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Infrared-Spectral Characteristics of *Camellia oleifera* Shell/Meal during Composting

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Abstract

The compost products of *Camellia oleifera* shell/meal mixed at different mass ratios were characterized by Fourier-transform infrared spectroscopy (FTIR) at different composting stages to monitor the structural changes of their components. The results showed that the amount of *Camellia oleifera* meal significantly affected the composting rate of the shell, but did not change the degradation order and decomposition of the related compounds. During the composting process, microorganisms used the highly decomposable carbon source materials, such as proteins and sugars, first to grow and multiply, and then decomposed hemicellulose, cellulose and lignin by oxidative cleavage after these nutrients were consumed to a certain extent. The decomposition products were then condensed into more stable humic acids. The degradation rates of the compounds were directly proportional to the amount of *Camellia oleifera* meal. The compounds in *Camellia oleifera* shell were composted faster with higher amounts of *Camellia oleifera* meals, resulting in less lignocellulose in the final products.

Keywords

Camellia oleifera Shell, *Camellia oleifera* Meal, Fourier-Transform Infrared Spectroscopy, Composting, Degradation

1. Introduction

Camellia oleifera is the largest woody oil crop in China [1], and the history of cooking oil extraction from *Camellia oleifera* seed can be tracked back to 2300 years ago [2]. The outer shell of fresh *Camellia oleifera* fruit accounts for more than 60% of its total weight [3]. *Camellia oleifera* meal is the residue left after the oil extraction from the seeds, and its weight is three times of that of the oil [4]. The production of both by-products, *Camellia oleifera* shell and meal, of tea oil

extraction have been significantly increasing with the rapid development of the tea oil industry. These by-products are rich in organic compounds and nutrients, which makes them excellent renewable resources. However, *Camellia oleifera* shell is mainly composed of cellulose, hemicellulose and lignin that are hardly degraded under natural conditions [5]. The *Camellia oleifera* meal contains large amounts of biotoxic substances, such as tannins and saponin. Therefore, the high production of *Camellia oleifera* shell and meal and their low utilization efficiency have imposed great threats to the environment.

Composting has been demonstrated an efficient approach to utilizing *Camellia oleifera* shell and meal. During composting, the unstable *Camellia oleifera* shell and meal are converted into stable humus substances by aerobic fermentation under artificially controlled conditions including water, C/N ratio and air, resulting in good soil improvers and organic fertilizers [6]. The rational development and utilization of *Camellia oleifera* shell and meal by composting can not only reduce waste pollution, but also partially alleviate the shortage of agricultural resources, fostering the environmental and economic developments.

Fourier-transform infrared spectroscopy (FTIR) provides the infrared spectrum of absorption or emission of a compound based on the constant vibrations and rotations of its atomic groups, which gives the composition information of atomic groups, and thus facilitates the understanding of structure of a compound. FTIR analysis has exhibited great advantages including low sample loss, easy operation, fast detection and good stability [7] [8], and thus has been widely used in medicine, agriculture and chemical production. Monitoring composting processes with an infrared spectroscopy can provide more information of the structural changes of the compounds in composting stack [9] [10] [11]. For example, Huang *et al.* successfully applied FTIR to the structural analysis of compounds in livestock manure composting [7]. They found that the contents of cellulose, hemicellulose and lignin were correlated with the composting temperature and germination index (GI) of the seeds, which could be used as an indicator of compost maturity [7]. Duan *et al.* studied the infrared-spectral characteristics of organic waste during composting and found that FTIR could provide detailed information on the degradation behavior of composting chemicals, and thus could be used for composting control and real-time monitoring [10]. However, different materials are composted differently, and there is not a universal compost maturity indicator established yet [12]. So far, to the best of our knowledge, the application of FTIR in the compost of *Camellia oleifera* shell/meal mixture has not been reported.

In the present work, the composted *Camellia oleifera* shell/meal was characterized by FTIR to investigate the effects of the ratio of shell to meal of on the degradations of various compounds during composting, aiming to establish the scientific foundation for the utilization of *Camellia oleifera* shell and meal and the corresponding compost maturity indicators.

2. Experimental Materials and Methods

2.1. Materials

Camellia oleifera shells with the sizes < 3.5 cm were collected from Dongfanghong Forest Farm, Jinhua City, Zhejiang Province, China and *Camellia Oleifera*seed meal provided by Zhejiang Tiantai Kangneng Tea Oil Co., Ltd.. White Urea granular was purchased from Henan Jinkai Chemical Holdings Group Co., Ltd. The microorganisms (EM, 1.05×10^{12} CFU/ml) was purchased from Henan Nanhua Qianmu Biotechnology Co., Ltd. Other bacterial strains included *aspergillus awamori* for the degradation of tannin and *Bacillus amyloliquefaciens* and *Meyerozyma guilliermondii* for the degradation of saponins. The additive amount of bacterial strains (submerged culture) was 1.5% of the weight of Camellia oleifera shells used in composting. The basic properties of raw materials are shown in Table 1.

2.2. Composting

The composting was conducted in an insulated and highly ventilated ecological composter (73 cm × 115 cm × 80 cm, 220 L, BIOLAN). Four experimental groups with different shell/meal ratios were designed, and ech experiment was conducted in 3 replicates (Table 2). The initial C/N ratio of each group was adjusted to 30 with urea, and the contents of both EM and saponin-degrading bacteria were 1.5%. The initial moisture content was adjusted to 55% with water. The raw materials were stir thoroughly and put in the composter to initiate the aerobic compost fermentation. The temperature of compost materials and room temperature were measured every day at 3 pm. The material in the composter was turned over every 7 days in the first two weeks, and every 14 days thereafter. The compost material was sampled on day 0, 3, 6, 9, 12, 18, 24, 30, 40 and 60. For each sampling, 200 g samples were taken from the upper, middle and lower positions of the composter, respectively, mixed well, sealed and stored in a 4˚C refrigerator before use.

Table 1. Properties of the raw materials for composting experiments (%).

Raw material	Cellulose	Hemicellulose	Lignin	C	N	C/N	Tannins	Saponins
Camellia oleifera shell	18.62	49.34	29.71	48.6	0.42	116.00	2.26	4.80
Camellia oleifera meal	21.01	24.76	21.59	47.8	1.22	39.18	1.03	16.35

Table 2. Design of composting experiments.

Compost group	Raw materials
1/3 *Camellia oleifera* meal	*Camellia oleifera* shell + 1/2 dry wt. *Camellia oleifera* meal
1/4 *Camellia oleifera* meal	*Camellia oleifera* shell + 1/3 dry wt. *Camellia oleifera* meal
1/5 *Camellia oleifera* meal	*Camellia oleifera* shell + 1/4 dry wt. *Camellia oleifera* meal
1/10 *Camellia oleifera* meal	*Camellia oleifera* shell + 1/9 dry wt. *Camellia oleifera* meal

2.3. FTIR Analysis

The samples collected from composters were analyzed with a Fourier-transform infrared spectrometer (Nicolet iS50, Thermo Fisher Scientific, USA) using KBr pellets. Briefly, 0.001 g sample was dried at 105˚C for 1 h, mixed with 0.1 g KBr powder, and pressed into a thin and transparent disk by the pressed-disk technique for FTIR measurement. For each measurement, a 32-scan absorption interferogram was collected with the resolution of 4 cm^{-1} in the range of 400 - 4000 cm^{-1} at ambient temperature. Each measurement was repeated three times, and the peak positions and heights were measured in the software Origin 8.0.

2.4. Data Analysis

The spectra were plotted in EXCEL and Origin 2017 to determine peak position and height.

3. Results and Discussion

3.1. Temperature Change of *Camellia oleifera* Shell/Meal during Composting

As shown in Figure 1, the temperatures in the composters containing the *Camellia oleifera* shell/meal mixtures of different mass ratios increased dramatically at first, remained at high temperatures with minor fluctuations for a while, decreased to room temperature and remained at the room temperature eventually. This process can be divided into three stages: the heating stage in the first 4 days, high temperature stage from day 4 to 35, and cooling stage from day 35 to 40. A minor temperature rising was observed thereafter, yet the temperature decreased back to room temperature rapidly, reaching the compost maturity. The sample containing 1/2 dry wt. meal (the 1/3 group) reached the high temperature of 50˚C on day 2, one day earlier than the other three groups, and its high temperature stage lasted for 32 days, the longest among those achieved with all groups. The highest temperature of the 1/3 group was 72˚C, followed by that of the 1/4 group containing 1/3 dry wt. meal with the highest temperature of

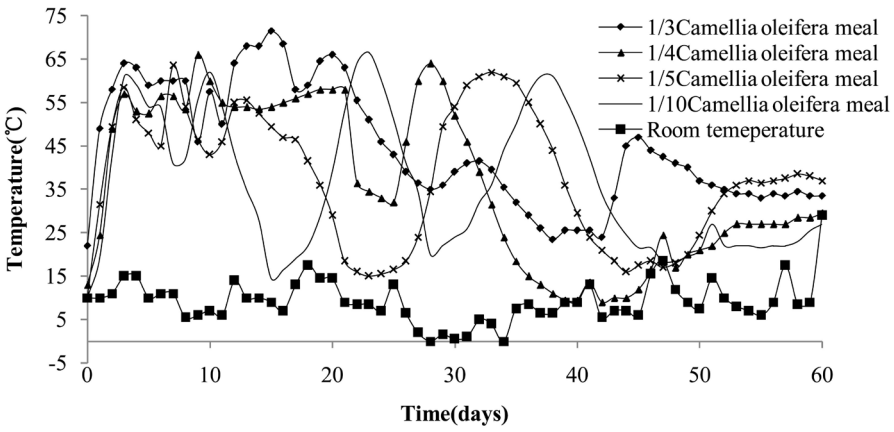

Figure 1. Temperature changes of *Camellia oleifera* shell/meal mixtures during composting.

68˚C and 29 days high temperature stage. The 1/10 group that contained 1/9 dry wt. meal reached the high temperature of 50˚C last with the shortest high temperature stage of 11 days, and its highest temperature was only 66˚C. The temperatures of all groups exhibited similar changing trends, but with different values and different lengths of each stage. It is clear that the high temperature stage was reached sooner, and was longer with more *Camellia oleifera* meals added. The compost stack temperature change was caused by the microbial activities that were also affected by the temperature. Therefore, the compost stack temperature can be used to evaluate the composting progress as an indicator of compost maturity. However, the temperature cannot directly reflect the changes in the composition of the stack [13]. Therefore, the compost samples were further analyzed by FTIR to determine the composition change of the stack, aiming to explore the possibility to monitor the composting progress of the *Camellia oleifera* shell/meal mixture with FTIR.

3.2. FTIR Analysis of Compost Samples

3.2.1. IR Spectra of Raw Materials

The *Camellia oleifera* shell sample exhibited three strong absorption peaks at 3415.69 cm^{-1}, 1617.33 cm^{-1} and 1049.51 cm^{-1}, respectively (**Figure 2**) and seven weak absorption peaks. Four strong peaks at 3415.69 cm^{-1}, 2295.88 cm^{-1}, 1654.68 cm^{-1} and 1049.51 cm^{-1} and five weak absorption peaks were found in the *Camellia oleifera* meal sample. The assignments of these peaks are shown in **Table 3** [3].

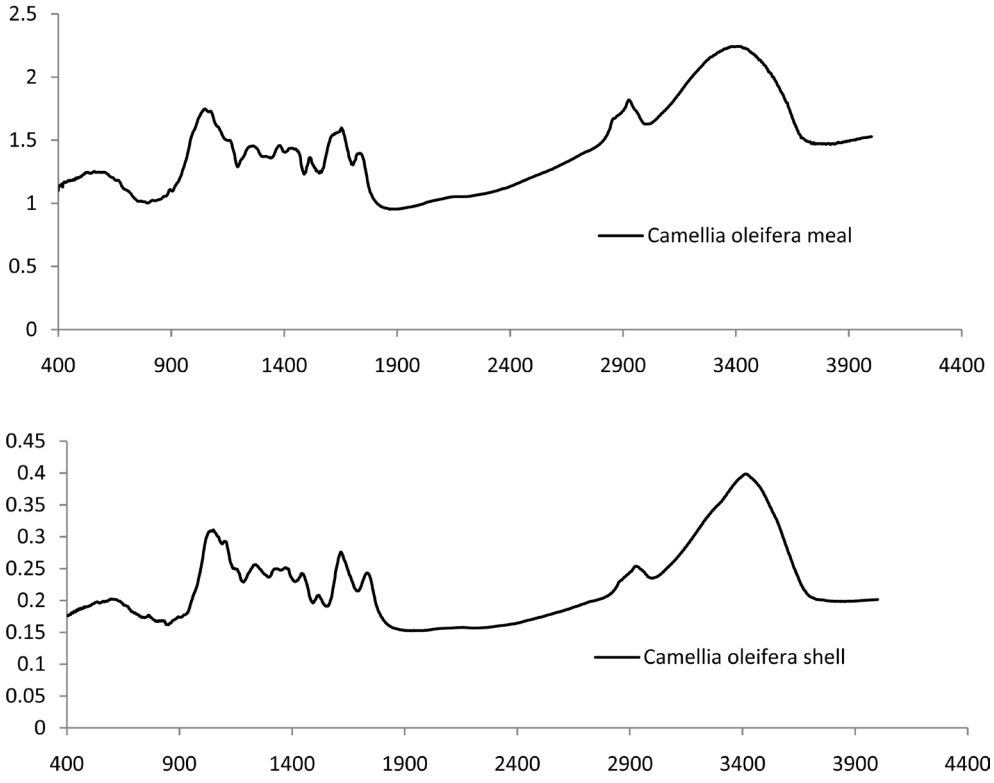

Figure 2. IR spectra of raw materials.

Table 3. Assignments of the infrared absorption peaks of the *Camellia oleifera* shell and meal samples and the representative compounds.

Wavenumber/cm^{-1}	Assignment	Representative compounds
3415.69	-OH vibration and N-H stretching vibration	Carbohydrates including cellulose, hemicellulose, and lignin and water
2926	Symmetric or asymmetric stretching vibrations of C-H in $-CH_3$ and $-CH_2$	Polysaccharides, lignin, fatty acids and saturated hydrocarbons
1737	Stretching vibration of C=O in non-conjugated ketones, carbonyl groups and esters	Polysaccharides, lignin, and hemicellulose
1654	Stretching vibration of C=O in p-substituted conjugated aromatic groups	Lignin
1617	Stretching vibration of C=O and skeletal vibration of aromatic groups	Lignin
1516 and 1513	Deformation of N-H and stretching vibration of C=N	Aminos and lignocellulose
1445	Bending vibration of C-H and skeletal vibration of benzene ring	Lignin and polysaccharides Lignin
1236 and 1261	Stretching vibration of CO-OR and Ph-O	Acetoxy group in hemicellulose and lignin
1049	Asymmetric stretching vibration of Si-O-Si and stretching vibration of C-O	Silicic compounds cellulose, polysaccharides, lignin, and hemicellulose

These characteristic IR peaks suggest that the *Camellia oleifera* shell and meal mainly contain carbohydrates, such as cellulose, hemicellulose, lignin, polysaccharides, and so on, proteins, amides, silicates etc. The peaks of *Camellia oleracea* meal at 2926 cm^{-1}, 1737 cm^{-1}, 1513 cm^{-1}, 1445 cm^{-1} and 1049 cm^{-1} are stronger than those in the shell sample, suggesting that the meal sample contains more polysaccharides, fatty acids and amides than the shell sample. No multiple complex bands of $-NH^{4+}$ at 2400 - 2200 cm^{-1} were found in the shell sample, indicating that it contained high amounts of lignocellulose and low amounts of proteins [13] [14].

3.2.2. FTIR Analysis of *Camellia oleifera* Shell and Meal Compost

The IR peak positions of the compost give the structural information of its compounds, and the peak intensities can be used to evaluate the degradation progress of these compounds [15]. As shown in **Figures 3-8**, the compost samples of different ratios of shell to meal exhibited similar IR spectra, suggesting that they contained similar functions groups, consistent with the IR spectra of garden compost waste reported by Xu *et al.* [16]. However, the peak intensities were varied significantly, yet regularly, during the composting. The peak intensity at 3400 cm^{-1} was weakened significantly at the heating and high temperature stages from day 0 to 30, indicating that the easily decomposable components

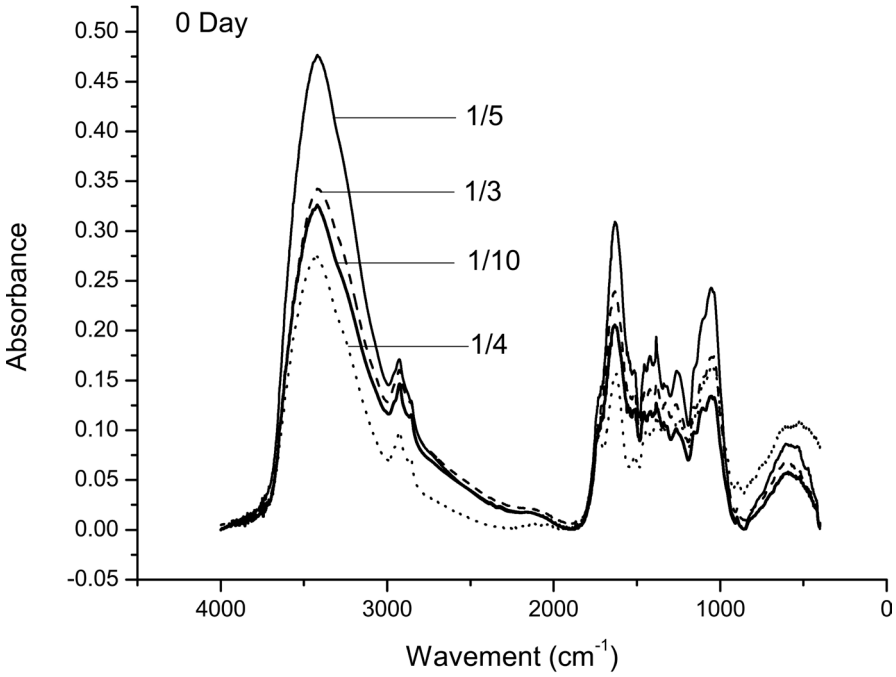

Figure 3. IR spectra of compost samples on 0 day.

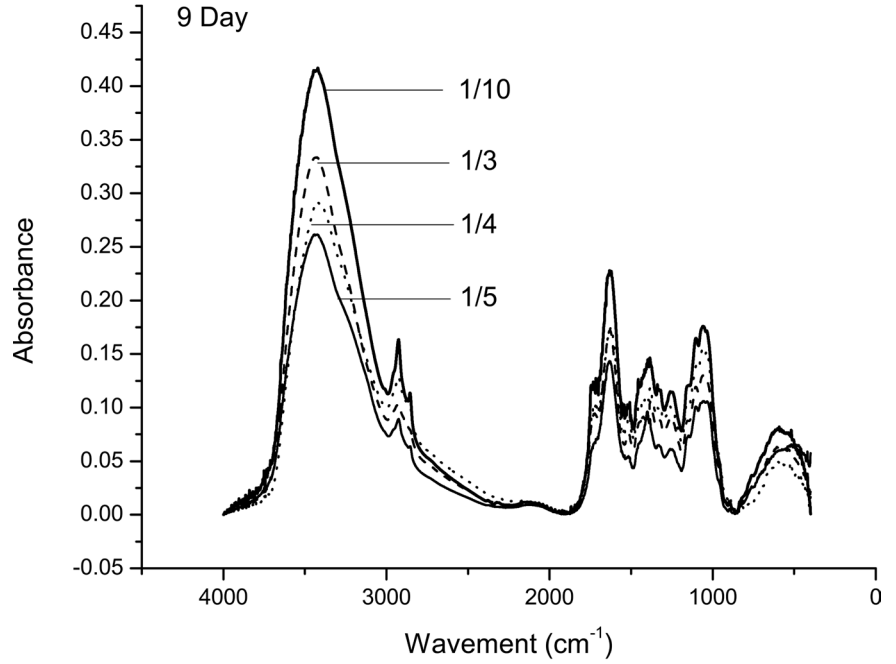

Figure 4. IR spectra of compost samples on 9 day.

including proteins and polysaccharides were degraded, consistent with the high temperatures during this period. The microorganisms used these proteins and polysaccharides to multiply and grow [16], which produced heats to raise the temperature of the stack. The peak intensity was slightly increased thereafter, and remained constant from day 40 to 60, indicating that the proteins and polysaccharides were completed degraded at the heating and high temperature stages.

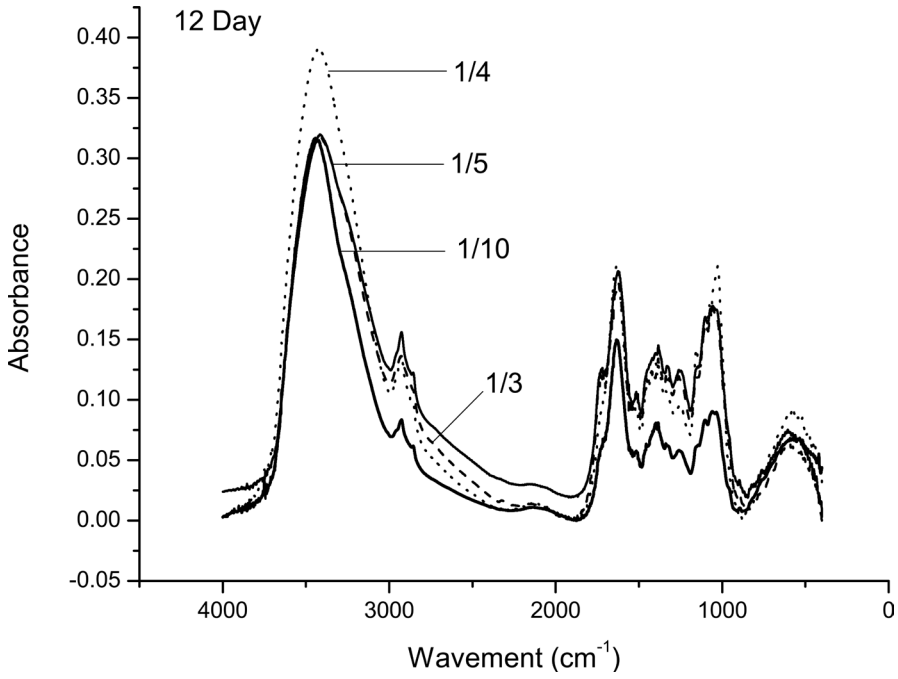

Figure 5. IR spectra of compost samples on 12 day.

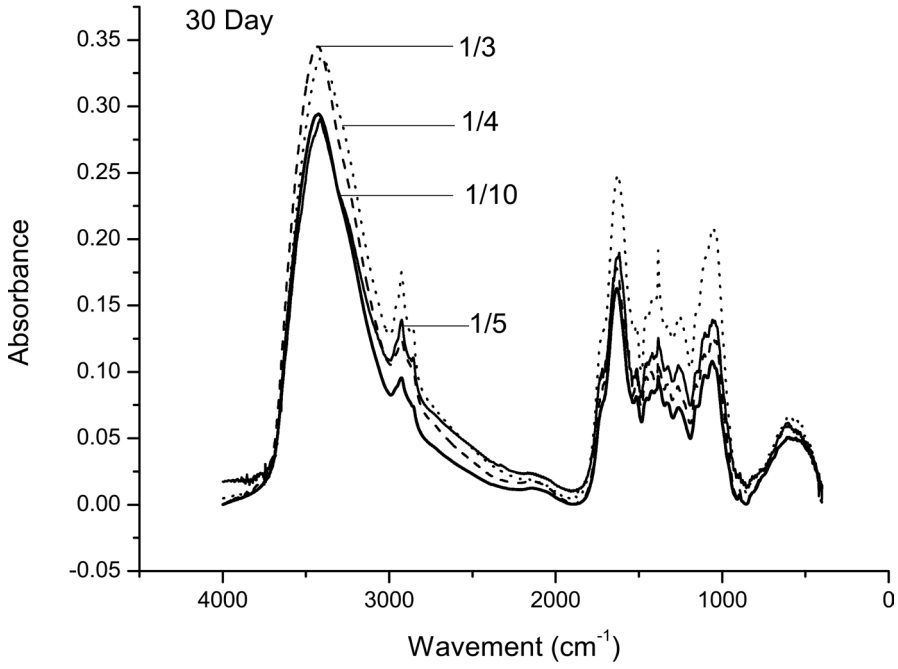

Figure 6. IR spectra of compost samples on 30 day.

The peak intensity at 2920 cm^{-1} exhibited an increasing trend from day 0 to 30, decreased thereafter and remained constant from day 40 to day 60, indicating that the decomposition of large amounts of macromolecules increased the numbers of methylene and carboxyl groups in the first 30 days, and then those degradation products were further consumed to afford humic acids. The intensities of the characteristic peaks of cellulose, hemicellulose and lignin at 1420 cm^{-1},

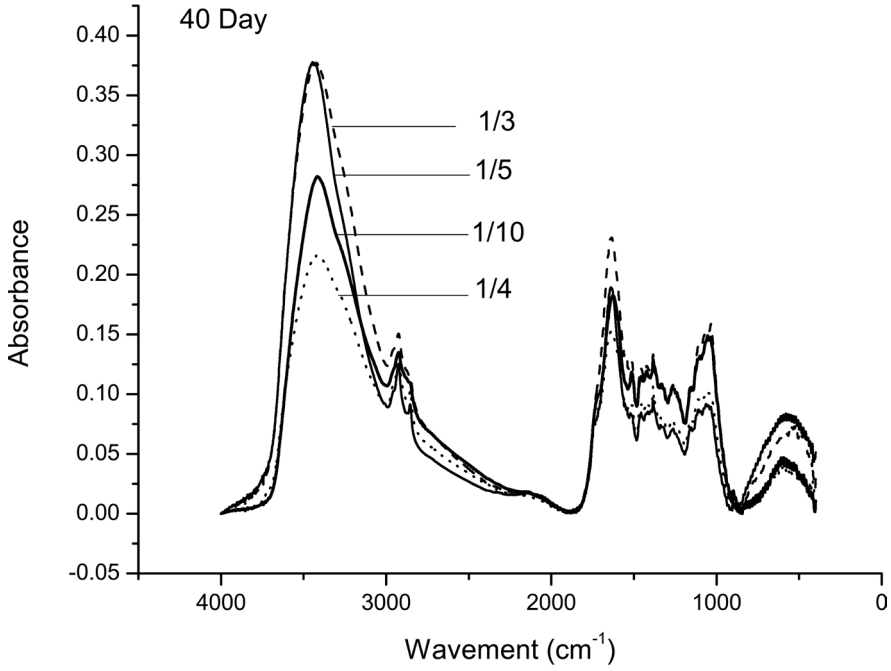

Figure 7. IR spectra of compost samples on 40 day.

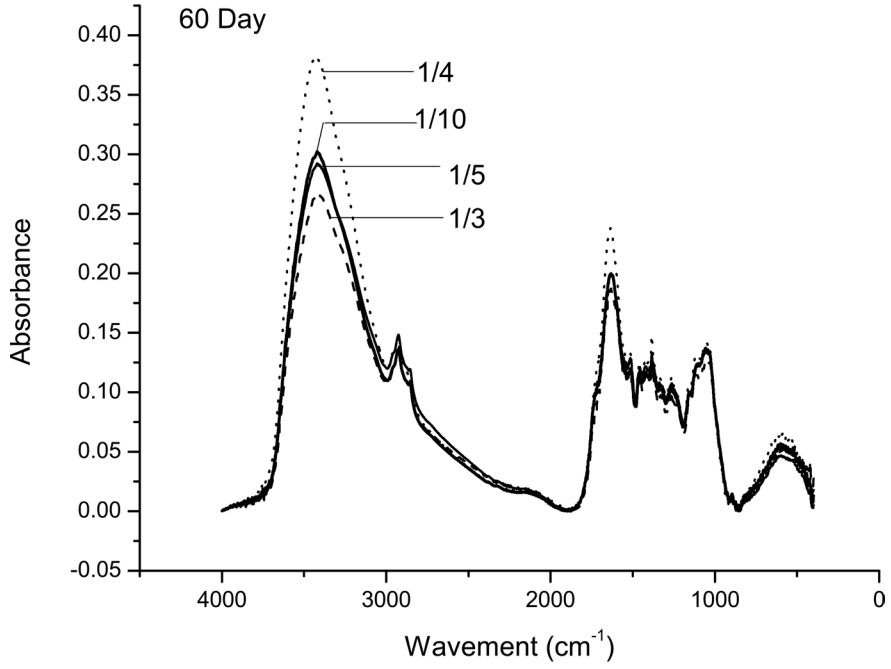

Figure 8. IR spectra of compost samples on 60 day.

1640 cm^{-1}, 1320 cm^{-1} and 1030 cm^{-1} were dramatically decreased from day 0 to 12 because of the degradation of large amounts of hemicellulose, slightly increased right before day 30, decreased again from day 30 to 40 and increased slightly thereafter. The second decrease and increase fluctuation might be due to the burst growth of microorganisms for the degradation of cellulose and lignin at appropriate temperatures and accumulated nutrition during the cooling stage.

The increased absorptions at 1420 cm^{-1} and 1640 cm^{-1} indicated that some of the degradation products were converted into humus in the composter [16]. These results suggest that, during the composting, the microorganisms used the easily decomposed carbon sources including proteins and polysaccharides first for growth and multiplication, and after these nutrients consumed, degraded the hemicellulose, cellulose, lignin etc. via oxidative cleavage. The degradation products were then further condensed into relatively stable humic acids [16], a major component of composting product. The composting processes of the mixtures containing different amounts of *Camellia oleifera* meal are similar. The variations in their IR peak intensities indicate that the amount of *Camellia oleifera* meal does not affect the degradation order of their compounds, and does affect the degradation degrees of these compounds.

The relative intensity changes of peaks at 1640 cm^{-1} for aromatic carbon, 1030 cm^{-1} for polysaccharide carbon, 1420 cm^{-1} for carboxyl carbon and 3400 cm^{-1} for aliphatic carbon can be used to evaluate the degrees of decomposition of different compounds, as well as their degrees of aromatization, during the composting [16]. As shown in **Figures 3-8** and **Table 4**, the peak height ratios of peak 3400 cm^{-1} to peak 1640 cm^{-1} (3400/1640) of the 1/3, 1/4, 1/5 and 1/10 groups decreased 49.8%, 31.9%, 25.9% and 23.6%, respectively after the composting, indicating that the amount of *Camellia oleifera* meal significantly affected the relative contents of aromatic and aliphatic carbons. The most significant declines of 1/3 and 1/4 group were found on day 40, and those of 1/5 and 1/10 groups appeared on day 60. The maximum decline in the peak height ratio of peak 1030 cm^{-1} to peak 1640 cm^{-1} (1030/1640) was found to be 47.1%, 49.4%, 62.7% and 52.7% for the 1/3, 1/4, 1/5 and 1/10 groups, respectively, indicating that the contents of aromatic carbons increased and those of polysaccharides decreased after the composting. The polysaccharides in the 1/5 and 1/10 groups were degraded rapidly, resulting in their short high temperature stages. Those in the 1/3 and 1/4 groups were decomposed slower, which explained their longer high temperature stages. The maximum decline in the intensity ratio of peak 1420 cm^{-1} to peak 1640 cm^{-1} (1420/1640) was calculated to be 27.1%, 26.3%, 39% and 34.4% for the 1/3, 1/4, 1/5 and 1/10 groups, respectively, indicating that the

Table 4. Relative peak intensities of major IR absorption peaks of the compost stack during composting.

Time/day	1/3			1/4			1/5			1/10		
	3400/1640	1030/1640	1420/1640	3400/1640	1030/1640	1420/1640	3400/1640	1030/1640	1420/1640	3400/1640	1030/1640	1420/1640
0	1.99	1.27	0.728	1.99	1.27	0.728	1.99	1.27	0.728	1.99	1.27	0.728
9	1.940	0.738	0.531	1.677	0.885	0.616	1.847	0.747	0.578	1.861	0.767	0.584
12	1.668	0.895	0.640	1.864	1.00	0.584	1.557	0.845	0.637	2.104	0.600	0.477
30	1.936	0.692	0.560	1.411	0.833	0.620	1.563	0.734	0.601	1.811	0.631	0.567
40	0.998	0.677	0.536	1.354	0.663	0.606	1.583	0.473	0.444	1.549	0.810	0.655
60	1.431	0.672	0.617	1.601	0.642	0.536	1.473	0.670	0.612	1.521	0.683	0.587

contents of carboxyl groups in each group decreased, and those of aromatic carbons increased, yet with different reduction degrees at different times. In addition, the absorption peaks at 1030 cm^{-1} and 1420 cm^{-1} were significantly weakened at the heating stage, indicating that the polysaccharides were degraded rapidly at the high temperatures. All groups exhibited similar change trends and final values of 1030/1640. Those results, along with the temperature change trend of each group during the composting indicate that the protein degradation is more vigorous, and the composting is faster with the higher amounts of *Camellia oleifera* meal. The 1/3 group exhibited the highest 1420/1640 and that of the 1/10 group was the lowest, suggesting that *Camellia oleifera* meal could increase the degradation degrees of cellulose, hemicellulose and lignin.

In summary, *Camellia oleifera* meal can significantly affect the decomposition degrees of the compounds in *Camellia oleifera* shell during composting but does not change their degradation order. The amount of *Camellia oleifera* meal affects the degradation rate and the quality of the final composting product of the shell.

4. Conclusions

The variation trend of absorption peaks in IR spectra of compost samples with different amounts of *Camellia oleifera* meal was basically consistent, but the temperature during composting increased more rapidly at the heating stage and the high temperature stage lasted longer as more meal added, reflected as increasing rate of change of height of the infrared characteristic peaks. Compared with temperature, IR spectra are less affected by the environment, and the height of the characteristic peak is directly related to the content of substances in composting. Therefore, IR spectra can be used as one of the indicators for judging compost maturity.

According to the infrared characteristic peaks, the amount of *Camellia oleifera* meal affected the progress of composting, but did not change the degradation order of the components in the shell. The microorganisms used the easily decomposable carbon source materials including proteins and sugars to grow and multiply first, and, after these nutrients were consumed to a certain extent, oxidatively cleaved the compounds, mainly hemicellulose, cellulose and lignin, and decomposed them. The decomposition products were then condensed into more stable humic acids. The degradation rate of *Camellia oleifera* shell is proportional to the amount of *Camellia oleifera* meal. The compounds in the shell were degraded more rapidly as higher amounts of meal added, resulting in less lignocellulose in the final compost. Therefore, *Camellia oleifera* meal can be used to promote the composting of *Camellia oleifera* shell, and improve the quality of composting products.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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