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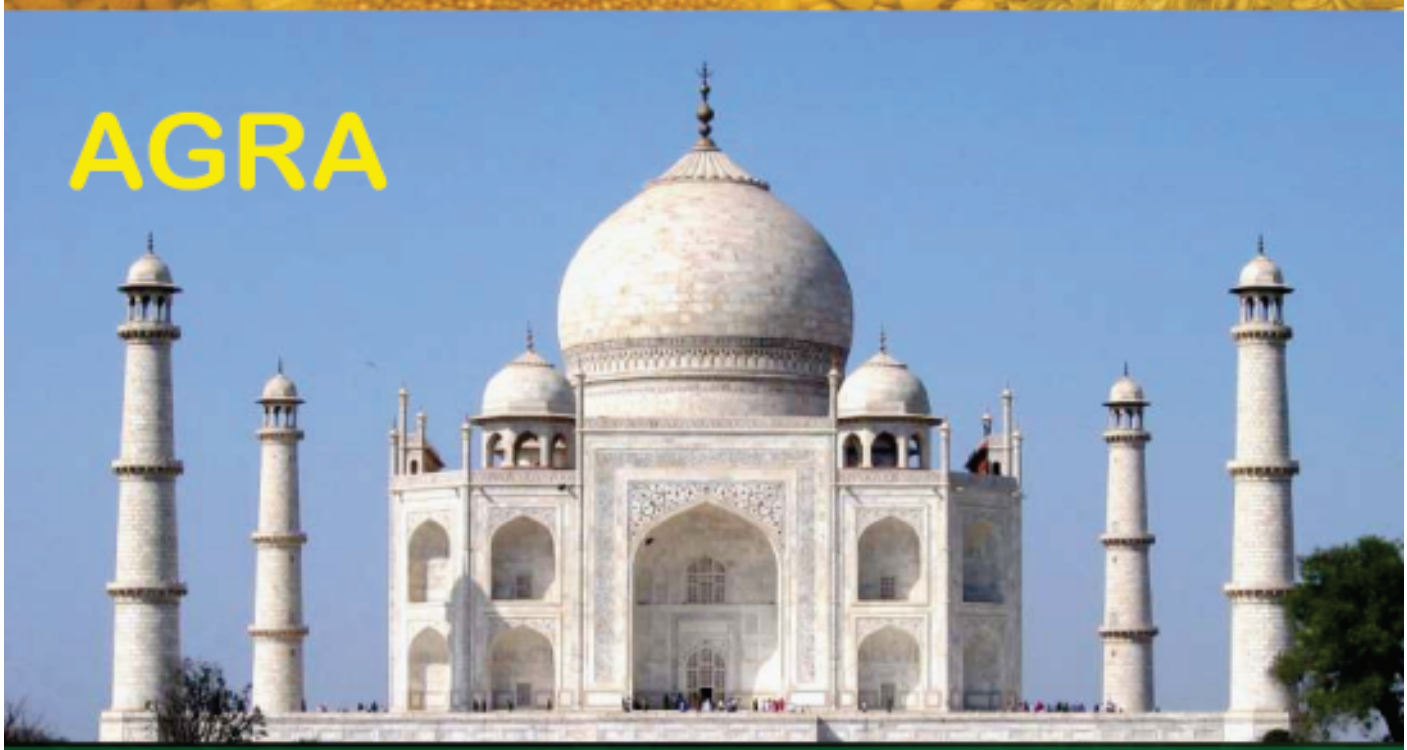

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CONTENTS

From Editor's Desk

In early eighties, supercritical fluid extraction was projected worldwide as a promising alternative to hexane extraction of oils and fats. Though promising results were reported by many researchers in both laboratory and pilot scale studies, the technology was not commercialized for oils and fats extraction. The major drawback was the high capital investments and this was restricted only to extraction of high value products. After three decades of better understanding of the process and advent of more critical fluids like sub and super critical propane, sub critical water, n-butane etc., this particular extraction process is once again gaining its importance. In the era of green technologies, the environmentally benign nature of the process is expected to play a vital role. The health aspects, safety hazards and the impact on environment of organic solvents are widely discussed in the public media. Public awareness has increased significantly about the possible contamination of residual solvents in final finished products, foods and pharmaceutical products in particular. The supercritical fluids selectively extract the desired compounds without leaving any traces of toxic residues and it also lowers the risk of thermal degradation. This technology has already been commercialized for extraction of various antioxidants from flowers like marigold, purification of herbal medicines, extraction of specific components from spices and the process is being tried for extraction of alkaloids like caffeine, morphine, emetine, pilocarpine etc. from natural products for different applications including medicinal uses. In recent years, a renewed interest was observed for the supercritical fluid extraction in the field of oils & fats. Extraction of palm oil, canola oil, soybean oil etc. was carried out and their nutritional values were evaluated and compared with that of hexane-extracted oil. It was observed that considerable nutritional benefits can be derived by using this technology. Currently, scientists are working on extraction of fats and particularly for reduction of cholesterol from dairy products as cholesterol has higher solubility in supercritical fluids like SC-CO_2 and supercritical ethane. Combination of supercritical carbon dioxide and supercritical ethane and propane were also tried to reduce the cost of the process. Supercritical fluid extraction of algal lipids was also carried out for getting the raw material for biodiesel industry and also for obtaining a PUFA-rich fraction. With these recent developments, one can see tremendous scope and possibilities for indigenous oils like rice bran oil and sesame oil as these oils contain hosts of minor compounds having nutritional benefits and these can be targeted for high value branding. Since the oils and fats industry will prefer a continuous process of extraction, some engineering interventions on the existing technology are also required, particularly for continuous feeding of the solid materials into high pressure extractors. The need of the hour is to form a team consisting of varying expertise and work on this particular green technology for development of commercially feasible processes.

Happy reading!!

(PRADOSH PRASAD CHAKRABARTI)

INDEX TO ADVERTISEMENTS / ANNOUNCEMENTS

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Comparative Study of Physicochemical Properties, *in vitro* Digestion and Gastrointestinal Absorption of Medium Chain Fatty Acid Rich Rice Bran Oil and Native Rice Bran Oil

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ABSTRACT

In the present study, the preparation of different medium chain fatty acid rich rice bran oils were carried out and comparison of their in vitro digestion study and in vivo intestinal absorption in the single-pass perfusion rat model with that of rice bran oil was studied. Medium chain fatty acid rich rice bran oil was prepared by enzyme catalysis technique which resulted in substitution of long chain fatty acids in rice bran oil with medium chain fatty acids. In vitro digestion study showed that medium chain fatty acid rich rice bran oil was better digested in comparison to native rice bran oil. In situ absorption efficiency of the oils was measured in laboratory acclimatized adult Sprague–Dawley rats. Subsequent analysis (e.g. percent volume absorption, percent lipid absorption) have shown that the medium chain fatty acid rich rice bran oil has significantly enhanced the absorption of lipids from the emulsion system, in the small intestine of the rats.

KEYWORDS: Medium chain fatty acids(MCFA), rice bran oil, physicochemical analysis, in vitro digestion study, *in vivo* absorption study, *Rhizomucor meihei.*

INTRODUCTION

Medium chain triglycerides (MCTs) are a family of triglyceride, composed mainly of caprylic and capric acids with a minor contribution of caproic and lauric acids. The concept of MCTs was introduced into clinical nutrition in the 1950s for the dietary treatment of malabsorption syndromes because of their rapid absorption and solubility[1]. MCT is mostly used to treat malabsorption and the rationale for the use of MCT on malabsorption is related to the circumstance that the small molecules of medium chain fatty acids (MCFAs) are more easily hydrolyzed by pancreatic lipase and is thus more rapidly absorbed[2]. The rationale for the use of MCT is based on differences in digestion, absorption, transport and catabolism between MCT and long chain triglycerides (LCT). Bile salts and micelle formation are not required for dispersion or absorption of MCT. MCT are transported across the mucosal more rapidly than LCT. MCT do not enter the lymph system and are transported through the portal venous system as albumin-bound free fatty acids. They are incorporated into chylomicrons and therefore do not require lipoprotein lipase for oxidation[3]. It has been observed that in comparison to LCT there is decrease in food intake in case of MCT consumption. Therefore replacing dietary LCT with MCT can increase weight maintenance programme. MCT can be used for clinical purposes such as the treatment of disorders of lipid absorption and as an energy source for enteral and parenteral nutrition[4].

Rice bran oil is a widely used cooking oil in Asian countries. It is well known for the presence of phytochemicals and for its stability as frying oil. Gamma-oryzanol is the important phytochemical present only in RBO which exhibits antioxidant properties including free radical scavenging and lipoperoxidation prevention. It is also reported to be hypolipidemic[5].

MCT rich mustard oil has already been proved to contribute towards protection against different lifestyle diseases in our previous studies. The food intake, growth of animals and lipid content of mesentry showed that capric acid rich mustard oil has anti-obese properties in comparison to mustard oil. Mustard oil enriched with capric acid significantly lowered plasma and liver lipids which are high risk factors of cardiovascular diseases[6]. Consumption of capric acid rich mustard oil improves the haematological and histological conditions which were disturbed due to hypercholesterolemia[7]. It seems to produce an inhibitory effect on platelet aggregation thus reducing the chances of vascular diseases and finally atherosclerosis by reducing the interaction between platelets and vessel wall. In another study it was observed that the deformity and fragility of erythrocyte membrane caused

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by cholesterol rich blood was partially reversed by capric acid rich mustard oil by virtue of their ability to lower the extent of hypercholesterolemia[8]. It was also proposed that dietary supplementation with capric acid might benefit humans leading to improved antioxidant defenses in individuals with hypercholesterolemia and thereby lowering atherosclerosis risk[9].

The in vitro digestion of lipids and their associated health effects is the subject of extensive research[10]. The consumption of structured lipid containing MCFA has shown to offer various health benefits. The behavior of those structured lipids during digestion has been poorly studied. There is also insufficient data regarding the absorption study of structured lipid containing MCFA. In the present study we have utilized single-pass perfusion method in rat model to compare the intestinal absorption of RBO and MCFA rich RBOs. The study also encompasses the in vitro intestinal digestion study of MCFA rich RBOs in comparison to native RBO. The analysis of the physico-chemical properties of MCFA rich RBO is also under the scope of this study.

MATERIALS AND METHODS

Materials

Refined rice bran oil was procured from the market and the acid value was checked. Caprylic acid (C8:0), Capric acid (C10:0) and Lauric acid (C12:0) were obtained from Sigma Chemical Company, India. Lipase TLIM was a complimentary sample from Novozymes India Pvt. Ltd. All other reagents used were of analytical grade and procured from Merck India Ltd., Mumbai, India.

Methods

Preparation of Oils: The reaction between caprylic acid, capric acid and lauric acid with rice bran oil was carried out in a packed-bed bioreactor. The reactor consisted of a tubular glass column of 10 mm ID and was of 50 cm long. It was also provided with a water jacket for temperature control. The immobilised enzyme (*Rhizomucor mehei*) packed into the reactor was retained in place by means of a sintered plate. The substrates were fed from the top and the products were collected at the bottom. The substrates were previously blended and well mixed at the reaction temperature before conducting the packed-bed reaction and were poured into the enzyme bed, maintaining a fixed sample head. Water from a constant temperature bath was circulated through the jacket by a peristaltic pump. A partial suction was given to maintain the constant flow rate (0.4 mL/min; optimized in the previous study); 20 g of enzyme was closely packed into the column by repeated tapping to avoid any air gaps. Transesterification reactions were then carried out by passing the substrate through the column. The temperature was maintained at 60ºC by passing water through the column jacket. The product mixture was collected at the outlet, steam sripped and the fatty acid composition of the oils was determined by gas chromatography (GC).

*Chromatographic analysis of oils:*Fatty acid compositions of native and MCFA rich rice bran oil were analysed by GC. The oils were saponified with 0·5 M KOH and methylated with boron trifluoride in methanol. The gas chromatograph (Agilent 6890 N; J&W Scientific, Wilmington, DE, USA) was fitted with a DB-Wax capillary column (30m x 0·32mm x 0·25 mm) and a flame ionization detector. N2, H2 and airflow rate were maintained at 1, 30 and 300 ml/min, respectively. Inlet and detector temperatures were kept at 250ºC and the oven temperature was programmed to increase from 150 to 190°C at a rate of 15°C/min, then to hold for 5 min, and then to increase to 230°C at a rate of 48°C/min, and then again to hold for 10 min.

Physicochemical Property Analysis:

Saponification value (SV): It was determined using AOCS method[11]. 2.0 g oil samples were added with ethanolic potassium hydroxide 0.5N and boiled for 60 min in a reflux condenser. The mixtures were cooled and subsequently titrated with 0.5N hydrochloric acid until the colour of the mixtures changed from pink to the original colour.

Iodine value (IV): The determination of IV was carried according to AOCS method [12]. Samples were reacted with the Wij's solution and left in the dark for 1 h. Mixture was consequently titrated with sodium thiosulphate solution.

Viscosity: The viscosity of the formulations was determined using Brookfield DV III ultra V6.0 RV cone and plate rheometer (Brookfield Engineering Laboratories, Inc., Middleboro, MA) using spindle # CPE40 at 25 ± 0.5 °C. The software used for the calculations was Rheocalc V2.6[13].

Refractive Index: Refractive index was determined using an Abbes type refractometer (Nirmal International, New Delhi, India) at 25 ± 0.5 °C[14].

Slip Melting Point: Slip melting point was determined using slip melting apparatus by capillary tube method[15].

In vitro intestinal digestion study: The in vitro gastric digestion protocol simulated fasted-state conditions in humans with a pH between 1 and 3[16]. First, 10 mL of simulated gastric fluid (SGF) (per liter, 2 g of NaCl and 7 mL of HCl at pH 1.226) was mixed with 20 mL of milk, which was then acidified to pH 1.5 with 6 M HCl and incubated at 37°C for 10 min in a shaking water

bath at 95 revolutions/min. Then, pepsin was added at the physiologically relevant substrate/enzyme ratio (w/w) of 20:1, and the temperature and pH were kept constant for 1 h. Samples were collected periodically for further characterization.

The simulated intestinal fluid (SIF) (per liter, 6.8 g of K_2HPO_4 and 190 mL of 0.2 M NaOH at pH 7.527) contained 150 mM NaCl to simulate the in vivo intestinal ionic strength and bile extract (5mg/mL). No calcium was added because bile extract may already contain physiological concentrations of calcium[17]. Experimental oils were subjected to gastric digestion for 1 h, as described above. Then, thein vitro intestinal digestion carried out by mixing the experimental oils with SIF (1:3, v/v) to a total of 30 mL in a conical flask. The pH was adjusted to 7, and the mixture was placed in a shaking water bath (95 revolutions/min) at 37 °C. Pancreatin (1.6 mg/mL) was added to the mixture; the pH was maintained at 7 with 1 M NaOH; and samples were taken periodically over 2 h for characterization. The activity of pancreatic lipase was measured over 2 h using a pH stat titration method (TitraLab 856, Radiometer Analytical, Villeurbanne, France) with 0.05 M NaOH and an end point of pH 7.0. The total free fatty acids released were back-titrated at different time points of intestinal digestion, as described in literature [18].

In vivo absorption study rats: In the present study, we have used the single pass perfusion method in rat model [19]. Experiments were carried out under the supervision of Animal Ethical Committee of the department of Chemical Technology, University of Calcutta. Male Sprague-Dawley rats (150-250 g) were acclimatized for a week in laboratory condition, gave diet food and water ad libidum. Each animals were fasted overnight and then anesthetized with intra-muscular injectrion of Ketajet 50 @ 35mg/kg body weight and intra-peritoneal injection of Xylocaine 2% @ 5mg/kg body weight. The peritoneal cavity was then opened by a midline incision. The small intestine was cannulated proximally (just downstream to the pyloric sphinter) and distally (about 5mm upstream to the illeo-caecal junction) so that the perfusate (emulsion in this case) entering the small intestine, traversed through it and finally left through the distal cannula, provided with a stoppered cap. The cannula was tied in place with a loop of silk suture placed tightly about the intestine at its both end. A similar tie-up has been given on gastric end of oesophagus to prevent any accidental backflow of the perfusate though the nasopharyngeal channel and subsequent choking of the respiratory system. The cannulated intestine is arranged in the peritoneal cavity so that it was not kinked or twisted. The cannulated intestine is kept covered throughout the experimental time-period with a cotton cloth soaked in phosphate buffer saline (PBS) to prevent drying. Firstly the intestine is flushed with the perfusate until the outflow fluid became clear and clean. Now a fixed volume (6ml) of the experimental oils is flown into the cannulated small intestine and after a stipulated time period of residence there (different time intervals in between 0 and 30 min) the outflow-fluid is collected for subsequent analysis. The difference of volume between the perfusate-oil and the outflow-oil was taken as the 'absorbed volume'.

Total lipid content from the experimental from the experimental oils was determined using standard method[20]. The difference between the lipid content of initial oil and outflow oil was taken as 'absorbed lipids'.

Statistical Analysis: All the data are presented as means with their standard errors. Statistical comparisons between groups were performed using one way ANOVA.

RESULTS AND DISCUSSION

Changes in fatty acid composition: Analysis of the MCFA rich RBO showed that caprylic acid rich RBO contained 14.00% caprylic acid (C8), capric acid rich RBO contained 13.43% capric acid (C10) and lauric acid rich RBO contained 13.11% lauric acid (C12). The fatty acid compositions of the MCFA rich RBOs, are given in Table 1.

TABLE 1

Fatty Acid Composition of Native Rice Bran Oil and Medium Chain Fatty Acid Rich Rice Bran Oils

Fatty acid Sample	Fatty Acid (% w/w)								
	$C_{8:0}$	$C_{10:0}$	$C_{12:0}$	$C_{14:0}$	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$
Rice Bran Oil	-	-	-	0.28	17.10	1.90	48.27	31.35	1.1
Caprylic acid rich RBO	**14.00**	-	-	0.29	13.77	1.90	40.76	28.28	1.0
Capric acid rich RBO	-	**13.43**	-	0.27	10.44	1.89	43.39	29.58	1.0
Lauric acid rich RBO	-	-	**13.11**	0.27	10.56	1.88	45.29	27.89	1.0

Changes in saponification value (SV): The SV of all experimental oils showed values ranging from 191-206. The highest SV was from C8 rich RBO and the lowest was recorded in RBO (Fig 1). The SV basically refers to the mean molecular mass of the fats and oils and have an inverse relationship with the chain length of the fatty acid present in the fats and oil. This means, longer the average fatty acid chain length, the smaller the SV. Thus in this case as the chain length of fatty acids present in RBO was long it had lowest SV. Similarly since caprylic acid rich RBO had the lowest chain length, it had the highest SV.

Changes in Iodine Value: The iodine value performed on the experimental oils is shown in Fig 2. The range of IV of all samples was between 86-99. The lowest IV was obtained in case of MCFA rich RBO and highest in case of RBO.

The low IV in case of medium chain fatty acid rich RBO was low owing to the high degree of saturation. This highlights the low likeliness of MCFA rich RBO to become rancid from lipid oxidation[21]. The IV would have effects on the overall quality of the MCFA rich RBO such as shelf life of the oils, appearance as well as taste and smell.

Changes in viscosity: The viscosity of RBO is shown to portray lowest viscosity as depicted in Fig 3. In comparison to RBO MCFA rich RBO showed higher viscosity. Among the three MCFA rich RBOs lauric acid rich RBO showed the highest viscosity and caprylic acid rich RBO showed the lowest viscosity.

Changes in slip melting point: From Fig 4 it was evident that RBO had highest slip melting point in comparison to MCFA rich RBO. This was due to the higher unsaturation of RBO than MCFA rich RBO. Among the three MCFA rich RBOs lauric acid rich RBO had the highest slip melting point due to the longer chain length of lauric acid in comparison to caprylic acid.

Changes in refractive index: Refractive index is a very important physical property of fats and fatty acids as it is a unique method for their identification. Refractive index of fats and fatty acids depends on the chain length and unsaturation. With increase in chain length and double bonds, refractive index increases. RBO showed the highest refractive index and caprylic acid rich RBO the lowest (Table 2).

Free fatty acid release after in vitro intestinal digestion: The release of total free fatty acids is depicted in Fig 5. From the curve it was evident that the rate of lipolysis was fastest in caprylic acid rich RBO and slowest in case of RBO. This was due to the presence of higher amounts of long chain fatty acids in RBO in comparison to MCFA rich RBO. The rate of lipolysis was high in MCFA rich RBO for the first 30 min and then slowed down. On the other hand the rate of lipolysis in case of RBO was gradually increasing till 90

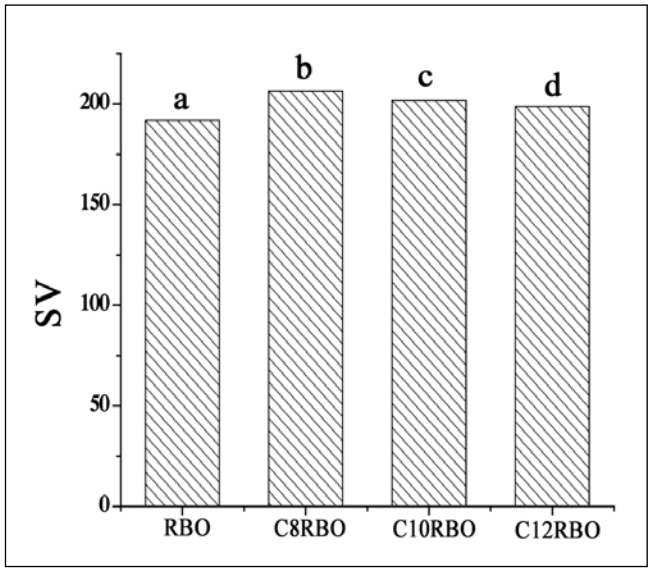

Fig. 1 : Changes in saponification value of the oil samples (RBO-Rice bran oil; C8RBO- caprylic acid rich rice bran oil; C10RBO-capric acid rich rice bran oil; C12RBO-lauric acid rich rice bran oil) Values are Mean±S.D Values not sharing common superscript are significantly different (p<0.05)

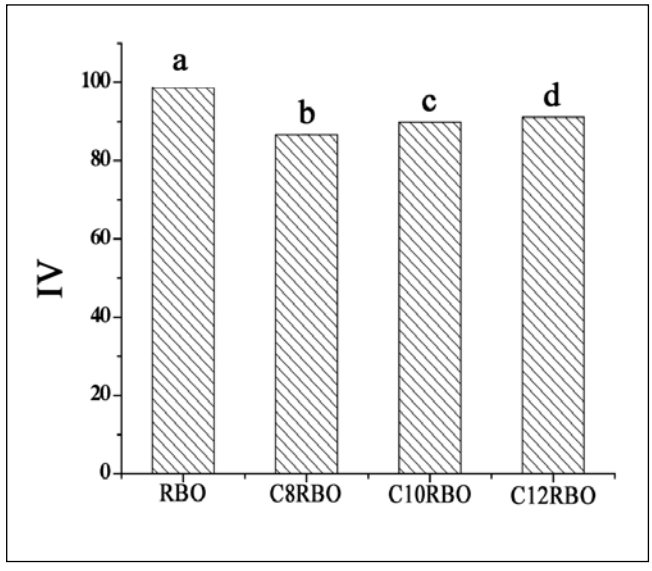

Fig. 2 : Changes in iodine value of the oil samples (RBO-Rice bran oil; C8RBO-caprylic acid rich rice bran oil; C10RBO-capric acid rich rice bran oil; C12RBO-lauric acid rich rice bran oil) Values are Mean±S.D Values not sharing common superscript are significantly different (p<0.05)

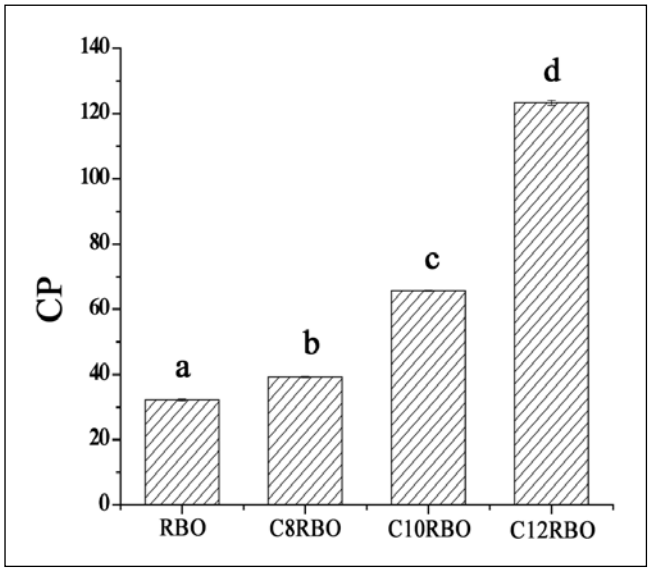

Fig.3 : Changes in viscosity in oil samples at 20ºC (RBO-Rice bran oil; C8RBO-caprylic acid rich rice bran oil; C10RBO- capric acid rich rice bran oil; C12RBO-lauric acid rich rice bran oil) Values are Mean±S.D Values not sharing common superscript are significantly different (p<0.05)

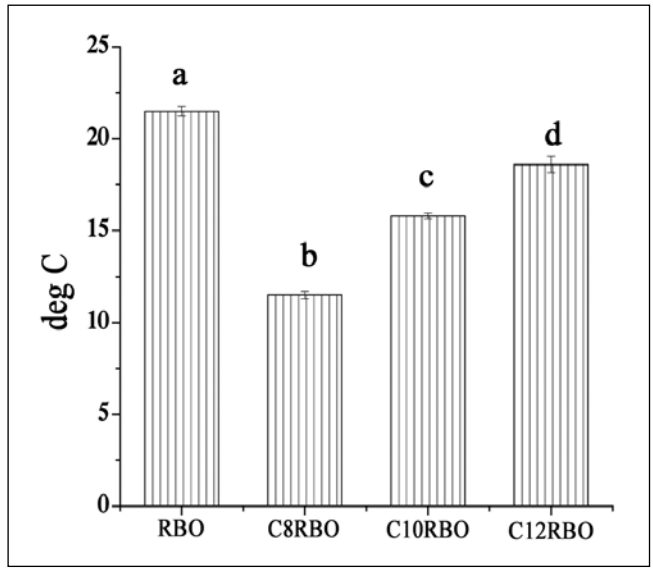

Fig. 4 : Changes in slip melting point in oil samples (RBO-Rice bran oil; C8RBO-caprylic acid rich rice bran oil; C10RBO-capric acid rich rice bran oil; C12RBO-lauric acid rich rice bran oil) Values are Mean±S.D Values not sharing common superscript are significantly different (p<0.05)

TABLE 2

Change in Refractive Indices of Oil Samples

Oil Samples	Refractive index
RBO	1.469±0.01[a]
Caprylic acid rich RBO	1.450±0.01[b]
Capric acid rich RBO	1.460±0.02[c]
Lauric acid rich RBO	1.463±0.02[d]

Values are Mean±S.D Values not sharing common superscript are significantly different (p<0.05)

min and then slowed down. The lipolytic products are further solubilized into phospholipid vesicles and mixed phospholipid-bile salt micelles[21]. No lag phase was observed in the titration curve of the release of titrable free fatty acids, suggesting that pancreatic lipase was rapidly adsorbed and activated at the surface of experimental oils. The rate of lipolysis slowed down progressively after sometime indicating that the free fatty acids were almost released by that time. MCFA rich RBOs were mostly lipolized by gastric lipase.

Changes in in vivo intestinal lipid absorption in rats: The results of in vivo absorption study based on intestinal perfusion model are depicted in Fig 6. RBO and all three MCFA rich RBOs were passed through the intestinal perfusion model and the gastrointestinal absorption was measured thereby. The absorption study was conducted for 2h. The sample was collected at every half an hour interval. The rate of absorption of MCFA rich RBOs was much faster than native RBO. Caprylic acid rich RBO was absorbed at a fastest rate. Fatty acid chain length affects aqueous solubility and also appears to have an important influence on the molecular mechanisms that govern uptake of these molecules. Importantly, MCFAs with 6–12 carbon atoms, have increased water solubility, and this means that they have measurable absorption via the paracellular route. A consequence of this is that such MCFAs appear to bypass the intracellular processing events that are encountered by the long chain fatty acids that predominantly enter the enterocyte cytosol. As a result, such fatty acids also follow a different route out of the gut, being exported chiefly via the portal circulation rather than the lymphatic route used

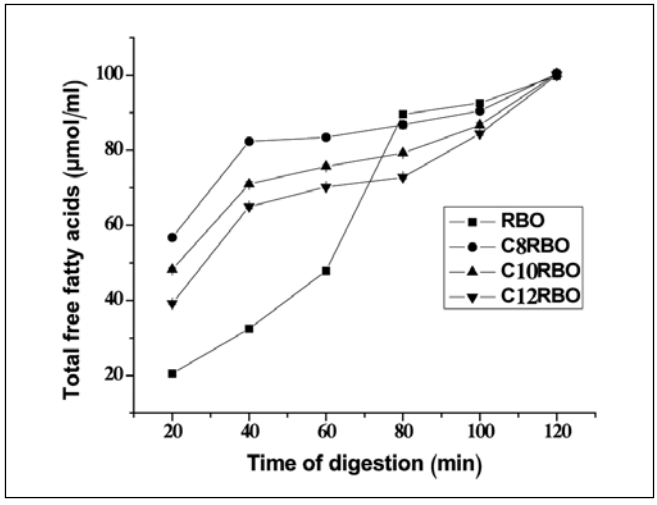

Fig. 5 : Total free fatty acid release from gastric digested oil samples during 120 min of intestinal digestion and measured after back titration (RBO-Rice bran oil; C8RBO-caprylic acid rich rice bran oil; C10RBO-capric acid rich rice bran oil; C12RBO-lauric acid rich rice bran oil) Values are Mean±S.D.

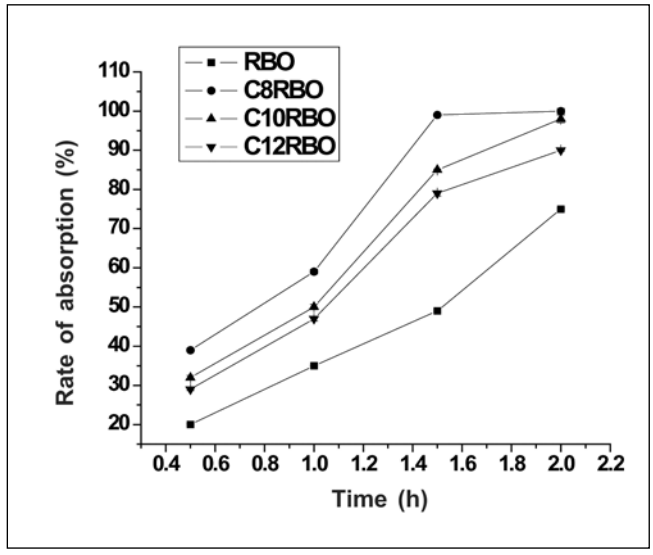

Fig. 6 : Rate of absorption of oil samples during 2 hr of intestinal absorption (RBO-Rice bran oil; C8RBO-caprylic acid rich rice bran oil; C10RBO-capric acid rich rice bran oil; C12RBO-lauric acid rich rice bran oil) Values are Mean±S.D.

by other lipids. The long chain fats, by contrast, are quite insoluble in water, the release of bile salts are required to emulsify these fats, allowing pancreatic lipase enzymes to start to break them down. The resulting micelles can diffuse across the brush border membrane of the gut and into the enterocytes. Once there, the long-chain fatty acids are re-esterified back into their triglyceride form, pumped toward the lymph system, the thoracic duct, and eventually the bloodstream via the water-soluble lipoproteins.

CONCLUSION

Rice Bran Oil is an unique oil which is well known for its oryzanol content which renders it high antioxidative property. Modification of RBO to MCFA rich RBO increased the digestion and absorption property of RBO due to the replacement of long chain fatty acid with medium chain fatty acid. Thus better absorption of RBO offers better availability of RBO to provide its antioxidative property. Among the three MCFA rich RBO, caprylic acid rich RBO has better ameliorative property.

ACKNOWLEDGEMENT

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REFERENCES

1. Seaton TB, SL Welle, MK Wareko, *et al.* **Amer. J. Clin. Nutr., 36,** 43 (1986).
2. Kaunitz H, **Coconuts Today** 18 (2001).
3. Babayan VK, **J. Amer. Oil Chem. Soc., 58,** 49A (1981).
4. Bell SJ, EA Mascioli, BR Bistrian, *et al.* **J. Amer. Dietary Association, 91,** 74 (1991).
5. Akiyama Y, K Hori, T Takahashi, Y Yoshiki, **Food Sci. Technol. Res. 11,** 295 (2005).
6. Sengupta A and M Ghosh, **Nutrition, 27**, 1183 (2011).
7. Sengupta A and M Ghosh, **Lipids, 45**, 393 (2010).
8. Sengupta A and M Ghosh, **Eur. J. Nutr., 50(6)**, 411 (2011).
9. Sengupta A and M Ghosh, **Br. J. Nutr., 107**, 845 (2012).
10. Armand M, **Curr. Opin. Clin. Nutr. Metab. Care**, **10**, 156 (2007).
11. AOCS **Cd 3-25,** Official Methods and Recommended Practices of the American Oil Chemists' Society (4th Edn), AOCS, Champaign, Illinois (1990).

12. AOCS **Cd 1-25,** Official Methods and Recommended Practices of the American Oil Chemists' Society (4th Edn), AOCS, Champaign, Illinois (1990).

13. Chong JS, EB Christiansen, AD Baer, **J. Applied Polymer Sci., 15,** 2007 (1971).

14. AOCS **Cc 7-25**, Official Methods and Recommended Practices of the American Oil Chemists' Society (4th Edn), AOCS, Champaign, Illinois (1990).

15. AOCS **Cc 1-25,** Official Methods and Recommended Practices of the American Oil Chemists' Society (4th Edn), AOCS, Champaign, Illinois (1990).

16. Kalantzi L, K Goumas, V Kalioras, B Abrahamsson, JB Dressman, C Reppas, **Pharm. Res., 23,** 165 (2006).

17. Tiss A, S Ransac, H Lengsfeld, P Hadvary, A Cagna, R Verger, **Chem. Phys. Lipids, 111,** 73 (2001).

18. Gallier S and H Singh, **Food Funct. 3**, 547 (2012).

19. Tarr BD and SH Yalkowsky, **Pharmaceutical Res., 6,** 40 (1989).

20. Folch J, I Ascoli, M Lees, JA Meath, N LeBaron, **J. Biol. Chem., 191,** 833 (1951).

21. Onyeike EN and GN Acheru, **Food Chem., 77**, 431 (2002).

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Low Temperature Synthesis of Fatty Acid Amide (Erucamide) Using Micro-emulsion

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ABSTRACT

A new method for synthesis of fatty acid amide using water-in-oil micro-emulsion was studied. This process is economical and it shortens the reaction time. It involves use of urea at atmospheric pressure in the presence of micro-emulsion in place of conventional processing using ammonia at high pressure and high temperature, for synthesis of fatty acid amides that results in poor colour of the product. At the same time formation of by-products is also there due to processing at high temperature. In the present study, the stable micro-emulsion was prepared by optimization of the conditions which were obtained using 46 % (w/w) of iso-amyl alcohol, 40 % (w/w) of soy bean oil, 7 % (w/w) of surfactant (sodium lauryl sulphate), and 7 % (w/w) of water. The reaction conditions were optimized and it was observed that the use of erucic acid and urea in molar ratio of 1:4, reaction time of 240 min, and temperature of 115°C with 20 ml micro-emulsion was found to be optimum. The process gives good yield comparable to any other commercial method with lighter colour erucamide in less reaction time with least amount of by-products.

KEYWORDS: micro-emulsion, erucamide, urea, sodium lauryl sulphate, soybean oil

INTRODUCTION

Fatty acid amides are produced in thousands of metric tons a year from the fatty acids by reaction with anhydrous ammonia at 200^{0}C and pressure of 345 – 690 kPa[1]. They are primarily used for their lubricating and surfactant properties. The market for refined fatty acid amides is dominated by the unsaturated fatty amides as oleamide (cis- 9-octadcenamide) and erucamide (cis-13-docosenamide) which are used as lubricants in plastic industry and printing ink industry.[1-3]

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Erucamide (CAS No.:112-84-5; $C_{22}H_{43}$ NO; M.W: 338), is one of the most important derivative of erucic acid. Erucamide is a plastic additive used as a slip agent, and anti block agent for the production of low linear density polyethylene films, moulded plastic, and polyvinyl chloride resins. Addition of 0.02 - 0.05% of erucamide reduces friction from 4.55 to 1.11 for the polypropylene films. Erucamide has a high melting point and good stability at higher temperature in comparison to other amides[2]. Therefore, it has advantages over oleamide and stearamide. The mono unsaturated oleamide is a good slip agent but a poor anti block agent whereas the saturated stearamide is a good anti block agent but a poor slip agent. Erucamide bridges the gap between the two providing good performance in both the areas. It is also used in high grade lube oils dye dispersants, water-proofing and antifogging agent for paper making, textile industries foam stabilizer, metal-wire drawing lubricating agent etc. Erucamide has low vapour pressure and is less volatile making it suitable for higher temperature processing. In addition, erucamide is less prone to thermal oxidation during processing and contributes less colour (yellowing) and odor to the final product[4]. It is also used in printing ink and dyes as a dispersing agent and to improve lubrication and helps in making high speed printing inks, magnetic ink, typing ribbons, carbon papers, and metal decoration[2].

Conventionally erucamide is produced by the reaction of erucic acid and ammonia at 200^{0}C and 345 – 690 kPa pressure. Use of urea in synthesis of erucamide has also been studied using chemical methods, enzymatic method and microwave synthesis[3-5]. Apart from that kinetic study of synthesis of fatty amide (erucamide) has also been studied[6]. In the present study, it was thought prudent to carry out the reaction in emulsion phase using micro-emulsion as it provides much large surface area for reaction to carry out. At the same time, it also helps in carrying out the reaction at lower temperature with the use of urea at atmospheric pressure instead of high temperature and high pressure used in conventional

synthesis This new method resulted in low reaction temperature and providing lighter coloured product with lower by-product formation.

MATERIALS AND METHODS

Materials

Refined soybean oil was purchased from the local market (Fortune brand) produced by M/s Adani Wilmar Ltd., India . This soybean oil was characterized and specifications are shown in Table 1. Sodium Lauryl Sulphate (L.R. grade) used as a surfactant was procured from M/s Thomas Baker (chemical) Pvt Ltd, India. Iso Amyl Alcohol (99 % pure) L. R. grade, used as a co-surfactant was procured from M/s Rankem, India. Double distilled water was used for this study wherever it was required.

Erucic Acid was received as a complimentary sample from M/s V.V.F. Ltd., Mumbai, India. The Erucic acid was characterized for saponification value, acid value and iodine value as per AOCS Methods and results are depicted in Table 1. Urea (L.R. grade) procured from RFC Ltd., India was used for the amidation of erurcic acid. Melting point of urea was determined and characterstics are given in Table 1. Di-ammonium hydrogen phosphate (L.R. grade, Anhydrous Purified) was procured from M/s C.D.H Ltd, Mumbai, India. It was used as catalyst. Other chemicals like petroleum ether (60-80°C), methanol (95%), sulphuric acid (98%) carbon tetra chloride (99%) chloroform (99.5%) of LR grade were procured from RFC Ltd, and were used for the study.

TABLE 1

Analysis of Raw Materials

Raw Material	Analytical Composition	
Erucic Acid	Acid Value Sap Value Iodine Value Melting Point	163.51 163.80 73.76 35.50°C
Urea	Melting Point	132.50°C
Soybean oil (refined)	Acid Value Sap Value Iodine Value	0.30 187.39 136.13

Methods

Acid Value, Saponification Value, Iodine Value were determined as per AOCS Standard Methods[10].

FTIR spectroscopic analysis

Fourier-transform infra-red (FTIR) is very useful instrument to determine the molecular structure of the material. FTIR spectra of the prepared samples were recorded on a Perkin-Elmer (Model Spectrum BX) infra-red spectrophotometer, using KBr pellets, in the wave length range of 400–4000 cm^{-1}.

^{1}H NMR spectroscopic analysis

Nuclear Magnetic Resonance (NMR) Spectroscopy is a technique which exploits the magnetic properties of a nucleus. ^{1}H-NMR spectra of the prepared samples were recorded on Bruker DRX 300 NMR spectrophotometer in $CDCl_3$. All $CDCl_3$ spectra were referenced to tetramethylsilane (TMS).

^{13}C NMR spectroscopic analysis

Carbon (^{13}C) NMR spectra were obtained in the same manner as the proton NMR spectra, however resonance frequency for ^{13}C NMR was 100 MHz. All chemical shifts (peaks) were referenced to tetramethyl silane (TMS).

GC-MS spectroscopic analysis

The Gas Chromatography/Mass Spectrometry (GC-MS) instrument separates chemical mixtures (the GC component) and identifies the components at a molecular level (the MS component). GC-MS of the prepared samples were recorded on HP 5988A GC-MS system using source temperature 230°C using concentration of 100 μg/mL and DB 17-HT Column (30m x 0.25mm x.15 μm). It was interfaced with a 5890A gas chromatograph (GC), and had the capabilities of separating volatile mixtures as well as mass analysis of low molecular weight, volatile, non-ionic and thermally stable components.

Preparation of microemulsion

Micro- emulsions (water in oil) were prepared in a beaker in which water and surfactant (SLS) were added using high speed shear mixer. Microemulsions were prepared by thoroughly mixing surfactant (SLS) with a co-surfactant (iso amyl alcohol) and water. The (refined soybean oil) was progressively added to the mixture in steps of 10% increase in the mixture, covering an oil composition range from 10 to 90%. The mixture was stirred for one hour and the oil addition was performed within 5 min intervals. The Microemulsion prepared was containing 40% oil, 46% iso amyl alcohol, 7% surfactants and 7% water. This emulsion was observed to be thermodynamically stable.

Synthesis of erucamide

For the synthesis of erucamide, a 500ml three necked round bottom flask was taken whose centre neck was equipped with stirrer with the help of a stuffing box. One side of the neck was equipped

with thermometer. The other side was kept open for evolution of ammonia and carbon dioxide gases produced in the reaction. The assembly was fitted in a thermostatically controlled oil bath for heating. Initially, known quantity of erucic acid, microemulsion, solvent medium and di-ammonium hydrogen phosphate were taken in the three necked flask and the mixture was heated with the help of oil bath. The molar ratio, temperature, and percentage of catalyst were varied in different sets of experiments. The contents of the flask were continuously stirred by mechanical stirrer and the reaction temperature was maintained.

As the reaction proceeded, the sample was drawn periodically for determination of acid value. The progress of the reaction was confirmed by determining the drop in acid value of the product due to conversion of fatty acid in to its amide. Thereafter, amide content and yield was also determined. The product was finally extracted with petroleum ether as a solvent followed by extraction with carbon tetra chloride and chloroform in the ratio of 3:1. The mixture was separated by gravity. The upper layer contained erucamide in solvent. The solvent was evaporated and the synthesized erucamide was recovered.

RESULTS AND DISCUSSION

Effect of molar ratio of erucic acid and urea on synthesis of erucamide without micro-emulsion and catalyst

For preparation of erucamide, the reaction was performed by varying molar ratio of erucic acid to urea from 1:1 to 1:5 at 70°C temperature and at atmospheric pressure. The drop in acid value at different time interval for various sets of experiments having different molar ratios of erucic acid to urea are depicted in Table 2. It is evident from the Table 2 that reduction in acid values of reaction mixture at 30 min reaction time was from163.32 to 157.12 with respect to molar ratio 1:1 to 1:5 respectively. In 60 min reaction time, reduction in acid value was from 163.13 to 155.49 with respect to molar ratio 1:1 to1:5 respectively. In 90 min reaction time, reduction in acid value was from 162.21 to 154.77 with respect to molar ratio 1:1 to 1:5 respectively. In 120 min reaction time, drop in acid value of reaction mixture was from 162.09 to 153.76 with respect to molar ratio 1:1 to 1:5 respectively. In 150 min reaction time, reduction in acid value was from 162.02 to 152.75 with respect to molar ratio 1:1to 1:5 respectively. In 180 min reaction time, drop in acid value was from 162.01 to 152.15 whereas in 210 min reaction time, drop in acid value was from 161.24 to 150.11. In 240 min reaction time, drop in acid value was found to be from 161.18 to 149.04 with respect to same molar ratio.

From these observations, it is clear that at a molar ratio of 1: 4 for erucic acid to urea, the drop in FFA was maximum and it was almost same as that at 1:5 molar ratio. Therefore, molar ratio of erucic acid to urea of 1:4 was considered to be optimum.

Effect of micro-emulsion addition on synthesis of erucamide

It was observed that the rate of drop in acid value in absence of micro-emulsion was very slow even at 70°C. However, it improved drastically in presence of micro-emulsion. Amounts of micro-emulsion (water in soybean oil) were varied keeping fixed molar ratio (1:4) of erucic acid to urea at 70°C. The results of addition of 5 ml, 10 ml, 15 ml, 20 ml, and 25 ml microemulsion in the reaction mixture are reported in Table 3. It was observed that increasing the amount

Table 2
Effect of Molar Ratio on Reduction in Acid Value of Product at Constant Temperature 70°C with 30 ml Solvent Medium without Catalyst and Microemulsion

Time in minute	Acid value with different molar ratio (erucic acid : urea)				
	1 : 1	***1 : 2***	***1 : 3***	***1 : 4***	***1 : 5***
0	163.51	163.51	163.51	163.51	163.51
30	163.32	163.14	161.89	157.37	157.12
60	163.13	160.62	158.87	155.55	155.49
90	162.21	158.72	155.67	154.92	154.77
120	162.09	157.65	153.55	153.76	153.76
150	162.02	155.89	152.98	153.05	152.75
180	162.01	155.70	151.56	152.65	152.15
210	161.24	156.56	150.32	150.20	150.11
240	161.18	156.11	149.56	149.12	149.04

of micro-emulsion in the reaction mixture resulted a higher decrease in the acid value. On addition of 5 ml microemulsion, the maximum drop in acid value was observed to be 95.65 with 240 min reaction time. On addition of 10 ml microemulsion the maximum drop in acid value was observed to be 91.56 with 240 minute reaction time; on addition of 15 ml microemulsion, the maximum drop in acid value was observed to be 86.91 with 240 min reaction time and similarly on addition of 20 ml microemulsion, the maximum drop in acid value was observed to be 77.15 with 240 min reaction time. The acid value was reduced upto 76.96 with 240 minute reaction time with addition of 25 ml of microemulsion and it was almost similar to that of addition of 20 ml of microemulsion. The decrease in acid value at different time intervals for the 20 ml and 25 ml microemulsion (Table 3) were also observed to be almost same.

The results indicate that the presence of microemulsion in the reaction mixture increases the rate of synthesis up to usage of 20 ml microemulsion and beyond 20 ml usage the rate almost becomes independent to quantity of micro-emulsion. Therefore, for the synthesis of erucamide from erucic acid and urea, the optimum condition of micro-emulsion has been considered to be 20 ml.

Effect of catalyst on synthesis of erucamide

The effect of catalyst (di- ammonium-hydrogen-orthophosphate) on the rate of synthesis of erucamide has been studied at different proportions of catalyst concentration i.e.,1%, 2%, 3%, and 4% keeping the other optimized conditions the same (erucic acid: urea ratio 1 : 4, microemulsion 20 ml, temp at 70°C at atmospheric pressure). The results are depicted in Table 4 and the results clearly indicate that on

Table 3

Effect of Mircoemulsion Addition on Reduction in Acid Value of Product at Constant Temperature 70°C and Molar Ratio 1:4 with 30 ml Solvent Medium and Without Any Catalyst

Time in minute	Acid value with microemulsion addition in various amounts				
	5 ml	***10 ml***	***15 ml***	***20 ml***	***25 ml***
0	163.51	163.51	163.51	163.51	163.51
30	109.63	105.97	102.93	99.71	99.52
60	104.93	101.97	97.89	93.96	92.86
90	101.89	98.21	93.16	89.09	88.07
120	99.04	95.86	90.37	86.09	85.84
150	97.89	93.89	88.19	83.87	83.55
180	96.82	92.45	87.91	80.92	80.84
210	95.94	91.87	87.16	77.63	77.12
240	95.65	91.56	86.91	77.15	76.96

Table 4

Effect of Catalyst Concentration in Reduction of Acid Value of Product at Constant Temperature 70°C with 30 ml solvent Medium and 20 ml Microemulsion

Time in Minute	Acid value with varying catalyst concentration			
	1 %	**2 %**	**3 %**	**4 %**
0	163.51	163.51	163.51	163.51
30	75.14	61.36	55.82	54.97
60	73.81	54.78	52.92	51.87
90	72.75	50.22	48.13	47.16
120	72.03	47.83	44.38	44.11
150	70.77	44.19	40.91	41.28
180	69.4	41.13	37.67	39.39
210	68.69	39.23	35.21	35.08
240	69.56	38.89	34.89	34.62

addition of 1% catalyst, drop in the acid value was low, however, on increasing in catalyst percentage, the drop in acid value was higher.

The maximum drop in acid value was observed to be 34.89 at 70° C temperatures with 30 ml solvent medium and 20 ml micro- emulsion. The results of drop in acid value were almost same in presence of 3% and 4% catalyst, therefore, 3% catalyst was considered to be optimum.

Effect of temperature on synthesis of erucamide

The reaction was performed at varying reaction temperature from 75° C to 125° C ± 2° C at atmospheric pressure and the yields of erucamide were determined by estimating unreacted fatty acid remaining in the reaction product. From Table 5 it is clear that the drop in acid value at temperatures of 75 to 125°C was 34.89 to 13.55 respectively, after 240 min at atmospheric pressure. The results clearly indicate that with increasing reaction temperature, the yield of erucamide continuously increased, but the boiling point of solvent medium (iso amyl alcohol) being only 128° C, therefore, further experiments were not carried out beyond 125° C. The optimum result was obtained at 115° C with 30 ml solvent medium, 20 ml micro-emulsion and 3% catalyst concentration. The maximum drop in acid value was observed to be 13.77.

Effect of reaction time on synthesis of erucamide

The reaction is performed at different time intervals from 30 min., to 270 min. From Table 6, it is clear that drop in acid value at different time intervals of 30, 60, 90, 120, 150, 180, 210, 240 and 270 min were 31.98, 27.66, 23.51, 21.01, 17.63, 15.56, 14.19, 13.77 and 13. 49 respectively at 115° C and atmospheric pressure with 20 ml microemulsion and 3 % catalyst concentration. As the reaction time increased, decreased in acid value was observed to be continuous as shown in the Table 6. However, maximum drop in acid value (13.49) was observed at 270 min but difference in drop in acid value between

Table 5

Effect of Temperature Variation on Reduction of Acid Value of Product with 30 ml Solvent Medium, 20 ml Mircoemulsion and 3% Catalyst Concentration

Time in minute	Acid value of the product with increasing temperature (°C)					
	75	85	95	105	115	125
0	163.51	163.51	163.51	163.51	163.51	163.51
30	55.82	52.38	41.19	34.56	31.98	31.455
60	52.92	48.62	35.79	30.04	27.66	27.63
90	48.13	44.35	31.24	27.39	23.51	23.34
120	44.38	41.27	28.58	24.81	21.01	21.23
150	40.91	38.88	25.11	21.17	17.63	16.87
180	37.67	36.24	23.68	19.77	15.56	15.27
210	35.21	34.93	22.14	18.59	14.19	14.17
240	34.89	34.41	21.56	18.12	13.77	13.55

Table 6

Effect of Time Intervals at 115°C, Atmospheric Pressure with 20 ml Microemulsion, Solvent Medium and 3% Catalyst

Time in minute	Acid value	Yield (%)
30	31.98	52
60	27.66	56
90	23.51	62
120	21.01	66
150	17.63	75
180	15.56	84
210	14.19	89
240	13.77	92
270	13.49	92.15

240 min and at 270 min was only 0.28. Hence 240 min reaction time was considered to be optimum under the reaction condition.

1 : 4 molar ratio of erucic acid to urea has been observed to be optimum as at this molar ratio the maximum drop in acid value was obtained. There was no drop in acid value below this ratio and above this also there was no significant drop in acid value. 20 ml micro-emulsion resulted in maximum conversion of acid to amide, 240 min time was considered to be optimum as conversion at this time was maximum. 115° C temperature gave maximum drop in acid value with good quality product. The yield of erucamide at optimised conditions was 92 %.The colour of erucamide synthesized with micro-emulsion at 115° C was 4.0 unit at gardner scale which was near to standard colour (3.0 unit).

Identification of erucamide by ^{1}H NMR spectrum

The ^{1}H NMR Spectrum of erucamide is shown in Fig. 1. It is clear from the figure that there is a broad triplet appeared at 0.86 ppm which might correspond to the methyl group protons. Appearance of multiplet at 1.28 ppm corresponds to the protons due to methylene group. A multiplet at 5.27 ppm and singlet in the region of 5.61-6.14 ppm, might be assigned to presence of protons attached to the –CH=CH– and $CONH_2$ group, respectively. A triplet at 2.25 ppm might be due to the protons of $–CH_2CONH_2$ group.

Identification of erucamide by ^{13}C NMR Spectrum

The ^{13}C NMR spectrum of erucamide confirmed the presence of –*C*=O at C_1 176.1 ppm; two olefinic carbons –*C*H=*C*H– at 129.7 ppm for C_{13} and C_{14}; 18 $–CH_2–$, ranging from 22.2 to 38.9 ppm ($C_{2–12, 15-21}$); and one $–CH_3$ at 13.8 ppm for C_{22}. The double bond might be of *cis* configuration as ^{13}C NMR showed chemical shift at 27.6 ppm (Fig. 2).

Identification of erucamide by GC-MS

GC-MS of erucamide indentified ionized atoms or molecules based on their mass-to-charge ratios (m/z). The molecular ion at m/z 337, 320, 184, 71, 69, 60 and 54 shows the fragmented ions $C_{22}H_{43}NO$, $C_{22}H_{40}O$, $(CH_2)_9CONH_2$, $(CH_2)_4CH_3$, $(CH_2)_4CH$, CH_2CONH_2 and $(CH_2)_2CH=CH$, respectively as shown in Fig. 3.

Identification of erucamide by FTIR spectrum

The identification of erucamide was confirmed by the presence of characteristic band combination of $–NH_2$, -C=O, $-CH_2$, -C=C groups in IR spectra. A band corresponding to C=C appear at 1648cm^{-1}. A broad band near 3312, 2841 and 1695 cm^{-1} showed the presence of $–NH_2$ group, methyl group and C=O linkages in the product. The IR spectra of prepared sample were also matched with standard spectra of erucamide as shown in Fig. 4.

Mechanism of reaction

Urea is weak base and in presence of acid forms cation by accepting proton from acid. The resonance stabilization of the cations is also reported. It is also reported that one of the amide nitrogen of urea is protonated by acid. On the basis of above facts and experimental results, the mechanism of synthesis of erucamide using fatty acid and urea is proposed as Scheme1.

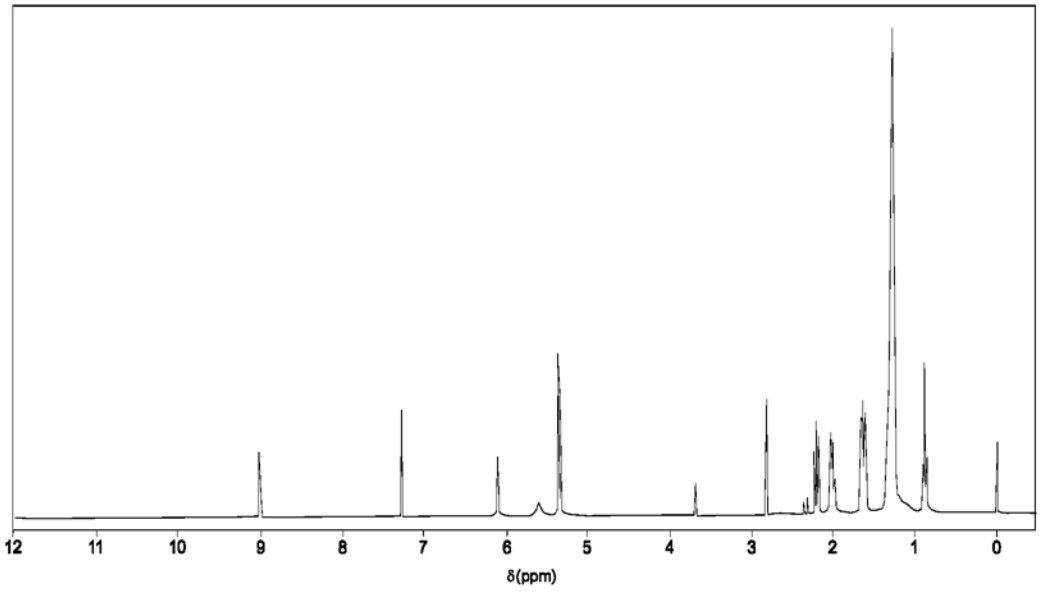


Fig. 1 : ^{1}H NMR Spectrum of Erucamide

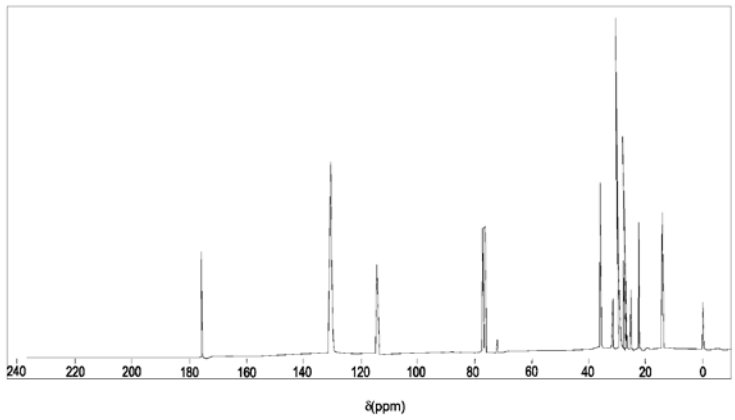


Fig. 2 ^{13}C NMR Spectrum of Erucamide

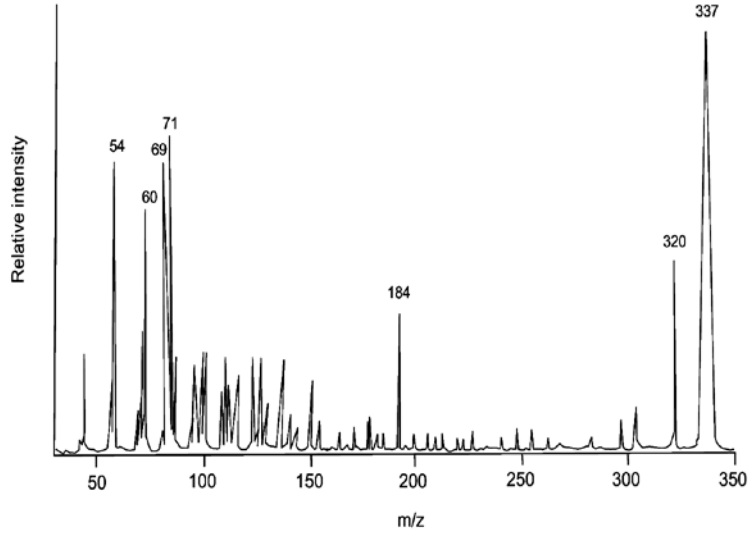


Fig. 3 GC-MS of Erucamide

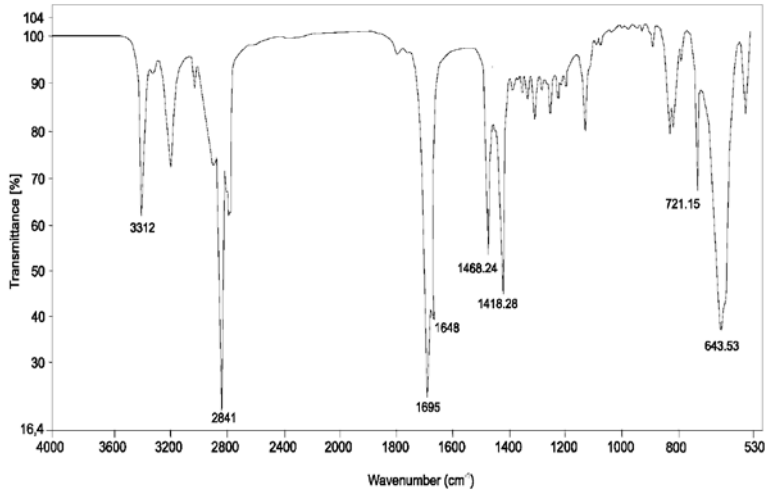
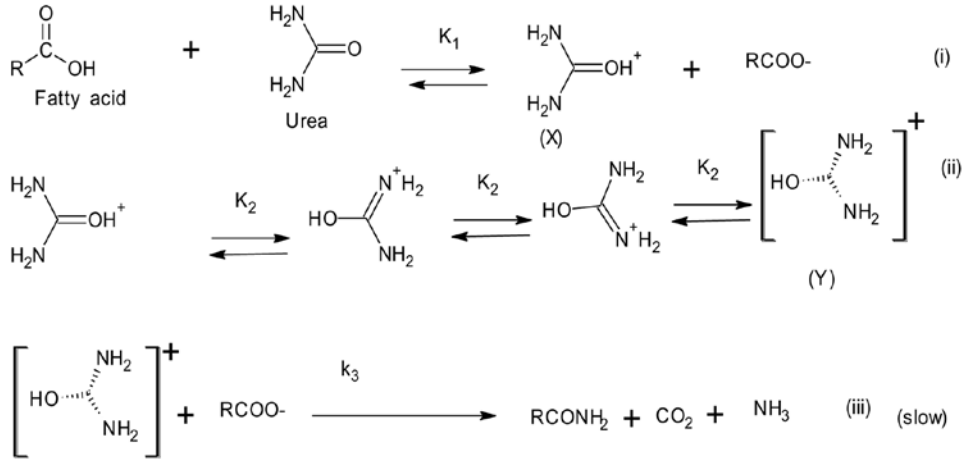


Fig. 4 FTIR Spectrum of Erucamide

Scheme1



Where R represents [- $(CH_2)_{11}$ CH= CH $(CH_2)_7$ CH_3]

Reaction

$$RCOOH\ (338) + NH_2CONH_2\ (60) \xrightarrow[(NH_4)_2HPO_4]{\text{Micro-emulsion}} R\,CONH_2\ (337) + NH_3\ (17) + CO_2\ (44)$$

Fatty acid Urea Fatty amide

CONCLUSION

In this study, a new method for preparation of erucamide is reported by the reaction of erucic acid and urea at 115°C at atmospheric pressure using (w/o) microemulsion. The reaction parametres were optimized and the erucamide produced was characterized. 1 : 4 molar ratio of erucic acid to urea, 240 min of reaction time using 3% diammonium hydrogen orthophosphate catalyst gave a very light colored (4'0 units Gardner scale) erucamide. The production cost is expected to be much lower compared to the conventional methods and the process is less polluting. This process has ample scope for commercial exploitation.

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REFERRENCES

1. Molnar, N M, **J. Amer. Oil Chem. Soc.**, **6**, 82 (1974).
2. De Zoete, M C, A C Kock-Van Dalen, F Van Rant Wijk, R A Sheldon, **J. Mol. Catal. B; Enzymatic, 3**, 141 **(**1996).
3. Awasthi N P, R P Singh, V Tripathi, **Brassica**, **8**, 1 (2007).
4. Awasthi N P, R P Singh, **J. Oleo Sci.**, **56,** 507 (2007).
5. Awasthi, N P, R P Singh, **Eur. J. Lipid Sci. Technol., 111,** 202 (2009).
6. Awasthi, N P, S K Upadhayay, R P Singh, **J. Oleo Sci.**, **57 (9),** 471 (2008).
7. Garrido, I Q, J M Barrrales-Rienda, J M Perena, **Polymer 20**, 5125-5135 (1997).
8. Hardwood, H.J., **J. Amer. Oil Chem. Soc., 11**, 559 (1954).
9. Markley, K.S, Simple Amides, Fatty Acids, **Int. Pub. Inc. New York**, pp 1579-1580 (1960).
10. Official and Tentative Methods of **Amarican Oil Chemists' Society (Link, W.E. ed.). 3rd edn. Am. Oil Chem. Soc., Champaign, Illions (1974).**

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Valorization of Glycerol to Cyclic Acetals Employing Heterogeneous Carbon Acid Catalyst Derived from Glycerol

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ABSTRACT

Glycerol-based SO_3H functionalized carbon catalyst was employed for conversion of glycerol to cyclic acetals with acetone and benzaldehyde for the preparation of isopropylidine glycerol (IPG) and benzylidine glycerol in high yields and selectivity. All the acetalization reactions were carried out at 80°C using 5 wt% of the catalyst to obtain excellent conversions (>99%) and selectivity towards 1,2-IPG (98%) and 1,2-benzylidine glycerol (92%) demonstrating the potential of SO_3H-carbon as a highly active, stable, water resistant and reusable heterogeneous solid acid catalyst. The same catalyst was also used for the deprotection of IPG and benzylidine glycerol in methanol at reflux temperature in 3 h. The catalytic activity of the solid acid catalyst was compared with p-TSA along with reusability studies. This methodology is highly advantageous to solve the problem of an over production of glycerol, which is a major co-product of the bio-carburant industry.

KEYWORDS: Glycerol, SO_3H functionalized carbon catalyst, solketal, benzylidine glycerol

INTRODUCTION

Glycerol, a renewable resource obtained from propylene oxide[1], microbial fermentation[2], hydrolysis of fats into fattyacids[3] and more recently, in huge amounts from the biodiesel industry[3,4] has great industrial importance due to the conversion to a variety of value-added products. Due to this surplus production of glycerol, as a by-product its utilization in different routes is a pressing need[5,6] and currently attracts the increasing interest for valorization[7-9]. In the last few years, the valorization of glycerol and its by-products is a major interest in the chemical industry for the preparation of a variety of compounds via etherification[10], oxidation[11], esterification, transesterification[12] and polymerisation[13] etc. Alternatively glycerol was also used for selective transformations by protecting the two hydroxyl groups as acetals and ketals and reacting the third group for desired reactions (e.g. oxidation or hydrogenation) and subsequent deprotection to the target product. Glycerol protected as cyclic acetals/ketals were employed as additives[14], bases[15] and in food and cosmetic industries as scents or flavours[16]. These protected glycerols are one of the important structural units for the synthesis of value added compounds (analogues) with biological applications which can be synthesized in a number of ways by selective hydroxylation using methods like enzymatic[17], solid acid[18] or base catalysts[19] and also spontaneously at higher temperatures. The cyclic acetals/ketals are also the potential intermediates for the different transformations in fine chemistry. These are to be used as a precursor for the development of new synthons in organic chemistry[20], for the production of 1,2/1,3 alkyl ethers[21], glycerol esters[20], monoglycerides[22], monoalkyl glycerols[23] and were also used for the synthesis of a variety of products in carbohydrate chemistry, dendrimer chemistry and hyper branched polymers[24].

The preparation of acetals/ketals of glycerol in the literature was reported by different catalysts. Glycerol protection as acetals/ketals which can be promoted by conventional acid catalysts[25-27] like H_2SO_4, HCl, HF, p-TSA. However, these catalysts suffer from lack of selectivity and are not eco-friendly due to formation of inorganic salts. To avoid this, researchers reported solid acids[28] like supported heteropolyacids, Amberlysts[29], promoted Zirconia[30], as well as zeolites[31] to catalyze acetalization with appreciable results in both catalytic activity and selectivity. However, ion exchange resigns (Amberlyst) and heteropoly acids exhibited the drawbacks such as poor thermal stability, solubility in polar media, poor regeneration ability and having low specific surface area. Zeolites and other catalysts are not affordable for industrial applications. Later, after the discovery of green chemical technologies, researchers used benign, novel and recyclable heterogeneous solid acid catalysts like Al-SBA-15[32], Ni(1.8)/MWCNTs[33], $[Cp^*IrCl_2]_2$[34], SnO2, MoO_3/SnO_2 and WO_3/SnO_2[35] for the protection of glycerol. The condensation of glycerol with benzaldehyde (1:1) in the presence of Al-SBA-15 (7 mol of acid groups per mmol of glycerol) showed,

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the conversion rate is 72% with selectivity of 83:17 (5-membered:6-membered), whereas the condensation with acetone, conversion rate was 6% with selectivity of 99:1 (5-membered:6-membered) in 8 h at 100 °C. In case of Ni(1.8)/MWCNT, the conversion rate is 96% with selectivity 72:28 in 3 h with 1:6 mole ratio of glycerol:acetone at 40°C. Glycerol acetalization with benzaldehyde was also studied using $[Cp^*IrCl_2]_2$ at 40°C and observed 55% conversion in 1 h with 79% selectivity for 5-membered compound. However, the reaction did not significantly proceed after 3 h. While the glycerol condensation with acetone over SnO_2, MoO_3/SnO_2 and WO_3/SnO_2 catalysts the conversion rate is 15, 55 and 61%, respectively with a 96% selectivity of solketal in 90 min. With further increase in reaction time, only a slight enhancement in the conversion of glycerol was noted. However, some of these catalysts are costly, slightly difficult to prepare and the conversion rate and selectivity is also low.

Recently, a stable, water-tolerant, inexpensive and reusable carbon-based solid acid catalyst was developed by this laboratory with excellent esterification activity from bioglycerol (biodiesel by-product), glycerol pitch (waste from fat splitting industry) and commercial glycerol by involving *in situ* partial carbonization and sulfonation in a single pot.[36] This carbon catalyst has showed excellent catalytic properties by demonstrating its effectiveness for different transformations[37-46] due to its high thermal stability, recyclability and strong acid sites of sulfonic acid functional groups. In continuation of our ongoing research towards exploring the applications of the carbon acid catalyst having 1.6 mmol/g acid density with surface area of 0.21 m^2/g[43], we present here a novel, simple and highly efficient green approach for the valorization of glycerol to isopropylidine and benzylidine glycerol.

MATERIALS AND METHODS

Materials

Glycerol, Acetone (AR grade), CH_3OH, Benzaldehyde, p-TSA and Na_2CO_3 were purchased from Sd. Fine chemicals (Mumbai, India), were used as it is without further purification. All reactions were performed using a magnetic stirrer. The compounds prepared were identified by thin-layered chromatography (TLC) which was performed on pre-coated silica gel 60 F procured from Merck (Darmstadt, Germany). ^{1}H NMR spectra were recorded in $CDCl_3$ using Bruker spectrometer (Avance 300 MHz, Bruker, Switzerland), with TMS as an internal standard. FT-IR spectra were recorded on a Perkin Elmer FT-IR spectrometer (Spectrum BX; Connecticut, USA). Mass spectra were recorded on Agilent GC 6890 (Agilent technologies, Palo Alto, USA) coupled with 5973N MSD instrument in the EI mode and are given in mass units (m/z). GC spectra were recorded on a capillary GC column HP-1 (30 m x 0.32 mm x 0.10 µm) mounted in a gas chromatograph GC 6850 system (Agilent technologies, Palo Alto, USA). The analysis of the products was performed in a temperature-programmed mode of 80 °C (0 min)- 10 °C/ min- 300 °C (5 min).

Catalyst preparation

A mixture of glycerol (10 g) and concentrated sulfuric acid (30 g) were taken in a 500 ml glass beaker and gently heated on hotplate from ambient temperature to 220 °C to facilitate *in situ* partial carbonization and sulfonation. The contents of the reaction were allowed at that temperature for about 20 min till the foaming was ceased. The resultant black crystalline product was cooled to ambient temperature and washed with hot water under agitation till the wash water becomes neutral. The product was filtered and dried in the oven for 2 h at 120 °C in order to ensure free of moisture to obtain glycerol based carbon acid catalyst (4.52 g).

Reaction procedure

Glycerol was used for the preparation of solketal and benzylidine glycerol by using the following methodologies:

Valorization of glycerol for the preparation of cyclic acetals (IPG and benzylidine glycerol)

Glycerol-based solid acid catalyst was employed for the preparation of IPG and benzylidine glycerol by condensing glycerol with acetone (as a reactant and solvent) or benzaldehyde (in toluene solvent) respectively at moderate temperature in excellent yield and the products were characterized by ^{1}H NMR, GC and GC-MS.

Synthesis of (2,2-Dimethyl-[1,3]dioxolan-4-yl)-methanol (2, IPG) or Solketal: To a mixture of acetone (120 mL) and glycerol (92 g, 1 mol), carbon acid catalyst (4.6 g, 5 wt% of glycerol) was added and the contents were stirred at reflux temperature over a period of 6 h. After cooling to room temperature, catalyst was filtered and the crude product obtained after complete removal of excess acetone was subjected to vacuum distillation (110-120 °C, 10 mm Hg) to get pure IPG as a colorless syrupy liquid (118 g, 98% purity by GC) in 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.29 (s, 3H),1.32 (s, 3H), 3.71-3.77 (2H), 3.9-4.0 (2H), 4.2 (1H, m); IR (neat): 3417, 2987, 2937, 2887, 2361, 1648, 1377, 1215, 1156, 1050, 844 cm^{-1}; EI-MS *m*/*z*: 117 [M^+ - 15].

Synthesis of (2-phenyl-1,3-dioxolan-4-yl)methanol (3, Benzylidine glycerol): To a mixture of glycerol (5

g, 0.054 mol) and benzaldehyde (5.7 g, 0.054 mol) in toluene (20 mL), glycerol based carbon acid catalyst (0.25 g, 5 wt% catalyst) was added and the contents were allowed to stir at 80 ºC by conventional method. The progress of the reaction was monitored by TLC and GC. At the end of 6 h reaction time, maximum amount of toluene was distilled out and the crude product was purified by silica gel column chromatography (60-120 mesh) using different proportions of hexane and ethyl acetate. The un-reacted benzaldehyde was recovered by running with hexane: ethyl acetate in the ratio of 97: 3 followed by 85: 15 hexane and ethyl acetate system for the separation of benzylidine glycerols as pale yellow colored liquid (9.3 g, 92% purity by GC) in 96.5% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 3.4-4.3 (m, 5H), 5.34-5.92 (s, 1H), 7.3-7.5 (m, 5H); IR (neat): 3414, 3038, 2864, 1454, 1393, 1219, 1149, 1084, 995, 918, 756, 699 cm^{-1}; EI-MS *m*/*z*: 180 $[M]^+$.

Analysis of the reaction products

The reaction product samples were qualitatively analyzed using gas chromatography (GC). Reaction sample (100 µl) was diluted in $CHCl_3$:MeOH (1:1, 2 ml) and 1 µl of the liquid was injected into a capillary non-polar GC column HP-1 (30 m x 0.32 mm x 0.10 µm) mounted in a gas chromatograph GC 6850 system (Agilent Technologies, USA). The analysis was performed in a temperature-programmed mode of 80 °C (2 min) 10 °C/min300 °C (10 min). EI-Mass spectra were recorded on Agilent GC 6890 coupled with 5973N MSD instrument performed in a temperature-programmed mode of 80 °C (2 min) 10 °C/min300 °C (10 min).

RESULTS AND DISCUSSION

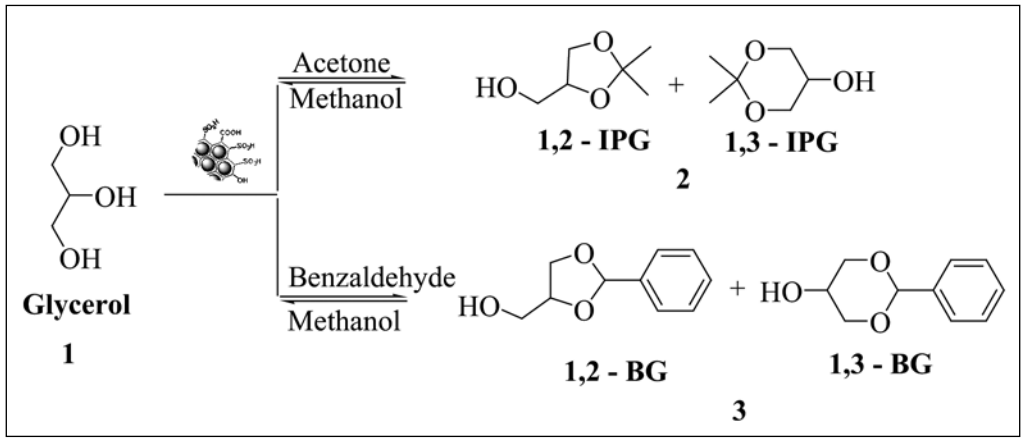
SO_3H-Carbon catalyst derived from glycerol was employed for the selective preparation of 1,2-IPG and 1,2-benzylidine glycerol in quantitative yields under mild reaction conditions (Scheme 1). In case of IPG, condensation of glycerol with acetone as ketal (2), at reflux temperature in presence of carbon acid catalyst (5 wt%) resulted 1,2-IPG as major isomer along with 1,3-IPG in 98:2 (5-membered:6-membered) ratio.

The formation of IPG isomers can be identified by the presence of two peaks (a, b) in GC (Fig 1) and can be further confirmed by mass spectral fragmentation in GC-MS (Fig 2). The mass spectral fragmentation peak at m/z 101 in Figure 2a is due to $[M^+ - CH_2OH]$ and this fragmentation is possible only for 1,2-isomer due to the presence of 1° hydroxyl group, whereas this peak is not observed in 1,3-isomer due to the absence of $-CH_2OH$ group indicating that Figure 2a is for 1,2-isomer and Figure 2b is for 1,3-isomer. The ^{1}H-NMR spectrum of IPG (Fig 3) shows peaks at 1.29-1.32 ppm for dimethyl groups, 3.71-4.0 ppm for glycerol backbone protons and at 4.2 ppm for 2° carbon. The IR spectrum of IPG shows characteristic stretching peaks for –OH at 3417 cm^{-1} and C-O-C at 1050-1150 cm^{-1}.

Similarly, during the condensation of glycerol with benzaldehyde as acetal (3), protection of the primary and secondary hydroxyl groups of glycerol with benzaldehyde was observed as shown in Scheme 1 with the formation of 1,2- and 1,3-benzylidine glycerol isomers in 92:8 ratio (i.e. 59:33 with total selectivity of 92% for 5-membered and 8% for 6-membered ring). Both the GC and GC-MS chromatogram (Fig 4 and 5) of benzylidine glycerol acetal showed 3 peaks (a, b and c) related to two diastereoisomers of 1,2-isomer (5-membered ring, a and b peaks) and 1,3-isomer (6-membered ring, c peak) of benzylidine glycerol. The formation of these isomers was confirmed by mass spectral fragmentation as shown in Fig 5. The presence of m/z 149 in Fig 5a and 5b is due to $[M^+ - CH_2OH]$, indicating that these fragmentations are

Scheme 1

Acetalization of Glycerol to Cyclic Acetals Employing SO_3H-Carbon Catalyst



possible in the diastereoisomers of 1,2-isomer having 1° hydroxy group, whereas this peak is not observed in Figure 5c due to the absence of (-CH_2OH) group specifies the fragmentation for 1,3-isomer. IR spectrum of benzylidine glycerol shows characteristic stretching peaks for –OH at 3414 cm^{-1}, aromatic –CH at 3038, 2864 cm^{-1} and C-O-C at 1050-1150 cm^{-1}. ^{1}H-NMR spectrum of benzylidine glycerol (Fig 6), shows peaks at 3.4-4.3 ppm for glycerol backbone protons and at 7.3-7.5 ppm for aromatic protons. The presence of isomers (1,2 diastereoisomers and 1,3-isomers) is further confirmed by the presence of four peaks in ^{1}H-NMR for -OCH(C_6H_5) in the region between 5.34-5.92 ppm (for two C-5 isomers at 5.78 and 5.92 and for C-6 isomers at 5.34 and 5.51 ppm). All the chemical shifts were found to be in agreement with the literature values[25,32]. Even though, the separation of mixtures of compounds 2 and 3 is somewhat difficult, the percentage of formation of these isomers (1,2 or 1,3) can be identified and quantified by GC and GC-MS chromatograms.

The catalytic activity and selectivity of the carbon acid catalyst for the preparation of benzylidine glycerol was compared with p-TSA under similar reaction conditions. Condensation of glycerol with benzaldehyde was carried out in presence of p-TSA (5 wt%) as catalyst at reflux temperature using Dean-stark apparatus for the removal of water as azeotropic mixture and the results are given in Table 1. The data indicate that, the SO_3H-carbon catalyst exhibited high selectivity towards the formation of 1,2-benzylidine glycerol (92%) when compared to p-TSA catalysed reaction which resulted only 62% of 1,2-isomer along with 33% of by-products. In addition, the SO_3H-carbon catalysed methodology has an added advantage of devoid of neutralization, water removal and without the formation of by-products.

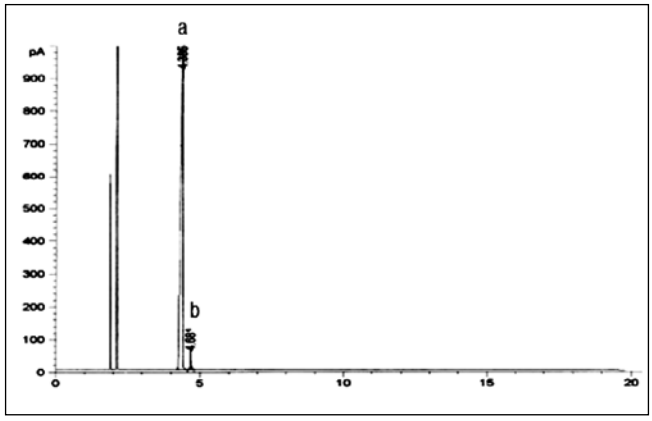


Fig. 1: Gas Chromatogram of Compound 2.

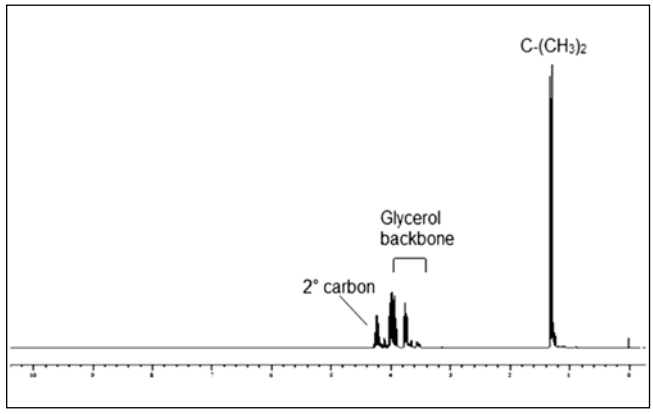


Fig. 3: ^{1}H-NMR Spectrum of Compound 2.

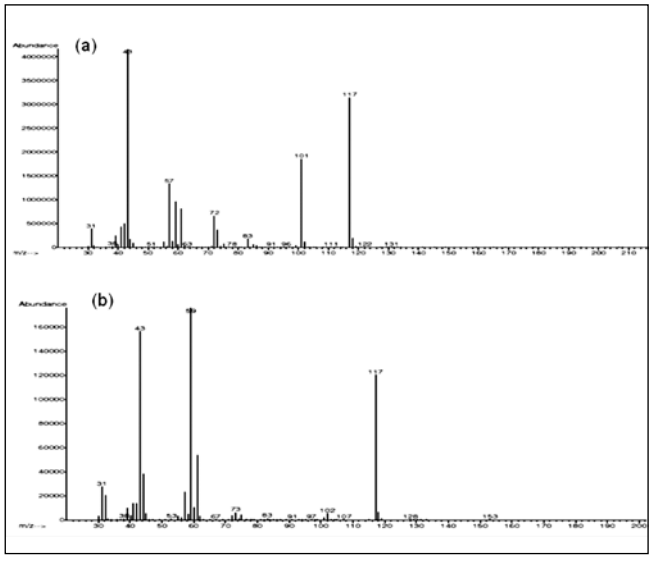


Fig. 2: GC-MS Spectrum of Compound 2 (a) 1,2- IPG, (b) 1,3- IPG.

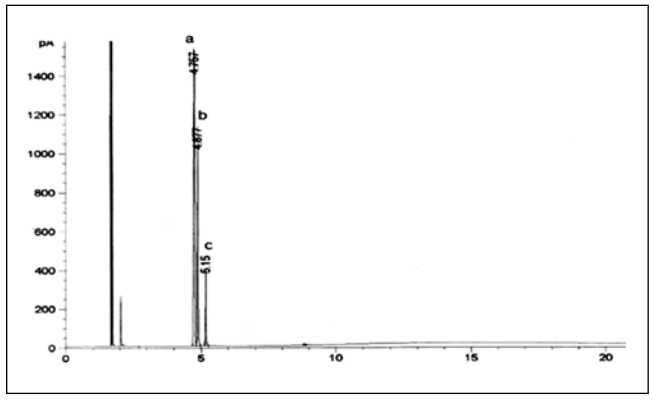


Fig. 4: Gas Chromatogram of Compound 3.

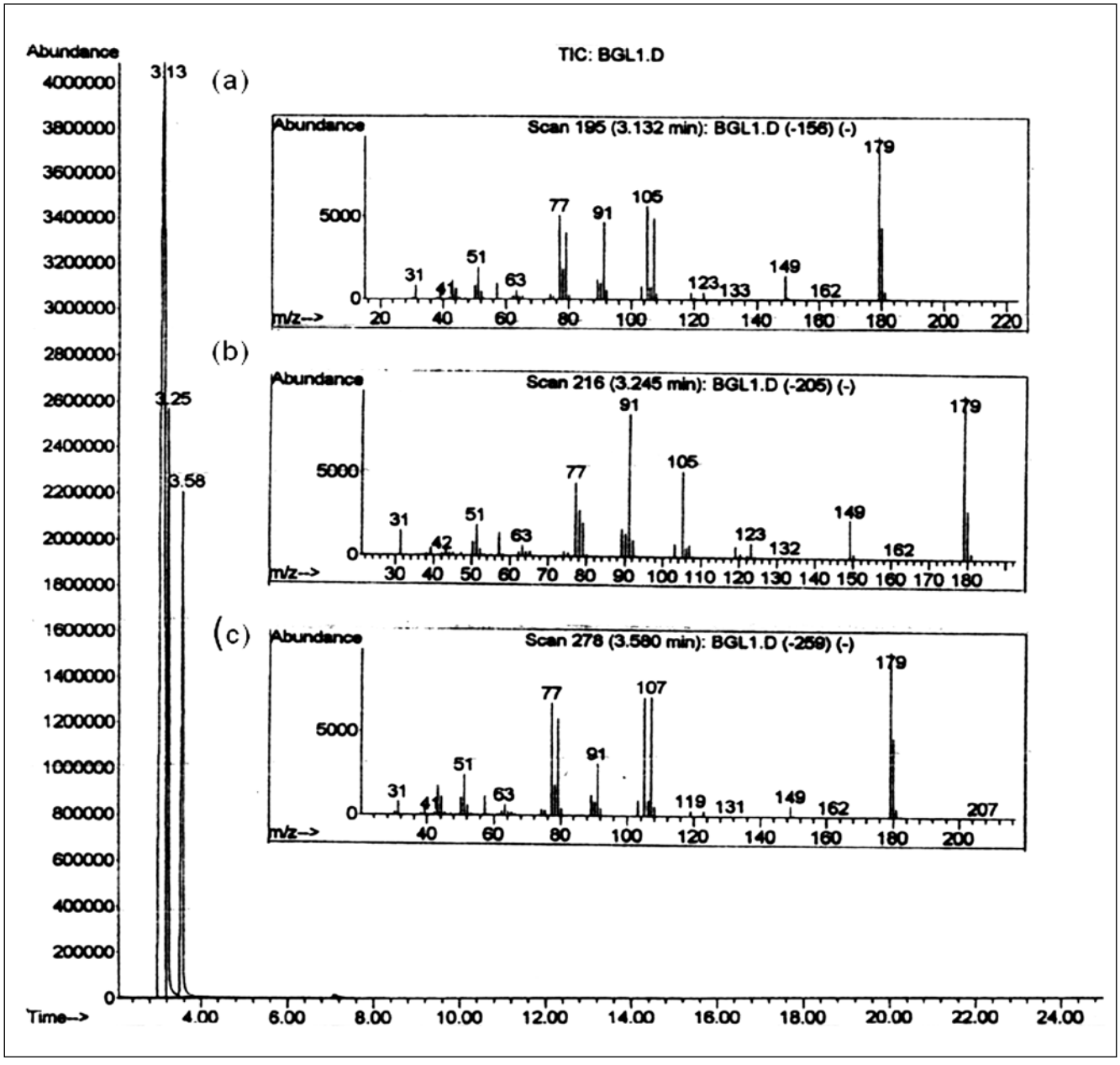


Fig. 5: GC-MS Spectrum of Compound 3 (a & b) 1,2- BG, (c) 1,3- BG.

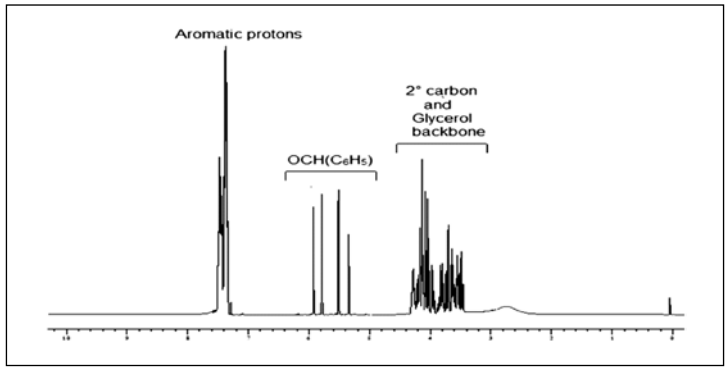


Fig. 6: ^{1}H-NMR Spectrum of Compound 3.

Table 1
Quantification of Benzylidine Glycerol Isomers (wt%) by GC

Catalyst	1,2-isomer	1,3-isomer	By-products
SO_3H-carbon	92	8	-
p-TSA	62	5	33

The SO_3H-carbon catalyst (5 wt%) was also found to be active for the deprotection of solketal and benzylidine glycerol in the presence of methanol at reflux temperature for 3 h. The catalyst used for the reaction is easily recoverable and recyclable for 4-5 cycles. The recyclability experiments (Fig 7) of the catalyst were conducted by condensation of glycerol (1 mmol) with benzaldehyde (1 mmol) at 80 °C in toluene as a test reaction. After completion of each cycle the catalyst from the reaction mixture was recovered by filtration, washed with methanol and then reused after drying in oven for 1 h at 110 °C. The catalyst shows excellent reusability without any significant loss in the activity and also reduction in the conversion rate of glycerol due to its high stability without any leaching and deactivation under the reaction conditions. Thus this methodology is very useful for the preparation of glycerol protected compounds (2 and 3) and also deprotection of these compounds to glycerol.

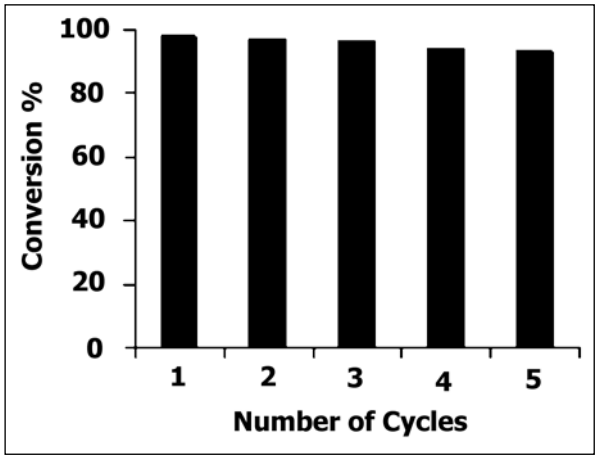


Fig. 7: Recyclability Study of Catalyst

CONCLUSIONS

The carbon acid catalyst derived from glycerol was demonstrated for its excellent catalytic activity for the acetalization of glycerol to cyclic acetals with acetone and benzaldehyde under mild reaction conditions. The catalyst exhibited high selectivity towards 1,2-IPG (98%) and 1,2-benzylidine glycerol (92%) with complete conversion of glycerol at 80 °C in 6 h. The catalyst recovery is simple and can be recycled for 5 times without any significant loss of activity, leaching and deactivation under the reaction conditions. The simplicity of the methodology and the catalyst recovery and reusability make this protocol potentially accessible for industrial applications with high selectivity and conversion rate for acid catalysed glycerol transformations to cyclic acetals.

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REFERENCES

1. Zhou C H C, J N Beltramini, Y X Fan, G Q M Lu, **Chem. Soc. Rev., 37,** 527 (2008).
2. Wang Z Z J, J Zhuge, H Fang, B A Prior, **Biotechnol. Adv., 19,** 201 (2001).
3. McCoy M, **Chem. Engg. News, 84,** 43 (2006).
4. Jerome F, Y Pouilloux, J Barrault, **ChemSusChem, 1,** 586 (2008).
5. Clark J H, V Budarin, F E I Deswarte, J J E Hardy, F M Kerton, A J Hunt, R Luque, D J Macquarrie, K Milkowski, A Rodriguez, O Samuel, S J Tavener, R J White, A J Wilson, **Green Chem., 8,** 853 (2006).
6. Pagliaro M, R Ciriminna, H Kimura, M Rossi, C D Pina, **Angew. Chem., Int. Ed., 46**, 2 (2007).
7. Papanikolaou S, **Aggelis, G. (Ed), Nova Science Publishers Inc.,** (2009) pp 137.
8. Meesters P A E P, G N M Huijberts, G Eggink, **Appl. Microbiol. Biotechnol., 45,** 575 (1996).
9. Papanikolaou S, S Fakas, M Fick, I Chevalot, M Gliotou Panayotou, M Komaitis, I Marc, G Aggelis, **Biomass Bioen., 32,** 60 (2008).
10. Ruppert A M, J D Meeldijk, B W M Kuipers, B H.Erné, B M Weckhuysen, **Chem. Eur. J., 14,** 2016 (2008).
11. Prati L, P Spontoni, A Gaiassi, **Top. Catal., 52,** 288 (2009).
12. Corma A, S B Abd Hamid, S Iborra, A Veity, **J. Catal., 234,** 340 (2005).
13. Clacens J M, Y Pouilloux, J Barrault, **App. Catal. A: Gen., 227,** 181 (2002).
14. Paille F, **Fr. Pat. 2 833 607 A1** (2003).

15. Piasecki A, A Sokolowski, B Burczyk, U Kotlewska, **J. Am. Oil Chem. Soc., 74**, 33 (1997).

16. Climent M J, A Veltry, A Corma, **Green Chem., 4**, 565 (2002).

17. Holmberg K, Osterberg E, **J. Am. Oil Chem. Soc., 65,** 1544 (1988).

18. Machado M S, J P Pariente, E Sastre, D Cardoso, A M Guereñu, **App. Catal. A: Gen., 203,** 3218 (2000).

19. Pouilloux Y, Métayer S, Barrault J, **Surface Chemistry and Catal., 3,** 589 (2000).

20. Villeneuve P, T A Foglia, T J Mangos, A Nuñez, **J. Am. Oil Chem. Soc., 75** (1998).

21. Damico R, R C Callahan, F H Mattson, **J. Lipid Res., 8,** 63 (1967).

22. Hess R, U Bomscheuer, A Capewell, T Scheper, **Enzyme. Microb. Technol., 17,** 725 (1995).

23. Se´bastien Q, B Pierre, T Didier, K Werner, A Jean-Marie, **Green Chem., 8,** 822 (2006).

24. Parzuchowski P G, M Grabowska, M Tryznowski, G Rokicki, **Macromol., 39 (21),** 7181 (2006).

25. Deutsch J, A Martin, H Lieske, **J. Catal., 245**, 428 (2007)

26. Ferreira P, I M Fonseca, A M Ramos, J Vital, J E Castanheiro, **Appl. Catal. B., 98,** 94 (2010).

27. Da Silva C X A, V L C Goncalves, C J A Mota, **Green Chem., 11**, 38 (2009).

28. Umbarkar S B, T V Kotbagi, A V Biradar, R Pasricha, J Chanale, M K Dongare, A S Mamede, C Lancelot, E Payen, **J. Mol. Catal. A: Chem., 310**, 150 (2009).

29. Ruiz V R, A Velty, L L Santos, A Leyva-Pe´rez, M J Sabater, S Iborra, A Corma, **J. Catal., 271,** 351 (2010).

30. Camino G A, P R Leticia, L Rafael, **Catal. Sci. Technol.**, **4**, 2287 (2014).

31. Li L, T I Koranyi, B F Sels, P P Pescarmona, **Green Chem., 14,** 1611 (2012).

32. Camino G A, A D A Rick, L Rafael, **Green Chem., 16,** 4985 (2014).

33. Khayoon M S, A Abbas, B H Hameed, S Triwahyono, A A Jalil, A T Harris, A I Minett, **Catal Lett., 144,** 1009 (2014).

34. Corrado C, F Erica, G Nicol Guidolin, **Green Chem., 12,** 2225 (2010).

35. Mallesham B, P Sudarsanam, G Raju, B M Reddy, **Green Chem., 15,** 478 (2013).

36. Prabhavathi Devi B L A, K N Gangadhar, P S Sai Prasad, B Jagannadh, R B N Prasad, **ChemSusChem., 2,** 617 (2009).

37. Prabhavathi Devi B L A, K N Gangadhar, K L N Siva Kumar, K Shiva Shanker, R B N Prasad, P S Sai Prasad, **J. Mol. Catal A: Chem., 345,** 96 (2011).

38. Ramesh K, S N Murthy, K Karnakar, Y V D Nageswar, K Vijayalakhsmi, B L A P Devi, R B N Prasad, **Tetrahedron Lett., 53,** 1126 (2012).

39. Karnakar K, S N Murthy, K Ramesh, Y V D Nageswar, T V K Reddy, B L A P Devi, R B N Prasad, **Tetrahedron Lett., 53,** 1968 (2012).

40. Ramesh K, S N Murthy, K Karnakar, K H Reddy, Y V D Nageswar, M Vijay, B L A P Devi, R B N Prasad, **Tetrahedron Lett., 53,** 2636 (2012).

41. Karnakar K, S N Murthy, K H Reddy, Y V D Nageswar, U Chandrakala, B L A P Devi, R B N Prasad, **Tetrahedron Lett., 53,** 3497 (2012).

42. Maheshwar Rao B, G Niranjan Reddy, T Vijaikumar Reddy, B L A P Devi, R B N Prasad, J S Yadav, B V Subba Reddy, **Tetrahedron Lett., 54,** 2466 (2013).

43. Gangadhar K N, M Vijay, R B N Prasad, B L A Prabhavathi Devi, **Green and Sustainable Chem., 3,** 122 (2013).

44. Prabhavathi Devi B L A, T Vijai Kumar Reddy, K Vijaya Lakshmi, R B N Prasad, **Bioresour. Technol., 153,** 370 (2013).

45. Chandrakala U, R B N Prasad, B L A Prabhavathi Devi, **Eur. J. Chem., 5,** 536 (2014).

46. Chandrakala U, R B N Prasad, B L A Prabhavathi Devi, **Ind. Eng. Chem. Res., 53,** 16164 (2014).

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News Section

RESEARCH ROUNDUP

Production of hydrogenated methyl esters of palm kernel and sunflower oils by employing rhodium and ruthenium catalytic complexes of hydrolysis stable monodentate sulfonated triphenylphosphite ligands

Christiana Vasiliou *et al* studied the hydrogenation of renewable polyunsaturated methyl esters of palm kernel and sunflower oils to the saturated (C18:0) methyl stearate (MS) catalyzed by rhodium and ruthenium complexes modified with hydrolysis stable monodentate sulfonated triphenylphosphite (STPP) ligands under mild reaction conditions in the absence or presence of organic solvents [**Applied Catalysis B: Environmental, 158–159,** 373-381, (2014)]. Superior selectivities up to 95.8 mol% of MS were achieved by Rh/STPP catalysts compared with the much lower selectivities (28.0–43.2 mol%) of MS obtained by rhodium catalysts modified with conventional triphenylphosphite or triphenylphosphine ligands. The bulkiness of transition metal STPP catalytic system which is in the form of a triisooctylammonium salt offers the possibility of the easy separation of the catalyst from the reaction mixture by means of a membrane. The hydrogenation reaction of the polyunsaturated C18 esters part of palm kernel oil and sunflower oil methyl esters toward the desired saturated product MS is an interesting catalytic reaction because it could acts as a model reaction for studying the hydrogenation of edible vegetable oil triglycerides to hardfats. Hardfats can be further subjected to interesterification reactions with liquid edible vegetable oils to yield foodstuffs with zero amounts of trans-fats. Very recent investigations have questioned whether there really are direct associations between hardfat consumption and a higher cardiovascular disease risk. Furthermore, MS could be used as a starting material of selective heterogeneous catalytic hydrogenolysis reaction of the C18:0 fatty ester to the corresponding saturated C18:0 stearyl alcohol which is an important industrial fatty alcohol.

Determination of carbamates in edible vegetable oils by ultra-high performance liquid chromatography–tandem mass spectrometry using a new clean-up based on zirconia for QuEChERS methodology

A fast, selective and sensitive multiresidue method based on QuEChERS methodology has been evaluated and validated by **David Moreno-Gonzalez *et al*** for the determination of carbamate pesticides, in edible vegetable oils by UHPLC–MS/MS [**Talanta, 128,** 299-304**, (**2014)]. A new clean-up sorbent, Supel™ QuE Z-Sep$^+$, has been successfully applied in vegetable oil extracts. Z-Sep$^+$ was compared with other sorbents (i.e. mixture of C18 and PSA) previously used for dispersive solid phase extraction of these matrices, reducing more effectively matrix effects without a significant decrease of analyte recoveries. Matrix effect was studied in different matrices (extra-virgin olive, sunflower, maize, linseed and sesame oil) being $\leq$ | 30 | % for most of the studied pesticides. Under optimum conditions, recoveries ranged from 74% to 101%, with relative standard deviations lower than 10%. Limits of quantification ranged from 0.09 to 2.0 μg kg^{-1}, allowing their determination at the low concentration levels demanding by current legislation.

Novel Approach To Evaluate the Oxidation State of Vegetable Oils Using Characteristic Oxidation Indicators

Four vegetable oils with typical fatty acid compositions were chosen by **Jun Cao Long Deng *et al*** to determine their indicators of lipid oxidation under the conditions of accelerated oxidation **[J. Agric. Food Chem., 62,** 12545–12552(2014)]. Good linear correlations were observed between the total nonpolar carbonyl amount and the total oxidation value (TOTOX, R2 = 0.89–0.97) or peroxide value (POV, R2 = 0.92–0.97) during 35 days of accelerated oxidation. Additionally, nonanal in camellia oil (oleic acid mainly) increased significantly, and correlated linearly with TOTOX (21.6 TOTOX – 595, R2 = 0.92); propanal increased significantly in perilla oil (linolenic acid mainly) and correlated linearly with TOTOX (8.10 TOTOX + 75.0, R2 = 0.90). Hexanal (9.56 TOTOX + 913, R2 = 0.90, and 7.10 TOTOX + 342, R2 = 0.78, respectively) and nonenal (10.5 TOTOX + 691, R2 = 0.95, and 6.65 TOTOX + 276, R2 = 0.84, respectively) in sunflower oil (linoleic acid mainly) and palm oil(palmitic and oleic acids mainly) also had good linear correlations with TOTOX. Considering the change patterns of these four aldehydes, it was found that the oxidation stability was in the order sunflower oil < camellia oil < perilla oil < palm oil, which was same as POV, TOTOX, and total nonpolar carbonyls. It was concluded that the four aldehydes nonanal, propanal, hexanal, and nonenal could be used as oxidation indicators for the four types of oils.

Lubricating and Waxy Esters. 6. Synthesis and Physical Properties of (E)-Didec-9-enyl Octadec-9-enedioate and Branched Derivatives

A fatty aliphatic "Jojoba-like" ester, didec-9-enyl octadec-9-enedioate, was synthesized by Steglish esterification, and C3-branched derivatives were prepared by **Shaojun Li *et al*** from its epoxide by a solvent-free epoxide ring-opening and one-pot normal condensation reaction [**Ind. Eng. Chem. Res. 53,** 20044–20055 (2014)] . The thermal stability, phase transition behavior, solid fat content, and flow behavior were investigated using thermogravimetric analysis, differential scanning calorimetry, p-NMR, and rotational rheometry, respectively. These properties were predictably varied as a function of branching, explained by the combined effects of mass, hydroxyl groups, and geometric steric hindrances imposed by the protuberant branches. The compounds demonstrated high thermal stability (>230 °C), competitive flow characteristics (210–773 cP at 40 °C and 31–66 cP at 100 °C) and superior low-temperature performance properties (–27 to –70 °C) suitable for exploitation in various applications such as lubricants, cosmetics, and pharmaceuticals.

Assessing the Potential of Crude Tall Oil for the Production of Green-Base Chemicals: An Experimental and Kinetic Modeling Study

Crude tall oil (CTO) is a cost-competitive biomaterial available from the Kraft pulping process that contains approximately 50% fatty acids, 30% resin acids and 20% neutral polycyclic oxygenated species such as sterols. Although CTO differs drastically from conventional fossil-derived feedstocks, it proves to be an interesting drop-in alternative to produce renewable base chemicals. **Ruben De Bruycker *et al*** proposed two-step process in which, first, CTO is converted into a highly paraffinic/naphthenic feedstock through hydrodeoxygenation (HDO) over a NiMo catalyst, followed by steam cracking, produces up to 34 wt % of ethylene, 15 wt % of propylene and 5 wt % of 1,3-butadiene [**Ind. Eng. Chem. Res. 53,** 18430–18442 (2014)]. A dedicated kinetic model was developed for HDO-CTO steam cracking containing over 500 species to further optimize its industrial potential. Reaction path analysis shows that the HDO severity must be optimized to remove all oxygen but dehydrogenation should be avoided so that valuable light olefins and aromatic production are maximized instead of low value fuel-oil.

Efficient Synthesis and Characterization of Ergosterol Laurate in a Solvent-Free System

Ergosterol and its derivatives have attracted much attention for a variety of health benefits, such as anti-inflammatory and antioxidant activities. However, ergosterol esters are advantageous because this compound has better solubility than the free ergosterol. In this work, ergosterol laurate was efficiently synthesized by **Wen-Sen He *et al*** for the first time by direct esterification in a solvent-free system [**J. Agric. Food Chem. 62,** 11748–11755 (2014)]. The desired product was purified, characterized by Fourier transform infrared spectroscopy, mass spectrometry, and nuclear magnetic resonance, and finally confirmed to be ergosterol laurate. Meanwhile, the effect of various catalysts, catalyst dose, reaction temperature, substrate molar ratio, and reaction time were studied. Both the conversion of ergosterol and the selectivity of the desired product can reach above 89% under the selected conditions: sodium dodecyl sulfate + hydrochloric acid as the catalyst, 2:1 molar ratio of lauric acid/ergosterol, catalyst dose of 4% (w/w), 120 °C, and 2 h. The oilsolubility of ergosterol and its laurate was also compared. The results showed that the solubility of ergosterol in oil was significantly improved by direct esterification with lauric acid, thus greatly facilitating the incorporation into a variety of oil-based systems.

Synthesis, Characterization, and Evaluation of 10-Undecenoic Acid-Based Epithio Derivatives as Multifunctional Additives

Novel epithio compounds from alkyl epoxy undecanoates (n-alkyl, C1, C4, and C6; isoalkyl, C3, C4, and C8) were synthesized using an ammonium thiocyanate in ionic liquid 1-methylimidazolium tetrafluoroborate/H2O (2:1) solvent system in 85–90% yields by gas chromatographic (GC) analysis. The synthesized products were characterized by **Gorla Geethanjali *et al*** by 1H and 13C nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy (FTIR), gas chromatography, and GC mass spectral (GC-MS) analyses and evaluated for their antioxidant, extreme pressure (EP), and antiwear (AW) properties in three different base oils, namely, epoxy jatropha fatty acid n-butyl esters (EJB), di-2-ethylhexyl sebacate (DOS), and mineral oil (S-105). Among the synthesized products, n-butyl epithio undecanoate exhibited superior antioxidant property (229.2 °C) compared to butylated hydroxytoluene (BHT, 193.8 °C) in base oil DOS and comparable performance in EJB and S-105 base oils [**J. Agric. Food Chem. 62,** 11505–11511(2014)]. All of the epithio derivatives exhibited significantly enhanced weld point for the base oils EJB and DOS at 2 wt % level and displayed moderate enhancement in S-105 base oil. Methyl epithio undecanoate at 0.6% concentration exhibited considerable improvement in the wear scar

of DOS base oil. The synthesized epithio derivatives have potential as multifunctional additives in lubricant formulations.

Rapid Determination of Ethyl Laurate from Supercritical Ethanol–Carbon Dioxide Transesterification by Full Evaporation Headspace Gas Chromatography

Qingqing Guan *et al* report on a full evaporation headspace gas chromatography (FE HS-GC) technique for rapid determination of the ethyl laurate content in supercritical ethanol–carbon dioxide mixtures [**Energy Fuels, 28,** 6995–6998(2014)]. The data show that, at an equilibration temperature of 150 °C, with a small volume (up to 75 μL) of sample, the full evaporation of ethyl laurate can be achieved in 3 min. The method had a relative standard deviation of less than 5.5% in replicate measurements; the limit of quantification (LOQ) was 26.0 μg; and the recovery ranged from 96 to 105%. The method is simple and rapid. It is quite suitable for use in the determination of ethyl laurate or similar compounds in an ethanol–carbon-dioxide-based supercritical reaction system.

Heterogeneous Interesterification of Triacylglycerols Catalyzed by Using Potassium-Doped Alumina as a Solid Catalyst

Heterogeneous interesterification of vegetable oils offers an environmentally more attractive option for the modification of edible oils to meet the specifications for certain food applications. In this work, potassium-doped alumina (KNO3/Al2O3) was prepared by **Wenlei Xie and Jing Chen** using an impregnation method, followed by calcinations at a temperature of 700 °C, and was then employed as heterogeneous catalysts for the interesterification of triacylglycerols [**J. Agric. Food Chem. 62**, 10414–10421 (2014)]. The solid catalyst was characterized by means of Hammett titration method, power X-ray diffraction, scanning electron microscopy, and nitrogen adsorption–desorption techniques. It was determined that the catalyst with KNO3 loading of 35% on alumina support and calcined at 700 °C exhibited the best catalytic activities toward the interesterification between soybean oil and methyl stearate under solvent-free conditions. Also, the solid base catalyst was successfully applied to the interesterification of soybean oil and lard blends in a heterogeneous manner. The physicochemical properties of the interesterified products were investigated using gas chromatography, high-performance liquid chromatography, and confocal laser scanning microscopy. It was found that the slip melting point and crystal morphology had a significant variation after the interesterification reaction as a result of the modification in the TAG profile. With the solid base catalyst, an environmentally friendly approach for the interesterification of triacylglycerols in a heterogeneous manner was developed.

Lipozyme RM IM-Catalyzed Acidolysis of Cinnamomum camphora Seed Oilwith Oleic Acid To Produce Human Milk Fat Substitutes Enriched in Medium-Chain Fatty Acids

In the present study, a human milk fat substitute (HMFS) enriched in medium-chain fatty acids (MCFAs) was synthesized by **Xian-Guo Zou *et al*** through acidolysis reaction from Cinnamomum camphora seed oil(CCSO) with oleic acid in a solvent-free system [**J. Agric. Food Chem. 62**, 10594–10603(2014)]. A commercial immobilized lipase, Lipozyme RM IM, from Rhizomucor miehei, was facilitated as a biocatalyst. Effects of different reaction conditions, including substrate molar ratio, enzyme concentration, reaction temperature, and reaction time were investigated using response surface methodology (RSM) to obtain the optimal oleic acid incorporation. After optimization, results showed that the maximal incorporation of oleic acid into HMFS was 59.68%. Compared with CCSO, medium-chain fattyacids at the sn-2 position of HMFS accounted for >70%, whereas oleic acid was occupied predominantly at the sn-1,3 position (78.69%). Meanwhile, triacylglycerol (TAG) components of OCO (23.93%), CCO (14.94%), LaCO (13.58%), OLaO (12.66%), and OOO (11.13%) were determined as the major TAG species in HMFS. The final optimal reaction conditions were carried out as follows: substrate molar ratio (oleic acid/CCSO), 5:1; enzyme concentration, 12.5% (w/w total reactants); reaction temperature, 60 °C; and reaction time, 28 h. The reusability of Lipozyme RM IM in the acidolysis reaction was also evaluated, and it was found that it could be reused up to 9 times without significant loss of activities. Urea inclusion method was used to separate and purify the synthetic product. As the ratio of HMFS/urea increased to 1:2, the acid value lowered to the minimum. In a scale-up experiment, the contents of TAG and total tocopherols in HMFS (modified CCSO) were 77.28% and 12.27 mg/100 g, respectively. All of the physicochemical indices of purified product were within food standards. Therefore, such a MCFA-enriched HMFS produced by using the acidolysis method might have potential application in the infant formula industry.

Dihydrophytol and phytol isomers as marker substances for hydrogenated and refined vegetable oils

Edible vegetable oils are an important part of the human diet. Products with different levels of processing are marketed for this purpose. Key-products are virgin oils, refined oils, and partly or fully hydrogenated oils.

Markus Schroder *et al* explored whether compounds derived from*trans*-phytol, i.e. the natural constituent of chlorophyll, could serve as marker compounds for identifying the processing type of oils, spreads and margarines [European Journal of Lipid Science and Technology, 116, **1372–1380 (2014)]**. The evaluation was based on the contribution of the native *trans*-phytol along with its transformation products*cis*- and *iso*-phytol as well as dihydrophytol. Gas chromatography with mass spectrometry operated in the selected ion monitoring mode enabled the detection of these compounds at >0.01 mg/100 g oil or fat. In virgin vegetable oils *trans*-phytol was the principle phytol related compound while *cis*-phytol was generally <0.05% and *iso*-phytol and dihydrophytol were not detected at all. Refined vegetable oils contained *trans*-, *cis*-, and *iso*-phytol but no dihydrophytol. Partly and totally hydrogenated vegetable oils contained dihydrophytol if at least 5% hydrogenated fat were present in the oil. The occurrence of *cis*- and *iso*-phytol in vegetable oils can be used as indicators for refined oils while the presence of dihydrophytol in vegetable oils is an indication for hydrogenation.

Tocopherol losses during pan-frying

Tocopherol losses were studied by **Jakub Fisnar *et al*** during pan-frying of bread and during heating of vegetable oils. During the heating experiments, 16 g of sunflower and olive oil was heated on a pan (internal diameter 17 cm) at maximum oil temperature 180 °C for 4, 8, and 12 min, as well as at 200 and 220 °C for 4 min [**European Journal of Lipid Science and Technology,116,** 1694–1700, (2014)]. The total tocopherol losses grew according to increasing heating time and temperature from 10 to almost 100% of the initial content. The absolute losses (in mg/kg) were higher in sunflower oil with a higher content of polyunsaturated fatty acids, while the relative losses (in % of the initial content) were higher in olive oil with a lower initial content of tocopherols. During the pan-frying, 16 g of oil (sunflower, olive, soybean, or rapeseed) was pre-heated on the pan for 4 min (at oil temperature 180 °C) and then two slices of bread (80 g) were fried in this oil for 8 min, while the oil soaked into the fried bread. Under these conditions, tocopherol losses did not depend prominently on the used oil and did not exceed 30% of the initial content.

Molecular distillation and characterization of diacylglycerol-enriched palm olein

Lipase-catalyzed glycerolysis of palm olein was used by **Chiou Moi Yeoh *et al*** to produce a mixture of acylglycerols with ~34-wt% of DAG. The reaction conditions were 5-wt% of Lipozyme TLIM at 55°C and 8 h of reaction time [**European Journal of Lipid Science and Technology**, **116**, 1654–1663, (2014)]. For commercial purposes, it is required to purify the product up to 80-wt% DAG and with free fatty acids (FFA) content below 0.1-wt%. A single-step distillation process was not sufficient to meet this product requirement. Two distinct 2-step short path distillation approaches were then studied. First scheme involved the removal of TAG by initial distillation step at 250°C, followed by separation of the MAG and FFA from distillate obtained at 180°C during second distillation step at vacuum pressure of 0.1 Pa. Second scheme involved the removal of MAG and FFA in first step at 180°C prior to purification of DAG from residue at 250°C during second distillation step at vacuum achieved up to 0.1 Pa. The results suggested that the first scheme of 2-step distillation operation was able to achieve 89.9-wt% of DAG purity without exceeding the limit of 0.1-wt% of FFA. A final yield of 21.5-wt% and DAG recovery of 47.8% were obtained using the first scheme. A detailed DAG profile was identified and product characterizations such as fatty acid composition, slip melting point, and solid fat content profile were also investigated. It was observed that purified-DAG product showed lower iodine value and higher slip melting point than raw material palm olein. The final product had 1134 ± 10 ppm tocols content.

Comprehensive two dimensional gas chromatographic separation of fatty acids methyl esters with online reduction

The accurate analysis of complex fats and oils often requires combining data from multiple GC separations, fractionation by LC prior to GC analysis, and identifying fatty acids or confirming their identities by mass spectrometry and synthetic reference materials. Comprehensive two dimensional gas chromatography markedly increases the number of resolved fatty acid methyl esters (FAME) in a single separation experiment by combining the separations of two capillary columns. **Pierluigi Delmonte *et al*** claimed that the addition of a capillary reducer in front of the second capillary column provides unique separation patterns and structural information for fatty acids based on simple elution rules [Lipid Technology 26, **256–259, (2014)**].

Sunflower oil and its applications

Monoj K. Gupta reviews sunflower as one of the oldest oilseeds in the Americas. It is the state flower of Kansas State and constitutes a significant segment of oilseeds produced in the former Soviet Union Block. Sunflower is admired worldwide for its vibrant beauty and is an important source of food. Its oil is viewed as a healthy vegetable oil and its seeds contain a wide range of nutrients that are enjoyed as a tasty snack as well as nutritious ingredient in many foods, such

as health bars, salad garnish and spreads similar to peanut butter. Sunflower is an important crop choice for US growers from the northern plains of Dakotas to Texas panhandle. The oil has very good taste and appearance. Today, there is the traditional sunflower oil, which is high in linoleic acid content that makes it excellent for both domestic and industrial use. The high linoleic acid content makes the oil unstable in industrial or institutional frying. Mid-oleic sunflower, which contains higher oleic acid and lower level of linoleic acid than the garden variety sunflower oil is more suitable for industrial and institutional frying along with the applications such as salad oil and cooking oil. High oleic sunflower oil, that contains 80% or higher oleic acid and very low linoleic acid, is one of the most stable oils for all applications, including industrial and institutional frying, and also for industrial non-food applications such as lubricant, as transformer oil and various other applications [**Lipid Technology, 26,** 260–263, (2014)].

Identification of critical parameters in liquid enzyme-catalyzed biodiesel production

Callera™ Trans L, a liquid formulation of *Thermomyces lanuginosus* lipase, has recently shown great promise as a cost-efficient catalyst for methanolysis of triglyceride substrates, specifically in the BioFAME process [**Biotechnology and Bioengineering,111,** 2446–2453, (2014)]. However, identifying the right combination of temperature and concentrations of catalyst, water and methanol to realize the full potential of the reaction system has remained a challenge. **Mathias Nordblad *et al*** presents an investigation of the impact of temperature, enzyme and water concentration on the reaction, as well as the effect of methanol feed rate for the conversion of rapeseed oil in a fed-batch reaction system. It was observed that the reaction can be divided into two distinct parts. The first part of the reaction, during which primarily tri- and diglycerides are converted, proceeded at a high rate and thus required a high rate of methanol supply. The second part of the reaction, where the remaining di- and monoglycerides are converted, proceeded at a much lower rate. Consequently, it is necessary to reduce the methanol feed rate during the latter part of the reaction to avoid inhibition or even inactivation of the enzyme. Since the second part of the reaction occupied most of the 24-h reaction time, it was concluded that this is the part of the process where further development efforts should be targeted. This point was demonstrated by partially substituting the catalyst with a lipase with a different specificity, which enhanced the performance during the second phase of the reaction

Hot-Air Drying Characteristics of Soybeans and Influence of Temperature and Velocity on Kinetic Parameters

The kinetics of the hot-air drying of soybeans was modeled by **Viviana Cocco Mariani *et al*** in order to evaluate the influence of temperature and velocity on the kinetic parameters. A convective dryer with air temperature from 30 to 195C and air flows of 0.75, 1.35, 2.0 and 2.5 m/s was used. Three different mathematical models were applied to simulate the drying process (two empirical equations, exponential and Page's, and Fick's diffusion model) and the diffusivity coefficient increased from 2.5×10^{-11} to 6.69×10^{-10} m^2/s for a range of air temperature between 30 and 195C. Both temperature and velocity influenced drying rate. The differential evolution optimization method was used toward parameter estimation. The goodness of fit of the proposed models, evaluated using linear regression coefficient (R^2), chi-squared parameter (χ^2) and root mean square error, indicated a satisfactory validation, mainly regarding to the exponential and Page's models [**Journal of Food Process Engineering, 37**, 619–627, (2014)].

Influence of industrial physical refining on tocopherol, chlorophyll and beta-carotene content in sunflower and rapeseed oil

The main purpose of this article by **Frantisek Kreps *et al*** was to investigate the influence of individual processes in physical refining on tocopherol content in sunflower and rapeseed oils. During refining some chemical parameters, the oxidative stability of oils and some minor compounds such as chlorophyll and beta-carotene, were determined . Those analytical data with explained chemical backgrounds gave more qualitative overview of what happened to the same lot of oils being processed in a continuous operation . Some processes were compared with a laboratory oil refining. Crude rapeseed oil contained 656 mg/kg of total tocopherols, followed by high oleic sunflower with 373 mg/kg of tocopherols and classic sunflower oil with 332 mg/kg of tocopherols. The most serious refining processes were bleaching and physical deodorization process, the tocopherol losses being 14.9–17.4% and 20.2–27.1%, respectively. In the refined oils, chlorophylls and FFAs were almost completely removed and the oxidative stability increased 2–3 times. Vegetable oil refining process caused relatively great losses of minor compounds but this, in turn, prolonged the shelf life of edible oils [**European Journal of Lipid Science and Technology,116,** 1572–1582, (2014)].

Oxidation and structural decomposition of fats and oils at elevated temperatures

A fast and reliable laboratory protocol allowing a holistic statement about thermo-oxidative structural changes of fats and oils at ambient temperatures, under accelerated conditions using 110°C and under elevated temperature usually used for frying at 170°C is proposed **Christian Gertz *et al***. The results demonstrate that two different routes of degradation may be responsible for fat deterioration at elevated temperatures. Depending on the temperature (at 20, 110, or 170°C) the composition of polar compounds changed. The content of di- and polymerized TAGs increased with time at elevated temperature, e.g., frying whereas the formation of oxidized products dominates at 110°C or lower. These different reaction mechanisms may explain the discrepancy between practical experiences during frying and the estimated oxidative resistance of fats and oils using accelerated tests like Rancimat or OSI [**European Journal of Lipid Science and Technology, 116**, 1457–1466, (2014)].

Preparation of PUFA concentrates as acylglycerols *via* enzymatic hydrolysis of hempseed oil (*Cannabis sativa* L.) in a homogeneous low-water medium

The growing demand for concentrated extracts of PUFA prompted us to undertake the preparation of natural glycerides containing linoleic acid and α-linolenic acid from hempseed oil. Hempseed is an exceptionally rich source of essential FA but is still underutilized. Hempseed oil was submitted to a lipase-catalyzed hydrolysis in a homogeneous medium based on oil and *t*-BuOH/water by **Pamela Torres-Salas *et al***. Seven commercial lipases were screened in this reaction medium, which resulted to be superior to the routinely used biphasic systems in terms of substrate/product solubility and biocatalyst stability **[European Journal of Lipid Science and Technology, 116**, 1496–1504, (2014)]. Lipase from *Pseudomonas cepacia* resulted to be sufficiently selective versus saturated FA and it was thus used to hydrolyze hempseed oil in order to obtain acylglycerols enriched with PUFA. The enzymatic reaction was scaled up and the acylglycerol components were purified and analyzed by GC-FID. In the fraction of monoacylglycerols (yield 22%) the total amount of PUFA reached 85% (against 77% of the crude oil) whereas the content of saturated FA was negligible. The omega-6/omega-3 ratio of the total glyceride component (purified acylglycerols, yield 29%) was maintained in the optimal range (4.6:1) for human nutrition. Therefore, PUFA concentrates from hempseed oil here obtained in the form of natural glycerides could be considered as valuable dietary supplements.

Kinetic analysis for the esterification of high free fatty acid feedstocks with a structural identifiability approach

Esterification is the first step in the biodiesel production process from low cost feedstock, which is typically characterized by its high content (>5%) of free fatty acids (FFAs). Although multiple attempts have been made to describe the kinetics of the esterification process for this feedstock, there is no consensus regarding which model is the most suitable. In this paper, two models were evaluated as candidates by **Efren Aguilar-Garnica *et al*** to describe the esterification of grease trap wastes, a synthetic mixture of tallow fat and canola oil, and oleic acid, which all have a high degree of acidity. The first model considers a pseudo-first order reaction, whereas the second model considers the reversibility of the reaction. All parameters involved in these models are structurally identifiable and are estimated with the Levenberg–Marquardt method. A statistical analysis based on Akaike's weights show that the reversible model provides the best fit for all experimental runs compared to the first order model. This result was obtained from variations in catalyst loading and moisture content [**European Journal of Lipid Science and Technology, 116**, 1598–1607 (2014)].

Preparation of Margarines from Organogels of Sunflower Wax and Vegetable Oils

It was previously reported that sunflower wax (SW) had high potential as an organogelator for soybean oil–based margarine and spread products. In this study, 12 other vegetable oils were evaluated by **Hong-Sik Hwang *et al*** in a margarine formulation to test feasibility of utilization of SW as an alternative to solid fats in margarine and spread products containing these oils. The minimum quantity of SW required to form a gel with these oils ranged from 0.3% to 1.0% (wt.) [**Journal of Food Science, 79**, C1926–C1932, (2014)]. Organogels were prepared from the vegetable oils with 3%, 5% and 7% SW and were tested for firmness as well as melting behaviors using differential scanning calorimetry. These organogels were also incorporated into a margarine formulation. All of the vegetable oil organogels produced relatively firm margarines. The margarines prepared from organogels containing 3% (wt.) SW had greater firmness than commercial spreads, whereas margarines made from 7% SW were softer than commercial stick margarines. However, dropping points of the margarine samples were higher than those of commercial spread and margarine products. Margarine firmness was modestly inversely correlated with the amount of polar compounds in the oils and did not correlate with fatty acid compositions. This

study demonstrates the feasibility of using a number of healthy vegetable oils rich in polyunsaturated fatty acids to make healthy margarine and spread products by utilizing SW as an organogelator.

Investigation of Oil Properties and Seed Composition in Some Safflower Lines and Cultivars

Fatty acid contents and physicochemical characteristics of a kind of oil extracted from seeds of 17 safflower genotypes from Iran along with three genotypes from Germany and Canada were studied. Oil content, refractivity index, specific gravity and peroxide, iodine, saponification, acid and tiobarbitoric acid values were measured according to AOCS official methods by **S. Ahmadzadeh *et al***. These determinations were carried out in triplicate. Fatty acids composition was determined by gas chromatography. Results indicated that there was a significant difference ($P < 0.01$) in all characteristics among genotypes. The seeds contained 22.03–36.73% oil and 15.64–21.50% protein. Linoleic acid (C18:2) was the most abundant unsaturated fatty acid, followed by oleic acid (C18:1) and linolenic acid (18:3) **[Journal of Food Biochemistry, 38**, 527–532 (2014)].

Mathematical modeling of the partial hydrogenation of vegetable oil in a monolithic stirrer reactor

Experimental and theoretical studies on the partial hydrogenation of vegetable oil in a monolithic stirrer reactor are reported by **Diego E. Boldrini *et al***. A complete mathematical model of the reactor was developed, including hydrogenation and isomerization kinetics, catalyst deactivation, external gas–liquid and liquid–solid as well as internal mass transfer. The experimental studies were carried out in a Pd/Al_2O_3/Al monolithic stirrer reactor, at a wide range of temperatures (353–373 K), pressures (414–552 kPa), and catalyst loadings (0.00084–0.00527 $kg_{Pd,exp}$ m^{-3}). Based on this model, simulated data can be used to evaluate the catalyst (Pd/Al_2O_3/Al) and the hydrogenation process in consecutive catalytic tests under different operating conditions [**AIChE Journal, 60**, 3524–3533, (2014)].

Enzyme-assisted deacidification of Jatropha crude oil by statistical design of experiments

Jatropha curcas L. crude oil has variable and often high free fatty acid content. As free fatty acids are corrosive, the crude oil has to be refined prior to its utilization in technical applications. Conventional refining processes have several environmental and energetic shortcomings, and there is a clear need for more sustainable pathways. In this study, an enzymatic method was studied for the neutralization of Jatropha oil by **Gabriele Gofferje *et al***. Detailed insight into the process was achieved by means of a statistical design of experiments utilizing an immobilized lipase from *Rhizomucor miehei*. The free fatty acids were esterified with glycerol. The most important impact factors and interactions between factors were identified with regard to acid number reduction and the MAG, DAG, and glycerol content. Validation experiments showed that the models obtained for acid number and, mono- and DAG development were valid and adequate for optimizing the esterification reaction for the desired application [**European Journal of Lipid Science and Technology, 116**,1421–1431,(2014)]. The results generated in this study open the possibility of modifying – within limits – the vegetable oil composition depending on the target application requirements. The acid number of the crude Jatropha oil could be decreased to 0.4 mg KOH per g oil by means of enzymatic esterification. The MAG content can be adjusted between 1.5 and 5.0% (w/w) and DAG content between 15.6 and 27.1% (w/w). The enzyme regeneration procedure that was developed allows multiple use of the enzyme at practically constant activity.

Effects of ultrasound-assisted extraction on yield of flaxseed oil, β- and γ- tocopherols optimized by orthogonal array design

Orthogonal array design ($L_9(3^4)$) was applied to optimize the flaxseed oil (FO) recovery, β- and γ-tocopherols yields and total oxidation value (totox value) using ultrasound-assisted extraction (UAE) by **Khamis Ali Omar *et al***. The optimized results were then compared with the one extracted by Soxhlet extraction (S.E.) at 8 h. The results revealed that 80.05% FO can be recovered by extraction for 30 min, 30°C and 10:1 solvent/solid ratio by UAE compared to 100% recovery obtained by 8 h, 60°C and 20:1 solvent/liquid ratio by S.E. (taken as reference and standard extraction). β- and γ-tocopherols yield was 40.39 mg/100 g oil at 30 min, 20°C and 10:1 solvent/liquid ratio by UAE compared to 56.37 mg/100 g oil by S.E. Totox value of FO by UAE was lower compared to S.E., which is a promising results for better quality and further processing of the oil. No significant differences were shown between the two extraction methods for fatty acids ($p < 0.025$). UAE is capable of reducing the financial [**European Journal of Lipid Science and Technology 116**, 1412–1420, (2014)].

Magnetic ionic liquid-based dispersive liquid–liquid microextraction for the determination of triazine herbicides in vegetable oils by liquid chromatography

Magnetic ionic liquid-based dispersive liquid–liquid microextraction (MIL- DLLME) was developed

for extracting triazine herbicides from vegetable oils by **Yuanpeng Wang *et al***. The MIL, 1-hexyl-3-methylimidazolium tetrachloroferrate ([C_6mim] [$FeCl_4$]), was used as the microextraction solvent. The magnetic separation time was shortened by simply mixing carbonyl iron powder with the MIL in the sample after DLLME. The effects of several important experimental parameters, including the amount of MIL, the time of ultrasonic extraction, the type and the volume of cleanup solvent were investigated. The MIL-based DLLME coupled with liquid chromatography gave the limits of detection of 1.31–1.49 ng mL^{-1} and limits of quantification of 4.33–4.91 ng mL^{-1} for triazine herbicides. When the present method was applied to the analysis of vegetable oil samples, the obtained recoveries were in the range of 81.8–114.2% and the relative standard deviations were lower than 7.7%. Compared with existing methods, the performances achieved by the present method were acceptable [**Journal of Chromatography A, 1373**, 9-16 (2014)].

Synthesis, structure and properties of fully biobased thermoplastic polyurethanes, obtained from a diisocyanate based on modified dimer fatty acids, and different renewable diols

Different innovative macromolecular architectures have been elaborated and characterized by **M. Charlon *et al*** . The synthesis of a set fully biobased thermoplastic polyurethanes (TPUs) was contingent on different renewable or potentially renewable building blocks such as 1,4-butanediol (BDO), isosorbide (ISO), and 2-heptyl-3,4-bis(9-isocyanatononyl)-1-pentylcyclohexane, the latter obtained after the chemical modification of a dimer fatty acid [**European Polymer Journal, 61**, 197-205, (2014)]. These TPUs were prepared in a one-step bulk process using different hard segment (HS) species with varying ratios of ISO/BDO contents. The final molar masses were found to decrease when BDO was progressively exchanged by ISO, presumably due to the high dissymmetry and lesser reactivity of the latter species (bearing exo and endo groups) with respect to the former. This substitution (BDO vs. ISO) altered the crystallinity, the thermal transitions and the stability of the resulting polymers. TPUs with low ISO content present good mechanical performances with high elongation and Young's Modulus. The deformation is however fully plastic, despite the "hard–soft" phase segregation proven by small-angle X-ray scattering analysis. These novel biobased materials are very attractive since they present highly tailorable properties by selecting appropriate HS content and suitable chemical structure.

Removal of dyes by lignocellulose adsorbents originating from biodiesel production

Zuy M. Magriotis *et al* used tucumã cake, *in natura* (TCN) and thermally treated (TCT), as potential alternative adsorbents for the adsorption of cationic and anionic dyes. The effects of the parameters: contact time, adsorbent: adsorbate mass ratio, and initial concentration of dye were analyzed. The adsorption isotherms were established from optimized adsorption parameters. The best conditions for adsorption were: equilibrium time of 7 h, concentration of 25 mg L^{-1} and ratio of 1:200 for the methylene blue dye; and pH 6.5, concentration of 25 mg L^{-1} and ratio of 1:200 for the congo red dye. The adsorption process was best represented by the Dubinin–Radushkevich and Sips isotherms. The kinetics of adsorption of the dyes were best described by the pseudo-second-order kinetic and Elovich models. TCT showed the best maximum adsorption capacity (Q_m) for the methylene blue dye (63.92 mg g^{-1}) [**Journal of Environmental Chemical Engineering, 2**, 2199-2210 (2014)].

Towards the development of a predictive model of the formulation-dependent mechanical behaviour of edible oil-based ethylcellulose oleogels

The functionality of the recently discovered ethylcellulose (EC) oleogel systems are highly dependent on the mechanical strength of these gels. This mechanical strength depends strongly on a variety of different compositional parameters. **Andrew J. Gravelle *et al*** report on a predicative model relating the mechanical strength of EC oleogels as a function of both gelator and surfactant concentration for a variety of oils, surfactants, and EC molecular weights. Predictive modelling was based on a goodness-of-fit approach achieved in a step-wise fashion. Two-dimensional fits were performed on the experimental data for gel strength as a function of both mass fraction ethylcellulose (0.07–0.15) and surfactant (fixed to three EC/surfactant ratios) to obtain candidate equations for the eventual three-dimensional model. It was discovered that gel strength increases with mass fraction of EC in a power law fashion for all conditions tested. Comparison of mechanical strength determined by back extrusion and texture profile analysis (TPA) showed similar trends in scaling behaviour. In addition, the behaviour of the elastic constant extracted from TPA was also found to follow a power law with increasing gelator concentration. Finally, the validity of the predictive model was investigated through interpolation [**Journal of Food Engineering, 143,** 114-122 (2014)].

[Contributed by KN Prasanna Rani]

FORTHCOMING EVENTS

1. **World Conference on Fabric and Homecare,** at Montreux Music and Convention Centre, Montreux, Switzerland during October 6-9, 2014. This meeting is organized by American Oil Chemists' Society. For details, contact: AOCS Meetings Department, Phone no. +1 217-693-4821; Fax: +1 217-693-4865; e-mail: meetings@aocs.org; website:http:// aocs.org/ meetings.

2. **Oils and Fats International Congress 2014 (OFIC 2014)** at Kualalampur Convention Centre, Kualalampur, Malaysia during November 5-7, 2014. For details, Contact: Ms. Michelle Lim, OFIC Secretariat, MOSTA, Selangor, Malaysia. E-mail: mosta.secretariat@gmail.com.

3. **69th Annual Convention of Oil Technologists' Association of India and International Conference on Sustainable Technologies and Futuristic Trends: Oilseeds, Oil Processing and Surfactants & Expo 2014** at Hotel Radisson Blue, Agra, India during November 14-16, 2014. For details, contact: Prof R K Trivedi, President, OTAI Central Zone. Phone: +91-9415024771. E-mail: otai2014@otaicentralzone.org; website:www.otaicentralzone.org.

4. **Fundamentals of Oilseed and Edible Oil Processing and Refining** at Hotel Crowne Plaza, Shanghai Pudong, Shanghai, China during November17-18, 2014. For details, contact: meetings@aocs.org.

5. **4th International Conference on Soaps, Detergents & Cosmetics** at Hotel Marriott, Panjim, Goa, India during December 7-9, 2014. For details, contact: Indian Home and Personal Care Industry Association. Tel. +91 2228771857; Fax.: +912228733619. E-mail: ihpcia@ihpcia.org.

6. **Refresher Course on Processing and Analytical Methodologies of Oils & Fats** at Centre for Lipid Research, CSIR-Indian Institute of Chemical Technology, Hyderabad, during February 25-27, 2015. The Members of SEA, India may avail concession for this course by mentioning their membership numbers. For further details, contact: Dr P P Chakrabarti, Convener, Refresher Course. Tel. +914027193179, +914027191851, Telefax: +914027193370. E-mail: pradosh@iict.res.in.

NEW BOOKS PUBLISHED

1. **Molecules That Amaze Us** by Paul May and Simon Cotton, CRC Press, Cheriton House, North Way, Andover, Hants, SP10 5BE, UK. ISBN : 9781466589605, $53.96, 2014.

2. **Chemistry of Sustainable Energy** by Nancy E Carpenter, CRC Press, Cheriton House, North Way, Andover, Hants, SP10 5BE, UK. ISBN : 9781466575325, $71.96, 2014.

3. **Industrial Biocatalysis** by Peter Grunwald, CRC Press, Cheriton House, North Way, Andover, Hants, SP10 5BE, UK. ISBN : 9789814463881, $359.96, 2014.

4. **Surface Chemistry Essentials** by K S Birdi, CRC Press, Cheriton House, North Way, Andover, Hants, SP10 5BE, UK. ISBN : 9781439871782,$129.95, 2013.

5. **Refining Used Lubricating Oils,** by James Speight and Douglas I Exall, CRC Press, Cheriton House, North Way, Andover, Hants, SP10 5BE, UK. ISBN: 9781466551497, $161.96, 2014.

6. **Differential Scanning Calorimetry: Applications in Fat and Oil Technology,** by Emma Chiavaro, CRC Press, Cheriton House, North Way, Andover, Hants, SP10 5BE, UK. ISBN: 9781466591523, $152.96, 2014.

7. **Lipids: Nutrition and Health,** by Claudia Leray, CRC Press, Cheriton House, North Way, Andover, Hants, SP10 5BE, UK. ISBN: 9781482242317, $89.96, 2014. .

8. **Improving Food Quality with Novel Food Processing Technologies** by Ozlem Tokusoglu and Barry G Swanson, CRC Press, Cheriton House, North Way, Andover, Hants, SP10 5BE, UK. ISBN: 9781466507241, $152.96, 2014.

9. **Methods in Food Analysis** by Rui M S Cruz, Igor Khmelinsku and Margarida Vieira, CRC Press, Cheriton House, North Way, Andover, Hants, SP10 5BE, UK. ISBN: 9781482231953, $116.96, 2014.

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

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Southern Zone : otaisz@gmail.com

Western Zone : otaiwz@gmail.com

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

OTAI ANNUAL MERIT AWARDS

1. Dr. S Hussain Zaheer Memorial Award (Single Person Award for Basic Research): Annual Cash Award of Rs. 5,000/- was instituted with the support of Zaheer Science Foundation, New Delhi. The award is for excellence in research contribution in Oil Chemistry and Technology, Surface Coatings and Allied Subjects, through research papers, which include applicant's name among the authors and which appeared during the previous three calendar years.
2. Dr. S D Tirumala Rao Memorial Award (Single Person Award for Applied Research): Annual Cash Award of Rs. 5,000/- was instituted with the support of Anantapur Chapter of OTAI (SZ). The award is for excellence in research contributions in relevant subject "Wealth from Waste" or "Value-added Products from the Waste generated in Vegetable Oil Industry" through research papers, which include applicant's name among the authors and which appeared during the previous three calendar years.
3. RBGV Swaika Memorial Award (Team Award for Applied Research): Annual Cash Award of Rs. 5,000/- was instituted with support of Shri B K Swaika and Shri N K Swaika of M/s Swaika Vanaspati Products, Kolkatta. The award is for excellence in Specific Process or Product Development or Innovation or Improvement in the Oils, Oilseeds, Surface Coating and Allied Field over three calendar years.
4. Dr. Santinath Ghosh Memorial Research Award: Annual Cash Award of Rs.10,000/- and citation was instituted by OTAI (EZ) with corpus fund donated by Dr. Pubali Ghosh Dhar in memory of Dr. Santinath Ghosh for the Young Researcher (age below 35 years as on 1st January of the particular year). The award is for excellence in the field of Oil Technology and Allied Sciences with Best Social / Industrial Implication through patent / research paper, which include applicant's name among the authors which appeared during the previous calendar year.
5. S R Bhatnagar (SARBI) Memorial Research Award: Annual Cast 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.

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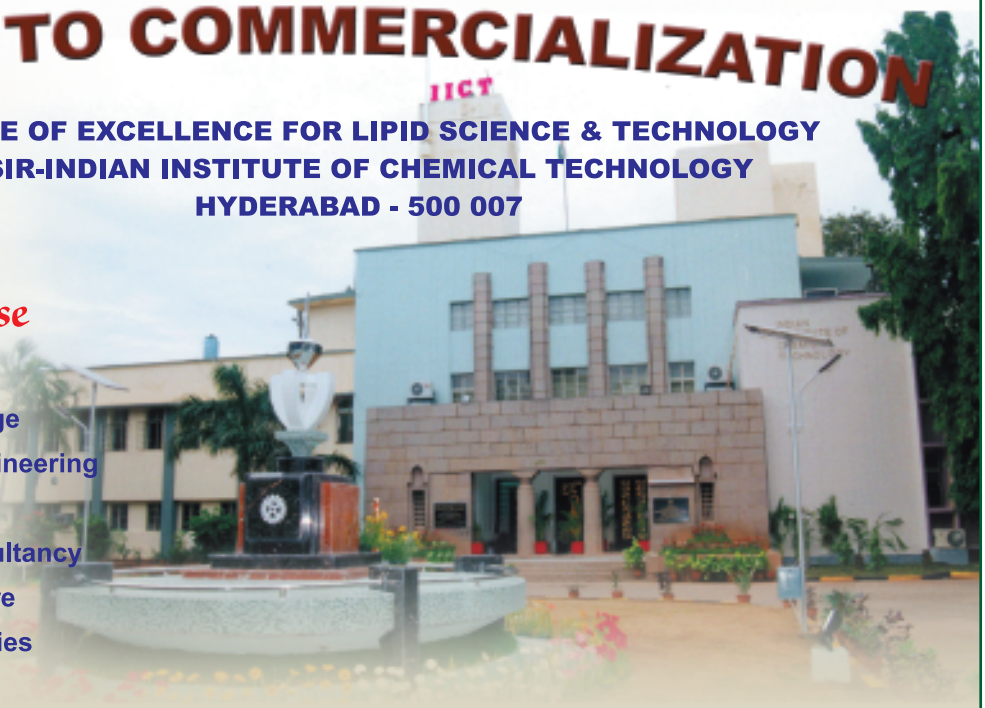

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- Sodium Stearoyl Lactylate

For Further Details Contact: Head, Lipid Science & Technology Division (Formerly Oils & Fats Division), CSIR-Indian Institute of Chemical Technology, Hyderabad–500 007, India; TEL: 91 40 27193179; Fax: 91 40 27193370 • e-mail: rbnprasad@iict.res.in • Website: www.iictindia.org

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