## Converting rubber seed oil into hydrocarbon fuels via supported Pd-catalyst

Chen Yubao<sup>1</sup>, Hao Yajie<sup>1\*</sup>, Zhao Yongyan<sup>1</sup>, Zhou Liming<sup>1</sup>, Yang Shunping<sup>1</sup>, Gao Yanni<sup>1</sup>, Ma Jiangli<sup>2</sup>, Du Junchen<sup>2</sup>, Dona Souliyathai<sup>1</sup>, Zhang Aimin<sup>2</sup>

> (1. The China-Laos Joint Lab for Renewable Energy Utilization and Cooperative Development, Yunnan Normal University, Kunming 650500, Yunnan, China;
> 2. Kunming Institute of Precious Metals, Kunming 650106, Yunnan, China)

**Abstract:** The one-step hydrotreatment of rubber seed oil to produce hydrocarbon fuels has been carried out via supported Pd-catalyst, and analyzed emphatically some elements affected catalytic cracking process, for example, temperature, hydrogen partial pressure and dosage of catalyst, etc. Through experimental research, the author found out the appropriate catalytic cracking conditions as follows: 310°C of reaction temperature, 2 MPa of hydrogen partial pressure, 15 of the ratio of oil to catalyst (m(oil)/m(catalyst)), 100 r/min of stirring speed. Under these conditions, effective component of hydrocarbon fuels in the converted oil accounts for 99.49%, and the proportion of  $C_8$ - $C_{16}$  can reach as high as 79.61%. The converted oil was similar to petroleum-based oil in chemical composition, and can be used for future the aviation biofuels development as the source of raw material because it contains a large amount of hydrocarbon in the range of  $C_8$ - $C_{16}$ .

**Keywords:** rubber tree seed oil, catalytic cracking, Pd based catalyst, hydrocarbon fuels, biofuel, renewable energy **DOI:** 10.25165/j.ijabe.20171006.2742

**Citation:** Chen Y B, Hao Y J, Zhao Y Y, Zhou L M, Yang S P, Gao Y N, et al. Converting rubber seed oil into hydrocarbon fuels via supported Pd-catalyst. Int J Agric & Biol Eng, 2017; 10(6): 201–209.

### 1 Introduction

With the increasing consumption of non-renewable

Received date: 2016-07-29 Accepted date: 2017-04-29 Biographies: Chen Yubao, PhD, Associate Professor, research interests: R&D of biomass energy, Email: c20072007@163.com; Zhao Yongyan, postgraduate student, research interests: R&D of bio-fuel, Email: 642979281@qq.com; Zhou Liming, postgraduate student, research interests: R&D of bio-fuel, Email: zhouliming622 @qq.com; Yang Shunping, postgraduate student, research interests: R&D of bio-fuel, Email: 442723154@qq.com; Gao Yanni, postgraduate student, research interests: R&D of bio-fuel, Email: 240221348@qq.com; Ma Jiangli, Engineer, research interests: catalytic materials, Email: amy.ma@spmcatalyst.com; Du Junchen, Engineer, research interests: catalytic materials, Email: junchen.du@spmcatalyst.com; Dona Soulivathai, postgraduate student, research interests: R&D of bio-fuel, Email: dona\_goodboy@hotmail.com; Zhang Aimin, Professor, research interests: catalytic materials, Email: aimin.zhang@spmcatalyst.com. \*Corresponding author: Hao Yajie, postgraduate student, research interests: R&D of bio-fuel, No.768 Juxian Street, Chenggong District, Kunming 650500, Yunnan, China. Tel: 0086-18487095572, Fax: 0086-871-65940983, Email: 834418734@qq.com.

energy, the rising of the fossil fuels' price and the gradual improvement of environmental regulations, energy shortage, energy conservation and emission reduction have been constraining the economic development. At present, researchers have been paying more attention to the R&D of renewable fuel<sup>[1]</sup>. Biomass resource as the environmental friendly energy which is abundant and renewable, will be an important supplement of fuels in the future and can substitute fossil fuel after the renewable matures<sup>[2]</sup>.

Rubber tree (*Hevea brasiliensis*) is the main economic tree species in *euphorbiaceae*, which has been planted on a large scale in Yunnan, Hainan and other provinces. According to the report delivered by China Natural Rubber Association, the planting area of natural rubber in China has reached 1.135 million hm<sup>2</sup> by 2012, being the third largest one in the world. Yunnan province is the second largest production base of natural rubber in China, and is also the province with the highest aviation biofuels.

utilization ratio of rubber seed. Generally, each mature rubber tree can yield 3 kg dry seeds every year and 2000 kg dry seeds can be yielded by each hectare of land. So the whole country can produce 570 000 t of rubber seed oil calculating by 25% of oil yield<sup>[3,4]</sup>. As rubber seed oil is extracted from rubber seed, it's better than any other plant oils in price or the acquisition of raw materials $^{[5,6]}$ . Due to the large population of China, the programs of extracting biofuels from grain plant oils are not supported by Chinese government. Especially in recent years, the regulations of 'not competing for grains with population', 'not competing for fields with grains' have been clearly raised by Chinese government. Consequently, the research about producing biofuels with non-grain plants liking rubber seed oil has great influence<sup>[7,8]</sup>. For the good external conditions, rubber seed oil will be one resource of abundant raw materials for developing hydrocarbon fuels in the future, and has the broader application prospect for further researches on

Plant oils can be converted into biofuels through the methods of transesterification and cracking<sup>[9-11]</sup>, etc. Transesterification is a method of applying widely to synthesize biodiesel. However, the biodiesel has a high production cost, high clouding point and is difficult to use in cold conditions<sup>[12]</sup>; Furthermore, the residual aliphatic acid during the transesterification process will result in corrosion problems<sup>[13]</sup>; meanwhile, biodiesel has low energy intensity, and 9% lower than the ordinary diesel in the calorific value<sup>[14,15]</sup>. All these disadvantages of biodiesel are attributed to the high content of oxygen in fatty acid methyl ester diesel<sup>[16,17]</sup>. It has been demonstrated by recent researches that oils generated from plant oils by catalytic cracking can be used as a substitute of fossil fuels because of its high energy intensity, low oxygen content, recyclability and renewability<sup>[18,19]</sup>. Researchers from National Renewable Laboratory of America (NREL) have researched that hydrogen consumption could be reduced through loading nickel on stable carrier or utilizing noble metal catalyst in the process of catalytic cracking, thereby the deoxygenation rate can be improved greatly.

Transition metal catalysts have already been widely applied in the catalytic cracking of oils, which has been reported by numerous literatures. Under the conditions of 300°C and 5% Pd/C as the catalyst, Wang et al.<sup>[20]</sup> have conducted the experimental on continuous thermal hydrolysis and furnace style catalytic thermal cracking of plant oil. They demonstrated that the decarboxylation of the saturated free fatty acids proceeded at the rate of 15.5 mmol/min, and about 90% free fatty acids were converted into alkanes in 5 h. These mixed alkanes can be converted into renewable hydrocarbon fuels and isomerization of alkanes quickly, and improved the low temperature fluidity of fuels. Immer et al.<sup>[21]</sup> carried on the experiment about catalytic liquid deoxygenation of stearic acid, oleic acid and linolenic acid by using 5% Pd/C catalyst; the catalytic deoxygenation of stearic acid was mainly conducted by decarboxylation, and its components of liquid products were heptadecane and heptadecene; after completed the conversion of stearic acid, hydrogenation of heptadecene was achieved by the transfer of defecate solvent, and acquired 97% yield of Kubičková et al.<sup>[22]</sup> studied about heptadecane. hydrocarbon fuels production with plant oil through decarboxylation; through using stearic acid ethyl ester as model compound. The plant oils were almost converted into the same final product of heptadecane under the temperature between 300°C-360°C and 5% Pd/C as catalyst. Stearic acid ethyl ester was converted by the intermedia of stearic acid, due to catalyst made the reaction products highly selective. The catalyst developed by our research group in this study is a new noble metal catalyst, which has the characteristics of low hydrogen consumption, high deoxygenation rate as well as quite good selective cracking property, etc.

#### 2 Materials and methods

#### 2.1 Equipment and materials

Instruments and equipment used in the experiment are shown as Table 1. Rubber seed oil: from Xishuangbanna Dai autonomous prefecture. The relative content of its major fatty acid with GC-MS analysis is shown as Table 2.

| No. | Name of instruments                                       | Specifications | Quantity | Manufacturer   |
|-----|---|----------------|----------|--|
| 1   | High temperature and high pressure reactor system         | GS-1L          | 4 sets   | Weihai city Zhengwei Mechanical Equipment Corporation, China   |
| 2   | Electric-heated thermostatic water bath                   | DZKW-D-6       | 2 sets   | Beijing city Yong Guang Ming Medical Instrument Factory, China |
| 3   | Electric-heated air dry oven                              | DHG-9203A      | 1 set    | Shanghai-heng Scientific Instrument Limited Company, China     |
| 4   | GC-MS   | TRACE 1300-ISQ | 1 set    | American Thermo Fisher Scientific corporation, USA             |
| 5   | Double-layer Vapour-bathing Constant Temperature Vibrator | HZQ-C          | 1 set    | Jintan city Da di Automation Instrument Factory, China         |

Table 1 Instruments and equipment used in the experiment

| Table 2 | Relative content of   | f maior f | attv acid in | rubber tree s | eed oil |
|---------|-----------------------|-----------|--------------|---------------|---------|
|         | iterative contents of |           |              |               |         |

| Composition | Palmitic acid | Stearic acid | Oleic acid | Linoleic acid | Linolenic acid | Eicosanoic acid |
|-------------|---------------|--------------|------------|---------------|----------------|-----------------|
| Wt%         | 10.24         | 8.19         | 24.73      | 31.14         | 23.17          | 1.08            |

#### 2.2 Characteristics of catalyst

The active component of 2% Pd was loaded on the functionalized silicon and aluminum oxide molecular sieve with the method of impregnation, then through high temperature at 500°C calcining, cooling and then grinding 5 h, it was activated on specific conditions of temperature at 300°C, hydrogen pressure at 1 MPa with response time for 6 h in experiment. The catalyst has certain selective cracking function under the conditions of controlling the temperature, hydrogen partial pressure and times.

The phases structure of the samples were analyzed by the D/MAX-2000 type full automatic X ray diffraction. The radiation source is Cu-K $\alpha$  ( $\lambda$ =0.15406 nm) operated at 40 kV, 40 mA. The morphology and composition of samples were analyzed by FEI Tecnai F30 at 300 kV with high-resolution transmission electron microscopy and energy dispersive X-ray spectrometry.

The specific surface area, pore volume and pore size were calculated by BET method, and the pore size distribution was calculated by the DFT method from the desorption curve through using NOVA2000 e-type surface and porosity analyzer the adsorption temperature of  $N_2$  was 77 K. Its characterization properties are shown as Table 3.

Table 3 Data of catalyst structure characterization

| Sample   | Specific      | Pore                             | Average pore | Total                 | Pd dispersion |
|----------|---------------|----------------------------------|--------------|-----------------------|---------------|
|          | surface area  | volume                           | diameter     | acid                  | degree        |
|          | $/m^2 g^{-1}$ | /cm <sup>3</sup> g <sup>-1</sup> | /nm          | /mmol g <sup>-1</sup> | /%            |
| Catalyst | 316.93        | 0.49                             | 3.09         | 1.42                  | 9.59          |

#### 2.3 Catalytic cracking of rubber tree seed oil

The whole physical and chemical process of catalytic cracking experiment was conducted in closed tank reactor (shown as Figure 1). Catalyst and rubber seed oil was mixed with specific ratio in the reactor. Adding hydrogen into the reactor and heating it to the reaction temperature, the catalytic cracking reaction will take place correspondingly; by the heat preservation continuously, the reaction will be slowed down and then ceased by some time; finally the product will be took out when the reaction is over. The liquid product consists of liquid fuel components and water (the content of water accounts for about 3%-5% of the raw materials of rubber seed oil), and will be analyzed the reaction products with GC-MS after a series of treatments.



 Hydrogen 2. Argon 3. Booster pump 4. Air compressor 5. Buffer tank
High temperature and high pressure reactor 7. Controller (adjusting reaction temperature and rotation speed) 8. Magnetic rotating stirrer 9. Gas collection and exhaust port.

Figure 1 Schematic diagram of experimental device

#### 2.4 Analysis of liquid fuel

The residual acid in the liquid production could cause the TRACE ISQ GC-MS Spectrometer damaged, so the liquid product which was taken out from the tank reactor would be methyl esterification firstly, then it was sealed and sent for analyzing. The component of the product was measured by THRACE ISQ GC-MS Spectrometer. Conditions of methyl esterification: measuring 3-5 g initial processing product, adding in 20 mL 1%  $H_2SO_4$ -methyl alcohol solution and shaking well; then placing the uniformly mixed solution into a water bath kettle backflow for 60 min under the temperature of 70°C; after that, extraction was conducted by adding 15 mL dichloromethane and stratification with adding 30 mL distilled water, removing the distilled water in the upper layer; then adding 5-10 mL dichloromethane once more for secondary extraction and washing it with distilled water for 2-3 times. Finally, pouring out the sample on the upper layer, adding enough anhydrous Na<sub>2</sub>SO<sub>4</sub> into it and shake well for desiccation, taking out the sample for analysis by filtration after 30 min standing. Gas chromatographic analysis condition, chromatographic column: CETM-5 (30 m × 0.25 mm × 0.25  $\mu$ m); 200°C of injection temperature; for temperature raising procedure, initial temperature is 80°C. Then heat preservation time is 3 min, and heating to 280°C at the rate of 10°C/min, then preserving the temperature for 3 min; 1.5 mL/min gas velocity of carrier gas. Mass spectrum analysis condition: electron impact (EI) ion source (electron energy 70 eV), 280°C of temperature of transmission line, 0.9 kV of detection voltage m/z 32-500 of mass scan range and 1-25 min of data acquisition time range.

Content of Hydrocarbons: The sum of the relative

percentages of non-oxygenated compounds converted from rubber seed oil was used as an index to evaluate the catalytic hydrodeoxygenation performance of the catalyst, namely deoxidation rate. Content of  $C_8-C_{16}$ hydrocarbons:  $C_8-C_{16}$  range of hydrocarbon components in the liquid reaction product as a percentage of the catalyst cracking performance evaluation index.

#### 2.5 Data processing

Components of the product can be identified by standard mass spectrum, based on the data analysis through searching the spectrogram data-base by data processing system automatically; after quantitative analysis, the relative percentage composition of the components will be calculated by the analysis of 'area normalization method' through data processing system.

#### **3** Results and discussion

# **3.1** Technological conditions for catalytic cracking of rubber seed oil

The catalytic cracking experiment's results of rubber seed oil under different conditions were different from each other, as is shown in Table 4.

| No. | Temperature/ $^{\circ}$ C | Hydrogen pressure/MPa | Ratio of oil and catalyst | Time/h | Stirring speed/r min <sup>-1</sup> | Content of hydrocarbons/% | $C_8 - C_{16} / \%$ |
|-----|---------------------------|-----------------------|---------------------------|--------|------------------------------------|---------------------------|---------------------|
| 1   | 300                       | 3.0                   | 10:1                      | 5      | 100                                | 95.16                     | 63.41               |
| 2   | 310                       | 3.0                   | 10:1                      | 5      | 100                                | 99.15                     | 71.46               |
| 3   | 320                       | 3.0                   | 10:1                      | 5      | 100                                | 96.84                     | 70.35               |
| 4   | 330                       | 3.0                   | 10:1                      | 5      | 100                                | 98.65                     | 69.32               |
| 5   | 340                       | 3.0                   | 10:1                      | 5      | 100                                | 98.52                     | 68.61               |
| 6   | 310                       | 1.0                   | 10:1                      | 5      | 100                                | 95.01                     | 76.25               |
| 7   | 310                       | 1.5                   | 10:1                      | 5      | 100                                | 95.80                     | 77.06               |
| 8   | 310                       | 2.0                   | 10:1                      | 5      | 100                                | 99.17                     | 78.22               |
| 9   | 310                       | 2.5                   | 10:1                      | 5      | 100                                | 96.50                     | 70.33               |
| 10  | 310                       | 3.0                   | 10:1                      | 5      | 100                                | 99.15                     | 71.46               |
| 11  | 310                       | 3.5                   | 10:1                      | 5      | 100                                | 99.14                     | 73.49               |
| 12  | 310                       | 4.0                   | 10:1                      | 5      | 100                                | 98.76                     | 71.38               |
| 13  | 310                       | 2.0                   | 10:1                      | 5      | 100                                | 99.17                     | 78.22               |
| 14  | 310                       | 2.0                   | 15:1                      | 5      | 100                                | 99.53                     | 79.58               |
| 15  | 310                       | 2.0                   | 20:1                      | 5      | 100                                | 98.99                     | 72.56               |
| 16  | 310                       | 2.0                   | 25:1                      | 5      | 100                                | 95.11                     | 73.23               |
| 17  | 310                       | 2.0                   | 30:1                      | 5      | 100                                | 93.97                     | 71.83               |
| 18  | 310                       | 2.0                   | 45:1                      | 5      | 100                                | 93.33                     | 71.24               |
| 19  | 310                       | 2.0                   | 90:1                      | 5      | 100                                | 91.39                     | 70.92               |
| 20  | 310                       | 2.0                   | 15:1                      | 4      | 100                                | 98.40                     | 69.11               |
| 21  | 310                       | 2.0                   | 15:1                      | 5      | 100                                | 99.53                     | 79.58               |
| 22  | 310                       | 2.0                   | 15:1                      | 6      | 100                                | 99.23                     | 72.52               |
| 23  | 310                       | 2.0                   | 15:1                      | 7      | 100                                | 98.66                     | 74.22               |
| 24  | 310                       | 2.0                   | 15:1                      | 8      | 100                                | 97.60                     | 73.85               |
| 25  | 310                       | 2.0                   | 15:1                      | 5      | 50                                 | 97.41                     | 70.52               |
| 26  | 310                       | 2.0                   | 15:1                      | 5      | 100                                | 99.53                     | 79.58               |
| 27  | 310                       | 2.0                   | 15:1                      | 5      | 150                                | 96.01                     | 76.40               |
| 28  | 310                       | 2.0                   | 15:1                      | 5      | 200                                | 96.89                     | 74.64               |

Table 4 Effect of each factor on content of components of hydrocarbon fuels in liquid product

Experiments were conducted to test the effect of reaction temperature on content of components of hydrocarbon fuels in liquid product generated by catalytic cracking, from 300°C to 340°C of reaction temperature (the corresponding experiment numbers are 1-5). The content of hydrocarbons in liquid product was 99.15% and content of C8-C16 was 71.46% when temperature was maintained at 310°C. Whereas, with the rising of temperature from 310°C to 340°C (the corresponding experiment numbers are 2-5), the proportion of hydrocarbons component is decreasing due to the proportion of every component is changing differently with temperature rising. As is shown in Figure 2, it can be also seen from the morphology that the products showed solid or semi-solid state, not fully converted and cracking extent below 300°C; when temperature was maintained above 300°C, the product mainly consisted of short-chain alkanes with the state of liquid. However, if the temperature gets too high, the catalyst will have obviously coking phenomenon. Furthermore, due to the coking taking place on the bottom of reactor, more catalyst would be adhered on the inner wall of reactor with temperature increasing. As could be seen in Figure 3, when the temperature was within the range of 300°C-340°C, the content of each hydrocarbon compound increased firstly and then followed by a decrease and later tended to be stable with increasing reaction temperature. Consequently, the optimal reaction temperature is 310°C.



Figure 2 Product morphology at the 290 °C condition



Figure 3 Effect of reaction temperature on content of each hydrocarbon fuel in liquid product

Experiments were conducted to test the effect of hydrogen partial pressure on content of hydrocarbon fuels in liquid product, from 1.0 MPa to 4.0 MPa of hydrogen partial pressure (the corresponding experimental number is 6-12). When hydrogen partial pressure was 2.0 MPa, the content of hydrocarbons in liquid product was 99.17% and content of  $C_8$ - $C_{16}$  was 78.22%. During the experiments, there was an obvious phenomenon that the coking of catalyst in reactor tank tended to be much more severe with decreasing hydrogen partial pressure. Kubičková et al.<sup>[23]</sup> reported that the reaction could proceed in inert atmosphere even without H<sub>2</sub>. However, hydrogen partial pressure had certain effect on coking of catalyst during the reaction process of selection and recombination as well as polymerization of unsaturated Different hydrocarbon. with saturation and deoxygenation reaction of double bond generally proceed in acid sites of the surface of catalyst, the cracking reaction of hydrocarbons proceeds in the channels of catalyst. Consequently, if the particle size of the formed molecules is smaller than the pore size of catalyst, then the molecules can flow through the channels when reaction completes. However, if the particle size of molecules is too large, the molecules generated will lead to channel plugging of catalyst, resulting in inactivation of catalyst, and the inactivated catalyst will congeal to form a clot and adhered on the bottom of the reactor. As is shown in Figure 4, it can be found that effect of hydrogen partial pressure on content of hydrocarbons in the product is not quite obvious, basically above on 95%, indicating that have a good effect of deoxygenation, but there is an obvious effect on the percentage of

hydrocarbons of  $C_8$ - $C_{16}$ . There is a rule that every content of each component increases firstly and then experiences a certain fluctuation and later followed by a decrease with increasing hydrogen partial pressure. Therefore, the optimal hydrogen partial pressure is 2 MPa.



Figure 4 Effect of hydrogen partial pressure on content of hydrocarbon fuels in liquid product

Experiments were conducted to test the effect of the catalyst dosage on components of hydrocarbon fuels in liquid product, from 10 to 90 of m (oil)/m (catalyst) (the corresponding experimental number is 13-19). When m (oil)/m (catalyst) is 15, content of hydrocarbons in liquid product was 99.53% and content of C8-C16 is 79.58%. As is shown in Figure 5, the content of each hydrocarbon component increased firstly and then decreased with the increase of the oil-catalyst ratio, because the greater the oil-catalyst ratio is, the more the contact between the rubber seed oil and the catalyst are, but the excess oil-catalyst ratio would the oil attach to the catalyst surface, which is unfavorable to the hydrogen and the catalyst contact, and accelerated the side reaction to occur when the amount of catalyst reached a certain level without promoting the progress of the reaction. Consequently, the optimal ratio of oil and catalyst is 15.

Experiments were conducted to test the effect of reaction time on content of components of hydrocarbon fuels in liquid product, from 4 h to 8 h of reaction time (the corresponding experimental numbers are 20-40). When reaction time was set as 5 h, content of hydrocarbons in liquid product was 99.53% and content of  $C_8$ - $C_{16}$  was 79.58%. As can be seen from Figure 6, with the increase of reaction time, content of each

hydrocarbon compound increased slightly and quite stable finally. The extension of the reaction time would promote the catalytic cracking reaction, but the side effects would occur over time, which would produce some aromatic hydrocarbons. Therefore, long reaction time is not beneficial, and 5 h is recommended as the appropriate reaction time.



Figure 5 Dosage of catalyst on content of hydrocarbon fuels in liquid product



Figure 6 Effect of reaction time on content of hydrocarbon fuels in liquid product

The faster the speed is, the greater the stirring speed will be. Stirring aims to promote the system of homogenization and mass transfer between the system and enhance heat transfer in reaction process. Experiments were conducted to test the effect of stirring speed on content of hydrocarbon fuels in liquid product, from 50 r/min to 200 r/min of stirring speed (corresponding experimental numbers are 25-28). When the stirring speed was set as 100 r/min, content of hydrocarbon compounds in liquid product was the maximum and the hydrocarbons proportion of  $C_8-C_{16}$  was also the maximum (the corresponding experimental number is 26). That is the reason that mixing degree of rubber seed oil and catalyst increased with increasing stirring speed in the initial stage, and exposure would also increase with it, therefore, both the degree of catalytic reaction and relative content of hydrocarbon compounds increased at the fixed reaction time of 5 h. However, as the stirring speed increased gradually, reactants had already been thoroughly exposed to the catalyst, so content of hydrocarbon compounds in liquid product would tend to be flat. Consequently, it can be seen from Figure 7 that the optimal stirring speed is recommended 100 r/min.



Figure 7 Effect of stirring speed on content of hydrocarbon fuels in liquid product

# **3.2** Further studies on catalytic cracking of rubber seed oil with proper conditions

On the basis of previous experiment, reaction temperature, dosage of catalyst and hydrogen pressure has been chosen as research factors, and deoxygenation rate and content of C8-C16 hydrocarbons were chose as test response value, furthermore response surface methodology was used to optimal the catalytic hydrogenation conditions. The results illustrate that no matter the deoxygenation effect or content of  $C_8$ - $C_{16}$ components, every factor has interactive effect on each other and not only the simple linear relation on response value. Based on the effect of deoxygenation, the effect of hydrogen pressure is not obvious, and the interactive effects with other factors are also not significant. But this does not mean that hydrogen pressure has no effect on experiment that is because the catalyst had already been activated before catalytic cracking reaction took place and had absorbed enough quantity of hydrogen, so the effect of hydrogen pressure on each response value is However, existence of hydrogen can not obvious.

preserve the activation of catalyst better, which is beneficial for the proceeding of experiment and can prolong service life of catalyst. Meanwhile, temperature and dosage of catalyst are two major influencing factors. These two factors have significant effect on deoxygenation effect and product distribution. There is no doubt that temperature has significant effect on catalytic cracking because chemical reaction is accompanied with energy change; the effect of the catalyst dosage in experimental demonstrated that after mixing rubber seed oil with catalyst, if the dosage of catalyst is not enough with the centrifugal force, the materials will not be able to thoroughly react with the molecules absorbed in the channel on the surface of catalyst, and will be constraint the following cracking reaction. After comprehensive discussion and analysis, the sequence of influencing factors is: temperature > dosage of catalyst > hydrogen pressure.

According to the experimental analysis and discussions above, the optimal condition are:  $310^{\circ}$ C of reaction temperature, 2 MPa of hydrogen pressure, 5 h of reaction time, 15:1 of ratio between oil and catalyst, 100 r/min of stirring speed. Under these conditions, liquid product with catalytic cracking experiment was analyzed by GC-MC, and contains 99.49% of the effective components of hydrocarbon fuels, in which the percentage of C<sub>8</sub>-C<sub>16</sub> could reach as high as 79.61% and the experimental results similar to the experimental number 26. Components of the product and their content are shown in Table 5, and the ion chromatogram is shown in Figure 8.

Compared with the conclusion of the paper by Sun<sup>[24]</sup>, raw material was 90 g, dosage of metal palladium catalyst was 3 g, the percentage of the catalyst was 3.33%, hydrogen partial pressure was 3 MPa, temperature was 300°C, the reaction speed was 100 r/min, the response time was 6 h, under the conditions of hydrocarbon content in the product can reach 100%, liquid hydrocarbons yield can reach 65.32%. This experiment adopts catalyst can achieve low hydrogen consumption, higher deoxygenation rate and better quality of crude oil products.

Open Access at https://www.ijabe.org

| Table 5 | Components of h | vdrocarbon fuels      | obtained under | proper condition | s and their content |
|---------|-----------------|-----------------------|----------------|------------------|---------------------|
|         |                 | , al 00001 0011 10010 | over a and o   | proper condition |                     |

| No. | Retention time/min | Compound                  | Molecular<br>formula           | Relative content/% | No. | Retention time/min | Compound                    | Molecular<br>formula | Relative content/% |
|-----|--------------------|---------------------------|--------------------------------|--------------------|-----|--------------------|-----------------------------|----------------------|--------------------|
| 1   | 1.35               | Hexane                    | C <sub>6</sub> H <sub>14</sub> | 0.51               | 20  | 6.22               | Styrene, 3,4-dimethyl       | $C_{10}H_{12}$       | 1                  |
| 2   | 1.60               | Heptane                   | C7H16                          | 3.64               | 21  | 6.92               | 2-Methyl-4-phenyl-2-butene  | $C_{11}H_{14}$       | 1.17               |
| 3   | 1.72               | Methylcyclohexane         | $C_{7}H_{14}$                  | 0.71               | 22  | 7.10               | Dodecane                    | $C_{12}H_{26}$       | 6.52               |
| 4   | 1.88               | Methylbenzene             | $C_7H_8$                       | 1.05               | 23  | 8.10               | 1-Ethyl-1-methylindane      | $C_{12}H_{16}$       | 0.61               |
| 5   | 1.95               | 3-Methylheptane           | C8H18                          | 1.42               | 24  | 8.23               | 2-Methylnaphthalene         | $C_{11}H_{10}$       | 1.64               |
| 6   | 2.11               | 1-octane                  | C8H18                          | 6.32               | 25  | 8.45               | 1-Ethylidene-1H-indene      | $C_{11}H_{10}$       | 0.98               |
| 7   | 2.55               | Ethylbenzene;             | C8H10                          | 1.76               | 26  | 8.51               | Tridecane                   | $C_{13}H_{28}$       | 5.38               |
| 8   | 2.63               | 1,4-Xylene                | C8H10                          | 4.64               | 27  | 9.56               | 2-Ethylnaphthalene          | $C_{12}H_{12}$       | 0.89               |
| 9   | 2.86               | 1,4-Xylene                | C <sub>8</sub> H <sub>10</sub> | 1.84               | 28  | 9.84               | Tetradecane                 | $C_{14}H_{30}$       | 3.35               |
| 10  | 3.00               | n-Nonane                  | C9H20                          | 8.27               | 29  | 9.90               | 1,7-Dimethylnaphthalene     | $C_{12}H_{12}$       | 1.6                |
| 11  | 3.54               | n-Propylbenzene           | C9H12                          | 1.6                | 30  | 10.98              | N/A                         | $C_{13}H_{14}$       | 0.49               |
| 12  | 3.86               | 1-ethyl-2-methyl-Benzene  | C <sub>9</sub> H <sub>12</sub> | 1.73               | 31  | 11.10              | Pentadecane                 | C15H32               | 6.67               |
| 13  | 4.05               | 1,2,3-trimethyl-Benzene   | C9H12                          | 1.75               | 32  | 12.29              | Hexadecane                  | C16H34               | 3.32               |
| 14  | 4.23               | Decane                    | $C_{10}H_{22}$                 | 7.73               | 33  | 13.42              | Heptadecane                 | C17H36               | 9.03               |
| 15  | 5.31               | 2,4-Dimethylstyrene       | $C_{10}H_{12}$                 | 1.74               | 34  | 14.49              | Heptadecane                 | C17H36               | 3.68               |
| 16  | 5.65               | Undecane                  | $C_{11}H_{24}$                 | 6.2                | 35  | 15.51              | 2,6,10-Trimethyltetradecane | C17H36               | 1.26               |
| 17  | 5.77               | Methyl octanoate          | $C_9H_{18}O_2$                 | 0.24               | 36  | 15.61              | Methyl hexadecanoate        | $C_{17}H_{34}O_2$    | 0.16               |
| 18  | 6.07               | 4-Methylindan             | $C_{10}H_{12}$                 | 0.99               | 37  | 17.19              | N/A                         | $C_{19}H_{34}O_2$    | 0.06               |
| 19  | 6.16               | 10,12-Octadecadiynoicacid | $C_{18}H_{28}O_2$              | 0.01               | 38  | 17.27              | N/A                         | $C_{19}H_{36}O_2$    | 0.04               |



Figure 8 GC-MS ion chromatogram of product obtained under proper conditions

### 4 Conclusions

Based on the experimental results, the optimal conditions of catalytic cracking craft are as follows:

310°C of reaction temperature, 2 MPa of hydrogen pressure, 5 h of reaction time, 15 of m (oil)/m (catalyst) and 100 r/min of stirring speed. Under these conditions, Liquid product with catalytic cracking experiment

contains 99.49% of the effective components of hydrocarbon fuels, in which the percentage of  $C_8$ - $C_{16}$  could reach as high as 79.61%. The quality of initial oil product of rubber seed oil through this technology will be improved, and this technology also has the low hydrogen consumption and high deoxygenation rate through Pd catalyst. Furthermore, this technology can maximize the synthesis of components of hydrocarbon fuels, and achieve that one-step method replacing the traditional two-step experimental procedure.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21266032) and International S&T Cooperation Program of China (No. 2015DFA60120). The authors also thank Liu Tiancheng from School of Chemistry and Environment, Yunnan Minzu University.

#### [References]

- Wang D J, Liu H Y, Liu Y X, He C H, Liu C G. Progress in the study of bio fuels hydrogenation catalysts. Pet. Technol., 2012; 41(10): 1214–1219.
- [2] Gao J S, Xu C M, He J, Duan X, He M Y. Development and strategy research of chemical engineering discipline. Sci. China Chem., 2014; 44(9): 1385–1393.
- [3] He M Y, Li G H, Li H Q. About Yunnan rubber seed oil with the development present situation and the thinking. Tropic Agric. Sci. & Technol., 2010; 33(4): 36–43.
- [4] Wang X L, Zhan L. The rubber seed oil refining research. China Oil and Fat, 2000; 25(4): 10–11.
- [5] Ramadhas A S, Jayaraj S, Muraleedharan C. Biodiesel production from high FFA rubber seed oil. Fuel, 2005; 84(4): 335–340.
- [6] Geo V E, Nagarajan G, Kamalakannan J, Nagalingam B. Experimental investigations to study the characteristics of rubber-seed-oil-fueled diesel engine supplemented with diethyl ether. Energy Fuels, 2009; 23(1): 533–538.
- [7] Li C Z, Li P W, Xiao Z H, Chen J Z, Zhang L B. Woody biodiesel raw materials research and development in our country present situation and the industrialization prospects. J. of China Agric. Uni., 2012; 17(6): 165–170.
- [8] Li L, Quan K J, Xu J M, Liu F S, Liu S W, Yu S T, et al. Liquid hydrocarbon fuels from catalytic cracking of rubber seed oil using USY as catalyst. Fuel, 2014; 123(1): 189–193.
- [9] James A, Yuan W, Boyette M D, Wang D, Kumar A.. In-chamber thermocatalytic tar cracking and syngas

reforming using char-supported NiO catalyst in an updraft biomass gasifier. Int. J. Agric. & Biol. Eng., 2014; 7(6): 91–96.

- Zhang H, Zhang K, Zhou X H, Hu J J, Jing Y Y, Liu S Y. Thermal properties of biomass tar at rapid heating rates. Int. J. Agric. & Biol. Eng., 2014; 7(2): 101–107.
- [11] Xie Z K, Liu Z C, Wang Y D. Technology innovation and prospect of petroleum and chemical industry based on resource and environment. Sci. China Chem., 2014, 44(9): 1394–1403.
- Yee K F, Wu J C S, Lee K T. A green catalyst for biodiesel production from jatropha oil: Optimization study. Biomass & Bioenergy, 2011; 35(5): 1739–1746.
- [13] Na J, Yi B E, Kim J N, Yi K B, Park S, Park J, et al. Hydrocarbon production from decarboxylation of fatty acid without hydrogen. Catal. Today, 2010; 156(1-2): 44–48.
- [14] Tian H, Li C Y, Yang C H, Shan H H. Alternative processing technology for converting vegetable oils and animal fats to clean fuels and light olefins. Chinese J. of Chem. Eng., 2008; 16(3): 394–400.
- [15] Demirbas A. Competitive liquid biofuels from biomass. Appl. Eneegy, 2011; 88(1): 17–28.
- [16] Wang Y P, Zhai Y, Zhang J L, Li W, Han Z T. Research progress of biodiesel preparation. Chem. Indu. and Eng. Prog., 2003; 22(1): 8-12.
- [17] Han W, Huang F H, Yang M, Liu C S, Huang Q D. Research progress of biological diesel low temperature fluidity and improved method. Chem. Indu. and Eng. Prog., 2007; 26(10): 1395–1399.
- [18] Santillan-Jimenez E, Morgan T, Lacny J, Mohapatra S, Crocker M. Catalytic deoxygenation of triglycerides and fatty acids to hydrocarbons over carbon-supported nickel. Fuel, 2013; 103(1): 1010–1017.
- [19] Morgan T, Santillan-Jimenez E, Harman-Ware A E, Ji Y Y, Grubb D, Crocker M. Catalytic deoxygenation of triglycerides to hydrocarbons over supported nickel catalysts. Chem. Eng. J., 2012; 189(2): 346–355.
- [20] Wang C, Thapaliya N, Campos A, Stikeleather L F, Roberts W L. Hydrocarbon fuels from vegetable oils via hydrolysis and thermo-catalytic decarboxylation. Fuel, 2012; 95(1): 622–629.
- [21] Immer J G, Jason Kelly M, Henry Lamb H. Catalytic reaction pathways in liquid-phase deoxygenation of  $C_{18}$  free fatty acids. Appl. Catal. A Gen., 2010; 375(1): 134–139.
- [22] Kubičková I, Snåre M, Eränen K, Mäki-Arvela P, Murzin D Y. Hydrocarbons for diesel fuel via decarboxylation of vegetable oils. Catal. Today, 2005; 106(1): 197–200.
- [23] Kubičková I, Kubička D. Utilization of triglycerides and related feedstocks for production of clean hydrocarbon fuels and petrochemicals: A review. Waste & Biomass Valorization, 2010; 1(3): 293–308(16).
- [24] Sun P P. Research of hydrocarbon production of vegetable oil and fat. Yunnan, Yunnan Normal University, 2014. (in Chinese)