



## Applied Studies on Application of Capric/Caprylic MCT Oils in Food Industries

Rabie S. Farag<sup>1</sup>, Hanafy A. Hashem<sup>2</sup>, Abdel-AI Rahman Naser<sup>3</sup>  
and Montaser. A. Mohamed<sup>4\*</sup>

<sup>1</sup>Department of Inorganic & Analytical Chemistry, Faculty of Science, Al-Azhar University, Egypt.

<sup>2</sup>Department of Food Science & Technology, Faculty of Agriculture, Al-Azhar University, Egypt.

<sup>3</sup>Department of Organic chemistry (Oils & Fats), Faculty of Science, Al-Azhar University, Egypt.

<sup>4</sup>Innovations – R&D Center, Savola Foods Company, Cairo, Egypt.

### Authors' contributions

*This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.*

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### ABSTRACT

Non healthy oils & fats consumption in foods is the major reason of obesity in human beings. Common cooking oils & fats are composed of medium and long chain triglycerides. Each triglyceride consist of fatty acids called medium and long chain fatty acids abbreviated as (MCFAs & LCFAs). The ratio of LCFAs is mostly higher than the MCFAs in common cooking oils to be suitable for heat stress applications like cooking and frying. On the other side there is natural dietary fats are rich in Medium-chain fatty acids (MCFAs) like coconut oil and dairy fats. Also there are synthetic medium-chain triglyceride (MCT) oils which are synthesized by a processes called fractionation that extracts the MCFAs as caprylic and capric acid from the other fatty acids in the coconut or palm kernel oil.

The MCFAs, shows substantial metabolic advantage compared to LCFAs. MCFAs are a preferred source of energy (b-oxidation). The last 20 years studies confirmed the potential of MCFAs to reduce body weight and may reduce fasting lipid levels more than oils rich in LCFAs. The same is true for glucose levels.

In this study, the authors did chemical and instrumental studies on dietary structured MLCT and non-structured MCT/LCT cooking oils which were used for producing for weight reduction and

\*Corresponding author: Email: [montaser20007@gmail.com](mailto:montaser20007@gmail.com);

obesity control purpose Capric /caprylic MCT oil was used as a source of MCFAs for producing of novel. Different sources of long-chain triglycerides (LCFAs) have been used including sunflower oil (SFO), Canola oil(CNO), high oleic sunflower oil (HOSFO), palm oil (PO) and double fractionated palm olein (DFOLEin).

The following techniques have been used for preparation of structured and non structured cooking oils in this study :

1-Physical blending.

2 - Chemical interesterification in a multipurpose batch reactor.

2- Enzymatic interesterification using immobilized Lipase enzyme in pilot scale packed bed reactor (PBR).

Different analytical and instrumental techniques were used in this study including Gas chromatography (GC), high-performance liquid chromatography (HPLC), Differential scanning calorimeter (DSC), Rancimate, and smoke point tester.

The study shown that the non-structured MCT/LCT oils gave reasonable heat stability, higher smoke points compared the structured MLCT oil which make it more suitable for cooking and frying applications.

The chemical and enzymatic interesterification (CIE & EIE) technique yield a real structured MLCT oil which is more effective in caloric reduction and obesity control purpose during long term consumption in dietary foods, however, due to its much lower smoke point compared to its relative LCFAs oil so it will be suitable only for cold applications like salad dressing and other culinary applications. But not suitable for heat stress applications like deep or shallow frying.

*Keywords: MCT oil; structured MLCT oil; MCFAs-LCFAs; dietary fats; low calories fats; obesity; interesterification; cooking; frying.*

## 1. INTRODUCTION

### 1.1 Medium Chain Fatty Acids (MCFAs)

Medium-chain fatty acids (MCFA) are composed of 6-10 carbon atoms and are found principally in tropical oil like coconut oils ,palm kernel oil, which contains about 50 to 60 percent MCFAs in its composition .Also there are synthetic medium chain triglyceride oil know as MCT oils which are composed of MCFAs .

(Marten et al. 2006) [1] in their review on Medium-chain triglycerides concluded that MCFAs has a potential uses to control body weight and reduce body fat if is consumed for long time. The root cause of this dietary effect of MCFAs compared with long-chain fatty acids (LCFAs) is that MCFAs shows a different metabolic pathway which leads to its non-accumulation in adipose tissues.

### 1.2 Medium Chain Triglycerides (MCTs)

-Medium-chain triglycerides (MCTs) are fatty acid esters of glycerol .These fatty acids having 6–12 carbons. MCTs are composed of several medium-chain fatty acids MCFA like C 6, C8, C10. MCT oil is known and traded in the edible oil market as a highly concentrated as Capric / caprylic MCT oil which is synthetic oil

manufactured by fractions of some oil like coconut oil. It's man-made via a process called fractionation. This involves extracting and isolating the MCTs from coconut or palm kernel oil.

MCT oils generally contain either 100% caprylic acid (C8), 100% capric acid (C10), or a combination of the two. Caproic acid (C6) is not normally included due to its unpleasant taste and smell. Meanwhile, lauric acid (C12) is often missing or present in only small amounts.

MCT oils are know to be used by medical consultants and food nutrition specialist for malnutrition patients who has a malabsorption syndromes.

According to Marten et al. [1], MCTs reduce fat mass and glucose levels as well as on lipid metabolism were observed.

Hiroyuki Takeuchi et al. [2] stated that MCFA are absorbed directly into the portal vein, transported rapidly to the liver for oxidation, however , LCFAs are absorbed via the intestinal lymphatic ducts and transported by chylomicrons through the thoracic duct into the systemic circulation.

MCT has disadvantages that it is of low smoking point and foaming during frying.

So authors developed Medium- and long-chain triacylglycerol MLCT by enzymatic transesterification and solved these problems. (Hiroyuki Takeuchi et al. [2].

### 1.3 Medium -Long -Medium Triglycerides (MLM)

Medium-long-medium type of structured lipid (MLM- SLS) is a type of structured lipid containing medium-chain fatty acids (MCFAs, C6-C12) at sn-1,3 positions, and long-chain fatty acids (LCFAs, C14-C24) at the sn-2 position. This structured lipid is appropriate for the management of obesity, fat malabsorption, and other metabolic disorders. The MCFA at sn-1,3 positions are easier to hydrolyze by pancreatic lipase and directly transported to the liver for the  $\beta$ -oxidation process. This mechanism supports MCFA as a potential rapid energy source. Moreover, MCFAs include a small tendency to accumulate in adipose tissues. In contrast, long-chain fatty acids at sn-1,3 positions include a low absorption coefficient due to their higher melting temperature, compared to body temperature. The long-chain fatty acids also include possibilities to form soaps when reacting with calcium. Therefore, the strategy of producing MLM-SLs (e.g. LCFA at sn-2 position) is further preferable to increase the absorption of LCFA. Qabul Dinanta Utama<sup>1</sup> et al (2020) [3]. In their review on the synthesis of MLM lipids by enzymatic interesterification, they gave detailed description of biocatalysts, substrates, reactors, and synthesis methods, and discusses the use of MLM lipids in food products.

Table 1 shown the potential substrates for medium-long-medium (MLM) structured lipid synthesis.

### 1.4 Medium -Long-chain Triglycerides (MLCTs) structured lipids (SLs)

Structured lipids based on MLCT have a induced effect in body weight and body fat reduction by suppressing body fat accumulation and increasing energy expenditure. (Hiroyuki Takeuchi et al (2008) [2], MLCT structure are shown (Fig. 1) & (Fig. 2).

The daily intake of the MLCT diet could result in a reduction in body weight and accumulation of body fat, and it could reduce serum total cholesterol [4].

MLCT structured oils produced by enzymatic interesterifications have several applications in

different food Industries. However, at least 12% of MCFA must be present in the product to see the beneficial effects of this food in body fat accumulation and body weight reduction [5].

As for the enzymatic production of MLCT structured oils among the 3 enzymatic processes discussed, (inter- esterification, esterification, and acidolysis), esterification gave the highest yield of MLCT though it may be costly when produced on large scale due to the substrates used.

Structured concentrated MLCT oil was produced through esterification synthesis of capric, oleic acid, and glycerol via Lipozyme RM IM lipase, using the optimum parameter determined in our previous study [6,7,8].

The Palm-based MLCT oil with different antioxidants showed better thermal-resistant oxidative strength than refined, bleached, and deodorized (RBD) palm olein throughout the five consecutive days of frying. Sensory evaluation and rancidity assessment on fried chips showed no significant differences ( $P > 0.05$ ) between chips fried in RBD palm olein and palm based MLCT oil.

MLCT-based salad dressings treated with different antioxidants showed similar rheological behaviors as compared to soybean-based salad dressings. These findings indicated that MLCT-based oil blends can be used as healthy functional oil for daily consumption. TBHQ addition to both palm- and soybean-based MLCT blends increased oxidative stability. Combination of BHA and BHT showed no significant improvement ( $P > 0.05$ ) inability to protect blends from oxidation compared to natural antioxidants such as sage or rosemary extracts [9].

The blending of MLCT oil with either palm olein or soybean oil improved its smoke point values and oxidative stability.

Yuehong Zhang [10] concluded in his published paper that the intake of MLCT might help reduce body fat and levels of fasting blood TAG and LDL-C in hyper triacylglycerol emic and overweight and control of abnormal TAG metabolism and body fat accumulation in overweight human beings subjects. However, a longer-term and larger sample size clinical trial is needed to confirm the substantial effects of MLCT in overweight and hypertriacylglycerolemic individuals.

The optimization of Process Parameters for enzymatic Synthesis of Medium- and Long-Chain Triacylglycerols (MLCT). The maximum concentration of MLCT yield was 59.76% which was produced by using 10 wt% enzymes Lipozyme RM IM type load, reaction temperature of 70°C, a reaction time of 14 h, and a substrate mole ratio of 3.5:1. [11].

The refined MLCT oil characteristics study showed this oil is suitable to be used for cooking/frying purposes as a high-value-added product.

Structured Lipids (SLs) was also produced through Lipase-Catalyzed Acidolysis of Canola Oil using the sn-1,3 specific lipase Lipozyme TL IM vs. the non-specific lipase Novozym 435. Novozym 435 indicated a higher capability to incorporate more caprylic acid in the oil than did Lipozyme TL IM. SLs produced by Lipozyme TL IM and by Novozym 435 were different in terms of their TAG. compositions.

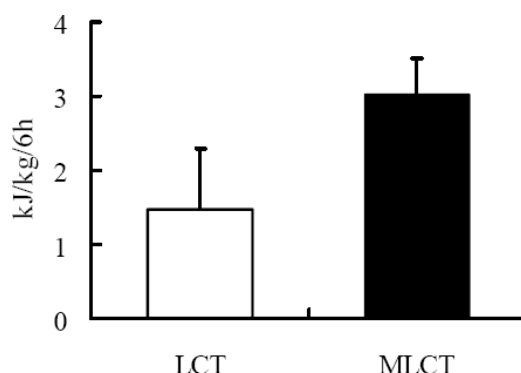
Application of the sn-1,3 specific Lipozyme TL IM lipase led to the production of more MLM-type TAGs and was more efficient in producing SLs of MLM structure than the non-specific Novozym 435 lipase. Although optimum enzyme loads for the acidolysis of canola oil as found in this study were 8% for Novozym 435 vs. 12% for Lipozyme TL IM. D. [12].

Structured lipids (SLs) containing medium-chain fatty acid (M) at position sn-1,3 and long-chain fatty acid (L) at the sn-2 position in a solvent-free system. (MLM), through lipase-catalyzed acidolysis of canola oil with caprylic acid to produce (Yingyoo Wnnq -2012) [13].

The results showed that Lipozyme RM IM resulted in the highest caprylic acid incorporation ability and the lowest acyl migration. The reaction parameters including substrate mole ratio, the enzyme load, reaction time, and temperature of Lipozyme RM IM were investigated. The incorporation of caprylic acid was higher when reactions were carried with 10% lipase of the total weight of substrates with a 1:4 mole ratio of (canola oil/caprylic acid). The optimal the time course was 15 h and the optimum temperature was 55 C. Lipozyme RM IM was suited to produce the high purity MLM-type of SL in canola oil and caprylic acid system.

Pilot-Scale Solvent-Free Packed Bed Reactor (PBR) was used for production of structured triacylglycerol via Enzymatic Interesterification of Medium-Chain Triacylglycerol and Soybean Oil using Lipozyme TL IM 1,3 selective enzyme [14].

Optimal conditions for this reaction process was determined as caprylic/capric TAG: SBO ratio of 45:55 w/w, reaction temperature of 75°C, and residence time of 16.0 min. Under the optimized reaction and refining conditions, a TAG mixture containing 80.07 wt % MLCT, 9.03 wt% MCT, and 10.89 wt % LCT was produced. The daily output of the pilot-scale PBR was 100 kg. The purified MLCT product had 82.74 wt% SFA at the sn-2 position, suggesting that it would serve as a suitably structured lipid for use in foods and medicines. The excellent performance of PBR, including continuity, stability, facility, and high efficiency, makes PBR a promising alternative industrial approach to the conventional production of MLCT.



**Fig. 1. Medium- and long-chain triacylglycerol (MLCT)- induced changes in body weight and body fat amount in hu- mans8). Eighty-two healthy subjects ate bread containing MLCT or long-chain triacylglycerol (LCT) for 12 weeks as breakfast under strict dietary control. The values are presented as the means ± SE. \*p<0.05 [3]**

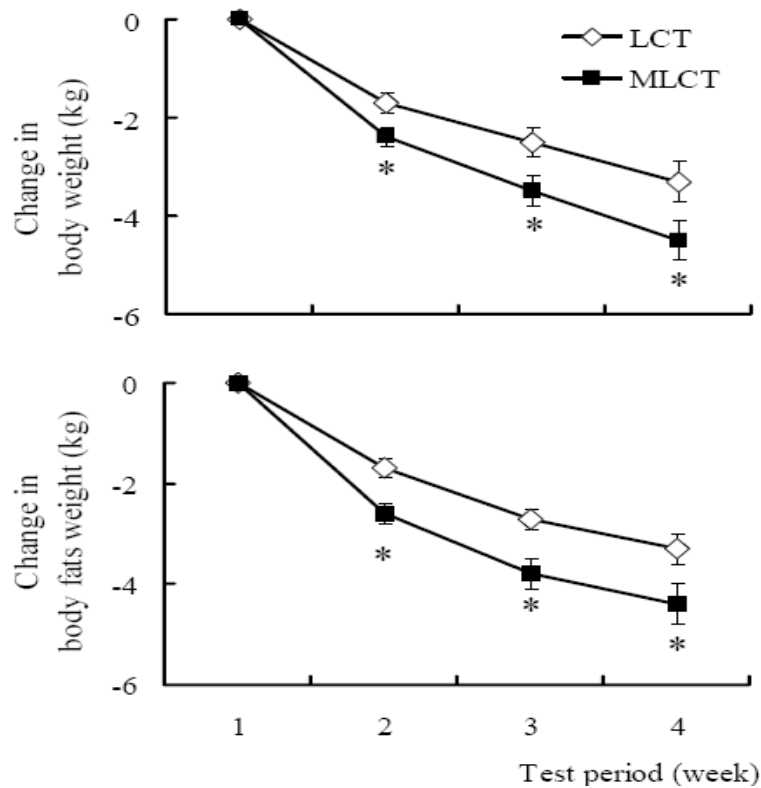


Fig. 2. Increase in energy expenditure after long-chain triacylglycerol (LCT) or medium- and long-chain triacylglycerol (MLCT) ingestion<sup>10</sup>. Fifteen healthy females ingested LCT or MLCT, and energy expenditure was measured for 6 hours. The values are presented as the means  $\pm$  SE. \*\* $p < 0.01$  [3]

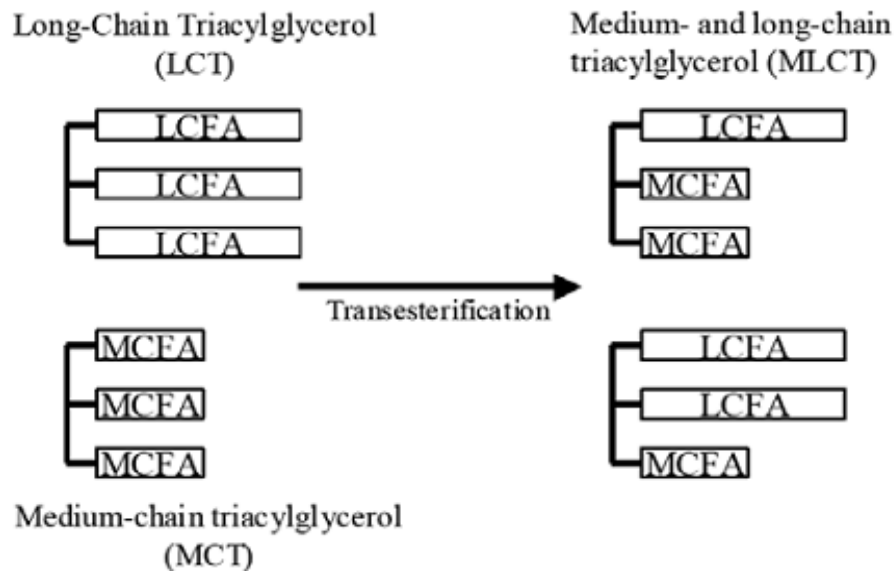


Fig. 3. Manufacture of medium- and long-chain triacylglycerol (MLCT) by transesterification. LCFA, long-chain fatty acid; MCFA, medium-chain fatty acid [3]

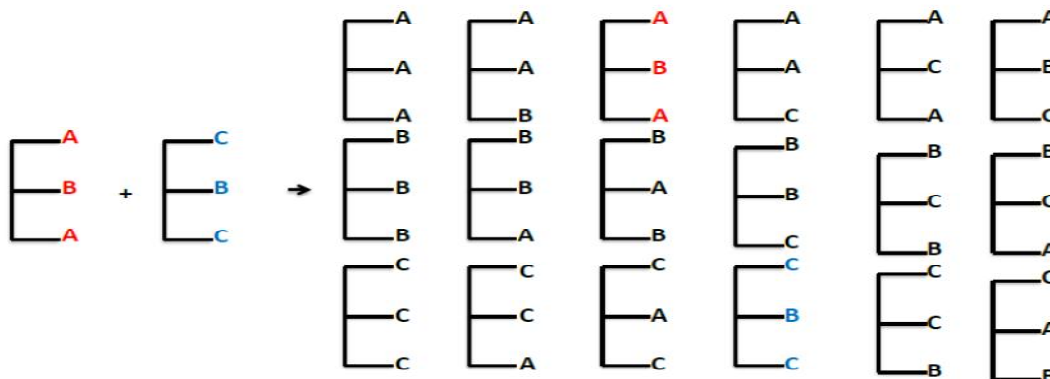


Fig. 4. Triacylglycerol mixture before and after chemical interesterification: (Alejandro G. Marangoni Saeed M. Ghazani- ILS-North America)

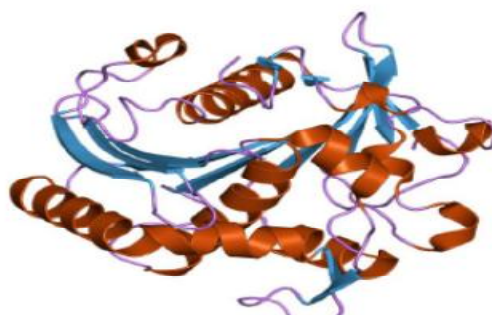
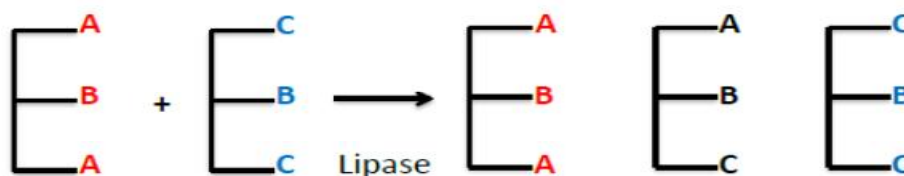


Fig. 5. Triacylglycerol mixtures before and after enzymatic interesterification (1,3-specific lipase) (Alejandro G. Marangoni Saeed M. Ghazani- ILS-North America)

### 1.5 Enzymatic Interesterification for Production of MLCT oil or Structured lipids (SLs)

Enzymatic interesterification methods that are used in the literatures for production of MLCT via the enzymatic process in 3 routes:

- (1) Interesterification
- (2) Acidolysis
- (3) Esterification

Intesterification is the reaction between esters or TAG molecules. Not much research has been reported on MLCT production via interesterification reaction.

For MLCT production through interesterification often involved coconut oil or palm kernel oil or saturated TAG such as tricaprylin that will provide the MCFA. LCFA part in MLCT is contributed by the vegetable oil such as soybean oil, rapeseed oil [15]; Lopez-Hernandez et al. [16]; Adhikari et al. 2011b) [17]. The progress of the interesterification reaction is measured by the changes in the TAG composition before and after the reaction (Fomuso and Akoh 1998 [15]; Lopez-Hernandez et al. 2005) [16].

For interesterification, substrate ratio is an important parameter that will affect the desirable yield. For example substrate mole ratio of trilinolein to tricaproin from 1: 1 to 1: 4, the mole

ratio of 1: 2 gave the highest yield of 50.7% di-caproyl linolein (ECN 33) and 23.6% mono-caproyldilinolein (ECN 45) (Fomuso and Akoh 1998) [15].

The first commercially available MLCT sold in the market by Nisshin Ollio Ltd. Group, Ltd also uses the interesterification process for its production. This MLCT oil was produced via an interesterification reaction involving coconut or palm kernel oil and edible vegetable oil, which are rapeseed, cottonseed, and soybean oil. This produced a randomly structured MLCT with TAG composition of LLL (49.5% to 52.7%) LLM or LML (37.3% to 39.6 3%) LMM or MLM (8.6% to 9.3 4%) and MMM (0.1% to 0.2%).

### 1.6 Chemical Interesterification (CIE) for Production of structured MLCT Oil

Upon CIE, extensive re-arrangement of fatty acids (FA) among triacylglycerols (TAG) was evident. Concentrations of several TAG were increased, some were decreased, and several new TAG was formed. The resulting changes in TAG profile were reflected in the solid fat content (SFC) of the blends. The SFC values of most chemically inter-esterified blends revealed that they were softer than their respective starting blends. H.M.D. Noor Lidaa, etal -2002 [18]. The sodium methoxide has been used by Yuandong Xu et al. [19] to catalyze the transesterification between soybean oil and glycerol trioxide to produce low-calorie oil. The optimal conditions were the substrate molar ratio of 3:1, reaction temperature of 120°C, a reaction time of 1.5 h, catalyst using an amount of 0.975%. Under such conditions, the product yield reached 73.14%. The calorific values of the soybean oil and the product were measured and the value for the latter was 32 450 J/g which was approximately 71% of the former. Yuandong Xu et al. [19].

## 2. MATERIALS AND METHODS

1- Lipozyme TL IM, a commercial immobilized 1, 3-specific lipase from *Thermomyces lanuginosa* sourced from Novozymes A/S (Bagsvaerd, Denmark). The specific activity of Lipozyme RM IM was 150 IU/g, having 0.35–0.45 g/mL bulk density, and 0.3–0.6 mm particle diameter.

2- Glycerin 99%-A.R. grade (ADWICK) – KOH (98%)-A.R. ( ADWICK) .-Phosphoric acid 85% (ADWICK).

3- Standards used for the determination of FAC is GLC-463 standard fatty acid methyl esters

(FAMEs) containing methyl esters C8–C20 saturated fatty acid was purchased from Nu-Chek Prep Inc. (Elysian, MN, USA).

4- Standard for Triacylglycerols composition (TAG%) analysis by GC were procured from Sigma- Aldrich Chemical Co. (St. Louis, MO, USA). For

5- 2 N methanolic KOH.(for methyl ester preparation).

6- N- Hexane or heptane (Analar grade).-Sigma-Aldrich. Co. (St. Louis, MO, USA). ( for methyl ester preparation).

7- alpha -beta -,gamma-,and delta tocopherol standards - Sigma- Aldrich Chemical Co. (St. Louis, MO, USA). for tocopherol composition determination by HPLC.

8- Organic Solvents for HPLC: Methanol, Dichloro methane, Hexane, Propane-2-ol (A.R, HPLC grade solvents)- Sigma-Aldrich. Co. (St. Louis, MO, USA).- HPLC mobile phase, Propane -2-ol in Hexane ( 1:99 V).

9- All other reagents used were of either analytical or chromatographic grade.

### 2.1 Oil's Sources and Sampling

1- Refined bleached winterized and deodorized Sunflower oil (RBDWSFO) sourced from EFKO-Trade LLC grain & oil export/import- .The fatty acid composition of SFO is shown in Table 2

2-Refined bleached deodorized High oleic sunflower oil ( RBD HOSFO)- sourced Lipidos Santiga .s.a Spain - Fatty acid composition of High oleic Sunflower oil is shown in Table 3.

3- Refined bleached deodorized Canola oil( RBD CNO), sourced from Riverland Oilseeds Pty. Ltd. The fatty acid composition of CNO is listed in Table 4.

4- Refined palm oil ( RBD PO) sourced from Wilmer SDN-Indonesia.- The fatty acid composition and solid fat content ( SFC) of RBD PO are shown in Table 5.

5- Refined super double fractionated olein ( RBD DF IV63-64) sourced from Wilmer SDN-Indonesia.- The fatty acid composition and solid fat content ( SFC) of RBD DF IV63-64 are shown in Table 6.

6- Refined bleached deodorized Caprylic/capric MCT oil ( RBD MCT oil) sourced from PT Musim Mas -Indonesia .The specifications and fatty acid composition of MCT oil are shown in Table 7.

The above oils have been sampled and refreshed in a Pilot deodorizer before usage in the Interesterification experiments:

Pilot deodorizer model used is Desmet -L800.

Deodorizer method for refreshing the specifications of pilot EIE prepared oil.

- 1- The amount of oil enter deodorizer =5-10 Kg per batch.
- 2-Maximum cooling temp = 75 C
- 3-Maximum sample quantity 130 gm
- 4- Heating rate = 2-2.2 C/min by thermal heat oil in the coil.
- 5- Thermal heat temperature: 300 C – Oil temperature in deodorizer :300 C.
- 6-Vacuum: 0.5-1 millibar.

### 3. INSTRUMENTS & APPARATUS

- 1- The determination of fatty acid composition (FAC %) and triacylglycerols (TAGs %)was carried out by gas chromatography type: Gas chromatograph (GC) with FID - Agilent7890B Series GC Custom under the following conditions:

Fatty acid composition by Gas Chromatography determined by capillary GC method, according to the AOCS Official Method Ce 1c-89, Ce 1f-96, Ce 1e-91.

**Preparation of fatty acid methyl ester** was done for oils prior to GC analysis by converting the triglycerides and fatty acids of oils to their corresponding methyl esters prior to the analysis by gas chromatography. The official AOCS Official Method Ce 2-66. Was followed in preparation.

**Analysis of the triacylglycerols composition (TAGs) of fats and oils** was determined by capillary GC method as per ISO /TS 17383 method.

- 2- **The determination of tocopherols was carried out by HPLC under the following parameters:** HPLC for tocopherol analysis.- Agilent HPLC 1260 -DAD detector.

Tocopherol analysis in oils by HPLC method:

Analysis of four tocopherol vitamers ( $\alpha$ ,  $\beta$ -,  $\gamma$ - and  $\delta$ -) that differ from each other by the number and position of methyl groups is done according to the standard AOCS Official Method Ce 8-89(revised 2017). Separation of tocopherols from most tocotrienols present in oil has also been obtained by using 0.5–1 % (v/v) of 2-propanol in hexane or heptane with a silica column.

**Table 1. The GC -capillary parameters followed**

|                    |                                     |
|--------------------|-------------------------------------|
| <b>Technique</b>   | GC-Capillary                        |
| <b>Column</b>      | Agilent CP-SIL 88 (Part No. CP7489) |
| <b>Temperature</b> | 100°C - 240°C, 4°C/min              |
| <b>Carrier gas</b> | Hydrogen, (17.7 psi)                |
| <b>Injector</b>    | Splitter, 14 ml/min, Temp.: 250°C   |
| <b>Detector</b>    | FID, Temp.: 270°C                   |
| <b>Sample Size</b> | 1.0 $\mu$ L                         |

**Table 2. The GC -capillary parameters followed**

|                    |   |
|--------------------|---|
| <b>Technique</b>   | GC-Capillary                                      |
| <b>Column</b>      | Agilent CP-TAP CB (Part No. CP7483)               |
| <b>Temperature</b> | 300°C - 310°C (1°C/min), 310°C - 355°C (15°C/min) |
| <b>Carrier gas</b> | Hydrogen, (15 psi)                                |
| <b>Injector</b>    | On Column Injector, Track Oven                    |
| <b>Detector</b>    | FID, Temp.: 370°C                                 |
| <b>Sample Size</b> | 0.2 $\mu$ L                                       |



### 3- The determination of thermodynamic Properties of Products:

A differential scanning calorimetry (DSC) system was used to monitor the melting and crystallization behavior of the products. DSC for crystallization and melting behaviors of fats METTLER - TOLEDO SWITZERLAND -STARE System DSC3.

The exotherm was obtained by holding the samples for 5 min at 80°C followed by cooling to -40°C at a rate of 5°C min<sup>-1</sup>. Endotherm was obtained by heating the samples to 80°C at 5°C min<sup>-1</sup>.

DSC operation parameters:

Technique DSC

Cooling Program 80°C: - 40°C (1°C/min)

Heating Program - 40°C: 80°C (1°C/min)

Sample Size 500 µg

- 4- **Determination of para anisidine value (p-A.V.) using UV-visible spectrophotometer** - Model: Agilent UV Carry 60(UV-Vis).
- 5- **Determination of Smoke point analyzer** for smoke point analysis -Semi-Automatic Cleveland Open Cup **Flashpoint Tester** - Model NCL 220- NORMALAB – FRANCE.
- 6- **Determination of oil stability determination by Rancimat method.** **Rancimat Model:** Metrohm 743 Apparatus (Metrohm, Switzerland).

The Rancimat induction period of oil was determined, where by 3 g oil was heated to 120°C under an air flow rate of 20 L/ h. According to the AOCS official method Cd 12b-92, edition 5.and Metrohm Rancimat instrument user manual.

- 7- **Pilot Enzymatic interesterification Packed bed column reactor (PPR): Model: Desmet pilot PBR reactor – LE2600):** Enzymatic interesterification Pilot plant description: The pilot contains 2 Enzyme reactor A & B with the flow of oil is four options are reactor are either reactor (A) only or Reactor (B) only or (A) to( B) or (B) to (A). (Desmet pilot EIE reactor - LE2600)
- 8- **Chemical interesterification CIE lab Apparatus components:**  
-Rotatory evaporator.

- Vacuum Reaction flat round bottom flask .
- Vacuum pump.

### Desmet Pilot deodorizer – Item L800.

Desmet Pilot oil deodorizer system – Item L800-

- 10- **Rotatory evaporator** for purifications of chemically interesterified (CIE)oil in lab CIE glass apparatus **Rotatory evaporator model used:** Phoenix Instruments GmbH  
-new Rotatory Evaporator RE-100D

## 4. EXPERIMENTAL METHODS

### 1- Chemical interesterification (CIE) Laboratory method:

- Melt oil blend
- Add to [0.4%(wt.) glycerine+0.4%(wt.) KOH+0.4%(wt.)water]
- Heat to 80°C and remove water under vacuum
- Increase temp to 120°C to react for 45min under vacuum
- Decrease temp to 80°C and add H3PO4 to it for neutralization and stir under vacuum for 15min
- Add 1%BE at 80°C under vacuum for 30min
- filter in filter bag 3-5 microns.

### 2-Enzymatic interesterifications (EIE) method: Pilot Enzymatic interesterification Packed bed column reactor (PPR):

- 1- Enzyme load: 5 kg dry enzyme / reactor
- 2- Number of reactors: 2
- 3- Enzyme consumption: 0.4 kg enzyme / ton oil
- 4- Flow rate: 0.5 – 2.0 kg oil / (kg enzyme. h)
- 5- Sieved particle size: 300-1000 m.

### 3-Purification of chemical and enzymatic inter-esterified oil (CIE & EIE):

#### A- Lab method for purifying CIE oil:

By vacuum distillation in Rotatory evaporator:

- Vacuum: 0.5- 1 millibar vacuum.
- Temperature: 180-190C
- Running time: 1 hour.

#### B- Pilot Deodorizer method for refreshing the specifications of for EIE oil

- 1-The amount of oil enter Deodorizer =5-10 Kg per batch)
- 2-Maximum cooling temp = 75 C

- 3-Maximum sample quantity 130 gm
- 4- Heating rate = 2-2.2 C/min by thermal heat oil in the coil.
- 5- Thermal heat temperature: 300 C – Oil temperature in deodorizer :300 C.
- 6-Vacuum: 0.5-1 millibar.

#### 4- Analyses of oils

Free fatty acid content (AOCS Ca 5a-40), peroxide value (AOCS Cd 8b-90), smoke point (AOCS Cc 9a-48) and anisidine value (AOCS Cd 18-90). All were determined using these AOCS Official Methods.

#### 5- Statistical Analysis:

All the results shown in this study, as mean  $\pm$  standard deviation, were subjected to analysis of variance.

(ANOVA). Duncan's multiple range test was used to determine the significance level of P value (P  $\leq$  0.05).

Analysis was done with the SPSS software (SPSS 20.0, SPSS Inc., Chicago, USA).

### 5. DESIGN OF THE STUDY

The experimental work was designed to study the physical, chemical characteristics of different physical blends of capric/ caprylic MCT with different LCT oils compared to MLCT structured oil formed from same oils blends through enzymatic interesterifications(EIE) in pilot packed bed reactor (PBR) and chemical interesterification(CIE) in laboratory CIE equipment .

### 6. RESULTS AND DISCUSSION

In this study, structured MLCT -type triacylglycerols and non-structured MCT/LCT oil blend. Both structured and non-structured healthy oils were prepared in the laboratory and pilot plants. Different long-chain triglycerides (LCT)source oils were used in the preparation which combined with medium-chain triglyceride (MCT) source oils. MCT oils used is caprylic/capric MCT oil as a synthetic source of medium-chain triglycerides (MCT) produced from coconut oil and supplied by PT Musim.

The produced MLCT structured oil and MCT/LCT non-structured oil blend was refined by short path distillation either in lab rotatory evaporator or pilot Desmet deodorizer.

The physical characteristics of oils and fats are determined by their chemical compositions such as the types of fatty acid (FA) and their distribution along the glycerol backbone. Most fats and oils have only limited application in their original forms. High oleic sunflower oil (HOSO), Canola oil, palm oil, palm olein, and double fractionation olein show high thermo-oxidative stability, due to the high levels of oleic acid. These types of oils could be of great value in foods (e.g., fried products, bakery products, and margarine, and frozen desserts) Fats and oils of vegetable origin are generally rich in unsaturated FAs (UFAs) in the central position (sn-2) of the triacylglycerols (TAGs), while the saturated FAs (SFAs) principally occupy the positions sn-1 and sn-3. SFAs in the sn-2 position of dietary TAG may elevate the LDL concentrations more than the same FA in the sn-1 or sn-3 positions, because the metabolic fat is different from that of the sn-1 and sn-3 positions Berry, S. E. E. [20].

The typical fatty acids composition(FAC) and triglycerides (TAGs)of different types of oils (triacylglycerol) used in the study have been analyzed by GC spectrometer. Results are summarized in (Table 9).

The LCT and MCT oils used in this study as follow:

#### 1-Long chain triglyceride ( LCT) oils included in the study were:

- a- Refined sunflower oil (SFO)
- b-Refined High oleic sunflower oil(HOSFO).
- c-Refined Canola oil. (CNO)
- d- Refined palm oil. (PO)
- e- Refined super double fractionated olein. (DFolein)

#### 2-Medium chain triglyceride (MCT) oils which are

- Refined MCT oil. (MCT).
- Three sets of experiments have been done to study the combination of LCT oils and MCT oils to prepare structured MLCT oils and non-structured MCT/LCT blends for producing a novel healthier cooking oil preparation: Bellow is the experiments set.

#### A-Physical blending of LCT & MCT oils for producing MCT/LCT blends:

1. Physical Blend 50%Super Olein+30%MCT+20%HOSFO.

2. Physical Blend 65% Super Olein+10%MCT+25%HOSFO,
3. Physical Blend 61% Super Olein+12% MCT+27%HOSFO.
4. Physical Blend 5% Super Olein+27%MCT+68%HOSFO.

**-Methods followed for preparation of structured MCLT oils by CIE and EIE:**

**A-Preparation of MLCT oil by EIE using lab apparatus and enzyme Lipozyme TL IM: -**

- The enzyme was pre-dried to remove any moisture traces that could hydrolyze the triglycerides by adding the oil blend under test to the enzyme and preheated to 70 °C in the reaction vessel, while gentle stirring for 30 minutes. The feed oil specification used are adjusted to ensure no deterioration of enzyme catalytic efficiency during the reaction: Phosphorus < 2ppm, Moisture < 0.05%, Peroxide value < 1 mEq/kg, p-Anisidine Value < 5 Iron content < 0.5 ppm.

**B-Chemical interesterification (CIE) of LCT & MCT oils for producing structured MLCT oils:**

- CIE Blend 50% Super Olein+30% MCT+ 20% HOSFO.

**C-Enzymatic interesterification (EIE) of LCT & MCT oils for producing structured MLCT oils:**

- EIE Blend 50% Super Olein+ 30% MCT+20% HOSFO.

**Table 3. Potential substrates for medium-long-medium (MLM) structured lipid synthesis Qabul Dinanta Utama1 et al. [3]**

| Fatty acid     | Source             | w(acid)/% |
|----------------|--------------------|-----------|
| Oleic acid     | Palm olein         | 39.8–46.0 |
|                | Canola oil         | 64.1      |
|                | Peanut oil         | 46.5      |
|                | Olive oil          | 55–83     |
|                | Rice bran oil      | 38–48     |
|                | Sesame seed oil    | 36.9–47.9 |
|                | Avocado oil        | 65.42     |
| Linoleic acid  | Soybean oil        | 48–59     |
|                | Cottonseed oil     | 46.7–58.2 |
|                | Sunflower oil      | 48.3–74   |
|                | Safflower seed oil | 67.8–83.2 |
| Linolenic acid | Flaxseed oil       | 50.28     |
|                | Krill oil          | 14.3–28.0 |
| EPA            | Menhaden oil       | 12.5–19.0 |
| DHA            | Tuna oil           | 21–42.5   |
|                | Anchovy oil        | 4.0–26.5  |
|                | Salmon oil         | 6.0–14.0  |
|                | Cod liver oil      | 6.0–18.0  |
| Lauric acid    | Palm kernel oil    | 45–55     |
|                | Coconut oil        | 45.1–53.2 |
|                | Babassu oil        | 40.5–55   |

**Table 4. Fatty acid composition of Sunflower oil (SFO)**

|       | Specifications range % | Test Method    |
|-------|------------------------|----------------|
| C12:0 | 0.2 max                | AOCS Ce 2-66 & |
| C14:0 | 5.0-7.6                | AOCS Ce 1e -91 |
| C16:0 | 2.7-6.5                |                |
| C18:0 | 14.0-39.4              |                |
| C18:1 | 48.3-74                |                |
| C18:2 | 0.3 max                |                |
| C18:3 | 0.1-0.5                |                |
| C20:0 | 0.3 max                |                |
| C22:0 | 1 max                  |                |
| C24:0 | 0.5 max                |                |

**Table 5. Fatty acid composition specifications of high oleic sunflower oil (HOSFO)**

|       | <b>Specifications range %</b> | <b>Test Method</b> |
|-------|-------------------------------|--------------------|
| C12:0 | -                             | AOCS Ce 2-66 &     |
| C14:0 | 0.1 max                       | AOCS Ce 1e -91     |
| C16:0 | 3.0-5.0                       |                    |
| C18:0 | 2.0-5.0                       |                    |
| C18:1 | 75-91                         |                    |
| C18:2 | 2.0-17                        |                    |
| C18:3 | < 0.3                         |                    |
| C20:0 | < 0.5                         |                    |
| C22:0 | < 0.5                         |                    |
| C24:0 | < 2                           |                    |

**Table 6. Fatty acid composition specification of Canola oil (CNO)**

|       | <b>Specifications range %</b> | <b>Test Method</b> |
|-------|-------------------------------|--------------------|
| C12:0 | -                             | AOCS Ce 2-66 &     |
| C14:0 | -                             | AOCS Ce 1e -91     |
| C16:0 | 0-0.6                         |                    |
| C18:0 | 0.8-3                         |                    |
| C18:1 | 51-70                         |                    |
| C18:2 | 15-30                         |                    |
| C18:3 | 5-14                          |                    |
| C20:0 | 0.2-1.2                       |                    |
| C20:1 | 0.1-4.3                       |                    |
| C22:0 | 0.6 max                       |                    |
| C24:0 | 0.3 max                       |                    |

**Table 7. Fatty acid composition and solid fat content of refined Palm oil**

|       | <b>Specifications range %</b> | <b>Test Method</b> |
|-------|-------------------------------|--------------------|
| C12:0 | 0.1-1.0                       | AOCS Ce 2-66 &     |
| C14:0 | 0.9-1.5                       | AOCS Ce 1e -91     |
| C16:0 | 41.8-46.8                     |                    |
| C18:0 | 4.2-5.1                       |                    |
| C18:1 | 37.3-40.8                     |                    |
| C18:2 | 9.1-11                        |                    |
| C18:3 | 0.6 max                       |                    |
| C20:0 | 0.2-0.7                       |                    |

**Table 8. Fatty acid composition and solid fat content of refined super double fractionation olein (IV 63-64)**

|       | <b>Specifications range %</b> | <b>Test Method</b> |
|-------|-------------------------------|--------------------|
| C12:0 | 0.1-1.0                       | AOCS Ce 2-66 &     |
| C14:0 | 0.9-1.4                       | AOCS Ce 1e -91     |
| C16:0 | 35.0-37.0                     |                    |
| C18:0 | 3.5-4.5                       |                    |
| C18:1 | 43.0-46.0                     |                    |
| C18:2 | 40.0-42.0                     |                    |
| C18:3 | 0.5 max                       |                    |
| C20:0 | 0.5 max                       |                    |

**Table 9. Specifications and fatty acid composition of MCT oil -PT Musim Mas**

| TEST                               | METHOD        | RESULTS | SPECIFICATION                                |
|------------------------------------|---------------|---------|--|
| APPEARANCE                         | VISUAL        | PASS    | COLOURLESS OR SLIGHTLY YELLOWISH OILY LIQUID |
| ACID VALUE, mg KOH/g               | AOCS Te 2a-64 | 0.04    | 0.1 MAX                                      |
| SAPONIFICATION VALUE, mg KOH/g     | AOCS TI 1a-64 | 334     | 325 - 345                                    |
| IODINE VALUE, g <sub>2</sub> /100g | AOCS Tg 1a-64 | 0.1     | 0.5 MAX                                      |
| HYDROXYL VALUE, mg KOH/g           | AOCS Cd 13-60 | 2       | 8 MAX  |
| PEROXIDE VALUE, meq/kg             | AOCS Cd 8-53  | 0.1     | 1 MAX  |
| COLOUR, APHA                       | AOCS Ea 9-65  | 12      | 70 MAX                                       |
| MOISTURE, %                        | AOCS Ca 2e-84 | 0.03    | 0.15 MAX                                     |
| <b>FATTY ACID COMPOSITION, %</b>   |               |         |  |
|                                    | ISO 5509      |         |  |
| C8                                 |               | 58.3    | 55 - 65                                      |
| C10                                |               | 41.5    | 35 - 45                                      |
| OTHERS                             |               | 0.1     | 2 MAX  |

**Table 10. Typical fatty acids and triglyceride compositions of oils used in the chemical and enzymatic interesterification**

|   | Carbon no.                             | SFO  | HOSFO | CNO  | PO    | DFOlein | MCT   |
|---|--|------|-------|------|-------|---------|-------|
| Fatty acid composition % by GC                        | C8 %                                   | ND   | ND    | ND   | ND    | ND      | 57.8  |
|   | C10%                                   | ND   | ND    | ND   | ND    | ND      | 41.6  |
|   | C12                                    | ND   | ND    | ND   | ND    | ND      | 0.1   |
|   | C14                                    | ND   | ND    | ND   | 1     | 1.2     | ND    |
|   | C16                                    | 6.2  | 0.1   | 5    | 43.05 | 38.5    | ND    |
|   | C18                                    | 5    | 5.4   | 2    | 4.46  | 4.5     | ND    |
|   | C18:1                                  | 20.3 | 81.3  | 61.2 | 39.16 | 45.5    | ND    |
|   | C18:2                                  | 60.5 | 9     | 21.8 | 10.43 | 12.5    | ND    |
|   | C18:3                                  | 0.3  | 0.2   | 8.8  | ND    | ND      | ND    |
|   | C20                                    | 0.3  | 0.4   | 0.7  | 0     | 0       | 0     |
| Triacyl glycerol's composition by GC                  | CLaLa                                  | ND   | ND    | ND   | ND    | ND      | ND    |
|   | CCC                                    | ND   | ND    | ND   | ND    | ND      | 34    |
|   | CaCaCa                                 | ND   | ND    | ND   | ND    | ND      | 38    |
|   | CCCa/CCaC/CaCaC                        | ND   | ND    | ND   | ND    | ND      | 14    |
|   | CCaCa/CaCCa/CaCaC                      | ND   | ND    | ND   | ND    | ND      | 13.88 |
|   | CaLaLa <sup>a</sup> /CLaM <sup>a</sup> | ND   | ND    | ND   | ND    | ND      | ND    |
|   | LaLaLa                                 | ND   | ND    | ND   | ND    | ND      | ND    |
|   | LaLaM                                  | ND   | ND    | ND   | ND    | ND      | ND    |
|   | LaLaO                                  | ND   | ND    | ND   | ND    | ND      | ND    |
|   | LLL                                    | 31.3 | ND    | 1.3  | ND    | ND      | ND    |
|   | LaLaP <sup>b</sup> /LaMM <sup>b</sup>  | ND   | ND    | ND   | ND    | ND      | ND    |
|   | SOL/LOS                                | 3.1  | ND    | 1.6  | ND    | ND      | ND    |
|   | SLL/LLS                                | 7.3  | ND    | ND   | ND    | ND      | ND    |
|   | LLM                                    | ND   | ND    | ND   | ND    | ND      | ND    |
|   | LMM <sup>c</sup> /LaOM <sup>c</sup>    | ND   | ND    | ND   | ND    | ND      | ND    |
|   | MMM <sup>d</sup> /LaPM <sup>d</sup>    | ND   | ND    | ND   | ND    | 0.54    | ND    |
|   | OLL/LLO                                | 26.5 | 3.1   | 8.6  | 0.4   | ND      | ND    |
|   | PLL/LLP                                | 10.4 | ND    | 1.4  | 1.2   | ND      | ND    |
|   | PLS                                    | 1.4  | ND    | ND   | ND    | ND      | ND    |
| LMO <sup>e</sup> /LaOO <sup>e</sup>                   | ND                                     | ND   | ND    | ND   | ND    | ND      |       |
| MPL <sup>f</sup> /LaOP <sup>f</sup> /MMO <sup>f</sup> | ND                                     | ND   | ND    | ND   | 2.99  | ND      |       |
| LaPP <sup>g</sup> /MMP <sup>g</sup>                   | ND                                     | ND   | ND    | ND   | 2.27  | ND      |       |
| OOL/OLO/LOO   | 7.3                                    | 5.8  | 22.5  | 1.5  | 0.77  | ND      |       |
| PLO/POL/LOP   | 4.9                                    | ND   | 5.7   | 8.9  | 13.56 | ND      |       |

| Carbon no.  | SFO | HOSFO | CNO  | PO   | DFolein | MCT |
|-------------|-----|-------|------|------|---------|-----|
| MOO         | ND  | ND    | ND   | ND   | ND      | ND  |
| PLP/PPL     | 1.1 | ND    | ND   | 9.2  | 10.14   | ND  |
| MOP         | ND  | ND    | ND   | ND   | ND      | ND  |
| PPM         | ND  | ND    | ND   | 0.2  | ND      | ND  |
| OOO         | 1.6 | 80.4  | 22.4 | 3.9  | 5.25    | ND  |
| POO/OPO     | 0.6 | 11.2  | 4.6  | 23.3 | 29.13   | ND  |
| POP/PPO     | 0.5 | 0.5   | ND   | 30.2 | 22.46   | ND  |
| PPP         | 0.8 | ND    | 0.2  | 6.7  | 0.9     | ND  |
| SOO/OSO/OOS |     | ND    | 2.8  | 2.9  | 4.17    | ND  |
| PSO/POS     | 0.5 | ND    | ND   | 6.7  | 3.97    | ND  |
| PPS/PSS/SPS | 0.4 | ND    | ND   | 1.1  | ND      | ND  |
| SSO/SOS     | 0.4 | ND    | ND   | 3.8  | 0.51    | ND  |
| LnLO        | 2.4 | ND    | 7.3  | ND   | ND      | ND  |
| LnLL        | ND  | ND    | 1.4  | ND   | ND      | ND  |
| LnOO        | ND  | ND    | 10.4 | ND   | ND      | ND  |
| LnOP        | ND  | ND    | 1.9  | ND   | ND      | ND  |
| LnLnO       | ND  | ND    | 1.8  | ND   | ND      | ND  |
| Others      | ND  | ND    | 6    | 0.3  | 3.3     | ND  |

Values show the means SD (n = 3).

Abbreviations: Fatty acid composition (FAC) PO, palm oil; SFO, sunflower oil; Canola oil :CNO ;DFolein : Double fractionated olein; Medium chain triglycerides: MCT oil ; C8:0, caprylic acid; C10:0, capric acid; C12:0, lauric acid; C14:0, myristic acid; C16:0, palmitic acid; C18:0, stearic acid; C18:1, oleic acid; C18:2, linoleic acid.: C18:3 Linolenic acid Others include caproic (C6:0), arachidic (C20:0) and Erucic (C22:1) acids. Triacylglycerol( TAG) C, capric acid; La, lauric acid; Ca, caprylic acid; M, myristic acid; O, oleic acid; P, palmitic acid; L, linoleic acid; Ln ,Linolenic acid S, stearic acid. TAG with the same roman superscript a–g are TAG, Others: group of other triglycerides of content of less than 1% including. Values show the means SD (n = 3)

#### Typical reaction parameters followed for laboratory EIE reaction:

- 1- Pretreatment to cut the moisture content of oil as low as possible (i.e., 0.01 %)
- 2- Enzyme addition dose : 8 %
- 3- Reaction temperature: 70 C.
- 4- Reaction duration time: 3-6 hours.
- 5- Sedimentation for removal of oil.
- 6- Filtering the oil through a polishing filter.

#### B-Preparation of structured MLCT oil by EIE using PBR and the enzyme catalyst Lipozyme TL IM:

Enzymatic production of MLCT was done in a pilot-scale packed bed reactor (PBR)based system, model.

(Desmet pilot EIE reactor - LE2600). at the optimal conditions recommended by Zhen Zhang et al 2000 [14] which are: MCT oil: LCT oil ratio of 45-50:55-45 w/w, reaction temperature of 75 °C, and residence time of 16.0 min.). The work parameter of the reaction is Oil temperature - feed rate – working. Pressure. The pilot contains 2 Enzyme reactor A & B with the flow of oil is four option are Reactor A only or Reactor B only or A to B or B to A. Every reactor contains 5 Kg of enzyme. Feeding or blending tank is app 70 kg.

Feed pump flow rate maximum 40 liter oil /h = 4 kg oil / Kg Enzyme/ h (A+B) = 8 Kg oil / Kg enzyme/ h (A only or B only). Pressure up to 3 bar 8- operation temperature: 70 -75 C. The purified MLCT product had 75.7 wt% SFA at the sn-2 position, suggesting that it would serve as a suitable structured.

Dietary cooking oil. The MLCT produced by the EIE pilot method was deodorized in a pilot deodorizer.

#### (Desmet Pilot oil deodorizer system).

#### C-Preparation of structured MLCT oil by CIE using lab apparatus.

The oil blend of MCT and LCT oils was completely melted, heated to 120 C, and mixed the chemical catalyst composed of glycerin and potassium hydroxide and set under vacuum. The reaction was known to be done by turning the mixture color to brownish and then the reaction was quenched by adding phosphoric acid.

-The generated soap content was removed by adding Add 1%BE at 80°C under vacuum for 30min a filter in filter bag 3-5 microns. The prepared MLCT structured oils by CIE and EIE oil were purified through. Vacuum distillation in a rotatory evaporator.

**Table 11. Analysis of Capric /Caprylic MCT -LCT oil blends before and after Interesterification**

|                   | <b>Blend 50%DFOlein+<br/>30%MCT+20%HOSFO</b> | <b>EIE Blend 50%DF<br/>Olein+30%MCT+20%HO<br/>SFO</b> | <b>CIE Blend 50%DF<br/>Olein+30%MCT+20%HO<br/>SFO</b> | <b>Blend 65%DF<br/>Olein+15%MCT+20%HO<br/>SFO</b> | <b>Blend 55%DF<br/>Olein+20%MCT+25%HO<br/>SFO</b> | <b>Blend 5%DF<br/>Olein+25%MCT+70%H<br/>OSFO</b> |         |
|-------------------|--|---|---|---|---|--|---------|
| FFA               | 0.08   | 0.12  | 0.1   | 0.07  | 0.07  | 0.08   |         |
| PV                | 0.8  | 1.5   | 1.2   | 0.9   | 0.8   | 0.76   |         |
| FAC %             |  |   |   |   |   |  |         |
| Caproic C 6:0     | 0.05   | 0.05  | 0.05  | 0.02  | 0.02  | 0.05   |         |
| Caprylic C 8:0    | 17.39  | 17.39   | 17.39   | 5.80  | 6.69  | 15.65  |         |
| Capric C10:0      | 12.29  | 12.29   | 12.29   | 4.10  | 4.92  | 11.06  |         |
| Lauric C12:0      | 0.19   | 0.19  | 0.19  | 0.22  | 0.21  | 0.05   |         |
| Myristic C14:0    | 0.51   | 0.51  | 0.51  | 0.66  | 0.62  | 0.05   |         |
| Palmitic C16:0    | 17.54  | 17.54   | 17.54   | 22.73   | 21.46   | 4.09   |         |
| Palmitoleic C16:1 | 0.12   | 0.12  | 0.12  | 0.15  | 0.14  | 0.10   |         |
| Stearic C18:0     | 2.47   | 2.47  | 2.47  | 3.16  | 3.08  | 2.32   |         |
| Oleic C18:1       | 39.87  | 39.87   | 39.87   | 50.96   | 50.71   | 57.75  |         |
| Linoleic C18:2    | 8.79   | 8.79  | 8.79  | 11.21   | 11.21   | 7.35   |         |
| Linolenic C18:3   | 0.20   | 0.20  | 0.20  | 0.24  | 0.24  | 0.22   |         |
| TAG % TGA type    |  |   |   |   |   |  |         |
| CCC               | 10.2   | 6.2   | 6.7   | 5.1   | 6.8   | 8.5  | MMM     |
| CaCaCa            | 11.4   | 4.3   | 4.1   | 5.7   | 7.6   | 9.5  | MMM     |
| CCCa/CCaC/CaCaC   | 4.2  | 2.1   | 2.1   | 2.1   | 2.8   | 3.5  | MMM     |
| CCaCa/CaCCa/CaCaC | 4.164  | 2.1   | 2.1   | 2.082   | 2.776   | 3.47   | MMM     |
| CCaLi/CLiCa       | ND   | 2.7   | 1.2   | ND  | ND  | ND   | MLM     |
| CCLi/CLiC         | ND   | 3.5   | 1.5   | ND  | ND  | ND   | MLM     |
| CCO/COC           | ND   | 2.5   | 1.3   | ND  | ND  | ND   | MLM     |
| CCP/CPC           | ND   | 1.6   | 1.1   | ND  | ND  | ND   | MLM     |
| CLiLn             | ND   | 3.5   | 2.5   | ND  | ND  | ND   | MLM     |
| CaCaLi/ CaLiCa    | ND   | 5.5   | 3.6   | ND  | ND  | ND   | MLM     |
| CCaO/COCa/CaOC    | ND   | 2.3   | 1.1   | ND  | ND  | ND   | MLM     |
| CCS/ CCaP         | ND   | 2.3   | 1.3   | ND  | ND  | ND   | MLM/MLL |
| CLiLi             | ND   | 3.6   | 5.4   | ND  | ND  | ND   | MLM     |
| CaCaO/CaOCa       | ND   | 0.3   | 3.7   | ND  | ND  | ND   | MLL     |
| CaOLn             | ND   | 3.4   | 3.4   | ND  | ND  | ND   | MLL     |
| CaLiLi            | ND   | 4.4   | 4.4   | ND  | ND  | ND   | MLL     |
| COLi              | ND   | 2.1   | 3.9   | ND  | ND  | ND   | MLL     |

|   | <b>Blend 50%DFOlein+<br/>30%MCT+20%HOSFO</b> | <b>EIE Blend 50%DF<br/>Olein+30%MCT+20%HO<br/>SFO</b> | <b>CIE Blend 50%DF<br/>Olein+30%MCT+20%HO<br/>SFO</b> | <b>Blend 65%DF<br/>Olein+15%MCT+20%HO<br/>SFO</b> | <b>Blend 55%DF<br/>Olein+20%MCT+25%HO<br/>SFO</b> | <b>Blend 5%DF<br/>Olein+25%MCT+70%H<br/>OSFO</b> |     |
|---|--|---|---|---|---|--|-----|
| CaOLi   | ND   | 3.4   | 3.7   | ND  | ND  | ND   | MLL |
| CaPLi   | ND   | 1.3   | 3.7   | ND  | ND  | ND   | MLL |
| CaSLi/ CaOO   | ND   | 1.6   | 2.8   | ND  | ND  | ND   | LLL |
| LiLiLi  | 0  | 1.6   | 2.3   | ND  | ND  | ND   | LLL |
| OLiLi   | 0  | 2.2   | 2.4   | ND  | ND  | ND   | LLL |
| PLiLi   | 0  | 2.1   | 2.1   | ND  | ND  | ND   | LLL |
| MPL/LMP   | 1.55   | 0.79  | 0.79  | 1.9   | 1.7   | 0.2  | LLL |
| MOM   | 0.31   | 0.23  | 0.28  | 0.31  | 0.31  | 0.31   | LLL |
| PPP   | 0.4  | 0.5   | 0.3   | 1.1   | 0.6   | 0.7  | LLL |
| OOL/OLO/LOO   | 1.17   | 0.4   | 0.5   | 1.2   | 2.45  | 4.1  | LLL |
| OLL/LLO   | 1.03   | 1.9   | 1.09  | 1.03  | 2.03  | 2.1  | LLL |
| PLO/POL/LOP   | 9.4  | 4.5   | 4.4   | 12.24   | 7.55  | 1.1  | LLL |
| PLP/PPL   | 5.2  | 2.1   | 2.3   | 6.42  | 5.6   | 0.58   | LLL |
| OOO   | 18.9   | 8.3   | 8.6   | 16.7  | 22.9  | 55.4   | LLL |
| SOO/OSO/OOS   | 1.55   | 0.86  | 0.86  | 2.1   | 1.8   | 0.2  | LLL |
| POS/PSO   | 2.1  | 0.66  | 0.45  | 2.7   | 2.24  | 0.3  | LLL |
| POO/OPO   | 18.3   | 7.1   | 6.88  | 23.7  | 19.2  | 8.6  | LLL |
| POP/PPO   | 10.9   | 6.33  | 6.56  | 14.45   | 12.3  | 1.28   | LLL |
| Others/MMP  | 0.14   | 1.2   | 1.06  | 0.76  | 1.3   | 0.3  | LLL |
| DSC analysis :  |  |   |   |   |   |  |     |
| Heat evolved during<br>Crystallization J/gm           | 44.17  | 35.15   | 30.08   | 44.17   | 44.17   | 44.17  |     |
| Temperature at which crystal<br>start to be formed °C | -23.95                                       | -23.8   | -28.85  | -23.95  | -23.95  | -23.95   |     |
| Temperature at which crystal<br>completely formed °C  | -31.13                                       | -36.13  | -37.8   | -31.13  | -31.13  | -31.13   |     |

*Triacylglycerol( TAG) abbreviations:  
C, capric acid; Ca, caprylic acid ;La, lauric acid; M, myristic acid; O, oleic acid; P, palmitic acid; Li, linoleic acid; Ln ,Linolenic acid S, stearic acid.  
Values show the means SD (n = 3).*



**Table 12. Chemical analysis of Capric/Caprylic MCT oil and different LCT oils used before and after chemical and enzymatic interesterification**

|  |  | FFA                                      | PV   | p.A.V. | Moisture | Smoke point | OSI (induction period) @110C Without A.O. | OSI (induction period) @110C with TBHQ 200 ppm |
|--|--|--|------|--------|----------|-------------|---|--|
| <b>Individual oils</b>                             | Caprylic /capric MCT oil                 | 0.07                                     | 0.5  | 3.2    | 0.06     | 143         | 8.5                                       |  |
|  | DF olein                                 | 0.1                                      | 1.5  | 4.8    | 0.07     | 222         | 9.8                                       |  |
|  | HOSF                                     | 0.07                                     | 0.5  | 4.3    | 0.08     | 236         | 8.5                                       |  |
| <b>Non structured MCT/LCT Blends</b>               | Blend(50%DFOlein +30%MCT +20%HOSFO)      | 0.07                                     | 0.5  | 4.2    | 0.05     | 205         | 8.1                                       | 12.1   |
|  | Blend (65%DF Olein+15%MCT +20%HOSFO)     | 0.06                                     | 0.8  | 4.6    | 0.06     | 213         | 8.3                                       | 11.8   |
|  | Blend (55%DF Olein+20%MCT +25%HOSFO)     | 0.07                                     | 0.6  | 4.6    | 0.08     | 210         | 8.15                                      | 12.5   |
|  | Blend (5%DF Olein+25%MCT +70%HOSFO )     | 0.32                                     | 1.4  | 4.5    | 0.07     | 214         | 8.46                                      | 12.5   |
| <b>Structured MLCT by Enzymatic Esterification</b> | EIE Blend (50%DFOlein +30%MCT +20%HOSFO) | 0.12                                     | 2.1  | 4.8    | 0.09     | 160         | 5.65                                      | 9.6  |
|  | <b>Chemical Esterification</b>           | CIE Blend (50%DFOlein +30%MCT +20%HOSFO) | 0.16 | 2.4    | 6.2      | 0.11        | 156                                       | 3.78   |

Values show the means SD (n = 3). 201

**Table 13. Tocopherol content in different LCT oils and Its blends with MCT oil before and after chemical and enzymatic inter-esterification according to HPLC chromatograph analysis results**

| Oil                                 | Tocopherols | Content (ppm) |
|-------------------------------------|-------------|---------------|
| MCT                                 | alpha       | 0.1           |
|                                     | beta+ gamma | 0             |
|                                     | delta       | 0             |
|                                     | Total       | 0.1           |
| CNO                                 | alpha       | 261.2         |
|                                     | beta+ gamma | 314.6         |
|                                     | delta       | 0             |
|                                     | Total       | 575.8         |
| Palm oil                            | alpha       | 294.1         |
|                                     | beta+ gamma | 132.5         |
|                                     | delta       | 0             |
|                                     | Total       | 426.6         |
| HOSF/SFO 50:50 blend                | alpha       | 192.2         |
|                                     | beta+ gamma | 158.2         |
|                                     | delta       | 0             |
|                                     | Total       | 350.4         |
| CIE (HOSF/SFO 50:50 blend)          | alpha       | 261.2         |
|                                     | beta+ gamma | 314.6         |
|                                     | delta       | 0             |
|                                     | Total       | 121.6         |
| EIE (HOSF/SFO 50:50 blend)          | alpha       | 261.2         |
|                                     | beta+ gamma | 314.6         |
|                                     | delta       | 0             |
|                                     | Total       | 198.1         |
| Blend (HOSFO/SFO - MCT ). 50:50     | alpha       | 98.2          |
|                                     | beta+ gamma | 80.2          |
|                                     | delta       | 0             |
|                                     | Total       | 178.4         |
| CIE (HOSFO/SFO - MCT ). 50:50 blend | alpha       | 53.1          |
|                                     | beta+ gamma | 27.5          |
|                                     | delta       | 0             |
|                                     | Total       | 80.6          |
| EIE (HOSO/SFO-MCT oil) 50:50        | alpha       | 78.3          |
|                                     | beta+ gamma | 63.8          |
|                                     | delta       | 0             |
|                                     | Total       | 142.1         |
| Blend of Palm-MCT ( 50:50) .        | alpha       | 146.3         |
|                                     | beta+ gamma | 65.0          |
|                                     | delta       | 0             |
|                                     | Total       | 211.3         |
| CIE(Palm-MCT) 50:50 blend .         | alpha       | 91.3          |
|                                     | beta+ gamma | 25.7          |
|                                     | delta       | 0             |
|                                     | Total       | 137           |
| EIE Palm-MCT (50:50)                | alpha       | 116.3         |
|                                     | beta+ gamma | 41.5          |
|                                     | delta       | 0             |
|                                     | Total       | 167.8         |
| Blend of CNO-MCT (50:50)            | alpha       | 128.2         |
|                                     | beta+ gamma | 163.6         |
|                                     | delta       | 0             |
|                                     | Total       | 278.1         |
| CIE CNO-MCT                         | alpha       | 56.4          |

| Oil                        | Tocopherols | Content (ppm) |
|----------------------------|-------------|---------------|
| (50:50)                    | beta+ gamma | 84.3          |
|                            | delta       | 0             |
|                            | Total       | 134.7         |
| EIE CNO-MCT oil<br>(50:50) | alpha       | 101.5         |
|                            | beta+ gamma | 128.7         |
|                            | delta       | 0             |
|                            | Total       | 230.2         |

Values show the means SD (n = 3).

#### **-Studies done on prepared non structured MCT / LCT blends and structured MLCT oils:**

Structured MLCT oil prepared by Enzymatic interesterification was done by pilot bed reactor (PBR) and chemical interesterification was done in laboratory CIE apparatuses.

Also, the prepared non-structured MCT / LCT blends, both were studied using different analytical and instrumental analysis tools to conclude the optimum composition that achieves both dietary.

health cooking oil which meet the heat stress application requirements like in shallow frying or cooking.

These studies included the following:

#### **1-Physicochemical Properties of MCT/ LCT blends and MLCT structured oils produced:**

-The chemical analysis of different blends of LCT and MCT oils as well as the CIE and EIE structured oils have been analyzed for the oxidation, hydrolytic stability parameters peroxide value (PV), free fatty acid (FFA), para anisidine (p-A.V.), Oxidation stability index (OSI).

The analysis of free fatty acids (FFA), peroxide value (PV) for the non-structured MCT/LCT blends of refined Capric / caprylic MCT blends with different LCT oils (Super olein, HOSF, SFO).

The smoke point of the structured MLCT oil produced by chemical and enzymatic interesterification of Capric /Caprylic MCT with different LCT oils (Super olein, HOSF,) shown in (Table 10) shows a good smoke point above 180 C for both non-structured MCT/LCT blends and structured MLCT oils which shows.

Suitability for heat stress applications like cooking and frying.

The reason is also may be attributed to the low free fatty acid content of structured MLCT oil produced as shown in **Table 10**.

#### **2-Fatty acid and triglycerides composition of MCT/LCT blends and MLCT structured oils produced:**

-The fatty acid compositions and triglycerides composition of both capric/caprylic MCT oil and different LCTs oils used in MCT/LCT blends have been analyzed before, after chemical and enzymatic interesterifications by GC spectrometer. Results of the above analysis for different blends as shown before and after EIE and CIE are shown in Tables 10.

The fatty acid composition of the substrate (before interesterification) and (after interesterification) was similar because the reaction only rearranges acyl chains on the TAG backbone.

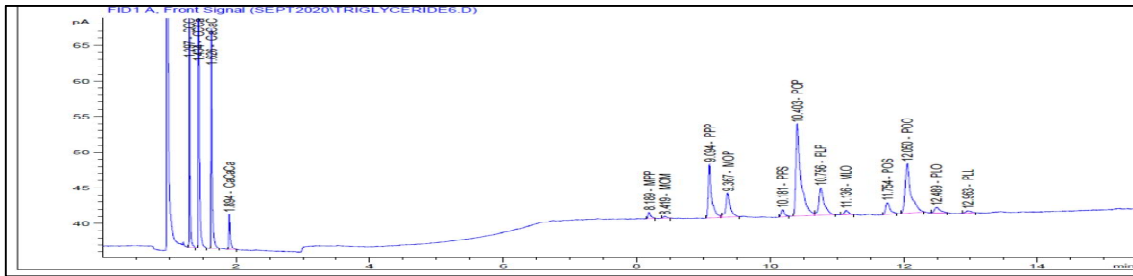
#### **3-Triacylglycerols TAG analysis study of the following MCT & LCT blends before and after chemical and enzymatic interesterification was done:**

- 1- TAG Chromatogram of Blends of 50%Super Olein+30%MCT+20%HOSFO before interesterification.
- 2- TAG Chromatogram of EIE Blend of 50%Super Olein+30%MCT+20%HOSFO.
- 3- TAG Chromatogram of CIE Blend of 50%Super Olein+30%MCT+20%HOSFO.
- 4- TAG Chromatogram of a Blend 65%Super Olein+15%MCT+20%HOSFO.
- 5- TAG Chromatogram of a Blend 55%Super Olein+20%MCT+25%HOSFO.
- 6- TAG Chromatogram of a Blend 5%Super Olein+25%MCT+70%HOSFO.

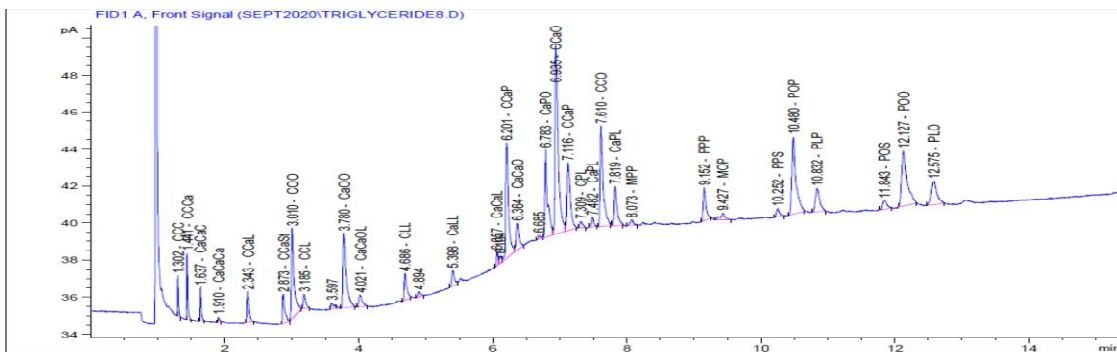
TAG composition results of these blends are shown in Table 10.

TAG -Chromatograms diagrams are shown in Diagram 1.

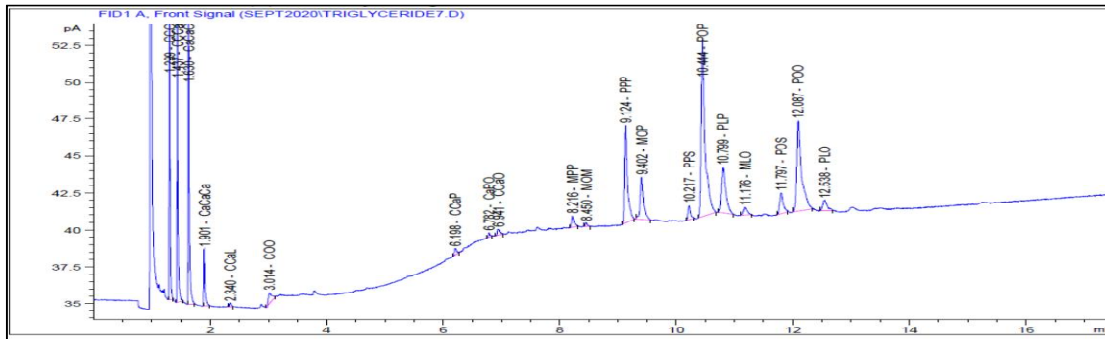
**1-Blend of 50%Super Olein+30%MCT+20%HOSFO**



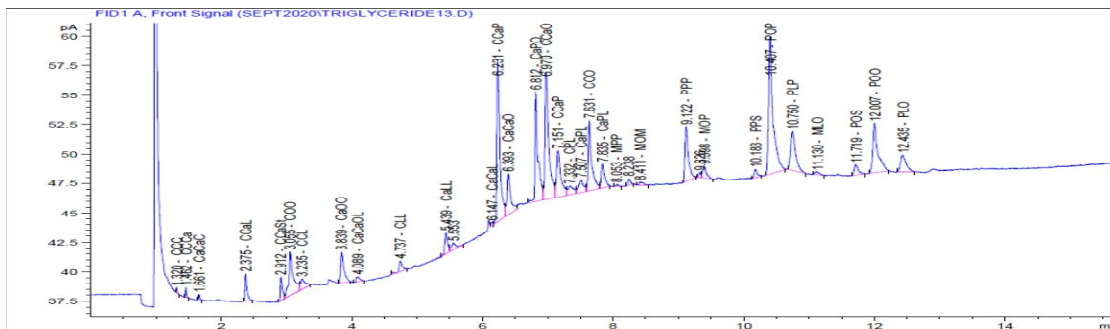
**2-EIE Blend of 50%Super Olein+30%MCT+20%HOSFO**



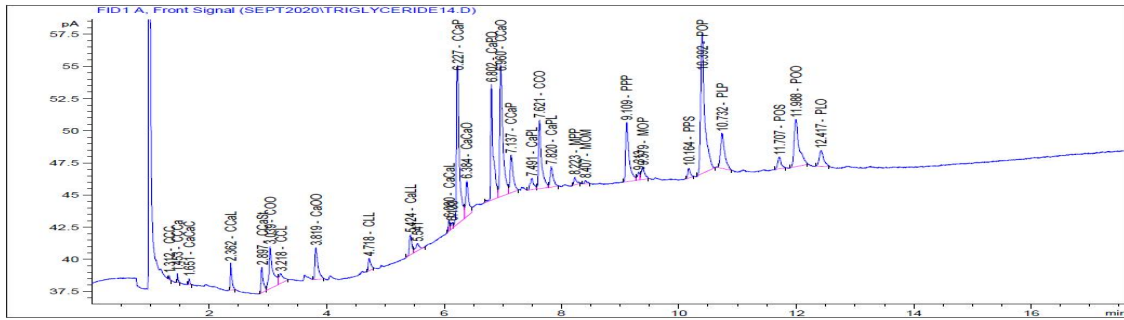
**3-CIE Blend of 50%Super Olein+30%MCT+20%HOSFO**



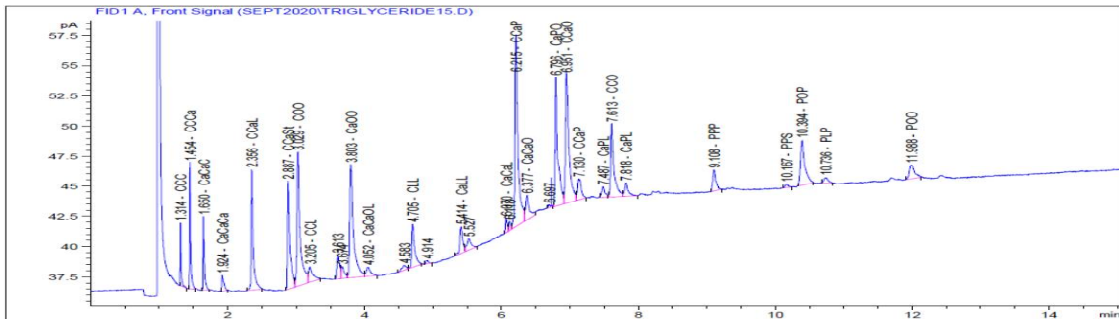
**4-Blend 65%Super Olein+15%MCT+20%HOSFO**



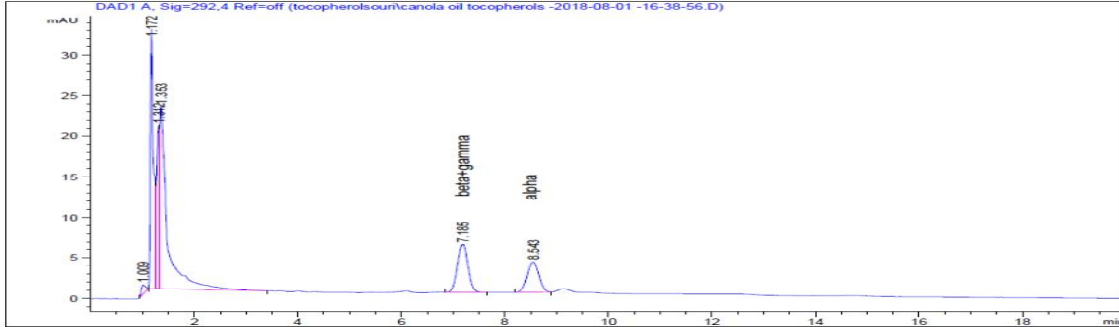
**5-Blend 55%Super Olein+20%MCT+25%HOSFO**



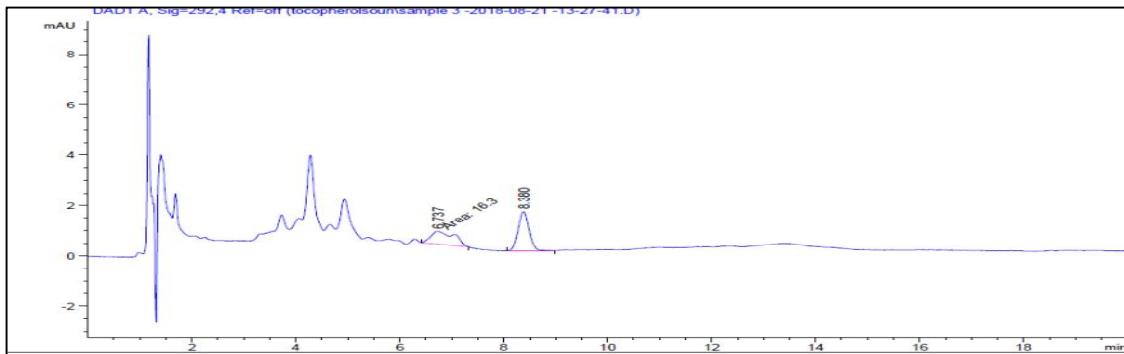
6-Blend 5%Super Olein+25%MCT+70%HOSO



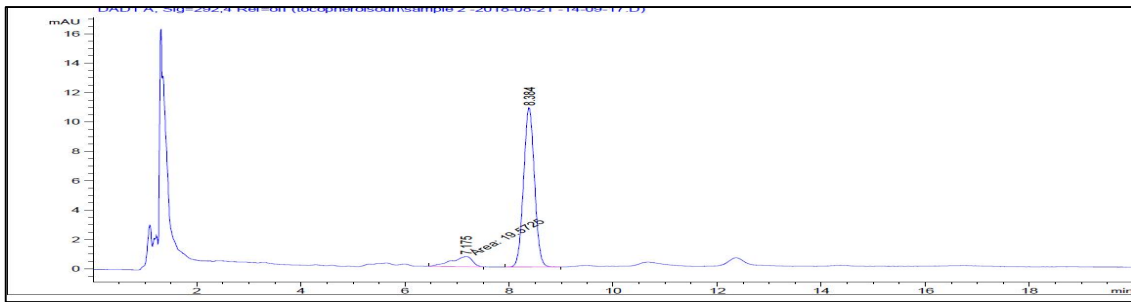
Diagrams 1. TGA Chromatogram of MCT -LCT oil blends before and after Interesterification



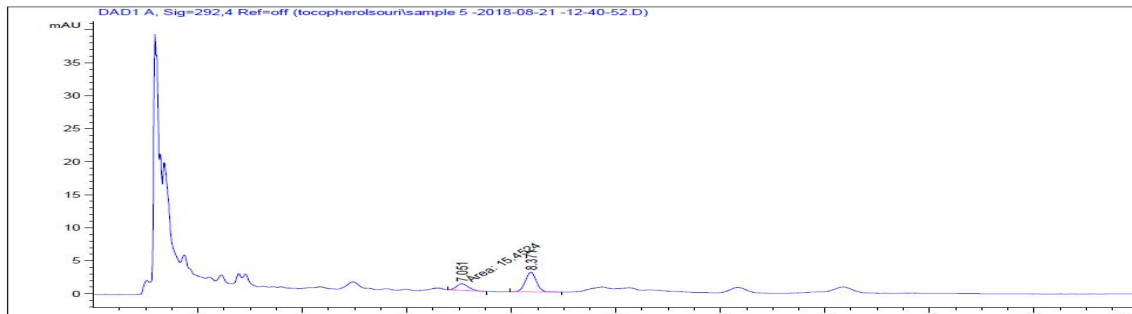
Diagrams 2.1. HPLC chromatogram for tocopherol content in Canola oil (CNO)



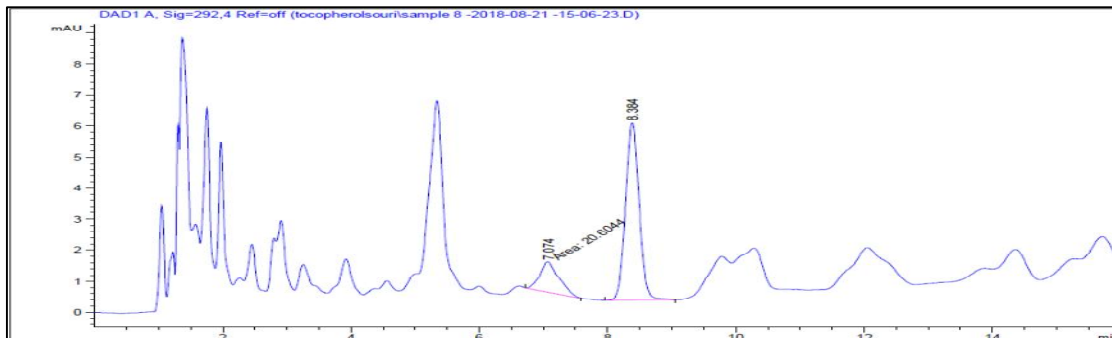
Diagrams 2.2. HPLC chromatogram for tocopherol content in Palm oil.



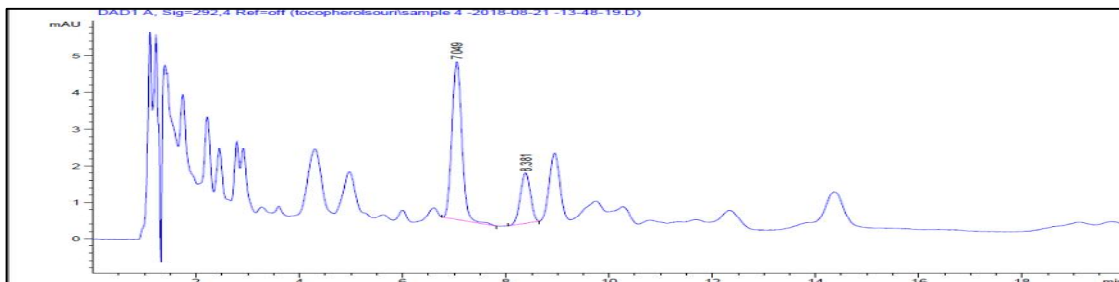
Diagrams 2.3. HPLC chromatogram for tocopherol content 50:50 blend of MCT and SFO /HOSF



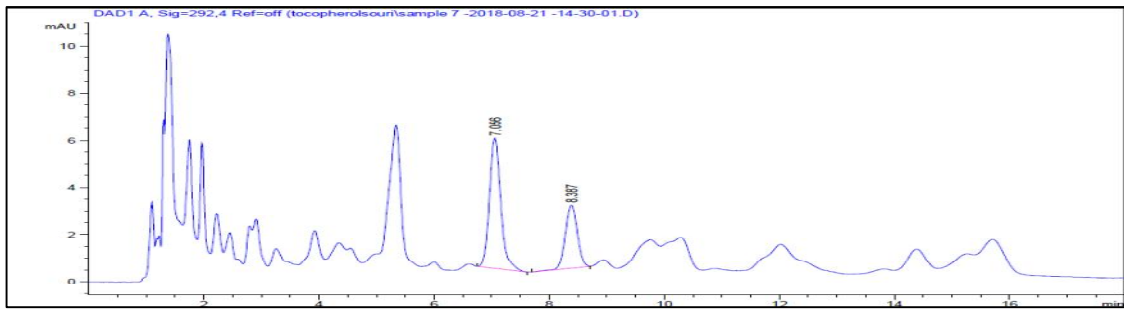
Diagrams 2.4. HPLC chromatogram for tocopherol content in 50:50 MCT - HOSFO+SFO after CIE



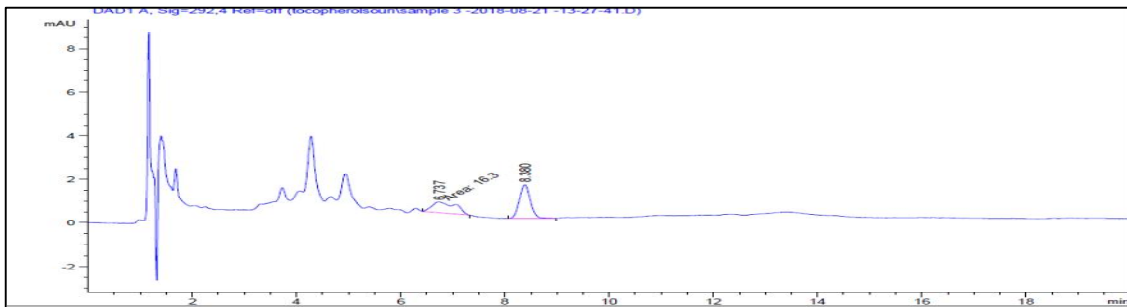
Diagrams 2.5. HPLC chromatogram for tocopherol content in 50:50 MCT - HOSFO/SFO after EIE



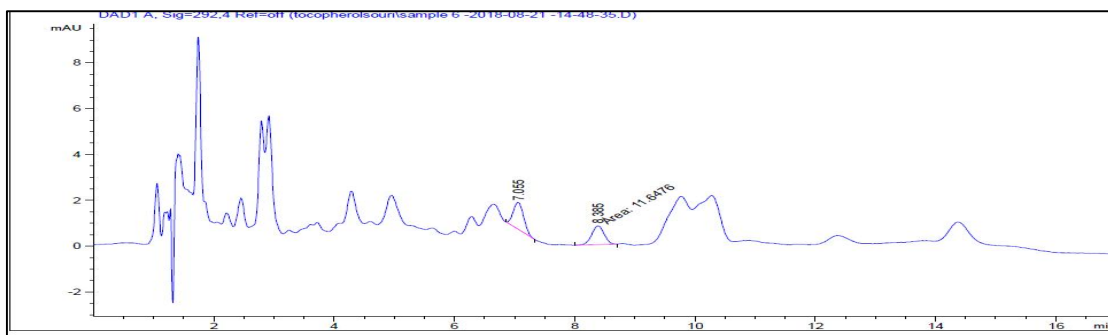
Diagrams 2.6. HPLC chromatogram for tocopherol content in 50:50 MCT -Canola (CNO)-after CIE



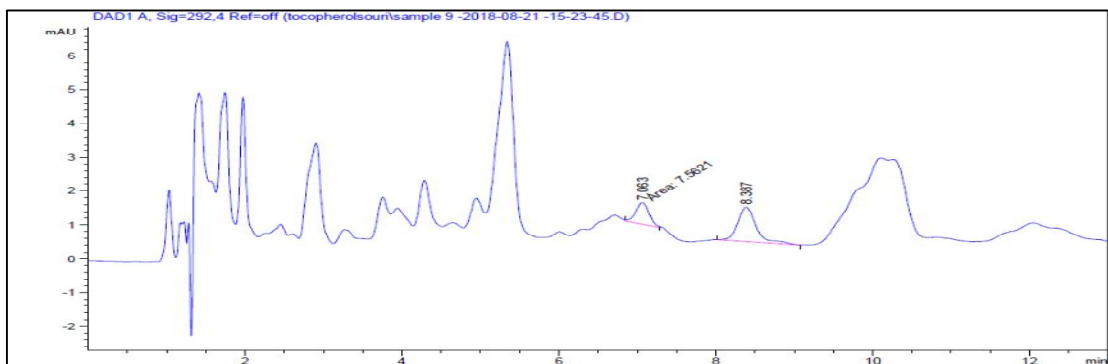
Diagrams 2.7. HPLC chromatogram for tocopherol content in 50:50 MCT-CNO-after EIE



Diagrams 2.8. HPLC chromatogram for tocopherol content in Palm oil

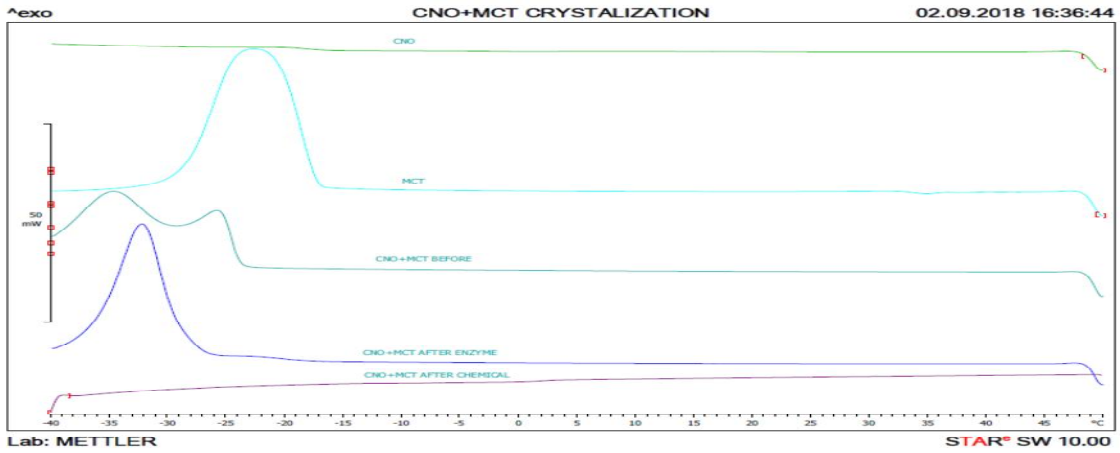


Diagrams 2.9. HPLC chromatogram for tocopherol content in 50:50 MCT-Palm after CIE

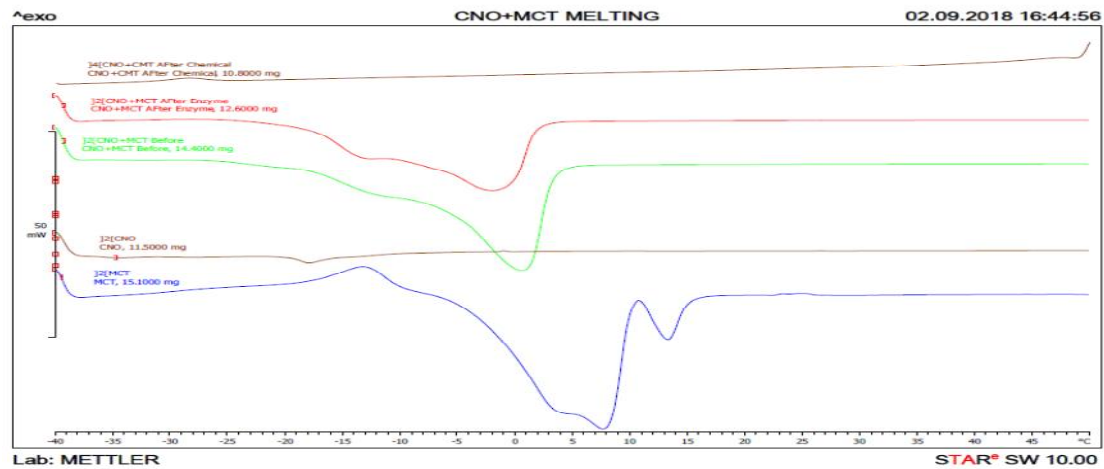


Diagrams 2.10. HPLC chromatogram for tocopherol content in 50:50 MCT-Palm after EIE

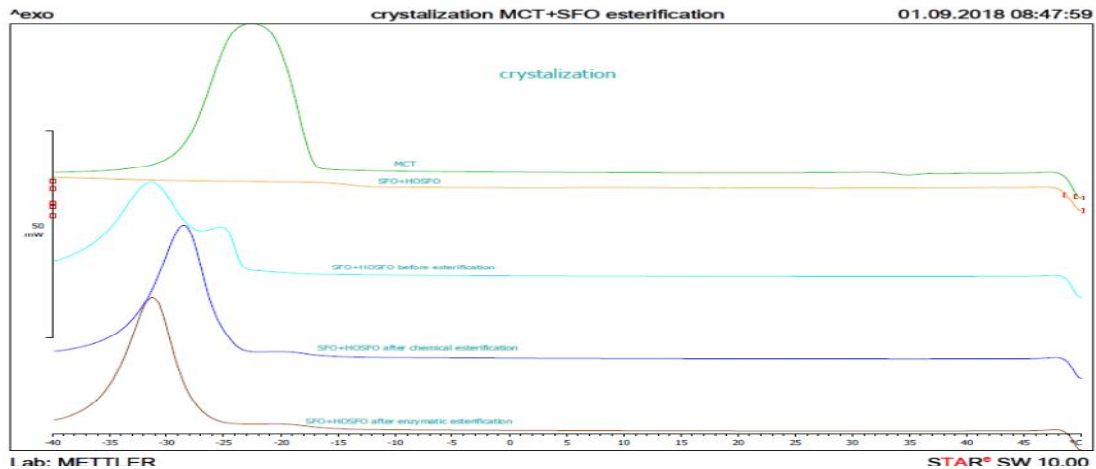
### 1-crystallization behavior of Blend of 50%MCT +50% canola ( CNO) before and after CIE and EIE



### 2-Melting behavior of Blend of 50% MCT +50% canola (CNO) before and after CIE and EIE

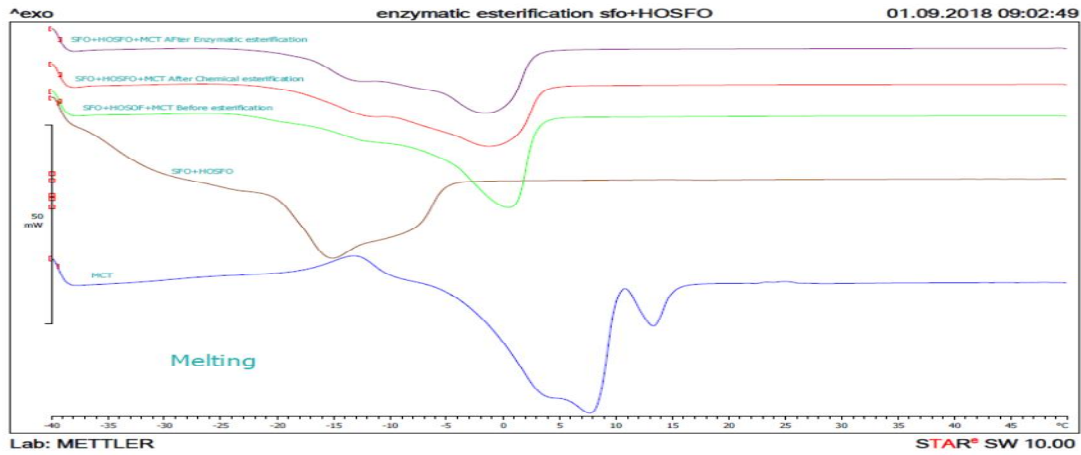


### 3-Crystallization behavior of Blend 50% (SFO/ HOSFO) and 50 % MCT oil before and after CIE and EIE

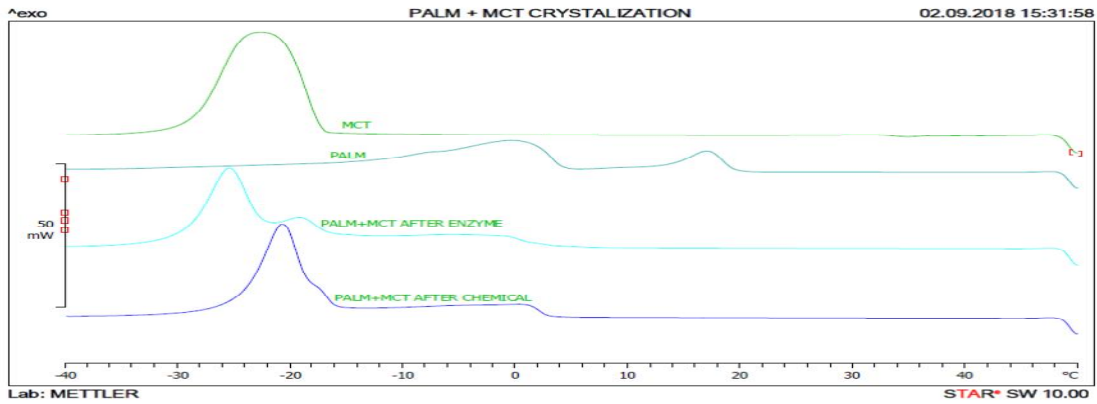




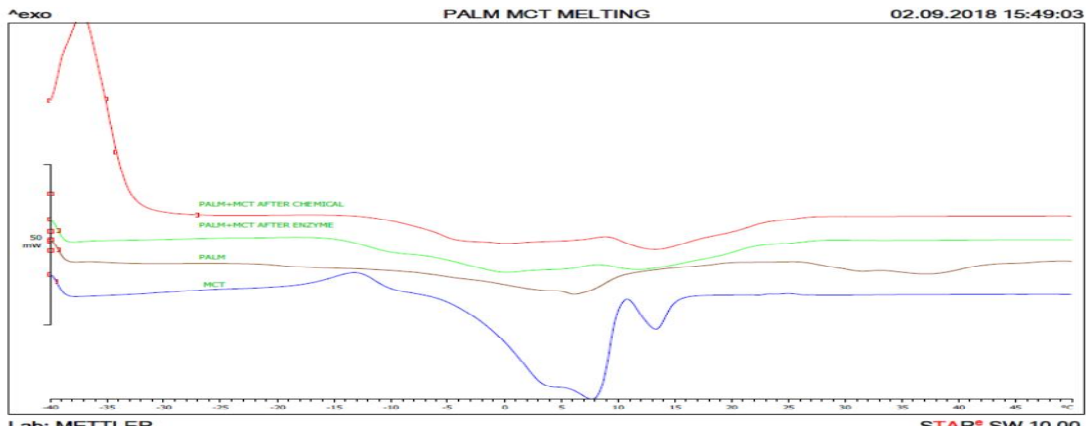
#### 4-Melting behavior of Blend of 50 % (SFO/ HOSFO) and 50 % MCT oil before and after CIE and EIE



#### 5-Crystallization behavior of Blend of 50% MCT oil +50% palm oil ( PO ) before and after CIE and EIE



#### 6-Melting behavior of Blend of 50% MCT oil +50% palm oil ( PO ) before and after CIE and EIE



Diagrams 3. DSC diagrams of MCT -LCT oil blends before and after CIE&EIE

The triacylglycerols profile of structured MLCT oil is divided into three categories, MLM, MML, LMM, MLL, and LLM. Medium-long-medium (MLM) structured lipids typically contain.

Medium-chain fatty acids (C6- C12) at sn-1,3 and long-chain fatty acids (C14-C24) at sn-2 positions. An MCFA that is located at sn-1,3 position is easily hydrolyzed by the lipase, shown by a higher possibility to be absorbed than any LCFA (Mu H, Porsgaard T- 2005. [21], Holm R, Porter CJH-2003 [22], Michalski MC-2013 [23].

Structured lipids containing combinations of LCFA at sn-2 and MCFAs at the sn-1,3 position, so-called medium-long-medium (MLM) TAG, will provide lipids with high coefficient absorption [14,15]. It has been reported that MLM structured lipids have a low caloric value, and can be used to control obesity, fat malabsorption, and other metabolic disorders. Osborn HT et al. 2002 [24]. Lee YY et al 2012 [25]; Lee YY et al. 2018 [26]. However, an MLM lipid is rarely found in nature in a high concentration, therefore, there is a need for developing its preparation.

The MMM yield should be kept at a very low level as MMM has a high foaming tendency and lower smoke point. In this study, The MMM yield was reduced by 50% (from 4 to 2 %) than non-structured LCT/MCT blends by doing the CIE or EIE for the blend of 50%Super Olein+30% Capric / Caprylic.

MCT+20%HOSFO to produce structured MLCT oils from those MCT/LCT blends. So the structured oils have better heat stress stability with lesser foaming, oxidation and so can serve for multipurpose food and cooking applications.

-However, in this study, MLM content in the EIE Blend 50%Super Olein+30%MCT+20%HOSFO was higher than CIE for the same blend. MLM content in lab CIE unit was 13.6 % its content in enzymatic.

Inter-esterified blend produced in pilot PBR EIE unit was 23.9 %. The reason behind higher MLM content in the EIE blend compared to CIE is due to the enzyme used in the EIE reaction which is Lipozyme TL IM, which is a 1,3-specific lipase. So it re-distributes that MCFAs on carbon numbers 1,3 on triglyceride backbone selectively while keeps the LCFAs in Carbon 2 unaffected, so favor the formation of MLM triglycerides.

The other medium long-chain triglycerides (MCTs) of types MLL, MML , LMM, etc... were

also produced during the interesterification and represent and its yields were 20.1 % and 31% for enzymatic and chemical interesterification reactions respectively. Its role in the health benefits of structured MLCT oils is less important than MLM and may be attributed mainly due to its content of MCFAs in its triglyceride composition.

The major TAG species occurring before the enzymatic reaction were CCC, CCCa, CCaCa from caprylic/capric MCT oil TAG, and OLnL, LLO, PLL, LLS/PLO from LCT oils (Canola, SFO/HOSFO, Canola and Palm oil), which is consistent with the fatty acid compositions (Table,9). The results show that 8:0 and 10:0 (from caprylic/capric MCT oil ) has been successfully inter-esterified into super olein and HOSFO forming mixed LCT with 16:0, 18:0, 18:1, 18:2, and 18:3.

#### **4-Tocopherol content of MCT/LCT blends and MLCT structured oils produced:**

The impact of the conversion process including chemical and enzymatic interesterification on the residual natural tocopherol content of common LCT oils as refined Canola oil, palm oil , Sunflower / high oleic sunflower oil to produce structured MLCT oil have been analyzed using HPLC .

HPLC chromatograms for the tocopherol analysis for the MCT oil, Canola, HOSFO/SFO blend, Palm Oil before and after chemical and enzymatic interesterification.

The following are the tocopherol content analysis by HLC for the studied oil blends:

- (1) 50:50 blend of SFO/HOSF,
- (2) Canola oil (CNO).
- (3) MCT oil.
- (4) Palm oil.
- (5) 50:50 MCT - HOSFO+SFO after CIE.
- (6) 50:50 MCT - HOSFO+SFO after EIE.
- (7) 50:50 MCT -Canola (CNO)-after CIE.
- (8) 50:50 MCT -Canola (CNO)-after EIE.
- (9) 50:50 MCT-Palm after CIE.
- (10) 50:50 MCT-Palm after EIE.

Results of the tocopherols analysis for different blends before and after EIE and CIE are shown in Table 12.

#### **HPLC chromatograms are shown in Diagrams set no. 2**

The results show that chemical interesterification reaction destroys much of the tocopherol content

in the oil. The total tocopherol content in HOSF/SFO 50:50 blend was 350.4 ppm while after chemical. interesterification (CIE) reduced to 121.6 ppm, however the tocopherol content in the enzymatic interesterification (EIE) was 198.1 ppm which is higher than CIE but still part of tocopherol content has been reduced and destroyed during the EIE reaction. This is due to the EIE process is milder in reaction. Conditions as the reactions takes place @ 70 C in presence of Lipase enzyme compared to CIE which needs heating to 120 C in presence of sodium methoxide. This favors the EIE process to produce structured MLCT oil over CIE.

The same is applicable for other blends between MCT oil which is nearly free from any natural Tocopherol (as it is synthetic MCT), and other LCT oils included in the study which is refined Palm oil, Canola oil, HOSFO/SFO 50:50, (Table 12).

For Ex. 50:50 blend MCT -palm oil, total tocopherol content was 211 ppm, however, CIE was down to 137 ppm, and after EIE was down to 167 ppm.

This reflects that the produced structured MLCT oil by any of the two techniques will lack oxidation stability and needs to be fortified by adding an external antioxidant system either from the same natural type (tocopherol) or synthetic types like TBHQ or BHA/BHT or propyl Gallate or natural identical like ascorbic palmitate (vitamin C palmitate). However Enzymatic interesterification method is more mild that does not destroy the majority of natural antioxidant as tocopherol compared to chemical interesterification method.

The addition of natural or synthetic antioxidants to bring up the anti-oxidative strength of MLCT oil blends against thermal oxidation (Koh et al., 2009) [8]. Or to blend the refined MLCT oil was blended with another LCT oil, either palm olein or soybean to have at least 12% MCFA in MLCT oil blends as per Kasai's study (2003) [27].

#### **5-Oxidation stability study (OSI analysis by Rancimat):**

The Rancimat induction period, free fatty acid content, anisidine value, E1% 1cm at 232 and 268nm can be used as oil quality parameters to indicate the oxidation stability of any oil during heat stress applications as well as refer to the expected degree of oil deterioration against

frying periods. Also, the change in saturated fatty acids/unsaturated fatty acids (SFA/USFA) ratio cross frying days indicated good thermal-oxidative stability of palm-based MLCT oil. Palm-based MLCT oils have inherently higher levels of polar of the medium- and long-chain triacylglycerols structure and also the presence of partial glycerides (Shimizu et al., 2004) [28]. The ratio of total polar compounds is not a good quality indicator for the palm-based MLCT oil since many European countries have established a regularity limit of total polar compounds of 25 – 27% as the discard point for frying oil (Mellema 2003 [29]; Sanibel and Mancini-Filho, [30].

Nevertheless, we considered in our study the free fatty acid (FFA) for hydrolytic stability, peroxide value (PV) for lipid hydroperoxides generated through primary oxidation, para Anisidine value (p-A.V.) for secondary oxidation, oxidation stability index (OSI) by Rancimat stability @ 110C.

The CIE and EIE of MCT/LCT blends showed a big reduction in the OSI of the same blends before interesterification.

The results of the analysis of the above parameters for individual oils, non-structured MCT/LCT blends, and structured MLCT oils prepared by chemical and enzymatic interesterification are shown in Table 11.

Soo Peng Koh et al. [9] concluded that the addition of a natural or synthetic antioxidant to both palm- and soybean based MLCT blends, showed better oxidative stability, both natural and synthetic antioxidants showed similar antioxidative strength, except for TBHQ-added MLCT blends, which had a significantly ( $P < 0.05$ ) higher oxidative stability in both palms- and soybean-based MLCT blends.

Accordingly, in this study, the TBHQ @ 200 ppm was added to non-structured MCT/LCT blends as well as the structured MLCT oils produced by EIE and CIE.

The induction period showed improved oxidation stability for the MLCT blends with TBHQ compared to without as shown in **Tables 10**. This improved induction period results by the effect of added.

Antioxidants improve the heat stability of MLCT oils to make them suitable for high-temperature.

Applications such as cooking oil or shallow - frying operation.

### 6-Smoke point analysis:

Smoke point is an important characteristic in deciding the suitability of any oil for a heat stress application like deep or shallow frying or cooking. The smoke points depends almost entirely on free fatty acid content and the molecular weight of the fatty acids. A comparison of the smoke point of individual MCT & LCT oils used in the study, as well as the non-structured. MCT/LCT, blends before interesterification and finally, the structured MLCT oil formed from CIE and EIE are shown in Table 11. Capric/Caprylic MCT oil is the lowest smoke points oil below 150 C due to distinctive fatty acid composition containing the majority content are short-chain medium-chain triglycerides, (C8, C10, C12). However, the LCT oils used in the study are palm olein, palm oil, canola oil, sunflower oil, high oleic sunflower (HOSFO), all having a much higher smoke point above 210 C due to the long-chain fatty acid composition which is composing these oils. As MLCT oil prepared in this study contained both medium- and long-chain fatty acids in the same triacylglycerol, it has a much lower smoke point value below 180 °C which is the frying temperature, as opposed to palm olein or soybean oil, which is made up of 1 kg kg<sup>-1</sup> long-chain triacylglycerols. So in this study, the structured MLCT oils produced from Capric / Caprylic MCT oils are not suitable for frying application but suitable for less heat stress applications like cooking, baking, and cold applications like salad dressing. Nevertheless, the non-structured MCT /LCT blended oils prepared in this study showed a higher smoke point of more 180 °C which is the common frying temperature, while pure Capric / caprylic MCT oil showed (143°C) and the structured MLCT oil prepared by enzymatic interesterification in this study showed a smoke point of (150-160 °C). This enables this non-structured MCT/LCT oil blend to be suitable for deep-frying applications in addition to cooking and cold applications better than structured MLCT.

To solve the problem of low smoke point of structured MLCT oil we had to follow, Soo Peng Koh et al. [9] recommendations to blend MLCT oil with LCT oil as palm olein or soybean oil. This blending will impact a cost reduction for producing this healthy cooking oil by focusing on the production of concentrated medium- and long-chain triacylglycerols that can be used to

blend with various oils to widen the application range. The second purpose is to increase the smoke point and oxidative stability of the final products by blending MLCT oil.

As expected, the smoke point of palm-based MLCT blends with LCT oil decreased gradually from 225 to 218°C when the amount of MLCT oil in the blends increased from 500 to 800 g kg<sup>-1</sup>. The same phenomenon was observed for soybean-based MLCT blends, whereby smoke point decreased from 229 to 219 °C for the same blending composition.

So to get a multipurpose cooking application of structured MLCT oil while achieving the health effect of less fat accumulation and use in lesser calories diet applications, it has to be blended at different ratios either with palm olein or soybean oil to increase its smoke point and heat stability in heat stress applications.

But for cold food applications like salad dressing and maybe mild hot applications like normal cooking the structured MLCT oils prepared in this study are recommended for healthy cooking applications without blending as the normal cooking temperature is about 100 C which is much lower than smoke point of pure structured MLCT oil prepared which is (150-160 °C).

### 6-Thermal profile of structured and non-structured lipid product:

Differential scanning calorimeter (DSC) is commonly used to evaluate the thermal behavior of oils. The DSC curves of the substrate mixture before and after chemical and enzymatic interesterification between Capric/Caprylic MCT TAG substrates and different LCT oils at different mix ratios (super olein & HOSFO & SFO/HOSFO blend & Canola, palm oil) are shown in Diagrams set no. 3.

These diagrams include groups of the DSC diagrams that were studied by Mettler Toledo DSC equipment.

MCT /LCT oil blends before and after chemical and enzymatic interesterification for MLCT structured oils based on capric/ Caprylic MCT oil as follow:

1-crystallization behavior of Blend of 50%MCT +50% canola (CNO) before and after CIE and EIE.

2-Melting behavior of Blend of 50% MCT +50% canola (CNO) before and after CIE and EIE.

3-crystallization behavior of Blend of 50% MCT +50% (SFO/HOSF) before and after CIE and EIE.

4-Melting behavior of Blend of 50% MCT +50% (SFO/HOSF) before and after CIE and EIE.

5-crystallization behavior of Blend of 50% MCT +50% palm oil (PO) before and after CIE and EIE.

6-Melting behavior of Blend of 50% MCT oil +50% palm oil (PO) before and after CIE and EIE.

Although the physical properties did not change greatly after chemical or enzymatic interesterification, however, the crystallization and melting profile were altered. The substrate mixture before interesterification had more than one primary crystallization peak, however, after interesterification, it has one sharp crystallization peak. A higher crystallization temperature was observed for the substrate after interesterification compared to before interesterification. The Onset crystallization temperature of the chemical interstratified substrate based MLCT oil was higher than enzymatic inter-esterified substrates.

The melting temperature behavior of the substrate of non-inter-esterified substrate showed a slightly higher. Onset melting temperature with a sharper melting point than the inter-esterified substrate.

The substrate mixture before interesterification had one primary crystallization peak. The melting temperature of the inter-esterified 50% MCT +50% canola blend was slightly increased from  $-(-0.5-(-1))^{\circ}\text{C}$  to  $(0-0.5)^{\circ}\text{C}$ . Same for the blend of 50 % (SFO/ HOSFO ) and 50 % MCT oil.

However, the melting curves for 50:50 palm: MCT blends gave non-sharp melting points for both inter- esterified and non-inter-esterified substrates blends. According to Zhen Zhang et al (2020) [14], the increase in the onset crystallization temperature of inter-esterified MCT/LCT substrate (from  $-30.06^{\circ}\text{C}$  to  $-27.67^{\circ}\text{C}$ ) and widening of the melting range after enzymatic interesterification likely reflect the change of acylglycerol composition and profile of TAG species According to Wang et al., 2016 [31], TAG hydrolysis occurred as a side-reaction during enzymatic transesterification observed by the formation of MAG (2.93%) and DAG (8.61%).

DAG also has a higher melting temperature and will be more likely to occur in the solid-state than the corresponding TAG of the same fatty acids (Wang et al., 2010), which may explain the higher melting.

Temperature after interesterification. Hence, the inter-esterification process altered the positions of the fatty acids on the glycerol backbones, and hence the triglyceride composition of fat which caused the change of crystallization and melting properties of inter-esterified fat.

## 7. CONCLUSION

The study concluded that the usage of dietetic Capric/ caprylic synthetic MCT oil for multipurpose cooking applications including heart stress applications like shallow or deep frying is not suitable.

The reason is the MCT oil has a low smoking point (about  $140^{\circ}\text{C}$ ), which make it easily foams, spatter and heavily smoke during frying, This is an addition its very high cost for its sourcing due to multiple process which h it goes through to produce it from natural oils rich in medium chain fatty acids (MCFAs) which make it very expensive compared to classical edible oils.

Medium-long-chain (MLCT) structured lipids have great potential as functional ingredients in food and nutraceutical products. In his study, capric / caprylic MCT was used as a source for MCFAs in the interesterification reaction for preparing non-structured MCT/LCT oil blends and structured MLCT oil with different long-chain triglycerides oils (Canola, HOSFO/SFO, Palm oil, DFOlein). The study concluded that non-structured MCT/LCT oil produced by physical blending between caprylic/caprylic MCT oil blended oils with above LCT oils at different ratios shows a higher smoke point finished which is suitable for heat stress applications like cooking and frying than structured MLCT oils produced by EIE or CIE of same blends. However, structured MLCT oils can be improved their smoke points by blending with other LCT oils like palm olein and soybean oil @ different ratios depending on targeted smoke points and healthier MLCT ratio targeted. The interesterification (chemical or enzymatic) reaction was found to reduces the smoke point of the MCT/LCT blend with a higher reduction in EIE than CIE. The triglyceride composition analysis done in the study confirmed that

interesterification is an important process to distribute Caprylic & Capric medium-chain fatty acids MCT oils in triglyceride backbone in the MLCT structured oil. DSC Results confirm that the interesterification process is important to improve the cloudiness of MCT blends. The structured MLCT oils [produced by CIE or EIE have a much lower OSI value measured by Rancimate @110 C compared to its related non structure MCT/LCT blended oils. The induction period(OSI value) gave much improved \ results by the effect of added antioxidant synthetic antioxidants @200 ppm TBHQ which improved the heat stability of MLCT structured oils. The results show that chemical interesterification is destroying much of the tocopherol content in the oil, while the residual tocopherol content in MLCT produced from the enzymatic interesterification (EIE) is higher than that from chemical interesterifications (CIE). So the produced structured MLCT oil by any of the two techniques will lack oxidation stability and needs to be fortified by adding an external antioxidant system either from the same natural type (tocopherol ) or synthetic types like TBHQ or BHA/BHT or propyl Gallate or natural identical like ascorbic palmitate (vitamin C palmitate).

A pilot-scale packed bed reactor (PBR)based system was used successfully for Enzymatic production of MLCT at the optimal conditions recommended by Zhen Zhang et al 2000.

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## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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