International Journal of Research in Engineering and Science (IJRES)
ISSN (Online): 2320-9364, ISSN (Print): 2320-9356
www.ijres.org Volume 09 Issue 10 ǁ 2021 ǁ PP. 60-64

Clay Catalyzed Dimerization of Linseed Oil: Synthesis of Linseed Oil Dimers

[*1]Gaurav Singh,[2]Surabhi Rajwani,[3]P. K. S. Yadav
[*1]*Department of Oil Technology, School of Chemical Technology, Harcourt Butler Technical University, Kanpur*
[2]*Department of Oil Technology, School of Chemical Technology, Harcourt Butler Technical University, Kanpur*
[3]*Department of Oil Technology, School of Chemical Technology, Harcourt Butler Technical University, Kanpur*
Corresponding Author:Gaurav Singh

Abstract
Vegetable oil based raw materials are one of the vital renewable feedstock for chemical industries in all the time. A tremendous shift has been observed from petrochemical based and synthetic feedstock towards oleochemical based products. Fatty acid dimers are a class of essential intermediates that are frequently used in various industrial applications such as development of polyamides, polyurethanes, polyesters, adhesives, lubricants, paints, coatings etc. This study reports formation of fatty acid methyl esters of linseed oil by transesterification reaction followed by an advanced catalytic dimerization of linseed oil methyl esters using acid activated bentonite clay as catalyst. The synthesis of product is confirmed and detailed qualitative analysis of dimers is done by Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR).

Keywords: *Dimer, Transesterification, Clay Catalysis, Methyl Ester, Polyamide, Polyurethane, oleochemicals.*

Date of Submission: 25-09-2021 Date of acceptance: 10-10-2021

I. INTRODUCTION

The unsaturated fatty acids can be dimerized by mainly two methods i.e. thermal dimerization at high temperature and dimerization by using suitable catalysts. Poly unsaturated fatty acids can readily be dimerized by heating at high temperature whereas monounsaturated acids require some catalyst along with the heat treatment. The structure of dimers and their properties depends on the raw material as well as catalysts and the process of reaction. The process of dimerization of the fatty acids can be performed by dimerization of the oil/fatty acids as well as dimerization of the methyl esters of oil/fatty acids. The latter is preferred to the former one as it provides better yield.

The catalytic process can also be categorized in two groups which include homogeneous and heterogeneous catalysis. The homogeneous catalytic dimerization is traditional process where some sort of alkaline metal salt or lewis acid is used as a catalyst. Heterogeneous catalysts are more eco friendly, readily available, easy to separate from the products, reusable, and commercially more attractive as compared to the former one [8].

Catalysts used in heterogeneous catalytic processes are Montmorillonite (MMT) [2], Zirconia [7], Molecular sieves [3,5], Lewis acids [4] andIonic liquids [6].Due to the availability and desirable properties such as elevated cationic exchange capacity, high active surface area, and better aspect ratio, the montmorillonite clay is considered the most frequently used catalyst [2].

1.1. Materials and Method

1.1.1. Materials

Crude linseed oil was obtained from Anuradha oil mills, Fazalganj,Organic bentonite clay was purchased from Shri Sai Products Kanpur, Sodium Methoxide from Qualikems Fine Chemical Pvt. Ltd., Sodium Sulfite Anhydrous from Rankem RFCL Ltd. and Methanol from RankemAvantor Performance Materials India Ltd. All the reagents used in the synthesis and characterization procedures were of analytical grade.

1.1.2 Method of Synthesis

1.1.2.1. Instrumentation

Transesterification reaction was conducted in a three necked flat bottom borosil flask (1000 mL capacity) attached with a cold water condenser and temperature measuring pocket while heating and stirring was done using a magnetic stirrer hot plate. Dimerization reaction was done in a high pressure Parr Autoclave (1500

ml capacity), fitted with a mechanical stirrer, pressure gauge, thermocouple and pressure removing valves. Fourier-transform Infrared Spectroscopy (FT-IR) was conducted using a ABB laboratory spectrometer MB3000. Nuclear magnetic resonance (NMR) spectra was done using a JEOL ECX-300 spectrometer at room temperature with deuterated chloroform (CDCl3) as a solvent in the experiment.

1.1.2.2. Synthesis of fatty acid methyl esters

Linseed oil (500g), methanol (450 ml) & sodium methoxide (7.5g, 1.5 wt%) were heated at 65°C for 150-180 minutes. After of the reaction, remaining methanol was evaporated and recovered under vacuum with the help of a rotary vacuum evaporator. The product was filtered to remove the catalyst and passed from sodium sulfate anhydrous. The synthesized methyl ester of linseed oil was analyzed by Fourier-transform Infrared Spectroscopy.

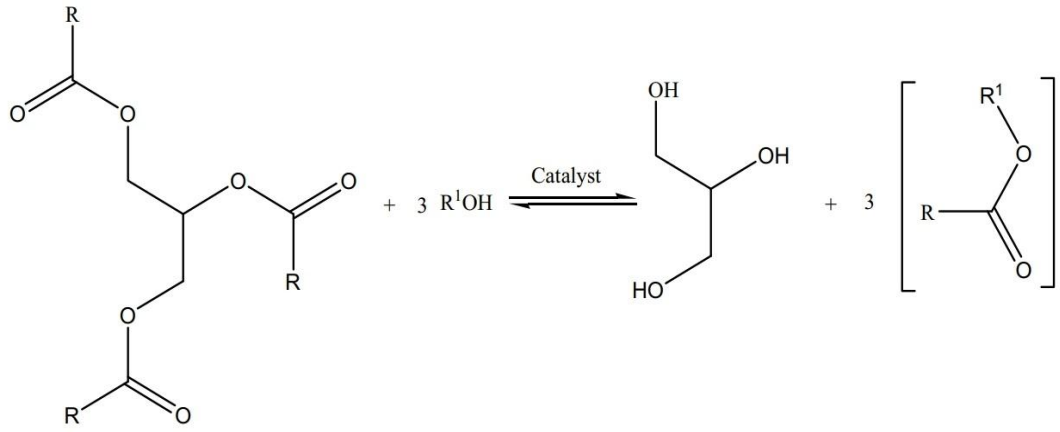

Figure 1: Transesterification reaction of triglyceride [1]

1.1.2.3. Synthesis of fatty acid dimers

Linseed oil methyl ester (500), obtained from transesterification, bentonite clay (75g, 15 wt %), distilled water (25g, 5 wt%) were taken in the high pressure Parr autoclave and heated up to 100°C then pressure released to isolate air from the reactor. The suspension was agitated (60 pulsations per minute) and heated up to 280°C. The temperature in the reactor was measured with a thermocouple, controlled within a 5°c deviation from the desired temperature and recorded. After the completion of reaction, the product is cooled and filtered by a Whatman filter paper.

1.2. Results and Discussion

1.2.1. Physicochemical characteristics of linseed oil

For the determination of IV, AV, SV and PV was calculated using standard) of oil was determined using AOCS Cd 3d-63 and AOCS Cd 3-25 standard methods respectively. The peroxide value was determined. The physicochemical characteristics are given in table 6.

Table 1: Physicochemical characteristics of linseed oil

Properties	Mean value
Refractive index	1.4686
Iodine value	179
Saponification value	192
Acid value	1.1
Peroxide value	0.85

1.2.2. Fatty acid Composition of linseed oil

The fatty acid composition of linseed oil is depicted in Table 7 Gas Chromatography-Mass Spectroscopy (GC-MS) technique was used for the determination of fatty acid composition. GC-MS analysis of the samples was performed on Agilent 5975C & 7890A model equipped with a capillary column (HP-5MS crosslined 5% PHME Siloxane, 30m *0.25mm i.d., 0.25µm film thickness) and MS detector.

Table 2: Fatty acid Composition of linseed oil

Fatty acids	Content (%)
Palmitic acid	7
Stearic acid	5
Oleic acid	17
Linoleic acid	18
Linolenic acid	51

1.2.3. FT-IR analysis

The FT-IR of linseed oil methyl ester (LOME) and linseed oil dimer (LOD) were recorded using ABB laboratory spectrometer MB3000 instrument, equipped with DTGS detector and KBr beam splitter. The spectrum for all the analysis was averaged over 16 scans with 4cm^{-1} resolution. The FT-IR spectrum of LOME and LOD are shown in Figure 6 and Figure 7 respectively. The spectrum reveals:

LOME: 3009, 2924, 2854 (C-C), 1744(C=O), 1458 (C=C), 1365(C-H), 1242(C-O), 1173(C-O), 987(C-O-C)

LOD: 2924, 2854 (C-C), 1744(C=O), 1450 (Aromatic), 1358 (C-H), 1196 (C-C-C), 1018 (C-H) 879, 725 (C-O-C)

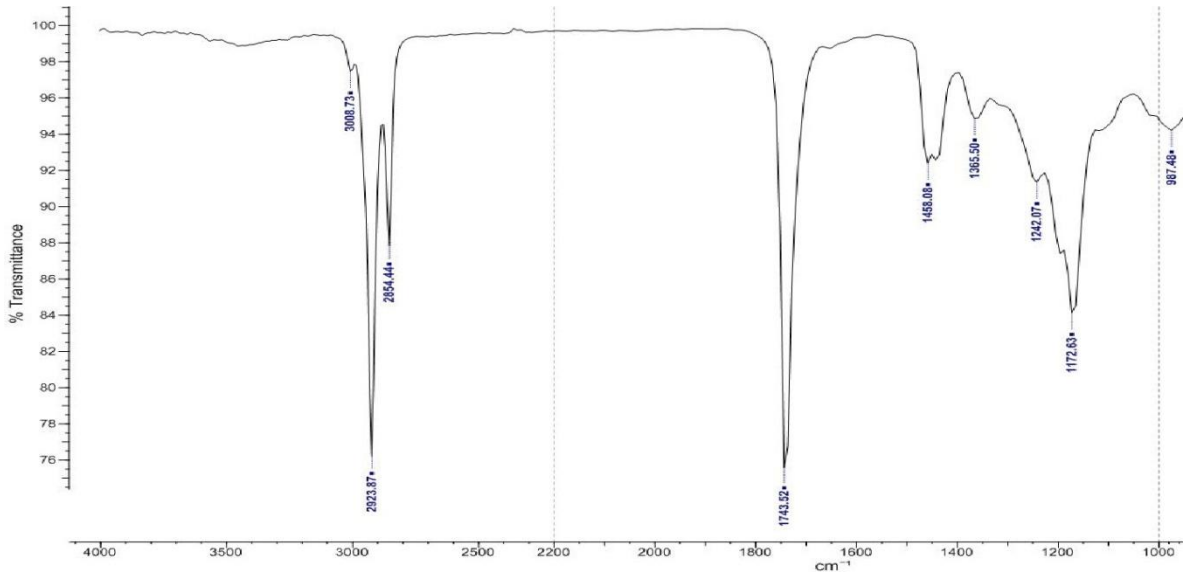

Figure 2: FTIR analysis of Linseed oil methyl ester

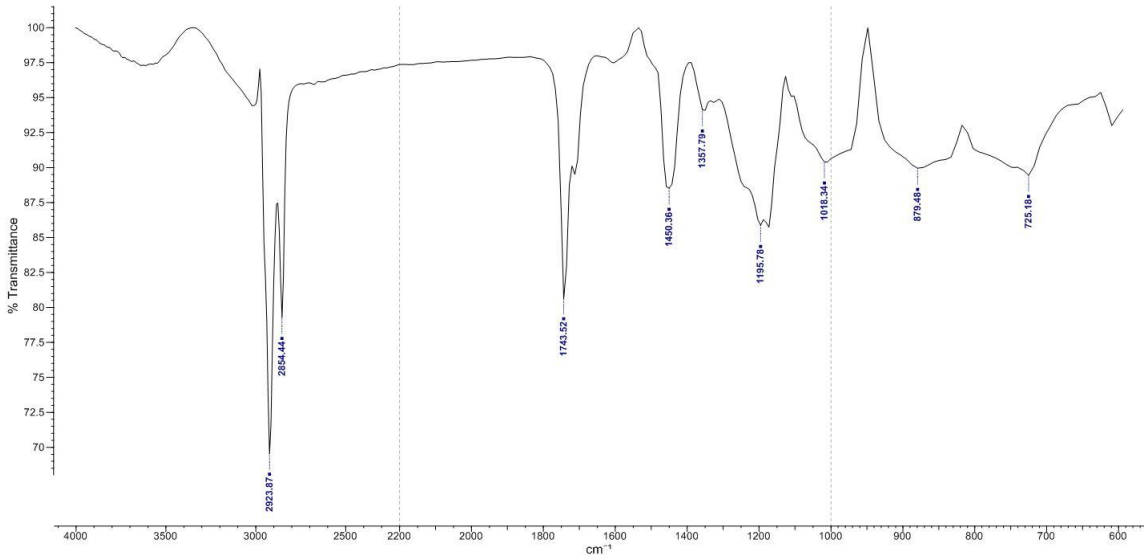

Figure 3: FTIR analysis of Linseed oil dimer

Rather slight differences could be observed between the spectra, since the methyl ester is chemically identical to its dimerized form up to an extent. The peaks observed in 2800-3200 cm^{-1} region attributes to the stretching of C=O, representing ester group, hence identical in both samples. The region which discriminates

between LOME and LOD lies in the range 1400-800 cm^{-1}, also called fingerprint region. The peak at 1458 cm^{-1} corresponds to the aromatic hydrocarbon present in LOD which confirms the synthesis of mono or bi-cyclic dimer. The peak at 1358 cm^{-1} can be attributed to the glycerol group. Another peak that differentiates LOME to LOD is 1018 cm^{-1} which corresponds to C-O-C group.

1.2.4. 1H NMR analysis

^1H NMR was recorded using JEOL ECX-300 spectrometer. The ^1H NMR spectrum in Figure-8 reveals the formation of linseed oil dimer. The spectrum represents. With the aid of NMR spectra information can be acquired about the number of different environments in which protons are located and the relative number of protons of each type. For our investigation this means that the presence of many branched fatty acids in the monomer, as found in NMR spectra as a decreased CH_2/CH_3-ratio. The disappearance of double bonds involves the disappearance of the -CH= proton signal. However, since the absorption coincides with the normal CH_2-absorption.

^1H NMR ($CDCl_3$): 3.6624(s, C-O-CH_3), 2.3191-2.2893 carboxylic acid (t, 1H, C=O), 1.6412-1.6137(t, trimer (-C-$(CH_2)_3$), 1.2758-1.2163 dimer (d, R-CH_2-R), 0.9094-0.8830(t, alkane(-CH3-CH2)).

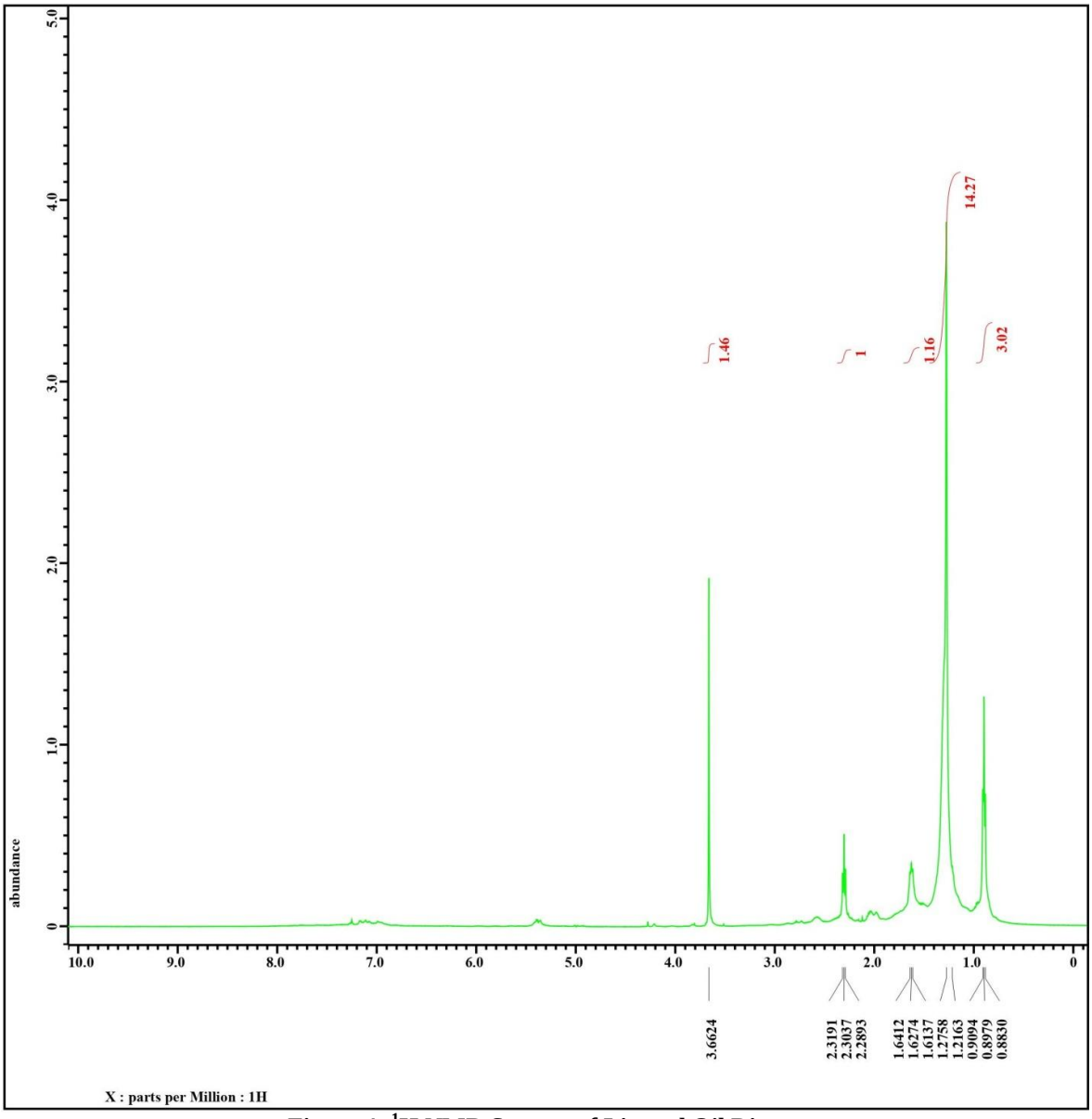

Figure 4: ^1H NMR Spectra of Linseed Oil Dimer

II. CONCLUSION

In this study, the dimers of linseed oil fatty acid were formed using crude linseed oil. Initially the crude oil was transesterified with ethanol using sodium methoxide as catalyst which was further dimerizedin an autoclave using montmorillonite clay as catalyst. The spectroscopic data i.e. FT-IR and 1H NMR indicate the formation of a cyclohaxene ring and elimination of a double bond which confirms that C=C converts into its corresponding cyclic dimer.

REFERENCES

[1]. E. F. Rico, I. Minondo, D. G. Cuervo. (2007) The effectiveness of PTFE nanoparticle powder as an E.P. additive to mineral base oils, ***Wear. 262***, 1399-406.
[2]. L. A. Utracki, M. Sepehr, E. Boccaleri. (2010) Clay-containing polymeric nanocomposites and their properties,***Polymers for Advanced Technologies*.26**, 8-15.
[3]. P. Tolvanen, P. Mäkiarvela, K. Eränen, J. Warna, B. Holmbom, T. Salmi, D. Y. Murzin. (2008) Thermal Polymerisation and Autoxidation of Technical Grade Linoleic Acid, ***Journal of the American Oil Chemists Society*.85**, 567-572.
[4]. R. M. Koster, M. Bogert, B. D. Leeuw, E. K. Poels, A. Bliek. (1998) Active sites in the clay catalyseddimerisation of oleic acid, ***Journal of Molecular Catalysis A: Chemical134***, 159-169.
[5]. S. J. Reaume, N. Ellis. (2011) Optimizing Reaction Conditions for the Isomerization of Fatty Acids and Fatty Acid Methyl Esters to Their Branch Chain Products, ***Journal of the American Oil Chemists Society*.88**, 661-671.
[6]. S. W. Liu, H. X. Zhou, S. T. Yu, Z. Q. Song. (2011) Dimerization of fatty acid methyl ester using Brönsted–Lewis acidic ionic liquid as catalyst, ***Chemical Engineering Journal.174***, 396-399.
[7]. S. Zhang, J. Zhou, Z. C. Zhang. (2009) Isomerization and Arylation of Oleic Acid on Anion Modified Zirconia Catalys, ***Catalysis Letter*.127**, 33-38.
[8]. X. Huang, Y. Yin, B. Zhang, G. Feng. (2018)Effects of the Structureand Composition of Montmorillonite on the Dimerization of Unsaturated Fatty Acids, ***Chemical Society*. 29**, 1516-152.