

PROCEEDING

BOOK I



bio energy chemicals materials

BIOENCHE 2013

International Seminar on Chemical Engineering
In conjunction with
Seminar Teknik Kimia Soehadi Reksowardojo (STKSR)2013

“Biorenewable Resources Utilization for Energy, Chemicals, and Materials”

Bandung, Indonesia
10-11 October 2013

Organized by :
Department of Chemical Engineering
Faculty of Industrial Technology
Institut Teknologi Bandung

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SURAT TUGAS

No. : 95 /ST/LP3M-ITI/X/2013

Pertimbangan : bahwa dalam rangka mengikuti International Seminar on Chemical Engineering Bio Energy, Chemicals and Materials (BioenChe2013) in conjunction with Seminar Teknik Kimia Soehadi Reksowardojo di ITB, maka perlu dikeluarkan Surat Tugas.

Dasar : 1. Surat Ka. Prodi Teknik Kimia ITI No. : 97/PSTK-ITI/PL200/X/2013 tanggal 7 Oktober 2013
2. Kepentingan ITI

DITUGASKAN

Kepada : **Dr. Ir. Joelianingsih, MT**

Untuk : 1. Mengikuti International Seminar on Chemical Engineering Bio Energy, Chemicals and Materials (BioenChe2013) in conjunction with Seminar Teknik Kimia Soehadi Reksowardojo sebagai pemakalah yang berjudul "EN14105 Modification Method for Determination of Free Glycerol and Mono-Di-Triglyceride Content in Biodiesel" dan "Controlled Hydrogenation of Nyamplung Biodiesel to Improve the Oxidation Stability" pada tanggal 9 – 11 Oktober 2013 bertempat di Institut Teknologi Bandung Jawa Barat.
2. Melaporkan hasil tugas kepada Direktur LP3M ITI
3. Biaya seminar diambilkan dari dana penelitian Insentif Riset Sistem Inovasi Nasional (Sinan) Kementerian Riset dan Teknologi.
4. Dilaksanakan dengan seksama dan penuh rasa tanggung jawab.

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dan Pemberdayaan Masyarakat
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Dr. rer. nat. Abu Amar

Tembusan Yth.

1. Wakil Rektor
2. Ka. Prodi Teknik Kimia
3. Ka. Divisi Adm SDM



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CERTIFICATE

is hereby presented to

Joelianingsih

as

Paper Presenter

International Seminar on Chemical Engineering
in conjunction with

Seminar Teknik Kimia Soehadi Reksowardojo 2013

"Renewable Resources Utilization for Energy, Chemicals, and Materials"

10-11 October 2013 Aula Timur Institut Teknologi Bandung Indonesia

Dr. Tjokorde Walmiki Samadhi
Chemical Engineering
Undergraduate Program Chairman

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BIOENCHE 2013
Dr. Tirta Prakoso, MEng.
Conference Chairman



October 10-11, Bandung, Indonesia

International Seminar on Biorenewable Resources Utilization for Energy and Chemicals 2013
In conjunction with Chemical Engineering Seminar of Soehadi Reksowardojo 2013

PREFACE

This BioEnChe-STKSR2013 proceeding contains of the collections of research works presented in International Conference of Bio Energy Chemicals and Materials 2013 (BioEnChe 2013) that was held in Institut Teknologi Bandung. The conference is in conjunction with annual Chemical Engineering Seminar of Soehadi Reksowardojo (Seminar Teknik Kimia Soehadi Reksowardojo, STKSR 2013).

The international conference provides an opportunity to publicize research works which done or in ongoing ones in many research institution. As the use of fossil base energy and other derivate become harmful for human life, the uses of renewable resource become more interest in our daily life. Therefore, the science and technology for utilization of those resources become enhanced to get more effective and efficient process to produce their products.

We have expectation in this occasion is not only a good place to exchange and discuss the progress of their research in bioenergy, biochemical and biomaterials, but also a venue to collect and to disseminate the most updated technologies and the researches of regional issue and public interest in order to contribute to the community and to draw support from the industrial and the governmental sectors. As this conference has main theme of biorenewable resources utilization for bioenergy, biochemical and material, hopefully this conference will contribute to enhance the utilization of renewable resources for many uses.

We would like to grateful to all participants and sponsors who has contributed to the conference, to the organizing committee for their commitment in their busy days so that the conference is possible to be held and conducted successfully.

Thank you,

Dr. Tirto Prakoso, MEng.
Conference Chairman

October 10-11. Bandung, Indonesia

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International Seminar on Chemical Engineering Bio Energy, Chemicals and Materials (BioEnChe2013)

in conjunction with Seminar Teknik Kimia Soehadi Reksowardojo (STKSR) 2013

September 11, 2013

ABSTRACT ACCEPTANCE LETTER

Dear

Joelianingsih, Imansyah Indra, and Is Sulistyati

Thank you for your interest to attend International Seminar on Biorenewable Resources Utilization for Energy and Chemicals 2013. We are appreciated your abstract submission. We would like to inform you that your abstract entitled "**EN14105 Modification Method for Determination of Free Glycerol and Mono-Di-Triglyceride Content in Biodiesel**" has been accepted in the sub topic **Biodiesel** and will be presented as **Oral** presentation at the conference.

Your presentation code is : **BD.21**

You need to do registration to attend and present paper in the conference in October 10th -11th, 2013, so that your full paper can be published in the proceeding. We encourage you to register before 23 September 2013 or lately you can inform us by email when you can register so that you can pay registration fee.

For your information, if you want to publish your paper in "Journal of Engineering and Technological Sciences" you have to fulfill confirmation letter for publishing in the journal and send back to the committee by email.

Please visit our website for more information about the registration and the conference, www.che.itb.ac.id/stksr2013.

We are looking forward to see you in Bandung.

Best regards,

Committee of
International Seminar on Biorenewable Resources Utilization for Energy and Chemicals 2013
in conjunction with Chemical Engineering Seminar of Soehadi Reksowardojo 2013

Dr. Tirto Prakoso, MEng
Conference Chairman



Modification Method of EN14105 for Determination of Free Glycerol and Mono-Di-Triglycerides Contents in Biodiesel

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Abstract. Determination of free glycerol and mono-, di-, triglycerides contents in biodiesel is the most critical parameter for the successful of transesterification reaction. Gas Chromatography (GC) is one apparatus to get the composition detail of glycerol and its derivative that formed after the transesterification reaction. Highly boiling point of that compounds cause problem in GC analysis. Method of EN14105 offer the solution for this problem, since in this method the compounds is transformed into more volatile and stable silyl derivatives in the presence of pyridine and MSTFA (N-methyl-N-trimethylsilyl-trifluoroacetamide). To prevent the decomposition of compounds, the EN14105 suggests to providing GC with the OCI (On Column Injector Programmed Temperature Vaporization) Unit. This method also use the internal standard for determination of the sample concentration. High cost of the OCI unit and the Internal Standard solution are the reasons why the modification of this method is should be done. Method modification was done by replaced the OCI with standard injector, followed by trial of external standard calculation method, and arrange program temperature of column. Identification of compounds was done by comparing retention time of standard materials to reference chromatogram provide by the EN14105. Unfortunately, the analysis of experiment results produce bad repeatability due to the unstable of detector responds. Experimental result indicated that the modicication method of EN 14105 is appropriate only for free glycerol content determination

Keywords: *analysis method, biodiesel, gas chromatography, glycerol, glyceride.*

1. Introduction

Fatty Acid Methyl Esters (FAME) is known as biodiesel can be produced by transesterification reaction of animal fat or vegetable oil. The major component of animal fat and vegetable oil are triacylglycerols (often also called triglycerides/TG) [1]. In a transesterification or alcoholysis reaction one mole of triglyceride reacts with three moles of alcohol (generally methanol) to form one mole of glycerol (GL) and three moles of the respective FAME. The process is



a sequence of three reversible reactions. Triglyceride reacts with methanol (MeOH) to produce diglyceride (DG) which further reacts with methanol to produce monoglyceride (MG). Finally, MG reacts with methanol to produce GL. At each reaction step, one molecule of FAME is produced for each molecule of methanol consumed [2]. This reaction mechanism can be represented by the reactions as shown in following equations :



Determination of free glycerol and mono-, di-, triglyceride contents in FAME is the most critical parameter for the successful of transesterification reaction and purification process. In the EN 14214 method, free glycerol is limited to a maximum amount of 0.02% (m/m) [3]. Free glycerol separates within the fuel tank, collects at the bottom, where it attracts other polar compounds, such as water, monoglyceride, and soap, and causes damage to the injection system. Vicinal hydroxy groups contained in glycerol is responsible for the corrosion of non-ferrous metals (especially copper and zinc) and chromium alloys due to complexation [4]. Moreover, glycerol depositions in the fuel filter and increased aldehyde emissions have been reported [3].

The EN 14214 limits the amounts of mono-, di-, and triglyceride up to $\leq 0.80\%$, $\leq 0.20\%$ and $\leq 0.20\%$ (m/m) respectively, and defines a maximum amount of 0.25% (m/m) for total glycerol (i.e the sum of the concentrations of free glycerol and glycerol bound in the form of mono-, di-, and triglyceride). Fuels composition that exceeding the limits are prone to coking and may cause the formation of deposits on injector nozzles, pistons and valves. Indirect hints of high glyceride contents in biodiesel samples are correspondingly increased value of viscosity and carbon residue [3].

The Gas Chromatography (GC) procedure is applicable to biodiesel sample derived from the most frequently used of oil and fat sources. Detection limits are 0.001% (m/m) for GL and 0.02% (m/m) for MG, DG and TG. Analyses are conducted on a non polar, high-temperature capillary column, applying on-column injection and flame ionization detection. Compounds that suitable for GC analysis must follow some criteria, such as, it must possess appreciable volatility at temperatures below 350–400 °C. In other words, all or a portion of the compound molecules have to be in the gaseous or vapor state below 350–400 °C [5]. Due to highly boiling point of biodiesel compounds, causing problem in GC analysis. The EN14105 is another analytical GC method that



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might be provide a better solution for GC analysing. The analytical standard method prescribed in EN 14105 is a further development of an approach suggested by Plank and Lorbeer [6]. In this method, pyridine and N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA) are added to the samples to transform reaction of compound into more volatile and stable silyl derivatives [7]. In addition, to prevent decomposition of sample compounds, the EN 14105 is provided with the OCI (On Column Injector Programmed Temperature Vaporization) unit [8]. For determining the analytical result in this method, internal standard solution is used. The OCI unit and internal standard solution are costly for routine biodiesel analysis, especially for students doing biodiesel experiments with vegetable oil as feedstock. In this experiment, laboratory study was done to modify the EN14105 method. Instead of using OCI unit, the standard injector available in our GC apparatus was still used but experiment was carried out by trial the external standard calculation method instead of using the internal one and arrange oven temperature program of column.

2. Methodology

2.1. Reagents, Solvents and Standards

Reagents and solvents were used for standard and sample preparation : N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA) chromatography grade reagent Pyridine max 0.1% and N-heptane 99,9% m/m.

Free glycerol 5,000 ug/L in pyridine, monolein (1-mono[cis-9-octadecenoyl]-racglycerol) 5,000 µg/mL in pyridine, diolein (1,3-di[cis-octadecenoyl] glycerol) 5,000 µg/mL in pyridine, triolein (1,2,3-Tri[cis-octadecenoyl]glycerol) 5,000 µg/mL in pyridine were used as A SRM to get the respond factor of each compound.

2.2. Gas Chromatography Condition.

The apparatus used in the experiment is Shimadzu GC 2010 gas chromatograph with flame ionization detector (GC-FID). The chromatograph was configured with injector in split mode, sample injection volume = 1mL, Injector temperature was set at 350°C, Detector temperature at 370°C, carrier gas : He, run with ramp of column temperature : Initial temperature of 50°C and hold for 5 min, and the second stage is reached by rate of 15 °C /min until temperature reached to 150 °C and hold for 2 min, the third stage is reached by rate of 15 °C/min until 250 °C and hold for 2 min. The fourth stage is reached by rate of 10 °C/min until 300 °C, hold for 20 min. The fifth stage is reached by rate of 5°C/min until 320 °C and hold for 20 min. The sixth stage is reached by rate



5°C/min until 350 °C and hold for 20 min . The final stage is reached by rate of 5°C/min until 370 °C and hold for 40 min. The column temperatur setting is extremely different from the EN14105 column temp guide. The lower ramp temperature modification were done to prevent the bleeding of the stationary phase from column. The column specification used is: Capillary Column RTX-1 restex nonpolar phase; Crossbond® dimethyl polysiloxane, with column length: 30 M, and column diameter : 0.32 mMID 0.5uM..

2.3. Analysis Procedure

The homogenized sample was put in a 2 ml vial and weighed approximately 300 mg (accuracy ± 0,1 mg) The silylation process are done by adding 40 ul of MSTFA in presence of pyridine and 1 mL of N-Heptane to dilute the solution. Each step of reagent addition was weighed to measure the final concentration of sample in prepared solution. 1 uL of prepared solution were analyzed with the same condition of GC program that mentioned above.

2.4. Identification of Compounds.

Identification of samples compounds was done by comparing retention time reference compounds respectively to retention time of same compounds available in the EN14105 [7]

2.5. Respond Factor Calculation.

Respond factor of each compound were determined by perform the pre test run of standard. The pre test shall be done according to the same condition with analysis procedure. By comparing area and actual concentration of SRM, the Respond Factor of each compound can be calculated. This Respond Factor will be used for reference calculation for External Standard Calculation Method.

The respond factors for each compound were obtained by integrating the areas of peak versus dilution concentration, as shown in equation (4). Dilution concentration of standard shall be determined first as shown in equation (5) [5, 9]

$$\text{Respond Factor} = \frac{C_{dilcon}}{\text{AREA}} \quad (4)$$



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different of oven column temperature and of column length used between these two methods.

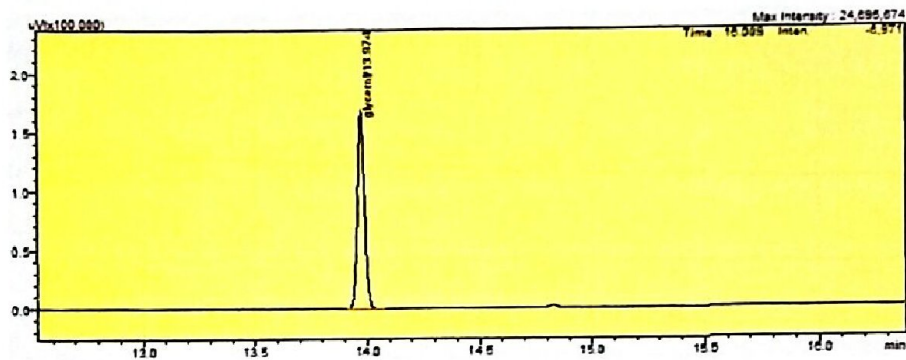


Figure 1 Chromatogram window of free glycerol.

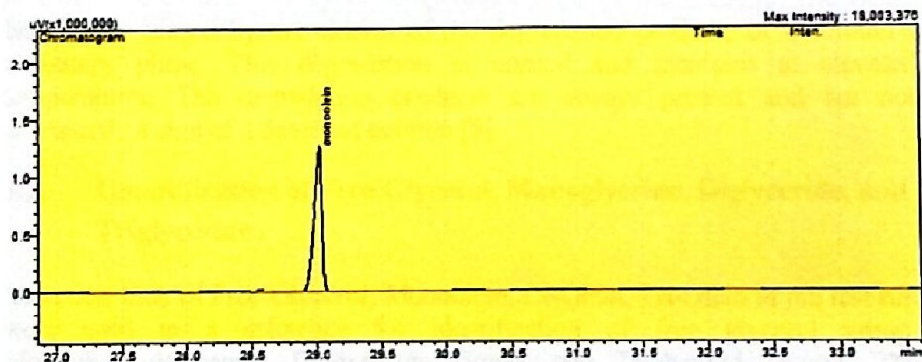


Figure 2 Chromatogram window of monoolein.

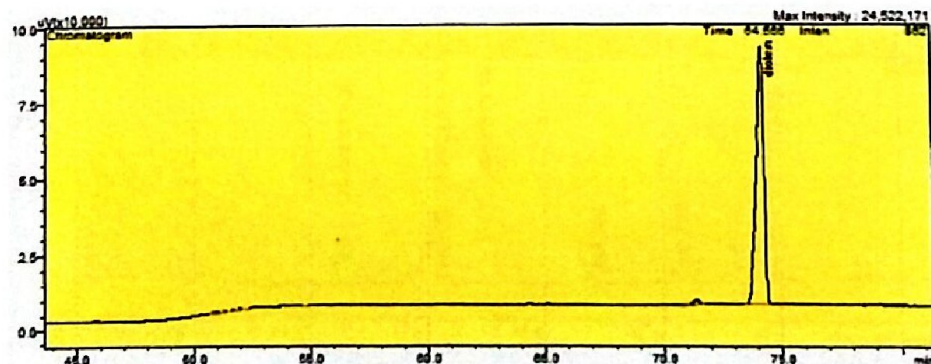


Figure 3 Chromatogram window of diolein.

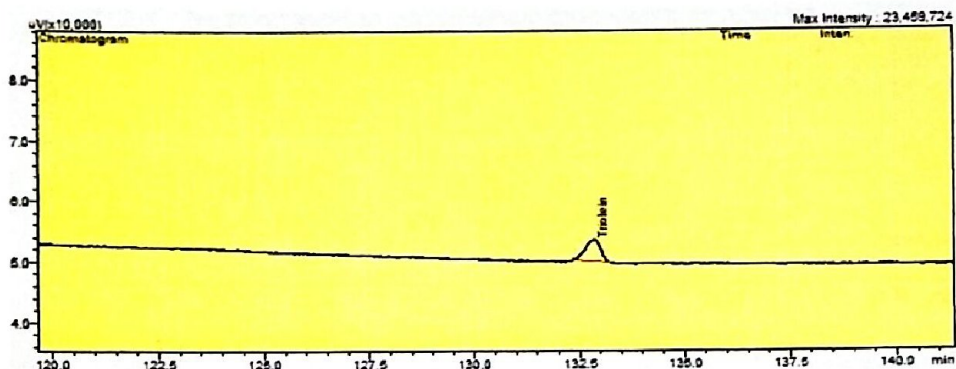


Figure 4 Chromatogram window of triolein.

In this experiment, column bleeding was evident as a rising or elevated baseline at temperatures near the upper temperature limit of the column. The rising baseline is caused by the elution of the degradation products of a column's stationary phase. This degradation is normal and increases at elevated temperatures. The degradation products are always present and are not necessarily a sign of a damaged column [5].

3.2. Quantification of Free Glycerol, Monoglyceride, Diglyceride, and Triglyceride .

Retention time of Free Glycerol, Monoolein, Di-Olein, Tri-Olein in pre test run were used as a reference for identification of free glycerol group, Monoglyceride group, DiGlyceride Group, and Triglyceride group. The identification of groups are shown in Figures 5, 6, 7, 8.

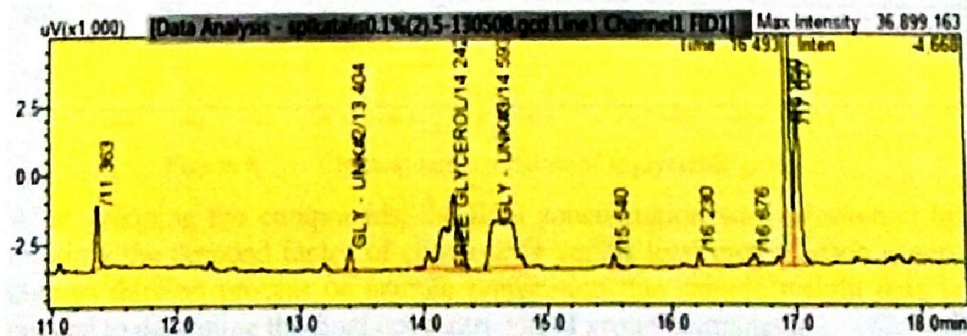


Figure 5 Chromatogram window of free glycerol group

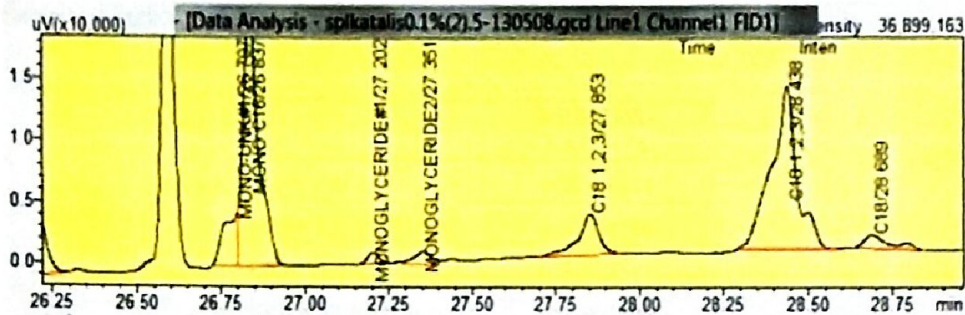


Figure 6 Chromatogram window of monoglyceride group

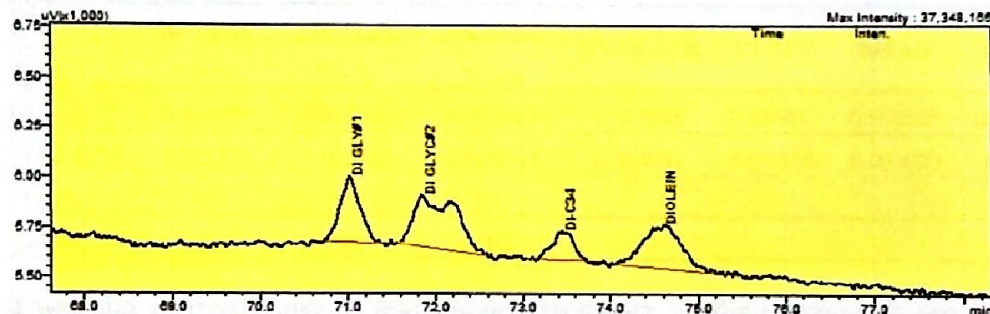


Figure 7 Chromatogram window of diglyceride group

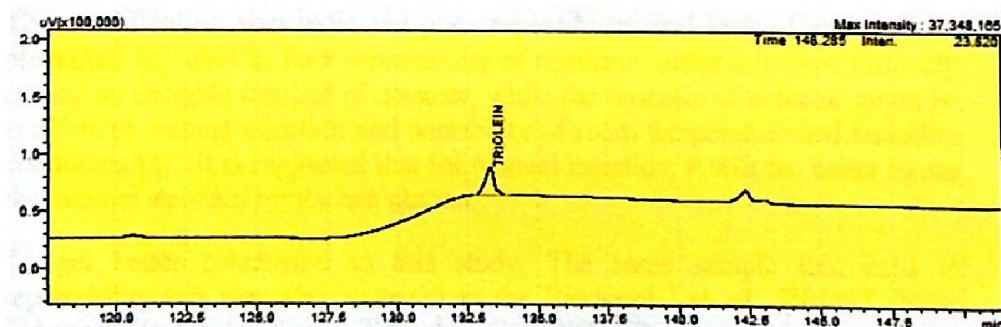


Figure 8 Chromatogram window of triglyceride group

After grouping the compounds, the final concentration was determined by multiply the respond factor of compounds versus total area of each group. Due to dilution process on sample preparation, the sample weight data is needed to determine the final concentration of group compounds.

The result of respond factor for each compound is given in Table 1. The triplicate test result is shown in Table 2.



Respond factor for each component

	RESPOND FACTOR
GLYCEROL	0.00106147
MONOGLYCERIDE	0.00044159
DIGLYCERIDE	0.00123587
TRIGLYCERIDE	0.01961206

Table 1. Triplicate result and deviation

	1st TEST	2nd TEST	3rd TEST	AVERAGE	STDEV	MEAN	DEV
	%w/w	%w/w	%w/w				
GLYCEROL	0.004679	0.002609	0.003589	0.003626	0.001035	0.003589	28.84%
MONOGLYCERIDE	0.001138	0.001022	0.000964	0.001041	0.000089	0.001022	8.68%
DIGLYCERIDE	ND	ND	ND				
TRIGLYCERIDE	ND	ND	ND				

It was shown from Table 1, that respond factor for all the compounds pre tested were very low, except for TD . Repeatability of sample was checked by running the same sample in triplicates.

The modification also indicated poor repeatability and lack of accuracy as presented in Tabel 2. Poor repeatability of triplicate analysis is most probably caused by unstable respond of detector, while the unstable of detector might be is effect of manual injection and unstability of room temperature and humidity conditions [5]. It is suggested that for manual injection, it will be better to use the internal standard for the calculation.

To get better conclusion to this study, The same sample that used in repeatability test was also analyzed in the Biodiesel Lab of BRDST (Balai Rekayasa Desain dan Sistem Teknologi) - BPPT. The comparison results was presented in Table 3.

Table 2. Comparison result

	EN 14105 modified	BPPT	DEV
	%w/w	%w/w	%
FREE GLYCEROL	0.004679	0.0053	11.73%
TOTAL GLYCEROL	0.005817	0.2200	97.36%



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BIODIESEL
BD.21

International Seminar on Biorenewable Resources Utilization for Energy and Chemicals 2013
In conjunction with Chemical Engineering Seminar of Soehadi Reksowardojo 2013

The comparison result table show that deviation between these two methods for free glycerol determination is more than 11 %, while the deviation for total glycerol determination was reached to 97 %.. The BPPT is using the FBI-A02-03 to determine the free glycerol and total glycerol content. In this experiment, total glycerol was calculated by summed the result of Mono-, Di-, and Tri-glyceride group calculation.

The experimental result indicated, that the modification of the EN 14105 method for determining of free glycerol and mono, di, and triglycerides content in biodiesel is still produce poor repetability and lack of accuracy. Although this modification is still appropriate to determine glycerol content in which showed 11 % deviation to BPPT result. But the detection of mono, di-, and tri-glyceride was still poor. This poor detection might be caused by over heated of compounds in the injector. Excessvely high temperatures may cause degradation of thermally untable compounds.

The modification method of EN 14105 can be continued while still using the manual injector by manually increase the injection temperature slowly. This action was to minimize the decomposition of compound. The modification of external standard calculation is valid only if using the auto injector. For next improvement need to use the internal standard method for the quantification, trial program temperature of injector, and do Internal Lab check using the CRM

4. Conclusion

Based on the experimental result, it is concluded that the modification of the EN 14105 method for determination of free glycerol and mono, di, and triglycerides content in biodiesel is appropriate only for free glyserol content determination. For mono, di, and triglycerides content determination, still need some modification improvement.

5. Acknowledgement

This research was supported by Kementerian Riset dan Teknologi (Kemenristek) Republik Indonesia, under Insentif Riset Sistem Inovasi Nasional (SINas) Scheme with Contract Number 40/SEK/INSINAS/PPK/I/2013.



6. References

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Question and Answer

1. Why productivity mono, di, tri glycerol responnya rendah?
 - kalo mono cdomnya lebih panjang
 - External standar operation we use auto injection