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Impact of hydrothermal process on the nutrient ingredients of restaurant garbage

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Abstract: In order to recover the nutrient resource from restaurant garbage, a complete trial with 2 factors on 5 levels of experiments was carried out. The temperature and heating time are the main factors influencing on hydrothermal process (HP) by which improves the degradability and digestibility of the restaurant garbage favorably to make animal feeds or fertilizer. The results showed the variation of protein, saccharide, and oil in the garbage. It showed that protein dissolved and liquefied during hydrothermal process, which made organic nitrogen in solid phase transfer to liquid phase. After heating at 180℃ for 60 min, organic nitrogen in liquid phase began to transform into ammonia. It also showed that hydrothermal process could promote the dextrinization, dissolution of the starch and its hydrolysis to reducing sugar, due to that starch in the restaurant garbage decreases and reducing sugar increases. When the temperature reached 140℃, the reducing sugar started to decrease due to chemical reactions. The cellulose was stable at 100—180℃. The floatable oil increased markedly in the hydrothermal process. The suitable condition for de-oil was observed at 160℃ heating for 80 min. Furthermore, the extraction of grease from the solid phase accords with first-order reaction dynamic model.

Keywords: restaurant garbage; hydrothermal process; protein; saccharide; lipid

Introduction

There are plenty of nutrients such as protein, carbohydrates and grease in the restaurant garbage. The structure of the nutrient ingredients and their occurrence have great influence on the disposal of the restaurant garbage and its recycle, e.g. if the garbage has a high nutrient value, we can consider to make it feedstuff for animals after proper treatment; if the organics are high, the garbage could be made into organic fertilizer after biochemical stabilization; if there is a more occurence of grease in the garbage, the grease could be extracted out to prepare biological fuel, and so on. Therefore, it is very important for the disposal of restaurant garbage and the popularization of the treatment process to determine how to make the nutrients change in a proper way from the garbage. Lai (2001) and Urbano *et al.* (2003) found that the hydrothermal process markedly influenced the physicochemical properties of protein, carbohydrates and grease. During hydrothermal process, pathogens are removed, while the nutrients such as protein, saccharide, and oil also change (Lai, 2001; Urbano *et al.*, 2003; Miyazaki and Morita, 2005). To make clear what reactions take place and how to control them, is important for the resource reclamation from restaurant garbage. However, few reports on it were published presently.

In this work, the influence theory and procedure of the hydrothermal process on the main nutrients including protein, carbohydrates and grease in the restaurant garbage were studied to investigate their variation generalization during this process. The results are expected to be favorable for optimizing the hydrothermal process of the restaurant garbage and for constructing the systematic hydrothermal theory.

1 Experimental materials and methods

1.1 Test samples of restaurant garbage

The test sample of restaurant garbage was taken from the 9th Canteen of Tsinghua University. Its physico-chemical properties are shown in Table 1. Of these, the true protein, starch, raw cellulose, reducing sugar, raw fat and floatable oil content were measured on the dry basis of the restaurant garbage.

Table 1 Physico-chemistry properties of restaurant garbage (% (w/w))

Item	pH	Moisture*	True protein*	Starch*	Raw cellulose*	Reducing sugar*	Raw fat*	Floatable oil from garbage* × 10⁻⁶
Average	6.58	79.01	21.75	12.51	0.14	15.24	27.61	9.4

Note: * Data measured on dry weight basis of the restaurant garbage

1.2 Hydrothermal treatment test on restaurant garbage

In order to make the treated products into feedstuff or fertilizer to recover the nutrients resource in the restaurant garbage fully, here treated the restaurant garbage hydrothermally according to the

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experimental arrangement as shown in Table 2, to investigate the effects of temperature and heating time on the content of nutrients such as protein, saccharide, and lipid. The structure of hydrothermal equipment is shown in Fig.1.

Before each test, the hydrothermal reactor was washed for three times with double-deionized water. The restaurant garbage sample 600 g was fed into the airproofed reactor and 300 ml water was added and the reactor was heated up to a prescribed temperature.

Table 2 Hydrothermal experiment conditions

No.	Temp.,℃	Heating time, min	No.	Temp.,℃	Heating time, min	No.	Temp.,℃	Heating time, min
1	100	20	10	120	100	18	160	60
2	100	40	11	140	20	19	160	80
3	100	60	12	140	40	20	160	100
4	100	80	13	140	60	21	180	20
5	100	100	14	140	80	22	180	40
6	120	20	15	140	100	23	180	60
7	120	40	16	160	20	24	180	80
8	120	60	17	160	40	25	180	100
9	120	80						

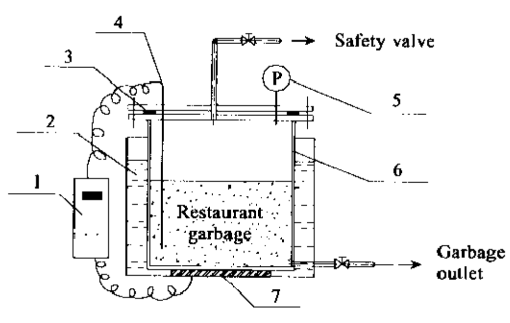


Fig.1 Diagram of hydrothermal equipment for restaurant garbage
1. temperature controller; 2. heat-conducting oil; 3. packing washer; 4. temperature sensor; 5. manometer; 6. body of the hydrothermal reactor; 7. heating cord

The time was noted as a starting point, and then during the course heating temperature was recorded for a prescribed period. When time was over, the pressure was released and treated sample was taken out. The treated sample was dewatered for 30 min by centrifuging at a speed of 3000 r/min to obtain the solid phase and water-oil mixture. The solid phase of the treated sample was dried in a vacuum drying oven to get the absolute dry sample for the measurement. The water-oil mixture was separated by a separatory flask. Then the protein, starch, raw cellulose, reducing sugar and raw fat in the solid product were measured, while the pH, the organic nitrogen, ammonia and floatable oil content in the liquid phase were measured. Here the floatable oil amount should be converted to the amount on the basis of per weight unit of dry garbage. The measurement methods are shown in Table 3.

1.3 X-diffraction tests of the starch

The starch sample was food grade, bought from Shenyang 5th Chemical Agent Factory in China. In

Table 3 Measurement methods

No.	Item	Measurement method	Method resource
1	Organics	Potassium dichromate method	GB 9834-88
2	True protein	Kjeldahl's methods	MAFIC-LAB/METH-004-2001
3	Ammonia	Nash reagent colorimetric method	GB 7479-1987
4	Starch	Enzyme-colorimetric method	GB/T 16287-1996
5	Reducing sugar	Direct assay method	GB 5009.7-85
6	Raw cellulose	Gravimetric method	GB/T 6436-1994
7	Raw fat	Soxhlet method	GB/T 6433-1994
8	Floatable oil	Volumetric method	

order to investigate the effect of hydrothermal process on the co-structure of the starch, we compared the X-diffraction spectra of the hydrothermally treated starch with its origin state at wavelength of 1.5406 × 10^{-1} nm (D/max1200 X-diffractometer, Rigakv Company, Japan). The nickel filter sheet was used. The scanning scope of 2θ was from 4° to 60 °. The scanning velocity was 10°/min.

1.4 Infrared spectral analysis of the lipid in the garbage

The waste oil sample taken from the restaurant garbage was purified and mixed with the barium sulfate, then was scanned by a Fourier transform infrared spectrometer (Bruker Company), the barium sulfate powder was used as background material for the infrared scan. In order to investigate the impact of the hydrothermal process on the oil, the infrared diffuse reflection spectrum of the waste oil was compared with that of the clean oil used to cook in the restaurant.

2 Results and discussion

The experimental results are shown in Table 4.

Table 4 Results of experiments

No.	True protein, dw%	Organic nitrogen in solid phase, dw%	Organic nitrogen in liquid phase, × 10^{-6} ww%	Ammonia in liquid phase, × 10^{-6} ww%	Starch, dw%	Reducing sugar, dw%	Raw cellulose, dw%	Raw fat in solid phrase, dw%	Floatable oil, × 10^{-6} dw%
1	21.56	3.45	240.14	92.11	10.21	16.11	0.24	26.30	1.52
2	24.38	3.90	259.90	95.21	8.54	17.05	0.23	24.23	2.12
3	27.19	4.35	255.48	105.46	7.62	29.21	0.43	21.98	2.31
4	30.63	4.90	304.95	114.68	5.98	28.33	0.32	19.94	2.54
5	24.06	3.85	322.05	120.33	5.13	29.3	0.23	16.46	3.62
6	22.19	3.55	305.17	114.05	9.33	18.03	0	26.21	2.45
7	26.00	4.16	365.32	141.01	6.52	30.15	0.17	24.07	3.52
8	31.44	5.03	334.54	176.10	4.25	49.64	0.22	20.47	5.13
9	23.94	3.83	361.47	190.07	3.11	66.61	0.01	17.95	6.52
10	22.00	3.52	389.10	211.04	2.56	53.15	0.15	14.78	7.53
11	22.94	3.67	315.75	115.51	8.69	65.42	0.19	25.11	5.04
12	22.94	3.67	368.69	157.02	5.23	70.86	0.25	22.06	6.14
13	21.50	3.44	437.40	193.00	3.64	68.59	0.31	17.91	7.03
14	18.38	2.94	527.85	214.06	2.45	65.32	0.21	14.35	7.32
15	14.25	2.28	516.67	243.00	1.56	50.17	0.05	10.60	7.41
16	23.56	3.77	191.68	217.43	6.14	69.56	0.30	23.38	4.11
17	26.44	4.23	376.72	244.62	4.21	65.21	0.37	19.96	7.78
18	28.81	4.61	445.26	260.03	2.56	53.54	1.05	14.21	10.70
19	21.13	3.38	441.46	307.00	1.03	35.34	0.01	9.39	13.17
20	10.63	1.70	443.94	363.00	0.66	35.15	0.34	5.57	7.53
21	28.06	4.49	143.13	337.07	6.01	29.64	1.64	22.77	7.34
22	25.38	4.06	303.95	378.00	3.02	25.53	0.30	16.58	9.31
23	14.38	2.30	310.48	393.85	1.14	18.15	3.56	10.10	10.63
24	8.38	1.34	186.45	523.61	0.35	15.32	2.96	5.66	8.79
25	7.00	1.12	210.47	646.00	0.27	7.91	15.52	1.96	5.58

2.1 Impact of hydrothermal process on the protein in the restaurant garbage

As one of the main nutrients in restaurant garbage, protein in the product is significant for the recycling of the treated garbage. At the beginning of the hydrothermal process, the protein in the garbage changes inappreciably as shown in Fig.2. If it continues to be heated, part of the carbohydrates and lipids dissolve or liquefy to enter the liquid phase, the protein content in the product relatively increases and it gets 31.44% as the highest value at 120℃ for 60 min. Then, the protein absorbs water and swells to make the auxiliary bond of the spherical peptide chain break because of being heated. Hence, the origin folded parts of the peptide chain were loosened and more readily affected by the digestion enzymes. Consequently, the digesting efficiency of the protein and the biological effectiveness of the essential amino acid in the product are improved which benefits for the treated product being made into feedstuff (Han, 2003a). Subsequently, the organic nitrogen content in the solid phase decreases while the organic nitrogen in liquid phase increases, as shown in Fig.3. Then the main changes of the protein are solution and liquation. The heating time when the protein content begins to decrease at 100, 120, 140, 160 and 180℃ were 80, 60, 60, 60 and 20 min respectively. When it gets 180℃ and the heating time reaches 60 min, the organic nitrogen concentration in liquid phase begins to decrease and the ammonia in liquid phase begins to increase which indicates that, at present, the protein joins chemical reaction besides solution. In fact, while the protein dissolves, it also hydrolyzes to form multipeptide, dipeptide and amino acid. The amino acid further hydrolyzes to form organic acid, NH_4^+ and CO_2 (Wand and Wang, 2003; Schieder *et al.*, 2000). This reaction leads to the loss of the nutrients which dose harm to make the treated garbage into feedstuff or fertilizer.

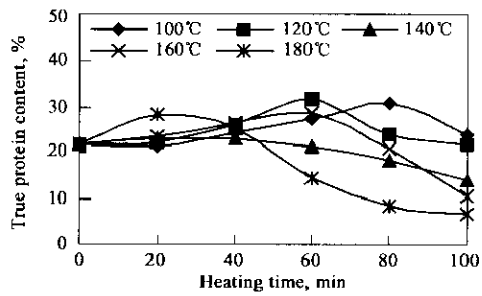


Fig.2 True protein vs. heating time

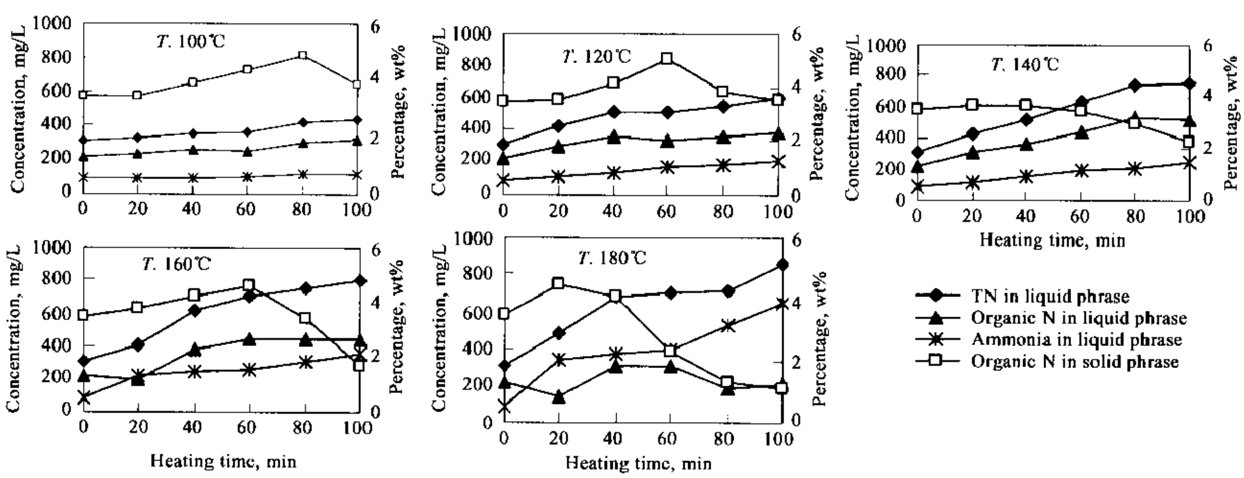
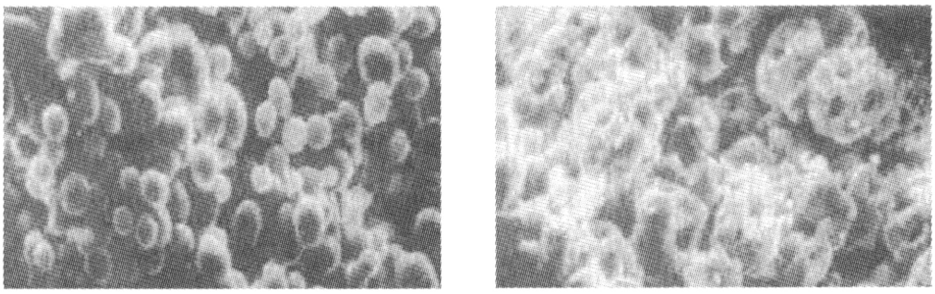


Fig.3 Occurrence of the nitrogen in the garbage at different temperatures

2.2 Impact of hydrothermal process on the carbohydrates in the restaurant garbage

The hydrothermally treated starch was observed compared with the raw starch through SEM (scanning electron microscope) pictures by American A2MARY21000B SEM, as shown in Fig.4. It shows that the hydrothermal process makes the particles of starch swelling and the SEM drive to be fuzzy which indicates gelling took place. Then the variation of the crystal structure of the starch is investigated by X-diffraction spectrum analysis, as shown in Fig.5. The diffraction peak of the raw starch in the curve is sharper which indicates the gelled starch has certain crystallinity. However, the diffraction peaks of the hydrothermal treated starch at 110, 140 and 180℃ in the curve become low and flat which have no noticeable characteristic diffraction peak. Furthermore, this trend does not change with the variation of temperature. This indicates that almost no crystal structure occurs in the gelled particles of starch. The formation of the gelled particles are the tangling of multi-molecules simply resulting from the hydrogen bonds among several points in the starch molecular chains. The hydrogen bonds do not occur among long molecular segments. Generally, the chemical structure of the gelled starch particles behaves similarly to that of raw starch, while it loses the noticeable crystal diffraction peak in the physical structure. It shows the variation of the starch molecular chains on the physical arrangement and the features on the actions of hydrogen bonds between the molecular chains.

Animals cannot absorb polysaccharide directly, so the carbohydrates such as starch must be hydrolyzed into low-carbon saccharides to be transferred into the humor of animals and plants. It



a. Raw starch b. Treated starch with hydrothermal process

Fig.4 SEMs of the starch particles amplified by 1000 times

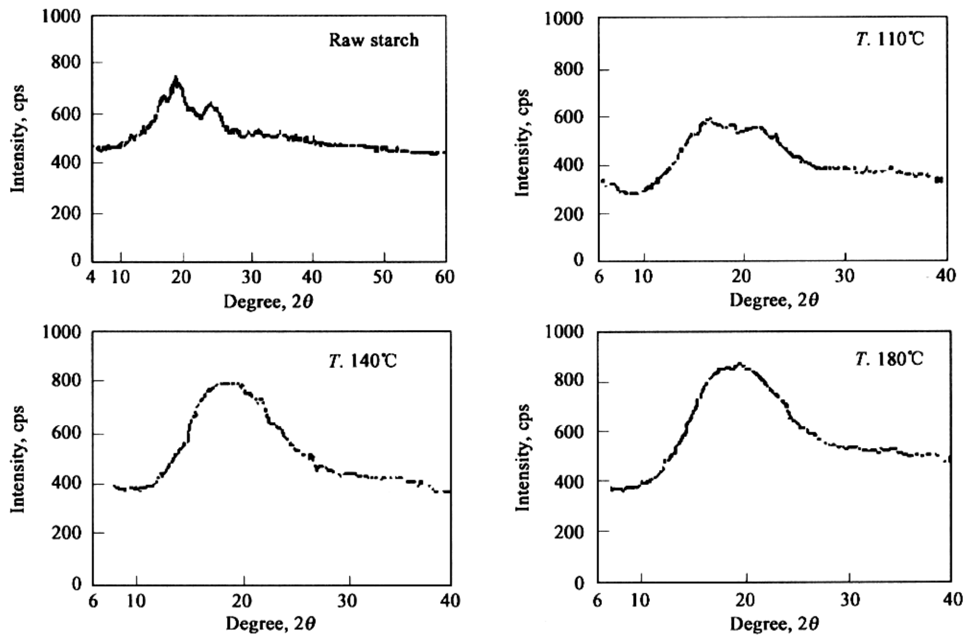


Fig.5 X-diffraction curve of the starch treated with hydrothermal process under different temperature

means that low-carbon saccharide content in the processed products plays an important role in its dissolving and digesting performance. During the hydrothermal process, the reducing sugar in the processed product mainly comes from the hydrolysis of the carbohydrates, especially from starch in the garbage. With the temperature rising and the heating time increasing, the starch swells, dextrinizes and hydrolyzes to reducing sugar, the starch content in the garbage is therefore decreases as shown in Fig.6. Meantime, the content of reducing sugar in the product starts to increase as shown in Fig.7. However, when the temperature reaches 140℃, the reducing sugar in the garbage starts to decrease. This is mainly because the reducing sugar reacts chemically to form other substances, wherein, one of the important chemical reactions is maillard reaction between the reducing sugar and amino acids. The C– in the open-chain carbonyl radicals in reducing sugar are attacked by the lone pair electrons on the N in the amino group nucleophillically to lose H_2O and closed chain to form a kind of spicy substance—glucosamine. This results in the decrease of the reducing sugar and the loss of amino acids which makes the nutrients value of the products decrease (Henle, 2001; Slot, 1997; Marrtins, 2001). The SEM of the hydrothermal treated starch is shown in Fig.8. In the picture of the starch treated at 140℃, there appears brown dots partially which indicates the reducing sugar from starch hydrolysis has happened maillard reactions with amino acids at this temperature. Furthermore, this kind of coloration reaction happens much more heavily as the brown dots approximately full of the sight in the SEM of the treated starch at 180℃. This illustrates the nutrients are destroyed severely at this temperature. Therefore, in order to avoid the loss of the nutrients effectively, the temperature should be controlled below 140℃.

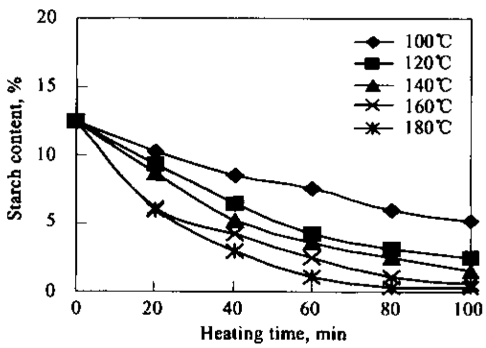


Fig.6 Starch content vs. heating time

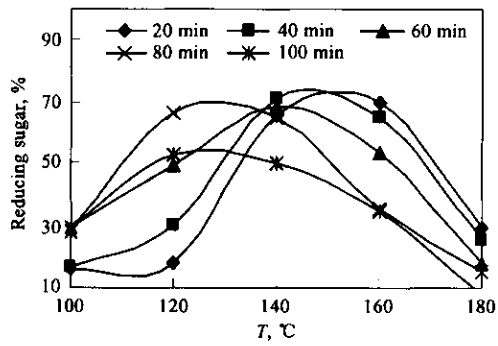


Fig.7 Reducing sugar vs. temperature

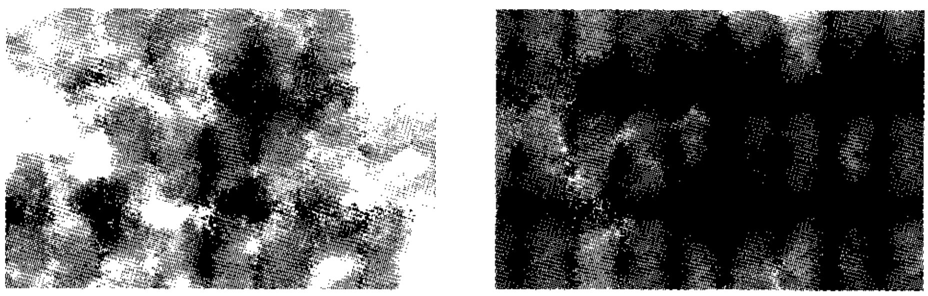


Fig.8 SEMs of the treated starch with hydrothermal process amplified by 400 times

The variation of the cellulose in the garbage during hydrothermal process can be seen from the data in Table 4. Under the experimental conditions, the cellulose is relatively stable.

2.3 Impact of hydrothermal process on the variation of the lipids in the restaurant garbage

2.3.1 Infrared spectrum analysis of the hydrothermal treated lipids

According to the methods described in section 1.4, the infrared spectrum of the lipid taken from the hydrothermal treated restaurant garbage was compared with that of the clean oil used to cook in the restaurant as shown in Fig.9. The absorption peak of the C=O double bond in the clean oil occurs on the point of 1740 cm^{-1} as shown in Fig.9a, while the absorption peak of the C=O double bond in the hydrothermal treated lipid generates red shift and appears on the point of 1540 cm^{-1} as shown in Fig.9b. This indicates that the hydrothermal process enabled the chemical changes of the molecular structure of the lipid. The chemical reaction involved might be saponification as the C=O double bond still exists.

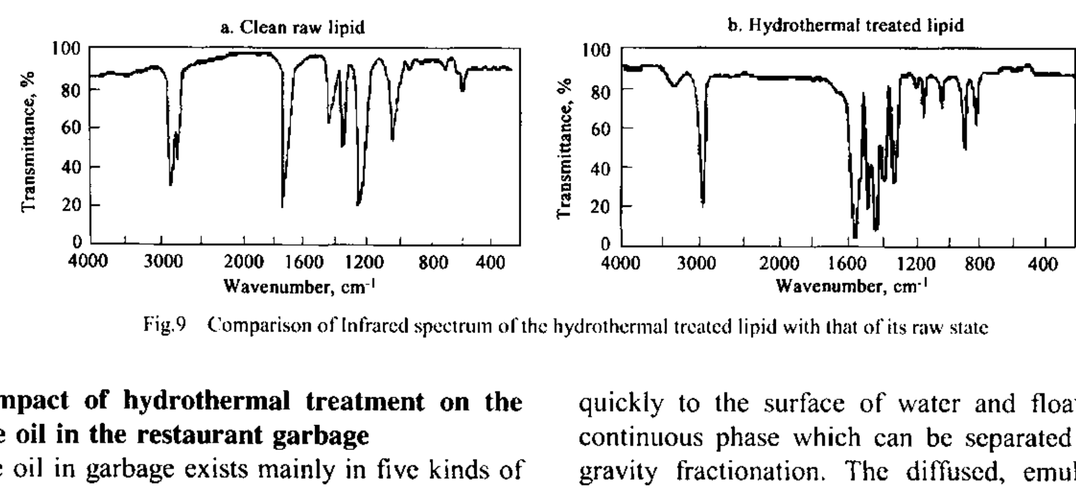


Fig.9 Comparison of Infrared spectrum of the hydrothermal treated lipid with that of its raw state

2.3.2 Impact of hydrothermal treatment on the floatable oil in the restaurant garbage

The oil in garbage exists mainly in five kinds of states including floatable, diffused, emulsified, dissolved and inside solid oil. Of these, the floatable oil occurs in large drops and if being held still, it rises quickly to the surface of water and floats there in continuous phase which can be separated simply by gravity fractionation. The diffused, emulsified and dissolved oil have smaller drops in size and bind with water tightly that are separated much harder. As for the inside solid oil, it always combines with the solid garbage in solid state so that can not be separated directly at all. Therefore, the content of floatable oil should be the critical factor for the de-oil performance of the garbage (Han and Hou, 2000).

The content of floatable oil in the restaurant garbage varies according to the heating time and temperature as shown in Fig.10. Hydrothermal process makes the content of floatable oil tend to increase. Furthermore, the higher temperature enhances the floatable oil increases more quickly. At present, the molecular mobility (M_m, i.e., the rotating mobility and translating mobility of the molecule) of the garbage is strengthened and its diffusing performance of water and lipid is improved. Because of the chemical potential difference between the interior and exterior of the solid phase in the garbage, water goes inside and the fat is extracted outside to form floating oil. At the temperature range from 100—120℃, the content of floatable oil increases continuously. When the temperature and heating time reach 160℃ and 80 min respectively, the floatable oil content per unit weight of garbage reaches the highest level as 131.7 ml/kg. After that, floating oil content begins to decrease. That means that the lipid inside the solid phase has extracted completely and continuous heating will promote the chemical reactions of lipid. For example, lipid would hydrolyze into free fatty acid and glycerine. Additionally, the glucose from the hydrolysis of starch will esterify with fatty acid and forms monoester, diester and triester with HLB value (hydrophilia-lipotropic balanced value) range from 1 to 16, which helps oil and water form O/W type system (oil-in-water type and water is continuous phase). It makes part of floating oil convert into emulsifying oil, which multiplies the difficulty of separating oil from water (Han, 2003b). In conclusion, the suitable condition for de-oiling of the restaurant garbage is that the temperature and heating time are 160℃ and 80 min, respectively.

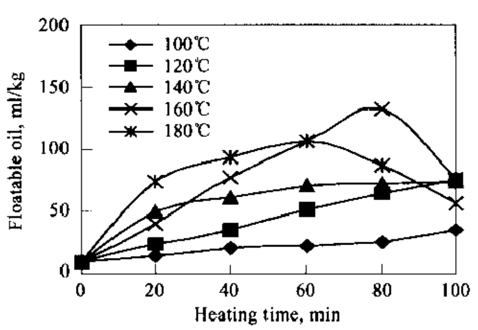


Fig.10 Floatable oil per unit weight of garbage vs. heating time

2.3.3 Kinetic analysis on the extraction of lipids from the restaurant garbage in hydrothermal process

Lipids in the solid phase of the garbage extracts out continuously during the hydrothermal process, which means the raw fat (RF) content in the solid phase decreases as shown in Fig.11. The RF content in the treated garbage varies regularly along with the heating time. We make an assumption that the extracting course accords with first-order reaction dynamic model which can be written as the following equations:

$$-\frac{dC_{RF}}{dt} = KC_{RF} \quad (1)$$

$$C_{RF} = C_0\exp(-Kt) \quad (2)$$

Where, C_{RF} is the raw fat content in the garbage measured in % when heating time is t. C_0 is the initial raw fat content in the garbage measured in %. K is extraction rate constant of lipid measured in min^{-1}. t is heating time measured in minutes.

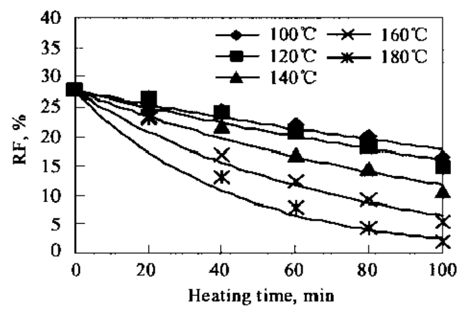


Fig.11 Raw fat content vs. heating time

Utilizing Origin Software to edit Equation (2), we fit the extration of raw fat in restaurant garbage with heating time. The results are listed in Table 5.

Table 5 shows that rate constants of lipid extraction rises with the increase of heating temperature and they are well relevant at different temperatures as all the correlation coefficients are greater than 90%, which illustrates that the extraction of solid grease from interior accords with first-order reaction dynamic model. According to Arrhenius Equation as follows:

$$\ln K = -\frac{E_\alpha}{RT} + \ln A \quad (3)$$

or

$$K = A\exp(-\frac{E_\alpha}{RT}) \quad (4)$$

where, A is the constant measured in min^{-1}; R is the gas constant which equals to 8.31×10^{-3} kJ/(K·mol); T is absolute temperature measured in K. E_α is activation energy measured in kJ/mol.

According to the results shown in Table 5, we use Origin Software to edit Equation (4) and fit the rate constant (K) with temperature (T) as shown in Fig.12. The involved parameters are: A = 64.07, E_a = 30.17 KJ/mol; the correlation coefficient is 96.6% which demonstrates that rate constants of lipid extraction and heating time accords with Arrhenius

Equation. Thus, with Equations (2) and (4), the lipid extraction of treated restaurant garbage can be predicted at any temperature between 100℃ and 180℃ during hydrothermal process.

Table 5 Rate constants of lipid extraction under different temperatures

Temperature, ℃	K, min^{-1}	Error	Correlation coefficient
100	0.0044	±0.0005	0.9374
120	0.0055	±0.0006	0.9418
140	0.0086	±0.0008	0.9618
160	0.0145	±0.0011	0.969
180	0.0237	±0.0027	0.958

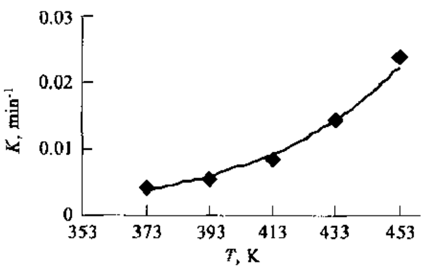


Fig.12 Rate constants of extraction vs. temperature (T)

3 Conclusions

Hydrothermal process makes the protein in the restaurant garbage dissolve and liquefy. In hydrothermal process, the organic N transforms from solid phase to liquid phase. When the temperature and the heating time reach 180℃ and 60 min respectively, the organic N starts to translate into ammonia.

During the hydrothermal process, the starch swells, gelatinizes and hydrolyzes to reducing sugars. The gelling simply results in the change of the physical structure of starch. The hydrolysis leads to the decrease of the starch in the garbage and the increase of the reducing sugar. However, when the temperature reaches 140℃, the reducing sugar starts to decrease because of the chemical reaction. The cellulose under the experimental conditions is stable.

During the hydrothermal process of the restaurant garbage, the floatable oil content increases which indicates that the de-oiling performance of the garbage is improved. The suitable condition for de-oiling of the restaurant garbage is that the temperature and the heating time are 160℃ and 80 min respectively. Additionally, the extraction of inside solid lipids from the garbage accords with first-order reaction dynamic model. And the relationship of the extraction rate constant to the temperature accords with Arrhenius equation.

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