Research Article

Solvent-free esterification of stearic acid and ethylene glycol with heterogeneous catalysis in a stirred batch microwave reactor

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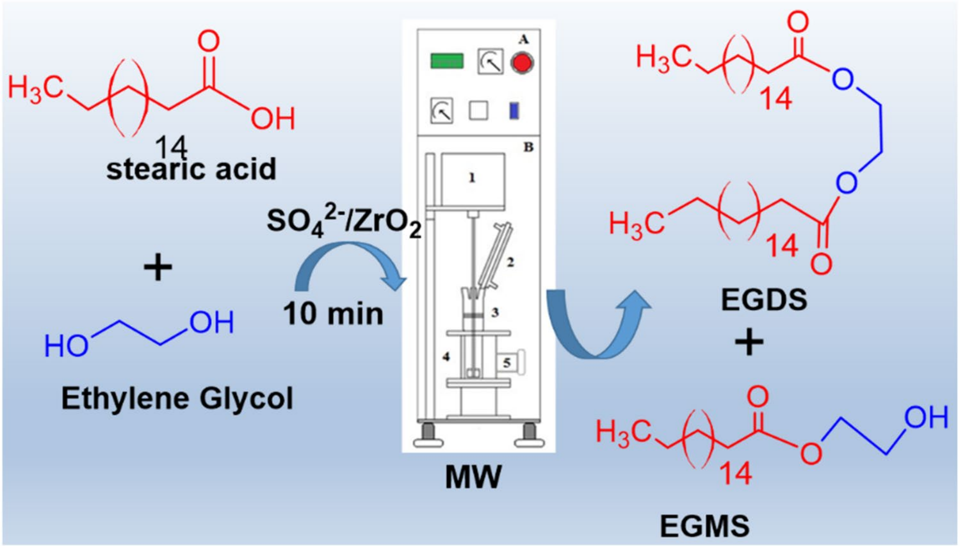
Abstract

Ethylene glycol distearate (EGDS) is extensively used in the pharmaceutical and cosmetics industries. Even in textile industries as a softener, EGDS is in demand. In this paper, synthesis of EGDS by esterification of ethylene glycol and stearic acid has been described using a solid acid catalyst under microwave (MW) irradiation in a solvent-free system. Conventional heating takes more than 4–6 h to give a mixture of EGDS and ethylene glycol monostearate (EGMS). Under MW irradiation, the highest conversion of 97% of the acid was obtained in 10 min. The reaction mixture was analyzed by acid value, FT-IR, ^{1}H-NMR and mass spectroscopy. The EGDS synthesis was optimized concerning various parameters such as reaction time, different catalysts, catalyst loading (wt/wt%), temperature, and MW power. Heterogeneous catalysis, intensified with MW irradiation, makes the esterification process more promising route for possible application at industrial scale.

Graphic abstract



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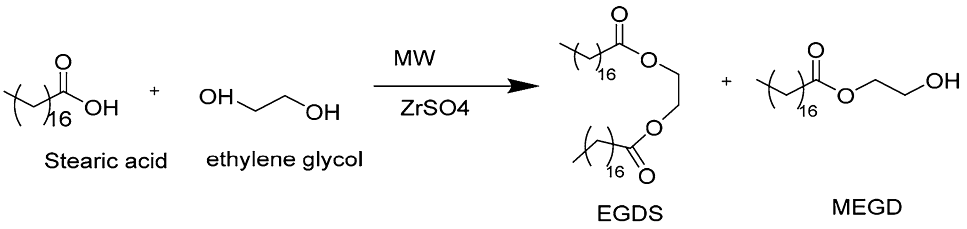
Keywords EGDS · Esterification · Microwave · Heterogeneous catalysis · Intensification

1 Introduction

Ethylene glycol distearate (EGDS) is used in cosmetic materials like shampoo, conditioners, body washes and soaps, hair colouring, acne treatment, and anti-ageing products [1]. It is also incorporated in the heating, ventilation and air conditioning systems of electronic cars. EGDS has important property as a phase-changing material [2]. Current studies in its synthesis aim to replace homogenous acid catalysts by heterogeneous catalysts. There are many heterogeneous catalysts reported to synthesize industrially important esters [3–6]. In addition to polymer-based catalysts, such as Amberlyst, sulfated zirconia has been studied by many researchers for catalyzing esterification reactions [7]. Biocatalysts are also incorporated in the synthesis of ethylene glycol di-stearate [8].

The well-established conventional method of synthesis of EGDS uses strong homogeneous acid catalysts, such as sulfuric acid [9]. Synthesis of EGDS with a homogeneous catalyst, usually conducted at higher temperatures, is a non-greener method as the catalyst acid is highly corrosive in the presence of water that is produced in equimolar quantities in the esterification reaction and has to be neutralized. There is increasing interest, therefore, in employing heterogeneous catalysts in these esterification reactions to avoid waste generation when the homogeneous acid catalyst is neutralized. There are, however, a few drawbacks of heterogeneous catalysis, including mass transfer limitations that lead to longer times for completion of the reaction. For example, esterification of stearic acid using acid-activated bentonite as a catalyst and *o*-xylene as the dehydrating solvent reportedly took 7 h to give 76% yield of the diester [10].



Reaction scheme for stearic acid and ethylene glycol esterification

Organic synthesis under microwave (MW) radiation is being investigated by a number of researchers for several reactions because of the intensification of the reactions by many folds. In many cases, the rates are enhanced enough to complete the reactions in just a few minutes. Commonly, these reactions are conducted without any solvent [11]. Avoiding the use of organic flammable solvents is one of the most important points in green chemistry, apart from process intensification. A solid acid-catalyzed reaction is easy for operation as the solid catalyst can be separated from the reaction mixture by simple physical processes such as filtration. It also allows continuous operation with the catalyst packed in a bed reactor. Heterogeneous catalysis combined with MW irradiation is an interesting area as the MW energy can be absorbed directly by the solid catalyst, if selected appropriately. The catalytic sites can then be activated specifically where the actual reaction takes place, improving the energy utilization [12, 13].

In this paper, we have focused on intensifying the ethylene glycol distearate synthesis by MW irradiation using solid acid catalysts. This reaction reportedly takes place over several hours when conducted using solid catalysts [14]. The main aim of this work was to investigate the microwave effect on the EDGS synthesis. To the best of our knowledge, there is no report on the synthesis of EGDS under solvent-free conditions and/or under microwave irradiation using the solid heterogeneous catalysts.

2 Experimental

2.1 Materials

Stearic acid and ethylene glycol were purchased from s.d. Fine Chemicals Limited, Mumbai, and were used without any purification. Zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) was procured from Loba Chemie, Mumbai. *p*-Toluene sulfonic acid, ammonia (aq.) and sulfuric acid (98%) were purchased from Thomas Baker Pvt. Ltd, Mumbai.

The solid polymer-based catalysts, Amberlyst-15 and Indion 130, both in ionic H^+ form, were procured from s.d. Fine Chemicals Ltd., and Ion Exchange (I) Ltd, Mumbai, respectively. These resin catalysts were washed with methanol followed by water and then dried in an oven at 100 °C.

The acidic sulphated zirconia catalyst was prepared by following the reported method [14]. $ZrOCl_2{\cdot}8H_2O$ was dissolved in double distilled deionized water followed by dropwise addition of aq. ammonia solution with vigorous stirring till the pH of the solution reached to 8. The white precipitate was filtered and washed with DI water several times to completely remove chloride ions. The solid was dried for 12 h at 100 °C and then added with stirring into 1.0 M sulfuric acid solution for 4 h. The solid was then filtered and calcined for 5 h at 600 °C in an oven.

2.2 Characterization of catalyst

An X-ray powder diffractometer (Bruker make, Model-D8 Advance) was used to obtain the XRD pattern using operating conditions set on 40 kV, 40 mA, scan speed of 6°/min with CuKα radiation (k = 1.54 Å) in the 2θ scan range of 10°–70°. The infrared spectrum of the catalyst was recorded as a KBR pellet on a Bruker Vertex 80 V vacuum FTIR in the wavenumber range of 3500–570 cm^{-1} with the resolution of 0.2 cm^{-1}. Surface area, pore volume and pore size of the catalyst were measured on ASAP-2010 instrument (Micromeritics, USA). Temperature programmed desorption (TPD) of ammonia was conducted on AutoChem II-2920 (Micrometrics V4.06) to characterize the acidity of sulphated zirconia. The acidity of polymer-based acidic resin catalysts was measured by acid–base titration.

2.3 Microwave reaction system

The schematic diagram of the microwave batch reactor system, designed and fabricated in our laboratory, is shown in Fig. 1. It consisted of a cylindrical metal cavity with a waveguide welded on its cylindrical surface for tangential entry of microwave into the cylindrical cavity hosting the glass reactor. The magnetron was mounted on the waveguide. The control system (*A*) was designed to adjust the time of exposure of the reaction mixture to the microwave radiation. The glass reactor was placed inside the microwave cavity at a place identified for maximum microwave radiation exposure. The reactor was equipped with an overhead motor and a pitched blade glass stirrer for agitating the reaction mixture. The temperature reached by the reaction mixture in the glass reactor was measured by an IR sensor at the end of each run.

2.4 Reaction procedure

Esterification of stearic acid (SA) with ethylene glycol (EG) was conducted in a cylindrical glass reactor equipped with a refluxing condenser. The reactor was placed in the cylindrical microwave cavity of the Microwave System for irradiation. Stearic acid was first charged into the reactor and was melted using MW irradiation of 900 W for time duration from 30 to 60 s. The solid catalyst was then added into the reactor while the liquid reaction mixture was agitated using the impeller, followed by the addition of EG. The molar ratio of SA to EG was maintained at 2:1 in all experiments.

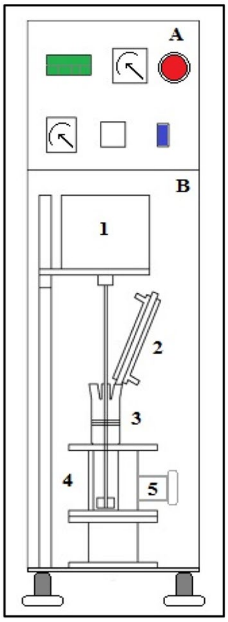


Fig. 1 Batch microwave reactor set-up (A: Electric panel, B: reactor assembly section, 1: mechanical stirrer, 2: heat exchanger, 3: glass batch reactor, 4: MW cavity, 5: MW waveguide)

The reaction mixture was then irradiated with microwave at 900 W power for a specified time. The temperature reached by the reaction mixture was more than 150 °C at the end of each run. After exposure to the MW irradiation, under well-stirred conditions for a specified time, the reactor was allowed to cool to room temperature in 5–10 min. The reaction mass was then poured into deionized (DI) water. Unreacted stearic acid and product(s) precipitate out as off-white waxy material and float on the surface while the catalyst settles down. The product precipitate was separated by filtration and washed 3–4 times with DI water to remove adhering ethylene glycol.

The experiments were conducted with sulfated zirconia, Amberlyst-15 and Indion-130 as heterogeneous catalysts and also with p-TSA, as a homogeneous catalyst, for comparison.

3 Analytical methods

The progress of the reaction was checked by conversion of stearic acid. The sample was analyzed for unreacted stearic acid in the reaction mass by titration. The sample aliquot was dissolved in 20 mL toluene and isopropyl alcohol (IPA)

(50:50 v/v) mixture and titrated against standard 0.1 N alcoholic KOH solution using phenolphthalein as an indicator to estimate the unreacted stearic acid in terms of its acid value.

$$\text{Acid value} = \frac{56.1 * M{*}V}{W} \tag{1}$$

where V is the volume of KOH solution (in mL), M is the molarity of the titrant (mol/L), and W is the weight of the sample (g).

The percentage conversion was calculated based on the unreacted stearic acid in the reaction mass by using the following Eq. (2).

$$\%\text{Conversion of stearic acid} = \frac{A0 - A1}{A0} * 100 \tag{2}$$

where A_0 the starting acid value and A_1 is the acid value after a specific time.

The esters were separated from the reaction mass by dissolving the product mixture in ethyl acetate in 1:10 ratio and transferred to a separating funnel for washing with water, first to remove EG, followed by dilute alkali wash to remove unreacted acid, if any. A small quantity of the product was grounded with dry IR grade KBr using a mortar and pestle and then pelletized. The FTIR spectrum of the esters as KBr pellet was recorded on a Bruker Vertex 80v vacuum FTIR in the range of 3500–570 cm^{-1}. The ^1H Nuclear Magnetic Resonance (^1H NMR) spectrum in $CDCl_3$, was recorded using a Bruker BioSpin (Advance AV500WB, Germany) spectrometer at 400 MHz using trimethyl silane as an internal reference standard. The mass spectrum was recorded on 6550 iFunnel Q-TOFs Agilent Technologies (USA) through atmospheric pressure chemical ionization technique (APCI).

3.1 Monoester and diester percentage determination

A known amount of the reaction mass was dissolved in 30 mL of toluene and IPA (50:50 v/v) mixture. The reaction mass contained unreacted stearic acid, monoester and diester. The solution was used for both acid value and hydroxyl value determination. The acid value was used to estimate the unreacted acid content while the hydroxyl value was useful for the determination of terminal hydroxyl content in ester [15].

$$\text{Weight of fatty acid} = \frac{\textit{acid value}}{1000} * \frac{1}{56.1} * \frac{\textit{Fatty acid molecular weight}}{\textit{sample weight}} \tag{3}$$

$$\text{Weight of monoester} = \frac{\textit{hydroxylvalue}}{1000} * \frac{1}{56.1} * \frac{\textit{Monoester molecular weight}}{\textit{sample weight}} \tag{4}$$

$$\text{Weight of diester} = 1 - (\textit{Wt. of fatty acid} + \textit{Wt. of monoester}) / \textit{sample Wt} \tag{5}$$

4 Results and discussion

In the initial experiments, Indion 130, a polymeric resin with sulfonic acid groups, was used as the catalyst. The particle size of resin was in the range of 0.42–1.2 mm. The BET surface area of the fresh Indion 130 resin catalyst was 19 m^2/g. [16] The pore volume and pore diameter were, 0.39 cm^3/g and 295 Å, respectively. The concentration of acidic sites in Indion 130 resin catalyst, as determined by acid–base titration, was 4.8 meq/gm. Amberlyst-15, also with SO_3-H functional groups, was having the particle size in the range 0.3–0.42 mm. The concentration of the active acid sites in the catalyst was 4.7 meq/gm. The nitrogen BET surface area of the catalyst was 53 m^2/gm while total pore volume was 0.40 cm^3/gm and the average pore diameter was 300 Å.

The freshly prepared sulphated zirconia catalyst showed 81 m^2/g of surface area, pore volume was 0.52 cm^3/g and pore diameter of 60 Å. The pore size of all three catalysts is sufficiently large to be in the mesoporous region. The sulfated zirconia catalyst showed type-II N_2 adsorption with mesoporous pore size without any hysteresis loop in the adsorption and desorption cycles [17] (Figure S1, supporting information). The adsorption isotherm, however, showed deviation from the Langmuir model of adsorption. The acid value, calculated by acid–base titration, of the sulphated zirconia was 3.06 meq/g sample. The acid site concentration of fresh sulphated zirconia catalyst by thermal desorption of ammonia was, however, lower at 0.414 mmol/g.

The powder X-ray diffraction spectrum (Fig. 2) shows the crystalline phase of sulfated zirconia when calcinated

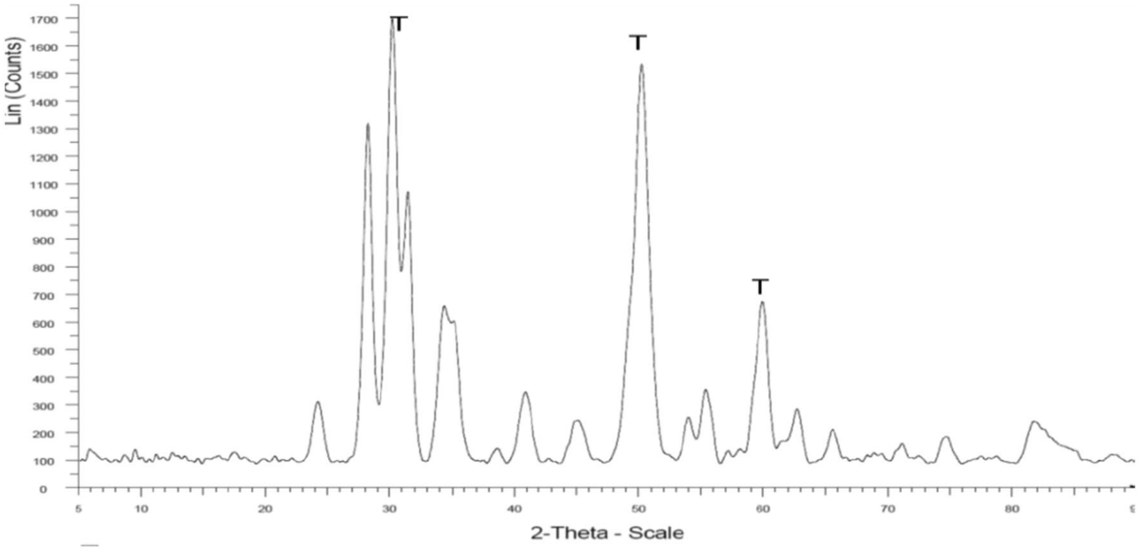


Fig. 2 XRD pattern of SO_4^{2-}/ZrO_2 calcined at 600 °C

at 600 °C temperature. The process of formation of the crystalline structure of sulfated zirconia is starts at 500 °C [18]. The sharp and prominent peaks in the diffraction spectrum at 2θ values of 30°, 50° and 60° indicate crystalline structure and presence of the catalyst mainly in the tetragonal form, which is known to be more active form of the catalyst when compared with reported X-ray diffraction pattern of sulfated zirconia [19].

The FT-IR spectrum of the SO_4^{2-}/ZrO_2 catalyst (Fig. 3), shows the presence of S–O bond in the range of 900–1244 cm^{-1} indicating the presence of Bronsted acid sites in the catalyst, whereas the peak at 1383 cm^{-1} indicates the presence of S=O covalent bond which is responsible for Lewis acidity of the sulfated zirconia [20].

4.1 Esterification reaction

Stearic acid (SA) reacted with EG in 2:1 molar ratio in the presence of homogeneous acid catalyst (p-TSA) and heterogeneous acid catalysts (Amberlyst 15, Sulphated zirconia, Indion 130) under MW irradiation. Esterification usually produces a mixture of monoester and diester. Conversion of stearic acid under MW irradiation with sulphated Zirconia solid acid catalyst was 92% with 10% (w/w) solid loading while the homogeneous catalyst, p-TSA, gave

Fig. 3 FT-IR spectrum of sulfated zirconia

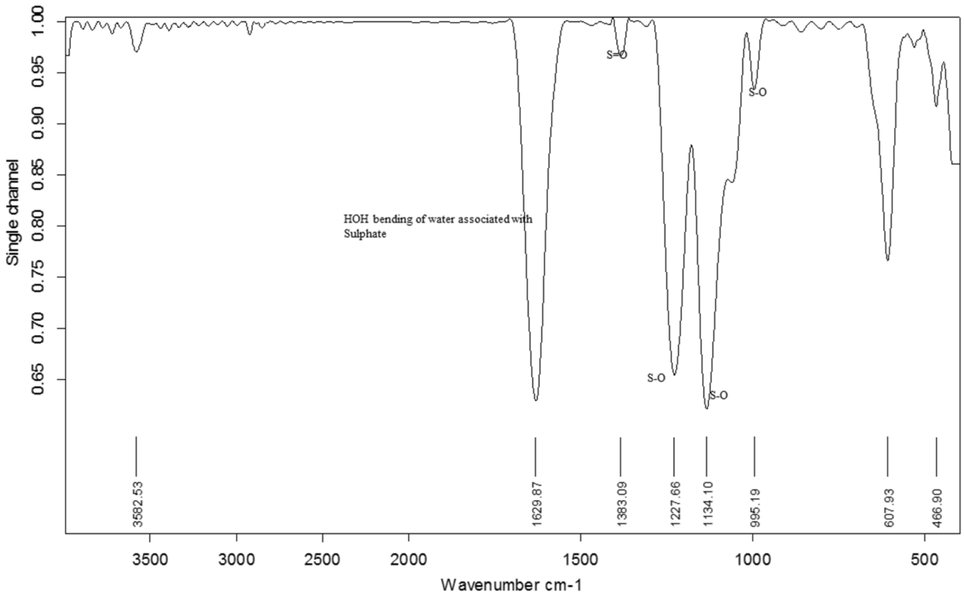


Table 1 Performance of different catalysts for conversion of stearic acid

Catalyst (10% w/w)	Final acid value	Time (min)	Final temperature of reaction mixture (°C)	Conversion of acid %	Yield % (EGDS)	Monoester–diester ratio
SO_4/ZrO	17.4	10	165	91.82	61.11	0.39/0.61
Amberlyst 15	23.7	10	162	88.84	54.58	0.46/0.54
Indion 130	29.5	10	168	86.12	51.64	0.48/0.52
p-TSA (0.3% w/w)	6.33	10	162	97.02	63.42	0.37/0.63

the highest conversion of acid at 97% that too at a much lower concentration of just 0.3% (w/w). The acid value, SA conversion, monoester–diester ratio and the % yield of EGDS, obtained with different catalysts, are reported in Table 1. Since the emphasis was on microwave effect on the reaction, no optimization of the catalyst characteristics was attempted, although the acid site concentration of sulfated zirconia measured by ammonia thermal desorption was low.

The time taken for the esterification of acid and alcohol under MW irradiation was restricted to just 10 min. The same reaction was reported in the literature by conventional heating at 120 °C using *p*-TSA as a homogeneous acid catalyst using toluene as a solvent in 4 h [21]. Under the influence of microwave, the reaction time is thus reduced significantly, i.e. 24 times, with all catalysts. Thus, microwave accelerates the rate of the reaction by an order of magnitude.

Ethylene glycol, being a polar solvent, strongly absorbs microwave irradiation. The water formed in the reaction is also a strong microwave absorbing material. Rapid internal heating of the reaction mixture, therefore, should remove the water of esterification from the reaction mixture and accelerate the esterification reaction by thermal effect. *p*-TSA, being a homogenous catalyst, gave the highest conversion (97%) of stearic acid. Solid catalysis provided slightly lower conversions in comparison. *p*-TSA is uniformly distributed throughout reaction mixture at the molecular level and thus provides a better conversion of stearic acid. Heterogeneous catalyst particles, on the other hand, are discretely distributed in the reaction mixture and, therefore, the MW effect is expected to be lesser because of localization of the active sites. The effect of microwave on the reaction rate is considered to be purely thermal and no catalytic effect is ascribed to it.

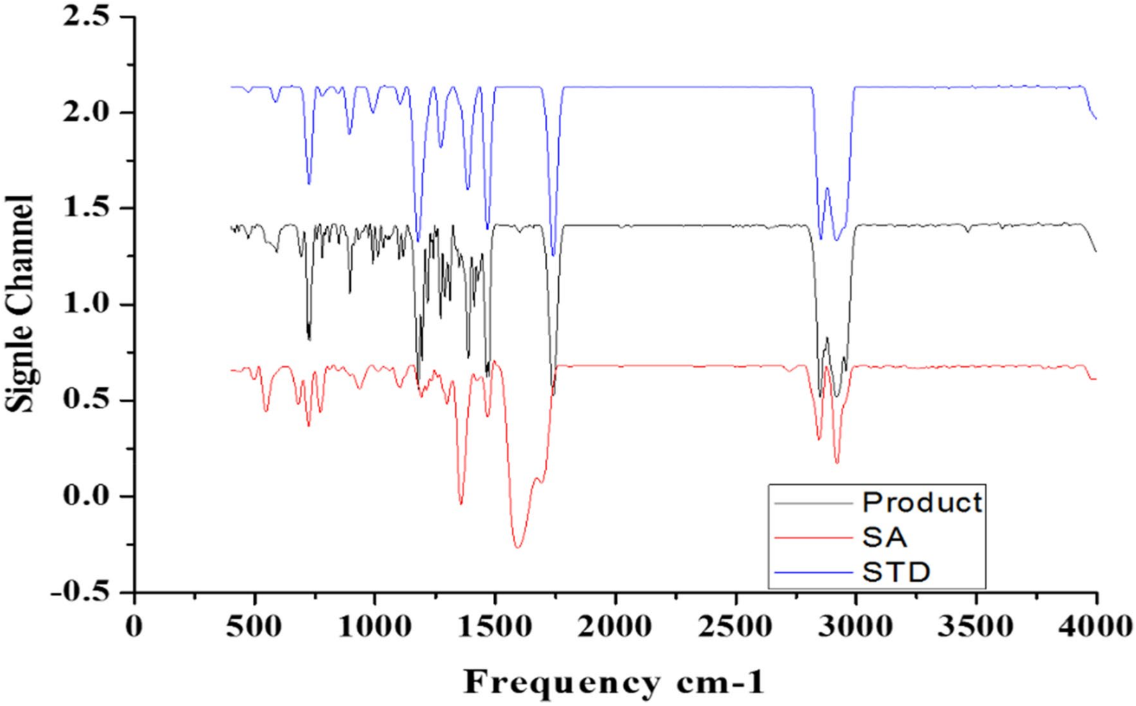


Fig. 4 FTIR spectra of EGDS synthesized under MW irradiation. Stearic acid and standard EGDS

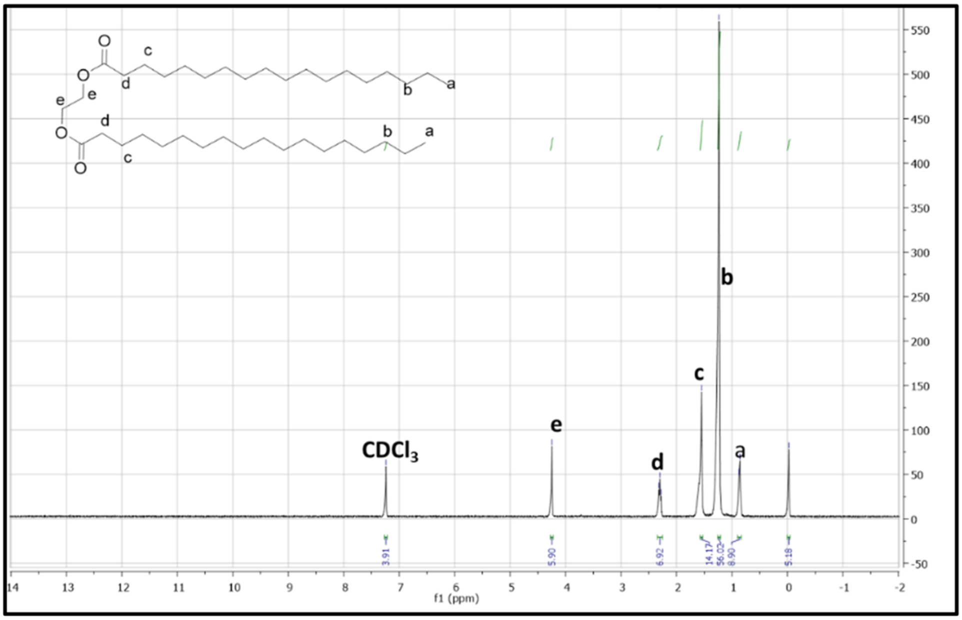


Fig. 5 ^{1}H NMR spectrum—EGDS synthesized under MW irradiation

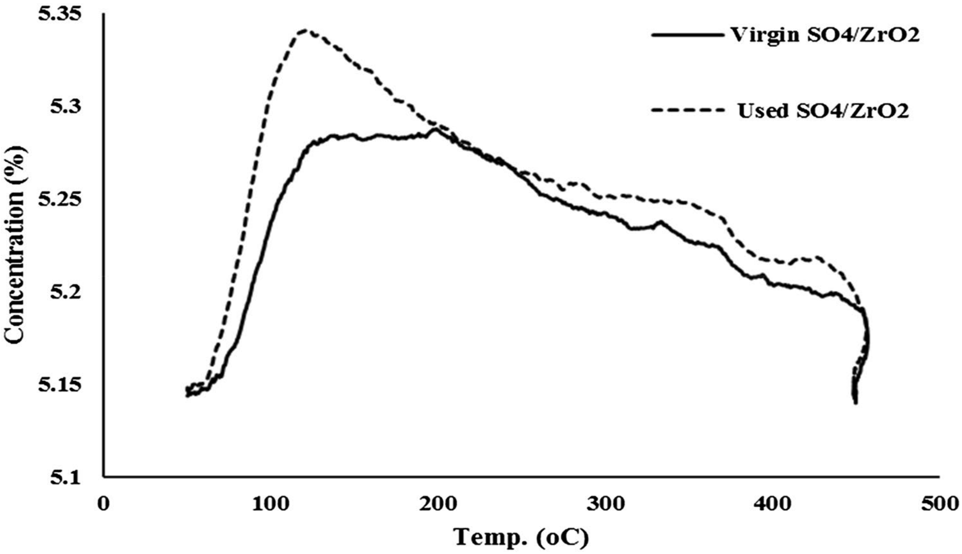


Fig. 6 Ammonia-TPD profiles of fresh and used SO_4^-/ZrO_2 catalysts

The FT-IR spectrum of the ester (Fig. 4) shows the band at 1738 cm^{-1} which was attributed to the carbonyl bond of the ester, resulting from the reaction between hydroxyl and carboxyl groups. In stearic acid, the spectrum shows the presence of carbonyl –C=O group of an aliphatic acid at 1701 cm^{-1}. The spectrum also shows the C–O bond of ester at 1180 cm^{-1}. The ^{1}H-NMR spectrum (Fig. 5) shows the protons of terminal methyl (a) R-$\mathbf{CH_3}$ (δ 0.845), (b) multiplets of alkyl group –CH_2– (δ 1.23–1.26), (c) R-COO-CH_2-$\mathbf{CH_2}$-R at (δ 1.53), (d) R-COO-$\mathbf{CH_2}$-R (δ 1.52) and (e) protons of ethylene group R-COO-$\mathbf{CH_2}$-$\mathbf{CH_2}$-OOC-R (δ 4.25) which confirmed the diester formation [22]. The mass spectra of the product was confirmed by MS (ES): m/z 595 [M + H$^+$], 283, 311 (Figure S2 Supporting information).

Table 2 Catalyst optimization

SO_4/ZrO (% w/w)	Time (min)	Conversion (%)	Yield of EGDS (%)	Monoester–diester ratio
3	10	51.2	17.5	0.83/0.17
5	10	87.1	52.7	0.48/0.52
10	10	91.82	61.1	0.39/0.61

Sulphated zirconia has good water-tolerant property. The ammonia thermal desorption analysis for the catalyst activity showed no loss of the active sites [23]. Acid site concentration of fresh sulphated zirconia catalyst was 0.414 mmol/g while 0.467 mmol/g was detected for the used catalyst as presented in Fig. 6. The additional acidity was because of SA adsorbed on the catalyst surface. The pore volume of the SO_4^-/ZrO_2, however, showed significant decrease (~ 90%) when no treatment was given to the recovered catalyst. Optimisation mentioned in Table 2 indicates that sulfated zirconia catalyst at 10% of loading gave 91.8% as the best conversion in 10 min. It must be noted that sulfated zirconia had lower number of active acid sites as compared to the polymeric catalyst, and yet gave better results in terms of the reaction rate and yield of the product.

The physical properties of fresh catalyst, Indion 130, were compared with those of the used catalyst after the reaction. The surface area of 12 m^2/g, a pore volume of 0.35 cm^3/g and pore diameter of 260 Å of used resin catalyst dropped as compared to the fresh resin. The desorption of reaction mass from the catalyst surface may resist the contact of fresh reactants with the active sites, which leads to loss of the catalytic activity of the resin over recycles. Changes in the physical properties of the Amberlyst catalyst were observed too. The surface area of the used Amberlyst-15 catalyst was 48 m^2/g, pore volume 0.38 cm^3/g and pore diameter of 285 Å. Microwave may heat these polymeric catalysts too as the heat of the reaction mixture is also transferred to the solid catalyst. The polymeric backbone of the catalysts may lose stability if the temperatures are too high. Sulfated zirconia, on the other hand, shows better thermal stability.

The conversion of stearic acid, however, decreased marginally over four cycles of reusing the catalyst (Fig. 7). The decrease in the pore volume of the catalyst was not reflected in the catalytic activity of the sulfated zirconia catalyst that not all pores were accessible to the reacting species. The microwave effect is because of selective dielectric heating of polar compounds which interact with the microwave electromagnetic field [24]. Heat is generated due to rapid molecular rotation in the reaction mixture reducing thermal gradients. It provides advantages over conventional heating such as reduction of process steps, faster heating of the reaction mixture and the catalyst. Selective heating of reactants and solid catalyst increases the rate and then yield of the esterification reaction as compared to conventional heating under similar reaction parameters [13].

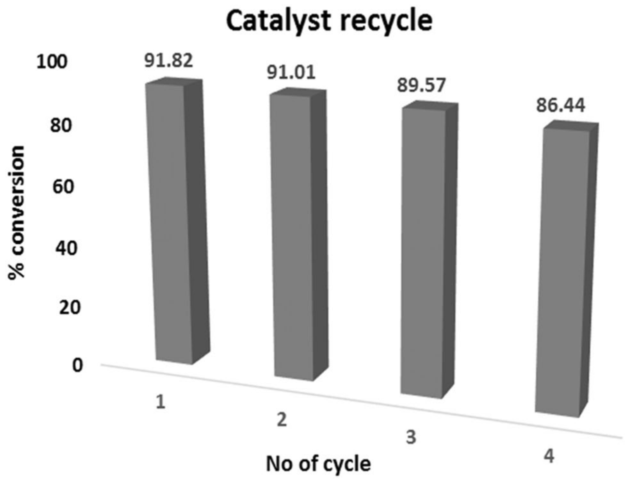


Fig. 7 Sulfated zirconia catalyst recycle

Ionescu et al. [21] have reported the diester synthesis using p-toluene sulfonic acid (5%) as the catalyst and toluene as an entrainer to remove water, with 85% yield of the product in 4 h. In the present case, the yield of the esters was higher, under solvent-free conditions, with just 0.3% of *p*-TSA loading as the catalyst. The water formed in the reaction quickly evaporates because of the temperature reached by the mixture due to microwave heating. Most importantly, there was no colouration of the product, normally exhibited when concentrated H_2SO_4 is used as the homogeneous catalyst.

Li et al. [25] reported the distearate synthesis with a silica gel based solid catalyst. The reaction took 4 h at a temperature of 260–270 °C to give 97% conversion under solvent-free conditions. Higher temperatures are reportedly responsible for coloration of the product under such conditions [25]. It thus appears that reaction temperature under microwave radiation did not go beyond these limits. Nevertheless, there was a substantial enhancement in the rate of the esterification reaction because of the microwave with, both homogeneous as well as heterogeneous catalysts.

5 Conclusion

A solvent-free synthesis of the diester of stearic acid and ethylene glycol was intensified by microwave irradiation. The rate of reaction was enhanced by microwave by at least an order of magnitude with both, homogeneous and heterogeneous, catalysts. The reaction time decreased markedly from a few hours in the absence of microwave to 10 min when the reaction mixture was irradiated, with good conversion and yield. The polymeric catalyst showed substantial loss of physical properties after exposure to microwave radiation while the effect on the activity of sulfated zirconia was minimal. The conversion achieved with p-TSA as homogeneous catalyst was, however, higher at 97% at much lower catalyst loading(0.3%) as compared to all heterogeneous catalyst. But heterogeneous catalyst provides much easier separation from the reaction mixture as compared to p-TSA and allows catalyst recycle over multiple reaction batches without much loss of the activity.

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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest.

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