

Continuous Deoxygenation of Triglycerides to Biofuels Over 15Co5Ni/ γ -Al₂O₃ Catalyst

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Received: 2 April 2014;

Accepted: 15 May 2014;

Published online: 10 January 2015;

AJC-16646

Bio fuels production was carried out in an electrically heated fixed bed tubular reactor. During the experimental work, all kinds of factor were investigated. It was found that reaction temperature played key role and the rate between nickel and cobalt is an important role in decarboxylation and decarbonylation reaction. Technological conditions are optimized at reaction temperature, the oil flow rate, the gas flow rate and the rate between nickel and cobalt, 450 °C, 0.1 mL/min, 12 mL/min and 3:1, respectively. The alkanes content and alkenes content of liquid products is 44.86 and 49.08 %, respectively under the optimized condition. The product is mostly under C₁₈ hydrocarbon compounds. The results of GC online and trace water determination show that the oxygen in the oils are mainly removed through decarboxylation and decarbonylation reaction. The oxygen in the oils are tiny removed through the dehydration of alcohol. Characterization of technologies including TG, XRD, BET, FT-IR, GC-MS and temperature programmed reduction were performed to demonstrate more details. The catalyst deactivation was due to coke deposition, relatively to sintering.

Keywords: Biofuels, Decarboxylation, Decarbonylation, 15Co5Ni/Al₂O₃ Catalyst, Deoxygenation.

INTRODUCTION

Petroleum and coal are not renewable resource, the quality and quantity of crude oils is poorer and poorer¹. But the rapid development of the world economy, the resources have been in greater demand by 26 % from the level of 1995¹. With the exhaustion of chemical fossil resources, a financial tsunami initiated by soaring crude oil prices has negative effects on the global economy in 2008, which still do not eliminate²⁻⁴. The global resource has been tensed once again, for the soaring of the price of crude oil in the international market in recent years. Consequently, the world economy driven only by oil has come to appear to be weak⁵. In addition the environmental problems to follow resulting from the extensive use of fossil fuels have become more and more serious. Seeking and development of renewable energy is very prerequisite and important. Renewable energy sources (RES), which include hydro energy, wind energy, solar energy, biomass energy, geothermal energy, tidal energy and wave energy. With the health consciousness of people, a renewable energy economy and the environment consciousness of the government are became more and more strong, all countries are revising the increasingly strict emission standards and the standards of fuel would further improved, European Union has adopted a target of 10 % of energy for transportation coming from renewable sources, including bio

fuels, by 2020 to tackle the increasing greenhouse gas emissions problem and reduce dependency on fossil fuels⁶.

Bio fuels has zero net emission of CO₂ and has very low contents of sulfur and nitrogen, which gives lower emissions of SO₂, NO_x than conventional fossil fuels⁷. Biomass is the only renewable energy containing carbon. People pay more and more attention to bio fuels⁸. Conversion of renewable resources the biomass-derived into hydrocarbon is regarded as a carbon neutral process due to carbon-cycling between chemical conversion (biomass → hydrocarbon + CO₂) and photosynthesis (light + CO₂ + H₂O → biomass)^{9,10}.

The concept and experimental process of converting vegetable oils into biodiesels was first attempted more than 100 years ago because of the shortage of petroleum and coal, particularly in those areas of the world that lack petroleum deposits^{11,12}. The first generation bio fuels, also named as fatty acid methyl ester (FAME), is an alternative fuel obtained from renewable biological sources by the transesterification of triglycerides or the esterification of free fatty acids with methano^{11,12}. Bio fuels are typically carried out at near atmospheric pressures, direct liquefaction¹³⁻¹⁵, direct cracking¹⁶⁻¹⁷, catalytic cracking and transesterification of triglycerides are the most common method¹⁸⁻²⁰. Biodiesel production can also be carried out by homogeneous alkali, homogeneous acid or enzyme-catalyzed²¹⁻²⁶ processes or in catalyst-free supercritical

methanol²⁷⁻²⁹. Direct transformation of triglycerides into hydrocarbons has been patented by several companies and already commercially demonstrated³⁰⁻³².

Fatty acid methyl ester (FAME) has many undesirable physical-chemical relative to petroleum-derived diesel, such as higher cloud point, higher viscosity, freeze point, pour point; above all poor oxidation stability and lower energy density because of oxygen content of FAME is high³³, hence, Kubicková *et al.*³⁴, Simakova *et al.*³⁵ and Takemura³³ paid to research and development of deoxygenation of triglycerides to non-esterified renewable diesel (NERD)-so-called second generation bio fuels^{10,36}. Deoxygenation of triglycerides can be achieved over these catalysts such as sulfided CoMo, NiMo, NiW supported on alumina and Pd/SBA-15 catalysts and Pd/C³⁷⁻³⁹ and Li *et al.*³⁶ and Watanabe *et al.*⁴⁰ employed ZrO₂, CeO₂ and Y₂O₃ as a solid base catalyst to get fuels from the waste vegetable oils and animal fats by use of the SCW decarboxylation technique.

The most oxygen was rejected as the forms of CO and CO₂ via decarboxylation (-CO₂) and decarbonylation (-CO) of fatty acids, the oxygen in the oils are tiny removed through the dehydration of alcohol and their methyl esters has been studied extensively over Pt/Al₂O₃⁴¹ and Pd/C⁴² catalysts.

Co/ γ -Al₂O₃ is a good catalyst in Fischer-Tropsch synthesis and hydrogenation activity⁴³⁻⁴⁵, Co/ γ -Al₂O₃ is a good catalysts deoxygenation activity and Ni/ γ -Al₂O₃ is a good catalysts hydrogenation activity⁴⁶. In the paper, the objective is to explore deoxygenation of triglycerides to non-esterified renewable diesel (NERD) by low-cost transition metal as catalyst at under mild operating conditions. A kind of bimetallic Co-Ni/Al₂O₃ catalysts by incipient wetness impregnation method was developed to catalyze the decarboxylation and decarbonylation of triglycerides. During the experimental work, the loading of NiO of Co-Ni bimetallic catalyst was immobility about 5 %, Catalysts were prepared with various cobalt loadings but only the samples with 5, 10 and 15 wt. % cobalt were characterized in detail and then K⁺ was added to the optimized catalyst to reduce the carbon deposition and improve the liquid yield.

The result of FT-IR, GC-MS and GC show reaction temperature and the rate between nickel and cobalt is a very important factor to bio fuels product, oils velocity is an important factor to bio fuels product. During the experimental work, all kinds of factor were optimized at reaction temperature, the oil flow rate, the gas flow rate and the rate between nickel and cobalt, 450 °C, 0.1, 12 and 3:1, respectively. Under the optimized condition, the alkanes content and alkenes content of liquid products is 44.86 and 49.08 %, respectively; deactivated carbon deposition, H₂O content and oxygenates product content is 2.13, 0.061 and 3.26 %, respectively. In this paper, the research result of continuous deoxygenation of triglycerides to renewable and sustainable bio fuels provides a good theoretical foundation and scientific basis for solving the problem of energy shortage and greenhouse gas emissions.

EXPERIMENTAL

Catalyst preparation: The support γ -Al₂O₃ pellets was crushed and sieved to 0.2-0.35 mm (40-60 mesh) particle size fraction. Prior to adding nitrate, the γ -Al₂O₃ support was

calcined in air at 700 °C for 5 h in order to stabilize the surface area. Aqueous solution of nickel nitrate, cobalt nitrate and cerium nitrate (> 99 % purity) were prepared and then impregnated on γ -Al₂O₃ by wetness impregnation. After impregnation, the solution was stirred and then placed at room temperature for 24 h, thereafter dried in an oven at 120 °C overnight and calcined at 500 °C for 6 h in the muffle furnace at a rate of 10 °C/min. The loading of NiO of Co-Ni bimetallic catalyst was immobility about 5 %. The catalysts were prepared with various cobalt loadings but only the samples with 5, 10 and 15 wt. % cobalt were characterized in detail. K⁺ modified Co-Ni bimetallic catalyst was obtained by adding desired amount of potassium nitrate into the mixture solution of nickel nitrate and cobalt nitrate before drying in oven.

XRD: X-ray diffraction (XRD) measurements are performed on the catalysts using the monochromic CuK α radiation of a Bruker AXS D8 focus diffractometer instrument at 40 kV and 30 mA. The XRD patterns are recorded for 2 θ = 10-80° with a step width of 0.01 degree at a rate of 1.25°/min.

BET: The textural characteristics of the supports and catalysts were analyzed by N₂ physisorption method. N₂ adsorption and desorption isotherms were performed at 77 K on micromeritics ASAP2020C equipment. The samples were outgassed for 5 h before the measurement under vacuum (\approx 1 μ m Hg) and temperature (573 K). The pore diameter and pore volume were calculated from the analysis of desorption branch of the isotherm by the BJH method.

Temperature programmed reduction: Temperature programmed reduction (TPR) measurements were performed with a Chemisorb2750 instrument. The catalyst samples (about 100 mg) were purged with argon at 150 °C for 0.5 h and cooled to 20 °C, then heated to 840 °C at a rate of 10 °C min⁻¹ while flowing a 5 vol % H₂/Ar (50 cm³ min⁻¹) through the sample. The consumption of hydrogen was monitored by a thermal conductivity detector (TCD).

Thermogravimetric analysis: Deposited coke was measured by temperature programmed combustion, performed on a thermogravimetric TGA/SDTA851 device. The used catalysts were dried at 120 °C for 12 h. Analysis of coke deposits on used catalysts was performed by a thermogravimetric technique. The spent catalyst (10 mg) previously heated to 450 °C for 1 h in N₂ (100 mL/min flowing-rate) in order to remove the volatile compounds. Once the sample had been cooled to 295 °C, a 20 % O₂/N₂ gas mixture (65 mL/min) was introduced into the analysis vessel and the coke was burnt in a Mettler Toledo TGA/SDTA 851 instrument. The temperature ramp of 10 °C/min was applied, heated to 850 °C and the catalyst weight loss as a function of temperature was registered.

Gas products analysis: The gas products were on line analyzed by using SP6800 GC from Shandong, China. GC equipped with a thermal conductivity detector (TCD) and carbon molecular sieve column TDX-01 (2 m, 2 mm), were used to analyze the contents of CO and CO₂ of the different reaction with a constant temperature of column 190 °C, current 110 mA and detector 160 °C, respectively.

Liquid products FT-IR analysis: 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.

Liquid products GC-MS analysis: GC-MS analysis using an Agilent 7890A GC (HP-5 column, 30 m \times 0.25 mm \times 0.25 μ m) coupled to an Agilent 5975C Inert MSD with a quadruplicate axis detector. Liquid products were dried for decrease water with dried Na₂SO₄. Liquid products were diluted 1:1 in cyclohexane and 0.2 μ L of the diluted sample was injected onto a HP-5 column. Helium was used as the carrier gas with velocity rate of 53.4 mL/min and split ratio was 50:1. Oven temperature was programmed from an initial temperature of 70 °C followed by a 10 °C/min to a final temperature of 280 °C, the following chromatographic temperature program was used for analysis: 150 °C (constant 5 min) - 180 °C (constant 5 min) - 250 °C (constant 3 min) - 280 °C (5 °C/min, constant 20 min). After a solvent delay of 3 min, full scan mass spectra were obtained. 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 (GC-MS).

Trace water content measurement of liquid products: Karl-Fisher coulometric titration method has been adopted to conduct trace water content measurement to different substances. SF-3 (made in Zibo Instrument Co., Ltd, China) trace water content meter has successfully adopted this method.

Experimental setup and procedure: The experiments of conversion of triglycerides to biofuels were performed in an electrically heated fixed bed tubular reactor (reactor dimension: length, 300 mm, internal diameter, 4.4 mm). The simple device chart can be seen in Fig. 1. The catalysts were placed between a layer of quartz sand and quartz wool and thermocouple was placed inside the reactor body. A layer of the inert quartz sand was placed above the catalyst bed to preheat triglycerides and hydrogen. While the oil is pumped independently through the catalyst bed with various volumetric velocity. The velocity of H₂ was controlled by mass flowmeter. These two streams are mixed in the reactor. All kinds of factor were respectively investigated from reaction temperature, the oil flow rate and the gas flow rate.

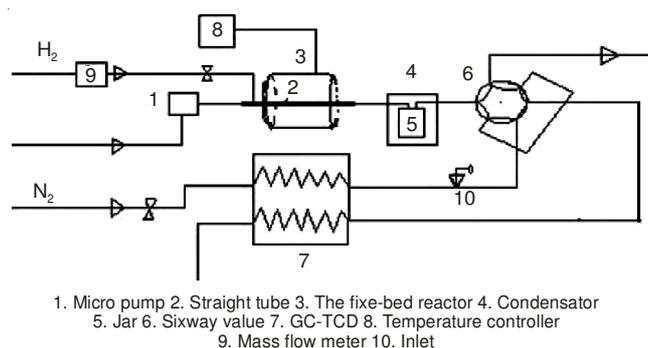


Fig. 1. Simple patterns of the reaction device

RESULTS AND DISCUSSION

X-ray powder diffraction: The XRD result is shown in Fig. 2. As can be seen from Fig. 2, Ni20 exhibited peaks of NiAl₂O₄ at 44° and 62°, as well as peaks of γ -Al₂O₃ at 17°, 25.45°, 37°, 43.39° and 67° 5. There were no obvious peaks relating to cobalt oxide and nickel oxide, indicating highly dispersed in the support or cobalt and nickel interacted with the support.

As cobalt content or the total content of cobalt and nickel were increased, new peaks at 44.9°, 57.57° and 67° appeared for the catalysts of Ni20,10Co5Ni, 15Co5Ni and Co20 are agree very well with the mixed phase of NiAl₂O₄ and CoAl₂O₄ can be formed⁵. This interacted result means the bimetallic CoNi/Al₂O₃ catalysts can enhance the effect of decarboxylation and decarbonylation of triglycerides, which has been shown to perform better than the Ni or Co catalyst alone.

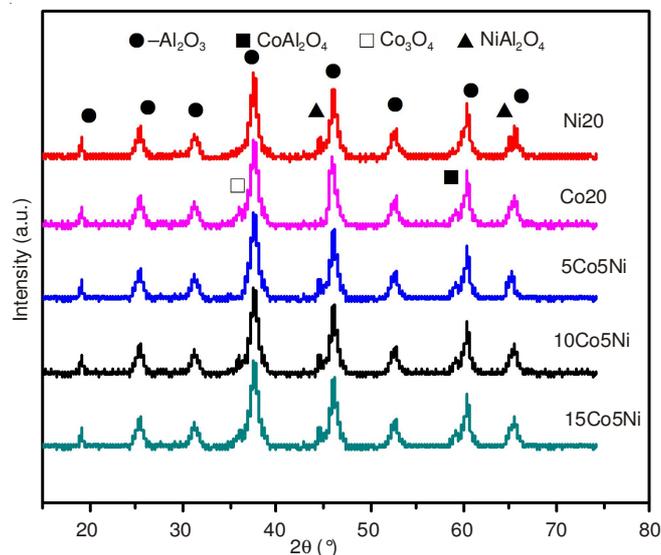


Fig. 2. XRD patterns of all kinds of the reaction catalyst

Temperature programmed reduction: The result is shown in Fig. 3. It can be found from Fig. 3 that for the Ni20 catalyst, the reduction temperature of 358 °C is likely attributed to reduction of Ni²⁺ in the NiO phase and the second peak of 437 °C may be associated with the reduction of Ni²⁺ in NiAl₂O₄. For the Co20, 5Co5Ni and 10Co5Ni catalyst, the only reduction temperature of 370 °C is likely attributed to reduction of Co₃O₄, with subsequent reduction of CoO to Co. However, bimetallic 15Co5Ni catalyst presents two reduction peaks at 420 and 650 °C and the lubricity peak at 650 °C-probably implied the reduction of NiAl₂O₄ and CoAl₂O₄ species. Thus,

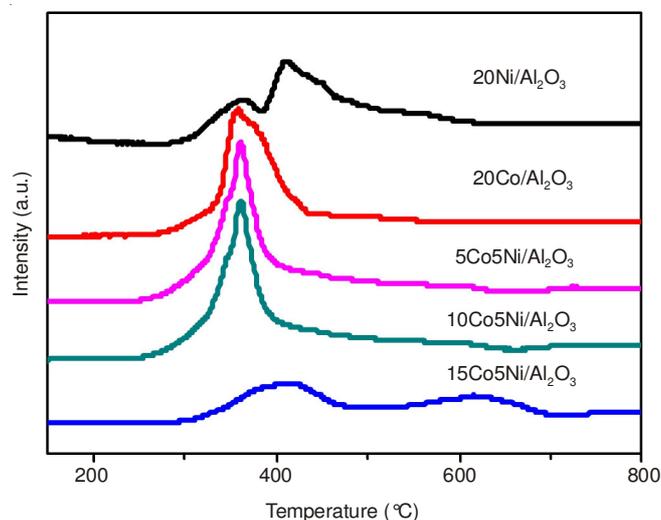


Fig. 3. Temperature programmed reduction patterns of the different catalysts

it implies the synergic effect between nickel and cobalt species was produced during the process of catalyst preparation. The temperature programmed reduction result of bimetallic 15Co5Ni catalyst is agree very well with FT-IR and GC-MS of liquid product.

BET: The results of BET were analyzed on the fresh and used catalysts. It can be seen from Table-1, Figs. 4 and 5 that the stability of the catalyst was excellent. The surface areas and pore volume of the catalyst show no significant difference before and after reaction and are a very slight decrease from 182.97, 165.29, 161.42 to 158.16 m² g⁻¹, 0.3434, 0.3015, 0.3043 to 0.3052 cm³ g⁻¹, respectively. Therefore, the capability of 15Co5Ni catalysts is very stable and the reproducible. The catalyst deactivation was due to coke deposition, relatively to sintering.

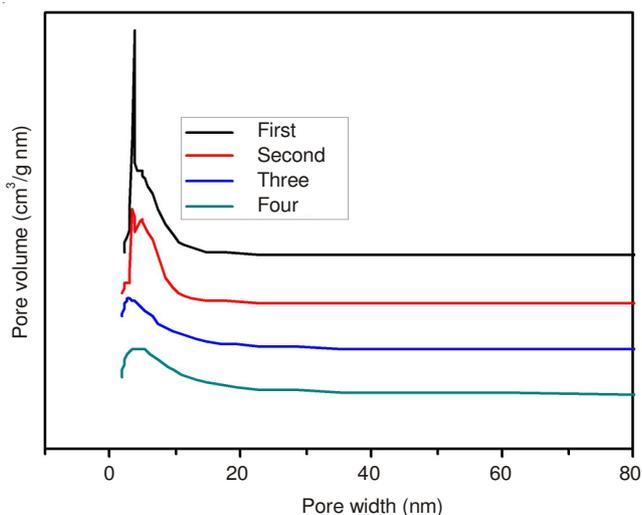


Fig. 4. Pore width and pore volume patterns of the fresh catalyst

Selection of the catalyst: The capability of five catalyst were performed in an electrically heated fixed bed tubular reactor at reaction temperatures, the oil flow rate and the carrier gas flow rate, 450 °C, 0.1 and 10 mL/min, respectively. The gas-phase product is most consisted of CO and CO₂. The gas product was on line analyzed by using SP6800 GC. The raw oil and the liquid products were characterized by FT-IR, SF-3 and GC-MS. Each FT-IR spectrum was normalized by the intensity of the absorption band centered at 2930 cm⁻¹ (the strongest band). The C=O band stretch is observed in the range 1800-1600 cm⁻¹. It can be found from Fig. 6, the carbonyl absorption peak of 1750 cm⁻¹ is not exist in the different liquid product compared to the raw oil, but the carbonyl absorption peak at 1705-1720 cm⁻¹ exists. This shows that the product

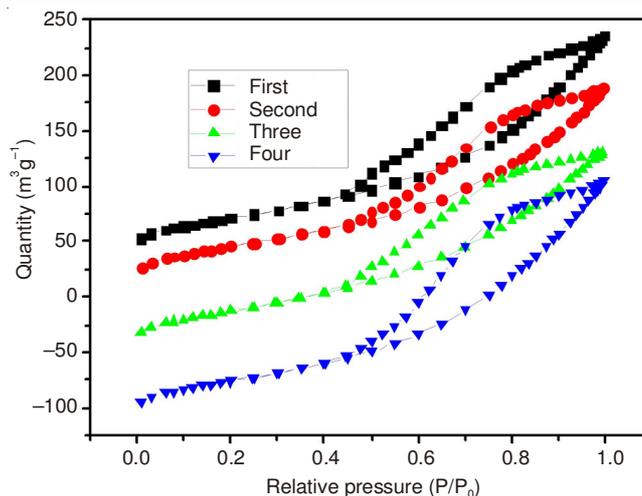


Fig. 5. BET patterns of the fresh and used catalyst

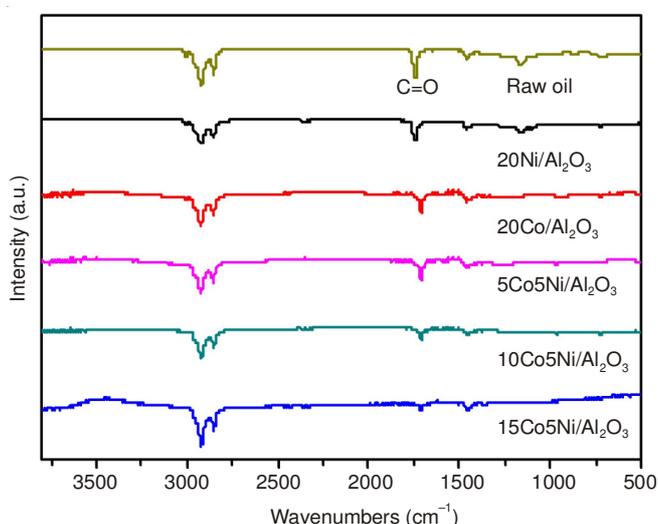


Fig. 6. FT-IR spectra of the different liquid products over the different catalysts

have small amount of ketone derivatives containing oxygen. The peak intensity of C=O reduced as follow the order 15Co5Ni > 10Co5Ni > Co20 > 5Co5Ni > Ni20. The liquid product of Co20, 5Co5Ni and Ni20 have the higher content of oxygenates compound compared to the product of 15Co5Ni. The gaseous, oxygenates, coke deposition and liquid hydrocarbons of products were described in Table-2. As Table-2 displays, 15Co5Ni catalyst has the best capability in catalytic deoxygenation. Oxygenates product, liquid hydrocarbons, H₂O content and coke deposition of 15Co5Ni catalyst are 3.36, 93.46, 0.063 and 2.20 %, respectively. Oxygenates product content of Ni20 catalyst and Co20 catalyst are 16.05 and

TABLE-1
BET PARAMETER OF THE FRESH AND USED CATALYST

	First	Second	Three	Four
BET Surface area (m ² /g)	182.97	165.29	161.42	158.16
Single point adsorption total pore volume of pores (cm ³ /g)	0.3177	0.2766	0.2851	0.3012
BJH Adsorption cumulative volume of pores (cm ³ /g)	0.3443	0.3015	0.3043	0.3052
BJH Desorption cumulative volume of pores (cm ³ /g)	0.3402	0.2982	0.3009	0.3486
Adsorption average pore width (nm)	6.9455	6.6933	6.7113	7.3356
BJH Adsorption average pore diameter (nm)	7.1115	6.6662	6.2453	7.0062
BJH Desorption average pore diameter (nm)	5.6161	5.5429	5.07886	5.4359

TABLE-2
ANALYSIS RESULT OF CONVERSION OF TRIGLYCERIDES TO BIO FUELS IN DIFFERENT CATALYSTS

	Ni20	Co5Ni5	Co10Ni5	Co20	Co15Ni5
Liquid yield (%)	83.2	83.11	83.2	83.59	85.64
Gas yield (%)	12.21	12.31	12.24	11.85	12.1
H ₂ O (%)	0.082	0.070	0.068	0.067	0.063
Coke yield (%)	4.51	4.51	4.49	4.49	2.2
Composition of the liquid product					
Cyclic compounds	3.91	7.65	6.69	8.54	1.44
Alkanes	37.43	39.84	40.25	39.4	44.57
Alkenes	41.53	40.24	42.35	40.49	48.89
Oxygenates	16.05	10.86	10.6	11.45	3.36
C ₈ -C ₁₀ (wt %)	11.37	10.26	10.32	10.98	5.48
C ₁₁ -C ₁₈ (wt %)	77.48	81.08	82.06	80.46	82.39
C ₁₈ ⁺ (wt %)	9.97	8.13	7.36	8.28	11.71
	98.82	99.47	99.74	99.72	99.58

11.45 %, Oxygenates product content of 5Co5Ni catalyst and 10Co5Ni catalyst are 10.86 and 10.60 %. Therefore, 15Co5Ni exhibit the highest catalytic performance for deoxygenation amongst the five catalysts. The FT-IR results are in good agreement with the GC-MS analysis. Thus, it implies the synergic effect between nickel and cobalt species was produced during the process of catalyst preparation. The temperature programmed reduction result of bimetallic 15Co5Ni catalyst agrees very well with FT-IR and GC-MS of liquid product. The components were classified into five portions: carbonyl compounds, alkanes, alkenes, cyclic compounds and some alcohols. Peak assignment was done by comparison with the NIST08. L database with more than 95 % similarity.

Selection of the optimized condition on the 15Co5Ni/ γ -Al₂O₃ catalyst: Biofuels production was carried out in an electrically heated fixed bed tubular reactor with 15Co5Ni/ γ -Al₂O₃ catalyst.

Effect of different reaction temperature to conversion of triglycerides to biofuels: The experiments of several different reaction temperatures were performed at 480, 450, 420, 390 and 360 °C, respectively. The products of five different reaction temperatures were obtained in an electrically heated fixed bed tubular reactor at raw oils flow rate and the carrier gas flow rate 0.1 and 10 mL/min, respectively. The products in all sorts of various different reaction temperatures were marked as H561, H531, H562, H563 and H564, respectively and in order. Liquid yield, gaseous products, H₂O

content, coke deposition and distribution of liquid hydrocarbons were described as shown in Table-3. As Table-3 display, reaction temperatures decreased, from 480, 450, 420, 390 and 360 °C. Liquid yield was, respectively obtained from 85.45, 85.64, 86.92, 87.01 and 87.82 %; H₂O content, respectively was obtained from 0.073, 0.063, 0.089, 0.102 and 0.116 %; Coke deposition rate changed from 3.17, 2.20, 2.82, 3.18 % and 3.23, oxygenates content changed from 1.18, 3.36, 5.98, 7.66 and 9.87 %. Liquid yield of the products of five different reaction temperatures have tiny aggrandizement. Coke deposition of different reaction temperatures increase more than 1.5 times, H₂O content increase about 2 times, Oxygenates content increase more than four times, which shows that reaction temperatures is a very important factor to deoxygenation of triglycerides to biofuels product from coke deposition, oxygenates content and H₂O content. Gaseous products, cyclic compounds and short chain liquid hydrocarbons were increased in reaction products with increasing temperature.

The gas products were on line analyzed by using SP6800 GC. Reaction gas are collected and analyzed after 0.5 h by GC online in order. The molar ratio of CO₂ and CO is in Fig. 7 under various temperatures conditions. The result of GC online, GC-MS and SF-3 show that the most oxygen in the triglycerides of vegetable oils was released in the forms of CO and CO₂, with a minimal amount of H₂O. The result of GC online shows that the oxygen in the oils are mainly removed-through

TABLE-3
ANALYSIS RESULT OF CONVERSION OF TRIGLYCERIDES TO BIOFUELS IN DIFFERENT REACTION TEMPERATURES

	H561	H531	H562	H563	H564
Liquid yield (%)	85.45	85.64	86.92	87.01	87.82
Gas (%)	11.31	12.1	10.17	9.71	8.83
H ₂ O (%)	0.071	0.063	0.089	0.102	0.116
Coke yield (%)	3.17	2.2	2.82	3.18	3.23
Composition of the liquid product					
Cyclic compounds	5.23	1.44	2.43	3.86	3.58
Alkanes	44.88	44.57	43.93	40.93	40.13
Alkenes	48.21	48.89	46.87	46.87	46.38
Oxygenates	1.18	3.36	5.98	7.66	9.87
C ₈ -C ₁₀ (wt %)	7.88	5.48	5.36	5.24	4.62
C ₁₁ -C ₁₈ (wt %)	80.01	82.39	80.27	78.93	78.59
C ₁₈ ⁺ (wt %)	12.02	11.71	13.97	15.34	16.58
Total (%)	99.91	99.58	99.6	99.51	99.79

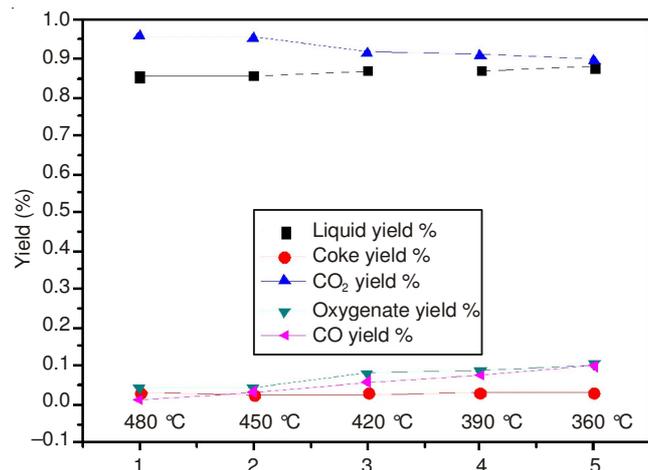


Fig. 7. Patterns of the products of different reaction temperature to conversion of triglycerides to biofuels

decarboxylation and decarbonylation are the main reactions of catalytic reaction.

From FT-IR spectra, the carbonyl absorption peak of C=O band and C-O band are change from 1720-1705 cm^{-1} migration to 1750-1740 cm^{-1} because of the oxygen that a electronic groups exist and through the interaction of thermal and catalytic cracking, the intensity of the C=O band stretch is almost disappeared compared with FT-IR graph of the raw materials when the reaction temperature to 420 °C (H562), 450 °C (H531) and 480 °C (H561) as shown in Fig. 8, but the carbonyl absorption peak at 1720-1705 cm^{-1} exists and intensity of the absorption peak is weak. This shows that the product have small amount of ketone derivatives containing oxygen and the results are consistent with the GC-MS data analysis.

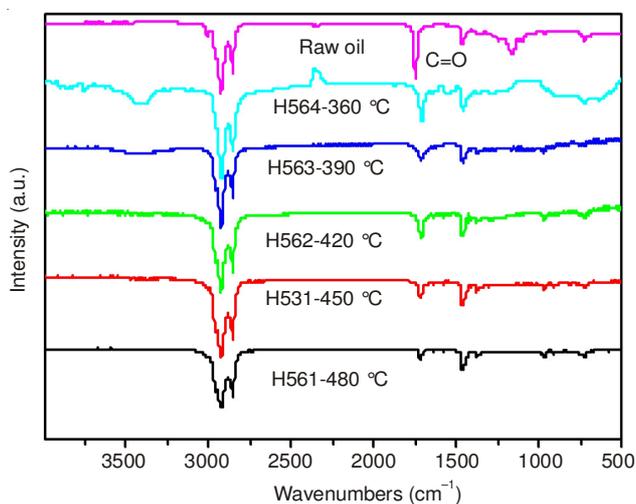


Fig. 8. FT-IR spectra of the different liquid products over the 15Co5Ni catalyst at different reaction temperatures

The intensity of the absorption peak in the area of 1750-1740 cm^{-1} is strong and the intensity of the absorption peak in the area of 3340-3320 is weak in the products of H564 (360 °C) and H563 (390 °C). This shows that the product have large amount of ketone and small amount fatty acids derivatives containing oxygen. The results are consistent with the GC-MS data analysis, which shows that reaction temperatures is a very important factor to deoxygenation of triglycerides to biofuels.

According to the data of GC-MS, as Table-3 display, reaction temperatures decreased, from 480, 450, 420, 390 and 360 °C, respectively. The oxygenate content changed from 1.18, 3.36, 5.98, 7.66 and 9.87 %. The alkanes content of liquid products changed from 44.88, 44.57, 43.93, 40.93 and 40.01 %. The alkenes content of liquid products changed from 48.21, 48.89, 46.87, 46.87 and 46.38 %. Total content of alkanes and alkenes is high in the product of H561 and H531 and the product is mostly under C₁₈ hydrocarbon compounds.

Moreover, the total content of alkanes and alkenes is low in the product of H562, H563 and H564 compare to the product of H561 and H531, the content of oxygenate compound are high compare to the product of H561 and H531, the product of H562, H563 and H564 is easy to deterioration, not easy to preserve and poor liquidity. The effect of thermal cracking and catalytic cracking will be decrease because of drop in temperature, the result of decarboxylation and decarbonylation reaction are not good and the product of H562, H563 and H564 have higher coke deposition, the higher content of oxygenates compound.

Despite of product of H561 has the higher than the product of H531 in the content of alkanes, the product of H561 has the lower than the product of H531 about the total content of alkanes and alkenes. The product liquid yield of H561 (480 °C) has the lower than the product liquid yield of H531 (450 °C). The product coke deposition of H561 has the higher than the product coke deposition of H531. Technology of H561 (480 °C) is not better than craftwork of H531 from the total content of alkanes and alkenes, coke deposition, economic benefits and liquid products yield.

Effect of different reaction gas flow rate to conversion of triglycerides to biofuels: The tests of several carrier gas flow rate were performed at gas flow rate from 18, 15, 12, 10 and 8 mL/min, respectively. The products of five various carrier gas flow rate were obtained in an electrically heated fixed bed tubular reactor at reaction temperatures and the oil flow rate, 450 °C and 0.10 mL/min, respectively. The products in all sorts of various conditions were marked as H554, H553, H552, H531 and H551, respectively and in order. Liquid yield, gaseous products, H₂O content, coke deposition and distribution of liquid hydrocarbons were described as shown in Table-4. As Table-4 display, Gas flow rate declined from 18, 15, 12, 10 and 8 mL/min, liquid yield, respectively obtained from 86.21, 86.04, 85.99, 85.64 to 85.53 %; H₂O content respectively was obtained from 0.061, 0.059, 0.057, 0.063 and 0.056 %. Coke deposition rate changed from 2.71, 2.35, 2.23, 2.20 change to 2.21 %, the change of liquid yield, H₂O content and coke deposition rate are not large. Furthermore, oxygenated compounds content changed from 5.03, 4.56, 3.34, 3.36 change to 5.42 %, which shows that gas velocity is a secondary factor to conversion of triglycerides to biofuels.

The FT-IR spectra of the liquid phase samples were recorded by a Nicolet 570027 infrared spectrophotometer. From FT-IR spectra Fig. 9, the carbonyl absorption peak of C=O band and C-O band are change from 1720-1705 cm^{-1} migration to 1750-1740 cm^{-1} because of the oxygen that electronic groups exist and through the interaction of thermal and catalytic cracking, as shown in Fig. 9, the intensity of the C=O band stretch is almost disappeared compared with FT-IR

graph of the raw materials in the reaction temperature 450 °C, but the carbonyl absorption peak of 1705-1720 cm⁻¹ is exist and intensity of the absorption peak is weak. This shows that the product have small amount of ketone derivatives containing oxygen. The results are consistent with the GC-MS data analysis. The content of oxygenated compound is under 5.42 %, which shows that gas velocity is a secondary factor relative to the reaction temperature.

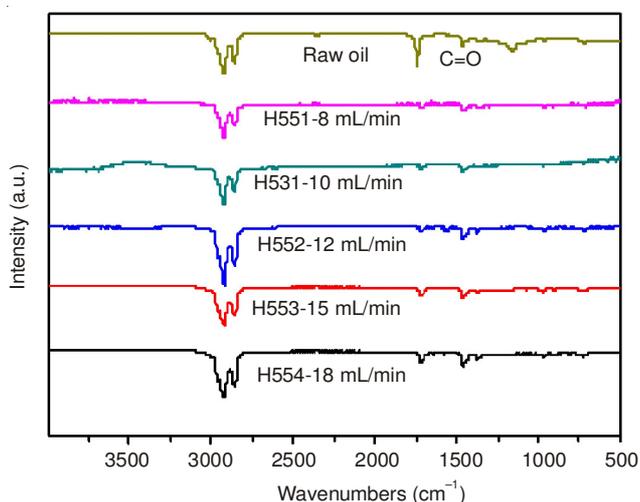


Fig. 9. FT-IR spectra of the different liquid products over the 15Co5Ni catalyst at the different gas flow rate

The gas products were on line analyzed by using SP6800 GC. Reaction gas are collected and analyzed after 0.5 h by GC online in order. The tests of several carrier gas flow rate were performed at gas flow rate from 18, 15, 12, 10 and 8 mL/min, respectively. The molar ratio of CO₂ and CO are change from 95.41, 95.52, 95.54, 95.55 and 95.62 %, respectively and 4.59, 4.48, 4.46, 4.45 and 4.38 %, respectively. The result of GC online shows that the oxygen in the oils are mainly removed through decarboxylation and decarbonylation are the main reactions of catalytic reaction. The molar ratio of CO₂ and CO, liquid yield, H₂O content and Coke deposition rate are listed in Fig. 10 under various gas flow rate conditions.

The results of GC and GC-MS show the most of the oxygen in the triglycerides of vegetable oils was released in the forms of CO and CO₂, with a minimal amount of H₂O.

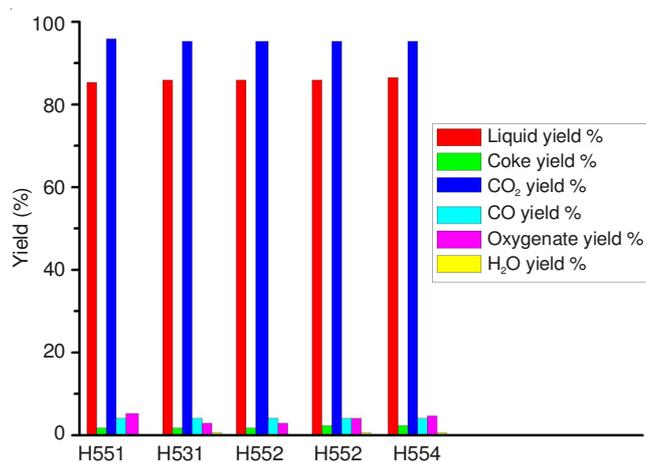


Fig. 10. Patterns of the products of different reaction gas flow rate to conversion of triglycerides to biofuels

Table-4 displays, the product of H552 (12 mL/min) which is higher than the product of H531, H551, H553 and H554 in the content of alkanes and alkenes and the product of H552 has the lower in the content of oxygenated compounds. The technology of H552 (12 mL/min) is better than other craftwork from the total content of alkanes and alkenes, the content of oxygenates compound and distribution of liquid C₁₈ hydrocarbons.

Effect of different reaction oil flow rate to conversion of triglycerides to biofuels: The tests of several oil flow rate were performed at oil flow rate from 0.08, 0.10, 0.12, 0.15, 0.18 and 0.20 mL/min, respectively. The products of six various oil flow rate were obtained in an electrically heated fixed bed tubular reactor at reaction temperatures and the reaction gas flow rate, 450 °C and 10 mL/min, respectively. The products in all sorts of several conditions were marked as H541, H531, H543, H544, H545 and H546, respectively and in order. Liquid yield, gaseous products, H₂O content, coke deposition and distribution of liquid hydrocarbons were described as shown in Table-5. As Table-5 displays the oil flow rate increased from 0.08, 0.10, 0.12, 0.15, 0.18 and 0.20 mL/min, respectively, liquid yield was, respectively obtained from 85.62, 85.64, 85.98, 86.15, 86.50 to 86.53 %; H₂O content, respectively was obtained from 0.062, 0.063, 0.078, 0.082, 0.087 and 0.097 %; Coke deposition rate changed from 2.21, 2.20,

TABLE-4
ANALYSIS RESULT OF CONVERSION OF TRIGLYCERIDES TO BIO FUELS IN DIFFERENT GAS FLOW RATE

	H551	H531	H552	H553	H554
Liquid yield (%)	85.53	85.64	85.99	86.04	86.21
Gas (%)	12.2	12.1	11.72	11.55	11.02
H ₂ O (%)	0.056	0.063	0.057	0.059	0.061
Coke yield (%)	2.21	2.2	2.23	2.35	2.71
Composition of the liquid product					
Cyclic compounds	4.45	1.44	1.43	1.89	3.23
Alkanes	41.26	44.57	44.62	43.25	42.86
Alkenes	46.85	48.89	49.12	49.38	48.25
Oxygenates	5.42	3.36	3.34	4.56	5.03
C ₈ -C ₁₀ (wt %)	6.23	5.48	5.89	4.38	4.27
C ₁₁ -C ₁₈ (wt %)	78.65	82.39	82.45	80.12	79.87
C ₁₈ ⁺ (wt %)	13.23	11.71	11.41	14.23	14.64
Total (%)	98.11	99.58	99.75	98.73	98.78

2.22, 2.35 and 2.71 % change to 3.19 %, the change of liquid yield is increased very less, H₂O content and coke deposition rate are large augment. Furthermore, oxygenated compounds content changed two times from 3.18, 3.36, 3.88, 5.27, 6.87 % change to 7.23 %, which shows that oil velocity is an important factor to deoxygenation conversion of triglycerides to biofuels.

From FT-IR spectra, the carbonyl absorption peak of C=O band and C-O band are change from 1720-1705 cm⁻¹ migration to 1750-1740 cm⁻¹ because of the oxygen exist. Through the interaction of thermal and catalytic cracking, as shown in Fig. 11, the peaks intensity of C=O in the liquid product of H545 and H546 in comparison with raw oils is still strong about 1750-1740 cm⁻¹. The peak intensity of C=O almost disappear in the 0.1 and 0.08 mL/min oils velocity, which show that the product have small amount of ketone derivatives containing oxygen, the deoxygenation efficiency of raw oils was reduced with increasing the oils flow rate from 0.08 to 0.2 mL/min. The results are consistent with the GC-MS data analysis. According to the data of GC-MS, as Table-5 displays, oxygenated content of different liquid products changed from 3.18, 3.36, 3.88, 5.27, 6.87 change to 7.23 %, alkanes content of liquid products changed from 41.88, 44.57, 43.23, 42.12, 40.18 to 39.15 %, alkenes content of liquid products changed from 49.12, 48.89, 48.87, 48.76, 48.38 to 49.15 %. The content of alkanes and alkenes in the H531 is 93.46 % and the product is mostly under C₁₈ hydrocarbon compounds. The technology of H531 is better than craftwork of H541 from the LHSV, oxygenated content, coke deposition rate and economic benefits. the results are consistent with the GC-MS data analysis.

The gas products were analyzed on line by using SP6800 GC. Reaction gas are collected and analyzed after 0.5 h by GC online in order. The tests of several carrier gas flow rate were performed at gas flow rate from 0.08, 0.1, 0.12, 0.15, 0.18 and 0.20 mL/min, respectively. The molar ratio of CO₂ and CO changed from 95.65, 96.55, 95.44, 95.15, 95.11 and 94.88 %, respectively and 4.35, 4.45, 4.56, 4.85, 4.89 and 5.12 %, respectively. The molar ratio of CO₂ and CO, liquid yield, H₂O content and coke deposition rate are listed in Fig. 12 under various oil flow rate conditions.

The result of GC-MS and GC online shows that the oxygen in the oils are mainly removed through decarboxylation and decarbonylation are the main reactions of catalytic reaction, with a minimal amount of H₂O.

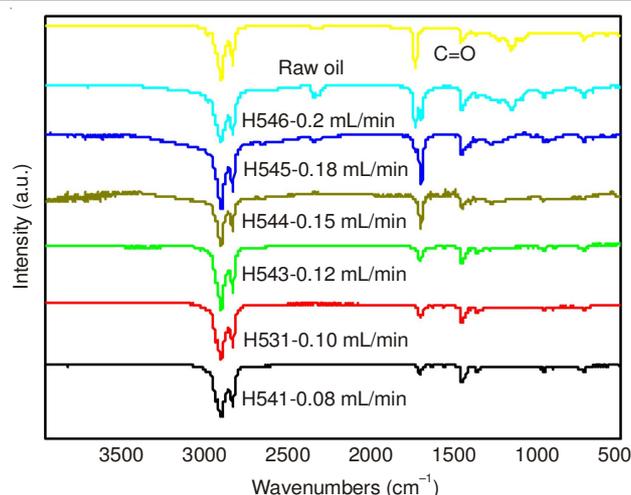


Fig. 11. FT-IR spectra of the different liquid products over the 15Co5Ni catalyst at the different oil flow rate

Conversion of triglycerides to biofuels in optimized conditions: The technology was optimized at reaction temperature, the oil flow rate to the gas flow rate, 450 °C, 0.1 and 12 mL/min, respectively. The liquid products in optimized conditions were marked as H566. The liquid products were analyzed by FT-IR, GC-MS and SF-3, the gas product was on line analyzed by using SP6800 GC. The GC-MS distribution of liquid hydrocarbons was described as shown in Table-6. The yield of CO₂ is 95.66 % and the yield of CO is 4.34 %. The result of GC online that the reaction of decarboxylation and decarbonylation occurred at the same time and decarboxylation reaction was the main reaction. The gas yield and liquid yield of liquid products is 12.03 and 85.78 wt. %, H₂O content, oxygenated product content and coke deposition of liquid products is 0.061, 3.26 and 2.13 wt. %, the alkanes content and alkenes content of liquid products is 44.86 and 49.08 %, respectively under the optimized condition. The compound distribution in the liquid product is mostly under C₁₈ hydrocarbon compounds.

Stability and deactivity of catalyst: The stability of 15Co5Ni catalyst was performed in an electrically heated fixed bed tubular at reaction temperature, the oil flow rate and the gas flow rate 450 °C, 0.1 and 12 mL/min, respectively. The used catalysts were calcined to remove any carbon residue at

TABLE-5
ANALYSIS RESULT OF CONVERSION OF TRIGLYCERIDES TO BIO FUELS IN DIFFERENT OIL FLOW RATE

	H541	H531	H543	H544	H545	H546
Liquid yield (%)	85.62	85.64	85.98	86.15	86.5	86.53
Gas (%)	12.1	12.1	11.72	11.42	10.7	10.18
H ₂ O (%)	0.062	0.063	0.078	0.082	0.087	0.097
Coke yield (%)	2.21	2.2	2.22	2.35	2.71	3.19
Composition of the liquid product						
Cyclic compounds	3.83	1.44	2.13	2.87	3.28	3.87
Alkanes	41.88	44.57	43.23	42.12	40.18	39.15
Alkenes	49.21	48.89	48.87	48.76	48.38	49.15
Oxygenates	3.18	3.36	3.88	5.27	6.87	7.23
C ₉ -C ₁₀ (wt %)	7.56	5.48	6.36	6.54	7.62	6.85
C ₁₁ -C ₁₈ (wt %)	79.55	82.39	81.27	79.88	76.59	76.26
C ₁₈ ⁺ (wt %)	12.28	11.71	11.89	13.38	15.58	15.82
Total (%)	99.39	99.58	99.52	99.8	99.79	98.93

TABLE-6
GC-MS ANALYSIS RESULT OF CONVERSION OF TRIGLYCERIDES
TO BIO FUELS IN THE OPTIMIZED TECHNOLOGY CONDITION

No.	RT	Area (%)	Molecular formula	Chemical name
1	3.298	0.17	C ₈ H ₁₀	Ethylbenzene
2	3.39	0.14	C ₈ H ₁₀	<i>p</i> -Xylene
3	3.699	1.87	C ₉ H ₂₀	Nonane
4	3.779	0.21	C ₉ H ₁₈	2-Nonene, (E)-
5	4.214	0.16	C ₉ H ₁₈	Cyclopentane, butyl-
6	4.529	0.3	C ₉ H ₁₈	2-Nonene, (E)-
7	5.152	1.73	C ₁₀ H ₂₂	Decane
8	5.747	0.45	C ₁₀ H ₂₀	Cyclopentane, pentyl-
9	6.085	0.66	C ₁₀ H ₂₀	4-Decene, (E)-
10	6.6	1.0	C ₁₁ H ₂₂	5-Undecene, (E)-
11	6.703	2.06	C ₁₁ H ₂₄	Undecane
12	6.777	1.98	C ₁₁ H ₂₂	4-Undecene, (E)-
13	8.053	0.19	C ₁₂ H ₂₄	3-Dodecene, (Z)-
14	8.122	0.87	C ₁₂ H ₂₄	4-Dodecene
15	8.214	1.82	C ₁₂ H ₂₆	Dodecane
16	8.288	1.68	C ₁₂ H ₂₄	6-Dodecene, (E)-
17	9.53	0.5	C ₁₃ H ₂₆	1-Tridecene
18	9.587	0.39	C ₁₃ H ₂₆	3-Tridecene, (E)-
19	9.644	1.54	C ₁₃ H ₂₈	Tridecane
20	9.713	0.3	C ₁₃ H ₂₆	2-Tridecene, (E)-
21	10.302	1.07	C ₁₃ H ₂₆	6-Tridecene, (Z)-
22	10.834	0.18	C ₁₄ H ₂₈	7-Tetradecene, (E)-
23	10.874	0.26	C ₁₄ H ₂₈	1-Tetradecene
24	10.989	3.12	C ₁₄ H ₃₀	Tetradecane
25	11.91	1.86	C ₁₅ H ₃₀	1-Pentadecene
26	12.213	0.36	C ₁₅ H ₃₀	Cyclopentadecane
27	12.265	5.73	C ₁₅ H ₃₂	Pentadecane
28	13.06	0.31	C ₁₅ H ₃₀	<i>n</i> -Nonylcyclohexane
29	13.123	0.21	C ₁₅ H ₂₈	Cyclohexene, 1-nonyl-
30	13.232	0.55	C ₁₆ H ₃₂	3-Hexadecene, (Z)-
31	13.289	1.45	C ₁₆ H ₃₂	1-Hexadecene
32	13.375	0.84	C ₁₆ H ₃₂	Z-8-Hexadecene
33	13.461	3.07	C ₁₆ H ₃₄	Hexadecane
34	13.569	0.16	C ₁₆ H ₂₆	Benzene, (1-methylnonyl)-
35	13.638	0.41	C ₁₆ H ₃₂	5-Hexadecene, (E)-
36	13.97	0.44	C ₁₇ H ₃₆	Hexadecane, 7-methyl-
37	14.164	2.77	C ₁₇ H ₃₄	1-Heptadecene
38	14.296	0.6	C ₁₇ H ₃₄	3-Heptadecene, (Z)-
39	14.428	19.24	C ₁₇ H ₃₄	8-Heptadecene
40	14.542	0.85	C ₁₇ H ₃₄	2-Methyl-E-7-hexadecene
41	14.622	12.29	C ₁₇ H ₃₆	Heptadecane
42	14.771	1.83	C ₁₇ H ₃₄	3-Heptadecene, (E)-
43	15.057	1.19	C ₁₇ H ₃₆	Hexadecane, 2-methyl-
44	15.297	0.31	C ₁₇ H ₃₄	Cyclohexane, undecyl-
45	15.332	0.69	C ₁₈ H ₃₆	9-Octadecene, (E)-
46	15.429	1.09	C ₁₈ H ₃₆	1-Octadecene
47	15.492	2.28	C ₁₈ H ₃₆	5-Octadecene, (E)-
48	15.669	4.06	C ₁₈ H ₃₈	Octadecane
49	15.847	0.34	C ₁₈ H ₃₆	3-Octadecene, (E)-
50	16.316	0.71	C ₁₉ H ₃₈	1-Nonadecene
51	16.385	0.41	C ₁₉ H ₃₈	5-Nonadecene (E)-
52	16.453	0.66	C ₁₉ H ₃₈	3-Nonadecene (E)-
53	16.516	1.12	C ₁₉ H ₃₈	5-Nonadecene (Z)-
54	16.642	0.31	C ₁₉ H ₃₈	9-Nonadecene (E)-
55	16.688	1.11	C ₁₉ H ₄₀	Nonadecane
56	16.734	1.36	C ₁₇ H ₃₄ O	2-Heptadecanone
57	17.443	1.31	C ₁₇ H ₃₄ O	9-Heptadecanone
58	17.495	0.78	C ₂₀ H ₄₀	1-Eicosene
59	17.661	1.57	C ₂₀ H ₄₂	Eicosane
60	18.399	0.26	C ₂₁ H ₄₂	10-Heneicosene (c,t)
61	18.593	1.31	C ₂₁ H ₄₄	Heneicosane
62	18.668	0.59	C ₁₉ H ₃₈ O	2-Nonadecanone
63	19.492	0.54	C ₂₂ H ₄₆	Docosane
64	20.19	1.49	C ₂₂ H ₄₆	Heneicosane, 9-methyl-
	Total	99.11		

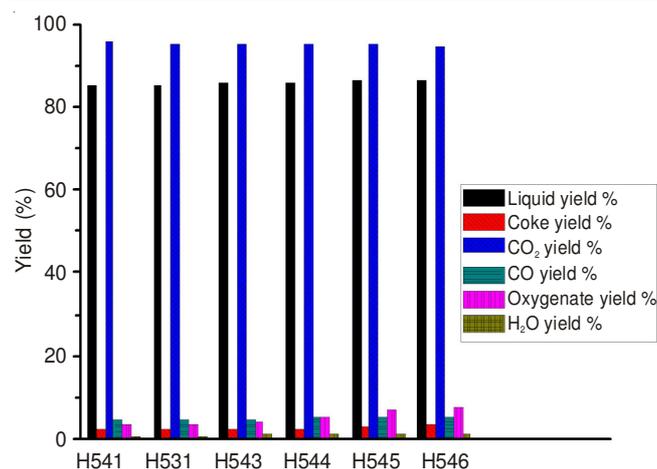


Fig. 12. Patterns of the different products over the 15Co5Ni catalyst at the different oil flow rate

550 °C for 6 h in the muffle stove. The result of liquid hydrocarbon yields, H₂O content, oxygenated product yield and coke deposition can be seen from Table-7. Liquid hydrocarbon yields and H₂O content have little diversification. Liquid hydrocarbon yields are reduced from 85.78, 85.28, 84.88 and 83.96 %. H₂O content, respectively was obtained from 0.061, 0.071, 0.078 and 0.085 %. Meanwhile, oxygenated product yield and coke deposition yield are increased from 3.36, 7.74, 11.62 to 11.52 %, from 2.20, 2.68, 3.16 to 3.35 %, respectively. The content of oxygenated compounds content changed about four times and coke deposition rate changed about 1.5 times. Nevertheless, the result of GC shows that decarboxylation reaction is main reaction and the decarbonylation reaction is secondary. It agreed very well with the thermodynamics of the decarboxylation reaction is easy in comparison with the decarbonylation reaction⁹. The most oxygen in the triglycerides of vegetable oils was released in the forms of CO₂. The CO₂ yield is reduced from 95.55, 95.15, 94.14 and 93.44 % and CO yield is enhanced from 4.45, 4.85, 5.86 and 6.56 %.

	First	Second	Three	Four
Liquid yield (%)	85.78	85.28	84.88	83.96
Gas yield (%)	12.03	11.97	11.88	12.6
CO yield (%)	4.34	4.85	5.86	6.56
CO ₂ yield (%)	95.66	95.15	94.14	93.44
H ₂ O (%)	0.061	0.071	0.078	0.085
Coke yield (%)	2.13	2.68	3.16	3.35
Composition of the liquid product				
Cyclic compounds	1.44	2.38	4.36	5.68
Alkanes	44.86	42.96	41.58	40.86
Alkenes	49.08	46.92	43.44	42.94
Oxygenates	3.26	7.74	11.62	11.52
C ₈ -C ₁₀ (wt. %)	5.69	7.12	7.16	8.07
C ₁₁ -C ₁₈ (wt. %)	82.56	80.16	80.05	78.75
C ₁₈ ⁺ (wt. %)	10.86	11.85	12.23	12.53
Total (%)	99.11	99.13	99.44	99.35

FT-IR spectra of the different times liquid products over the 15Co5Ni catalysts as shown in Fig. 13. The intensity of

the C=O band stretch is weak at the first and the second, but the intensity of the C=O band stretch became little stronger at the three and the four, which show the capability of decarboxylation (-CO₂) and decarbonylation (-CO) became weakened. The selective deoxygenation on the 15Co5Ni catalyst can be done in the many times, the decarboxylation and decarbonylation reaction was fulfilled excellently.

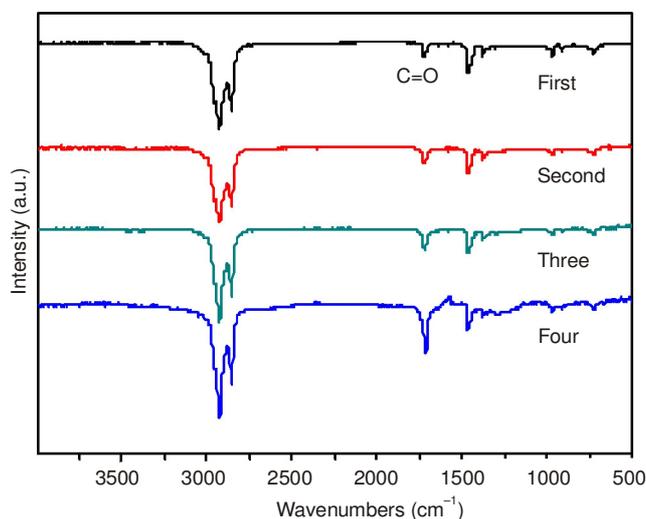


Fig. 13. FT-IR spectra of the different liquid products over the 15Co5Ni catalyst at the different times

The results of BET were analyzed on the fresh and the used catalysts. It can be seen from Table-1 that the stability of the catalyst was excellent. The surface areas and pore volume of the catalyst show no significant difference before and after reaction and are a very slight decrease from 182.97, 165.29, 161.42 to 158.16 m² g⁻¹, 0.3434, 0.3015, 0.3043 to 0.3052 cm³ g⁻¹, respectively. Therefore, the capability of 15Co5Ni catalysts is very stable and the reproducible.

Conclusion

The catalysts by incipient wetness impregnation method were prepared and examined by BET, temperature programmed reduction and TGA analyses. The catalyst has good thermal stability. The catalyst deactivation was due to coke deposition, relatively sintering. The result of FT-IR, GC-MS and GC show reaction temperature played key roles and the rate between nickel and cobalt is important roles in decarboxylation reaction, oils velocity is a very important factor to biofuels product, gas velocity and reaction pressure is a secondary factor to biofuels product. It is optimized at reaction temperature, the oil flow rate, the gas flow rate and the rate between nickel and cobalt, 450 °C, 0.1 and 12 mL/min and 3:1, respectively. The alkanes content and alkenes content of liquid products is 44.86 and 49.08 %, respectively under the optimized condition. The product is mostly under C₁₈ hydrocarbon compounds. The results of GC online and trace water determination that the oxygen in the oils are mainly removed by the reaction of decarboxylation (-CO₂) and decarbonylation (-CO) and decarboxylation reaction was the main reaction, the oxygen in the oils are removed very less through the form of H₂O.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of this study by the Foundation of Educational Department of Jiangxi Province (No.GJJ11276 and No.GJJ11409) and the Important Foundation of Technological Department of Jiangxi Province (No.20111BBF60028).

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