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by Desneli Desneli

Submission date: 16-Apr-2023 07:09AM (UTC+0700)
Submission ID: 2065518795
File name: 1-s2.0-S1876619615002752-main-procedia.pdf (260.12K)
Word count: 1477
Character count: 7805

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Procedia Chemistry 17 (2015) 44 – 48

Procedia Chemistry

3rd International Seminar on Chemistry 2014

The Olefin Reaction between Crude Palm Oil Fatty Acid Methyl Ester (CPO FAME) and Ethylene Using Grubbs II Catalyst

Desnelli[a,b], D. Mujahidin[a], Y. Permana[a], C.L. Radiman[a,*]

[a]*Inorganic and Physical Chemistry Research Division, Institut Teknologi Bandung, Jalan Ganesha 10, Bandung 40132, Indonesia*
[b]*Chemistry Department of Universitas Sriwijaya, Jalan Palembang-Prabumulih Km 32 Indralaya, Indonesia*

Abstract

Renewable materials derived from vegetable oils are now widely developed for obtaining green polymers. One of the applications of those polymers is in the field of Enhanced Oil Recovery (EOR) where the polymers are put in the injection wells to increase water viscosity resulting in higher efficiency of oil production. Indonesia is very rich in crude palm oil and therefore, it was chosen as the starting material for polymer synthesis. The objective of this work is to prepare the monomer first, by doing the olefin metathesis reaction between crude palm oil FAME (fatty acid methyl ester) and ethylene. The reaction was carried out using a Grubbs II catalyst in order to obtain methyl 9-decenoate which is used later as the monomer for EOR application. The resulting product was characterized using Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared (FTIR) spectroscopy as well as Gas Chromatography Mass Spectrometry (GC-MS). Based on the functional group analysis, it was found that methyl 9-decenoate has successfully been synthesized.

Keywords: Crude palm oil, Grubbs II catalyst, methyl 9-decenoate, metathesis.

* Corresponding author. Tel.: +62-22-250-2103; fax: +62-22-250-4154.
E-mail address: cynthia@chem.itb.ac.id.

1. Introduction

Palm oil is one of the vegetable oils which contain unsaturated fatty acids such as oleic acid. The content of oleic acid in palm oil is about 30-40%. Oleochemical industries use oleic acid as the starting material for many important chemical reactions such as olefin metathesis, ozonolysis and epoxidation[1].

Olefin metathesis is an important catalytic reaction in organic synthesis where the internal double bond is converted into new product through the rupture and reformation of C-C double bond[2]. Among other organic reactions, the olefin metathesis reaction gives opportunity to new routes in industries in order to produce petrochemical materials, polymers, oleochemicals and specialty chemicals[3]. Metathesis reactions use various

Peer-review under responsibility of Department of Chemistry, Faculty of Mathematics and Natural Sciences, Padjadjaran University
doi:10.1016/j.proche.2015.12.127

transition metal complexes such as tungsten, molybdenum and ruthenium[4]. According to Astruc, the Schrock and Grubbs catalysts are the most efficient catalysts as they are more compatible with functional groups responsible for the metathesis reaction[5].

Unsaturated fatty acid methyl esters (FAME) and natural oils are renewable feedstock that can be used as starting materials in the metathesis reactions considered as green chemistry[6]. These materials are available abundantly in nature. Indonesia is the largest palm oil producer in the world since its plantations can be found in almost every region of Indonesia.

One of the applications of olefin metathesis is the transformation of internal alkene to terminal alkene via cross metathesis. The objective of this research is to carry out the reaction between unsaturated fatty acid ester (FAME) of crude palm oil and ethylene to produce methyl 9-decenoate monomer. This monomer is an essential chemical for the production of polymer in Enhanced Oil Recovery (EOR) application.

2. Experimental section

2.1. Reagents

Crude palm oil (FAME), Grubbs II catalyst (Sigma), toluene, n-hexane (Merck), activated alumina, silica gel, Mg_2SO_4, distilled water.

2.2. Procedure

Crude palm oil (CPO) is a reddish vegetable oil obtained from extraction or compression process of palm fruit meat. The crude palm oil (FAME) was first passed through active alumina to remove the impurities present in the crude palm oil (CPO FAME). Then the crude palm oil was put in the reactor and purged with nitrogen gas. Then, the Grubbs II catalyst (with a ratio of 1:500 to crude palm oil) was dissolved in toluene and poured into the reactor. The reactor was then connected to an ethylene pipeline. The metathesis reaction was carried out with ethylene at 10 bars and 50 ^{o}C. After a certain time the sample was removed from the reactor. Then water and *n*-hexane were added to the mixture and placed in a separating funnel. The water layer was removed and the organic layer was washed with water twice. The organic layer was poured into a small column of silica to eliminate the excess of catalyst. It was dried afterwards with anhydrate Mg_2SO_4 and filtered. The product was a clear liquid with a characteristic odor. The sample was then characterized by NMR, FTIR and GC-MS spectroscopy.

3. Results and discussion

Figure 1 shows the scheme of metathesis reaction between methyl oleate and ethylene. The Grubbs II catalyst used in this reaction has more tolerance to compounds containing oxygen. Palm oil contains also oxygen that comes from fatty acids. It can be seen that the product of the methyl oleate transformation is methyl 9-decenoate monomer which has a terminal double bond. The side product of this reaction is 1-decene.

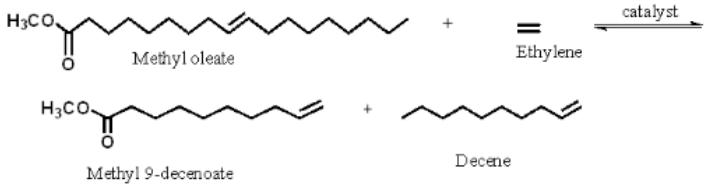


Fig. 1. Scheme of metathesis reaction between methyl oleate and ethylene

Figure 2 shows the ^{1}H-NMR spectrum of the metathesis product. The chemical shift values at 4.98 ppm and 5.77 ppm show a terminal alkene. The peak at chemical shift of 4.98 ppm indicates the presence of protons of -CH=C**H**$_2$ and chemical shift at 5.77 ppm indicates the proton of –C**H**=CH$_2$.The presence of chemical shift near 5.33 ppm is assigned to internal double bond of -CH=CH- proton. The presence of internal double bond is derived from the unreacted methyl oleate.

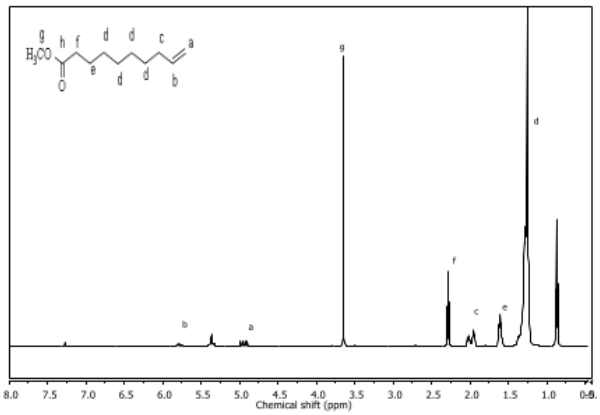


Fig. 2. ^{1}H-NMR spectrum of metathesis product between CPO FAME and ethylene

The analysis result of ^{1}H-NMR spectrum was supported by analysis of ^{13}C-NMR spectrum. The ^{13}C-NMR spectrum can be seen in Figure 3. The ^{13}C-NMR spectrum indicates the presence of alkene terminal of methyl 9-decenoate by the appearance of chemical shift at 114.1 ppm and 139.0 ppm. The chemical shift value at 114.1 ppm is assigned to the carbon of -CH=**C**H$_2$. Furthermore, the chemical shift at 139.0 ppm is assigned to the carbon atom of -**C**H=CH$_2$. The presence of chemical shift at 130.3 ppm indicates the presence of internal alkene of methyl oleate residue.

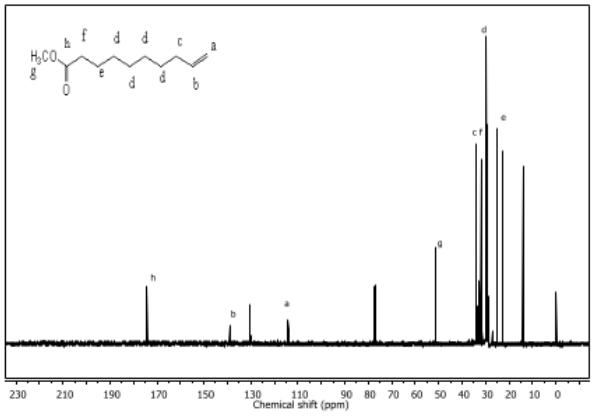


Fig. 3. ^{13}C-NMR spectrum of olefin metathesis product using CPO FAME and ethylene as reactants

The FTIR spectrum of the metathesis product can be seen in Figure 4. The absorption bands at 910 cm^{-1} and 3074 $cm^{-1}$are assigned to alkene terminals where the terminal double bond is derived from the methyl-9-decenoate. It is concluded that methyl 9-decenoate has been formed by this reaction.

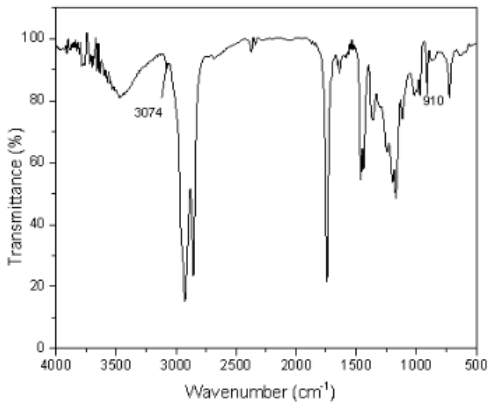
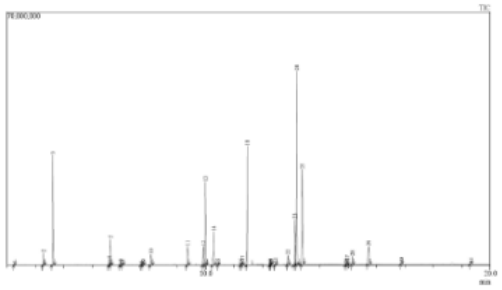
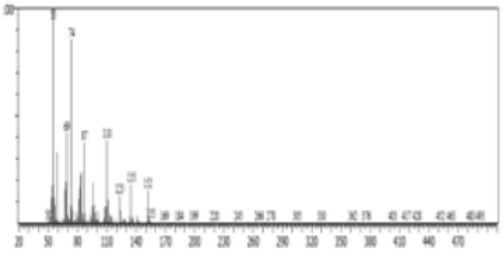


Fig. 4. FTIR spectrum of metathesis product using CPO FAME and ethylene as reactants

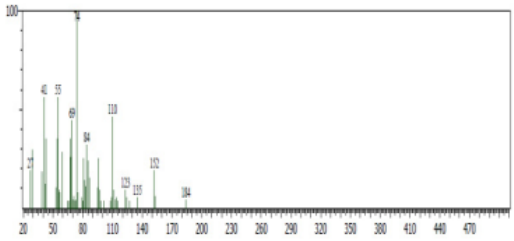
The GC-MS spectrum of the reaction product using CPO FAME and ethylene as reactants can be seen in Figure 5. Based on chromatogram GC, the metathesis reaction products showed several peaks. The peak number 3 is the peak of methyl 9-decenoate at a retention time of 4.618 minutes with an area of 13.14%. Unfortunately, the peak number 24 represented the methyl oleate from unreacted CPO FAME is still dominant.



(a)



(b)



(c)

Fig. 5. GC-MS spectrum of the metathesis product using CPO FAME and ethylene as reactants (a) GC Chromatogram; (b) MS spectrum of methyl 9-decenoate; (c) MS spectrum from the literature.

Conclusion

We have successfully synthesized the methyl 9-decenoate monomer from CPO FAME using olefin metathesis reaction (ethenolysis reaction) in the presence of Grubbs II catalyst. The presence of methyl 9-decenoate is confirmed by various spectroscopic methods including NMR, FTIR and GC-MS.

Acknowledgements

This work was financially supported by the LPPM-ITB under a contract No. 2259/AL-J/DIPA/PN/SKP/2014; for which the authors are very grateful.

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