

Synthesis of Fatty Acid Dimers and Their Applications: An Overview

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ABSTRACT

Vegetable oil-based raw materials are the most important renewable feedstock for chemical industries in all the time. A tremendous shift has been observed from petrochemical-based and synthetic feedstock toward oleochemical-based products. That's why it has become necessary to cultivate more oil crops containing fatty acids with interesting and desired properties for their utilization in chemical industries, simultaneously increasing the agricultural biodiversity. Fatty acid dimers are a class of important intermediates that are frequently used in various industrial applications such as development of polyamides, polyurethanes, polyesters, adhesives, lubricants, paints, and coatings. This paper is focused on study of various methods used for the synthesis of fatty acid dimers, and the effect of process parameters, namely, temperature, pressure, catalyst concentration, and molecular distillation of dimerized products along with their industrial applications.

Keywords: Oleochemical, Dimers, Dimerization, Molecular Distillation, Biodiversity, Clay Catalysis

1. INTRODUCTION

Polymerization reactions of fatty oils have been known for a long time. In the middle ages, viscous products for paints were prepared by heating certain oils in contact with air. Thermal polymerization of linseed oil in its present form was first carried out in 1830 [1]. During the 1st world war, a high-quality lubricant was produced by exposing the fatty acids into a high voltage of about 5000–10,000 V in an inert atmosphere which was expected to occur because of formation of the dimers containing a cyclobutane ring. The thermal and catalytic dimerization started since early of 1929 [2]. In 1940, Bradley *et al.* gave the reaction mechanism of the formation of dimers using conjugated and non-conjugated fatty acid methyl esters [3].

Fatty acid dimer is an important raw material for chemical industries with excellent physicochemical properties. These materials are widely used for the development of polyamide resins [4,5], lubricants [6,7], adhesives [8], corrosion inhibitor [9], inks [10,11], and other products. The unsaturated fatty acids can be dimerized by mainly two methods, that is, thermal dimerization at high temperature and dimerization using suitable catalysts. The catalytic dimerization has the advantages of better selectivity and comparatively moderate reaction conditions [12]. The catalytic process for the synthesis of fatty acid dimers has also two groups which include homogeneous catalysis 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 [13].

Catalysts used in heterogeneous catalytic processes are montmorillonite (MMT) [14], Zirconia [15], Molecular sieves [16,17], Lewis acids [18], and Ionic liquids [19]. The most commonly used clay mineral is montmorillonite clay because of its plenty availability and valuable properties such as high cationic exchange capacity, high active surface area, and large aspect ratio [14]. The major components, present in montmorillonite, are Si and Al ions, and

its general chemical formula is $(Al^{2-x}Mg_x)Si_4O_{10}(OH)_2 \cdot (M \cdot nH_2O)$ (where $M = Na^+, Ca^{2+}, Mg^{2+}$, etc.). It is a typical 2:1 structure with three sheets (octahedral/tetrahedral/octahedral). Montmorillonite surfaces are negatively charged due to the tetrahedral and octahedral substitution of Mg^{+2} or Fe^{+2} ions by Al^{+3} ions. The negative charge of montmorillonite surfaces is balanced by the cations (Li^{+1} , Na^+ , K^+ , Ca^{+2} , and Mg^{+2}) coordinated between montmorillonite layers enclosed by the water molecules [20]. The surface of the montmorillonite clay is hydrophilic in nature due to the hydrated state of the interlayer cations and Si-OH groups at the edges. The interlayer cations are transferable with organic cations such as primary, secondary, and quaternary ammonium compounds and they are also transferable with each other [21,22]. The affinity of cation transfer is an important property of the montmorillonite clay minerals, which denotes the degree to which hydrophilicity of montmorillonite clay can be converted into hydrophobicity or organophilicity, where the organic cations are exchanged with interlayer cations [23] which provide suitable reaction conditions for the dimerization reaction.

The recent researches on fatty acid dimers have been focused on improving the yield of dimer produced and reducing the byproducts. Zhang and Nunez explained the zeolite catalysis process using plant-based soybean oil fatty acid to reduce the use of non-renewable clay catalyst [24]. Abu Hassan and Armylisas, 2019, elaborated properties of dimer fatty acid esters as biolubricant produced by catalyst- and solvent-free esterification [25]. Colja and Laane studied the bio-

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ISSN NO: 2320-0898 (p); 2320-0928 (e)

DOI: 10.22607/IJACS.2022.1001009

Received: 26th July 2021;

Revised: 12th October 2021;

Accepted: 12th January 2022

dimerization of unsaturated fatty acids using lipoxygenase enzyme, extracted from soybean pellets [26].

A report, published by Market Watch group on August 31, 2020, says that the “dimer acid market is valued at 1525.3 million USD in 2020 and expected to reach 2163.1 million USD by the end of 2026, growing at a CAGR of 5.1% during 2021–2026 in the global market especially in North America, Europe and Asia-Pacific, South America, Middle East, and Africa [27].

2. SYNTHESIS OF FATTY ACID DIMERS

Polyunsaturated 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.

2.1. Preparation of Fatty Acid Methyl Esters: Transesterification

Synthesis of fatty acid alkyl esters by reacting fatty acid or oil with alcohol is called transesterification. The reaction can be catalyzed by both homogeneous and heterogeneous catalysts. Sodium methoxide is one of the most common catalysts used for industrial production of fatty acid methyl esters but in case of high FFA content, sodium methoxide catalyst is replaced with acid catalysts to reduce the possibility of soap formation. But again acid catalysts have the drawback of slower reaction rate as compared to base catalyst. Moreover, exclusive acid-resistant reactors should be used because of the corrosive nature of acid catalysts. In general, short-chain alcohols such as methanol/ethanol and low-quality feed stocks, including non-edible vegetable oils, animal fats, waste cooking oil, and grease, having a significant amount of unsaturation, are preferred as raw materials for the synthesis of dimers. Therefore, the FFA present in the oil should be transformed into esters using an acid catalyst to convert a low-quality feedstock into their corresponding fatty acid methyl esters. The triglycerides in the second step are transesterified with methanol, catalyzed by a base to obtain the methyl esters [28]. The reaction is depicted in Figure 1.

2.2. Thermal Dimerization

Thermal dimerization indicates dimerization of fatty acids exclusive of a catalyst simply by maintaining the reaction temperature to about 300°C in the absence of oxygen. Thermal dimerization occurs in significant amounts only with polyunsaturated fatty acids. For thermal dimerization, methyl esters of polyunsaturated fatty acids and glycerides are typically favored as raw materials, since saturated fatty acids readily give decarboxylation and anhydride formation leading to a lesser yield and an inferior color [30].

Scheiher suggested that the isomerization of non-conjugated to conjugated esters is must for their dimerization [31]. Thereafter,

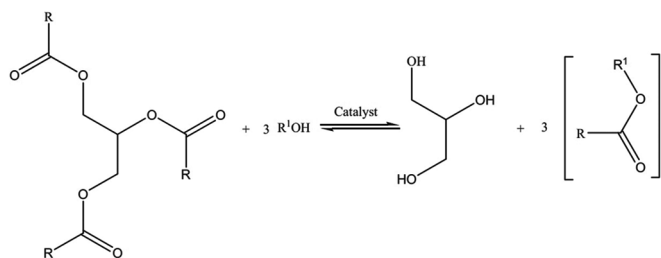


Figure 1: Transesterification reaction of triglyceride [29].

Kappelmeier brought forward that polymerization of drying oils, that is, the glycerol esters of polyunsaturated fatty acids can be elaborated by Diels–Alder reaction as a condensation of two conjugated fatty acids. In this way, the rapid polymerization of tung oil, which consists mainly of elaeostearic esters, could be explained [32], whereas Bradley and Johnston asserted that the non-conjugated and conjugated esters would yield identical dimers. For methyl linoleate, this would lead to the formation of monocyclic dimers or to isomers of it. For the dimerization of methyl linolenate containing three ethylenic bonds, they postulated that the above reaction is followed by an additional intramolecular ring closure, leading to a bicyclic dimer or to isomers of it as depicted in Figure 2 [33].

2.2.1. Mechanism for the formation of methyl linoleate dimer

Formation of conjugated linoleate is the second order with respect to methyl linoleate, is inconsistent with the conjugation hypothesis which can be explained by a bimolecular hydrogen transfer free radical mechanism, where the methyl linoleate acts both as hydrogen donor and as hydrogen acceptor (Figure 3) [1].

2.3. Dimerization by Atomic Hydrogen

The reaction of atomic hydrogen with fatty acids causes hydrogenation as well as polymerization. The atomic hydrogen can be produced by gas discharge in a hydrogen atmosphere at low pressure, thermal dissociation, or photochemical fission of H₂ molecules. The formation of dimers and polymers by this process can be explained by free radical addition reactions. When a free radical is formed, it can be hydrogenated by hydrogen atom or can form dimers by joining two radicals. Atomic hydrogen can dimerize saturated fatty acids also but the process is relatively slow with lower yield. The dimers formed by atomic hydrogen are not cyclic [34].

2.4. Dimerization by Electric Discharge

When fatty acids or oils are exposed to a high-voltage electric discharge, in a hydrogen or inert atmosphere and low pressure, they form a high viscous fluid. This process is widely adopted in preparation of high-

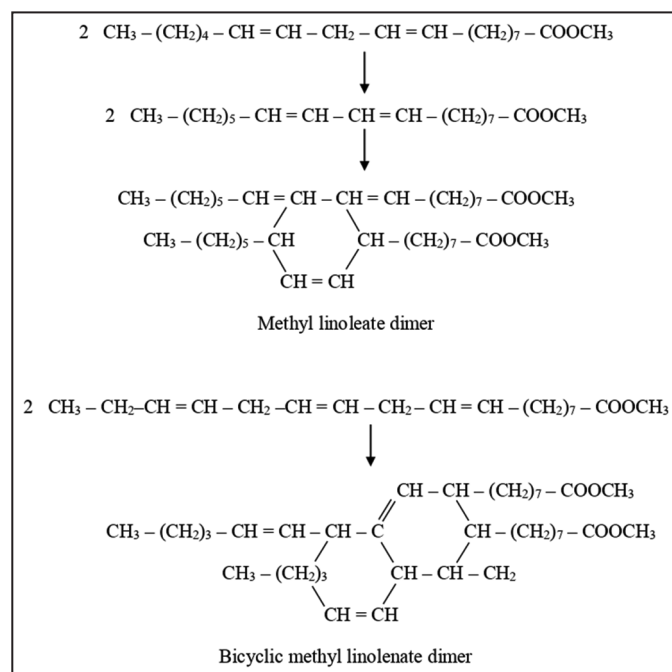


Figure 2: Chemical reactions for the synthesis of mono- and bi-cyclic methyl linoleate dimers using thermal dimerization process.

quality lubricants during the First World War on a commercial scale. The increase in viscosity occurs due to the polymerization. Unsaturated as well as saturated compounds can be polymerized by this process because of the formation of free radicals. These radicals cause an addition polymerization and form various dimers and polymers. Slansky and Goldenstien investigated the applicability of the electric discharge process for the preparation of polymerized oil in the paint industries according to them, the linseed oil polymerized by electric discharge is better in several aspects than thermally polymerized oil [35,36].

Boelhouwer *et al.* studied the polymerization of linseed oil by electric discharge process, also called as voltol process. The experiment was conducted in a rotating cylindrical Pyrex tube of 500 × 90 mm diameter voltol apparatus. In the reactor, approx. 600 ml of oil could be treated at once. The linseed oil was subjected into the voltol apparatus for electric discharge in hydrogen atmosphere at a pressure of 80 mm and 70°C temperature. The reaction of voltol process is exclusively intermolecular and the conversion of fatty acid monomers into polymers was noted about 60% [37].

2.5. Dimerization by Peroxides

Early in 1953, Clingman and Sutton dimerized methyl linoleate by heating it for 10 h with di-tertiary-butyl peroxide at 134°C in vacuum. They investigated that the di-*t*-butyl peroxide had been transformed into *tert*-butyl alcohol, the tertiary-butoxy radicals had not been converted into the linoleate and the degree of unsaturation was unchanged [38]. Harrison *et al.* also observed the synthesis of dimers of monounsaturated fatty acids using peroxide. They took 20 g (0.071 mol) of oleic acid (IV = 88.7, AV = 198.4) and heated with 0.75 g of di-tertiary butyl

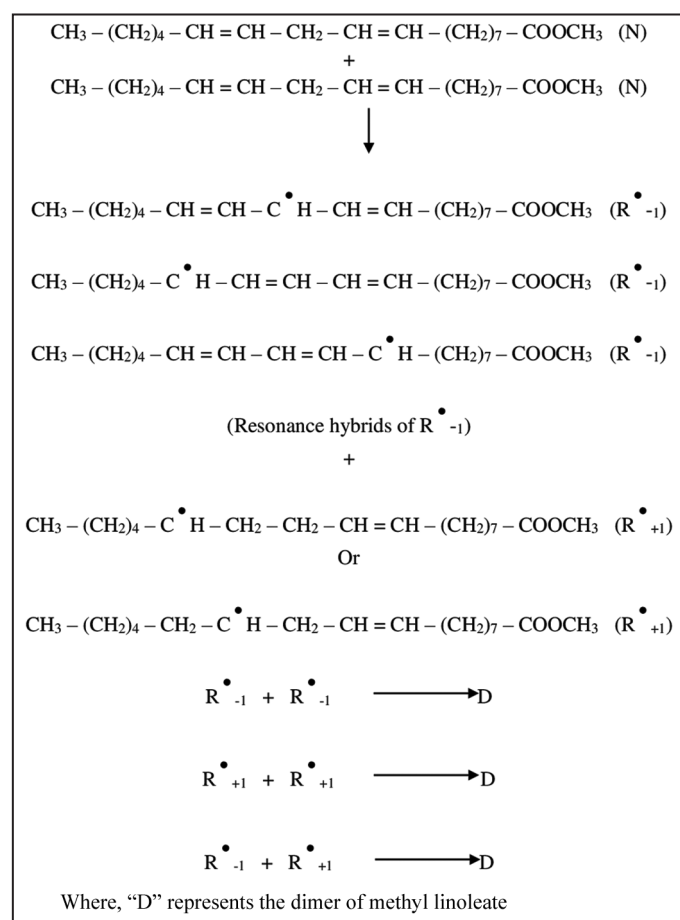


Figure 3: Bimolecular hydrogen transfer free radical mechanism for the synthesis of methyl linoleate dimer9-5.

peroxide without any agitation for 24 h in a closed vessel. The product was stripped under vacuum to remove the volatiles and monomers. The dimer, formed by this process, was of molecular weight – 548, IV – 91.7, AV – 186.5, and UV–vis. absorption spectrum – 231 μm.

2,2-bis-*t*-butylperoxy propane, 2,2-bis-*t*-butylperoxy butane, 2,2-bis-*t*-butylperoxy pentane, and 3,3-bis-*t*-butylperoxy pentane can also be used under the same conditions and are obtained similar results [39]. The peroxide is not a catalyst, since for each dimer molecule, one molecule peroxide is converted into the corresponding alcohol by abstraction of hydrogen from the molecule to be dimerized [40]. The possible structures of the dimer formed by Wheeler's experiment are given in Figure 4a-d:

2.6. Dimerization by Super Acids (Cationic Dimerization)

Boron trifluoride and its complexes are very important catalyst for various chemical reactions such as alkylation, condensation polymerization, and rearrangement polymerization reactions. Croston *et al.* investigated the effect of BF₃ and HF₃ acids on the polymerization of soybean oil. They polymerized soybean oil methyl esters which were prepared by methanolysis of commercial alkyl refined soybean oil using sodium hydroxide catalyst in a round-bottom flask with reflux condenser. 100–200 g of methyl ester was weighted into the flask and then BF₃ was bubbled into the flask with the help of a storage cylinder until the desired increase in weight was registered. The flask was heated up to 250°C and one atmospheric pressure and for the desired period of time. They found that the polymer formed was a dark brown viscous liquid which was due to the less yield of dimers and high yield of polymers. The refractive index of the synthesized product was 1.4810–1.4860 at 30°C and acid value was 25–50 [41].

Ionescu and Petrovic also investigated the cationic polymerization of fatty acids of biological oils using super acid catalyst. The super set catalyst may be defined as an acid having pK_a more than H₂SO₄ (pK_a from 3 to 25). It was suggested that the use of anhydrous very strong super acid, such as BF₃, HBF₃, CF₃SO₃H, and HSbF₆, as a catalyst provides a very high efficiency and superior yield under mild reaction conditions. The concentration of super acid preferably ranges between 0.1% and 0.5 wt% and the reaction is carried out at 60–110°C for about 20–120 min at normal pressure. The viscosity of the product ranges from 10 to 200 units which is approx. 10–40 times greater than thermal process. The cationic process provides such a viscous oil that it can be used for synthesizing solid oils, meltable on heating, which can be used for processing ads in rubber industries. This process is also suitable for synthesizing polyurethane, epoxy resins, hydroxyls, carbonyls, aminos, aldehydes, etc. The number of double bonds, used in polymerization, is low in this process thus provides the polymer oil of higher IV [42].

2.7. Photodimerization

Suzuki and Hashimoto studied the photodimerization of conjugated fatty acid methyl esters. Tung oil and dehydrated castor oil fatty acids were converted into their conjugated methyl ester by refluxing it with methanol for 1 h. These esters were separated and purified by solvent crystallization method using a mixture of ethyl alcohol and acetone at

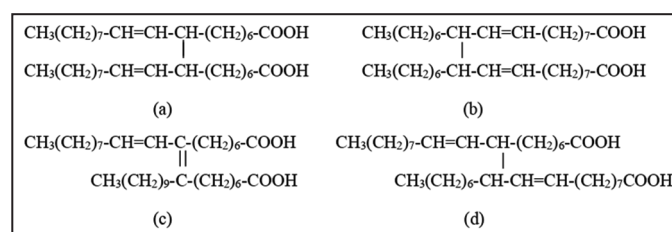


Figure 4: Structure of dimers formed by peroxides.

60°C and then again the hydrated by heating at 235°C under vacuum. The conjugated fatty acid ester was then dimerized by following three methods to obtain dimers;

- i. Photochemical reaction with high-pressure mercury lamp, in which 20 g of conjugated fatty ester was taken and dissolved in 300 ml of organic solvent with 2 g of methyl stearate as an internal reference. The photochemical reactions were performed under the nitrogen atmosphere at $25 \pm 2^\circ\text{C}$ by irradiation with high-pressure mercury lamp illumination (100 W) in a water cooled quartz well placed in the solution
- ii. Photochemical reaction with low-pressure mercury lamp, in which 5 g of conjugated ester were dissolved in 300 ml of solvent with 0.5 g of methyl stearate. The temperature of the photochemical reactions was $35 \pm 2^\circ\text{C}$ and the reaction was performed by irradiation with low-pressure mercury lamp illumination (30 W)
- iii. Photochemical reactions with monochromatic irradiation, which was carried out with monochromatic irradiation apparatus JASCO CRM-50 equipped with 2 KW xenon lamp. The monochromatic light was dispersed into the reactants by diffraction grating. The solutions of the esters prepared with a similar procedure to the reactions with the low-pressure mercury lamp were irradiated under the nitrogen atmosphere in quartz tubes of 5 mm internal diameter arranged in the tube holder, where the each tube was lighted with the different monochromatic light [43].

The concentration of the fatty acid methyl esters was noted 0.2 M for high-pressure mercury lamp and 0.05 M for low-pressure mercury lamp. The dimers were separated from the photochemical products by column chromatography further analyzed by thin-layer chromatography and gas-liquid chromatography following with mass spectra and IR spectra. The photoreactions were found different under the different irradiation of and depend on the wavelength of light source. Neither the rate of dimerization nor the yield can be compared between high-pressure lamp and low-pressure lamp.

2.8. Dimerization by Enzyme Catalysts

Colja and Laane studied the biodimerization of soya fatty acids using lipoxygenase enzyme which was obtained by the extraction of soya pallets with 0.1 molar sodium acetate/acetic acid buffer (pH 4.5). It is suggested that soybean lipoxygenase is capable of catalyzing the linoleic acid to form dimeric fatty acids by anaerobic process. The process was done by incubating lipoxygenase-1 enzyme with linoleic acid and [R,S-(2)-13-(hydroperoxy)-9-octadecenoic acid (13-ROOH) in the absence of oxygen.

The process was conducted in a bioreactor at ambient conditions. Formerly the linseed oil is digested with enzyme in the presence of oxygen which caused the formation 13-ROOH. Once enough 13-ROOH was formed, the supply of oxygen was limited or completely shut off and 13-ROOH was allowed to react with the remaining linoleic acid in the absence of oxygen to form, the desired dimers.

Theoretically, maximum overall yield for soya fatty acids is 58%. In that case, all available linoleic (51%) and linolenic acids (7%) would have been converted into dimers. Monounsaturated and saturated acids are not substrates for lipoxygenase. This implies that, for soya, 42% of the starting material is inert toward biodimerization. Attempts to increase the overall biodimerization yield above 9% by varying reaction temperature (20–60°C).

The mechanism of the enzymatic dimerization is completely different from the chemical process. The lipoxygenase-catalyzed reactions are quite selective and proceed through a radical mechanism, while the chemical mechanism involves carbenium ions, hydrogen transfer

reactions, and possibly Diels–Alder reactions. Clearly, this difference is reflected in the products generated by the two processes. Typically, the chemical process yields about 40% branched fatty acids, 5% lactones, 45% dimers, and 10% trimers and higher oligomers. At present, all these products have found a commercial outlet: The branched acids as a valuable ingredient in lubricants and cosmetics, and the dimers and trimers mainly in the polymer industry. Compared to the chemical process, the enzymatic process is less productive. Only 9% of the total feedstock is converted into a product of commercial interest. Further processing and/or biochemical treatment of the remaining fatty acids is required to make the “bio-route” economically attractive. However from economic aspect, well-established chemical process is more attractive than the bio-option [44].

2.9. Dimerization by Clay Catalyst

Johnston claimed dimerization of fatty acid esters using clay catalyst in 1944. He described the dimerization of polyunsaturated fatty acid esters at 280–300°C temperature in an inert atmosphere using activated bentonite clay as catalyst [45]. In 1947, Goebel discovered that for thermal dimerization, the presence of a small amount of water (1–5%) prevents both dehydration and decarboxylation of fatty acids [46–48]. In 1957, Goebel investigated the dimerization using both clay (10–25%) and water (1–5%). In their patent, they formulated the fatty acid dimers of mono and polyunsaturated fatty acid such as oleic acid. Dimerization reaction begins at 180°C and the maximum conversion occurs at the temperature between 200 and 260°C 5–11 atm pressures. The process requires 2–4 h and the mixture is continuously agitated to keep the catalyst in suspension during the reaction. They stated that all common clay can be used as catalyst such as kaolinite, bentonite, hectorite, and halloysite but montmorillonite is preferred. After that clay, catalyzed method became the most adaptable process for the production of dimeric fatty acids and many patents have been filed to this process, for example, US Patent No's. 3157681 [49], 3632822 [50], 2793219 [51], 2793220 [52], 2955121 [53], 4776983 [54], 5001260 [55], and 4895982 [56] describe the formation of C-36 dimers using clay catalysts.

Milks *et al.* elaborated the two-stage polymerization of monounsaturated fatty acids. In the first step, a mixture of tall oil and soybean oil fatty acids was polymerized at 180–260°C using 4% activated clay and 0.5–5% water. The polymerized product was filtered and distilled under vacuum and the residue was again polymerized at same reaction conditions in the second step. The overall yield of the reaction was calculated 70% of which 50% portion was of dimers [57].

Miller investigated the dimerization of unsaturated fatty acid using clay catalyst which was stabilized by the acetic acid anhydride and a lithium compounds. Three catalysts were activated and synthesized using acetic acid anhydride and lithium compounds and used them as catalysts for the dimerization of unsaturated fatty acids. The first catalyst was synthesized by refluxing the 400 g of natural clay (having montmorillonite in major quantity, moisture = 11.4%, and pH = 8.3) with 500 ml of acetic acid anhydride with stirring for 3 days in a bottle. The acid activated product was filtered using Buchner filter and residue was washed with benzene several times and placed in a desiccator having NaOH pallets for several days until the moisture became 0.9% (measured by Karl Fischer method). The second catalyst was synthesized by the same method and refluxed with 1000 ml of acetic acid anhydride and desiccated till the moisture became 3.05%. Moreover, the third catalyst was prepared by refluxing 100 g of clay and 250 g of acetic acid anhydride for 24 h then cooled to 70°C, filtered with the help of Bucher funnel, and again reflected with 1000 ml of toluene at 70°C till the moisture became 0.1%.

These catalysts were heated with tall oil in an autoclave using lithium compounds such as (lithium carbonate, lithium acetate, lithium caproate, lithium propionate, lithium fluoride, lithium chloride, lithium bromide, and lithium iodide) under vacuum. N₂ was flashed into the system twice to create inner environment. After reaching at desired temperature, that is, 250–300°C, the temperature was maintained for the desired length of time and the final product was cooled, washed with a mixture of HCL + H₂O 2:1 and filtered to remove the catalysts. In general, the lithium compound was taken about 0.25 to 3 meq. per gram of the clay catalyst [58].

3. FRACTIONATION OF POLYMERIZED FATTY ACIDS

The reaction product obtained from the autoclave consists of monomers, dimers, trimers, polymers, and some unrelated products as well, which has to be separate to obtain the desired dimeric compound. The most common and industrial technique, applied for the fractionation of dimers from polymerized product, is molecular distillation. Besides it, there are some other methods such as solvent extraction using supercritical fluid as solvent and some analytical methods are also there for laboratory scale extraction.

3.1. Molecular Distillation

Molecular distillation is a short path vacuum distillation which is operated at very low vacuum pressure (0.01 torr or below) using a molecular still. The apparatus for the molecular distillation of the dimeric fatty acids is depicted in Figure 5;

The air, present apparatus, is evacuated by means of a rotary oil pump and an oil vapor-jet pump. The pressure is kept less than 0.01 torr which is measured by a manometer, as shown in Figure 2. The polymerized product, which has to be distilled, is subjected through dosing valve,

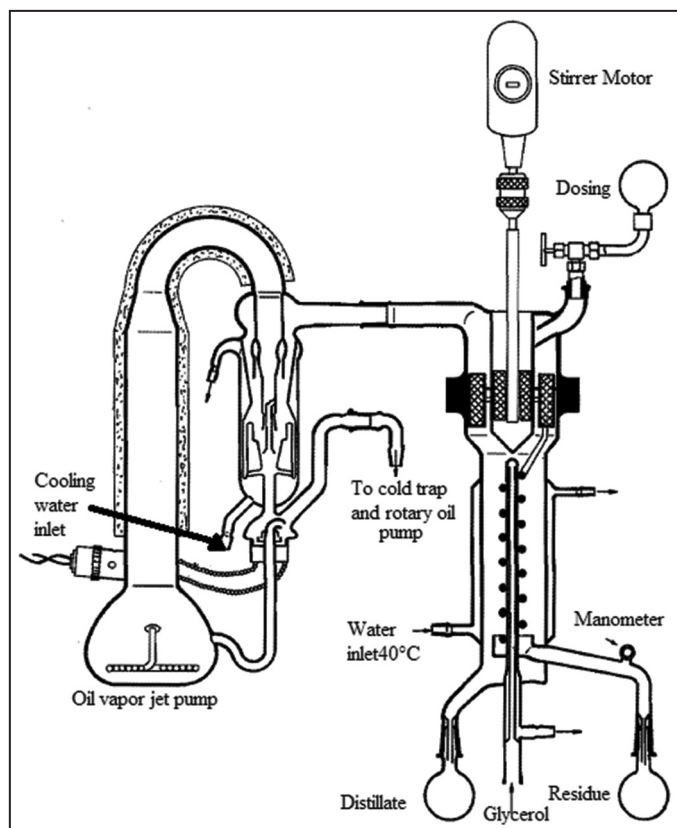


Figure 5: Apparatus for the molecular distillation of the dimeric fatty acids

falls on the top of the glass tube drop wise (approx. 15 drops/min). The tube is heated by the circulating hot oil. The slowly rotating coil causes the film formation and separates on the tube entirely. The monomer evaporates, condenses on the cooled surface (40°C), and is collected in a flask. The residue is moved downward by the helix and is also collected. The dimerization yield can be represented by:

$$\frac{\text{Residue}}{\text{Residue} + \text{Distillate}} \times 100 \text{ (in wt\%)}$$

3.2. Fractionation by Supercritical Fluids

Frihart and Lawrenceville invented the separation of the trimers, dimers, and monomers from polymerized product using supercritical fluids as solvent. The supercritical fluid was selected based on their solubility to the components of polymerized fatty acids, for example, hydrocarbon gases such as methane, ethane, propane, butane, and ethylene and carbon dioxide at their supercritical conditions accordingly. Hydrocarbon gases are preferred to separate dimers and trimers, whereas carbon dioxide shows better solubility with monomers. Supercritical solvents were brought into contact with polymerized product under supercritical conditions and the selected supercritical solvent dissolves one of the components present in the mixture either monomer, dimer, or trimer. The pressure of the system ranges from 3000 to 5000 psi and temperature from 0 to 200°C. The extracted materials were carried out through an expansion valve. Finally, the extracted component is separated from supercritical fluid by reducing the pressure or increasing the temperature. In the given experiment, a mixture of polymerized fatty acid is fractionated, before fractionation, the qualitative analysis of the chemicals was done by gas chromatography. The following results are as given below:

- Monomers – 2.7%
- Dimers – 80.7%
- Trimers – 16.6%.

The first fluid taken by Frihart and Lawrenceville was liquid carbon dioxide at 60° centigrade temperature and 3200 psi pressure which extracted monomers, the second fluid was ethylene, under 200 PSI pressure and 70° centigrade temperature which extracted dimers, and the third fuel was supercritical profile in at 107° centigrade and 2000–5000 PSI pressures which extracted primers from the residue [59]. The extracts obtained from Frihart's experiment are shown in Table 1:

4. APPLICATIONS OF FATTY ACID DIMERS

Dimer acids are high-molecular-weight compounds yet liquid at 25°C. They have an excellent viscosity index with respect to temperature and rheological characteristics which are a consequence of their balancing and cyclic structure and the variety of isomers. Therefore, dimer acids become suitable for wide range of industrial applications.

4.1. Lubricants

The liquidity of long-chain fatty acid dimers provides suitability to use them as lubricants and coolants for high-speed metal rolling machineries. Dwyer and Jedenoff prepared fatty acid dimers and polymers using tallow oil sperm oil, Textilana, and palm oil in a variety of compositions and studied their rheological and cooling properties over high carbon steel at a rolling speed of 500 rpm under 6000 pound pressure. It was concluded that dimer-based lubricants were comparatively more suitable for use as a cooling lubricant on cold-working metals than petroleum-based lubricants [60].

Burg and Kleiman prepared meadowfoam dimer acids and esters using clay catalyzed reactions and demonstrated their uses as

Table 1: Compositional analysis of extracts using CO₂, C₂H₄, C₃H₈, and supercritical fluid solvents at different temperature and pressure

Gas used	Temp (°C)	Pressure (psi)	Amount extracted (g)	% analysis of the extract		
				Monomer	Dimer	Trimer
CO ₂	60	3200	0.09	29.2	70.8	-
CO ₂	70	3700–5500	0.35	-	98.6	3.4
CO ₂	70	6500	0.19	13.3	80.7	6
C ₂ H ₄	70	2000–5000	0.98	-	93.7	6.3
C ₂ H ₄	70	5500	2.4	-	90.2	9.8
C ₂ H ₄	77	5500	1.56	-	80.4	19.6
C ₂ H ₄	107	2000	0.5	-	24.2	75.8
C ₂ H ₄	107	5000	0.1	-	22.8	77.2

Source: US patent 4568495, approved on February 4, 1986

lubricants and gave a comparison between tall oil fatty acid dimers and meadowfoam dimer. Dibutyl dilinoleate dimers were prepared by meadowfoam fatty acids which showed better properties as high temperature lubricants [61]. Many other patents such as Japanese patent 58144311 [62] and 62153208 [63], US patent 2922763 [64] and 2930758 [65] suggest the use of dimer fatty acids as metal-working lubricants, gear oils, and compressor lubricants.

4.2. Polyurethanes

Polyurethane is the most varietal product produced by dimer fatty acid. Rajput *et al.* prepared two novel packs of polyurethane for wood finishing and coating from fatty acid dimers by condensation polymerization and observed their thermal behavior and investigated that oleic acid dimers can be utilized for synthesizing wood finishing polyurethanes [66]. Paraskar and Kulkarni synthesized green polyurethane coating using dimer fatty acid-based polyester, polyols, and isosteric acids which were further modified through structurally different di-isocyanates. Polyurethane coatings exhibit excellent performance due to their cross-link density and provide a remarkable glass transition temperature and better thermal degradation temperature [67].

4.3. Polyamide Resins

Dimer base polyamides have the characteristics of low crystallinity, softening properties, transition temperature rangers, and excellent adhesiveness [68] as well as hydrophobicity. These properties contrast with the other nylon-based polyamide alternatives [69]. The condensation reaction of tall oil fatty acid dimers with higher ethylene amines such as diethylenetriamine (DETA, H₂N–CH₂CH₂–NH–CH₂CH₂–NH₂) or triethylenetetramine (TETA, H₂N–CH₂CH₂–NH–CH₂CH₂–NH–CH₂CH₂–NH₂) yields lower molecular weight (1000–2000) dimer acid-based polyamides [70]. Fan *et al.* synthesized polyamide resins using soy fatty acid dimers (1,4-phenylene diamine) at 250°C and studied their physicochemical properties and concluded that they provide excellent flexibility and strength [71,72].

5. CONCLUSION

It is concluded that vegetable oils are immensely useful for the synthesis of dimeric fatty acids. The polyunsaturated fatty acids can be readily dimerized by thermal treatment without any catalyst. Chemical reaction of thermal dimerization follows the Diels–Alder mechanism. Polyunsaturated fatty acids can be readily dimerized by thermal treatment without any catalyst whereas monounsaturated fatty acids or fatty acid methyl esters require some special conditions,

such as catalysts, moisture, and catalyst amplifier, for gaining the better yields. Chemical reaction of thermal dimerization follows the Diels–Alder mechanism. Dimers can be synthesized by thermal process, atomic hydrogen, electric discharge, peroxides, super acids, photo catalysis, enzyme catalysis, and clay catalysis methods. Clay catalyst method has an advantage of being economically efficient as compared to other methods. The dimerized product consists of some undesirable impurities, namely, trimers, polymers, and unreacted products which have to be removed. Molecular distillation and supercritical extraction techniques have been widely used for the removal of these impurities.

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