Progress in comprehensive development and utilization of pecan resources

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Abstract. The pecan (Carya illinoinensis) is one of the most important woody oil and dried fruit trees in the world. The kernels, peels, husks, inflorescences, leaves, etc. of pecans have many industrial values and are widely used in industrial fields such as chemicals, medicines, pesticides, additives, and vegetable proteins. This article reviews the current process and utilization status of pecans and their nutritional value, including the kernels, skins, shells, inflorescences, leaves, etc. of pecans with shells, and puts forward relevant suggestions for problems in development.

1. Introduction

Carya illinoinensis K. Koch, also known as pecan, is a deciduous tree of the genus Pecan in the Juglans family. It is one of the world-famous woody oil and dried fruit species. Its nuts are not only high-quality food, but also high-quality edible oil raw materials, which have many industrial values. Related products are widely used in food, chemicals, medicine, pesticides, additives, plant protein and other fields; after hundreds of years of introduction and domestication, pecans with shells have shown good adaptability in many parts of China and have great development potential.

In order to develop and utilize the resources of pecan scientifically and rationally, give better play to its value, accelerate the development of the pecan industry, this paper systematically summarized and analyzed the research status of the development and utilization of its kernel, peel, shells, leaves, inflorescence and other aspects, and put forward relevant suggestions according to the problems existing in the development.

2. The resource status of pecan

2.1. Distribution in nature

Pecan (Carya illinoinensis) is naturally distributed in the Mississippi River Basin and its tributaries on both sides [1]. Its northern edge extends to the southern part of Nebraska, Iowa, Illinois and Indiana, its southern edge extends to the central part of Mexico, its eastern edge extends to the western part of Kentucky and Tennessee, and its western edge extends to the western part of Texas.
Pecans are also introduced and planted in South Africa, Australia, Brazil, China, Argentina, Chile and other countries, and the distribution range is mainly between latitude $25^\circ \sim 40^\circ$ [2]. According to statistics in 2019, the world's pecan production was 309,909 t, of which Mexico and the United States led the world in production, accounting for 47% and 43% respectively [3], and South Africa, Australia and Brazil accounted for the remaining 10%. As South Africa's new planting areas begin to bear fruit, its production has maintained steady growth. In 2020, China's total output is about 1,000 t. The annual output of main pecan producing countries in 2017 are listed in Table 1.

| Major producing countries | Peacan yield (t) |
|---------------------------|------------------|
| U.S.A                     | 146,200          |
| Mexico                    | 133,300          |
| South Africa              | 16,510           |
| Australia                 | 2,505            |
| Argentina                 | 1,100            |
| China                     | 1,10             |

2.2. Introduction and development of pecan in China

The introduction and cultivation of pecan has been carried out in China for more than 100 years. Roughly experienced 4 different stages: the spontaneous introduction stage (from the end of the 19th century to the beginning of the 20th century), the first stage of conscious introduction (from the early 20th century to the eve of 1950s), the second stage of conscious introduction (after 1950s to the early 1960s) and the third stage of conscious introduction (From the end of the 1970s to the present). The spontaneous introduction stage and the first stage of conscious introduction were small in scale, most were direct introduction, mostly as garden greening tree species. The scale of spontaneous introduction in the second stage gradually expanded, but the reserved area and number were not large. Until the third stage of conscious introduction, the introduction and domestication of pecans in China has made new progress, and domestic indirect introduction activities have increased significantly [1].

In recent years, it has been developed rapidly in the middle and lower reaches of the Yangtze River and the mountainous areas in southwest China. As of 2020, 22 provinces (autonomous regions and municipalities) in China have carried out the introduction and cultivation of pecans [1], and the cultivation area is about $666.67 \text{ km}^2$. They are mainly distributed in Yunnan, Anhui, and Jiangsu, and part of Shandong, Zhejiang, Jiangxi, Hunan, and Guangxi. At present, most orchards are in the early stage of construction and have not yet entered the period of high yield. In addition, some areas showed poor growth traits, delayed fruit setting or low yield, and even a large number of forest stands were abandoned in the middle.

China is currently rich in resources of pecans with a large number of varieties. According to incomplete statistics, there are currently more than 100 varieties of pecans imported and preserved in China. Among them, 51 varieties of pecans imported from the United States are collected in the germplasm resource nursery of Nanjing Luzhou Pecan Science and Technology Co., Ltd. And there are 22 domestic breeding varieties and 112 excellent individual plants. Through the screening and regional cultivation experiments, 6 excellent varieties, including Mahan, Pawnee, Shawnee, Wichita, Elliott, and Xenix, were selected for promoting in Jiangsu and surrounding provinces. Among them, Mahan and Boni were recognized as provincial superior varieties by the New Forestry Variety Committee of Jiangsu Provence [3].

The Yunnan Academy of Forestry has introduced 54 varieties from home and abroad for 53 years. It has established a gene pool for introduced species at the Walnut Research Station in Yangbi County, China. Through experiments, 8 varieties were screened out suitable for growth in Yunnan [4]. Today,
Mahan, Boni, Jinhua, and Shaoxing are all excellent varieties that are widely promoted in China. Jinhua has been widely spread in Yunnan and expanded from Yunnan to Zhejiang, Jiangsu, Anhui, Hubei, Guizhou, Hunan and Chongqing [5]. ‘Poni’ was introduced in the 1990s, and was mainly planted in Jiangsu, Yunnan, Hubei, Anhui and other provinces in the Yangtze River Basin, and all of them showed good adaptability [6]. In 2019, Lv et al. selected and bred 5 fine varieties of Puziley, Jinhua, Pawnee, Tejas, and Mississippi in Hunan Province, which greatly promoted the development of the local industry [7]. All these germplasm resources and their large-scale planting provide a solid raw material foundation for resource development and utilization.

3. Status of comprehensive development and utilization of pecans

In recent years, the comprehensive utilization of pecans in China has become more and more diversified, from nuts to oil processing, from the kernel to the substances extraction from peel, shell, flower and leaf. The implementation of multi-purpose development, mainly reflected in the fruit development and utilization of oil and its by-products.

3.1. Nuts

Pecan, as a nutritious and delicious nut food, is rich in crude fat, amino acids, sugars, nitrogen, phosphorus, magnesium, potassium, calcium and other mineral elements. Its seed kernels are rich in crude fat, amino acids, carbohydrates, nitrogen, phosphorus, magnesium, potassium, calcium and other mineral elements, phenols, vitamin E, as well as the content of flavonoids. Studies have shown that the fat and protein content of Carya pecan kernels is mostly higher than that of walnuts and other pecans [8]. Wu et al. [9] compared the phenolic content of eight kinds of nuts including almonds, Brazilian chestnuts, cashews, hazelnuts, macadamia nuts, pine nuts, pistachios and walnuts, and concluded that the pecans are phenolic substances. One of the nuts with the highest content, reaching 2016 mg/100 g. In addition, it is concluded that the pecan is the nut with the highest flavonoid content, reaching 34.01 mg/100 g. Katherine et al. [10] compared the vitamin E in seven kinds of nut oils including almonds, Brazilian chestnuts, hazelnuts, pecans, pine nuts, pistachios and walnuts, and concluded that pecans have the highest vitamin E, at 711mg/kg. Among them, vitamin E and phenolic substances have certain antioxidant activity, and their antioxidant compounds can delay aging, reduce diseases, and prolong life; some unsaturated fatty acids and trace elements can promote development of brain cells and reduce cholesterol synthesis. At present, there are many kinds of finished products, which can be made into foods such as nut foods, pecan powder, pecan milk beverages, and pecan crisp candy [11].

3.2. Pecan oil

Pecan oil is rich in polyunsaturated fatty acids, which can reduce the risk of cardiovascular diseases, regulate lipid metabolism, regulate the immune system, fight cancer, promote growth and development, and delay aging, etc. [12]. It is a precious nutritional health oil. In addition, it can also be used as a seasoning food. Its kernel oil content is as high as 70%, and the unsaturated fatty acid in the fat is as high as 940 g/kg. Compared with other woody oil species, it is better than tea oil (910 g/kg), walnut oil (890 g/kg), olive oil (850g/kg), and is more acid-resistant than olive oil [13].

Its relative content of monounsaturated fatty acid (oleic acid) is 58.76% ~ 73.01%, and the main polyunsaturated fatty acid is linoleic acid, with the relative content of 19.69% ~ 32.20% [14].

Zhang et al. [15] found that the content of polyunsaturated fatty acid (25.92%) of Carya illinoensis was the highest by comparing many kinds of pecans, such as Hunan pecan, Dabieshan pecan, Carya illinoensis and Carya chekiangensis, et al. Through comparison, it can be found that Carya illinoensis is a kind of high-yield and high-quality oil raw material, which has been widely used as the raw material for extracting vegetable oil [16-18]. The comparison of nutritional components of different vegetable oils are listed in Table 2.
Table 2. Comparison of nutritional components of different vegetable oils

| Items            | Pecan oil | Rapeseed oil | Olive oil | Soybean oil | Palm oil | Peanut oil | Tea oil |
|------------------|-----------|--------------|-----------|-------------|----------|------------|--------|
| Fat (g/100g)     | 99.9      | 99.9         | 99.9      | 99.8        | 100      | 99.9       | 99.9   |
| Energy (kJ/100g) | 3700      | 3761         | 3696      | 3757        | 3766     | 3761       | 3761   |
| Saturated fatty acids (%) | 8.11 | 10          | 13.5      | 13          | 51       | 19         | <10    |
| Monounsaturated fatty acids (%) | 68.88 | 80          | 72.5      | 25          | 39       | 48         | 80     |
| Polysaturated fatty acids | Linoleic acid (%) | 21.81 | 10        | 7.9        | 55       | 10         | 33     |
|                   | Linolenic acid (%) | 1.19   | 0         | 0.6        | 7        | 0          | 10     |
| Vitamin E (mg/kg) | 711       | 608         | 150       | 930         | 152      | 420        | 279    |
| Phytosterol (mg/kg) | 1800~2620 | 4500~11300 | ≥1000     | 4500        | 700      | 2900       | 5713.48 |

3.3. Plant natural antioxidants

All parts of pecans such as the shells, kernels, flowers, leaves, and exocarp of pecans, have certain antioxidant properties. The main components are polyphenols, which can inhibit the oxidation of polyunsaturated fatty acids. However, the main substances that play an antioxidant role in each part are not completely the same, and there are certain differences in the antioxidant substances and antioxidant capacity of different parts, which have the potential to develop into plant natural antioxidants.

Chen et al. [19] found that the outer shell of pecan contains tannins, anthraquinones, flavonoids, coumarins and other phenolic substances. In addition, the pecan shells were extruded at 70°C with 150rpm, and the polyphenols content is doubled, and the activity of scavenging free radicals is significantly improved [20]. The content of tocochromanol in Carya illinoensis kernel, in dynamic change, is the main antioxidant component. Xu et al. [21] studied the polyphenols, flavonoids and antioxidant activity in the defatted kernel of Carya illinoensis, and concluded that its defatted kernel contains rich polyphenols and flavonoids, the total polyphenols content and total flavonoids content are significantly positively correlated with antioxidant activity. Xu et al. [22] found that the change of tocochromanol content during kernel ripening was higher in the early stage of kernel development, decreased rapidly with the development, and increased slightly after ripening. The tocochromanol content also decreased gradually with time during storage. Wang et al. [23] used ethyl acetate to extract the active components from peach blossom, and the IC50 value reached 30.7 μg. Pang et al. [24] found that Carya cathayensis leaves have antioxidant activity, among which polyphenols are the main components of inhibiting superoxide anion free radical and providing reducing power, and there are other components with certain DPPH free radical scavenging ability. Li et al. [25] found in the study on the effect of walnut leaf water extract on spatial learning and memory ability of mice that the extract water can improve the spatial learning and memory ability of aging model mice, and it is related to its antioxidant effect. In the study of the effect of walnut leaf water extract on the spatial learning and memory ability of mice by Li et al. [25], it was found that walnut leaf water extract can improve the spatial learning and memory ability of aging model mice, and it is related to its antioxidant effect. The antioxidant activity of walnut green peel is closely related to the content of polysaccharides. The antioxidant activity of walnut green peel is closely related to the content of polysaccharides. Xie et al. [26] showed that the two polysaccharides had strong antioxidant activity and could scavenge hydroxyl free radical and DPPH free radical, and the scavenging ability was dependent on the sample concentration. The antioxidant capacity of different parts is different. For example, the content and antioxidant capacity of phenolic compounds in hickory shell are higher than those in pericarp [27].
3.4. **Bacteriostatic agent**

The epicarp and leaves of pecans contain certain antibacterial components, which has a certain potential in the development of botanical fungicides. Different organic phase extracts have different bacteriostatic effects on different microorganisms. The antibacterial components of pecan leaves are complex [28], among which n-butanol extract and ethyl acetate extract have the best antibacterial effect, and have obvious inhibitory effect on gram-positive and gram-negative bacteria.

The ethanol extract from its leaves had significant inhibitory effect on *Staphylococcus aureus*, yeast, *Escherichia coli*, *Penicillium* and *Aspergillus niger* [29]. The methanol extract of pecans exocarp had obvious bactericidal effect under appropriate conditions on cucumber anthracnose, *Sclerotinia sclerotiorum*, apple rot, pepper blight, *Rhizoctonia solani*, *Sclerotinia sclerotiorum*, etc., but the inhibition degree was also different [30].

3.5. **Adsorbent**

Activated carbon can be prepared from the shell of pecans. Busscher *et al*. treated the soil with biochar generated from the pyrolysis of *Carya illinoensis* shell at 700 °C. The results showed that the biochar could increase the carbon content in the soil and improve its physical and chemical properties, such as the polymerization, infiltration and water holding capacity [31]. Shawabkeh *et al*. [32] used sodium dodecyl sulfonate to treat the surface of activated carbon obtained from pecan shell after chemical activation with phosphoric acid, so as to remove phenol and methylene blue from aqueous solution. The activated carbon obtained has the performance of adsorbing phenol and methylene blue. Vaghetti *et al*. studied the feasibility of *Carya illinoensis* shell as a biosorbent to remove Cr$^{3+}$, Fe$^{3+}$, Zn$^{2+}$, Cu$^{2+}$, Mn$^{2+}$, Pb$^{2+}$ and other metal ions in aqueous solution, revealed that it has good absorption effect on these toxic heavy metal substances, and can be used for the treatment of agricultural waste [33-34]. Liang *et al*. [35] treated alkaline dye wastewater with biochar adsorbent prepared from *Carya cathayensis* epicarp activated by phosphoric acid, which can adsorb malachite green and methylene blue in water with high removal rate. Therefore, *Carya cathayensis* epicarp adsorbent is an efficient alkaline organic dye adsorbent.

All the above studies showed that the activated carbon prepared from *Carya cathayensis* shell had strong adsorption capacity, and it also had a certain absorption effect on heavy metals in water, so *Carya cathayensis* shell was a potential material for biomass adsorbent.

3.6. **Pigment**

The components of pericarp, shell and flower of pecans are very similar to those of walnut. Brown pigment, natural edible pigment and walnut green pigment can be extracted from walnut exocarp. Using water at 60 °C as the extraction agent, the mass ratio of water to green peel was 1:5 for the first time and 1:3 for the second time, the brown pigment extract was obtained from the dried walnut exocarp (green peel) [36]. Tan *et al*. [37] used walnut pericarp as raw material, added sodium hydroxide solution, stirred and filtered to extract safe and non-toxic natural edible pigment. Walnut shell can be used to extract and purify natural brown pigment. Chen *et al*. [38] ground walnut shell into powder. Take a certain amount of walnut shell powder which has passed through 30 mesh sieve and dried, take aqueous ethanol as solvent, heat in water bath, reflux, cool, filter, reduce pressure and concentrate to obtain brown solid, wash with a certain amount of petroleum ether, and then vacuum dry to obtain a brown pigment. The properties of the pigment were tested. The pigment has light fragrance, good heat resistance and antioxidant properties. Li *et al*. [39] improved the extraction process of pigment. By comparing the adsorption of different resins on walnut shell brown pigment and the elution effect of different eluents on walnut shell brown pigment, it was concluded that AB-8 resin had higher adsorption capacity on walnut shell brown pigment. After adsorption, 50% ethanol was used as eluent to extract walnut shell brown pigment with higher quality, better color and better stability.

The results showed that the melanin of peach blossom was soluble in water and ethanol. Yu *et al*. [40] used purified water as the extraction solvent to extract the melanin from peach blossom, and obtained the best process conditions as follows: the solid-liquid ratio was 1:150, the extraction time was
1.5h, the extraction order was one, the extraction rate could reach 28.96%, and the color value was 48.08.

3.7. Food nutrition additive

The results showed that the staminate flower inflorescence of pecans had low fat content and rich protein and crude fiber content. Inflorescence is rich in K, Ca, Mg, Se and other mineral nutrients, which can be a way to supplement trace elements. In addition, there are many kinds of amino acids in inflorescence, such as aspartic acid, lysine, threonine and so on. The content of aspartic acid is the highest, which can reduce the occurrence of heart disease, liver disease and hypertension.

Lysine and threonine are the first and second limiting amino acids in human body. By taking staminate inflorescence as supplementary food, the waste of protein can be reduced and give full play to its nutritional value. The staminate inflorescence also contains high content of polysaccharides, polyphenols and flavonoids, and it is found to have strong antioxidant activity by DPPH method [41]. Based on the above characteristics, the pollen of pecans contains a lot of basic nutrients, which shows high nutritional value and can be used as food nutrition additives.

3.8. Others

The pecans shell can be used as anti-polymerization agent, plugging agent and filter material in chemical industry. Sun et al. [42] used the empyreumatic oil of hickory shell to process anti polymerization agent, and determined the distillation process, operation parameters, operation methods, abnormal phenomena and elimination methods in the production process. Using the empyreumatic oil of pecans instead of wood to produce anti polymerization agent can reduce the consumption of wood and is conducive to the stability of ecological environment. The empyreumatic oil of pecans anti-polymerization agent has the characteristics of high phenol content and good anti polymerization performance.

Xu et al. [43] used walnut shell as a compound plugging material and mixed with high water loss plugging agent (DTR). The results show that the combination of high water loss plugging agent (DTR) and walnut shell can enhance its plugging performance, which is very effective to deal with the leakage of large and medium fractures. Walnut shell filter has become the main filtration equipment in oily wastewater treatment. Walnut shell filter material has hydrophilic and oleophobic properties, which is easy to be washed and regenerated after oily wastewater treatment. Zhang et al. [44] carried out the test of walnut shell filter for filtration of produced water, defined some important operating parameters, and the test results showed that walnut shell filter had a certain sewage interception capacity.

4. The current problems

4.1. Single form of resource utilization

Carya illinoensis is a kind of multi-functional resource. At present, the utilization of pecan mainly focuses on the edible value and other aspects. The product type is single, and the pharmacological effect of each part of pecan and the deep processing and utilization of nut are less. In fact, the polyphenols and flavonoids contained in pecan have great potential in the development of new drugs and new cosmetics. For example, Forino et al. [45] isolated and identified oligosaccharides from its leaf extract, and conducted in-depth study on their effects on glucose uptake of Hep G2 and Caco-2 cells, indicating that walnut leaf extract has the potential to reduce glucose uptake, and can be made into functional drinks containing walnut leaf extract to treat diabetes. The flavonoids from the leaves of pecan can accelerate the elimination of free radicals, inhibit lipid peroxidation and delay the aging of the body [46]. Therefore, pecan can be used to develop anti-aging drugs. In addition, the leaves and exocarp of pecan all contain certain anti-tumor active ingredients [47-48], which is expected to be used in the production of anti-tumor drugs. Studies have shown that the leaves can reduce the cardiac contractility without affecting the heart rate, which may alleviate the angina pectoris in the elderly [49]. At the same time, the polyphenol extract from pecan has good inhibitory, antioxidant and reducing melanin deposition. Therefore, pecan polyphenols can be used to develop natural skin care products, which can not only
achieve the effect of removing freckles and moisturizing, but also have no toxic and side effects on the skin.

4.2. The utilization rate of resources is not high
The waste of pecans resources is serious, the utilization rate is not high, and there are many production wastes, such as pecans shell, exocarp, inflorescence and so on. Furthermore, some waste may cause environmental pollution problems, so it is necessary to improve the value of waste, and it should also be paid attention to in the production process of nutritional products related to pecans. In addition, by studying the toxicity of water extract from pecans shell on mice, it was found that inorganic trace elements such as manganese, aluminum, copper and iron accumulated in pecans shell may be harmful [50]. Therefore, attention should be paid to its toxicity and control its dosage reasonably.

4.3. Lack of improved varieties with low levels of cultivation and management
Due to the high requirements of site conditions and planting techniques, there is a lack of high and stable yield demonstration bases in China. In addition, its cultivation and management level in China is generally low, and the cultivation and management techniques are not perfect, resulting in the late fruiting and low yield in a large area, and the limitations of large-scale promotion and cultivation, and the shortage of resources and materials.

5. Conclusion
Pecans, as the world famous raw material of dried fruit and health edible oil, as well as excellent timber and afforestation tree species, is favored by all countries in the world. It is of great significance to develop pecan to enrich domestic nut varieties, ensure national food and edible oil security, overcome poverty and increase farmers' income. Making full use of modern technology, including phytochemistry, traditional Chinese medicine, food science, pharmacognosy, etc., to develop and utilize Carya illinoensis resources, improve the yield and quality of Carya illinoensis, and realize the full utilization of resources, has become an important direction of China's agricultural products processing, and will become a major focus of Carya illinoensis research in the future.

Acknowledgement
This study was supported by the Changsha Key Research and Development Project (KQ1907084); the Demonstration of Central Government Guided Local Scientific and Technological Development Scientific and Technological Innovation Projects (YDZX2019XF5052); the National Science and Technology Infrastructure Platform Project (2005 DKA32200-0G).

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