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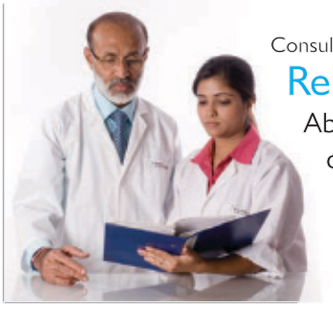

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CONTENTS

From Editors Desk

There is a steep rise in import of RBD palmolein (up 225% in the last 5 months) which is hurting the domestic industry. Presently the landed cost of RBD palmolein is lesser than crude palm oil and for this reason the domestic refining industry is facing severe crisis of less capacity utilization. Due to this reason the Indian industry wants the reduction of import duty on CPO to 5% whereas retaining the 15% import duty on RBD palmolein.

The severe El nino and the effects of dry weather are being noticeably felt in CPO production at present. The Indonesian government and industry have also got together and finally their "Bio-diesel" programme has got underway. At present monthly production and consumption of palm biodiesel is over two lakh tonnes.

India's growth remains very good and the Indian economy remains an island of high growth in an otherwise shaky world. This has also translated into a high growth of consumption and import. So far in accordance with official MPOB figures, Malaysian production for January and February is running over 1.0 lac tonnes less than Jan – Feb 2015 and by the end of the March quarter, the deficit may extend to 3.5 lakh tonnes which may further go up drastically in the near future. It is, therefore, expected that there will be increase in palm oil prices in the international market in near future.

In the recent past a lot of palm oil is being fractionated and the less valued palm stearin fraction can be made a valuable product by it's sulfonation and derivitisation, it can go very well in the surfactant industry. Although, a greater part is going into fat splitting plant, thereby, yielding fatty acids for toilet soap manufacture.

R. P. Singh

(R.P. SINGH)

INDEX TO ADVERTISEMENTS / ANNOUNCEMENTS

The views and opinions expressed in this journal are those of the contributors; Oil Technologists'Association of India does not necessarily concur with the same. All correspondence should be addressed to the Honorary Editor, Journal of Lipid Science and Technology, 7/105-E, Ratan Kunj, Villa-3,Swaroop Nagar, Kanpur-208002, e-mail: rpshbti@rediffmail.com and lst.journal@gmail.com. ***Annual Subscription: Rs.500 (India) / US$ 60 (Overseas).***

Physico-chemical Properties and Fatty Acid Profile of *Erythrina variegata* Seeds

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ABSTRACT

Erythrina variegata seed were collected from wildly grown trees of Hyderabad region of Telangana, India and was investigated for physico-chemical and fatty acid composition. The extracted lipid was characterized employing standard AOCS methods, gas chromatography and gas chromatography–mass spectrometry. The seeds were found to contain 14.3% lipid and 24.1% protein. Peroxide and iodine values were 6.6 meq O_2/kg and 64 mg I_2/100g fat respectively. Neutral lipids (89.9%) were the major classes found in total lipid of seeds. The total lipid showed high oleic acid, palmitic and behenic acids (55.1, 13.6, and 8.9% respectively). Palmitic and stearic acids were the major fatty acids in glycolipid, while oleic and palmitic acids in phospholipids. Linoleic acid (6.6-8.3%) was found in good quantities in all the lipid classes and linolenic acid (4.5%) in the phospholipid fraction. Oleic acid was found in more than 50% in all the lipid Results indicated oleic acid content was found to be higher (> 50%) and hence there is a scope for determining its suitability for chemical modifications to produce biolubricant base stocks or biofuel applications.

KEYWORDS: *Erythrina variegata,* Seed lipid, Physico-chemial properties Lipid quality, Lipid classes

INTRODUCTION

Erythrina variegata, also known as Tiger's Claw, Indian coral tree and Sunshine tree, is a specimen of *Erythrina* native to the tropical and subtropical regions of Eastern Africa, Southern Asia, Northern Australia, and the islands of the Indian Ocean and the Western Pacific Ocean east to Fiji. The tree grows to a maximum height of 60-90 feet[1]. The leaf of this plant is used as fodder for cattle[2]. The seed flour of *Erythrina variegata* was extracted using hexane to remove oil (14%) to yield a meal with protein content of 40.3% as compared to 24.3% in the whole seed[3]. Protein extractability from defatted seeds of *Erythrina variegata* in aqueous solutions of various pH values or by different concentrations of NaCl, KCl, $CaCl_2$ and $MgSO_4$ at pH 7.0 were studied[4]. Nitrogen content of the seeds and deoiled seeds showed good protein content. Albumin, globulin, prolamine and glutelin were fractionated. Amino acid analysis of the protein isolates and the fractions identified 17 amino acids, most of which were found to be essential.

Bioassay-directed fractionation of the roots of *Erythrina variegata* resulted in the isolation of several known compounds: warangalone (scandenone), 5,7,4′-trihydroxy-6,8-diprenylisoflavone, erycristagallin, erythrabys-sin-II, phaseollin, phaseolidin, and isobavachin. A new cinnamylphenol, eryvariestyrene, were isolated and characterized by spectroscopic means[5]. Most of the literature of the *Erythrina variegata* was concentrated on the protein and bio active components present in different parts of the plant. However, the oil was not characterized for the lipid components. In the present investigation, *Erythrina variegata* seeds were collected from Hyderabad region and analysed for their chemical composition, lipid quality and fatty acid composition using chromatographic techniques such as GC, GC-MS.

MATERIALS & METHODS

Materials

Erythrina variegata seeds (5 kg) were collected from the trees at Hyderabad, Telangana, India during 2009-11. Solvents and chemicals used in the study were of laboratory grade obtained from M/s. Sd. Fine Chem, Mumbai, India. Standard fatty acid methyl esters (FAMES, C_4-C_{24}) were procured from M/s. Sigma-Aldrich, St Louis, USA.

METHODS

Sample preparation: Seeds of *Erythrina variegata* were manually cleaned from dust and ground to obtain uniform sample using a laboratory mixer (Sumeet Food Processor, Nasik, India).

Physico-chemical Properties of seed sample

Estimation of moisture: Moisture was determined using hot air oven method[6]. The powder (5 g) weighed in a glass dish was placed in a hot air oven at 103 ± 2 ˚C for 12 hr. The dish was cooled in a desiccator, and weighed. Loss on drying is calculated and expressed as percent moisture.

Estimation of total ash:

The seed powder 5 g was weighed into silica dish and the contents were ignited on Bunsen burner for combustion of organic matter and determination of the inorganic metals. Further, the material was exposed to 525 ˚C for 6 hr in a muffle furnace (Adair Dutt and Company, Chennai, India). The crucibles were cooled and weighed and the difference in weight gives the total ash content, which is expressed as percentage.

Estimation of protein: Nitrogen content in seed powder (2g) was estimated by the Kjeldahl method, which is based on determination of the amount of reduced nitrogen (NH_2 and NH) present in the sample. Various nitrogenous compounds are converted into ammonium sulphate, when digested with concentrated sulphuric acid (40 ml) in the presence of a digestion mixture (2g) consisting of copper sulphate, potassium sulphate and selenium dioxide for 6h till the appearance of clear solution. The contents were made up to 100ml volume with distilled water. Ammonia is liberated by boiling the aliquot 10 ml with 20ml of NaOH (40%), which is absorbed in neutral boric acid solution (2%) and was titrated with a standard

hydrochloric acid (0.1N). Percent protein was calculated using a general conversion factor N × 6.25.

Extraction of total lipid: The total lipid of *Erythrina variegata* seed sample was obtained by extracting the seed powder with a mixture of chloroform:methanol (2:1, v/v) at room temperature (RT, 27 ± 2 °C) under magnetic stirring[7]. Extraction was repeated for 5 times for maximum recovery of lipids. The solvent was recovery at <50 °C using a rotary evaporator.

Lipid analysis: The total lipid was analysed for chemical parameters such as free fatty acids (FFA), saponification value (SV), peroxide value (PV) and iodine value by using standard methods[8-11].

Chromatographic separation of lipid classes: The total lipid was quantitatively chromatographed by eluting with chloroform, acetone and methanol separately to recover neutral, glyco- and phospholipids employing silicic acid column[12]. TLC identification was employed for neural lipids, glycolipids and phospholipids using different solvent systems (90:10, hexane:ethyl acetate, v/v; 170:25:24:4 chloroform:methanol:aceticacid:water, v/v/v/v; 65:25:4 chloroform:methanol:water, v/v/v), respectively.

Determination of fatty acid composition of lipid classes: The total lipids and the lipid classes were converted into their respective fatty acid methyl esters (FAMEs) by refluxing with methanol containing 2% sulphuric acid for 6 h. The reaction mixture was extracted into ethyl acetate and the excess acid was washed off with water. The extracts were concentrated by removing the solvent.

The GC-FID analysis of FAMEs was performed with an Agilent 6850 (Agilent Technologies, Palo Alto, CA, USA) series gas chromatograph equipped with an FID detector, DB-225 capillary column (30 m × 0.25 mm i.d. and 0.25 µm film) with temperature programming maintaining at 160 °C for 2 min, increasing to 230 °C at 6 °C/min, and finally maintained for 10 min at 230 °C[13]. The carrier gas was nitrogen at a flow rate of 1.5 ml/min. The injector and detector temperatures were 230 and 250 °C, respectively with a split ratio of 50:1.

The GC-MS analysis was conducted using Agilent (Paolo Alto, USA) 6890N gas chromatograph equipped with a HP-5 MS capillary column (30 m × 0.25 mm i.d. 0.25 µm film) connected to an Agilent 5973 mass spectrometer operating in the EI mode (70 eV; *m/z* 50-550; source temperature 230 °C and a quadruple temperature 150 °C). The column temperature was programmed as 200 °C for 2 min, increasing to 300 °C at a rate of 4 °C/min, and maintaining at 300 °C for 20 min. The carrier gas used was Helium at a flow rate of 1.0 mL/min. The inlet temperature was 300 °C and split ratio was 50:1. Comparison of retention times as well as fragmentation pattern of authentic compounds from the Wiley and NIST libraries was utilized for structural assessment.

RESULTS AND DISCUSSION

Chemical composition: The photographs of the *Erythrina variegata* plant and seeds are presented in Fig. 1. The sample prepared from seed was analysed for chemical composition and it is presented in Table 1. The processed seed after solvent extraction at room temperature yielded 14.3% total lipid. The seed possessed 24.1% protein, total ash 1.9% and a moisture content of 5.8%. Similar composition was observed in de-hulled seeds of quamachil (*Pithecellobium dulce* L) where the lipid yield was 27.3% and protein content of 22%, as reported by Prabhakara Rao *et al*.,[14]; Narsing Rao *et al*.,[15]. Similarly, it was reported that *Sterculia foetida* seed flour contained a protein content of 15% and yielded a crude fat of 20%[16]. *Sterculia urens* seed cotyledons were found to be rich in total lipid (39.2%) and protein (30.9%)[17]. The karanja (*Pongamia pinnata*) seed was reported to contain 27% fat, and 17.4% protein[18].

Lipid quality: The results of total lipid quality such as free fatty acids (FFA), saponification value (SV), peroxide value (PV) and iodine value are presented in Table 2. Free fatty acid content 28 mg/g, peroxide value 6.6 meq O_2/kg, saponification value 181.3 mg KOH/g and iodine value of 64 mg I_2/100 g are observed in the total lipid. Similar free fatty acid content of 26% and lower peroxide value 1.3 meq O_2/kg was reported in *Sterculia urens* seed cotyledons lipid and palash seed oil of 40 mg/g[17,19]. Saponification value of 188 mg KOH/g and higher iodine value of 103 I_2/100 g lipid was reported in *Trachyspermum copticum* seed lipid by Prabhakara Rao *et al*.,[20]. In karanja seed lipid, a saponification value of 185 mg KOH/g and iodine value of 80 mg I_2/100 g were observed[18]. *Psophocarpus tetragonolobus* seed oil showed an acid value of was 1.2 mg KOH/g oil, saponification value of 172.6 mg KOH/g and iodine value of the oil was 127.7 g KOH/100 g oil[21]. These oils have been found to be potential raw materials in biolubricant base stock and biodiesel preparation.

Lipid classes of Erythrina variegate: The composition of different classes of lipids and total lipid in *Erythrina variegata* seed is presented in Table 3. Higher triglyceride (89.9%) content followed by glycolipids (8.6%) was observed. The composition of lipid classes is similar to many vegetable oils such as buckwheat, which contain 81% neutral lipid, 8% phospholipid and 2% glycolipid in total lipid fraction[22].

Fatty acid composition of total lipid: The GC and GC-MS chromatograms of the seed lipid are presented in Fig. 2. The fatty acid composition of *Erythrina variegata* seed total lipid by GC and GC-MS is presented in Table 4. The total lipid was composed of high concentration of monounsaturated fatty acids (59.4%) with oleic acid (18:1) as the major fatty acid (55.1%) followed by eicosenoic acid (3.8%). Saturated fatty acids were also prominent (33.2%) wherein palmitic (13.6%), behenic (8.9%) and stearic (6.1%) acids were found in considerable quantities. Among the polyunsaturated fatty acids (7.4%), linoleic acid alone contributed 91.8%. Neutral and phospholipids followed a similar trend of fatty acids as in total lipids. The phospholipids showed higher polyunsaturated fatty acids (12.8%) with linolenic acid was as the major fatty acid (8.3%). However, glycolipids showed higher saturated fatty acids (94.7%) with palmitic (58.8%) and oleic (34.8%) acids as the major fatty acids. Earlier works on forest seeds such as jatropha, Brazilian nuts, walnut and entada possessed higher lipid contents which can be exploited for food and industrial

applications. Jatropha seed oil possessed palmitic acid (14.2%) and linoleic acid (32.8%)[23]. Derewiaka *et al.,*[24] reported the presence of 17.9% palmitic acid in the Brazilian nuts, and oleic acid 23.9% in pine nuts and 17.8% in walnuts. Lipid classes and fatty acid composition of Adavi chinta (*Entada pursaetha*) seed oil was reported by Prabhakara Rao *et al*.,[25]. They found that the palmitic acid (8.8%), oleic acid (37.2%), linoleic acid (43.9%) and eicosanoic acid (1%) were the major fatty acids of total lipid. Similar trend in fatty acid composition such as oleic (41-43%), palmitic (13-14%) and stearic acid (6-7%) was reported by Satheesh Kumar *et al.,*[26] in Jatropha seed lipid. Alkyd resins were prepared using different amount of jatropha oil (40–80%) by employing two stage alcoholysis-polyesterification process. Palash seed oil with almost similar composition was found to be a potential source for biodiesel preparation[19]. It was reported that the total lipid contained oleic (23.8%) and linoleic acids (40.4%) as major fatty acids. Hence *Erythrina variegata* seed lipid with oleic (55.1%) and linoleic acids (6.8%) can be explored for bio diesel production.

CONCLUSIONS

In the present study, seeds of *Erythrina variegata* L. were studied for chemical, lipid and fatty acid composition. The results revealed that total lipid content was 14.3%. Seed oils from *Erythrina variegata* possessed neutral lipids to an extent of 89.9%, with major fatty acids of the of palmitic, oleic, linoleic and linolenic acids. The lipid is rich source of monounsturated fatty acids (59.4%) and polyunsaturated fatty acids (7.4%). The composition reveals that *Erythrina variegata* L can be chemically modified to develop biolubricant base stocks, alkyd resins or biofuels.

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TABLE 1	
Physico - chemical characteristics of seed	
Parameter %	**Erythrina variegata**
Moisture	5.8 ± 0.45
Total Ash	1.9 ± 0.05
Total Lipid	14.3 ± 0.13
Crude Protein	24.1 ± 1.44

Values are mean of triplicate analysis

TABLE 2	
Chemical characteristics of Erythrina variegata seed lipid	
Parameter	**Quantity**
Free fatty acid content (mg/g)	28 ± 0.45
Peroxide value (meq O_2/kg)	6.6 ± 0.08
Saponification number (mg KOH/g)	181.30 ± 2.07
Iodine number (mg I_2/100 g fat)	64 ± 0.91
Phosphorus (mg/100g)	Traces

Values are mean of triplicate analysis

TABLE 3	
Composition of lipid classes (wt%) of seed lipids determined using column chromatography	
Lipid Class	**Composition (wt%)**
Neutral lipids	89.9 ∓ 0.75
Glycolipids	8.6 ∓ 0.63
Phospholipids	1.5 ∓ 0.35

Values are mean of triplicate analysis

TABLE 4				
Fatty acid composition (wt.%) of total and individual lipid classes of Erythrina variegata seeds				
Fatty acid	**Total lipid**	**Neutral lipids**	**Glycolipids**	**Phospho-lipids**
14:0	0.1 ± 0.01	0.1 ± 0.01	1.1 ± 0.12	0.8 ± 0.01
16:0	13.6 ± 0.13	13.9 ± 0.28	58.8 ± 2.00	27.8 ± 0.72
18:0	6.1 ± 0.12	6.5 ± 0.36	34.8 ± 0.75	9.9 ± 0.26
20:0	2.9 ± 0.08	3.2 ± 0.11	–	–
22:0	8.9 ± 0.30	7.9 ± 0.36	–	–
24.0	1.6 ± 0.16	1.5 ± 0.19	–	–
Saturated	**33.2**	**33.1**	**94.7**	**38.5**
17:1	0.1 ± 0.01	1.2 ± 0.15	1.6 ± 0.03	0.8 ± 0.01
18:1	55.1 ± 0.70	53.7 ± 0.78	1.9 ± 0.15	47.9 ± 1.04
20:1	3.8 ± 0.38	4.5 ± 0.10	1.8 ± 0.01	–
22:1	0.4 ± 0.02	0.2 ± 0.01	–	–
Mono Unsaturated	**59.4**	**59.6**	**5.3**	**48.7**
18:2	6.8 ± 0.46	6.6 ± 0.10	–	8.3 ± 0.22
18:3	0.6 ± 0.01	0.7 ± 0.01	–	4.5 ± 0.17
Poly Unsaturated	**7.4**	**7.3**	**0.0**	**12.8**

Values are mean of triplicate analysis

Fig. 1: Photograph of *Erythrina variegata* (a) plant pods (b) seeds

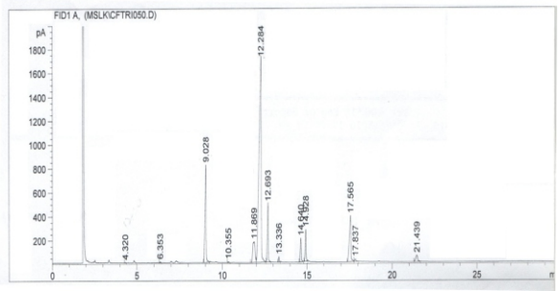
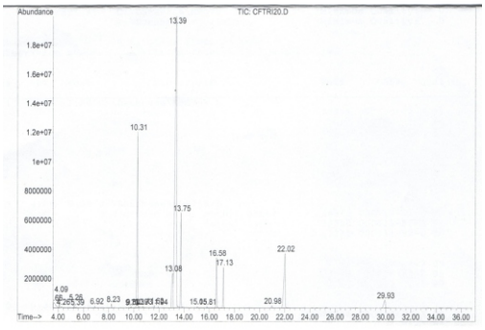


Fig. 2: The (a) GC and (b) GC-MS chromatograms of the Erythrina variegata seed lipid



Synthesis of Fructose Laurate using Candida Antarctica *NOVOZYME 435* lipase

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*Keywords : Esterification, Novozyme 435, Molecular Sieves (MS), Solvent

ABSTRACT

The process of synthesis of Sugar Fatty Acid Ester using Fructose and Lauric acid substrate was studied by varying all parameters such as molar ratio from 1:2 to 1:4, temperature from 50^0 to 60^0C, agitation speed or revolution per minute from 150 to 250, presence of molecular sieves (MS) from 0.5 to 1.5% and enzyme load from 2 to 8% in solvent acetone, n-butanol and iso-propyl alcohol with time varying from 2 to 20 h.

The highest yield approx 98.0% was obtained at molar ratio 1:3, temperature 55^0C, 1% molecular sieves (MS), 200 rpm in n-butanol solvent and 7% enzyme load (*Novozyme 435*) for 18 h.

1. Introduction

Fatty acid sugar esters, well known as bio-surfactants, are produced from renewable resources [1]. Since they are tasteless, odorless, non-toxic and non-irritating, non-ionic and biodegradable, their application has been expanded in numerous areas including pharmaceuticals, cosmetics, detergents, and food industry [2,3]. In addition, their tunable physicochemical properties, suit potential applications by varying the sugar head group size, and the length and number of alkyl chains offer a full range of hydrophilic/lipophilic balance (HLB) values from 1 to 16, with all grades displaying exceptionally good surfactant properties [1,4]. One of the important fatty acid derivatives is fatty acid fructose ester, which exhibits interesting surface properties and higher interfacial tension values compared with commercial sucrose esters [5]. While most of these compounds are chemically synthesized, the enzymatic synthesis of sugar esters has gained considerable interest because of milder and simpler conditions, higher selectivity, and greener processes [6,7].

Enzymatic sugar esters synthesis is based on esterification reaction catalyzed by hydrolases. Because esterification is a reversible reaction, the esterification reaction products such as water in media should be removed to shift the equilibrium of the reaction away from hydrolysis to obtain a maximum yield of sugar ester [3]. The water librated by the reaction can be removed by evaporation under reduced pressure [6] and azeotropic distillation [7] during the reaction. In this study, the key parameters of enzymatic sugar ester synthesis catalyzed by an immobilized lipase were investigated, including the solvent, molecular sieves, molar ratio and effect of enzyme percentage with reaction time and revolution per minute (rpm).

2. MATERIALS AND METHODS

2.1 Materials

The chemicals used like lauric acid, sucrose were procured from M/s S. D. Fine Chem. Ltd., Mumbai and Candida Antarctica (Novozyme 435) was supplied by M/s Novo Nordisk, Denmark. All organic solvents, including n-butanol were of Analytical grade. The chemicals used for FTIR and HPLC were of HPLC grade procured from M/s. Ranbaxy Laboratories Ltd., S. A. S. Nagar, India.

2.2 Methods

Reaction Procedure: A typical reaction mixture that consists of 1:8 molar ratio of sucrose and lauric acid with 8% (wt/wt)[1] of Novozyme 435 was taken in 50 ml t-butanol. After addition of molecular sieves (1%), reaction was carried out in stoppered vessel by shaking the contents at 250 rpm in orbital shaker for 20 h. The reaction was terminated by separating the enzyme and molecular sieves by centrifugation. Ester formation was monitored based on acid value of the reaction mixture measured before and after the incubation time with a procedure suggested by Novo Nordisk A/S (Novozyme 435 Product sheet, 1999) [8]. At the end of each batch of reaction, the enzyme was removed by filtration and the solvent was recovered.

The product was identified by thin layer chromatography (TLC), using Kiesilgel 60 and using solvent system of chloroform/methanol/water (64/10/ 1:v/v/v) [6]. The product was dissolved in ethyl acetate and unreacted sugar was removed by filtration. Ethyl acetate was separated by evaporation and unreacted free fatty acid was separated employing silica gel chromatography by eluting with chloroform to separate the unreacted fatty acid followed by the ester of sugar with a mobile phase of acetone/water (64/10 vol/vol). The solvents were recovered under reduced pressure.[2]

Analysis: Acid value, saponification and iodine value of Lauric acid were determined by AOCS Method (Cd 3a-63). Acid value, saponification and iodine value of Lauric acid were found to be 265.1, 280.2 and 40.1, respectively. The Fatty acids of sucrose esters were confirmed by FTIR.

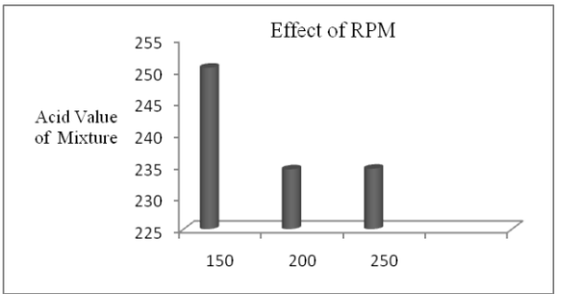
3. RESULTS AND DISCUSSIONS

3.1 Optimization of Different Parameters of Fructose and Lauric Acid with Novozyme 435

3.1.1 Effect of RPM on Synthesis of Sugar Fatty Acid Ester

For getting maximum conversion, the effect of rpm was studied at 50^{0}C, reaction time 6h in 50 ml acetone with 1:2(w/w) molar ratio, 5% catalyst (*Novozyme 435*) and with 0.5% MS. High agitation speed gave high rate of reaction but after 200 rpm it was not yielding better results. On varying the agitation speed from 150-250, the acid value of mixture decreased from 250.4 to 234.8. However, maximum reduction in AV from 265.1 to 234.3 was observed to be at 200 rpm, hence it was considered as optimum.

Figure. 1 Effect of RPM on AV during synthesis of SFAE[a,b]



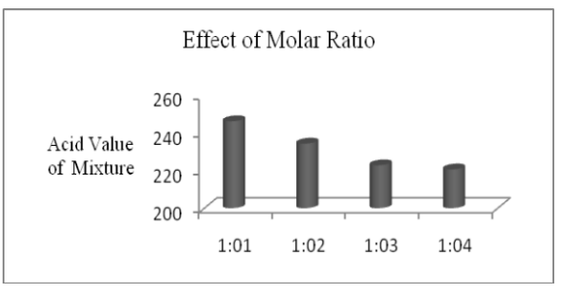
a. Reaction temperature 50^{0}C, reaction time 6h in 50 ml acetone with 5% catalyst (*novozyme 435*) and 0.5% MS at 1:2 molar ratio

b. Average of two determinations[5]

3.1.2 Effect of Molar Ratio on Synthesis of Sugar Fatty Acid Ester

Reaction at different molar ratio of fructose to lauric acid were performed at 50^{0}C, reaction time 6h and 200 rpm in 50 ml acetone with 5% catalyst (*novozyme 435*) with 0.5% MS. When we vary molar ratio of fructose to lauric acid (1:1 to 1:4), Acid value of mixture decreased. It had insignificant change in AV of mixture when molar ratio was increased from 1:3 to 1:4[3] (w/w) as depicted in figure 2. It was concluded that 1:3 is the optimum molar ratio for maximum esterification.

Figure.2 Effect of molar ratio on AV during synthesis of SFAE[a,b]



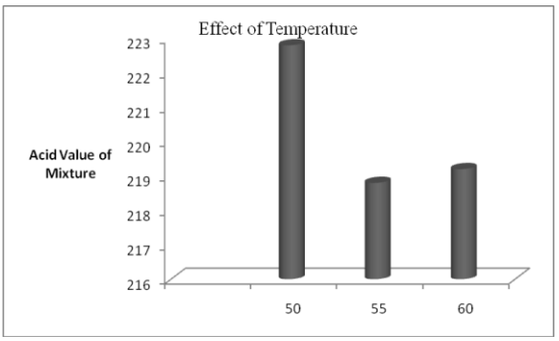
a. Reaction temperature 50^{0}C, reaction time 6h and 200 rpm in 50 ml acetone with 5% catalyst (*novozyme 435*) and 0.5% MS

b. Average of two determinations

3.1.3 Effect of Temperature on Synthesis of Sugar Fatty Acid Ester

Reaction was carried out at the three temperatures to evaluate the influence of temperature on the esterification. As we reduce the temperature, reaction rate is slower. Effect of temperature at reaction time 6h and 200 rpm in 50ml acetone with 1:3 molar ratio 5% catalyst and 0.5% ms. AV of mixture decreased from 222.8 to 219.2 only. However, when the temperature increased from 50^{0}C to 55^{0}C, the decrease in AV was from 222.8 to 218.8 and on further increase from 55^{0}C to 60^{0}C AV was observed to increase from 218.8 to 219.2 which was undesirable, hence 55^{0}C temperature was considered to be optimum.

Figure. 3 Effect of temperature on AV during synthesis of SFAE[a,b]



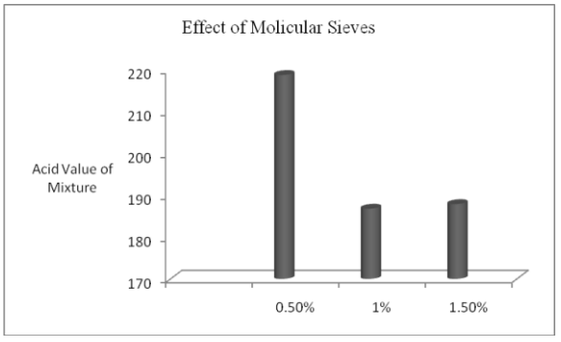
a. reaction time 6h and 200 rpm in 50 ml acetone with 5% catalyst (*novozyme 435*) and 0.5% ms

b. Average of two determination

3.1.4 Effect of Molecular Sieves on Synthesis of Sugar Fatty Acid Ester

During the reaction between sugar and fatty acid, water is one of the reaction products, which has to be removed for getting maximum conversion. When we vary the MS from 0.5-1.5 at 55^{0}C, reaction time 6h and 200 rpm in 50ml acetone with 1:3 molar ratio, 5% catalyst, the AV of reaction mixture decreased. It was found that AV decreased to 186.8 with 1% MS and with1.5% MS usage AV decreased to 187.1. Therefore, it was concluded that 1% MS was optimum for the synthesis of SFAE.

Figure. 4 Effect of molecular sieves on AV during synthesis of SFAE[a,b]



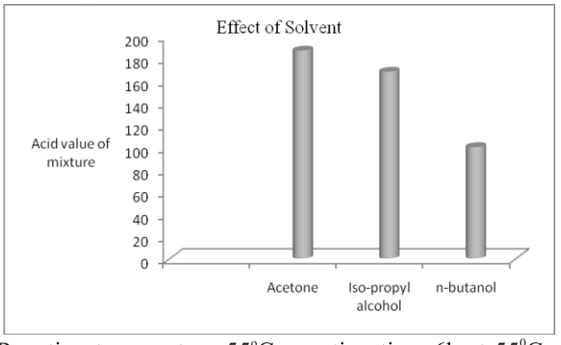
a. Reaction Temperature 55°C reaction time 6h and 200 rpm in 50 ml acetone with 5% catalyst (*novozyme 435*)

b. Average of two determinations

3.1.5 Effect of Solvent on Esterification Reaction

Suitable organic solvent should dissolve enough substrate to allow the lipase-catalyzed esterification reaction. To choose suitable organic solvent study was carried out at 55^{0}C reaction time 6h and 200 rpm in 1% MS with 1:3 molar ratio, 5% catalyst using different solvent namely actone, iso-propyl alcohol and n-butanol. The AV of mixture decreased under above conditions from 265.1 to -100.1, i.e., it decreased from 265.1 to 186.8 using acetone, decreased up to 167.8 with iso-propyl alcohol, however with n-butanol it decreased upto 100.1. Therefore, it was concluded to use n-butanol as solvent for the synthesis of SFAE.

Figure. 5 Effect of Solvents on AV during synthesis of SFAE[a,b]



a. Reaction temperature 55°C, reaction time 6h at 55^{0}C and 200 rpm in 50 ml acetone with 5% catalyst (*novozyme 435*) and 1% MS

b. Average of two determinations

3.1.6 Effect of Reaction Time on Synthesis of Sugar Fatty Acid Ester

As indicated in earlier literatures, long reaction times normally favor the synthesis of SFAE and also give high conversions. To study the effect of reaction time for this reaction at 55^{0}C & 200 rpm in 50ml n-butanol with 1:3(w/w) molar ratio of fructose to lauric acid, 5% catalyst and with 1.0 MS, the study was under taken from 0 to 20h. It was observed that in 10h AV decreased from 265.1to 54.6 but after that rate of reaction was slow from 10h-18h AV. During this time the AV decreased from 54.6 to 12.6. After that hardly any decrease in AV was observed and therefore 18h was considered as optimum time of the reaction for the synthesis of SFAE.

Table 1. Effect of reaction time on AV during synthesis of SFAE[a,b]

Time (h)	Acid value of product
0	265.1
2	197.7
4	138.6
6	100.1
8	74.7
10	54.6
12	34.3
14	21.5
16	19.4
18	12.6
20	12.5

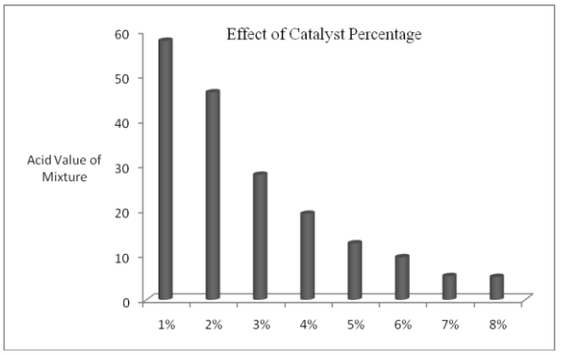
a. 55^{0}C & 200 rpm in 50ml n-butanol with 1:3 molar ratio of fructose to lauric acid, 5% catalyst and with 1% MS

b. Average of two determinations

3.1.7 Effect of Enzyme Load on Synthesis of Sugar Fatty Acid Ester

Lipase catalyzed synthesis of fructose laurate on different enzyme concentrations was investigated. If no mass transfer limitation is present, the relation between reaction rate and enzyme concentration should be linear. Due to the nature of the highly concentrated and mainly solid reaction mixtures, it is obvious that effective mixing of reactants and enzyme is important to provide good transport and contact of the reaction partners. The optimum enzyme concentration highly depends on the stirring status. It was found that the AV of product decreased (57.8-5.1) with varying enzyme concentration (1%-8%). Maximum value was reached at 7-8% (w/w) enzyme load i.e. 5.3-5.4, whereas using 8%concentration of enzyme had limited effect in comparison of 7% as stated in figure 4.2.7. Optimum enzyme load was 7% at 55^{0}C and 200 rpm in 50ml n-butanol with 1:3 molar ratio of fructose and lauric acid, and with 1.0% MS for 18 h reaction condition.

Figure. 6 Effect of catalyst on AV during synthesis of SFAE[a,b]



a. 55^0C & 200 rpm in 50ml n-butanol with 1:3 molar ratio of fructose and lauric acid, and with 1% MS for 18 h
b. Average of two determinations

1. Analysis of SFAE

The presence of ester was also confirmed by FTIR spectrophotomter analysis which showed that the product had adsorption bands at wave number 3464 cm^{-1} (for the OH band), 2854-2925 (for the C–H band in $–CH_2$ or $–CH_3$), 1743 (for the C=O, ester band), 1463-1363 (for $–CH_2$, $–CH_3$), 1017-1246 (for the C–O, ester band), and 722 (for the CH_2 band) as shown in Figure 7.

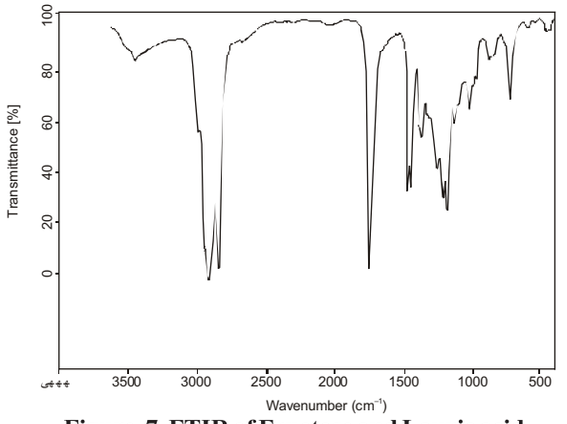


Figure. 7 FTIR of Fructose and Lauric acid

One of the most important characteristics of a surfactant is its ability to reduce surface tensions. The fructose ester prepared in this experiment could reduce the surface tension of water from 74.2 to 38.3 dynes cm^{-1} as shown in Figure.8.

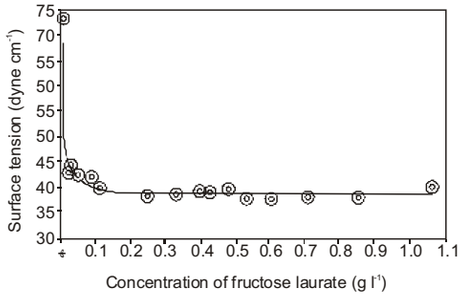


Figure. 8 Surface Tension of fructose laurate (g l^{-1})

HLB, an important characteristics of a surfactant, was determuined for the synthesized biosurfactant derived from fructose and lauric acid and was found to be 6.5.[7]

1. Conclusion

The optimum reaction conditions for the synthesis of fructose-laurate were molar ratio (fructose : lauric acid) 1:3 at 55^0C in n-butanol solvent at 200 rpm in 7% enzyme for 18 hour.

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Synthesis and Characterization of Novel 10-Undecenoic Acid based Acyloxy Ether Derivatives

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Abstract
Synthesis of novel 10-undecenoic acid based acyloxy ether derivatives was done in a two step reaction. Methyl epoxy undecanoate on oxirane ring opening by alkoxy anions from two different alcohols namely, methanol and n-butanol in presence of K 10 clay as a green reusable heterogeneous catalyst yielded a mixture of regioisomeric forms of hydroxyl ether undecanoates. These products on acylation of hydroxyl group with two different anhydrides gave acyloxy ether derivatives in good yields (90-92%). The synthesized products were characterized using different spectroscopic techniques like FTIR, ^{1}H NMR and ^{13}C NMR, GC, GC-MS and ESI-MS. These products could prove useful as biodegradable cold flow improvers for diesel and biodiesel fuels and potentially as lubricants.

1. Introduction

Epoxidation is one of the most important double bond addition reactions. Epoxides are highly versatile intermediates in organic synthesis owing to their relatively easy synthesis and ability to undergo facile ring opening reactions with various nucleophiles. Ring opening reactions of epoxide with nucleophiles are considered as an interesting approach in organic synthesis of many functionalized oxygenated compounds. The reaction with nucleophiles such as oxygen compounds (water, alcohols, phenols, acids)[1-5] (Olah et al., 1981; Otera et al., 1985; Chini et al., 1992; Tamami et al., 1993; Iranpoor et al., 2002). Nitrogen compounds (amine and derivatives of amines, azide, nitrate, isocyanate)[6-8] (Scriveni and Turnbull, 1988; Chini et al., 1994; Iranpoor and Salehi, 1995). Halides[9] (Tamami et al., 2002) and various carbon nucleophiles[10] (Ciaccio et al., 1992) have been performed in both organic and aqueous solvents.

In the case of unsaturated fatty acid esters, it is often performed in situ using the performic acid method. This process is industrially performed on a large scale and at present the vegetable oil epoxides are used in PVC and stabilizers[11](Biermann et al., 2000). Furthermore, they are also used to improve the lubricity in lubricants[12,13](Sammaiah et al., 2014; Adhvaryu and Erhan, 2002). Because of their good lubricity and high oxidation stability in comparison to rapeseed oil, pure epoxidised rapeseed oil can also be used as a lubricant base fluid[14](Wu et al., 2000). The strained three-membered ring of epoxides makes them highly susceptible to ring-opening reactions. Ring opening takes place through cleavage of one of the carbon-oxygen bonds. It can be initiated by either electrophiles or nucleophiles, or catalyzed by either acids or bases[15-18](Salimon et al., 2012; Salimon et al., 2011; Geethanjali et al., 2013; Lathi and Mattiasson, 2007). For example, the acid catalyzed hydrolysis of an epoxide is a useful procedure for preparing vicinal-dihydroxy compounds (glycols). In acid catalyzed ring opening, the nucleophile attacks the protonated epoxide ring from the side opposite the epoxide group. The carbon being attacked undergoes an inversion of configuration. The new C-O bond is always formed from the side opposite that of the original epoxide ring because the ring-opening reaction is an S_N^2 reaction. Acid catalysis assists epoxide ring-opening by providing a better leaving group (an alcohol) at the carbon undergoing nucleophilic attack. This catalysis is especially important if the nucleophile is a weak one such as water or an alcohol. In the absence of an acid catalyst the leaving group must be a strongly basic alkoxide ion, but this kind of reactions are not so environment concerned. Such reactions do not occur with other ethers, but they are possible with epoxides, provided the attacking nucleophile is strong enough. Besides the reaction variables regarding the nucleophile, already mentioned, stearic effects also may play an outstanding role on the reaction rate and reaction pathway especially with alcohols bearing branches in β position because it is expected these branches will sterically hinder the new functions created by the ring-opening of the epoxide with the alcohols, i.e. the ether and hydroxyl groups, increasing the hydrolytic and oxidative stability of the products in their application as lubricants[19](Moser and Erhan 2006) Keeping this in view, an approach was undertaken in this study in which two alcohols namely methanol and butanol in the presence of acid catalyst clay K10 were added to an oxirane moiety in methyl epoxy undecanoate to afford hydroxy ethers. Methanol was chosen because being the simplest alcohol, it allows a first approach to the reactions system to obtain valuable information that can be applied in the addition of other alcohols. Besides, the addition product from methanol could have interesting lubricant properties itself. The other alcohol butanol was selected as it is a short chain alcohol. Montmorillonite Clay K 10 was chosen as catalyst for ring opening studies because of its high acid site accessibility provided by the open high surface area combined with the relatively high amount and strength of Brönsted acid sites. The introduction of branching to the fatty epoxide may impart lower cloud point and pour point by affecting macro crystalline formation at low temperatures. Applied to fatty acid esters, these products could prove useful as biodegradable cold flow improvers for biodiesel and potentially as lubricants in diverse applications such as hydraulic fluids, metalworking fluids, crankcase oils, drilling fluids, two-cycle engine oils, wear-resistant fluids, and greases[20](Sharma et al., 2006).

Experimental Description

2.1. Materials

10-Undecenoic acid was procured from Jayant Oil Mills (Mumbai, India). All the chemicals and solvents were of analytical grade purchased from Sigma Aldrich and Sd. Fine Chemical companies. Montmorillonite K 10 was procured from Fluka (Montmorillonite is a subclass of smectite, a 2:1 phyllosilicate mineral characterized as having greater than 50% octahedral charge. Chemically, it is hydrated sodium calcium aluminium magnesium silicate hydroxide $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$. Potassium, iron, and other cations are common substitutes, and the exact ratio of cations varies with source) Gas Chromatography was recorded on Agilent 6850 series.^{1}H and ^{13}C-NMR Spectra were recorded on a Varian 300 and 75 MHz, respectively and TMS was used as an internal standard. Mass spectra were recorded on Waters e2695 Seperators module (Waters, Milford, MA, USA) Mass Spectrometer using electron spray ionization. IR spectra were recorded on a on a Perkin-Elmer Fourier Transform (FT-IR) Spectrum BX instrument (Model: Spectrum BX; Connecticut, USA) using dichloromethane.

2.2. Methods

Synthesis of methyl-10-epoxy undecanoate: Methyl undecenoate (3 g, 0.015 mol) and m-chloroperbenzoicacid (3.9 g, 0.023 mol) were dissolved in 50 ml of dichloromethane (DCM) and kept under magnetic stirring for about 3 hr at refluxing temperature. The progress of the reaction was monitored by TLC, using solvent system hexane/ethyl acetate (90:10 v/v). After completion of the reaction DCM was evaporated under reduced pressure. Crude product was extracted with hexane and the insoluble m-chloro benzoic acid was separated out from the product by filtration. Methyl-10-epoxy undecanoate was purified by passing through basic alumina column with solvent hexane to yield the product (3.02 g). General procedure for the synthesis of methyl-11(10)-alkoxy-10(11)-hydroxy undecanoates:To a stirred solution of methyl-10-epoxy undecanoate (0.005 mol) in an alcohol (0.0075 mol) was added clay K 10 (10 mg, 0.1% based on weight methyl-10-epoxy undecanoate) and stirring continued at 80˚C until GC–MS analysis indicated that methyl-10-epoxy undecanoate was consumed (6 h). Hexane (100 mL) was then added, and the solution was washed with $NaHCO_3$ (sat. aq., 1 × 0.5 mL) and brine (2 × 1 mL), dried (Na_2SO_4), filtered, concentrated in vacuo, and placed for 6 h under vacuum to yield hydroxy ethers. The product was purified using silica gel column with n-hexane: ethyl acetate (94:6 v/v) to afford methyl-11(10) alkoxy-10(11) -hydroxy undecanoates.

Methyl 11(10)-butoxy-10(11)-hydroxy undecanote: FT-IR (Neat, v, cm^{-1}): 3462 (OH),2929(C-H), 1740 (C=O), 1171 (C-C(=O)-O);^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm):0.96(t, CH_3-); 1.25-1.4 (m, -C<u>H</u>$_2$-CH_3); 1.55-1.65 (m, C<u>H</u>$_2$-CH_2-CO-); 2.3 (t, -CH_2-C=O); 3.24-3.56(m, -C<u>H</u>-O); 3.65 (s, O-CH_3);^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm):13.8,19.2,24.8, 25.3, 25.4, 29.2, 29.6, 30.8, 32.1, 33.0,34.1, 51.3, 64.2, 69.3, 70.2, 71.1, 75.2, 79.9, 174.3;ESI-MS (m/z): 311 $(M+Na)^+$.

Methyl 10(11)-hydroxy-11(10)-methoxy undecanoate: FT-IR (Neat, v, cm^{-1}): 2929 (C-H), 1740 (C=O), 1171(C-C(=O)-O);^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.25-1.4 (m, -C<u>H</u>$_2$-CH_3), 1.6-1.65 (m, C<u>H</u>$_2$-CH_2-CO-), 2.3 (t, -CH_2-C=O), 3.24(t, OCH_3), 3.39-3.64 (m, -C<u>H</u>$_2$-O), 3.65 (s, $COOCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 24.8, 25.9, 29.1, 29.3, 32.3, 33.9, 51.3, 52.2, 63.8, 70.1, 81.5, 174.2; ESI-MS (m/z): 269 $(M+Na)^+$.

General procedure for the synthesis of methyl 10(11) -acyloxy-11(10) –alkoxy undecanoates: Methyl-11(10) alkoxy-10(11) -hydroxy undecanoates (1.7mmol), acid anhydride (2.55 mmol) (propionic and butanoic), DMAP (0.1% DMAP based on weight of methyl-11(10) alkoxy-10(11) -hydroxy undecanoates) and xylene (30 mL) were taken in a three necked round bottom flask and stirred at 110ºC for a period of 6 h. The reaction was monitored by TLC and IR. The crude product was distilled at 80-140˚C temperature to remove excess acid anhydride and xylene. The resultant product was extracted with ethyl acetate and washed with water, filtered over Na_2SO_4, concentrated in vacuo, and dried under vacuum to afford methyl 10(11) -acyloxy-11(10) –alkoxy undecanoate. The product was passed over basic alumina to recover the product having an acid value less than 0.1.

Methyl 11(10)-butoxy-10(11)- cm^{-1}): (propionyloxy) undecnoate: FT-IR (Neat, v, 2929 (C-H), 1740 (C=O), 1171 (C-C(=O)-O); ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.96 (t, -C<u>H</u>$_3$), 1.15(t, -CH_3), 1.25-1.42 (m, -C<u>H</u>$_2$-CH_3), 1.48-1.68 (m, C<u>H</u>$_2$-CH_2-CO-), 2.3 (t, -CH_2-C=O), 3.24-3.53(m, CHO-), 3.67 (s, -OCH_3),5.0 (m, CH-OCO);^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 9.0, 13.8, 19.8, 24.8, 25.3, 25.4, 29.2, 29.6, 30.8, 32.1, 33.0, 33.7, 51.3, 65.6, 69.8, 71.1, 71.8, 72.5, 174.2 174.3; ESI-MS (m/z): 367 $(M+Na)^+$.

Methyl 11(10)-butoxy-10(11) (butyryloxy) undecnoate: FT-IR (Neat, v, cm^{-1}) : - 2931(C-H), 1740 (C=O), 1179 (C-C(=O)-O); ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.93(t, CH_3), 1.25-1.57 (m, -CH_2-), 1.6-1.67 (m, C<u>H</u>$_2$-CH_2-CO-), 2.3 (t, -CH_2-C=O), 3.48-3.73(m, -CH_2-O), 4.28(m, CH-O), 3.65 (s, O-CH_3), 5.0 (m, CH-OCO); ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.6, 13.9, 18.4, 19.3, 25.3, 25.4, 29.2, 29.6, 30.8, 32.1, 33.0, 33.8, 51.4, 65.8, 69.8, 71.1, 71.8, 72.4, 173.3, 174.3; ESI-MS (m/z): 381 $(M+Na)^+$.

Methyl 11(10)-methoxy-10(11) (propionyloxy) undecanoate: FT-IR (Neat, v, cm^{-1}): - 2931(C-H), 1740 (C=O), 1195(C-C(=O)-O); ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.14(t, CH_3), 1.25-1.48 (m, -C<u>H</u>$_2$-CH_3), 1.58-1.65 (m, C<u>H</u>$_2$-CH_2-CO-), 2.3 (t, -CH_2-C=O), 2.75 (m, C<u>H</u>$_2$-O); 3.36(s, -OCH_3), 3.40(m, C<u>H</u>$_2$-O), 3.65 (s, $COOCH_3$), 5.0 (m, C<u>H</u>-OCO;^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 9.1, 25.4, 29.2, 29.6, 30.8, 32.1, 33.0, 33.9, 51.3, 52.2, 65.4, 72.3, 73.7,78.9, 174.3;ESI-MS (m/z): 325 $(M+Na)^+$.

Methyl 10(11)-(butyryloxy)-11(10) methoxyundecanoate: FT-IR (Neat, v, cm^{-1}) : 2930(C-H), 1740 (C=O), 1177(C-C(=O)-O); ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.95 (t, CH_3); 1.25-1.4 (m, -C<u>H</u>$_2$-CH_3), 1.56-1.65 (m, C<u>H</u>$_2$-CH_2-CO-), 2.3 (t, -CH_2-C=O), 3.35-3.44(m, CH_2O-), 3.24(s, -OCH_3), 3.65 (s, $COOCH_3$), 5.0 (m, C<u>H</u>-OCO); ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 13.5, 18.4, 25.3, 25.4, 29.2, 29.6, 30.8, 32.1, 33.0, 33.8, 51.3, 52.2, 64.8, 65.2, 71.5, 72.2, 73.9, 78.9, 173.3, 174.2; ESI-MS (m/z): 365 $(M + Na)^+$.

3. Results & discussion

In the present study methyl 10(11) -acyloxy-11(10) –alkoxy undecanoates were synthesized by epoxy ring opening of methyl epoxy undecanoate using K 10 clay as catalyst and after acylation of hydroxyl group with two different anhydrides namely, propionic and butyric anhydrides (Fig. 1). The products were characterized by GC, ESI-MS, GC-MS, IR, ^{1}H NMR and ^{13}C NMR spectral analysis. 10-Undecenoic acid was esterified with methanol in presence of H_2SO_4 (0.2% based on 10-undecenoic acid) to obtain methyl 10-undecenoate in 96.5 % yield. Methyl 10-undecenoate was reacted with mCPBA using dichloromethane as solvent to obtain methyl epoxy undecanoate in 93% yield. The purity of the product was determined by GC and was characterized by GC-MS, IR, and NMR spectral analysis.

Fig. 1: Synthesis of 10-undecenoic acid based acyloxy ether derivatives - Placed just after the conclusion.

The epoxy group of methyl epoxy undecanoate was opened with two different alcohols namely methanol and n-butanol in presence of K 10 clay (0.1% based on weight methyl-10-epoxy undecanoate) to prepare alkyl-11(10) alkoxy-10(11) -hydroxy undecanoates monitoring by TLC analysis for the disappearance of epoxide. In the ring opened products, the yield of methyl-11(10) methoxy-10(11) -hydroxy undecanoate was 86% and methyl-11(10) butyroxy-10(11) -hydroxy undecanoate was 82%. FTIR spectra confirmed the ring opening reaction of methyl epoxy undecanoates with alcohols. disappearance of epoxy band (835 cm^{-1}) and a new broad band at 3466 cm^{-1}, attributed to the addition of hydroxyl group in the product and a band at 1171 (C-C(=O)-O) characteristic of the ether group confirmed the presence of hydroxyl and ether groups in the product. In ^{1}H NMR spectra absence of peaks at 3.2-2.8 ppm (-CH- protons of the epoxy ring) indicate complete epoxy ring opening. A signal at 3.39-3.64 ppm confirmed oxirane ring opening and introduction of hydroxy groups into the molecule. In ^{13}C NMR signal at 70.1 ppm indicated the presence of hydroxyl group and another signal at 81.5 ppm confirmed the presence of ether group. Molecular ion of m/z 269 $[M+Na]^{+.}$ confirmed the structure of the compound. Regiochemistry of 11-alkoxy-10-hydroxy undecanoate vs. the equally likely 11- hydroxy-10 –alkoxy undecanoate regioisomer was observed by GC by their retention time difference and by GC-MS by fragmentation pattern. For methyl 11-hydroxy-10-methoxy undecanoate the retention time was 12.21 min and for methyl 10-hydroxy-11-methoxy undecanoate the retention time was 12.43 min. The ratio of these isomers is 40:60. The yield of isomer methyl 10-hydroxy-11-methoxy undecanoate is higher due to stearic hindrance. In butanol opened products the methyl 11-hydroxy-10-butoxy undecanoate retention time was 14.82 min and for methyl 10-hydroxy-11-butoxy undecanoate the retention time was 14.91 min. Molecular ion of m/z 311 $[M+Na]^{+.}$ confirmed the structure of the compound methyl-11(10) butoxy-10(11) -hydroxy undecanoate.

Methyl-11(10) alkoxy-10(11) -hydroxy undecanoates were acylated with acid anhydrides (propionic and butyric) in presence of dimethly amino pyridine (DMAP) in a water azeotrope forming solvent xylene at a temperature 100-150°C for a period required for complete conversion to obtain methyl 10(11) -acyloxy-11(10) - alkoxy undecanoates in 90-92 % yield. The molecular ion of proionoylated methyl 10(11) -acyloxy-11(10) –methoxy undecanoates m/z 325 $[M+Na]^+$ and molecular ion of butanoylated methyl 10(11) -acyloxy-11(10) – methoxy undecanoates m/z 339 $[M+Na]^+$ confirmed their respective structures. The molecular ion of proionoylated methyl 10(11) -acyloxy-11(10) –butoxy undecanoates m/z 367 $[M+Na]^+$ and molecular ion of butanoylated methyl 10(11) -acyloxy-11(10) – butoxy undecanoates is m/z 381 $[M+Na]^+$ confirmed their respective structures.

The admirable quality of the clay catalyst could be the recovery and reusability. After the reaction, the product was extracted into ethyl acetate, catalyst from aqueous layer was separated by simple filtration, washed with methanol, dried and reused. The reusability study of the catalyst for the under optimized conditions for methyl-11(10) alkoxy-10(11) -hydroxy undecanoates five catalytic runs was observed to be no considerable loss of activity of the catalyst.

Additional physical property characterization such as thermal and oxidative stability, viscosity, lubricity, surfactant behavior, etc. may provide interesting insight into the utility of these derivatives for lubricant applications.

4. Conclusion

In the present study novel methyl 10(11) -acyloxy-11(10) –akoxy undecanoates were synthesized by epoxy ring opening of methyl epoxy undecanoate using K 10 clay as catalyst and after acylation of hydroxyl group with two different anhydrides namely, propionic and butyric anhydrides. The introduction of branching to the fatty epoxide may impart lower cloud point and pour by affecting macro crystalline formation at low temperatures. Hence, the hydroxyl ethers can be used as pour point depressants for biodiesel and lubricants. The acylated derivatives may prove to be potential base stocks for industrial lubricant applications.

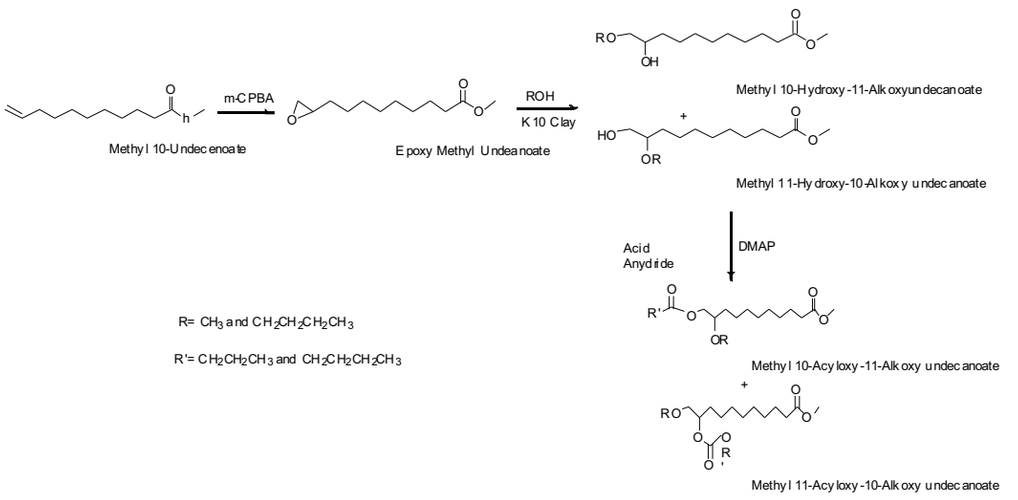

Fig. 1 : Synthesis of 10-undecenoic acid based acyloxy ether derivatives

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RESEARCH ROUNDUP

July – September 2016

Analytical method for the trace determination of Esterified 3- and 2-monochloropropanediol and glycidyl fatty acid esters in various food matrices

Fatty acid esters of 3-monochloro-1,2-propanediol (3-MCPDEs), of 2-monochloro-1,3-propanediol (2-MCPDEs) and of 2,3-epoxy-1-propanol or glycidol (GEs), which are considered to be deleterious to human health, may occur in a broad variety of food samples. A proper risk assessment of those substances requires the availability of robust occurrence data; in this respect concerns have been raised regarding the reliability of results obtained with the currently available methods to determine those substances in processed food. This article by **Vasilios G. Samaras *et al*** presents an indirect analytical procedure for the simultaneous determination of 3-MCPDEs, 2-MCPDEs and GEs in a wide variety of food products after extraction by pressurised liquid extraction (PLE) and determination by gas chromatography mass-spectrometry (GC–MS) **[Journal of Chromatography A, 1466**, 136-147, (2016)]. For the differentiation of MCPDEs and GEs, the latter were first converted to monobromopropanediol esters (MBPDEs) in acid aqueous solution of sodium bromide. MCPDEs and MBPDEs were then hydrolysed under acidic conditions followed by derivatisation of the released free (non-esterified) form in ethyl acetate with phenyl boronic acid (PBA). Quantification of the analytes was carried out using the isotopic labelled analogues of both MCPDEs and GEs. Limits of detection (LODs) and limits of quantitation (LOQs) were in the range of 7–17 mg kg^{-1} and 13–31 mg kg^{-1} respectively, while the working range of the method was between LOQ and 1850 mg kg^{-1} expressed on fat basis. The developed method was successfully applied for the analysis of the target compounds in more than 650 different food samples covering the following commodities: bread and rolls, fine bakery wares, smoked fish products, fried and roasted meat, potato based snacks and fried potato products, cereal-based snacks and margarines.

Multi residue analysis of environmental pollutants in edible vegetable oils by gas chromatography tandem mass spectrometry

A novel multiresidue determination of polycyclic aromatic hydrocarbons (PAHs), phthalate esters (PAEs) and alkylphenols (APs) in edible vegetable oils was developed by **Rui-Ze Zhou *et al***. The samples were extracted with hexane-saturated acetonitrile, and after concentration, the extract was directly qualitatively and quantitatively analyzed by gas chromatography–tandem mass spectrometry (GC–MS/MS) with multiple reaction monitoring (MRM) in positive ion mode **[Food Chemistry, 207,** 43-50, (2016)]. The calibration curve displayed good linearity in the range of 2–100 µg/L, with correlation coefficients greater than 0.99. The mean recoveries were 70.0–110.8% by analysis of spiked oil, and the relative standard deviations (RSDs) were 2.1–10.2% (n = 6), respectively. The limits of detection (LODs) for the 23 PAHs, 17 PAEs and 3 APs were 0.1–1.0 µg/kg, 0.1–4.0 µg/kg and 1.2–3.0 µg/kg, respectively. The established method effectively avoided interference from large amounts of lipids and pigments. It was applied to real sample and shown to be a rapid and reliable alternative for determination and confirmation in routine analysis.

The effect of frying on glycidyl esters content in palmoil

The changes in palm oil, as affected by frying temperature, and content of the glycidyl esters (GEs) were studied by **Magda Aniołowska and Agnieszka Kita**. Potato chips were fried intermittently in palm oil, which was heated for 8 h daily over five consecutive days. Frying was conducted at three frying temperatures: 150, 165 and 180 °C **[Food Chemistry, 203,** 95-103, (2016)] . Thermo-oxidative alterations of the oil were measured by acid and anisidine values, changes in fatty acid composition, total polar components, polar fraction composition and colour components formation. Content of GE was measured by liquid chromatography–mass spectrometry. Results showed that amount of products of hydrolysis, oxidation and polymerization (excluding decrease of degree of unsaturation) increased significantly as a function of frying temperature and time. Between GEs of fatty acids the most abundant were esters of palmitic and oleic acids. With increasing temperature and frying time, the content of GE decreased. The extent of GE decrease was correlated with degree of oil degradation.

Determination of phthalate esters in drinking water and ediblevegetableoilsamples by headspace solid phase microextraction using graphene/polyvinyl chloride nanocomposite coated fiber coupled to gas chromatography-flame ionization detector

In the current study, a graphene/polyvinylchloride nanocomposite was successfully coated by **Hatam Amanzadeh *et al*** on a stainless steel substrate by a simple dip coating process and used as a novel headspace solid phase microextraction (HS-SPME) fiber for the extraction of phthalate esters (PEs) from drinking water and edible vegetable oil samples **[Journal of Chromatography A, 1465**, 38-46, (2016)]. The prepared SPME fibers exhibited high extractability for PEs (due to the dominant role of π-π stacking interactions and hydrophobic effects) yielding good sensitivity and precision when followed by a gas chromatograph with a flame ionization detector (GC-FID). The optimization strategy of the extraction process was carried out using the response surface method based on a central composite design. The developed method gave a low limit of detection (0.06–0.08 µg L^{-1}) and good linearity (0.2–100 µg L^{-1}) for the determination of the PEs under the optimized conditions (extraction temperature, 70 ± 1 °C; extraction time, 35 min; salt concentration, 30% w/v; stirring rate, 900 rpm; desorption temperature, 230 °C; and desorption time, 4 min) whereas the repeatability and fiber-to-fiber reproducibility were in the range 6.1–7.8% and 8.9–10.2%, respectively. Finally, the proposed method was successfully applied to the analysis of PEs in drinking water and edible oil samples with good recoveries (87–112%) and satisfactory precisions (RSDs < 8.3%), indicating the absence of matrix effects in the proposed HS-SPME method.

Large multiresidue analysis of pesticides in ediblevegetableoilsby using efficient solid-phase extraction sorbents based on quick, easy, cheap, effective, rugged and safe methodology followed by gas chromatographytandem

mass spectrometry

The aim of this research by **P. Parrilla Vázquez *et al*** was to adapt the QuEChERS method for routine pesticide multiresidue analysis in edible vegetable oil samples using gas chromatography coupled to tandem mass spectrometry (GC–MS/MS) **[Journal of Chromatography A, 1463**, 20-31(2016)]. Several clean-up approaches were tested: (a) D-SPE with Enhanced Matrix Removal-Lipid (EMR-Lipid™); (b) D-SPE with PSA; (c) D-SPE with Z-Sep; (d) SPE with Z-Sep. Clean-up methods were evaluated in terms of fat removal from the extracts, recoveries and extraction precision for 213 pesticides in different matrices (soybean, sunflower and extra-virgin olive oil). The QuEChERS protocol with EMR-Lipid d-SPE provided the best reduction of co-extracted matrix compounds with the highest number of pesticides exhibiting mean recoveries in the 70–120% range, and the lowest relative standard deviations values (4% on average). A simple and rapid (only 5 min) freeze-out step with dry ice (CO_2 at −76 °C) prior to d-SPE clean-up ensured much better removal of co-extracted matrix compounds in compliance of the necessity in routine analysis. Procedural Standard Calibration was established in order to compensate for recovery losses of certain pesticides and possible matrix effects. Limits of quantification were 10 μg kg^{-1} for the majority of the pesticides. The modified methodology was applied for the analysis of different 17 oil samples. Fourteen pesticides were detected with values lower than MRLs and their concentration ranged between 10.2 and 156.0 μg kg^{-1}.

Determination of pesticides in edibleoilsby liquid chromatography-tandem mass spectrometry employing new generation materials for dispersive solid phase extraction clean-up

Jonatan V. Dias *et al* evaluated the efficiency of several sorbents on removal fats from edible oils (olive, soya and sunflower) during the clean-up step for posterior determination of 165 pesticides by UHPLC-QqQ-MS/MS system **[Journal of Chromatography A, Volume 1462**, 8-18 (2016)]. The extraction procedure employed in this work was the citrate version of QuEChERS method followed by a step of freezing out with dry ice and clean-up evaluation using i) PSA with magnesium sulfate (d-SPE); ii) magnesium sulfate and Z-sep sorbent (d-SPE); iii) Z-sep (column SPE) and iv) Agilent Bond Elut QuEChERS Enhanced Matrix Removal-Lipid (EMR-Lipid). After evaluation of the recovery results at 10, 20 and 50 μg kg^{-1}, the EMR-Lipid showed important advantages comparing to the other sorbents evaluated, such as better recovery rates and RSD%. The method was validated at the three concentrations described above. Analytical curves linearity was evaluated by spiking blank oil samples at 10, 20, 50, 100 and 500 μg kg^{-1}. The method demonstrated good recoveries values between the acceptable range of 70–120% and RSD% < 20 for most of evaluated pesticides. In order to evaluate the performance of the method, this same procedure was employed to other oils such as soya and sunflower with very good results.

Techno-economic comparison of biojet fuel production from lignocellulose,vegetableoil and sugar cane juice

In this study, a techno-economic comparison was performed by **Gabriel Wilhelm Diederichs *et al*** considering three processes (thermochemical, biochemical and hybrid) for production of jet fuel from lignocellulosic biomass (2G) versus two processes from first generation (1G) feedstocks, including vegetable oil and sugar cane juice **[Bioresource Technology, 216**, 331-339 (2016)]. Mass and energy balances were constructed for energy self-sufficient versions of these processes, not utilising any fossil energy sources, using ASPEN Plus® simulations. All of the investigated processes obtained base minimum jet selling prices (MJSP) that is substantially higher than the market jet fuel price (2–4 fold). The 1G process which converts vegetable oil, obtained the lowest MJSPs of $2.22/kg jet fuel while the two most promising 2G processes- the thermochemical (gasification and Fischer-Tropsch synthesis) and hybrid (gasification and biochemical upgrading) processes- reached MJSPs of $2.44/kg and $2.50/kg jet fuel, respectively. According to the economic sensitivity analysis, the feedstock cost and fixed capital investment have the most influence on the MJSP.

Exploration of upstream and downstream process for microwave assisted sustainable biodiesel production from microalgaeChlorella vulgaris

Amit Kumar Sharma *et al* explore the integrated approach for the sustainable production of biodiesel from*Chlorella vulgaris* microalgae **[Bioresource Technology, 216**, 793-800 (2016)]. The microalgae were cultivated in 10 m^2 open raceway pond at semi-continuous mode with optimum volumetric and areal production of 28.105 kg/L/y and 71.51 t/h/y, respectively. Alum was used as flocculent for harvesting the microalgae and optimized at different pH. Lipid was extracted using chloroform: methanol (2:1) and having 12.39% of FFA. Effect of various reaction conditions such as effect of catalyst, methanol:lipid ratio, reaction temperature and time on biodiesel yields were studied under microwave irradiation; and 84.01% of biodiesel yield was obtained under optimized reaction conditions. A comparison was also made between the biodiesel productions under conventional heating and microwave irradiation. The synthesized biodiesel was characterized by ^{1}H NMR, ^{13}C NMR, FTIR and GC; however, fuel properties of biodiesel were also studied using specified test methods as per ASTM and EN standards.

Extraction of microalgal lipids and the influence of polar lipids on biodiesel production by lipase-catalyzed transesterification

In order to obtain microalgal saponifiable lipids (SLs) fractions containing different polar lipid (glycolipids and phospholipids) contents, SLs were extracted by **Elvira Navarro López *et al*** from wet *Nannochloropsis gaditana* microalgal biomass using seven extraction systems, and the polar lipid contents of some fractions were reduced by low temperature acetone crystallization **[Bioresource Technology, 216**, 904-913, (2016)]. We observed that the polar lipid content in the extracted lipids depended on the polarity of the first solvent used in the extraction system. Lipid fractions with polar lipid contents between 75.1% and 15.3% were obtained. Some of these fractions were transformed into fatty acid methyl esters (FAMEs, biodiesel) by methanolysis, catalyzed by the lipases Novozym 435 and *Rhizopus oryzae* in tert-butanol medium. We observed that the reaction velocity was higher the lower the polar lipid content, and that the final FAME conversions achieved after using the same lipase batch to catalyze

consecutive reactions decreased in relation to an increase in the polar lipid content.

Optimization of 1,3-dihydroxyacetone production from crude glycerol by immobilized Gluconobacter oxydansMTCC 904

Pritam Kumar Dikshit and Vijayanand S. Moholkar carried out optimization of production of the value added product, dihydroxyacetone, from crude glycerol using immobilized cells of *Gluconobacter oxydans*. Statistical optimization of the fermentation medium revealed $MgSO_4{\cdot}7H_2O$, $(NH_4)_2SO_4$ and KH_2PO_4 as the significant components, in addition to small concentration of yeast extract **[Bioresource Technology**, 216, 1058-1065 (2016)]. As per previous literature, these components augment the activity of glycerol dehydrogenase enzyme in metabolism and provide assimilable nitrogen and sulfur source for cell growth. Yeast extract not only provides essential growth factors, but also accelerates production of alcohol dehydrogenase enzyme due to amino acids present. The DHA yield from crude glycerol (20 g/L) with optimized medium is 14.08 g/L, which is just 12% lower than the yield for pure glycerol .This study has thus established that proper optimization of fermentation medium reduces the adverse effect of impurities in crude glycerol on fermentation process and DHA yield.

Value-added processing of crude glycerol into chemicals and polymers

Crude glycerol is a low-value byproduct which is primarily obtained from the biodiesel production process. Its composition is significantly different from that of pure glycerol. Crude glycerol usually contains various impurities, such as water, methanol, soap, fatty acids, and fatty acid methyl esters. Considerable efforts have been devoted by **Xiaolan Luo *et al*** to finding applications for converting crude glycerol into high-value products, such as biofuels, chemicals, polymers, and animal feed, to improve the economic viability of the biodiesel industry and overcome environmental challenges associated with crude glycerol disposal **[Bioresource Technology, 215**, 144-154 (2016)]. This article reviews recent advances of biological and chemical technologies for value-added processing of crude glycerol into chemicals and polymers, and provides strategies for addressing production challenges.

Evaluation of poly(90% biscyanopropyl/10% cyanopropylphenyl siloxane) capillary columns for the gas chromatographic quantification oftransfatty acids in non-hydrogenated vegetableoils

Current gas chromatographic (GC) methods for the analysis of fatty acids (FA) were optimized by **Pierluigi Delmont** primarily for the quantification of the *trans* 18:1 FAs (18:1 *t*FAs) produced during the partial hydrogenation of fats and oils **[Journal of Chromatography A, 1460**, 160-172, (2016)]. Recent regulatory action regarding the application of partial hydrogenation in the processing of edible fats and oils may reshape the FA composition of these products. The higher content in 18:3 *t*FAs compared to 18:1 *t*FAs of most refined non-hydrogenated vegetable oils (RNHVO), and the challenge in their quantification applying current methods, suggest the need for new methodologies. This manuscript describes a simple GC method for the analysis of FAs in RNHVOs utilizing a 100 m (0.25 mm I.D.) capillary column coated with poly(90% biscyanopropyl/10% cyanopropylphenyl siloxane) (90% BCS). The optimization of the chromatographic conditions and the detection of co-eluting compounds were carried out by applying comprehensive two dimensional gas chromatography with online reduction (GC-OR × GC). Results showed that 90% BCS capillary columns operated at the elution temperature of 162 °C provide the separation of the 18:1, 18:2 and 18:3 *t*FAs, contained in RNHVOs, from other components. A minor constituent of Canola oil, 16:3n-3, partially co-eluted with trans-18:1 FAMEs. This simple GC method showed the ability to measure trans-fat in RNHVOs at the level of 0.5 g/100 g, providing comparable quantitative results to the more complex GC × GC methodology.

A novel process for low-sulfur biodiesel production from scum waste

Scum is an oil-rich waste from the wastewater treatment plants with a high-sulfur level. In this work, a novel process was developed by **Huan Ma *et al*** to convert scum to high quality and low sulfur content biodiesel **[Bioresource Technology, 214**, 826-835, (2016)]. A combination of solvent extraction and acid washing as pretreatment was developed to lower the sulfur content in the scum feedstock and hence improve biodiesel conversion yield and quality. Glycerin esterification was then employed to convert free fatty acids to glycerides. Moreover, a new distillation process integrating the traditional reflux distillation and adsorptive desulfurization was developed to further remove sulfur from the crude biodiesel. As a result, 70% of the filtered and dried scum was converted to biodiesel with sulfur content lower than 15 ppm. The fatty acid methyl ester profiles showed that the refined biodiesel from the new process exhibited a higher quality and better properties than that from traditional process reported in previous studies.

Scale-up and economic analysis of biodiesel production from municipal primary sewage sludge

Municipal wastewater sludge is a promising lipid feedstock for biodiesel production, but the need to eliminate the high water content before lipid extraction is the main limitation for scaling up. This study by **Magdalena Olkiewicz *et al*** evaluates the economic feasibility of biodiesel production directly from liquid primary sludge based on experimental data at laboratory scale **[Bioresource Technology, 214**, 122-131(2016)]. Computational tools were used for the modelling of the process scale-up and the different configurations of lipid extraction to optimise this step, as it is the most expensive. The operational variables with a major influence in the cost were the extraction time and the amount of solvent. The optimised extraction process had a break-even price of biodiesel of 1232 $/t, being economically competitive with the current cost of fossil diesel. The proposed biodiesel production process from waste sludge eliminates the expensive step of sludge drying,

Biodiesel production from different algaloilusing immobilized pure lipase and tailor made rPichia pastoriswith Cal A and Cal B genes

B. Bharathiraja *et al* performed oil extraction in marine macroalgae *Gracilaria edulis*, *Enteromorpha compressa* and *Ulva lactuca*. The algal biomass was characterized by Scanning Electron Microscopy and Fourier Transform-Infra Red Spectroscopy **[Bioresource Technology, 213**, 69-78 (2016)].

Six different pre-treatment methods were carried out to evaluate the best method for maximum oil extraction. Optimization of extraction parameters were performed and high oil yield was obtained at temperature 55 °C, time 150 min, particle size 0.10 mm, solvent-to-solid ratio 6:1 and agitation rate 500 rpm. After optimization, 9.5%, 12.18% and 10.50 (g/g) of oil extraction yield was achieved from the respective algal biomass. The rate constant for extraction was obtained as first order kinetics, by differential method. Stable intracellular Cal A and Cal B lipase producing recombinant *Pichia pastoris* was constructed and used as biocatalyst for biodiesel production. Comparative analysis of lipase activity and biodiesel yield was made with immobilized *Candida antarctica* lipase.

Converting paper mill sludge into neutral lipids by oleaginous yeastCryptococcus vishniacciifor biodiesel production

Farha Deeba*et al* worked on paper mill sludge (PMS) and assessed it as cheap renewable lignocellulosic biomass for lipid production by the oleaginous yeast *Cryptococcus vishniaccii* (MTCC 232) **[Bioresource Technology, 213**, 96-102 (2016)]. The sonicated paper mill sludge extract (PMSE) exhibited enhanced lipid yield and lipid content 7.8 ± 0.57 g/l, 53.40% in comparison to 5.5 ± 0.8 g/l, 40.44% glucose synthetic medium, respectively. The accumulated triglycerides (TAG) inside the lipid droplets (LDs) were converted to biodiesel by transesterification and thoroughly characterized using GC–MS technique. The fatty acid methyl ester (FAME) profile obtained reveals elevated content of oleic acid followed by palmitic acid, linoleic acid and stearic acid with improved oxidative stability related to biodiesel quality.

Complete utilization of non-edibleoilseeds ofCascabela thevetiathrough a cascade of approaches for biofuel and by-products

Lipid-rich biomass, generally opted for biodiesel production, produces a substantial amount of by-product (de-oiled cake and seed cover) during the process. Complete utilization of *Cascabela thevetia* seeds for biofuel production through both chemical and thermochemical conversion route is investigated in the present study by **Debashis Sut *et al***. Various properties of biodiesel produced was characterized and compared with those obtained from similar oil seeds **[Bioresource Technology, 213**, 111-120 (2016)]. The by-products of the chemical process were used as a feedstock for pyrolysis at different temperatures in a fixed bed reactor. Maximum bio-oil yields of 29.11% and 26.18% were observed at 500 °C. The bio-oil obtained at optimum yield was characterized by CHN analyzer, NMR and FTIR spectroscopy. The biochar produced was further characterized by SEM–EDX, XRD and FTIR along with elemental analysis to explore its utilization for various purposes. The present investigation depicts a new approach towards complete utilization of lipid-rich bio-resources to different types of biofuels and biochar.

Biosurfactant production throughBacillussp. MTCC 5877 and its multifarious applications in food industry

In this study *Bacillus* sp. MTCC5877 was explored by **Farhan Anjum *et al*** for the production of biosurfactant (BSs) and various carbon sources 1% (w/v), 0.5% (w/v) nitrogen sources were tested at different pH, and temperature **[Bioresource Technology, 213**, 262-269 (2016)]. Yield was measured in terms of Emulsification index (EI), Oil Displacement Area (ODA) and Drop Collapse Area (DCA) and maximum emulsification activities of BSs were found (E_{24}) 50%, 76% and 46%, respectively, and maximum ODA of 5.0, 6.2 and 4.7 cm, were shown respectively. The BS was able to reduce the surface tension of water from 72 to 30 mN/m and 72 to 32 mN/m. Structural compositions of BS were confirmed by FTIR, GC–MS and NMR. Anti-adhesive property of BS was determined and found effective against biofilm formation. It could remove 73% Cd from vegetable which confirms its application in food industry.

Pyrogenic transformation ofNannochloropsis oceanicainto fatty acid methyl esters withoutoilextraction for estimating total lipid content

Jieun Kim *et al* investigated the pseudo-catalytic transesterification of dried *Nannochloropsis oceanica* into fatty acid methyl esters (FAMEs) without oil extraction, which was achieved in less than 5 min via a thermo-chemical pathway **[Bioresource Technology, 212**, 55-61(2016)]. This study presented that the pseudo-catalytic transesterification reaction was achieved in the presence of silica and that its main driving force was identified as temperature: pores in silica provided the numerous reaction space like a micro-reactor, where the heterogeneous reaction was developed. The introduced FAME derivatization showed an extraordinarily high tolerance of impurities (*i.e.*, pyrolytic products and various extractives). This study also explored the thermal cracking of FAMEs derived from *N. oceanica*: the thermal cracking of saturated FAMEs was invulnerable at temperatures lower than 400 °C. Lastly, this study reported that *N. oceanica* contained 14.4 wt.% of dried *N. oceanica* and that the introduced methylation technique could be applicable to many research fields sharing the transesterification platform.

Lipase cocktail for efficient conversion ofoilscontaining phospholipids to biodiesel

The presence of phospholipid has been a challenge in liquid enzymatic biodiesel production. Among six lipases that were screened by **Jerome Amoah *et al*** lipase AY had the highest hydrolysis activity and a competitive transesterification activity **[Bioresource Technology, 211**, 224-230 (2016)]. However, it yielded only 21.1% FAME from oil containing phospholipids. By replacing portions of these lipases with a more robust bioFAME lipase, CalT, the combination of lipase AY–CalT gave the highest FAME yield with the least amounts of free fatty acids and partial glycerides. A higher methanol addition rate reduced FAME yields for lipase DF–CalT and A10D–CalT combinations while that of lipase AY–CalT combination improved. Optimizing the methanol addition rate for lipase AY–CalT resulted in a FAME yield of 88.1% at 2 h and more than 95% at 6 h. This effective use of lipases could be applied for the rapid and economic conversion of unrefined oils to biodiesel.

Biorefinery of corn cob for microbial lipid and bio-ethanol production: An environmental friendly process

Microbial lipid and bio-ethanol were co-generated by **Di Cai *et al*** an integrated process using corn cob bagasse as raw material

[Bioresource Technology, 211, 677-684 (2016)]. After pretreatment, the acid hydrolysate was used as substrate for microbial lipid fermentation, while the solid residue was further enzymatic hydrolysis for bio-ethanol production. The effect of acid loading and pretreatment time on microbial lipid and ethanol production were evaluated. Under the optimized condition for ethanol production, ~131.3 g of ethanol and ~11.5 g of microbial lipid were co-generated from 1 kg raw material. On this condition, ~71.6% of the overall fermentable sugars in corn cob bagasse could be converted into valuable products. At the same time, at least 33% of the initial COD in the acid hydrolysate was depredated.

Bioconversion of volatile fatty acids derived from waste activated sludge into lipids by Cryptococcus curvatus

Pure volatile fatty acid (VFA) solution derived from waste activated sludge (WAS) was used to produce microbial lipids by **Jia Liu *et al*** as culture medium in this study, which aimed to realize the resource recovery of WAS and provide low-cost feedstock for biodiesel production simultaneously **[Bioresource Technology, 211**, 548-555 (2016)]. *Cryptococcus curvatus* was selected among three oleaginous yeast to produce lipids with VFAs derived from WAS. In batch cultivation, lipid contents increased from 10.2% to 16.8% when carbon to nitrogen ratio increased from about 3.5 to 165 after removal of ammonia nitrogen by struvite precipitation. The lipid content further increased to 39.6% and the biomass increased from 1.56 g/L to 4.53 g/L after cultivation for five cycles using sequencing batch culture (SBC) strategy. The lipids produced from WAS-derived VFA solution contained nearly 50% of monounsaturated fatty acids, including palmitic acid, heptadecanoic acid, ginkgolic acid, stearic acid, oleic acid, and linoleic acid, which showed the adequacy of biodiesel production

Microwave, ultrasound, thermal treatments, and bead milling as intensification techniques for extraction of lipids from oleaginousYarrowia lipolyticayeast for a biojetfuel application

In the present work, two different ways of lipids extraction from *Yarrowia lipolytica* yeast were investigated by **Alice Meullemiestre *et al*** in order to maximize the extraction yield **[Bioresource Technology, 211**, 190-199 (2016)]. Firstly, various modern techniques of extraction including ultrasound, microwave, and bead milling were tested to intensify the efficiency of lipid recovery. Secondly, several pretreatments such as freezing/defrosting, cold drying, bead milling, and microwave prior two washing of mixture solvent of chloroform:methanol (1:2, v/v) were study to evaluate the impact on lipid recovery. All these treatments were compared to conventional maceration, in terms of lipids extraction yield and lipid composition analysis. The main result of this study is the large difference of lipid recovery among treatments and the alteration of lipids profile after microwave and ultrasound techniques.

Kinetic study on microwave-assisted esterification of free fatty acids derived fromCeiba pentandraSeedOil

Recently, a great attention has been paid to advanced microwave technology that can be used to markedly enhance the biodiesel production process. *Ceiba pentandra* Seed Oil containing high free fatty acids (FFA) was utilized by **Thanh Lieu *et al*** as a non-edible feedstock for biodiesel production **[Bioresource Technology, 211**, 248-256 (2016)]. Microwave-assisted esterification pretreatment was conducted to reduce the FFA content for promoting a high-quality product in the next step. At optimum condition, the conversion was achieved 94.43% using 2 wt% of sulfuric acid as catalyst where as 20.83% conversion was attained without catalyst. The kinetics of this esterification reaction was also studied to determine the influence of factors on the rate of reaction and reaction mechanisms. The results indicated that microwave-assisted esterification was of endothermic second-order reaction with the activation energy of 53.717 kJ/mol.

Determination of pesticides in edibleoilsby liquid chromatography-tandem mass spectrometry employing new generation materials for dispersive solid phase extraction clean-up

Jonatan V. Dias *et al* evaluated the efficiency of several sorbents on removal fats from edible oils (olive, soya and sunflower) during the clean-up step for posterior determination of 165 pesticides by UHPLC-QqQ-MS/MS system**[Journal of Chromatography A, 1462**, 8-18 (2016)] . The extraction procedure employed in this work was the citrate version of QuEChERS method followed by a step of freezing out with dry ice and clean-up evaluation using i) PSA with magnesium sulfate (d-SPE); ii) magnesium sulfate and Z-sep sorbent (d-SPE); iii) Z-sep (column SPE) and iv) Agilent Bond Elut QuEChERS Enhanced Matrix Removal-Lipid (EMR-Lipid). After evaluation of the recovery results at 10, 20 and 50 $\mu g\ kg^{-1}$, the EMR-Lipid showed important advantages comparing to the other sorbents evaluated, such as better recovery rates and RSD%. The method was validated at the three concentrations described above. Analytical curves linearity was evaluated by spiking blank oil samples at 10, 20, 50, 100 and 500 $\mu g\ kg^{-1}$. The method demonstrated good recoveries values between the acceptable range of 70–120% and RSD% < 20 for most of evaluated pesticides. In order to evaluate the performance of the method, this same procedure was employed to other oils such as soya and sunflower with very good results.

Two-step cleanup procedure for the identification of carotenoid esters by liquid chromatography-atmospheric pressure chemical ionization-tandem mass spectrometry

Carotenoids are naturally found in both free form and esterified with fatty acids in most fruits; however, up to now the great majority of studies only evaluated their composition after saponification. This fact is easily explained by the difficult to analyze carotenoid esters. Preliminary studies by **Daniele Bobrowski Rodrigues *et al*** showed that cleanup procedures in the extract are necessary for further analysis by LCMS/MS since triacylglycerols (TAGs) impair the MS detection**[Journal of Chromatography A, 1457**, 116-124 (2016)] . Considering these facts, we developed a new cleanup procedure to remove TAGs and other lipids from carotenoid fruit extracts. This procedure is based on physical removal of solid lipids at low temperature followed by open column chromatography on MgO and diatomaceous earth. Before cleanup, four carotenoid diesters and two free xanthophylls were identified in murici (*Byrsonyma crassifolia*), corresponding to about 65% of the

total chromatogram area. After carrying out the two-step cleanup procedure, 35 carotenoids were identified, being 14 monoesters, six free carotenoids and 15 carotenoid diesters. We can conclude that this two-step procedure was successfully applied to murici, an Amazonian fruit, which contains high amounts of lipids.

Comparison of gas chromatography-combustion-mass spectrometry and gas chromatography-flame ionization detector for the determination of fatty acid methyl esters in biodiesel without specific standards

GC-FID has been effectively used as a universal quantification technique for volatile organic compounds for a long time. In most cases, the use of the ECN allows for quantification by GC-FID without external calibration using only the response of a single internal standard. **Laura Alonso Sobrado *et al*** compare the performance characteristics of GC-FID with those of post-column ^{13}C Isotope Dilution GC-Combustion-MS for the absolute quantification of organic compounds without the need for individual standards **[Journal of Chromatography A, 1457**, 134-143(2016)]. For this comparison we have selected the quantification of FAMEs in biodiesel. The selection of the right internal standard was critical for GC-FID even when ECN were considered. On the other hand, the nature of the internal standard was not relevant when GC-Combustion-MS was employed. The proposed method was validated with the analysis of the certified reference material SRM 2772 and comparative data was obtained on real biodiesel samples. The detection limit for GC-combustion-MS was found to be 4.2 ng compound/g of injected sample. In conclusion, the quantitative performance of GC-Combustion-MS compared satisfactorily with that of GC-FID constituting a viable alternative for the quantification of organic compounds without the need for individual standards.

Encapsulation of ω-3fattyacidsin nanoemulsion-based delivery systems fabricated from natural emulsifiers: Sunflower phospholipids

Nanoemulsions have considerable potential for encapsulating and delivering ω-3 fatty acids, but they are typically fabricated from synthetic surfactants. This study by **Jennifer Komaiko *et al*** shows that fish oil-in-water nanoemulsions can be formed from sunflower phospholipids, which have advantages for food applications because they have low allergenicity and do not come from genetically modified organisms **[Food Chemistry, 203**, 331-339 (2016)]. Nanoemulsions containing small droplets (d < 150 nm) could be produced using microfluidization, by optimizing phospholipid type and concentration, with the smallest droplets being formed at high phosphatidylcholine levels and at surfactant-to-oil ratios exceeding unity. The physical stability of the nanoemulsions was mainly attributed to electrostatic repulsion, with droplet aggregation occurring at low pH values (low charge magnitude) and at high ionic strengths (electrostatic screening). These results suggest that sunflower phospholipids may be a viable natural emulsifier to deliver ω-3 fatty acids into food and beverage products.

A novel method for qualitative analysis of edible oil oxidation using an electronic nose

An electronic nose (E-nose) was used by **Lirong Xu *et al*** for rapid assessment of the degree of oxidation in edible oils **[Food Chemistry, 202**, 229-235 (2016)]. Peroxide and acid values of edible oil samples were analyzed using data obtained by the American Oil Chemists' Society (AOCS) Official Method for reference. Qualitative discrimination between non-oxidized and oxidized oils was conducted using the E-nose technique developed in combination with cluster analysis (CA), principal component analysis (PCA), and linear discriminant analysis (LDA). The results from CA, PCA and LDA indicated that the E-nose technique could be used for differentiation of non-oxidized and oxidized oils. LDA produced slightly better results than CA and PCA. The proposed approach can be used as an alternative to AOCS Official Method as an innovative tool for rapid detection of edible oil oxidation.

Delivery of dietary triglycerides toCaenorhabditis elegansusing lipid nanoparticles: Nanoemulsion-based delivery systems

The nematode *Caenorhabditis elegans* is a powerful tool for studying food bioactives on specific biochemical pathways. However, many food bioactives are highly hydrophobic with extremely low water-solubilities, thereby making them difficult to study using *C. elegans*. **Daniel Colmenares *et al*** developed nanoemulsion-based systems to deliver hydrophobic molecules in a form that could be ingested by*C. elegans*. Optical microscopy showed that oil-in-water nanoemulsions with a range of particle diameters (40–500 nm) could be ingested by *C. elegans*. The amount of lipid ingested depended on the size and concentration of the nanoparticles**[Food Chemistry, 202**, 451-457(2016)]. Fatty acid analysis showed incorporation of conjugated linoleic acid and there was a significant reduction in the fat levels of *C. elegans* when they were incubated with nanoemulsions containing conjugated linoleic acid, which suggested that this hydrophobic lipid was successfully delivered to the nematodes. The incorporation of hydrophobic molecules into nanoemulsion based-delivery systems may therefore enable their activities to be studied using *C. elegans*.

Reactive Desorption of Fatty Acid Adsorbed on γ-Alumina Using Supercritical Methanol

A novel method for regeneration of fatty acid-adsorbed γ-alumina using supercritical methanol was developed by **Hee Suk Woo *et al*** . This method is based on a difference in the affinity of a fatty acid and the corresponding fatty acid methyl ester (FAME) for γ-alumina ***[Ind. Eng. Chem. Res, 55***, 10420–10426 (2016)]. Palmitic acid was selected as a model fatty acid. Batch-type reactors were used to investigate the effect of the operating parameters (temperature, methanol to γ-alumina weight ratio, and reaction time) on supercritical methanol regeneration. Almost all of the adsorbed palmitic acid was desorbed at temperatures above 300 °C, or when the weight ratio of methanol to γ-alumina was higher than 75:1, and/or if the reaction time was longer than 15 min. The crystal structure and BET surface area of γ-alumina were unchanged after supercritical methanol regeneration. The developed technique requires relatively lower operating temperature, is ecofriendly, and generates fuel, although the process is more complex than the thermal regeneration method.

Hybrid Cross-Linked Lipase Aggregates with Magnetic Nanoparticles: A Robust and Recyclable Biocatalysis for the Epoxidation of Oleic Acid

Highly stable and easily recyclable hybrid magnetic cross-linked lipase aggregates (HM-CSL-CLEAs) were prepared by **Jiandong CuiLili *et al*** by coaggregation of lipase aggregates with nonfunctionalized magnetic nanoparticles and subsequent chemical cross-linking with glutaraldehyde ***[J. Agric. Food Chem, 64,*** pp 7179–7187 (2016)]. Analysis by SEM and CLSM indicated that the CLEAs were embedded in nanoparticle aggregates instead of covalently immobilized. The resulting HM-CSL-CLEAs exhibited higher thermostability, storage stability, and reusability than standard CLEAs. For example, HM-CSL-CLEAs maintained >60% of their initial activity after 40 min of incubation at 60 °C, whereas standard CLEAs lost most of their activities. The HM-CSL-CLEAs can be easily recovered from the reaction mixture by an external magnetic field. Moreover, the H_2O_2 tolerance of the lipase in HM-CSL-CLEAs was also enhanced, which could relieve the inhibitory effect on lipase activity. A high conversion yield (55%) for the epoxidation of oleic acid using H_2O_2 as oxidizing agent was achieved by HM-CSL-CLEAs.

Poly(ester amide)s from Soybean Oil for Modulated Release and Bone Regeneration

Designing biomaterials for bone tissue regeneration that are also capable of eluting drugs is challenging. Poly(ester amide)s are known for their commendable mechanical properties, degradation, and cellular response. In this regard, development of new poly(ester amide)s becomes imperative to improve the quality of lives of people affected by bone disorders. In this framework, a family of novel soybean oil based biodegradable poly(ester amide)s was synthesized by **Janeni Natarajan *et al*** based on facile catalyst-free melt-condensation reaction ***[ACS Appl. Mater. Interfaces*, *8***, pp 25170–25184 (2016)]. The structure of the polymers was confirmed by FTIR and ^{1}H -NMR, which indicated the formation of the ester and amide bonds along the polymer backbone. Thermal analysis revealed the amorphous nature of the polymers. Contact angle and swelling studies proved that the hydrophobic nature increased with increase in chain length of the diacids and decreased with increase in molar ratio of sebacic acid. Mechanical studies proved that Young's modulus decreased with decrease in chain lengths of the diacids and increase in molar ratio of sebacic acid. The in vitro hydrolytic degradation and dye release demonstrated that the degradation and release decreased with increase in chain lengths of the diacids and increased with increase in molar ratio of sebacic acid. The degradation followed first order kinetics and dye release followed Higuchi kinetics. In vitro cell studies showed no toxic effects of the polymers. Osteogenesis studies revealed that the polymers can be remarkably efficient because more than twice the amount of minerals were deposited on the polymer surfaces than on the tissue culture polystyrene surfaces. Thus, a family of novel poly(ester amide)s has been synthesized, characterized for controlled release and tissue engineering applications wherein the physical, degradation, and release kinetics can be tuned by varying the monomers and their molar ratios.

Thermal (Catalyst-Free) Transesterification of Diols and Glycerol with Dimethyl Carbonate: A Flexible Reaction for Batch and Continuous-Flow Applications

An innovative thermal transesterification protocol for the synthesis of linear and alkylene carbonates was investigated by **Sandro Guidi *et al*** under both batch and continuous-flow (CF) conditions. Accordingly, model 1,*n*-diols (n = 2–4) and glycerol were set to react with dimethyl carbonate (DMC) at T and$p$ of 150–260 °C and 1–50 bar, respectively, in the absence of any catalyst ***[ACS Sustainable Chem. Eng, 4,*** 6144–6151(2016)]. 1,2-diols afforded the corresponding five-membered ring carbonates as the main products with a quantitative conversion and a selectivity up to 94%, whereas 1,3-diols gave the six-membered ring products along with linear mono- and dicarbonate derivatives. A complete conversion was attained also for glycerol, but the products distribution depended on reaction conditions: the CF mode allowed the synthesis of glycerol carbonate, whereas batch reactions yielded either glycerol carbonate or its derivative from a further transesterification reaction, i.e., methyl (2-oxo-1,3-dioxolan-4-yl)methyl carbonate. The selectivity toward these two compounds was in the range of 83%–94%. An addition of gaseous CO_2 (up to 20 bar) allowed to control further the selectivity of batch reactions.

Glycerol Upgrading via Hydrogen Borrowing: Direct Ruthenium-Catalyzed Amination of the Glycerol Derivative Solketal

Hydrogen borrowing provides an efficient and atom economical method for carbon–nitrogen and carbon–carbon bond formation from alcohol precursors. Glycerol is a renewable nontoxic polyol and a potential precursor to small functional organic molecules. **Anna Said *et al*** report the direct amination of solketal, a 1,2-hydroxy-protected derivative of glycerol, via ruthenium-catalyzed hydrogen borrowing, affording up to 99% conversion and 92% isolated yield using $[Ru(p\text{-cymene})Cl_2]_2$ as the catalyst precursor ***[ACS Sustainable Chem Eng*, *4***, 5730–5736 (2016)]. The synthesis of an antitussive agent in 86% overall yield from solketal was also demonstrated using this methodology.

Clean Enzymatic Preparation of Oxygenated Biofuels fromVegetable and Waste CookingOilsby Using Spongelike Ionic Liquids Technology

The biocatalytic synthesis of oxygenated biofuels (fatty acid solketal esters, FASEs) and biodiesel (fatty acid methyl esters, FAMEs) was carried out by **Pedro Lozano *et al*** by both the direct esterification of fatty acids (i.e., lauric, myristic, palmitic, and oleic acids, respectively) with solketal or methanol, and the transesterification of vegetable oils (i.e. sunflower, olive, cottonseeds, and waste cooking oil) with the same alcohols, in hydrophobic ionic liquids (ILs) based on cations with long alkyl side-chains (e.g., octadecyltrimethylammonium bis(trifluoromethylsulfonyl)imide $[C_{18}tma][NTf_2]$) ***[ACS Sustainable Chem. Eng*, *4***, 6125–6132 (2016)] . These hydrophobic ILs are temperature switchable ionic liquid/solid phases that behave as sponge-like system. As liquid phases, they are excellent monophasic reaction media for proposed biotransformations with all the assayed fat substrates, e.g. near to 100% yield of fatty acids solketyl esters (FASEs) and fatty acid methyl esters (FAMEs) in 6 h at 60 °C. By using waste cooking oil mixed with free fatty acids as substrate, green biofuels containing either both FAMEs and FASEs (e.g., aprox. 80% FAMEs and 20% FASEs, etc.) can easily be prepared. Moreover, the reaction mixture can be easily fractionated by iterative centrifugations at controlled temperature into three

phases, i.e. solid IL, water, and FAMEs + FASEs mixture leading to a straightforward and clean approach allowing the full recovery of the biocatalyst/IL system for further reuse and the simple product isolation. Furthermore, the enzyme did not shown any loss in activity during reuse in these reaction systems after six operation cycles.

–LiquidLiquid Equilibrium Data for the Pseudoternary Model System of Refined Sunflower Seed Oil + (n-Hexanal, or 2-Nonenal, or 2,4-Decadienal) + Anhydrous Ethanol at 298.15 K

Experimental liquid–liquid equilibrium data for three pseudoternary systems containing {refined sunflower seed oil + aldehyde + anhydrous ethanol} were determined at a temperature *T* of 298.15 K with u(*T*) = 0.05 K and atmospheric pressure by **Perci O. B. Homrich and Roberta Ceriani**. Binodal curves and tie line compositions are reported for *n*-hexanal, 2-nonenal, or 2,4-decadienal as solutes ***[J. Chem. Eng. Data, 61,*** 3069–3076(2016)]. The nonrandom two-liquid1 and universal quasichemical models satisfactorily correlated experimental tie line data. Othmer–Tobias3 and Hand4 methods attested the quality of experimental data. Further, the predictive capabilities of four versions5−9 of the UNIFAC10 method were analyzed.

Engineering Green Lubricants IV: Influence of Structure on the Thermal Behavior of Linear and Branched Aliphatic Fatty Acid-Derived Diesters

Fatty acid-derived aliphatic diesters and their branched derivatives are lubricating compounds that demonstrate predictable viscosity temperature profiles and remain fluid at extremely low temperatures. In this work, the influence of molecular structure on the high temperature thermal behavior of several series of aliphatic fatty acid-based diesters was investigated by **Latchmi Raghunanan and Suresh S. Narine** using thermogravimetric analyses (TGA) ***[ACS Sustainable Chem. Eng, 4,*** 4868–4874(2016)]. Evaporation behavior was determined as a function of molecular weight, saturation, symmetry and double bond position, and decomposition behavior as a function of molecular weight, branching, saturation and symmetry. The results revealed that the diol-derived diesters underwent predictable molecular weight-mediated evaporation, and that further refinement of the predicted evaporation temperatures could be obtained by accounting for saturation in the fatty acid moieties. Double bond position and symmetry did not measurably influence the evaporation temperatures of the diesters. Evaporation was successfully suppressed with increasing molecular weight, with the fatty acid chain length and the nature of the branched group being most important in the linear and branched diesters, respectively. Overall, these results are fundamentally significant because they provide the background necessary to make informed changes to molecular structure so as to effect the desired high temperature behavior in renewably sourced specifically engineered materials for lubricant applications.

Highly Functional Unsaturated Ester Macromonomer Derived from Soybean Oil: Synthesis and Copolymerization with Styrene

A highly functional unsaturated ester macromonomer was synthesized from soybean oil (SBO), by **Chengguo LiuYan *et al*** and its chemical structure was confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR, and gel permeation chromatography ***[ACS Sustainable Chem. Eng, 4,*** 4208–4216 (2016)]. The monomer was prepared through modifying epoxidized soybean oil (ESO) first with a synthesized precursor, hydroxyethyl acrylated maleate (HEAMA), and then employing maleic anhydride (MA) to modify the produced ESO-HEAMA. The obtained SBO-based monomer (ESO-HEAMA-MA) possessed a C=C bond functionality of 6.75–8.15 per ESO. Effects of styrene concentration, feed ratio, and initiator concentration on the dynamic mechanical properties of the cured bioresins were investigated carefully. When the monomer with the highest C=C bond functionality was used, the cured resins with 20–60 wt % styrene demonstrated cross-link densities of 5.07–9.52 (10^3 mol)/m^3, storage moduli at 25 °C of 1.32–2.16 GPa, glass transition temperatures of 69.9–114.1 °C, and tensile strengths and moduli of 19.7–33.1 MPa and 1.17–2.11 GPa, respectively. Microstructural morphologies of tensile-fractured surfaces of the cured resins were studied by scanning electron microscopy. Finally, curing behaviors of the resultant resin was studied by differential scanning calorimetry. The developed eco-friendly biomaterials have potential applications in the industry of unsaturated polyester resins.

Developments and challenges in biodiesel production from microalgae: A review

The imminent depletion of fossil fuels and the surging global demand for renewable energy have led to the search for nonconventional energy sources. After a few decades of trial and error, the world is now testing the sources of the third generation of fossil fuels, which contain for most parts microalgae. With more than 80% oil content, being adaptable in growth parameters and highly versatile, microalgae are highly promising sources of biofuels in the present time. The present article by makes a sweeping attempt to highlight the various methods employed for cultivation of microalgae **Tanvi Taparia *et al***, techniques to harvest and extract biomass from huge algal cultures, as well as their downstream production and processing procedures [Biotechnology and Applied Biochemistry, 63, 715–726, (2016)]. The advantages, limitations, and challenges faced by each of them have been described to some extent. Major concerns pertaining to biofuels are supposed to be their environmental sustainability and economic viability along with their cost effectiveness. This would require a great deal of empirical data on existing systems and a great deal of optimization to generate a more robust one. We have concluded our article with a SWOT analysis of using algae for biodiesel production in a tabulated form.

Fatty acid profile of new promising unconventional plant oils for cosmetic use

Oils have been used on the cosmetic application since antiquity. With the growing interest in cosmetic formulation of strictly natural origin there has been also an increased interest in the use of alternative oils obtained from nuts, herbs, fruit and vegetable seeds. Due to lack of good scientific reports on the cosmetic plant oils available in Poland, **A. Bialek *et al*** characterized fatty acids (FA) profile and oxidative quality of selected unconventional plant oils, which are used as cosmetics or potential cosmetic ingredients **[International Journal of Cosmetic Science, 38,** 382–388, (2016)]. Oxidative quality and FA composition of examined oils varied widely among

analyzed oils. Cluster analysis revealed three clusters. Clusters S1 and S3 include only one oil (Perilla and sea buckthorn, respectively). Perilla oil is characterized by relatively small content of both saturated FA (8.5%) and monounsaturated FA (14.2%) and much higher amount of polyunsaturated FA (73.5%) whereas in sea buckthorn these proportions are opposite (saturated FA and monounsaturated FA – 33.5% and 51.0% respectively, and the lowest amount of polyunsaturated FA – 5.2%). In cluster S2 two sub-clusters were distinguished and the content of linoleic ($p = 0.0015$), α-linolenic ($p = 0.0092$) and oleic ($p = 0.0015$) acid caused this distinction. PI ranged from 8.9 in sea buckthorn oil to 135 in Perilla oil. Perilla oil and raspberry seed oil were also characterized by the highest PV (225 ± 14.9 mEq O/kg oil and 232 ± 13.8 mEq O/kg oil, respectively), whereas the lowest PV was determined for walnut oil (0.82 ± 0.18 mEq O/kg oil) and carrot seed oil (0.87 ± 0.21 mEq O/kg oil) oils.

Density functional theory study of the reactivity and electronic structure of the transesterification of triacetin in biodiesel production via a sulfated zirconia heterogeneous catalysis

DFT study examined by Jesus Muniz et al for the interaction of a sulfated zirconia (SZ) slab model system (heterogeneous catalyst) and triacetin (a precursor in biodiesel production) using explicit methanol solvent molecules [International Journal of Quantum Chemistry, 116, 988–999, (2016)]. Full geometry optimizations of the systems were performed at the B3LYP level of theory. Gibbs free energies provide insight into the spontaneity of the reactions along a three-step reaction mechanism for the transesterification of triacetin. Charge decomposition analysis revealed electronic charge transfer between the metallic oxide and the organic moieties involved in the reaction mechanism. Fukui indices indicate the likely locations on the SZ surface where catalysis may occur. The quadratic synchronous transit scheme was used to locate transition structures for each step of the trans esterification process. The results are in agreement with the strongly acidic catalytic character of zirconium observed experimentally in the production of biodiesel.

Identification of waste cooking oil and vegetable oil via Raman spectroscopy

Furong Huang et al made a qualitative identification of ordinary vegetable oil and waste cooking oil based on Raman spectroscopy. Raman spectra of 73 samples of four varieties oil were acquired through the portable Raman spectrometer [Journal of Raman Spectroscopy, 47, 860–864, (2016)]. Then, a partial least squares discriminant analysis (PLS-DA) model and a discrimination model based on characteristic wave band ratio were established. A classification variable model of olive oil, peanut oil, corn oil and waste cooking oil that was established through the PLS-DA model could identify waste cooking oil accurately from vegetable oils. The identification model established based on selection of waveband characteristics and intensity ratio of different Raman spectrum characteristic peaks could distinguish vegetable oils from waste cooking oil accurately. Research results demonstrated that both ratio method and PLS-DA could identify waste cooking oil samples accurately. The identification model based on characteristic waveband ratio is simpler than PLS-DA model. It is widely applicable to identification.

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 R K Srivastava, 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.

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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