A Brief Review on Propionic Acid: A Renewal Energy Source

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ABSTRACT

Over the last 3 decades, there has been a resurgence of interest in large-scale production of fermentation chemicals due to the sharp increase in petroleum cost. So the potential role of a new energy efficient fermentation technology is receiving growing attention. Carboxylic acids like as propionic, lactic, citric, tartaric acid etc. have been used as the most efficient fermentation chemicals. Propionic acid produced by fermentation is widely used in chemical, pharmaceutical and food industries. It is used primarily for animal feed preservation, including hay, silage, and grains, and in human foods, mainly in baked goods and cheeses. The growing demand of this acid draws attention towards the more economical energy efficient technology. The conventional method of recovery of the propionic acid 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. Thus there is a need to look at other methods of producing propionic acid. Reactive extraction with specified extractant giving a higher distribution coefficient has been emerged as a promising technique for the recovery of acids. This paper covers fermentation technology for the production, most efficient recovery methods from the fermentation broths and various applications of propionic acid.

Keywords: Carboxylic Acids; Propionic Acid; Fermentation technology; Recovery; Reactive Extraction.

1. INTRODUCTION

Over the last 3 decades, there has been a resurgence of interest in large-scale production of fermentation chemicals due to the sharp increase in petroleum cost. So the potential role of a new energy efficient fermentation technology is receiving growing attention.

The current economic impact of fermentation chemicals, however, is still limited, in large part because of difficulties of product recovery. Thus, for fermentation products to penetrate the organic chemicals industry, substantial improvements in the existing recovery technology are needed.

Carboxylic acids are obtained by the aerobic fermentation of glucose via the glycolytic pathway and glyoxylate bypass. Corn meal hydrolyzed with amylases was used as the carbon source for producing acetic, propionic, and butyric acids via anaerobic fermentations.

The propionic acid is a naturally occurring carboxylic acid with chemical formula CH_3CH_2COOH. In the pure state, it is a colorless, corrosive liquid with a sharp, somewhat unpleasant odor.

Propionic acid is used in the manufacture of herbicides, chemical intermediates, artificial fruit flavors, pharmaceuticals, cellulose acetate propionate, and preservatives for food, animal feed, and grain. Its present U.S. market is estimated at 235 million pounds per year (Chemical Marketing Reporter, 1997) and is growing at 4% annually.

2. FERMENTATION TECHNOLOGY FOR PROPIONIC ACID

Commercial production is chiefly carried out by chemical synthesis from petroleum feedstocks (Playne, 1985), but fermentation is an attractive alternative route to produce this acid from renewable resources. Several carbon sources have been used for this fermentation such as glucose (Emde and Schink 1990a; Lewis and Yang 1992a), xylose (Carrondo et al. 1988), maltose (Babuchowski et al. 1993), sucrose (Quesada-Chanto et al. 1994), and whey lac-tose (Lewis and Yang 1992b; Colomban et al. 1993).

Propionic acid bacteria have long been used in the dairy industry. These bacteria play important roles in the development of the characteristic flavor and eye production in Swiss-type cheeses. Propionibacteria are Grampositive, nonspore-forming, rod-shaped, facultative anaerobes.

Like most organic acid fermentations, the propionic acid fermentation is inhibited by acidic pHs and the major fermentation product, propionic acid (Blanc and Goma, 1987b; Ibragimova et al., 1969; Neronova et al., 1967). The conventional fermentation technology for propionate production is thus limited by low fermentation rate and low product concentration. Furthermore, the fermentation is heterogeneous; i.e., propionate is produced along with other byproducts. This not only results in a low product yield but also renders product purification difficult and expensive. Consequently, the conventional fermentation route for propionic acid production is inefficient and it competes with difficulty with petrochemical routes. Presently, only small amounts of propionate are produced by fermentation of whey and are used as a natural product in foods for the labeling purpose.

In order to make the fermentation route economically viable, it is necessary to develop novel fermentation processes that use highly efficient bioreactors and separations techniques. Recently, integrated fermentation-separation systems have been successfully used to reduce end-product inhibition and, thus, to improve the overall process efficiency (Daugulis, 1988; Roffler et al., 1984).

3. RECOVERY METHODS

Organic acids, widely used in the food, pharmaceutical and chemical industries, are important chemicals. Fermentation technology for the production of organic acids in particular has been known for more than a century and acids have been produced in aqueous solutions. They have severe inhibiting effects on the rate of conversion and thus several separation methods, such as liquid extraction (Hauer and Marr, 1994), reverse osmosis (Timmer et. al, 1994), electro dialysis (Nomura et. al, 1987), liquid surfactant membrane extraction (Sirman and Grandison, 1991), anion exchange (Cao et. al, 2002), precipitation and adsorption (Dai, 1996) etc. have been practiced to remove acids. Reactive liquid-liquid extraction of the organic acids by a suitable extractant has been found to be a promising alternative to the conventional processes (Kertes and King, 1986).

3.1. Precipitation

A process is described for the purification of lactic acid by precipitation. The fermentation liquor is filtered and evaporated. In the calcium precipitation process, the separation and final purification stages account for up to 50% of the production costs and produces a large quantity of solid waste.

3.2 Electro-dialysis

Electro dialysis is a recovery process where ion exchange membranes are used for removing ions from an aqueous solution under the driving force of electrical field. Hongo at al., (1986) proposed the possibility of electro dialysis for *in situ* recovery of lactic acid to reduce product inhibition in batch fermentation. The amount of lactic acid was 5.5 times greater than that produced in non-pH- controlled fermentation.

3.3 Adsorption

Carboxylic acids may be recovered by adsorption on solid adsorbent. Kawabata et al. (1982) separated carboxylic acid by using a polymer adsorbent of pyridine skeletal structure and a cross-linked structure. The polymer adsorbent showed good selectivity and high adsorption capacity for carboxylic acids even in the presence of inorganic salts. The selected elutants were aliphatic alcohol, aliphatic ketones and carboxylic esters. Chen and Ju (2002) studied the coupled fermentation and adsorption to prevent the product concentration from reaching inhibitory levels for lactic acid production.

3.4 Reverse Osmosis

Reverse Osmosis has also studied for recovery of carboxylic acids from fermentation broths (Timmer et. al, 1994). They concluded that the reverse osmosis could effectively concentrate lactic acid from 10 to120 gdm^{-3} at a 6.9 MPa trans-membrane pressure at energy use lower than multiple effect evaporators.

3.5 Reactive Extraction

Reactive extraction with a specified extractant giving a higher distribution coefficient has been proposed as a promising technique for the recovery of carboxylic and hydroxycarboxylic acids (Wasewar et. al, 2003). Reactive liquid-liquid extraction has the advantage that acid can be removed easily from the fermentation broth, preventing lowering of the pH. Due to use of a high concentration substrate as the process feed, process waste and production cost can be reduced. Further, acid can be re-extracted and the extractant recycled to the fermentation process (Weilnhammer and Blass, 1994).

Conventional solvents such as alcohols, ketones, ethers, and aliphatic hydrocarbons are not efficient when applied to dilute, carboxylic acid solutions because of the low aqueous activity of carboxylic acids resulting in low distribution coefficients (Kertes and King, 1986). Organic bases or amines can provide much higher equilibrium distribution coefficient (K_D) for extraction of carboxylic acids than conventional solvents. Long-chain, aliphatic amines are effective extractants for separation of carboxylic acids from dilute aqueous solution (Yang et. al, 1991 and Kertes and King, 1986). Generally, the amine extractants are dissolved in a diluent, an organic solvent that dilutes the extractant. It controls the viscosity and density of the solvent phase.

Reactive extraction strongly depends on various parameters such as the distribution coefficient, degree of extraction, loading ratio, complexation equilibrium constant, types of complexes (1:1, 2:1, etc.), rate constant of carboxylic acid-extractant reaction, properties of the solvent (extractant and diluent), type of solvent, temperature, pH and acid concentration.

4. EXTRACTIVE FERMENTATION

Several extractive fermentation systems also have been studied for organic acid production (Yabannavar and Wang, 1991). Extractive fermentation removes the inhibitory, acidic product from the reactor and, therefore, provides better pH control on the reactor and results in higher reaction rates. Also, products are present in relatively pure and concentrated forms. Thus, savings in the downstream recovery and purification costs can be realized. However, all prior extractive fermentation studies dealt with homo fermentative products, such as lactic, acetic, and citric acids.

An extractive fermentation process was developed to produce propionate from lactose. The bacterium Propionibacterium acidipropionici was immobilized in a spiral wound, fibrous matrix packed in the reactor. Propionic acid is the major product from lactose fermentation, with acetic acid and carbon dioxide as byproducts. Propionic acid is a strong inhibitor to this fermentation (Lewis and Yang, 1992).

Despite the great variety of substrates studied for propionic acid production, glycerol has rarely been considered (Emde and Schink 1990b; Barbirato et al. 1997). However, a better efficiency of propionic acid production from glycerol could be ex-pected because of its higher reduction level compared to conventional substrates. Effectively, a propionic acid yield of 0.84 mol/mol, a final concentration in propionic acid of 42 g/l and a low acetic acid production have been obtained from glycerol with P. acidipropionici (Barbirato et al. 1997). Similar data have been also reported with P. thoeni (Boyaval et al. 1994).

Himmi et. al (2000) compared the kinetics of glycerol and glucose fermentation and product formation for two propionibacteria: *P. acidipropionici*, which has been widely studied, and *P. freudenreichii ssp. shermanii* scarcely used for glycerol fermentation. In all cases, fermentation end-products were the same and consisted of propionic acid as the major product, acetic acid as the main byproduct and two minor metabolites, n-propanol and succinic acid. Evidence was provided that greater production of propionic acid by propionibacteria was obtained with glycerol as carbon and energy sources. P. acidipropionici showed higher efficiency in glycerol conversion to propionic acid with a faster substrate consumption. The almost exclusive production of propionic acid from glycerol by this bacterium suggested an homo propionic tendency of this fermentation.

5. CONCLUSION

The growing demand of propionic acid draws attention to the improvement of a conventional process for the production. Commercial production is chiefly carried out by chemical synthesis from petroleum feedstocks, but fermentation is an attractive alternative route to produce this acid from renewable resources. It is important to have an efficient and sustainable process for the separation of these acids from the fermentation broth. Although commercial processes for acid recovery are based on the classical method of separation and this separation and final purification stages account for up to 50% of the production costs. The productivity of these fermentation processes can be significantly increased by *in-situ* recovery of propionic acids from fermentation broths by reactive extraction. Extractive Fermentation process has many advantages over the conventional propionic acid fermentation, including improved productivity, propionate yield, final product concentration, and product purity.

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