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Effects of Physico-Chemical Properties of the Blended Diesel and Waste Cooking Oil Biodiesel

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Biodiesel is a renewable fuel with similar chemical and physical properties to diesel. The study used waste cooking oil to make biodiesel because reusing waste cooking oil harms human health by raising FFA levels above the norm. Transesterification was performed at 60 °C using a 1:5 methanol to waste cooking oil volume ratio, 30 min reaction time, 600 rpm stirring speed and 1% wt. KOH was employed as a homogenous base catalyst. Biodiesel samples of B0, B2, B5, B20, B40 and B100 were processed at 25 ºC in combination with petrodiesel. Samples were tested for density, kinetic viscosity, flash point, acid value and pH. The fuel economy and flue gas analysis were performed using three-wheeler diesel. The amount of waste cooking oil biodiesel increases the density, kinematic viscosity, flash point, acid value and pH of the sample. In blended diesel, the amount of biodiesel also lowered CO_2, CO, NO, NO_x, hydrocarbon (HC) and SO_2 emissions.

Keywords: Biodiesel, Blended biodiesel, Flue gas emissions, Renewable energy, Transesterification.

INTRODUCTION

In recent times, energy consumption has increased dramatically due to lifestyle changes and significant population growth [1]. This increase in energy demand has been fueled by fossil resources, which have a significant environmental impact on global warming and deforestation [2]. The industries and the transportation sector uses fuels made from fossil resources that release large amounts of greenhouse gases (GHGs) and other harmful air pollutants which are hazardous to the environment and human health [3]. Diesel takes precedence over black smoke emissions and SO_2 emissions among automotive fuels, contributing to one-third of greenhouse gas emissions. The study of global energy consumption trends revealed that fossil fuel-powered vehicles contribute more than 70% of all CO emissions and 19% of corresponding CO_2 emissions [4]. As fossil fuels disappearing fast, there is a great need to find alternative fuels to meet global energy demand and reduce green house gas and pollution emissions [5]. Fossil fuels are a limited energy source and their combustion causes various environmental problems [6]. This has led to the search for alternative renewable fuels such as biodiesel derived from vegetable, animal or waste oil feeders [1,7]. Biodiesel is more suitable than conventional diesel due to its lower sulphur content, higher aromatic content and higher flashpoint. According to the literature, conventional diesel can contain up to 500 ppm SO_2 and 20-40 wt.% aromatic compounds [5,8].

Compared to biodiesel, vegetable oil as a fuel source is simpler and the production cost is lower. However, vegetable oils generally have adverse factors such as high viscosity, high ignition point, poor volatility, high cloud point and turbidity and contain phosphorus, reducing abrasion resistance [9]. Diesel engines are at risk of piston ring exhaust, oil pipeline or filter freezing, difficult cold start, poor atomization, incomplete combustion and large fuel consumption. Long-term use of vegetable oils can cause serious carbon dioxide emissions and other problems [9]. To avoid these problems, the properties associated with the combustion of vegetable oil must be changed to bring them closer to petroleum diesel. Modifications used include micro-emulsion, pyrolysis (thermal cracking) and transesterification. Transesterification is one of the major and most important steps in producing clean and environmentally safe biodiesel from vegetable oils [10].

Biodiesel exhibits chemical and thermal properties which are significantly similar to diesel fuels. Biodiesel has a higher cetane number; and thus more suitable for combustion in a diesel engine. Biodiesel has a good lubricant and can compensate for the loss of lubricant due to the removal of sulphur from the blend with low sulphur diesel fuel [11]. Instead of using biodiesel, blended biodiesel can be used for the diesel engine; blended biodiesel is a blend of diesel and biodiesel. Biodiesel is completely miscible with diesel. Blending can be done at any rate to improve fuel properties. However, due to the variant chemical nature of biodiesel and diesel, changes in physico-chemical properties can occur, which can affect engine performance and emissions.

Biodiesel blends can be developed by volume from a precision beaker glass and stirred at 2000 rpm for 15 min to ensure homogeneity. Although there is an advantage in preparing the mixture on a weight basis, the weight fraction does not change with temperature. Still, the general practice in the fuel industry is to perform the mixing process based on volume at the ambient temperature of the mixing site [12].

Many workers have examined the biodiesel-diesel blend in different types of car engines. Subsequent results revealed that the diesel engine can operate satisfactorily with biodiesel and its blends without any mechanical issues [13]. These performance characteristics can be better explained by studying the biodiesel-diesel blend's composition and prop-erties [14]. In customary, biodiesel derived from palm oil has different properties than other biodiesels and mineral diesel made from other organic sources. Compared to mineral diesel, palm oil has a higher viscosity and density. Moreover, various studies have shown that the biodiesel derived from alternative feedstock with different fatty acid profiles has higher variable engine performance and emission profile. Therefore, the data on biodiesel's physical properties and emission profile and their blended fuels are required to analyze the characteristics of biodiesel when operating with conventional diesel engines [7,14]. The use of biodiesel-diesel blends increases the oxygen content of fuels and reduces CO emissions. A study with biodiesel containing 10, 20, 30, 50 and 100% blends shows that blends generally reduce black smoke emissions than petroleum diesel. However, as the percentage of ester increases, fuel consumption and NO emissions also increase [11].

According to the literature, low calorific value, high density and viscosity of the biodiesel blends, the brake thermal efficiency (BTE) of the engine was slightly lower than that of all the biodiesel blends tested at all loads compared to the petroleum diesel fuel [15]. The BTE can be defined as the indication of how much of the fuel is converted into beneficial work. Low cylinder pressure and heat release rate were observed with biodiesel mixtures due to the slow oxidation reaction rate at low combustion temperatures.

The high cost of biodiesel compared to today's petroleum-based diesel is a significant barrier to its commercialization. Approximately 70-85% of the total biodiesel production cost arises from the cost of raw materials. As such using a readily available feedstock such as waste cooking oil (WCO) helps to produce biodiesel competitive with petroleum diesel. This opens up a golden opportunity for WCO to use its products as nutrients [16]. Therefore, it is important to assess the chemical and physical properties of different biodiesel blends, flue gas composition and fuel economy compared to conventional diesel and biodiesel products from WCO.

EXPERIMENTAL

Preparation of reused cooking oil: The marinated chicken was fried in fresh cooking oil to replicate the restaurant's cooking process. Once the cooking process completed, used cooking oil was allowed to cool for the second round. Once it reached room temperature, 20 mL of ample was taken for free fatty acid (FFA%) analysis. This oil sample was considered the "1st attempt" of frying. After the first sample was taken, the remaining used oil was reheated and at the appointed time, a same quantity of fresh chicken was fried. A 20 mL portion of used cooking oil was removed and added into a clean bottle and it was considered the "2nd attempt" of frying. This procedure was followed up to the "10th attempt" to generate waste cooking oil similar to the restaurant process.

Determination of FFA content of used cooking oil: The used cooking oil, which was taken into a sample bottle of 1 g, was added to a titration flask containing 125 mL of isopropyl along with 5-6 drops of phenolphthalein as an indicator. The mixture was titrated with 0.1 M KOH and the volume which required a colourless solution to turn pale pink was recorded (V1). A similar procedure was followed for the blank sample, which does not contain oil and recorded the KOH consumption (V2). The entire procedure was performed three times for each sample to minimize personal errors. The FFA content was then calculated for each corresponding sample based on the following equations (eqns. 1 and 2).

$$\text{Acid value} = 56.1 \times 0.1 \times (V_2 - V_1) \quad (1)$$

$$\text{FFA (\%)} = \frac{\text{Acid value}}{2} \quad (2)$$

where: V_1 is the 0.1 M KOH volume required for the sample, V_2 is the 0.1M KOH volume required for the blank sample.

Transesterification process: The transesterification reaction was performed in 300 mL of the batch reactor. A 100 mL of pre-treated waste cooking oil sample was stirred at 600 rpm at 60 ºC. A mixture of methanol and catalyst was added to the oil as a form of methoxide. The transesterification reaction was then performed at 60 ºC and a catalyst of KOH (1 wt.%) of the oil sample. After 30 min, the reaction was completed and the reaction mixture was poured into a separate funnel. The separation process was left overnight to obtain two layers, glycerol (lower layer) and methyl ester (upper layer). Biodiesel purification was done by rinsing with warm distilled water, which is 50% of the biodiesel volume, for 20 min. After that biodiesel was heated to 120 ºC for 20 min to remove residual water and unreacted chemicals.

Blended biodiesel: According to Table-1, biodiesel and conventional diesel were mixed based on volume and mixed biodiesel samples were prepared at B0, B2, B5, B20, B40 and B100 at 25 ºC. The physical properties such as density, kinematic viscosity, flash point and the chemical parameters such as acid value and prepared samples' pH were examined accordingly. Fuel economy and flue gas analysis were tested using

TABLE-1
REQUIRED VOLUMETRIC RATIO OF BIODIESEL AND CONVENTIONAL DIESEL AT A CONSTANT TEMPERATURE TO OBTAIN THE PROPOSED BLENDED SAMPLES

Blended biodiesel/ biodiesel/conventional diesel	Volume ratio of conventional diesel (%)	Volume ratio of biodiesel (%)
B0	100	0
B2	98	2
B5	95	5
B20	80	20
B40	60	40
B100	0	100

a diesel three-wheeler. The vehicle's specifications are listed in Table-2.

TABLE-2
TECHNICAL SPECIFICATIONS OF THE VEHICLE-DIESEL THREE-WHEELER

Parameter	Value
Fuel type	Diesel
Engine type	Single cylinder-Naturally aspirated, Air-cooled, DI
Wheel base (mm)	1920
Displacement	436 cc
Kerb weight (Kg)	420
Fuel tank capacity (L)	10.5
Gear type	Constant mesh (4 forward, 1 reverse)
Max. power	W @ 3600 + 50 rpm

RESULTS AND DISCUSSION

Waste cooking oil (WCO) properties with frying attempts: Ten WCO samples were prepared by increasing the reusing attempts. The samples were numbered 1-10 for easy identification. The percentage of free fatty acid (FFA%) of WCO samples was analyzed before biodiesel production. The Sri Lanka Food Act, mention the acceptable limit of the FFA% of coconut oil, palm oil and other vegetable oils (less than 1%) [17]. According to this act, the oil we consume for food processing should not exceed the given FFA%. When waste cooking oil reusing for cooking purposes, its percentage of free fatty acid is gradually increasing. Based on the experiments, FFA% variation with the reusing attempts is given in Fig. 1 for the coconut oil sample. According to Fig. 1, it can be clearly seen that only fresh cooking oil and the one-time reusing of oil falling within the standard limits (FFA% < 1) given in the Food Act.

Properties of biodiesel blends: Blended diesel properties were analyzed and presented in Table-3. Only the blends which is given in Table-3, perform the diesel three-wheeler to check the engine performance even though B30, B50, B60, B70, B80, B90 are also produced.

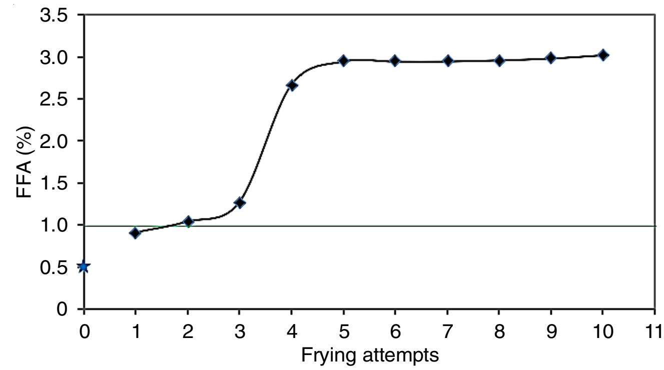

Fig. 1. FFA% variation with frying attempts for coconut oil samples

Effect of blending on kinematic viscosity (V): Fuel with a higher viscosity has poor atomization characteristics and narrow spray angle during the combustion process [18]. The petroleum diesel has a viscosity of 3.1062 mm^2/s, while biodiesel produced from waste cooking oil (WCO) has a kinematic viscosity of 4.2336 mm^2/s. According to the ASTM D6571 standards, biodiesel should have a viscosity of between 1.9-6.0 mm^2/s [19].

It is noted that B100 (pure biodiesel) is having 1.4 times higher viscosity than the pure diesel which is B0. Therefore, with the increase of the blended ratio from B0, B2, to B100, kinematic viscosity should increase and the experimental values were found to obey this fact.

With the increasing waste cooking oil biodiesel percentage, the sample's viscosity was found to increase (Fig. 2). In order to get the better quality, B2 to B100 biodiesel blends are produced with a 10-point gap to fill the missing points. Those samples were only produced and analyzed the parameters to develop the relationship of the parameters only. Selected samples were used for engine performance testing.

The relation between the kinematic viscosity (v) of the blend and the biodiesel percentage (X) blended can be defined with the mathematical expression as:

$$V = 0.011X + 2.961 \quad (3)$$

where V = kinematic viscosity and X = biodiesel percentage.

The kinematic viscosity of the biodiesel can be estimated using eqn. 3, which is a variable of the percentage of biodiesel in the diesel blend. The equation can validate with a new sample. The validated results for the biodiesel sample, B25, are given in Table-4.

Effect of blending on density (ρ): There is a relationship between the density of biodiesel and the amount of fuel consumption. It is preferred to have less dense fuel to reduce fuel con-

TABLE-3
BLENDED DIESEL PROPERTIES

Property	Test method	B0	B2	B5	B10	B20	B40	B100
Density at 15 °C (g/cm^3)	ASTM D4052	0.8080	0.8110	0.8150	0.8170	0.8200	0.8350	0.8592
Kinematic viscosity at 40 °C/mm^2/S	ASTM D445 - 19a	3.0062	3.0542	3.067	3.0921	3.1294	3.3748	4.2336
Flash point (°C)	ASTM D93 - 20	66	72	76	80	82	84	124
Acid value (mg KOH/g)	ASTM D664	0.7012	0.7012	0.9817	1.2622	1.2622	1.5427	1.8232
pH	Bench top pH meter	6.92	7.03	7.72	7.88	7.18	7.83	7.34

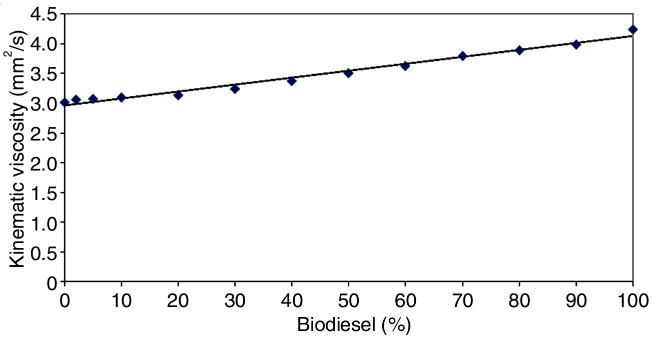

Fig. 2. Variation of kinematic viscosity of the blends with the biodiesel percentage blended

TABLE-4
COMPARISON OF VISCOSITIES PREDICTED USING eqn. 3 AND THE EXPERIMENTAL VALUES

Biodiesel blend	Predicted viscosity by eqn. 3	Experimental viscosity
B20	3.181	3.1294
B25	3.236	3.1758
B30	3.291	3.2356

sumption. Table-3 showed that biodiesel is slightly denser than petroleum diesel. The relationship between blended percentage and the density of the biodiesel blend is given in Fig. 3. According to the EN14214 standards, biodiesel should have a density of between 0.860-0.900 g/cm^3 [16].

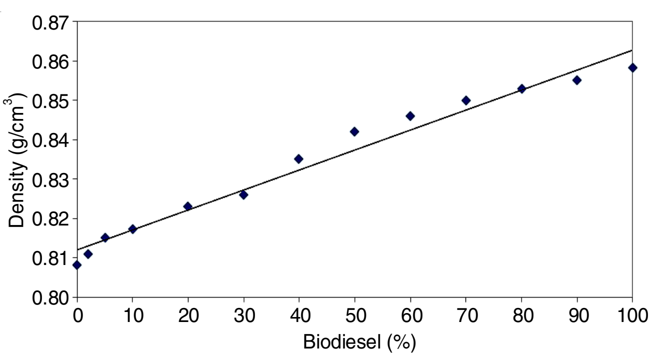

Fig. 3. Variation of the density of the blends with the biodiesel percentage blended

The relationship between the density of the blended biodiesel and the percentage of biodiesel is given in eqn. 4:

$$\rho = 0.0005X + 0.8121 \quad (4)$$

where ρ = density, X = biodiesel percentage.

The density of the biodiesel can be estimated using eqn. 4, which is a variable of the percentage of biodiesel in diesel blend. The validated results for the biodiesel sample (B25) are given in Table-5. Produced blended diesel satisfied with the ignition requirements. The flashpoint of the blended diesel also increases with the increase in the biodiesel percentage in the diesel blend.

TABLE-5
COMPARISON OF DENSITIES PREDICTED USING eqn. 4 AND THE EXPERIMENTAL VALUES

Biodiesel blend	Predicted density by eqn. 4	Experimental density
B20	0.822	0.823
B25	0.825	0.824
B30	0.827	0.826

The acid value is defined as the amount of free fatty acids in the biodiesel sample. The petroleum diesel shows the lowest acid value, which is 0.7012 mg KOH/g and the B100 has the highest, which is 1.8232 mg KOH/g. The acid value of the blended biodiesel-diesel fuel increases with increasing biodiesel fuel in the blend.

Engine performance with blended diesel: The blended diesel applied to the diesel three-wheeler and analyzed the exhaust gas emission to check the emission reduction. Table-6 represents the flue gas emission values of biodiesel after applied to the diesel three-wheeler. According to the percentage of CO_2 emission, it is clear that the percentage decrease with the increase of biodiesel content in the blend. The reason may be the lower carbon to hydrogen ratio of biodiesel [20].

Moreover, CO emission also decreased with the increase of biodiesel percentage in the blended diesel. Similarly, NO and NO_2 are also decreasing from petroleum diesel which is B0, to pure biodiesel, B100. However, those emissions should have impacts from other factors as well. Therefore, closer consideration should be taken into account, before concluding the emission levels with blended diesel.

The fuel economy of the biodiesel was recorded for a diesel three-wheeler. The number of kilometers travels with the 1 L of biodiesel has also been recorded (Table-7). There is no impact on the engine efficiency with the biodiesel or blend of biodiesel. It has almost similar fuel efficiency with biodiesel and with blended biodiesel. However, fuel efficiency varies with other variables such as the vehicle engine, power, load of the vehicle and the driving style. Therefore, it is only possible to analyze the variation of the mileage per liter of fuel.

Conclusion

Waste cooking oil (WCO) can be used for biodiesel production as a low-cost feedstock that cannot be reused for cooking

TABLE-6
FLUE GAS EMISSION COMPARISON FOR BLENDED DIESEL

Exhaust emission	B2	B5	B10	B20	B40	B100	Petro diesel
CO_2 (%)	0.9	0.9	0.9	0.9	0.8	0.8	1
CO (ppm)	278	275	270	205	166	146	278
NO (ppm)	9	9	9	8	7	7	9
NO_X (ppm)	27	27	26	25	22	20	28
HC (ppm)	15	15	13	12	8	4	15
SO_2 (ppm)	16	16	14	14	12	4	16

TABLE-7
FUEL ECONOMY

Diesel type	Fuel economy (km/L)
B2	39.6
B5	39.2
B10	39.2
B20	39.6
B40	40.8
B100	41.0
Petroleum diesel	40.0

purposes because of its high FFA level. Depending on the FFA% of the waste cooking oil with the results of the frying attempts, the standard level of FFA was increased by more than 1% after a one-time reusing of oil. It was found that the kinematic viscosity of the sample increases as the percentage of the blend of biodiesel increases. All samples had a viscosity that conforms to the ASTM D6571 standard range. In parallel with the kinetic viscosity, the density of the B0, B2, B5, B20, B40 and B100 samples was increased from 0.8080 to 0.8592, respectively. The lowest acid value at 0.7012 mg KOH/g was recorded for B0 while the highest at 1.8232 mg KOH/g was recorded for B100. As the biodiesel fuel in the blend increases, the acid value of the blended biodiesel-diesel fuel increases. In terms of engine performance with blended diesel, emission levels of CO_2, CO, NO, NO_x, hydrocarbons and SO_2 were reduced by increasing the percentage of biodiesel. However, those emissions must be influenced by other factors as well. Therefore, emissions levels with blended diesel should be considered more carefully. Fuel efficiency varies according to the engine, power, weight of the vehicle and the driving style of the driver. No effect was recorded on engine performance with biodiesel or biodiesel blend. It has the same fuel efficiency as biodiesel and blended biodiesel.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. R. Avtar, S. Tripathi, A.K. Aggarwal and P. Kumar, *Resources*, **8**, 136 (2019); https://doi.org/10.3390/resources8030136
2. M.C. Bobadilla, R.L. Lorza, R.E. García, F.S. Gómez and E.V. Vergara-González, *Energies*, **10**, 130 (2017); https://doi.org/10.3390/en10010130
3. R.T. Wadanambi, L.S. Wandana, K.K.G.L. Chathumini, N.P. Dassanayake, D.D.P. Preethika and U.S.P.R. Arachchige, *J. Res. Technol. Eng.*, **1**, 86 (2020).
4. H. Du, Z. Huque and R.R. Kommalapati, *J. Renew. Energy*, **2018**, 7350715 (2018); https://doi.org/10.1155/2018/7350715
5. H. Emaish, K.M. Abualnaja, E.E. Kandil and N.R. Abdelsalam, *Sci. Rep.*, **11**, 9811 (2021); https://doi.org/10.1038/s41598-021-89287-0
6. F. Perera, *Int. J. Environ. Res. Public Health*, **15**, 16 (2017); https://doi.org/10.3390/ijerph15010016
7. K.A. Abed, M.S. Gad, A.E.K. El Morsi, M.M. Sayed and S.A. Elyazeed, *Egyptian J. Petrol.*, **28**, 183 (2019); https://doi.org/10.1016/j.ejpe.2019.03.001
8. U.S.P.R. Arachchige, K.I.A. Wijenayake, K.A.V. Miyuranga, D. Thilakarathne, N.A. Weerasekara and R.A. Jayasinghe, *Int. J. Scientific Eng. Sci.*, **5**, 1 (2021).
9. J. Li, W. Wang and F. Li, *Energy Sources A* (2020); https://doi.org/10.1080/15567036.2020.1811431
10. M. Kurañska and E. Malewska, *Ind. Crops Prod.*, **162**, 113294 (2021); https://doi.org/10.1016/j.indcrop.2021.113294
11. M.A. Hazrat, M.G. Rasul and M.M.K. Khan, *Energy Procedia*, **75**, 111 (2015); https://doi.org/10.1016/j.egypro.2015.07.619
12. A.S. Silitonga, H.H. Masjuki, T.M.I. Mahlia, H.C. Ong, W.T. Chong and M.H. Boosroh, *Renew. Sustain. Energy Rev*., **22**, 346 (2013); https://doi.org/10.1016/j.rser.2013.01.055
13. X.J. Man, C.S. Cheung, Z. Ning, L. Wei and Z.H. Huang, *Fuel*, **180**, 41 (2016); https://doi.org/10.1016/j.fuel.2016.04.007
14. T. Kaya, O.A. Kutlar and O.O. Taskiran, In Proceedings of the 14th International Combustion Symposium, Karabük, Turkey, pp. 52-60 (2018).
15. A.K. Sharma, P.K. Sharma, V. Chintala, N. Khatri and A. Patel, *Int. J. Environ. Res. Public Health*, **17**, 3896 (2020); https://doi.org/10.3390/ijerph17113896
16. H. Liu, X. Ma, B. Li, L. Chen, Z. Wang and J. Wang, *Fuel*, **209**, 62 (2017); https://doi.org/10.1016/j.fuel.2017.07.066
17. The Gazette of the Democratic Socialist Republic of Sri Lanka, THE FOOD ACT, No. 26 OF 1980 (1990); http://eohfs.health.gov.lk/food/images/pdf/regulations/food_standards_regulations_1990_en.pdf.
18. A. Sarin, Biodiesel: Production and Properties, Royal Society of Chemistry: U.K. (2012).
19. R.B. Kiran, T.S. Rahul and K. Sivaji, V.G. and Vardhan, *IOP Conf. Series: Mater. Sci. Eng.*, **330**, 012092 (2018); https://doi.org/10.1088/1757-899X/330/1/012092
20. T. Kaya, O.A. Kutlar and O.O. Taskiran, *Energies*, **11**, 2814 (2018); https://doi.org/10.3390/en11102814