PRODUCTION OF NON-ESTER RENEWABLE DIESEL BY THE HYDROGENATION OF VEGETABLE OIL ON THE 15Co5Ni-10Ce / Al_2O_3 CATALYST

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ABSTRACT

The catalysts by incipient wetness impregnation method were prepared and characterized by XRD, BET, H_2 -TPD, NH_3 -TPD and H_2 -TPR analysis, and the catalyst activity was detected by WFSM-3060 high-pressure reactor. Effective double metal catalysts were produced by using $\gamma\text{-Al}_2\text{O}_3$ as carrier and Co and Ni as activity center, and more effectiveness by using Ce to modify. The results revealed that the 15Co5Ni-10Ce catalyst was the best in producing bio-fuels. The catalyst had good thermal stability, three kinds of adsorbed sites and three kinds of acidic sites. Compared with sintering, the catalyst deactivation was due to coke deposition. The results of FT-IR, SF-3, GC and GC-MS indicated that reaction temperature is the key factor and that oil velocity is a very important factor. The optimized condition was at reaction temperature of 450°C, reaction pressure of 3.0 MPa, oil velocity of 0.1 mL/min and the gas velocity of 35 mL/min, respectively. The alkanes and alkenes content of liquid products are 50.02% and 40.03% under the optimized condition. The main products are the hydrocarbon compounds under C_{18} . The results of GC online and trace water determination showed that the main products of oxygen in the oil are CO and CO_2 , and that the minor product is H_2O . The importance and the economical production of the Non-ester renewable diesel from vegetable oil are presented. From the results of FT-IR, SF-3 and GC-MS, the generating mechanism of Non- ester renewable diesel was deduced.

Keywords: Bio-fuels, 15Co5Ni-10Ce/ $\gamma\text{-Al}_2\text{O}_3$ catalyst, decarboxylation, deoxidization, hydrogenation.

INTRODUCTION

Coal and petroleum are the promising fossil fuels for energy supply in the future. But the quantity of petroleum and coal are becoming less, and the quality of the crude oil is becoming poorer and poorer every day. However, the demand of the crude oil has been on the increase by 26% every year since 1995 caused by the rapid growth of the world economy¹⁻³, so the price of the crude oil in the international market in recent years has been soaring⁴. In addition, the environmental problems caused by the extensive use of fossil fuel have been more serious. Many countries are revising the strict emission standards and developing renewable energy sources (RES), the aim of which is to reduce the significant dependence on import energy and the crude oil. Biomass is the only renewable energy containing carbon and can be converted into liquid fuels and fine chemicals⁵⁻⁸. The conversion of biomass into bio-fuels is regarded as a carbon-cycling between the chemical conversion ($\text{Biomass} \rightarrow \text{hydrocarbon} + \text{CO}_2$) and the photosynthesis ($\text{light} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Biomass}$), so bio-fuels can be considered to be zero emission of CO_2 . Compared with fossil fuels, biomass contain less of sulfur and nitrogen, so the content of sulfur and nitrogen is less in bio-fuels, which leads to lower emissions of SO_2 and NO_x ⁹⁻¹¹. The potential and importance of RES was evaluated and examined from the economic and environmental viewpoints in Slovenian⁵. By 2020, the E.U. has adopted a target that the 10% energy of the transportation energy is used by the conversion of different triglycerides to different bio-fuels⁶. The use of RES is considered to be a solution to the problems of energy shortage and the pollution in the long-term.

Nowadays fatty acid methyl esters (FAME), called as first generation bio-diesel, could be produced from a variety of biomass feed-stock using suitable conversion technique, especially use the nonfood plant that is rich in triglycerides or sugars¹²⁻¹⁵. Bio-diesel production can also be carried out by homogeneous alkali, acid and enzyme¹⁶⁻²⁵. The use of FAME plays a positive and important role in solving the problems of energy shortage and the pollution in a period of time. Compared with petroleum-derived fuels, FAME has many physical-chemical disadvantages (e.g. the higher cloud point, the higher viscosity, the freezing point, the pour point, the poor oxidation stability etc.)²⁶. To overcome these disadvantages and to reach better quality fuel, the most viable way is the deoxidization of triglyceride to Non-ester renewable diesel (NERD), which is called second generation bio-fuels. Snåre M. et al.²⁷, Kubičková I. et al.²⁸, Katikaneni S. P. R. et al.²⁹ and Vonghia E. et al.³⁰ are earlier concerned about the research of the deoxidization of triglyceride to NERD. The deoxidization of fatty acids and their methyl esters has been studied extensively on the Pd/C³¹, Pd/SBA-15³² and Pt/ $\gamma\text{-Al}_2\text{O}_3$ ³³ noble metal catalysts. Moreover, the deoxidization of triglycerides can be achieved on these catalysts such as sulfided CoMo, NiMo, NiW supported on $\gamma\text{-Al}_2\text{O}_3$ ³⁴ and Ni-

Mo/ $\gamma\text{-Al}_2\text{O}_3$ /F³⁵ Catalysts.

Co/ $\gamma\text{-Al}_2\text{O}_3$ is an effective catalyst in Fischer-Tropsch synthesis³⁶, and the Ni/ $\gamma\text{-Al}_2\text{O}_3$ is a good catalyst in the hydrogenation activity³⁴. In the paper, economical and non-sulfide transition metal catalysts were produced by using $\gamma\text{-Al}_2\text{O}_3$ as carrier and Co and Ni as activity center, and more effectiveness by using Ce to modify, and the non-ester renewable diesel by the hydrogenation of vegetable oil on the 15Co5Ni-10Ce / Al_2O_3 catalyst was produced. The standards of bio-fuels had been further improved because of low oxygen content and high content of the alkanes and alkenes in the bio-fuels. The research result of continuous conversion of vegetable oil to bio-fuels provided a scientific basis for solving the problem of energy shortage.

1 EXPERIMENTAL

1.1 Experimental materials and setup

Rapeseed oil (industrial grade) with the following mass distribution of fatty acids (purchased from FuLinMen Co. Ltd, Beijing, China) was used as a starting material: palmitic acid: 5.4%, stearic acid: 1.87%, oleic acid: 46.04%, linoleic acid: 20.36%, linolenic acid: 7.98%, eicosanoic acid: 0.63%, eicosenoic acid: 1.75%, erucic acid: 15.75%.

The experiment of the conversion of vegetable oil to bio-fuels was carried out by WFSM-3060 high-pressure reactor. The velocity of H_2 and the crude oil were controlled by a mass flow-meter. These two streams were mixed in the reactor. All kinds of factors were respectively investigated from reaction temperature, reaction pressure, the oil speed and the velocity of H_2 . The support ($\gamma\text{-Al}_2\text{O}_3$) was crushed and sieved to 0.2 - 0.35 mm particle size fraction. The mass of the catalyst is 1.0 g and the catalyst-bed length is about 0.95 - 1.0 cm.

All kinds of catalysts by incipient wetness impregnation method were prepared. After impregnation, the solution were stirred and placed at room temperature for 24 h, and dried in an oven at 120°C overnight and calcined at 500°C for 5 h in the muffle furnace at a rate of 10°C / min.

During the experimental work, the total loading of NiO and CoO was immobility about 20%, and the loading of NiO and CoO of Co-Ni bimetallic catalyst was immobility about 5% and 15 %. K⁺ and Ce were added to the catalysts for reducing the carbon deposition and improving the activity of the catalysts. All sorts of the catalysts were marked in order as 20Ni, 20Co, 15Co5Ni, 15Co5Ni-5Ce and 15Co5Ni-10Ce, respectively.

1.2 Catalyst characterization

The textural characteristics of the support and the catalysts were analyzed by N_2 physisorption method. N_2 adsorption and desorption isotherms were performed at 77 K on Micromeritics ASAP2020C equipment. The samples were outgassed in vacuum ($\approx 1 \mu\text{m Hg}$) at 573 K for 3 h before the measurement. The pore diameter and pore volume were calculated from the analysis of desorption

branch of the isotherm by the Barrett-Joyner-Halenda (BJH) method. X-ray diffraction (XRD) measurements were performed on the catalysts using the monochromatic Cu K α radiation of a Bruker AXS D8 Focus diffractometer instrument at 40 kV and 30 mA. The XRD patterns were recorded for $2\theta = 10 \sim 80$ degrees with a step width of 0.01 degree at a rate of 1.25°/min. Temperature programmed reduction (TPR) measurements were performed with a Chemisorb2750 instrument. The catalyst samples were purged with argon at 150°C for 30 min and cooled to 30°C, then heated to 840°C at a rate of 10°C min⁻¹ and the 5 vol% H₂/Ar flowing rate with 30 cm³·min⁻¹. The consumption of hydrogen was monitored by a thermal conductivity detector (TCD). Temperature programmed desorption (TPD) measurements were performed with a Chemisorb2920 instrument. The catalysts were purged with argon at 150°C for 30 min and cooled to 50°C before the measurement of H₂ or NH₃ adsorption. When the base line is stable, the samples were heated to 800°C at a rate of 10°C ·min⁻¹. The signal of H₂ or NH₃ was monitored by a thermal conductivity detector. Deposited coke was measured by temperature programmed combustion by TGA/SDTA851 device.

1.3 Gas products analysis

The gas products were analyzed by GC online. GC equipped with a thermal conductivity detector and carbon molecular sieve column TDX-01 (2.0 m, 2.0mm) were used to analyze the contents of CO and CO₂ at a constant temperature of column 190°C, current 110 mA and detector 160°C, respectively. Reaction gas are collected and analyzed by GC online every 10 minute in order.

1.4 Liquid products analysis of FT-IR

The FT-IR spectra of the liquid product samples were recorded by a Nicolet 5700 27 Infrared Spectrophotometer in 4000-400 cm⁻¹ with KBr pellet sample.

1.5 Liquid products analysis of GC-MS

GC-MS analysis using an Agilent 7890A GC (HP-5 column, 30 m × 0.25 mm × 0.25 μ m) coupled to an Agilent 5975C Inert MSD with a quadruplicate axis detector. Liquid product was dried for decrease water with dried Na₂SO₄. Liquid product was diluted 1:1 in cyclohexane and the diluted samples were injected onto a HP-5 column. Helium was used as the carrier gas at velocity rate of 54 mL/min and that the split ratio was 50:1. The mass range from m/z 50 - 550 was scanned with a speed of 0.3 s decade. Product identification was validated with a gas chromatograph-mass spectrometer.

1.6 The determination of trace water in the liquid products

Karl-Fisher coulometric titration method has been adopted to trace water content measurement of different substances. SF-3 (made in Zibo Instrument Co., Ltd, China) trace water content meter has successfully adopted this method. The yield was calculated by the following equation³:

$$\text{Liquid product yield\%} = \frac{\text{Weight of Liquid bio-fuels}}{\text{Weight of the crude oil}} \times 100\%$$

$$\text{H}_2\text{O yield\%} = \frac{\text{Weight of H}_2\text{O}}{\text{Weight of the crude oil}} \times 100\%$$

$$\text{Coke yield\%} = \frac{\text{Weight of coke}}{\text{Weight of the crude oil}} \times 100\%$$

$$\text{Gas product yield\%} = 1 - \text{Liquid product yield\%} - \text{H}_2\text{O yield\%} - \text{Coke yield\%}$$

2 RESULT AND DISCUSSION

2.1 XRD

The XRD results were shown in Figure 1. As can be seen, the peaks of γ -Al₂O₃ exhibited at 17.0°, 25.45°, 37.0°, 43.39° and 67.0°, and the peaks of NiAl₂O₄ exhibited at 44.0° and 62.0° in the Ni20 catalyst. Compared with the peaks of γ -Al₂O₃, there were no obvious peaks of nickel oxide, which indicated that the phases highly dispersed in the support. As the content of cobalt or the total content of cobalt and nickel increased, new peaks at 44.9°, 57.57° and 67.0° appeared for the catalysts of 20Ni, 15Co5Ni, 15Co5Ni-5Ce, 15Co5Ni-10Ce and 20Co, which indicated that the mixed phase of NiAl₂O₄ and CoAl₂O₄ can be formed. It is not surprise to know that the bimetallic Co-Ni / γ -Al₂O₃ catalysts are better than the Ni or Co catalyst alone in the activity of the decarboxylation and the decarbonylation of triglyceride to bio-fuels.

Fig. 1 XRD patterns of all kinds of the Catalysts

2.2 BET

The BET results of 15Co5Ni-10Ce catalyst were analyzed and showed in the table1 and Figure 2 on the fresh and the used catalysts. It can be seen from table1 that the surface areas and the pore volume of the catalyst show no significant difference before and after reaction, and the surface areas decreased from 166.4865 m²·g⁻¹ to 143.65 m²·g⁻¹, and the pore volume were obtained from 0.3226 cm³·g⁻¹ to 0.2878cm³·g⁻¹. The 15Co5Ni-10Ce / γ -Al₂O₃ catalyst of the fresh and multiple used could keep structure stability in this reaction. Compared with sintering, the catalyst deactivation was due to coke deposition. Therefore, the capability of 15Co5Ni-10Ce catalysts is very stable.

Fig. 2 BET patterns of the fresh and used catalysts.

2.3 TPR

The TPR result can be found from Figure 3 that the reduction peak of 358 °C in the 20Ni catalyst is attributed to the reduction of Ni²⁺ in the NiO phase, and the second peak of 437°C is associated with the reduction of Ni²⁺ in NiAl₂O₄. For the 20Co catalyst, the only reduction temperature of 370°C is likely attributed to the reduction of Co²⁺ in the Co₃O₄ phase. Moreover, the bimetallic 15Co5Ni catalyst has two reduction peaks at about 420°C and 650°C, and the peak of 420°C is associated with the reduction of Ni²⁺ in NiAl₂O₄, and that the peak of 650°C is associated with the reduction of Co²⁺ in CoAl₂O₄ species. What' more, the 15Co5Ni-5Ce catalyst has two reduction peaks at 360°C and 485°C, and the 15Co5Ni-10Ce catalyst have two reduction peaks 360°C and 525°C. The peak height of the reduction peak changed little, but the reduction peak temperature is shifted to lower temperature, which implies that the synergic effect was produced in the process of the preparation among cerium nitrate, nickel nitrate and cobalt nitrate species. The results revealed that the adding of cerium plays an important role in the reduced process.

Table 1 BET parameter of the fresh and used catalysts.

	the fresh	the second	the third	the fourth
BET Surface Area (m ² /g)	166.487	154.164	151.25	143.65
Single point adsorption total pore volume of pores(cm ³ /g)	0.3226	0.2768	0.2697	0.2878
BJH Adsorption cumulative volume of pores(cm ³ /g)	0.3452	0.2969	0.2918	0.2979
BJH Desorption cumulative volume of pores(cm ³ /g)	0.3426	0.2941	0.2912	0.2957
Adsorption average pore width(nm)	7.7507	7.3654	7.3207	8.1434
BJH Adsorption average pore diameter(nm)	6.9188	6.8437	6.8335	7.5806
BJH Desorption average pore diameter(nm)	5.4113	5.4353	5.6897	6.0355

Fig. 3 TPR patterns of the different catalysts**2.4 NH₃-TPD**

The acidic sites of the catalysts were measured by NH₃-TPD. For all catalysts, an intense desorption peak was observed at 120°C in Figure 4, which can be attributed to weakly adsorbed NH₃. One peak of moderate acidity sites can be seen at around 220°C in all kinds of catalysts. Moreover, the NH₃-TPD profile in Fig. 4 showed that three peaks at 220°C, 300°C and 420°C can be seen in the 20Co and 15Co5Ni catalysts, which indicated that 20Co and 15Co5Ni had two kinds of moderate acid sites and one strong acid site on their surface. What's more, one peak of strong acid site appeared at 550°C in the 15Co5Ni, 15Co5Ni-5Ce and 15Co5Ni-10Ce catalysts, which indicated that the surfaces of the 15Co5Ni, 15Co5Ni-5Ce and 15Co5Ni-10Ce catalysts had three kinds of acidity sites on their surface: weak acid, moderate acid and strong acid. With the introduction of Ce into the 15Co5Ni framework, the NH₃ adsorption peak at 300°C and 550°C increased significantly in the 15Co5Ni-5Ce and 15Co5Ni-10Ce catalysts, which induced the formation of a large amount of Lewis on their surface. The strong acid site is beneficial to the catalyst activity of the hydrogenation reaction and the deoxygenation reaction³².

Fig.4 NH₃-TPD patterns of the different catalysts**2.5 H₂-TPD**

The results of H₂-TPD were given in Figure 5. The H₂-TPD profile in Figure 5 showed that two similar intense desorption peaks of hydrogen at 120°C and 220°C in all kinds of catalysts. Moreover, there was a different hydrogen desorption curve over 400°C for 20Co catalysts, and the shoulder desorption peaks were centered at 450°C for the 20Ni and 15Co5Ni catalysts. What's more, the H₂-TPD profile in Figure 5 shows that one peak at 550°C can be seen in the 15Co5Ni-5Ce and 15Co5Ni-10Ce catalysts, which indicates that the 15Co5Ni-5Ce and 15Co5Ni-10Ce catalysts have three adsorbed sites. The higher desorption temperature makes desorption of reaction H₂ harder, which is beneficial to the hydrogenation reaction³. The strong adsorbed site is beneficial to the catalyst activity of the hydrogenation reaction, which implied that the adding of cerium plays an important role in the reduced process.

Fig.5 H₂-TPD patterns of the different catalysts**2.6 The selection of the catalyst**

The capability of five catalysts were performed at reaction temperature of 450°C, the oil flow rate of 0.1 mL/min, reaction pressure of 2.5 MPa and the H₂ flow rate of 30 mL/min.

It can be seen from Figure 6 that each FT-IR spectrum had the strongest absorption band centered at 2930 cm⁻¹ (CH₂ stretching). Compared with the FT-IR graph of the crude oil, all cracking products have no 1740 ~ 1750 cm⁻¹ peak, while the carbonyl absorption peak of 1705 ~ 1720 cm⁻¹ existed and the intensity of the absorption peak was weak, which showed that the liquid products have small amount of oxygenated compound. It can be found from Figure 6 that the peak intensity of C=O of liquid products reduced as the following order: 15Co5Ni-10Ce > 15Co5Ni-5Ce > 15Co5Ni > Co20 > Ni20 in the range 1720 cm⁻¹ to 1700 cm⁻¹. The peak intensity of C=O almost disappeared in the product produced on the 15Co5Ni-10Ce, which showed that the activity of the deoxygenation was very efficient on the 15Co5Ni-10Ce.

The FT- IR results are consistent with the result of NH_3 -TPD, H_2 -TPD and GC-MS analysis. The 15Co5Ni-10Ce catalyst had the best capability of the deoxidization in the conversion of vegetable oil to bio-fuels.

Gas yield, oxygenated compound, coke rate and liquid yield were shown and described in the table 2. As the table 2 displays, the content of oxygenated compound are high in the products of Co20, 15Co5Ni and Ni20, and that oxygenated product content of Ni20 catalyst and Co20 catalyst are 5.45%, 4.38% and 4.68%. Moreover, oxygenated compound content of the 15Co5Ni-5Ce catalyst and the 15Co5Ni-10Ce catalyst are 3.56% and 2.64%, respectively. Oxygenated compound content is the lowest in the liquid product produced on the 15Co5Ni-10Ce catalyst, and the total content of the alkanes and alkenes is the highest. Therefore, the 15Co5Ni-10Ce catalyst in the five different catalysts is the best in the deoxygenated activity in the conversion of vegetable oil to bio-fuels. The GC-MS results are consistent with the NH_3 -TPD, H_2 -TPD and FT- IR analysis.

Fig.6 FT-IR spectra of the different liquid products on the different catalysts.

Table 2 the result of the conversion of vegetable oil to bio-fuels on different catalysts.

	Ni20	Co20	15Co5Ni	15Co5Ni-5Ce	15Co5Ni-10Ce
Liquid yield%	85.89	85.94	86.02	86.34	86.9
Gas yield %	12.08	12.13	12.36	12.24	11.89
$\text{H}_2\text{O}\%$	0.087	0.084	0.079	0.074	0.063
Coke yield %	1.94	1.85	1.54	1.35	1.15
Composition of the liquid product					
aromatics	7.54	6.44	6.63	5.89	5.96
alkanes	40.4	42.57	42.93	43.05	46.51
alkenes	46.33	45.89	45.66	47.13	44.68
Oxygenated product	5.45	4.68	4.38	3.56	2.64
$\text{C}_8\text{-C}_{10}$ wt%	10.89	10.8	10.59	8.42	5.23
$\text{C}_{11}\text{-C}_{18}$ wt %	69.59	72.21	72.44	76.97	74.92
C_{18}^+ wt %	19.24	16.59	16.57	14.24	19.64
Total, wt%	99.72	99.58	99.6	99.63	99.79

2.7 Selection of the optimized condition

Bio-fuels production was carried out by using the 15Co5Ni-10Ce catalyst. During the experimental work, all kinds of factors were investigated from the reaction temperature, the oil flow rate, the reaction pressure and the gas flow rate.

2.7.1 Effect of reaction temperature

The experiments of several different reaction temperatures were performed from 470°C to 370°C. The products of six different reaction temperatures were obtained at reaction pressure of 2.5 MPa, the crude oil flow rate of 0.1 mL/min and the H_2 flow rate of 30 mL/min, respectively. Liquid yield, gas yield, H_2O

content, coke deposition rate and the distribution of liquid hydrocarbons were described and shown in table 3. As table 3 display, when reaction temperature reduced, liquid yield of the products of six different reaction temperatures had tiny aggrandizement, and the alkanes content of liquid products had biggish aggrandizement, and the coke deposition rate at different reaction temperatures increased more than 2 times. The content of oxygenated compound and H_2O increased more than four times, which showed that reaction temperatures is a very important factor in bio-fuels producing from coke rate, oxygenated product content and H_2O content.

Table 3 the analytical result of the conversion of triglycerides to bio-fuels at different reaction temperatures.

	470°C	450°C	430°C	410°C	390°C	370°C
Liquid yield%	85.94	86.9	87.08	87.63	87.94	88.1
Gas%	12.89	11.89	11.49	10.72	10.13	9.39
H ₂ O%	0.037	0.063	0.087	0.126	0.138	0.145
Coke yield %	1.13	1.15	1.34	1.52	1.79	2.36
Composition of the liquid product						
Cyclic compounds	7.42	5.96	5.89	3.8	3.8	6.74
alkanes	48.45	46.51	42.91	39.94	31.43	30.68
alkenes	41.72	44.68	46.98	45.22	53.66	51.24
Oxygenated compounds	2.28	2.64	4.02	10.53	10.77	10.88
C ₈ -C ₁₀ wt%	7.14	5.23	6.96	2.87	3.8	6.61
C ₁₁ -C ₁₈ wt %	71.36	74.92	70.26	63.93	73.97	69.78
C ₁₈ ⁺ wt %	21.37	19.64	22.58	32.46	22.08	23.15
Total, wt%	99.87	99.79	99.8	99.49	99.56	99.54

When the temperature was raised, liquid yield reduced and gas yield increased, and the total content of oxygenated compound became lower. The total content of alkanes and alkenes in the products produced at 410°C, 390°C and 370°C are lower than the 430°C, 450°C and 470°C products, and the content of oxygenated compound and coke deposition rate are higher. Moreover, the total alkanes and alkenes content are higher in the products produced at 470°C and 450°C, and the total content of oxygenated compound is low, and the main products are the hydrocarbon compounds under C₁₈. Although the content of oxygenated compound in the 470°C product was the lowest in all products, liquid yield and total content of alkanes and alkenes were lower than the product produced at 450°C. What's more, gas yield and total content of aromatic hydrocarbon and cyclic compound in the 470°C product was higher than the 450°C liquid product. The optimized reaction temperature is 450°C.

It can be seen from Figure 7, all kinds of FT-IR spectrum were normalized by the strongest intensity of the absorption band centered at 2930 cm⁻¹. Compared with FT-IR graph of the crude oil, the intensity of the C=O bond stretch in the 1740 ~ 1750 cm⁻¹ almost disappeared in the 410°C, 430°C, 450°C and 470°C liquid products while the carbonyl absorption peak of 1705 ~ 1720 cm⁻¹ exists, which shows that the liquid products have tiny compound containing oxygen. The carbonyl absorption peak is weak and decreasing when the reaction temperature was raised from 370°C to 470°C. But the intensity of the absorption peak in the area of 1740 ~ 1750 cm⁻¹ is strong, and the intensity of the absorption peak in the area of 3340 ~ 3320 cm⁻¹ is weak in the products produced at 370°C and 390°C, which showed that the liquid products have tiny fatty acids derivatives containing oxygen. The result is in agreement with literature and in particular with the work of Katikaneni S. P. R et al.²⁹ and Vonghia E. et al.³⁰. The fatty acid and the enol are unstable intermediate products when the reaction temperature increased. When the reaction temperature increases, the kinetic energy of the molecules increased, and molecular effective collision increase, and that the effect of the decarboxylation (-CO₂) and the decarbonylation (-CO) are advanced. The carbonyl absorption peak of 1705 ~ 1720 cm⁻¹ disappeared when the reaction temperature was 450°C. The FT-IR result showed that the activity of deoxidization was very efficient at 450°C, and reaction temperature is a very important factor in bio-fuel producing.

Fig.7 FT-IR spectra of the liquid products of different reaction temperatures

The distribution of CO and CO₂ were listed in table 4 under various conditions. It can be seen from table 4, the proportional relationship of CO and CO₂ is changing with the time. The molar ratio of CO₂/CO increased firstly and then decreased as the reaction progresses. But the molar ratio of CO₂/CO is more than twice in most cases, and the molar ratio of CO₂/CO change at about 0.88~24.54. The molar ratio of CO₂/CO may changed more than five times in the middle period (for 5~8 times). This is in agreement with literature and in particular with the work of Kovács S. et al.³⁵. The reaction of the decarboxylation and the decarbonylation occurred at the same time and the decarboxylation reaction was the main reaction. Analytical result of GC online and H₂O test indicated that the most oxygen in the crude oil were rejected by the forms of CO and CO₂, and small part was rejected by the form of H₂O.

Table 4 the GC result of the conversion of oil to bio-fuels at different reaction temperatures.

	470°C	450°C	430°C	410°C	390°C	370°C
No.	CO ₂ /CO	CO ₂ /CO	CO ₂ /CO	CO ₂ /CO	CO ₂ /CO	CO ₂ /CO
1	3.68	3.56	2.84	1.87	0.97	0.88
2	6.09	5.87	3.16	3.03	1.46	1.25
3	8.79	9.67	5.66	4.89	2.46	1.69
4	14.74	12.15	7.10	6.78	2.85	2.09
5	18.29	14.18	10.28	11.37	4.87	3.61
6	24.54	13.25	14.36	13.28	7.56	3.87
7	15.54	10.76	10.68	11.87	8.05	3.32
8	12.75	7.45	7.55	9.87	7.43	2.67
9	6.35	4.45	6.13	5.56	4.38	2.45
10	4.28	3.11	3.24	3.18	2.97	1.46

2.7.2 Effect of different oil flow rates

The experiments of several different oil flow rates were performed from 0.16 mL/min to 0.06 mL/min. The experiments of several crude oil flow rates were performed at reaction pressure of 2.5 MPa, reaction temperature of 450°C and the H₂ flow rate of 30 mL/min. Liquid yield, gas yield, H₂O content, coke deposition rate and the distribution of liquid hydrocarbons were described and shown in table 5. When the crude oil flow rate decreased from 0.16 mL/min to 0.06 mL/min, the change of the liquid yield and H₂O content is small, and the change of oxygenated compound content and coke yield increased more than twice, and the alkanes content of liquid products have biggish aggrandizement, which showed that oil velocity is a very important factor in bio-fuels producing.

Compared with the other products produced at 0.10 mL/min, 0.08 mL/min and 0.06 mL/min oil speed, the total content of alkanes and alkenes in the products produced at 0.16 mL/min, 0.14 mL/min and 0.12 mL/min oil speed are

lower, and the content of oxygenated compound of their products are higher. Their products are easy to be oxidized and have poor liquidity. When the oil flow rates are increased, the crude material and other middle product stay time became shorter, and the effect of the decarboxylation and the decarbonylation reaction would get bad. The total content of alkanes and alkenes in the products produced at 0.10 mL/min, 0.08 mL/min and 0.06 mL/min oil speeds are 91.19%, 93.82% and 91.64%, respectively. The main products are hydrocarbon compounds under C₁₈, moreover, odd carbon hydrocarbon with C₁₅ and C₁₇ are the main compounds. The oxygenated compound content is 2.64%, 2.45% and 2.44%, which showed that the activity of the deoxidization was very efficient at the 0.1 mL/min, 0.08 mL/min and 0.06 mL/min oil velocity. From the LHSV, liquid yield, gas yield and economic benefit, the oil velocity with 0.10 mL/min is suitable.

Table 5 the analytical result of the conversion of oil to bio-fuels at different oil flow rates.

	0.16	0.14	0.12	0.10	0.08	0.06
Liquid yield%	88.32	88.11	87.04	86.9	86.51	85.9
Gas%	8.05	10.2	11.55	11.89	12.35	12.97
H ₂ O%	1.37	0.097	0.078	0.063	0.054	0.058
Coke yield %	2.26	1.59	1.33	1.15	1.08	1.07
Composition of the liquid product						
Cyclic compounds	5.59	3.48	5.18	5.96	4.52	5.64
alkanes	39.18	39.26	40.81	46.51	46.66	47.2
alkenes	49.24	52.61	50.89	44.68	46.16	44.44
Oxygenated compounds	5.53	4.45	2.84	2.64	2.45	2.44
C ₈ -C ₁₀ wt%	3.1	2.77	5.52	5.23	6.79	5.87
C ₁₁ -C ₁₈ wt %	66.84	63.23	69.33	74.92	71.21	68.06
C ₁₈ ⁺ wt %	29.6	33.8	24.87	19.64	21.79	25.79
Total, wt%	99.54	99.74	99.72	99.79	99.79	99.72

It can be seen from Fig.8, the intensity of the absorption peak decreased when the oil velocity reduced. Compared with FT- IR graph of the crude oil, most cracking products except the products produced at 0.16 mL/min and 0.14 mL/min oil velocity almost have no 1740 ~ 1750 cm⁻¹ peak, but the carbonyl absorption peak of 1705 ~ 1720 cm⁻¹ exists, which showed that the products have small amount of ketone compound. The peak intensity of C=O almost disappeared in the liquid product produced at 0.1 mL/min oil velocity. The FT-IR result showed that the effect of the deoxidization was very efficient at the

crude oil velocity of 0.1 mL/min. The intensity of the absorption peak in the area of 1740 ~ 1750 cm⁻¹ is strong in the liquid products produced at 0.16 mL/min and 0.14 mL/min oil velocity, and the intensity of the absorption peak in the range of 3340 ~ 3320 cm⁻¹ is weak, which showed that the product produced at 0.16 mL/min and 0.14 mL/min have small amount of ketone and fatty acids derivatives containing oxygen. The FT-IR results are consistent with the GC-MS data analysis, which showed that reaction oil velocity among 0.06 mL/min to 0.16 mL/min is an important factor in bio-fuels producing.

Fig.8 FT-IR spectra of the liquid products of different oil flow rates

The molar ratio of CO and CO₂ are listed in table 6 under various conditions. It can be seen from table 6, the proportional relationship of CO and CO₂ is changing with the time. The molar ratio of CO₂/CO increased firstly and then decreased as the reaction progresses. But the molar ratio of CO₂/CO is more than twice in most cases, and the molar ratio of CO₂/CO change at about 0.87 ~ 28.63. The molar ratio of CO₂/CO may change more than five times more than five times for 3 ~ 8 times in the collected gas.

Table 6 the GC analytical result of different oil flow rates.

	0.16	0.14	0.12	0.10	0.08	0.06
No.	CO ₂ /CO	CO ₂ /CO	CO ₂ /CO	CO ₂ /CO	CO ₂ /CO	CO ₂ /CO
1	0.87	1.68	1.71	3.56	3.75	2.28
2	1.22	3.29	2.00	5.87	5.53	6.29
3	7.51	6.09	5.62	9.67	6.10	9.00
4	9.60	8.84	8.80	12.15	7.92	14.02
5	11.68	9.12	18.81	14.18	10.76	28.63
6	10.45	18.09	14.35	13.25	11.74	27.7
7	6.68	13.74	11.14	10.76	18.16	15.53
8	3.08	5.76	8.78	7.45	10.16	9.37
9	2.06	2.69	6.94	4.45	5.72	7.84
10	1.48	2.39	3.56	3.11	4.34	4.54

2.7.3 Effect of different reaction pressures

The experiments of different reaction pressures were performed from 3.5 MPa to 1.0 MPa. All kinds of the products were obtained at oil flow rate of 0.1mL/min, reaction temperature of 450 °C and the carrier gas flow rate of 30mL/min. Liquid yield, gas yield, H₂O content, coke rate and the distribution of liquid hydrocarbons were described and shown in table 7. The change of liquid yield, H₂O content and coke rate is small from 3.5 MPa to 1.0 MPa. The change of oxygenated compound content increased from 2.62% to 3.38%, which showed that the activity of the deoxidization and the hydrogenation was very efficient among 3.5 MPa to 1.0 MPa.

According to the data of GC-MS, the total content of alkanes and alkenes

in the products produced at 3.5 MPa, 3.0 MPa and 2.5 MPa are 91.54%, 92.53% and 91.19%, respectively. The main products are hydrocarbon compounds under C₁₈, and odd carbon hydrocarbon with C₁₅ and C₁₇ are the main compounds. The total content of alkanes and alkenes in the product produced at 3.0 MPa is higher than other products produced at other reaction pressure. Moreover, the content of alkanes in the product produced at 3.0 MPa is 50.19%. What's more, the oxygenated compound content is 2.62%, which showed that the activity of the deoxidization and the hydrogenation was very efficient at 3.0 MPa, which showed that reaction pressure with 3.0 MP is suitable among 1.0 MPa to 3.5 MPa under the same LHSV condition.

Table 7 the analytical result of different reaction pressures.

	3.5	3.0	2.5	2.0	1.5	1.0
Liquid yield%	87.05	87.08	86.9	86.63	86.71	86.30
Gas%	11.79	11.78	11.89	12.04	11.86	12.09
H ₂ O%	0.059	0.055	0.063	0.067	0.061	0.073
Coke%	1.1	1.08	1.15	1.26	1.36	1.53
Composition of the liquid product						
aromatics	5.64	4.60	5.96	5.67	7.36	6.72
alkanes	50.1	50.19	46.51	46.3	46.05	43.88
alkenes	41.44	42.36	44.68	44.43	43.16	45.62
oxygenates	2.64	2.62	2.64	3.14	3.08	3.38
C ₈ -C ₁₀ wt%	5.87	5.17	5.23	5.86	6.61	6.61
C ₁₁ -C ₁₇ wt%	72.26	75.08	74.92	69.49	69.31	68.44
C ₁₈ ⁺ wt %	21.69	20.52	19.64	24.19	23.73	24.55
total%	99.82	99.77	99.79	99.54	99.65	99.60

The distribution of CO and CO₂ are listed in table 8 under various conditions. It can be seen from table 8, the proportional relationship between CO and CO₂ is changing with the time. The molar ratio of CO/CO₂ increased firstly and then decreased as the reaction progresses. But the molar ratio of CO₂/CO is more than three times in most cases, and the molar ratio of CO₂/CO changed at about 1.12~25.46.

The analytical results of GC online and trace H₂O test indicated that the most oxygen in the oil were rejected by the forms of CO and CO₂, and the minor oxygen were rejected by the form of H₂O.

Table 8 the GC result of different reaction pressures.

	3.5MPa	3.0MPa	2.5MPa	2.0MPa	1.5MPa	1.0MPa
No.	CO ₂ /CO	CO ₂ /CO	CO ₂ /CO	CO ₂ /CO	CO ₂ /CO	CO ₂ /CO
1	4.34	3.68	3.56	2.24	1.69	1.12
2	6.09	6.09	5.87	5.82	5.15	1.87
3	10.56	7.92	9.67	8.36	7.84	2.85
4	17.89	8.79	12.15	10.91	10.94	8.86
5	19.28	13.74	14.18	11.61	12.69	9.53
6	25.46	18.09	13.25	13.44	13.62	11.62
7	23.24	12.54	10.76	9.67	9.55	10.29
8	13.45	8.75	7.45	7.87	5.81	6.86
9	8.96	6.35	4.45	5.68	5.12	5.56
10	6.47	3.28	3.11	3.56	1.63	2.86

It can be found from Fig.9 that the peak intensity of C=O bond of liquid products reduced as the following order: 3.5 MPa ≥ 3.0 MPa > 2.5 MPa > 2.0MPa > 1.5 MPa > 1.0 MPa in the range 1705~1720 cm⁻¹, and the peak intensity of C=O almost disappeared in the product produced at 3.0 MPa. The result of FT-IR showed that the activity of the deoxidization and the hydrogenation was very efficient at 3.0MPa.

Fig.9 FT-IR spectra of the liquid products of different reaction pressures

2.7.4 Effect of different H₂ flow rates

The tests of several H₂ flow rate were performed at H₂ flow rate from 15 mL/min to 40 mL/min. The products of various H₂ flow rates were obtained at reaction pressure of 2.5 MPa, reaction temperature of 450°C and the oil flow rate of 0.10 mL/min. Liquid yield, gas yield, H₂O content, coke rate and the distribution of liquid hydrocarbons were described and shown in table 9. As table 9 displays, the change of liquid yield, H₂O content, the content of alkanes and coke deposition rate is small, which showed that H₂ velocity is a secondary factor in the conversion of triglyceride to bio-fuels.

As table 9 display, the total content of alkanes and alkenes in the liquid product produced at 35 mL/min is 93.26%, and the content of alkanes is the highest and the content is 48.36%, and the content of oxygenated compounds in the 35 mL/min liquid product is lower than other H₂ flow rates products. The main products are hydrocarbon compounds under C₁₈, and odd carbon hydrocarbon with C₁₅ and C₁₇ are the main compounds. Although the content of alkanes in the liquid product produced at 40 mL/min is 48.09%, the content of oxygenated compounds and coke rate in the 40 mL/min liquid product is higher than the liquid product produced at 35 mL/min. When the H₂ flow rate increased, the crude oil and other middle products stay time become short, and the activity of decarboxylation and decarbonylation reaction would not be good. The good technique is that H₂ flow rate is 35 mL/min from the consumption of H₂, liquid products yield, the total content of alkanes and alkenes, coke rate and the content of oxygenated compounds.

Table 9 the analytical result of different gas flow rates.

	15	20	25	30	35	40
Liquid yield%	86.06	86.12	87.03	86.9	87.06	86.16
Gas%	12.48	12.46	11.74	11.89	11.79	12.65
H ₂ O%	0.082	0.087	0.068	0.063	0.056	0.059
Coke yield %	1.37	1.33	1.16	1.15	1.09	1.13
Composition of the liquid product						
Cyclic compounds	6.74	6.53	7.42	5.96	3.99	2.64
alkanes	43.78	45.92	46.35	46.51	48.36	48.09
alkenes	45.62	44.38	43.22	44.68	44.9	45.49
Oxygenated compound	3.38	2.84	2.78	2.64	2.41	3.25
C ₉ -C ₁₀ wt%	6.61	4.91	6.94	5.23	4.61	4.81
C ₁₁ -C ₁₈ wt %	68.36	67.12	68.85	74.92	74.77	70.88
C ₁₈ ⁺ wt %	24.55	27.64	23.98	19.64	20.28	23.78
Total, wt%	99.52	99.67	99.77	99.79	99.66	99.47

It can be seen from Fig.10, all kinds of FT-IR spectrum were normalized by the strongest intensity of the absorption band centered at 2930 cm⁻¹. Compared with FT-IR graph of the crude oil, all cracking products had no 1740 ~ 1750 cm⁻¹ peak while the carbonyl absorption peak of 1705 ~ 1720 cm⁻¹ existed and the intensity of the absorption peak was small, which showed that the product had small amount of derivatives containing oxygen and the activity of deoxidization was very efficient in the different H₂ flow rates. Compared with the reaction temperature, H₂ velocity was a secondary factor in producing bio-fuels.

The distribution of CO and CO₂ are listed in table 10 under various conditions. It can be seen from table 10, the proportional relationship between CO and CO₂ is changing with time, and the molar ratio of CO₂/CO changed at about 1.56~29.56. The molar ratio CO₂/CO increased firstly and then decreased as the reaction progresses. But the molar ratio of CO₂/CO was more than three times in most cases. The molar ratio of CO₂/CO changed more than four times in the reaction middle period. The results of GC online and trace water test showed that the oxygen in the oil was mainly removed by the forms of CO and CO₂, and a small quantity of oxygen was rejected by the form of H₂O.

Fig.10 FT-IR spectra of the liquid products of different gas flow rates

Table 10 the GC result of different gas flow rates

	15	20	25	30	35	40
No.	CO ₂ /CO	CO ₂ /CO	CO ₂ /CO	CO ₂ /CO	CO ₂ /CO	CO ₂ /CO
1	1.56	2.18	3.84	3.56	6.46	5.24
2	2.68	2.95	5.08	5.87	10.35	9.88
3	3.58	5.68	8.15	9.67	14.56	10.68
4	5.89	9.87	10.46	12.15	20.35	11.24
5	8.45	10.89	12.12	14.18	29.56	14.87
6	6.36	10.75	11.15	13.25	25.45	12.54
7	4.98	10.24	9.46	10.76	17.45	8.76
8	3.56	8.45	8.45	7.45	15.35	7.45
9	2.35	6.56	5.35	4.45	6.78	4.45
10	2.14	2.84	3.22	3.11	4.26	2.47

2.7.5 The optimized result of the conversion of vegetable oil to bio-fuels

The technique was optimized at reaction temperature of 450°C, reaction pressure of 3.0 MPa, the oil flow rate of 0.1 mL/min and the gas flow rate of 35 mL/min. The fresh and used catalysts were analyzed by BET. The molar ratio of CO₂/CO may changed at about 5.05~26.85. The results of GC online showed that the reaction of the decarboxylation and the decarbonylation occurred at the same time and the decarboxylation reaction was the main reaction. The gas

yield and liquid yield of liquid products were 11.79 wt % and 87.11 wt%; H₂O content, oxygenated compound content and coke rate of liquid products were 0.053 wt%, 2.32 wt% and 1.05 wt%; the alkanes content and alkenes content of liquid products were 50.02% and 40.03% under the optimized condition. The distribution in the liquid product analyzed by GC-MS was showed in table 11. The main products were hydrocarbon compounds under C₁₈.

Table 11 the GC-MS analytical result of the conversion of oil to bio-fuels under the optimized condition

No.	RT	Area%	molecular formula	chemical name
1	3.59	0.21	C ₉ H ₁₈	1-Nonene
2	3.699	0.53	C ₉ H ₂₀	Nonane
3	3.779	0.11	C ₉ H ₁₈	2-Nonene,(E)-
4	4.924	0.2	C ₉ H ₁₂	Benzene,1-ethyl-4-methyl-
5	5.015	0.32	C ₁₀ H ₂₀	1-Decene
6	5.141	0.83	C ₁₀ H ₂₂	Decane
7	5.227	0.22	C ₁₀ H ₂₀	4-Decene,(E)-
8	6.085	0.3	C ₁₀ H ₁₄	Benzene,butyl-
9	6.28	0.46	C ₁₀ H ₁₄	Benzene,1-methyl-3-propyl-
10	6.566	0.97	C ₁₁ H ₂₂	5-Undecene,(E)-
11	6.692	0.91	C ₁₁ H ₂₄	Undecane
12	6.772	0.45	C ₁₁ H ₂₂	4-Undecene,(E)-
13	6.915	0.23	C ₁₁ H ₂₂	3-Undecene,(E)-
14	7.132	0.19	C ₁₁ H ₂₂	Cyclohexane,pentyl-
15	7.327	0.37	C ₁₁ H ₂₂	Cyclopentane,hexyl-
17	7.561	0.22	C ₁₀ H ₁₂	Indan,1-methyl-
18	7.636	0.52	C ₁₁ H ₁₆	Benzene,pentyl-
19	7.767	0.57	C ₁₀ H ₁₂	Naphthalene,1,2,3,4-tetrahydro-
20	8.082	0.85	C ₁₂ H ₂₄	3-Dodecene,(Z)-
21	8.202	0.53	C ₁₂ H ₂₆	Dodecane
22	8.282	0.29	C ₁₂ H ₂₄	6-Dodecene,(E)-
23	9.141	1.1	C ₁₂ H ₁₈	Benzene, hexyl-
24	9.518	0.89	C ₁₃ H ₂₆	1-Tridecene
25	9.633	1.55	C ₁₃ H ₂₈	Tridecane

26	9.702	0.22	$C_{13}H_{26}$	3-Tridecene,(Z)-
28	10.388	0.46	$C_{13}H_{26}$	6-Tridecene,(E)-
29	10.525	0.82	$C_{13}H_{20}$	Benzene, heptyl-
30	10.64	0.28	$C_{13}H_{20}$	1-Methyl-2-n-hexylbenzene
31	10.875	2.07	$C_{14}H_{28}$	1-Tetradecene
32	10.978	3.1	$C_{14}H_{30}$	Tetradecane
33	11.184	0.1	$C_{14}H_{28}$	5-Tetradecene,(E)-
34	11.647	0.22	$C_{14}H_{28}$	Cyclopentane, nonyl-
36	11.784	0.55	$C_{14}H_{26}$	Cyclopentene,1-octyl-
37	11.904	0.54	$C_{14}H_{22}$	Benzene, octyl-
38	11.973	0.21	$C_{14}H_{22}$	Benzene,(1-methylheptyl)-
39	12.151	3.72	$C_{15}H_{30}$	1-Pentadecene
40	12.248	7.82	$C_{15}H_{32}$	Pentadecane
41	12.448	0.26	$C_{15}H_{30}$	Cyclopentane, decyl
42	12.923	1.23	$C_{15}H_{30}$	n-Nonylcyclohexane
43	13.163	1.11	$C_{16}H_{32}$	Z-7-Hexadecene
44	13.278	0.49	$C_{16}H_{32}$	1-Hexadecene
45	13.352	0.82	$C_{16}H_{32}$	Z-8-Hexadecene
46	13.438	1.23	$C_{16}H_{34}$	Hexadecane
47	13.621	0.52	$C_{16}H_{32}$	5-Hexadecene,(E)-
48	14.147	1.41	$C_{17}H_{36}$	Tetradecane,2,6,10-trimethyl-
49	14.21	0.79	$C_{17}H_{34}$	1-Heptadecene
50	14.342	3.15	$C_{17}H_{34}$	3-Heptadecene,(Z)-
51	14.405	4.42	$C_{17}H_{34}$	8-Heptadecene
52	14.491	1.24	$C_{17}H_{34}$	7-Heptadecene
53	14.577	6.3	$C_{17}H_{36}$	Heptadecane
54	14.76	1.13	$C_{17}H_{34}$	3-Heptadecene,(E)-
55	14.868	0.95	$C_{12}H_{24}$	Cyclohexane,1-methyl-3-pentyl-
56	15.086	0.58	$C_{17}H_{36}$	Hexadecane,2-methyl-
57	15.2	1.3	$C_{17}H_{34}$	Cyclohexane,undecyl-
58	15.401	0.62	$C_{18}H_{36}$	8-Octadecene
59	15.486	0.5	$C_{18}H_{36}$	6-Octadecene,(E)-
60	15.572	0.83	$C_{18}H_{36}$	1-Octadecene
61	15.647	1.95	$C_{18}H_{38}$	Octadecane
62	15.853	2.3	$C_{18}H_{36}$	3-Octadecene,(E)-
63	16.379	0.16	$C_{19}H_{38}$	5-Nonadecene(E)-
64	16.385	0.91	$C_{19}H_{40}$	Nonadecane
65	16.442	0.34	$C_{19}H_{38}$	3-Nonadecene(E)-
66	16.499	0.39	$C_{19}H_{38}$	5-Nonadecene(Z)-
67	16.717	3.02	$C_{18}H_{36}$	4-Methyl-7-Heptadecene
68	16.734	0.22	$C_{17}H_{34}O$	2-Heptadecanone
69	17.312	5.4	$C_{18}H_{36}$	Heptadecane,8-methyl-
70	17.432	1.07	$C_{18}H_{36}$	Heptadecane,9-methyl-
71	17.655	3.91	$C_{20}H_{42}$	Eicosane
72	18.45	3.25	$C_{21}H_{42}$	Heneicosene
73	18.582	0.65	$C_{21}H_{44}$	Heneicosane

74	18.656	1.03	C ₁₉ H ₃₈ O	2-Nonadecanone
75	19.017	4.65	C ₂₁ H ₄₄	Eicosane,3-methyl
76	19.166	2.32	C ₂₂ H ₄₄	1-Docosene
77	19.349	2.29	C ₂₂ H ₄₆	Docosane
78	19.509	0.97	C ₂₂ H ₄₄	10-Docosene
79	20.03	0.9	C ₂₂ H ₄₆	Heneicosane,5-methyl-
80	20.087	0.67	C ₂₂ H ₄₆	Heneicosane,7-methyl-
81	20.213	1.07	C ₂₂ H ₄₆	Heneicosane,9-methyl-
82	20.344	0.24	C ₂₂ H ₄₆	Heneicosane,11-methyl-
Total,wt%		99.52		

2.8 The stability of 15Co5Ni-10Ce in different reaction times

The stability of 15Co5Ni-10Ce/ γ -Al₂O₃ catalyst were performed at reaction temperature with 450°C, reaction pressure with 2.5 MPa, the oil flow rate with 0.1mL/min and the gas flow rate with 30 mL/min. The used catalysts were calcined at 550°C for 6 h to remove any carbon residue in the muffle stove. Liquid hydrocarbon yields, H₂O content, oxygenated product content and coke rate were listed in the table 12. It can be seen from table 12, the change of oxygenated compound content and coke deposition rate was about 1.5 times. The change of the total content of alkanes and alkenes and the liquid yield was

small, which showed that the stability of 15Co5Ni-10Ce catalyst was good.

The FT-IR spectra of liquid products were described and shown in Fig.11. The peak of 1740 ~ 1750 cm⁻¹ almost have no appearance, while the carbonyl absorption peak of 1705 ~ 1720 cm⁻¹ existed and the intensity of the absorption peak was weak in the different times' product, which showed that the decarboxylation and decarbonylation reaction were excellently fulfilled on the fresh and multiple used catalysts. The reason is that the 15Co5Ni-10Ce/ γ -Al₂O₃ catalyst can keep structure stability in this reaction.

Table 12 the analytical result of the conversion of triglyceride to bio-fuels at different times

	the fresh	the second	the third	the fourth
Liquid yield%	86.9	86.63	86.19	85.90
Gas yield %	11.89	12.05	12.35	12.52
H ₂ O%	0.063	0.068	0.073	0.083
Coke yield %	1.15	1.26	1.38	1.49
Composition of the liquid product				
aromatics	5.96	6.3	6.54	6.74
alkanes	46.51	45.86	44.66	43.15
alkenes	44.68	43.92	45.16	45.58
oxygenates	2.64	3.16	3.45	4.22
C ₈ -C ₁₀ wt%	5.23	5.82	6.79	6.46
C ₁₁ -C ₁₈ wt %	74.92	68.85	67.23	67.18
C ₁₈ ⁺ wt %	19.64	24.57	25.79	26.05
Total, wt%	99.79	99.24	99.81	99.69

2.9 The related mechanism and possible equations

The bond energy of C = O is about 736 ~ 749 KJ·mol⁻¹, and the bond energy of C - O bond with 360 KJ·mol⁻¹ and the bond energy of C - C with 347 KJ·mol⁻¹, so the reaction of C - O and C - C bond breaking is more easy at the beginning of the reaction when the reaction temperature increased, and the crude oil easily changed into fatty acid and short chain hydrocarbon fracture.

Vegetable oil can be deoxygenated via three pathways³⁵: decarboxylation, which produces paraffinic hydrocarbon via the removal of the carboxyl group with the release of carbon dioxide; or decarbonylation, which produces olefinic hydrocarbon by the removal of the carboxyl group and the release of carbon monoxide; or hydrodeoxygenation, which produces paraffinic hydrocarbon via the removal of the carboxyl group with release of water. When the methanation reaction is negligible, the molar ratio of CO₂/CO can serve as an indicator for evaluating the reaction pathways of decarboxylation and decarbonylation.

According to the data of GC-MS of the different reaction conditions, the main products were the hydrocarbon compounds under C₁₈, and the minor product was the ketone compounds. Most alkanes and alkenes were hydrocarbons with C₁₁~C₁₈, moreover, odd carbon hydrocarbons with C₁₃, C₁₅ and C₁₇ were the main compounds. From the results of GC-MS, GC, SF-3 and the FT-IR, we speculated that the first mechanism is one or more fatty acid ester chain γ -H transfer, directly generate less of a carbon atom chain, fatty acid and the unstable intermediate enol. The triglycerides changed into fatty acids and other middle products when the reaction temperature increased, and fatty acids partly became alcohol and small quantity of H₂O was produced by dehydration of alcohol. The above interpret is agreed with the literature and in particular with the work of Kovács et al.³⁵, Katikaneni et al.²⁹ and Vonghia E. et al.³⁰. The related mechanism and equations are listed below.

Decomposition of the triglycerides and the unstable intermediate enol:

(1)

(2)

Decomposition and isomerism of the unstable intermediate enol:

(3)

(4)

Decarboxylation (- CO₂) and decarbonylation (- CO) reaction of fatty acids:

Decarboxylation and decarbonylation reactions of fatty acids generate odd carbon alkenes and alkanes and CO and CO₂ gas. In the H₂ condition, odd alkenes and alkenes are the formation of partial olefins by the hydrogenation reaction.

(5)

(6)

(7)

The even carbon alkanes and alkenes are the formation by the hydrogenation and the deoxidization of fatty acids in the H₂ condition:

(8)

(9)

Splitting decomposition of fatty acids and paraffin:

According to the data of GC-MS, the liquid product contained a small amount of C₈~C₁₁ alkanes and aromatic hydrocarbon and alkenes. Because the number of carbon atoms of the fatty acid in the crude oil is mainly made of C₁₄, C₁₆, C₁₈, C₂₀ and C₂₂ carbon atoms, alkanes and aromatic hydrocarbon and alkenes of C₈~C₁₁ mostly caused by the common effect of thermal cracking and catalytic cracking.

(10)

(11)

(12)

CONCLUSIONS

The catalysts were prepared and characterized by XRD, BET, H₂-TPD, NH₃-TPD and TPR analysis, and the 15Co5Ni-10Ce catalyst had good thermal stability and three adsorbed sites and three kinds of acidity sites on the surface. Compared with sintering, the catalyst deactivation was due to coke deposition. The decarboxylation reaction and decarbonylation reaction were excellently fulfilled on the fresh and multiple used catalysts.

The results of FT-IR, SF-3, GC and GC-MS indicated that reaction temperature and oil velocity were very important factors and that reaction pressure was a less important one in producing bio-fuels. The technique was optimized at reaction temperature of 450°C, reaction pressure of 3.0 MPa, oil velocity of 0.1 mL/min and the gas velocity of 35 mL/min. The alkanes content and alkenes content of liquid products are 50.02% and 40.03% under the optimized condition. The main products were hydrocarbon compounds under C₁₈.

The results of GC online and trace water determination indicated that the reaction of the decarboxylation and decarbonylation occurred at the same time and the decarboxylation reaction was the main reaction, and the main oxygen in the oil were removed by the forms of CO₂ and CO, and the oxygen in the oil was partly removed by the form of H₂O.

From the results of FT-IR, SF-3 and GC-MS, researchers deduce the generating mechanism of Non-ester renewable diesel. The isomerism of the unstable intermediate enol was added to the possible equations about the related mechanism. The research result of continuous conversion of triglyceride to bio-fuels provided a theoretical foundation and scientific basis for solving the problems of energy shortage.

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