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Fatty Acid Profile Optimization in Edible Oil Blend Through Linear Programming

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Linear programming as versatile optimization tool could successfully be applied to engineer the properties of oil in order to improve the quality aspects respecting the multiple linear constraints variables. Spreadsheets based software with the solver function may successfully be used to solve the purpose. The possibility to obtain the desired ratio of saturated, mono unsaturated and poly unsaturated fatty acid ratio with the optimal range of omega-6 (ω-6) to omega-3 (ω-6) fatty acid ratio having minimal cost in oil blend was assessed. Palm oil, rice bran oil, linseed oil and sunflower oil were used to develop the model oil blend to confirm the ideal fatty acid ratio as laid down by health agencies. Blending of oil has altered the fatty acids composition of saturated fatty acid, mono unsaturated fatty acid and poly unsaturated fatty acid to a desired level and thus resulted in a significant change in physico-chemical characteristics. As the developed model oil has an optimal combination of fatty acids with an appropriate ratio of ω-6:ω-3 fatty acids, makes it healthier alternative.

Keywords: Fatty acids, Fatty acid profile, Linear programming, Oil, Oil blending.

INTRODUCTION

It is well recognized that the incidence of chronic disorders is escalating in India and fat consumption trends play a prominent role in obesity and related disorders, including type II diabetes, hypertension, cardiovascular diseases, non-alcoholic fatty liver disease, obstructive sleep apnea, gastro-esophageal reflux disease, musculoskeletal disorders, a variety of cancers and a number of psychosocial concerns[1,2]. Functional role of fat as one of the major macro nutrient in the diet is manifold. It is a most concentrated source of energy. It helps in increased absorption and mobilization of lipid-soluble vitamins (A, D, E and K) and antioxidants (α-tocopherol, β-carotene and lycopene). Fat and oil in the diet fulfills the major calorific requirements and needs of essential fatty acids in body, which regulate body functions such as heart rate, blood pressure, blood viscosity, muscle contraction, pain relief, blood clotting, mail fertility, female conception and play a role in immune function by regulating inflammation and encouraging the body to fight infection[3,4]. Associated with subcutaneous tissues it serves as thermal insulator and being non polar act as electrical insulators allowing rapid propagation of depolarization waves along myelinated nerves[5]. Fatty acids that occur in nature usually contains even number of carbon atoms as synthesized from 2-carbon unit and straight chain derivatives. The dietary fat formed from the chain may be saturated having no double bond or unsaturated having one or more double bonds. The quality and quantity of dietary fat thus play an important role in either providing a healthy system or metabolic disorders leading to coronary heart disease , obesity and cancer[6]. Reduction in the dietary intake of total fat with a limited amount of saturated fatty acid and polyunsaturated fatty acid has been suggested. The Indian Council of Medical Research and American Heart Association (AHA) recommended that best possible health benefits can be attained by consuming equal proportions of saturated fatty acid, mono unsaturated fatty acid and poly unsaturated fatty acid[3,7-10] with the consumption of total fat should not exceed 30 % of total calories[11]. The low level of linoleic acid (ω-6) and virtual absence of linolenic acid (ω-3) make the oil relatively stable to oxidative deterioration[12] but higher levels of saturated fatty acid raises the oxidative stress, levels of serum total cholesterol[13] and low density lipoprotein cholesterol (LDL-C) responsible for increased risk of artherosclerosis (hardening of arteries) and cardio vascular disease. Replacing saturated fatty acid (palm oil) with unsaturated essential fatty acids comprised of linoleic acid (poly unsaturated fatty acid) and linolenic acid (poly unsaturated fatty acid) through sunflower oil and linseed oil, respectively may linked to lower the serum LDL-C and decrease the chance of cardio vascular disease and arthritis[14]. But at the same time higher level of poly unsaturated fatty acid intake could also lead to impaired antioxidant system in body and thereby enhance the risk of cancer.

The World health organization (WHO) recommends an ideal intake a ratio of poly unsaturated fatty acid to saturated fatty acid as 0.8 to 1 and ω-6 to ω-3 fatty acids as 5 to 10[15,16]. The imbalance ratio of ω-6/ω-3 fatty acids and deficiency of essential fatty acid is linked with serious health conditions, such as accelerated aging, arthritis, asthma, cancer, cardio vascular disease, depression, diabetes, obesity and stroke[4]. The unsaponifiable ingredient such as oryzanol, a family of ferulic acid esters or triterpene alcohols and plant sterols associated with physically refined rice bran oil has plasma lipid and cholesterol lowering ability by creating interference in the absorption of cholesterol with the increased fecal excretion of bile acids[11].

None of the known edible oil alone provides the balanced composition of saturated and unsaturated fatty acid (Table-1); therefore adhering to particular single oil for long term use must be avoided or a combination or blend of oils may be preferential for dietary usage. The oil blending is the physical mixture of two or more oils a potential alternative as model oil with balanced fatty acids profile. Presently, the oil blending process is gaining popularity worldwide mainly due to improvement in nutritional benefits, thermal and oxidative stability[17,18].

Product optimization is controlled and systematic approach for the development of best formulation under available situation. Linear programming, a mathematical optimization technique is more often used in process and product optimization[19]. It uses objective function, decision variables and constraints as the three major components in defining and solving the optimization problem. Objective function is usually applied to formulate the ingredients amount as per the decision variables either for cost minimization or for maximization of nutritional attributes in order to achieve profit maximization and constraints control the possible solutions by defining criteria that all solutions must meet in food formulations[20-22]. Linear programming approach was applied in the present investigation to develop and characterize the cost effective model oil blend from the use of palm oil, rice bran, sunflower and linseed oils.

EXPERIMENTAL

All chemicals and reagents used were either of analytical reagent or high-performance liquid chromatography (HPLC) grades of Himedia Laboratories Pvt. Ltd. (Mumbai, India) or Sigma-Aldrich Chemical Company, st. Louis, MO, USA.

Oil and model oil blend samples: Refined, bleached, deodorized palm oil, sunflower oil and linseed oil with physically refined rice bran oil samples were procured from the departmental store, Ludhiana (Table-2). The oil samples were transferred in amber colored glass bottles and kept in the refrigerator at 4 °C. Before the experimentation the required oil samples were transferred to another glass jars and allowed to stand for at least 0.5 h outside the refrigerator for thermal equilibration to ambient temperature. Model oil blend was prepared by using the optimum proportion of oils acquired through linear programming as 48.7 % palm oil, 24.4 % rice bran oil, 21 % sunflower oil and 5.9 % linseed oil to get desired ration of saturated fatty acid, mono unsaturated fatty acid and poly unsaturated fatty acid. The model oil blend was stirred at 40 °C for 1 h using a magnetic stirrer prior to initial analysis.

TABLE-2
DIFFERENT TYPES OF OILS AND THEIR SOURCE

Sr. No.	Oil name	Source
1	Palm oil	Vijaya enterprises, Mumbai, Maharashtra, India
2	Rice bran oil	Vijaya enterprises, Mumbai, Maharashtra, India
3	Sunflower oil	Tara health foods limited, Sangrur, Punjab, India
4	Flaxseed oil	Chem Tech Industries Private Limited, Ahmedpur, Maharashtra , India

Linear programming: Linear programming is a technique that minimizes a linear function of a set of variables with respecting the multiple linear constraints on selected variables. The proposed linear programming formulation was developed in Microsoft Excel 2007 as illustrated in Tables-3 and 4 using

TABLE-1
TYPICAL RANGE OF FATTY ACID COMPOSITION (%) OF MAJOR EDIBLE OILS

	C 14:0 (Myristic)	C 16:0 (Palmitic)	C 18:0 (Stearic)	C 18:1 (Oleic)	C 18:2 (Linoleic)	C 18:3 (Linolenic)	References
Almond oil	-	4-9	1.1-3	60-80	16.3-30	-	27,28
Canola oil	< 0.2	2.5-6	0.9-2.1	50-66	18-30	6-14	29,30
Coconut oil	16.8-19.2	7.7-9.7	2.3-3.2	5.4-7.4	1.3-2.1	-	31-33
Corn oil	< 0.1	8-19	0.5-4	19-50	34-62	0.1-2	29,31,34
Cottonseed oil	0.6-1	21.4-26.4	2.1-3.3	14.7-21.7	46.7-58.2	0-1	31,32,35
Flaxseed oil	0.5-0.8	4-7.7	2-4.4	12-34	17.4-24	35-60	36,37
Mustard oil	-	2.7-6.1	0.4-3.5	9.6-81.5	5.2-45.5	1.8-14.8	36,38
Niger seed Oil	-	4-18.9	0.3-10	11-40	7-18	45-63	39,40
Olive oil	< 0.1	7.5-20	0.5-5	55-83	3.5-21	<0.9	29,31,41
Palm oil	0.9-1.5	41.8-46.8	4.5-5.1	37.3-40.8	9.1-11	0.4-0.6	42,43
Peanut oil	< 0.1	8.3-14	1.9-4.4	36.4-67.1	14-43	<0.1	31,32,44,45
Rice bran oil	0.4-1	12-25.5	0.9-3	37.4-50	29-42	0.5-1.1	6,46,47,48
Safflower oil	< 0.4	4-7.7	1-4.9	12-24.7	62.4-79	<0.4	31,49,50
Sesame oil	< 0.5	7-17	3.5-6	35- 50	35-50	<1	27,36
Soybean oil	< 0.2	8-13.3	2.4-5.4	17.7-26.1	49.8-57.1	5.5-9.5	31,49,51
Sunflower oil	< 0.2	5.6-7.6	2.7-6.5	14-39.4	48.3-74	<0.2	29,30,31

solver option and was applied to meet the constraints of achieving desired fatty acids composition and essential fatty acids ratio (ω-6 to ω-3) in the range of 5-10 using palm oil (X_1), rice bran oil (X_2), linseed oil (X_3) and sunflower oil (X_4) with market price of oil. The linear function to be minimized in this case is the cost of model oil blend, as expressed mathematically below:

$$\text{Cost of model oil blend} = X_1C_1 + X_2C_2 + X_3C_3 + X_4C_4 \quad (1)$$

where, C_1, C_2, C_3 and C_4 are the cost ratio (Rs. per unit) of the palm oil (X_1), rice bran oil (X_2), linseed oil (X_3) and sunflower oil (X_4), respectively. The provided constraints that must be satisfied with the objective function for cost minimization[23] of model oil blend. Mathematically all the constraint terms have been expressed by a set of inequalities. All these formulated constraints are linear in nature as they consist of a simple sum of products having inequality operators (Table-3).

Fatty acid profile: The fatty acids composition of different oil and model oil blend was estimated using agilent gas chromatograph fitted with a DB-225 polar column (30 m, 0.322 mm, 0.25 μ) and flame ion detector (FID) was used for the analysis of fatty acid composition of four different oils and the developed model oil blend. The oil (20-25 mg) was treated with 0.55 sodium methoxide solution (5 mL) in a glass stopper flask. The content was heated to around 50 °C for 10-15 min and then glacial acetic acid (0.1 mL) was added followed by water (5-10 mL). The organic phase was extracted with hexane (15 -20 mL) and washed with water till neutral pH. The hexane extract was dried over anhydrous sodium sulphate and concentrated under reduced pressure to get the methyl ester. The temperature of oven, injectors and detector blocks were maintained at 210, 230 and 250 °C respectively. Nitrogen was used as the carrier gas. Peaks were identified by comparison with relative retention times of the standard fatty acid methyl esters (FAMEs). Concentration of each fatty acid was recorded by normalization of peak areas using gas chromatograph post run analysis software, manual integration and reported as % of the particular fatty acid.

Physico-chemical characteristics: The viscosity of oils and model oil blend was measured at 33 ºC using bench top brookfield viscometer installed with the programmable temperature controller model 106 and thermosel. The refractive index of oil samples was determined using abbe's refractometer. Peroxide value was determined following the standard method of Association of official analytical chemist[24]. 0.50 g sample in a conical flask, 30 mL of the acetic acid and chloroform (mixture 2:3) were added to it followed by 0.5 mL of a saturated potassium iodide solution. Kept on a rotary shaker for 1 min and then 30 mL of distilled water were added to it. It was then titrated with a 0.01 M $Na_2S_2O_3$ solution with vigorous shaking until the disappearance of the yellow color, 0.5 ml of 1 % starch indicator was added and titration continued till until the blue color had just disappeared. Iodine value (IV) as the measure of the degree of unsaturation of fat was determined using Wijs method[24]. The sample was taken nearest to 0.001 g according to its IV and was dissolved in 15 mL acetic acid and cyclohexane solution (3:2 v/v), 25 mL of Wijs solution was added and kept undisturbed in the dark following the IV scale, after that time sample was kept in uncovered beakers at room temperature during this time. Saponification value (SV) was determined by the AOAC official Method[24]. N/10 KOH solution was prepared using 95 % ethyl alcohol and distilled. 5 g of oil sample were weighed in a conical flask, the flask was connected to an air condenser and boiled until the oil was completely saponified, cooled and titrated with 0.5 M HCl using phenolphthalein as indicator until the pink color just disappear.

Statistical analysis: All statistical analyses were performed on triplicate data and the results were expressed as mean ± standard deviation. The data were compared using one-way analysis of variance (ANOVA) using statistical program SPSS Version 16. Statistical differences were represented at 5 % level of significance using Duncan's multiple range test.

RESULTS AND DISCUSSION

Table-4 summarizes the fatty acid composition of palm oil, rice bran oil, sunflower oil and linseed oil determined using gas chromatography. The prominent fatty acids associated as palmitic acid (43.23 %) and oleic acid (40.18 %) with palm oil, oleic acid (38.19 %) and linoleic acid (37.50 %) with rice bran oil, linoleic acid (77.05 %) with sunflower oil while linseed oil has found abundance with linolenic acid (53.09 %). Rice bran oil confirms to have almost equal ratio of mono unsaturated fatty acid and poly unsaturated fatty acid (Fig. 1). None of the edible oil from plant origin has the required equal ratio of SFA:MUFA:PUFA (Table-1). This ratio as found in the fatty acid profiling was 1.5:1.2:0.3 for palm oil, 0.7:1.1:1.2

TABLE-3
LINEAR PROGRAM MATRIX OF OIL BLENDING FORMULATION FOR MINIMIZATION OF COST

Cost minimization	Palm oil (X_1)	Rice bran oil (X_2)	Linseed oil (X_3)	Sunflower oil (X_4)	Optimization constraints	
Cost ratio of oil (Rs.)	0.72	0.96	0.88	0.93		
Subject to						
Saturated fatty acid	0.51	0.23	0.11	0.09	=	33
Mono unsaturated fatty acid	0.4	0.38	0.22	0.14	=	33
Poly unsaturated fatty acid	0.09	0.39	0.67	0.77	=	34
ω–6 fatty acid	0.09	0.375	0.14	0.77	≥	20
ω–3 fatty acid	0	0.015	0.53	0	≥	3
Oil fraction	1	1	1	1	=	100
Rice bran oil (X_2)	0	1	0	0	≥	20.5
Sunflower oil (X_4)	0	0	0	1	≥	21
Optimized level					Cost (Rs.)	
Variable values (%)	48.72	24.44	5.84	21.00	83.21	

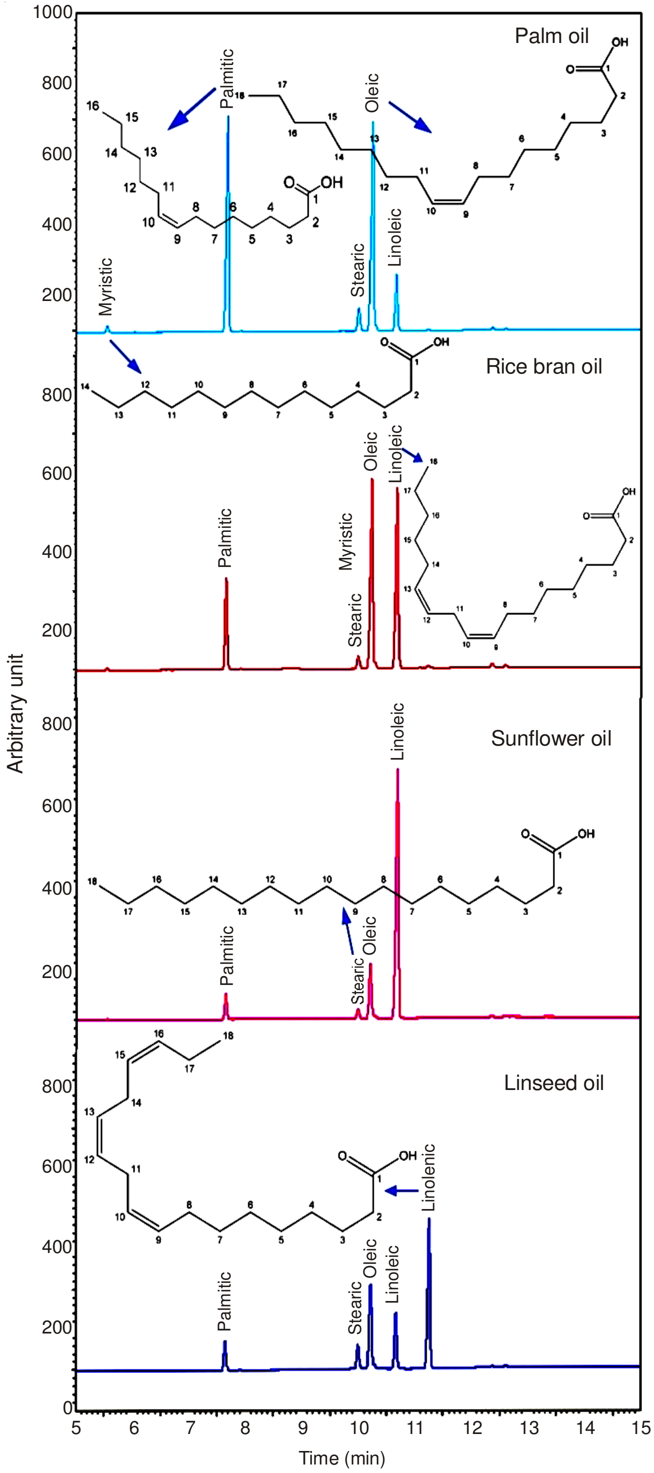

Fig. 1. Gas chromatogram of palm oil, rice bran oil, sunflower oil and linseed oil

for rice bran oil, 0.3:0.7:2 for linseed oil and 0.3:0.4:2.3 for sunflower oil (Table-4), which further confirm non fulfilling the American Heart Association recommendation of equal proportions of SFA:MUFA:PUFA. Further the ω6:ω3 ratio was also not found to be in the desired ratio of 5-10 for the selected oils (Table-4). The oil blend combinations as obtained using linear programming (Table-3) for the desired proportion of SFA:MUFA:PUFA with the ω6:ω3 ratio in the range of 5 to 10 (Fig. 2).

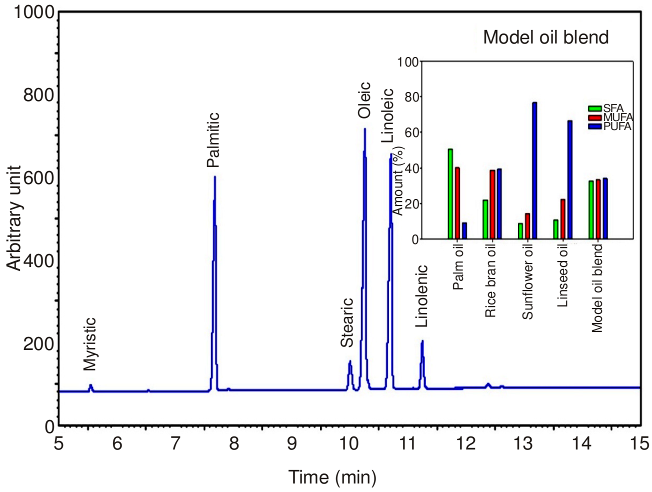

Fig. 2. Gas chromatogram of the oil blend and inset picture - fatty acid compositions

It indicates minor variation in the use of selected oil to get the desired ω6:ω3 ratio, the variations found were 48.65-49.79 % in palm oil, 20.50-24.76 % in rice bran oil, 5.13-10.05 % in linseed oil and 18.23-21.47 % in sunflower oil (Fig. 3) and affected the overall price variations of Rs. 0.55. The balanced amount of fatty acids in model oil blends not only provide the better storage stability of oil but also provide the engineered aspects of multipurpose oil usage with health and nutritional aspects. Thus the model oil blend prepared having recommended fatty acids profile results conformity to Indian Council of Medical Research[7,8] and having appropriate ω6:ω3 fatty acid ratio which might be useful against various ailments being a healthy oil blend.

Physico-chemical characteristics: Table-5 shows the physico-chemical characteristics in terms of viscosity, refractive index, peroxide value, iodine value and saponification value of palm oil, rice bran oil, linseed oil and sunflower oil with their model oil blend. Blending of oils have significantly ($P \leq 0.05$) affected the observed characteristics of oils. The

TABLE-4
FATTY ACID COMPOSITION (%) OF DIFFERENT EDIBLE OILS AND OIL BLEND

Fatty acids	Palm oil	Rice bran oil	Linseed oil	Sunflower oil	Oil blend
C 14:0 (Myristic)	1.03	-	-	-	-
C 16:0 (Palmitic)	43.23	18.92	5.33	6.25	25.95
C 18:0 (Stearic)	6.32	3.89	5.30	2.53	7.04
C 18:1 (Oleic)	40.18	38.19	22.07	14.17	32.96
C 18:2 (Linoleic)	9.24	37.50	14.21	77.05	30.57
C 18:3 (Linolenic)	-	1.50	53.09	-	3.48
SFA:MUFA:PUFA	1.5:1.2:0.3	0.7:1.1:1.2	0.3:0.7:2	0.3:0.4:2.3	1:1:1
Cost (Rs./litre)	72	96	88	93	83.21

TABLE-5
PHYSICO-CHEMICAL CHARACTERISTICS OF DIFFERENT EDIBLE OILS AND OIL BLEND

	Viscosity (cP)	Refractive index	Peroxide value (meq/kg)	Iodine value	Saponification value
Palm oil	79.350 ± 2.833[a]	1.461 ± 0.001[d]	0.403 ± 0.080[e]	60.980 ± 3.052[e]	199.033 ± 0.507[a]
Flaxseed oil	48.147 ± 1.150[c]	1.482 ± 0.001[a]	13.243 ± 1.189[c]	175.630 ± 3.018[a]	192.277 ± 1.197[c]
Sunflower oil	35.820 ± 0.822[e]	1.468 ± 0.001[c]	10.263 ± 0.870[d]	148.500 ± 2.591[b]	196.170 ± 0.316[b]
Rice bran oil	43.120 ± 0.636[d]	1.471 ± 0.001[b]	40.963 ± 2.061[a]	100.130 ± 2.033[d]	191.060 ± 0.728[c]
Oil blend	55.103 ± 1.017[b]	1.472 ± 0.001[b]	17.887 ± 0.924[b]	136.290 ± 1.678[c]	195.137 ± 0.746[b]
SE	0.770	0.001	0.690	1.425	0.437
CD ($p \leq 0.05$)	2.511	0.002	2.251	4.648	1.425
CV (%)	2.550	0.074	7.222	1.986	0.389

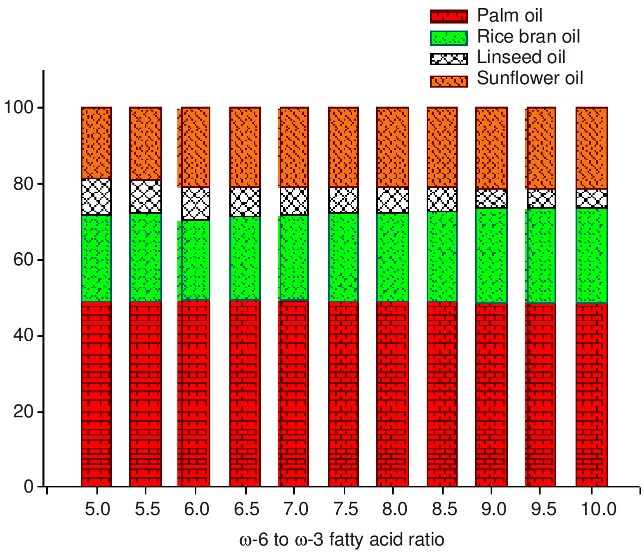

Fig. 3. Amount of edible oil for specific ω-6:ω-3 fatty acid ratio in oil blend

results obtained were found similar to previous finding that viscosity decreased with increased in poly unsaturated fatty acid[25] having direct relationship with the quality and stability of foods. The refractive index of the oils ranges 1.461 to 1.482.

The peroxide values of the oils are significantly different and varied from 0.403 to 40.963 meq/kg, while model oil blend found to have peroxide value of 17.887 meq/kg. The iodine value of oil blend is 136.29, the increase was due to an increase in the predominance of mono unsaturated fatty acid and poly unsaturated fatty acid in model oil blend used as measure the oil quality[26]. The saponification value of the respective oils and the model oil blend ranges from 191.06 to 199.03 and having a significant difference ($P \leq 0.05$). The observed properties of the model oil blend resulted in the intermediate values to the selected oils (Table-5).

Linear programming could result in a best possible combination under the applied constraints in order to get model oil blend of appropriate fatty acids composition and desired level of ω6:ω3 fatty acid ratio. Linear programming could also be successfully used to fulfill the demand of desired physico-chemical characteristics of fat and fat products suitable for food and allied industries to achieve desired nutritional and functional characteristics. The study leads to the conclusion that not only the quantity and the availability oil may be considered for the edible use but the proportion of fatty acids are critical to be decided for the types of oil to be used. The developed model oil blend thus can be the potential fat alternative in human diet in order to maintain the healthy body.

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