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# Production of Bio-Gasoline with High Octane Number, as a Renewable Transportation Biofuel, via Thermochemical Conversion of Castor Oil

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## ABSTRACT

Vegetable oils are proved as valuable feedstocks in the biofuel production. Some common issues of cracking of vegetable oils—as an effective method for the biofuel production—are related to the glycerol decomposition during the cracking process. Transesterification, which can remove glycerol from vegetable oil molecules, is performed before the thermal cracking to adjust the problems. This study has been aimed at surveying the efficiency of transesterification and the thermal cracking integration to produce bio-gasoline and bio-oil from castor oil. In transesterification, methanol as alcohol and KOH as catalyst were used, and the catalyst concentration, reaction temperature, and alcohol to oil ratio were effective variables. Statistical studies demonstrated the interactions among parameters and the yield of the methyl ester production as 96.7 % under the optimized conditions. Results showed that in the thermal cracking two parameters, of the feed flowrate and temperature, influenced the product yield significantly without any interaction. Under the optimum conditions, to maximize the bio-gasoline production, 28 % of bio-gasoline and 88.6 % of bio-oil were produced. The lack of acrolein, as a toxic component, the negligible amount of the generated water in the product, the high octane number, the significant amount of the heat of combustion of bio-gasoline, and being in criteria of standard gasoline as per ASTM D4814 for the distillation curve and RVP of bio-gasoline, were the great advantages of the cracking of the transesterified castor oil. Therefore, the bio-gasoline produced via the thermochemical conversion of castor oil could be used as a fuel for spark-ignition engines or as an octane enhancer with gasoline, i.e., by adding 10 % of bio-gasoline to the refinery gasoline, the octane number increased from 95 to 105.

## 1. Introduction

The supply of fossil fuels will be limited in the future, and this is aside from the associated environmental pollution caused by using these fuels. These drawbacks spurred the search to find alternative renewable fuel

sources like biofuels. Biofuel, a gaseous or liquid fuel, can be generated from the biomass substrates and is consumed as a transportation fuel. Triglycerides (TG) derived from vegetable oils or animal fats have the potential to be a suitable source for the

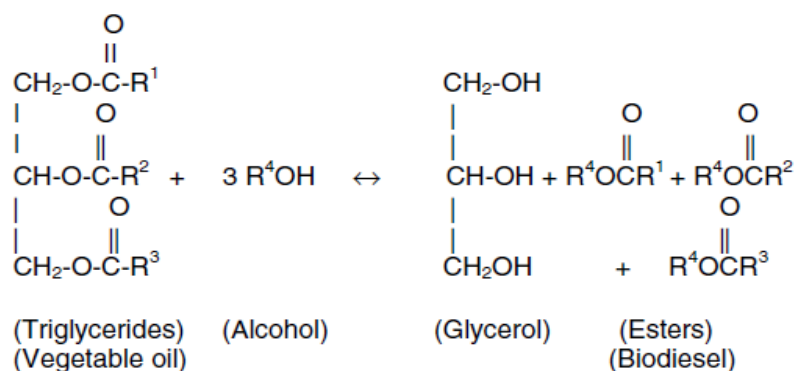
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biofuel production due to their linear chain and similar structure to that of the linear hydrocarbons [1, 2].

One of the known methods to convert TG to biofuel is cracking or pyrolysis [3, 4]. The pyrolysis of TGs involves the biomass decomposition at high reaction temperatures (400–700 °C) without injecting air into the feed. The biofuel production through this process can be achieved in the cracking unit of existing petroleum refineries, with minor modifications [5]. The advantages of pyrolysis include the fact that it is simple and inexpensive to execute [6]. The disadvantages of TG pyrolysis mainly relate to the glycerol decomposition which results in the production of rather reactive chemicals [4], acrolein (a

very toxic component) [7, 8], and considerable water content of the liquid product [1, 9, 10]. Therefore, removing glycerol from the backbone of TG before the thermal cracking seems to be essential for removing the aforementioned drawbacks. Transesterification is an efficient method for this purpose.

Transesterification is a reaction that converts an ester into another ester by means of alcohol. This reaction leads to the separation of glycerol. Transesterification can be done via a catalytic or non-catalytic reaction which is mainly named supercritical transesterification [11, 12]. The following figure illustrates the transesterification of TG.



**Figure 1.** Transesterification reaction [13].

The cracking of TG also produces more residues in comparison to that of the FAME (fatty acid methyl ester), which is the product of TG transesterification with methanol. Due to TG fatty acids bonding with glycerol subsequently, the coke deposition occurs and the drop in pressure increases during the reaction. In this study, transesterified castor oil was used instead of the initial castor oil for the separation of glycerin from triglycerides.

The FAME starts to decompose at 270 °C and the molecules with higher thermal stability, like more saturated molecules and

shorter chain length, postpone the decomposition to higher temperatures [14, 15]. Pyrolysis at a high temperature with a short residence time yields alkanes, alkenes, and also unsaturated fatty acid methyl esters with a few aromatics [16]. However, pyrolysis at a low temperature and longer residence time and accompanied by a catalyst yields decarboxylation reaction [16]. Unlike TGs, FAMEs do not result in remarkable amounts of fatty acids in the thermal cracking process [17].

Roy et al. used castor seed oil to synthesize

biodiesel with the catalyst of potassium promoted lanthanum oxide. 97.5 % conversion of castor oil resulted at the transesterification reaction at the temperature 65 °C, time of 150 min and the methanol to oil ratio of 16:1. Although the homogeneous catalysts are commonly used in transesterification, the heterogeneous catalyst of K promoted  $\text{La}_2\text{O}_3$  has been used in this research. Roy et al. investigated the kinetics and thermodynamics of the reaction, and their study showed 47.13 kJ/mol of the energy of activation [18].

Roman-Figueroa et al. evaluated the supercritical (non-catalytic) transesterification of castor oil by methanol. The highest yield of FAMES was 96.5 % in 300 °C, 90 min, and 21 MPa and in that state, FAMES were not thermally decomposed. The consumption of high alcohol (43-mole of alcohol to 1-mole of oil) has been the drawback of this research [19].

The thermal cracking of transesterified vegetable oils like canola oil and soybean oil was developed by Luo et al. in a single study, using a batch reactor at the high temperature and pressure, for the production of bio-jet fuel [16, 17]. The liquid product yielded 72-86 wt % of methyl esters but the production of acrolein and water was not investigated.

The previous researches of the thermal cracking mainly focused on the biodiesel production whereas the study on the bio-gasoline production has rarely been done. Likewise, the production of acrolein and water, which is the drawback of the TG cracking, has not been investigated in literatures [20, 21]. The process of the thermal cracking to upgrade FAME has never been considered. In addition, all of experiments in literatures have been evaluated with the classical method, consequently, it has

been neglected to investigate the interaction of parameters.

This research was designed to study the applicability of cracking transesterified vegetable oils as a new path of producing biofuels to remove the drawbacks of TG cracking (the production of acrolein and water) and also this study aimed to produce bio-gasoline with appropriate properties. The comprehensive investigation of the transesterification reaction proves the value of this work. In this study, castor oil, which is one of the main sources of TG for the biofuel production in Iran and has seldom been investigated in the previous researches, has been opted as the feed [22]. Castor oil methyl ester was used for the thermal cracking aimed at the production of bio-gasoline and the evaluation of the acrolein and water production. In addition, the mathematical models were introduced for each stage to explain the relationships between parameters and the outcome. Ultimately, the process was optimized.

## **2. Materials and methods**

### **2.1. Materials**

Purified castor oil was bought from market in Tehran and was used in the esterification and thermal cracking processes. The analysis of fatty acids of the oil was done by the GC model Perkin Elmer-Clarus 580 and the BPX-BIOD5 column with FID detector. Methanol with 99 % purity has been provided by Dr. Mojalali Company and sodium methoxide of 95 % has been purchased from Fluka Company (St. Gallen, Switzerland). KOH and phenolphthalein have been obtained from Merck Company [20].

### **2.2. Transesterification and thermal cracking apparatus**

The transesterification was done in a batch reactor. For the reaction, the mixture of methanol, as an alcohol, KOH, as a homogeneous catalyst, and castor oil, before being fed to the reactor, was heated to reach the reaction temperature. The temperature of the reaction was controlled by a thermometer and at the end of the time for terminating the reaction, the products were put in the cold bath and ultimately methyl ester as the product was separated.

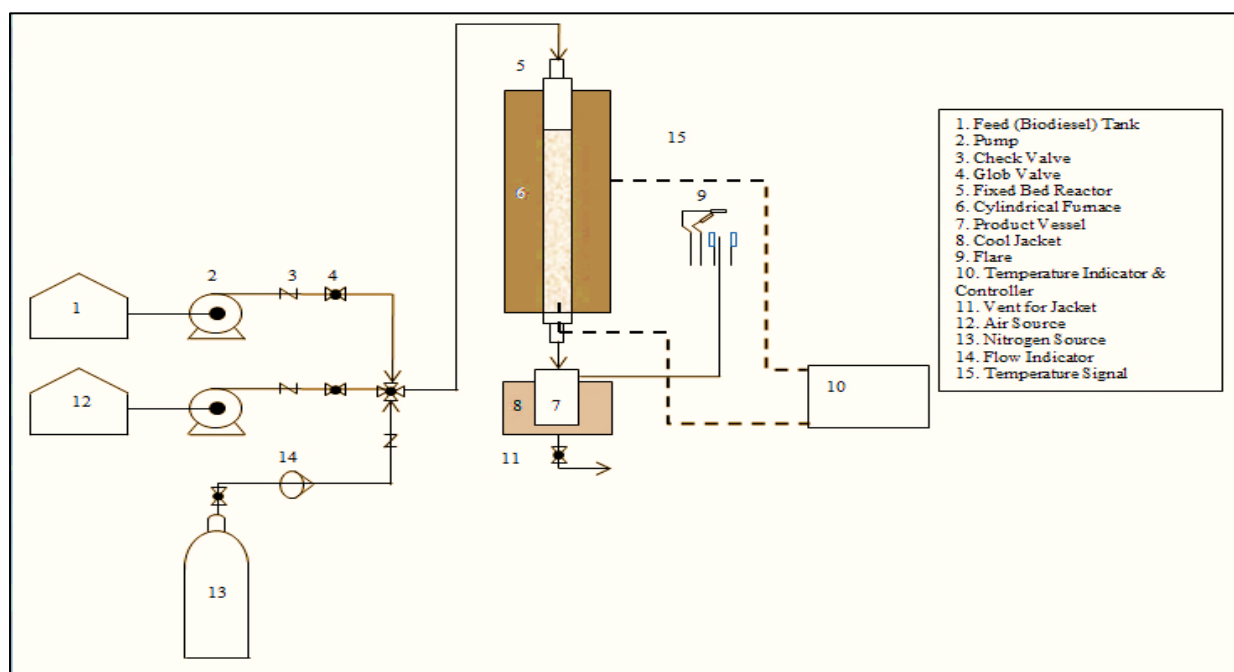
The schematic diagram for the apparatus, designed for the thermal cracking of castor methyl esters, is shown in Figure 2. The reaction system consists of a cylindrical reactor made of quartz with a volume of  $210 \text{ cm}^3$ . The reactor was heated to the desired temperature by means of an electrical cylinder furnace surrounding it and then the methyl esters were fed to the reactor from the top end. Nitrogen has been flown to the reactor as an inert gas during the heating

process. One dispenser uniformly distributed the feedstock through the reactor. The gaseous products of the reactor were injected into a collecting container equipped with an ice jacket. Consequently, non-condensable gas was separated from the condensable fractions, and this gas was passed out via a flare. Ultimately, liquid product was collected in the container.

The distillation of bio-oil was done based on the ASTM D86 to segregate it into three cuts like below:

- Bio-gasoline (IBP-160 °C)
- Green diesel (160-350 °C)
- Heavy bio-oil (more than 350 °C)

Data about the green diesel was summarized in the previous survey [20]. In the first pretests, the amount of formed coke was very low and negligible. Therefore, the coke was ignored for mass balance, and the feed led to liquid and gaseous products.



**Figure 2.** Schematic diagram of the thermal cracking apparatus.

### 2.3. Experimental design

The statistical design of experiments removes

the systematic errors and reduces the number of tests to its minimum [23]. For a statistical

model being generated, prior knowledge related to the process is required. In the experimental design, firstly, the experiments are designed statistically. Then, a mathematical model is introduced to predict the response. Finally, the model's applicability is analyzed.

In this study, the experiments were divided into two parts; the transesterification and thermal cracking. In the preliminary experiments of transesterification, the effects of the reaction time and stirrer RPM have been investigated and since they did not affect the results, they have been fixed (one hour reaction time and 500 RPM) for all of the experiments. According to literatures, only the reaction temperature (25-45 °C), catalyst concentration (0.5-2 % wt/wt of oil), and alcohol to oil ratio (5-10) have been used to analyze the experimental design using the Box-Behnken method [19, 20, 24]. The dependent response in these experiments has been the yield of methyl ester production.

In the thermal cracking step, the experiments were done in a central composite design with two response variables including yields of bio-gasoline and bio-oil. Based on literatures and primary experiments, the ranges for the effective parameters were designed. Cracking temperature (457-493 °C which in the  $-\alpha$  and  $+\alpha$  is 450-500 °C) and feed flow rate (23-37 g/h which in the  $-\alpha$  and  $+\alpha$  is 20-40 g/h) were the independent variables, and each was considered at five levels. The experiments were done in a random order. The experiment in the central point was repeated five times for the sake of the reproducibility.

As a result, 13 experiments were carried out with 8 experiments in the factorial points and 5 tests in the central points. In order to conduct a precise analysis of the thermal

cracking process, 2 dependent responses, which were yield of bio-gasoline and yield of bio-oil, were investigated. Likewise, the amount of gaseous products can be calculated by mass balances.

#### 2.4. Statistical analysis

To study the relationships between the variables and responses, a quadratic regression model was utilized. The design-Expert 7.0.0 software was used for the estimation of the polynomial coefficients, resulted from the least square fitting method. The quadratic polynomial is generally represented as:

$$Y = a_0 + \sum_{i=1}^2 a_i X_i + \sum_{i=1}^2 \sum_{j=1}^2 a_{ij} X_i X_j \quad (1)$$

In this equation, Y is the response;  $a_0$ ,  $a_i$ , and  $a_{ij}$  are the polynomial coefficients;  $X_i$ , and  $X_j$  indicate design variables [25].

The results were analyzed through the analysis of variance<sup>1</sup> with the design-Expert 7.0.0 software. Then, three-dimensional surface plots were created using the fitted quadratic model obtained from the regression analysis. From these plots, the effect of parameters on responses has been evaluated and the optimum combinations of reaction parameters were analyzed.

#### 2.5. Analytical method

Karl-Fischer method was used for the investigation of bio-oil water content. The bio-gasoline fraction was characterized and compared with the standard motor gasoline according to ASTM D4814. Different methods, used for analyzing each property of the bio-gasoline, are shown in Table 10. For measuring the octane number, Octane Tester SHATOX SX-200 was used. The precise

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<sup>1</sup> ANOVA

composition of bio-gasoline was characterized by GC-MS analysis. The search program of NIST Ms Spectral was used as the reference for the identification of species. Helium (1 ml/min), a carrier gas, was used in the instrumentation. The column oven was heated with a program of 5 °C/min. The detectors of mass spectrometry utilized Ion Trap ionization in the mass analysis with the scanning capability ranging from 10 to 500 m/z. Also, the VARIAN Capillary Column (30 m length and 0.25 mm diameter) was used. The program of changing the temperature started at 40 °C and continued with an increase of 5 °C/min to the final temperature (250 °C), then remained at that temperature for 20 min. Ultimately, the product was identified by means of matching the retention time with the standard.

### 3. Results and discussion

**Table 1**

Results of the production of methyl ester from castor oil.

Run	Temperature (°C)	Catalyst concentration % wt/wt of oil	Alcohol/oil molar ratio	Reaction conversion % wt/wt of oil
1	35	2	10	81.46
2	45	1.25	5	89.85
3	25	0.5	7.5	79.3
4	35	1.25	7.5	88.1
5	25	1.25	5	83.82
6	45	0.5	7.5	74.7
7	25	1.25	10	82.22
8	45	2	7.5	88.16
9	35	1.25	7.5	90
10	25	2	7.5	82.05
11	35	2	7.5	89
12	35	1.25	7.5	88.5
13	35	2	5	90.03
14	35	0.5	5	77.87
15	35	0.5	10	79.75
16	45	1.25	10	82.71
17	35	1.25	7.5	87

The response surface methodology was used for the investigation of results and those

#### 3.1. Model and ANOVA

Results of the experiments for the production of methyl ester are in Table 1. Although the maximum yield of transesterification for different oils occurs around the alcohol boiling point (60 °C), in this study the temperature of maximum yield is 35 °C, which is the advantage of castor oil in the biofuel production because of the lower energy consumption. As it is shown in Table 1, the alcohol ratio and catalyst concentration in the maximum yield of methyl ester are 5 and 2 % wt/wt of oil respectively.

In this design, the fractional points (+1 and -1) are 45 °C and 25 °C for temperature, 2 and 0.5 for catalyst concentration, and 10 and 5 for the molar ratio of alcohol/oil. The central points (0) for the temperature, concentration of catalyst, and alcohol/oil ratio are 35 °C, 1.25, and 7.5 respectively [25].

results were fitted into an equation accurately. ANOVA for the quadratic model was



performed at a 95 % level of confidence to establish its significance (Table 2). The F-value of 30.46 and p-value of less than 0.05 for the model demonstrate the significance of it [25].

In this case, all three parameters are significant model terms. Likewise, there are interactions among variables that the classic method can not be used for designing of experiments in methyl ester production.

**Table 2**

Analysis of the variance for the methyl ester yield model.

Source	S.O.S.	D.F.	M.S.	F Value	p-value	Prob > F
Model	362.53	9	40.28	30.46	< 0.0001	Significant
X <sub>1</sub> -temperature, °C	8.06	1	8.06	6.09	0.0429	
X <sub>2</sub> -catalyst concentration, % wt/wt of oil	113.10	1	113.1	85.54	< 0.0001	
X <sub>3</sub> -molar ratio of alcohol to oil	29.76	1	29.76	22.5	0.0021	
X <sub>1</sub> X <sub>2</sub>	28.67	1	28.67	21.68	0.0023	
X <sub>1</sub> X <sub>3</sub>	7.67	1	7.67	5.8	0.0468	
X <sub>2</sub> X <sub>3</sub>	27.3	1	27.3	20.64	0.0027	
X <sub>1</sub> <sup>2</sup>	27.32	1	27.32	20.66	0.0026	
X <sub>2</sub> <sup>2</sup>	101.92	1	101.92	77.08	< 0.0001	
X <sub>3</sub> <sup>2</sup>	7.36	1	7.36	5.56	0.0503	
Residual	9.25	7	1.32			
Lack of Fit	4.34	3	1.44	1.18	0.4220	Not significant
Pure Error	4.9	4	1.22			
Total	371.78	16				

S.O.S.: Stands for Sum of Squares  
D.F.: Stands for Degree of Freedom  
D.F.: Stands for Degree of Freedom

Experimental results of methyl ester yield were fitted to Eq. 2 (coded factors) and Eq. 3 (actual factors).

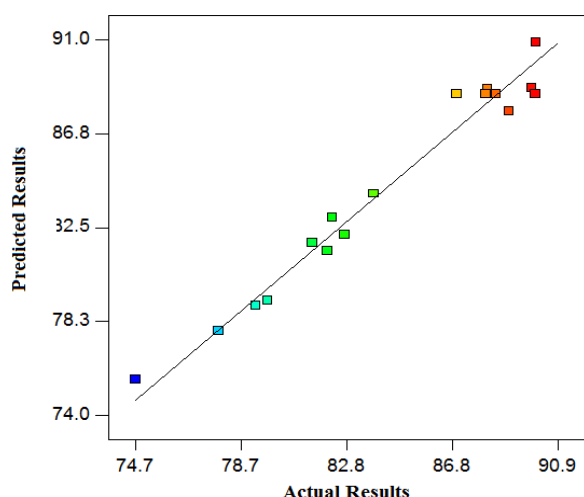
$$Y = 88.52 + X_1 + 3.76 X_2 + 1.93 X_3 + 2.68 X_1 X_2 - 1.39 X_1 X_3 - 2.61 X_2 X_3 - 2.55 X_1^2 - 4.92 X_2^2 - 1.32 X_3^2 \quad (2)$$

$$Y = 14.128 + 1.919T + 24.088C + 6.310 A + 0.357 TC - 0.055 TA - 1.393 CA - 0.0262T^2 - 8.365C^2 - 0.227A^2 \quad (3)$$

In Eq. 2, the parameters are in code as +1 for the maximum levels and in code as -1 for the minimum levels. In Eq. 3, the amount of each variable is in its original units.

In Eq. 2, X<sub>1</sub>, X<sub>2</sub>, and X<sub>3</sub> are temperature, catalyst concentration, and the alcohol to castor oil ratio respectively. In Eq. 3, T is the reaction temperature (°C), C denotes the catalyst concentration, (% wt/wt), and A is the alcohol to castor oil molar ratio.

The statistical model is verified by the verification curve (Figure 3). This figure compares the amount of the experimental transesterification with its predicted amount via the statistical model. As it is seen in Figure 3, the points are scattered along the diagonal line, which is an indication of plausible fitting for experimental results [25].



**Figure 3.** Actual vs. predicted results for transesterification.

The thermal cracking of castor methyl ester produced bio-oil separated into three fractions

namely: bio-gasoline, green diesel, and heavy bio-oil. Table 3 summarizes bio-gasoline and bio-oil yields at different cracking temperatures and feed flow rates. Results showed that bio-oil yield was ranged from 80 to 93.6 wt % of the feedstock. The bio-gasoline yield ranged from 21.2 % to 29 %.

In these experiments, the axial points (+ $\alpha$  and - $\alpha$ ) are 500 °C and 450 °C for the temperature and 40 g/h and 20 g/h for the flow rate. The fractional points (+1 and -1) are 493 °C and 457 °C for the temperature and 37 g/h and 23 g/h for the flow rate. Ultimately, the center points (0) are 475 °C and 30 g/h for the temperature and flow rate respectively [25].

**Table 3**

Experimental design and product distribution of the thermal cracking.

Experiment number	Feed flow (g/h)	Reaction temperature, °C	Yield of bio-oil (%)	Yield of bio-gasoline (%)
1	23	457	89.1	23.4
2	30	500	82	23.7
3	37	457	93.6	21.6
4	20	475	87	25.4
5	37	493	86.5	23.8
6	30	450	92.3	21.2
7	40	475	92.9	23.5
8	23	493	80	24.7
Center point				
1	30	475	89.37	28.1
2	30	475	88.9	27.6
3	30	475	87.1	29
4	30	475	88.7	28.6
5	30	475	88.6	28.4

Experimental data were fitted to polynomial equations to quantify the relationship of the response with independent variables. ANOVA analysis revealed that experimental data were fitted well into an equation. The quadratic model for the production of bio-gasoline through the thermal cracking of methyl esters in terms of coded (Eq. 4) and

actual (Eq. 5) factors are as follows. Table 4. shows the ANOVA analysis of the bio-gasoline yield model.

P-value is a sign to indicate the model terms are significant. A P-value < 0.05 shows that the term is significant. The F-value of 106.27 and p-value of < 0.0001 for the model prove the significance of it. The P-value of both

reaction parameters ( $X_1$  and  $X_2$ ) and their quadratic effects ( $X_1^2$  and  $X_2^2$ ) revealed they were significant and the interaction between

reaction parameters ( $X_1X_2$ ) did not have a significant influence on the response.

**Table 4**

Analysis of the variance for the bio-gasoline yield model.

Source	S.O.S.	D.F.	M.S.	F value	p-value Prob > F	
Model	87.91	5	17.58	106.27	< 0.0001	Significant
$X_1$ -temperature, °C	6.06	1	6.06	36.62	0.0005	
$X_2$ -flow, g/hr	3.67	1	3.67	22.17	0.0022	
$X_1X_2$	0.20	1	0.20	1.23	0.3039	
$X_1^2$	60.78	1	60.78	367.36	< 0.0001	
$X_2^2$	26.30	1	26.30	158.99	< 0.0001	
Residual	1.16	7	0.16			
Lack of fit	0.010	3	0.003	0.01	0.9979	Not significant
Pure error	1.15	4	0.29			
Total	89.07	12				

The pure errors and residual errors are compared by “Lack of Fit”. The P-value > 0.05 proves the lack of fit is not significant, thereby, the mathematical model is significant. The p-value of 0.9979 for Lack of Fit indicates this parameter is not significant regarding the pure error. In other words, the model fitted well with the experimental data of bio-gasoline yields.

The regression coefficient ( $R^2$ ) and adjusted regression coefficient ( $R^2_{\text{adjusted}}$ ) are used to analyze the accuracy of the model. These coefficients are positive and less than 1, and their proximity to 1 demonstrates the acceptable approximation of the model and response. The obtained  $R^2$  and  $R^2_{\text{adjusted}}$  values for the response were  $R^2=0.9875$  and  $R^2_{\text{adjusted}}=0.9786$ .

Through the determined coefficients, quadratic polynomial regression models of bio-gasoline were obtained:

$$Y = -2135.6 + 8.981 X_1 + 1.38 X_2 + 0.0018 X_1X_2 - 0.00946 X_1^2 - 0.0389 X_2^2 \quad (4)$$

$$Y = 28.34 + 0.88T - 0.67F + 0.23TF - 2.96 T^2 - 1.96 F^2 \quad (5)$$

In Eq. 4,  $X_1$  and  $X_2$  are the temperature and feed flow rate respectively. In Eq. 5, T is the temperature (°C) and F is the feed flow rate (g/hr).

Experimental results of the bio-oil (like bio-gasoline) were fitted into the quadratic equation (Eq. 6 and Eq. 7).

As it is mentioned, a p-value < 0.05 confirms the significance of the model. Based on Table 5, the ANOVA for the bio-oil yield, a p-value of the model is <0.0001, therefore, the introduced model for the bio-oil yield is highly significant. Although the linear terms of the temperature and flow rate significantly affect the bio-oil yield, there is no interaction between them.

$$Y = -482.47 + 2.728X_1 - 2.028X_2 + 0.004X_1X_2 - 0.003X_1^2 + 0.008X_2^2 \quad (6)$$

$$Y = 88.53 - 3.85 T + 2.42 F + 0.5 TF - T^2 + 0.4 F^2 \quad (7)$$

In Eq. 6,  $X_1$  and  $X_2$  are the temperature and feed flow rate respectively. In Eq. 7, T is the temperature (°C) and F is the feed flow rate

(g/hr). In Eq.6, the largest absolute coefficient for variables is for  $X_1$ , which means the temperature has the highest influence on the bio-oil yield.

$R^2=0.9602$  and  $R^2_{adjusted}=0.9317$  prove the

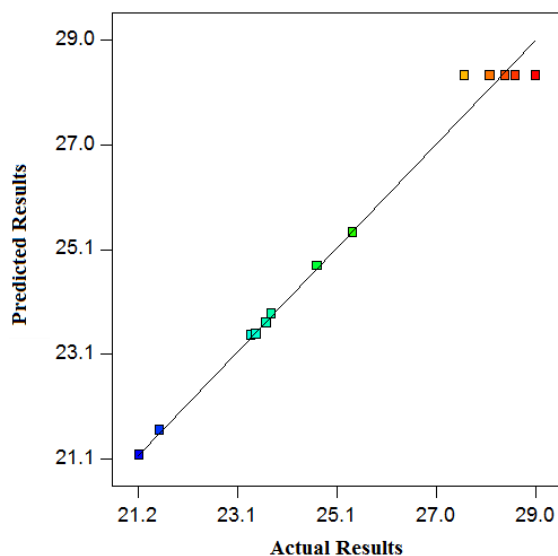
accuracy of the mathematical model for the bio-oil yield. On the other hand, the p-value of 0.2629 for lack of fit is another reason for the significance of the model for the bio-oil yield.

**Table 5**

Analysis of the variance for the bio-oil yield model.

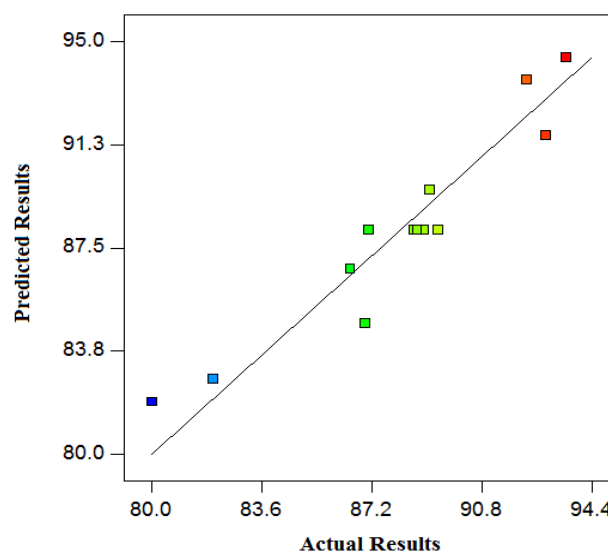
Source	S.O.S.	D.F.	M.S.	F value	p-value	Prob > F
Model	175.1	5	35.02	33.57	< 0.0001	Significant
$X_1$ -temperature, °C	118.32	1	118.32	113.42	< 0.0001	
$X_2$ -flow, g/hr	46.77	1	46.77	44.83	0.0003	
$X_1X_2$	1	1	1	0.95	0.3601	
$X_1^2$	7.07	1	7.07	6.78	0.0352	
$X_2^2$	1.06	1	1.06	1.02	0.3457	
Residual	7.3	7	1.04			
Lack of fit	4.34	3	1.44	1.95	0.2629	Not significant
Pure error	2.96	4	0.74			
Total	182.4	12				

Verification curves, illustrated as follows, verify the statistical models for bio-gasoline and bio-oil.



**Figure 4.** Actual vs. predicted results for bio-gasoline.

The non-significant lack of fit, highly significant model, and acceptable fitting for verification curves all confirm the statistical models of this study.



**Figure 5.** Actual vs. predicted results for bio-oil.

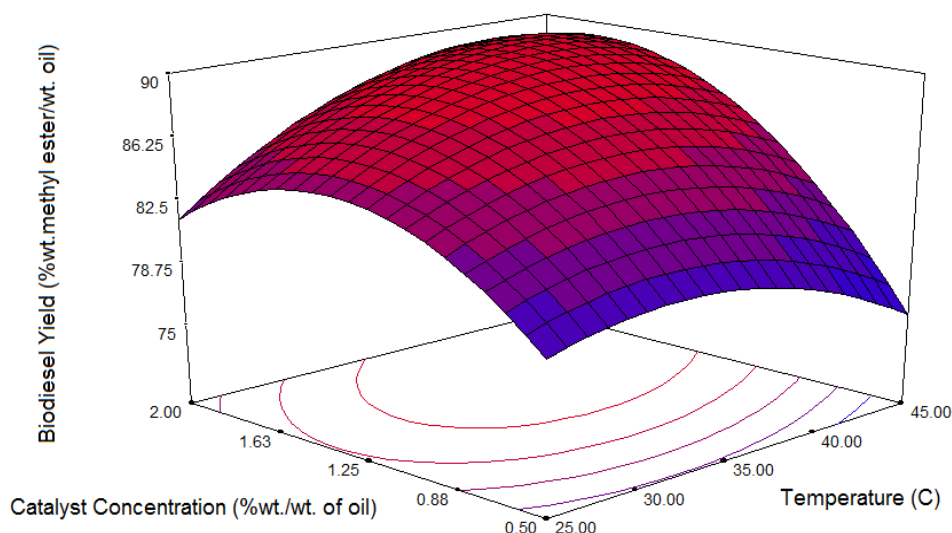
### 3.2. Effects of reaction parameters

The influence of parameters on the yield of transesterification was evaluated in the Figures 6, 7, and 8. Figure 6 illustrates the effects of the temperature and concentration of catalyst on the yield while the ratio of alcohol/oil is 7.5.

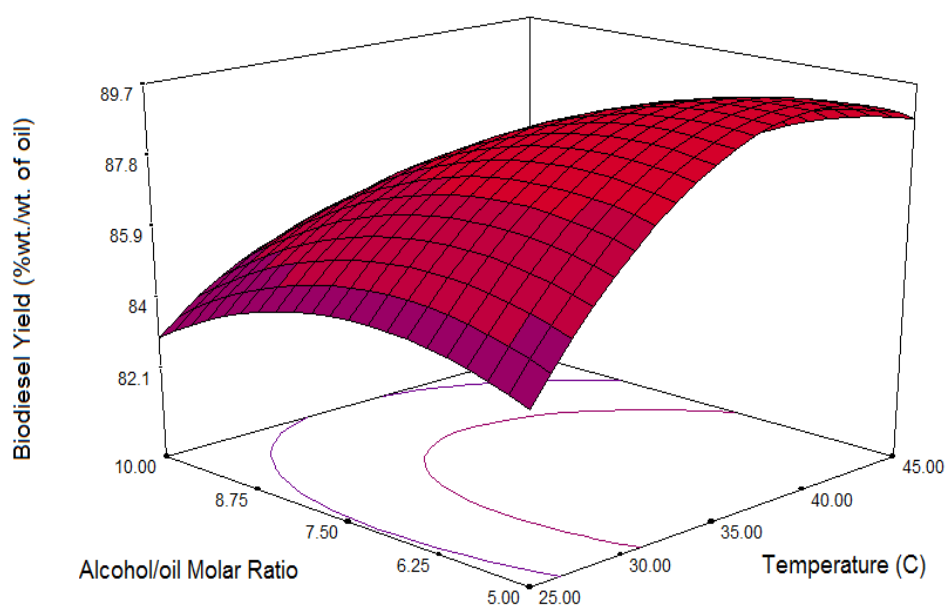
A major part of castor oil is formed by Ricin oleic acid, which can be solved in the

methanol due to its hydroxyl bond in the chain of hydrocarbon. The solubility of castor oil, in comparison with other oils, in methanol contributes to the well-doing of reaction in

the low temperature [24]. In addition to the reaction of the production of methyl ester, other side reactions like the saponification reaction are being done [26].



**Figure 6.** Methyl ester yield response surfaces (the molar ratio of alcohol/oil=7.5).



**Figure 7.** Methyl ester yield response surfaces (the catalyst concentration of 1.26 % wt/wt of oil).

According to Figure 6, in the high catalyst concentration, with the rise of temperature, the yield of reaction increases. While in the low catalyst concentration with the increase in temperature after 40 °C, the yield declines

because of the selectivity reduction for transesterification against saponification. The transesterification reaction is endothermic and reversible, therefore the growth of temperature will enhance the production of

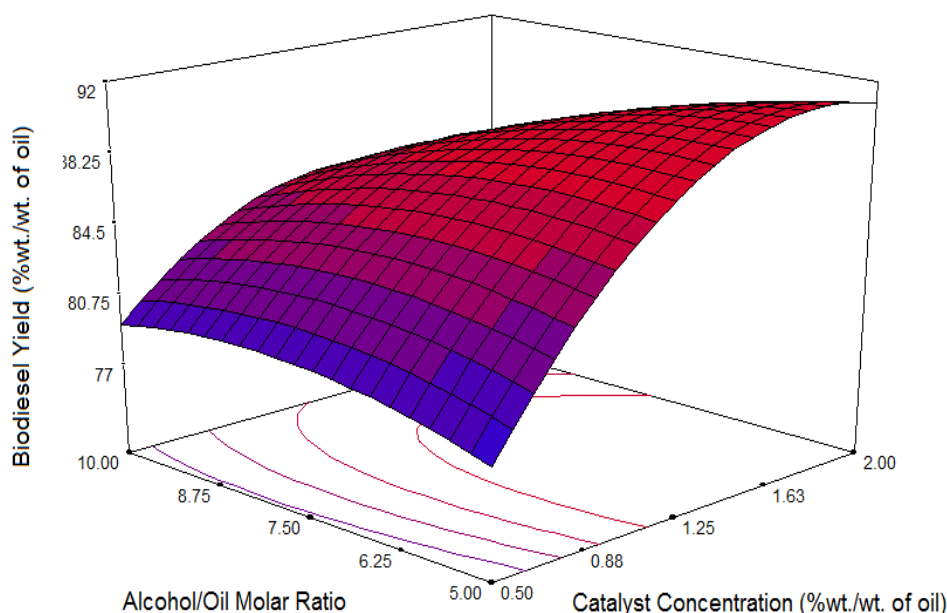
methyl ester [1]. When the concentration of the catalyst is low, in the competition of reactions, the rise of temperature leads to a higher rate of saponification, consequently, the yield declines. In other words, with the reduction of the catalyst concentration and increase in temperature, more saponification than transesterification is done.

Figure 7 indicates the effects of temperature and the ratio of alcohol/oil on the yield under the condition that the catalyst concentration is 1.26 % wt/wt.

Based on Figure 7, in the low molar ratio, the rise of temperature increases the yield of

the reaction. While in the high molar ratio, first, the increase in temperature has an additive influence on the yield and then reduces it. In other words, in the presence of excessive amounts of alcohol in the reactor, the increase in temperature plays a negative role in the yield of the reaction.

The interaction between temperature and the molar ratio has a negative effect and this indicates that in the high temperature and molar ratio, the selectivity of transesterification and of the methyl ester yield reduces.



**Figure 8.** Methyl ester yield response surfaces (Temperature = 35 °C).

Transesterification is an equilibrium reaction, and based on Le Chatelier's principle, with the rise of the alcohol/oil ratio, the methyl ester yield should grow [1]. But ricin oleic acid in castor oil, which has a hydroxyl group (OH), with the creation of a hydrogen bond, destroys castor oil and glycerol. When there is more alcohol than its stoichiometric ratio in the reaction, the extra alcohol causes the spoilage of alcohol in the generated glycerol and ultimately leads to the

reversibility of the reaction, as the result of Roy et al. study verifies it [23].

In Figure 10 the temperature is 35 °C and the effects of the catalyst concentration and the ratio of alcohol to oil on the yield are shown. As it can be understood from this figure, the rise of the catalyst concentration in the reaction is more effective when the molar ratio of alcohol/oil is low in comparison with the state of a high molar ratio.

While the alcohol/oil ratio is low, the

increase in the concentration of catalyst plays a positive role in the yield. But this rise is less effective when the alcohol/oil ratio is high. The plausible reason for this event might be the destructive influence of the high alcohol/oil molar ratio existing in the transesterification.

In the thermal cracking section, increasing the cracking temperature and decreasing the feed flowrate lead to severe thermal cracking conditions and more molecular decomposition. More cleavage of bonds and shortening the chains lead to the production of lighter fractions, like gasoline and gas. On the other hand, decreasing the feed flowrate (meaning increasing the residence time) can favor polymerization or addition reactions which lead to the production of heavier fractions [28]. Therefore, it is expected to produce more light fractions by increasing the temperature of cracking.

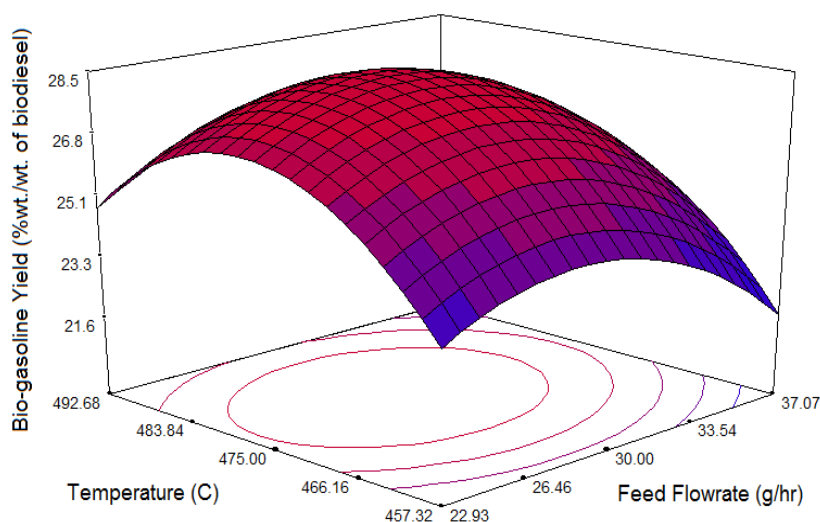
The response surface of the bio-gasoline yield, created by polynomial fitting is shown in Figure 9.

The light fractions of the methyl ester thermal cracking laid in the bio-gasoline cut. It means the cracking of methyl ester molecules, occurred in the range of 450 °C to

500 °C. This finding is verified by Seames et al. that proves the light fractions are generated in the range of 400 °C to the boiling point of the mixture [29].

According to Figure 9, the yield of bio-gasoline has steadily increased with the rise of temperature from 457 °C to 478 °C and then has declined. The rise of temperature to 478 °C, strengthens the severity of the cracking and enhances the light fractions that are included in the bio-gasoline cut. The negative influence of the temperature rising after 478 °C might be attributed to the generation of too light molecules, separated from the liquid as the non-condensable gas and reduce the yield of bio-gasoline. This negative effect at this temperature range is properly confirmed by Koul et al.[30].

The feed flow rate, like temperature, influences the yield. On the one hand, the reduction in the feed flow (an increase in the residence time) with the production of light fractions boosts the bio-gasoline yield. On the other hand, if the feed flow rate is lower than approximately 29 g/hr, it would increase the production of non-condensable gas, thereby, the bio-gasoline yield will diminish.



**Figure 9.** Bio-gasoline yield response surfaces.

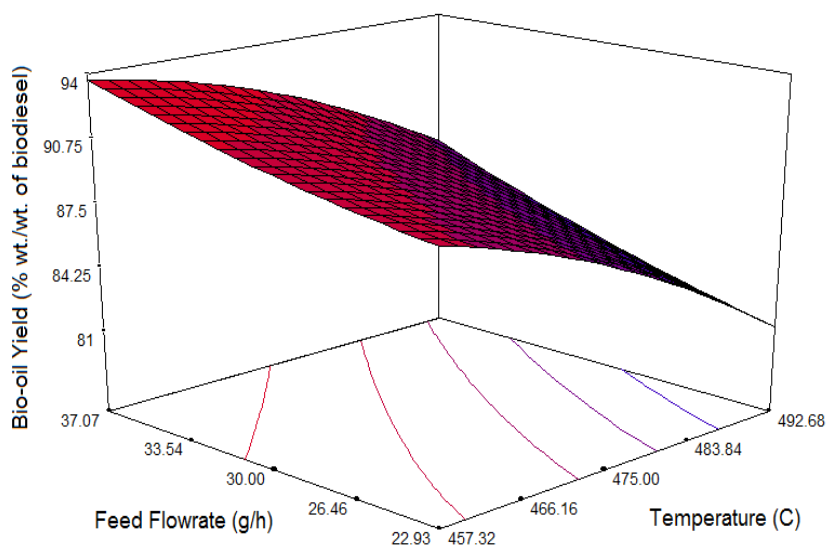


Figure 10. Bio-oil yield response surfaces.

For the bio-oil as the product of the thermal cracking, the response surface of the bio-oil yield is illustrated in Figure 10. Based on this figure, the rise of temperature in this range has decreased the bio-oil yield. When the temperature increases, the more molecules are cracked and more molecules are converted into the non-condensable gases and this result is verified by the result of Bridgwater studies [31].

In the feed flow rang, the increase of the feed flow enlarged the yield of bio-oil. The rise of the feed flow leads to the decline in the residence time. Thereby, the cracking of molecules is reduced and the fewer molecules are converted into the non-condensable gases

which grow the yield of the bio-oil.

### 3.3. Process optimization

A numerical method was chosen for the optimization of reaction parameters. In the transesterification step, the yield as a target was set to maximum. The criteria for optimization are in Table 6.

The optimized condition introduced by the software was the temperature = 47 °C, the catalyst concentration = 2 % wt/wt, and the molar ratio of alcohol to oil = 3, which led to the 96 % yield. The experimental result verified that yield by the obtained yield of 96.7 %.

Table 6

Criteria for the process optimization of transesterification.

Parameter	Goal	Limits	
<b>X<sub>1</sub>-temperature</b>	Extrapolated	15	55
<b>X<sub>2</sub>-catalyst concentration</b>	Extrapolated	0.01	2
<b>X<sub>3</sub>-molar ratio</b>	Extrapolated	3	10
<b>Y:Conversion</b>	Maximize	74.7	100

In this study, the maximum yield of methyl ester production resulted in the alcohol to oil ratio of 3, which in the comparison with the

result announced by Roman-Figueroa et al. (molar ratio of 43) was a great achievement [19]. Likewise, The optimized catalyst



concentration and temperature for this research are confirmed by the result obtained by Karatay et al. [26].

In the numerical optimization of reaction

parameters for the thermal cracking, the bio-gasoline yield was set to the maximum range. The desired criteria are in Table 7.

**Table 7**

Criteria for the process optimization of the thermal cracking.

Criteria	Goal	Minimum limit (wt %)	Maximum limit (wt %)	Results (wt %)
Bio-oil yield	In range	80	99	88
Bio-gasoline yield	Maximum	20	99	28.5

The optimized values of the temperature of 478 °C and feed flow rate of 29 g/hr were obtained to maximize the yield of the bio-gasoline. Under this condition, 88 % bio-oil and 28.5 % bio-gasoline would be yielded, according to the optimization computing.

The optimized temperature is lower than the results obtained by Botton et al. and Hu et al. (which are more than 500) and this means the reduction in the energy consumption [28, 32].

The thermal cracking of castor methyl ester under optimized reaction conditions yielded 88.6 % of the bio-oil and 28 % of the bio-gasoline, that were more than the result announced by Jairo et al. [33]. Experimental and computational results were in accordance with each other as quadratic equations were fitted well with the experimental results. Moreover, results indicate that the thermal cracking of castor methyl ester is a valuable method to produce transportation fuels. Heavy oil yielded 12.4 % under the optimized conditions. This fraction includes mostly high-MW FAMES and polymers and could be burned in the furnaces of the same process.

### 3.4. Bio-gasoline chemical composition

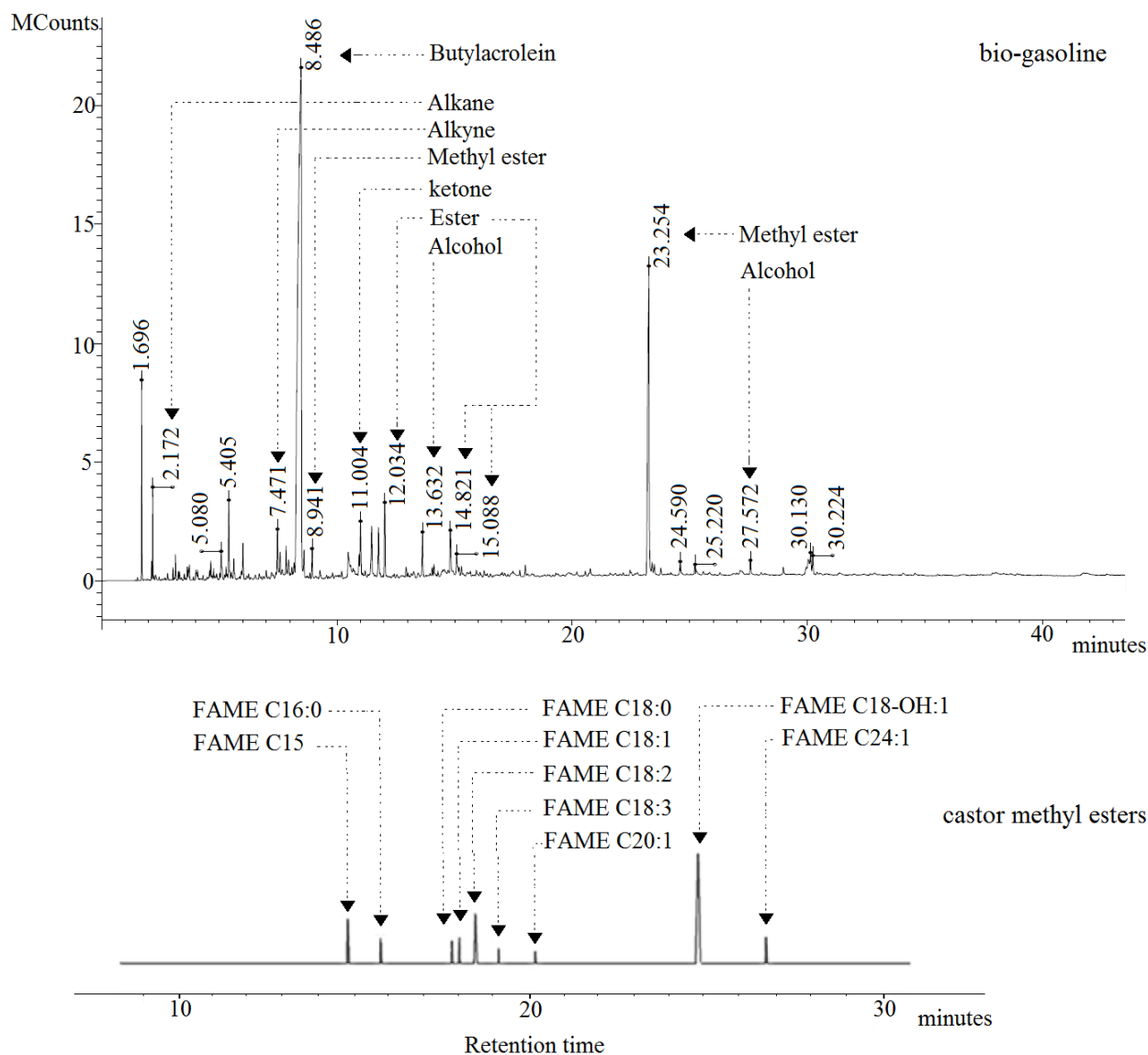
The chromatograms of the original castor methyl ester feedstock and bio-gasoline (produced under the optimum conditions) are shown in Figure 11 in which the occurrence

of FAMES, aldehydes, ketones, alcohols, and aromatics in the bio-gasoline are illustrated. The predominance of deoxygenated hydrocarbons (ketones and alcohols) among the bio-gasoline composition revealed that the deoxygenation reactions were more common. The composition of the bio-gasoline was enriched with Butyl acrolein, which has not been mentioned as a dangerous component in any references. Acrolein has not been found in the composition of the bio-gasoline and this shows the advantage of the TG methyl ester cracking comparing to the TG cracking like what showed in the research of Prado et al., in which acrolein was produced [8].

A major fraction of the bio-gasoline is related to FAMES, which indicates in FAMES the ester bond survives to be cracked. Since there has been no hydroxy fatty acid in the bio-gasoline, it can be inferred that the ricin oleate has decomposed via the C-C bond cleavage. Also, traces of aromatic compounds in the bio-gasoline prove that aromatization occurred in the cracking of castor methyl ester. In most of the countries, strict regulations are laid to control the benzene content in gasoline [5]. Small amounts of aromatics in the bio-gasoline is an advantage that is found in the castor methyl ester cracking and this amount is lower than that of the presented result by Beims et al. which

have done the thermal cracking of soybean oil [34]. Tables 8 and 9 show the identified

compounds in the castor methyl esters and bio-gasoline respectively.



**Figure 11.** Chromatograms of the bio-gasoline and castor methyl esters.

**Table 8**

Compositions for castor oil and castor methyl esters.

Component	Molecular formula	wt %
Pentadecanoic acid	C15:0	7.38
Palmitic acid	C16:0	3.51
Linolenic acid	C18:3	1.03
Linoleic acid	C18:2	12.15
Oleic acid	C18:1	1.38
Stearic acid	C18:0	3.67
Ricin oleic acid	C18:1-OH	60.81
Gondoic acid	C20:1	0.61
Nervonic acid	C24:1	9.46

**Table 9**  
Bio-gasoline composition.

Compound	Retention time (min)	Area (%)
Alkene	2.172	1.274
Alkyne	7.471	1.429
Alkene	7.84	0.721
Aromatic	7.942	0.565
Butylacrolein	8.486	56.829
Ester	8.599	0.546
Methyl ester	8.941	0.746
Ketone	11.004	1.687
Aldehyde	11.479	2.055
Ester	12.034	2.336
Alcohol	13.632	1.278
Ester	14.821	1.701
Ester	15.088	0.864
Methyl ester	23.254	15.095
Alcohol	27.572	0.542
Unidentified	-	12.332

### 3.5. Bio-gasoline properties analysis

The Karl-Fischer test's result showed a low water content (3 % Vol./Vol. of the bio-oil) in the liquid product. This means the water production has been reduced in this method by using the transesterified TG.

This low water content is less than the produced water in the thermal cracking which has been done by Jairo et al. [33]. Therefore, the thermal cracking of the transesterified TG has the advantage of producing less amounts of water compared to the same in the TG cracking.

The characteristic of the bio-gasoline (produced under the optimum conditions) was investigated and compared with the criteria of ASTM D4814 (shown in Table 10). This specification describes the various requirements of automotive fuels for use in ground vehicles equipped with spark-ignition engines.

The compressibility of the fuel before ignition is shown by a standard measure

named octane number. This property is essential for investigating the performance of the aviation fuel. The bio-gasoline, produced under the optimized condition, was tested for octane number, and the test was done twice to ensure the results and both times, the same values were obtained. Results revealed the fact that the bio-gasoline produced from the methyl ester thermal cracking had a very high octane number representing its compatibility with gasoline engines, that would require higher compression ratios. The high quantity of branched and oxygenized compounds increases the octane number of the bio-gasoline [35]. Likewise, it can be blended with the conventional gasoline as a bio-based octane enhancer. In this regard, the blending octane numbers of the bio-gasoline and petrol gasoline were analyzed and shown in Table 11.

Moreover, the vapor pressure and distillation curve of the bio-gasoline were in accordance with the standard gasoline

according to ASTM D4814 as shown in Table 10. The bio-gasoline showed high combustion heat, which was very close to the petrol gasoline. Thus the bio-gasoline,

produced in this study, can be used as fuel in spark-ignition engines or as an additive for improving the octane number of the conventional gasoline.

**Table 10**

Property analysis of the bio-gasoline.

Property	Measuring method	Bio-gasoline	ASTM D4814 (Class AA)
Heat of combustion (MJ/Lit)	ASTM D3338	27.3698	
Vapor pressure, max (KP)	ASTM D5482	34.474	53.779
Distillation temperatures (°C) at 10 %			
vol. recovered, max		64	70
50 % vol. recovered, min-max	ASTM D86	140	77-121
90 % vol. recovered, max		158	190
End point, max		160	225
Specific gravity	ASTM D287	0.75	

**Table 11**

Blending octane numbers of the bio-gasoline and petrol gasoline.

Volume percent in blend		RON
Bio-gasoline	Petrol Gasoline	
0	100	95
10	90	105
15	85	114
20	80	>120
100	0	>120

#### 4. Conclusions

The non-catalytic cracking with the pre-transesterification of castor oil was found to be an efficient method to produce the bio-gasoline. The pre-transesterification of vegetable oils removed some important problems which were common in the TG cracking. In the transesterification, three parameters of temperature, the catalyst concentration, and the molar ratio of alcohol to oil were optimized by the response surface methodology. Also, an accurate mathematical model was developed to predict the response. While the model predicted that the methyl ester yield would be 96.7 %, the experimental

result with the yield of 96 % confirmed the accuracy of the model. In the following and in the thermal cracking steps, the developed mathematical model resulted in the yield of 28.5 % and 88 % for the bio-gasoline and bio-oil production respectively, under the optimized condition of the temperature of 478 °C and flow rate of 29 g/hr. The test under the optimized condition led to 28 % for bio-gasoline and 88.6 % for bio-oil. Therefore, all of the introduced models in this study are valid. While only a small amount of water was generated, the toxic acrolein was not produced in the thermal cracking. Another noticeable finding in this research has been

less aromatic compounds in the bio-gasoline. In addition, the property analysis showed that the bio-gasoline was compatible with standard specifications of gasoline (ASTM D4814) representing its applicability as a fuel of spark-ignition engines. The high octane number of the bio-gasoline ensures its suitability. Adding 10 % of the bio-gasoline to the refinery gasoline resulted in an octane number enhancement of 95 to 105. Further studies are required for the economic analysis of this method. The overall study showed that the thermochemical conversion (transesterification followed by the thermal cracking) was an effective method to address the drawbacks of the thermal cracking to produce valuable biochemicals.

### Acknowledgement

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### Competing interests

All of the authors claim that they do not have a competing interest.

### References

- [1] Molefe, M., Nkazi, D. and Mukaya, H., "Method selection for bio-jet and bio-gasoline fuels production from castor oil: A Review", *Energy Fuels*, **33**, 5918 (2019).
- [2] Hu, X. and Gholizadeh, M., "Biomass pyrolysis: A review of the process development and challenges from initial researches up to the commercialisation stage", *J. Energy Chem.*, **39**, 109 (2019).
- [3] Kozliak, E., Mota, R., Rodriguez, D., Overby, P., Kubatova, A., Stahl, D., Niri, V., Ogden, G. and Seames, W., "Non-catalytic cracking of jojoba oil to produce fuel and chemical by-products", *Ind. Crops Prod.*, **43**, 386 (2013).
- [4] Seifi, H. and Sadrameli, S. M., "Bound cleavage at carboxyl group-glycerol backbone position in thermal cracking of the triglycerides in sunflower oil", *J. Anal. Appl. Pyrolysis*, **121**, 1 (2016).
- [5] Ong, Y. K. and Bhatia, S., "The current status and perspectives of biofuel production via catalytic cracking of edible and non-edible oils", *Energy*, **35**, 111 (2010).
- [6] Onay, O. and Kockar, O. M., "Fixed-bed pyrolysis of rapeseed (*Brassica napus* L.)", *Biomass Bioenergy*, **26**, 289 (2004).
- [7] Oliveira, L. P., Montenegro, M. D. A., Lima, F. C. A., Suarez, P. A. Z., Silva, E. C. D., Meneghetti, M. R. and Meneghetti, S. M. P., "Biofuel production from *Pachira aquatic* Aubl and *Magonia pubescens* A St-Hil: Physical-chemical properties of neat vegetable oils, methyl-esters and bio-oils (hydrocarbons)", *Ind. Crops Prod.*, **127**, 158 (2019).
- [8] Prado, C. M. R. and Filho, N. R. A., "Production and characterization of the biofuels obtained by thermal cracking and thermal catalytic cracking of vegetable oils", *J. Anal. Appl. Pyrolysis*, **86**, 338 (2009).
- [9] Lima, D. G., Soares, V. C. D., Ribeiro, E. B., Carvalho, D. A., Cardoso, É. C. V., Rassi, F. C., Mundim, K. C., Rubim, J. C. and Suarez, P. A. Z., "Diesel-like fuel obtained by pyrolysis of vegetable oils", *J. Anal. Appl. Pyrolysis*, **71**, 987 (2004).
- [10] Maher, K. D. and Bressler, D. C., "Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals", *Bioresour. Technol.*, **98**, 2351 (2007).
- [11] Sawangkeaw, R., Bunyakiat, K. and

- Ngamprasertsith, S., "A review of laboratory-scale research on lipid conversion to biodiesel with supercritical methanol (2001-2009)", *J. Supercrit. Fluids*, **55**, 1 (2010).
- [12] Rathnam, V. M. and Madras, G., "Conversion of *Shizochitrium limacinum* microalgae to biodiesel by noncatalytic transesterification using various supercritical fluids", *Bioresour. Technol.*, **288**, 121538 (2019).
- [13] Sinha, S., Agarwal, A. K. and Garg, S., "Biodiesel development from rice bran oil: Transesterification process optimization and fuel characterization", *Energy Convers. Manage.*, **49**, 1248 (2008).
- [14] Shin, H. Y., Lim, S. M., Bae, S. Y. and Oh, S. C., "Thermal decomposition and stability of fatty acid methyl esters in supercritical Methanol", *J. Anal. Appl. Pyrolysis*, **92**, 332 (2011).
- [15] Lin, R., Zhu, Y. and Tavlarides, L. L., "Mechanism and kinetics of thermal decomposition of biodiesel fuel", *Fuel*, **106**, 593 (2013).
- [16] Luo, Y., Ahmed, I., Kubátová, A., Šťávoová, J., Aulich, T., Sadrameli, S. M. and Seames, W. S., "The thermal cracking of soybean/canola oils and their methyl esters", *Fuel Process. Technol.*, **91**, 613 (2010).
- [17] Kubatova, A., Luo, Y., Šťavova, J., Sadrameli, S. M., Aulich, T., Kozliak, E. and Seames, W., "New path in the thermal cracking of triacylglycerols (canola and soybean oil)", *Fuel*, **90**, 2598 (2011).
- [18] Roy, T., Sahani, S. and Sharma, Y. C., "Green synthesis of biodiesel from *Ricinus communis* oil (castor seed oil) using potassium promoted lanthanum oxide catalyst: Kinetic, thermodynamic and environmental studies", *Fuel*, **274**, 117644 (2020).
- [19] Figueroa, C. R., Carrillo, P. O., Paneque, M., Nereo, F. J. P. and Medina, J. Q., "High-yield production of biodiesel by non-catalytic supercritical methanol transesterification of crude castor oil (*Ricinus communis*)", *Energy*, **107**, 165 (2016).
- [20] Parvizsedghy, R., Sadrameli, S. M. and Darian, J. T., "Upgraded biofuel diesel production by thermal cracking of castor biodiesel", *Energy Fuels*, **30**, 326 (2016).
- [21] Laksmono, N., Paraschiv, M., Loubar, K. and Tazerout, M., "Biodiesel production from biomass gasification tar via thermal/catalytic cracking", *Fuel Process. Technol.*, **106**, 776 (2013).
- [22] Ghobadian, B., "Liquid biofuels potential and outlook in Iran", *Renewable and Sustainable Energy Rev.*, **16**, 4379 (2012).
- [23] Kuehl, R. O., Design of experiments: Statistical principles of research design and analysis, Second Edition, Duxbury Press, Pacific Grove, (2000).
- [24] Marcon, N. S., Colet, R., Bibilio, D., Graboski, A. M., Steffens, C. and Rosa, C. D., "Production of ethyl esters by direct transesterification of microalga biomass using propane as pressurized fluid", *Appl. Biochem. Biotechnol.*, **187**, 1285 (2019).
- [25] Montgomery, D. C., Design and analysis of experiments, Sixth Edition, John Wiley & Sons Inc., United States, (2005).
- [26] Karatay, S. E., Demiray, E. and Dönmez, G., "Efficient approaches to convert *Coniochaeta hoffmannii* lipids into biodiesel by in-situ transesterification", *Bioresour. Technol.*, **285**, 121321 (2019).

- [27] Roy, T., Sahani, S. and Sharma, Y. C., "Study on kinetics-thermodynamics and environmental parameter of biodiesel production from waste cooking oil and castor oil using potassium modified ceria oxide catalyst", *J. Clean. Prod.*, **247**, 119166 (2020).
- [28] Botton, V., Souza, R. T., Wiggers, V. R., Scharf, D. R., Simionatto, E. L., Ender, L. and Meier, H. F., "Thermal cracking of methyl esters in castor oil and production of heptaldehyde and methyl undecenoate", *J. Anal. Appl. Pyrolysis*, **121**, 387 (2016).
- [29] Seames, W., Luo, Y., Ahmed, I., Aulich, T., Kubatova, A., Stavova, J. and Kozliak, E., "The thermal cracking of canola and soybean methyl esters: Improvement of cold flow properties", *Biomass Bioenergy*, **34**, 939 (2010).
- [30] Koul, M., Shadangi, K. P. and Mohanty, K., "Thermo-chemical conversion of Kusum seed: A possible route to produce alternate fuel and chemicals", *J. Anal. Appl. Pyrolysis*, **110**, 291 (2014).
- [31] Bridgwater, A. V., "Renewable fuels and chemicals by thermal processing of biomass", *Chem. Eng. J.*, **91**, 87 (2003).
- [32] Hu, H. B., Park, K. W., Kim, Y. M., Hong, J. S., Kim, W. H., Hur, B. K. and Yang, J. W., "Optimization of production temperatures of heptaldehyde and methyl undecenoate from methyl ricinoleate by pyrolysis process", *J. Ind. Eng. Chem.*, **6**, 238 (2000).
- [33] Jairo, M. J. and Isabel, F., "Bio-oil production by pyrolysis of metal soaps derived from macauba pulp oil", *J. Anal. Appl. Pyrolysis*, **135**, 101 (2018).
- [34] Beims, R. F., Botton, V., Ender, L., Scharf, D. R., Simionatto, E. L., Meier, H. F. and Wiggers, V. R., "Experimental data of thermal cracking of soybean oil and blends with hydrogenated fat", *Data Brief*, **17**, 442 (2018).
- [35] Palanna, O. G., Engineering chemistry, Tata McGraw-Hill Education, New Delhi, (2009).