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# Feasibility Studies for Conventional Refinery Distillation with a (1:1) w/w of a Biocrude Blend with Petroleum Crude Oil

Anil Kumar Sarma\* and D. Konwer

Department of Energy, Tezpur University, Napaam-784028, Assam, India

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Biocrude produced by the catalytic cracking of plant seed oil has the potential for use as a substitute of petroleum crude oil. The distillation characteristics of a biocrude blend prepared by mixing 50 wt % of Oil India Limited (OIL) petroleum crude with the biocrude prepared from the methyl esters of *Mesua ferrea* L. seed oil are reported in this paper. More than 63% of the distillate can be recovered from the blend at atmospheric pressure, compared to 43% for the OIL crude. The recovery of aviation turbine fuel (JP-8), which normally has a boiling range of 175–250 °C was determined to be much higher: 26% in biocrude and 22% in the blend, compared to 16% for the OIL crude alone. This finding is significant, considering the increased demand for air transportation fuel. Blending shows great economic promise. Using vacuum distillation, the product recovered is ~89% for the blend, whereas this recovery is only 76% for the OIL crude. The fractions obtained from blend distillation have characteristics that are similar to those of the petroleum crude. However, some additional treatment may need to be undertaken to reduce the stickiness and odor of the blended crude.

## Introduction

The production of liquid biofuels has been gaining popularity recently, because of environmental concerns and diminishing petroleum reserves. These can be made from renewable biological sources, such as vegetable oils and animal fats. It is a well-established fact that the triglycerides derived from the plant seed oil, animal fats, waste cooking oil, etc. can be transformed to cracked oil, which has properties similar to those of petroleum crude oil.<sup>1–8</sup> The substitution of petroleum diesel with methyl esters derived from rapeseed oil is already a commercial activity in many European countries.<sup>1</sup> It is also observed that the biodiesel produced by the transesterification of vegetable oil has higher density, viscosity and a narrow range of boiling points, thus requiring an additional distillation for end use in many cases.<sup>1</sup> Methyl esters prepared from rapeseed oil can also be used as feedstock for the preparation of liquid hydrocarbons, as reported by Billaud et al.<sup>8</sup>

*Mesua ferrea* L. is a timber plant that grows naturally in the northeastern parts of the Himalayan regions of India. The plant flowers normally in the months of March and April every year, and seeds are harvested in the month of September. A normal 15- to 20-year-old tree produces in an average of 30 kg of oil seeds. Currently, these oil seeds can be obtained inexpensively and have no obvious end use. The oil seed contains ~55–57 wt % nonedible, reddish-brown-colored oil (the shelled kernel contains >75 wt % oil), which had been traditionally used as a fuel.

Konwer and co-workers<sup>9–11</sup> reported a method of steam cracking of *Mesua ferrea* L. oil seeds. In their experiments, the ground seeds (500 g) were mixed thoroughly with anhydrous sodium carbonate (0.5 g) in water (~50 mL) and the mixture was placed in a vertical cast-iron retort (40 cm × 20 cm inside diameter), which was connected to a receiver flask. The retort was heated to 250–500 °C, at which point decomposition of the seeds occurred, yielding two layers of liquids. The upper layer was black crude-type hydrocarbon mixture, whereas the lower layer was water. The renewable crude oil (i.e., the biocrude) fraction was separated from the water layer and fractional distillation was performed using the true boiling point (TBP) distillation process. They concluded that the fraction distilled between the initial boiling point (IBP) and 140 °C may be a substitute of gasoline, whereas the fractions obtained within the boiling ranges of 140–300 °C and 140–370 °C may be kerosene and diesel equivalents, respectively. Therefore,

\* Author to whom correspondence should be addressed. E-mail address: anil\_tu@yahoo.co.in.

(1) Graboski, M. S.; McCormick, R. L. *Prog. Energy Combust. Sci.* **1998**, *24*, 125–164.

(2) Twaiq, F. A.; Mohammad, A. R.; Bhatia, S. *Microporous Mesoporous Mater.* **2003**, *64*, 95–107.

(3) Reed, T. B.; Graboski, M. S.; Gaur, S. *Biomass Bioenergy* **1992**, *3*, 111.

(4) Ikwaagwu, O. E.; Ononogbu, I. C.; Njoku, O. U. *Ind. Crops Prod.* **2000**, *2*, 57–62.

(5) Alcantara, R.; Amores, J.; Canoira, L.; Fidalgo, E.; Franco, M. J.; Navarro, A. *Biomass Bioenergy* **2000**, *18*, 215–217.

(6) Idem, R. O.; Katikaneni, S. P. R.; Bakshi, N. N. *Fuel Process. Technol.* **1997**, *51*, 101–105.

(7) Billaud, F.; Guitard, Y.; Tran Minh, A. K.; Zahraa, O.; Lozano, P.; Pioch, D. *J. Mol. Catal., A: Chem.* **2003**, *192*, 281–288.

(8) Billaud, F.; Dominguez, V.; Broutin, P.; Busson, C. *J. Am. Oil Chem. Soc.* **1995**, *72*, 1149–1154.

(9) Konwer, D.; Taylor, S. E.; Gordon, B. E.; Otvos, J. W.; Calvin, M. *J. Am. Oil Chem. Soc.* **1989**, *66* (2), 223–226.

(10) Konwer, D.; Baruah, K. *Chem. Ind. (London)* **1984**, 184.

(11) Konwer, D.; Baruah, K. *Chem. Ind. (London)* **1985**, 15.

**Table 1. Properties of Oil India Limited (OIL) Crude Oil, Biocrude, and Blend**

property	Value		
	OIL crude	biocrude	blend
density at 15 °C (g/cm <sup>3</sup> )	0.871	0.853	0.862
API gravity (°API)	30.950	34.381	32.654
sediment (wt %)	0.006	0.004	0.005
H <sub>2</sub> O content (vol %)	0.900	0.810	0.851
salt content (mg/L)	14.810	0.600	7.812
sulfur content (wt %)	0.222	0.041	0.122
initial boiling point, IBP (°C)	68	97	75
Scotch set point <sup>a</sup> (°C)	42.0	41.5	41.0

<sup>a</sup> Fraction of ASTM D86 distillation.

it evoked interest to determine if these cracked products could be obtained conveniently from distillation in conventional refineries. In this paper, the authors report the distillation characteristics of a biocrude produced by the catalytic cracking of methyl esters of *Mesua ferrea* L. seed oil and a blend of the biocrude with Oil India Limited (OIL) crude (collected in February 2004) in a 1:1 (w/w) ratio, as well as the petroleum crude. The characteristics of different fractions of the biocrude blend are also reported, along with the expected possibilities of distillation of this biocrude blend in conventional refineries.

### Experimental Section

Approximately 10 L of oil were extracted using the Soxhlet extraction method<sup>9</sup> with petroleum ether (40–60 °C) as a solvent. The methyl esters (85% purity) of *Mesua ferrea* L. seed oil were prepared using potassium hydroxide (KOH) as a catalyst, and their properties were reported elsewhere.<sup>12</sup> A superficial observation of the properties of this biodiesel indicated that it could not possibly be used in diesel engines, either directly or in blends (>10%), because of its high density (0.925 g/cm<sup>3</sup> at 15 °C), very high viscosity (38.6 cSt at 40 °C), and high amount of carbon deposits (0.5 wt %). Therefore, an organized experiment was conducted, using this biodiesel as the feedstock for catalytic cracking.

**Biocrude Preparation.** In this experiment, a 1-L-capacity iron-made reactor (batch-type) was used. The top cover of the reactor was vapor-leak-proof; it had a screw-passe type gasket that was attached and can be opened from time to time. The long conical outlet pipe was connected to a Leibig condenser (30° vertical), and the other end of the condenser was connected to the two-inlet collector flask. One inlet of the collector flask was connected to a gas jacket. The reactor was placed properly above a heater for uniform heating. The cracking process was continued with 500 mL of feedstock at 450 °C, at a rate of 3–5 mL of product formed per minute, using 0.5 g of Na<sub>2</sub>CO<sub>3</sub> as a catalyst<sup>9</sup> (0.1 wt % of the feedstock used). The conversion rate of waste biodiesel to biocrude was 85 wt % of the feedstock used. Four liters of biocrude were prepared using this method.

**Testing of the Biocrude, OIL Crude, and Blended Crude.** The biocrude thus produced and the OIL petroleum crude were tested separately for their necessary characteristics. The two crude samples were then mixed to obtain a 50:50 biocrude blend (w/w, 2 kg each), and their preliminary characteristics were determined using the ASTM procedure.<sup>13</sup> The results are reported in Table 1.

**Table 2. ASTM Distillation D86 of Biocrude, OIL Petroleum Crude, and Blend**

temperature (°C)	Recovery (vol %)		
	biocrude	OIL crude	blend
75	0	1.0	0
100	4.0	5.5	1.0
125	9.0	10.0	5.0
150	14.0	13.5	14.0
175	19.5	18.5	19.5
180	21.0	20.5	20.6
200	25.5	22.0	23.5
225	32.0	29.0	30.5
250	44.0	34.0	41.0
275	60.5	38.5	51.0
280	64.0	39.0	57.0
300	77.0	43.0	63.0

**Fractional Distillation.** Atmospheric distillation was performed for the OIL crude, biocrude, and the biocrude blend, as per ASTM Standard D86, and the volume percentages of distillates recovered are reported in Table 2.

The true boiling point (TBP) distillation of each of the three samples was performed using an Oldershaw column (vacuum jacket, 50 cm length) that had 10 actual plates, as per ASTM Standard D2892. The distillation of the higher-boiling-point fraction was performed under reduced pressure at a reflux ratio of 1:5 throughout the distillation process, to avoid further cracking. The details of the distillation conditions and the percentages of distillates recovered by weight from the TBP distillation are reported in Table 3.

**Characterization of Gasoline, Kerosene, and Diesel.** The fractions obtained at 40–140 °C were tested for gasoline, whereas the fractions obtained at 140–180 °C and 180–300 °C were tested for kerosene and the fractions at 300–325 °C and 325–370 °C were tested for diesel. All the important fuel properties, such as density, specific gravity, °API, flash point, aniline point, viscosity, pour point, calorific value, diesel index, etc., as applicable, were determined using ASTM<sup>13</sup> and IP methods.<sup>15</sup>

### Results and Discussion

The results obtained from the characterization of crude oil are reported in Table 1. The significant decrease in density and increase in API gravity of the biocrude blend clearly indicated an increase of lighter fractions. Sedimentation showed no significant alterations, whereas the salt content and sulfur content were reduced by almost one-half after blending, as shown in the Table 1. A lower salt content contributes to the longevity of the distillation column, whereas a low sulfur content implies environmental benefits.

To ascertain the feasibility of refinery distillation, the ASTM Standard D86 and the TBP distillation (ASTM Standard D2892) experiments were conducted. The ASTM Standard D86 results (see Table 2) showed that 50% of the blended crude could be distilled at ~275 °C, whereas only 38.5% of the OIL crude could be distilled at the same temperature. When the temperature reached a maximum of 300 °C, 43% of the OIL crude was recovered, whereas, the recovery at the same temperature was 63% for the blends. Certainly a recovery of 20% of the distillation products is advantageous, from the standpoint of energy conservation that requires no

(12) Konwer, D. *World Renewable Energy Congress VIII*, August 29–September 3, 2004, Denver, CO; World Renewable Energy Congress (WREC): 2004; pp 1–5.

(13) *2000 Annual Book of ASTM Standards*; American Society for Testing and Materials: Philadelphia, PA, 2000; Vol. 05.01–05.05.

(14) Arkoudeas, P.; Kalligeros, S.; Zannikos, F.; Anastopoulos, G.; Karonis, D.; Korres, D.; Lois, E. *Energy Conserv. Manage.* **2003**, *44*, 1013–1025.

(15) *IP Standards for Petroleum and Its Products, Part I*; Institute of Petroleum: London, 1993.

**Table 3. True Boiling Point (TBP) Distillation of OIL Crude, Biocrude Blend and Biocrude (via ASTM Standard D2892)**

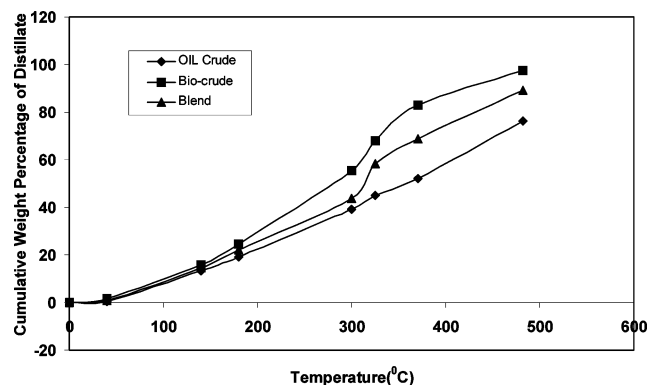
sample number	cut temperature (°C)	vapor temperature (°C)	pressure (mm Hg)	OIL Crude		Biocrude Blend		Biocrude	
				weight percentage of distillate	cumulative weight percentage of distillate	weight percentage of distillate	cumulative weight percentage of distillate	weight percentage of distillate	cumulative weight percentage of distillate
1	gas + loss			0.48	0.48	1.02	1.02	1.55	1.55
2	40–140	140	760	12.96	13.44	13.52	14.54	14.32	15.87
3	140–180	180	760	5.92	19.36	7.42	21.96	8.67	24.54
4	180–300	160	10	19.98	39.34	27.19	49.15	31.76	55.30
5	300–325	180	10	5.50	44.84	9.10	58.24	12.54	67.84
6	325–370	218	10	7.40	52.24	10.69	68.93	12.15	82.99
7	370–482	297	5	23.93	76.26	20.20	89.13	18.54	97.53
8	482+			23.84	100.0	10.87	100.0	6.47	100.0

**Table 4. Properties of the Refined Oil Obtained from TBP Distillation of Biocrude Blend at Different Boiling Ranges/Fractions**

property	Value						
	A (40–140 °C)	B (140–180 °C)	C (180–300 °C)	D (300–325 °C)	E (325–370 °C)	F (375–482 °C)	G (residue)
initial boiling point, IBP (°C)	49	145	189	276			
final boiling point, FBP (°C)	141	174	272	305			
50% distillation (°C)	101	169	232	287			
density @ 15 °C (g/cm <sup>3</sup> )	0.769	0.801	0.837	0.855	0.871	0.902	0.986
kinematic viscosity (cSt)							
at 40 °C		0.902	2.037	3.420	4.163		
at 50 °C						20.537	
octane number	70						
aniline point (°C)			52	64	68		
diesel index			47	55	48		
smoke point (mm)		20	19.5				
flash point (°C)		36	72	105	110		
pour point (°C)	−27	−15	−9	−9	0	9	
calorific value (kJ/g)	38.544	44.626	44.434	45.015	46.810	46.522	45.537

additional cracker or vacuum distillation units. The recovery of aviation turbine fuel (JP-8), which normally has a boiling range of 175–250 °C, was determined to be much higher: 26% in biocrude and 22% in the blend, compared to 16% for the OIL crude alone. It is a significant finding, considering the increased demand for air transportation fuel.

The TBP distillation results (Table 3) show that the 40–140 °C fraction of the hydrocarbon (i.e., the gasoline fraction) was observed to increase by 1% after blending. The kerosene fraction (140–300 °C) was ~36% in the biocrude blend, compared to only 25% in the OIL crude. The diesel fraction in the range of 140–370 °C was observed to be 43% in the OIL crude, whereas it was significantly higher (54%) in the blended crude. The most significant result is the fact that ~89% of the hydrocarbon could be recovered through atmospheric and vacuum distillation at <482 °C, whereas 76% recoverable products were observed in the OIL crude.

**Figure 1.** True boiling point (TBP) distillation curves.

The marketability of the different distillates is emphasized by their respective properties, which are tabulated in Table 4.

The comparative study of the TBP curves (Figure 1) is a clear indicator of the advantages of biocrude blend distillation. It has been observed that the blending of biocrude with petroleum crude leads to higher recovery of distillates at low temperature and pressure, which may reduce the prices of petroleum distillates. Lower sulfur content in biocrude blends can also mitigate pollution problems. The sticky nature of the biocrude blend, because of the presence of oil gums, and the irritating odor (which is due to the presence of cracked products) are minor disadvantages that would require some treatment. It is expected that the blending of biocrude with mineral crude might solve the problem of fossil fuel crisis in the future.

## Conclusions

(1) The overall efficiency (i.e., the amount of usable cracked product recovered from the waste biodiesel) is ~82.5%, which is significantly higher, compared to the cracking of raw *Mesua ferrea* L. seed oil, which was observed to be only 48 wt % of the raw oil seeds.<sup>10</sup> The weight percentage of distillate product (89%) of the biocrude blend is also much higher than that of the OIL crude alone.

(2) A major portion of the biocrude blend (63% by Vol) can be recovered without the use of a cracker or a vacuum distillation unit. This means that a huge amount of energy input for the operation of vacuum distillation unit can be saved.

(3) The important properties of the fractions obtained as listed (including calorific values of the oils) clearly indicate the feasibility of the process under examination.

(4) Some initial treatment of the biocrude and the blend may be applied to reduce the stickiness; this could be a promising research area. Hydrocracking of the oil or the waste biodiesel is also expected to improve the quality of different fractions, which provides ample scope for research.

Overall, the entire existing refinery systems can easily be used for the fractional distillation of the biocrude blend.

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**Note Added after ASAP Publication.** This article was published on the Web on 05/03/05 with an incorrect reference citation in item 1 of the Conclusions section. The version posted 05/19/05 and the print version are correct.

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