Preparation and application of a new catalyst to produce bio-oil from microalgae liquefaction

Wang Yipeng, Nan Ge, Wang Wenjia, Zhang Jinglai*, Han Wei

(*School of Environment & Natural Resources, Renmin University of China, Beijing 100872, China*)

Abstract: In this study, hydrothermal catalytic liquefaction method was adopted to produce bio-oil from microalgae. The influence of supported Ni-Catalysts doped neodymium (Nd) on the bio-oil yield from microalgae liquefaction was investigated, aiming to find the optimal preparation procedure of bio-oil. It proved that under the condition of a temperature of 270°C and a reaction period of 30 min, the bio-oil yield of hydrothermal catalytic liquefaction of *spirulina* powder could reach 55.1% by means of the catalyst prepared with 1 mol/L neodymium nitrate as the dipping solution after a calcination for 4 h at 800°C. In addition, the characterization on catalyst was discussed in this research.

Keywords: catalyst, bio-oil, microalgae, catalytic liquefaction, *spirulina* powder

DOI: 10.3965/j.ijabe.20171001.2599

Citation: Wang Y P, Nan G, Wang W J, Zhang J L, Han W. Preparation and application of a new catalyst to produce bio-oil from microalgae liquefaction. Int J Agric & Biol Eng, 2017; 10(1): 169–175.

1 Introduction

Traditional fossil fuels are still dominant in the global energy consumption structure. In 2013, the world's major energy consumption increased by 2.3%, and fossil oil is still the main fuel, accounting for 32.9% of global energy consumption. In 2013, China's energy consumption structure was dominated by coal (67.50%), while the percentages of oil, natural gas, hydropower and nuclear power were 17.79%, 5.10%, 7.23% and 0.88%, respectively[1]. However, biomass energy, the world's fourth energy and the largest renewable energy, has a greater development potential for its wide variety, abundance, renewability, biodegradability and environmental friendliness[2,3].

At present, the main raw materials for bio-oil preparation are several kinds of lignocellulose biomass[4,5]. However, the application of lignocellulose biomass is restricted by plenty energy consuming for its pretreatment. From the point of sustainable development, microalgae, which multiplies rapidly and does not occupy farmland, is thought to be an ideal raw material for bio-oil production[6-8]. And the *spirulina*, without cell walls, can be liquefied directly instead of crushing pretreatment. Xu et al.[9] studied the hydrothermal liquefaction of *spirulina* using Ni/TiO_2 catalyst, but the bio-oil production by this technology has the problems of low-yield, poor-quality, high-cost and high N, S, O element contents. Thus, low yield is the biggest problem of hydrothermal liquefaction technology and the key point in our future research.

On the basis of above studies, a new catalyst of Nd-Ni/TiO_2 was developed in this research, which had a significant increase in bio-oil preparation efficiency of microalgae liquefaction and a reduction in S and O element contents. Then the effects of the concentration of the neodymium nitrate solution, dipping time,

---

Received date: 2016-09-08 **Accepted date:** 2016-12-06

Biographies: Wang Yipeng, Master, research interests: environmental science, Email: wayzx@126.com; **Nan Ge,** Undergraduate, research interests: environmental science, Email: nancyjltx@163.com; **Wang Wenjia,** Master student, research interests: biomass liquefaction, catalysis, chemical engineering, Email: 752636881@qq.com; **Han Wei,** Associate Professor, Master, research interests: ecological economy, Email: hanwei@ruc.edu.cn.

***Corresponding author: Zhang Jinglai,** PhD, Professor, research interests: environmental and chemical engineering, Mailing address: School of Environment and Natural Resources, Renmin University of China, No. 59 Zhongguancun Street, Haidian District, Beijing 100872, China. Tel/Fax: +86-10-82502695; Email: zhangjl@ruc.edu.cn.

calcination time and temperature on catalyst preparation and the bio-oil yield were investigated.

2 Materials and methods

2.1 Materials and experimental instruments

The *spirulina* powder was provided by Shandong Binzhou TianJian Biotechnology Ltd. And experimental instruments used in this study are shown in Table 1.

Table 1 Experimental instruments

Device name	Model	Manufacturer
High temperature and high pressure reactor	4578	PARR
Elemental analyzer	CE-440	EAI Ltd. of America
Digital temperature control electric heating jacket	98-1-C	Tianjin Taisite Instrument Co., Ltd.
Full-automatic calorimeter	YX-ZR/R	Changsha U-therm Instrument Manufacturing Co., Ltd.
Bar thin layer chromatograph	MK-5	Iatron Ltd. of Japan
GC-MS	QP2010	Shimadzu Co., Ltd., Japan

2.2 Analysis methods

Ni/TiO_2 was selected as the catalyst that was prepared by mixing TiO_2 with Ni loading on the above by impregnation method and then modified by transition metal Nd. And bio-oil was prepared in high temperature and high pressure reactor using hydrothermal catalytic liquefaction method. Then the effects of concentration of the neodymium nitrate solution, dipping time, calcination time and temperature in catalyst preparation process on the bio-oil yield were investigated by single factor test. Only one factor was selected as the single variable and the other three constants of each test remained unchanged, and then the relationships between the given experimental variables and oil yield were discussed. Therefore, the optimal condition to liquefy *spirulina* was obtained.

2.3 Catalyst preparation

When Ni/TiO_2 catalyst was selected to prepare bio-oil from microalgae by hydrothermal catalytic liquefaction, the nitrogen content of the bio-oil was significantly decreased. Lanthanide metal Nd can remove NOx in the petroleum industry[10], and therefore a new catalyst was prepared by modifying Ni/TiO_2 with transition metal Nd. A quantity of 36 g TiO_2 was acidified with 5% dilute acid for 4 h, added 0.75 mol/L nickel chloride, dipped for 24 h at room temperature, and then added with certain concentration of neodymium nitrate, dipped for 24 h at room temperature. After filtration, the remaining solution was dried at 105°C in oven. Finally, after calcination in Muffle furnace, $Nd-Ni/TiO_2$ catalyst has been produced. Variables set in each single factor test are shown in Table 2.

Table 2 Experimental variables

Variable name	Test 1	Test 2	Test 3	Test 4
Concentration of the neodymium nitrate solution /mol·L^{-1}	0.5, 0.75, 1.0, 1.25 and 1.5 (experimental variable)	1.0	1.0	1.0
Dipping time /h	24	24	24	12, 24, 48, 72 and 96 (experimental variable)
Calcination temperature /°C	675	675	600, 675, 700, 800 and 900 (experimental variable)	675
Calcination time /h	4	2, 3, 4, 5 and 6 (experimental variable)	4	4

2.4 Catalytic liquefaction

The experiments were carried out in a pressure reaction kettle of 2 L, which composed of a kettle body, a stirring device and a controller. One hundred and twenty grams of algae powder was added to 480 mL distilled water, fully stirred to mix well, and added with 12 g $Nd-Ni/TiO_2$ as catalyst. Then the system was sealed, and the inside air was replaced with 0.2 MPa N_2. The high temperature and high pressure reactor was heated with electric furnace from room temperature to 270°C in 2 h. The reactor was kept at 270°C for 30 min, and then it was kept at room temperature when the residual pressure almost entirely provided by N_2 was between 0.2 MPa to 0.3 MPa. Then the liquid in kettle body was separated by filtration, and extracted by methylene chloride. Finally, the methylene chloride layer was evaporated at 45°C and negative pressure of 0.01 MPa, and the oil-like substance was collected as the bio-oil product of about 50 g from 120 g algae powder.

3 Results and discussion

3.1 Characteristics of *spirulina*

The *spirulina* powder used in this study was analyzed by GB/T16919-1997 method. The results are shown in Table 3.

The mainly organic composition of *spirulina* is protein (66%), sugar and lipid are less. The mainly liquefaction reaction is the conversion from protein to bio-oil.

Table 3 Characteristics of *Spirulina* (wt%)

Component	Value
Protein	66
Ash	6.8
Moisture	6.5
C	47.08
H	8.772
O	30.58
N	9.972
S	2.082

3.2 Effects of supported Ni-catalysts doped Neodymium (Nd) on the yield of bio-oil

3.2.1 Effects of neodymium nitrate solution concentration on microalgae liquefaction

Generally, the concentration of dipping solution has a great influence on the catalytic performance of the catalyst. When the concentration is high, the active component is easy to disperse, which helps to reach maximum adsorption capacity. However, loading of active components is difficult to control. On the contrary, it is easy to control the loading of active components when the dipping solution is dilute, but dispersion will be poor. The results of test on neodymium nitrate hydrate concentration are shown in Figure 1. The element analysis results of the oil are shown in Table 4.

It can be seen from Figure 1, bio-oil yield increased when neodymium nitrate solution concentration increased from 0.25 mol/L to 1 mol/L, but decreased when it continued to rise to 1.5 mol/L. The catalyst made by 1 mol/L neodymium nitrate helped the oil yield reach the highest.

Concentration of ions in the solution affects the concentration of supported element on catalyst surface. With the increase of dipping solution concentration, the concentration of neodymium element on the surface of the titanium dioxide increases, the catalytic effect is better. However, when the impregnating solution concentration increases to a certain extent, excessive loading makes the active components on carrier's surface agglomerate, and active sites on the catalyst surface covered, reduces the binding probability of reactants, and so is bio-oil production. Compared to the maximum oil yield 35.26 g in Xu's experiment using Ni/TiO_2 as catalyst[9], the oil production has increased significantly in this study. Figure 1 shows that comparing to bio-oil without adding catalyst, sulfur element content significantly reduced, and oxygen element content also decreased when the concentration of dipping solution was 1.5 mol/L.

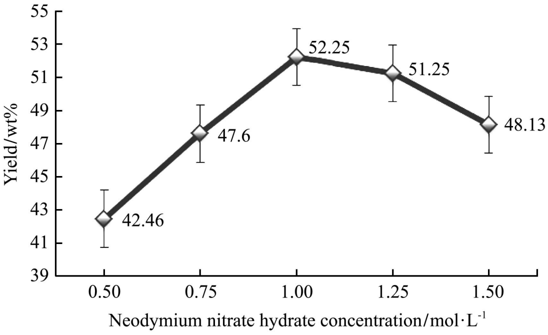


Figure 1 Effects of neodymium nitrate hydrate concentration on bio-oil yield

Table 4 Results of elemental analysis

Catalyst	C/N	C/%	H/%	N/%	S/%	O/%
Nd-Ni/TiO_2 (0.5 mol/L)	8.37	68.580	10.150	8.194	0.572	12.504
Nd-Ni/TiO_2 (1.0 mol/L)	7.093	64.960	10.920	9.158	0.631	14.331
Nd-Ni/TiO_2 (1.5 mol/L)	8.258	69.720	10.810	8.442	0.639	10.389
Ni/TiO_2 (data from Xu et al.[9])	7.777	69.286	8.909	6.747	0.367	14.691
No catalyst added	7.246	70.50	9.729	7.676	1.065	11.653

3.2.2 Effects of calcination time on microalgae liquefaction

Catalyst is typically calcined to stabilize itself and remove volatile components, retain the chemical composition. Therefore the catalyst has a certain crystal form. The effects of calcination time on bio-oil yield from microalgae liquefaction are shown in Figure 2. The element analysis results of the oil are summarized in Table 5.

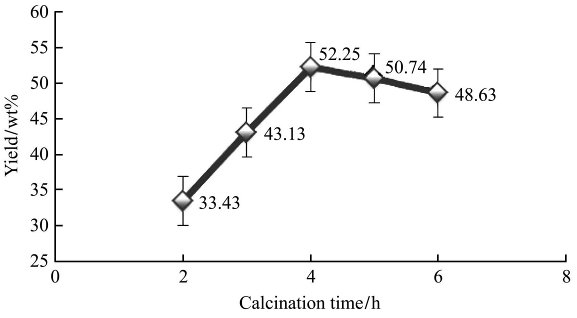


Figure 2 Effects of calcination time on bio-oil yield

Table 5 Results of elemental analysis

Catalyst	C/N	C/%	H/%	N/%	S/%	O/%
Nd-Ni/TiO_2 (3h)	8.087	67.450	10.300	8.340	0.572	13.338
Nd-Ni/TiO_2 (4h)	7.093	64.960	10.920	9.158	0.631	14.331
Nd-Ni/TiO_2 (5h)	7.566	67.190	10.730	8.881	0.744	12.455
Ni/TiO_2 (data from Xu et al.[9])	7.777	69.286	8.909	6.747	0.367	14.691
No catalyst added	7.246	70.50	9.729	7.676	1.065	11.653

It can be seen from Table 5 that bio-oil yield first increased and then decreased as the calcination time extended. The yield reached a peak of 52.25%, when the catalyst was baked for 4 h. Calcination time affects catalyst's specific surface area and pore volume. If the baking time is too short, there will be no stable and suitable crystal structure, less adhesion to the surface of carrier, low concentration of Ni and Nd, and therefore the catalytic effect will not be good. On the contrary, excessive calcination will make the particle size and bulk density of catalyst increase, the contact area between catalyst particles and algae powder reduces and so does catalytic effect[11]. From Table 5, when the calcination time was 3 h, N and S element contents were relatively low. While the calcination time was 5 h, O element content was relatively low; comparing to bio-oil without adding catalyst, S element content was significantly reduced.

3.2.3 Effects of calcination temperature on microalgae liquefaction

The calcination temperature has an important influence on the catalyst preparation, which can directly affect the crystal form of the catalyst. When the calcination temperature were set at 600°C, 675°C, 700°C, 800°C and 900°C, the oil yields are shown in Figure 3. Element analysis results of the oil are shown in Table 6.

It can be seen from Figure 3 that the oil yield first increased rapidly as the calcination temperature was raised from 600°C to 800°C then decreased after the calcination temperature was raised higher than 800°C. When the calcination temperature was 800°C, the maximum yield reached a peak of 55.1%. Compared to the conversion by hydrothermal liquefaction from *Chlorella vulgaris* and *Spirulina* to bio-oil in [13], of which the maximum yields of 19.5 wt% from *Spirulina* and 15.7 wt% from *Chlorella* were achieved in a high pressure batch reactor at 350°C using Acetic acid as catalyst, this study has improved the oil yield from low lipid microalgae significantly. Toor et al.[14] and Jazrawi et al.[15] found that the maximum bio-crude yield was 38 wt% by common hydrothermal liquefaction experiments and 41.7 wt% in a continuous reactor. TiO_2 in rutile form could increase the catalyst's specific surface area, pore volume and Ni adhesion to the surface of carrier, so is catalytic effect. But excessively high temperature will cause the agglomeration on catalyst surface, pore volume to decrease, pore diameter to increase and a reduction in effective reaction area of active components, even cause deactivation of catalyst[12]. The maximum yield reached 55.1% at a calcination temperature of 800°C, when N element content was significantly reduced compared to the bio-oil produced by Ni/TiO_2 catalyst and with no catalyst adding. The lowest S element content was achieved when the temperature was 900°C, which is much lower than bio-oil prepared without catalyst.

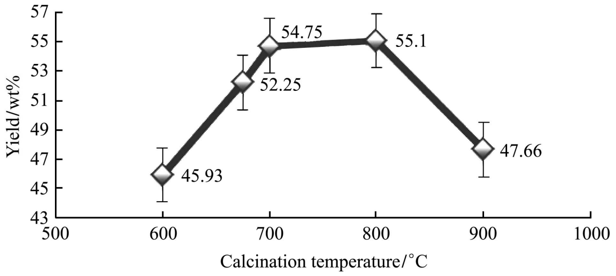


Figure 3 Effects of calcination temperature on bio-oil yield

Table 6 Results of elemental analysis

Catalyst	C/N	C/%	H/%	N/%	S/%	O/%
Nd-Ni/TiO_2 (700°C)	8.02	69.390	9.261	8.653	0.554	12.142
Nd-Ni/TiO_2 (800°C)	7.883	45.650	6.384	5.790	0.423	41.753
Nd-Ni/TiO_2 (900°C)	8.19	67.270	10.350	8.214	0.395	13.771
Ni/TiO_2 (data from Xu et al.[9])	7.777	69.286	8.909	6.747	0.367	14.691
No catalyst added	7.246	70.50	9.729	7.676	1.065	11.653

3.2.4 Effects of dipping time on microalgae liquefaction

When dipping time was 12 h, 24 h, 48 h, 72 h and 96 h, the oil yields from microalgae liquefaction are shown in Figure 4. Element analysis results of the oil are shown in Table 7.

It can be seen from Figure 4 that the oil yield first increased rapidly when dipping time extended from 12 to 24 h, then reduced and finally flattened. When the catalyst dipped for 24 h, oil yield reached a peak of 52.25%. Table 6 shows that N element content reached the lowest at a dipping time of 72 h. S reached the lowest at a dipping time of 48 h; O reached the lowest at a dipping time of 12 h.

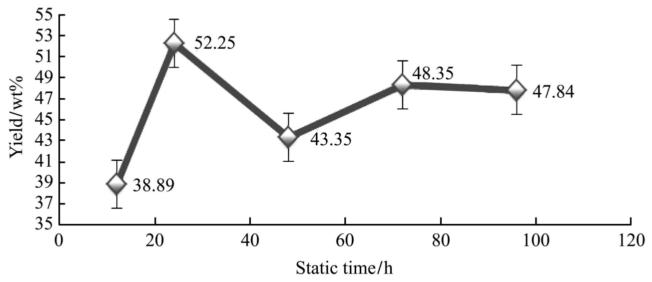


Figure 4 Effects of static time on bio-oil yield

Table 7 Results of elemental analysis

Catalyst	C/N	C	H	N	S	O
Nd-Ni/TiO_2 (12 h)	8.368	67.930	10.590	8.117	0.647	12.716
Nd-Ni/TiO_2 (24 h)	7.093	64.960	10.920	9.158	0.631	14.331
Nd-Ni/TiO_2 (48 h)	8.468	68.260	10.090	8.061	0.582	13.007
Nd-Ni/TiO_2 (72 h)	8.331	66.980	10.030	8.040	0.612	14.338
Ni/TiO_2 (data from Xv et al.[9])	7.777	69.286	8.909	6.747	0.367	14.691
No catalyst added	7.246	70.50	9.729	7.676	1.065	11.653

3.3 Characterization of catalyst

According to the experimental results above, supported Ni-Catalysts doped neodymium (Nd) cannot only improve the oil yield of microalgae hydrothermal catalytic liquefaction, but also reduce the content of nitrogen and sulfur in bio-oil, improve oil quality. The catalyst was characterized in the following categories.

The catalyst was analyzed by X-ray diffraction (XRD). The composition and content of this catalyst are clearly shown in XRD diagram. As Figure 5 shows that the obvious diffraction peaks of this carrier in anatase phase (101), (004), (200), (211) and (004) diffraction direction make it clear that the carrier contains anatase crystallite. Diffraction peaks in rutile phase (210), (211), (002), (310), (311) make it clear that the carrier contains rutile phase, and peaks were higher and sharper for bigger crystallite of titanium dioxide. Samples contained TiO_2 (74% in anatase phase; 10% in rutile phase) and Nd_2TiO_7 (16%). The diffraction peaks of Ni particles are at 44.5°, 52° and 76°. Metal peak is not obvious or exist, and Nd peak is not obvious, which is because of its good active phase dispersion and smaller crystallite.

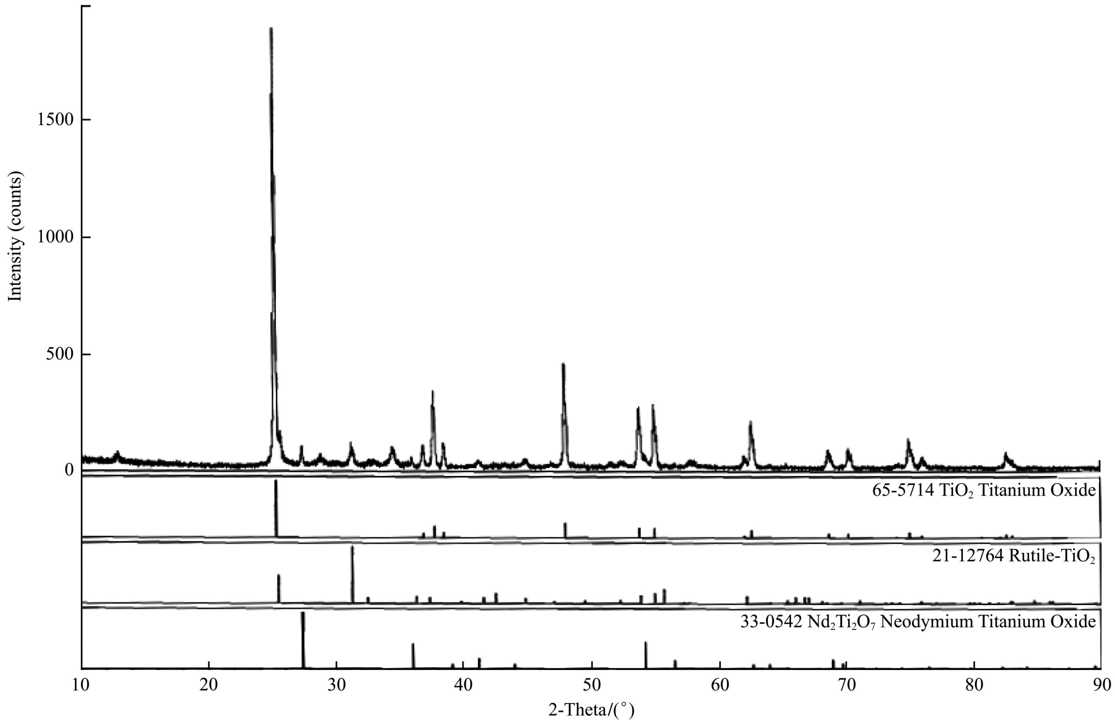
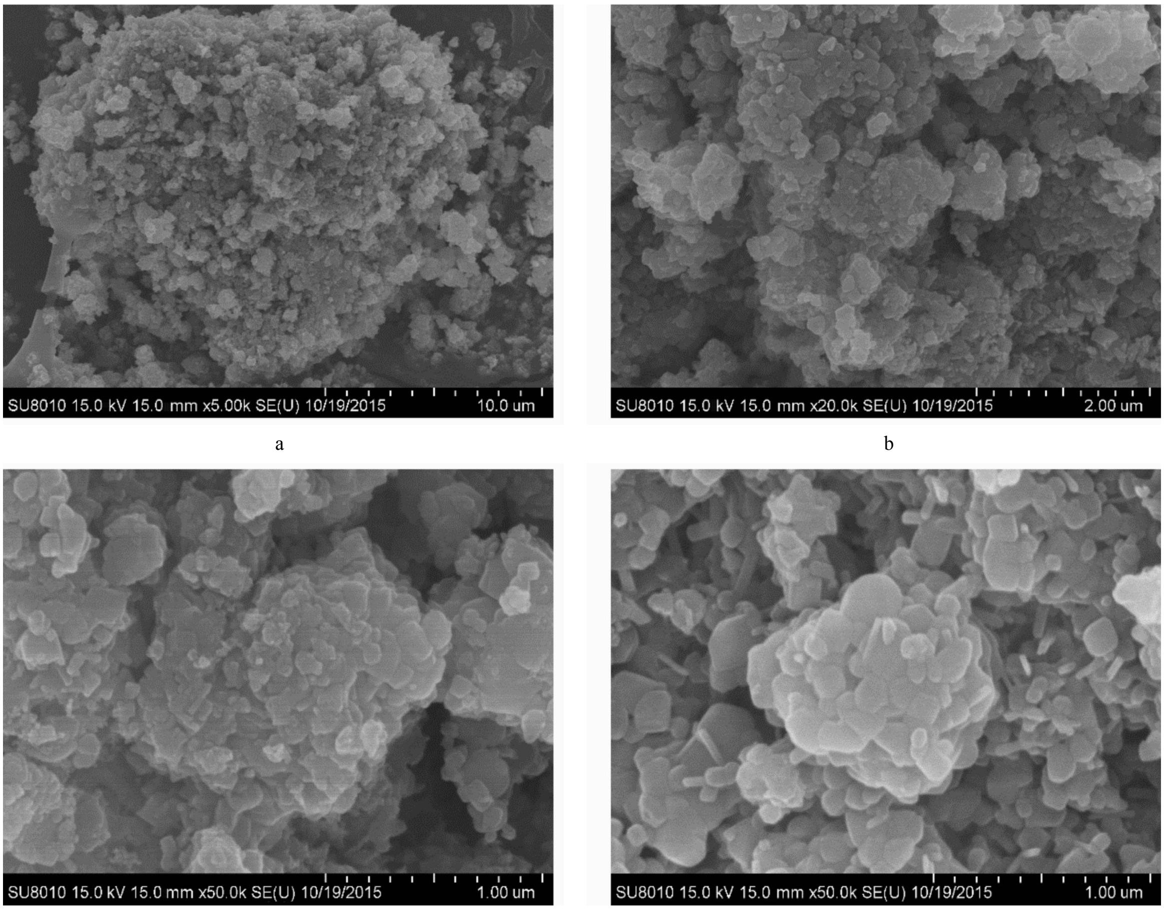


Figure 5 XRD diagram of catalyst

The catalyst was also analyzed by scanning electron microscope (SEM). SEM is a microscopic appearance observation method by transmission electron microscope and optical microscope, which can directly show the material properties of the sample surface by microscopic imaging. The SEM images of catalyst are shown in Figure 6.

Nd-Ni/TiO_2 dispersed well in solution, and was adsorbed uniformly to the surface of catalyst' carrier with even distribution, but did not form a common crystalline phase. In addition, the particles of active components were too small to be detected by XRD, thus there were no other diffraction peaks.

Finally, the catalyst was analyzed by energy dispersive spectroscopy. EDS can carry out qualitative and quantitative analysis of elements quickly and efficiently, and then clearly describe all the elements contained in the catalyst. EDS energy spectra at different locations of the catalyst are shown in Figure 7. Nd, Ni elements are well attached to the catalyst surface. The mass ratio of Nd and Ni is close to their molar ratio, which shows good dispersion of catalyst. Large specific surface and good dispersion of Nd-Ni/TiO_2 catalyst both contribute to improve oil yield from microalgae liquefaction.



a b

c d

Figure 6 SEM images of catalyst

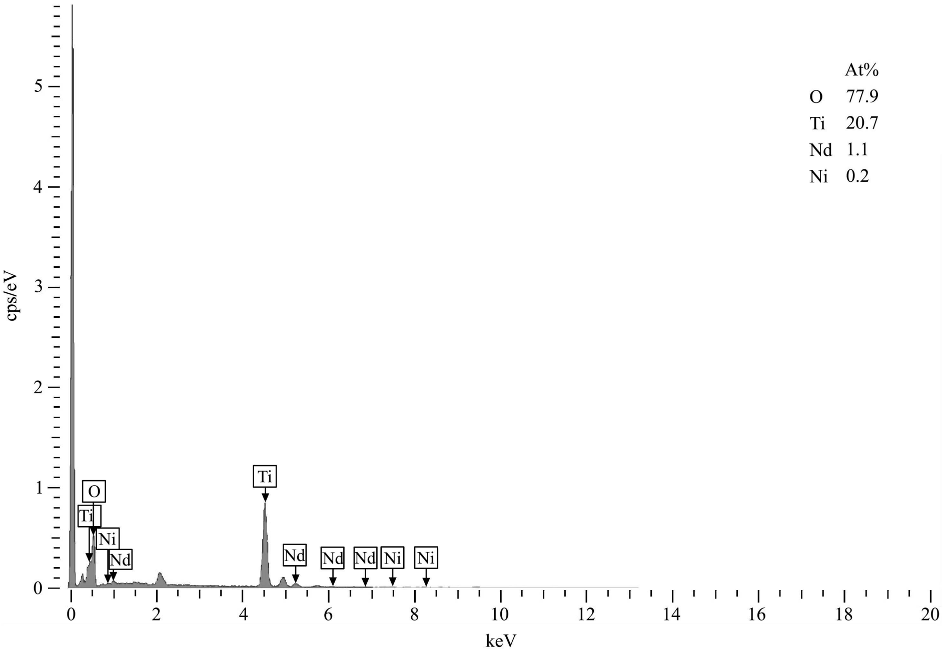


Figure 7 EDS diagram of catalyst

4 Conclusions

This study describes the preparation method and application effect of supported Ni-Catalysts doped neodymium (Nd) for microalgae liquefaction. Compared with Ni/TiO_2 catalyst, Nd-Ni/TiO_2 Catalyst has a significant increase in efficiency of bio-oil preparation from microalgae liquefaction. Effects of the calcination temperature, calcination time, dipping time and neodymium nitrate solution concentration of Nd-Ni/TiO_2 catalyst preparation on bio-oil yields have been studied. The results show that the influences of such four factors are declining. When using the catalyst prepared with 1 mol/L neodymium nitrate as dipping solution for 24 h and after a calcination for 4 h at 800°C, the bio-oil yield from hydrothermal catalytic liquefaction of *spirulina* powder containing low lipid contents could reach a peak of 55.1%, improved by 19.17% compared with no catalyst added. In addition, the contents of S and O elements of products also decreased considerably. Through the characterization of the catalyst, Nd-Ni/TiO_2 catalyst is of large specific surface and good dispersion.

Acknowledgments

The authors acknowledged the financial support by Reinvent the Toilet Challenge-China (4332155000521) and Pre-research Project of Renmin University of China (297516503421).

[References]

[1] BP Group, BP Statistical Review of World Energy, 2014.

[2] Chu S, Majumdar A. Opportunities and challenges for a sustainable energy future. Nature, 2012; 488(7411): 294–303.

[3] Gai C. A study on hydrothermal liquefaction of low-lipid microalgae to produce bio-crude oil through experimental investigation and mechanism analysis. PhD dissertation, Shandong University, 2014. (in Chinese)

[4] Pütün A E, Apaydın E, Pütün E, Tsatsaronis G, Moran M J, Cziesla F, et al. Rice straw as a bio-oil source via pyrolysis and steam pyrolysis. Energy, 2004; 29(12): 2171–2180.

[5] Mourant D, Wang Z, He M, Wang X S, Garcia M, Ling K, et al. Mallee wood fast pyrolysis: Effects of alkali and alkaline earth metallic species on the yield and composition of bio-oil. Fuel, 2011; 90(9): 2915–2922.

[6] Rasoul S, Montazeri N, Mobasher M A, Hoseini S, Ghasemi Y. *Chlorella* sp.: A new strain with highly saturated fatty acids for biodiesel production in bubble-column photobioreactor. Applied Energy, 2011; 88(10): 3354–3356.

[7] Singh A, Nigam P S, Murphy J D. Renewable fuels from algae: An answer to debatable land based fuels. Bioresource Technology, 2011; 102(1): 10–16.

[8] Konur O. The scientometric evaluation of the research on the algae and bio-energy. Applied Energy, 2011; 88(10): 3532–3540.

[9] Xu Y T, Liu Q Y , Yang L, Sun Z, Han W, Zhang J L. Study on the impacts of the montmorillonite-supported Ni in the liquefaction of *spirulina* to produce bio-oil. Renewable Energy Resources, 2015; 33(9): 1427–1433.

[10] Wu Q S, Chen Y L. Synthesis, characterization, and de-NOx performance of lanthanum-doped MCM-41. Inorganic Chemicals Industry, 2014; 46(7): 71–74. (in Chinese)

[11] Wang Y J, Zhu Y M, Pang C J, Wang Z T. Study of catalytic esterification by modified solid super acid SO_4^{2-}/TiO_2. Journal of Shenyang Institute of Chemical Technology, 1998; 12(3): 188–192. (in Chinese)

[12] Sun F Y, Wu M, Li W Z, Li X Y, Gu W Z, Wang F D. Effect of TiO_2 preparation conditions on photocatalytic activity. Chinese Journal of Catalysis, 1998; 19(3): 229–233. (in Chinese)

[13] Ross A B, Biller P, Kubacki M L, Li H, Lea A, Jones J M. Hydrothermal processing of microalgae using alkali and organic acids. Fuel, 2010; 89(9): 2234–2243.

[14] Toor S S, Reddy H, Deng S G, Hoffmann J, Spangsmark D, Madsen L B, et al. Hydrothermal liquefaction of spirulina and nannochloropsis salina under subcritical and supercritical water conditions. Bioresource Technology, 2013; 131(3): 413–419.

[15] Jazrawi C, Biller P, Ross A B, Montoya A, Maschmeyer T, Haynes B S. Pilot plant testing of continuous hydrothermal liquefaction of microalgae. Algal Research, 2013; 2(3): 268–277.