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LETTER TO THE EDITOR

Nano-catalyzed Pyrolysis at 550°C for Resourcing of *Robinia Pseudoacacia* Flowers

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Robinia pseudoacacia has been planted all over the world, while *R. pseudoacacia* flowers (RPFs) are not enough utilized except edibility. The high value resourcing of RPFs were explored by nano pyrolysis. The original powder of RPFs and the sample treated with the nanocatalysts (NiO, Fe_2O_3, 1/2 NiO + 1/2 Fe_2O_3) were pyrolyzed at 550°C. This result indicates that the pyrolysis at 550°C can increase the content of bioenergy and cosmetics in the pyrolysis products in RPFs, while the nano-Fe_2O_3 cannot play a positive catalytic role. The findings here suggested that RPFs have great potential in high value resourcing for biomedicine and chemical materials.

I Introduction

Robinia pseudoacacia is a native species of the North America. Nowadays, it has been introduced to Asia, Europe and other regions, and it has been widely cultivated in the world. The canopy of *R. pseudoacacia* is tall and the leaves are bright green, which can be used as a street tree and a shade tree in landscaping. *R. pseudoacacia* heartwood is a good species in timber forest (Kolyada and Kolyada 2018). Its seed oil is rich in linoleic acid, traces of azelaic acid and perylenetetracarboxylic acid fatty acids, so it can be used to extract oil or make soap (Zhang and Zhang 2018).

The *R. pseudoacacia* flowers (RPFs) contain oleic acid, enamel and flavonoids and it is an excellent honey plant (Akatov 2016). The production of RPFs increased dramatically from April to May each year and cannot be utilized in a timely and effective way which has caused great waste (Gao and Wang 2017, Rawat et al. 2019). In this study, adding nano catalysts in the raw powder of RPFs, and quantitative analysis of bioactive components of RPFs raw powder by Pyrolysis Gas Chromatography-Mass Spectrometer at 550°C.

II Materials and Methods

(1) Materials and reagents

The RPFs were picked in mid-April and after air drying the RPFs at room temperature, they were pulverized into a powder using a FW100 micronizer (Cheng et al. 2018).And then the sample powder was sieved with a 200 mesh sieve and stored under dry and ventilated conditions.

(2) Methods

Detection and analysis by DSC-TG. Sample Weight: 186.797 mg. Initial Conditions: Temperature 30.00°C. End Condition: Go To Load. Method Steps: Pre-Run Actions, start the Run, action occurs Immediately, switch the Gas to Nitrogen at 20.0 ml/min, action occurs Immediately, heat from 30.00°C to 800.00°C at 10.00°C/min. Load Temperature: 30.0°C, go To Temp Rate 50.0°C/min(Lam et al, 2019).

Detection and analysis by Py-GC/MS. Pyrolysis conditions: 50°C, held for 1 sec, 20°C to 700°C, held for 10 s. Interface conditions: 80°C, 100 °C/min, increased to 300°C, held for 2 min. Instrument: Gas chromatograph mass spectrometer (Agilent 7890--5977). Meteorological chromatographic analysis conditions for the capillary column using a HP-5 capillary column [30 m× 0.25 mm× 0.25 μm] (Agilent, USA), carrier gas is helium, carrier gas flow rate 1.0 mL/min. injection volume: 1.0 μL. Inlet temperature: 280°C, split ratio of 5:1. Temperature program: initial temperature of 50°C for 2 min, 10 °C/min to 300°C, and held for 10 min. Ion source temperature: 230°C, quadrupole temperature 150°C, detection range: 30-550°C.

III Results

(1) Thermogravimetric behavior of RPFs

Pyrolysis is commonly used for the gasification of biomass, which is a key process also used for processing crude oil into gasoline and diesel. The weight loss of the sample can be roughly divided into four major stages (Figure 1). From the beginning to approximately 100°C is the first stage, where the sample begins to lose weight, and there is a small exothermic peak in the DSC curve. In the second stage between 100°C and 250°C, it can be seen a slight weight loss peak appears on the corresponding DTG, and there is no significant absorption peak appearing on the DSC curve. The sample decreased a little, some substances in the sample may have sublimed. At the third stage, from 250°C to 350°C, the obvious weight loss peak appeared in the DTG curve. During the entire process, the temperature point with the fastest weight loss of the sample appears during the third stage. Between 350°C and 800°C, there is no large change in the DTG or DSC curves for the sample, but the sample weight is still in a decreasing state, and the rate of reduction is significantly slower than that of the previous stage. The whole process indicated that there appear some potential components in the RPFs.

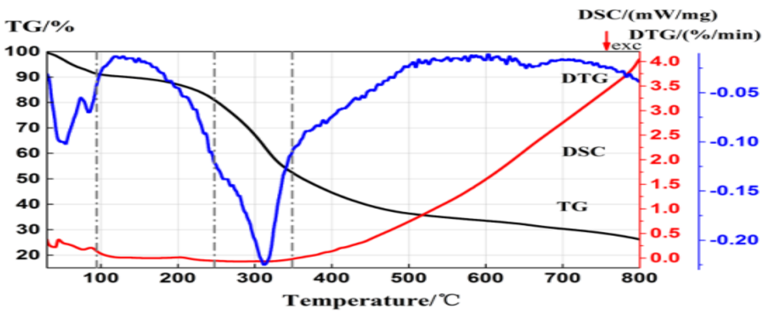

Figure 1: DSC-TG-DTG curves were obtained by increasing the temperature of the original powder of the sample at the rate of 10 °C/min

(2) Diverse bioenergy and bioactive components of nano-catalyzed pyrolyzates from RPFs

Pyrolysis-gas chromatography-mass spectrometry is an instrument for the qualitative and quantitative analysis of volatile complex matrix components. It requires a small amount of sample and is used in a wide range of applications (He et al. 2018). The main purpose of this thermal cracking-meta chromatography-mass spectrometer is to identify the volatile constituents in the RPFs. At the same time, a qualitative and quantitative analysis of the identified components is performed (Chen et al. 2018).

In this term, different nano catalysts were added to three identical samples. The number of the original powder is

A, the number of nano- NiO added is B, the number of nano-Fe_2O_3 is C, and the sample of the same amount of nano- NiO and nano- Fe_2O_3 is D. And all these substances are mainly divided into chemical raw materials, bio-energy, bio-pharmaceuticals, spices, food additives, and cosmetics. And many substances have multiple functions, which are cumulatively calculated in the following figures.

There are 154 active substances in the 198 peaks detected by pyrolysis of sample A at 550°C. The main substances (Figure 2) that can be used as chemical raw materials are ethylene oxide. Ethylene oxide is used as an organic chemical raw material and solvent for the production of ethylene glycol, ethanolamine and nonionic surfactants (Qin et al. 2017). In terms of bioenergy, o-xylene can be used as an aviation gasoline additive. Adding n-hexadecanoic acid to combustible materials can make it gelatinized when making napalm. Biomedicine mainly consists of 9, 12-octadecadienoic acid (z, z) -, which is a drug that can be used to lower blood fat. There exist some spices and some substances that can be used as food additives. Maltol is mainly used to prepare strawberries, coffee and various fruit flavors. Maltol itself is a broad-spectrum fragrance synergist and it has the functions of flavoring, solidifying and sweetening. Therefore, it can also be used to formulate cosmetic flavors.

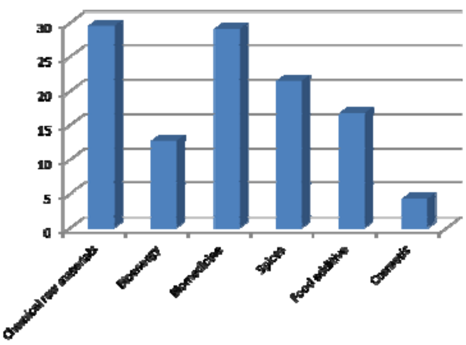

Figure 2: Classification of the functions of sample A after pyrolysis at 550°C.

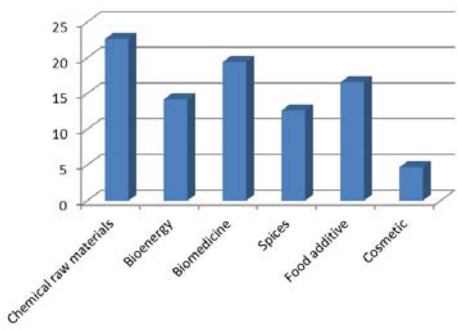

Figure 3: Classification of the functions of sample B after pyrolysis at 550°C.

175 effective substances were detected in 210 peaks obtained by pyrolysis of sample B at 550°C. Phenol (Figure 3) is an important organic chemical raw material, which can be used to prepare chemical products and intermediates such as phenolic resin, caprolactam. As a bioenergy substance, 9H-pyrido [3, 4-b] indole is a petroleum additive while pyridine is a raw material for the manufacture of explosives (Xu et al. 2018). In biomedicine, acetic acid, phenyl ester can be translocated to obtain hydroxylacetophenone, which is effective in the treatment of acute and chronic jaundice hepatitis and cholecystitis. Flavors mainly include cis-7, cis-11-hexadecadien-1-yl acetate, indole and oxacyclohexadecan-2-one.Octadecanoic acid is a fatty acid widely found in nature and it can be used in cosmetics.

177 active substances were detected in 214 peaks obtained by pyrolysis of substance C at 550°C.Chemical raw materials include ethylene oxide and acetic acid. As a derivative of ethylene industry, the importance of Ethylene oxide is mainly based on its series of products. The species produced by ethylene oxide are much more abundant than various ethylene derivatives. The main bioenergy sources include heptadecane and ethylene oxide. Ethylene oxide can generate huge energy when it is automatically decomposed, and can be used as a power for rockets and jet propellers. The mixed fuel has good combustion performance, low freezing point, and stable nature.

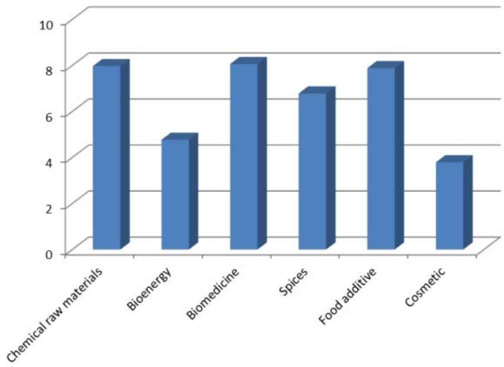

Figure 4: Classification of the functions of sample C after pyrolysis at 550°C.

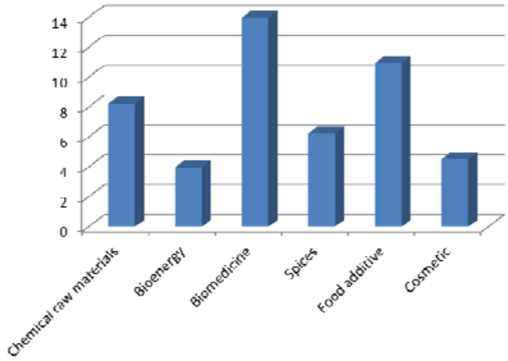

Figure 5: classification of the functions of sample C after pyrolysis at 550°C.

157 active substances were detected in 191 peaks obtained from sample D at 550°C. Chemical raw (Figure 5) materials are mainly including oleic acid. Oleic Acid is an organic chemical raw material, epoxidizedoleate can be used as plastic plasticizer (Liu et al. 2018). 2-Furanmethanol is a good solvent for resin, varnish and rocket fuel. Biomedicine mainly includes octacosanol. Octacosanol as a health food mainly enhances physical strength and endurance, which is valuable in the treatment of early stage Parkinson's disease in the elderly. 2-Furanmethanol is a food flavoring additive that is mainly used to formulate aroma flavor. Vanillin is mainly used in food additives.

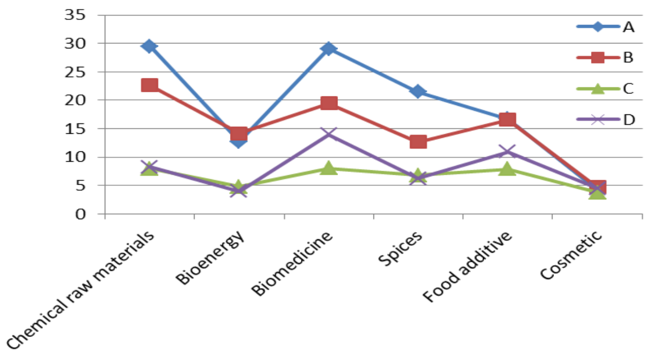

Figure 6: comparison of the functional classification of samples A, B, C, and D after pyrolysis at 550 ° C, the A sample can be used as a chemical raw material, biomedicine, and the content of the fragrance is the highest, and the content of the bioenergy substance and the cosmetic material which can be obtained is the highest under the temperature condition in the B sample. This result indicates that the pyrolysis at 550°C can increase the content of bioenergy and cosmetics in the pyrolysis products in RPFs, while the nano-Fe_2O_3 cannot play a positive catalytic role.

The results of Py-GC-MS indicating there exists active ingredients in RPFs which have huge potential to be utilized. When producing production at a temperature of 550°C (Figure 6), if you want more bioenergy and cosmetic raw materials, you can choose nano NiO as a catalyst to add to RPFs.

IV Conclusion

Comparing the products obtained by pyrolyzing four different samples at 550°C, it was found that the three nano-catalysts do not actively catalyze the target pyrolysis product throughout the process. The pyrolysis products of the original powder can be used as chemical raw materials, the biomedical and spices are the most, the product obtained by pyrolysis of the sample added with nano NiO has the most bioenergy components, while all the components obtained by pyrolysis in the addition of nano- Fe_2O_3 are the least. This indicates that when pyrolysis at a temperature of 550°C, the addition of nano-NiO as a catalyst to RPFs is beneficial to increase the bioenergy content. Compared with common catalysts, nano catalysts have larger specific surface area, and stronger ability to adsorb substances. Therefore, the catalytic effect of the nano-catalyst is more obvious than that of the conventional catalyst.

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