International Journal of Applied Chemistry.
ISSN 0973-1792 Volume 13, Number 3 (2017) pp. 385-391

http://www.ripublication.com

Assessment Of Biosolar Quality By Measuring Its Carbon-14 Activity Through Liquid Scintillation Technique

Rahmawati[1*], Alfian Noor[2], Maming[2] and Muhammad Zakir[2]

[1]Health Analysts Academy Muhammadiyah, Makassar 90132, South Sulawesi-Indonesia.

[2]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Hasanuddin University, Makassar 90245, South Sulawesi-Indonesia.
**Corresponding author*

Abstract

Assessment of biosolar quality by measuring its carbon-14 activity through liquid scintillation technique has been investegated. The purpose of this study was to determine the concentration of the component in biodiesel samples by measuring Carbon-14 of specific activity using Liquid Scintillation Counting (LSC). Sample counting was carried out in two steps. The first step is to determine optimum counting time have to obtain best value of disintegration per minute (DPM) and efficiency (Triple to Double Counting Ratio, TDCR) respectively and secondly is to determine the average value of counting results of the samples at the optimum time. ^{14}C activity measurements were performed by mixing 8 ml of the sample and standard solutions of biosolar and 12 mL scintillator solution into a 20 mL plastic vial with counting span of 5-240 minutes. The results showed that specific activity (As) found for each standard solution (in dpm/gC), namely biosolar S1 5% 2.1184; S2 10% 5.1981; S3 15% 10.6071; S4 20% 13.0885, and S5 25% 14.5958. while for biosolar sample, X1 was 1.9218 for concentration, C = 4.04%, X2 2.6502 for C 5.14%, and X3 2.0744 for C 4.27%. It can be concluded that a strong tool to verify the quality of biosolar produced by a seller.

Keywords: Carbon-14, LSC, biosolar, activity, quality, assessment

INTRODUCTION

Due to limited world oil reserves, renewable energy is introduced as an alternative energy source such as biodiesel made from palm oil. Biofuel was authorized to be developed untill 2025 by Indonesian government. Biofuel is mixture between fossil fuel and biodiesel, generally from palm oil[1]. The ratio between fuel source and plant source were prepared carefully so that engine motor can be working properly without substantial damage. Generally the mixing ratio, between fossil and biodiesel source and which is called biosolar, can be between 5%; 10%; 15%; 20%; and 25% of biodiesel contribution. Quality assurance need to be made so that biosolar product released in the market by Pertamina is the true number as mentioned in its label. Therefore, it is necessary to instill confidence in users of biodiesel blends that the fuel they are using indeed conforms to regulations, standards, and expected blend levels.

The quality control of biosolar is greatly important to the successful commercialization of this fuel and its blends. The determination of blend levels is another key point of biosolar analyses since its use has been increasing considerably. Several techniques are therefor applied for monitoring purposes, taking in to consideration different biofuels characteristics. Nuclear magnetic resonance[5], gas chromatography[10], accelerator mass spectrometry (AMS)[4,9] and infra-red spectrometry[6], can be used for characterisation of specific bio-components related to diesel, usually for fattyacid methylesters. Time consuming analytical techniques usually require skilfull operators for complex sample preparation and expensive equipment.

Carbon -14 on the other hand can provide the amount of this radioactive concentration found in the sample. The result will show us the real quality of biosolar used. If radioactive concentration is zero, that means no biodiesel source found in the sample. In other word, only fossil origin was in the sample. The existence of radioactive carbon in the sample showed that plant oil in certain concentration was in the sample together with fossil fuel origin [3,11,12,14].

In Liquid Scintillation Counting (LSC), the quantity of ^{14}C in the sample is the criterion for biofuel presence in the fuel taking into account that the concentration of ^{14}C in the recent grown bio component is the same as in the atmosphere, while there is no ^{14}C in the fossil component because it has already disappeared given its decay half-life of 5700 years [3]. Different approaches regarding LSC are performed for measurements of bio components in fuels: one of the LSC methods is described also in the ASTM D6866 standard. The method has
excellent accuracy and can be performed on all types of bio components [10].

The investigation is carried out in three ways; first to prepare pure biodiesel from palm oil, as standardized amount of biodiesel in relation to carbon-activity, secondly to prepare biosolar as a mixture of fossil origin and biodiesel at the various percentages, namely 25; 15; 10 and 5 percents of biodiesel in biosolar, and last one is to sample several real samples taken from gasoline station of Pertamina to measure the actual concentration of biodiesel found in commercial biosolar sold by Pertamina.

EXPERIMENTAL

Preparation of Standard Biosolar

Standard biosolar prepared at a concentration of 5%; 10%; 15%; 20% and 25% by way of pipette 5.0; 10.0; 15.0; 20.0; 25.0 mL of solution then matched volume biodiesel up to 100 mL with diesel fuel.

Measurement of Activity of Carbon-14 in The Samples

Eight milliliter of each sample (biodiesel or biosolar) is mixed with twelve ml of scintillator solution Ultimagold XR (Packard) and then put into 20 mL vial. After that, radiation of the sample is measured using LSC (Liquid Scintillation Counter) Hidex 300 SL for 5 – 240 minutes. It is important for an LSC to apply background radiation as bases for counting carbon-14 activity of samples. The difference between background and sample reflects real sample radioactivity which shows the amount carbon-14 remain in sample after a certain period of decaying time. On the other hand, carbon-14 activity in biodiesel samples were generally showed the time passed in the palm oil formation in other words the standardized carbon-14 in palm oil. In biosolar samples, the amount of palm oil compounded is directly related with their carbon-14 radioactivity so that the number of carbon-14 activity in biosolar sample represents the percentage of biodiesel in biosolar sample [8].

RESULTS AND DISCUSSION

Table-1 below represents counting result of standard solution between 5 – 240 cpm as well as standard biosolar.

Table-1. Activity of Standard Biosolar at Various Percentages

Samples	CPM	DPM	TDCR
Background	49.950	112.693	0.444
S1 (5%)	51.892	119.326	0.435
S2 (10%)	57.756	127.568	0.452
S3 (15%)	66.540	144.258	0.461
S4 (20%)	60.212	144.148	0.418
S5 (25%)	62.754	159.004	0.396

In standard biosolar is seen that the higher the concentration the higher the value of DPM. This is due to the rich content of biodiesel contained in the sample so that the value of its activity is also higher. While the CPM values obtained fluctuate. CPM impairment occurs because the number of nuclei decay during certain time intervals decreased exponentially. The decline in the value of CPM a sample proportional to the decline in value of DPM but inversely proportional to the value TDCR samples.

The specific activity of a sample can be determined from the difference between the results of the count Disintegration Per Minute (DPM) sample of the results of the count

Disintegration Per Minute (DPM) divided by the background levels of total carbon in 8 mL of sample was mixed with 12 mL of scintillator solution. From these explanations it can be conducted to determine the specific activity of the sample. The specific activity average (As) sample from the calculation of disintegrations per minute (DPM) per unit carbon future standards.

Table-2. Specific Activities of Standard Biosolar

Samples	DPMs	DPMb	DPMk	Carbon-Total (g)	As (DPM/gC)
S1 (5%)	119.326	112.693	6.633	3.1311	2.1184
S2 (10%)	127.568	112.693	14.875	2.8616	5.1981
S3 (15%)	142.100	112.693	29.407	2.7724	10.6071
S4 (20%)	150.948	112.693	38.255	2.9228	13.0885
S5 (25%)	159.004	112.693	46.311	3.1729	14.5958

Based on data from a sample census results in Table 2, shown specific activity of ^{14}C in the standard S1 5%, S2 10%, S3 15%, S4 20%, and S5 25% respectively were 2.1184 dpm/gC; 5.1981 dpm/gC; 10.6071 dpm/gC; 13.0885 dpm/gC; and 14.5958 dpm/gC. The higher the concentration of biosolar, the higher the specific activity because these concentrations show the rich content of biodiesel contained in the biosolar sample.

Table-3. Background and Biosolar Sample Counts

Samples	CPM	DPM	TDCR
Background	49.950	112.693	0.444
X1	65.382	114.180	0.572
X2	66.868	118.014	0.567
X3	67.590	116.010	0.583

Table-4. Specific Activities Biosolar Samples

Samples	DPMs	DPMb	DPMk	Carbon-Total (g)	As (DPM/gC)
X1	121.980	112.693	9.287	4.8324	1.9218
X2	118.814	112.693	6.121	2.3096	2.6502
X3	124.610	112.693	11.917	5.7449	2.0744

Information:
CPM : Counts Per Minute
DPM : Disintegration Per Minute
TDCR : Triple To Double Coincidance Ratio
DPMs : Disintegration Per Minute Standard
DPMb : Disintegration Per Minute Background
DPMk : DPMs – DPMb (Correction)
As : Specific Activities

The sample X1, X2, and X3 respectively shown in Table 4 is 1.9218 dpm/ gC; 2.6502 dpm/ gC and 2.0744 dpm/ gC. Activities obtained shows the magnitude of the decay of carbon atoms that takes place every minute (DPM) in one gram of carbon.

The value of a specific disintegration (specific activity) average ^{14}C obtained from the sample is lower compared to the specific activity of an average standard modern carbon often used in practice in the range of 15.3 ± 0.1 dpm/gC [7,13]. The value of a specific disintegration average ^{14}C obtained indicates the actual number of atoms of ^{14}C that decays per minute (DPM) in every single gram of carbon elements in 8 mL sample.

Specific disintegration value indicates that there has been a decay of the atomic nucleus that starts from the sample dead so that the activity of ^{14}C contained in the sample is reduced and smaller than modern carbon specific activity of 15.3 ± 0.1 dpm/gC [7].

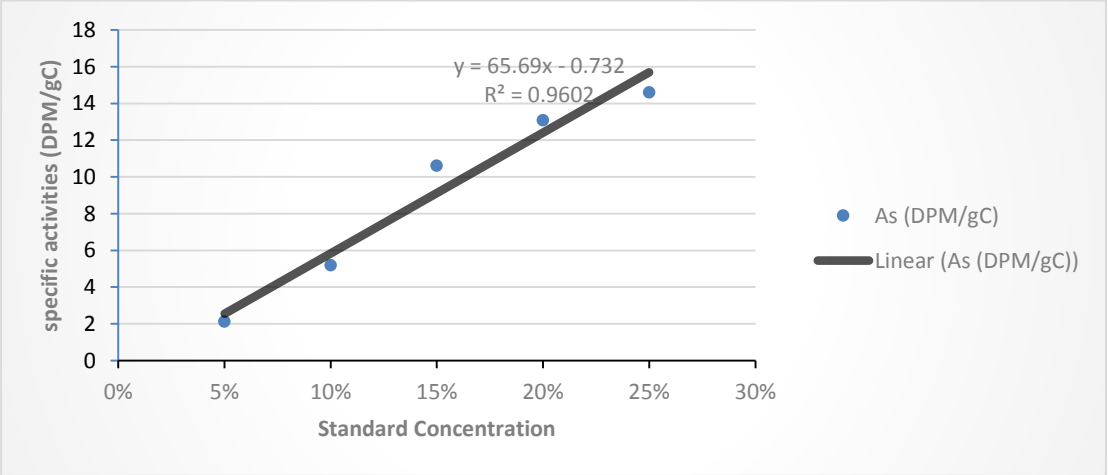

Figure 1. Graph of relation of standard concentration with specific activities

The concentration of each sample of biosolar can be determined from the graph in Figure 1 obtained X1 4.04%, X2 5.14% and X3 4.27% (Table 5). Concentration values obtained vary and be around 5%, in accordance with Presidential Decree No. 5 of 2006, which is 5% of national energy needs met from biofuel energy sources until 2025[1]. Since 2006, Pertamina has been selling biodiesel with a mixture of 95% diesel and 5% biodiesel.

Table 5. Biosolar Samples Concentrations

Samples	As (DPM/gC)	Concentration (%)
X1	1.9218	4.04%
X2	2.6502	5.14%
X3	2.0744	4.27%

CONCLUSIONS

Based on the research that has been done can be concluded that the concentration of biosolar samples were obtained by measuring the specific activity of the radiocarbon method using a Liquid Scintillation Counting Hidex 300 SL were X1 4.04%, X2 5.14%, and X3 4.27%. Therefore, this method can be proposed as an alternative method for measuring the quality of biosolar.

ACKNOWLEDGEMENTS

The authors would like to thank Directorate General of Higher Education Ministry of Indonesia for financial support.

REFERENCES

[1] Azmi, Riza dan Hidayat Amir. 2014. *Energy Security: Concepts, Policies and Challenges for Indonesia,* Jakarta.

[2] Canducci, C., Bartolomei, P., Magnani, G., Rizzo, A., 2013, Upgrade Of The CO_2 Direct Absorption Method For Low Level ^{14}C Liquid Scintillation Counting, *Radiocarbon*, **55** (2-3), 260-267.

[3] Dijs, I.J, Vander Windt, E., Kaihola, L., Vander Borg, K., 2006. Quantitative Determination By ^{14}C Analysis Of The Biological Component In Fuels. *Radiocarbon,* **48** (3):315–323.

[4] D.J.Donahue, 1995, Radiocarbon Analysis by Accelerator Mass Spectrometry, *Int.J.Mass Spectrom. Ion Processes*, 143: 235–245.

[5] G. Knothe, 2001, Determining the Blend Level of Mixtures of Biodiesel with Conventional Diesel Fuel by Fiber-Optic Near-Infrared Spectroscopy and 1H Nuclear Magnetic Resonance Spectroscopy, *J. Am. Oil Chem. Soc*. **78**(10): 1025–1028.

[6] J.S.Oliveira, R.Montalv~ao, L.Daher, P.A.Z.Suarez, J.C.Rubim, 2006, Determination of Methyl Ester Contents in Biodiesel Blends by FTIR-ATR and FTNIR Spectroscopies, *Talanta*, **69**(5): 1278–1284.

[7] Libby, W.F., 1960, Radiocarbon Dating, *Nobel Lecture*, Elsevier Publishing Company, Amsterdam.

[8] Maming, Noor, A., Zakir, M., Raya, I., Jauhari, Kartika, S.A., 2014, Aplication in Liquid Scintillation Method on Carbon Dating in Determination of Coral Ages from Spermonde Archipelagos, *Mar. Chim. Acta*, **15**(1): 31-35.

[9] M.Oinonen, H.Hakanp¨a¨a-Laitinen, K.H¨am¨al¨ainen, A.Kaskela, H.Jungner, 2010, Biofuel Proportions in Fuels by AMS Radiocarbon Method**,** *Nucl. Instrum.Meth.Phys.Res.B: Beam Interact.Mater.Atoms*, **268**(7-8):1117–1119.

[10] M.Monteiro, A. Ambrozin, L.Liao, A.Ferreira, 2008, Critical Review on Analytical Methods for Biodiesel Characterization, *Talanta*, **77**(2): 593–605.

[11] Noakes, J., Norton, G., Culp,R., Nigam,M., Dvoracek,D., 2006. A Comparison Of Analytica Lmethods For The Certification Of Biobased Products. In:

Chalupnik, S., Schonhofer,F., Noakes, J. (Eds.), LSC 2005, Advances in Liquid Scintillation Spectrometry. *Radiocarbon*, Tuscon, pp. 259–271.

[12] Takahashi, Y., Sakurai,H., Inui,E., Namai,S., Sato,T., 2011. Radiocarbon Measurement Of Biodiesel Fuel Using The Liquid Scintillation Counter Quantulus. In: Cassette, P.(Ed.), LSC 2010, Advances in Liquid Scintillation Spectrometry. *Radiocarbon*, Tuscon, pp.41–46.

[13] Yuliati, H., Akhadi, M., 2005, *For Cosmogenic Radionuclide Dating, Center for Biomedical Radiation and Nuclear Safety* . Radiation Center. Batam.

[14] Yunoki, S., Saito, M., 2009. A Simple Method To Determine Bioethanol Contentin Gasoline Using Two-Step Extraction And Liquid Scintillation Counting. *Bioresour. Technol*. **100**: 6125–6129.