*Article*

# Thermal Cracking of *Jatropha* Oil with Hydrogen to Produce Bio-Fuel Oil

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**Abstract:** This study used thermal cracking with hydrogen (HTC) to produce bio-fuel oil (BFO) from *jatropha* oil (JO) and to improve its quality. We conducted HTC with different hydrogen pressures ($P_{H2}$; 0–2.07 MPa or 0–300 psig), retention times ($t_r$; 40–780 min), and set temperatures ($T_C$; 623–683 K). By applying HTC, the oil molecules can be hydrogenated and broken down into smaller molecules. The acid value (*AV*), iodine value, kinematic viscosity (*KV*), density, and heating value (*HV*) of the BFO produced were measured and compared with the prevailing standards for oil to assess its suitability as a substitute for fossil fuels or biofuels. The results indicate that an increase in $P_{H2}$ tends to increase the *AV* and *KV* while decreasing the *HV* of the BFO. The BFO yield ($Y_{BFO}$) increases with $P_{H2}$ and $t_r$. The above properties decrease with increasing $T_C$. Upon HTC at 0.69 MPa (100 psig) $H_2$ pressure, 60 min time, and 683 K temperature, the $Y_{BFO}$ was found to be 86 wt%. The resulting BFO possesses simulated distillation characteristics superior to those of boat oil and heavy oil while being similar to those of diesel oil. The BFO contains 15.48% light naphtha, 35.73% heavy naphtha, 21.79% light gas oil, and 27% heavy gas oil and vacuum residue. These constituents can be further refined to produce gasoline, diesel, lubricants, and other fuel products.

**Keywords:** *jatropha* oil (JO); hydrogenation; cracking; bio-fuel oil

## 1. Introduction

Animal fats and vegetable oils have been widely used as alternative feedstocks for biodiesel production in order to reduce the dependence on fossil-fuel-based diesel [1–14]. To increase usage of these feedstocks, much attention has been paid to its use in the production of diesel-like fuels and/or other value-added chemicals [15]. Common production methods are pyrolysis [16,17], catalytic pyrolysis [18–22], and hydrogenation [23].

In a study on the pyrolysis of *babassu*, *piqui*, and palm oils in a glass apparatus at 573–773 K, Alencar et al. [17] obtained mixtures of the major products (*n*-alkanes and 1-alkenes) at yields (v/v)

of 94.46%, 68.20%, and 95.55%, respectively. Adebanjo et al. [16] performed pyrolysis of lard with continuous feeding into a fixed bed at 873–1073 K, using nitrogen as the carrier gas. This produced a diesel-like fuel with a cetane index of 46, specific gravity of 0.86, and heating value (*HV*) of 40 MJ/kg.

Catalysis has been incorporated into pyrolysis to enhance production. Dos Anjos et al. [19] investigated the decomposition of vapors of crude and pre-hydrogenated soybean oils by passing them through a solid acid, $Al_2O_{3-n}$, and a base, MgO, in a tubular reactor at 573–773 K. The crude oil gave oxygen-containing products and hydrocarbons (HCs) with a low mean molecular weight (MW), while the pre-hydrogenated oil produced HCs with a mean MW comparable to those of HCs in diesel. They also found that $Al_2O_3$ was better than MgO at producing a diesel-like fuel. Konar et al. [21] pyrolyzed dried raw sludge from Atlanta sewage over activated alumina at 723 K and 1 atm. The products consisted of low-viscosity liquids (10.7–67.5 wt%), non-condensable gases (12.1–15.6 wt%), semisolids, and water. The liquid products comprised mixtures of HCs containing mainly alkanes. Using a reactor with a fractionating packed column at 673 and 693 K, Dandik and Aksoy [18] studied the pyrolysis of used sunflower oil in the presence of sodium carbonate. An increase in the pyrolytic temperature and catalyst content enhanced the yields of liquid HCs and gases while reducing the formation of aqueous compounds, acids, and coke-residual oil. The major constituents of the liquid HCs and gases were $C_5$–$C_{11}$ and $C_1$–$C_3$ HCs, respectively. Lima et al. [22] conducted pyrolyses of soybean, palm, and castor oils in a 5 L batch reactor at 623–673 K. Gaseous products immediately produced during catalytic pyrolysis were then directly fed into a fritted-bottom glass-tube deoxygenating reactor packed with HZSM-5 zeolite. The yields of product fractions at distillation temperatures (DTs) of <353, 353–413, 413–473, and >473 K were 7–10, 9–15, 9–20, and 60–75 wt%, respectively. Instead of applying conventional transesterification, pyrolysis using Pd/C catalyst was used by Ito et al. [20] to convert waste animal fat and cooking oil into light-oil HCs in an autoclave reactor at 633–693 K. This approach enhanced the selectivity for light oil at 453–623 K.

Catalytic hydrogenation of *jatropha* oil (JO) at 10.34 MPa (1500 psig) $H_2$ pressure ($P_{H2}$) and 613–653 K was studied by Kumar et al. [23]. When sulfided $Ni$–$Mo/Al_2O_3$, $Ni$–$W/SiO_2$–$Al_2O_3$ and $Co$–$Mo/Al_2O_3$ were used, 98%, 81% and 49% yields of $C_{15}$–$C_{18}$ diesel range HCs were obtained, respectively. The use of $Co$–$Mo/Al_2O_3$ also yielded 36% kerosene. Co-processing a mixture of JO with refinery gas oil while using sulfided $Ni$–$Mo/Al_2O_3$ resulted in a diesel yield of 88%–92%. These results indicate that sulfided $Ni$–$Mo/Al_2O_3$ is a suitable catalyst for hydro-processing.

Kumar et al. [23] conducted catalytic hydrogenation of JO at high $P_{H2}$, and Ito et al. [20] studied the catalytic pyrolysis of triglycerides without hydrogen. The present study, on the other hand, performed non-catalytic hydrogenation at low to moderate $P_{H2}$, which can save on catalyst and $H_2$ while maintaining the hydrogenation process. Here we also determined the feasibility of processing JO via thermal cracking with hydrogen (HTC) for bio-fuel oil (BFO) production and the role of hydrogenation, which may compete with thermal cracking. The effects of hydrogen on the yield and key properties of the resulting BFO were also addressed. Simulated distillation of the BFO was carried out to analyze its fuel content, and the results were compared against those of various fuels.

## 2. Results and Discussion

### 2.1. Characteristics of Jatropha Oil

The acid value (*AV*), iodine value (*IV*), kinematic viscosity (*KV*), and density ($\rho_{LO}$) of the JO used are about 36.07 mg KOH/g, 113.8 g $I_2$/100 g, 33.56 $mm^2$/s, and 917.8 $kg/m^3$, respectively, which are similar to those obtained by Andrade-Tacca et al. [3,4]. Except for the *IV* (<120 g $I_2$/100 g max), the other properties do not meet the standards for biodiesel. The *AV* of JO (36.07 mg KOH/g) indicates that it contains about 18.04 wt% free fatty acids (FFAs), which is substantially high. Moreover, the JO contains unsaturated bonds, as reflected by its *IV*. These properties need to be improved to allow the value-added use of JO. The *HV* of JO (37.46 MJ/kg or 34.38 MJ/L), however, is much higher than that of coal (24.17 MJ/kg, dry basis) [24] and similar to that of diesel (35.15 MJ/L) [25].

## 2.2. Thermal Cracking of Jatropha Oil

Table 1 presents the yield and properties of the liquid product BFO ($Y_{BFO}$) obtained from JO thermal cracking at 683 K set temperature ($T_C$) and 60 min retention time ($t_r$) for run 1. The reactions involved can be found in studies by Ito et al. [20], who investigated biodiesel production from waste animal fats and cooking oils using pyrolysis. The reaction products are triacylglycerol (TG), diglyceride (DG), monoglyceride (MG), FFAs, HCs, organic gases, and carbon dioxide. Cleavage of the ester bond generates unsaturated and saturated FFAs, while breakage of the unsaturated bonds forms short-chain HCs and FFAs. Decarboxylation of the FFAs then yields light-oil HCs while releasing $CO_2$. Further decomposition of the HCs may produce some organic gases. Thus, chain-breaking and decomposition reactions of the unsaturated and saturated fractions take place during thermal cracking. Both condensable and non-condensable fragments are formed. The BFO obtained is essentially the pyrolysis oil.

**Table 1.** Yield and properties of BFO obtained from thermal cracking of JO at $T_C$ = 683 K. $Y_{BFO}$: yield of *jatropha* oil (JO) derived bio-fuel oil (BFO); $T_C$: setting temperature; $t_r$: retention time; $P_{H2}$: $H_2$ pressure; *IV*: iodine value; *KV*: kinematic viscosity; $\rho_{LO}$; density; *HV*: heating value; and N/A: not applicable.

| Run No. | $T_C$ | $t_r$ | $P_{H2}$ | $Y_{BFO}$ | *AV* | *IV* | *KV* | $\rho_{LO}$ | *HV* |
|---|---|---|---|---|---|---|---|---|---|
| | K | min | Mpa (psig) | wt% | mg KOH/g | g $I_2$/100 g | mm$^2$/s | kg/m$^3$ | MJ/kg |
| Raw JO | N/A | N/A | N/A | N/A | 36.07 | 113.8 | 33.56 | 917.8 | 37.46 |
| 1 | 683 | 60 | 0 (0) | 72.5 | 46.48 | 77.49 | 1.76 | 863.6 | 39.15 |

$Y_{BFO}$ is maintained at 72.5 wt% after thermal cracking. About 27.5 wt% of the JO decomposes into gases. The increase in *AV* of the BFO produced by JO thermal cracking (from 36.07 to 46.48 KOH/g) is due to FFA formation during thermal breakage of the ester bonds of glycerides. The decrease in *IV* (113.8 to 77.49 g $I_2$/100 g) is attributed to the cleavage of double bonds of unsaturated glycerides and fatty acids. The decrease in *KV* from 33.56 to 1.76 mm$^2$/s and $\rho_{LO}$ from 917.8 to 863.6 kg/m$^3$ results from the formation of short-chain HCs and FFAs. All of these results are consistent with the findings of Ito et al. [20] in a study on waste animal fats and cooking oils. The decomposition of the volatile matter and light components of the JO subjected to carbonization via thermal cracking also results in an increase in *HV* from 37.46 to 39.15 MJ/kg.

## 2.3. Thermal Cracking of Jatropha Oil with Hydrogen

### 2.3.1. Effects of $P_{H2}$

The performance of HTC processing of JO at $P_{H2}$ of 0–2.07 MPa (0–300 psig) at $T_C$ of 683 K and $t_r$ of 60 min is summarized Table 2. Hydrogenation has functions of: (1) saturating the unsaturated bonds, which decreases the *IV*; (2) assisting in bond breaking of long-chain molecules, thus forming smaller fragments; and (3) inhibiting carbonization. Thermal cracking of BFO increases its *AV* and *HV* while reducing the *IV*, *KV*, and $\rho_{LO}$, as noted in Section 2.2. Hydrogenation during thermal cracking may have both enhancing and inhibiting effects. Saturation of unsaturated bonds via hydrogenation facilitates breakdown of saturated components during thermal cracking. However, radicals formed by thermal cracking may be attacked by hydrogen, as indicated by Ito et al. [20]. The hydrogen may be derived from the feed or may be abstracted from alkyl HCs. Thus, an excess of hydrogen may inhibit the effectiveness of radicals formed by thermal cracking. The increase in *AV* with $P_{H2}$ is due to the assistance of hydrogenation in thermal cracking, which breaks ester bonds and forms more FFAs. *IV* generally decreases with increasing $P_{H2}$ as hydrogenation saturates the unsaturated bonds that otherwise need to be broken down via thermal cracking. At a high $P_{H2}$ (2.07 MPa or 300 psig), however, the inhibitory effect of hydrogen on radicals reduces the propagation of decomposition reactions that decrease *IV*, resulting in an *IV* of 76.67 g $I_2$/100 g. This value is higher than that obtained at a $P_{H2}$ of 1.38 MPa (200 psig), 54.62 g $I_2$/100 g. The inhibitory effect of hydrogen on radicals also causes a

high *KV* (4.08 mm$^2$/s) and a high $\rho_{LO}$ (874.6 kg/m$^3$) at 2.07 MPa (300 psig) H$_2$ pressure. The low *HV* (30.30 MJ/kg) at 2.07 MPa (300 psig) H$_2$ pressure is due to the retardation of carbonization by H$_2$. The presence of H$_2$ leads to retention of more HCs in the liquid state, thus giving a $Y_{BFO}$ of about 86–89 wt%, which is higher than that obtained in the absence of H$_2$ (72.5 wt%).

**Table 2.** Yields and properties of BFO obtained from treating JO via thermal cracking with hydrogen (HTC) at various $P_{H2}$.

| Run No. | $T_C$ | $t_r$ | $P_{H2}$ | $Y_{BFO}$ | *AV* | *IV* | *KV* | $\rho_{LO}$ | *HV* |
|---------|-------|-------|----------|-----------|------|------|------|-------------|------|
|         | K     | min   | Mpa (psig) | wt%     | mg KOH/g | g I$_2$/100 g | mm$^2$/s | kg/m$^3$ | MJ/kg |
| Raw JO  | N/A   | N/A   | N/A      | N/A       | 36.07 | 113.8 | 33.56 | 917.8 | 37.46 |
| 1       | 683   | 60    | 0        | 72.5      | 46.48 | 77.49 | 1.76  | 863.6 | 39.15 |
| 2       | 683   | 60    | 0.69 (100) | 86      | 70.56 | 59.41 | 4.08  | 849.1 | 36.09 |
| 3       | 683   | 60    | 1.38 (200) | 87      | 85.43 | 54.62 | 3.00  | 865.0 | 36.59 |
| 4       | 683   | 60    | 2.07 (300) | 89      | 85.09 | 76.67 | 4.08  | 874.6 | 30.30 |

### 2.3.2. Effects of $t_r$

Table 3 illustrates the time variation of $Y_{BFO}$ during the HTC of JO at $T_C$ of 683 K and $P_{H2}$ of 2.07 MPa (300 psig). $Y_{BFO}$ increases from 80 to 93 wt% as $t_r$ increases from 40 to 80 min, as more HCs form.

**Table 3.** Yields and properties of BFO obtained from treating JO via HTC at various $t_r$.

| Run No. | $T_C$ | $t_r$ | $P_{H2}$ | $Y_{BFO}$ | *AV* | *IV* | *KV* | $\rho_{LO}$ | *HV* |
|---------|-------|-------|----------|-----------|------|------|------|-------------|------|
|         | K     | min   | Mpa (psig) | wt%     | mg KOH/g | g I$_2$/100 g | mm$^2$/s | kg/m$^3$ | MJ/kg |
| Raw JO  | N/A   | N/A   | N/A      | N/A       | 36.07 | 113.8 | 33.56 | 917.8 | 37.46 |
| 5       | 683   | 40    | 2.07 (300) | 80      | 79.79 | 71.62 | 3.15  | 858.7 | 41.36 |
| 6       | 683   | 60    | 2.07 (300) | 89      | 85.09 | 76.67 | 4.08  | 874.6 | 30.30 |
| 7       | 683   | 80    | 2.07 (300) | 93      | 73.82 | 53.20 | 1.86  | 845.6 | 37.13 |

One may refer to the studies of Ito et al. [20] on the pyrolysis of waste animal fats and cooking oils to understand the effects of $t_r$ on $Y_{BFO}$ and the properties of the liquid BFO product. Their results indicate that increasing the pyrolysis time reduces the yields of TG, DG, MG, and FFAs while increasing those of HCs, organic gases, and CO$_2$. The decrease in *AV*, *IV*, *KV*, $\rho_{LO}$, and *HV* with the increase in $Y_{BFO}$ and with the increase in $t_r$ from 40 to 80 min for the HTC of JO in the present study are consistent with the time-dependent trends of TG, DG, MG, FFAs, and HCs reported by Ito et al. [20]. An increasing $t_r$ enhances the decomposition reactions of starting and intermediate compounds and the formation of final products. Hydrogenation also inhibits carbonization, lowering the *HV* as $t_r$ increases from 40 to 80 min.

At an intermediate $t_r$ (60 min), hydrogenation is dominant, enhancing the breakage of ester bonds in the formation of FFAs via thermal cracking. This results in an *AV* (85.09 mg KOH/g) higher than that obtained at 40 min (79.79 mg KOH/g). With further increase in $t_r$ to 80 min, thermal cracking becomes dominant, thus lowering the *AV* via decarboxylation of FFAs. The inhibitory effect of hydrogenation on radicals at 60 min is more severe than that at 40 min, resulting in hindered cleavage of double bonds during thermal cracking. This results in an increase in the *IV* as $t_r$ increases from 40 to 60 min. However, the domination of thermal cracking at 80 min contributes to further breakage of double bonds, thus reducing the *IV*. The inhibitory effect of hydrogenation on radicals at 60 min and the enhancement of thermal cracking at 80 min also explain the increase in *KV* and $\rho_{LO}$ as $t_r$ increases from 40 to 60 min, which is in contrast to a decrease as $t_r$ increases from 60 to 80 min. The decrease in *HV* with increasing $t_r$ from 40 to 60 min and from 60 to 80 min may be attributed to the inhibitory effect of hydrogenation and to the enhancement of thermal cracking with carbonization, respectively.

### 2.3.3. Effects of $T_C$

The $Y_{BFO}$ for the HTC of JO at $T_C$ at 623–683 K at $P_{H2}$ of 2.07 MPa (300 psig) and $t_r$ of 80 min is shown in Table 4. With high $P_{H2}$ and long $t_r$, which result in a high $Y_{BFO}$ (93–94 wt%), the effect

of $T_C$ on $Y_{BFO}$ is insignificant. However, its effects on the formation of different product species are significant. A higher $T_C$ induces vigorous thermal cracking, facilitating the decarboxylation of FFAs and thereby reducing the *AV*. It also promotes the cleavage of double bonds, thus decreasing the *IV*. In addition, the higher thermal energy at a higher $T_C$ enhances the decomposition of large molecules to small ones through bond breaking. This then generally lowers the *KV* and $\rho_{LO}$. The decrease in *HV* (from 41.47 to 37.13 MJ/kg) with increasing $T_C$ (623–683 K) may arise from the inhibitory effect of hydrogenation on the carbonization, which is more pronounced at a higher *T*, thus reducing the *HV*.

**Table 4.** Yields and properties of BFO obtained from treating JO via HTC at various $T_C$.

| Run No. | $T_C$ | $t_r$ | $P_{H2}$ | $Y_{BFO}$ | *AV* | *IV* | *KV* | $\rho_{LO}$ | *HV* |
|---|---|---|---|---|---|---|---|---|---|
| | K | min | Mpa (psig) | wt% | mg KOH/g | g $I_2$/100g | mm²/s | kg/m³ | MJ/kg |
| Raw JO | N/A | N/A | N/A | N/A | 36.07 | 113.8 | 33.56 | 917.8 | 37.46 |
| 8 | 623 | 80 | 2.07 (300) | 94 | 162.00 | 92.40 | 6.54 | 919.6 | 41.47 |
| 9 | 653 | 80 | 2.07 (300) | 93 | 104.03 | 69.34 | 6.85 | 882.3 | 37.69 |
| 10 | 683 | 80 | 2.07 (300) | 93 | 73.82 | 53.20 | 1.86 | 845.6 | 37.13 |

### 2.3.4. Simulated Distillation Characteristic of Bio-Fuel Oil

Figure 1 compares the SDCs of the BFO derived from the HTC of JO at $T_C$ of 683 K, $t_r$ of 60 min, and $P_{H2}$ of 0.69 MPa (100 psig) with those of various fuels. The comparison indicates that the BFO from HTC possesses SDCs close to those of diesel, while being superior to those of heavy and boat oils. About 57.52% of the BFO constituents have boiling points in the range of 366–573 K.
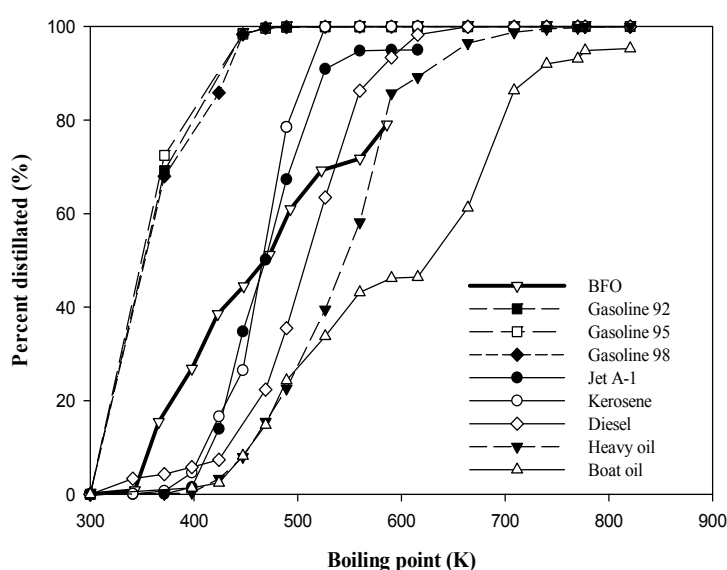


**Figure 1.** Simulated distillation characteristic of BFO for HTC of JO at $T_C$ = 683 K, $t_r$ = 60 min and $P_{H2}$ = 0.69 MPa (100 psig) comparing with those of different fuels. BFO: this study; fuels other than BFO: Chang et al. [26].

More detailed classifications based on the fractionating temperature are presented in Table 5. The amounts of light naphtha, heavy naphtha, light gas oil, and heavy gas oil with vacuum residue are about 15.48%, 35.73%, 21.79%, and 27%, respectively. Thus, the BFO obtained can be further refined to value-added fuels and chemicals.

### 2.4. Comparison of Results with Those of Others

A comparison of some of the results of this work with those of others is presented in Table 6. The main products obtained by HTC are C6–C16 (heavy naphtha and light gas oil, at about 57.52 wt%), while those of other studies are HCs in various carbon fractions or diesel-like fuels.

**Table 5.** Fuel contents of BFO obtained from treating JO via HTC at $T_C$ = 683 K, $t_r$ = 60 min and $P_{H2}$ = 0.69 MPa (100 psig). HCs: hydrocarbons.

| Constituent | Fractionating Temperature, K | Number of Carbons of HCs | Percent of Content |
|---|---|---|---|
| Light naphtha | 343–366 | $C_5$–$C_6$ | 15.48% |
| Heavy naphtha | 366–478 | $C_6$–$C_9$ | 35.73% |
| Light gas oil | 478–573 | $C_9$–$C_{16}$ | 21.79% |
| Heavy gas oil + vacuum residue | >573 | >$C_{16}$ | 27% |

**Table 6.** Comparison of some results of this work with those of others. DG: diglyceride; FFA: free fatty acid; HTC: Thermal cracking with hydrogen; MG: monoglyceride; TG: triacylglycerol; Py: pyrolysis; CPy: catalytic pyrolysis; pre $H_2$: pre-hydrogenation; $DT$: distillation temperature; $Y_{HC}$: yield of HC; CHy: catalytic hydrogenation; NiMo: Sulfide Ni-Mo/$Al_2O_3$; Ni-W: sulfide Ni-W/$SiO_2$-$Al_2O_3$; and CoMo: sulfided Co-Mo/$Al_2O_3$.

| References | Conditions | Yield of Liquid Products or as Specified | Some Product Constituents | Key Products |
|---|---|---|---|---|
| This study | HTC; 683 K, 60 min, 100 psig $H_2$; JO | 86 wt% | Liquid HCs; organic and inorganic gases | $C_6$–$C_{16}$ |
| Alencar et al. [17] | Py; 573–773 K; *babassu*, *piqui* and palm oils | 68.2–95.56 vol% | *n*-alkanes, 1-alkenes, cyclic HCs, $CO_2$. | *n*-alkanes, 1-alkenes. |
| Adebanjo et al. [16] | Py; 873–1073 K; lard | - | Diesel-like fuel, gaseous fuel | Diesel-like fuel |
| Dos Anjos et al. [19] | CPy with $Al_2O_3$ and MgO; 573 to 773 K; vapors of crude and pre $H_2$ soybean oil | 55–65 wt% for crude oi; 39–57 wt% for pre $H_2$ oil | HCs and oxygen containing products for crude oil; HCs for pre $H_2$ oil | HCs comparable to diesel oil. |
| Konar et al. [21] | CPy with activated alumina; 723 K, 1 atm; dried sewage sludge | 10.7–67.5 wt% | Liquid HCs | Alkanes |
| Dandik and Aksoy [18] | CPy with $Na_2CO_3$; 673 and 693 K; sunflower oil | 36.4 wt% $C_5$–$C_{11}$ | HCs, acids, coke residual oil, gases (CO, $CO_2$, $H_2$, others), $H_2O$ | $C_5$–$C_{11}$ (liquid) and $C_1$–$C_3$ (gas) HCs |
| Lima et al. [22] | CPy with HZSM-5, 623–673 K, soybean, palm and castor oils | 7–10, 9–15, 9–20, 60–75 wt% for $DT$<353, 353–413, 413–473, >473 K | Olefins, parraffins, carboxylic acids, aldehydes | HCs comparable to petrol-based fuels |
| Ito et al. [20] | CPy with Pd/C, 633–693 K, animal fats and waste cooking oil | At 693 K and 120 min, $Y_{HC}$ (wt%) = 58 for Py, = 82.5 for CPy, animal fat | TG, DG, MG, FFA, HC, organic gas, $CO_2$. | HC |
| Kumar et al. [23] | CHy, 613–653 K, 1500 psig $H_2$, NiMo, NiW, CoMo, JO, gas oil | Yields of $C_{15}$–$C_{18}$ HCs = 98%, 81%, 49%, using NiMo, NiW, CoMo for JO, = 88%–92% using NiMo for JO + gas oil | TG, paraffins, $C_{15}$–$C_{18}$ HCs, $CO_2$ | $C_{15}$–$C_{18}$ HCs of diesel range |

The $Y_{BFO}$ obtained with HTC in the present work (86 wt%) is comparable to or better than that obtained using pyrolysis and catalytic pyrolysis; however, it is less than that of a process of Kumar et al. [23], which uses sulfided Ni–Mo/Al$_2$O$_3$ catalysts for treating JO (98%) and a mixture of JO and gas oil (88%–92%). The degree of deoxygenation of the BFO produced from JO by HTC is worth examining, as this parameter is important for its proper use. A higher degree of deoxygenation gives better fuel properties and a lower oxygen content. Although we did not perform deoxygenation analyses in the present study, the work of Huang [27] concerning the hydrogenation and upgrade of tung oil is a useful reference. Upon catalytic hydrogenation using $MoS_2/\gamma$–Al$_2$O$_3$ in a continuous continuous-flow process through a packed bed, the dry-basis oxygen content of tung oil (16.01 wt%) decreases to that of BFO derived from the tung oil at 623–673 K (0.24–0.36 wt%); that is, extensive deoxygenation was achieved. Thus, it is expected that HTC would can also reduce the oxygen content of the BFO derived from JO. That said, further study may help in understanding the effect of HTC on the deoxygenation of JO.

## 3. Experimental Methods

### 3.1. Materials

The JO used was supplied by Ozone Environmental Technology Co. (Yi-Lan, Taiwan) and was imported from Indonesia. Hydrogen and nitrogen of 99.995% purity were provided by Ching-Fong Co. (Taipei, Taiwan). Other chemicals that were used include isopropyl alcohol, toluene, acetic acid, cyclohexane, Wijs solution, KI, and Na$_2$S$_2$O$_3$.

### 3.2. Equipments and Procedures

An autoclave reactor (HP/HT 4570 bench top reactor; Parr Instrument Co., Moline, IL, USA) with a volume of 600 mL, maximum pressure of 20.67 MPa (3000 psig), and maximum temperature of 773 K (500 °C) was used for the batch-wise HTC of JO. The reaction system, shown as a schematic diagram in Figure 2, features a temperature controller, pressure gauge, and circulating cooling bath. The $T_C$ variation in the reactor during heating, constant-temperature reaction, and cooling at $T_C$ values of 623, 652, and 683 K is presented in Figure 3. The trends of these values are similar and consistent, indicating good temperature control. A lower $T_C$ at the same $t_r$ means that the plateau in the $T_C$ is reached more quickly, and that cooling down to end the reaction at room temperature is likewise swifter. A time of 28–33 min is required for heating, and about 81–96 min is needed for cooling at a rate of about 4 K/min.
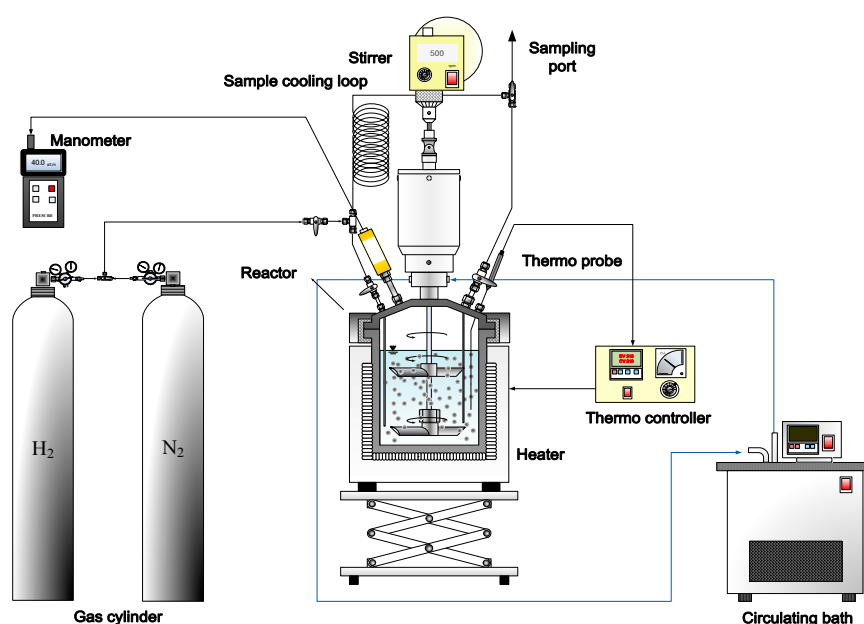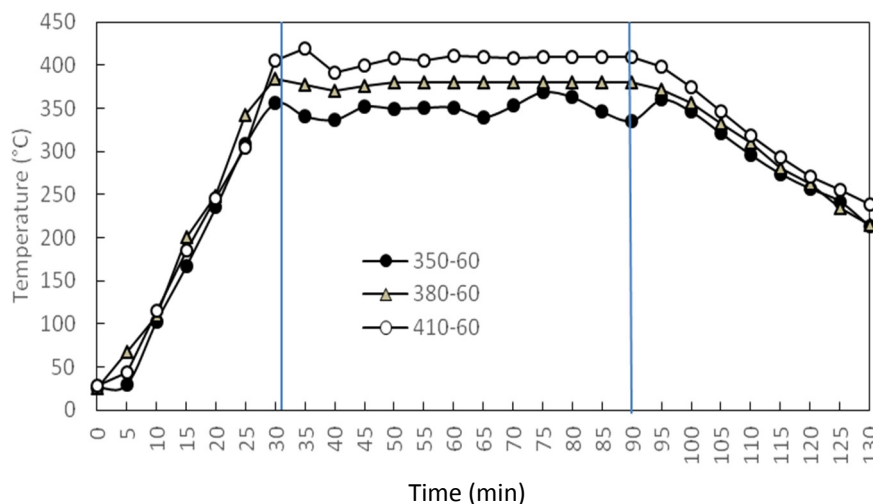


**Figure 2.** Schematic diagram of the HTC reaction system.

**Figure 3.** Time (*t*) variations of temperature (*T*) during heating, constant-temperature reaction and cooling for three $T_C$. Retention time = 60 min; 350-60: $T_C$ in °C-*t* in min.

JO (100 mL) was injected into the reactor. Nitrogen was then introduced for about 1 min to purge the residual air. This was followed by charging with hydrogen at $P_{H2}$ of 0, 0.69, 1.38, or 2.07 MPa (0, 100, 200, and 300 psig, respectively). A $P_{H2}$ of 0 psig was used in the case of thermal cracking without hydrogen. The stirring speed was held at 600 rpm. $t_r$ values during the constant-temperature reaction period were 40, 60, and 80 min.

*3.3. Analyses*

The *AV* was determined according to the method BS EN 14104 [28], which uses an automatic potentiometric titrator (KEN AT-510; Kyoto Electronics Manufacturing Co., Shinjuku-ku, Tokyo, Japan). The chemicals used included isopropyl alcohol and toluene. The *IV* was also measured using the KEN AT-510 and the reagents acetic acid, cyclohexane, Wijs solution, KI, and $Na_2S_2O_3$, in accordance with the procedure of BS EN 14111 [29]. The *KV* was analyzed at 313 K (40 °C) using a Firstek B801-2 (Taipei, Taiwan) on the basis of BS EN ISO 3104 [30]. The viscosity tubes 100 T803 (with coefficient of viscometer $C_V$ = 0.01574 cSt/s) and 100 T 851 ($C_V$ = 0.01398 cSt/s), which were supplied by Cannon Instrument Co. (State College, PA, USA), were used for samples with different ranges of viscosity. The process time for each sample flowing through the viscometer was multiplied by the $C_V$ to obtain the *KV*. Measurement of $\rho_{LO}$ was conducted using the DMA 35 Anton Parr density meter (Anton Paar Benelux, Oosterhout, The Netherlands) set at API Density B at 15 °C (288 K), in accordance with the Chinese National Standard CNS 14474 [31]. Analysis of the *HV* was performed using a calorimeter (oxygen bomb plain jacket calorimeter, model 1341; Parr Instrument Co., Moline, IL, USA) according to NIEA R214.01C [32]. The SDCs were deduced by gas chromatography using a flame ionization detector (5890 Series II; Hewlett Packard Inc., Wilmington, DE, USA) and a Supelco fused-silica capillary column (SBR-5, Supelco, Bellefonte, PA, USA).

## 4. Conclusions

(1) Thermal cracking of JO can produce a BFO with lower *IV*, *KV*, and $\rho_{LO}$ and higher *HV* compared with those of JO.

(2) An increase in $P_{H2}$ and $t_r$ increases the $Y_{BFO}$ during HTC treatment of JO.

(3) A higher $T_C$ generally results in lower *AV*, *IV*, *KV*, $\rho_{LO}$, and *HV* at the same retention time.

(4) At 683 K, 60 min, and 0.69 MPa (100 psig) $H_2$, the major constituent of the resulting BFO is heavy naphtha (about 35.73 wt%).

(5) The BFO obtained via HTC exhibits SDCs better than those of boat oil and heavy oil, while being similar to those of diesel oil.

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**Conflicts of Interest:** The authors declare no conflict of interest.

## Nomenclature

| | | |
|---|---|---|
| $AV$ | Acid value | mg KOH/g |
| $C_V$ | Coefficient of viscometer | cSt/s |
| $DT$ | Distillation temperature | K |
| $HV$ | Heating value | MJ/kg or kcal/kg |
| $IV$ | Iodine value | g $I_2$/100 g |
| $KV$ | Kinematic viscosity | mm$^2$/s |
| $P$ | Gas pressure during HTC | kPa or psi |
| $P_{H2}$ | Hydrogen pressure | kPa, or psi (1 psi = 6.89 kPa) |
| $T$ | Temperature | K or °C |
| $T_C$ | Setting temperature for HTC | K or °C |
| $T$ | Time | min |
| $t_r$ | Retention time at constant setting temperature $T_C$ | min |
| $Y_{BFO}$ | Yield of *jatropha* oil derived bio-fuel oil (BFO) | wt% |
| $Y_{HC}$ | Yield of HC | wt% |
| $\rho_{LO}$ | Density | kg/m$^3$ |

## Abbreviation

| | |
|---|---|
| BFO | Bio-fuel oil |
| CPy | Catalytic pyrolysis |
| DG | Diglyceride |
| FFA | Free fatty acid |
| HC | Hydrocarbon |
| HTC | Thermal cracking with hydrogen |
| JO | *Jatropha* oil |
| MG | Monoglyceride |
| MW | Molecular weight |
| TG | Triacylglycerol |

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