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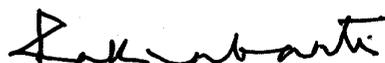
RP Singh

From Editor's Desk



A large number of countries from different corners of the globe have come up with very ambitious biofuel programmes and most of these programmes have economic incentive driven policies attached to it. It is obvious that the biofuel demand will grow tremendously if the decision makers of these countries stick to their mandates very seriously. Biodiesel is also an integral part of this biofuel programmes and biodiesel production will also be revived. Though some European countries are seriously thinking to re-orient themselves towards bioethanol production because of higher energy contents of ethanol crops compared to that of biodiesel crops, the European Union still continues to be the major biodiesel producer. China is also focusing on biofuel programmes with well defined growth plan. India, though, fell behind the planned schedule, is also looking forward with renewed interests. Indian Railways is seriously thinking of replacing around 5% of their diesel consumption with bio-diesel. Similarly, many state-owned transport agencies are also looking forward to add 5% biodiesel into the diesel fuel they use. The major hurdle will be the non-availability of the raw materials. The jatropha crop did not have the predicted yield and the farmers did not receive expected returns. Karanja was also not cultivated and collected in an organized manner. No other crop was persuaded as a potential alternative and the biodiesel programme in India did not experience any growth. However, with the changed circumstances, the biodiesel producers have to chalk out a strategic plan to match the demand of biodiesel in near future. Like many other countries, India can also make biodiesel from different palm oil fractions. However, since India is producing only a very little fraction of the total consumption of palm oil, it has to depend on imports. This will lead to a situation where the import of crude petroleum oil would be replaced with import of oil palm. The economics and the environmental benefits are to be calculated and a long term policy has to be derived for revival of biodiesel programme.

Happy reading!!



(PRADOSH PRASAD CHAKRABARTI)

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Optimization of Aqueous Enzymatic Extraction of Virgin Coconut Oil through Coconut Milk

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ABSTRACT

The aim of the present work was to optimize the simultaneous extraction of milk and oil from coconut by means of aqueous enzymatic extraction process using the commercial enzyme Viscozyme-L. To this purpose, the combine effect of grinding time (2- 4 min), amount of Viscozyme-L enzyme [60-180 FBGU (Fungal β -Glucanase Units)] and incubation time (2-7 h), were optimized using Response Surface Methodology. The study showed that the method can produce best yield of coconut milk ($73.88 \pm 0.5\%$, w/w) and virgin coconut oil (VCO) ($21.57 \pm 0.4\%$, w/w) 86.14% of fat present in fresh coconut kernel could be recovered by using grinding time (3 min), amount of enzyme (120 FBGU) and incubation time (4.5 h). The experimental results were significantly ($P < 0.05$) comparable with the predicted yield of coconut milk (73.33%) and coconut oil (21.12%). These results were confirmed by validation model that performed within the selected ranges of variable, microscopic image of cell wall and particle distribution in coconut milk. The results suggested that the use of Viscozyme-L could enhance the extraction of oil with quality.

KEYWORDS: *Aqueous enzymatic extraction, Optimization, Virgin coconut oil, Coconut milk, Viscozyme-L*

INTRODUCTION

In the present trend of focusing on the enhanced functional properties of foods in food industry, commercialization of the extraction methods that could sustain the nutritional, functional and sensory characteristics of extracted oils from their sources have become very important. Industrially, copra oils are extracted from dried copra using mechanical pressing and solvent extraction processes. The solvent extraction process recovers the maximum amount of oil from coconut kernel. However, the need of further refining, bleaching and deodorization lead to the depletion of nutrients and environmental pollution specific to the

use of solvents¹. Virgin Coconut Oil (VCO), the non-copra oil, is extracted from fresh coconut kernel using physical and natural processes such as centrifugation, fermentation, and aqueous extraction process (AEP) under ambient temperature without further chemical treatment². Particularly VCO retains the nutrient components Vitamin A, E and phenolic compounds that could enhance the antioxidant activity^{3,4}. Aqueous extraction process (AEP) to extract oil has been studied over the last five decades. AEP, where water is used as an extraction and separation medium, has regained considerable interest during the past decade as an environmental friendly approach for extraction of oil from oil sources. However, the oil recovery has not reached the maximal efficiency that would be necessary for their economic viability. The oil is localized in lipid bodies, which are bounded by cell wall and cell membrane⁵. The extraction efficiency of AEP could be enhanced with the combined enzymatic action by using Aqueous Enzymatic Extraction Process (AEEP). It ruptures the biological membrane and hydrolyze the protein to destabilize the milk emulsion from vegetative cells of coconut kernel⁶. Aqueous Enzymatic Extraction Process is a sustainable extraction process and involves in experimental conditions. It increases the yield of oil⁷, with the sustenance of nutrients and native flavor of coconut kernel acceptable to the consumers and thus attracted the attention of researchers⁸. In the past decades, AEEP has been attempted to extract oil from oil bearing materials such as peanut⁹, Soybean¹⁰, Sesame¹¹, Sunflower¹², Corn-germ¹³ and Rapeseed¹⁴.

AEEP requires enzymatic system that can hydrolyze carbohydrates (starch, cellulose, hemicellulose and pectin) linked to the cell wall. Viscozyme L is a multi-active carbohydrase enzyme, which can effectively hydrolyze the polysaccharides in plant cells and cleave the linkages within the polysaccharide matrix to liberate more intercellular components, such as fat, protein etc, and enhances the ease of extraction of lipid bodies. AEEP can thus be carried out for the extraction of VCO using Viscozyme L. Few studies were reported on the extraction of VCO from fresh coconut kernel using Viscozyme L.

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Response Surface Methodology (RSM) is an effective tool for optimizing processes¹⁵ wherein the interaction among factors (independent variables) has to be tailored for desired responses (dependent variables). RSM considers interaction among process parameters and optimize them to a reasonable range, with the advantage of the relevant information in the shortest time with the least number of experiments¹⁶. The basic principle behind response surface methodology (RSM) analysis is to relate the observed value (response) to process parameters (independent variables) using statistical methods. RSM has been widely reported for the optimization of extraction of oil using enzymatic action as in peanut oil¹⁷, olive oil^{18,19} virgin olive oil²⁰, soyabean oil²¹, coconut oil²² and rapeseed oil^{23,24}.

In the present study, grinding time, amount of Viscozyme L enzyme and incubation time were selected as independent variables and their interactive effects on the yield of coconut milk and recovery of virgin coconut oil was optimized using response surface methodology. The microstructural changes associated with enzymatic action on the cell wall of coconut kernel and the effect of grinding time on reducing the size of particles in coconut milk emulsion for the release of oil bodies were also examined.

MATERIALS AND METHODS

Materials

Fresh and mature (10-12 months old) coconuts (*Cocos nucifera* L.) of East Coast tall variety procured from a local garden of Pondicherry (India). Coconuts were randomly selected for each experiment. Liquid enzyme Viscozyme L in a multi enzyme complex containing a broad range of carbohydrases including cellulase, hemicellulase, arabanase, xylanase, and β -glucanase) from *Aspergillus* sp. The activity of Viscozyme L was 120 Fungal β -Glucanase Units (FBGU) ml⁻¹. This was obtained from Sigma- Aldrich (USA). All other reagents were of analytical grade and procured from Merck Chemicals, Mumbai, (India).

Methods

Aqueous enzymatic extraction processes (AEEP): For each experiment, the fresh grated white coconut kernel was ground with distilled water by fixed ratio of coconut kernel to water (1:1,w/w) in a mixer grinder for different grinding time. The resulting slurry was subsequently adjusted to the optimum pH (5 \pm 0.5) using 0.1N HCl and temperature (45°C \pm 2) for maximum activity of Viscozyme L enzyme for 1h. Viscozyme L was added in different amount and incubated for different time in a shaking water bath. The slurry obtained was filtered through double layer of cheesecloth to obtain milk emulsion, which was then centrifuged at 5000 rpm for 10 min to obtain coconut cream and the aqueous

phase was discarded. The obtained cream was kept in freezer at 0°C for 30min, and after thawing at room temperature, it was centrifuged at 5000 rpm for 20min and the floating oil layer was removed immediately after centrifugation. Viscozyme L assisted extraction process was optimized using response surface methodology with a selected ratio of grinding time, amount of enzyme and incubation time by screening experiment for the maximum recovery of milk which in turn could result in maximum yield of oil.

Extraction yield: The percentage yield of coconut milk (Y_{milk}), virgin coconut oil (Y_{oil}) and percentage recovery of extracted oil (R) were calculated using Eq.1, 2 and 3 respectively.

$$Y_{milk} (\%) = (\text{Weight of coconut milk} / \text{Weight of grated coconut kernel plus water added}) \times 100 \quad (\text{Eq. 1})$$

$$Y_{oil} (\%) = (\text{Weight of extracted oil by AEEP} / \text{Weight of fresh grated coconut kernel}) \times 100 \quad (\text{Eq. 2})$$

$$R (\%) = (A / B) \times 100 \quad (\text{Eq. 3})$$

where,

A = Weight of oil extracted from fresh coconut kernel by AEEP

B = Weight of oil extracted from fresh coconut kernel
Weight of oil extracted from wet residue by Soxhlet method²⁵.

Selection of suitable extraction conditions: The preliminary phase of the study was conducted for the selection of range of each factor based on yield of milk and oil. The factors included grinding time (1-4 min), amount of Viscozyme L enzyme (20-200FBGU) and incubation time (1-10 h) for sequential optimization at the constant ratio of coconut kernel to distilled water (1:1), pH (5.0) and temperature (45°C) for the maximum yield of coconut milk and virgin coconut oil. Grinding time was first optimized and was followed by the optimization of the amount of enzyme at the optimized grinding time and then incubation time at the optimized grinding time and amount of enzyme. From the results of preliminary study, the range of grinding time (2-4 min), amount of Viscozyme L enzyme (60-180FBGU) and incubation time (2-7 h) were found to be significant for the yield of VCO. The interaction of these independent factors on the yield of coconut milk and virgin coconut oil was determined through central composite rotatable design (CCRD) using response surface methodology.

Experimental design for AEEP: The central composite rotatable design (CCRD) was applied to study the interactive effect of three independent factors

(grinding time, amount of Viscozyme L enzyme and incubation time) at five different level ($-\alpha$, -1 , 0 , $+1$, $+\alpha$) on the responses (yield of coconut milk and virgin coconut oil). The actual and coded value of the three independent factors and test designed are summarized in Table 1. According to the design, the total number of experiment combinations were 20 with eight (2^3) factorial points, six axial points (star points) and six repetition of experiments at the central point. The experiments run in random order to minimize the effect of unexpected inconsistency in the observed responses due to extraneous factors. The yield of coconut milk and oil was measured in triplicates in 20 different experimental runs and their observations were fitted to the following second order polynomial equation using multiple regression procedure²⁷.

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC \quad (\text{Eq. 4})$$

Where Y is the predicted response; β_0 is the regression coefficient at center point, β_1 , β_2 and β_3 are the linear coefficients, β_{11} , β_{22} and β_{33} are the quadratic coefficients, β_{12} , β_{13} and β_{23} are the second order interaction coefficient, and grinding time (A), amount of enzyme (B), incubation time (C) are the independent variables. All experiments were carried out in triplicates and randomized order to minimize the effect of unexplained variable on the observed responses due to extraneous factors.

Validation of the model: Optimal conditions including grinding time, amount of enzyme and incubation time for the extraction of coconut milk and virgin coconut oil were obtained using the predictive equations of RSM. The yield of coconut milk and virgin coconut oil were determined under optimal conditions. The experimental and predicted values were compared in order to determine the validity of the model.

Particle size analysis: Particle size distribution of coconut milk emulsions with the effect of different grinding time (1-4 mins) was determined using a laser light scattering instrument (Malvern Zetasizer Nano S, Malvern Instruments Ltd, UK). The fixed refractive index ratio (1.33) and viscosity (0.887cP) were used to calculate the oil body size distribution in coconut milk at 25°C.

Scanning electron microscopy: Control and Viscozyme L treated grated coconut were freeze-dried (-40°C) and mounted on an aluminum stubs using double side sticky tape followed by coating employing a sputter coater. SEM images illustrating the effect of Viscozyme L on rupturing the cell wall to release the oil bodies were captured employing a field emission scanning

microscope (Hitachi model S-3400N). The images were studied using secondary electron detectors at an operating voltage of 5kV.

Statistical analysis: The Statistical software “Design-Expert” trial version 8.0.7.1 (State-Ease Inc., Minneapolis, MN, USA) was employed for regression analysis and graphical visualization respectively. The quality of the fitted model was determining by its F-value and determination coefficient of (R^2). Statistical analysis was performed by Analysis of variance (ANOVA) for multiple comparisons and to evaluate the adequacy of the generated mathematical models.

RESULTS AND DISCUSSION

Fitting the model: The central composite design employed for 20 experiments planned at different combinations of the significant factors in quadratic model for aqueous enzymatic extraction process demonstrates in Table 1. It shows the predicted and observed yield of coconut milk and VCO corresponding to the combined effect of all the three significant variables in the specified ranges. From the results of CCRD and regression analysis of experimental results, a second order polynomial equation was tested to estimate the relationship of variables on the yield of coconut milk or virgin coconut oil.

The following regression equation was obtained for the yield of milk:

$$Y_{\text{milk}} (\%) = (73.33) + (0.79 A) + (0.54B) + (0.35C) + (0.30 AB) - (0.055AC) - (0.100BC) - (2.27A^2) - (1.78B^2) - (0.54C^2) \quad (\text{Eq. 5})$$

The following regression equation obtained for the yield of VCO:

$$Y_{\text{oil}} (\%) = (21.12) + (0.040A) + (0.19B) + (0.39C) - (0.099AB) - (0.14AC) - (0.56BC) - (1.40A^2) - (1.52B^2) - (1.09C^2) \quad (\text{Eq. 6})$$

The statistical significance of the models were evaluated by ANOVA as shown in Table 2 and 3. The model F-value of 55.86 for the yield of coconut milk and 45.23 for the yield of virgin coconut oil indicates both the models were significant ($P < 0.05$). In the case of coconut milk yield (Eq.5), the linear term of grinding time (A), amount of enzyme (B), and Incubation time (C) as well as the quadratic term (A^2 , B^2 , and C^2) were shown to be significant ($P < 0.05$). In the case the yield of virgin coconut oil (Eq.6), only linear term of incubation time (C), interactive term of amount of enzyme and Incubation time (BC) and quadratic term of all factors (A^2 , B^2 , C^2) were significant in model terms ($P < 0.05$). Further the models were statistically analysed for being appropriate to predict their respective responses. The

TABLE 1
Central Composite Rotatable Design (CCRD) Layout in Actual Value (Coded Value) for Yield of Coconut Milk and VCO

Run	A Grinding time (min)	B Enzyme concentration (FBG)	C Incubation time (h)	Yield of Milk (%,w/w)		Yield of VCO (%,w/w)	
				Observed	Predicted	Observed	Predicted
1.	2 (-1)	60 (-1)	2 (-1)	67.26	67.20	15.92	15.69
2.	4 (+1)	60 (-1)	2 (-1)	68.82	68.31	16.51	16.25
3.	2 (-1)	180 (+1)	2 (-1)	67.84	67.89	17.12	17.38
4.	4 (+1)	180 (+1)	2 (-1)	70.04	70.18	18.05	17.55
5.	2 (-1)	60 (-1)	7 (+1)	68.43	68.20	17.48	17.87
6.	4 (+1)	60 (-1)	7 (+1)	69.23	69.09	18.24	17.86
7.	2 (-1)	180 (+1)	7 (+1)	68.07	68.49	17.18	17.32
8.	4 (+1)	180 (+1)	7 (+1)	70.59	70.56	16.81	16.92
9.	1.32 (- α)	120 (0)	4.5 (0)	65.72	65.57	17.47	17.08
10.	4.68(+ α)	120 (0)	4.5 (0)	67.96	68.24	16.66	17.22
11.	3 (0)	19.09 (- α)	4.5 (0)	66.88	67.39	16.28	16.51
12.	3 (0)	220.91(+ α)	4.5 (0)	69.59	69.21	17.19	17.13
13.	3 (0)	120 (0)	0.3 (- α)	71.03	71.22	17.01	17.38
14.	3 (0)	120 (0)	8.7 (+ α)	72.44	72.38	18.89	18.68
15.	3 (0)	120 (0)	4.5 (0)	72.38	73.33	20.84	21.12
16.	3 (0)	120 (0)	4.5 (0)	73.1	73.33	21.08	21.12
17.	3 (0)	120 (0)	4.5 (0)	73.49	73.33	21.10	21.12
18.	3 (0)	120 (0)	4.5 (0)	73.6	73.33	21.12	21.12
19.	3 (0)	120 (0)	4.5 (0)	73.87	73.33	21.02	21.12
20.	3 (0)	120 (0)	4.5 (0)	73.56	73.33	21.57	21.12

(-1): indicates the lowest coded value; (0): indicates the mean level; (+1): indicates the highest coded value

error analysis revealed the non-significant lack of fit for both the models. The values of determination coefficient (R^2) of 0.980 for the yield of coconut milk and 0.976 for the yield of VCO were satisfactory to validate the models. Moreover, the lowest coefficient of variance (C.V.) for both the yield of coconut milk 0.71% and VCO (2.28%) evinced the better precision and reliability of the model²⁷. In the present study, ratios for the yield of coconut milk (22.02) and VCO (18.32) were greater than 4 indicating the adequacy of the models to navigate the design space.

The maximum yield of coconut milk and virgin coconut oil predicted by regression quadric equation were 73.33% (w/w) and 21.12 % (w/w) respectively, under the extraction conditions including grinding time of 3 minutes, amount of enzyme 120 FBGU and 4.5

h of incubation time. The percentage recovery of VCO was found to be 86.14% of total fat content in fresh coconut kernel. The increase in the recovery of oil in the present study could be credited to the enzymatic action of Viscozyme L enzyme as compared to the recovery of oil (83.12%) observed in aqueous extraction process without enzyme. It was clear that the optimum conditions for Viscozyme-L assisted AEEP had comparatively improved the yield of oil effectively²⁸. The 65.5% of oil was recovered from copra using mixture of protease, cellulase and hemicellulose²⁹. Similarly, the 73% of oil was recovered from grated coconut kernel using mixture of protease, cellulase, α -amylase and polygalactouranase³⁰. The effect of Viscozyme-L action on the extraction of sunflower oil using aqueous extraction process confirmed that Viscozyme-L treatment alone could be the most efficient, producing

TABLE 2
Analysis of Variance and Lack of Fit as Per CCRD for the Percentage Yield of Coconut Milk
Applying Response Surface Quadratic Model

Source	SS ¹⁾	DF	MS	F-Value	p-value*
Model	124.91	9	13.88	55.86	0.0001
A-Grinding time	8.62	1	8.62	34.68	0.0002
B-Amount of enzyme	3.96	1	3.96	15.95	0.0025
C-Incubation time	1.64	1	1.64	6.60	0.0280
AB	0.70	1	0.70	2.80	0.1251
AC	0.024	1	0.024	0.097	0.7614
BC	0.080	1	0.080	0.32	0.5829
A ²	74.36	1	74.36	299.27	0.0001
B ²	45.57	1	45.57	183.42	0.0001
C ²	4.22	1	4.22	16.96	0.0021
Residual	2.48	10	0.25		
Lack of Fit	1.09	5	0.22	0.78	0.6058
Pure Error	1.40	5	0.28		
Correlation Total	127.40	19			
R ²	0.98				
C.V.	0.71%				
Adequate precision	22.018				

¹⁾ SS: sum of squares; DF: degrees of freedom; MS: mean square; *p< 0.05 indicates significance

TABLE 3
Analysis of Variance and Lack of Fit as per CCRD for the Percentage Yield of Virgin Coconut Oil
Applying Response Surface Quadratic Model

Source	SS ¹⁾	DF	MS	F-Value	p-value*
Model	71.37	9	7.93	45.23	0.0001
A-Grinding time	0.022	1	0.022	0.13	0.7307
B-Amount of enzyme	0.47	1	0.47	2.70	0.1317
C-Incubation time	2.03	1	2.03	11.61	0.0067
AB	0.078	1	0.078	0.44	0.5198
AC	0.16	1	0.16	0.91	0.3625
BC	2.50	1	2.50	14.24	0.0036
A ²	28.36	1	28.36	161.76	0.0001
B ²	33.28	1	33.28	189.79	0.0001
C ²	17.12	1	17.12	97.65	0.0001
Residual	1.75	10	0.18		
Lack of Fit	1.46	5	0.29	4.99	0.0512
Pure Error	0.29	5	0.059		
Correlation Total	73.12	19			
R ²	0.976				
C.V.	2.28%				
Adequate precision	18.317				

¹⁾ SS: sum of squares; DF: degrees of freedom; MS: mean square; *p< 0.05 indicates significance.

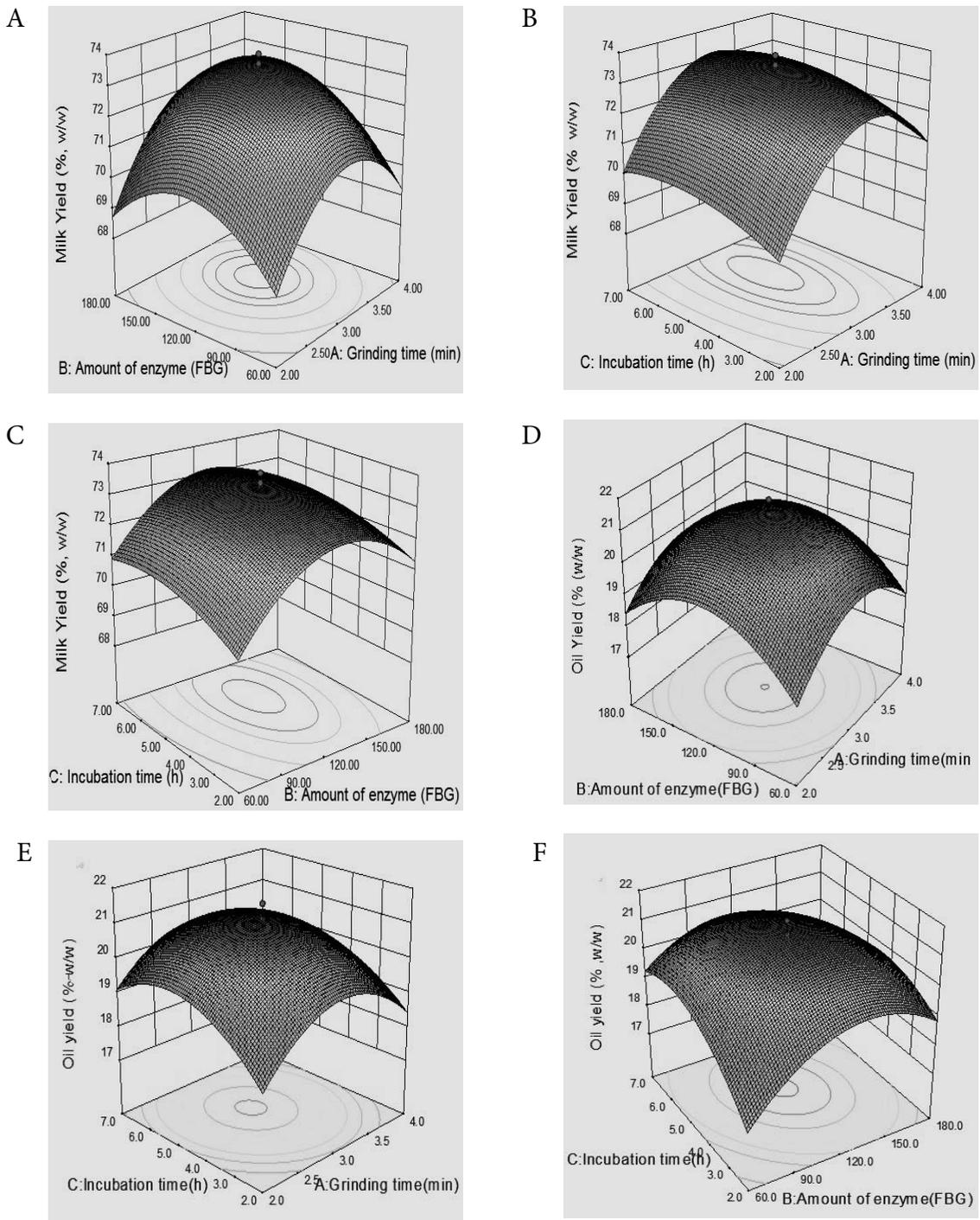


Fig.1 : Response surfaces for percentage yield of Coconut milk as a function of (a) grinding time and amount of enzyme, (b) grinding time and incubation time (c) amount of enzyme and incubation time; for percentage yield of oil as function of (d) grinding time and amount of enzyme, (e) grinding time and incubation time, (f) amount of enzyme and incubation time.

oil yield of 34.05%, which represented 61.46% of the total extractable oil³¹. The effect of interaction between the independent variables on the yield of coconut milk and oil was demonstrated by the three-dimensional response plot shown in Figure 1(a, b, c) and (d, e, f) respectively. In Fig. 1a and Fig. 1d, illustrated

to be increasing up to moderate level of both the grinding time and amount of enzyme for the yield of coconut milk and oil. The higher level of enzyme was insignificant to increase the yield of both the coconut milk and virgin coconut oil whereas the higher level of grinding time decreased the yield of coconut milk

and virgin coconut oil. A similar result between grinding time and incubation time on the yield of coconut milk and VCO was encountered as shown in Fig.1b and Fig.1e respectively.

There was also a moderate interactive effect of amount of enzyme and incubation time on increasing the yield of coconut milk and virgin coconut oil as shown in Fig.1c and Fig.1f respectively. However, the slight increase in the yield of coconut milk and rapid increase in the yield of oil due to the moderate interaction between incubation time and amount of enzyme could be observed from the variation in the shape of the curve in Fig. 1c and 1f respectively.

Validation of the model: In order to maximize the response and to validate the adequacy of the quadratic model, optimum extraction conditions were estimated by the desirability method³². The prediction of the models was validated through additional independent experiments in triplicates under the optimum conditions. The experimental value of 73.88% (w/w) for the yield of coconut milk and 21.57% (w/w) for virgin coconut oil were found in agreement to their respective predicted values. Therefore, the extraction conditions for coconut milk and virgin coconut oil determined by RSM were practical.

Particle size: The effect of grinding time (1-4 min) on particle size distribution in coconut milk emulsion were evaluated. The average particle size distribution of milk emulsion was found to be 1521nm, 929.2nm, 667.7nm, and 567.5nm for 1, 2, 3, 4 minutes of grinding time respectively. From the results, the particle size from 1521 to 667.7 nm corresponding to the grinding time for 1 to 3 minutes was found to increase the release of oil as depicted in Response surface plot (Fig. 1). The increase in oil recovery for smaller size particles could be attributed to the diffusion of water-soluble

components as well as the enhanced enzyme diffusion rate to act more easily on substrates. However, excessive grinding (4 min) favored the formation of stable emulsion of coconut milk and reduced the yield of oil.

Scanning electron microscopy (SEM): The effect of enzymatic action on the degradation of cell wall for enhancing the release of oil bodies from vegetative cells could be observed from the changes in microstructure of Viscozyme L treated coconut kernel as compared to that of untreated grated coconut kernel (Fig.2). Fig. (2a) showed the regular arrangement of cells enclosed with cell wall for control whereas the microstructure of Viscozyme L (complex of multi enzyme) treated coconut kernel was observed with the collapse of cell wall structure due to the breakdown of complex arrangement of polysaccharides in cell wall as shown in Fig. 2b. This is in accordance with the results obtained by the earlier studies done with seed kernels of *Irvingia gabonensis*³³.

CONCLUSION

The present study concludes that the maximum yield of coconut milk was dependent on the grinding time, amount of Viscozyme L enzyme and incubation time. However, the yield of virgin coconut oil was dependent on linear term of incubation time and quadratic terms of all three independent factors. It also depends on amount of enzyme and incubation time in aqueous enzymatic extraction process optimized using response surface methodology. The proposed quadratic regression model showed the optimum level of independent factors such as grinding time (3 min), amount of Viscozyme L (120FBGU) and of incubation time (4.5 h) for the maximum yield of coconut milk (73.33% w/w) and virgin coconut oil (21.12% w/w). This was in agreement to the verified experimental yield of coconut milk (73.88% w/w) and virgin coconut

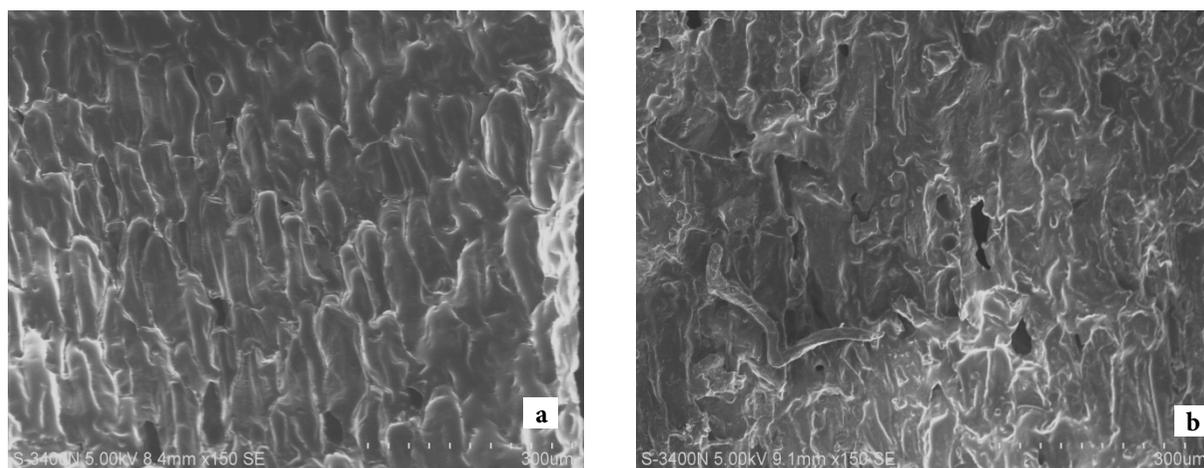


Fig.2 : Scanning electron micrographs of (a) untreated and (b) Viscozyme L treated grated coconut meat

oil (21.57% w/w). The maximum recovery of virgin coconut oil was about 86.14% of total fat content in fresh coconut kernel. The extracted oil was transparent like water and had the characteristics pleasant coconut aroma. Moreover, the SEM image showed the action of Viscozyme-L on the degradation of cell wall of coconut kernel. It was observed that 3 min of grinding was helpful for reducing the size of particles (667.7nm) in coconut milk emulsion. Therefore, in the present study the addition of Viscozyme L can facilitate the penetration of the cell wall to release the oil bodies, which results in the maximum yield of VCO.

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Oil Content and Fatty Acid Composition of Four New Minor Tree Borne Oilseeds

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ABSTRACT

Fatty acid composition of four new seed oils were determined and reported for the first time. Oil was extracted from tree borne seeds of *Adina cordifolia*, *Anogossious latifolia*, *Anthocephalus cadamba*, *Callitris glauca* and the oil contents varied from 0.4 to 4.4 %. Fatty acid compositions of all the four oils were analyzed and it was observed that all of the oils were found to contain linoleic acid as a major fatty acid. The content of linolenic acid was higher in *Adina cordifolia* (74.6%) and *Anogossious latifolia* (54.6%) compared to *Anthocephalus cadamba* (38.6%) and *Callitris glauca* (28.4%). *Anthocephalus cadamba* and *Callitris glauca* were also found to contain linolenic acid.

KEYWORDS: Tree borne oil seeds, Oil content, Fatty acid composition, Gas chromatography.

INTRODUCTION

In recent years, interest in finding new sources of food that will meet the health and nutritional needs of the world's population has been increasing¹. Plant seeds from lesser known varieties can be important sources of oils with industrial and nutritional applications. In this connection, from the past several years, many studies have been carried out in India aiming at the utilization of wild plants as a source of unconventional oil for edible and non-edible applications. Several oil seed plants of Indian origin such as *Terminalia chebula*, *Pterocarpus marsupium*, *Melia dubia*, *Chukrasia tabularis*, *Lannea coromandelica*, *Albizia lebeck*, *Dalbergia sissoo*, *Cassia siamea*, *Bridelia retusa*, *Ailanthus excels*, *Simarouba glauca*, etc were characterized for their physico-chemical properties²⁻¹¹. However, India's forest base is rich in a variety of tree-borne oilseeds which can be targeted for screening. As part of this strategy the present study was aimed at screening of oil seeds

from forest origin and evaluation of oil content and fatty acid composition. The four seeds screened were from *Adina cordifolia*, *Anogossious latifolia*, *Anthocephalus cadamba*, *Callitris glauca* and there were no reports on the oil content and fatty acid composition for these species.

Adina cordifolia is a deciduous tree over 20 m high belonging to the subfamily *Cinchonoideae* and family Rubiaceae. It is native to Southern Asia, from India and Srilanka to southern China and Vietnam. It is found scattered in deciduous forests throughout the greater part of India, ascending to an altitude of 900 m in sub-Himalayan tract. It is also common in forests of South India¹². The plant is reported to be employed in treatment of deep wounds and jaundice, stomach ache, malarial fever, swelling in stomach and root is useful for dysentery¹³.

Anogeissus latifolia (Roxb.) belongs to the family Combretaceae, commonly known as 'Dhawara'. It is a small to medium sized tree distributed throughout India and ascending up to 1200 m in the hilly regions of south India. Roots are astringent, acrid and stomachic. The bark is used as an anti-inflammatory and urinary astringent. Some parts of the tree have been reported to be used in the treatment of piles, diabetes, and anaemia¹⁴.

Anthocephalus cadamba (Roxb.) is widely distributed throughout India and is used as a folk medicine in the treatment of fever, anaemia, uterine complaints, blood diseases, skin diseases, leprosy, dysentery, and for improvement of semen quality. The leaves are recommended as a gargle in cases of stomatitis. Some scientific studies have been carried out to reveal its antimalarial and antihepatotoxic activities. The major constituents of bark were reported to be triterpenes, tripernoid glycosides, saponins, indole alkaloids cadambine, dihydrocadambine, cadamine, isocadamine and isodihydrocadambine¹⁵.

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Callitris glauca is a shrub or slow growing tree and is a native of southern Australia, eventually coming up to 80 feet high with hard furrowed, greenish brown bark. Leafy branches divided into fine bushy sprays. Leaves about 1/10 inch long commonly glaucous, dorsal surface rounded giving the branchlets textured, non-ribbed appearance. The presence of flavonoids and glycosides in the leaves were reported in the literature¹⁶.

MATERIALS AND METHODS

Materials

Seeds were provided by Forest Department, Research and Development, Aranya Bhavan, Saifabad, Hyderabad, India. All solvents, chemicals and reagents were purchased from SD Fine Chemical Ltd., Mumbai and were of analytical grade.

Methods

Isolation of oil: Seeds were ground to powder using laboratory mixer and the seed powder was extracted in a Soxhlet extractor using hexane as solvent. The oil content was determined as a percentage of the extracted oil to the sample weight (w/w). The extracted oil was stored in a refrigerator (4 °C) in a glass bottle under nitrogen blanket for further analysis.

Fatty acid composition of extracted oils: The extracted oils were converted to fatty acid methyl esters according to the reported method¹⁷. Briefly, the oil (about 20 mg) was refluxed in 20 ml of 2% sulphuric acid in methanol reagent for 3 hr after which methanol was evaporated and the methyl esters were extracted into ethyl acetate (15 ml) and washed with water (4 x 30 ml) until neutral and dried over anhydrous sodium sulphate. Solvent was removed using rotary evaporator to obtain the fatty acid methyl esters for gas chromatographic analysis for determining the fatty acid composition.

Gas Chromatographic (GC) analysis: GC was performed on an Agilent 6890 gas chromatograph equipped with a flame ionization detector. The column used was a DB-225 column having a length of 30 m, 0.25 mm i.d and 25 µm film thickness. The carrier gas was nitrogen at a flow rate of 1 mL·min⁻¹. The oven programming

was as follows: 160 °C for 2 minutes, which rose to 230 °C at a rate of 5 °C min⁻¹ and held at 230 °C for 20 minutes. The injector and detector temperatures were maintained at 220 and 250 °C respectively.

RESULTS AND DISCUSSION

Seeds of *Adina cordifolia*, *Anogessious latifolia*, *Anthocephalus cadamba*, *Callitris glauca* which have not been exploited for oil content and fatty acid composition have been selected for the present study. The seeds of *A. cordifolia* were very small with grass like appearance and yellow-brown in colour. *A. latifolia* plant seeds were small, round in shape, similar to coriander seeds in appearance and yellow in colour. *A. cadamba* plant seeds were small and dark brown in colour. The seeds of *C. glauca* plant were small and reddish brown colour in appearance. All the seeds were small in appearance measuring about a few millimeters in size. The characteristics and compositions of four seeds and oils are given in Tables 1 and 2 respectively. Table 1 shows the oil content of the four seeds and it is observed that the oil content was 4.4, 0.4, 0.8, 2.0% for *A. cordifolia*, *A. latifolia*, *A. cadamba* and *C. glauca* respectively.

From Table 2, it can be observed that *A. cordifolia* was found to be rich a source for linoleic acid (74.6%) which was the major fatty acid. Oleic and palmitic acids were found to be next major fatty acids present in 11.4 and 9% respectively. Similarly, the fatty acid composition of *A. latifolia* showed that linoleic acid (54.6%) was the major fatty acid followed by oleic (17.5%) and palmitic acids (15.8%) as the next major fatty acids. Lauric (2.2%), myristic (5.9%), stearic acids (2.2%) were the minor fatty acids present in *A. latifolia*. In *A. cadamba* and *C. glauca* seed oils, linoleic acid was found to be present in 38.6 and 28.4% where as oleic was present in 32.6% and 24.1% respectively. Palmitic acid was found to be next major fatty acid present in both the species. It was interesting to observe linolenic acid in both the species of *A. cadamba* and *C. glauca*. Linolenic acid content was found to be high in *C. glauca* which was present in about 15.7% where as in *A. cadamba* the level of linolenic acid was 5%. It can be observed that in all the four species linoleic acid was the major fatty acid present. *A. cordifolia*,

TABLE 1
Oil Content (%) for the Seeds

S.No.	Botanical name	Common name	Oil content (%)
1	<i>Adina cordifolia</i>	Bandaru	4.4
2	<i>Anogessious latifolia</i>	Thirman	0.40
3	<i>Anthocephalus cadamba</i>	Kadamba	0.80
4	<i>Callitris glauca</i>	-	2.0

GLC analyses were performed for determining the fatty acid composition of all the four oils and the data is given in Table 2.

TABLE 2
Fatty Acid Composition (wt %) for the Seed Oils

FA	<i>A cordifolia</i>	<i>A latifolia</i>	<i>A cadamba</i>	<i>C glauca</i>
12:0	-	2.2	-	0.5
14:0	0.7	5.9	1.9	0.8
16:0	9.0	15.8	15.9	17.3
16:1	-	-	0.5	-
18:0	1.0	2.2	3.8	7.9
18:1	11.4	17.5	32.6	24.1
18:2	74.6	54.6	38.6	28.4
18:3	-	-	5.0	15.7
20:0	-	-	0.6	1.6
20:1	-	-	0.3	0.8
20:2	-	-	-	1.2
22:0	-	-	0.1	1.1
UI/HC	3.3	1.8	0.7	0.6

UI: unidentified; HC: hydrocarbons.

A. latifolia, *A. cadamba*, *C. glauca* seed oil methyl esters showed no unusual components.

CONCLUSIONS

The oil content and fatty acid composition of four new seeds were reported for the first time. The oil content was low in all the four seeds and the fatty acid composition revealed that linolenic acid was the major fatty acid in all the four seed oils.

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Assessment of Shelf Stability and Heat Transfer Coefficient of Mustard and Sesame Oil Blends during Frying

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ABSTRACT

The primary objective of this work was to ascertain the shelf stabilities of mustard and sesame oils and their blends by physicochemical assays. The secondary objective was to determine the heat transfer coefficient (h) for the least oxidized oil (or blend), employing deep frying. Mustard and sesame oils and their blends (90:10, 80:20, 50:50) were stored for 60 days and assayed for physicochemical properties at an interval of 10 days, post frying of potato wedges using shallow frying. The blend of mustard and sesame (90:10) was found to be least affected by oxidation with storage and shallow frying. The SFA: MUFA: PUFA ratio of the same was found to be 1:3.98:2.33. This blend was used for computation of ' h ', both by direct and indirect methods ('with' and 'without bubbling' effects) using deep frying at 130, 150 and 170°C. Our studies recommend 150°C as the most preferred temperature for industrial scale frying operations. The ' h ' values obtained by indirect method were significantly different in presence and absence of bubbling. We advocate indirect method of estimation of ' h ' and bubbling effect to be crucial in modeling frying operations.

KEYWORDS: *Mustard oil, sesame oil, blends, frying, physicochemical property, heat transfer coefficient*

INTRODUCTION

India is one of the largest oilseed producing countries in the world and mustard is one of the major edible oilseed crops¹. 10 million tonnes of edible oils are consumed per annum in India and the per capita consumption is around 11 kg per year including native and blended oils². Blending of oils is a common practice in manufacture of edible oils wherein two oils are mixed in definite ratios to extend shelf life, meet new product specifications and for cost reduction³.

Frying is a major food processing operation which generates flavourful products that have crispy crusts, enticing aroma and visual appeal. French fries, in

particular, are a global snack and they are appreciated for their taste and texture⁴. A reputed snack food manufacturer, McDonald's alone serves about 3.5 MMT of French fries to about 33 million customers daily worldwide⁵. In India, fried potato wedges are very popular snacks. These are produced through sequential steps of blanching, drying and frying, wherein each step contributes significantly to the quality attributes of the final product.^{6,7}

Frying is generally carried out industrially by deep fat or immersion frying. However, due to health hazards (such as higher oil uptake by the fried food, higher oxidation and generation of acrylamide) of deep frying, alternative frying techniques, primarily shallow frying is also highly recommended. The aim of our study was to optimize shallow frying conditions for potato wedges using blends of mustard and sesame oil in different ratios, so as to minimize the oil uptake in the fried products during frying and improve the nutritional value and organoleptic potential of the fried products and also to ascertain the shelf-life of the blended oils by physicochemical tests including antioxidant assay.

The mechanism of frying is a very complex phenomenon due to coupled heat and mass transfer between the food and oil. Therefore, in order to optimize the frying process modeling of the same is required. There are various frying parameters which are involved in developing an empirical model for frying, which include: temperature of oil (T in °C), time of the frying (t in sec), moisture content (m in %), heat transfer coefficient (h in $W/m^2°C$), specific heat (c_p in J/kgK) and area of the frying material (A in m^2). The second objective of this study was to develop a model for deep frying using the best blend of mustard and sesame oils obtained in the first part of the study.

MATERIALS AND METHODS

Mustard oil, sesame oil, raw potatoes-*Solanum tuberosum* (Kufri Jyoti variety), aluminium foil, low density polyethylene (LDPE) self-sealable pouches

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bags (20 μ thickness) were purchased from a local supermarket in Kolkata, India. All the chemicals used for analyses were of AR grade, unless specified. Shallow frying was carried out in a domestic pan fryer while deep frying was carried out in a 5 l table-top deep fat fryer for determination of heat transfer coefficient. These were procured from M/s Shiva Kitchen Appliances, Kolkata, India. A T-type thermocouple (2 mm diameter) with a transducer-display was procured from M/s G.B Enterprises, Kolkata, India. A metal piece of SS 304 (70 mm x 10 mm x 10 mm) was specially fabricated for the determination of 'h' value by indirect method.

Preparation of oil blends and storage: The blends of mustard and sesame oils were prepared in the following ratios, B1 (100:0 = mustard: sesame), B2 (90:10 = mustard: sesame), B3 (80:20 = mustard: sesame), B4 (50:50 = mustard: sesame) and B5 (0:100 = mustard: sesame). We have used a higher proportion of mustard oil compared to sesame oil because mustard oil is nutritionally beneficial owing to its ω6:ω3 ratio equaling 2.6:1 and also because it is the most popular edible oil in eastern India. The oil samples were divided into 7 batches and they were stored up to 60 days before shallow frying at 130°C. The shelf lives of the oils were ascertained through several physicochemical tests. All oils and blends were stored in nitrogen flushed screw-capped polyethylene bottles in dark at 23±2°C.

Pre-Frying and Frying processing of potato wedges: Pre-frying of potato wedges such as peeling, cutting, blanching and drying were carried out according to the method described by Ghosh *et al*⁶.

Frying of potato wedges: For the study of physicochemical characteristics of stored oils, potato wedges were shallow fried in batches of 100 g each in a pan fryer (M/s Shiva Kitchen Appliances, Kolkata, India), with temperature controlled in the range of 90-170 (±1)°C using a standard thermometer. The fryer was filled with 200 g oil in every batch of frying. Post frying, the potato wedges were placed on blotting papers to remove the excess surface oil. Five batches of frying were carried out in a day for five blends with an interval of 10 days between two successive frying cycles. No repeat frying was conducted. The blend showing least oxidation post frying was used for determination of heat transfer coefficient (h), employing deep frying. For determination of 'h' value, deep frying was performed in the commercial fryer of 5 l capacity with a thermostat having automated temperature cut-off for oil temperature regulation. Additionally, a glass disc type agitator (70 mm x 10 mm x 10 mm) was placed into the fryer to attain uniform heating. Oil temperature was also monitored using a thermocouple to ensure

isothermal conditions during frying. The temperature of the frying oil was maintained at three temperature regimes of 130±1°C, 150±1°C and 170±1°C, which are the normal temperature ranges employed in domestic and commercial frying operations⁹.

Assay of physical properties of oils: The physical properties of the oils were assessed by estimation of specific gravity, viscosity (Brookfield Synchro-electric Rotovisco Viscometer, M/s Brookfield Engineering Company, Middleboro, MA, USA) with LVT model spindle (spindle No.2) at 25±1°C, with speed of 60 rpm, and Lovibond colour (The Tintometer Ltd, Waterloo Road, Salisbury, Wilts, SP1 2JY, UK, Model F) assays, after frying.

Assay of chemical properties of oils: Acid value, peroxide value, para anisidine value and Totox value: The acid and peroxide values of oils and blends were determined by standard methods AOCS¹⁰. Para-anisidine value was determined according to IUPAC¹¹ method. Total oxidation value (TOTOX) was derived from peroxide and para-anisidine values as follows:

$$\text{TOTOX} = 2 \text{ PV} + \text{p-AV} \quad \dots\dots\dots (1)$$

where, PV is peroxide value, p-AV is para-anisidine value.

Conjugated dienes and triene: The presence of conjugated compounds in the oils and blends post frying was determined. The absorbance at 233 and 268 nm were used to assess conjugated dienes and trienes, respectively¹².

Total antioxidant capacity of oil blends by DPPH radical scavenging assay: The antioxidant activities of oils and blends were determined by DPPH radical scavenging activity, according to the method reported by Gorinstein *et al*¹³.

DPPH Scavenging activity (%) =

$$\frac{[(\text{Abs}_{\text{control}} - \text{Abs}_{\text{sample}})]}{(\text{Abs}_{\text{control}})} \times 100 \quad \dots\dots\dots (2)$$

where, Abs_{control} is the absorbance of DPPH radical + methanol and Abs_{sample} is the absorbance of DPPH radical + sample. The antioxidant activities were reported as IC₅₀ (mg/ml) values.

Compositional analysis of blended oils by FAME-GC
Preparation of fatty acid methyl esters of oils: All oil samples were analysed for their fatty acid composition to investigate the effects of storage and frying on fatty acid composition. Fatty acid methyl esters were prepared according to the method described by Fernandez *et al*¹⁴.

FAME (Fatty Acid Methyl Ester) analysis by GC-FID: The gas chromatograph (GC Varian, UK) attached with WCOT, VF-1MS 15m x 0.25mm x 0.25 μ m Factorfour™ capillary column and equipped with FID was used for the analyses (M/S Varian Inc. California, USA). 1 μ l FAME was injected into the GC column. Nitrogen was used as the carrier gas at a flow rate of 1 ml/min. The oven was programmed as follows: 70°C (1 min hold), 70-260°C at 5°C/min and held at 260°C for 5 min. The detector temperature was set at 280°C. The standard FAME mix (M/s Supelco, CA, USA) was used to quantify the fatty acids using area normalisation method and the composition was reported as % fatty acids.

Product analysis of potato wedges: Potato wedges were analyzed by shelf life study. Each sample was analyzed thrice and values reported as mean \pm S.D.

Shelf life studies of potato wedges

Storage of potato wedges: The fried potato wedges were wrapped in aluminium foil and packaged in self-sealable LDPE pouches. Thereafter, the packets were N₂ purged, sealed and stored at -18°C for 0, 10, 20, 30, 40, 50 and 60 days. The packets were withdrawn at respective intervals for organoleptic and texture studies.

Sensory evaluation of potato wedges: Sensory evaluation of fried potato wedges was carried out by a 10-member panel consisting of university staff and students. The sensory evaluation was conducted between 10-12 AM and 3-5 PM as recommended by Ranganna¹⁵. The panellists used standard 9-point hedonic scale for evaluating the samples.

Texture analysis: The texture of the fried potato wedges was analyzed by Instron Texture Analyzer (M/s Instron Inc., Buckinghamshire, UK model number 4301). The fried wedges were fractured longitudinally with a wedge shaped probe (60° cutting angle, 7 cm width) at a crosshead speed of 20 mm/min. A force-distance diagram was constructed from the resistance that the probe encountered during the fracture. Texture analysis parameters of the fried potato wedges were expressed as hardness (N).

TBARS assay for malondialdehyde in fried potato wedges: To assess the wholesomeness and safety of the fried potato wedges prior to consumption, malondialdehyde (MDA) was determined in shallow frying using TBARS assay, in accordance to the method reported by Okhawa *et al*¹⁶.

Determination of heat transfer coefficient 'h': The oil blend which showed the least oxidation in shallow frying was employed for determination of 'h' value, employing deep frying in accordance to Haradwala and Bhattacharjee¹⁷. Two methods were adopted for

calculation of 'h' value: direct and indirect methods. Under indirect method, two approaches were investigated- with bubbling and without bubbling effect while frying potato wedges.

Statistical analyses: All experiments were conducted in triplicate and reported as mean \pm SD of three independent experiments (i.e., three independent batches of fried potato wedges). A p value of 0.05 was used to verify significance of all tests. Statistical analyses of the variation in the results were carried out by one-way ANOVA using STATISTICA 8.0 software (Statsoft, OK, USA).

RESULTS AND DISCUSSION

Assay of physical properties of oils and blends:

Specific gravity of oils and blends: The specific gravity of the oils increased with storage. In B1, the specific gravity value increases linearly from 0.9088 on day zero to 0.9120 after 60 days. In B5, the value was 0.9143 on day zero and 0.9167 on the 60th day. B2 (90:10) showed 0.9072 (0 day) and 0.9110 (60 days), B3 (80:20) showed 0.9100 (0 day) and 0.9121 (60 days), and B4 (50:50) showed 0.9118 (0 day) and 0.9134 (60 days). The three blends had higher specific gravity values than B1 and B5 with frying. Among the blends, B2 had the lowest values. The increase in specific gravity values observed in the remaining blends may be attributed to the formation of polymeric fractions of higher molecular weight and increased oil density due to oxidation reactions during frying; in accordance to that reported by Ahoh and Min¹⁸.

Viscosity of oils and blends: From the rheological study, all oils and blends showed Newtonian flow. All oil samples showed an increase in viscosity with frying and storage. The viscosities of B2, B3 and B4 were significantly lower ($p = 0.041$) than B1 but higher than that of B5 (Fig. 1). For the native oils, viscosity of B1 was 53.50 cP (0 day) and 65.00 cP (60 days); while the viscosity of B5 was 44.00 cP (0 day) and 55.50 cP (60 days) at 25 \pm 1°C. For B2, viscosity was 52.50 cP (0 day) and 64.00 cP (60 days); for B3 53.00 cP (0 day) and 63.50 cP (60 days) and for B4 49.50 cP (0 day) and 60.50 cP (60 days). As seen, B5 had minimum change in viscosity. Sesame oil being refined did not show changes in viscosity while the blends having higher proportion of unrefined mustard oil showed significant changes in viscosity. The increase in viscosity in oils and blends may be due to polymeric materials generated by polymerization reactions during frying and/or owing to faster rate of oxidation of unsaturated fatty acids; in agreement with reports of Berger¹⁹.

Lovibond colour of oils: In the past, oils have almost invariably been graded on the basis of colour by visual

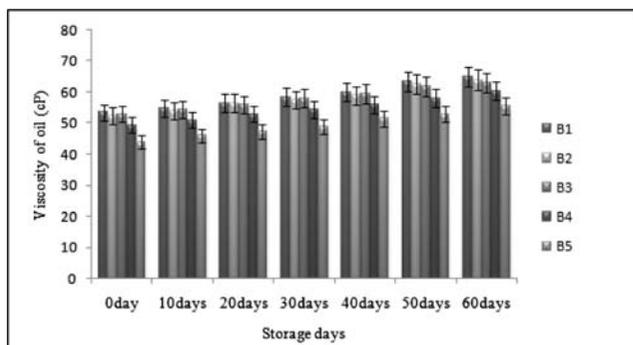


Fig. 1: Viscosity of Oils and Blends with Storage

comparison with standard Lovibond red and yellow glasses. The changes in the lovibond colour value of selected oil blends during storage are shown in (Fig. 2). The change in colour of B1 was found to from 48.50 to 90.00 units; while in B5, it changed to 30 (60 days) from 26.00 unit (0 days). All the oil blends showed an increase in colour indices with storage period. For B2, the lovibond colour ranged from 46.00 to 77.50 units; in B3, it was from 45.50 (0 day) to 65.00 units (60 days); in B4, the change was from 40.00 (0 day) to 60.00 units (60 days). The intensity of the colour was seen to be lighter in B5, possibly because it was refined. The colour of B5 was deep yellow while the other blends were darker since they contained mustard oil in higher proportion. Further, darkening could have been enhanced during storage due to oxidative effects. This is well correlated to PV, TV and p-AV values reported later. From physical analyses, we therefore, inferred that colour of blend B5 was most stable with storage and frying.

Chemical assay of oils and blends:

Determination of acid value of oils and blends: The changes in acid values (expressed as % oleic acid) of oils and blends for the storage period of 60 days are

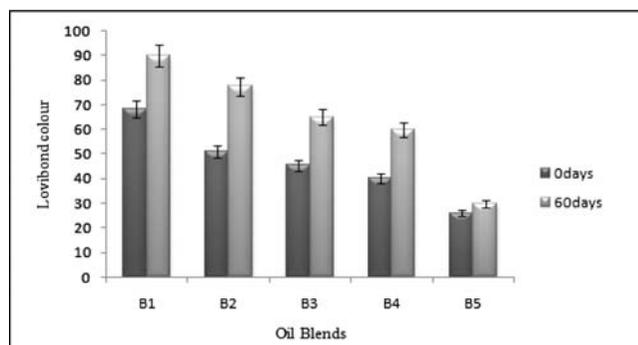


Fig. 2: Lovibond Colour (Y+5R) of Oil Blends with Storage

depicted in Table 1. The initial acid value of native oil B1 was 0.21 on day zero which increased to 0.97 (60 days) and similarly for B5, the values were 0.92 on day zero and 1.89 at the end of 60 days. For blends, B2, values were 0.22 (0 day) and 0.78 (60 days); for B3, 0.45 (0 day) and 1.18 (60 days) and for B4, 0.57 (0 day) and 1.39 (60 days); showing minimum oxidation in B2 among all oils and blends. The increase in the acid values could be attributed to the increase in rate of hydrolytic rancidity when water is introduced into the frying oil from the potato wedges (at initial stages of frying) followed by formation of secondary oxidation products.

Analysis of peroxide value (PV) oils and blends: The PV of all blends registered a progressive increase with storage duration. Our results are in agreement with that reported by Gulla *et al*²⁰, who reported a steady increase in PVs in blends of mustard and sesame oil. The increase in PV of B1 was from 4.31 (0 day) to 14.68 mEq/Kg (60 days) while for B5 it was from 2.78 (0 day) to 14.79 mEq/Kg (60 days). For B2, the values ranged from 4.78 to 14.36; for B3, from 5.85 to 15.22 mEq/Kg and for B4, from 5.97 to 16.73 mEq/Kg, for 0 day and 60 days respectively (Table 2). Although, peroxides

TABLE 1
Changes in the Acid Value (% oleic acid) of Oil Blends During Storage Days

Storage days	Oils				
	B1	B2	B3	B4	B5
0	0.15±0.03	0.22±0.03 ^a	0.45±0.04 ^a	0.57±0.05	0.92±0.03
10	0.43±0.02	0.47±0.03 ^b	0.55±0.03 ^b	0.81±0.04	1.11±0.04
20	0.57±0.04	0.59±0.04 ^c	0.68±0.04 ^c	0.85±0.03	1.34±0.04
30	0.72±0.06	0.68±0.05 ^d	0.78±0.04 ^d	0.96±0.05	1.52±0.03
40	0.89±0.03	0.79±0.04 ^e	0.90±0.03 ^e	1.20±0.03	1.75±0.04
50	0.91±0.05	0.86±0.03 ^f	0.99±0.05 ^f	1.35±0.04	1.83±0.04
60	0.97±0.07	0.95±0.04 ^g	1.10±0.05 ^g	1.39±0.04	1.89±0.06

Mean ± S.D of three independent experiments

B1=100% mustard, B2=90:10, B3=80:20, B4=50:50, B5=100% sesame.

^{a-g} Different letters in a row in a particular test category are not significantly different (p<0.05)

are possibly not directly responsible for the taste and odour of rancid fats, their concentration is useful in assessing the extent of oxidative rancidity. During frying, oils are hydrolysed to form FFA and mono- and diglycerides, and these compounds accumulate in the frying oil. In addition, oils also oxidize to form hydroperoxides, conjugated dienoic acids, epoxides, hydroxides, aldehydes, and ketones. These compounds may undergo fission into smaller fragments or may remain in the triglyceride molecule and cross-link with each other, leading to dimeric and higher polymeric triglycerides. An increase in these volatile compounds could be attributed to an increase in FFA content and PV in the oil samples²¹. According to the Prevention of Food and Adulteration Act (PFA, 1954), fresh oil usually have peroxide value well below 10 mEq/Kg. A rancid taste is noticeable when the peroxide value is >20 mEq/Kg. This observation is in accordance to our sensory panel data, elaborated later. Unlike in the present study, the changes in the PV of edible oils

stored at room temperature were not regular which has also been reported by Murthy *et al*^{3,22, 23, 24}.

Estimation of para-anisidine value (p-AV) of oils and blends: The formation of secondary oxidation products was determined at an interval of 10 days by p-AV. There was an increase in p-AV in individual oils (B1 and B5), but not in the blends on day zero of frying. The initial p-AV of B1 was found to be 1.675 on 0 day and 4.085 units after 60 days; for B5, it was 1.78 (0 day) and 2.01 units (60 days); for B2, it was 1.020 (0 day) and 3.121 units (60 days); for B3, 1.240 (0 day) and 3.519 units (60 days); and for B4, it was 0.870 (0 days) and (3.021 units) after 60 days with frying (Table 3). Typically, p-AV increases as aldehydes are produced and subsequently further oxidized or participate in dimerization or condensation reactions. According to p-AV values, B5 was most stable since it showed least change. This value mainly reflects the oxidation history of the oil. Since B5 is refined sesame

TABLE 2
Changes in the Peroxide Value (mEq/kg) of Oil Blends During Storage Days

Storage days	Oils				
	B1	B2	B3	B4	B5
0	4.31±0.06	3.78±0.05 ^a	4.78±0.07 ^a	5.85±0.03	5.97±0.05
10	5.35±0.04	4.85±0.04 ^b	5.90±0.04 ^b	6.87±0.09	8.98±0.01
20	7.38±0.06	6.18±0.02 ^c	8.25±0.05 ^c	8.40±0.02	9.12±0.02
30	8.92±0.03	9.14±0.09 ^d	9.10±0.07 ^d	9.39±0.02	10.49±0.07
40	10.14±0.09	12.50±0.08 ^e	11.92±0.05 ^e	12.40±0.01	13.64±0.02
50	13.93±0.02	14.32±0.06 ^f	13.34±0.04 ^f	15.29±0.06	14.72±0.03
60	14.68±0.06	14.36±0.05 ^g	14.79±0.07 ^g	15.22±0.05	15.73±0.03

Mean ± S.D of three samples of one experimental set

B1=100% mustard, B2=90:10, B3=80:20, B4=50:50, B5=100% sesame.

^{a-g} Different letters in a row in a particular test category is not significantly different ($p < 0.05$)

TABLE 3
Changes in the Para-anisidine Value of Oil Blends During Storage Days

Storage days	Oils				
	B1	B2	B3	B4	B5
0	1.675±0.006	0.51±0.04 ^a	0.870±0.050 ^a	1.020±0.035	1.240±0.030
10	1.734±0.007	1.25±0.03 ^b	0.980±0.050 ^b	1.120±0.045	1.430±0.040
20	2.120±0.035	1.82±0.03 ^c	1.220±0.045 ^c	1.345±0.005	1.625±0.005
30	2.320±0.005	1.98±0.02 ^d	1.450±0.024 ^d	1.532±0.003	1.821±0.003
40	2.831±0.003	2.21±0.02 ^e	2.095±0.025 ^e	1.983±0.006	2.431±0.006
50	3.015±0.002	2.43±0.02 ^f	2.252±0.005 ^f	2.032±0.007	2.619±0.007
60	3.685±0.006	3.01±0.02 ^g	3.021±0.005 ^g	3.121±0.002	3.120±0.002

Mean ± S.D of three samples of one experimental set

B1=100% mustard, B2=90:10, B3=80:20, B4=50:50, B5=100% sesame.

^{a-g} Different letters in a row in a particular test category is not significantly different ($p < 0.05$)

oil, it was least oxidised and therefore, showed highest stability in terms of p-AV.

Totox value (TV) oils and blends: Similar to changes in PV and p-AV, TV also showed significant rise during the entire storage period. Table 4 gives the changes in TV values of the oil blends during storage. The TV of B1 was found to increase from 10.295 to 31.905 units after 60 days and in B5, it increased from 4.070 to 26.371 units after 60 days. These increases were due to increase of both PV and p-AV. The highest increase was seen in B4 from 15.83 units for 0 day to 36.481 units after 60 days. B5 had the lowest value of TV and therefore, it can be concluded that B5 was most stable among all blends studied.

Conjugated dienes and trienes in oils and blends by absorbances at 232 and 268 nm: The longer the frying time, higher the absorbance of oils. The results obtained were closely related to PV. The conjugated compounds showed there was a trend of increasing

diene content with storage and frying. The % diene content of B1 increased from 0.384 to 0.648 after 60 days; in B5, it increased from 0.283 to 0.653 after 60 days; in B2 the increase was 0.283 to 0.645; in B3, from 0.243 to 0.679 and in B4, from 0.476 to 0.692 after 60 days (Table 5). The magnitudes of the differences were different for different blends. A relatively smaller increase in diene content was observed in B2 at later stages of frying, possibly when equilibrium between the rate of formation of conjugated dienes and the rate of formation of polymers was attained. According to this data and from PVs, we found that the blend B2 underwent least oxidation. The absorbance at 268 nm measures particularly, the diethylenic ketones. The triene value of B1 increased from 0.060 to 0.180 after 60 days; in B5, from 0.066 to 0.182; in B2, from 0.085 to 0.178; in B3, from 0.090 to 0.195 and in B4, from 0.132 to 0.221 after 60 days (Table 6).

TABLE 4
Changes in the Totox Value (2PV+p-AV) of Oil Blends During Storage Days

Storage days	Oils				
	B1	B2	B3	B4	B5
0	10.295±0.004	10.070±0.032 ^a	12.944±0.022 ^a	15.830±0.082	10.580±0.034
10	12.434±0.018	13.355±0.069 ^b	15.175±0.088 ^b	18.944±0.075	12.922±0.016
20	16.880±0.390	17.180±0.024 ^c	18.425±0.070 ^c	19.460±0.345	16.508±0.390
30	20.160±0.202	19.265±0.344 ^d	20.601±0.204 ^d	22.430±0.155	19.732±0.346
40	23.111±0.392	22.216±0.027 ^e	27.231±0.190 ^e	29.375±0.533	25.823±0.204
50	30.875±0.198	27.273±0.028 ^f	33.199±0.125 ^f	35.965±0.105	30.712±0.198
60	31.905±0.320	31.371±0.204 ^g	33.959±0.115 ^g	36.481±0.100	31.401±0.039

Mean ± S.D of three samples of one experimental set

B1=100% mustard, B2=90:10, B3=80:20, B4=50:50, B5=100% sesame.

^{a-g} Different letters in a row in a particular test category is not significantly different ($p < 0.05$)

TABLE 5
Changes in the Values of Conjugated Dienes at 233nm of Oil Blends During Storage Days

Storage days	Oils				
	B1	B2	B3	B4	B5
0	0.384±0.003	0.283±0.007 ^a	0.243±0.003 ^a	0.476±0.006	0.283±0.007
10	0.412±0.004	0.324±0.005 ^b	0.341±0.004 ^b	0.525±0.004	0.324±0.005
20	0.483±0.006	0.376±0.003 ^c	0.389±0.004 ^c	0.583±0.006	0.376±0.003
30	0.495±0.007	0.392±0.004 ^d	0.412±0.006 ^d	0.625±0.005	0.392±0.004
40	0.596±0.002	0.600±0.005 ^e	0.654±0.007 ^e	0.651±0.003	0.600±0.005
50	0.611±0.006	0.615±0.006 ^f	0.663±0.002 ^f	0.682±0.005	0.615±0.006
60	0.648±0.005	0.645±0.008 ^g	0.679±0.006 ^g	0.692±0.007	0.653±0.008

Mean ± S.D of three samples of one experimental set

B1=100% mustard, B2=90:10, B3=80:20, B4=50:50, B5=100% sesame.

^{a-g} Different letters in a row in a particular test category is not significantly different ($p < 0.05$)

TABLE 6

Changes in the Conjugated Trienes Value at 268 nm of Oil Blends During Storage Days

Storage days	Oils				
	B1	B2	B3	B4	B5
0	0.060±0.045	0.085±0.003 ^a	0.090±0.003 ^a	0.132±0.002	0.066±0.004
10	0.072±0.002	0.094±0.005 ^b	0.115±0.007 ^b	0.153±0.003	0.083±0.002
20	0.136±0.065	0.121±0.005 ^c	0.139±0.008 ^c	0.185±0.003	0.145±0.005
30	0.142±0.002	0.135±0.006 ^d	0.149±0.002 ^d	0.196±0.005	0.153±0.007
40	0.158±0.004	0.149±0.002 ^e	0.161±0.005 ^e	0.211±0.004	0.162±0.008
50	0.169±0.006	0.158±0.004 ^f	0.181±0.002 ^f	0.224±0.006	0.171±0.003
60	0.180±0.025	0.178±0.005 ^g	0.195±0.005 ^g	0.221±0.006	0.182±0.007

Mean ± S.D of three samples of one experimental set

B1=100% mustard, B2=90:10, B3=80:20, B4=50:50, B5=100% sesame.

^{a-g} Different letters in a row in a particular test category is not significantly different ($p < 0.05$)

Antioxidant activity of oil blends: The antioxidant activities of oils were evaluated by the DPPH radical scavenging assay. The results depicted the higher antioxidant capacity of B1 compared to other blends. Also with frying, the increment in IC₅₀ value of B4 was significantly higher ($p = 0.043$) compared to other blends (Fig. 3). This indicates that mustard oil has better antioxidant potential in shallow frying. This observation could possibly be owing to the most abundant antioxidant present in mustard oil -melatonin, which has temperature stability until 117°C while sesamol and sesamolein antioxidants of sesame oil degrade at 93°C or above ^{25, 26}.

Effect of storage on Fatty acid composition of oils by FAME-GC: The objective of this part of the study was to determine the optimum fatty acid ratio to achieve a balance between the storage stability, frying stability and health aspect. In our study, the gradual increase in saturated fat and decrease in unsaturated fats

were observed with storage. This effect was more pronounced in the blends than in the individual oils (i.e., B1 and B5). This may probably be due to oxidative cleavage of fatty acids on storage which has also been reported by Gulla and Waghyar²⁷.

Based on the fatty acid composition of various oil blends, proportion of SFA: MUFA: PUFA was calculated. These values indicate that although the ideal proportion of 1:1:1 (as per the recommendations of American Health Association) could not be achieved; it is closer to this recommendation compared to those obtained for B1 and B5 (Table 7). In the oil blends studied, it was seen that B3 blend showed a near ideal fatty acid ratio followed by the B2 blend. From one-way ANOVA, there was no significant difference ($p = 0.047$) between blends B2 and B3. The physicochemical studies showed that B2 blend was more stable than B3 blend. The GC chromatogram of FAME of B2 blend is shown in Figure 4. Furthermore, B1, B4 and B5 have higher ratios of SFA: MUFA: PUFA than B2 (Table 7). Therefore, from physicochemical assays we concluded that B2 blend was the most shelf-stable with storage and frying. This study indicated that mustard oil had lost its MUFA: PUFA ratio on frying although its antioxidant efficacy survived. This observation suggests further studies on health beneficial aspects of mustard oil.

Sensory analysis of fried potato wedges: For B3 blend, it was observed that the fried potato wedges were crispier compared to those obtained by other oil blends. The wedges fried in B3 were acceptable until 40 days of storage, after which it lost its hardness and became soggy and unacceptable. The B2-fried potato wedges had acceptability up to 50 days of storage while B1,

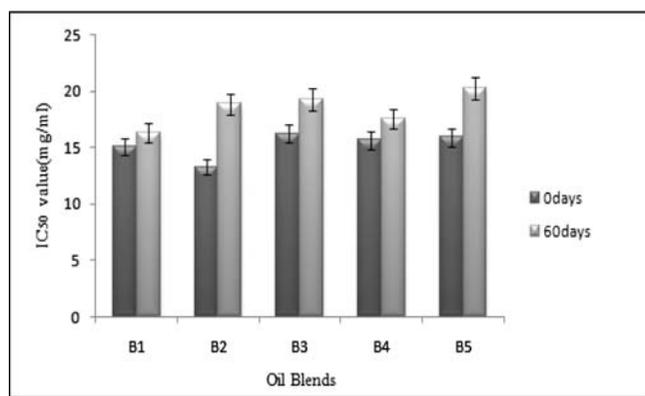


Fig. 3: DPPH Antioxidant Activity of Oil Blends with Storage

TABLE 7
Proportion of SFA: MUFA: PUFA (S:M:P) Composition of the Oil Blends as a Function of Storage Time

Storage days	Oils				
	B1	B2	B3	B4	B5
	S:M:P	S:M:P	S:M:P	S:M:P	S:M:P
0 (unfried)	1:2.85:13.17	1:0.30:8.83	1:0.18:8.99	1:6.34:4.94	1:1.04:4.96
0 (fried)	1:3.43:10.23	1:2.94:4.56	1:0.30:8.16	1:6.91:4.25	1:2.34:4.68
60 (fried)	1:7.33:2.90	1:3.98:2.33	1:0.56:6.74	1:8.38:3.89	1:4.65:2.51

B1=100% mustard, B2=90:10, B3=80:20, B4=50:50, B5=100% sesame

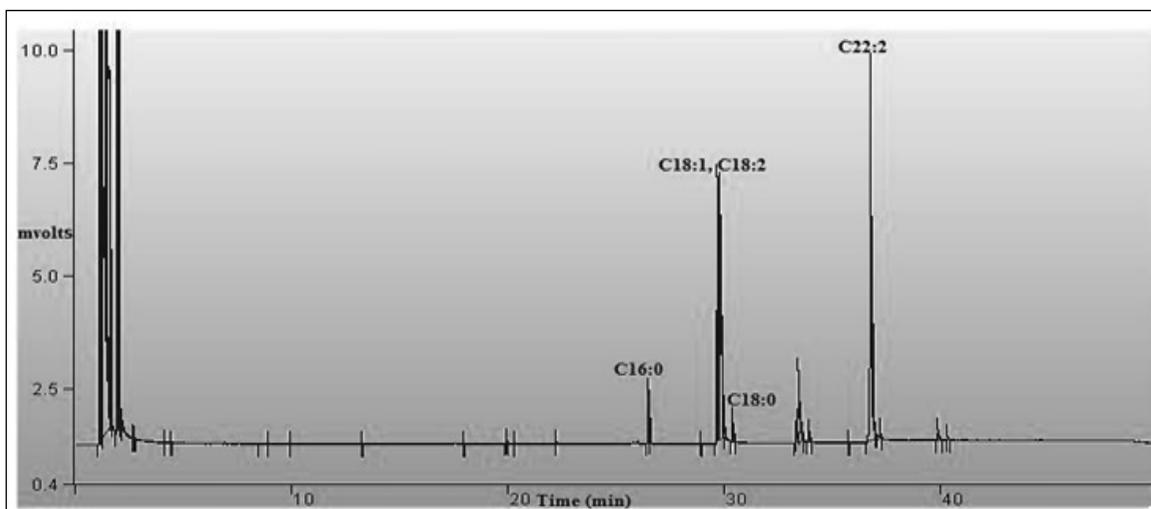


Fig. 4: FAME-GC of Mustard: Sesame (90:10) Blended Oil

B4 and B5-fried potato wedges were acceptable until 40 days of storage.

Thus, B2 blend-fried potato wedges (wrapped in aluminium foil and stored in nitrogen- flushed LDPE packs at -18°C), had the highest acceptability for the maximum duration of storage and obtained the highest scores among all batches. According to sensory analysis, B2 blend-fried wedges were more acceptable than other blended oil-fried potato wedges (Fig. 5).

Texture analysis of the fried potato wedges: It was observed that for all the samples, highest values of hardness were obtained for potato wedges fried in B1. It was also observed that the 'shear force' (hardness) values decreased with number of storage days. This is due to loss of firmness during storage, as has been reported in our sensory evaluation studies. Among all oils and blends, B1-fried potato wedges had maximum hardness, i.e., desired crispness, showing suitability of the oil in frying.

TBARS assay for formation of malondialdehyde in fried potato wedges: The TBARS assay for fried potato

wedges showed trends similar to that obtained in physicochemical tests and by antioxidant assay. We observed greatest content of MDA (μ moles malon dialdehyde/kg potato wedges) in wedges shallow fried in oil blends. MDA in potato wedges fried in B1 was 0.46 on day 0 and increased to 0.741 after 60 days. For B5-fried wedges, MDA was 0.140 on day 0 and 0.219 for 60 days. The MDA values were comparatively lower in blends than in individual oils B1 and B5. In

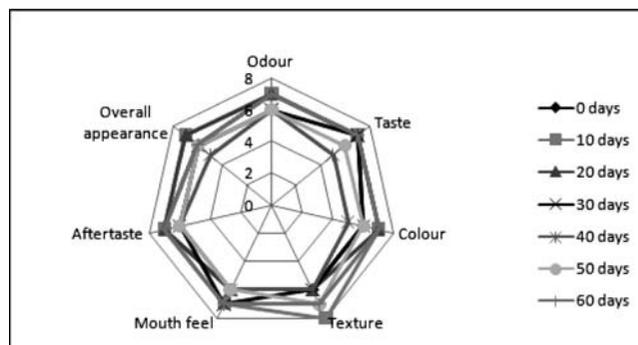


Fig. 5: Effect of Sensory Characteristics of Fried Potato Wedges Fried in (Mustard: Sesame, 90:10) Blended Oil

B2, the MDA was 0.347 (0 days) and increased to 0.731 (60 days). In B3 (80:20), MDA was 0.303 (0 days) and it increased to 0.612 (60 days) and in B4 (50:50), it increased from 0.209 (0 days) to 0.598 after 60 days (Table 8).

MDA values in the fried wedges were found to be very low than that reported by Cheman and Tan²⁸, who worked on palmolein-fried wedges in deep frying. Low MDA content in potato wedges shallow fried in sesame and mustard oils, indicated generation of lesser secondary oxidation products during frying.

MDA values of the fried potato wedges increased steadily with frying time in agreement with Cheman and Tan. To the best of our knowledge, there are no set standards and reports in literature that indicate the acceptable level of malonaldehyde in fried potato wedges. According to our data, B5 blend-fried wedges had lowest MDA compared to those obtained in the remaining blends.

After evaluating all the physiochemical properties, it was observed that blend of Mustard: Sesame (90:10) had the edges over the other oil or oil blends, used for deep frying. It was, therefore, selected for computation of 'h' in deep frying mode.

Determination of heat transfer coefficient

Indirect method for measurement of 'h' with bubbling effect: The temperature profile (Fig. 6a-c) represents the values of temperature in case of indirect method of measurement (with bubbling) at the geometric centre of the metal piece, until constant values of

the same were obtained in the transducer. The final temperatures were recorded as 121.7, 144.6, 158.4°C when the temperature of the oil was 130, 150 and 170°C, respectively.

The 'h' values estimated by indirect method with bubbling effects at different frying temperatures were in the range of 141.44±3.22 to 249.00±4.56 W/m²°C at 130°C; 214.67±3.76 to 274.76±4.66 W/m²°C at 150°C and 426.15±5.66 to 456.44±6.77 W/m²°C at 170°C. Lowest values were obtained at 130°C. Since frying temperature regime of 150- 170°C is generally employed in commercial frying, it is recommended to consider the effect of bubbling for determination of 'h' in indirect method of estimation. Bubbling may possibly have pronounced effect on boundary layer mixing at the metal surface during frying.

Indirect method for measurement of 'h' without bubbling effect: The temperature profile shown in (Fig. 7a-c) represents the constant values of temperatures displayed in the transducer. The final temperatures were recorded as 116.2, 133.3 and 155.5 °C without bubbling effect at frying temperature regimes of 130, 150 and 170°C respectively.

In absence of bubbling, the 'h' values ranged from 166.74±4.19 to 301.89±7.74 W/m²°C at 130°C, 168.29±5.01 to 890.21±8.08 W/m²°C at 150°C and 196.52±5.19 to 950.22±8.51 W/m²°C at 170°C. The higher rates of heating, i.e. higher values of 'h' were observed with increase in frying temperature in case of indirect method without bubbling effect in accordance to that reported by Costa *et al*²⁹. This may be attributed to the fact that higher temperature resulted in water

TABLE 8
Changes in the MDA (µmole/kg potato wedges) of Oil Blends During Storage Days

Storage days	Oils				
	B1	B2	B3	B4	B5
0	0.460±0.002	0.347±0.022 ^a	0.303±0.032 ^a	0.209±0.021	0.140±0.040
10	0.555±0.004	0.446±0.064 ^b	0.481±0.026 ^b	0.331±0.048	0.153±0.052
20	0.630±0.006	0.582±0.082 ^c	0.492±0.048 ^c	0.485±0.037	0.162±0.034
30	0.680±0.002	0.675±0.026 ^d	0.549±0.069 ^d	0.525±0.073	0.171±0.026
40	0.710±0.005	0.702±0.041 ^e	0.582±0.033 ^e	0.573±0.045	0.192±0.088
50	0.738±0.004	0.725±0.037 ^f	0.589±0.052 ^f	0.591±0.081	0.212±0.070
60	0.741±0.008	0.731±0.048 ^g	0.612±0.087 ^g	0.598±0.026	0.219±0.032

Mean ± S.D of three samples of one experimental set

B1=100% mustard, B2=90:10, B3=80:20, B4=50:50, B5=100% sesame.

^{a-g} Different letters in a row in a particular test category is not significantly different (p<0.05)

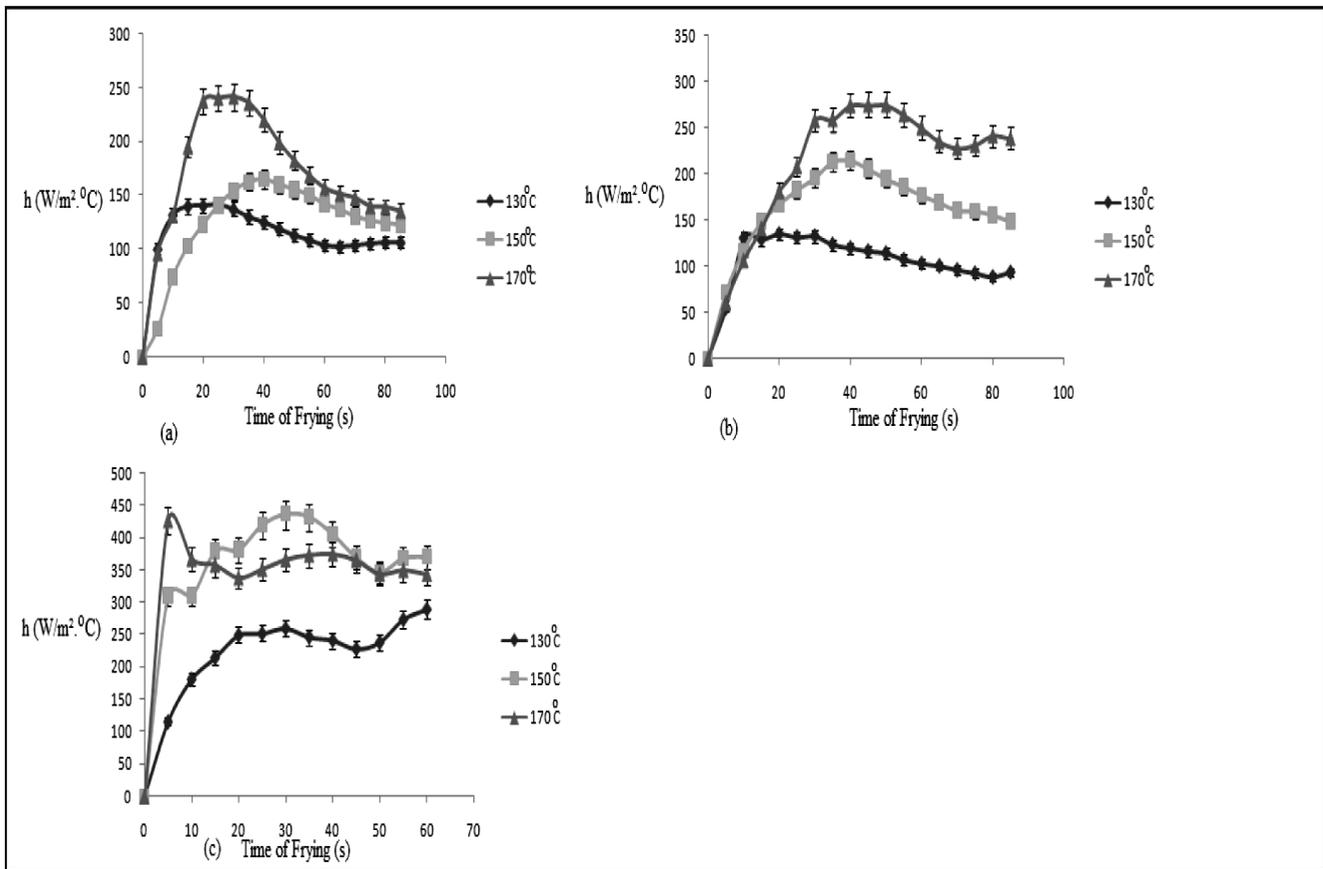


Fig. 6: The Temperature Profile for Indirect Method Using SS 304 Metal Block at Different Temperature Regimes With the Effect of Bubbling in (a) Mustard Oil, (b) Sesame Oil, (c) Blended Oil Mustard: Sesame Oil 90:10)

loss from the product at a higher rate and therefore, contributed to higher 'h' values.

Direct method for measurement of 'h': In case of direct method, temperature was measured at three different locations in the potato wedges. The temperature at the surface increased rapidly compared to that at the geometric centre of the potato wedge while the temperature at the bottom surface was relatively higher than the top surface owing to its proximity to the heating coil. The initial temperature of the potato wedge was in the range of 22.8-24.5°C at 0 sec and it increased with frying to 74-101°C at 300 sec for all three temperature ranges. A lower rate of increment was observed at around the boiling point of water owing to vaporization of moisture in wedges.

For direct method, at 130°C, the bubbling effect was minimum owing to less agitation surrounding the surface of potato wedge and insufficiently contributed to heat transfer. Consequently, a higher deviation in minimum and maximum values (28.03 %, 32.86 %, 73.77 %) of 'h' was observed. At 170°C, higher bubbling caused resistance to heat flow to the potato surface and therefore, caused increased deviation (38.56 %,

40.52 %, and 84.86 %) in the minimum and maximum values of 'h'.

The 'h' values for different frying temperatures in case of direct method ranged from 105.72±4.52 to 1080.29±27.5 W/m²·°C, 190.49±5.3 to 1488.09±21.75 W/m²·°C and 151.20±2.67 to 1789.83±32.87 W/m²·°C at 130, 150 and 170°C, respectively. All these values are in the range of 105-1789 W/m²·°C (Fig. 8). The highest deviation of 'h' value in case of direct method was obtained at 170°C. The reason for this observation could be that in the preliminary phase of frying, potato wedges come in influence of high temperature gradient vis-à-vis ambient (23±2°C) temperature and at the latter stages, the moisture diffusivity within the product is considerably high, resulting in decreased temperature gradient and therefore lower 'h' value. Based on these observations, we inferred 150°C as the optimum deep frying temperature to obtain uniformity in heat transfer in the vicinity of the potato wedge.

Moisture content of potato wedges during frying: The moisture content of the potato wedges decreased with progression of frying. The results also depicted that rate of moisture loss was higher for higher oil

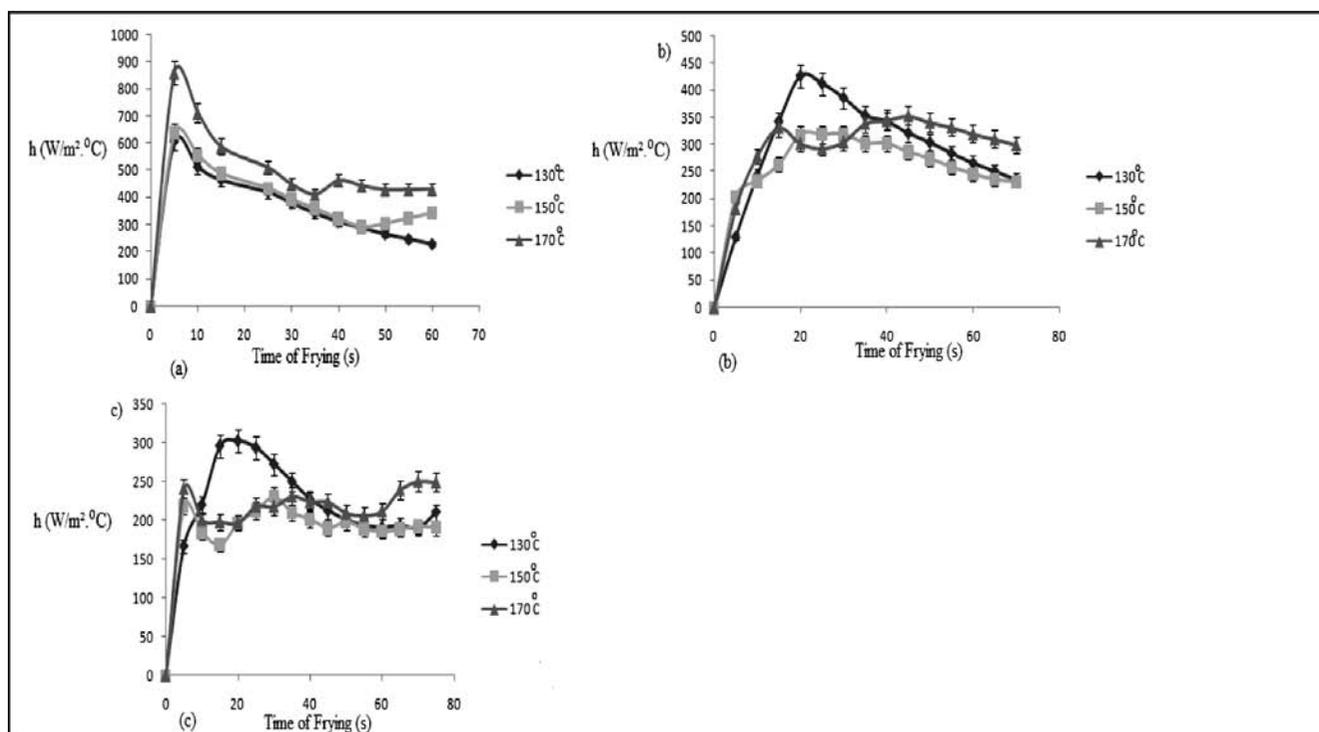


Fig. 7: The Temperature Profile for Indirect Method Using SS 304 Metal Block at Different Temperature Regimes without the Effect of Bubbling in ((a) Mustard Oil, (b) Sesame Oil, (c) Blended Oil Mustard: Sesame Oil 90:10)

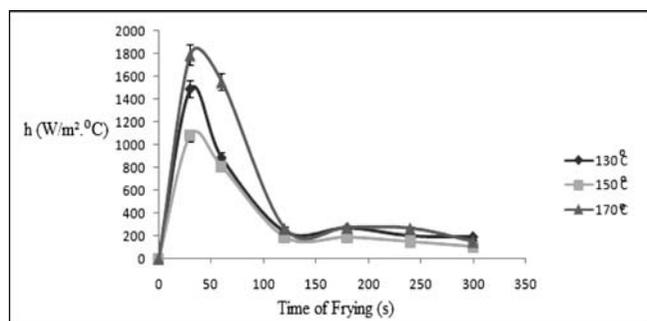


Fig. 8: Heat Transfer Coefficient Measured by Direct Method in Different Temperature Regime

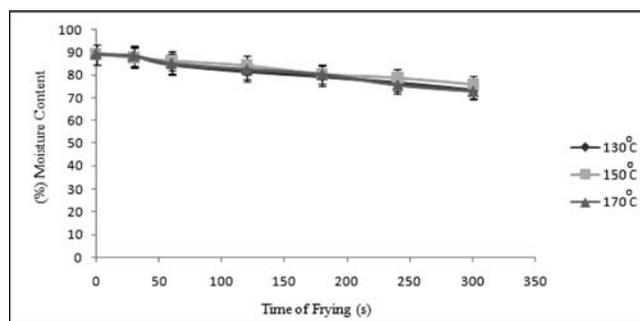


Fig. 9: Moisture Content Profile of Potato Wedges at Different Temperature Regime

temperature. Also, a lower decrease in moisture content was observed at the beginning of the frying process as shown in (Fig. 9). Moisture losses of 2.925, 3.802 and 4.671% in the first 60 s of frying at 130, 150 and 170°C could have been the result of drying, post blanching. The highest moisture losses of 5.825, 6.804 and 7.754% at 130, 150 and 170°C, respectively were observed during 60 to 120 s of frying time. The moisture curves thereafter were flat until 300 s of frying at all temperature regimes of frying oil temperature. From our studies, we found indirect method (with bubbling effect) to be the most suitable method of estimation of heat transfer co-efficient in deep frying. For domestic purpose, we recommend 130°C as the frying temperature but for large scale processing in industries, 150°C is recommended,

although 180°C is most used. Appreciable 'h' values have been obtained at 150°C and adverse oxidative deterioration of the fried potato wedges is expected to be lower than that at 180°C.

CONCLUSIONS

Blends of mustard: sesame was used for frying in this study, B1 (100:0), B2 (90:10), B3 (80:20), B4 (50:50) and B5 (0:100). Physicochemical studies indicated that among all blends, B2 (90:10 = mustard: sesame) was the most stable and underwent least oxidation on storage and frying. However, fatty acid compositional analyses by FAME-GC of the blends suggested that B3 blend was the best blend since its composition complied nearly to 1:1:1 = SFA:MUFA:PUFA as per recommendations of American

Heart Association, followed by B2 (1:3.98:2.33) and B3(1:0.56:6.74) blends. From one-way ANOVA, no significant difference ($p=0.043$) between B2 and B3 blends was obtained. Therefore, holistically, it was adjudged that B2 blend (mustard:sesame = 90:10) is most recommended and has nutritional significance in shallow frying applications. The 'h' values obtained in B2 by both direct and indirect methods were appreciably different.

The minimum value of 'h' obtained was $105.72 \pm 4.52 \text{ W/m}^2\text{C}$; while the maximum value was $1789.83 \pm 3.87 \text{ W/m}^2\text{C}$, in case of direct method. In case of indirect method, the values ranged from $141.44 \pm 3.22 \text{ W/m}^2\text{C}$ to $456.44 \pm 6.77 \text{ W/m}^2\text{C}$ in deep frying temperature (130- 170°C) regime considering bubbling effect. In absence of bubbling effect, the values ranged from $166.74 \pm 4.19 \text{ W/m}^2\text{C}$ to $950.22 \pm 8.51 \text{ W/m}^2\text{C}$ at in the 130-170°C frying temperature regime. The 'h' values obtained by indirect method were significantly different in presence and absence of bubbling. Therefore, we consider the bubbling effect to be crucial and recommend evaluation of 'h' value using indirect method of estimation for modeling frying operations in industrial/ commercial purposes.

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Membrane Processing of Biodiesel Wastewater for Possible Reuse

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ABSTRACT

Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. In down stream process of the alkali catalyzed transesterification, or in acid catalyzed esterification a significant amount of wastewater is generated. This wastewater is to be treated before discharge. In the present study, the wastewater generated in a biodiesel production plant was treated. In pretreatment steps, alum was used as coagulant. The alum dosage, stirring time and settling time were optimized to 50 mg/L, 1 h and 2 h respectively. After coagulation treatment, the treated water was subjected to adsorbent treatment using powdered activated charcoal (PAC) for the removal of color and odoriferous compounds. It was found that the optimized dosage of PAC in adsorbent treatment was 0.5 g/L and stirring time was 2 h. After the pretreatment, the pretreated water was first passed through ceramic microfiltration membranes having the pore size of 0.2 μm and then it was followed by spiral wound nanofiltration and reverse osmosis membranes. All the major contaminants could be separated significantly by the combinations of these membrane separation techniques. The processing conditions were also optimized for various membrane separations. The quality of processed water after membrane separation was found to be suitable for reuse in the process or for various other purposes.

KEYWORDS: *Biodiesel wastewater; coagulants; alum; microfiltration (MF); nanofiltration (NF); reverse osmosis (RO)*

INTRODUCTION

India is heavily dependent on imports of crude petroleum oil. There is an urgent need to develop alternative source of energy. Biodiesel is projected to be one of the most viable alternatives. Biodiesel, an alternative diesel fuel, is primarily long chain fatty acid methyl ester (FAME) made from renewable biological

resources such as vegetable oils and animal fats. It has become more attractive because of environmental benefits such as biodegradability, low carbon emission profiles, high combustion efficiency, low sulfur and aromatic contents and high cetane number¹⁻³. But, India is importing more than 50% of its edible oil requirement and hence India has to depend on non-edible oils for the production of biodiesel. Various non-edible oils such as karanja, jatropha, mahua, palash etc are available in India and can be used for biodiesel production. Unlike the edible grade oils used in production of biodiesel in USA, European countries or even in Malaysia, these two oils have impurities like high FFA, gums and mucilages and other toxic components that may affect the properties of biodiesel prepared from these oils. Therefore, they require elaborate pretreatment before the final transesterification reaction to produce biodiesel if the biodiesel produced has to meet stringent specification prescribed by organizations like BIS or ASTM or EN14214. Every steps of these treatments generates considerable amount of contaminated waste water.

Several methods of biodiesel production, using alkali catalysts, acid catalysts, enzymes, supercritical methanol, ultrasonic irradiation and thermal decomposition of oil have been developed. Ma and Hanna² had given a review on the production of biodiesel from the cooking oils, vegetable oils and animal fats etc by the method of transesterification, micro-emulsions, thermal cracking or pyrolysis. Preliminary studies on usage of frying oils to convert to biodiesel by transesterification with different alcohols and potassium hydroxide as catalysts was shown by Nye⁴. Kusdiana and Saka⁵ studied on the esterification of free fatty acids of rapeseed oil by supercritical methanol. Experimental studies on the influence of low frequency ultrasounds (28 and 40 kHz) versus mechanical stirring on alkali (NaOH) catalyzed transesterification was described by Stavarache⁶.

Amongst all the methods available for the production of the biodiesel, the alkali catalyzed transesterification is the most attractive method

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because of high conversion of triglycerides (Oil) to fatty acid methyl esters (Biodiesel) by a simple chemical reaction in a short time. Due to these advantages, most of the people follow this method for biodiesel production. In the alkali catalyzed transesterification process, huge amount of wastewater is generated. For 100 L of production of biodiesel fuel, about 20 L of wastewater is generated⁷. The Indian perspective is entirely different. In India, the major raw materials are non-edible oils. Most of these oils have higher amount of free fatty acids and gums. As a pretreatment process, degumming has to be done and it generates huge wastewater. If phosphoric acid is used, the pollution level is also increased. As most of these oils have higher FFA, these are to be converted to methyl esters by confirmation of acid catalyzed esterification reaction and base catalyzed transesterification reaction. The wastewater generated in these processes has to be neutralized. This process, thus, generates highly salt contaminated wastewater and that has to be treated.

Various environmental protection agencies had imposed more stringent rules and stipulated their standards for the discharge of industrial wastewater. Researchers all over the world are trying to develop some methodologies to treat the wastewater so that it could be reused or recycled. The treatment processes include physical process such as screening, flocculation, flotation and sedimentation etc⁸, chemical processes such as chemical coagulation, disinfection, neutralization, precipitation, oxidation, stabilization and chemical scale control etc and biological process such as aerobic, anaerobic, anoxic and lagoon processes⁹. The type of the process that can be used to treat wastewaters will depend on the type and extent of contamination of pollutants. These processes, however, are used only to treat the water before discharge. Most of these processes have limitations and the treated water could not be reused/recycled.

The membrane separation technique is already a proven technology in the treatment and recycling of wastewater streams coming out from the various vegetable oil industries¹⁰⁻¹², chemical industries¹³, textiles industries¹⁴, food processing industries¹⁵⁻¹⁶ and other industries¹⁷. India is looking forward to biodiesel production in a big way. Considerable amount of wastewater will be generated. It was, therefore, felt that a process for treatment of wastewater coming out of biodiesel industries should be developed. Application of membrane processing techniques might produce a quality of water that can be reused.

Pretreatment using conventional coagulating agents namely alum, polyaluminium chloride, ferric chloride and chitosan before the membrane separation are well known technique to remove suspended solids,

fouling substances so that the permeation flux and the life of the membranes are increased¹⁸⁻²¹. In this study pretreatment was done with alum as coagulant.

The information available on treatment of biodiesel wastewater is very little. Different approaches were followed by different scientists for the treatment of the biodiesel wastewater. Suehara worked on biological treatment of wastewater using an oil degradable yeast, *Rhodotorula mucilaginosa*⁷. The process had its limitations and can be useful for small-scale production plants. Kawai and his fellow workers also have done microbiological treatment of biodiesel wastewater by using seed culture of same yeast²². Later Chavalparit and Ongwande has optimized the electrocoagulation process for the treatment of biodiesel wastewater²³. In this process, they could reduce the COD, FOG, SS upto a certain extent before discharge. Srirangan and Chavalparit have reported electrocoagulation process for treatment of biodiesel wastewater²⁴. In a recent communication, a two stage process for treatment of biodiesel wastewater at laboratory scale was described by Jaruwat²⁵. However, this process showed the presence of considerable amount of biodiesel in the waste stream that may be avoided by following well designed downstream processing. This shows that there exists lots of gap in knowledge and tremendous scope to develop a process for treatment of biodiesel wastewater. Most of the processes, till reported have tried to reduce the pollution level before discharge instead of trying for reuse of the treated water.

In this study, attempts were made to treat the wastewater from a vegetable oil based biodiesel industry for possible reuse. The biodiesel wastewater found to contain high values of conductivity, fats, oils and grease (FOG), chemical oxygen demand (COD), biological oxygen demand (BOD) etc. Initially, coagulation treatment was done followed by pretreatment and the pretreated water was then subjected to membrane separation to get the required quality of the water for reuse.

MATERIALS & METHODS

Materials

Wastewater Samples: Wastewater sample was collected from various stages of commercial production of biodiesel from a local biodiesel plant Southern Online Biotechnologies Ltd, Hyderabad, India, before any treatment. The wastewater samples from different stages were mixed and a composite wastewater sample was prepared. For laboratory scale study, biodiesel wastewater was collected from our laboratory where biodiesel was produced from karanja oil.

The oily layer from the composite wastewater sample was skimmed off as much as possible and the resultant water was passed through ordinary filter paper and then taken for further studies. The resultant raw wastewater samples had the following characteristics as shown in the Table 1.

Reagents: Alum was procured from local market. Acetic acid, barium chloride, sodium acetate, magnesium chloride, calcium chloride, magnesium sulphate and anhydrous sodium sulphate were of analytical grade and were procured from S.D. Fine Chem Ltd, Mumbai, India. Potassium nitrate (AR Grade) was procured from Qualigens Fine Chemicals, Mumbai, India. All the analytical grade reagents namely potassium hydrogen phosphate, dipotassium hydrogen phosphate, disodium hydrogen phosphate and ammonium chloride were also purchased from S.D. Fine Chem Ltd, Mumbai, India. Sulfuric acid (AR grade) was obtained from Ranbaxy Fine Chemicals Ltd, New Delhi, India. NaOH (LR grade) was procured from S.D. Fine Chem Ltd, Mumbai, India. Distilled water was prepared using laboratory scale distillation unit in the laboratory itself.

Membranes:

For lab scale studies: Microfiltration flat sheet membrane having the pore size of 2.5 micron was procured from Whatman International Ltd, Maid stone, England, U.K. Flat sheet polyvinyl alcohol nanofiltration membrane (NF-500) was procured from Permionics India Ltd,

Vadodara, India. TW30-1812 flat sheet thin film composite polyamide reverse osmosis (RO) membrane with the rejection characteristics of 98% rejection of NaCl was procured from FilmTec Corporation, Dow Chemical Company, Minneapolis, USA.

For pilot scale studies: The ceramic microfiltration membrane having 0.2 micron pore size used in pilot scale studies was procured from Orelis, France. This membrane is having the tubular configuration and the length of 800 mm and 0.167 m² surface area. The nanofiltration and reverse osmosis membranes used in the pilot scale studies were spiral wound module type and were made up of thin film composite polyamide. The NaCl rejection characteristics of NF & RO was 80 and >99% respectively and whereas NF membrane showed 98.5% hardness rejection. The surface area of the NF & RO membranes was 2.5 m² and 1 m² respectively. The nanofiltration membrane was purchased from Koch membrane systems, USA and the RO membrane was acquired from Permionics Membranes Pvt Ltd, Vadodara, India.

Analytical methods: Raw wastewater samples and various water samples after coagulant treatment and membrane processing were investigated for total suspended solids (TSS), total dissolved solids (TDS), sulfate ion concentration (SO₄⁻²), chloride ion concentration, methanol content and fats, oil and grease content (FOG) according to the APHA standard

TABLE 1
Characteristics of Biodiesel Composite Raw Wastewater

Properties	Industrial Sample	Laboratory Sample
pH	3.83	5.9
Conductivity, μS/cm	12,100	2,390
TDS (Total Dissolved Solids), mg/L	11,833	2,678
TSS (Total Suspended Solids), mg/L	2,173	650
SO ₄ ⁻² (Sulphate Ion Concentration), mg/L	49.63	73
FOG (Fats, Oils and Grease), mg/L	3,932	150
COD (Chemical Oxygen Demand), mg/L	4752.48	8,000
BOD (Biological Oxygen Demand), mg/L	2,250	3,750
Methanol Content, mg/L	200.67	Nil
Cl ⁻ (Chloride Ion Concentration), mg/L	479.85	-
Appearance	Turbid and Pale yellow	Turbid
Odor	Mal odor	Slight Odor

methods¹². pH and conductivity were measured with the help of digital pH meter (Model: DI 707) supplied by Digisun Electronics, Secunderabad and Digital Conductivity Meter (DCM 900) supplied by Global Electronics, Hyderabad respectively. For COD estimation, the digestion of the sample was done in a COD reactor, supplied by HACH, Colorado, USA followed by titration with standard Ferrous Ammonium Sulfate. 5 day 20°C BOD values were measured by using YSI-5100 dissolved oxygen meter, supplied by YSI Incorporated, Ohio, USA.

Methods:

Pretreatment studies

Coagulant treatment: The biodiesel composite wastewater was taken into a separating funnel and oily layer and aqueous layer were separated. After skimming of the oily layer, the aqueous layer was taken as composite raw wastewater sample. After adjusting the pH of the composite raw wastewater to 7, it was subjected to coagulant treatment by using alum at different dosages.

Adsorbent treatment: After coagulant treatment, the treated water was subjected to adsorbent treatment using powdered activated charcoal (PAC) as adsorbent. After treatment, the sample was filtered using filter paper.

Membrane separation: The pretreated sample was then passed through microfiltration membrane followed by nanofiltration. The permeate was then passed through reverse osmosis membrane.

For laboratory scale studies: The microfiltration were performed in a dead-end glass test cell having maximum pressure limit of 6 bar supplied by Millipore Corporation, MA, USA. The nanofiltration and reverse osmosis experiments were done in a stainless steel test cell of dead-end type having the maximum pressure limit of 50 bar and this was supplied by Snowtech Pvt. Ltd., Mumbai, India. Both the test cells were fitted with magnetic stirrer. The trans-membrane pressure (TMP) was generated by nitrogen gas.

For pilot scale studies: Cross flow membrane separation unit having 50 L stainless steel feed tank was taken for pilot scale studies. This was procured from Nishotech Systems Pvt. Ltd., Mumbai, India.

The Schematic diagram of the process developed is presented in Fig.1.

RESULTS AND DISCUSSION

Biodiesel is produced by acid catalyzed esterification of fatty acids or the alkali catalyzed transesterification of vegetable oils with methanol.

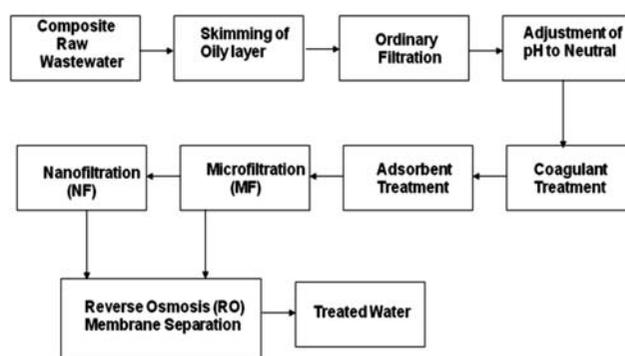


Fig. 1: Schematic diagram of developed process

During this process, wastewater containing high amounts of salts, fats, oils and grease (FOG), chemical oxygen demand (COD), biological oxygen demand (BOD) are produced. This creates serious threats to the environment and to aquatic life if discharged into the environment without proper treatment. Though, some researchers have tried to treat this wastewater for matching the discharge limits, no attempts were made to reuse the treated water. In the present investigation, attempts were made to treat the wastewater using membrane separation to get a quality of water that can be reused and recycled. At the initial stage of this study, experiments were carried out on the laboratory scale in order to check the feasibility of the process. Once feasibility studies were established experiments were carried out on the pilot scale having the capacity of 50 L of wastewater.

Initially, the wastewater sample was subjected to coagulant treatment using alum and settling of colloidal particles were observed to be good at 50 mg/L of alum dosage, 60 min of stirring time and 2 h of settling time gave the best results in coagulant treatment.

The treated water after coagulant treatment was still found to have mal odor. It was, therefore, treated using powdered activated charcoal as adsorbent. The dosages were varied from 0.1 to 1 g/L. For complete removal of odor, it was observed that the optimum dosage of PAC and stirring time were 0.5 g/L and 2 h respectively for laboratory scale study. After the adsorbent treatment and filtration, the pH of the treated water sample was adjusted to neutral and passed through microfiltration having the pore size of 2.5 micron. The permeate of microfiltration was then passed through nanofiltration followed by thin film composite polyamide reverse osmosis membrane on a dead-end test cell. The characteristics of treated water after reverse osmosis were shown in the Table 2 below.

TABLE 2
Characteristics of Treated Water after Reverse Osmosis at Laboratory Scale

Properties	Reverse osmosis permeate
pH	7
Conductivity, $\mu\text{S/cm}$	46
TDS, mg/L	20
TSS, mg/L	0
SO_4^{-2} , mg/L	0
FOG, mg/L	0
COD, mg/L	0
BOD, mg/L	0
Methanol Content	0
Cl ⁻ , mg/L	0
Appearance	Clear
Odor	Odorless

The results showed that conductivity and TDS were found to be very low and TSS, FOG, COD, BOD, sulfate and chloride ion were completely removed from wastewater. The laboratory scale results, thus, showed that the final quality of treated water was very well and can be reused. It was then planned to performed a pilot scale study by taking around 50 L of composite raw wastewater sample. The characteristics of composite raw wastewater obtained from a local industry are shown in the Table 3.

TABLE 3
Characteristics of Composite Raw Wastewater for Pilot Scale Study

Properties	Raw wastewater sample
pH	3.83
Conductivity, $\mu\text{S/cm}$	12,100
TS, mg/L	13,560
TDS, mg/L	11,833
TSS, mg/L	2,173
SO_4^{-2} , mg/L	49.63
FOG, mg/L	3,932
COD, mg/L	4500
BOD, mg/L	2,250
MeOH Content	200.67
Cl ⁻ , mg/L	479.85
Appearance	Pale yellow
Odour	Mal odour

Based on the optimized conditions on the laboratory scale, the coagulant treatment was done

using alum. The treated water sample was then subjected to adsorbent treatment with PAC. After PAC treatment, the sample was filtered by using ordinary filter paper. The characteristics of water samples at various stages of coagulant and adsorbent studies were shown in the Table 4.

TABLE 4
Characteristics of Treated Water in Pretreatment Studies on Pilot Scale

Properties	After pH of the waste water to 7	After coagulant treatment	After adsorbent treatment
pH	7	6.99	6.86
Conductivity, $\mu\text{S/cm}$	12,780	12,620	11740
TDS, mg/L	11,617	13,580	11540
TSS, mg/L	2,013	0	0
SO_4^{-2} , mg/L	50.51	71.87	72.09
FOG, mg/L	2,961	1,944	201
COD, mg/L	4752.48	5,400	5,148.52
BOD, mg/L	2,250	3,000	2,250
Cl ⁻ , mg/L	484.85	485.85	484.85
Appearance	Pale yellow	Colorless	Colorless
Odour	Mal odor	Mal odor	Odorless

A minor increase in all parameters is due to addition of alkali while adjusting the pH to 7. The results showed that suspended solids were completely removed by alum treatment and a slight increase in sulphate ion concentration is due to addition of alum. Significant removal of fats, oils and grease content could also be achieved.

In order to safe guard nanofiltration and reverse osmosis membranes and to remove larger particles, the filtrate of ordinary filtration was passed through microfiltration membrane using cross-flow ceramic membrane separation system. While separation, the average flux was 142.4 LMH at trans-membrane pressure of 1-1.5 kg/cm². The permeate of MF was passed through spiral wound polyamide NF membrane followed by RO membrane as described in the section 2.6. In nanofiltration, the average flux obtained at trans-membrane pressure of 4 kg/cm² was 386.9 LMH and 141.61 LMH in case of RO separation at TMP of 25 kg/cm². The characteristics of treated water at different stages of pilot scale membrane separation were shown in the Table 5.

TABLE 5

Characteristics of Treated Water at Different Stages of Membrane Processing on Pilot Scale

Properties	Microfiltration permeate	Nanofiltration permeate	Reverse Osmosis permeate
pH	7.02	7.01	6.99
Conductivity, $\mu\text{S}/\text{cm}$	11,130	9,420	79
TDS, mg/L	10,250	9,120	6.7
TSS, mg/L	0	0	0
SO_4^{-2} , mg/L	71.65	0	0
FOG, mg/L	0	0	0
COD, mg/L	3960.4	3485.15	141.6
BOD, mg/L	2,100	1,800	0
Cl^- , mg/L	485.35	392.38	0/2.50
Appearance	Colorless	Colorless	Colorless
Odor	Odorless	Odorless	Odorless

The treated water after reverse osmosis was completely clear and TDS and BOD were almost completely removed. FOG was completely reduced by MF membrane and sulphate ion by NF. This is due the fact that macromolecules, divalent ions were well handled by MF and NF membranes respectively.

The quality of the final treated water, the permeate of RO membrane, was compared to actual process water used in the biodiesel production. The results of the corresponding study are shown in the Table 6.

CONCLUSION

The results clearly showed that the final treated water quality was much better compared to actual process water. Hence, the treated water can be recycled back to process stream or can be used for other purposes.

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TABLE 6

Comparison of Quality of Final Treated Water with Actual Process Water

Properties	Final treated water	Actual process water
pH	6.99	7.62
Conductivity, $\mu\text{S}/\text{cm}$	79	1,187
TDS, mg/L	6.7	300
TSS, mg/L	0	0
SO_4^{-2} , mg/L	0	0
FOG, mg/L	0	0
COD, mg/L	158.42/141.6/ 144.16	136.2
BOD, mg/L	0	0
MeOH Content	0	0
Cl^- , mg/L	2.50	4.0
Appearance	Colorless	Colorless
Odor	Odorless	Odorless

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RESEARCH ROUNDUP

Standardization of non-edible *Pongamia pinnata* oil methyl ester conversion using hydroxyl content and GC–MS analysis

The non-edible *Pongamia pinnata* is unsuitable plant for human lives which is grown in many parts of India and it contains several toxic and unsaponifiable components. The free fatty acids (FFA) in this oil are very high (<20%). For the effective utilization of *P. pinnata* oil as a source for the conversion of alternative fuel we have standardized the methyl ester conversion protocol by estimating the hydroxyl content of the *P. pinnata* oil and its methyl esters. The methyl ester conversion estimated from the hydroxyl content was statistically analyzed with the results obtained from gas chromatography mass spectrometry (GC–MS). The calibration curve was developed by **Muthulingam Seenuvasan *et al*** for the methyl ester conversion from the *P. pinnata* oil at 97% confidence level under Chi-square test [**Journal of the Taiwan Institute of Chemical Engineers**, **45**, 1485-1489, (2014)]

Kinetics of the pre-treatment of used cooking oil using Novozyme 435 for biodiesel production

The pre-treatment of used cooking oil (UCO) for the preparation of biodiesel has been investigated by **Kathleen F. Haigh *et al*** using Novozyme 435, *Candida antarctica* Lipase B immobilised on acrylic resin, as the catalyst [Chemical Engineering Research and Design, **92**, 713-719, (2014)]. The reactions in UCO were carried out using a jacketed batch reactor with a reflux condenser. The liquid chromatography–mass spectrometry (LC–MS) method was developed to monitor the mono-, di- and triglyceride concentrations and it was found that the method was sensitive enough to separate isomers, including diglyceride isomers. It was found that the 1,3 diglyceride isomer reacted more readily than the 1,2 isomer indicating stereoselectivity of the catalyst. This work showed that Novozyme 435 will catalyse the esterification of free fatty acids (FFAs) and the transesterification of mono- and diglycerides typically found in UCO when Novozyme 435 is used to catalyse the pre-treatment of UCO for the formation of biodiesel. A kinetic model was used to investigate the mechanism and indicated that the reaction progressed with the sequential hydrolysis esterification reactions in parallel with transesterification.

Enzymatic process for biodiesel: Challenges and opportunities

The chemical-catalyzed transesterification of vegetable oils to biodiesel has been industrially

adopted due to its high conversion rates and low production time. However, this process suffers from several inherent drawbacks related to energy-intensive and environmentally unfriendly processing steps such as catalyst and product recovery, and waste water treatment. This has led to the development of the immobilized enzyme catalyzed process for biodiesel production which is characterized by certain environmental and economical advantages over the conventional chemical method. These include room-temperature reaction conditions, elimination of treatment costs associated with recovery of chemical catalysts, enzyme re-use, high substrate specificity, the ability to convert both free fatty acids and triglycerides to biodiesel in one step, lower alcohol to oil ratio, avoidance of side reactions and minimized impurities, easier product separation and recovery; biodegradability and environmental acceptance. This paper by **Lew P. Christopher *et al*** provides a comprehensive review of the current state of advancements in the enzymatic transesterification of oils [**Applied Energy**, **119**, 497-520, (2014)] . A thorough analysis of recent biotechnological progress is presented in the context of present technological challenges and future developmental opportunities aimed at bringing the enzyme costs down and improving the overall process economics towards large scale production of enzymatic biodiesel. As the major obstacles that impede industrial production of enzymatic biodiesel is the enzyme cost and conversion efficiency, this topic is addressed in greater detail in the review. A better understanding and control of the underpinning mechanisms of the enzymatic biodiesel process would lead to improved process efficiency and economics. The yield and conversion efficiency of enzymatic catalysis is influenced by a number of factors such as the nature and properties of the enzyme catalyst, enzyme and whole cell immobilization techniques, enzyme pretreatment, biodiesel substrates, acyl acceptors and their step-wise addition, use of solvents, operating conditions of enzymatic catalysis, bioreactor design. The ability of lipase to catalyze the synthesis of alkyl esters from low-cost feedstock with high free fatty acid content such as waste cooking oil, grease and tallow would lower the cost of enzymatic biodiesel. Discovery and engineering of new and robust lipases with high activity, thermostability and resistance to inhibition are needed for the establishment of a cost-

effective enzymatic process. Opportunities to create a sustainable and eco-friendly pathway for production of enzymatic biodiesel from renewable resources are discussed.

An improved rapid stigmastadiene test to detect addition of refined oil to extra virgin olive oil

Extra virgin olive oil is a premium food product that is likely to be the target of adulteration with refined olive oils or seed oils. Refining produces steroidal alkenes (sterenes) including stigmastadiene. **Colin Crews et al** describes a rapid GC-MS method for the determination of stigmastadiene which is faster and more sensitive than the current official procedure based on GC-FID [**Food Research International**, **60**, 117-122, (2014)]. The method does not require a saponification procedure for cold pressed oils, uses a stigmastadiene standard for quantification, has a low limit of quantification (0.015 mg kg⁻¹) and gives excellent confirmation of peak identity at the current regulatory limit of 0.5 mg kg⁻¹.

Transesterification of canola, palm, peanut, soybean and sunflower oil with methanol, ethanol, isopropanol, butanol and tert-butanol to biodiesel: Modelling of chemical equilibrium, reaction kinetics and mass transfer based on fatty acid composition

Mechanism of alcoholysis (e.g. methanolysis) using different oils, alcohols and homogeneous base catalysts was utilized to devise chemical kinetics and thermodynamics based on fatty acid composition, differentiating among triglycerides, diglycerides, monoglycerides and fatty acid alkyl esters (e.g. fatty acid alkyl esters, FAME) with bonded gadoleic, linoleic, linolenic, oleic, palmitic and stearic acid-originating substituents. Their concentrations were measured by **Blaz Likozar and Janez Levec** using an optimized high-performance liquid chromatography (HPLC) method. Hydrodynamics and diffusion limitations in emulsion were considered in overall model by determining diffusivities, distribution coefficients, molar volumes, boiling points and viscosities of individual components [**Applied Energy**, **123**, 108-120, (2014)]. Pre-exponential factors and activation energies were related with structure of reactants, intermediates and products acknowledging number of carbons, double bonds and alkyl branches by linear and mixed response surface methodology. Developed model may be used with batch and continuous flow reactors, e.g. for novel micro-structured or industrial-scale process intensification, different vegetable or non-edible oils (waste cooking *Jatropha* or microalgae lipids).

The wastewater treatment in the biodiesel production with alkali-catalyzed transesterification

Biodiesel has been studied in last few decades because of limited energy resources and a huge increase of the energy demand. The basic feedstocks for the production of biodiesel are vegetable oils and animal fats that contain primarily triacylglycerols while the main reaction is transesterification. This reaction is most frequently conducted at commercial scale in the presence of the homogeneous alkali catalyst. Previous studies on biodiesel were mainly focused on its production and fuel properties, while its environmental management is rarely considered. The present work by **Vlada B. Veljkovic et al** is a review of the previous studies on treating wastewaters generated by the biodiesel production processes involving alkali-catalyzed transesterification [**Renewable and Sustainable Energy Reviews**, **32**, 40-60, (2014)]. The attention is focused on physical, chemical, physico-chemical, electrochemical, biological and integrated treatment processes of biodiesel wastewaters. Both advantages and disadvantages of different biodiesel wastewater treatment processes are discussed. Since different input biodiesel wastewaters are employed in different studies, it is difficult to compare different treatments with respect to their contaminant removal efficiencies. Proper acidification and chemical coagulation/flocculation or electrocoagulation remove grease and oil successfully but they are unsuccessful in removing COD. The combinations of acidification, coagulation and the electrochemical treatment improve the removal efficiencies of COD and BOD. Advanced oxidation technologies appear not to be effective in removing the contaminants from raw biodiesel wastewaters. The performance of biological processes is improved by the pretreatment of biodiesel wastewater with acidification, chemical coagulation, electrocoagulation or photo-Fenton. When selecting a treatment process, it should be evaluated with respect to its treatment efficiency and operational requirements. The right choice is probably an integration treatment involving acidification, coagulation/flocculation or electrocoagulation and a biological process. The reuse of the pretreated wastewater is also an interesting alternative.

Simultaneous quantitative analysis of the acetate, formate, chloride, phosphate and sulfate anions in biodiesel by ion chromatography

A quantitative ion chromatographic analytical method for the simultaneous determination of the acetate, formate, chloride, phosphate, and sulfate anions in biodiesel is proposed by **Eva Lúcia Cardoso Silveira et al**. Samples of biodiesels prepared from soy, canola and sunflower vegetable oils, from crude soy oil, and from bovine fat were analyzed [**Fuel**, **124**, 97-101, (2014)]. The extraction of the anions

from the matrixes was performed using water with the assistance of ultrasound. The observed limits of detection and of quantitation in mg kg⁻¹ and the mean relative standard deviation in percent were, respectively: acetate, 0.32, 0.97 and 4.4; formate, 1.36, 4.12 and 6.2; chloride, 0.098, 0.30 and 6.5; phosphate, 0.81, 2.47 and 7.1; and sulfate, 0.087, 0.264 and 7.8. The procedure can be considered to be green because it uses small volumes of water, is simple, and can be performed rapidly

Biocatalysis combined with physical technologies for development of a green biodiesel process

Biodiesel derived from the transesterification of vegetable oils or animal fats with alcohol is composed of saturated and unsaturated long chain alkylesters. The process has some technical problems that must be resolved to reduce the high cost of operation. Limitation of mass and heat transfers, reaction equilibrium, batch mode operation and product purification affects conversion yield, time of reaction, productivity and energy cost. **Camilo Barroso Teixeira et al** highlighted some recent advances in process innovation for the biodiesel industry to develop a sustainable continuous process, environmentally benign and cost effective. Eco-friendly physical technologies as microwave, ultrasound and membrane reactors and their possible combination have successfully improved the enzymatic transesterification for biodiesel production [**Renewable and Sustainable Energy Reviews**, **33**, 333-343, (2014)].

Production of bio-hydrogenated diesel by catalytic hydrotreating of palm oil over NiMoS₂/γ-Al₂O₃ catalyst

Catalytic hydrotreating of palm oil (refined palm olein type) to produce bio-hydrogenated diesel (BHD) was carried out in a continuous-flow fixed-bed reactor over NiMoS₂/γ-Al₂O₃ catalyst by **Atthapon Srifa et al**. Effects of dominant hydrotreating parameters: temperature: 270–420 °C; H₂ pressure: 15–80 bar; LHSV: 0.25–5.0 h⁻¹; and H₂/oil ratio: 250–2000 N(cm³/cm³) on the conversion, product yield, and a contribution of hydrodeoxygenation (HDO) and decarbonylation/decarboxylation (DCO/DCO₂) were investigated to find the optimal hydrotreating conditions [**Bioresource Technology**, **158**, 81-90, (2014)]. All calculations including product yield and the contribution of HDO and DCO/DCO₂ were extremely estimated based on mole balance corresponding to the fatty acid composition in feed to fully understand deoxygenation behaviors at different conditions. These analyses demonstrated that HDO, DCO, and DCO₂ reactions competitively occurred at each condition, and had different optimal and limiting conditions. The differences in the hydrotreating reactions, liquid product

compositions, and gas product composition were also discussed.

Rhazya stricta Decne seed oil as an alternative, non-conventional feedstock for biodiesel production

Rhazya stricta Decne (*R. stricta*) is a hardy, drought-resistant, and arid land plant that is widely distributed from the Middle East to South Asia. The aim of this study by **Imededdine Arbi Nehdi et al** was to evaluate the use of *R. stricta* seed oil as an alternative source of triacylglycerols that may be suitable for the synthesis of biodiesel [**Energy Conversion and Management**, **81**, 400-406, (2014)]. The oil content of the seeds was approximately 14% and was mainly composed of the fatty acids linoleic (60.95%) and oleic (25.48%) acid. *R. stricta* methyl esters (RSME) were prepared by a base-catalyzed transesterification reaction. The conversion rate of the triacylglycerols to the corresponding methyl esters was determined by ¹H-NMR to be approximately 97%. This study showed that the fuel properties of the RSMEs are comparable to other vegetable oil methyl esters that are commonly used as biodiesels. *R. stricta* plantations will therefore be suitable for promoting sustainable agriculture and for producing biodiesel with viable prices in arid and semi-arid regions throughout the world

Liquid hydrocarbon fuels from catalytic cracking of rubber seed oil using USY as catalyst

The catalytic cracking of rubber seed oil (RSO) to produce liquid hydrocarbon fuels using USY (ultrastable Y zeolite) as a heterogeneous catalyst has been studied by **Lu Li et al**. Under the optimum cracking conditions of RSO 10 g, m(USY)/m(RSO) = 1:50, and 420 °C for 90 min, the yield of liquid product reached 75.6%, and the chemical composition and properties of the liquid fuel were similar to those of gasoline-based fuels (C₈–C₉ content >70%, low acid value, good cold-flow properties, and high calorific value) [**Fuel**, **123**, 189-193, (2014)]. The stability of USY has been studied, and the results showed that it could be reused with negligible loss of activity over at least six cycles. USY appears to be a suitable heterogeneous catalyst for the production of liquid hydrocarbon fuels from RSO.

Homogeneous catalysis of soybean oil transesterification via methylic and ethylic routes: Multivariate comparison

An experiment to establish the best reaction conditions for the transesterification of soybean oil is described by **Karen Araújo Borges et al**. They conducted the ethylic and methylic routes using two different protocols, and evaluated how the variables time, stirring, alcohol/oil molar ratio, catalyst (%), catalyst type, and temperature affected the process [**Energy**, **67**, 569-574, (2014)] . The highest yield of

biodiesel was obtained using the following conditions: ethylic route – t = 60 min, stirring: 100 rpm, ethanol/oil molar ratio = 12:1, catalyst relative to oil (%) = 0.2%, catalyst = potassium ethoxide, temperature = 35 °C; methylic route – t = 30 min, stirring: 100 rpm, methanol/oil molar ratio = 6:1, catalyst (%) = 0.2%, catalyst = KOH, temperature = 55 °C. We analyzed the acidity, moisture content, density at 20 °C, kinematic viscosity at 40 °C, oxidative stability, and carbon residue at the biodiesels obtained under optimal conditions. The results were consistent with the values allowed by the Brazilian ANP (Resolution 07/2008). We also conducted the physicochemical analysis of the soybean oil used as feedstock to produce biodiesel

Absorption of carbon dioxide in alkanolamine and vegetable oil mixture and isolation of 2-amino-2-methyl-1-propanol carbamate

The carbon dioxide emission has to be efficiently controlled due to environmental, economic and social demands. Among the various technologies, gas absorption technology is of great importance for the capture of CO₂ and to prevent global warming. In the present work, the absorption of carbon dioxide in alkanolamines in aqueous and vegetable oil medium was assessed by **A. Uma Maheswari and K. Palanivelu** and it was found that the absorption in organic medium is higher than in aqueous medium. Among the alkanolamines in various vegetable oil media, 2-amino-2-methyl-1-propanol (AMP) in the coconut oil medium was found to exhibit the highest absorption capacity for CO₂ gas [**Journal of CO₂ Utilization**, **6**, 45-52, (2014)]. The precipitate resulting after passing CO₂ through AMP in the vegetable oil medium was analyzed by FT-IR, 1H NMR and 13C NMR spectroscopic techniques and identified as AMP-carbamate. The influence of various operating conditions such as amine concentration, reaction time, temperature and pressure of CO₂ gas on the AMP-carbamate yield was analyzed. Under optimized conditions, the maximum yield of 52% of AMP-carbamate was obtained. Thus the AMP in vegetable oil medium emerges to be a promising candidate for capturing CO₂ and for isolation of value added product (AMP-carbamate)

Design of soft lipid nanocarriers based on bioactive vegetable oils with multiple health benefits

Ioana Lacatusu et al designed and synthesized soft and functional nanocarriers based on vegetable oils (Pumpkin and Amaranth oils) able to co-encapsulate and co-deliver two UV-A and UV-B filters (Avobenzone, Octocrylen) and to explore their efficiency in developing advanced bio-cosmetic prototypes [**Chemical Engineering Journal**, **246**, 311-321, (2014)]. The exploitation of vegetable oils with safe

utilization and biological efficiency in obtaining soft nanocarriers represent an innovative approach that provides a significant advance in the nanotechnology field. The obtained vegetable nanocarriers having mean diameters of 100 and 160 nm were tested in vitro for their antioxidant, photoprotective and drug release properties. The in vitro ability to capture free radicals was superior when the nanoparticles were prepared in Amaranth oil/solid lipids system. Study of UV absorbing effect revealed that co-loaded vegetable nanoparticles have greatly improved the photoprotective properties, the obtained SPF being of 40–45 and FP-UVA of 27–34. These values are associated with a high protective effect, e.g. more than 99% against UV-B and 92% against UV-A radiation. In vitro co-release experiments demonstrated that both Avobenzone and Octocrylen filters were released in a prolonged manner. The ultimate objective was to formulate the newly co-loaded nanoparticles into advanced cosmetic prototype and compare it with conventional cream. The soft vegetable-nanocarriers produced significantly higher UV-protection than the conventional cream. The use of appropriate renewable vegetable sources for obtaining soft bio-active nanostructures with broad health benefices has the potential to satisfy both the industrial and consumer needs, thanks to their safety and sustainability.

Physical properties of (jojoba oil + biodiesel), (jojoba oil + diesel) and (biodiesel + diesel) blends

Jojoba plant product (seeds) contains about 40–50% of seed dry weight oil, which is more than the amount produced by other oilseed crops such as soybeans and rapeseed. Unlike vegetable oils and animal fats, jojoba oil (JO) is not a triglyceride but a mixture of long straight chain monoesters esters. Therefore, JO appears to be a promising energy source that can be used separately or in mixtures with petroleum diesel (PD) and/or biodiesel (BD) fuels in many applications without being esterified. In this study, the dynamic viscosity, density, flash point and heating value of jojoba oil (JO) and its blends with PD and BD have been investigated by **Zayed Al-Hamamre and Ahmed Al-Salaymeh**. The effects of temperature and volume fraction on the density and viscosity of blends were examined [**Fuel**, **123**, 175-188, (2014)]. The results are described by means of specific mathematical correlations. The constants of these correlations differ depending on the type of fuel blend. Furthermore, some previously reported models that have been presented for the prediction of viscosity and density of PD–BD blends are examined with the experimental data obtained in this work.

Reduction of saturated fat in traditional foods by substitution of ghee with olive and sunflower oils – A case study with halwa

Diet related diseases are increasing at an alarming rate all over the world. Restriction in dietary saturated fat intake is one of the major components in healthy diet as a mean of preventing cardiovascular and other associated diseases. Ghee is one of the high saturated fat types (around 60% saturated fat) which is consumed along with many Asian traditional foods. As a model food, halwa, a traditional confection in Oman, which is popular in domestic and many other gulf countries is modified by **A. Manickavasagan and J.N. Al-Sabahi** replacing ghee with healthy vegetable oils and tested for their acceptability [**Journal of the Association of Arab Universities for Basic and Applied Sciences**, **15**, 61-67, (2014)]. Three types of halwa, olive oil halwa, sunflower oil halwa and ghee halwa (control) were produced in a commercial production facility and their textural and sensorial attributes were determined. In instrumental texture profiles, there were no significant differences in cohesiveness, springiness, chewiness and gumminess between olive oil, sunflower oil and ghee halwa samples. The hardness of olive oil halwa was the highest and sunflower oil halwa was the lowest among three tested samples. In sensory evaluation of developed halwa products, there was no significant difference in the overall acceptability between ghee and sunflower oil halwa. In blind sensory test, 60% of females and 80% of males selected sunflower oil halwa, and only 10% of females and 10% males selected olive oil halwa as their first choice of preferences. But in informed sensory test, the selection of olive oil halwa as the first choice was increased to 55% in females and 30% in males. About 80% of the panelists in informed sensory test were ready to accept non-ghee halwa the way it was prepared or with product improvement. There are opportunities to modify traditional foods which are rich in saturated fat by replacing with healthy oils, and to educate the people about the health benefits of these modifications.

Solid Fat Content of vegetable oils and simulation of interesterification reaction: Predictions from thermodynamic approach

The Solid Fat Content (SFC) of vegetable oils is a fundamental property in fatty foods. Also, chemical interesterification (the exchange of fatty acids within and between triacylglycerols) has been used to enhance the melting profile of vegetable oils blends used in food industry. The present work by **M. Teles dos Santos et al** uses a computational approach using Solid-Liquid Equilibrium (SLE) to predict SFC and simulate the chemical interesterification reaction (CI) for different formulations using palm oil (PO), sunflower oil (SFO) and palm kernel oil (PKO) [**Journal of Food**

Engineering, **126**, 198-205, (2014)]. More than 3696 SLE problems are solved, allowing the evaluation of how the fraction of each oil, the temperature and the CI reaction impacts the SFC. The calculated SFC values are compared with experimental data taken from literature. For systems composed of two or one single vegetable oil, the average absolute error (AAE) is 5.2% before CI and 4.2% after CI. For systems composed of three vegetable oils, the AAE is 6.3% before CI and 4.2% after CI. The predictions of SFC before and after CI reaction can aid the food makers to face the combinatorial problem imposed by the choice of the vegetable oil and its fraction in the blend. Future improvements in the pure component properties, thermodynamic model and distribution model of fatty acids in the triacylglycerols can increase the use of computational approaches allowing the experiments to be focused on the most promising formulations in terms of melting profile.

Oxidative stabilization of mixed mayonnaises made with linseed oil and saturated medium-chain triglyceride oil

Mayonnaises, made with either saturated medium chain triglyceride (MCT) oil or unsaturated purified linseed oil (LSO), were mixed by **Piret Raudsepp et al**. Raman confocal microspectrometry demonstrated that lipid droplets in mixed mayonnaise remained intact containing either MCT oil or LSO [**Food Chem.**, **152**, 378-385, (2014)]. Peroxide formation during storage was lower in mixed mayonnaise compared to LSO mayonnaise, while in mixed oil mayonnaise the level of peroxides was constantly low. Mixed oil mayonnaise had a lower rate of oxygen consumption than mixed mayonnaise, LSO mayonnaise having the highest rate. The decay of water-soluble nitroxyl radicals showed radicals are formed in the aqueous phase with the same rate independent of the lipids. This was also reflected in decay of α -tocopherol during storage being similar in MCT and LSO mayonnaises, but being stable in mixed oil mayonnaise and mixed mayonnaise. Results suggest that other effects than simply diluting unsaturated triglycerides with saturated triglycerides is causing the oxidative stabilization observed for mixed mayonnaise and mixed oil mayonnaise

Glycerin-Free Synthesis of Jatropha and Pongamia Biodiesel in Supercritical Dimethyl and Diethyl Carbonate

To overcome the fear of glycerin glut formation based on biodiesel production process, the present study by **Vivek Rathore et al** is aimed at investigation of glycerin-free biodiesel process under nonconventional synthesis conditions [**Ind. Eng. Chem. Res.**, **53**, 10525–10533, (2014)]. Accordingly, glycerin-free synthesis

of biodiesel from nonedible oils viz. jatropha and pongamia oils under supercritical conditions has been investigated with either dimethyl carbonate (DMC) or diethyl carbonate (DEC) as methylating agent. Typically, supercritical conditions with 40:1 molar ratio of DMC or DEC to oils at 325 °C/150 bar have been found to be adequate to achieve nearly complete conversion in 45 min. Furthermore, reaction kinetics has been investigated under supercritical conditions of DMC and DEC in the temperature range 250–350 °C at 150 bar. Estimated activation energies (E_a), are on the order of 38.0 ± 2 and 35.5 ± 2 kJ/mol for DMC and 40.4 ± 2 and 38.2 ± 2 kJ/mol for DEC, for conversion of jatropha and pongamia oils, respectively, with pseudo-first-order kinetics. The prepared biodiesel samples have been found to align with ASTM D6751/EN 14214/IS 15607 specifications. In view of this, noncatalytic glycerin-free supercritical biodiesel process is conceptualized for its development and possible implementation.

Estimation of Density of Biodiesel

Density of biodiesel is an important physical property of liquid fuel and biodiesel. A slight change in density can affect engine output power. In this work by **Suriya Phankosol et al** density of a saturated, unsaturated fatty acid methyl ester or a biodiesel was estimated from either (1) its number of carbon atoms (of fatty acid, z) and number of double bonds (nd): $\ln \rho = -0.435 - 0.0025z + 85.98/T + 0.792z/T + 4.0 nd/T$ or (2) its saponification number (SN) and iodine value (IV): $\ln \rho = -0.427 - 10/SN + 83.38/T + 3168.95/(T \times SN) + 11 IV/(T \times SN)$, where T is absolute temperature [**Energy Fuels**, **28**, 4633–4641, (2014)]. The predicted densities at different temperatures from both equations agree well with the reported literature values.

Study of the Surfactant Properties of Aqueous Stream from the Corn Milling Industry

Corn steep liquor (CSL) is a liquid byproduct generated by the corn wet-milling industry. This agroindustrial residue is obtained when corn is digested with warm water and SO_2 in the presence of different spontaneously growing microorganisms. The microbial population of CSL includes lactic acid bacteria, which are widely known to produce biosurfactants. However, there is no information available about the possible existence of surface-active compounds in CSL. In this work the surface tension activity of CSL was evaluated by **X. Vecino et al** and the biosurfactant contained in this residue was extracted with different organic solvents and characterized [**J. Agric. Food Chem.**, **62**, 5451–5457, (2014)]. The biosurfactant obtained from CSL was analyzed by Fourier transform infrared spectroscopy, and the composition in fatty acid was analyzed by gas chromatography–mass spectrometry. The hydrophobic chain of the biosurfactant contained in

CSL comprised 50–55.2% linoleic acid, 15.7–22.2% oleic and/or elaidic acid, 5.9–14.6% stearic acid, and 14.9–19.6% palmitic acid

Biodiesel Potential of Oleaginous Yeast Biomass by NMR Spectroscopic Techniques

Analytical strategies based on NMR (1H and ^{13}C), IR (infrared), and GC (gas chromatography) techniques have been developed by **A. S. Sarpal et al** for the molecular level characterization of Soxhlet and ultrasonic solvent extracts of yeast biomass samples generated on a lab scale by different yeast, feed, and diverse culture conditions, with an objective to explore biodiesel potential [**Energy Fuels**, **28**, 3766–3777, (2014)]. The extraction efficiency of each solvent (cyclohexane, chloroform, methanol) toward extraction of neutral lipids (total glycerides (TG), free fatty acids (FFA), and polar lipids have been determined and compared with regards to the nature of fatty acid components extracted in each solvent fractions. The fatty acid composition of yeast extracts has been found to be similar to vegetable oils, mostly rich in C16:0, 18:0, and C18:N ($N = 1-3$) fatty acids as indicated by the combined NMR, GC, and GC-MS analyses. The analytical protocol developed has established that 1H NMR techniques can be used directly and rapidly without any sample treatment and prior separation to determine total neutral lipid content (TG, FFA), nature of fatty acids/ester, polyunsaturated fatty esters (PUFE), iodine value, etc. NMR results of nature of unsaturated fatty acids/esters (C18:N, $N = 1-3$) have been validated by GC and GC-MS analyses. The results have shown the presence of C18:1 and C18:2 as the predominant unsaturated fatty acid components besides common saturated fatty acids. The content and composition of biomass has been found to be specific to types of yeast and feed used for cultivation. The NMR methods offer great potential for rapid screening of yeast for generation of yeast biomass with desired lipid content, quality, and biodiesel potential and value added PUFE, keeping in view of the cost economics of overall generation cost of the biomass.

Statistical Optimization for Biodiesel Production from Soybean Oil in a Microchannel Reactor

Microreactors are efficient with regard to the continuous production of biodiesel, because of their enhanced mass transfer. In this study by **Jian-Ying Dai et al**, a novel structure of microchannel reactor was studied to synthesize biodiesel from soybean oil via alkali-catalyzed transesterification [**Ind. Eng. Chem. Res.**, **53**, 9325–9330, (2014)]. Response surface methodology (RSM) was applied to evaluate the relationship between biodiesel yield and reaction parameters, such as residence time, reaction

temperature, catalyst amount, and molar ratio of methanol to oil. A three-level four-factor Box–Behnken design (BBD) was used to fit the available response data to a second-order polynomial regression model. Under the optimum conditions of a residence time of 14.9 s, a methanol/oil molar ratio of 8.5, 1.17 wt % KOH, and 59 °C, the biodiesel yield reached 99.5%. The effect of moisture and free fatty acid on biodiesel production were also explored.

Kinetic Study of the Hydrodesulfurization of a Heavy Gasoil in the Presence of Free Fatty Acids Using a CoMo/ γ -Al₂O₃ Catalyst

The effect of an acidic vegetable oil (AVO) on the hydrodesulfurization (HDS) reaction of an atmospheric heavy gasoil over a commercial CoMo/ γ -Al₂O₃ catalyst was studied by **Andreas Vonortas and Nikos Papayannakos**. The coprocessing of the two liquid feeds was carried out in a trickle-bed bench-scale reactor at the typical HDS reaction conditions used in most refineries; namely, the reaction temperature ranged from 310 to 350 °C, while the total pressure was kept constant at P = 33 bar [**Ind. Eng. Chem. Res.**, **53**, 9646–9652, (2014)]. The AVO content in the liquid feed varied from 0 to 20 wt %, and it was found that its presence inhibited the HDS reaction in all different conditions tested, which reflects an obvious decrease in the HDS reaction rate constant. Catalytic selectivity concerning the hydrodeoxygenation reaction was determined via analysis of the gaseous products. Decarboxylation cannot be distinguished from a decarbonylation mechanism because of the simultaneously occurring water–gas shift reaction. It was obvious that the overall selectivity for decarboxylation and decarbonylation reaction paths decreased with increasing AVO content in the feed and increased with the reaction temperature. During the experimental tests, the catalyst activity was measured and deactivation was found to be negligible.

Simultaneous Determination of Seven Anions of Interest in Raw *Jatropha curcas* Oil by Ion Chromatography

Various ions are of interest to the quality of biodiesel feedstock and products. In this study, a simple and labor-saving analytical method was developed by **Yi Zhang et al** to directly and simultaneously measure seven anions of interest in oil, utilizing an ion chromatography system with function of sample matrix elimination [**Energy Fuels**, **28**, 2581–2588, (2014)]. Various eluent profiles were explored and calibration curves were made to analyze 13 raw *Jatropha curcas* oils for their contents of formate, acetate, nitrite, nitrate, sulfite, sulfate and phosphate. A 23 min program was found to sufficiently separate all the ions, and

linear correlation higher than 99% was achieved for all the ions except formate (98.6%). High diversity was found in both the presence and concentration range of these ions. Formate, nitrate, and phosphate were more prevalent among the ions tested, such that 12, 10, and 11 samples showed their presence, respectively. Nitrite was found in only two samples with the concentrations lower than 10 mg kg⁻¹. Formate concentration ranged from 0 to over 3000 mg kg⁻¹, and nitrate and phosphate showed ranges of 0 to 100 and 0 to 300 mg kg⁻¹, respectively. Acetate was less common than formate, and its concentration was universally lower (0 to 500 mg kg⁻¹). In addition, the occurrence of acetate and nitrite seemed to be correlated to that of formate and nitrate, respectively, whereas sulfite and sulfate showed mutual exclusion. This method showed reasonably good detection limits and reproducibility, that concentrations of around 0.2 mg L⁻¹ can be detected in the organic samples, and in most cases the ratio of standard deviation to average was below 25%. However, for phosphate, the accuracy and reproducibility need further improvement, possibly by decreasing sample dilution ratio and optimizing eluent profile.

Detection of Chemlali Extra-Virgin Olive Oil Adulteration Mixed with Soybean Oil, Corn Oil, and Sunflower Oil by Using GC and HPLC

Fatty acid composition as an indicator of purity suggests that linolenic acid content could be used as a parameter for the detection of extra/virgin olive oil fraud with 5% of soybean oil. The adulteration could also be detected by **Hazem Jabeur et al** by the increase of the trans-fatty acid contents with 3% of soybean, oil 2% of corn oil, and 4% of sunflower oil [**J. Agric. Food Chem.**, **62**, 4893–4904, (2014)]. The use of the Δ ECN42 proved to be effective in Chemlali extra-virgin olive oil adulteration even at low levels: 1% of sunflower oil, 3% of soybean oil, and 3% of corn oil. The sterol profile is almost decisive in clarifying the adulteration of olive oils with other cheaper ones: 1% of sunflower oil could be detected by the increase of Δ 7-stigmastenol and 4% of corn oil by the increase of campesterol. Linear discriminant analysis could represent a powerful tool for faster and cheaper evaluation of extra-virgin olive oil adulteration.

Preparation of Low Calorie Structured Lipids Catalyzed by 1,5,7-Triazabicyclo[4.4.0]dec-5-ene(TBD)-functionalized Mesoporous SBA-15 Silica in a Heterogeneous Manner

1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD, a strong bicyclic guanidine base) functionalized SBA-15 material has been found to be an efficient solid catalyst by **Wenlei Xie and Cong Qi** for the interesterification between tributyrin and methyl stearate in a solvent-

free system for the production of low-calorie structured lipid (LCSL) [**J. Agric. Food Chem**, **62**, 3348–3355, (2014)]. The solid base catalyst was characterized by using small-angle X-ray scattering, Fourier transform infrared spectra, thermo gravimetric analysis, scanning electron microscopy, transmission electron microscopy, nitrogen adsorption–desorption, and elemental analysis techniques. The obtained LCSL was analyzed by reverse-phase high-performance liquid chromatography for triacylglycerol composition. The influence of various reaction parameters, such as the substrate ratio, reaction temperature, and reaction time, on the interesterification reaction was investigated systematically. More than 90% LCSL was obtained at 80 °C within 1 h when the methyl stearate/tributyrin molar ratio of 2:1 was employed. The obtained solid catalyst could be recovered easily and reused for several recycles with a negligible loss of activity. By using the solid base catalyst, an eco-friendly more benign process for the interesterification reaction in a heterogeneous manner was developed

Effect of Different Alcohols and Palm and Palm Kernel (Palmist) Oils on Biofuel Properties for Special Uses

The properties of biodiesel are determined by its oleaginous composition and the alcohol used in the transesterification. **Claudia Cristina Cardoso Bejan *et al*** performed using palm and palmist oils and methyl, ethyl, isopropyl, and benzyl alcohols to investigate their influence on the cold flow properties, density, and viscosity of the resulting biofuel [**Energy Fuels**, **28**, 5128–5135, (2014)]. The products were also characterized by ¹H nuclear magnetic resonance (NMR) and high-performance liquid chromatography (HPLC) analyses. Biofuel produced from palmist oil had different properties compared to biofuel synthesized from palm oil because of its lower average chain length and lower content of unsaturation. Biodiesel produced with palmist oil and isopropyl alcohol had the lowest values of cold filter plugging point (CFPP) (–16 °C) and density (860 kg/m³). The use of benzyl alcohol yielded a biofuel with high viscosity and density values that do not adhere to any international specifications for biodiesel.

Boiling Points of Short-Chain Partial Acylglycerols and Tocopherols at Low Pressures by the Differential Scanning Calorimetry Technique

Boiling points of monocaprylin, monocaprin, dicaprylin, and dicaprin were measured by **Daniela S. Damaceno *et al*** at low pressures (1.0 kPa up to 13.2 kPa) using a differential scanning calorimetry technique and correlated by empirical equations (Clapeyron and Antoine) [**J. Chem. Eng. Data**, **59**, 1515–1520, (2014)]. Parameters of the Design Institute

for Physical Property Research (DIPPR) equations were also regressed considering calculated values of normal boiling points and critical points using the Marrero and Gani method. Heats of vaporization were estimated using the Clausius–Clapeyron relation with the inclusion of a correction term to account for deviations at higher pressures. Boiling points of α -, β -, δ -, and γ -tocopherol were measured at 1.1 kPa. A DIPPR equation was also proposed for estimating the vapor pressure of this class of compounds, and an equation for predicting heat of vaporization was derived. Data presented in this work can be valuable for process design in the edible oil industry and for development of biodiesel purification steps.

Physicochemical properties and stability of black cumin (*Nigella sativa*) seed oil as affected by different extraction methods

Black cumin (*Nigella sativa*) oil (BCO) was recovered using different extraction techniques including solvent free system (cold-pressing) and solvent extracted systems (Soxhlet and microwave assisted) by **Mustafa Kiralan *et al***. Oils were analyzed for the composition of fatty acids and bioactive compounds (sterols, tocopherols, chlorophyll, carotenoid and phenolics profile) and for some physicochemical properties [free fatty acid, peroxide value (PV), refractive index, and ultraviolet (UV) absorption at K232 and K270] [**Industrial Crops and Products**, **57**, 52–58, (2014)]. Antiradical power (AP) of oils was also evaluated, wherein cold-pressed oil had stronger AP than solvent extracted oils. Phenolic profiles analyzed by HPLC revealed that thymoquinone was the main phenolic compound wherein high levels of benzoic and p-hydroxy benzoic acids were found in cold pressed-BCO. Oxidative stability (OS) of oils was evaluated during accelerated oxidation conditions (oven test at 60 °C and Rancimat test at 110 °C). The greatest induction period was 19.6 h for Soxhlet-extracted BCO, and the lowest induction period was 3.48 h for cold-pressed BCO. PV of cold-pressed BCO reached 85.3 meq O₂/kg oil, while PV of the other extracted oils were under 27.0 meq O₂/kg oil at the end of storage period.

Vegetable-oil-based polymers as future polymeric biomaterials

Vegetable oils are one of the most important classes of bio-resources for producing polymeric materials. The main components of vegetable oils are triglycerides – esters of glycerol with three fatty acids. Several highly reactive sites including double bonds, allylic positions and the ester groups are present in triglycerides from which a great variety of polymers with different structures and functionalities can be

prepared. Vegetable-oil-based polyurethane, polyester, polyether and polyolefin are the four most important classes of polymers, many of which have excellent biocompatibilities and unique properties including shape memory. In view of these characteristics, vegetable-oil-based polymers play an important role in biomaterials and have attracted increasing attention from the polymer community. Here **Shida Miao *et al*** comprehensively review recent developments in the preparation of vegetable-oil-based polyurethane, polyester, polyether and polyolefin, all of which have potential applications as biomaterials [**Acta Biomaterialia**, **10**, 1692-1704, (2014)].

Study on the thermal degradation of 3-MCPD esters in model systems simulating deodorization of vegetable oils

The establishment of effective strategies for the mitigation of 3-MCPD esters in refined vegetable oils is restricted by limited knowledge of their mechanisms of formation and decomposition. In order to gain better understanding on the thermal stability of these compounds, a model system for mimicking oil refining conditions was developed by **Alessia Ermacora and Karel Hrnčirik** [**Food Chemistry**, **150**, 158-163, (2014)]. Pure 3-MCPD esters (3-MCPD dipalmitate and 3-MCPD dilaurate) were subjected to thermal treatment (180–260 °C) and the degradation products were monitored over time (0–24 h). After 24 h of treatment, both 3-MCPD esters showed a significant degradation (ranging from 30% to 70%), correlating with the temperature applied. The degradation pathway, similar for both compounds, was found to involve isomerisation (very rapid, equilibrium was reached within 2 h at 260 °C), dechlorination and deacylation reactions. The higher relative abundance of non-chlorinated compounds, namely acylglycerols, in the first stages of the treatment suggested that dechlorination is preferred over deacylation with the conditions applied in this study.

Purification technologies for crude biodiesel obtained by alkali-catalyzed transesterification

For commercial application, the ester product of alkali-catalyzed transesterification of vegetable oil or animal fats should be refined after glycerol separation by settling to fulfill the biodiesel standard specifications. This crude biodiesel, after neutralization and methanol removal, should be further cleaned by either one of the following methods: wet washing, dry washing, membrane extraction or using ion liquids. This paper by **Ivan J. Stojkovic *et al*** presents a review on the traditional (wet and dry washing) and novel (membrane separation technology and usage of ion liquids) methods of crude biodiesel purification [**Renewable and Sustainable Energy Reviews**, **32**,

1-15, (2014)]. It also provides a comparison of crude biodiesel purification methods. Each method has its advantages and disadvantages, which should be carefully analyzed when choosing the proper one for refining crude biodiesel.

Monte Carlo simulation based prediction of blended oil composition containing mustard, rapeseed and soybean oil

High erucic acid rapeseed and mustard seed (HEARM) oils are popular cooking oil in various southeast Asian countries (e.g. Nepal, India, Bangladesh) due to the preference of the local consumer for its strong pungency. Low erucic acid rapeseed (LEAR) oil having lower pungency is frequently mixed with the pungent HEARM oil to increase its sensory appeal to the local consumer. Moreover, these oils are also prone to be adulterated with the cheaper oil available in the local market like soybean oil for economical reasons. In order to detect this fraud in a quick and easy manner, a Monte Carlo simulation based approach was developed by **Kshitij Shrestha *et al*** for the estimation of blend composition using only the fatty acid composition of the sample [**Food Research International**, **60**, 108-116, (2014)]. The limits of detection (LODs) of soybean oil in HEARM oil and LEAR oil were 14% and 13%, respectively. The LODs of LEAR oil in HEARM oil and soybean oil were 11 and 9%, respectively. Similarly, the LODs of HEARM oil in LEAR oil and soybean oil were 9% and 3%, respectively. The prediction from the developed method was evaluated both in real oil blends (prepared in the laboratory) and in theoretically simulated blends. The method was applied on forty-nine samples (labeled as mustard/rapeseed oil) collected from the Nepalese market. Among them, twenty-seven samples were found to be adulterated with soybean oil. The predicted adulteration was further supported by their δ -tocopherol content and trans fatty acid content, as an indicator for the adulteration with refined oil. The developed Monte Carlo simulation method is based on a single analytical run of determining the fatty acid composition of the suspected oil blend and thus useful for a quick segregation of samples in routine analysis.

A simplified procedure for the determination of organochlorine pesticides and polychlorobiphenyls in edible vegetable oils

A one-step extraction–purification multiresidue method for the determination of 14 organochlorine pesticides (OCPs) and 7 polychlorinated biphenyls (PCBs) in edible vegetable oils based on matrix solid-phase dispersion (MSPD) has been developed by Jindong Li *et al*. The experimental parameters affecting the recoveries and the efficiency of the

cleanup procedure were thoroughly evaluated. Under an optimised condition, 0.5 g of oil sample was blended with 3.5 g of sulfuric acid-impregnated silica and 0.8 g of silica gel was used as co-column absorbent [Food Chemistry, 151, 47-52, (2014)]. The PCBs and OCPs were eluted by 10 mL of n-hexane/dichloromethane (70:30, v/v) and determined by gas chromatography equipped with an electron capture detector (GC-ECD). Good recoveries were obtained in the range of 69.6–105.3% with relative standard deviations (RSD) values below 15% in most cases. The limits of detection (LOD), based on a signal-to-noise ratio (S/N) of 3, were in the range of 0.04–0.74 ng/g.

Analytical pyrolysis of the kernel and oil of babassu palm (*Orbignya phalerata*)

Babassu palm has a great economic importance. The kernel oil can be used as fuel in production of biodiesel, and in food and cosmetics industry. The kernel cake is used generally like food supplement for animals and organic fertilizer. Analytical pyrolysis (Py-GC/MS) was used in this work by **Jonas O. Vinhal *et al*** to characterize babassu palm oil and kernel. In first step, the pyrolysis temperature was optimized and detailed descriptions of the pyrolysis compounds released after pyrolysis at 650 °C is reported [Journal of Analytical and Applied Pyrolysis, 107, 73-81, (2014)]. The products identified from the oil pyrolyzed at 650 °C included alkanes, alkenes, cyclic ketones, aldehydes, esters and carboxylic acids. These compounds were produced by the pyrolysis of free fatty acids and triglycerides. The products identified from the pyrolysis of the kernel included alkanes, alkenes, aldehydes, ketones, alcohols, esters, carboxylic acids and amides, which were derived from the fatty acids and triglycerides that were present in the oil, as well as the carbohydrates and proteins present in the kernel cake. Analytical pyrolysis has several advantages, such as speed and simplicity, for identification of organic compounds, like observed in this work. However, this technique proved effective to obtain a lipid profile by analysis of babassu oil and kernel together with other data previously reported.

Two-stage thermal conversion of inedible lipid feedstocks to renewable chemicals and fuels

The aim of this work by **Justice Asoaming *et al*** was to study the conversion of inedible, low cost lipid feedstocks to renewable hydrocarbons using a two stage thermal hydrolysis–pyrolysis method [Bioresource Technology, 158, 55-62, (2014)]. Beef tallow, yellow grease, brown grease and cold pressed camelina oil were first hydrolyzed and the fatty acids produced were recovered and pyrolyzed in batch reactors. The pyrolysis products were identified and quantified using gas chromatography and mass

spectrometry. The pyrolysis product yields were similar for all the feedstock used with the organic liquid fraction (OLF) accounting for 76–80% of the product. The OLF consisted predominantly of n-alkanes. Approximately 30% OLF constituted a gasoline-equivalent fraction and 50% a diesel fraction. Other fuel property test showed that the OLF met the specifications set out by the Canadian general standards board. This research demonstrated a novel two-stage thermal hydrolysis–pyrolysis conversion method for producing OLF from inedible and low-value lipids.

Two-step thermal conversion of oleaginous microalgae into renewable hydrocarbons

Isabel Espinosa-Gonzalez *et al* evaluated the conversion of microalgal biomass to renewable chemicals and fuels through a two-step reaction and separation process [Bioresource Technology, 158, 91-97, (2014)]. High density *Chlorella protothecoides* culture with 40% lipid accumulation (dwb) was produced in 10 L bioreactors and hydrolyzed in batch stainless steel reactors under subcritical conditions. After hydrolysis, fatty acids free of sulfur and low in nitrogen and salts, were recovered by hexane extraction. The fatty acids were pyrolyzed at 410 °C for 2 h under N₂ yielding n-alkanes, α -olefins and internal olefins and low molecular weight fatty acids. This study demonstrated the direct conversion of microalgal biomass into valuable platform chemicals and fuels compatible with the existing industrial hydrocarbon infrastructure.

Pyrolysis of polyunsaturated fatty acids

The primary goal of this work by **Justice Asoaming *et al*** was to study the thermal conversion of polyunsaturated fatty acids to hydrocarbon for use as renewable chemicals and fuels [Fuel Processing Technology, 120, 89-95, (2014)]. Linoleic acid (cis,cis-9,12-octadecadienoic acid) was selected as a model polyunsaturated fatty acid. Batch pyrolysis reactions were conducted at temperatures from 350 to 450 °C for 0.5 to 8 h reaction times. Gas chromatography and mass spectrometry were used to analyze and identify products in the gas and liquid product fractions. Analysis of the gas phase showed concurrent production of CO and CO₂, indicating that deoxygenation reaction proceeded through both decarbonylation and decarboxylation mechanisms. The gas product encompassed alkanes and alkenes with carbon numbers ranging C₁–C₅ with ethane and propane as the major products. Analysis of the liquid fraction revealed series of n-alkanes, alkenes, cyclic alkanes and alkenes, and fatty acids. The presence of the unsaturation resulted in cracking at the allylic C–C and predominance of C₆ to C₁₀ hydrocarbons and C₉ and C₁₀ fatty acids. This work uncovers the dominant reaction pathways in the pyrolysis of

free polyunsaturated fatty acids and demonstrates the viability of this pyrolysis to produce renewable hydrocarbons immediately compatible with the existing petrochemical infrastructure.

Thermal cracking of free fatty acids in inert and light hydrocarbon gas atmospheres

Justice Asomaning *et al* studied the pyrolytic conversion of free fatty acids to renewable hydrocarbons in the presence of short-chain alkane and alkene hydrocarbon gases [**Fuel**, **126**, 250-255, (2014)]. Oleic acid (cis-9-octadecanoic acid) was used as model for fatty acids produced from hydrolysis of lipids from animal and plant feedstock. Batch pyrolysis reactions were conducted at 410 °C for 2 h at an initial pressure between 130 psi (896.3 kPa) and 500 psi (3447.4 kPa) under constant agitation. Identification and quantification of the pyrolysates in the gas and liquid phase were carried out using gas chromatography and mass spectrometry. Under inert N₂ atmosphere liquid product yields were between 74 and 81 wt% of feed with lower pressure giving the highest product yields. Liquid product was composed mainly of alkanes and alkenes ranging in carbon number from 6 to 19 and fatty acids from carbon numbers 4 to 18. Pyrolysis reactions conducted in the presence of short-chain alkane gases did not appreciably influence the liquid product yield and the composition compared to the inert atmosphere. On the other hand, pyrolysis reaction in presence of short-chain alkene gases resulted in a marked increase in the liquid product yield, the production of branched alkanes and alkenes and increased fatty acid decarboxylation. This work demonstrates a novel approach to concurrently increase the liquid product yield in pyrolysis of free fatty acids and produce highly valuable branched hydrocarbons for fuel and solvent applications.

Catalyst free esterification of fatty acids with methanol under subcritical condition

This study by **Alchris Woo Go *et al*** provides an alternative way to produce biodiesel from low quality feedstock oil. Feedstock oil with high water and free fatty acid contents can be hydrolyzed into fatty acids using conventional methods or subcritical water processes [**Energy**, **70**, 393-400, (2014)]. Fatty acids produced can be reacted with methanol to produce fatty acid methyl esters under conditions developed in this work, which is much milder than the supercritical methanol condition and without the use of catalyst. Using palmitic acid and oleic acid as the model free fatty acid, at 175–205 °C, 2.0–2.8 MPa and with a fatty acid:methanol:water ratio of 1:2:0.05 (w/w/w), a conversion of 96.5% can be achieved in 3–4 h. The

method can be applied to feedstock with water content up to 15%.

A novel method for determining peroxide value of edible oils using electrical conductivity

In this study, a new method for determining peroxide value (PV) of edible oils was described by **Yandie Yang *et al***. The basis of this method was the determination of changes in the electrical conductivity (EC) values of the aqueous phase during the reaction of potassium iodide (KI) with the hydroperoxides presented in oil samples [**Food Control**, **39**, 198-203, (2014)]. The effect of various analytical conditions was evaluated, such as temperature, holding time, oscillating time, stability of the saturated KI solution and oil types. The calibration was developed and validated using the EEC, AOCS, IUPAC, and AOAC methods. The results showed that the analytical conditions had no significant ($P > 0.05$) influence on the EC determination at room temperature; the calibration equation of PV was obtained as $y = 150.54x - 0.0327$ (where x is the change in EC values, S/m; y is PV, mmol/kg), with $R = 0.9980$ and $SD = 0.4045$. The linear correlativity between the proposed method and AOCS method was very high ($R = 0.9992$), and the standard deviation of the blind samples used in the experiments was slightly better than that of the EEC, AOCS, IUPAC, and AOAC procedures, which illustrates the feasibility of determining PV of edible oils using the proposed method.

A short note on the use of an equation of state (EOS) based approach to modelling the thermodynamics of biodiesel systems

An initial attempt to adapt the Peng–Robinson EOS, with Huron–Vidal mixing rules, for the prediction of phase equilibrium in the production of biodiesel is described by **Sergio Zerpa *et al***. Six vegetable oils and methanol were chosen to constitute the feedstock [**Fuel Processing Technology**, **121**, 70-75, (2014)]. In order to describe the chemical composition of the vegetable oils, a fuel surrogate technique was employed. In regressing the binary interaction parameters for the equation of state, it was found that the necessary binary phase equilibrium data were seldom available in the literature. Thus, the EOS was formulated as a predictive model in which the KT-UNIFAC method was used to assist in generating binary interaction parameters. The EOS was subsequently tested by computing phase equilibrium and then comparing the

results to the small amount of available experimental data. It was found that the predictions ranged from less than satisfactory to very good.

Production of Novel “Functional Oil” Rich in Diglycerides and Phytosterol Esters with “One-Pot” Enzymatic Transesterification

Diglycerides and phytosterol esters are two important functional lipids. Phytosterol esters mixed with dietary diglyceride could not only influence body weight but also prevent or reverse insulin resistance and hyperlipidemia. In this study, a kind of novel “functional oil” rich in both diglycerides and phytosterol esters was prepared by **Ming-Ming Zheng et al** with “one-pot” enzymatic transesterification [*J. Agric. Food Chem.*, **62**, 5142–5148, (2014)]. First, lipase AYS (*Candida rugosa*) was immobilized on the porous cross-linked polystyrene resin beads (NKA) via hydrophobic interaction. The resulting immobilized AYS showed much better transesterification activity and thermal stability to freeways. On the basis of the excellent biocatalyst prepared, a method for high-efficiency enzymatic esterification of phytosterols with different triglycerides to produce corresponding functional oils rich in both diglycerides and phytosterol esters was developed. Four functional oils rich in both diglycerides and phytosterol esters with conversions >92.1% and controllable fatty acid composition were obtained under the optimized conditions: 80 mmol/L phytosterols, 160 mmol/L triglycerides, and 25 mg/mL AYS@NKA at 180 rpm and 50 °C for 12 h in hexane. The prepared functional oil possessed low acid value (≤ 1.0 mgKOH/g), peroxide value (≤ 2.1 mmol/kg), and conjugated diene value (≤ 1.96 mmol/kg) and high diglyceride and phytosterol ester contents (≥ 10.4 and $\geq 20.2\%$, respectively). All of the characteristics favored the wide application of the functional oil in different fields of functional food.

Calculating the Thermodynamic Characteristics and Chemical Equilibrium of the Stepwise Transesterification of Triolein Using Supercritical Lower Alcohols

A comparative study of triolein transesterification using three individual supercritical alcohols (methanol, ethanol, and isopropanol) was performed using thermodynamic analysis by **Dan Zeng et al**. The correlative properties were calculated for all components, including boiling point, critical parameters, acentric factor, enthalpy, entropy, and constant-pressure heat capacity [*Ind. Eng. Chem. Res.*, **53**, 7209–7216, (2014)]. Chemical equilibria of the three reaction systems were discussed and

diagrams of reaction enthalpy, Gibbs free energy and the chemical equilibrium constant as a function of temperature were constructed for the temperature range from 300 to 700 K. The results illustrated that, in the supercritical state, the triolein transesterification reaction proceeds primarily with methanol under the proper reaction conditions, but rarely occurs with ethanol or isopropanol. This observation was consistent with the experimental results reported in literature. This study provides a reliable method for analyzing analogous reaction systems for biodiesel synthesis with supercritical fluids.

Alcoholysis of canola oil using a short-chain (C1–C3) alcohols

The conversion characteristics and fuel properties of biodiesel were investigated by **In Kwon Hong et al** according to carbon numbers of the short-chain alcohols that were used as reactants in the biodiesel manufacturing process [*Journal of Industrial and Engineering Chemistry*, **20**, 3689-3694, (2014)]. As the carbon numbers of the short chain alcohols increased, the fatty acid alkyl ester content of biodiesel decreased, and the optimum reaction temperature and time increased. The optimal conditions for short-chain alcoholysis were as follows: methanolysis (55 °C, 60 min), ethanolysis (65 °C, 80 min), and propanolysis (85 °C, 100 min). Also, according to the fuel properties analysis of the manufactured biodiesel with increasing carbon numbers, the heating value increased to 39.6–41.1 MJ/kg, and oxidation stability improved with methanolysis (6.68 h), ethanolysis (7.03 h), and propanolysis (7.51 h). But the kinematic viscosity increased from 4.24 to 4.68 cSt with increasing carbon numbers of the short chain alcohols.

Surface and foaming properties of polyoxyethylene glycerol ester surfactants

Polyoxyethylene glycerol esters derived from cocoa oil are non-ionic surfactants obtained from a renewable source which fulfil the environmental and toxicological requirements to be used as ecofriendly foaming and/or emulsifying agents. **L.A. Trujillo-Cayado** reported a study on the equilibrium adsorption, surface rheology and foaming properties of two commercial polyoxyethylene glycerol ester surfactants which differ in the number of ethylene oxide (EO) groups [*Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **458**, 195-202, (2014)]. Dynamic and equilibrium surface pressure values were obtained with a drop profile tensiometer. The oscillating drop technique was used to study the dilatational rheology of adsorbed surfactant layers. The foaming

properties of aqueous solutions of these surfactants were characterized in a commercial foam scan column. Dynamic surface pressure measurements showed two adsorption processes in which a slower condensation of the adsorbed film followed a fast diffusion step. Surface rheology and equilibrium surface pressure data fitted an extended Frumkin model which takes into account the compressibility of the adsorbed layer. The polyoxyethylene glycerol ester with the highest number of EO groups turned out to be more surface active, leading to lower cmc and higher adsorption constant. Both surfactants exhibited similar overall foam capacity at a given concentration. However, the time evolution of the liquid volume in the foam and the size of the air bubbles pointed to the formation of a more homogeneous and stable foam with smaller bubbles for the most hydrophilic polyoxyethylene glycerol ester studied. This is considered to be related to its surface dilatational rheology properties.

Kinetic study and thermoxidative degradation of palm oil and biodiesel

A.G.D. Santos et al investigated the synthesis of biodiesel from palm oil, its thermal stability using the Ozawa–Flynn–Wall and Vyazovkin kinetic models and its thermoxidation using thermogravimetry [*Thermochimica Acta*, **592**, 18-22, (2014)]. The obtained biodiesel was in accordance with the specifications of Resolution No. 7/2008 of the ANP. The 97.4% wt conversion of palm oil to methyl esters confirmed the efficiency of the conversion of fatty acids into esters. The thermal analysis was performed on a thermobalance using heating rates of 5, 10 and 20 °C min⁻¹. The oil exhibited two mass losses, and the biodiesel exhibited only one mass loss. The average values of the obtained apparent activation energies were 184.6 and 191.3 kJ mol⁻¹ for palm oil and 64.1 and 65.3 kJ mol⁻¹ for biodiesel. Additionally, the results indicate that thermal analysis can be used as a tool for monitoring the thermoxidation of biodiesel as a function of time.

Enzymatic biodiesel production of microalgae lipids under supercritical carbon dioxide: Process optimization and integration [*Biochemical Engineering Journal*, **90**, 103-113, (2014)]

Enzymatic biodiesel production in supercritical CO₂ (SC-CO₂) has recently received an increasing attention, as an alternative to the conventional chemical processes. In this study, enzymatic production of biodiesel from microalgal lipids was investigated in batch and integrated extraction-reaction systems by **Hanifa Taher** et al. In the batch system, the effect of enzyme loading (15–50 wt%), temperature (35–55 °C)

and methanol to lipid molar ratios (3–15:1) were studied, and response surface methodology was employed to optimize selected factors effect. The optimum transesterification yield of 80% was obtained at 47 °C, 200 bar, 35% enzyme loading, and 9:1 molar ratio after 4 h reaction in the batch system. The experimental results were also used to determine the kinetics parameters of the Ping-Pong Bi Bi model, with methanol inhibition, suggested to describe the reaction. In the continuous integrated extraction-reaction system, the effect of methanol to lipids molar ratio was investigated, and enzyme operational stability and reusability were tested. Bed regeneration by tert-butanol washing was also assessed. The optimum methanol to lipid ratio was found to be 10:1. At this ratio, the enzyme was able to attain 78% of its original activity when reused for 6 continuous cycles, and the bed was successfully reused by washing with tert-butanol

Ceramic hollow fibres catalytic enhanced reactors for glycerol steam reforming

NiO/MgO/CeO₂ catalysts with Ni content from 5% to 30% were synthesized by sol–gel method and tested by **E. Gallegos-Suárez et al** in a fixed-bed reactor (FBR) in the glycerol steam reforming (GSR) reaction [*Catalysis Today*, **233**, 21-30, (2014)]. The catalysts were characterized by N₂ adsorption isotherms at –196 °C (S_{BET}), X-ray diffraction (XRD), H₂ temperature programmed reduction (H₂-TPR), transmission electron microscopy (TEM) and energy dispersive X-ray (EDX). The 20% NiO/MgO/CeO₂ catalyst, which showed the highest catalytic activity in GSR reaction, was selected to be deposited in the finger-like region of the asymmetric Al₂O₃ hollow fibre and the sponge-like region of the symmetric Al₂O₃ hollow fibre in the development of the asymmetric hollow fibre reactor (AHFR) and symmetric hollow fibre reactor (SHFR), respectively. The impregnated ceramic substrates were characterized by scanning electron microscopy (SEM), EDX and TEM. The performances of the AHFR and SHFR were compared with that in a conventional FBR during the GSR reaction. Both AHFR and SHFR were operating at “dead-end” configuration at a temperature range from 250 °C to 550 °C, atmospheric pressure and in a reactant mixture of steam and glycerol (16:1 molar ratio). At 550 °C the glycerol conversion in the AHFR and SHFR was 70% and 46%, respectively, which are 5 and 2 times higher than that obtained in the FBR. The different performances of the AHFR and SHFR could be explained due to the unlike catalyst particle size deposited in the asymmetric and symmetric substrates, 8 nm and 3 nm, respectively.

Acidic solvent extraction of gossypol from cottonseed meal

To expand the use of cottonseed protein in animal feeding, cottonseed meal was extracted with acetone- and ethanol-based solutions to remove gossypol by **Scott M. Pelitire et al.** Phosphoric acid and water were included in the solutions to catalyze the hydrolysis of protein-bound gossypol [**Animal Feed Science and Technology, 195**, 120-128, (2014)]. Both solvents were effective at reducing the total gossypol level in meal to between 5% and 10% of its initial value. Gossypol extraction occurred much faster in the ethanol-based extractions than it did in the acetone-based extractions. Treated meals tended to retain phosphorus but most of this could be removed by conducting a final water wash. Water washing also removed hydrophilic components resulting in reduced product yields but increased protein levels. Other acids, e.g., oxalic, citric, or sulfuric acid, were also effective at reducing meal gossypol. In contrast, extractions conducted without acid were not effective. The process can be used to produce low-gossypol cottonseed meals that should be useful in a broader range of feed applications.

Vegetable oil based eco-friendly coating materials: A review article

Vegetable oils (VO) constitute the single, largest, easily available, low cost, non-toxic, non-depletable, biodegradable family yielding materials that are capable of competing with fossil fuel derived petro-based products. The outstanding feature of VO is their unique chemical structure with to unsaturation sites, epoxies, hydroxyls, esters and other functional groups along with inherent fluidity characteristics. These enable them to undergo various chemical transformations producing low molecular weight polymeric materials with versatile

applications, particularly as chief ingredients in paints and coatings. **Manawwer Alam et al** described important VO derived materials such as alkyds, polyesteramides, polyetheramides, polyurethanes, epoxies, polyols, along with their preparation and applications as protective coatings [**Arabian Journal of Chemistry, 7**, 469-479, (2014)]. A small portion of the review is also dedicated to the future perspectives in the field. In spite of their extensive utilization in the world of coatings, literature survey revealed that in the past (from 1990s to date) no review has come up describing the chemistry and applications of VO polymer based coating materials.

A kinetic study of quicklime-catalyzed sunflower oil methanolysis

The quicklime-catalyzed sunflower oil methanolysis was studied at mild reaction conditions by **Marija R. Miladinovic et al**. Quicklime (calcined at 550 °C for 4 h) in amounts of 1.0, 2.5, 5.0 and 10.0% (based on the oil weight) and different molar ratios of methanol-to-oil (6:1, 12:1 and 18:1) were employed to investigate their influence on the methyl esters content and the kinetics of the methanolysis reaction [**Chemical Engineering Research and Design, 92**, 1740-1752, (2014)]. The optimal methanol-to-oil molar ratio and quicklime amount for achieving the highest fatty acid methyl esters content were established to be 12:1 and 5% (based on the oil weight), respectively. The sigmoidal kinetics of quicklime-catalyzed methanolysis reaction was described by a model which included the changing mechanism of the reaction and the triacylglycerols mass transfer limitation. The kinetic parameters were determined and correlated with the process variables. A good agreement between the kinetic model and the experimental data for all applied reaction conditions was observed.

[Contributed by KN Prasanna Rani]

Inauguration of Dr S D Thirumala Rao Memorial Hall

Dr Sirdesai Thirumala Rao Memorial Hall was inaugurated by Prof. K Lal Kishore, Honorable Vice Chancellor of JNTU, Ananthapuramu in a function organized by OTAI (SZ), Ananthapuramu



Local Chapter. The hall was constructed and donated by Dr O S Ramchandraiah and Brothers during the Golden Jubilee Celebrations of OTRI. This is done by Dr Thirumala Rao's students and friends as a tribute to the great scientist.



Book Review**Agricultural Plant Biochemistry by Dr G Nagaraj**

Published by New India Publishing Agency, India. ISBN No. 9789383305551

Plant Biochemistry is an important emerging field in the agricultural sciences. Basic knowledge of the chemistry and the biochemical mechanisms of the plant in synthesizing various components are essential for advancements needed in other areas of agriculture like plant breeding, plant production, etc. In the recent times, biotechnology and biochemistry are moving hand in glove to solve many problems related to humans and other living beings. This book is aimed as a text book for U.G. and P.G. students in Agriculture and P.G. students in biology and as a reference book for most researchers in areas of Biochemistry and biology. This book deals with primary metabolites like sugars, lipids, amino acids and proteins, their structure, properties and utility. Nucleic acids (DNA and RNA), their structure, properties and their role in protein synthesis and inheritance also find a place. Secondary metabolites like pigments, terpenoids, steroids, phenolics, alkaloids, vitamins and phytohormones, their properties and uses in day to day life and in medicines are also discussed. Nitrogen metabolism in plants and their importance in agriculture are also presented

The author, Dr. G. Nagaraj has served the Indian Council of Agricultural Research, Govt. of India, for over 40 years as a scientist in plant biochemistry. He retired as a Principal Scientist from the Directorate of Oilseeds Research, Hyderabad. His vast knowledge and experience was the driving force in writing this book.

OTAI - AOCS Joint Membership

Oil Technologists' Association of India and American Oil Chemists' Society have come out with an attractive Joint Membership proposal for the members of OTAI. Members are requested to contact the Honorary Secretaries of the respective zones for availing this opportunity.

OBITUARY

Dr. B. P. Baliga, one of the Senior Most Members of Oil Technologists' Association of India left for the heavenly abode on March 2, 2014 at Michigan, USA. Dr. Baliga, former Director of Research of erstwhile Tata Oil mills Co. Ltd, and consultant of Shree Renuka Sugars Pvt.Ltd. was President of AFST (I) Head Quarters during 1979-80 and Vice-President of Oil Technologists Association of India (WZ) and took keen interest in the activities of the associations. Dr. Baliga had many academic distinctions both in India and abroad in the field of edible oils, vegetable proteins, animal feeds, soaps & detergents. He served on many committees of BIS and CSIR. He was responsible for collaboration on a Vegetable Protein Project between TOMCO, Mumbai and CFTRI, Mysore. The OTAI members pray for his soul to rest in peace in heavenly abode.

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&
International Conference on Sustainable Technologies and Futuristic
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November 14 - 16, 2014
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FORTHCOMING EVENTS

1. 13th Practical Short Course on Fundamentals of Edible Oil Refining, Processing and Quality Management at Crown PlazaMontpellier Corum, Montpellier, France, September 13-14, 2014. For details, contact: Dr Ignace Debruyne. Tel: +32476460798; e-mail: info@smartcourses.com.
2. Globeoil India 2014 at Renaissance Mumbai Convention Centre, Renaissance Hotel, Mumbai, during 26-28 September, 2014. For details, contact: Tefla's, Phone: 91-22-28710245/28710246; Fax: 91-22-28710247; e-mail: teflas@gmail.com.
3. World Conference on Fabric and Homecare, at Montreux Music and Convention Centre, Montreux, Switzerland during October 6-9, 2014. This meeting is organized by American Oil Chemists' Society. For details, contact: AOCS Meetings Department, Phone no. +1 217-693-4821; Fax: +1 217-693-4865; e-mail: meetings@aocs.org; website: <http://aocs.org/meetings>.
4. Oils and Fats International Congress 2014 (OFIC 2014) at Kualalumpur Convention Centre, Kualalumpur, Malaysia during November 5-7, 2014. For details, Contact: Ms. Michelle Lim, OFIC Secretariat, MOSTA, Selangor, Malaysia. E-mail: mosta.secretariat@gmail.com.
5. 69th Annual Convention of Oil Technologists' Association of India and International Conference on Sustainable Technologies and Futuristic Trends: Oilseeds, Oil Processing and Surfactants & Expo 2014 at Hotel Radisson Blue, Agra, India during November 14-16, 2014. For details, contact: Prof R K Trivedi, President, OTAI Central Zone. Phone: +91-9415024771. E-mail: otai2014@otaicentralzone.org; website: www.otaicentralzone.org.
6. Fundamentals of Oilseed and Edible Oil Processing and Refining at Hotel Crowne Plaza, Shanghai Pudong, Shanghai, China during November 17-18, 2014. For details, contact: meetings@aocs.org.
7. 4th International Conference on Soaps, Detergents & Cosmetics at Hotel Marriott, Panjim, Goa, India during December 7-9, 2014. For details, contact: Indian Home and Personal Care Industry Association. Tel. +91 2228771857; Fax.: +912228733619. E-mail: ihpcia@ihpcia.org.

NEW BOOKS PUBLISHED

1. The Science of Defoaming: Theory, Experiment and Applications by Peter R Garrett, CRC Press, Cheriton House, North Way, Andover, Hants, SP10 5BE, UK. ISBN : 9781420060416, \$199.95, 2013.
2. Introduction of Physical Chemistry of Foods by Christos Ritzoulis, CRC Press, Cheriton House, North Way, Andover, Hants, SP10 5BE, UK. ISBN : 9781466511750, \$89.95, 2013.
3. Chemical Reaction Engineering: Beyond the Fundamentals by L K Doraiswami and Deniz Uner, CRC Press, Cheriton House, North Way, Andover, Hants, SP10 5BE, UK. ISBN : 9781439831229, \$129.95, 2013.
4. Surface Chemistry Essentials by K S Birdi, CRC Press, Cheriton House, North Way, Andover, Hants, SP10 5BE, UK. ISBN : 9781439871782, \$129.95, 2013.
5. Advances in Biofuel Production: Algae and Aquatic Plants, by Barnabas Gikonyo, CRC Press, Cheriton House, North Way, Andover, Hants, SP10 5BE, UK. ISBN: 9781926895956, \$149.95, 2013.
6. Introduction to Chemical Processes, Principles, Analysis and Synthesis, Reginar Murphy, McGraw Hill Education (India) Pvt. Ltd., B 4, Sector 63. Noida. Uttar Pradesh 2010301. Tel. +911204383400.. ISBN : 9781259064869, Rs.580/-, 2013.
7. Mass Production of Beneficial Organisms, Edited by Joan A Morales-Ramos, M Guadalupe Rojas and David I Slapiro-Ilan, Academic Press, Elsevier Ltd., The Boulevard, Longford Lane, Kidlington, Oxford, OX5 1GB, UK.. Tel.+441865844731. ISBN : 9780123914538, 2013.
8. Industrial Catalysis and Separations: Innovations for Process Intensification, Edited by K V Raghavan and B M Reddy, CRC Press, Cheriton House, North Way, Andover, Hants, SP10 5BE, UK. ISBN : 9781926895963, \$179.95, 2014.

All the members of OTAI are requested to update their membership details and send the information to their respective zonal secretaries

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The e-mails of zonal secretaries are given below:

Central Zone : otaicz@gmail.com

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Eastern Zone : otaiez@gmail.com

Southern Zone : otaisz@gmail.com

Western Zone : otaiwz@gmail.com

Please mark a copy to : lst.journal@gmail.com

OTAI ANNUAL MERIT AWARDS

1. Dr. S Hussain Zaheer Memorial Award (Single Person Award for Basic Research): Annual Cash Award of Rs. 5,000/- was instituted with the support of Zaheer Science Foundation, New Delhi. The award is for excellence in research contribution in Oil Chemistry and Technology, Surface Coatings and Allied Subjects, through research papers, which include applicant's name among the authors and which appeared during the previous three calendar years.
2. Dr. S D Tirumala Rao Memorial Award (Single Person Award for Applied Research): Annual Cash Award of Rs. 5,000/- was instituted with the support of Anantapur Chapter of OTAI (SZ). The award is for excellence in research contributions in relevant subject "Wealth from Waste" or "Value-added Products from the Waste generated in Vegetable Oil Industry" through research papers, which include applicant's name among the authors and which appeared during the previous three calendar years.
3. RBGV Swaika Memorial Award (Team Award for Applied Research): Annual Cash Award of Rs. 5,000/- was instituted with support of Shri B K Swaika and Shri N K Swaika of M/s Swaika Vanaspati Products, Kolkatta. The award is for excellence in Specific Process or Product Development or Innovation or Improvement in the Oils, Oilseeds, Surface Coating and Allied Field over three calendar years.
4. Dr. Santinath Ghosh Memorial Research Award: Annual Cash Award of Rs.10,000/- and citation was instituted by OTAI (EZ) with corpus fund donated by Dr. Pubali Ghosh Dhar in memory of Dr. Santinath Ghosh for the Young Researcher (age below 35 years as on 1st January of the particular year). The award is for excellence in the field of Oil Technology and Allied Sciences with Best Social / Industrial Implication through patent / research paper, which include applicant's name among the authors which appeared during the previous calendar year.
5. S R Bhatnagar (SARBI) Memorial Research Award: Annual Cash Award of Rs 15,000/- and citation was instituted by OTAI (WZ) with the Corpus fund of donated by Mrs. Cherry Churi, Director, Ms Sarbi Petroleum & Chemicals Pvt. Ltd. in memory of Late Mr. S R Bhatnagar for the post graduate students. The award is for excellence in the research in the field of Tribology / Lubricant and allied fields for the research papers published which include applicant's name among the authors which appeared during the previous or current calendar year.
6. O P Narula – OTAI (SZ) Technology Award: Annual Cash Award of Rs. 7,500/- was instituted with the support of Shri O P Narula, New Delhi and OTAI (SZ). The award is for the best project report prepared for a specific topic identified by OTAI (SZ). The applicant has to submit a 10 to 15 page report (5 copies) on the above topic to the Secretary, OTAI (SZ).
7. O P Narula – OTAI (SZ) Young Scientist Award: Annual Cash Award of Rs. 5000/- was instituted with the support of Shri O P Narula, New Delhi and OTAI (SZ). This award is for a researcher who is engaged in Oils & Allied Products and should not have completed 35 years of age as on 1st January of the particular year. The award is for Publications/Patents which include applicant's name among the authors.

For further details and prescribed proforma for Award Nos. 1, 2 & 3, the applicants may contact Shri Sanjay Tandon, Hony. General Secretary, Oil Technologists' Association of India, C/o. HBTI, Kanpur – 208 002. For Award No. 4, the applicants may contact Dr. Mahua Ghosh, Hony. Secretary (EZ), C/o. Dept. of Chemical Technology, University of Calcutta, 92, A.P.C. Road. Kolkata 700 009, West Bengal. For Award No. 5, the applicants may contact Dr Rajeev Churi, C/o Oils, Surfactants & Oleochemicals Div., ICT, Matunga, Mumbai-19. For Award No. 6 and 7, the applicants may contact Dr. B V S K Rao, Hony. Secretary, OTAI (SZ), C/o CSIR-IICT, Hyderabad – 500 007. Any member of the OTAI engaged in an Academic or Industrial Research Organization or in industry is eligible for all the awards. The same award may be given second or more times to the same person, but only after the lapse of three years.

8. Prof. R K Khanna Memorial Award: Annual Cash Award of Rs. 5,000/- was instituted with the support of OTAI (Central Zone) in memory of Prof. R K Khanna. This team award is for the best research paper published in all issues of the Journal of Lipid Science and Technology, which appeared during previous calendar year. No application is required for this award.



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