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Gas Chromatography analysis on the performance evaluation of the palm oil cross-metathesis using 1-octene

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A R T I C L E I N F O

A B S T R A C T

Palm oil is one of the important raw materials in the oleochemical industry for downstream expansion and sustainability. The built-in functionality and availability of oil worldwide make palm oil more attractive. It can be further modified using the cross-metathesis process for the production of bio-based polyol. In this study the cross metathesised palm oil was pre-treated with different types of pre-treatment methods namely transesterification, silylation, methylation and dilution to find the best pre-treatment method. Moreover, the pre-treated samples were analysed using two different Gas chromatography columns installed to the Gas chromatography flame ionisation detector (GC-FID). The best pre-treatment method was then used to prepare the samples taken from the palm oil octenolysis at different molar ratio of palm oil to 1-octene. According to the findings of this research, dilution method outperformed other pre-treatment methods.

1. Introduction

During the 21st century, polyurethane production from renewable resources-derived polyol has been intensively researched due to environmentally benign development (Rybak et al., 2007). The usage of renewable sources has become an imperative component in green chemistry (Pillai et al., 2016; Mol, 2004). Natural oil has been considered as one of the paramount sources in the oleochemical industry has been used substantially in making chemical products. Malaysia produces approximately 1.48 million metric tonnes of palm oil yearly (Nitin et al., 2020; Embong et al., 2021; Bhuyar et al., 2021) . In Germany, plant oil plays an important role by bestowing 30% of 2.7 million tonnes of oil for the production of polyols every year (Meier, 2009). In the view of sustainable development, plant oil being one of the renewable sources significantly contributes to the production of polyol which is used for polyurethane production (Li et al., 2017).

The triglyceride structure of the plant oil can be affected by the degree of unsaturation and the length of carbon chains of the fatty acids (Meier, 2009). Meanwhile cross-metathesis has been enhanced to instigate a wide variety of functional groups by tuning the properties of plant oils for the application of polymers (Sinclair et al., 2017; Sumathi et al., 2008). Compounds with increased molecular diversity and reactivity that are more appropriately used

as feedstock for the formulation of bio-based materials, in particular polyols for the production of polyurethanes (PUs), can be generated by cross-metathesis of plant oil using external alkene (Alkenolysis), as opposed to self-metathesis(Ferreira et al., 2021). In terms of providing access to olefins and oleochemicals, a bio-refinery plant in Indonesia process up 180000 metric tonnes of plant oil using cross-metathesis (CM) process (Ogba et al., 2018; Nickel et al., 2012).

Palm oil, the second most cultivated oil in the world specifically in tropical countries, consists of 45% of palmitic acid, 40% of monounsaturated oleic acid, 10% of polyunsaturated linoleic acids, and 5% stearic acid (Sumathi et al., 2008). Palm oil which has a longer unsaturated fatty acid chain length is the best raw material to cross metathesize. With the help of an olefin, the longer unsaturated fatty acid chain will be sundered and hence producing terminal double bonds (Mol et al., 1998).

Cross-metathesis of high molecular weight substrates like triglyceride or a mixture of triglycerides can be efficiently performed with alpha olefins, especially with lower alpha olefins, to produce low molecular weight products that can be easily separated or purified. Previous studies have derived polyols through cross metathesis of various plant oil such as Rapeseed oil, Canola oil, Soybean oil, Sunflower oil, Corn oil, Peanut, Olive oil, and Linseed oil with different olefins namely, butene, ethylene, propene, and 1-octene(Thangavel et al., 2020). As an industrial intermediate, 1-octene is a linear organic compound, mainly used in the manufacture of polyethylene. By using terminal olefin, 1-octene inhibits the formation of side products. It can be further enhanced by the catalyst with high activity and stability (Pease et al., 2016). The use of liquid cross-metathesis partner instead of gaseous cross-metathesised partner such as 1-octene is more advantageous. Here 1-octene is preferred as it declines the formation of ruthenium methylidene which promotes catalyst decomposition(Kuhn et al., 2009).

The reaction performance of the octenolysis of palm oil can be measured by the reactant conversion, product selectivity and yield. The number of reactants and products after the reaction can be quantified using High Temperature Gas chromatography (GC) equipped with fused silica capillary column. The selection of the column is important to analyse the sample whereas inappropriate usage of the column can give meaningless result. Typically, fatty acids and oils can be analysed using the commercially available CP-TAP and Rtx-65TG columns which possessing a more polar stationary phase (Ruiz-Samblás et al., 2015). In oils and fats analysis prior to GC injection, derivatization procedure is considered to be the essential step because it reduces the elution temperature of TAGs in oil.

2. Materials and Methods

2.1. Chemicals

Analytical grade chemicals and solvents were used without further purification. The following chemicals were purchased from Sigma Aldrich except the raw material, palm oil.Tris(hydroxymethylphosphine) (reagent), 1-octene (98%) (reactant), 2-propanol (>99.5%) (solvent), Ethyl Acetate (99.8%) (solvent to dissolve catalyst), hexadimethylsilazane (98%) (reagent), trimethylchlorosilane (reagent), Methanol (99%) (solvent used for stock solution), Hoveyda Grubbs second generation catalyst, Dichloromethane (99.5%) (reagent) and n-hexane (99.8%) (solvent for GC sample preparation).

2.2. Experimental Procedure for Cross-metathesis of Palm Oil

The octenolysis of palm oil was carried out according to the following general procedure. The palm oil and 1-octene were mixed in a round bottom flask with a capacity of 50 mL using a magnetic stirrer. The reaction was carried out at molar ratio of (1:3) palm oil to 1-octene. The reaction mixture was heated up to 40 °C. A solution of the Hoveyda Grubbs second-generation ruthenium-based catalyst was prepared in ethyl acetate green solvent and added to the palm oil/1-octene mixture via syringe through the Teflon-seal while stirring. The catalyst loading was 1 ppm (mole of catalyst per mole of the double bond in the substrate). The reaction mixture was maintained at 40°C for 4 hrs. The resulted products were subjected to different derivatization methods prior to the GC analysis.

2.3. Procedure for different pre-treatment methods of GC sample

2.3.1 Method A(Transesterification)

Prior to GC analysis, 0.5 mL of a 1.0 M of tris(hydroxymethyl)phosphine (THMP) isopropanol solution was added to the sample. The mixture was then heated at 60 °C for 1 h, diluted with 2.5 ml of distilled water and 2.5ml of hexane. The organic phase was separated and analysed by GC-FID (Alto, 2011).

2.3.2 Method B(Silylation)

A simple silylation method was carried out by dissolving 50 mg of the sample with 3 ml of pyridine. Then 0.4 ml of hexadimethylsilazane and 0.3 ml of trimethylchlorosilane were added. The solution was stirred for 30 sec and left for a certain time to ensure complete silylation (Quigley et al., 2014; Chin et al., 2018). It was then refluxed for 1 hour, filtered through a microfilter and injected into GC-FID.

2.3.3 Method C (HMD (Methylation)

Sample derivatization using hexamethyldisilazane was done by adding 5% of hexamethyldisilazane in 50 μl of methanol to the stock solution of (450ul). The reaction mixture was sonicated for 30 min and was thereafter kept at room temperature for 24 hrs to achieve complete derivatization. Then, 140 μl of internal standard stock solution was added and the solution was further diluted with 1.5ml of dichloromethane (DCM) before it was injected into GC-FID (Tammekivi et al., 2019).

2.3.4 Method D (Dilution)

The sample was diluted with n-hexane by following the dilution factor of 1.25 and 2(Qian et al., 2020).

2.4 Procedure for GC-FID Analysis

The pre-treated samples were analysed using GC equipped with flame ionization detector (FID), CP-TAP column (25 m length x 0.25 mm i.d. x 0.1 μm film thickness) and Rtx-65TG (cap. column 30 m,0.25 mm ID,0.10μm). The specification of the method is as follows; the oven temperature was ramped from 100°C (hold for 1 min) to 200°C at a rate of 20 °C/min to 350 °C at a rate of 21.7 °C/min to 365 °C at a rate of 1.2°C/min (hold 5min). The injection volume was 0.1 μl and the split ratio were 25:1 and 10:1. The injection temperature and detector temperature were 250 °C and 365 °C respectively. The flow rate of H_2 carrier gas was set at 0.5 ml/min or 1.28 ml/min. The make-up gas with a flow rate of 30 ml/min was used to sweep the components through a detector to minimize band broadening and can improve sensitivity, the air flow rate was 370 ml/min and the data rate was 50 Hz.

3.Results and Discussion

3.1 Screening of the GC Column

The samples prepared with different pre-treatment methods were analysed using GC equipped with flame ionization detector (FID) and CP-TAP column (25 m length x 0.25 mm ID x 0.1 μm film thickness) or Rtx-65TG column (30 m x 0.25 mm ID x 0.1 μm) with the method stated in 2.4 with the split ratio of 25:1.

Here from Figure 1, it can be noticed that no 1-decene and triglyceride peak was detected. It is due to the contamination of the column. Triglycerides being the high molecular weight compound and setting the GC's maximum oven temperature causes contamination in the column and its peak does not get eluted (Ruiz-Samblás et al., 2015). This is because the residues do not elute but accumulating in the column. The contaminants are relatively non-volatile and they accumulate in the column over time. The column becomes coated with these residues which interfere with the proper partitioning of solutes in and out of the stationary phase.

The retention time of the 1-octene peak obtained was 3.736 mins (Method A), 3.876 mins (Method B), 3.636 mins (Method C), 3.788 mins (Method D) as shown in Figure 1(a) and 1(b). From Figure 1(b), it can be noticed that the peaks were well separated if the sample was treated using method D and analysed through Rtx-65TG column. Method D has reduced the concentration of the analyte and hence help eliminating the interference from other substances that may be present in the sample which would alter the analysis. If the sample is too concentrated the shape of the peak will be broad and flattened on top and possibly can overlap.
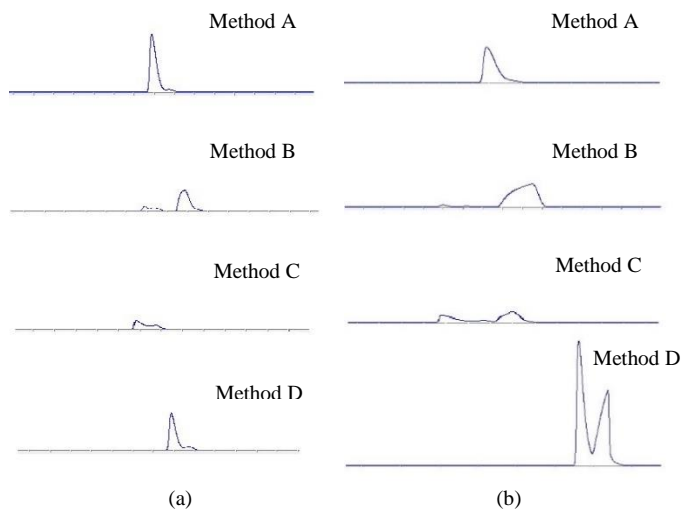

Figure 1 Chromatogram of pre-treated samples using Method A, Method B, Method-C and Method D analysed through CPTAP column-Figure 1 (a) and Rtx-65TG column-Figure 1 (b)

3.2 Sample analysis using Rtx-65TG Column with different split ratio

The split ratio of the GC analysis was set at 25:1 or 10:1. Separation of peaks with different split ratio is shown in Figure 2 (a) for 25:1 and Figure 2 (b) for 10.1. The peaks were well separated using 25:1 split ratio. Split ratio is defined as the ratio of split vent flow rate to the ratio of column flow rate, Usually, the split ratio determines the sharpness of the peak. The peak shape would be blunt if the split ratio is very low. The narrowest and sharpest peaks would result from the best split ratio. Typically, the split ratio varies from 20:1 to 100:1. It is also found that split ratios between 10:1 and 400:1 are usually accurate for ensuring that the target analyte of interest has good peak symmetry. Here the effective dynamic split ratio range for Rtx-65TG column is found to be 25:1.

The sample was prepared with different dilution factor. Figure 3(a) represents that the peaks were well separated when the dilution factor was 1.25. From Figure 3(b), it has been found that using the dilution factor 2 the peak separation was not as good as the one shown in Figure 3(a). From the above figures it was noted that the peaks were efficient in Method D with the dilution factor of 1.25 by using Rtx-65TG column. Though this column is one of the industrial most rugged and reliable columns for accurate and precise analysis it is very efficient for the separation of 1-octene and hexane.
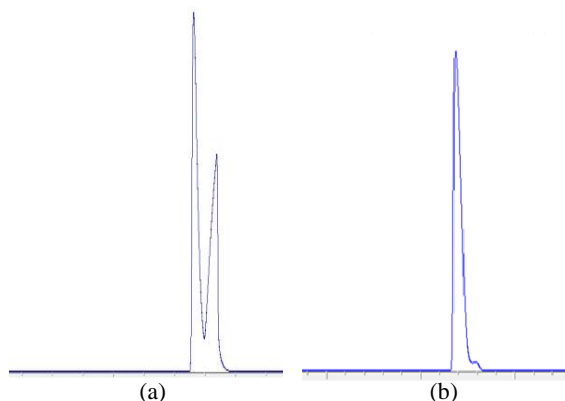
Figure 2 The resulted chromatogram of the sample pre-treated using Method D from the GC analysis with the (a)-Split ratio- 25:1 (b) Split ratio-10:1

3.3 Sample analysis using Rtx-65TG Column with different dilution factor
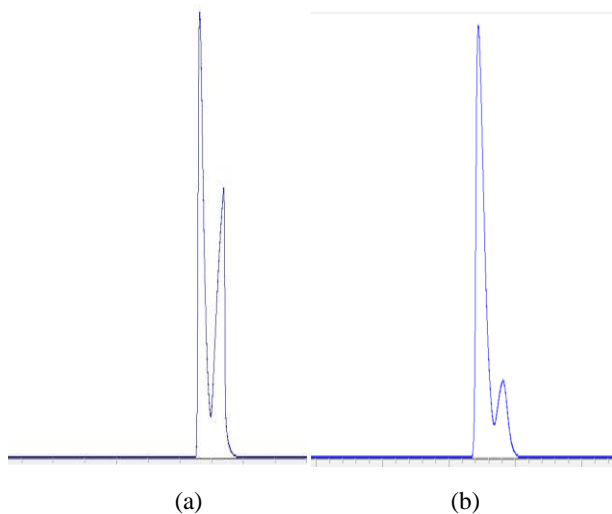

Figure 3 The resulted chromatogram of the sample pre-treated using Method D with (a)-Dilution factor-1.25 (b)-Dilution factor-2 from the GC analysis with Rtx-65TG column

4.Conclusion

The 1-decene and other triglyceride peaks were not able to be found using the GC-FID analysis though the compound in the oil have contaminated the column. In this situation the separation of 1-octene and hexane peaks were able to be found with different pre-treatment methods. The separation of 1-octene and hexane have been observed successfully using chromatographic methods.

The GC analysis ostensibly showed, that the performance of method D was satisfactory. To prove that higher separation capacity can be achieved using capillary column Rtx-65TG showed valuable results. The samples prepared and pre-treated using method D with the dilution factor of 1.25 is considered to be the best pre-treatment method. The peaks were nicely separated with the retention time of 3.7 mins with the operating conditions: column flow rate of 0.5 ml/min, the oven temperature was ramped from 100 ºC (hold 1 min) to 200 ºC at a rate of 20.7 ºC/min, 200 ºC to 350 ºC at a rate of 21.7 ºC/min and 350 ºC to 365 ºC at a rate of 1.2 ºC/min (hold 5mn). The injector temperature was 250 ºC whereas the detector temperature was 365 ºC. It was noted that the 1-octene and hexane peak obtained using the sample which was pre-treated using method D with dilution factor of 1.25 and 2 were distinct from one another when compared to Method A, B and C.

References

Alto, P. 2011. (12) United States Patent s San. 2(12).

Bhuyar, P., Sundararaju, S., Rahim, M. H. A., Ramaraj, R., Maniam, G. P., & Govindan, N. (2021). Microalgae cultivation using palm oil mill effluent as growth medium for lipid production with the effect of CO2 supply and light intensity. Biomass Conversion and Biorefinery, 11(5), 1555-1563.

Chin, S.Y., Hong, C.S., Kamaruzaman, M.R., and Chua, G.K. 2018. Chromatography strategies for the composition determination of bio-based sorbitol azelaic acid ester. Polymer Testing 65(December 2017): p.270–280.

Embong, N. H., Hindryawati, N., Bhuyar, P., Govindan, N., Rahim, M. H. A., & Maniam, G. P. (2021). Enhanced biodiesel production via esterification of palm fatty acid distillate (PFAD) using rice husk ash (NiSO4)/SiO2 catalyst. Applied Nanoscience, 1-9.

Ferreira, L.A., Silva, J.T., Alves, R.G., Oliveira, K.C.B., and dos Santos, E.N. 2021. Spicing up olefin cross metathesis with the renewables estragole and methyl sorbate. Applied Catalysis A: General 620(February): p.118173.

Kuhn, K.M., Bourg, J.B., Chung, C.K., Virgil, S.C., and Grubbs, R.H. 2009. Effects of NHC-backbone substitution on efficiency in ruthenium-based olefin metathesis. Journal of the American Chemical Society 131(14): p.5313–5320.

Li, S., Bouzidi, L., and Narine, S.S. 2017. Polyols from self-metathesis-generated oligomers of soybean oil and their polyurethane foams. European Polymer Journal 93(February): p.232–245.

Meier, M.A.R. 2009. Metathesis with Oleochemicals: New approaches for the utilization of plant oils as renewable resources in polymer science. Macromolecular Chemistry and Physics 210(13–14): p.1073–1079.

Mol, J.C. 2004. Catalytic metathesis of unsaturated fatty acid esters and oils. Topics in Catalysis 27(1–4): p.97–104.

Mol, J.C., and Buffon, R. 1998. Metathesis in oleochemistry. Journal of the Brazilian Chemical Society 9(1): p.1–11.

Nickel, A., et al. 2012. A highly efficient olefin metathesis process for the synthesis of terminal alkenes from fatty acid esters. Topics in Catalysis 55(7–10): p.518–523.

Nithin, B. R., Bhuyar, P., Trejo, M., Rahim, M. H. A., Maniam, G. P., & Govindan, N. (2020). Culturing of green photosynthetic microalgae (Chlorella sp.) using palm oil mill effluent (POME) for future biodiesel production. Maejo International Journal of Energy and Environmental Communication, 2(1), 1-8.

Ogba, O.M., Warner, N.C., O'Leary, D.J., and Grubbs, R.H. 2018. Recent advances in ruthenium-based olefin metathesis. Chemical Society Reviews 47(12): p.4510–4544.

Pease, B., Dreyer, B., and Pauls, R.E. 2016. Detailed Compositional Analysis of Vegetable Oil Metathesis Products Using Microfluidic Switching Multidimensional Gas Chromatography. JAOCS, Journal of the American Oil Chemists' Society 93(8): p.1025–1036.

Pillai, P.K.S., Li, S., Bouzidi, L., and Narine, S.S. 2016. Metathesized palm oil & novel polyol derivatives: Structure, chemical composition and physical properties. Industrial Crops and Products 84: p.205–223.

Qian, Y., Rudzińska, M., Grygier, A., and Przybylski, R. 2020. Determination of triacylglycerols by HTGC-FID as a sensitive tool for the identification of rapeseed and olive oil adulteration. Molecules 25(17).

Quigley, B.L., and Grubbs, R.H. 2014. Ruthenium-catalysed Z-selective cross metathesis of allylic-substituted olefins. Chemical Science 5(2): p.501–506.

Ruiz-Samblás, C., González-Casado, A., and Cuadros-Rodríguez, L. 2015. Triacylglycerols Determination by High-temperature Gas Chromatography in the Analysis of Vegetable Oils and Foods: A Review of the Past 10 Years. Critical Reviews in Food Science and Nutrition 55(11): p.1618–1631.

Rybak, A., and Meier, M.A.R. 2007. Cross-metathesis of fatty acid derivatives with methyl acrylate: Renewable raw materials for the chemical industry. Green Chemistry 9(12): p.1356–1361.

Sinclair, F., Alkattan, M., Prunet, J., and Shaver, M.P. 2017. Olefin cross metathesis and ring-closing metathesis in polymer chemistry. Polymer Chemistry 8(22): p.3385–3398.

Sumathi, S., Chai, S.P., and Mohamed, A.R. 2008. Utilization of oil palm as a source of renewable energy in Malaysia. Renewable and Sustainable Energy Reviews 12(9): p.2404–2421.

Tammekivi, E., et al. 2019. Comparison of derivatization methods for the quantitative gas chromatographic analysis of oils. Analytical Methods 11(28): p.3514–3522.

Thangavel, M., and Chin, S.Y. 2020. Cross metathesis of plant oil: A mini review on reaction condition and catalysis. IOP Conference Series: Materials Science and Engineering 991: p.012073.