Ekoloji 28(108): 33-38 (2019)

LETTER TO THE EDITOR

# Pyrolysis-based Resource Utilization of Rapeseed Cake Treated with Benzene/Ethanol Extraction

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New ways of rapeseed cake resource utilization were explored by pyrolysis. The results showed that the largest component types at 600°C, at 300°C pyrolysis produced mainly esters (accounting for 41.68% of the total), followed by ketone (30.73%); at 450°C (41.46%) mainly ketones and esters (40.63%) were produced and small amounts of alkane (1.35%) and alcohol (2.36%) began to appear in the substance; at 600°C (37.42%) ketones were mainly found and the ester content decreased to 14.36%, and a new category emerged: ethers and amine, but to a lesser content, below 5%; at 750°C,mainly esters (29.68%), as well as the content close to ketone (16.04%), aldehyde (16.68%), olefin (15.67%), and hydroxyl acids (12.73%) were found, while ethers and composition of amine disappeared. 48 and 45 compounds were identified from 450 and 600°C Pyrolyzates of extraction residues, respectively. The types of pyrolyzate at 450°C are up to 15, and the highest content is ketone (20.90%), followed by heterocyclic (20.33%). At 600°C, 14 types of pyrolyzate were found, the highest content is heterocyclic (29.22%), followed by ketone (21.33%), and hydrocarbons (20.75%). Component analysis showed many new substances in the pyrolyzates of rapeseed extract and extraction residue.

## I Introduction

China has a vast territory and rape planting is widely common (Cheng et al. 2018a), throughout the country, particularly north to Heilongjiang and south to Hainan Island, west of Uygur Autonomous Region Xinjiang, east to the coastal provinces (Yang and Tian 2015), from the plains to above 4600 m height in the Tibet plateau rape is sown, grown, and harvested in the field all year round (Gao and Wen 2018).

These articles used the modern testing means (Lee and Lee 2018), and for describe thermal cracking of rapeseed dregs at different temperatures via Py- GC/MS triplet technical identification of chemical compositions of pyrolyzates, analytical pyrolyzates compositions under the condition of different change rules (Jiang and Ge 2017).

In view of this, this study first extracted rapeseed cake from benzene/ethanol (2:1), prepared the extract, and extracted the residue, and then the following experiments were conducted: the Py-GC/MS analysis of pyrolyzates under different temperature of rapeseed extraction (Yang and Tian 2015), and analytical pyrolysis law; Based on the extract study, the Py-GC /MS of the pyrolyzates in different temperatures of rapeseed cake was further studied, and the pyrolysis law was analyzed; (Kang et al., 2018) Infrared spectra of the extract and extraction residue of rapeseed were analyzed to clarify the change rules of the groups; A comparison and analysis pyrolyzates of rapeseed extraction and extraction residue was conducted to select the optimum extraction technology of rapeseed.

**II Materials and Methods**

**(1) Materials**

After drying rapeseed cake, it was processed into about 40-60 target powder via pulverizer, then dried to absolute dry at 55°C (0.01 MPa). The benzene used in the test was set aside. Ethanol was chromatographic pure, and water was first grade ultrapure water. Filter paper was fully extracted by benzene/alcohol solution for 24 h (Liu et al. 2018).

**(2) Benzene/ethanol extraction**

10 g samples (accuracy 0.1 mg/g) were taken respectively and 150 mL benzene/ethanol solution was added (volume ratio of benzene to ethanol is 2:1). The mixed solvent was extracted via fully automatic Soxhlet extractor FOSS. The extraction conditions were as follows: soaking at room temperature for 12 h, then extracting at 85°C for 5 h (Ouyang and Hou 2017). The benzene/ethanol extract filtrate of the rapeseed cake was obtained via filter paper with full extraction of benzene/alcohol solution. The extracted filtrate was evaporated at 45°C/0.01 MPA vacuum and concentrated to 10 ml (Cheng et al. 2018b).

**(3) Preparation of benzene/ethanol residue**

Weigh 0.1mg benzene/ethanol extraction residue, a quartz tube laid flat in pyrolysis, the ends of which are covered with quartz cotton. The tube is placed in a solid automatic sampler and the pyrolysis chamber is a conical quartz tube. (Ahamed and Loganathan 2017) The controller of the pyrolyzer controls the furnace heating to a set temperature. Benzene/ethanol extracts were instantly clicked in the pyrolysis chamber at 450-600°C. The pyrolysis products were collected via gas chromatographic injection port, and the injection temperature was kept at -50°C. Liquid nitrogen condensed, gas reheated after pyrolysis, swept into GC/MS (Lou and Zhao 2018).

**(4) Py-GC/MS analysis**

The PY-2020iS pyrolyzer produced by Frontier Company of Japan is used in the Py-GC/MS triad system (Lou and Zhao 2018). GC/MS adopts the Agilent 5975C/6890N gas chromatography-mass spectrometer produced by Agilent Company of USA. The pyrolyzer is a single-click pyrolyzer, instant pyrolysis using standard gas chromatographic conditions: the chromatographic column is DB-5 MS (30 m × 0.25 mm × 0.25 um) produced by Agilent Company, and the carrier gas is helium. Injection port temperature 250°C; The chromatographic column rising conditions were as follows: the velocity of 10°C/min was increased from 50°C to 300°C, and the mass spectrum conditions were as follows: the ionization mode was EI and the electron energy was 70 EV. The flow rate of he is 1 ml/min, and the scanning mass range is 35-550 AMU (m/z) (Chen et al. 2018).

**(5) Infrared spectrum analysis**

The situation of molecular absorption of infrared light is recorded via instrument, the infrared spectrum is collected, and the spectrum is smoothed and baseline corrected. Infrared spectrogram usually uses spectral wave number as abscissa to indicate the location of the absorption peak, and the transmittance (T%) is used as ordinate to indicate absorption intensity (Tian and Zhong 2018; Lam et al. 2019).

**III Results**

**(1) Identification of pyrolyzates of benzene/ethanol extractives**

The pyrolyzates of rapeseed cake benzene/ethanol (2:1) extract had 300 peaks under the condition of 300°C for gas phase chromatography, and 26 peaks were found. After MS analysis, combined with literature research, 23 compounds were identified, accounting for 99.91% of the total peak area; the gas chromatogram of pyrolyzateshas19 peaks at 450°C, and 15 compounds have been identified via MS analysis and literature review, accounting for 98.26% of the total peak area. At 600°C, 45 peaks were found in the pyrolyzates of gas chromatogram, and 40 compounds were identified via MS analysis and literature review, accounting for 98.74% of the total peak area. (Prabhakaran and Raj 2018)The gas chromatogram of pyrolyzates have 21 peaks at 750°C, and 21 compounds have been identified via MS analysis and literature review, accounting for 99.99% of the total peak area. 300°C pyrolysis temperature the products are mainly esters (41.68% of the total), followed by ketones (30.73% of the total). Other content is less; at the pyrolysis temperature of 450°C, the main products were esters and ketones, accounting for 40.63% and 41.46% of the total amount, respectively. Alkanes and alcohols began to appear, but the relative contents remained comparatively small. It was 1.35% and 2.36, respectively. At a pyrolysis temperature of 600°C, the main products were ketones, which accounted for 37.42% of the total amount. The contents of esters decreased to 14.36%, and a new category appeared on the basis of cracking products at 450°C: ethers and amines. However, the content is less, not higher than 5%; at the pyrolysis temperature of 750°C, the main products were esters, which accounted for 29.68% of the total amount. The contents of ketones, aldehydes, olefins and hydroxyl acids were almost identical with 16.04% and 16.68%, respectively. 15.67% and 12.73% ethers and amines disappeared.

At the pyrolysis temperature of 750°C, the relative content is 41.68% and 14.36%, respectively. The reason for this trend may be that the chemical components in rapeseed cake decompose under heating conditions to form hydrolytic monoesters and pyrolytic monoesters. The decomposition of pyrolytic esters occurs when the temperature continues to increase and the content decreased at 600°C pyrolysis temperature. When the temperature increased to 750°C, both alcohols may be dehydrated to form double bonds, and the contents of esters with hydroxyl groups in the branched chain may increase slightly. The content of ketones is 300 and 450. At the pyrolysis temperatures of 600 and 750°C, the relative content was 30.73-41.46% and 37.32-16.04%, respectively, at 600°C. The relative content of ketones reached the maximum value and decreased greatly at 750°C. The reason for this phenomenon may be that the cracking of ketones increases with increasing temperature. However, when the temperature is above750°C, ketones will be decomposed and destroyed; so, for ketones, the pyrolysis temperature should not exceed 600°C, and the temperature should not be too high.

**(2) Identification of pyrolysis products of benzene/ethanol-extracted residues**

Compared to the pyrolysis of rapeseed cake benzene/ethanol extract, extraction residue pyrolysis products of different types, different types of content varied significantly. 450°C pyrolysis temperature, pyrolysis products of rapeseed cake benzene/ethanol extract, product type was only 5%, not containing heterocyclic hydrocarbons or aldehydes. The chemical composition of phenol, amine, amide, nitrile sulfone, phosphine, oxime and the material content was highest in esters (up to 44%), followed by ketones, accounting for 41.82% of the total; rapeseed cake benzene/ethanol extraction residue at 450°Cin pyrolysis products, up to 15 types, containing material with the highest amount of ketones, accounting for 20.90% of the total, followed by heterocyclic, accounted for 20.33%.600°C pyrolysis temperature, rapeseed cake benzene/ethanol extract pyrolysis products. There are nine types of products, which do not contain heterocyclic, aldehyde, phenol, sulfone, nitrile, phosphonate, oxime, the highest content is ketones, up to 38.44%, followed by esters, accounting for 28.19% of the total; among the pyrolysis products of benzene/ethanol extraction from rapeseed cake at 600°C, there are 14 types of products, the highest content of which is heterocyclic, accounting for 29.22% of the total amount, followed by ketones and hydrocarbons. Class substances, 21.33% and 20.75% of the total amount, respectively. Because the relative content of rapeseed residue was only at 450°C and 600°C, the relative content was less; therefore, the longitudinal comparison was not made.

**(3) Groups change identification via Infrared Spectroscopic analysis**

**a** **b** **c**

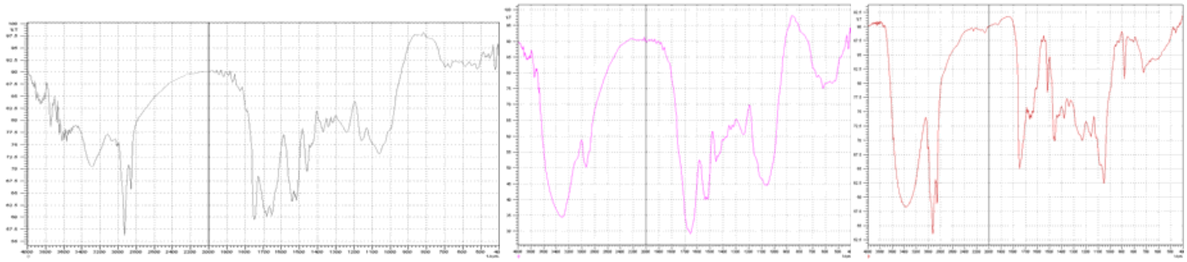

**Figure 1. a Infrared spectroscopy of rapeseed cake, Infrared spectroscopy results of the extractives (a), extracting residues (b) of rapeseed cake by benzene/ethanol (2:1) solvent**

From the above analysis of the whole IR spectra of rapeseed cake samples, it is found that there are many types of substances in rapeseed cake samples, such as alcohols, phenols, ketones, hydrocarbons, ethers, amides, amines, and other substances (Figure 1-a).

Observed and compared to the infrared spectrum of benzene/ethanol extract and extraction residue of rapeseed meal, Both extracts and extraction residue have the same material category respectively are ether ketone, alcohol, phenol, hydrocarbon, carboxylic acid, oramide substances. In the infrared spectra of rapeseed cake benzene/ethanol extract (Figure 1-b), in 2855, 1750, 1180 $cm^{-1}$ near the absorption peak belonged to the symmetric stretching vibration peak, carboxylic acid (ester), and carbonyl stretching vibration of C-O, which contains the material categories aldehydes and ketones, carboxylic acids, alcohols, and phenols type of material; in the infrared spectra of benzene/ethanol extraction of rapeseed meal residue (Figure 1-c), in 3760, 1380, 1600-1450, 620 $cm^{-1}$ (peak) appears near the absorption peaks belong to N-H stretching vibration absorption and C-CH2 group, N-H, C=C deformation vibration skeleton vibration C=C, and C-H outside the plane bending, namely the material category for heterocyclic, aldehydes, amines, and nitriles (Duan et al. 2018).

## IV Conclusion

The extraction of rapeseed cake products was conducted via pyrolysis and a variety of useful components were detected; however, under different temperature conditions the organic ingredients are very different from that of benzene/ethanol (2:1) extraction product at 300°C temperature. Pyrolyzates of the highest relative content of esters, which accounted for 41.68% of the total, 450°Ctemperature pyrolyzates the highest relative content are esters and ketones, respectively accounting for 40.63% and 41.46%, 600°C temperature pyrolyzates of the highest relative content are ketones, accounting for 37.42% of the total, 750°C cracking temperature relative content was esters in the product, accounting for 29.68% of the total. The rapeseed extraction residue through pyrolysis, benzene/ethanol (2:1) at 450°C cracking temperature products in relatively high content of ketones and heterocyclic compounds, accounting for 20.90% of the total, 20.33%, 600°C temperature pyrolysis products show a relatively high content of heterocyclic ketones and hydrocarbons, respectively. 29.22% of the total, 21.33%, 20.75%; rapeseed cake extraction residue containing trace amounts of pyrrole (4.51%). Infrared spectrum analysis of rapeseed cake, solvent extract, and extract residue showed that there were many types of substances in rapeseed cake powder extracted by solvent, such as alcohols, phenols, ketones, hydrocarbons, ethers, amides, and amines. If these organic compounds are released into the atmosphere, they will cause air pollution. If these substances can be transformed into available resources and improve rapeseed cake utilization efficiency, they will better protect the environment.

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