Optimization of Bio-Hydrogenated Gasoline Production from Rice Bran Oil via Catalytic Hydrocracking over Pd/Al₂O₃ Catalyst

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(Received January 5, 2021)

This work aims to study biofuel production from rice bran oil (RBO) using a hydrocracking reaction over 0.5%Pd/Al₂O₃ catalyst. The Central Composite Design (CCD) was used to find optimal bio-hydrogenated gasoline (BHG) production conditions. The effects of pressure and temperature, including the interaction of the parameters under the constant liquid hourly space velocity (LHSV), were determined by the statistical methodology of surface response (RSM). The yields of liquid biofuel products and BHG, as well as BHG selectivity, were used as response values for optimizing BHG production. The results remarkably showed that pressure and temperature significantly influenced BHG production in terms of yield and selectivity. The optimal condition for BHG production was found to be at 516°C and 4.8 MPa, with the BHG yield of 44.21%. However, the optimal BHG selectivity was found to be at 532°C and 4.4 MPa with a selectivity of 69.74%. Moreover, temperature appeared to be a more dominant parameter on biofuel product yield than the pressure. This parameter had greater effects on both linear and square terms in ANOVA analysis of the biofuel product yield. Furthermore, hydrocracking was discovered to improve the heat of combustion of BHG as compared with the initial feedstock and commercial gasoline. The total acid value of BHG was also found to increase because the reaction could break the ester bond between glycerol and carboxyl groups; thus, free fatty acids were formed, causing the high value of total acid in the sample.

Key Words
Green gasoline, Green fuel, Biofuel, Hydroprocessing, Central composite design

1. Introduction

The aim to find alternative solutions to the globally increasing energy shortage and environmental issues caused by the extensive use of fossil fuels has been dedicated to developing renewable sources of transportation fuels 1). Vegetable oil, an abundant renewable energy source, is an organic feedstock produced by photosynthesis. One of the benefits of using vegetable oil as an energy source is carbon neutrality. Triglycerides (TG) and fatty acids contained in vegetable oil can be used with appropriate biochemical and thermo-chemical processing for producing valuable chemicals and renewable fuels 2) ~ 4). Biofuels obtained from TG-based feedstocks consist of hydrocarbons with similar properties as fossil fuels 5). Nevertheless, these feedstocks cannot be used directly in the engines of vehicles because they have high viscosities, about ten times those of gasoline or diesel fuels. Several pieces of research were investigated on the reduction of the oil viscosity either by various techniques, including adding viscosity depressants, heating and blending with excess transportation fuel, and using thermal cracking 6).

Hydrocracking, one of the thermal cracking reactions, is a modern technology that offers a high yield of hydrocarbon products with good fuel properties. Also, the process can readily be carried out in existing petroleum refineries. Hydrocracking can use TG-based feedstock to produce clean gasoline that meets commercial fuel standards. The transformation mechanism of TG into
hydrocarbon by hydrocracking has been described in many works. TG is broken down by the severe condition of hydrocracking into various intermediate substances, which are mostly carboxylic acids \(^7\) \(^8\). The intermediates are transformed into alkane hydrocarbons by three main pathways: hydrodeoxygenation, decarboxylation, and decarbonylation. Huber et al. (2007) have explained the conversion of carboxylic acid that they used as a reactant for alkane production. They reported that the decarboxylation pathway converted a carboxylic group to alkane hydrocarbon with no hydrogen requirement, and it involved converting carboxylic acid into the methyl groups and CO\(_2\) without the presence of water. On the other hand, CO was produced by the decarbonylation pathway, where the carboxylic groups reacted with hydrogen to produce methyl groups, CO and H\(_2\)O. The hydrodeoxygenation pathway converted carboxylic acid by reacting with hydrogen to produce alkane hydrocarbon and water. Moreover, decarboxylation and decarbonylation yielded liquid alkane products that had an odd number of carbon atoms that are not generally found in TG \(^7\).

Rice bran is available as an agricultural waste in a massive quantity, especially in Southeast Asia, and is obtained from the rice milling process. Only 10% or less portion of rice bran oil (RBO) is used as edible oil, whereas the rest of the oil which is rich in free fatty acid (FFA), hence is not suitable for human consumption. For this reason, it offers huge potential as an inexpensive feedstock for biofuel production \(^6\) \(^9\). Nevertheless, based on our literature review, many research on the utilization of other TG-based feedstocks such as palm oil, jatropha oil, and sunflower oil to produce green diesel was found but research on rice bran oil was rather limited, and even more so on the application of hydrocracking technology to produce bio-hydrogenated gasoline \(^2\) \(^9\) ~\(^13\). Since it is known that the operating condition plays an important role in product selectivity, bio-hydrogenated gasoline selectivity increases with operating temperature while green diesel selectivity decreases \(^9\) \(^14\) \(^15\). This work attempted to find the most appropriate operating condition, which gave the best bio-hydrogenated gasoline yield and selectivity from rice bran oil hydrocracking.

2. Methodology

2.1 Feedstock and chemicals

Refined rice bran oil was used as feedstock in this study. The fatty acid components of the rice bran oil feedstock compared with other feedstocks that are often used in the hydrocracking process are shown in Table 1. It is evidenced from the table that most of the fatty acid components of rice bran oil are saturated and monounsaturated fatty acids which are similar to those of palm oil.

Hydrogen gas with 95% purity was used as reactant gas during the reaction, and nitrogen gas with 99% purity was used for checking gases leak and cooling down the system. A 0.5% Pd/Al\(_2\)O\(_3\) commercial-grade catalyst (Heze Development Zone Dayuan Chemical Co., Ltd. China) was used as the reaction catalyst.

2.2 High pressure-packed bed reactor (HPPBR)

Hydrocracking reaction was operated in the high-pressure-packed bed reactor (HPPBR). In brief, the HPPBR is comprised of three systems, including feed system, reaction system, and separation system, as shown in Fig. 1. The feed system is the first system of the reactor, and it consists of the feedstock tank, pump, gas cylinders, and regulators. The feedstock was pumped from the feedstock tank at the volumetric flow rate of 100 mL/h at room temperature and mixed with the hydrogen gas before entering the reaction system with the gas-oil volumetric ratio of 500:1 at STP. The mixed reactant was continuously fed to a stainless-steel tubular reactor (2.3 cm inner diameter and 43 cm long) at the bottom of the

| Table 1 Fatty acid components of rice bran oil compared with palm oil, soybean oil, and sunflower oil \(^{16}\) |
|-----------------------------------------------|
| Fatty acids (%) | Palm oil \(^{16}\) | Soybean oil \(^{16}\) | Sunflower oil \(^{16}\) | Rice bran oil (This study) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Undecanoic (C11:0) | -               | -               | -               | 12.36           |
| Myristic (C14:0) | 1.23            | -               | -               | 3.20            |
| Palmitic (C16:0) | 41.78           | 14.04           | 6.52            | 25.19           |
| Steric (C18:0)  | 3.39            | 4.07            | 1.98            | 13.23           |
| Palmitoleic (C16:1) | -             | -               | -               | 5.43            |
| Oleic (C18:1)   | 41.90           | 23.27           | 45.39           | 13.99           |
| Linoleic (C18:2) | 11.03           | 52.18           | 46.02           | 3.94            |
| Linolenic (C18:3) | -              | 5.63            | 0.12            | -               |
| Eicosapentaenoic (C20:5) | -        | -               | -               | 12.16           |
reactor through the catalyst that was carefully packed to fill the reactor with the working volume of 100 mL. It is worth mentioning here that the catalyst was of a cylindrical shape (4 mm diameter and 8 mm long). The reaction was performed in this system under the controlled severe condition. The reaction temperature was measured and controlled by thermocouples installed at the top and bottom of the reaction zone. The hydrocracked product was exported from the top of the reactor as an up-flow current and continuously flowed to a heat exchanger of the product separation system to condense and separate the liquid and gas products. Gases were released into the atmosphere while the liquid product was collected in the product tank. The liquid product consisted of several types of fuel; therefore, it needs to be further separated by a distillation apparatus.

2.3 Biofuel optimization

The statistical tool of central composite design (CCD) was used in the experimental design of this study. It yielded a set of 13 experiments with different combinations of temperature and pressure. Factors and their levels were interpreted to find their effects, interaction, and optimal condition by Minitab 16 statistical software (Minitab, Inc, Pennsylvania, USA).

The experiment of BHG production was designed by using CCD to determine the influence of pressure and temperature on BHG yield and selectivity. The HPPBR was employed to conduct the catalytic hydrocracking reaction. Operating hydrogen pressure and temperature were controlled under the range as shown in Table 2, while the feedstock flow rate was fixed at 1 h⁻¹ in terms of liquid hourly space velocity (LHSV), which is the ratio of rice bran oil volume flow per hour to the working volume of the reactor. The pressure and temperature were so selected based on our literature review and preliminary experimental results. It was reported in the literature that the reaction that took place at a temperature below 465 °C yielded rather low gasoline selectivity ² ⁵ ¹ ⁴ ⁻ ¹ ⁰ ⁻ ¹ ³ ⁵ ⁻ ¹ ⁵, and this was confirmed by our preliminary tests. Our preliminary tests also revealed that the reaction temperature below 450 °C yielded grease-like material, and combustion took place at a temperature above 535 °C. In addition, at 3 MPa, the reaction also gave grease-like material. To avoid the occurrence of the grease-like material, the pressure was selected to be above 3.6 MPa, and the maximum pressure was chosen to be 6.4 MPa for safety reasons. For the chosen initial pressure of 6.4 MPa, the actual operating pressure could be 8-9 MPa due to the high operating temperature.

The experiments were carried out in the HPPBR. The obtained liquid biofuel product was collected in the separation system, and its volume was determined. The liquid biofuel product yield, together with the operating temperature and pressure, as input to the Minitab16 software to determine a mathematical model relating the yield as a function of pressure and temperature. The

![The experimental design of the high-pressure-packed bed reactor](image)

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**Table 2. Parameters and levels used for the experimental design in BHG production**

| Parameters     | Code | Code Levels |
|----------------|------|-------------|
| Pressure (MPa) | X₁   | -α 0 +1 +α  |
| Temperature (°C)| X₂  | 36 4 5 6 6.4 |
|                | 465 475 500 525 535 |
obtained liquid biofuel product was distilled by using Petotest Instrument (Anton Paar, Germany) followed by ASTM D86 \(^{(1)}\) to obtain BHG selectivity and yield. In brief, the biofuel sample was heated at ambient pressure. The operating temperature was indicated by a thermometer that was connected to the distillation flask. The range of boiling point was used to separate biofuel types. The boiling point between 50 to 170 °C was classified as BHG and 170 °C to 360 °C as green diesel. Since this study focused on these two valuable products, the other outcome, which has a boiling point over 360 °C, was assumed to be an unconverted feedstock.

In this work, yields of biofuel product and BHG and BHG selectivity were investigated for use as the responses in the Minitab software to determine the best operating conditions for BHG production.

3. Results and discussion

Each experimental run provided a different biofuel yield due to the different operating conditions designed by CCD, based on the parameters and their levels, as presented in Table 2. The biofuel obtained from the reactor had dark-brown color with less viscosity than the initial viscosity of the feedstock due to the fact that its carbon chain was changed to a shorter structure. Hydrocracking usually provided liquid/gas-based hydrocracked products and water. Gasses were released to the atmosphere with unreacted H\(_2\). Liquid products and water were collected from the reactor, which was separated into two layers. Water occurred from oxygen removal in the decarbonylation and hydrodeoxygenation reactions, and it was removed by fractionation funnel while the liquid biofuel part was further distilled to identify the type of bio-hydrogenated biofuels. Only the biofuel layer was further determined as biofuel product yield before distilled by a distillation unit for verifying BHG. Therefore, biofuel product yield was the first response and could be calculated by Equation (1).

\[
\text{Biofuel product yield (%vol.)} = \left(\frac{V_p}{V_f}\right) \times 100 \tag{1}
\]

where \(V_p\) represented the volume of product distillate obtained between 50 °C to 360 °C, and \(V_f\) is the volume of the feedstock used for biofuel production. It should be noted that the distillation higher than 360 °C was sorted as the un-converted feedstock and was not included in the biofuel product. Normally, the boiling point of light oil and middle distillate starts from 50 °C and ends at 360 °C, and the BHG was also included in this range.

Table 3 presents the biofuel product yield, BHG selectivity, and BHG yield from several conditions statistically designed by CCD. The yield of biofuel product obtained from each condition given by CCD can be interpreted as the main and interactive effects of the pressure and temperature.

The effects of the pressure and temperature on the biofuel product yield were demonstrated in Table 4. The \(F_{\text{value}}\) of main, square, and interaction parameters were considered at a 95% confidence interval, as presented in Table 4. The ANOVA table also showed \(F_{\text{value}}\) of linear, square, and interaction terms for biofuel product yield to be 31.90, 13.55, and less than 0.00, respectively. These values were compared with \(F_{\text{critical}}\), to determine the significance of the linear, square, and interaction terms. If the \(F_{\text{value}}\) of a term is greater than \(F_{\text{critical}}\) of the term, the term is significant, and vice versa. The results also showed that the effect of pressure and the interaction between pressure and temperature showed an insignificant effect on biofuel product yield. On the contrary, the effect of temperature and the square terms of both parameters exhibited

| Run | Pressure (MPa) | Temperature (°C) | Biofuel product yield (%) | BHG selectivity (%) | BHG yield (%) |
|-----|---------------|------------------|---------------------------|---------------------|--------------|
| 1   | 4.0           | 475              | 81.29                     | 24.47               | 19.89        |
| 2   | 6.0           | 475              | 76.93                     | 43.85               | 33.73        |
| 3   | 4.0           | 525              | 60.64                     | 61.96               | 37.57        |
| 4   | 6.0           | 525              | 56.43                     | 51.89               | 29.28        |
| 5   | 3.6           | 500              | 75.31                     | 36.02               | 27.12        |
| 6   | 6.4           | 500              | 57.83                     | 56.40               | 32.62        |
| 7   | 5.0           | 465              | 76.80                     | 23.86               | 18.33        |
| 8   | 5.0           | 535              | 58.86                     | 75.74               | 44.58        |
| 9   | 5.0           | 500              | 75.80                     | 54.02               | 41.29        |
| 10  | 5.0           | 500              | 79.29                     | 53.54               | 43.54        |
| 11  | 5.0           | 500              | 77.94                     | 54.86               | 42.10        |
| 12  | 5.0           | 500              | 77.31                     | 54.68               | 41.94        |
| 13  | 5.0           | 500              | 78.45                     | 53.16               | 42.86        |
significant effects.

The definitions of the parameters in the table may be found at elsewhere 18). Furthermore, the coded second-order mathematical model was found and represented by Equation (2).

\[ Y_1 = 77.7580 - 4.1613X_1 - 8.3151X_2 - 5.1884X_1^2 - 4.5584X_2^2 + 0.0375X_1X_2 \] (2)

When insignificant terms are removed, Equation (2) becomes

\[ Y_1 = 77.7580 - 4.1613X_1 - 8.3151X_2 - 5.1884X_1^2 - 4.5584X_2^2 \] (3)

where \( Y_1 \) represents the biofuel product yield (%). \( X_1 \) and \( X_2 \) represent coded variables of pressure and temperature, respectively. While \( X_1^2 \) and \( X_2^2 \) are the square terms of each coded variable.

It is worth noting here that \( R^2 \) of Equation (2) and \( R^2_{\text{adj}} \) of Equation (3) were determined to be 92.85% and 87.74%, respectively. Since the difference between \( R^2 \) and \( R^2_{\text{adj}} \) is 5.11%. This indicated that Equation (3) was an adequate approximation of the experiment.

In addition, the \( F_{\text{value}} \) of lack-of-fit was greater than the \( F_{\text{critical}} \), and the lack-of-fit was thus significant. This was also confirmed by the \( P_{\text{value}} \) of 0.015, which was less than 0.05. However, the accuracy of the obtained mathematical model can be alternatively determined by evaluating the residuals between the predicted values with the experimental values. Fig. 2 depicts a plot of the experimental values against the predicted values.

Even though the Minitab software revealed the lack-of-fit was significant, visual examination of the plot in Fig. 2 showed the distribution of the data points clustering around the 45-degree line, indicating fair agreement between the model and the experiment. With the complex nature of the experiment, the limitations of the equipment, and data collection, the model was considered a fair representation of the actual experiment.

Fig. 3 presents the surface plot of biofuel product yield based on Equation (3) with the interaction between both parameters. It was found that the yield of biofuel product can be obtained in the wide range of 40-90% under the temperature ranging from 470 to 530 °C, and pressure from 4 to 6 MPa. However, the plot revealed an interesting result: the yield decreased when the reaction pressure and temperature increased. This phenomenon could be due to the unsaturated fatty acids in triglycerides being polymerized to polymers under high temperature and
pressure conditions which were evidenced by the gum and grease found in the reactor system. In addition, some research has reported that liquid hydrocarbon yield slightly decreased as the reaction temperature increased because the initial substrate was cracked into gaseous products.

Furthermore, the model predicted the optimal condition for converting RBO into liquid biofuel at 477°C of temperature and 4.6 MPa pressure, with a yield of 82.40%.

### 3.1 Bio-gasoline production

The liquid biofuel, obtained from every experimental run given by CCD, was further refined by the distillation method to separate BHG. The selectivity of the BHG range was calculated by Equation (4) and shown in Table 3. Also, it was used as a response in the Minitab software for determining the optimal condition for BHG selectivity.

\[
S = \frac{V_g}{V_p} \times 100
\]

where \( S \) is BHG selectivity, \( V_g \) is the volume of BHG fraction with the boiling point between 50°C and 170°C, and \( V_p \) is the volume of all distillation products between 50°C and 360°C.

The Minitab software was also used to analyze the direct and interaction effects of pressure and temperature on the BHG selectivity. The results were used to identify the significant and insignificant terms of both parameters by comparing the \( F_{\text{value}} \) of each term to the \( F_{\text{critical}} \) as presented in Table 5.

Therefore, the coded second-order mathematical model was also obtained and presented in Equation (5).

\[
Y_2 = 54.09 + 4.77X_1 + 14.86X_2 - 4.56X_1^2 - 7.36X_1X_2
\]

When insignificant terms are removed, Equation (5) becomes

\[
Y_2 = 54.09 + 4.77X_1 + 14.86X_2 - 7.36X_1X_2
\]

where \( Y_2 \) is the BHG selectivity (%).

Similarly, the \( R^2 \) of Equation (5) and \( R^2_{\text{adj}} \) of Equation (6) were compared and found to be less than 5%, and it could be concluded that Equation (6) was an adequate approximation of the experiment.

Although the lack-of-fit was thus significant, as shown in Table 5, the correlative values between the predicted and actual experimental values were laying along the 45-degree line as presented in Fig. 4. This result indicated a fair agreement between the model and the experiment.

| Source                  | DF | \( F_{\text{value}} \) | \( P_{\text{value}} \) | Result   |
|-------------------------|----|------------------------|------------------------|----------|
| Regression              | 5  | 2064                   | <0.001                 | significant |
| Linear                  | 2  | 42.91                  | <0.001                 | significant |
| Pressure                | 1  | 8.00                   | 0.025                  | significant |
| Temperature             | 1  | 77.82                  | <0.001                 | significant |
| Square                  | 2  | 3.91                   | 0.072                  | insignificant |
| Pressure × Pressure     | 1  | 6.36                   | 0.040                  | significant |
| Temperature × Temperature| 1  | 2.33                   | 0.170                  | insignificant |
| Interaction             | 1  | 9.55                   | 0.018                  | significant |
| Temperature × Pressure  | 1  | 9.55                   | 0.018                  | significant |
| Residual Error          |    | 88.54                  | <0.001                 | significant |
| Lack-of-Fit             | 734|                        |                        |          |
| Pure error              |    |                        |                        |          |
| Total                   | 12 |                        |                        |          |

The influence of both parameters on selectivity is...
displayed as a surface plot in Fig. 5. The figure disclosed that the BHG selectivity increased with temperature and pressure. Although the graph does not show a clear optimal point, the Minitab software predicted the optimal selectivity of 69.74% at 532 °C and 4.4 MPa. It should be mentioned here that the optimal response also depended on the selected ranges of the parameters, which are limited by the equipment used. As discussed by Dujjanutat et al. (2019) and Dujjanutat et al. (2020), the selection of the parameter’s range had an impact on product selectivity extension 10,24.

Moreover, the yield of BHG was also investigated to determine the optimal condition. It could be calculated by Equation (7) with the calculational results shown in Table 3.

\[
\text{BHG yield (\% vol.)} = \frac{V_g}{V_f} \times 100
\]

where \( V_g \) represented the volume of BHG distillate between 50–170 °C, and \( V_f \) is the volume of the feedstock used as previously defined.

Similarly, the Minitab software was also employed to determine the influence of the parameters on BHG yield, as shown in Table 6.

The significance of the parameters and their interaction were determined by comparing the \( F_{value} \) with the \( F_{critical} \) and shown in the table. The coded second-order mathematical model was given by the software as in Equation (8), where \( Y_3 \) is the BHG yield (%).

| Source            | DF |  \( F_{value} \) |  \( P_{value} \) | Result       |
|-------------------|----|------------------|------------------|--------------|
| Regression        | 5  | 16.74            | <0.001           | significant  |
| Linear            | 2  | 15.70            | 0.003            | significant  |
| Pressure          | 1  | 2.06             | 0.195            | insignificant|
| Temperature       | 1  | 29.34            | <0.001           | significant  |
| Square            | 2  | 20.48            | <0.001           | significant  |
| Pressure \( \times \) Pressure | 1 | 26.17            | <0.001           | significant  |
| Temperature \( \times \) Temperature | 1 | 20.07            | 0.003            | significant  |
| Interaction       | 1  | 11.34            | 0.012            | significant  |
| Temperature \( \times \) Pressure | 1 | 11.34            | 0.012            | significant  |
| Residual Error    | 7  |                  |                  |              |
| Lack-of-Fit       | 3  | 31.93            | 0.003            | significant  |
| Pure error        | 4  |                  |                  |              |
| Total             | 12 |                  |                  |              |

| Source | DF1 | DF2 |  \( F_{critical} \) |
|--------|-----|-----|---------------------|
| Fixed  | 2   | 7   | 4.74                |
| Fixed  | 1   | 7   | 5.59                |
| Fixed  | 3   | 4   | 6.59                |
When insignificant terms are removed, Equation (8) becomes

\[ Y_3 = 42.346 + 1.666 X_1 + 6.294 X_2 - 6.374 X_1^2 - 5.582 X_2^2 - 5.532 X_1 X_2 \]  

(8)

Furthermore, the \( R^2 \) of Equation (8) and \( R^2_{adj} \) of Equation (9) were determined to be 92.28% and 86.77%, respectively. Since the difference between \( R^2 \) and \( R^2_{adj} \) is 5.51%. This indicated that Equation (9) was an adequate approximation of the experiment. Fig. 6, which shows a plot of the predicted BHG yields and the corresponding experimental values, confirmed a fair agreement between the model and the experiment.

Furthermore, the surface plot presented the influence of both parameters, as displayed in Fig. 7. It could be found from this figure that at low-temperature, BHG yield increased with the pressure. Similarly, at low pressure, the yield increased with temperature. On the contrary, at high temperatures, the yield decreased as the pressure increased. At high pressure, the yield increased with temperature until a certain temperature value, after which the yield decreased. This phenomenon may be explained as follows. Normally severe conditions can crack large molecules of hydrocarbon substrate into light oil and gaseous products. However, the isomerization of long-chain hydrocarbons increased with pressure; thus, green-diesel yield increased. This hypothesis can be supported by Deily and Simakova (2008), who studied the catalytic activity of the VIII groups metals in the hydrogenation and hydrogenation by varying the ranges of temperature and pressure. They reported that a Pd-based catalyst could promote the highest catalytic activity in double bond isomerization of \( \alpha \)- and \( \beta \)-pinenes under high hydrogen pressure \(^{25}\). Nevertheless, the Minitab software predicted the optimal BHG yield of 44.21% at 516 °C and 4.8 MPa.

The regression models exhibited a lack of fit when they failed to adequately describe the functional relationship between the experimental parameters and the response variables. Although this study showed a significant level of lack-of-fit for all response variables due to the complexity of the reaction, the differences between \( R^2 \) and \( R^2_{adj} \) were at about 5%; hence it could be concluded that the models were sufficiently acceptable \(^{10,26}\).

In order to compare the results of this study with those of other researchers, the comparison was made and shown in Table 7. The comparison was made in terms of gasoline yield. It was found that the highest gasoline yield was that of this study. It should be noted that RBO seemed to have more advantages than other biological feedstocks in terms of BHG yield.

### 3.2 BHG properties

The distillation result of BHG produced from rice bran oil via hydrocracking reaction compared with the Standard Specification for Automotive Spark-Ignition Engine Fuel D4814 - 15a is illustrated in Table 8. The result demonstrated that each volumetric distillate portion was in line with the specifications. The maximum temperature was 200 °C at the endpoint of distillation, and only 1.8 mL of distillation residue was obtained.

Furthermore, other properties of BHG were also analyzed. Important physical, thermal, and chemical properties of BHG from RBO were compared with those.
of commercial gasoline, as demonstrated in Table 9. The results showed that the viscosity and density of BHG were much lower than the feedstock but comparable with those of commercial gasoline. It is important to note that hydrocracking improved the heat of combustion. The net heat of combustion of BHG was determined to be about 44.8 MJ/kg, which was higher than those of RBO and commercial gasoline. It is also important to note that the total acid value increased because the reaction broke the ester bond between glycerol and carboxyl groups, resulting in the free fatty acid being formed, thus increasing the value of total acid in the sample.

4. Conclusion

In this work, RBO was demonstrated as a potential substrate for producing BHG via hydrocracking. Pressure and temperature were found to play important roles in BHG yield and selectivity. The experimental data were used to obtain the regression models for predicting biofuel product yield, BHG selectivity, and BHG yield. The models were found to be sufficiently acceptable and predicted the optimal BHG yield and BHG selectivity to be 44.21% (516 °C, 4.8 MPa) and 69.74% (532 °C, 4.4 MPa), respectively.

Acknowledgment

This research project was supported by the Center for Alternative Energy Research and Development, Khon Kaen University under grant number DOL/2558, Research Fund of the Faculty of Engineering, Khon Kaen University, and Graduate School, Khon Kaen University, Khon Kaen, Thailand.

References
1) Lu, Y.; Hu, J.; Han, J.; Yu, F., J. Energy Inst., 89(4), 782 (2016)
2) Emori, E. Y.; Hirashima, F. H.; Zandonai, C. H.; Ortiz-Bravo, C. A.; Fernandes-Machado, N. R. C.; Olsen-Scaliante, M. H. N., Catal. Today, 279, 168 (2017)
3) Llamas, A.; Garcia-Martinez, M. J.; Al-Lal, A. M.; Canoira, L.; Lapuerta, M., Fuel, 102, 483 (2012)
4) Tye, C. T.; Looi, P. Y.; Meow, T. L., Adv. Mater. Res., 560-561, 538 (2012)
5) Hengst, K.; Arend, M.; Pfützenreuter, R.; Hoelderich, W. F., Appl. Catal. B Environ., 174-175, 383 (2015)
6) El Khatib, S. A.; Hanafi, S. A.; Barakat, Y.; Al-Amrousii, E. F., *Egypt. J. Pet.*, 27(4), 1325 (2018)
7) Huber, G. W.; O’Connor, P.; Corma, A., *Appl. Catal. A Gen.*, 329, 120 (2007)
8) Sankaranarayanan, T. M.; Banu, M.; Pandurangan, A.; Sivasanker, S., *Bioresour. Technol.*, 102(22), 10717 (2011)
9) Zullaikah, S.; Lai, C. C.; Vali, S. R.; Ju, Y. H., *Bioresour. Technol.*, 96(17), 1889 (2005)
10) Dujjanutat, P.; Neramittagapong, A.; Kaewkannetra, P., *Energies*, 12(16), 3196 (2019)
11) Verma, D.; Rana, B. S.; Kumar, R.; Sibi, M. G.; Sinha, A. K., *Appl. Catal. A Gen.*, 490(1), 108 (2015)
12) Anand, M.; Farooqui, S. A.; Kumar, R.; Joshi, R.; Kumar, R.; Sibi, M. G.; Singh, H.; Sinha, A. K., *Fuel Process. Technol.*, 151, 50 (2016)
13) Liu, Y.; Sotelo-Boyas, R.; Murata, K.; Minowa, T.; Sakanishi, K., *Energy and Fuels*, 25(10), 4675 (2011)
14) Kiatkittipong, W.; Phimsen, S.; Kiatkittipong, K.; Wongsakulphasatch, S.; Laosiripojana, N.; Assabumrungrat, S., *Fuel Process. Technol.*, 116, 16 (2013)
15) Dujjanutat, P.; Neramittagapong, A.; Kaewkannetra, P., *Defect Diffus. Forum*, 364, 104 (2015)
16) Chowdhury, K.; Banu, L.; Khan, S.; Latif, A., *Bangladesh J. Sci. Ind. Res.*, 42(3), 311 (1970)
17) Ferris, A. M.; Rothamer, D. A., *Fuel*, 182, 467 (2016)
18) Quality Engineering Software | JMP, https://wwwjmp.com/en-au/offers/quality-engineering-software.html?gclid=Cj0KCQjwytOEBlhD5ARIsAAnnRjVjSr0gD3oKglMEy9UVXj5PX1xuodNae1FSk94jzWbDIOziEnmQoaApYaEALw_web, (accessed: May 7, 2021)
19) Li, F.; Marks, D. W.; Larock, R. C.; Otaigbe, J. U., *Polymer (Guildf)*, 41(22), 7925 (2000)
20) Li, F.; Larock, R. C., *J. Polym. Environ.*, 10(1–2), 59 (2002)
21) Xia, Y.; Larock, R. C., *Green Chem.*, 12(11), 1893 (2010)
22) Meiorin, C.; Aranguren, M. I.; Mosiewicki, M. A., *Eur. Polym. J.*, 67, 551 (2015)
23) Cheng, J.; Li, T.; Huang, R.; Zhou, J.; Cen, K., *Bioresour. Technol.*, 158, 378 (2014)
24) Dujjanutat, P.; Kaewkannetra, P., *Renew. Energy*, 147, 464 (2020)
25) Deliy, I. V.; Simakova, I. L., *Russ. Chem. Bull.*, 57(10), 2056 (2008)
26) Suwannaruang, T.; Rivera, K. K. P.; Neramittagapong, A.; Wantala, K., *Surf. Coatings Technol.*, 271, 192 (2015)