that there were errors less than 8% for the mole fraction shock results.

Liquid phase esterification of acetic acid with ethanol over dodecatungstophosphoric acid (DTPA) supported on K10 montmorillonite was systematically studied and optimization of process parameters was carried out by V. V. Bokade et al.<sup>48</sup> The 20% m/m DTPA/K10 was found to be the optimum catalyst with 90% acetic acid conversion and 100% ethyl acetate selectivity. Authors were also explored to see the feasibility of 20% m/m DTPA/K10 as a catalyst for the alkylation of acetic acid with other alcohols like methanol, isopropanol and n-butanol.

A tubular hydroxy sodalite (SOD) membrane was successfully applied in the esterification of acetic acid with ethanol and acetic acid with 1-butanol, by Freek Kapteijn et al.<sup>49</sup> The reactions were carried out using equimolar solutions of acetic acid with the appropriate organic alcohol at 90°C using Amberlyst 15 as acid catalyst. The hybrid process drove the esterification reactions almost to completion. The SOD-membrane showed absolute selectivity towards water and retained its stability under the reaction conditions. The membrane exhibited a stable water pervaporation

performance at pH values above 2.9 for acetic acid–water mixtures.

Recently, the reaction of direct transformation of ethanol to ethyl acetate was investigated on reduced Cu/ZrO<sub>2</sub> catalysis prepared by a co-precipitation procedure.<sup>50</sup> These catalysts were characterized by N<sub>2</sub> adsorption, XPS, XRD, TPR, and NH<sub>3</sub>-TDP. The catalytic performances of these Cu-Zr mixed oxides were considerably influenced by changing the molar ratio of Cu to Zr. The highest selectivity to ethyl acetate was found over Cu/ZrO<sub>2</sub> (1) catalyst (molar ratio of Cu and Zr was one). The studied revealed that the presence of a certain amount of Cu<sup>+2</sup> species may play very important role in improving the selectivity to ethyl acetate of the Cu/ZrO<sub>2</sub> catalyst.

In the next decades, ethanol produced from cellulosic residues will be in large supply all over the world. Undoubtedly, bio-ethanol will be used as a gasoline substitute or additive. Taking its future large availability into account, its use as feedstock for the chemical industry can also be foreseen. The ethyl acetate one-pot synthesis from ethanol is a good example of this new industry. The dehydrogenative route of the ethyl acetate one-pot synthesis and also the role of the support using physical mixtures comprised of a dehydrogenation catalyst and four different oxides have been studied by P. C. Zonetti et al.<sup>51</sup> These catalysts were characterized employing TPD of ethanol, CO<sub>2</sub> and acetaldehyde and also pyridine adsorption. Authors have verified that acetaldehyde synthesized on the dehydrogenation catalyst migrates towards the oxide and reacts with the ethoxide species which are generated by the oxide basic sites. The resulting hemiacetal is dehydrogenated and the ethyl acetate

obtained is desorbed. Oxides with strong basic sites generate the most active and selective systems for the ethyl acetate synthesis.

Recently, direct transformation of ethanol into ethyl acetate through catalytic membranes containing Pd or Pd-Zn has been reported by P. R. De La Piscina et al.<sup>52</sup> Authors were studied the ethanol dehydrogenating coupling at 250°C and 1 MPa over catalytic membrane reactors (CMRs) conventional supported catalysts based on Pd or Pd-Zn on CeO<sub>2</sub>-ZrO<sub>2</sub>. They have prepared CMRs through a wet impregnated method based on evaporation crystallization was used to deposit Pd or Pd and Zn on membrane reactors of TiO<sub>2</sub> with a top layer of CeO<sub>2</sub>-ZrO<sub>2</sub> and a pore size of 5 nm. These systems were compared with conventional CeO<sub>2</sub>-ZrO<sub>2</sub> supported Pd or Pd-Zn catalysts. Monometallic Pd systems favoured the decomposition of ethanol giving CO and CH<sub>4</sub> as the main product. The presence of Zn in both Pd/CeO<sub>2</sub>-ZrO<sub>2</sub> and CRMs containing Pd inhibited ethanol decomposition and favoured the production of acetaldehyde, which was subsequently transformed to ethyl acetate.

### 3. PATENTS

The production of esters by a reaction between organic acids or their anhydrides and olefin hydrocarbons in the presences of halide catalysis and it's pertains more particularly to the direction of reaction toward the formation of particular esters<sup>53</sup> and the avoidance of side reactions such as polymerization. The preferred catalyst is boron fluoride promoted with a hydrogen halide such as hydrogen chloride or hydrogen fluoride. Such catalysts offer many advantages over sulphuric acid; phosphoric acid, aluminium chloride, etc.

Because of the remarkable effectiveness of the boron fluoride-hydrogen halide catalyst and the catalyst may be separated from reaction products and recovered for reuse.

M. Gruffaz et al.<sup>54</sup> invented a process for the preparation of ethyl acetate by vapour phase reaction of ethylene with acetic acid, the improvement which comprise conducting said reaction in the presence of a catalytic amount of a solid, ion-exchange fluoropolymer comprising sulfonic acid moieties and its activity is virtually constant over a long period of time as well as virtually no by-products are formed.

A process for the preparation of ethyl acetate by hydrogenating acetic anhydride or mixture of acetic anhydride and ethylidene diacetate in the presence of a Raney Nickel catalyst<sup>55</sup> and an organic sulfonic acid (p-toluene sulfonic acid) to produce ethyl acetate is disclosed in US P. 4 471 136.

Carboxylic acid esters, and in particular ethyl acetate, are produced by esterification of an organic carboxylic acid ester with an alcohol (methanol, ethanol, propanol, the isomeric butanols and the isomeric pentanols) in the presence of alkyl sulfonic acid having desulphonation temperature in excess of that of p-toluene sulfonic acid is invented by John Russell et al.<sup>56</sup> They also claimed corrosion inhibitor-copper acetate, to reduce corrosion of the vessel.

Process for the preparation of ethylidene diacetate and/or ethyl acetate by hydrogenating acetic anhydride<sup>57</sup> in the presence of a homogeneous ruthenium catalyst, methyl iodide and lithium iodide are disclosed in US P. 4 886 905. The process can also by utilize to hydrogenate mixtures of acetic anhydride and ethylidene diacetate to produce ethyl acetate.

In another process, ethyl acetate is synthesized from a one step process of an

oxidation of liquid ethanol in the presence of excess liquid ethanol and a supported oxidation catalyst by a solid ion-exchange resin in the acid form (Amberlyst 15 in acid form).<sup>58</sup> In this process, the acetic acid produced in the oxidation is absorbed by the excess liquid ethanol, which esterifies to ethyl acetate. The oxidation portion of process is preferred with a metallic oxidation catalyst on a hydrophobic support. The esterification portion of the process is preferred with an acidic solid ion-exchange resin to promote the esterification.

US P. 6 768 021 B2 describes another approach based on the use of a membrane separation unit to remove water from the resultant product ethyl acetate-stream<sup>59</sup>. An improved process for producing acetic acid and ethanol in a reaction zone in the presence of an acid catalyst (a variety of homogeneous or heterogeneous acid, Rohm and Hass A-16), distilling formed vapours and condensing to form an organic phase rich in ethyl acetate and an aqueous phase rich in water, separating the phases and further distilling each phase to obtain a final purified ethyl acetate product and a water stream low in organic components, the improvement comprising directing the organic phase from the first distillation to the reaction zone.

US P. 0 255 072 A1 reveals a process for the production of ethyl acetate by reacting ethylene with acetic acid and water in presence of a heteropoly acid catalyst<sup>7</sup> in which the concentrations of reactants in the feed stream to the reactor are such as that the mole ratio of ethylene to water lies in the range 8.0 to 17.0 and the mole ratio of acetic acid to water lies in the range 1.25 to 1.40.

Recently, a process for the selective production of ethyl acetate by vapour phase reaction of acetic acid over a hydrogenating

catalyst composed of a supported bimetal catalyst<sup>60</sup> such as for example, platinum or palladium and copper or cobalt supported on a suitable catalyst to form ethyl acetate is disclosed in US 0029980 A1.

#### 4. APPLICATIONS

Ethyl acetate has a wide range of applications<sup>61</sup> across many industries, including:

##### **Surface coating and thinners:**

Ethyl acetate is one of the most popular solvents and finds wide use in the manufacture of nitrocellulose lacquers, varnishes and thinners, to dissolve the pigments for nail varnishes. It exhibits high dilution ratios with both aromatic and aliphatic diluents and is the least toxic of industrial organic solvents.

##### **Pharmaceuticals:**

Ethyl acetate is an important component in extractants for the concentration and purification of antibiotics. It is also used as an intermediate in the manufacture of various drugs.<sup>62</sup>

##### **Flavors and essences:**

Ethyl acetate finds extensive use in the preparation of synthetic fruit essences, flavors and perfumes.

##### **Flexible packaging:**

Substantial quantities 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.

##### **Occurrence in wines:**

Ethyl acetate is the most common ester found in wine, being the production of the most common volatile organic acid-acetic acid and the ethanol alcohol created during the fermentation of wine. The aroma of ethyl acetate is most vivid in younger wines and contributes towards the general perception

of "fruitiness" in the wine. Sensitivity varies with most people having a perception threshold around 120 mg/lit. An excessive amount of ethyl acetate is considered a wine fault. Exposure to oxygen can exacerbate the fault due to the oxidation of ethanol creating acetaldehyde. This can leave the wine with sharp vinegar like taste.

##### **Electronics:**

Small quantities of ethyl acetate are also used in the manufacture of video/audio tapes. Magnetic media of tapes are purified with ethyl acetate. It is also used for head cleaning. In fact, ethyl acetate of 99.7% quality is the best solvent for cleaning, etc.

##### **Miscellaneous:**

Ethyl acetate is used in the manufacture of adhesives, cleaning fluids, nail polish removers and silk, coated papers, textiles, explosives, artificial leather etc. In the field of entomology, ethyl acetate is an effective poison for use in insect collecting and study. In a killing jar charged with ethyl acetate, the vapours will kill the collected (usually adult) insect quickly without destroying it. Because it is not hygroscopic, ethyl acetate also keeps the insect soft enough to allow proper mounting suitable for a collection. High purity product (ethyl acetate) can be used as a viscosity reducer for resins used in photo resist formulations in the electronics industry.

Ethyl acetate is also used as a solvent in a variety of coating formulations including epoxies, urethanes, cellulose, acrylics and vinyls. These coatings are used for wood furniture and fixtures, agricultural, construction and mining equipment, containers and closures, auto refinishing, and maintenance and marine applications. Over the past twenty years, ethyl acetate coatings have been losing share to waterborne and high solids coatings, powder

and two-component coatings systems, due to environmental constraints on volatile organic compound (VOC) emissions. Ethyl acetate is used as a solvent in inks for flexographic and rotogravures printing, where it's main function is to dissolve the resin, control the viscosity and modify the drying rate. As with industrial coatings, the decline in the use of acetate because of environmental constraints has largely been completed.

### CONCLUSION

Survey of the literature reveals that ethyl acetate has been used for a multitude of applications. We believe that the almost all the important results presented in this review will open up a potentially new chapter in the "chemistry of ethyl acetate".

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