Chapter 15
Cereal Vinegars Made by Solid-State Fermentation in China

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15.1 Introduction

In China there is a proverb saying that, in daily life, the seven indispensable substances are firewood, rice, edible oil, salt, sauce, vinegar and tea. From this proverb, we can see the vinegar has a very important position in Chinese daily life. In the historical literature, we find that vinegar originated more than 3000 years ago in China. It is reported that the first written mention of vinegar was in 1058 BC in a book named *Zhou Li* about the rites of the Zhou Dynasty, and a professional workshop for vinegar making appeared in the Chunqiu Dynasty (770-476 BC) (Zhao, 2004; Hu, 2005; Zhao and Li, 2005; Shen, 2007). At that time, vinegar was so costly that only the rich noblemen could afford it. Vinegar first became popular with ordinary people in the Donghan Dynasty (25-220 AD) (Shen, 2007). Up until the Northern and Southern Dynasties (420-581 AD), a book named *Qi Ming Yao Shu*, about the essential techniques of farming, written by Sixie Jia, recorded in detail 23 different methods for brewing vinegars (Zhao, 2004; Hu, 2005).

Besides a seasoning, vinegar is regarded as a herbal medicine in China. In the book, *Compendium of Materia Medica*, written by Shizhen Li in 1857, the medicinal functions of vinegar were described as dissipating blood stasis, treating the diseases of jaundice and yellow sweat, improving appetite and nourishing the liver (Qin and Wu, 2001; Zhao, 2004; Hu, 2005). In the *Dictionary of Chinese Medicine*, it was also stated that vinegar had a curative effect for acute and chronic hepatitis (Qin and Wu, 2001).

There are many legends in China about the origins of vinegar. For example, Zhenjiang aromatic vinegar, one of the famous China-style vinegars, was invented by Heita, the son of Dukang, who was considered to be the inventor of rice wine in China (Shen, 2007). One day, after Heita had prepared rice wine, he put it aside. Twenty-one days later, when he remembered it, the wine had become a sour liquid. As soon as he tasted it, he was aware that the sour rice wine could be used as a seasoning with a concordance of sourness and sweetness. Gradually, the sour rice wine was used in cooking and was named vinegar.

L. Solieri, P. Giudici (eds), *Vinegars of the World*

Nowadays, in Chinese markets, there are more than 20 types of homemade vinegars, most of which are brewed with starchy materials such as rice, sorghum, corn (maize), barley and wheat, even though there are now also some fruit vinegars and fruit vinegar drinks which have been available since the early 1990s (Liu et al., 2004; Ma, 2005). Traditional Chinese vinegars are therefore also called cereal vinegars. Among these, the most famous Chinese vinegars are Shanxi aged vinegar, Zhenjiang aromatic vinegar, Sichuan bran vinegar and Fujian *Monascus* vinegar, respectively using sorghum, sticky rice, wheat bran and red yeast rice as the main raw materials or the starter (Chen, 1999a; Huang and Cai, 1998; Liu et al., 2004). These vinegars are also highly prized as four famous China-style vinegars due to their unique flavour, long production history, massive yields and characteristic fermentation processes, and are described in detail in Section 15.5. Besides their raw materials, Chinese vinegars can be classified into different groups according to their colour, their special flavour and their production processes; such as black (brown) vinegar, red vinegar, white vinegar, smoky vinegar, herbal vinegar, and so on.

In this chapter, we describe the general process, the raw materials, and the main microorganisms for brewing cereal vinegars, as well as four famous China-style vinegars. We also cover the analysis of cereal vinegars.

15.2 Solid-State Fermentation Process for Cereal Vinegars

Chinese cereal vinegars may be brewed either by a solid-state fermentation (SSF) process or a liquid-state fermentation (LSF) process, although most of them, especially the traditional Chinese vinegars, are produced by a SSF process (Chen, 1999a; Huang and Cai, 1998; Liu et al., 2004). SSF refers to the growth of the microorganisms on moist solid substrates without or in the near absence of free-flowing water (Liu et al., 2004). SSF has been widely used since ancient times in the oriental food industry in China to produce vinegar, as well as distilled spirits, rice wine, soy sauce, fermented soy bean curd, and other local fermented foods. In recent years, SSF has shown much promise in the development of several bioprocessing end-products, such as industrial enzymes and metabolites (Wang and Yang, 2006). Compared with LSF, also called ‘submerged fermentation’, SSF is considered to be a more suitable and useful technique for the production of food and industrial goods, due to its low technology and energy requirements, its use of cheap unrefined agricultural products as substrates, its moderate capital investment and operating costs, high productivity in a low reactor volume, and less stringent aseptic processing methods (Liu et al., 2004).

15.2.1 SSF Flowchart for Cereal Vinegars

Although SSF is complex, uncertain and empirical for the different sorts of fermented foods, its general scheme in cereal vinegar preparation includes the following five stages.

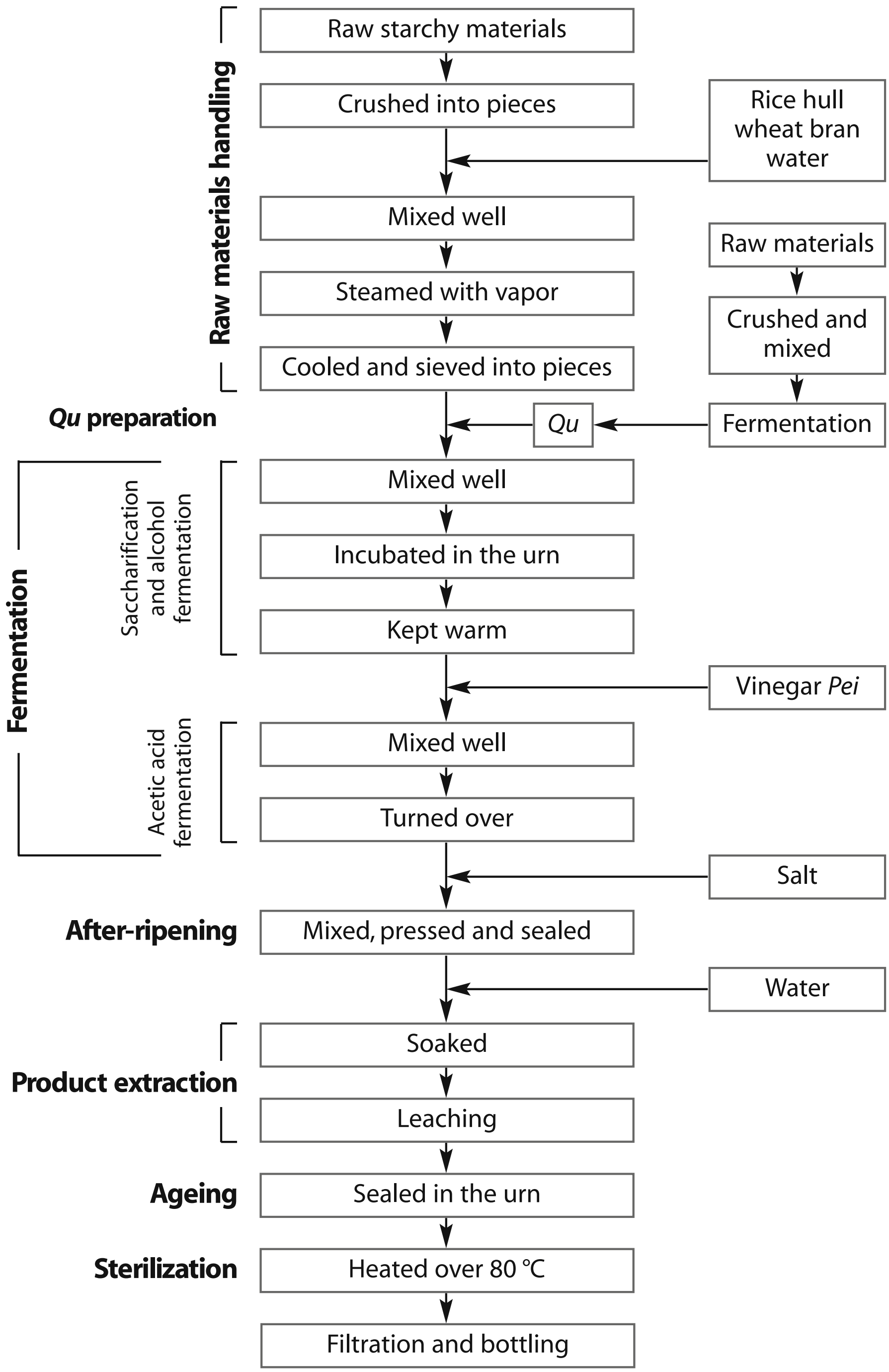

Figure 15.1 Flowchart of a general SSF process for cereal vinegars

- Starter (called *Qu* in Chinese) preparation, during which the dominant microorganisms are enriched by choosing the raw materials and controlling the cultural conditions.
- Saccharification and alcohol fermentation, during which the dominant microorganisms, such as moulds and yeasts from the starter, grow in fermentation substrates to hydrolyse starch into sugar and convert sugar to ethanol.
- Acetic acid fermentation, during which ethanol is fermented into acetic acid by acetic acid bacteria.
- Leaching vinegar, during which the final products are dissolved from fermented materials (called *Pei* in Chinese).
- After-ripening or ageing, during which the flavour components are formed (Huang and Cai, 1998; Chen, 1999a; Liu et al., 2004).

Figure 15.1 shows a generalized flowchart for cereal vinegar production by the SSF process.

15.2.2 Qu Preparation

Qu (*koji* in Japanese) is the starter used in SSF, which is made from grains such as rice, sorghum, wheat, barley, and beans such as peas and soy beans, in a loose form or various pressed forms. Microorganisms from the raw materials, water and

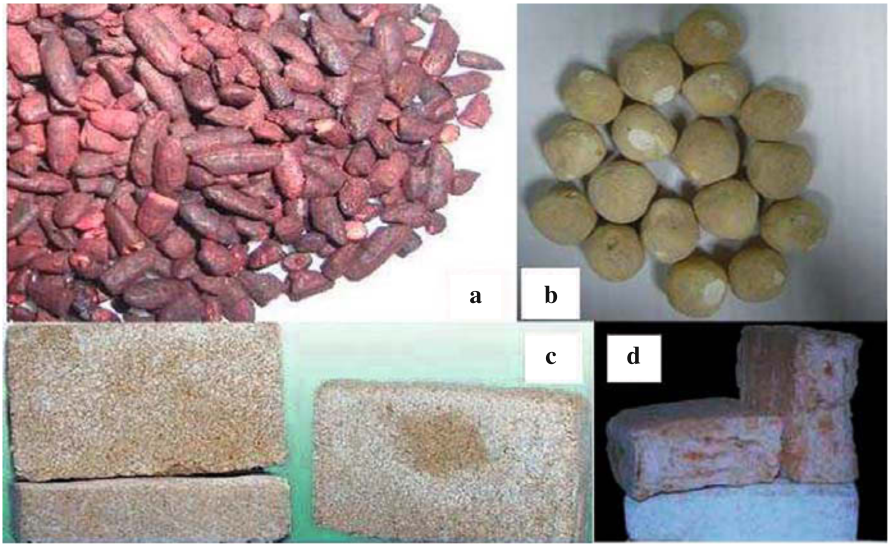

Figure 15.2 Some kinds of Qu in China: **a** Hong Qu, also called red yeast rice; **b** Xiao Qu, made of rice and rice chaff in an egg-shaped form; **c** Da Qu, made of barley, wheat and peas, looks like a brick; **d** Da Qu, with a red core, used especially for Shanxi aged vinegar production

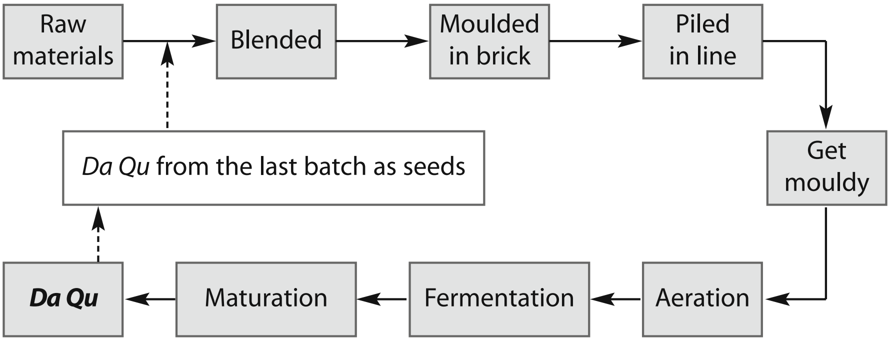

Figure 15.3 Typical flowchart for Da Qu preparation

atmosphere, including moulds, yeasts and bacteria, grow on/in it spontaneously. The dominant microorganisms can be enriched by controlling the temperature, moisture and air content in a Qu preparation house (called *Qu Fang* in Chinese). The main microorganisms in Qu are moulds of the genera *Aspergillus*, *Rhizopus* and *Monascus*, yeasts of the genus *Saccharomyces*, as well as lactic acid bacteria. Besides microorganisms, Qu contains more than 50 types of enzymes produced by microbial cells, including α-amylase, glucoamylase, acid protease and lipase (Steinkraus, 2004).

There are several kinds of Qu in China, namely *Mai Qu*, *Xiao Qu*, *Da Qu*, *Hong Qu* and *Fu Qu* (Huang and Cai, 1998; Chen, 1999a); some of them are shown in Figure 15.2. Mai Qu, originating in the north of China, is made with wheat in brick-shaped form and its main microbe is *Aspergillus* spp. Xiao Qu is produced in the south of China and is made with rice and rice chaff in an egg-shaped form and its main microbe is *Rhizopus* spp. Da Qu is derived from Mai Qu and also looks like a brick. It is made of barley, wheat and peas, and the dominant microbes are *Mucor* spp. and *Rhizopus* spp. Hong Qu, also called red yeast rice or red fermented rice, is made of rice in a loose form and the main microorganism is *Monascus* spp. Fu Qu, which has just been developed recently, is made of wheat bran by inoculating a pure culture of *Aspergillus* spp.

Figure 15.3 outlines a typical flowchart for Da Qu preparation.

15.2.3 Raw Materials Handling

Normally, the starchy raw materials, such as corn (maize), wheat and barley, are crushed into pieces to expand the area in contact with microorganisms and to utilize the components of the raw materials effectively. After being soaked in water for about 12 h in summer, or 24 h in winter, the materials are steamed with vapour to turn the starch granules into a sol-shaped form to make the starch hydrolyse more easily. In addition, the raw materials are partly sterilized during steaming (Chen, 1999a).

15.2.4 Saccharification and Alcohol Fermentation

After the steamed materials have been cooled and sieved into pieces (Figure 15.1), they are mixed with Qu powder, and put into a ceramic urn with a rice hull or rice straw cover to keep warm. Starch is immediately hydrolysed by enzymes and microbes from Qu to produce saccharified mash. Simultaneously, as alcohol fermentation starts, the temperature in the urn is increased. In order to keep the temperature at about 28 °C, the mixture of raw materials and Qu – also called *Pei* in Chinese – is transferred into another empty urn once a day to decrease the temperature and, meanwhile, to improve the air content and reduce the evaporation of ethanol in Pei. Normally, after 2-3 days, the temperature gradually decreases. The simultaneous reactions of saccharification and alcohol production take about 5 days (Huang and Cai, 1998; Chen, 1999a).

15.2.5 Acetic Acid Fermentation

After alcohol fermentation, vinegar 'seeds', which come from the last batch of vinegar Pei, are added into the urn and mixed well with some coarse rice hull, which is used to increase the porosity for oxygen uptake and heat discharge. With sufficient oxygen, acetic acid bacteria grow and metabolize rapidly, producing a large amount of acetic acid, which inhibits mould and yeast growth at 1-2% content. During this phase, the temperature in the urn should be stabilized at 38-40 °C by turning over and pressing the vinegar Pei to reduce oxygen supply and decrease the rate of ethanol consumption and heat production. Normally, vinegar Pei is turned over once a day, and this stage lasts at least 12 days (Huang and Cai, 1998; Chen, 1999a).

15.2.6 Adding Salt

Salt has the ability to strongly inhibit acetic acid bacteria at more than 1% concentration (Miao and Ma, 2006). So, at the end of acetic acid fermentation, salt at 2-5% of vinegar Pei weight is added into the urn and mixed with vinegar Pei to prevent the oxidization of acetic acid to carbon dioxide and the production of off-flavours (Chen, 1999a). Moreover, salt can modify the flavour and taste of the finished cereal vinegars.

15.2.7 After-ripening

After adding salt, the vinegar Pei should be kept in the urn for several days for esterification and further oxidization of ethanol to acetic acid (Shen, 2007). This step is named after-ripening, which promotes the aroma and colour of the vinegar.

15.2.8 Leaching Vinegar

Leaching vinegar is the progress of adding water to vinegar Pei to dissolve out any soluble components such as acids, amino acids, sugar and other metabolites. The leached solution is called 'fresh vinegar'. Normally, vinegar Pei should be leached three times (Chen, 1999a; Shen, 2007). The fresh vinegar leached for the first time is called first-level vinegar; at the second time, it is named second-level vinegar; and at the last time, it is called third-level vinegar. In practice, the second-level vinegar is used to soak vinegar Pei to obtain the first-level vinegar, the remaining solid is soaked with the third-level vinegar to get the second-level vinegar and, after that, water is used to immerse the residue to get the third-level vinegar. Figure 15.4 shows a typical flowchart for leaching vinegar.

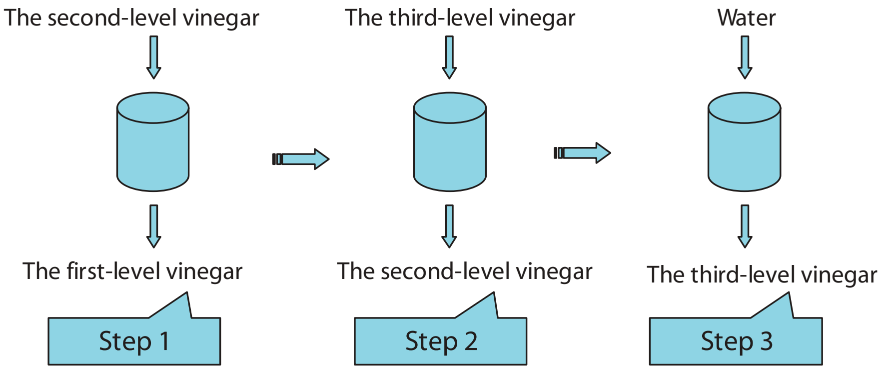

Figure 15.4 Typical flowchart for leaching vinegar

15.2.9 Ageing

Ageing is a kind of storage and ripening progress, during which many flavour substances of vinegar can be formed by chemical reactions. There are two general ways in which the cereal vinegars can be aged: one is to age the vinegar in sealed or open ceramic urns for several months or years; the other is to age the vinegar Pei, which is deposited for several months after adding salt and before leaching vinegar, and subsequently to age the fresh vinegar (Shen, 2007). After ageing, vinegar will take on a bright colour and lustre and a scented mellow flavour.

15.2.10 Sterilization and Packaging of Finished Products

After the concentrations of acetic acid and other components in the aged vinegar have been adjusted, the vinegar should be heated to over 80 °C for sterilization before filtering and packaging (Chen, 1999a).

15.3 Raw Materials of Cereal Vinegars

15.3.1 Main Raw Materials

The main raw materials of cereal vinegars are grains, such as rice in the south of China, and sorghum in the north of China.

Recently, other starchy materials, such as barley, corn (maize), wheat, potato, sweet potato, cassava and so on, have been used as the main materials of vinegar (Huang and Cai, 1998; Chen, 1999a) (Table 15.1).

Table 15.1 Composition of raw materials employed in cereal vinegar production (%)

Materials	Carbohydrate	Protein	Lipid	Moisture
Sticky rice	69-73	5-8	2.4-3.2	13-15
Sorghum	62-68	8-15	3-5	10-14
Barley	58-65	12-18	1.8-3.7	10-12
Wheat	66.4	13	1.5	14.4
Corn (maize)	62-70	8-16	3-5.9	11-19
Potato	68.5	3.8	–	12.8
Sweet potato	65-75	6	0.5	12
Cassava	67-72	3-9.5	0.9-1.3	14

–, not detected.

Adapted from: Huang and Cai, 1998; Chen, 1999b

15.3.2 Supplementary and Filling Materials

Besides the main materials, many supplementary materials, including rice bran, wheat bran, soybean meal and peas are included in cereal vinegar production (Huang and Cai, 1998; Chen, 1999a). They do not only contain a certain amount of carbohydrates, but also proteins and minerals, which can provide nutrients for the microorganisms during brewing and increase the amino acid and mineral contents of the vinegar. Additionally, supplementary materials also play important roles in absorbing water, loosening vinegar Pei and storing air. In the SSF process of vinegar production, some filling materials, such as rice hulls, sorghum hulls, cornstalks, corn cores and so on, are used to loosen vinegar Pei and improve air content, which is good for the acetic acid bacteria in aerobic fermentation.

15.3.3 Other Materials

Other materials, including salt, sugar, parched rice and some spices, are added to the cereal vinegar to adjust the colour, improve the flavour, and modify the taste (Huang and Cai, 1998; Chen, 1999a). Salt is a very important additive for cereal vinegar. When the vinegar Pei is fermented to a certain extent, salt is put into the urn to restrain the acetic acid bacteria and prevent decomposition of acetic acid. Salt also plays a role in reconciling vinegar flavour and inhibiting pathogenic bacteria growth (Miao and Ma, 2006).

Normally, sugar such as sucrose is added to the vinegar to increase sweetness and thickness. Some spices, such as ginger, garlic, cloves and fennel, are included in order to produce characteristically flavoured vinegars (Li et al., 2004). For Zhenjiang aromatic vinegar, the parched rice is used to improve colour and modify flavour (Shen, 2007).

15.4 Main Microorganisms

The microorganisms involved in cereal vinegar production by SSF include moulds, yeasts and bacteria. Nowadays, some manufacturers use pure cultures of microbes to brew vinegar in China, but the traditional method of vinegar brewing still uses spontaneous and mixed culture fermentation in the majority of vinegar factories (Huang and Cai, 1998; Chen, 1999a; Liu et al., 2004).

15.4.1 Moulds

Qu is the main source of moulds to brew cereal vinegars. The dominant moulds depend on the type of Qu (Huang and Cai, 1998; Chen, 1999a). For example, in Da Qu for brewing Shanxi aged vinegar, *Mucor* spp. and *Absidia* spp. are the main moulds, while *Rhizopus* spp. and *Aspergillus* spp. are present to a lesser extent, and *Monascus* spp. is in the minority (Wu, 2004) (Table 15.2).

Moulds can secrete an abundance of enzymes such as amylase, glucoamylase, protease, lipase, tanninase and so on, which play important roles in hydrolysing macromolecule substances, like starch and protein, to small molecular substances like dextrin, glucose, peptides and amino acids, which provide nutritional sources for yeasts during the ethanol fermentation (Figure 15.1) (Huang and Cai, 1998; Chen, 1999a).

Table 15.2 Amount of the main mould in Da Qu[a] for Shanxi aged vinegar, expressed as cfu/g Da Qu

Sampling parts of Da Qu	*Mucor* spp.	*Absidia* spp.	*Rhizopus* spp.	*Aspergillus* spp.	*Monascus* spp.
On the surfaces	2.23×10^8	2.10×10^8	4.02×10^7	7.32×10^7	ng
At edges and corners	3.72×10^8	2.84×10^8	8.24×10^7	1.00×10^7	ng
In the core	1.41×10^8	3.27×10^7	1.28×10^7	8.00×10^6	3.10×10^6

[a] Da Qu refers to the starter prepared with barley, wheat and peas, which looks like a brick. When brewing cereal vinegar, it should be milled into powder and mixed with the raw materials.

ng, not grown.

Adapted from Wu, 2004

15.4.2 Yeasts

Saccharomyces cerevisiae, *Hansenula anomala* and *Candida berkhout* are the main yeasts in the alcohol fermentation during vinegar brewing (Mao, 1998; Chen, 1999a; Wu, 2004). Sugar turns into alcohol and carbon dioxide mainly by the yeast glycolysis pathway. After the alcoholic fermentation, yeast cells remaining in the vinegar Pei can undergo autolysis, which provides nutritional material to support the growth of acetic acid bacteria.

15.4.3 Bacteria

Acetic acid bacteria are the main bacteria at the stage of acetic acid fermentation, which oxidizes ethanol into acetic acid. Several species of acetic acid bacteria are present in SSF of cereal vinegars, such as *Acetobacter pasteurianus*, *A. aceti*, *A. liquefaciens*, *A. rancens*, *A. hansenii*, *A. xylinum* and *Gluconobacter* spp. (Mao, 1998; Hu and Hao, 2004; see chapter 3 for the up to date AAB classification).

Lactic acid bacteria, mainly belonging to the genus *Lactobacillus*, contribute a great deal to the content of lactic acid in the vinegar, which can moderate the irritating sour smell and promote a soft taste of the vinegar. Wu (2004) reported that 70-90% of non-volatile acids in some Chinese traditional vinegars was lactic acid.

Bacillus spp. is a group of aerobic microorganisms which can occur in cereal vinegar. They produce organic acids, such as citric acid, succinic acid and malic acid, through the tricarboxylic acid cycle pathway (Wu, 2004). These organic acids can modify the irritating sour taste caused by a high concentration of acetic acid and create a softer taste. Moreover, the high activity of protease produced by *Bacillus* spp. can digest proteins into amino acids, which play an important role in the taste and colour of the vinegar (Wu, 2004).

15.5 Four Famous China-Style Vinegars

Chinese vinegars have specific local features. Every region has its own vinegar factories depending on particular raw materials, local climate and a specific production process (Liu et al., 2004; Zhao and Li, 2005). Consequently, each type of vinegar has its own taste, flavour and market. In China, there are more than 20 types of homemade vinegar on the market (Liu et al., 2004). Among these vinegars, Shanxi aged vinegar, Zhenjiang aromatic vinegar, Sichuan bran vinegar and Fujian *Monascus* vinegar are well-known as four famous traditional Chinese vinegars, whose geographical distribution is shown in Figure 15.5.

15.5.1 Shanxi Aged Vinegar

Although vinegars in Shanxi province can be traced to 479 BC, the traditional brewing technique for Shanxi aged vinegar was created in 1368 in the workshop called

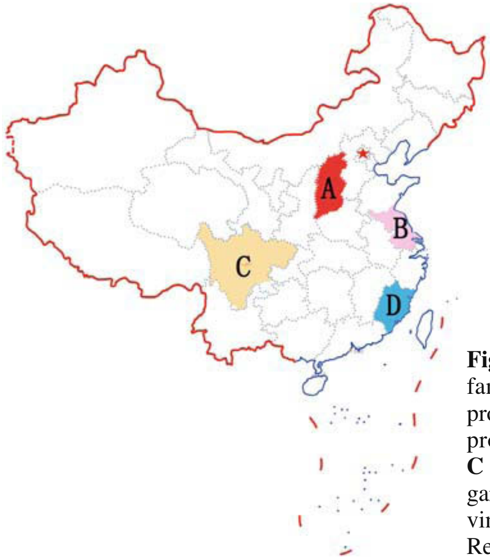

Figure 15.5 Original locations of four famous China-style vinegars: **A** Shanxi province (Shanxi aged vinegar); **B** Jiangsu province (Zhenjiang aromatic vinegar); **C** Sichuan province (Baoning herbal vinegar); **D** Fujian province (Fujian *Monascus* vinegar); ★ Beijing, the capital of People's Republic of China

Mei He Ju in Qingxu county (Wang and Chen, 2004; Hu, 2005;Yan et al., 2006). Nowadays, the traditional brewing technique has been developed successfully by the Shanxi Aged Vinegar Group Co., which is the authority for Shanxi aged vinegar.

Unlike Zhenjiang aromatic vinegar (see Section 15.5.2), the raw materials for brewing Shanxi aged vinegar are sorghum, wheat bran, barley and pea. Among these grain materials, barley and pea are mainly used to make Da Qu with a red core (Figure 15.2), which is a source of enzymes and microbes specially tailored for Shanxi aged vinegar (Wang, 1999; Wang and Chen, 2004). During brewing, the ratio of Da Qu to sorghum, the main raw material, is up to 0.6 : 1, while the dosage of Xiao Qu or Mai Qu for other Chinese vinegars is usually less than one-tenth of the raw materials (Huang and Cai, 1998; Yan and Yan, 2003). The large amount of Da Qu used in the vinegar brewing process contributes a great deal to the complex flavours and nutrient components of Shanxi aged vinegar. Therefore the quality of Da Qu has an important effect on the quality of the vinegar. It is often said that Da Qu is the soul of Shanxi aged vinegar.

Besides the raw materials, the brewing process of Shanxi aged vinegar has some distinct characteristics (Huang and Cai, 1998; Yan and Yan, 2003; Wang and Chen, 2004). For example, after acetic acid fermentation (Figure 15.1), the vinegar Pei is taken out and put into another urn once a day , and its temperature is gradually heated to 80-90 °C on the third day by a moderate fire, and then decreased to about 50 °C on the sixth day. As a result, the vinegar Pei turns from yellow to brown in colour, and takes on a distinctive smoky flavour. This special process can greatly improve the quality of Shanxi aged vinegar with regard to colour, fragrance, lustre and taste.

Another important step in Shanxi aged vinegar production is the ageing. As mentioned above (see Section 15.2.9), there are two traditional vinegar ageing methods

Figure 15.6 Two ageing methods for the traditional vinegar production in China: **a** fresh vinegar is put into open urns in an open room for at least 1 year; **b** ageing vinegar Pei by mixing mature vinegar Pei with salt and covering with plastic sheet to keep for 1-3 months before vinegar leaching; **c** ageing the vinegar – after leaching, the fresh vinegar is sealed in ceramic urns for several months or years

in China. The first is just to age the vinegar; the other is to age both vinegar Pei and vinegar. Shanxi aged vinegar belongs to the first category, while Zhenjiang aromatic vinegar belongs to the second (Figure 15.6). The fresh vinegar is put into an open urn in an open room for at least one year. In summer, exposure of the urn to the sun causes intense vaporization, whilst in winter, ice in the urn is removed. As a result, the volume of vinegar decreases to one-third of its original amount, the concentrations of soluble solid and non-volatile acids increase, esterification of acids and alcohols occurs greatly, while the content of volatile acids reduces (Yan and Yan, 2003; Wang and Chen, 2004). Finally, Shanxi aged vinegar with an excellent flavour, good mouth-feel and mild acidity, is obtained.

15.5.2 Zhenjiang Aromatic Vinegar

Zhenjiang aromatic vinegar can be traced back as far as 1400 years ago in the city of Zhenjiang, located in the eastern coastal province of Jiangsu. Nowadays, the most famous corporation producing Zhenjiang aromatic vinegar is Jiangsu Hengshun Vinegar Industry Co., which was established in 1840 (Shen, 2007).

In the brewing process, the traditional brewing technique for Zhenjiang aromatic vinegar embodies the quintessence of brewing Chinese spirit (Bao, 2000). Both Xiao Qu and Mai Qu are used for brewing this kind of vinegar, whereas only one kind of Qu is applied in the brewing of other vinegars. During the saccharification and alcohol fermentation, Xiao Qu powder, about 0.4% of the rice weight, is added and mixed with the steamed rice, and the mixture is kept for about 48 h at about 30 °C. Then Da Qu powder, about 6% of the rice weight, and water, 1.5 times the weight of the rice, are poured into the urn and mixed. After that, the mixture solution (called *Lao* in Chinese) is kept for about 5 days at approximately 28 °C for the saccharification and alcohol fermentation.

In Xiao Qu, which is made with rice, the main microbes are *Rhizopus* spp. and yeasts, while in Mai Qu, which is made of wheat, barley and pea, the dominant microbes are *Aspergillus* spp. The combined use of Xiao Qu and Mai Qu contributes a large amount to the flavour substances of the vinegar, including amino acids and organic acids, and makes the saccharification and alcohol fermentation more efficient, due to the mix of microbes and hydrolytic enzymes from both sorts of Qu.

In Zhenjiang aromatic vinegar production, a multilayer SSF is employed (Huang and Cai, 1998; Liu et al., 2004; Shen, 2007). A vinegar Pei mixture of wheat bran, rice hull, alcoholic solution (obtained from the saccharification and alcohol fermentation), and vinegar seed from last batch of vinegar Pei, is poured into an urn to half-fill it, and is kept warm with a rice straw cover for 2-3 days in summer or 5-6 days in winter. When the temperature in the top layer of the mixture reaches 45-46 °C, some rice hull is added and mixed. After that, once a day, another batch of rice hull is put into the urn and mixed with the vinegar Pei for about 10 days until the vinegar Pei fills the urn. Finally, the whole vinegar Pei is turned over into another urn and kept for about 7 days to obtain the mature vinegar Pei, which is then mixed with salt and covered with a plastic sheet to store for 1-3 months to age before leaching the vinegar (Figure 15.6).

Another distinctive feature of brewing Zhenjiang aromatic vinegar is the use of parched rice as a colourant to increase the vinegar's colour and lustre (Huang and Cai, 1998; Shen, 2007). Non-glutinous rice is parched in a heated wok until the colour of the rice is coal black. Then water is added to the parched rice and it is cooked for 15 min; the filtrate is added to the vinegar to modify its colour and flavour during the leaching phase.

15.5.3 Sichuan Bran Vinegar

In Sichuan province, vinegars are mainly brewed with wheat bran, and Baoning herbal vinegar is the most famous one (Huang and Cai, 1998). According to historical records, Baoning herbal vinegar originated in Langzhong City in 1618, where the history of vinegar brewing is longer than 2000 years (Chen, 1999b). Up until now, Sichuan Baoning Vinegar Co., has been the only company authorized to produce the traditional Baoning herbal vinegar (Chen, 1999b; Liu, 2003).

Sichuan bran vinegars, and especially Baoning herbal vinegar, are the only medicinal vinegars among the four famous China-style vinegars, and this is due to the use of 60 kinds of Chinese traditional herbs, such as eucommia bark (*Eucommia ulmoide*), villous amomum fruit (*Amomum villosum*) and licorice roots (*Glycyrrhiza glabra*), in Qu preparation. Some compounds from the medicinal herbs, such as polyphenol and flavone, can affect the microbial composition in Qu preparation through the inhibition of some bacteria such as lactic acid bacteria, while promoting some fungi, such as *Rhizopus* spp. and *Aspergillus* spp., and also make an important contribution to the special flavour of the vinegar (Shang, 2003).

As a kind of bran vinegar, the ratio of wheat bran to rice used for brewing is high – up to 25:1 – while it is only about 2:1 for Zhenjiang aromatic vinegar (Huang and Cai, 1998; Shang, 2003). As no rice hull is added, wheat bran also serves as a filling material. After inoculating with herbal Qu, the mixed materials are put loosely into a wooden trough 2.4 m long, 1.25 m wide and 0.7 m deep, rather than into an urn (Huang and Cai, 1998). In the trough, saccharification, alcohol fermentation and acetification take place in sequence. The air content and temperature in vinegar Pei are controlled by turning. Then the mature vinegar Pei in the wooden troughs is pressed into the urns and covered with a 3 cm-thick layer of salt on the surface to age for at least 1 year.

15.5.4 Fujian *Monascus* Vinegar

Fujian province is well known for red yeast rice produced by *Monascus* spp. The application of red yeast rice in vinegar was prevalent in Yongchun county during the early years of the North Song Dynasty (960-1125 AD), according to ancient records. Thus, Fujian *Monascus* vinegar is also referred as Yongchun *Monascus* vinegar, which gets its name from the red yeast rice and the producing area. In the past, Fujian *Monascus* vinegar was brewed in the traditional way, with the method being handed down from generation to generation. In 1955, the first vinegar plant, the Yongchun brewing plant, was established, which contributed a great deal to the industrial production of Fujian *Monascus* vinegar.

Red yeast rice, especially *Gutian Hong Qu*, is used as the saccharifying agent, owing to the large quantities of hydrolytic enzymes, such as α-amylase, β-amylase, glucoamylase, protease and lipase, produced by *Monascus* spp. during Fujian *Monascus* vinegar brewing (Huang and Cai, 1998; Yuan, 2000; Bao, 2001). Sesame and white sugar are used to improve the flavour of the vinegar.

Unlike other traditional Chinese vinegars brewed by SSF, Fujian *Monascus* vinegar is brewed from sticky rice by LSF (Huang and Cai, 1998; Yan, 2004). Neither wheat bran nor rice hull is used during brewing Fujian *Monascus* vinegar. At the end of the alcohol fermentation, red rice wine with a high ethanol and amino acid concentration is put into the first urn at half volume with 1-year-old vinegar, and mixed well. One year later, a half volume of vinegar from the first urn is poured into the second urn with a half volume of 2-year-old vinegar. One year later, a half volume of vinegar from the second urn is poured into the third urn with a half volume of 3-year-old vinegar, and kept for one more year. Therefore, the Fujian *Monascus* vinegar is at least 3 years old when it is taken out as a commercial product (Huang and Cai, 1998).

15.6 Analysis of Cereal Vinegars

The Chinese government has been concerned about the safety and quality of foods, including vinegars, of which more than 3.2 million litres are consumed every day in China. The hygienic standards for the vinegars in China have been revised four times since the first national hygienic standard of vinegar (GBn5-1977) was published in 1977. Tables 15.3 and 15.4 show the recent national hygiene standards for vinegar (GB2719-2003), in which the contents of free mineral acids, arsenic, lead, aflatoxin B_1 and the number of total plate colony, coliform group and pathogens such as *Salmonella* spp., *Shigella* spp. and *Staphylococcus aureus* are strictly limited. Methods of analysis for the hygiene standard of vinegar were also published in GB/T 5009.41-2003.

Table 15.3 Physical and chemical indexes required by Vinegar Hygiene Standard GB2719-2003

Item	Index
Free mineral acids	Not to be found
Total arsenic (counted with As), mg/L	≤ 0.5
Lead, mg/L	≤ 1
Aflatoxin B_1, μg/L	≤ 5

Table 15.4 Microbial indexes required by Vinegar Hygiene Standard GB2719-2003

Item	Index
Total plate colony (cfu/mL)	≤ 10,000
Coliform group (MPN/100 mL)	≤ 3
Pathogenic bacteria (*Salmonella* spp., *Shigella* spp. and *Staphylococcus aureus*)	Not to be found

Besides the hygiene standards, the quality standards of fermented vinegar have also recently been modified in GB18187-2000. According to the standards, the quality of fermented vinegar should be analysed for colour, fragrance, taste and body, as well as for the contents of total acids, non-volatile acids and soluble solids. The parameters for the sensorial properties and physico-chemical indexes of fermented vinegar are listed in Tables 15.5 and 15.6.

With regard to studies on qualities and flavours of cereal vinegars, Zhang et al. (2006, 2008) have recently established a gas-sensing fingerprint database of Chinese vinegars through the use of an 'electronic nose' which they used to analyse 17 different commercial Chinese vinegars. Liu et al. (2005) analysed the flavour

Table 15.5 Organoleptic properties of fermented vinegar required by GB18187-2000

	Requirement	
Item	**SSF vinegar**	**LSF vinegar**
Colour and lustre	Amber or reddish brown	Depending on special requirements of the products
Fragrance	The unique aroma of solid-state fermentation vinegar	Depending on special requirements of the products
Taste	Softly sour, long aftertaste, no foreign odour	Softly sour, no foreign odour
Body state	Clarification	

Table 15.6 Physical and chemical indexes of fermented vinegar, according to GB18187-2000

Item	Index	
	SSF vinegar	LSF vinegar
Total acids (counted with acetic acid, g/100 mL)	3.50	3.50
Non-volatile acids (counted with lactic acid, g/100 mL)	0.50	–[a]
Soluble solids without salt (g/100 mL)	1.00	0.50

[a] Contents of non-volatile acids in LSF vinegar are without requirements.

compounds of cereal vinegars by HS-SPME-GC-MS and found more than 130 kinds of trace ingredients, including alcohols, aldehydes and phenols; the particular compound and their proportions being dependent on the kind of vinegar analysed.

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