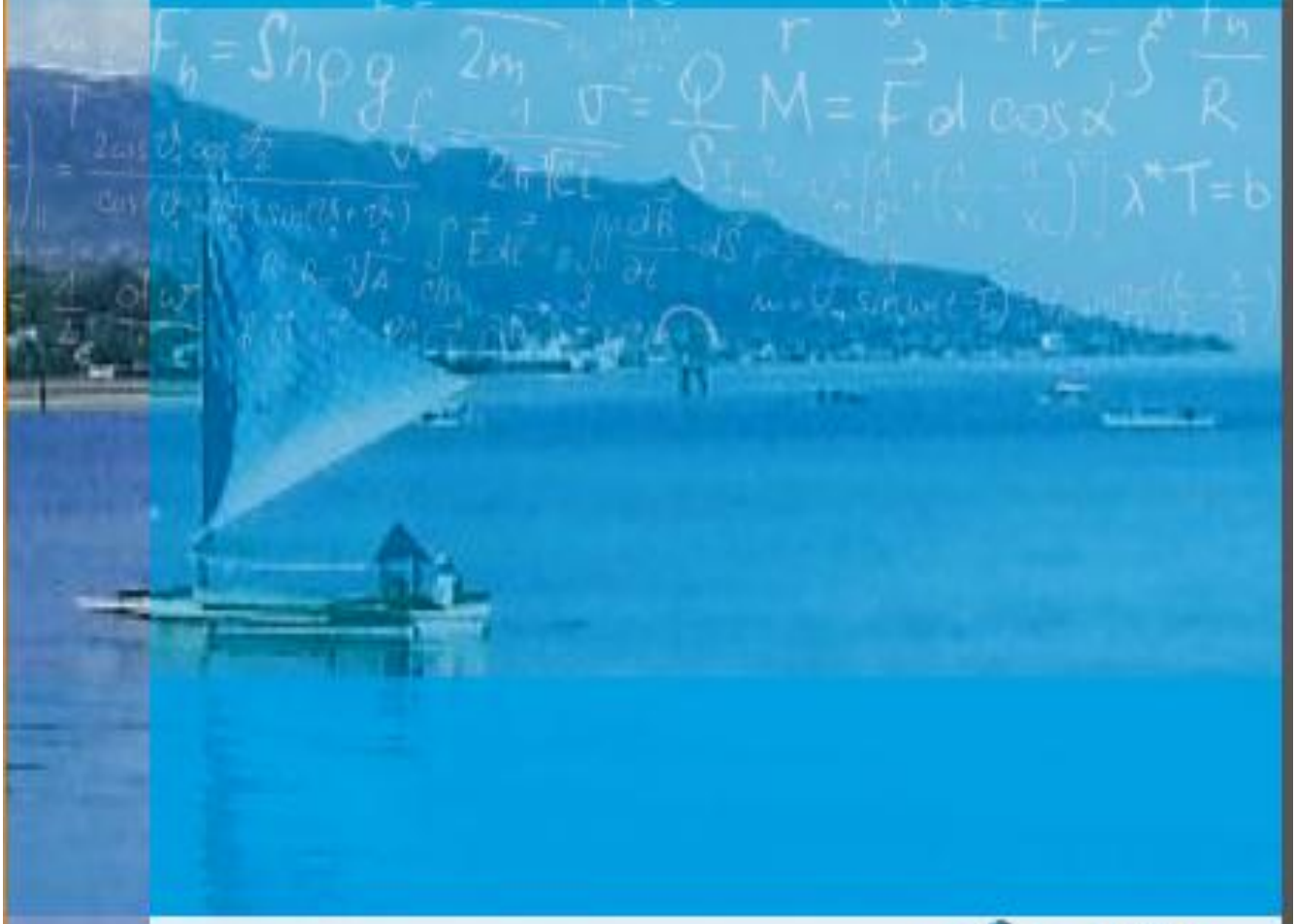
Basic Science
for Sustainable Marine Development

PROCEEDING
INTERNATIONAL SEMINAR 2015

Ambon, 3-4 June 2015



Organized by
Faculty of Mathematics and Natural Sciences
Pattimura University

PROCEEDINGS

1st International Seminar of Basic Science, FMIPA Unpatti - Ambon
June, 3rd – 4th 2015

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Welcoming Address by The Organizing Committee

The honorable, the rector of Pattimura University

The honorable, the vice rector of academic affair, Pattimura University

The honorable, the vice rector of administration and financial affair, Pattimura University

The honorable, the vice rector of planning, cooperation and information affair, Pattimura University

The honorable, all the deans in Pattimura University

The honorable, the key note speakers and other guests.

We have to thank The Almighty God for the blessings that allow this International seminar can be held today. This is the first seminar about MIPA Science in which the Faculty of MIPA Pattimura University becomes the host. The seminar under the title Basic Science for Sustainable Marine Development will be carried out on 3 June 2015 at Rectorate Building, the second floor. There are 250 participants from lecturers, research institute, students, and also there are 34 papers will be presented.

This International seminar is supported by the amazing people who always give financial as well as moral supports. My special thanks refer to the rector of Pattimura University, Prof. Dr. Thomas Pentury, M.Si, and the Dean of MIPA Faculty, Prof. Dr. Pieter Kakissina, M. Si. I also would like to express my deepest gratitude to Dr. Kotaro Ichikawa, the director of CSEAS Kyoto University, Prof. Bohari M. Yamin, University of Kebangsaan Malaysia, Prof. Dr. Budi Nurani Ruchjana (Prisident of Indonesian Mathematical Society/Indo-MS), Dr. Ir. A. Syailatua, M.Sc (Director of LIPI Ambon), and Hendry Ishak Elim, PhD as the key note speakers. We expect that this international seminar can give valuable information and contribution especially in developing basic science for sustainable marine development in the future.

Last but not least, we realize that as human we have weaknesses in holding this seminar, but personally I believe that there are pearls behind this seminar. Thank you very much.

Chairman

Dr. Netty Siahaya, M.Si.

Opening Remarks
By Dean of Mathematic and Natural Science Faculty

I express my deepest gratitude to The Almighty God for every single blessing He provides us especially in the process of holding the seminar until publishing the proceeding of International Seminar in celebrating the 17th anniversary of MIPA Faculty, Pattimura University. The theme of the anniversary is under the title Basic Science for Sustainable Marine Development. The reason of choosing this theme is that Maluku is one of five areas in Techno Park Marine in Indonesia. Furthermore, it is expected that this development can be means where the process of innovation, it is the conversion of science and technology into economic value can be worthwhile for public welfare especially coastal communities.

Having the second big variety of biological resources in the world, Indonesia is rich of its marine flora and fauna. These potential resources can be treated as high value products that demand by international market. Basic science of MIPA plays important role in developing the management of sustainable marine biological resources.

The scientific articles in this proceeding are the results of research and they are analyzed scientifically. It is expected that this proceeding can be valuable information in terms of developing science and technology for public welfare, especially people in Maluku.

My special thanks refer to all researchers and reviewers for your brilliant ideas in completing and publishing this proceeding. I also would like to express my gratefulness to the dies committee-anniversary of MIPA Faculty for your creativity and hard working in finishing this proceeding, God Bless you all.

Dean of Mathematic and Natural Science Faculty

Prof. Dr. Pieter Kakisina, M.Si.

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Metathesis of Ethyloleate

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ABSTRACT

The discovery of less air sensitive catalysts and more tolerance towards functional groups has widen the scope of metathesis reaction as a tool to synthesize many organic compounds and polymers. In Asia the market trend of using liquid detergents based on plant fatty acid is increasing compare to animal fatty acids in Europe. Lubricant is also another example of the potential of plant based fatty acid applications. The metathesis of methyl ester as model study is the right approach to begin with before embarking into the bulk oil that contains various components of fatty acids. In this presentation the focus will be on the preliminary study of self and cross metathesis of ethyloleate with some chalcogens looking into diversification of products based on vegetable or plant oils.

***Keywords**: metathesis, ethyl oleate, Grubbs 2nd generation.*

INTRODUCTION

Catalytic metathesis reaction of vegetable oil such as soybean and palm oils have attracted many researchers to investigate its application to produce new products. In the early study Chauvian tungsten and Schrock, molybdenum complexes[1] were available for the study. Since the analysis of vegetable oil is quite difficult because of their low volatility, it is more convenient to study their methyl esters before begining with the bulk oil. Therefore, methyl oleate being the simplest unsaturated methyl ester fatty acid has been studied in both homogenous and heterogenous catalytic conditions. Alternatively it should be possible to do metathesis on the bulk oil followed by esterification for the analysis.

Among the early reports on the metathesis of vegetable oil was self metathesis of methyl oleate by using $WCl_6/SnMe_4$ catalyst[2]. According to Van Dem *et al* (1972), active metal tungsten could undergo reduction due to alkyltin promoter.

Early study of palm oil metathesis reaction by $WCl_6/SnMe_4$ catalyst showed that the products were 6-pentadecene, 9-octadecene and dimethyl 9- -octadecenedioate[3]. It has been reported that the composition of the oil would give quality effect of oil either positive or negative by changing the oil composition[4]. However, the air sensitive and low functional group tolerance of the catalyst are the problems in extending the study and the design to scale up the process. Some progress on the self metathesis of methyloleate by 2nd generation Grubbs has also been reported.

In this preliminary study, Grubbs 2nd generation (Fig.1) is tested for the self metathesis of ethyl oleate both in homogeneous and heterogeneous conditions.

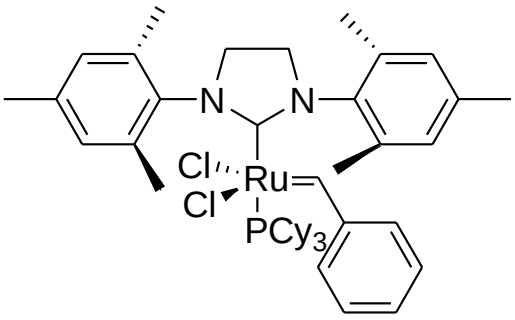


Figure 1. Grubbs 2nd generation

METHODOLOGY

Chemicals

Ethyl oleate, Grubbs 2nd generation catalyst were purchased from Aldrich. Other chemicals were analytical grades and used as received. All solvents such as dichloromethane and hexane were distilled before used.

Instruments

The gas chromatograph mass spectrometer (GC/MS) analysis were performed on an Agilent 7890A gas chromatograph (GC) directly coupled to the mass spectrometer system (MS) of an Agilent 5975C inert Mass Selective Detector (MSD) with triple-axis detector. SGE column model BP-20 30 m length, 0.25 mm in diameter and film thickness and polyethylene glycol stationary phase was used throughout the experiment.

Procedure

Preparation of heterogenous catalyst

1 g β-alumina powder was calcinated at 300 °C for 6 hours. The alumina was then placed in a vial containing 1 mL CH_2Cl_2 solution of (0.00005 mol, 0.0040 g) catalyst. The vial was tightly closed and left for overnight. The solvent was removed and the solid supported catalyst was dried under vacuum. The workout was carried out in vacuum box. The alumina powder catalyst was heated at 150 °C for 1 hour.

Homogenous self metathesis reaction

(0.01 mmol, 1 mL) ethyl oleate in 1 mL hexane was added into 1 mL catalyst (0.00005 mol, 0.0040 g) solution in 20 mL vial. Then it was stirred for 24 hours at room temperature. The sample was then kept in refrigerator. GC-MS analysis was carried out on the sample.

Heterogeneous metathesis reaction

(0.01 mmol, 1 mL) ethyl oleate was placed inside the 1.5 mL vial containing 0.5 g supported catalyst and left without stir for 24 hours at room temperature.

RESULTS AND DISCUSSION

Homogeneous reaction

Addition of ethyl oleate into the red catalyst solution gave slight change in the colour of the solution. After 24 hours, dark brown solution was obtained. The gas chromatogram showed four major peaks (Fig.2) together with several other peaks indicating the extent of the reaction after 24 hours at room temperature.

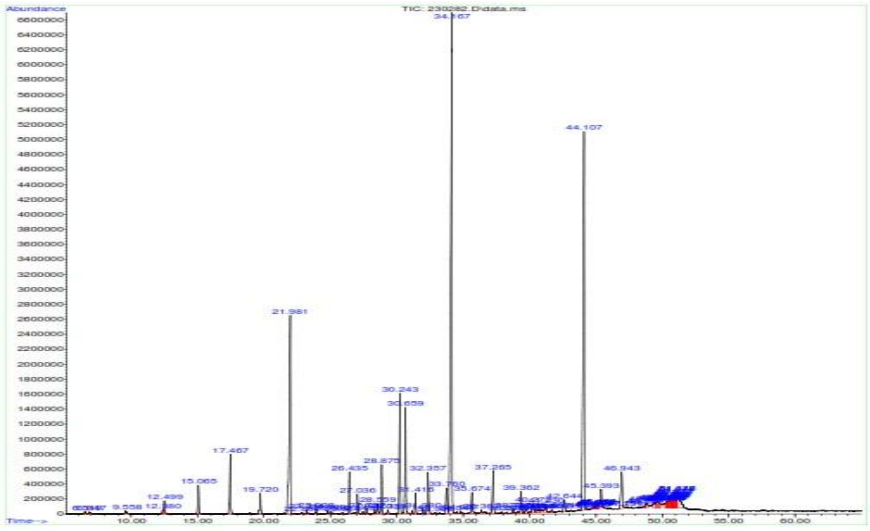


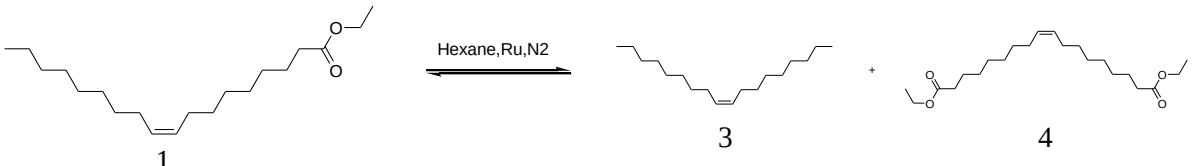
Figure 2. Chromatogram of the homogeneous reaction solution.

The m/z values for the peaks at 21.98, 30.24, 34.16, 44.10 min retention times are given in Table 1.

Table 1. Mass spectral analysis of 4 important products

Peak No.	Retention time/min	m/z values
1.	21.98	55.1 (100%), 69.1, 83.1, 97.1, … **252.3**
2.	30.24	88.1 (100%), 157.1, 241.2... **256.2**, 284.3
3.	34.16	55.1(100%), 83.0, 101.0, 264.0, 281.0, **310.3**
4.	44.10	55.1 (100%), 81.1... 345.8, **368.3**,

The mass spectra of the four peaks indicate the formation of 9-octadecene, ethyl oleate, hexadecanoic acid and diethyl 9-octadecenedioate as major products.



1
(m/z= 310.29)

3
(m/z= 252.28)

4
(m/z= 368.29)

Other small peaks possibly due to isomerisation and products from continuous reaction are not considered until detailed studies are carried out.

Heterogenous reaction

The gas chromatogram of the reaction solution showed almost exactly the same (Fig.3) with four major peaks at 21.98, 30.24, 34.17 and 44.10 min retention times. Therefore, the Grubbs catalyst also work very well under heterogeneous condition.

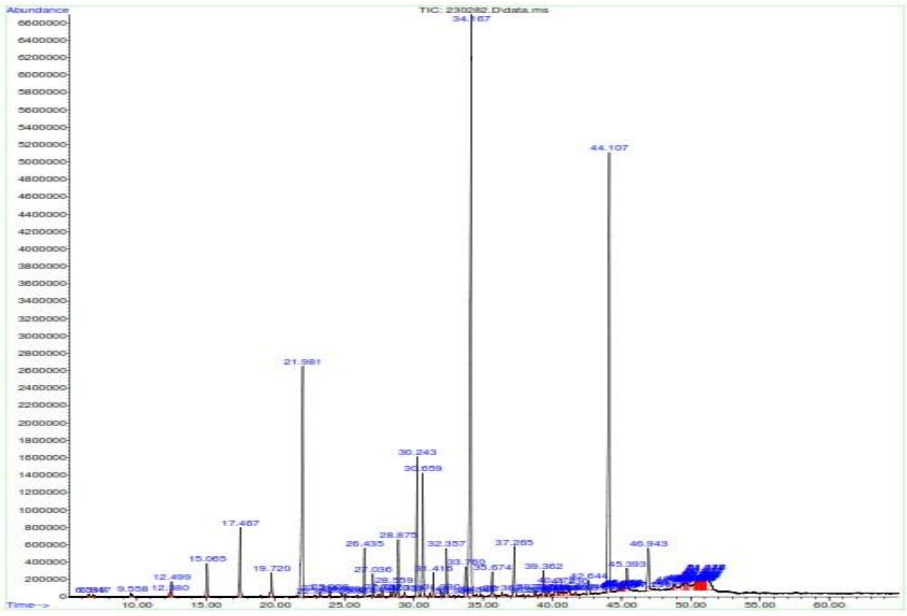


Figure 3. Chromatogram of the heterogeneous reaction solution

Heterogeneous reaction has certain advantages over the homogeneous that it can always be recycled provided the catalytic activity still functioning. Fig.4 shows the chromatogram of the reaction solution when the same catalyst support system was used for the second time.

There are 5 major peaks at 31.21, 34.75, 35.01, 37.86 and 44.68 min retention times (Table 2). The catalyst are still active and additional products are produced. The mass spectra for the five peaks indicate the formation ethyl 9-hexadecanoate, ethyl oleate, ethyl 9-octadecadionate and 9-octadecyne as the major products for second time reaction.

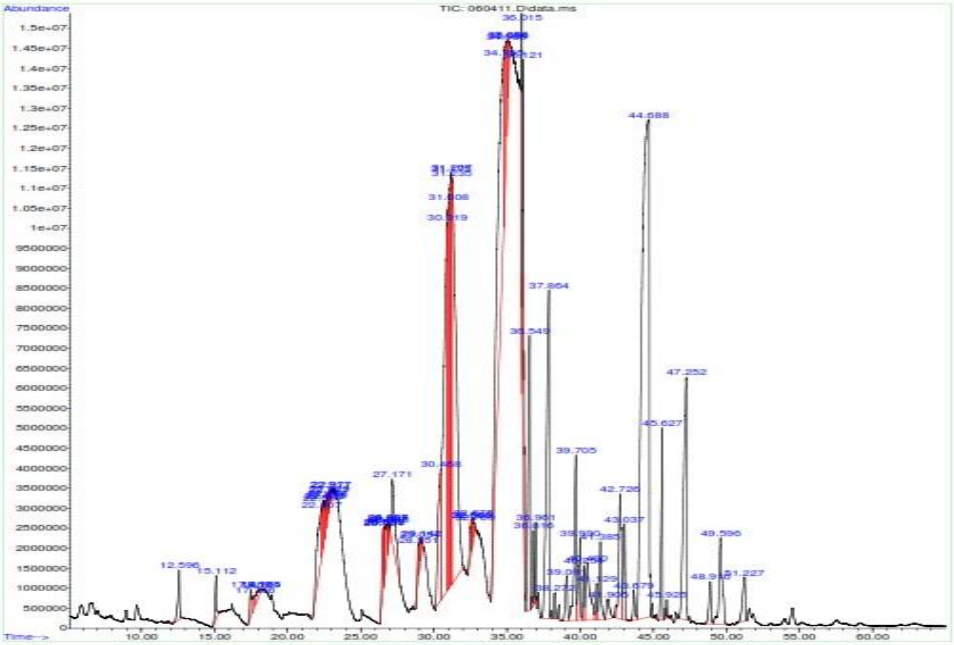


Figure 4. Chromatogram of the heterogeneous reaction solution for the second time reaction with the same catalyst

Table 2.

Peak No.	Retention time/min	m/z values
1.	31.21	55.1, 88.1(100%), 157.2... 241.2, **284.3**
2.	34.75	55.1 (100%), 88.1... 222.3, 264.3, **310.3**
3.	35.01	55.1 (100%), 83.1... 264.3, **310.3**
4.	37.86	55.1 (100%), 81.1... 345.8, **368.3**
5	44.68	55.1 (100%), 83.1, 250.3... 292.3,**309.2**

This preliminary study is a good basis for extensive and more detailed work on the metathesis of ethyl oleate exploring for new products by crossing with other olefinic compounds including optimisation study of the reaction.

CONCLUSIONS

The Grubbs 2nd generation catalyst is suitable for the metathesis reaction of ethyl oleate in both homogenous and heterogenous system. The products of the heterogenous reaction are similar with the homogenous system. However, additional products were observed when the same catalyst under heterogenous condition was used for the second time. Therefore, further study on the optimisation of the reactions and cross metathesis to obtain new products are on progress.

ACKNOWLEDGEMENT

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