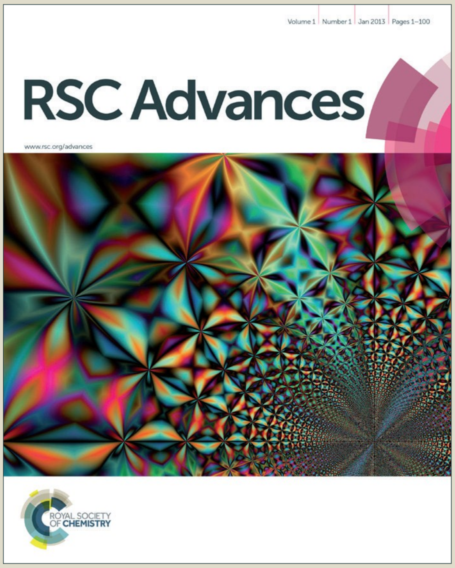
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances RSCPublishing

ARTICLE

Preparation of functionalized castor oil derivatives with tunable physical properties using heterogeneous acid and base catalysts

Cite this: DOI: 10.1039/x0xx00000x

Received 00th March 2015,
Accepted 00th April 2015

DOI: 10.1039/x0xx00000x

www.rsc.org/

Sivashunmugam Sankaranarayanan[ab] and **Kannan Srinivasan***[ab]

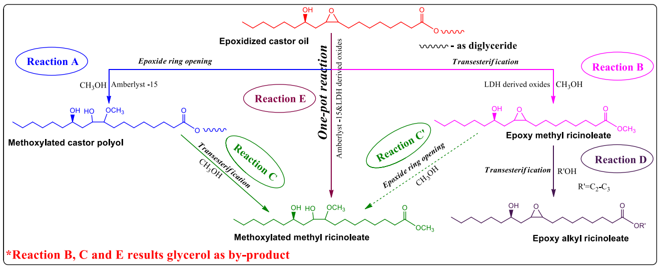
Functionalized castor oil derivatives namely ring-opened glyceryl ricinoleates, epoxy alkyl ricinoleates, and ring-opened alkyl ricinoleates were successfully prepared through two reaction chemistry viz., ring opening and transesterification using epoxidized castor oil (ECO) as a raw material. Amberlyst 15, the most active catalyst among several acid catalysts screened, showed a maximum conversion of 82% for ring opening of ECO with methanol. In another chemistry, 91% yield of epoxy methyl ricinoleate was achieved through transesterification of ECO with methanol using CaAl-layered double hydroxide (LDH) derived oxides as base catalyst. The scope is extendable to many nucleophiles and alcohols for both reactions respectively. Ring-opened alkyl ricinoleates were prepared both in two-pot and one-pot using both acid and base catalysts together. The catalysts were recyclable and were successfully scaled at 25 g. The physical properties of these castor-based derivatives bestow opportunity to design tailor-make materials suiting industrial needs.

Introduction

Due to limited availability, demand, vacillating cost, geopolitical reasons and environmental concerns associated with petroleum products, biomass has gained interest in last two decades as an alternate source for the production of bio-based products.[1] The term bio-based products include fuels as well as chemicals derived from renewable carbon sources which are eco-friendly.[2] Vegetable oils, one of the large-segment category of such biomass sources, have fatty acid triglycerides in their structure and are effectively utilized for the production of diverse oleochemicals.[3] Presence of unsaturated centres in vegetable oils and their fatty derivatives causes low cold flow and lesser oxidative stability that limits their use in commercial applications.[4] Though hydrogenation is the commonly explored commercial option, epoxidation of double bond followed by ring opening with alcohols[5] (or) acids[6] are some of the interesting and potential ways to achieve the desired physical properties. Further, functionalized oil/fatty derivatives have huge market value and are the best replacement for petroleum products which can be utilized either directly (or) as potential intermediate for making derivatised chemicals thanks to their functional flexibility and reactivity.[7]

In recent years, non-edible and used cooking oils have earned impetus for producing energy molecules (or) chemicals for averting food vs fuel issues.[8] Castor oil, one of such promising non-edible oils, is effeciently used in many industrial processes for making various chemicals besides being used for centuries for medicinal purposes.[9] Castor oil, being highly stable (longer shelf life) and relatively inexpensive, coupled with their unique functionality make it superior over many other vegetable oils.[10] In world, ~1.2 million tons of castor oil are produced every year and India occupies the top place for castor production with nearly ~60%[11] of overall production followed by China and Brazil. Presence of >85% of ricinoleic acid (a functionalized fatty acid which has ester linkage, hydroxyl group and unsaturated centre) makes castor oil an important raw material for various commercial applications.[12] Generally in vegetable oils, reactions can occur at ester region (or) fatty region and functionalization in one region without affecting the other will leads to molecules with entirely different physical properties.

Epoxides of oils and fatty derivatives are valuable intermediates for the production of several chemicals that have many industrial applications.[13] Owing to the presence of highly active oxirane ring, fatty epoxides can easily undergo various chemical transformations.[5, 14] The products derived from fatty epoxides are useful in bioplasticizers,[15] surfactants and coatings,[14a] polymers,[16] lubricant additives,[14g] hydraulic and dielectric fluids,[17] as antifriction/antioxidant and anti-wear in automotives[14d, 14e] and as lubricants.[14j] Ring opening of epoxidized oils with alcohols is an interesting pathway to produce polyols that are used as starting materials for polyurethane.[15b] Besides, thus obtained hydroxyl ethers can be further processed chemically into lubricants as well.[18]



Scheme 1 Preparation of functionalized castor oil derivatives (mainly represented as methyl derivatives).

Transesterification of vegetable oils with alcohol is a known method for the preparation of fatty acid alkyl esters (commonly called biodiesel)[19] and the same process can be extended for epoxidized oils and the resulting epoxidized fatty acid alkyl esters are useful as surfactants, fuel additives and in other industrial products.[20] Given the abundant availability of castor oil in India besides steady growth and considering the industrial application potential of functionalized derivatives for oils, it is prudent to study the value addition of castor oil or its derivative. In recent years, heterogeneous catalysts are preferred for industrial processes due to their well-known advantages over homogeneous catalysts. To our best knowledge, no report is available for the ring opening of epoxidized castor oil as well as transesterification of epoxidized castor oil (including for epoxidized vegetable oils) using heterogeneous catalysts. In this work, we report the preparation of functionalized castor oil derivatives namely ring-opened glyceryl ricinoleates and epoxy alkyl ricinoleates with tunable physical properties through two reaction chemistry using epoxidized castor oil (ECO) as raw material using heterogeneous acid and base catalysts. Furthermore, ring-opened alkyl ricinoleates (functionalized in both regions) is also prepared from ECO in a two-pot as well as one-pot reactions (Scheme 1).

Experimental

Materials

Commercial resin based materials such as Amberlite IR 120, Amberlite 200 C, Amberlite IRA 67 and Amberlite IRA 402Cl were purchased from sd fine chemicals limited, Mumbai, India. Amberlyst 15 was purchased from Lancaster while Amberlyst A 26 (OH) and zinc triflate were purchased from Sigma-Aldrich. Sulphated zirconia was gifted from Dr. Beena Tyagi's research group, CSIR-CSMCRI, Bhavnagar.

MgAl-LDH and CaAl-LDH were prepared by co-precipitation under low supersaturation as reported earlier.[21] The as-synthesized LDHs were calcined at 700 °C in static air in an electric furnace for 5 h and the calcined samples were denoted as M(II)M(III)x-$CLDH_{700}$ where M(II) & M(III) represents divalent and trivalent cations respectively and 'x' is the molar ratio of M(II)/M(III). Epoxidized castor oil (ECO; Molecular weight ~980) was provided by Jayant Agro Organics Ltd., Mumbai, India.

Characterization

Acidic strength of the materials (meq H^+/g) was determined by acid-base titration method. In a flask, 50 mg of material was taken with 5 ml of water and to that 5 ml of 0.1M NaOH solution was added. The contents in the flask were stirred well for 15 min. 2 drops of phenolphthalein indicator was added and then titrated against 0.1M HCl solution. Powder X-ray diffraction (PXRD) of the materials was carried out on a Rigaku Miniflex II system using Cu Kα radiation. The operating voltage and current were 30 kV and 15 mA, respectively. The step size was 0.04° with a step time of 0.2 s.

^1H NMR analysis was done using Bruker Avance DPX 200 instrument with an operating frequency of 200 MHz. FT-IR spectra were recorded in a Perkin-Elmer Spectrum-GX instrument using KBr pellets; 100 scans were recorded with a nominal resolution of 4 cm^{-1}, which were accumulated and averaged to improve the signal-to-noise ratio. For diffuse reflectance infra-red Fourier-transformed (DRIFT) measurements, neat samples were used using reflectance accessory.

ESI-MS studies were carried out in Waters 2487 Q-TOF Micro by dissolving samples in acetonitrile and diluted with methanol. Viscosity studies were carried out using Brookfield Viscometer (Model –LVOV-II+P) by keeping the samples at different rpm. Oxidative stability studies were done in Metrohm 873 Biodiesel Rancimat.

Ring opening reaction

In a 25 ml round bottom flask, 500 mg of epoxidized castor oil (ECO) was taken along with 3 ml of toluene as solvent. To that, known amount of methanol and catalyst were added and the flask was kept at different temperatures in a preheated oil bath. The contents in the flask were stirred vigorously for desired reaction time. The reaction mixture was then allowed to cool and the product mixture was collected by simple decantation (in particular for resin based catalysts). Collected mixture was subjected to rotary evaporation under reduced pressure to remove unreacted methanol and solvent. Finally, solvent free sample (15-25 μL) was analyzed by ^1H NMR using $CDCl_3$ as solvent. Duplicate experiments were conducted and the errors in the values are ± 3%. Conversion is calculated based on the decrease in the peak area of the oxirane ring protons of reactants and products (by keeping the terminal $-CH_3$ protons as internal standard in both the samples). Ring opening of epoxy methyl ricinoleate, epoxy ethyl linoleate and 1,2-epoxy hexadecane were also performed similar to the above procedure.

Transesterification reaction

In a 25 ml round bottom flask, 5 g of ECO and 3 g of methanol (methanol:oil = ~ 18:1 molar ratio) was taken and to that exactly 250 mg of CaAl2-CLDH$_{700}$ (mixed oxides derived by calcining CaAl2-LDH at 700 °C; 5 wt.% w.r.t. ECO) was added. The flask was placed in a 65 °C preheated oil bath and contents in the flask were stirred vigorously for 5 h. After the reaction, the catalyst was separated from reaction mixture by simple centrifugation and product mixture was collected. No glycerol layer was observed; water was added to this mixture to remove glycerol. Organic layer was extracted with hexane and subjected for rotary evaporation to remove unreacted methanol and hexane. Finally, solvent free sample (15-25 µL) was analyzed by ^{1}H NMR using $CDCl_3$ as solvent. Similar procedure was extended (except water addition step) for the transesterification of EMR with higher alcohols namely ethanol, *n*-propanol and *iso*-propanol using a alcohol:EMR molar ratio of 6:1.

Yield of epoxy methyl ricinoleate (EMR) was calculated based on the formation of new peak around 3.7 ppm for $-OCH_3$ protons in ^{1}H NMR by keeping methylene protons as internal standard. Same procedure was adopted for the transesterification of castor oil with methanol to obtain methyl ricinoleate with methanol:oil molar ratio of 10:1.

In the case of epoxy alkyl ricinoleates, conversion was calculated based on the decrease in the peak area at 3.7 ppm and the yield was computed assuming the products formed were only epoxy alkyl ricinoleates. The formation of transesterified products was ascertained by the appearance of characteristic peak at 4.2-4.1 ppm in ^{1}H NMR that corresponds to $-OCH_2$ protons in the alkyl ricinoleates.

One-pot reaction

In a 50 ml round bottom flask, 2 g of ECO and 12 g of methanol were taken along with 10 ml of toluene as solvent. To that exactly 200 mg of Amberlyst 15 (10 wt.% w.r.t. ECO) and 100 mg of CaAl2-CLDH$_{700}$ (5 wt.% w.r.t. ECO) were taken together. The flask was placed in a 105 °C preheated oil bath and contents in the flask were stirred vigorously for 5 h. The catalyst was then separated from the reaction mixture by simple centrifugation and the product mixture was collected. No glycerol layer was observed; water was added to this mixture to remove the glycerol. Organic layer was extracted with hexane and subjected for rotary evaporation to remove unreacted methanol, toluene and hexane. Finally, solvent free sample (15-25 µL) was analyzed by ^{1}H NMR using $CDCl_3$ as solvent. Conversion of oxirane ring and yield of transesterified products were calculated by the above mentioned calculation procedures.

Catalyst reusability studies

To assess the reusability of the catalyst, the Amberlyst 15 was separated from the reaction mixture by filtration. It was then washed with toluene to remove the oily nature of the catalyst. The catalyst was then washed well with methanol and kept in an oven for drying at 110 °C for 4 h. In the case of transesterification reaction, the catalyst was recovered by G3 crucible separation, washed well with methanol and kept in an oven at 110 °C. In another experiment with an endeavor to understand the effect of re-activation, the recovered catalyst was recalcined at 700 °C for 5 h in static air atmosphere (as done for as-synthesized LDH) and tested for the reaction.

Results and discussion

Ring opening reaction with methanol

For the initial screening, various catalysts were chosen for the ring opening of ECO with methanol (Scheme 1; Reaction A) as nucleophile at 60 °C for 4 h and the results are given in Table 1. Thermal heating of ECO (blank reaction) in toluene at 60 °C in the absence of catalyst showed only 2% conversion of oxirane ring suggests the thermal stability of ECO and also supports the authenticity of the methodology employed for calculating conversion using ^{1}H NMR spectroscopy. Reaction of ECO with methanol in toluene in the absence of catalyst gave only 2% conversion suggests the necessity of the catalyst for the ring opening reaction under the conditions studied. Resin based acidic and basic catalysts were studied that gave conversion in the range of 9-18% except for Amberlyst 15 which gave 34% conversion.

Though Nafion is a well-known acid catalyst, gave lesser conversion (15%) might be due to its rigid nature. Further, as Nafion was used as ‘as-received’ beads for the catalytic studies, there is likely that the reactant molecules do not have easy accessibility to the catalytically active sites. Solid base MgAl3-LDH catalyst gave 12% conversion which is comparatively lesser than Amberlyst 15. When comparing the results of Amberlyst A 26 (OH) and MgAl3-LDH with Amberlyst 15, one could infer that the acidity of the catalyst plays an important role in the conversion of oxirane ring. Under the reaction condition studied, homogeneous zinc triflate catalyst gave 53% conversion which is slightly higher than the heterogeneous Amberlyst 15 catalyst (comparison of ^{1}H NMR spectrum of ECO along with the reaction product mixture are given in ESI† Fig. S1). All the resin based materials have acidity in the range of 0.5-1 meq H^+/g whereas Amberlyst 15 has 4.9 meq H^+/g. Sulphonic acid is the main functional group in the resin based catalysts and it was found that compared to other resin catalysts/sulphated zirconia, Amberlyst 15 has higher sulphur content that supported well for its higher acidity. These results clearly show that higher acidity of Amberlyst 15 is the probable reason for the higher conversion of ECO. Hence, Amberlyst 15 was selected as catalyst for the ring opening of ECO with methanol for further studies.

Parametric variation studies

After the screening of catalysts, several reaction parameters such as methanol:ECO molar ratio, catalyst wt.%, time, temperature and solvent were varied to improve the conversion

RSC Advances RSCPublishing

ARTICLE

Table 1 Preliminary catalyst screening and catalyst characterization for the ring opening of ECO

Catalyst[a]	Conversion of oxirane ring (%)	Acidity (meq H^+/g)[b]	Sulphur content (%)[c]
Blank reaction[d]	2	-	-
Nil[e]	2	-	-
Amberlite IR 120	14	1	8.5
Amberlite 200 C	11	0.6	11
Amberlyst 15	34	4.9	12.9
Amberlite IRA 67	18	0.8	0.2
Amberlite IRA-402 Cl	16	0.9	0.2
Amberlyst A-26 (OH)	9	0	0
Sulphated zirconia	22	2.4	3.9
Nafion	15	-	-
MgAl3-LDH	12	0.6	-
Zinc triflate[f]	53	5.9	-

[a]ECO = 0.5 g, Methanol:ECO = ~60:1 molar ratio, Toluene = 3 ml, Catalyst = 5 wt.% w.r.t. ECO, Temp. = 60 °C, Time = 4 h; [b]Acid-base titration; [c]Based on CHNS analysis; [d]Reaction of ECO in Toluene in the absence of catalyst; [e]Reaction of ECO and methanol in toluene in the absence of catalyst; [f]Homogeneous reaction.

(ESI† Fig. S2; A-F). A maximum oxirane conversion of 82% was achieved with methanol:ECO molar ratio of ~180:1, 10 wt.% catalyst at 105 °C in 4 h using toluene as solvent. FT-IR spectra of ECO and methoxylated castor polyol (MCP; ring-opened glyceryl ricinoleate) are given in ESI† Fig. S3. The bands present around 840 and 1250 cm^{-1} for ring C-O-C stretching band in ECO were almost disappeared for the ring-opened MCP confirms the conversion of oxirane ring. The band appeared at 1220 cm^{-1} in MCP represents the C-O_{str} vibration of ether indicates the product formation. In both ECO and MCP, the band appeared at 1750 cm^{-1} corresponds to the ester carbonyl of glyceride moiety suggests the retention of glyceryl moiety. The bands appeared around 3500 cm^{-1} are attributed to ν_{OH} vibration present in both ECO and MCP. Though, maximum conversion was achieved at 105 °C, some of the studies were carried out at 60 °C to discern more scientific information at which 70% conversion was ECO was observed.

Activity of Amberlyst 15 in water

Interestingly, the conversion of ECO (70%) increased to 76 and 74% upon pre-treating the catalyst in reactant methanol (for 3 h) and by powdering the catalyst respectively suggests the influence of physical state of the material on the conversion. PXRD patterns showed a subtle increase in the crystallinity ((ESI† Fig. S4; although the sample is nearly amorphous irrespective of the physical state – bead or powdered) and DRIFT measurements (ESI† Fig. S5) showed an increase in the intensity of –OH and –S-O_{str} vibration bands for the crushed sample suggest crushing might have increased the number of available sites and thus improved the conversion.

Methanol used in the studies has (≤0.2%) water content and is well-known that epoxides (also castor oil due to the presence of -OH) are sensitive to react with moisture. To find out the role of water/moisture, reaction was performed with dry methanol that showed 81% conversion confirms its detrimental role on the conversion. To further confirm, studies were extended in presence of different concentrations of water (keeping the total nucleophile amount constant; Reaction conditions: ECO = 0.5 g, Methanol and water = 3 g, Toluene = 3 ml, Catalyst = 10 wt.% w.r.t. ECO, Temp. = 60 °C, Time = 4 h). Reaction without water gave 70% conversion while it decreased to 24 and 16% when 1 g (33 wt.%) and 2 g (66 wt.%) of water present in the system respectively. Reaction only with water gave 6% conversion suggests diol formation is less favourable than hydroxyl ether under the conditions studied. In addition, the presence of -OH group in ricinoleate may interfere strongly in the case of water as nucleophile and in turn result poorer conversion.

RSC Advances RSCPublishing

ARTICLE

Table 2 Ring opening ECO with different nucleophiles

Nucleophile[a]	**Conversion of oxirane ring (%)**	**Characteristic proton peaks in ^{1}H NMR (δ in ppm)**[b]
Methanol	82	3.5-3.4 (t, $-OCH_3$;ether)
Ethanol	60	3.8-3.6 (q, $-CH_2$;ether)
n-propanol	51	3.7-3.5 (q, $-CH_2$;ether)
Iso-propanol	47	4.0-3.9 (q, -CH ;next to -OH)
Water[c]	49	3.66-3.35 (s, -OH ;diol)
Acetic anhydride	69	3.4-3.5 (t, $-OCH_3$;ester)
Acetone	39	1.4 (s, $-CH_3$;ketal)
Diethyl amine	24	2.7-2.8 (q, $-CH_2$;amine)
Sodium azide/water	4	-

[a]ECO = 0.5 g, Nucleophile: ECO = ~180:1 molar ratio, Toluene = 5 ml, Catalyst = 10 wt.% w.r.t. ECO, Temp. = 105 °C, Time = 4 h; [b]Supports the yield of products. [c]White gel like material.

Leaching and hot filtration studies over Amberlyst 15

Calculated amount of water was taken along with catalyst (pH of the medium: 4.6) and stirred well at 60 °C for 4 h. Collected water (pH = 2.6) was used for the ring opening of ECO withmethanol at 60 °C for 4 h in the absence of catalyst which showed 22% conversion (similar to when the reaction was carried out in presence of catalyst with same wt. % of water in methanol; *vide supra*) while the recovered catalyst (dried) showed 45% conversion. This suggests homogeneous contribution of the reaction when aqueous methanol was used probably due to leaching of acidic moieties of Amberlyst 15. To unravel further, hot filtration studies were carried wherein the catalyst was removed by filtration at different time under hot conditions and the reaction was allowed further to continue in the absence of catalyst for 4 h (ESI† Fig. S6). A conversion of 11, 18 and 22% was observed in 4 h for the catalyst-removed at 0.5, 1 and 2 h filtrates respectively while 24% was observed in the presence of catalyst. This further confirms the significant homogeneous contribution of leached acidic moieties under the reaction conditions. Furthermore, FT-IR spectra of the water-treated Amberlyst 15 showed a sharp decrease in the intensity of the band around 1200 cm^{-1} that corresponds to the S-O$_{str}$ vibration corroborates the observed decrease in the activity (ESI† Fig. S7).

Role of glyceryl moiety and the functional group

In order to find out the role of glyceryl moiety present in the ECO, ring opening reaction was carried out for epoxidized methyl ricinoleate (EMR) with methanol. Under identical conditions (~60:1 molar ratio of methanol:substrate, 10 wt.% catalyst, 60 °C, 4 h) ECO gave 34% conversion whereas the same for EMR was 76% (ESI† Fig. S8). This shows that compared to viscous ECO, its corresponding methyl ricinoleate derivative can easily undergo epoxide ring opening probably due to the hindrance offered by glyceryl moiety present in former. Under identical conditions (Epoxide = 0.5 g, Methanol:substrate = ~45:1 molar ratio, Toluene = 3 ml, Catalyst = 10 wt.% w.r.t. substrate, Temp. = 60 °C, Time = 4 h), EMR, epoxidized ethyl linoleate (EEL) and 1,2-epoxy hexadecane showed 39, 64 and 75% conversion of oxirane ring respectively. These results suggest simple fatty epoxides and terminal epoxides can easily undergo ring opening reaction than functionalized fatty epoxides. The only structural difference between EMR and EEL is the presence of -OH group instead of unsaturated centre in the former. To further understand the variation in the activity, Amberlyst 15 was treated with EMR and EEL under neat condition at 60 °C for 4 h and the catalysts were recovered and FT-IR was recorded. A sharp decrease in S-O$_{str}$ vibration (at 1200 cm^{-1}) was observed for EMR treated catalyst (ESI† Fig. S9) indicates strong interaction of sulphonic groups with -OH group of EMR that in turn lead to lesser conversion.

Ring opening reaction with different nucleophiles

For scientific curiosity and expanding the scope, ring opening of ECO with different nucleophiles were studied and the results are given in Table 2. Increase in the chain length of alcohols (C_1-C_3) resulted a decrease in the conversion of ECO. Ring opening of ECO with water to produce polyol (diol formation in the place of oxirane) gave 49% conversion. The product mixture became white gel like material and FT-IR spectra

Table 3 Two-pot reactions for the preparation of ring-opened alkyl ricinoleates

Entry No.	Pathway	Reaction (as per Scheme 1)	Conversion of oxirane ring (%)	Yield of transesterified product (%)
1.	Ring opening of ECO with methanol followed by transesterification of methoxylated castor polyol (MCP) with methanol	Reaction A[a]	81	
		Reaction C[b]		83
2.	Transesterification of ECO with methanol followed by ring opening of epoxy methyl ricinoleate (EMR) with methanol	Reaction B[c]		91
		Reaction C'[d]	76	
3.[e]	Ring opening of ECO with *iso*-propanol followed by transesterification of isopropoxylated castor polyol (IPCP) with methanol	-[a]	47	
		-[b]		81

[a] Alcohol:ECO = ~ 180:1 molar ratio, Toluene = 5 ml, Catalyst (Amberlyst 15) =10 wt.% w.r.t. ECO, Temp. = 105 °C, Time = 4 h; [b] Methanol:Alkoxylated castor polyol (MCP/IPCP) = ~ 18:1 molar ratio, Catalyst (CaAl2-CLDH$_{700}$) = 5 wt.% w.r.t. oil, Temp. = 65 °C, Time = 5 h; [c] Conditions same like (b) except Methanol: ECO = ~ 18:1 molar ratio; [d] Conditions same like (a) except Methanol: EMR = ~ 60:1 molar ratio; [e] Isopropanol as nucleophile for ring opening reaction.

supported the conversion of oxirane ring as well as formation of -OH group (ESI† Fig. S10). Ring opening of ECO with acetic anhydride resulted 69% conversion which is comparatively higher in shorter time than a recent report.[14j] Ring opening of ECO with acetone gave 39% conversion with the formation of ketals while ring opening of ECO with diethyl amine gave 24% conversion which resulted aminated polyols. Sodium azide along with water is known for the preparation of nitrogen containing oil derivatives;[14b] but gave only 4% conversion under the studied reaction conditions. ^{1}H NMR profile of ring opening of ECO with different nucleophiles are given in ESI† Fig. S11 and S12.

Transesterification reaction

Transesterification of epoxidized castor oil with methanol (Scheme 1; Reaction B) in presence of 700 °C calcined CaAl-layered double hydroxides (CaAl2-CLDH$_{700}$) as heterogeneous base catalyst rendered 91% yield of epoxidized methyl ricinoleate (ESI† Fig. S13). Under identical conditions (Alcohol:oil = ~18:1 molar ratio, Catalyst = 5 wt.% w.r.t. ECO, Temp. = 65 °C, Time = 5h), mixed oxides derived from MgAl3-LDH gave only 22% yield of transesterified product. This indicates the presence of sites having higher basic strength range and higher density of basic sites in CaAl-LDH derived mixed oxides play a crucial role in the transesterification reaction.[21] Transesterification of castor oil with methanol (methanol:oil = ~12:1 molar ratio) using the same active catalyst showed 74% yield of methyl ricinoleate at 65 °C in 5 h (ESI† Fig. S14).

Depending on the availability of alcohol feedstock, transesterification reaction can be performed with different chain length alcohols which results fatty acid alkyl esters with different properties. Transesterification of ECO with ethanol (or) propanol did not work under the optimized reaction conditions adopted for methanol (reactions were carried out at reflux temperature). In order to synthesize epoxidized alkyl ricinoleates, epoxidized methyl ricinoleate (EMR) was further transesterified with different alcohols (Scheme 1; Reaction D) such as ethanol, *n*-propanol and *iso*- propanol which showed 49, 35 and 23% yield of corresponding epoxidized alkyl ricinoleates respectively (ESI† Table S1). In other words, an increase in the chain length decreased the yield of epoxidized alkyl ricinoleates as elucidated from the appearance of characteristic peak at 4.2-4.1 ppm in ^{1}H NMR that corresponds to -OCH$_2$ protons (ESI† Fig. S15).

Two-pot reactions

Ring-opened alkyl ricinoleates can be prepared by ring opening of epoxidized castor oil followed by transesterification of derived ring-opened glyceryl ricinoleate (Scheme 1; Reaction C) (or) transesterification of epoxidized castor oil followed by ring opening of derived epoxy alkyl ricinoleate (Scheme 1; Reaction C'). In the current study, both the pathways were studied and the results are given in Table 3 (Entry No. 1& 2). In both the cases, conversions of oxirane ring towards ring-opened products were 81 and 76% whereas the yields of transesterified products were 83 and 91% respectively. These results bestow that ring-opened alkyl ricinoleates (methoxylated methyl ricinoleate; MMR) can be effectively prepared by carrying the above mentioned reactions in a two-pot synthesis. Reaction C was also extended for transesterification of isopropoxylated castor polyol (IPCP) with methanol (Table 3; Entry No. 3) for the preparation of isopropoxylated methyl ricinoleate (IPMR).

RSC Advances RSCPublishing

ARTICLE

Table 4 Physical properties of neat and blended castor oil, epoxidized castor oil and ring-opened glyceryl ricinoleates

Property	**CO**[a]	**ECO**[b]	**CO + ECO**[c]	**Ring-opened glyceryl ricinoleates**				
				MCP[d]	**IPCP**[e]	**MCP+ IPCP**[c]	**HCP**[f]	**ACP**[g]
Appearance	Golden yellow (liquid)	Pale yellow (liquid)	Pale yellow (liquid)	Pale yellow (liquid)	Pale yellow (liquid)	Pale yellow (liquid)	Milky white (gel)	Brown Yellow (liquid)[m]
Chemical formula	$C_{57}H_{104}O_9$	$C_{57}H_{104}O_{12}$	-	$C_{60}H_{116}O_{15}$	$C_{66}H_{128}O_{15}$	-	$C_{57}H_{110}O_{15}$	$C_{69}H_{137}N_3O_{12}$
Molecular weight (g/mol)[h]	~933	~981	-	~1077	~1161	-	~1035	~1200
Density (kg/m^3)	0.94	1.03	0.99	0.97	0.98	0.99	-	0.95
Iodine number[i]	16.0	3.1	11.6	2.4	2.5	3.4	2.9	2.7
Oxirane group content (%)[i]	0	4.0	1.3	0.9	2.3	1.0	2.9	1.2
Relative oxirane conversion[i]	0	0.81	0.26	0.18	0.46	0.20	0.59	0.25
Viscosity (Cp)[j]	360	4625	972	1020	4007	1644	-	370
Oxidative stability at 30 °C (h)[k]	3581	-[l]	4951	42552	112016	1298	-	-
Oxidative stability at 110 °C (h)[k]	118.7	-[l]	15.0	43.9	61.1	3.2	-	194.4
Oxidative stability at 120 °C (h)[k]	77.6	-[l]	7.3	18.6	23.9	1.5	-	-[l]

[a]Castor oil; [b]Epoxidized castor oil; [c]Blended in 1:1 w/w%; [d]Methoxylated castor polyol; [e]Isopropoxylated castor polyol; [f]Hydroxylated castor polyol; [g]Aminated castor polyol; [h]Maximum molecular weight is given; [i]^{1}H NMR analysis; [j]at 25 °C; [k]Rancimat analysis; [l]Occurrence of solidification of sample restricted the analysis; [m]Nitrogen content is 2% (based on CHNS analysis).

Scale-up studies

Ring-opened glyceryl ricinoleates were successfully prepared up to 25 g (MCP and IPCP were prepared on 100 g scale) using various nucleophiles. Epoxy alkyl ricinoleates and ring-opened alkyl ricinoleates were also prepared up to 25 g (EMR and MMR were prepared on 50 and 250 g scale respectively). On higher scale for the ring opening reactions, alcohol:oil molar ratio was fixed as ~60:1 (except for hydroxylated castor polyol (HCP) preparation where ratio was 100:1). For transesterification reaction, methanol:oil molar ratio was fixed as ~18:1 and 12:1 for ECO and CO respectively. In all the cases, conversion/yield of the products were similar as that of normal reaction scale (0.5/5 g) that substantiate good efficacy of the catalysts even while working at higher scale. CO, ECO and formed products are confirmed by ESI-MS analysis (ESI† Fig. S16-S26) and interestingly in the case of transesterification reaction, along with EMR and MR diglycerides were also present which shows partial completion of reaction (suggest requirement of harsher reaction conditions).

Physical property measurements

Various physical properties were measured for neat, ring opened glyceryl ricinoleates, epoxy alkyl ricinoleates, ring opened alkyl ricinoleates and their blended forms whose values are summarized in Table 4 and 5. Density of castor oil is 0.94 kg/m^3 whereas the obtained products showed variable densities from 0.87-1.03 kg/m^3. Decrease in the iodine number of the functionalized castor derivatives compared to CO/MR further confirmed the participation of double bonds in the epoxidation reaction. Functionalized derivatives showed almost similar iodine number values as that of ECO/EMR while a decrease in the oxirane group (epoxy oxygen) content values were observed indicates the formation of ring opened products. ECO and MCP showed 12.8 and 2.8 times higher viscosity than CO whereas ACP showed almost same viscosity like CO. Interestingly, IPCP showed only 1.2 times lesser viscosity than ECO and may be due the presence of higher epoxide (lesser conversion of ECO). EMR (transesterified product) showed 96 times lesser viscosity than ECO and MR (transesterified product) showed 16.3 times lesser viscosity than CO. Ring-opened alkyl ricinoleates showed 1.5 to 4 times higher viscosity than MR

Table 5 Physical properties of neat and blended methyl ricinoleate, epoxidized alkyl ricinoleate and ring-opened alkyl ricinoleates

Property	**MR**[a]	**Epoxidized alkyl ricinoleates**		**Blended epoxy ricinoleates**		**Ring-opened alkyl ricinoleates**		
		EMR[b]	**EPR**[c]	**MR+ EMR**[d]	**EMR+ EPR**[d]	**MMR**[e]	**IPMR**[f]	**MMR+ IPMR**[d]
Appearance	Golden yellow (liquid)	Pale yellow (liquid)	Pale yellow (liquid)	Pale yellow (liquid)	Pale yellow (liquid)	Golden yellow (liquid)	Pale yellow (liquid)	Golden yellow (liquid)
Chemical formula	$C_{19}H_{36}O_3$	$C_{19}H_{36}O_4$	-	-	-	$C_{20}H_{40}O_5$	$C_{22}H_{44}O_5$	-
Molecular weight (g/mol)[g]	~312	~328	~356	-	-	~360	~388	-
Density (kg/m^3)	0.87	0.91	0.96	0.90	0.95	0.95	0.91	0.94
Iodine number[h]	15.4	0.6	0.4	11.5	0.5	0.4	0.5	0.4
Oxirane group content (%)[h]	0	3.95	3.66	1.95	3.56	0.78	0.50	0.63
Relative oxirane conversion[h]	0	0.81	0.75	0.40	0.73	0.16	0.10	0.13
Viscosity (Cp)[i]	22	48	60	24	72	91	70	103
Oxidative stability at 30 °C (h)[j]	342	5221	27067	5051	34510	195	93865	21.3
Oxidative stability at 110 °C (h)[j]	2.9	22.9	263.2	194.4	270.4	194.4	34.8	20.6
Oxidative stability at 120 °C (h)[j]	1.6	11.6	147.5	129.4	147.5	194.3	13.0	20.5

[a]Methyl ricinoleate; [b]Epoxy methyl ricinoleate; [c]Epoxy propyl ricinoleate; [d]Blended in 1:1 w/w%; [e]Methoxylated methyl ricinoleate; [f]Isopropoxylated methyl ricinoleate; [g]Maximum molecular weight is given; [h]^{1}H NMR analysis; [i]at 25 °C; [j]Rancimat analysis.

and epoxy derivatives. These studies show that glyceride moiety present in the CO/ECO is the reason for their higher viscosity than methyl ricinoleate (or) epoxy ricinoleates (or) ring-opened alkyl ricinoleates. Interestingly, compared to CO/MR, their corresponding epoxide derivatives showed higher viscosity suggests presence of oxirane ring enhances the viscosity of the oils/fatty derivatives. It was also observed that an increase in the chain length in fatty region/ ester region increased the viscosity of the derivatives except in the case of IPMR and it may be due to lesser oxirane content in it compared to EMR. Blended derivatives (1:1 w/w%) showed viscosity between the range of the individual derivatives suggests that viscosity can be altered by blending the derivatives in different ratios. Oxidative stability of MCP and IPCP improved 12 and 31% respectively than CO indicating the importance of functionalization of castor oils which can then be effectively utilized for industrial applications. On the other hand, oxidative stability of these derivatives decreased drastically than CO at higher temperature indicates the potential influence of atmosphere for faster degradation possibly due to free radical formation. Oxidative stability of epoxy alkyl ricinoleates is ~15 times greater than methyl ricinoleate whereas ring-opened alkyl ricinoleates exhibited lesser stability at 30 °C. Ring-opened glyceryl ricinoleates gave lesser oxidative stability which may be due to the occurrence of intramolecular functional group reactions (e.g. estolides formation) that might facilitate degradation of the molecules. However at higher temperature, the oxidative stability of ring-opened alkyl ricinoleates improved than methyl ricinoleate, epoxy alkyl ricinoleates and glyceryl ricinoleates.

One-pot reaction

Ring-opened alkyl ricinoleates are interesting molecule which can beprepared by earlier discussed two different reaction chemistries. Instead of two-pot reaction, this molecule can be prepared by one-pot reaction by taking both heterogeneous acid and base catalysts together (Scheme 1; Reaction E). Results of one-pot reaction for the preparation of methoxylated methyl ricinoleate (MMR) are given in ESI† Table S2. Reaction performed for 5 h reaction time resulted 61% conversion of ECO and 59% yield of transesterified products. A further increase in the reaction time to 48 h did not have any influence on the conversion of ECO whereas the yield of transesterified product slightly increased to 67%. Comparison of ^{1}H NMR spectra of MMR prepared by two-pot as well one-pot reactions are given ESI† in Fig. S27. The peaks appeared at 3.7 ppm corresponds to terminal methoxy (-OCH_3) protons confirms the occurrence of transesterification reaction whereas the peaks at 3.5-

3.3 corresponds to internal methoxy protons confirms the ring opening reaction. The peaks appeared at 3.2-2.8 ppm in one-pot reaction suggests lesser conversion of ECO.

ESI-MS analysis was done for the mixture obtained from one-pot reaction (5 h reaction time; as per the data Table S2; Entry No. 1) and the mass fragmentation patterns are given in ESI† Fig. S28. Molecules such as ECO, EMR and MMR showed intense signals corresponds to $[M+Na]^+$ rather than their original expected m/z values. Intense signal appeared at 1078 corresponds to $[M+1]^+$ for MCP. Also, m/z values appeared at 680-700 represents the presence of diglyceride in the mixture which indicates incomplete transesterification reaction. Oxirane group content and relative oxirane conversion are 1.57 and 0.32% respectively for the mixture obtained through one-pot reaction. These values are in between the values of ECO and MCP which supports lesser conversion of ECO to MCP under the studied conditions.

Recycle studies

Amberlyst 15 was recycled up to 4 cycles for the ring opening of ECO with methanol under the optimized reaction conditions with slight change in its activity (Fig. 1). Acidity measurements showed almost no change after every cycle (4.9 & 4.4 meq H^+/g in fresh catalyst & after first use); however, interestingly a subtle increase in the pH of the medium was observed after first cycle which was almost constant for subsequent cycles (pH of the medium before reaction for 1st cycle: 2.3; remaining all cycles: ~ 6).

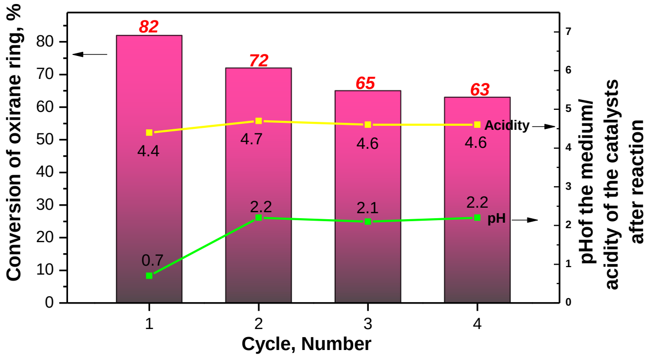


Fig. 1 Reusability studies of Amberlyst 15 for ring opening of ECO with methanol. Methanol:ECO =~180:1, Catalyst = 10 wt.% w.r.t. ECO, Toluene = 5 ml, Temp.=105 °C, Time =4 h.

Reusability studies of recovered CaAl2-CLDH$_{700}$ gave 27% yield of epoxy methyl ricinoleate during the second run. It was reported that recalcination of the recovered catalyst can improve the transesterification efficacy.[22] To retain the activity, the recovered catalyst was recalcined at 700 °C for 5 h in static air atmosphere. Reaction performed using the recalcined catalyst showed 60% yield of epoxy methyl ricinoleate during the third run (Fig. 2).

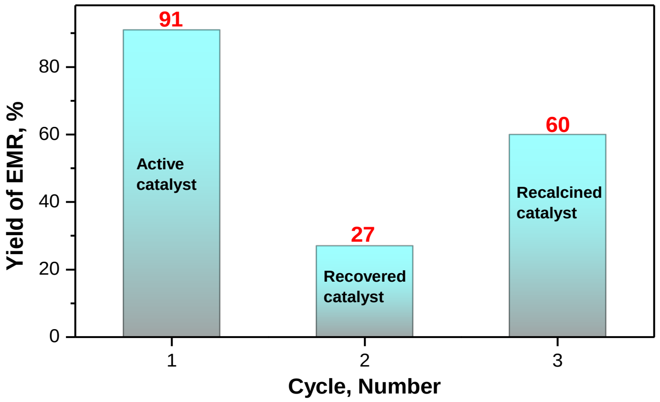


Fig. 2 Reusability studies of CaAl2-CLDH$_{700}$ for transesterification of ECO with methanol. Methanol:ECO = 18:1, Catalyst = 5 wt.% w.r.t. ECO, Temp. = 65 °C, Time = 5 h.

Reusability studies of the catalyst recovered from one-pot reaction (8 h reaction time; as per the data Table S2, Entry no. 2) resulted 29% conversion of ECO with 5% yield of transesterified product. This result suggests that the activity of the acid and base catalysts decreases drastically after first run when they were used together.

Conclusions

Among various heterogeneous acid catalysts screened, Amberlyst 15 is the most efficient catalyst for the ring opening of ECO with methanol. The high activity of this catalyst was attributed to its higher acidity. By optimizing the parameters, a maximum conversion of 82% was achieved at 105 °C in 4 h using toluene as solvent. The catalyst was successfully recycled up to 4 cycles with slight loss in its activity. The scope of this reaction was extended to various nucleophiles such as alcohols, acetone, diethyl amine and water with moderate conversion (24-70%). Transesterification of ECO with methanol gave 91% yield of EMR using mixed oxides derived from CaAl-LDH as heterogeneous base catalyst within 5 h at 65 °C without affecting oxirane ring. Transesterification of EMR with higher alcohols such as ethanol (or) n-propanol/iso-propanol rendered 49-23% yield of alkyl ricinoleates. This catalyst showed a decrease in its activity while recycling and could partially be restored by recalcining at 700 °C for 5 h. MMR was prepared from ECO and methanol with 61% conversion of oxirane ring and 59% yield of transesterified product by using both these acid and base catalysts together in a one-pot reaction. The physical properties measured for these ring opened and transesterifed derivatives suggest the possibility of tailoring the values by suitably choosing the appropriate nucleophiles, besides simple blending of them. The reaction chemistry presented here along with the propensity of modifying the physical properties endorse the potential use of these castor-based derivatives in industrial application in the field of lubricants, plasticizers and in rheology.

RSC Advances RSCPublishing

ARTICLE

Acknowledgements

CSIR-CSMCRI Communication No. 077/2014: Authors thank CSIR, New Delhi for financial support under the network project Indus MAGIC (CSC-0123). Authors thank “Analytical Division and Centralized Instrumental Facilities” for providing instrumentation facilities. Authors also thank M/s Jayant Agro Organics Ltd., Mumbai for providing castor oil derivative samples.

Notes and references

[a]Inorganic Materials and Catalysis Division, CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Council of Scientific & Industrial Research (CSIR), Gijubhai Badheka Marg, Bhavnagar- 364 002, (Gujarat), INDIA.

[b]Academy of Scientific and Innovative Research, CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Council of Scientific & Industrial Research (CSIR), Gijubhai Badheka Marg, Bhavnagar- 364 002, (Gujarat), INDIA

†Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [FT-IR spectra of products and catalysts, ^{1}H NMR spectra of reactant and different product molecules, reaction parameter variation studies, hot filtration leaching studies, ESI-MS analysis of reactants and products, transesterification with different alcohols, one-pot reaction using both acid and base catalysts]. See DOI: 10.1039/b000000x/

1 G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044.

2 A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick Jr., J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484.

3 (a) K. Hill, *Pure Appl. Chem.*, 2000, **72**, 1255; (b) U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger and H. J. Schafer, *Angew. Chem. Int. Ed.*, 2011, **50**, 3854.

4 P. A. Z. Suarez, M. S. C. Pereira. K. M. Doll, B. K. Sharma and S. Z. Erhan, *Ind. Eng. Chem. Res.* 2009, **48**, 3268.

5 B. R. Moser and S. Z. Erhan, *Eur. J. Lipid Sci. Technol.*, 2007, **109**, 206.

6 K. M. Doll, B. K. Sharma and S. Z. Erhan, *Ind. Eng. Chem. Res.*, 2007, **46**, 3513.

7 G. Du, A. Tekin. E. G. Hammond and L. K. Woo, *J. Am. Oil Chem. Soc.*, 2004, **81**, 477.

8 (a) C. C. Enweremadu and M. M. Mbarawa, *Renew. Sust. Energ. Rev.*, 2009, **13**, 2205; (b) P. Campanelli and M. Banchero, L. Manna, *Fuel*, 2010, **89**, 3675.

9 A. Nezihe, D. Elif, Y. Ozlem and E. A. Tuncer, *Ind. Eng. Chem. Res.*, 2011, 50, 398.

10 D. S. Ogunniyi, *Bioresour. Technol.*, 2006, **97**, 1086.

11 I. B. Banković-Ilić, O. S. Stamenković and V. B. Veljković, Renew. Sust. Energ. Rev., 2012, **16**, 3621.

12 A. Dupé, M. Achard, C. Fischmeister and C. Bruneau, *ChemSusChem*, 2012, **5**, 2249.

13 J. K. Satyarthi and D. Srinivas, *Appl. Catal. A: Gen.*, 2011, **401**, 189.

14 (a) Y. Guo, J. H. Hardesty, V. M. Mannari and J. L. Massingill Jr., *J. Am. Oil Chem. Soc.*, 2007, **84**, 929; (b) A. Biswas, B. K. Sharma. J. L. Willett, A. Advaryu, S. Z. Erhan and H. N. Cheng, *J. Agric. Food Chem.*, 2008, **56**, 5611; (c) A. Biswas, B. K. Sharma, K. Vermillion, J. L. Willett and H. N. Cheng, *J. Agric. Food Chem.*, 2011, **59**, 3066; (d) B. K. Sharma, A. Advaryu and S. Z. Erhan, *J. Agric. Food Chem.*, 2006, **54**, 9866; (e) A. Biswas, A. Adhvaryu, S. H. Gordon, S. Z. Erhan and J. L. Willett, *J. Agric. Food Chem.*, 2005, **53**, 9485; (f) K. M. Doll and S. Z. Erhan, *Green Chem.*, 2008, 10, 712; (g) K. M. Doll, G. B. Bantchev and R. E. Murray, *ACS Sustain. Chem. Eng.*, 2013, **1**, 39; (h) M. Guidotti, R. Psaro, N. Ravasio, M. Sgobba, F. Carniato, C. Bisio, G. Gatti and L. Marchese, *Green Chem.*, 2009, 11, 1173; (i) L. A. Rios, B. A. Llano and W. F. Hoelderich, *Appl. Catal. A: Gen.*, 2012, **445-446**, 346; (j) R. V. Sharma and A. K. Dalai, *Appl. Catal. B: Environ.*, 2013, **142-143**, 604.

15 (a) G. Fogassy, P. Ke, F. Figueras, P. Cassagnau, S. Rouzeau, V. Courault, G. Gelbard and C. Pinel, *Appl. Catal. A: Gen.*, 2011, **393**, 1. (b) B. K. Ahn, H. Wang, S. Robinson, T. B. Shrestha, D. L. Troyer, S. H. Bossmann and X. S. Sun, *Green Chem.*, 2012, **14**, 136.

16 K. Lee, L. L. C. Wong, J. J. Blaker, J. M. Hodgkinson and A. Bismarck, *Green Chem.*, 2011, **13**, 3117.

17 N. W. Higgins and J. F. Stults, U.S. Patent 7947847, May 24, 2011.

18 P. S. Lathi and B. Mattiasson, *Appl. Catal. B: Environ.*, 2007, 69, 207.

19 F. Ma and M. A. Hanna, *Bioresour. Technol.*, 1999, 70, 1.

20 R. A. Holser, *Ind. Crop. Prod.*, 2008, **27**, 130.

21 S. Sankaranarayanan, C. A. Antonyraj and S. Kannan, *Bioresour. Technol.*, 2012, **109**, 57.

22 S. Sankaranarayanan and S. Kannan, *Int. J. Adv. Eng. Sci. Appl. Math.*, 2013, **5**, 210.