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

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

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 (PH2; 0?2.07 MPa or 0?300 psig), retention times (tr; 40?780 min), and set temperatures (TC; 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 PH2 tends to increase the AV and KV while decreasing the HV of the BFO. The BFO yield (YBFO) increases with PH2 and tr. The above properties decrease with increasing TC. Upon HTC at 0.69 MPa (100 psig) H? pressure, 60 min time, and 683 K temperature, the YBFO 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.

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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) H₂ 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 Al₂O₃ 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) H₂ pressure (P_{H2}) and 613–653 K was studied by Kumar et al. [23]. When sulfided Ni–Mo/Al₂O₃, Ni–W/SiO₂–Al₂O₃ and Co–Mo/Al₂O₃ were used, 98%, 81% and 49% yields of C₁₅–C₁₈ diesel range HCs were obtained, respectively. The use of Co–Mo/Al₂O₃ also yielded 36% kerosene. Co-processing a mixture of JO with refinery gas oil while using sulfided Ni–Mo/Al₂O₃ resulted in a diesel yield of 88%–92%. These results indicate that sulfided Ni–Mo/Al₂O₃ 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 (ρ_{LO}) of the JO used are about 36.07 mg KOH/g, 113.8 g I₂/100 g, 33.56 mm²/s, and 917.8 kg/m³, respectively, which are similar to those obtained by Andrade-Tacca et al. [3,4]. Except for the *IV* (<120 g I₂/100 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].

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 CO₂. 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} : H₂ pressure; *IV*: iodine value; *KV*: kinematic viscosity; ρ_{LO} ; density; *HV*: heating value; and N/A: not applicable.

	T_C	t_r	P_{H2}	Y_{BFO}	AV	IV	KV	ρ_{LO}	HV
Kun No.	К	min	Mpa (psig)	wt%	mg KOH/g	g I ₂ /100 g	mm²/s	kg/m ³	MJ/kg
Raw JO 1	N/A 683	N/A 60	N/A 0 (0)	N/A 72.5	36.07 46.48	113.8 77.49	33.56 1.76	917.8 863.6	37.46 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 I₂/100 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 mm²/s and ρ_{LO} from 917.8 to 863.6 kg/m³ 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 decremposition 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 ρ_{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 I₂/100 g. The inhibitory effect of hydrogen on radicals also causes a

high *KV* (4.08 mm²/s) and a high ρ_{LO} (874.6 kg/m³) at 2.07 MPa (300 psig) H₂ pressure. The low *HV* (30.30 MJ/kg) at 2.07 MPa (300 psig) H₂ pressure is due to the retardation of carbonization by H₂. The presence of H₂ 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 H₂ (72.5 wt%).

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

	T_C	t _r	P_{H2}	Y_{BFO}	AV	IV	KV	ριο	HV
Kun No.	К	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 .

	T_C	t_r	P_{H2}	Y_{BFO}	AV	IV	KV	ρ_{LO}	HV
Kun No.	К	min	Mpa (psig)	wt%	mg KOH/g	g I ₂ /100 g	mm ² /s	kg/m ³	MJ/kg
Raw JO 5 6 7	N/A 683 683 683	N/A 40 60 80	N/A 2.07 (300) 2.07 (300) 2.07 (300)	N/A 80 89 93	36.07 79.79 85.09 73.82	113.8 71.62 76.67 53.20	33.56 3.15 4.08 1.86	917.8 858.7 874.6 845.6	37.46 41.36 30.30 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 CO₂. The decrease in AV, IV, KV, ρ_{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 ρ_{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 HVwith 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 ρ_{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.

	T_C	t_r	P_{H2}	Y_{BFO}	AV	IV	KV	ριο	HV
Kun No.	К	min	Mpa (psig)	wt%	mg KOH/g	g I ₂ /100g	mm ² /s	kg/m ³	MJ/kg
Raw JO 8 9 10	N/A 623 653 683	N/A 80 80 80	N/A 2.07 (300) 2.07 (300) 2.07 (300)	N/A 94 93 93	36.07 162.00 104.03 73.82	113.8 92.40 69.34 53.20	33.56 6.54 6.85 1.86	917.8 919.6 882.3 845.6	37.46 41.47 37.69 37.13

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

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.

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	C9-C16	21.79%
Heavy gas oil + vacuum residue	>573	>C ₁₆	27%

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.

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 H₂: pre-hydrogenation; *DT*: distillation temperature; Y_{HC} : yield of HC; CHy: catalytic hydrogenation; NiMo: Sulfide Ni-Mo/Al₂O₃; Ni-W: sulfide Ni-W/SiO₂-Al₂O₃; and CoMo: sulfided Co-Mo/Al₂O₃.

References	Conditions	Yield of Liquid Products or as Specified Some Product		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%	<i>n</i> -alkanes, 1-alkenes, cyclic HCs, CO ₂ .	<i>n</i> -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 ₂ O ₃ and MgO; 573 to 773 K; vapors of crude and pre H ₂ soybean oil	$\begin{array}{llllllllllllllllllllllllllllllllllll$		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 ₂ CO ₃ ; 673 and 693 K; sunflower oil	$36.4 \text{ wt}\% \text{ C}_5-\text{C}_{11}$	HCs, acids, coke residual oil, gases (CO, CO ₂ , H ₂ , others), H ₂ O	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 .	НС
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/Al₂O₃ 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 MoS₂/ γ –Al₂O₃ 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 Na₂S₂O₃.

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 Na₂S₂O₃, 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 $C_V = 0.01574 \text{ cSt/s}$ and 100 T 851 ($C_V = 0.01398 \text{ cSt/s}$), 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 ρ_{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 ρ_{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, ρ_{LO} , and HV at the same retention time.
- (4) At 683 K, 60 min, and 0.69 MPa (100 psig) H₂, 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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Nomenclature

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

Abbreviation

BFO	Bio-fuel oil
СРу	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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