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Article

Preparation, Characterisation and Evaluation of Brazilian Clay-Based Catalysts for use in Esterification Reactions

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Catalisadores a base de argilas naturais brasileiras foram preparados, caracterizados, e sua atividade catalítica foi avaliada em reações de esterificação. As argilas naturais foram ativadas por tratamento ácido como recebidas, sem qualquer tratamento prévio. As argilas naturais e as argilas ácidas foram caracterizadas por DRX, TPD-NH_3, termodessorção de *n*-butilamina, análise de adsorção de N_2, FT-IR, TGA e DTA. O desempenho catalítico foi investigado em reações de esterificação de diversos ácidos carboxílicos com diferentes álcoois. As reações foram realizadas com razão molar ácido carboxílico/álcool 1:3, a 100 °C e pressão atmosférica, por 3 h. As argilas ácidas forneceram boas conversões e apresentaram desempenho melhor que a argila comercial K10.

Natural Brazilian clay-based catalysts were prepared, characterised, and their catalytic activity was assessed in esterification reactions. The natural clays were acid activated as received, without any previous treatment. Both natural and acid-activated clays were characterised by XRD, NH_3-TPD, thermodesorption of *n*-butylamine, N_2 adsorption analysis, FT-IR, TGA and DTA. The catalytic performance was investigated in the esterification of several carboxylic acids with different alcohols. The reactions were carried out in a 1:3 carboxylic acid/alcohol molar ratio at 100 °C and atmospheric pressure for 3 h. The acid-activated clays provided good yields and better performance than commercial clay K10.

Keywords: acid activation, clay, smectite, esterification

Introduction

Esterification reactions are widely employed in a variety of chemical industries.[1] The procedure generally uses either sulfuric, hydrochloric or sulfonic acid as catalyst. These catalysts generate large quantities of acidic waste, which require appropriate treatment before disposal. The most widely used catalyst is sulfuric acid. It is a low cost reagent and is very active. However, it is also corrosive and presents problems of storage and control.[2]

To minimise the problems associated with the homogeneous process, intensive research has been recently devoted to the development of heterogeneous catalysts for esterification. Some examples include functionalised mesoporous materials,[3,4] ion-exchange resin,[1] oxides[5-7] and metal complexes.[8,9]

There is considerable interest in developing catalysts based on clays. In terms of their environmental aspect, these materials are one of the most friendly solid catalysts. Additionally, clay-based catalysts are very promising because of the low cost of the raw material, ease of properties manipulation and ease of recovery and reuse.[10] Ion exchange capacity and the potential for increased interlayer spacing are important characteristics of clay minerals that strongly influence their physical-chemical and technological properties. These characteristics, as well as their high surface area, have lead clay minerals to be explored as catalysts. The acid activation method is usually employed to modify the textural characteristics of clays.

Clays are being employed successfully in many organic reactions, and smectites are most often used.[11-17]

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There have also been studies using other minerals.[18-21] With respect to esterification, some studies have used commercial, metal-exchanged and heteropoly acid supported montmorillonite.[22-28] We report here the preparation, characterisation and catalytic activity of two Brazilian clay-based catalysts in esterification reactions at atmospheric pressure and without a Dean-Stark apparatus or co-solvent.

Experimental

Materials

The two natural clays were from Boa Vista District, Paraíba, Brazil. Sulfuric acid, lauric acid, sodium sulfate, hexanol and cyclohexanol were purchased from Vetec (Brazil). *n*-Butylamine, phenylacetic, benzoic and cyclohexanoic acids were from Aldrich (USA). Ethyl acetate, hexane and methanol were from Tedia (Brazil) and silica gel (70-230 mesh) was from Merck (USA).

Catalysts preparation

The two clays were completely crushed and passed through a 60 mesh sieve. The homogenised clays, called BBn and VLn, were acid-activated, without any previous treatment, in a round-bottom flask connected to a reflux condenser.[29] A 10% m/v suspension of clay in 4 mol L^{-1} sulfuric acid was stirred at 90 °C for 2 h. The solid was filtered under reduced pressure and washed with distilled water until the washing water has the same pH of the first. The material was dried in an oven at 110 °C for 24 h and finally ground until passage through a 60 mesh sieve again. The activated clays, called BBa and VLa, were kept in a dessicator.

Catalysts characterisation

XRD analysis was performed on a Rigaku D/Max-2A/C with Cu-Kα (λ = 1.5406 Å) at 40 kV and 20 mA. A 2θ range from 5° to 80° was scanned at 0.02° s^{-1}. BET specific surface area was measured by nitrogen adsorption data in a relative pressure range from 0.05 to 0.98, employing a Quantachrome NOVA 2200e. The average distribution of pore sizes was calculated using the BJH method. All of the adsorption and desorption isotherms were obtained at the temperature of –196 °C. Prior to each measurement, all samples were degassed at 110 °C for 5 h under vacuum.

Temperature programmed desorption of ammonia (NH_3-TPD) was performed using a CHEMBET-3000 apparatus (American Quantachrome Company). Each sample was treated at 250 °C for 50 min under a constant flow of helium (80 mL min^{-1}) prior to NH_3 adsorption. The TPD spectrum was obtained across a temperature increase from 100 °C up to 800 °C at a rate of 15 °C min^{-1}. The desorbed NH_3 was detected by a thermal detector.

The number of acid sites was estimated by thermodesorption of *n*-butylamine. Each sample was heated to 120 °C at a rate of 10 °C min^{-1} under He flow at 40 mL min^{-1}. After 30 min at 120 °C, the material was kept under He flow saturated with *n*-butylamine for 10 min. Next, pure N_2 percolated the sample during 20 min to remove any physiosorbed *n*-butylamine molecules. Thermogravimetric results were obtained under N_2 flow at 20 mL min^{-1} from 20 up to 800 °C at a rate of 10 °C min^{-1}, on a TGA-51 Shimadzu.

The thermal analysis (TGA and DTA) was done on a DTG-60 Shimadzu instrument under N_2 flow (50 mL min^{-1}). The samples were analysed from 25 to 1000 °C at a rate of 20 °C min^{-1}. The thermal analyser was a TA-60WS.

The infrared spectrum was obtained from a powder sample and KBr pellets. The analysis was performed on a Bruker Equinox 55 interferometer (Ettlingen, Germany) using a DTGS detector. The FT-IR spectrum in the range 4000 to 400 cm^{-1} is the average of 32 scans at a nominal spectral resolution of 4 cm^{-1}.

Esterification reactions

The catalysts were pre-activated in a microwave oven at 760 W for 5 min immediately before the catalytic test. This activation method does not modify the crystalline structure and the catalytic properties of clays.[30] The reaction medium was composed of carboxylic acid (4 mmol), alcohol (12 mmol) and catalyst (200 mg). The reaction was carried out in a 5 mL round-bottom flask connected to a reflux condenser and immersed in a heating bath at 100 °C. The suspension was kept under constant stirring at atmospheric pressure. After 3 h, the reaction mixture was cooled and ethyl acetate was added to extract the products. The catalyst was filtered; the organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. All of the reactions were performed in duplicate.

Conversion calculation

The conversion to ester was analysed by gas chromatography using a flame ionisation detector in a Hewlett Packard 5890 series II. A 25 m Carbowax 20M column with 0.2 mm i.d. and 0.2 µm phase film diameter was used. The carrier gas was hydrogen at a flow rate of 1.2 mL min^{-1}. The temperature program was 140 °C to 180 °C at a rate of 10 °C min^{-1}, followed by a second rate of 3 °C min^{-1} up to 220 °C. The injector and detector temperatures were held at 240 °C. A sample volume of 1.0 µL and the split mode with a 1:20 ratio were used.

The conversion to ester was determined by the internal standard (IS) addition method. Pentadecanoyl propanoate was used as IS.[31] The response factors were calculated for the carboxylic acids and for their esters. The ester standards were obtained by esterification using sulfuric acid as a catalyst. The product was purified by column chromatography over silica gel using hexane/ethyl acetate 8:1 as the eluent. GC-FID analyses indicated that the ester standards were more than 99% pure.

The standard solutions (acid and ester) and the sample solutions were prepared by mixing 10 mg of the standard (or reaction product) with 250 µL of 5000 mg L^{-1} IS solution and completing the volume to 5 mL with ethyl acetate.

Results and Discussion

Natural Brazilian clays were used without any previous treatment to eliminate organic materials, quartz, other materials or minerals. The objective was to simplify the preparation of clay-based catalysts to evaluate their potential for use in esterification reactions. Of course, for industrial use of these catalysts a deeply study is needed in order to evaluate the differences in the catalytic activity according to the composition of the clay which may vary in the mining site.

Characterisation of the catalysts

Figure 1 indicates the XRD patterns of the clays. As can be seen, the XRD shows a mixture of different minerals. The natural clays presented reflections at 14.9 Å (2θ = 5.9°), typical of smectite. The XRD analyses indicated that smectite is the dominant mineral in the two natural clays. The peaks at 2θ = 22.3° and 27.5° suggest the presence of quartz in the raw materials. Kaolinite (2θ = 12.5°), mica (2θ = 22.3°) and cristobalite (2θ = 20.8°) may also be present.

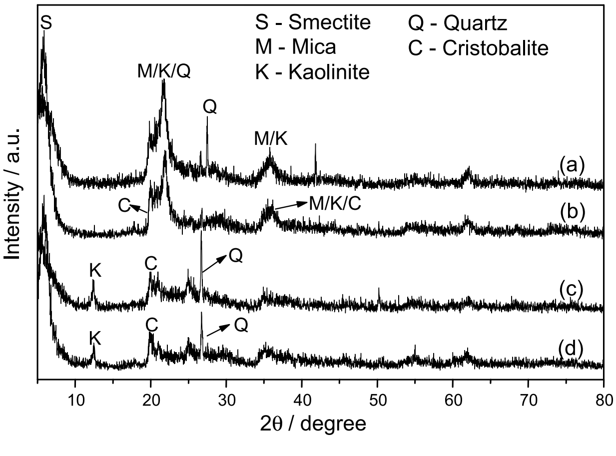

Figure 1. XRD diffraction patterns of clays: (a) BBa, (b) BBn, (c) VLa, (d) VLn.

The characterization of smectite was confirmed by the expansion of the interlayer distance by treatment with ethylene glycol. A heat treatment at 550 °C was also used to check the collapse of the structure. The XRD analyses indicated a peak at 17.2 Å (2θ = 5.1°) after the first treatment and a breakdown to 10.3 Å (2θ = 8.5°) after heating.

XRD analyses of the acid-activated clays BBa and VLa revealed that the d(001) smectite peak at 2θ = 5.9° was of a lower intensity compared with the natural samples, suggesting a partial destruction of the crystalline phase of the clays after acid treatment.

Nitrogen adsorption isotherms for the samples are indicated in Figure 2. All of the isotherms exhibit stepwise adsorption and desorption (type IV isotherms), indicating a typical mesoporous structure. The textural data are displayed in Table 1 and indicate that the surface area increased dramatically with the acid treatment. The maximum BET surface area with the maximum pore size occurred in VLa (238 m^2 g^{-1}). The corresponding pore size distributions indicate the presence of mesoporosity in the clays. The hysteresis loop observed in the isotherm can be classified as H4 type in the IUPAC system. This H4 hysteresis loop indicates that the structures are mesoporous, reinforcing the isotherm data.

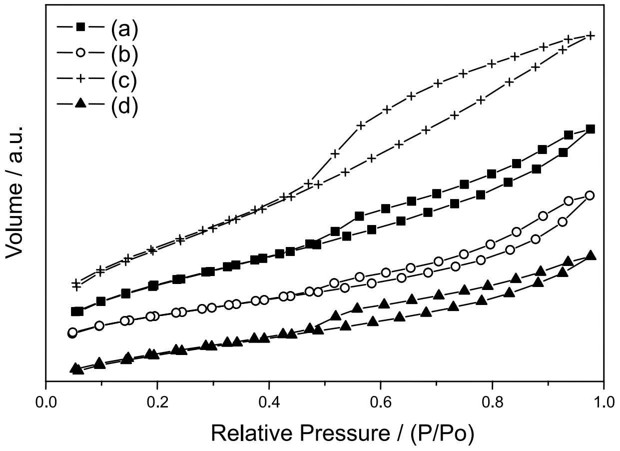

Figure 2. N_2 adsorption-desorption isotherms: (a) BBa, (b) BBn, (c) VLa, (d) VLn.

The range of NH_3 desorption temperatures for all of the catalysts are provided in Table 2. Note that the values in mV presented in Table 2 for the intensity of the peaks have a direct relation to the amount of desorbed ammonia,

Table 1. Textural properties of clays

Clays	S_{BET} / (m^2 g^{-1})	Pore diameter / Å	Pore volume / (cm^3 g^{-1})
BBa	170	40.6	0.17
BBn	123	45.8	0.14
VLa	238	41.4	0.25
VLn	71	41.0	0.07

and thus with the quantity of acid sites. Although it is not possible to obtain an absolute value, these results allow us to compare the relative surface acidities of the different catalysts studied here. The clays presented two peaks, one at lower temperatures (200 to 300 °C), related to Bronsted or weaker Lewis acid sites, and another at higher temperatures (300 to 800 °C), related to strong acid sites. The intensity of both peaks was low, leading to the conclusion that the catalysts present few acidic sites. However, it is possible to conclude that the acid treatment of BBn had not increased the acidity of the sample and that the treatment of VLn increased the weak acid sites.

Table 2. Temperature ranges and peak intensity (NH_3-TPD)

Clays	Temperature ranges / °C	Peak intensity / mV
BBa	200-300 and 300-800	6 and 11
BBn	200-300 and 300-800	8 and 11
VLa	200-350 and 350-800	15 and 8
VLn	200-300 and 300-800	6 and 13

The thermodesorption of *n*-butylamine analysis corroborate the NH_3-TPD results. The data showed that the acid treatment of VLn increased the weak acid sites but did not affect the number of moderate and strong sites. Moreover, the treatment of BBn slightly increases the weak acid sites. The number of acid sites as a function of temperature is summarized in Table 3.

Table 3. Number of acid sites (mmol g^{-1} clay) *per* range of temperature

Clays	50-150 °C	150-350 °C	350-500 °C
BBa	0.29	0.31	0.45
BBn	0.18	0.26	0.43
VLa	0.61	0.40	0.74
VLn	0.27	0.39	0.78

The TGA and DTA profiles obtained for the different clays are indicated in Table 4 and Figure 3, respectively. The DTA of the raw material revealed an intense endothermic peak between 25 and 100 °C, accompanied by a continuous loss of mass in the TGA. This peak can be attributed to the dehydration of the samples due to water molecules adsorbed in the interlayer or coordinated with exchangeable cations. The peak around 500 °C is a characteristic one and can be attributed to the loss of structural hydroxyls in iron-rich smectites. At 900 °C, a soft double endoexothermic peak appeared in the natural clays. The endothermic peak represents the destruction of the crystalline framework and structural dehydration, whereas the exothermic peak represents the formation of quartz. The TGA showed that the BBa clay is more thermally stable, losing only about 1% of its mass with increasing temperature.

Table 4. Loss of mass from the TGA curves

Temperature ranges / °C	Clays			
	BBn	BBa	VLn	VLa
25-100	4.5%	1.0%	5.0%	4.5%
100-600	3.5%	-	7.5%	3.5%
600-1000	1.5%	-	1.0%	1.0%

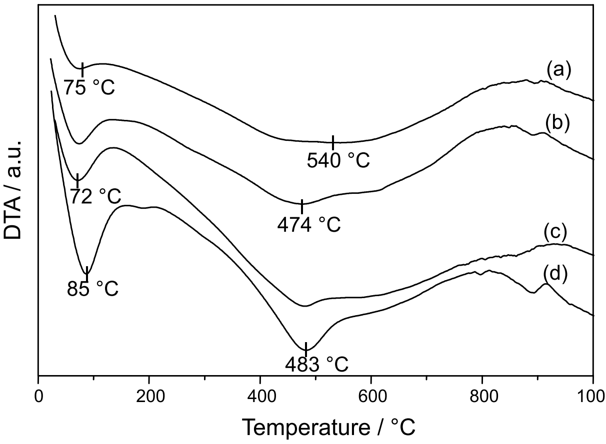

Figure 3. Differential thermal analysis (DTA) curves of clays: (a) BBa, (b) BBn, (c) VLa, (d) VLn.

The IR spectra of the clays are indicated in Figure 4. A strong band at 900-1300 cm^{-1} was assigned to asymmetric stretching of Si–O and Al–O. For BBn was observed an absorption band at 790 cm^{-1} related to the SiO_4 vibrations of non-structural silicates, which disappeared after the acid treatment. The most remarkable similarity between the natural clay spectra and those of the acid-activated clays were bands between 3700 and 3200 cm^{-1}, which can be related to structural OH^- in kaolinite (bands from 3700 and 3600 cm^{-1}), to free hydroxyl mode vibrations (at 3630 cm^{-1}), and to hydroxyl hydrogen bond at 3420 cm^{-1}, and the vibrations of associated hydroxyl groups at 1640 cm^{-1}.

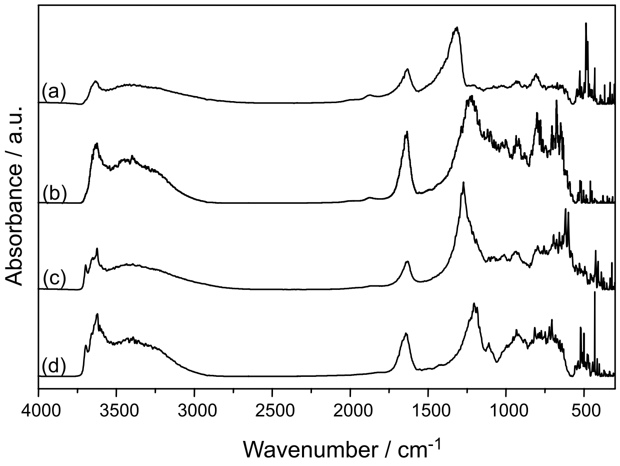

Figure 4. Infrared spectra of the studied clays: (a) BBa, (b) BBn, (c) VLa, (d) VLn.

Catalysts performance in esterification

The catalytic performance of BBn, VLn, BBa and VLa was investigated in the esterification of several carboxylic acids with different alcohols. The purpose was to evaluate the versatility of the acid-activated clays as catalysts in the synthesis of esters from carboxylic acids and alcohols with different chemical structures. The montmorillonite K10, a commercial catalyst produced by the acid treatment of raw clay,[32] was also used. The reactions were performed at atmospheric pressure, and neither a Dean-Stark apparatus nor a co-solvent was used. The duplicates presented a difference from 0.5 to 4% of conversion. The average results are summarised in Table 5.

The acid activation treatment markedly increased the catalytic activities of the clays. The conversion of lauric, cyclohexanoic and phenylacetic acids to their methyl esters was higher using BBa or VLa than with BBn or VLn. BBa and VLa also exhibited better results than did the commercial clay K10. Benzoic acid underwent no conversion under similar conditions. The selectivity of the esterification of aliphatic carboxylic acid using Fe^{3+}-K-10 montmorillonite has been demonstrated by Srinivas and Das.[23]

With the exception of the esterification of phenylacetic acid (wherein the two catalysts promoted the same conversion, *ca.* 90%), VLa presented slightly higher conversions to methyl esters than did BBa. These values can be attributed to the greater specific area and pore volume of the VLa catalyst. Both the natural and activated clays promoted the esterification of phenylacetic acid with methanol more efficiently than those of other carboxylic acids. This result may be associated with the presence of methylene in the phenylacetic acid structure, allowing the carboxyl group to rotate. This rotation increases the probability of access to the catalytic site in the clay.

The acid activation allows the esterification of phenylacetic acid with hexanol and cyclohexanol at high conversion rates. The reactions with these alcohols were carried out without cooled water circulation in the reflux condenser, which can help evaporate the water produced by the reaction. Even so, the results indicated a slightly reduced conversion to esters. This observation can be attributed mainly to steric effects.

BBn provided a slightly better conversion rate in the synthesis of methyl phenylacetate and hexyl phenylacetate than did VLn. This result is consistent with the characterisation data, which indicated that the latter has a lower specific area and less pore volume. After the acid treatment, VLa presented higher specific area and more pore volume than BBa. This difference between the textural properties of the two acid-activated clays could explain the higher conversion

Table 5. Esterification of different carboxylic acids with various alcohols

entry	Carboxylic acid	Alcohol	Conversion / %				
			BBn	BBa	VLn	VLa	K10
1	lauric acid	methanol	4	84	2	87	74
2	cyclohexanoic acid	methanol	3	70	11	82	24
3	phenylacetic acid	methanol	39	91	22	90	86
4	benzoic acid	methanol	< 1	< 1	< 1	< 1	< 1
5	lauric acid	hexanol	31	89	36	84	47
6	cyclohexanoic acid	hexanol	23	38	21	33	31
7	phenylacetic acid	hexanol	38	75	28	82	83
8	benzoic acid	hexanol	< 1	6	2	6	3
9	lauric acid	cyclohexanol	1	11	5	93	16
10	cyclohexanoic acid	cyclohexanol	9	48	4	76	8
11	phenylacetic acid	cyclohexanol	8	23	29	76	11
12	benzoic acid	cyclohexanol	< 1	3	< 1	4	< 1

BBn and VLn: natural clays; BBa and VLa: acid-activated clays; K10: commercial clay.

achieved by VLa because the NH_3-TPD analyses and the thermodesorption of *n*-butylamine results did not indicate a substantial difference in acidity between these catalysts.

As with the esterifications with methanol, hexyl benzoate and cyclohexyl benzoate were obtained in limited quantities, even when using the acid-activated clays.

The natural clays performed better in the formation of hexyl esters than cyclohexyl esters. The low conversion rates for cyclohexyl esters could be attributed to steric effects induced by the catalyst. Relative to primary alcohols, it is more difficult for a secondary cyclic alcohol to access the mesoporous system of a smectite.

BBa and VLa were very active for the esterification of lauric acid with hexanol (89% and 84%) and for that of phenylacetic acid with the same alcohol (75% and 82%). In the esterification of cyclohexanoic acid with hexanol, the acid-activated clays afforded conversions close to those of the natural clays. This result could be attributed to sterically hindered access of hexanol to the electrophilic site of cyclohexanoic acid.

The esterification of carboxylic acids with cyclohexanol was catalysed more efficiently by BBa and VLa than by BBn or VLn. Moreover, the VLa catalyst provided better conversions of cyclohexyl esters than did BBa. The VLa provided better catalytic performance than did K10 for all of the esterifications assessed in this study.

It was not done a mechanistic study on the esterification using the clays as catalysts. However, we assume that the mechanism involved is probably similar those proposed by our group in other works involving Bronsted or Lewis acid transesterification, esterification or hydrolysis.[5,6,8,9,33]

Conclusions

Two Brazilian clays mainly composed by smectite were acid activated without any previous treatment. The acid treatment significantly increased the surface area of the materials without changing their surface acidity. The catalytic activity of the clays for esterification was strongly enhanced after acid treatment. The acid-activated clays exhibited high efficiency even when the by-product (water) was not removed. These catalysts show potential use as catalyst for the esterification of multiple carboxylic acids with various alcohols, mainly because smectite is cheap and abundant in Brazil.

Supplementary Information

Supplementary information (Figures S1-S16, Table S1-S2) is available free of charge at http://jbcs.sbq.org.br as a PDF file.

Acknowledgments

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Supplementary Information

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Data for calculation of the response factors of acids and esters standards

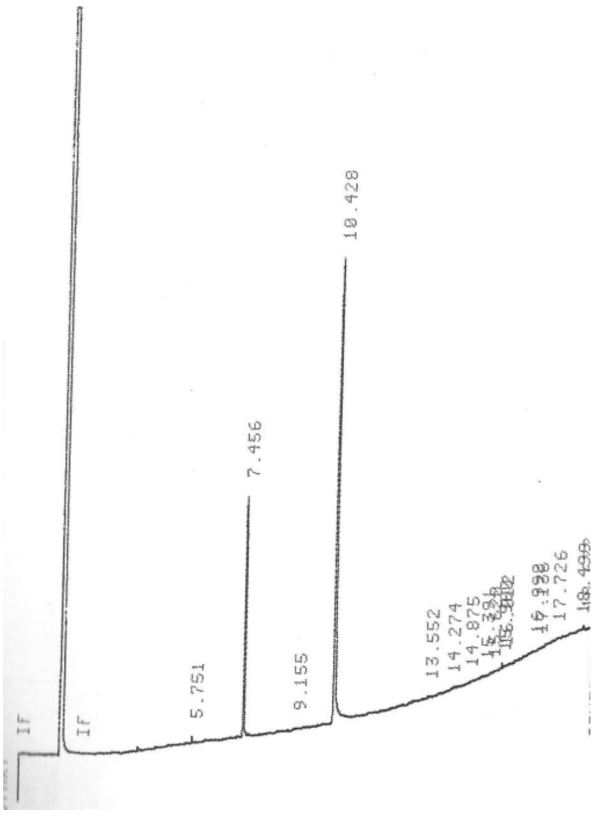

Figure S1. Chromatogram of lauric acid (t_R 10.4 min) and internal standard (t_R 7.5 min).

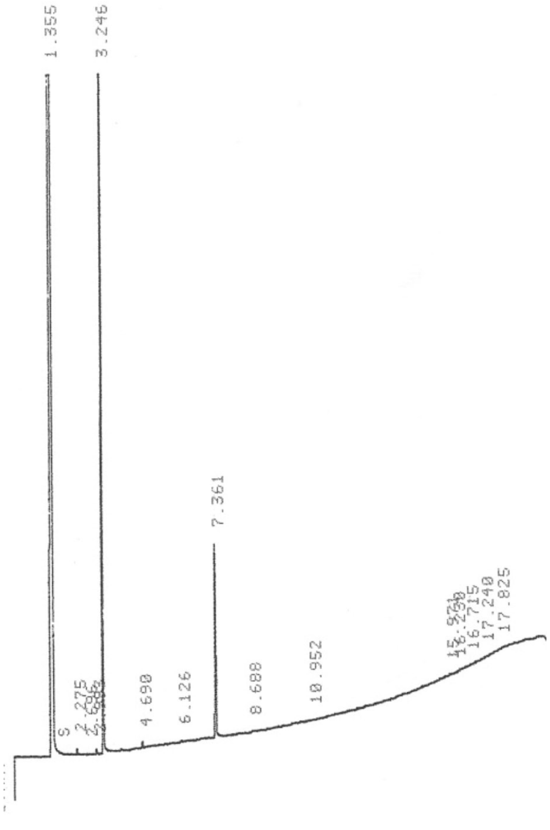

Figure S2. Chromatogram of methyl laurate (t_R 3.2 min) and internal standard (t_R 7.4 min).

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*e-mail: mjcrezende@gmail.com

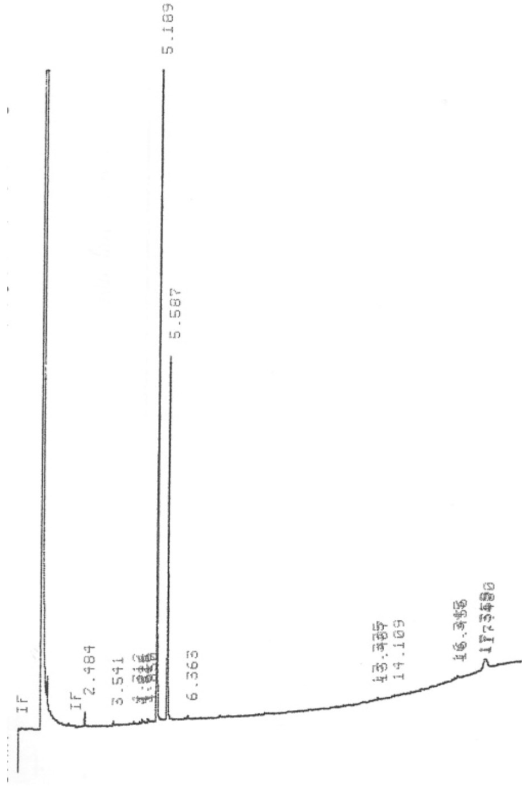

Figure S3. Chromatogram of hexyl laurate (t_R 5.2 min) and internal standard (t_R 5.6 min).

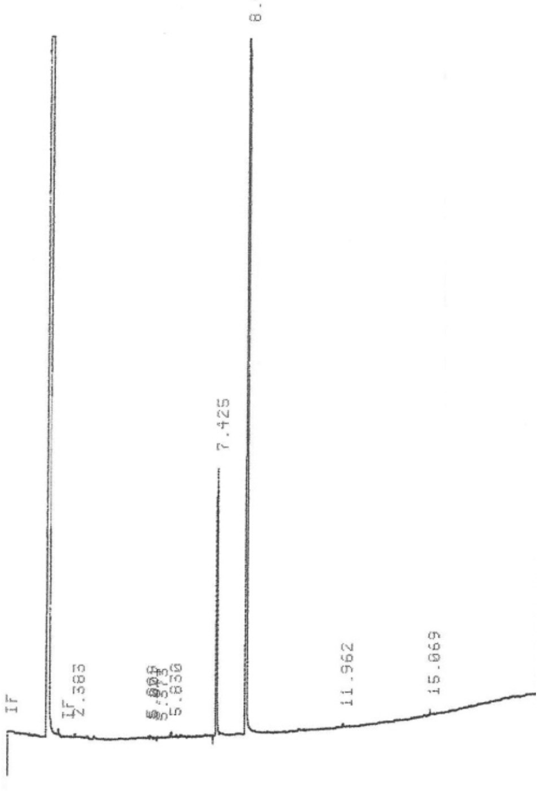

Figure S4. Chromatogram of cyclohexyl laurate (t_R 8.4 min) and internal standard (t_R 7.4 min).

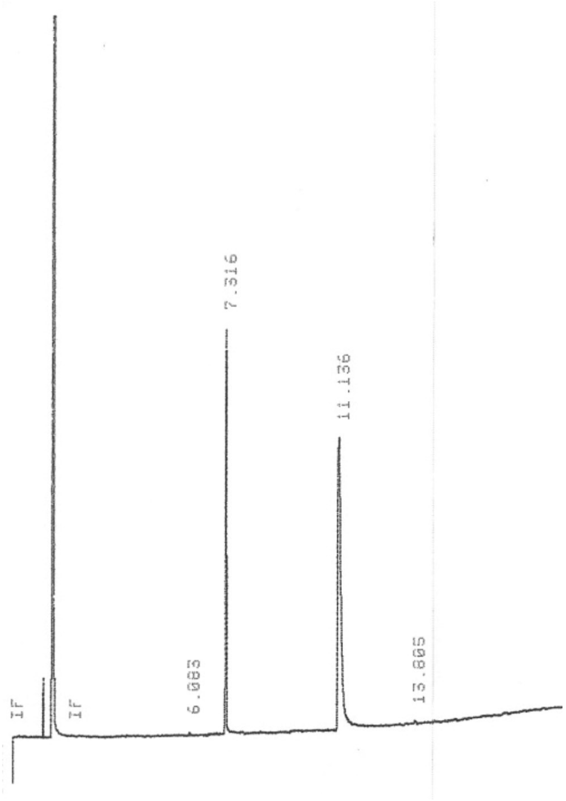

Figure S5. Chromatogram of phenylacetic acid (t_R 11.1 min) and internal standard (t_R 7.3 min).

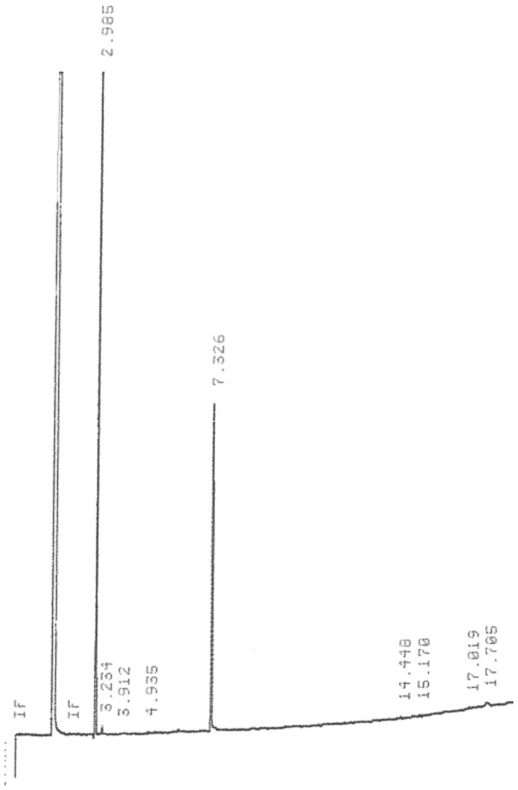

Figure S6. Chromatogram of methyl phenylacetate (t_R 3.0 min) and internal standard (t_R 7.3 min).

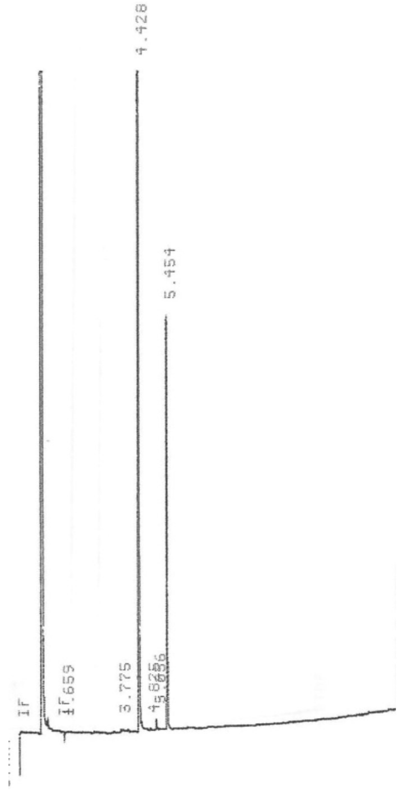

Figure S7. Chromatogram of hexyl phenylacetate (t_R 4.4 min) and internal standard (t_R 5.4 min).

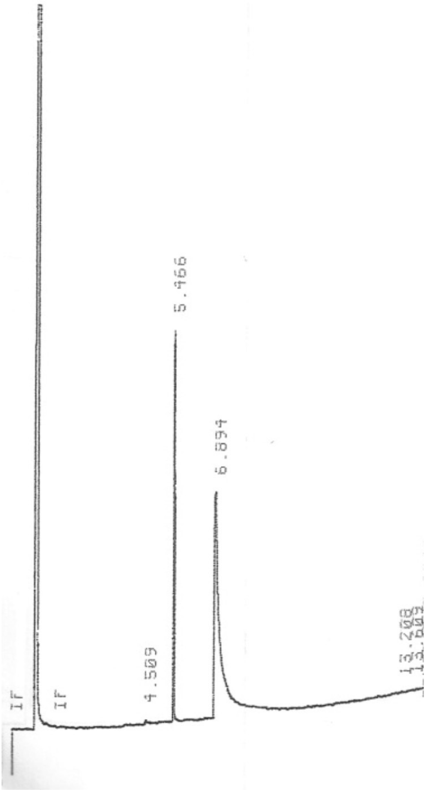

Figure S9. Chromatogram of benzoic acid (t_R 6.9 min) and internal standard (t_R 5.5 min).

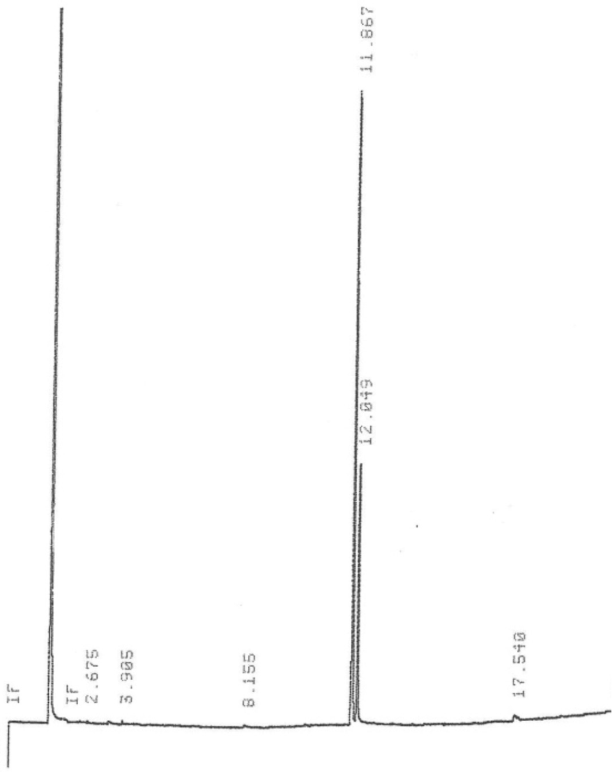

Figure S8. Chromatogram of cyclohexyl phenylacetate (t_R 11.9 min) and internal standard (t_R 12.0 min).

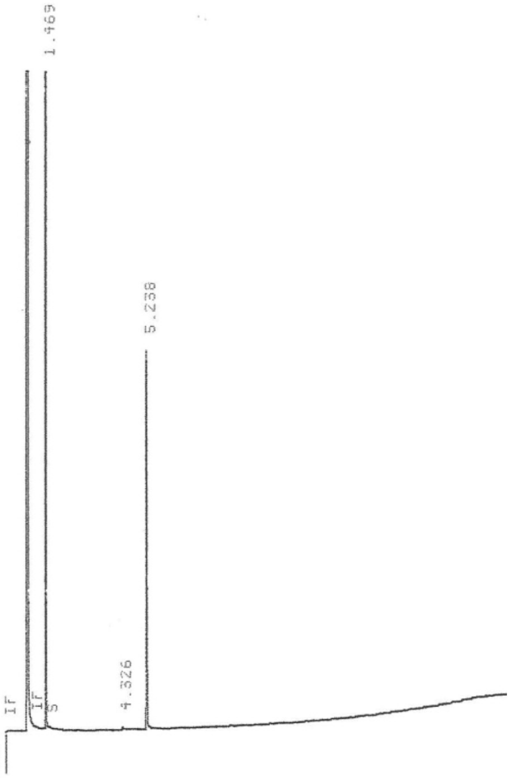

Figure S10. Chromatogram of methyl benzoate (t_R 1.5 min) and internal standard (t_R 5.2 min).

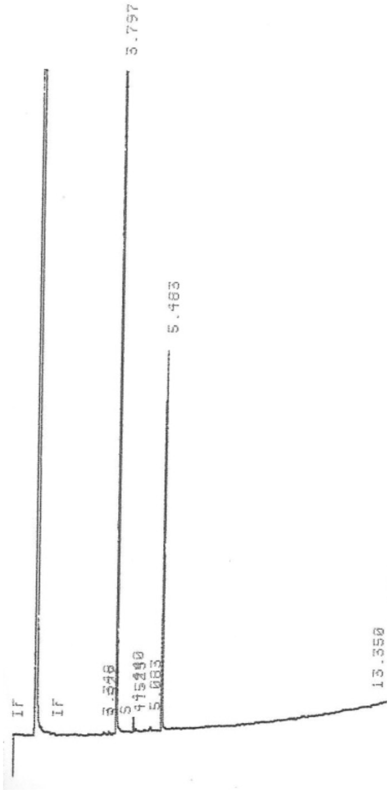

Figure S11. Chromatogram of hexyl benzoate (t_R 3.8 min) and internal standard (t_R 5.5 min).

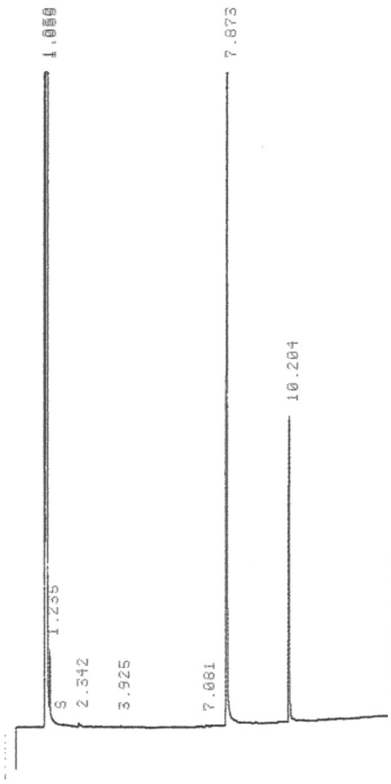

Figure S13. Chromatogram of cyclohexanoic acid (t_R 7.9 min) and internal standard (t_R 10.2 min).

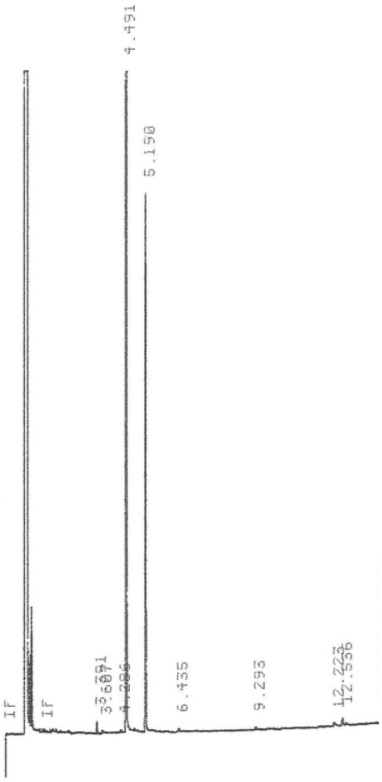

Figure S12. Chromatogram of cyclohexyl benzoate (t_R 4.5 min) and internal standard (t_R 5.2 min).

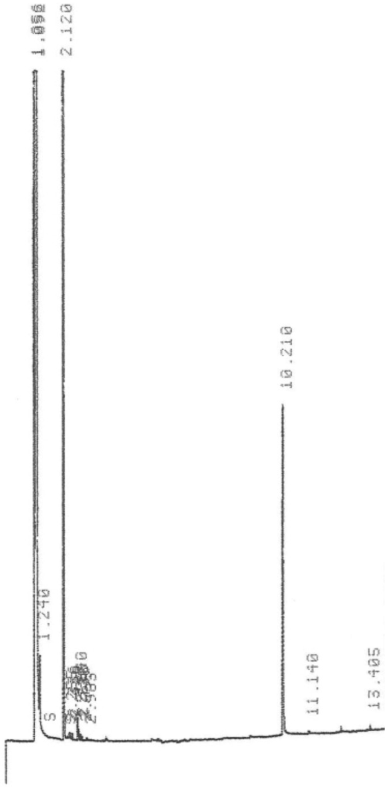

Figure S14. Chromatogram of methyl cyclohexanoate (t_R 2.1 min) and internal standard (t_R 10.2 min).

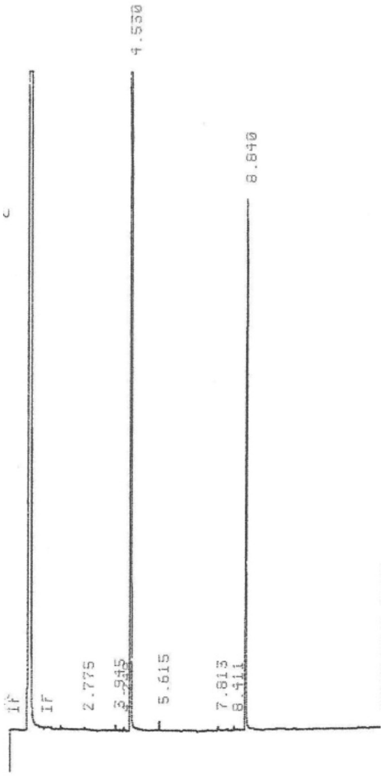

Figure S15. Chromatogram of hexyl cyclohexanoate (t_R 4.5 min) and internal standard (t_R 8.8 min).

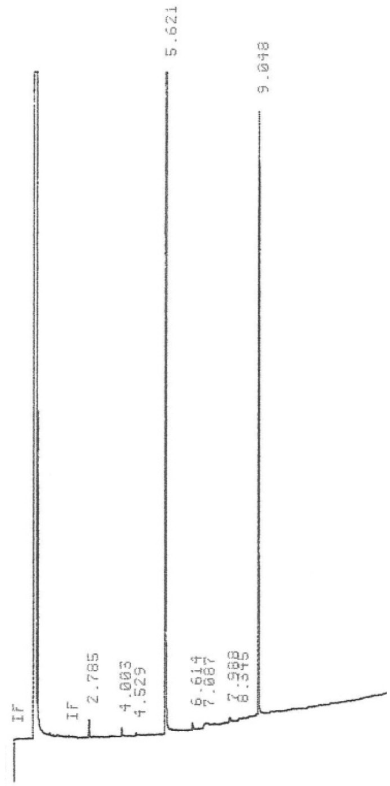

Figure S16. Chromatogram of cyclohexyl cyclohexanoate (t_R 5.6 min) and internal standard (t_R 9.0 min).

Table S1. Data for calculation of the response factors of acids and esters standards

Standard	S_{Area}	S_{Conc}	IS_{Area}	IS_{Conc}	F_R	F_R
lauric acid	218841	1020	83333	268	0.690	0.684
lauric acid	216720	1020	83928	268	0.678	
methyl laurate	492794	1040	71675	268	1.772	1.758
methyl laurate	539675	1040	79744	268	1.744	
cyclohexyl laurate	412109	1630	77671	268	0.872	0.876
cyclohexyl laurate	506955	1630	94774	268	0.879	
hexyl laurate	323411	1330	107778	238.5	0.538	0.534
hexyl laurate	368092	1330	124750	238.5	0.529	
phenylacetic acid	384842	1620	136902	248	0.430	0.421
phenylacetic acid	378276	1620	140893	248	0.411	
methyl phenylacetate	438196	1410	156421	248	0.493	0.509
methyl phenylacetate	366980	1410	122895	248	0.525	
cyclohexyl phenylacetate	1366540	1710	144943	248	1.367	1.375
cyclohexyl phenylacetate	1394862	1710	146311	248	1.383	
hexyl phenylacetate	904087	1670	122677	239	1.055	1.054
hexyl phenylacetate	927589	1670	126073	239	1.053	
cyclohexanoic acid	412674	1340	108036	265.5	0.757	0.727
cyclohexanoic acid	372292	1340	105803	265.5	0.697	
methyl cyclohexanoate	728707	1940	112690	265.5	0.885	0.913
methyl cyclohexanoate	596780	1940	86712	265.5	0.942	
cyclohexyl cyclohexanoate	891191	1630	159304	238.5	0.818	0.827
cyclohexyl cyclohexanoate	1070347	1630	187300	238.5	0.836	
hexyl cyclohexanoate	2038730	2870	167994	241	1.019	1.021
hexyl cyclohexanoate	1993908	2870	163741	241	1.022	
benzoic acid	262536	960	98661	265.5	0.736	0.756
benzoic acid	249880	960	89095	265.5	0.776	
methyl benzoate	263392	940	92042	265.5	0.808	0.806
methyl benzoate	279626	940	98359	265.5	0.803	
cyclohexyl benzoate	640039	1850	104871	238.5	0.787	0.785
cyclohexyl benzoate	568059	1850	93466	238.5	0.783	
hexyl benzoate	874892	1630	116861	239	1.098	1.101
hexyl benzoate	863688	1630	114751	239	1.104	

S_{Area} = standard area; S_{Conc} = standard concentration at mg L^{-1}; IS_{Area} = internal standard area; IS_{Conc} = internal standard concentration at mg L^{-1}; F_R = response factor; $F_R = (S_{Area}/S_{Conc})/(IS_{Area}/IS_{Conc})$.

Table S2. Oven temperature program used on GC-FID analyses

Product	Oven temperature program	tR / min		
		acid	ester	IS
methyl phenylacetate	140 °C to 180 °C at 10 °C min^{-1} followed by 180 °C to 220 °C at 3 °C min^{-1}	8.7	3.0	5.4
hexyl phenylacetate	140 °C to 180 °C at 10 °C min^{-1} followed by 180 °C to 220 °C at 3 °C min^{-1}	8.7	4.4	5.4
cyclohexyl phenylacetate	5 min at 140 °C followed to 180 °C at 8 °C min^{-1}. After 3 min at 180 °C followed to 220 °C at 3 °C min^{-1}	17.6	11.9	12.0
methyl laurate	140 °C to 180 °C at 10 °C min^{-1} followed by 180 °C to 220 °C at 3 °C min^{-1}	8.1	1.4	5.5
hexyl laurate	140 °C to 180 °C at 10 °C min^{-1} followed by 180 °C to 220 °C at 3 °C min^{-1}	8.1	5.1	5.5
cyclohexyl laurate	140 °C to 180 °C at 10 °C min^{-1} followed by 180 °C to 220 °C at 3 °C min^{-1}	8.1	8.4	5.5
methyl benzoate	140 °C to 180 °C at 10 °C min^{-1} followed by 180 °C to 220 °C at 3 °C min^{-1}	6.9	1.5	5.2
hexyl benzoate	140 °C to 180 °C at 10 °C min^{-1} followed by 180 °C to 220 °C at 3 °C min^{-1}	6.9	3.8	5.5
cyclohexyl benzoate	140 °C to 180 °C at 10 °C min^{-1} followed by 180 °C to 220 °C at 3 °C min^{-1}	6.9	4.5	5.2
methyl cyclohexanoate	100 °C to 180 °C at 10 °C min^{-1} followed by 180 °C to 200 °C at 3 °C min^{-1}	6.9	1.5	9.0
hexyl cyclohexanoate	100 °C to 180 °C at 10 °C min^{-1} followed by 180 °C to 200 °C at 3 °C min^{-1}	6.8	4.5	8.8
cyclohexyl cyclohexanoate	100 °C to 180 °C at 10 °C min^{-1} followed by 180 °C to 200 °C at 3 °C min^{-1}	6.9	5.6	9.0