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Production pathways of acetic acid and it's versatile applications in the food industry

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Abstract

Acetic acid is a commodity chemical with the global demand of approximately 15 million tons per year with several applications in the chemical and food industry. The production of acetic acid can be widely categorized into chemical and fermentative routes. In the current industrial practice, the chemical route is the predominant production route. In this chapter, we will reflect on the most recent developments in acetic acid production over the past two decades, including process intensification and catalysis, with the main emphasis on process sustainability. Acetic acid is used in several industrial sectors such as food and beverages, chemical, pharmaceutical, textile, polymer and paints. Acetic acid has several applications in food industry traditionally known as vinegar. It is used as flavouring agent in cocoa, beer to get characteristic sour smell and flavour. It is also used as an acidulant, to give a characteristic flavour profile to food. Indole-3-acetic acid plays a key role in banana ripening (phytohormone) and its degradation to 2-aminoacetophenone, during wine production can give untypical ageing off-flavour in wine. It is also used as a natural preservative and antimicrobial agent. Acetic acid is added to mayonnaise to deactivate Salmonella. It can be used for microbial decontamination of meat and as a mild descaling agent in the food industry. More recently, acetic acid is reported to be used as an antimicrobial edible food coating agent. The diversified food culture has a significant demand in the development of such kind of innovation and acetic acid can be an efficient solution.

Keywords: Acetic acid production, acetification, acidulant

1. Introduction

The bridge between chemistry and the day to day human life is always growing wider and stronger, and acetic acid is one of the perfect examples. Acetic acid is a clear liquid with a pungent odour, sharp taste, melting point of 16.73 °C and boils at 117.9 °C. Acetic acid, traditionally known as 'vinegar' is widely used as a food preservative, first discovered (c. 5000 BC) when unattended grape juice turned in wine. A famous physician Hippocrates II (c. 420 BC) used acetic acid to clean the wounds[1]. With direct and indirect applications of acetic acid, it has diversified into several chemical sectors such as food, pharma, chemical, textile, polymer, medicinal, cosmetics etc. Since then, acetic acid is proven to be a multi-application chemical building block resulting in ever-increasing demand. The production of acetic acid is expected to reach 18 million ton with an average growth of 5 % per year [2,3].

The overall routes for production and the applications of acetic acid are shown in Figure 1. Currently, the manufacturing demand is fulfilled via two main production routes, which are chemical and fermentative. Amongst the chemical manufacturing processes, the key processes are Cavita process (carbonylation of methanol), oxidation of aldehyde and oxidation of ethylene. The major players are BP chemicals and BASF which follow carbonylation route. The major consumption of acetic acid mainly comes from the preparation of vinyl acetate monomer (VAM), acetic anhydride, C1-C4 acetates and it is used as a solvent in synthesis of terephthalic acid (PET). VAM is a one of the main ingredients used in polymer industry with application in as emulsifier, resins, as intermediate in surface coating agent, acrylic fiber and polymer wires. It is also used in textile industry to generate synthetic fibers as a result of condensation rection. The other condensation reaction of acetic acid produces acetic anhydride used as typical acetylation agent, which is subsequently utilized to produce cellulose acetate, used in synthetic textiles and for silver-based photographic films. Most derived esters of acetic acid are ethyl acetate, n-butyl acetate, isobutyl acetate, and propyl acetate which are frequently used as solvents for inks, paints and coatings. Glacial acetic acid is an excellent polar protic solvent which is frequently used as a solvent for recrystallization to purify organic compounds. Several researchers are working on developing a sustainable process with the simple design to produce acetic acid that meets current demand. Several homogeneous, as well as heterogeneous catalytic systems, are reported for the production of acetic with carbonylation process[4].

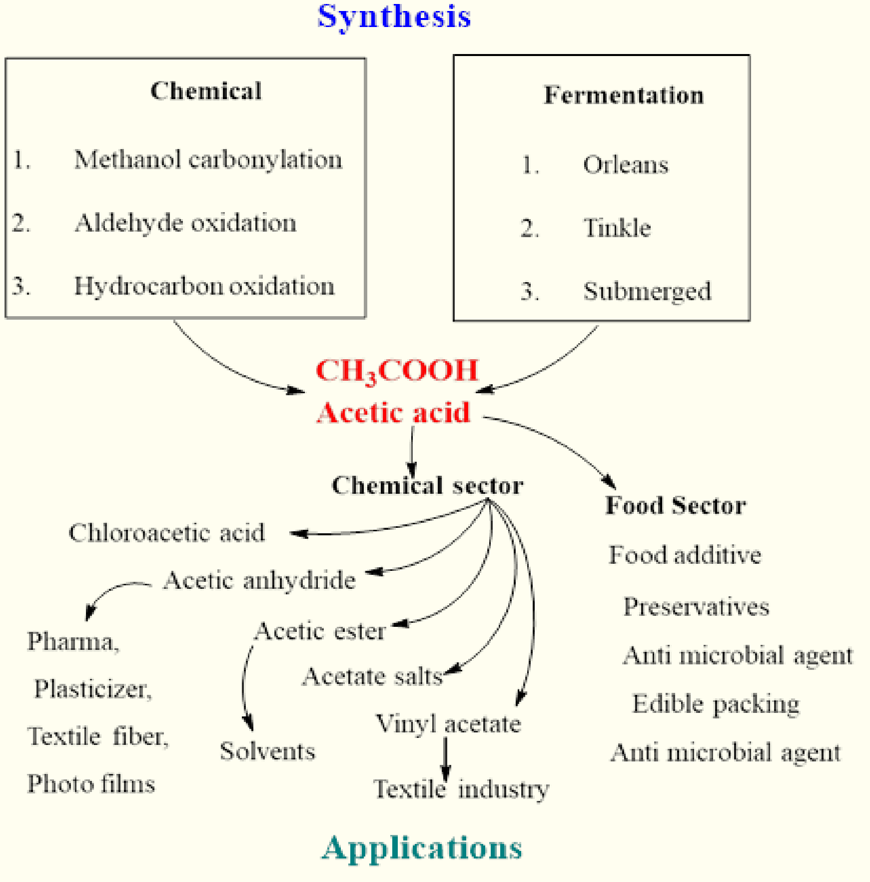


Figure 1: Commercial routes for synthesis of acetic acid and applications

Acetic acid produced via fermentation route is mainly utilized in the food industry in the form of vinegar. Use of vinegar is more diversified these days coming with more innovative ways to adjust and suit the current lifestyle and food culture. The different concentrations of acetic acid are used to sharpen the taste of food with a longer shelf life period and as a food preservative. Some new application has also come such as edible and non-edible antimicrobial coating[5,6].

This chapter reviews the current commercial processes for the synthesis of acetic acid to meet an ever-increasing global demand. The chapter also gives insight into the pros and cons associated with the process available and then how should we design a sustainable strategy to develop a simple commercial process. Further, the state of art to produce vinegar is discussed with exploitation as a multiapplication tool in the modern food industry.

2. Production of acetic acid

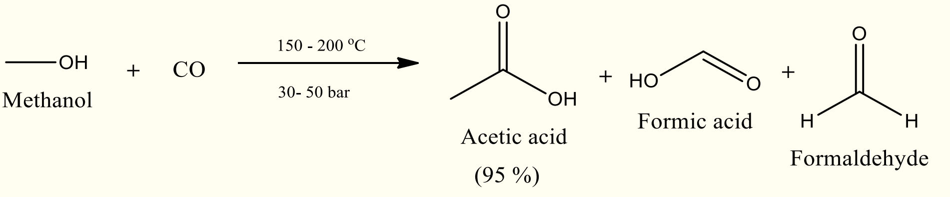
Acetic acid is mainly produced via chemical route which involves homogeneous as well as heterogeneous catalytic methods. The carbonylation of methanol via Monsanto process is the most adapted route, which further evolved as Cavita process with a choice of catalysts and process intensification. In the recent decade, the fermentative approach has also gained attention, however the commercial approach is not established yet. The current trends in sustainable manufacturing demand an urgent paradigm shift to develop and pursue more sustainable routes to reduce environmental burden. An approach is also made with the development of membrane-based technology which offers a very simple design with eco-friendly production[7].

2.1 Conventional process

I Methanol carbonylation process:

Carbonylation process is a most employed commercial route for synthesis of acetic acid, also known as Monsanto process (Scheme 1). Methanol and carbon monoxide are reacted in liquid phase in the presence of rhodium (Rh)-based catalyst at 150-200 ^{o}C temperature and 30-50 bar pressure to produce acetic acid with 95% selectivity and 5 % side products such as formic acid and formaldehyde[8]. Hydrogen iodide is used as an alkali promoter in this process. The reaction proceeds in liquid phase with methyl acetate as solvent using homogeneous catalyst. The controlled amount of water is required for the reaction which is generated *in situ* by reaction of methanol with hydrogen iodide. The rate of reaction in the Monsanto process depends on the concentration of water. CO_2, H_2 and methanol are obtained as byproducts in the reaction. The generated methanol in the reaction is recycled. The process has evolved with the time and different strategies were adapted to separate pure acetic acid from a mixture of water and byproducts. This process was modified by BP chemicals replacing rhodium-based catalyst with Iridium (Ir) catalyst known as Cavita process[4]. The choice of Ir as a coordination metal is relatively more economic process than rhodium. The use of an iridium catalyst improves the overall rate of reaction.

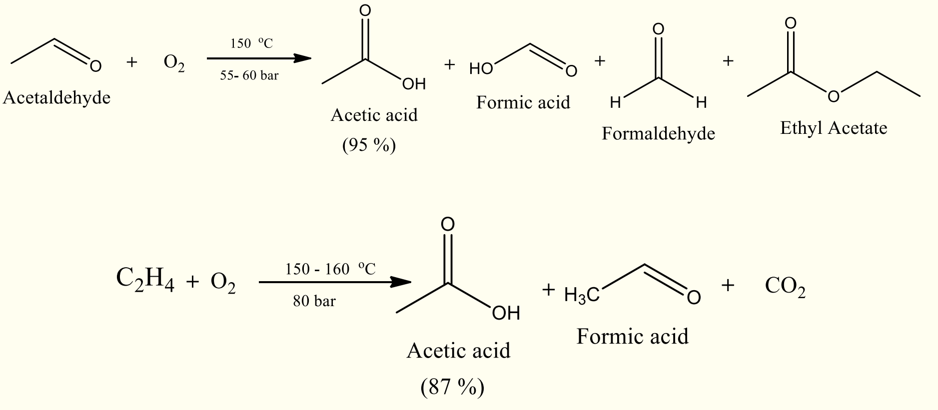
The safety and the environmental hazards arising from the current methods are a serious concern. Acetic acid is highly corrosive, and the production processes need to be more sustainable and environmentally benign by reducing the amount of energy required in production and subsequent separation technologies as well as using heterogeneous catalysts. The Japanese firm, Chiyodo developed a heterogeneous Rh catalysed process wherein, Rh metal was immobilized on the vinyl-pyridine resin. The use of heterogeneous catalyst prevails the loss of catalyst in the liquid phase and facilitates easy separation from the reaction mixture. The amount of water used in the reaction is very low and thus the separation of water from acetic acid is more energy-efficient compared to the other processes mentioned.



Scheme 1 Production of acetic acid by carbonylation method

II Acetaldehyde oxidation process

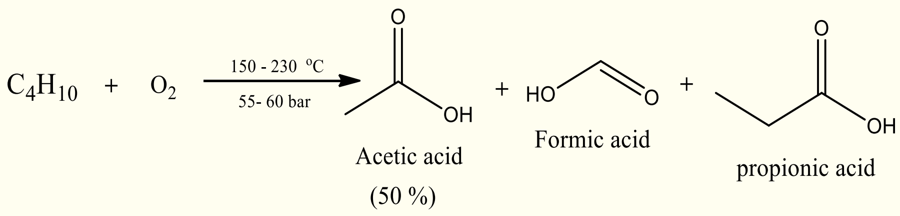
Acetaldehyde oxidation was the predominant process followed for the synthesis of acetic acid. Wherein, acetaldehyde is first prepared by oxidation of ethylene using palladium and copper chloride and it was further oxidized to form acetic acid (Scheme 2). The same process is reported using cobalt and chromium-based catalyst at 55 bar pressure and 150 ˚C temperature. The one-step process for conversion of ethylene to acetic acid is also practiced using lead and lead-platinum based catalyst at high pressure compared to the acetaldehyde oxidation process with a low yield of acetic acid [9].



Scheme 2 Production of acetic acid by acetaldehyde oxidation

III Hydrocarbon oxidation process

Hydrocarbons derived from petroleum stock such as butane and naphtha are utilized to generate acetic acid using cobalt acetate and chromium acetate catalyst (Scheme 3). The reaction proceeds at a comparatively higher temperature range (150-230 °C) and pressure (50-60 bar). The process involves petroleum feedstock which contains hydrocarbon mixture which leads to the formation of other byproducts such as acetone, formic acid, propionic acid along with acetic acid. Thus, this process fails to give pure acetic acid. This process is more suitable for manufacturing a mixture of volatile fatty acids.



Scheme 3 Production of acetic acid by hydrocarbon oxidation

2.1 Fermentation route

Fermentative route is mostly adapted for the generation of food-grade acetic acid i.e. vinegar. This process mainly involves the use of renewable carbon resources such as apple, grape, pears, honey, cane, coconut, date, syrup cereals, hydrolyzed starch, beer and vine [10]. The fermentation process is mainly divided into two steps: the treatment with yeast followed by acetic acid bacteria (AAB). Commercial production of vinegar is done via oxidative fermentation using AAB. *Acetobacter* and *Gluconacetobacter* are most used species among ten classified genera. *Acetobacter pasteurianus* is traditionally used for commercial production of vinegar with concentration not exceeding 6 % (v/v). Whereas, *Gluconacetobacter europaeus* is utilized to produce high concentration vinegar (10 % v/v). The price of the vinegar varies with the kind of source is used and the region where it is generated.

I) Orleans method:

This method is well established, traditional and preferred for low volume production of acetic acid. Derived from the French word Orléans, wooden barrels are used to ferment the feed in this process. This method is followed to prepare exotic brands of vinegar in different regions of the world with specific raw material available in the specific season. The traditional balsamic vinegar produced in different parts of the world such as sherry from Spain, oxos from Greece and Modena in Italy.

II) Trickling process:

This process was developed to overcome the slow rate of acetification in Orleans process[11]. The process intensification was done improve the acetic acid bacteria and substrate interaction. The alcoholic substrate was sprayed over the fermentation in continuous loop to achieve the desired concentration of acetic acid. The heat of the reaction was controlled by passing the air through the system. The process has drawback of accumulating gelatinous material on the surface the membrane which reduces the rate of reaction over the period.

III) The continuous submerged process:

This modern fermentation method is followed to produce vinegar in masses. This is the most widely method and has a high yield along with the fast rate of oxidation as compared to the previous method. This method is 30 times faster than the Orleans method with higher efficiency for production of acetic acid. This process requires comparatively small space with higher yields. The Fringe fermenter is used for this process to increase the rate of the acetification. The yield of acetic acid is 98 %. The pure substrates are required to achieve the high quality of acetic acid. This fermentation process is much economical, simple design with easy process control.

The Fermentation process for acetic acid is economically feasible with comparatively simple operations. The application of this process is very limited to the present global demand. Whereas, the conventional process involves several steps such as fractional distillation, condensation and crystallization, which add to the high machinery cost. The operating conditions are harsh considering the process temperature and pressure along with the corrosive nature of acetic acid [12]. The purification of acetic acid from water is a multi-step process which consumes a high amount of energy which makes overall process complex and critical. In addition to this, the process requires huge manpower with stringent safety protocols and norms.

3. Need for development of Novel sustainable technologies

Looking at the ever-increasing threats of global warming and ever-increasing global demand of acetic leads into it is an urgent need to develop a novel technological approach and sustainable feedstock for the generation of acetic acid. Even though many process and technological development are reported recently, they fail to sustain the production cost to profit margins. The separation of acetic acid remains the key issue to overcome the economical and energy consumption barriers. The different operations such as distillation, evaporation, absorption, filtration crystallization and alkali neutralization are time and energy consuming. Even though these processes involve multiple steps, the ever-growing demand forces to follow this path. On the other hand, fermentation process is reliable but cannot match the scale of current demand. Thus, the development of novel route for generation or process intensification in separation can drastically reduce the overall production cost of acetic acid. Utilization of CO and CO_2 as feed stock generated from natural gas can offer long term sustainability of acetic acid production. This technology offers high purity of acetic acid with eco-friendly production. Furthermore, membrane-based separation processes can provide efficient way to produce acetic acid. The pathways are discussed briefly.

3.1 CO and CO_2 as valuable feedstock:

Utilization of CO_2 and syngas can offer sustainable alternatives to produce acetic acid. BP has announced the breakthrough process wherein, acetic acid will be manufactured from syngas as a feedstock derived from natural gas. This will give an alternative to SaaBre process which produces acetic acid in three integrated steps.

The production of acetic acid from syngas will avoid the purification of CO and purchase of methanol. Though the technology is not fully developed, it provides better alternatives in terms of sustainability. Similarly, acetic acid can also produce via CO_2 and H_2 to produce methanol followed by subsequent carbonylation step. This route gives liberty to utilize CO_2 as value added feedstock

3.1 Membrane based technologies:

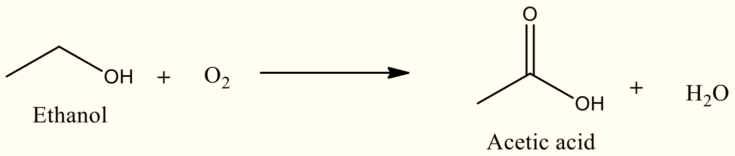
The membrane technology can offer the separation of liquid, vapor and gas selectively with controlled mass transfer rates. These processes are easy to operate and simple to design. The technology can offer development on energy intensification. Several types of processes are reported based on the pore size of the membrane for separation of different components. These are namely microfiltration, ultrafiltration and nanofiltration membrane. The operating pressure (varying from 1 – 20 bar) of the system varies according the pore size of the membrane are used. The reverse osmosis is another membrane technology with non-porous membrane. This process operates at pressure more than 20 bar. The membrane technologies collectively can be applied in downstream processing for separation of acetic acid in chemical process as well as fermentation processes. The combination of fermenter with acetic acid permeable membrane can help in separation of acetic acid to avoid the self-inhibition.

4. Application of acetic acid in food industry

Direct applications of acetic acid are reported from ancient times. It was used as a medicine and food preservative. Over the period of applications of acetic are diversifies as per the demands of modern life. Using the different concentrations, it is utilized as Food Additives, Food Preservation, Antimicrobial Agent, Acidulant, Flavor and Taste enhancer, Edible Packaging material, artificial food ripening agent etc. Some of the applications such as acidulent and as acetification agents are described in detail here.

4.1 Acetification

Acetification is simply bacterial oxidation of ethanol to produce acetic acid and water (Scheme 4). The process is also termed as oxidative fermentation. The rate of the reaction in acetification mainly depend on type of micro-organism used to catalyze and the concentration of available oxygen in the media[13].



Scheme 4 Production of acetic acid by fermentative oxidation of alcohol

There are different types of microorganisms which occur naturally in food which are responsible for the different natural process such as acetification, alcoholism, proteolysis and enzymatic reactions which alter the natural condition of the food.

This bioprocess technology is studied and systematically utilized to improve the quality of food s in terms of texture, taste, mouthfeel, colour and prolonged shelf life. The overall concept has grown into generating different types of food and beverages produces in a cheap and sustainable way.

Acetification of different food categories using acetic acid bacteria (AAB) has led to the production of several food products [14]. AAB are naturally found on fruits, flowers and plants which naturally react and convert carbohydrates sugars into organic acids in presence of oxygen. The same concept is biotechnologically utilized to prepare a diverse variety of food and beverages.

4.2 Flavoring agent: The different parts of the world have utilized the acetification process to generate a variety of foods and beverages. The famous Lambic beer is produced from malted barley, aged dry hops and unmalted wheat. The different AAB and yeast are responsible for the generation of this beer which is matured for over the period of three years. The typical acidic flavour of the beer is achieved with help AAB together with lactic acid. The sparkling water is another famous example which gives typical acidic and fruity flavour vis fermentation of water and natural sucrose. Water kafir is one of the examples of such type. Kombucha is another type of beverages produced by oxidative fermentation. It is prepared from Kombucha (tea fungus), water and sugar. Similarly, Cocoa is fermented from cocoa beans with the help of AAB and yeast which is used as raw material for chocolate production.

4.3 Acidulent

Acidulants are essential ingredients or additives which are generally used to improve the taste of food and make it sharper. There are naturally occurring acidulants such as acetic acid, citric acid, malic acid, fumaric acid, lactic acid, tartaric acid, succinic acid, phosphoric acid etc. having different taste profiles. Many fruits such as orange, lemon, apples, tomatoes, and yogurt contain natural acids with the most common example as citric acid. Citric acid comes with lemon flavour, acetic acid with strong familiar vinegar flavour, tartaric acid gives sharp taste and lactic acid is with a smooth taste [10]. Apart from taste enhancement, acidulants also act as a food preservative. The choice of the acidulent is usually made on their characteristic flavour and the physical state and solubility. Some food formulations require solid acidulants. In general, inorganic acids such as sulphuric acid, phosphoric acid, monosodium orthophosphate and diphosphates are used as dry acidulants in controlled concentrations. The composition of the acidulants is based on their selection and different concentrations calculated by total titratable acid. Acetic acid is mainly used in the form of vinegar with the pungent smell. As it appears in the liquid state, it is used as a preservative in pickles. It is also used in the manufacture of cheese to improve the shelf life period, good mouthfeel and taste. [15]

4.4 Edible packing:

Acidulants are also used as food coating, it may be edible or non-edible to prevent it from contamination with the surrounding environment, to protect it from bacterial infection and to improve the shelf life of the food. These films are easily biodegradable. The water-soluble non-edible coating is used for the packing of food [16]. The edible coating is used for breath freshening agent, in drug delivery and as flavour. Acetic acid is used in edible films to enhance sour flavour. Various compositions of acetic acid are used to develop antimicrobial food coating to stop the outgrowth of bacterial and fungal cells. It is also used in meat coating and preservation of meat products. The chitosan-based edible food coatings along with aqueous acetic acid is used to enhance anti-listerial activity.

4.5 Antibacterial agent: Acetic acid is commonly used in medicine since ancient times. The low concentrations (3 %) of acetic acid can be used as a local antiseptic against various micro-organisms. Acetic acid is always considered as an alternative It can be utilized as *in vitro* antimicrobial agent combined with other antiseptics. Acetic acid covers the vide range of spectrum with Gram-positive as well as Gram-negative bacteria.

5. Conclusion

Acetic acid has remained one of the key chemical molecules associated with human life. It is one of the main building blocks for developing several chemical entities. Cavita process shares a major part of the production to meet the global demand. The process utilizes methanol as a raw material which is obtained from biogas. Though the process utilizes bio-derived feedstock, it utilizes high energy and manpower with multiple separation steps. The innovative and simple technologies for separation of acetic acid can improve the overall process. The other well-known process i.e. fermentative route is slow and commercially unsuitable to meet the global demand. The fermentation process is globally followed to generate the food-grade acetic acid commonly known as vinegar. The demand for acetic acid will always keep growing which necessitates the development of an eco-friendly process. Utilization of CO_2 and syngas may offer excellent alternatives as a sustainable feedstock to develop innovative technologies to develop commercial processes. This offers development of 100 % bioderived feedstock process. Further, the modern food industry has come up with different innovative applications of the acetic acid in food preservations and improved quality of food.

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Conflict of Interest

"The authors declare no conflict of interest."

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