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LETTER TO THE EDITOR

Nanocatalysts Affect Bioactive Component Diversity of Pyrolyzates from Walnut Shell

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The huge resource of walnut shells were almost low efficient utilization. Therefore, the nano-catalytic technology was used to reveal the bioactive component characteristic by nanocatalysts. Three kinds of nanocatalysts (Ag, NiO, 1/2 Ag + 1/2 NiO) was added to the original powder of the walnut shell for pyrolysis at 300°C. The results showed that the main types of pyrolyzates are: bioenergy, biomedicine, food additive, spices and chemical raw materials. Among them, the original powder treaded with nano-Ag has higher component content of chemical raw materials and bioenergy. Treating with nano-NiO, the component content of chemical raw materials and perfumes in pyrolyzate is relatively higher. Treating with nano- 1⁄2Ag+1⁄2NiO, the component content of most functional substances increases more in pyrolyzate, especially, the proportions of biomedicine and bioenergy increase significantly. The findings suggested that the content of pyrolyzate is different with different nanocatalysts, and nanocatalyst 1⁄2Ag+1⁄2NiO can be used to produce pyrolyzate including bioactive components of bioenergy and biomedicine.

I Introduction

Juglans regia, a *Juglandaceae* plant, is also one of the important economic tree species (Bi et al. 2016). Because of its characteristics such as sunny habitats, cold resistance, drought resistance, disease and insect resistance (Kar et al. 2011), *J. regia* is widely grown around the world (Martínez et al. 2010). *J. regia* is not only an important nut product but also can be developed into a high value comprehensive product (Hayes et al. 2016). *J. regia* is an important edible oil resource because it contains a lot of fat and ranks first in all woody oils (Ros et al. 2009, Qin et al. 2017). It is also rich in protein and acknowledged as is a high-quality protein resource. As a result, there is a great demand for *J. regia*. Walnut green husk contains phenols, alcohols, hydrocarbons, ketones, vitamins and other organic components. Its inorganic components include potassium, calcium, iron, manganese, zinc, magnesium, copper and other trace elements (Naghizadeh et al. 2016). It can be used to prepare industrial potassium salts, cosmetics and drugs. Studies have proved that walnut polyphenols have many kinds of biological activities (Cao et al. 2014). As people's demand for walnuts and by-products grows, the area planted with walnuts continues to

expand (Fu et al. 2018). After the walnut kernel is developed and used, a large number of walnut shells are abandoned or burned as fuel directly (Jackson et al. 2014, Liu et al. 2018). This not only causes great waste of resources (Cao et al. 2008), but also brings many other problems (Casas-Agustench et al. 2011), such as polluting the environment. In order to improve the reuse of walnut shell resources, this paper uses pyrolysis gas chromatography-mass spectrometry to investigate the resource utilization law and bioactive components of walnut shell under different catalysts treatment conditions (Hardman et al. 2014, Alrawashdeh and Allouzi 2019). The paper it provides some methods for the rational development and utilization of walnut shell resources, and further improves the economic value of walnut shell (Babaranti et al. 2019, Yu et al. 2018).

II Materials and Methods

(1) Experimental materials

The walnuts were collected from the *J. regia* plantation of Henan Agricultural University. After fully dried at 40°C by air blowing thermostatic oven, the shell and diaphragma were separated from the nutmeat. The walnut shell raw powder was sifted through 200 mesh screen, and then the walnut shell raw powder and nanocatalysts were prepared according to 100:1, mixed evenly for detection.

(2) Methods

Thermostability analysis by TG. Detection was conducted using 10 mg samples placed in instrument. The temperature program of TG started at 30°C, and reached 850°C at 10 °C/min. The carrier gas is high purity nitrogen, with a flow rate of 40 mL/min (Lam et al. 2019).

Pyrolysis–gas chromatography–mass spectrometry. The walnut shells were powdered by thermal cracking–gas chromatography–mass spectrometry (CDS6250T-Agilent7890-5977). GC was conducted under the following conditions: quartz capillary column. 30 mm × 0.25 mm × 0.25 μm; helium as the carrier gas; carrier gas flow velocity, 1.0 mL/min; inlet temperature, 280 ºC, split ratio, 5:1. Heating procedure: The GC program started at 50ºC for 2 min, and rose to 300ºC at 10 ºC/min for 10 min.

III Results

(1) Thermogravimetric rules of walnut shell

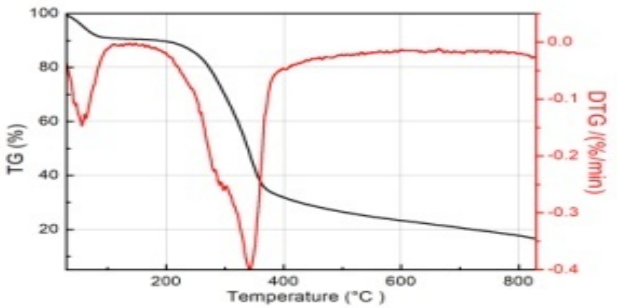

Figure 1 Thermogravimetric analysis of walnut shell

The TG curve declines continuously and the sample quality being lost continuously (Figure 1).The total weight loss of the sample was about 84%, ranging from 30°C to 850°C. At 58°C, the DTG curve has a corresponding weightlessness peak with mass loss of about 4.40%, which may be attributed to the evaporation of moisture from the sample. At 340°C, The DTG curve has a corresponding weightlessness peak with mass loss of about 53.70%, which may be related to the partial decomposition of the sample.

Bioactivity and bioactivity components of walnut shell nano-catalytic pyrolysis

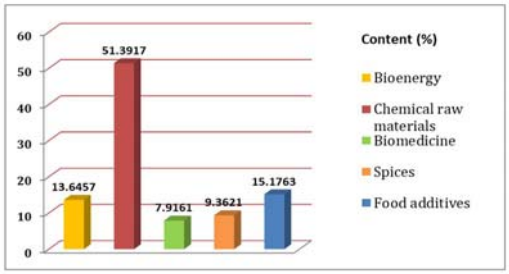

Figure 2. Comparison of the Content of Pyrolyzates under the Treatment of nano-Ag catalyst

At 300°C, the original pyrolysis products of walnut shells treated with nano-Ag catalyst. Some bioenergy components were detected in the original pyrolysis product of walnut shell treated with nano-Ag catalyst. For example, alkyl and n-twenty are flammable liquids that can be exploded when mixed with air (Peng et al. 2018). They can be flammable in open fire, high temperature, and oxidant, and may have the potential to develop bioenergy. The pyrolysis products of walnut shell raw powder treated with nano-Ag catalyst were detected and some components were used in biomedicine. For example, 2-methylnaphthalene is used as an intermediate in the production of vitamin K3 in medicine. Many ingredients containing food additives and spices were found in the pyrolysis products of the original powder of walnut shell treated with nano-Ag catalyst. 1-(1H-pyrrol-2-yl) - Ethanone is a food spice and is mainly used to prepare roasting food-type flavors. Nonanal can be used for roses, orange flowers, lily of the Valley, Peony, Iris, sunflower leaves, sweet orange, lemon, jasmine, late jasmine, windbreak roots and many other incense.

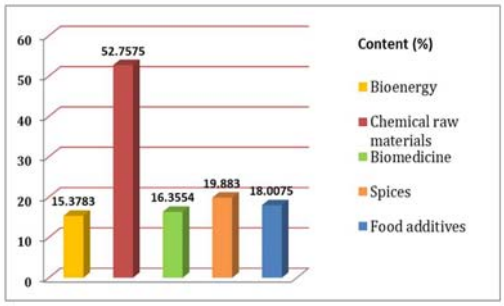

Figure 3. Comparison of the Content of Pyrolyzates under the Treatment of nano-NiO Catalyst

At 300°C, the original pyrolysis products of walnut shells treated with nano-NiO catalyst. The pyrolysis products of walnut shell raw powder treated with nano-NiO catalyst were detected to contain a small amount of bioenergy. For example, 2-Furanmethanol can be used as rocket fuel. A lot of ingredients containing food additives and spices were identified in the pyrolysis products of raw walnut shell processed by nano-NiO catalyst. For example, nonanal has a strong oily odor and sweet orange flavor, and its dilute ethanol solution has vanillin and aroma, and is used as a food additive. 4- Ethyl phenol is used as food flavoring for the preparation of whisky, rum, bacon, ham, coffee and other flavors.

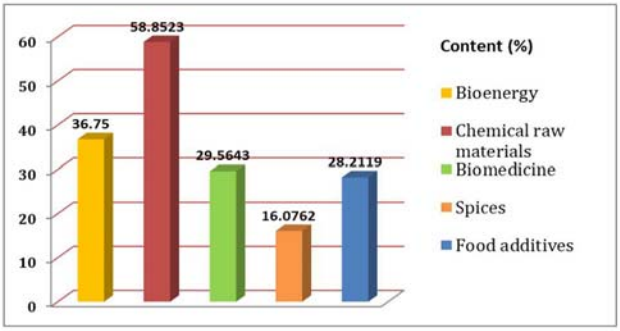

Figure 4. Comparison of the Content of Pyrolyzates under the Treatment of nano- 1/2Ag+1/2NiO Catalyst

At 300°C, the original pyrolysis products of walnut shells treated with nano-1/2Ag+1/2NiO catalyst. The pyrolysis products of walnut shell raw powder treated with nano-1/2Ag+1/2NiO catalyst were found to contain some bioenergy components. For example, 1, 2-ethylene glycol monoacetate, diisooctyl phthalate, dibutyl phthalate and 1-Decene are flammable liquids, which are explosive when mixed with air (Liu et al. 2017). They are flammable when exposed to open fire, high temperature and oxidant, and may have the potential to develop bioenergy.Some biomedical components were found in the pyrolysis products of walnut shell raw powder treated with nano-1/2Ag+1/2NiO catalyst. For example, silver acetate is used in the pharmaceutical industry, as well as a new preparation method for highly reflective and conductive silver polymer film. 1,3-dimethyl-benzene is used for the production of lidocaine, oxazoline, and pan shadow. Benzaldehyde is used as pharmaceutical raw material, anaesthetic and preservative. Para cresol is used as disinfectant in medicine. Catechol is an important pharmaceutical intermediate, which can be used to manufacture cough-killer, eugenol, berberine and isoproterenol, skin preservatives and fungicides. Adrenalin is the intermediate of anostol and non steroid hormones (Qin et al. 2017).

IV Conclusion

The mass change during the thermogravimetric process showed that walnut shell has the highest mass loss rate at two obvious peaks. This phenomenon may be caused by pyrolysis to convent macromolecule into small molecules with better volatility, suggesting that walnut shells can produce new bioenergy components by pyrolysis. At 300°C, the raw powder pyrolysis products of walnut shells treated with nanocatalysts were found to be rich in components that could be included in chemical raw materials, biomedicine, bioenergy, food additives and spices. Among them, under the condition of nano-Ag catalyst treatment, it was found that the material content used for chemical raw materials and bioenergy were very rich. Under the condition of nano-NiO catalyst treatment, it was found that more components could be used in chemical raw materials, biomedicine, and spices. Under the condition of nano-1/2Ag+1/2NiO catalyst treatment, it was found that the content of each substance was relatively high, especially for biomedicine and bioenergy. The results show that there are a lot of components in pyrolysis products of walnut shell which can be widely used in high value-added industries such as bioenergy and biomedicine.

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References

Alrawashdeh BH, Allouzi AM (2019) Importance of the united nations millennium declaration for international

environmental law development. Ekoloji 28(UNSP e107071107):115-121.

Babaranti O, Horn S, Jowett T, Frew R (2019) Isotopic signatures in mytilus galloprovincialis and ulva latuca as bioindicators for assessing discharged sewage effluent in coastal waters along Otago Peninsula, New Zealand. Geology, Ecology, and Landscapes 3(1):53-64.

Bernard A, Zhang K, Larson D, Tabatabaei K, Kauzlarich SM (2018) Solvent Effects on Growth, Crystallinity, and Surface Bonding of Ge Nanoparticles. Inorg Chem 57(9).

Bi D, Zhao Y, Jiang R, Wang Y, Tian Y, Chen X, Bai S, She G (2016) Phytochemistry, Bioactivity and Potential Impact on Health of Juglans: the Original Plant of Walnut. Nat Prod Commun 11(6).

Cao JS, Lin JX, Fang F, Zhang MT, Hu ZR (2014) A new absorbent by modifying walnut shell for the removal of anionic dye: kinetic and thermodynamic studies. Bioresour. Technol. 163.

Casas-Agustench P, Salas-Huetos A, Salas-Salvadó J (2011) Mediterranean nuts: origins, ancient medicinal benefits and symbolism. Public Health Nutr 14(12A).

Chen C, Jin X, Meng X, Zheng C, Shen Y, Wang Y (2011) Inhibition of TNF α-induced adhesion molecule expression by (Z)-(S)-9-octadecenamide, N-(2-hydroxyethyl, 1-methyl). Eur. J. Pharmacol. 660.

Cheng X, Yang T, Wang Y, Zhou B, Yan L, Teng L, Wang F, Chen L, He Y, Guo K, Zhang D (2018) New method for effective identification of adulterated Camellia oil basing on Camellia oleifera-specific DNA. Arab J Chem 11(6):815-826.

Fu H, Liu Z, Wang M, Wang Z (2017) Big data digging of the public's cognition about recycled water reuse based on the BP neural network. Complexity 1876861.

Gao Z, Han Y, Wang F (2018) Cooperative supramolecular polymers with anthracene–endoperoxide photo-switching for fluorescent anti-counterfeiting. Nat Commun 9(1).

Lam SS, Mahari WAW, Ma NL, Azwar E, Kwon EE, Peng WX, Chong CT, Liu ZL, Park YK (2019) Microwave pyrolysis valorization of used baby diaper. Chemosphere 230:294-302

Qin J, Wang Y, He G, Chen L, He H, Cheng X, Xu K, Zhang D (2017). High-efficiency Micropropagation of dormant buds in spine base of red pitaya (Hylocereus polyrhizus) for industrial breeding. International Journal of Agriculture and Biology, 19(1):193-198

Sun Y, Xue S, Li L, Ding W, Liu J, Han Y (2018) Sulfur dioxide and o-xylene co-treatment in biofilter: Performance, bacterial populations and bioaerosols emissions. J Environ Sci (China) 69.

Tabuchi T, Urabe D, Inoue M (2009) Asymmetric synthesis of a highly functionalized bicyclo [3.2.2]nonene derivative. Beilstein J Org Chem 9.

Vinothkumar R, Ceasar SA, Divyarupa A (2017) Chemosuppressive effect of plumbagin on human non-small lung cancer cell xenotransplanted zebrafish. Indian J Cancer 54(1).

Xu K, He G, Qin J, Cheng X, He H, Zhang D, Peng W (2015) High-efficient extraction of principal medicinal components from fresh Phellodendron barks (cortex phellodendri). Saudi J Biol Sci 25(4):811-815.

Yu D, Liu H, Bresser C (2018) Peak load management based on hybrid power generation and demand response. Energy 163:969-985.