BEST: International Journal of Management, Information Technology and Engineering (BEST: IJMITE)
ISSN (P): 2348-0513, ISSN (E): 2454-471X,
Vol. 4, Issue 3, Mar 2016, 27-34

TREATMENTS OF BIODIESEL WASHING WATER

AYOOLA A.A, ORESEGUN O. R, OLADIMEJI T. E & LAWAL S. A

Department of Chemical Engineering, Covenant University, Ogun State

ABSTRACT

The main objective of this study was to produce biodiesel from palm kernel oil and to purify the biodiesel washing water generated through adsorption, acidification, coagulation and filtration treatment processes. Removal efficiencies of these treatment processes were investigated by analysing biochemical oxygen demand (BOD), chemical oxygen demand (COD), pH, conductivity, total dissolved solids (TDS) and elements present in the biodiesel washing water (before and after treatments). The results of the trans-esterification process showed that the highest biodiesel yield of 87.6% was obtained at a reaction time of 65 minutes and methanol to oil mole ratio of 6:1.The overall removal efficiencies obtained using the stated water treatment processes were 65% (BOD), 38% (COD), 75% (TDS) and 94% (conductivity).The treated washing water met the waste water discharge standards of FEPA. Hence, adsorption, acidification, coagulation and filtration, were effective in treating biodiesel washing water.

KEYWORDS: Acidification, Adsorption, Biodiesel, Coagulation, Trans-esterification

INTRODUCTION

Biodiesel is a renewable, clean-smoldering diesel substitution, produced from the trans-esterification process between triglycerides of plant oils (or animal fats) and low carbon chain alcohol, in the presence of alkaline or acidic catalyst (Ayoola *et.al.*, 2013; Farha, 2008). That is, it is a fuel of mono-alkyl esters of long chain fatty acids (Veljković*et. al.*, 2014;Srivastava and Prasad, 2000).It can be utilized alone or mixed with diesel in any existing diesel engine without any modification or adjustment (Eevera*et. al.*, 2009).

Biodiesel is an alternative to diesel fuel due to the fact that it can reduce the dependence on crude oil foreign imports and enhance the energy security, it has favorable energy return on energy invested, it can reduce greenhouse emissions and lower harmful emissions, and it is biodegradable, nontoxic, and renewable. It helps to improve rural economies since it involves the use of biomass as the main raw material (Ayoola, 2015;Ngamlerdpokin*et. al.*, 2011).

During trans-esterification process, a product of two immiscible layers of glycerol and biodiesel (fatty acid alkyl ester) are formed. The biodiesel obtained from this reaction is impure and has to be washed, using warm water, to make it pure (Ayoola, 2015;Ngamlerdpokin*et. al.*, 2011).During washing process, the warm water dissolves all impurities in biodiesel and then becomes impure. Biodiesel washing water (waste water) generated is a viscous liquid with opaque white colour. It is alkaline and contains dissolvable salts, catalyst used, the unreacted oil or fat, glycerol, soaps and any other organic impurities present (Kuwornoo, 2010; Suehara, 2005).

The large amount of wastewater generated is hazardous to the environment if not treated before it is being discarded into the sewage systems, lakes, rivers (Suehara, 2005). The biodiesel waste water generated can be treated using physical, chemical, physico-chemical, electrochemical, biological and integrated treatment processes (Daud*et. al.*, 2014;

Romano, 1982).

Adsorption is a surface-based process that allows a film of pollutant molecules on the surface of the suspended solid particles in a packed in a column(Pitakpoolsil andHunsom, 2014; Liu *et. al*., 2009). The nature of bonding experienced depends on the manner of interaction of the the species on the surface of the adsorbent (Liu *et. al*., 2009). The adsorption of impurities from biodiesel wastewaters is mostly a physical interactions between the adsorbent surface and the impurity particles (Pitakpoolsil andHunsom, 2014; Liu *et. al*., 2009)

Acidification is generally utilized as a pretreatment step prior to chemical or other treatment of biodiesel wastewater treatment processes. This involves pH adjustment of biodiesel waste water by adding an acid to destabilize and annihilate emulsion of oil in the wastewater; therebydissolving the oily impurities before the coagulation process (Daud*et. al.*, 2014). Coagulation or flocculation aids in the removal of oil in biodiesel wastewater through the introduction of an appropriate coagulant, such as an inorganic salt (e.g. ferric chloride or aluminium sulfate) or a pre-polymerized inorganic compound (e.g. polyaluminium chloride).

Analysis of the impurity removal efficiency can be carried out through the determination of the wastewater biochemical oxygen demand (BOD), chemical oxygen demand (COD), pH, conductivity, total dissolved solids (TDS) and elements present, before and after each of the treatment processes (Daud*et. al.*, 2014; Suehara, 2005)

The aim of this study is to produce biodiesel from palm kernel oil trans-esterification process and to assess the effectiveness of adsorption, acidification, coagulation, flocculation and filtration treatment processes during the purification of the wastewater generated from the biodiesel production. Table 1 shows the typical properties of palm kernel oil (PKO).

Table 1: Properties of Palm Kernel Oil

Properties		Values
Iodine Value	(cg Iodine/g Oil)19.3	
Saponification Value	(mgKOH/g Oil)	250
Kinematic Viscosity	(@ 40 ^{0}C, mm^2/s)	30.1
Refractive Index	(@ 40 ^{0}C	1.398

Kuwornoo,2010

MATERIALS AND METHODS

Determination of Percentage of Acid Value

20g of absolute ethanol was added to 10g of crude PKO in a 250 ml. The mixture was shaken and slightly heated for 10 minuites so as to have homogeneous mixture. 2 drops of phenolphthalein indicator was added and titration was carried out with 0.1M NaOH. The End point at which the oil changed from light brown to deep purple was recorded in order to determine the oil acid value.

Removal of FFA Using Alkaline Treatment

100 grams of PKO was measured into a conical flask and heated up to 40^{0}C at a steady rate using a magnetic stirer. 10 ml of 0.125M of NaOH was added slowly into the heated oil. The mixture was maintained at temperature of 40^{0}C.After 20minutes of saponification reaction, the liquid mixture obtained was poured into a measuring cylinder and allowed to settle for 20 minutes. There was soap formation at the baseof the container, whileoil free of FFA was at the

upper lower (trace of soap formed at the top were first scrapped out). Separation of the two layers was carried out and the oil was dried in oven at 110^0C for 30 minutes, to remove water present. This procedure was repeated for the required amount of oil.

Trans-Esterification of Palm Kernel Oil

Minitab 17 software and Factorial method were used for the design of experiment. 100 grams of oil, 0.7 g of KOH catalystand 60^0C reaction temperature wereconstant during each of the trans-esterification experimental runs. Oil was preheated to a steady temperature of 55^0C using a magnetic stirer on a heating mantle. The temperature was constantly monitored with a thermometer that was fixed into the flask through one of the corks in one mouth of the three legged flat bottom flask. Through slight heating, KOH pellets were dissolved in the required amount of methanol in a conical flask which was corked to prevent loss of methanol. Potassium methoxideformed was poured into the pre-heated oil in the three legged flat bottom flask. The content of the flask was stirred with a magnetic stirrer at a steady speed of 400 rpm and heated to a steady temperature of 60^0C. The reaction time was varied for experimental runs. A product of two layers obtained was poured into a separating funnel mounted on a retort standfor a period of 6 hours to allow total separation. The lower phase of glycerin and upper phase of biodiesel were separated. Table 2 shows the variation of the two factors and the pure biodiesel yield obtained.

Generation of Biodiesel Washing Water

To remove any form of impurity present in the impure biodiesel produced the biodiesel was 'washed' with warm water in a separating funnel repeatedly, until the warm water leaving the funnel remained clear as it was before being introduced into the funnel.The washing water was collected and stored as waste biodiesel water.Also, pure, but wet, biodiesel obtained was then dried in the drying oven for 45 minutes, to remove moisture content.

Table 2: Pure Biodiesel Yield Obtained From the Varied Methanol/Oil Mole Ratio and Reaction Time

	Methanol/Oil		Reaction Time	Yield
Mole Ratio		(Minutes)	%	
	6.0		65	87.6
	7.5		55	87.4
	9.0		65	75.9
	9.0		45	86.2
	7.5		55	87.4
	6.0		45	67.4
	7.5		55	87.4
	7.5		55	84.6
	5.4		70	68.1
	9.6		55	61.7
	7.5		55	87.4
	7.5		45	66.7
	7.5		55	60.2

Washing Water Treatment

To determine the efficiency of the treatment, the following analyses were carried out on the waste water, before and after each of the treatment process: Biochemical Oxygen demand (BOD), Chemical Oxygen Demand (COD), pH, conductivity, Total Dissolved Solids (TDS), elements present (chloride, sulphate, nitrogen, phosphorus, iron, calcium,

magnesium).The physico-chemical water treatment processes carried out are: Adsorption, Acidification (pH adjustment), Coagulation/flocculation, and Sedimentation/ Filtration. The results of the treatment and analysis were shown in Table 1

Adsorption

2g of Activated Carbon was added to every 200ml of biodiesel wastewater in a beaker and continuously stirred for 1 hour.The sample was then filtered, and the process was repeated twice. After the third procedure of allowing activated carbon to adsorb impurities in biodiesel waste water, the sample was then analysed for BOD, COD, pH, conductivity, TDS andelements present.

Acidification of Waste Water

The pH of the alkaline waste water sample after adsorption process was reduced by adding drops of 0.1M H_2SO_4. The sample was then analysed for BOD, COD, pH, conductivity, TDS and likely elements present (chloride, sulphate, nitrogen, phosphorus, iron, calcium, and magnesium).

Coagulation and Flocculation

The acidic waste water sample was then neutralised by adding droplets of CaObefore coagulation. 0.6g of Aluminum sulphate was added to 300ml of the treated water sample in a 1L beaker placed on a magnetic stirrer for continuous stirring for 20 minutes. Floc formed was allowed to settle and then filtered. And the treated water sample was then taken for the determination of its physicochemical properties.

RESULTS AND DISCUSSIONS

Figure 1shows the biodiesel yield obtained from the variation of reaction time and methanol/oil mole ratio during palm kernel oil trans-esterification. From the figure, highest biodiesel yield was obtained at methanol/oil mole ratio and reaction time of 7.5 and 70 minutes respectively. This shows that increase in reaction time favours biodiesel production. There was decrease in the yield at the methanol/oil mole ratio which is greater or less than 7.5. At these two conditions, there was insufficient and excess methanol/oil mole ratio for the trans-esterification reaction. Insufficient methanol/oil mole ratio would only produce low biodiesel yield while excess methanol/oil mole ratio would hinder the further production of biodiesel.

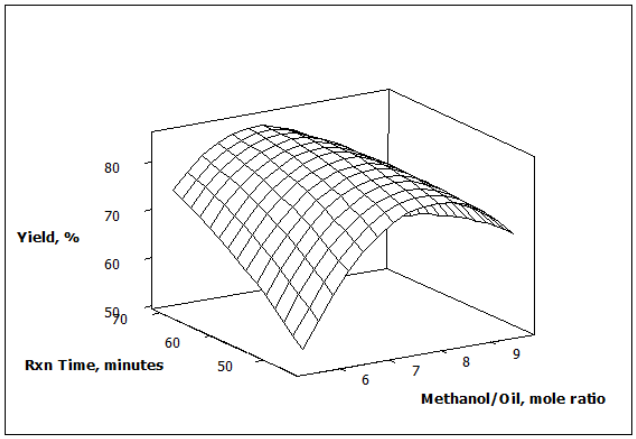

Figure 1: Biodiesel Yield Obtained From the Variation Reaction Time and Methanol/Oil Mole Ratio

Analysis of Wastewater after Adsorption

The biodiesel wastewater was subjected to adsorption process using activated carbon and the physico-chemical properties of the water were then determined Table 3. BOD and COD obtained were 90.32 mg/L and 36.2 mg/L respectively showing that the amount of oxygen required by the bacteria to oxidise organic matter in the waste water had been reduced significantly; that is from 168 mg/L to 90.32 mg/L for BOD and from 46.2mg/L to 36.2 mg/L for COD. The reduction in values also shows the BOD removal efficiency for adsorption is 46 % and COD removal efficiency is 22%. The total dissolved solids (TDS) was 371 g/l from an initial value of 397 g/l indicating that adsorption process can be used as one of the methods to remove dissolved solids in waste water; though further treatment is required as it had a removal efficiency of 6.54 %.

The pH of the waste water dropped from 9.42 to 6.54, showing a reduction in the alkalinity as the pH dropped from 9.42. There was a reduction in the dissolved ions present in the waste water during adsorption process; the conductivity became 61.2 µS/cm instead of the initial value of 66.1 µS/cm.

Analysis of Waste Water after Acidification

The biodiesel waste water was acidified to reduce the pH to 2.02 by adding drops of 0.1M H_2SO_4. This aids in the removal of the emulsion of oil and free fatty acids as reported by Veljkovic*et. al.* (2014).The reduction in BOD and COD could be attributed to the acidic environment created by reducing the pH, giving the acidification process a COD and BOD removal efficiency of 48% and 87% respectively. The amount of total dissolved solids was 278 mg/L which reduced immensely from a previous value of 371 mg/L showing a removal efficiency of 25%. The conductivity value was reduced to 10.28 µS/cm. The identifiable elements and anions present were Nitrate, Iron, Sulphates, Phosphorus and Chloride, the significant value of 160 mg/Lconcentration of sulphate recorded was as a result of the H_2SO_4 added.

Analysis of Waste Water after Coagulation & Filtration

The biodiesel waste water was coagulated usingAluminum Sulphate ($Al_2(SO_4)_3$) but the pH was first adjusted to 6.84 using CaO because Aluminum Sulphate ($Al_2(SO_4)_3$) would only function optimally at pH between of 6and7 (Daud*et. al.*, 2014). Coagulation process is based on the principle that the coagulant produces a gelatinous mass which attracts the atoms of the suspended particles.After coagulation the solid lumps of the suspended particles (flocs) were then filtered off. The BOD and COD of the waste water were 58.6 mg/L and 28.83 mg/L respectively; this reduction in values amounted to the COD andBOD removal efficiency of 31% and33% respectively. The TDS was 100mg/L showing a removal efficiency of 65%. The conductivity was 4.02 µS/cm. The detectable elements and anions found are Nitrate, Calcium, Magnesium, Iron, Sulphates, Phosphorus and Chloride.The significant value of 184 mg/L obtained as the concentration of Calcium wasas a result of the CaOadded which reacted with the H_2SO_4 to form $CaSO_4$.

Table 3: Wastewater Analysis

Parameters	Before Treatment	Adsorption	Acidification	Coagulation & Filtration
BOD, mg/L	168	90.32	60.05	58.6
COD, mg/L	46.2	36.2	22.24	28.83
pH	9.42	6.45	2.02	6.84
Conductivity, µS/cm	66.1	61.2	10.28	4.02
TDS, mg/L397	371	278	100	
Elements				
Nitrate, mg/L	34.2	33.0	31.7	23.2

Calcium, mg/L	-	-	-	184
Magnesium, mg/L	-	-	-	186
Iron, mg/L	51	49	32	16
Sulphate, g/L	157	160	160	360
Phosphorus, g/L	6.19	5.28	5.18	5.10
Chloride, g/L	20.0	16.0	120	500

Means Not Detected

The treated waste water properties were compared with the recommended effluent limitation guideline in Nigeria for all categories of industries and the results revealed that the treated biodiesel waste water can be discharge into the nearby streams Table 5. The water can be further treated, if it is to be consumed.

Table 4: Overall Removal Efficiency of the Treatment Processes

Parameters	Overall Removal Efficiency (%)
BOD	65
COD	38
Conductivity	94
TDS	75

CONCLUSIONS

The results of the analysis carried out showed that the three treatment processes of the wastewater were effective for the removal efficiency of BOD, COD and TDS obtained were high as a result of the waste water treatment Table 4. Comparatively, the values of the properties of waste water obtained after the treatment met the Federal Environment Protection Agency (FEPA) standards for waste water that can be discharged into the nearby streams Table 5.

Table 5: Comparison between FEPA Standards of Waste Water Quality and Quality of the Washing Water after Treatment

Parameters	*FEPA Standards	After Treatment Processes
BOD, mg/L	50	58.6
COD, mg/L	Not defined	28.83
pH	6 – 9	6.84
Conductivity, µS/cm	Not defined	4.02
TDS, mg/L	2000	100
Elements		
Nitrate, mg/L	20	23.2
Calcium, mg/L	200	184
Magnesium, mg/L	200	186
Iron, mg/L	20	16
Sulphate, mg/L	500	360
Sulphate, mg/L	600	400
Phosphorus	5	5.1

*FEPA standards, 1991

REFERENCES

1. Ayoola A.A. (2015), ‘Production and Life Cycle Assessment of Biodiesel Produced from Three Waste Oils’, Ph.D. Thesis, Chemical Engineering Department, Covenant University, Nigeria.
2. Ayoola A. A., Efeovbokhan V.E, Adeeyo O. A., Johnson O. (2013),‘Methanolysis of Triglycerides using Jatropha Oil and KOH Catalyst’,International Journal of Advanced Research in IT and Engineering,Vol.:2, No.:3, pg 61 – 69.

3. Daud N.M, Hasan H.A, Sheikh Abdullah S.R. (2014), 'Review: Application of Coagulation-Biological Aerated Filter (CBAF) System for Biodiesel Wastewater Treatment. Australian Journal of Basic and Applied Sciences', Vol.:8, No.:19, pg 296 – 298.
4. Eevera T., Rajendran K and Saradha S. (2009), 'Biodiesel Production Process Optimisation and Characterisation to Assess the Suitability of the Product for varied Environmental Conditions', Renewable Energy, Vol.:34, pg 762 – 765.
5. Farha, N. (2008). Biodiesel Production via Single-step Alkali Catalyst in Batch Process. M Sc. Thesis, Faculty of Chemical and Natural Resources Engineering Universiti Malaysia Pahang.
6. Federal Environmental Protection Agency, (1991), 'Interim Effluent Limitation Guidelines in Nigeria for All Categories or Industries, Retrieved January 2016, from Government Notice of 1991.
7. Kuwornoo D.K. (2010), 'Optimization of Factors Affecting The Production of Biodiesel From Crude Palm Kernel Oil andEthanol', International Journal of Energy and Environment, Vol.:1, No.:4, pg 675 - 682.
8. Liu S., Musuku S.R., Adhikari S., Fernando S(2009), 'Adsorption of Glycerol From Biodiesel Washwaters', Environmental Technology, doi: 10.1080/09593330902803019.
9. Ngamlerdpokin K., SasipanKumjadpai, PreeyaChatanon, UngsikaTungmanee, SulalitChuenchuanchom, PattaralukJaruwat, PrarinyaLertsathitphongs, Mali Hunsom, (2011), 'Remediation of Biodiesel Wastewater by Chemical and Electro-coagulation:
10. A Comparative Study', Journal of Environmental Management, Vol.:92, pg 2454 – 2460.
11. Pitakpoolsil W., Hunsom M. (2014), 'Treatment of Biodiesel Wastewater by Adsorption with Commercial Chitosan Flakes: Parameter Optimization and Process Kinetics', Journal of Environmental Management, doi: 10.1016/j.jenvman.2013.12.019
12. Romano S. (1982), 'Vegetable Oils: A New Alternative', ASAE Publ. (4 – 82, Veg. Oil Fuels), 106 – 116.
13. Srivastava A and Prasad R. (2000), 'Triglycerides-based Diesel Fuels', Renewable and Sustainable Energy Reviews, Vol.:4, pg 111 – 133.
14. Suehara K., Kawamoto Y., Fujii E., Kohda J., Nakano Y., Yano T. (2005), 'Biological Treatment of Wastewater Discharged FromBiodiesel Fuel Production Plant with Alkali-catalyzed Transesterification', Journal of Bioscience and Bioengineering, Vol.:100, No.:4, pg 437-442.
15. Veljković V. B., Olivera S. Stamenković and Marija B. Tasić , (2014), 'The Wastewater Treatment in the Biodiesel Production with Alkali-catalyzed Transesterification', Renewable and Sustainable Energy Reviews, Vol.:32, No.:C, pg 40 – 60.