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Energy Analyses and Operating Costs of Biodiesel Production

Phaedra Jaggernauth[a], Enoch Ghany[b], Puran Bridgemohan[c], and Ejae John [d,Ψ]

The University of Trinidad and Tobago, Waterloo Research Campus, Waterloo Estates, Carapichaima, Trinidad and Tobago;
[a]E-mail: phaedra.jaggernauth@utt.edu.tt
[b]E-mail: enoch.ghany123@gmail.com
[c]E-mail: puran.bridgemohan@utt.edu.tt
[d]E-mail: ejae.john@utt.edu.tt

[Ψ] *Corresponding Author*

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Abstract: *Fluctuating petroleum prices, environmental concerns and the understanding that petroleum is a finite resource have encouraged investigation into alternative fuels. Coconut oil can be potentially be used as the triglyceride feedstock for biodiesel production. The objective of this study was to complete energy performance analyses of four (4) coconut oil biodiesels. The energy performance metrics investigated were net energy ratio (NER), net energy balance (NEB), net renewable energy value (NREV) and fossil energy ratio (FER). NER values ranged from 0.51 to 0.77, NEB from -12.00 MJ/L to -46.21 MJ/L, NREV from 9.00 to 21.31 MJ/L and FER from 1.52 to 2.88. The energy metrics implied that the small-scale transesterification process is neither energy-efficient nor sustainable in Trinidad and Tobago. At the atom efficient 3:1 methanol to oil ratio, the NREV and FER values are improved, however, compared to the 6:1 methanol to oil ratio process. Additionally, since most of their physical properties are already within specification for use in the local vehicular market, all biodiesels are a prospective component of environmentally friendly blends with petrodiesel.*

Keywords: *Coconut oil, biodiesel, energy analysis, operating cost, NER, NEB, NREV, FER*

1. Introduction

Petrodiesel has been established as the preferred fuel for compression ignition engines due to its efficiency, low cost and availability. However, concerns about greenhouse gas emissions (Stern, 2006), the decline of global oil production (IEA, 2010; Hirsch, 2005), and the unpredictability of oil prices due to socioeconomic and political factors (IEA, 2010) have forced investigation into locally available, renewable, environmentally friendly liquid fuels.

Vegetable oils would have been an excellent option as a renewable liquid fuel if not for its high viscosity which is 11-17 times higher than petrodiesel (Meher et al., 2006), resulting in engine deposits due to poor atomization (Knothe et al., 2005). Consequently, four main methods have been investigated to lower the viscosity of the vegetable oils viz. transesterification, pyrolysis, dilution blending with petrodiesel, and microemulsification (Knothe et al., 2005; Balat and Balat, 2008). As carbon deposits and lubricating oil contamination still persist with pyrolysis, blending, and emulsifying (Ma and Hanna, 1999), transesterification is the most frequently used method to decrease viscosity (Knothe et al., 2005).

Transesterification is a chemical reaction whereby the fatty acid alkyl esters are produced from the parent triglyceride via a reaction with an alcohol, usually in the presence of a catalyst (Knothe et al., 2005). The process converts the large triglyceride molecule from the vegetable oil into three smaller alkyl ester molecules. Biodiesel's characteristics of renewability, cleaner emissions (Demirbas, 2008), ability to be used without modifications to the diesel engine (Vega-Lizama, et al., 2015), and high degradability (Veljković et al., 2015) make it one of the most rapidly growing alternative fuels in the world (Babu et al., 2015). The main challenge to biodiesel becoming a competitive alternative to diesel on the market is its price, which is 1.5-3 times more than diesel (Demirbas, 2009). High oil feedstock costs, the main cost component, can be up to 80% of the operating cost (Balat and Balat, 2008). Market implementation of biofuels will not be successful if the process is not economically viable (Müller-Langer et al., 2014). This has led to an interest in the field of energy economics specific to biodiesel production.

Energy metrics are a measure of the technical or overall efficiency of the process and indicate where the investment and production costs are located (Müller-Langer et al., 2014). A detailed understanding of the energy content and economics of a plant's process is the foundation to understanding how to increase energy efficiency and reduce process costs (Thumann and Mehta, 2008) as well as allow for better allocation of resources (Bhattacharyya, 2011). Energy and cost analyses of biodiesel production are therefore of vital importance in determining where resources should be assigned in order to lower production cost. When renewability is being investigated, such as in this biodiesel production study, net energy balance (NEB) and net energy ratio (NER) are the more appropriate metrics (Fore et al., 2011). Net renewable energy value (NREV) and fossil energy ratio (FER) are also relevant as they indicate the sustainability of the process.

The objective of this study was to determine the potential of coconut oil biodiesel for use in diesel engines based on its energy values. Additionally, the physical properties of the biodiesels of four different locally produced coconut oils were determined for their compatibility in diesel engines in Trinidad and Tobago.

2. Materials

Four locally available coconut oils were used in this study, namely, Eastern Brand, Palmola, Naisa, and Nariel. Analytical grade sodium hydroxide, methanol and sulphuric acid were used.

3. Transesterification Method

Free fatty acid (FFA) content was determined from AOCS Official Method Cd 3d-63 (AOCS, 2010). The FFA content of Eastern Brand, Palmola, Naisa, and Nariel were determined as 1.9%, 0.03%, 0.18% and 0.03%, respectively. Eastern Brand was the only oil with FFA>0.5%, thus requiring an acid esterification step (Meher et al., 2006; Ma and Hanna, 1999). Acid transesterification experimental conditions were 0.5wt% H_2SO_4 (Berchmans and Hirata, 2008; Jain & Sharma, 2010), 0.35 v/v methanol, 1 hour reaction time at 60°C (Nakpong and Wootthikanokkan, 2009) under reflux conditions with vigorous stirring. The top methanol-water layer was removed and the bottom oil layer was washed with 1/5 of the oil volume (Sharma, et al., 2008) of 0.001M NaOH solution at 50ºC until neutral after which it was dried.

Base transesterification experimental conditions were 60ºC (Jain and Sharma, 2010), vigorous stirring (Meher et al., 2006), 6:1 or 3:1 methanol to oil ratio (Meher et al., 2006; Ma & Hanna, 1999), 2 hour reaction time and 1 wt% NaOH (Meher et al., 2006; Ma and Hanna, 1999) under reflux conditions. Post reaction, the bottom glycerol layer was removed using a separatory funnel. The top biodiesel layer was washed to pH7 using warm distilled water. Complete drying was done using anhydrous magnesium sulphate. The physical properties of the final biodiesel product were then determined using ASTM methods and compared with local and international specifications.

4. Characterisation of bio-diesel

A qualitative GC-MS analysis of the reaction products was conducted to confirm that methyl esters were produced by the altered reaction. An Agilent 5975C Series GC/MSD was operated in split mode with 50:1 split ratio using a BD 14103 capillary column, 30m x 0.250 i.d. x 25µm film thickness. The front inlet was heated to 250ºC. Injection volume for all analyses was 2µL. The oven was heated to 60ºC for 2 mins, ramped at 10ºC/min to 200ºC, ramped at 5ºC/min to 240ºC and held for 7 min.

5. Determination of energy metrics

Net energy ratio (NER), net energy balance (NEB) (Fore et al., 2011), net renewable energy value (NREV) (Eshton et al., 2013) and fossil energy ratio (FER) (Mohammadshirazi et al., 2014) were determined using equations 1-4 in Table 1. In order to use these metrics, input and output values were converted to their energy equivalent value using equation 5 (Mohammadshirazi et al., 2014) from Table 1. Inputs were labour cost, coconut oil, methanol, and electricity. The main outputs were the biodiesels and glycerol. The actual quantities that were used in the laboratory were recorded and used in energy equivalent calculations.

Energy equivalent conversion values for labour, alcohol, electricity, biodiesel and glycerol in the biodiesel process were previously determined (Mohammadshirazi et al., 2014, Hossain et al., 2012). However, KOH was used as the catalyst and waste cooking oil was the feedstock in Mohammadshirazi et al. (2014). In Hossain et al. (2012), the biodiesel was derived from coconut oil. The present study used H_2SO_4, NaOH, and refined coconut oil. Lower heating values (LHV), or net calorific values, can be used as energy equivalent conversion values for the coconut oil feedstock (Farobie and Matsumura, 2015). LHVs were determined from net calorific value laboratory analyses of the coconut oils and biodiesel (see Table 2).

Table 1. Metrics equations

Equation #	Metric	Units	Equation for calculation
1	*NER*	-	$= \frac{Energy\ output\ (MJ/L)}{Energy\ input\ (MJ/L)}$
2	*NEB*	MJ/L	$= Energy\ Output\ (MJ/L) - Energy\ Input\ (MJ/L)$
3	*EREV*	MJ/L	$= \text{Energy output of biodiesel}\ (MJ/L) - \text{Fossil energy inputs}\ (MJ/L)$
4	*FER*	-	$= \frac{Renewable\ fuel\ energy\ output\ (MJ/L)}{Fossil\ energy\ input\ (MJ/L)}$
5	*Total energy equivalent*	MJ/L	$= Quantity\ per\ 1L\ of\ biodiesel\ (unit/L) \times Energy\ equivalent\ conversion\ (MJ/unit)$
6	*Total cost and income equivalent*	US$/L	$= Cost\ equivalent\ (US\$/unit) \times Quantity\ per\ 1L\ of\ biodiesel\ (unit/L)$

Table 2. Calorific values

Property	Test Method	Palmola	Nariel	Naisa	Eastern Brand
Net Calorific Value, BTU/lb	ASTM D4868	17973	18001	17973	18018
Net Calorific Value, MJ/kg	-	41.81	41.87	41.81	41.91

*Conversion Rate:*1 Btu/lb = 2.326 kJ/kg

Since energy can take many forms and is defined as anything that makes it possible to do work (Banks, 2000), it can be assumed that the standard heat of formation, in MJ/mol, of the catalysts is stored as potential energy and can be used as energy equivalent conversion values. The standard heat of formation for NaOH (crystalline) was listed at -101.99 kg-cal/mol (Lange and Forker, 1967), or 426.7 kJ/mol. For concentrated H_2SO_4 (aq), it was –887.3 kJ/mol (Lide, 2004).

6. Results and Discussion

6.1 Fuel Characterisation

All spectra of the biodiesels confirmed the presence of the expected methyl esters at similar retention times. The spectra for Naisa, which is representative of the other brands, is shown in Figure 1.

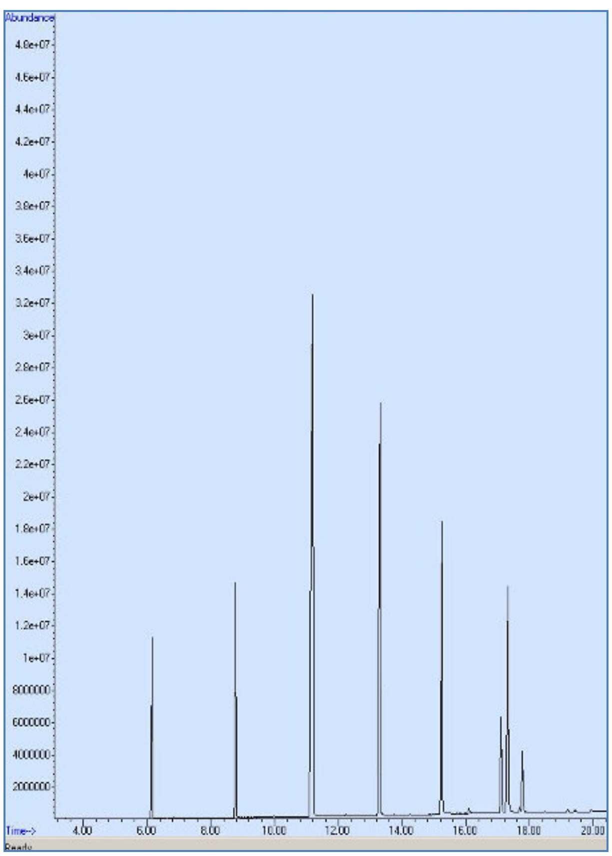

Figure 1. GC spectra for methyl esters present in Naisa biodiesel

Peaks were observed at retention times of 6.154, 8.761, 11.205, 13.279, 15.220 and 17.123 mins for methyl esters of octanoic acid, decanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid and octadecanoic acid. This agreed with the composition of the expected coconut oil methyl esters present in quantities >5% (Jayadas and Nair, 2006).

6.2 Fuel Properties

The main fuel properties specification used for comparison was the local TTS 569:2011 automotive vehicle specifications (TTBS, 2011). Although international specifications ASTM D975-08a for grade 2D diesel (Jääskeläinen, 2015) and ASTM D6751 and EN 14214 for biodiesel (Knothe, et al., 2005) are also listed in Table 3, it should be noted that this is for comparison only as the test methods differ.

All biodiesel properties were within specifications for the local automotive market except for density and cetane index, which are considered key properties for engine performance (Gülüm and Bilgin, 2015). Density for all biodiesels was higher than the TTS 569:2011 specification. Its value affects the engine output power, fuel consumption, combustion and exhaust emissions (Gülüm and Bilgin, 2015; Chinnamma et al., 2015) and its effect on engine performance is observed immediately (Chevron Corporation, 2015). However, as density values ranged from 873-875 kg/m3 they did fall within EN14214 specifications for biodiesel. Apart from Eastern Brand, all cetane numbers were lower than specification. However, the values, which ranged from 41 to 42 in this study, were similar to the cetane index value of 40.20 determined for coconut oil methyl esters in a previous study (Chinnamma et al., 2015). Low cetane numbers can cause the engine to misfire and slower engine warm-up (Knothe et al., 2005). These biodiesels therefore cannot be used in the local automotive market in their unadulterated form, but can be part of diesel-biodiesel blends that conform to specifications as is done in other countries (Santana et al., 2010).

6.3 Energy Analyses

The yield for acid transesterification of Eastern Brand was 99% to produce the lower FFA oil. Base transesterification yields were 94%, 92%, 94%, and 99%

Table 3. Properties of coconut oil biodiesels

Property	Test Method	TTS 569:2011 specifications	Palmola	Nariel	Naisa	Eastern Brand	International specifications		
							ASTM D975-08a	ASTM D6751	EN 14214
Flash point, ºC	ASTM D93	55 min	112	88	110	136	52	130 min	120 min
Water content, volume %	ASTM D95	0.05 max	<0.05	<0.05	<0.05	<0.05	NS	NS	*
Sediment, mass %	ASTM D473	0.01 max	<0.01	<0.01	<0.01	<0.01	NS	NS	NS
Cetane Index	ASTM D613	46 min	**42**	**41**	**41**	49	NS	NS	NS
Distillation temperature (90% volume recovered), ºC	ASTM D86	282-357	318	314	319	334	282- 338	360 max	NS
Pour point, ºC	ASTM D97	10 max	-9	-9	-9	3	NS	NS	NS
Copper strip corrosion resistance (3h at 50ºC)	ASTM D130	1	1b	1a	1b	1b	No.3 max	No.3 max	1
Kinematic viscosity (at 40ºC), cSt	ASTM D445	1.9-5.0	2.7	2.73	2.74	3.99	1.9-4.1	1.9-6.0	3.5-5.0
Density at 15ºC, kg/m^3	ASTM D1298	820-865	**873**	**874**	**875**	**875**	NS	NS	860-900

Keys: NS- Not specified; *- not specified in volume %; In **Bold** - Out of specification with reference to TTS 569:2011

for Eastern Brand, Palmola, Naisa, and Nariel, respectively.

Energy equivalents were first determined and are listed in Table 4. The total input and output values for each biodiesel from Table 4 were then used to calculate NER, NEB, NREV and FER (see Table 5).

NER, also termed as energy use efficiency, (Mohammadshirazi et al., 2014) values ranged from 0.55 to 0.63 for all biodiesels which meant that the process was 55-63% energy efficient. NER values from other literature included 3.23 for palm oil biodiesel (Cho et al., 2013), 0.92 for canola oil biodiesel (Farobie and Matsumura, 2015), and 1.49 for waste cooking oil (Mohammadshirazi et al., 2014). Values of 0.55-0.63 are therefore comparatively low. In this study, the calculations did not consider the unreacted methanol as an output because it was not purified and this would require additional labour and electricity as inputs. If considering the unreacted methanol similarly to that of other authors (Mohammadshirazi et al., 2014), the NER values increase from 0.79 to 0.89.

NEB was negative for all biodiesels, ranging from -34.41 to -29.09 MJ/L, and compared unsatisfactorily with the NEB of 14.9 MJ/L for waste cooking oil (Mohammadshirazi et al., 2014). A positive value of NEB was required for the fuel to be considered a sustainable source of energy (Kamahara et al., 2010). These negative values indicated that more energy was consumed than produced in the process.

Table 4. Energy analysis of inputs and outputs of biodiesel production (6:1 methanol to oil ratio)

Particulars	Unit	Quantity per 1L of biodiesel (unit/L)				Energy Equivalent Conversion value (MJ/unit)				Total energy equivalent (MJ/L)			
		Palmola	Nariel	Naisa	Eastern Brand	Palmola	Nariel	Naisa	Eastern Brand	Palmola	Nariel	Naisa	Eastern Brand
Inputs													
Human Labour	h	0.25	0.25	0.25	0.5	1.96	1.96	1.96	1.96	0.49	0.49	0.49	0.98
Coconut Oil	kg	0.95	1.02	0.94	0.95	41.81	41.87	41.81	41.91	39.72	42.71	39.30	39.81
Methanol	kg	1	1	1	1.1	33.7	33.7	33.7	33.7	33.7	33.7	33.7	37.07
NaOH	kg	0.008	0.009	0.008	0.009	10.67	10.67	10.67	10.67	0.09	0.10	0.09	0.10
H_2SO_4	kg	-	-	-	0.005	-	-	-	9.14	-	-	-	0.05
Electricity	KWh	0.0005	0.0005	0.0005	0.00075	11.93	11.93	11.93	11.93	0.006	0.006	0.006	0.009
ENERGY INPUT										**74.00**	**77.00**	**73.58**	**78.02**
Outputs													
Biodiesel	kg	0.86	0.86	0.86	0.86	40.37	41.87	40.37	48.95	34.72	36.01	34.72	42.10
Glycerol	L	0.33	0.26	0.3	0.27	25.3	25.3	25.3	25.3	8.35	6.58	7.59	6.83
ENERGY OUTPUT										**43.07**	**42.59**	**42.31**	**48.93**

Table 5. Energy performance metrics for 4 coconut oil biodiesels (6:1 methanol to oil ratio)

Items	Unit	Palmola	Nariel	Naisa	Eastern Brand
NER	-	0.58	0.55	0.57	0.63
NEB	MJ/L	-30.93	-34.41	-31.27	-29.09
NREV	MJ/L	0.92	2.22	0.91	4.98
FER	-	1.03	1.07	1.03	1.13

Net renewable energy value (NREV) and fossil energy ratio (FER) metrics indicate fossil energy content. Fossil energy inputs were, in this study, methanol, sodium hydroxide, sulphuric acid and electricity (Pradhan et al., 2009). NREV values were 2.22 MJ/L for Nariel, 0.92 MJ/L for Palmola, 0.91 for Naisa, and 4.98 MJ/L for Eastern Brand. The positive values indicated that less fossil fuel was used to generate the renewable fuel than was actually produced by the renewable fuel (Eshton et al., 2013). FER was 1.03 for Palmola and Naisa, 1.07 for Nariel, and 1.13 for Eastern Brand. This can be interpreted as 1.03-1.13 MJ/L of renewable energy that was obtained for every 1 MJ/L fossil energy input. Reported FER values were 1.3 for waste cooking oil (Mohammadshirazi et al., 2014), 4.56 (Pradhan et al., 2009) and 3.2 for soybean oil (Sheehan et al., 1998), all values of which were higher than reported in this study.

NEB and FER indicated that the process was not energy efficient. Improvement of these metrics can be achieved by either lowering the energy inputs and/or increasing the energy outputs. Table 4 indicated that coconut oil and methanol were the highest total energy equivalents input values. Whilst the coconut oil quantities cannot readily be changed, the methanol values in the process can be lowered. Although a 6:1 methanol to oil ratio is typically used (Ma and Hanna, 1999), the stoichiometric ratio is actually 3:1. NEB and FER indicated that too much fossil fuel was being utilised to produce the renewable fuel. Since a lowered methanol content should also improve these metrics, a follow-up experiment was conducted using the 3:1 stoichiometric ratio, with all other experimental parameters remaining the same.

Biodiesel yields using a 3:1 methanol to oil ratio for Palmola, Naisa and Nariel continued to be high at 97%, 98% and 94%, respectively. However, Eastern Brand was considerably less at 60% yield as compared to 94% with a 6:1 methanol to oil ratio. The energy analyses and metrics were then recomputed and are listed in Tables 6 and 7.

The metrics heavily dependent on fossil fuel content showed considerable improvement upon use of the 3:1 ratio. NREV increased from 0.92 – 4.98 to 9 – 21.31. FER increased from values close to 1 to values ranging from 1.52 -2.88. NER improved slightly with a lowered methanol to oil ratio, with the range increasing to 0.55-0.63. Although the values are still negative, NEB improved for Palmola, Naisa and Nariel, but not for Eastern Brand. NEB is used to determine loss or gain of energy. It indicates whether the process is sustainable (Cho, et al., 2013). Results show that even using a lowered methanol content, the process is not sustainable as the inputs are too high compared with the outputs. Another high energy input is that of coconut oil. As such, in terms of energy conversions, coconut oil is not a viable feedstock. Within the Caribbean, coconut oil is the most widely available local oil source. However, coconut oil biodiesel may not be a sustainable alternative to petrodiesel. Other feedstock inputs should therefore be investigated for a viable, sustainable process. Specifically, Mohammadshirazi et al. (2014) demonstrated via energy metrics that using waste cooking oil is one of the most sustainable options, and this is an option that can be explored in the Caribbean.

Table 6. Energy analysis of inputs and outputs of biodiesel production (3:1 methanol to oil ratio)

Particulars	Unit	Quantity per 1L of biodiesel (unit/L)				Energy Equivalent Conversion value (MJ/unit)				Total energy equivalent (MJ/L)			
		Palmola	Nariel	Naisa	Eastern Brand	Palmola	Nariel	Naisa	Eastern Brand	Palmola	Nariel	Naisa	Eastern Brand
Inputs													
Human Labour	h	0.25	0.25	0.25	0.50	1.96	1.96	1.96	1.96	0.49	0.49	0.49	0.98
Coconut Oil	kg	0.89	0.94	0.90	1.48	41.81	41.87	41.81	41.91	37.21	39.36	37.63	62.03
Methanol	kg	0.41	0.43	0.41	0.95	33.70	33.70	33.70	33.70	13.75	14.59	13.82	32.02
H_2SO_4					0.01				9.14				0.05
NaOH	kg	0.008	0.009	0.008	0.009	10.67	10.67	10.67	10.67	0.085	0.096	0.085	0.096
Electricity	KWh	0.0005	0.0005	0.0005	0.00075	11.93	11.93	11.93	11.93	0.006	0.006	0.006	0.009
ENERGY INPUT										**51.54**	**54.54**	**52.03**	**95.17**
Outputs													
Biodiesel	kg	0.85	0.86	0.86	0.84	40.37	41.87	40.37	48.95	34.31	36.01	34.72	41.12
Glycerol	L	0.13	0.18	0.21	0.31	25.30	25.30	25.30	25.30	3.29	4.55	5.31	7.84
ENERGY OUTPUT										**37.60**	**40.56**	**40.03**	**48.96**

Table 7. Energy performance metrics for 4 coconut oil biodiesels (3:1 methanol to oil ratio)

Items	Unit	Palmola	Nariel	Naisa	Eastern Brand
NER	-	0.73	0.74	0.77	0.51
NEB	MJ/L	-13.94	-13.98	-12.00	-46.21
NREV	MJ/L	20.47	21.31	20.81	9.00
FER	-	2.72	2.76	2.88	1.52

Cooking oil is one of the top ten imports in the Caribbean, accounting for $246.64M USD in 2011 (FAOSTAT, 2016). In 2013, Antigua and Barbuda, the Bahamas, Barbados, Jamaica, and Monstserrat alone spent 57.7 M USD on edible oils, importing 62,277 tonnes (FAOSTAT, 2016). Waste collection is paid for via taxation in Jamaica, and Belize, through government subventions in Trinidad and Tobago, Haiti, and Suriname, and direct billing or private companies in the Bahamas (Riquelme et al., 2016). In Barbados and Guyana, waste collection is supported via both taxes and government subventions (Riquelme et al., 2016). Through the use of waste cooking oil for biodiesel production, an opportunity exists for the sustainable production of biodiesel, reduction in food import spending, and reduction in the cost of waste collection.

7. Conclusions

The energy performance evaluation of four coconut oil biodiesels revealed the following:

1. With respect to fuel properties, coconut oil biodiesel could be used in the local market as a constituent in environmentally friendly, sustainable blends with diesel fuel.
2. NEB and NER energy metrics indicated that the process was not energy efficient at both the 6:1 and 3:1 methanol to oil ratios.
3. NREV and FER energy metrics indicated that too much fossil energy was being used to produce the renewable fuel when a 6:1 methanol to oil ratio was used. At the 3:1 ratio, NREV and FER values were comparable to the literature values. They can be further improved with added use of bioalcohols in the process, and renewable energy as the heat source.

It should be noted that a conventional energy metrics analysis cannot satisfactorily be reflective of certain important benefits associated with the use of biodiesels such as reducing oil imports and foreign debt, decreasing greenhouse gas emissions, stimulation of domestic agricultural production by expansion of demand for oil feedstock and generating rural employment (Nguyen et al., 2007), as well as conserving on current petroleum reserves. There has also been step-wise reduction of fuel subsidies in Trinidad and Tobago. This created a diesel price increase from TT$1.50/L (US$0.23/L) to TT$2.30/L (US$0.35/L) (GORTT, 2016) over a one-year period. These concerns, coupled with simultaneous concerns about international low oil prices (GORTT, 2016), have encouraged the investigation into alternative fuels as a reliable and competitive alternative to petroleum fuels, ensuring that this study is both timely and relevant.

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Authors' Biographical Notes:

Phaedra Jaggernauth *is a PhD Candidate and Research Assistant at The University of Trinidad and Tobago. Her qualifications include MSc. in Petroleum Engineering and BSc. in Chemistry and Management (Hons.) from The University of the West Indies, St. Augustine.*

Enoch Ghany *is a Mechanical Engineer with working experience in the T&T Petrochemical and Petroleum Industry. He holds a BSc. in Mechanical Engineering (Hons.) from The University of the West Indies, St. Augustine, and is completing the MSc. in Petroleum Engineering at the same institution.*

Puran Bridgemohan *is an Associate Professor in Crop Sciences at the Bio-Sciences, Agriculture and Food Technology Department of The University of Trinidad and Tobago. Dr Bridgemohan's professional experience extends across the Caribbean. He has held over 11 titles at various associations, including Specialist/ Consultant in Project Management for Caribbean Rice Improvement, Executive Member of TAC – WISBEN, Barbados, and Project Reviewer of the Common Fund for Commodities [CFC-United Nations], SIRI, Jamaica. He is currently the Chairman of the Board of Directors at the Trinidad and Tobago Bureau of Standards. His associations are part of an extensive list such as the Weed Science Society of America, the Caribbean Food Crop Society, the International Allelopathy Society, the International Society of Sugarcane Technologists, West Indies Sugarcane Breeder Network and the Caribbean Rice Network.*

Ejae John *is an Associate Professor in the Process Engineering Department of The University of Trinidad and Tobago. She has participated in interdisciplinary research (chemistry and chemical engineering) to address a variety of technical and environmental challenges throughout her career. Locally, this includes projects with the Chemical and Process industry such as optimising plants, green designs, and utilisation of waste as fuel. It is her goal to use her skills to address issues in sustainable processes and products, including catalyst optimisation, waste reduction, and fuel supplementation.*