History of the Acetone-Butanol-Ethanol Fermentation Industry in China: Development of Continuous Production Technology

Jui-shen Chiao^a Zhi-hao Sun^b

^aInstitute of Plant Physiology and Ecology, Shanghai Institutes for Biological Sciences, Chinese Academy of Sciences, Shanghai, and ^bSchool of Biotechnology, Southern Yangtze University, Wuxi, China

Abstract

The acetone-butanol-ethanol (ABE) fermentation industry in China was started in the early 1950s in Shanghai and expanded rapidly thereafter. At its peak, there were about 30 plants all over the country and the total annual production of solvents reached 170,000 tons. This large enterprise was compelled to complete shutdown at the end of the 20th century due to the rapid increase of petrochemicals. The success of the ABE industry in China had special features like the development of a continuous fermentation technology. Its main strategic considerations were as follows: maintaining maximal growth and acid production phase, adoption of multiple stages in the solvent phase to allow gradual adaptation to increasing solvent, and the incorporation of stillage to offer enough nutrients to delay cell degeneration. Due to the tremendous national demand for solvents, China has begun a new round of ABE fermentation research. It is expected that a new era in the ABE industry is on the horizon.

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Introduction

The historical development of the acetone-butanol-ethanol (ABE) industry in China and the future perspective of this industry are presented in this paper. Due to various reasons, China developed its own economy independently. During the planned market era, because of the cheap price of grain and the unavailability of self-made chemical synthesis equipment, acetone and butanol were mainly produced by the fermentative method to meet the domestic requirements, and the balance between supply and demand could be approximately reached. With the economic development and the adoption of opening and reforming policies, China imported many equipment systems used for chemically synthesizing acetone and butanol, and the grain prices were also gradually approaching the international price level. Under these circumstances, the fermentation process could not compete economically with the petrochemical process at all. Even though experiencing a transient period of relocating the solvent plants to the corn belts, the fermentative products still could not compete with the chemically synthesized products. As a result, all of the fermentative solvent plants in China were eventually closed down. However, the story is not complete yet, as this old technology is in the process of regeneration.

History of the Acetone-Butanol-Ethanol Industry in China

Since the 1950–1960s, the ABE fermentation industry has ceased completely in Europe, America, Japan, and other countries except Egypt, the Soviet Union, South Africa, and China, due to the competition of petrochemicals. Owing to its economic and blocked political situation, China developed its own ABE industry by a self-reliant effort. Around 1960, ABE plants were built in Shanghai, Beijing, and Wuxi, each with a yearly production of 1,000 tons. Between 1965 and 1970, ten more plants were constructed in Tianjin, Yunnan, Shanxi, Zhejiang, etc. The total national annual production amounted to 40,000–50,000 tons. The Shanghai Solvent Plant led the list with a yearly output of 10,000 tons.

Around 1980, the ABE fermentation industry underwent tremendous changes, many plants leaving big cities for agricultural districts, moving from Southern to Northern China, close to corn and coal production localities. At the same time, new plants were set up in Shandong, Hebei, North-Eastern provinces, each with a yearly output of 5,000–10,000 tons. The total national annual production of solvents reached 170,000 tons. However, the glorious period of ABE fermentation encountered a heavy blow by the end of 20th century, because of the rapid emergence of petrochemical synthetic processes. Solvent fermentation was stepped down successively to complete closure in 2004 along with the construction and operation of some industrial production sites of equipment used for chemical synthesis of butanol or acetone. During the first 5 years of this century, the situation of solvents supply and marketing in China had greatly changed, e.g., the national demand for butanol was 280,000 tons in 2000, of which 167,000 tons had to be imported. However, the amount of butanol required increased to 520,000 tons in 2005 and the annual productivity of synthetic butanol reached 500,000 tons, leading to a balance between supply and demand.

Strains

All ABE plants employed *Clostridium acetobutylicum* isolated locally, such as *C. acetobutylicum* AS 1.70 by the Institute of Microbiology, and phage-resistant culture *C. acetobutylicum* No. 2 by the Shanghai Solvent Plant. All these cultures were suitable for starch feedstocks, such as corn, cassava, potato, and sweet potato, with a total solvent yield amounting to 35–37% of starch and a solvent

ratio of A:B:E = 3:6:1, $\text{CO}_2\text{:H}_2$ = 60:40 by volume. At the Shanghai Institute of Plant Physiology and Ecology, Zhang et al. [1996, 1997] isolated hyper-butanol cultures of *C. acetobutylicum* EA2018 and EA2019; their butanol yield reached 70% of the total solvents. Results from 100-ton fermenters in the continuous process showed that the butanol ratio and starch conversion rates were 10 and 5% higher than the traditional cultures respectively. In addition, these hyper-butanol strains could utilize corn/potato chips (20%) or corn/sorghum (20–50%) mixtures efficiently.

On the other hand, some solvent plants based on molasses, abundant in Guangxi Province, used culture CLS004 to ferment this feedstock for solvent production. Application of enzymatic hydrolysates of vegetable wastes and rice straw for ABE fermentation with *C. butanolaceticus* GV (guard-Vim) or *C. acetobutylicum* C375 has been studied [Sun, 1990; Chen et al., 1998].

Fermentation Technology

Continuous Process

As mentioned above, the ABE industry in China was started in the early 1950s at Shanghai Solvent Plant, Pudong, Shanghai, by batch fermentation. Owing to the rapid expansion of the chemical industry and penicillin production, a study to boost the national ABE industry was started in 1958. Through investigation, the continuous process for solvent fermentation was successfully developed, in spite of classical literature opposing it [Chiao et al., 1960, 1964].

We started with a 5-liter laboratory fermenter system running continuously with 8% corn mash. Through a series of experiments, the optimal dilution rate for growth and acid production was found to be 0.5. The operation could be continued up to ca. 150 h, and then solvent production declined and cell morphology showed long threads. The incorporation of stillage up to 20%, as used by classical practice, reverted these abnormalities and the operation could be prolonged to ca. 200 h. The fermentation cycle was reduced to ca. 20 h. The successful results were transferred to serial 100-ton fermenters with similar results. For example, in one of the production tank experiments, the dilution rate was as follows: 0.5–0.25–0.25–0.25, the total retention time was $2 + 4 + 4 + 4 = 14$ h. The productivity was 2.3 times that of the batch process. Similar results were obtained in parallel experiments. The chief difficulty encountered was contamination. Whenever contamination was detected, fresh mash flow was

immediately stopped and new serial fermenters were connected and started. Seed tanks were always ready if needed. Contamination in the end fermenters did not cause serious loss in solvent production. The experience with the 100-ton fermenters was rapidly adapted to the newly-built 200-ton fermenters of that plant and transferred to other plants all over China.

Immobilization

Immobilized cell techniques for solvent fermentation have been studied [Sun et al., 1987, 1988; Fan et al., 1993]. Sun et al. [1987, 1988] reported the preparation of immobilized cells of *C. acetobutylicum* AS 1.70 absorbed by ceramic rings and its application in the acetone-butanol production. The average solvent concentration obtained after 20 repeated batch cultures for 60 days was 10.93 g/l, the average yield efficiency of starch was 30.6%. In a three-stage continuous system with a packed column reactor (5.18 l), the maximal concentration of total solvents from 8% corn mash reached 21.9 g/l. The productivity and the conversion efficiency of starch for the duration of 90 days was 24.73 g/l-day and 40.5%, respectively. However, this process has not been tested on a large scale yet.

Future Perspective of the ABE Industry in China

It is only recently that the whole situation has come to a turning point. Due to the recent increased price for petroleum and the global shortage of energy resources, the Chinese national authority began to look for renewable resources. China is an agricultural country and there is a plentiful supply of various kinds of biomass. Some old ABE plants have started to restore the fermentation production again and biotechnological enterprises are planning to establish new plants. Scientists of various institutions are actively engaged in genetic engineering to modify traditional cultures. Judging from these trends, a new era of ABE fermentation will be introduced in the near future in China. One thing for sure is that the continuous technology will play a major role in the revival of the ABE industry.

Acknowledgement

Sincere thanks to Prof. Y.-L. Yang for his help in writing this review.

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