Catal Lett
DOI 10.1007/s10562-014-1275-8

Cellulose Sulfuric Acid Catalyzed Esterification of Biodiesel Derived Raw Glycerol to Medium Chain Triglyceride: The Dual Advantage

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Received: 9 April 2014 / Accepted: 11 May 2014

Abstract Biodiesel derived raw glycerol represent a copious and inexpensive source which can be used as raw material for a variety of value added products such as 1,3-propanediol, poly hydroxyalkanoate, hydrogen, epichlorohydrin and also lactic acid. So, this work was investigated to study chemical conversion of biodiesel derived raw glycerol and lauric acid to triglycerides of lauric acid via esterification reaction over cellulose sulfuric acid as an efficient, biodegradable and recyclable solid acid catalyst. Synthesized catalyst was characterized by fourier transform infra-red spectroscopy (FT-IR) as well as BET surface area analysis. While, synthesized triglyceride of lauric acid was fittingly characterized by FT-IR as well as ^{1}H and ^{13}C Nuclear magnetic resonance spectroscopic techniques.

Keywords Glycerol · Cellulose sulfuric acid (CSA) · Epichlorohydrin · Biodiesel · Esterification

1 Introduction

The world continues to explore alternative source of energy and chemicals in order to reduce dependency on fossil fuels and to ensure the security of energy supply. Biodiesel production could play a significant role in this process [1, 2]. Large amounts of glycerol are obtained as waste products from biodiesel production, with about 1 kg of glycerol produced for every 10 kg of biodiesel [3]. In 2009, the biodiesel product from the european union and united states reached a massive share of 9 and 2.7 million tons respectively, from a total of 16 million tons worldwide [4]. Therefore, 1.6 million tons of glycerol was produced as an obligatory byproduct. Glycerol, also known as glycerin or propane-1,2,3-triol, is a chemical which has a multitude of uses in pharmaceutical, cosmetic, and food industries [5]. It can be produced as a by-product from saponification and hydrolysis reactions in oleochemical plants as well as transesterification reaction in biodiesel plants. Further crude glycerol is a low value product as its low purity limits its application as feedstock in industries [6].

The development of conversion processes for crude glycerol to other value added products is being thoroughly investigated [7]. However, the techniques are not widely commercially adopted at present in developing countries [8]. The purified glycerol can be sold as a commodity because it is still highly required as an important industrial feedstock especially in various chemical industries. Consequently, a development of purification methods is necessary to produce highly purified glycerol as feasible industrial feedstock [9]. Currently, almost two third of the industrial uses of glycerol are in food and beverage (23 %), personal care (13 %), oral care (20 %), tobacco (12 %), etc. [10]. The purification of crude glycerin from the biodiesel plants is a major issue. The disposal of glycerol by the emerging biodiesel industry is therefore a new engineering challenge in order to make it more competitive with the conventional fossil diesel. Also, with the ever increasing production of biodiesel, a glut of glycerin ($C_3H_8O_3$) is expected in the world market [11].

It is critical to explore alternative uses of glycerin. One promising way is to use glycerin to produce hydrogen or synthesis gas via steam reforming [12, 13]. Hydrogen is a clean energy source with uses including ammonia production, petroleum processing, and power generation in fuel cells. Also, it is known that, the demand for hydrogen

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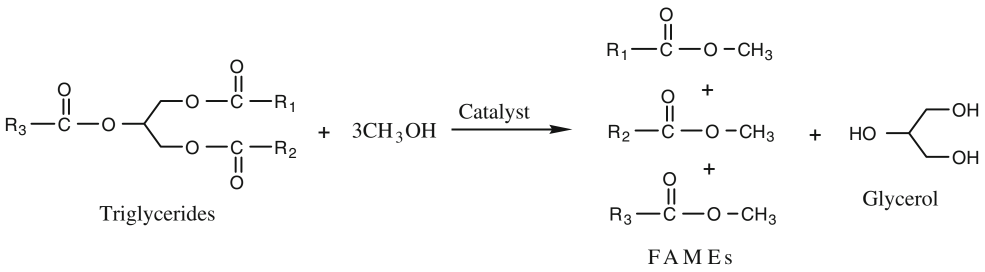

Fig. 1 Transesterification of triglyceride to biodiesel and glycerol

is expected to greatly increase globally in the future, due to the increasing environmental concerns [14, 15]. Triglyceride is an ester derived from glycerol and three fatty acid molecules. Triglycerides are blood lipids that help enable the bidirectional transference of adipose fat and blood glucose from the liver. Depending on the oil source, triglycerides can be named as an either highly unsaturated or saturated. Also, it is used in the synthesis of biodiesel fuel. Biodiesel and glycerol are generally produced via transesterification of triglyceride of fatty acids. Where, one molecule of triglyceride reacts with three molecules of alcohol to produce three molecules of fatty acid alkyl esters and one molecule of glycerol [16–18]. General reaction scheme for transesterification of triglyceride to biodiesel and glycerol is given in Fig. 1 [12].

Like other solid acid catalysts, cellulose sulfuric acid (CSA) can also be used as an acid catalyst in numerous organic synthesis reactions [19]. As being a heterogeneous catalyst, it easily gets recovered from the reaction media and also used for several repetitive cycles without significant loss of their activity. Cellulose is biodegradable polymer and it contains numerous hydroxyl functionalities. So, on chlorosulphonation of cellulose, almost all hydroxyl groups get converted into sulphonic acid groups. Therefore, it can able to give very good acidity. Furthermore, these types of catalysts are efficient, environmentally friendly and biodegradable in nature [20–22]. So, an effort was made to study chemical conversion of biodiesel derived raw glycerol and lauric acid to triglycerides of lauric acid via esterification reaction over CSA as green solid acid catalyst.

2 Experimental Methodology

2.1 General

All commercially available chemicals were purchased from Fluka and Merck companies and used without further purification. IR spectrum was recorded on a (Model RZX Perkin Elmer) FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Advanced DPX 400 MHz FT-NMR spectrometer using TMS as internal standard. Surface area measurements were done after pretreating the sample under high vacuum at 350 °C for 6 h, by nitrogen adsorption on a Micromeritics ASAP 2010 instrument. Specific surface area (S_{BET}) was calculated from the linear part by BET equation. Reaction monitoring was accomplished by TLC on silica gel Polygram SILG/UV 254 plates.

2.2 Materials and Methods

2.2.1 *Materials*

Raw glycerol was pulled down as a byproduct from our own biodiesel production process. Lauric acid, dichloromethane (DCM) and chlorosulfonic acid used in the present study were purchased from Sterling lab care, Surat, Gujarat, India.

2.2.2 *Preparation of Cellulose Sulfuric Acid (CSA) Catalyst*

In a magnetically stirred mixture of cellulose (5.00 g, Merck) in methylene dichloride (20 ml), chlorosulfonic acid (1.00 g) was added drop wise at 0 °C during 2 h. After addition was completed, the mixture was stirred for 2 h until HCl was removed from the reaction vessel under partial vaccum (Above −85.05 °C HCl is gaseous in nature). Then, the mixture was filtered and washed with acetonitrile (30 ml) and dried at room temperature to obtain CSA as a white powder (5.22 g). The sulfur content of the samples of conventional elemental analysis, was 0.55 mmol/g for CSA. The number of H^+ site of cellulose-SO_3H determined by acid–base titration was 0.50 meq/g. This value corresponds to about 90 % of the sulfur content, indicating that most of the sulfur species in the sample are in the form of the sulfonic acid groups. A general reaction scheme for the synthesis of CSA is given in Fig. 2.

2.3 General Procedure

2.3.1 *CSA Catalyzed Esterification of Raw Glycerol to Triglycerides of Lauric Acid*

The glycerol esterification processes were usually carried out under continuous water removal system. Water removal during esterification is a vital process as it is formed as a side product and will inhibit the activity of a

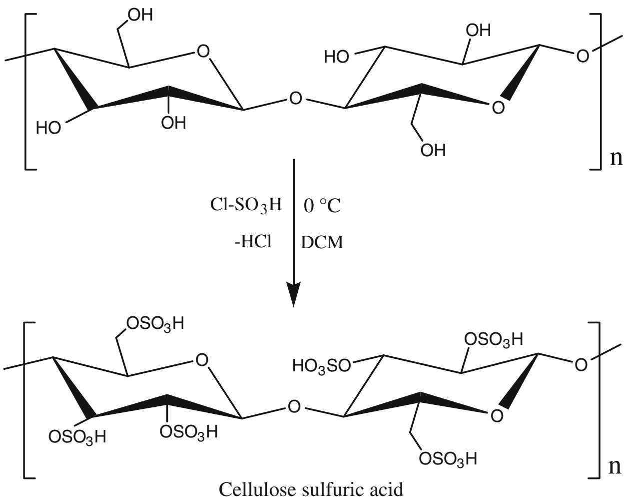

Fig. 2 Reaction scheme for synthesis of cellulose sulfuric acid (CSA) catalyst

solid acid catalyst. It can also promote reverse reaction. Besides, esterification is an equilibrium limited reaction in which full conversion can only be achieved when one of the products is removed. Therefore, anhydrous sodium sulphate (1.5 mol) was added to trape water formation during the reaction. So, in the present study, a three neck round bottom flask (equipped with a condenser, temperature indicator and continuous water removing system), a mixture of lauric acid (3 mol), raw glycerol (1 mol) and CSA (0.8 g) was added and stirred at 170 °C for the appropriate time. Completion of the reaction was indicated by TLC monitoring. Finally, the reaction mixture was cooled to ambient temperature; the CSA was filtered off. The filtrate was poured into a cold water to get triglycerides at upper layer. Furthermore, the unreacted lauric acid also tended to remain in the upper layer. So, it was filtered off from triglycerides and 94 % yield was obtained. Whereas, unreacted glycerol directly goes to the aqueous phase. So, isolation of the final product becomes easier. General reaction scheme for esterification of biodiesel derived raw glycerol to triglycerides of lauric acid is given in Fig. 3.

2.3.2 *Suggested Reaction Mechanism Pathway for CSA Catalyzed Esterification of Raw Glycerol to Triglycerides of Lauric Acid*

Mechanism of esterification of glycerol and lauric acid could be accomplished via three steps, in the first step acid catalyst will protonate the lauric acid molecule via liberation of the proton. The protonated lauric acid molecule will remove one molecule of water, followed by nucleophilic attack of oxygen will take place, which is lying in the one of the hydroxyl group of glycerol to form a tetrahedral intermediate. Finally, deprotonation of a tetrahedral intermediate gives monoglyceride of lauric acid. This entire sequence will repeat at twice to form a triglyceride of lauric acid and three molecules of water. But in second and third steps, monoglyceride of lauric acid and diglyceride of lauric acid will react with remaining hydroxyl groups in monoglyceride of lauric acid respectively. Overall, in the esterification of lauric acid and glycerol, three molecules of lauric acid and one molecule of glycerol reacted to form one molecule of triglyceride of lauric acid and three molecules of water. The General reaction mechanism scheme is given in the Fig. 4.

3 Results and Discussion

Triglycerides of medium chain length fatty acids, known as medium-chain triglyceride(s) or MCT(s), can be synthesized by esterifying glycerol with fatty acids [23]. Aluminium trichloride appeared to be as effective catalyst for esterification of glycerol but it has not been tested with a wide range of samples. Phenyl esters of fatty acids have been prepared by esterification of glycerol and lauric acid using *p*-toluenesulfonic acid as a catalyst [24]. Therefore,

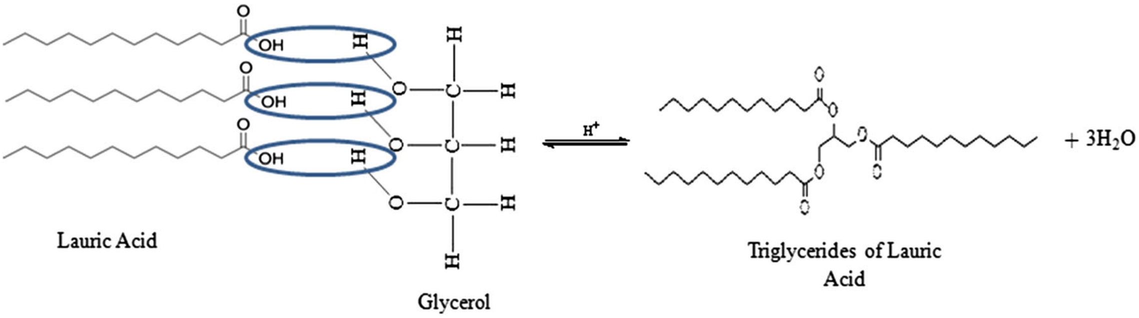

Fig. 3 Esterification of biodiesel derived raw glycerol and lauric acid to triglycerides of lauric acid

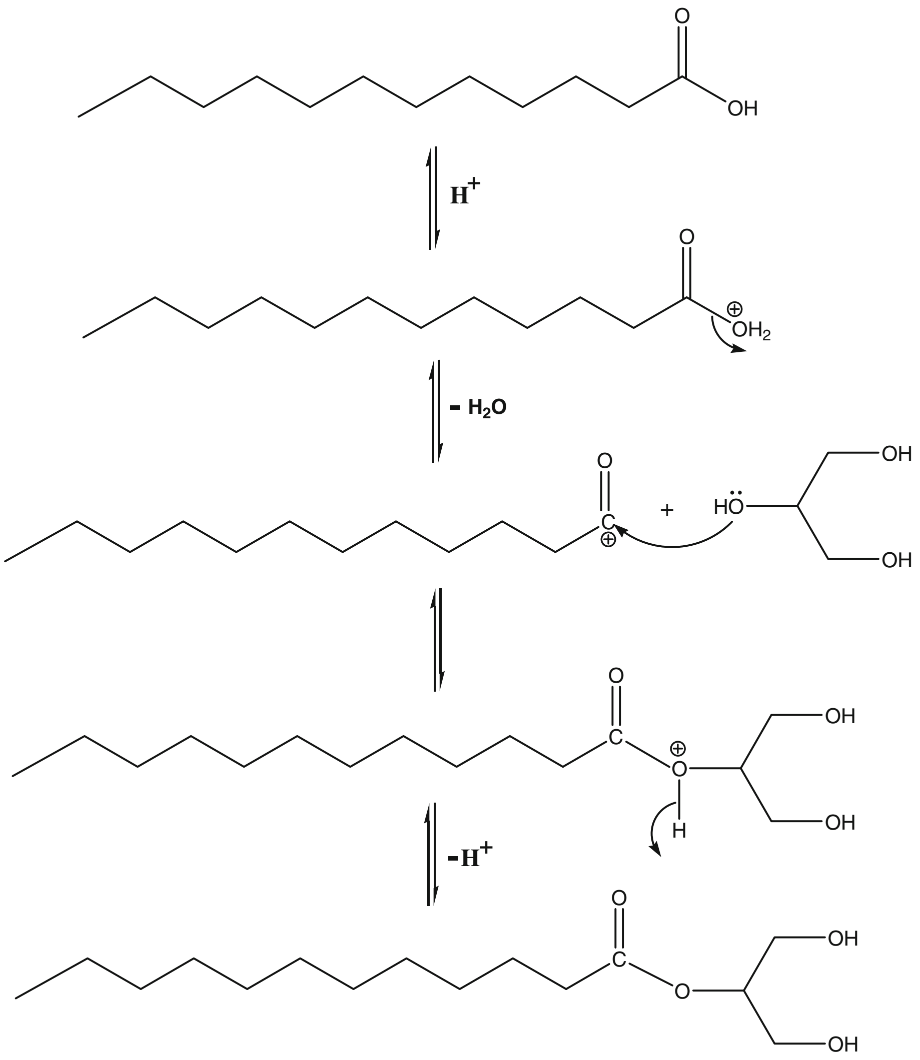

Fig. 4 Reaction mechanism pathway for CSA catalyzed esterification of raw glycerol to triglycerides of lauric acid

in present investigation the prepared CSA catalyst was evaluated for the synthesis of triglycerides of lauric acid under reaction conditions such as reaction temperature of 170 °C, stirring speed of 600 rpm, and 0.8 g catalyst. The best catalyst amount was chosen based on the yield of maximum triglycerides with minimum unreacted glycerol and lauric acid content in the final product. From the surface area analysis it has been found that BET surface area (S_{BET}) and microporous surface area (S_{micro}) of CSA are 100.7546 and 105.2088 m^2/g respectively. Synthesized catalyst was also investigated for their solubility in acid and organic solvents. CSA is soluble in water, methanol, propanol, 1-butanol, acetic acid and hydrobromic acid. Whereas, it is insoluble in methylene dichloride, hexane, carbon tetrachloride, chloroform, ethylene dichloride, benzene and phosphoric acid. It is decomposed in nitric acid and sulfuric acid.

Synthesized catalyst was also investigated for their reusability study. During the experiments, it was found that catalyst can also intended for three repetitive cycles without significant loss of their activity. Fresh catalyst can give maximum conversion of lauric acid to triglyceride up to 94 %. However, its first, second and third cycle can give maximum conversion up to 90, 87 and 84 % respectively. Raw glycerol is available in the commercial market at very low cost or no cost. Furthermore, downstreaming process for raw glycerol is very complex and requires high cost as well as plenty of manpower. Lauric acid available in the commercial market at somehow high cost. The cost of the lauric acid is already covered by glycerol, if it is raw glycerol. Because, purification cost of raw glycerol is much more high then cost of commercial grade lauric acid. One of the major advantage associated with this process is the formation of water as a byproduct rather then other toxic chemicals. So, this process offering environmental sustainability also. Overall, this process offering economical viability for the commercial production of triglycerides of lauric acid.

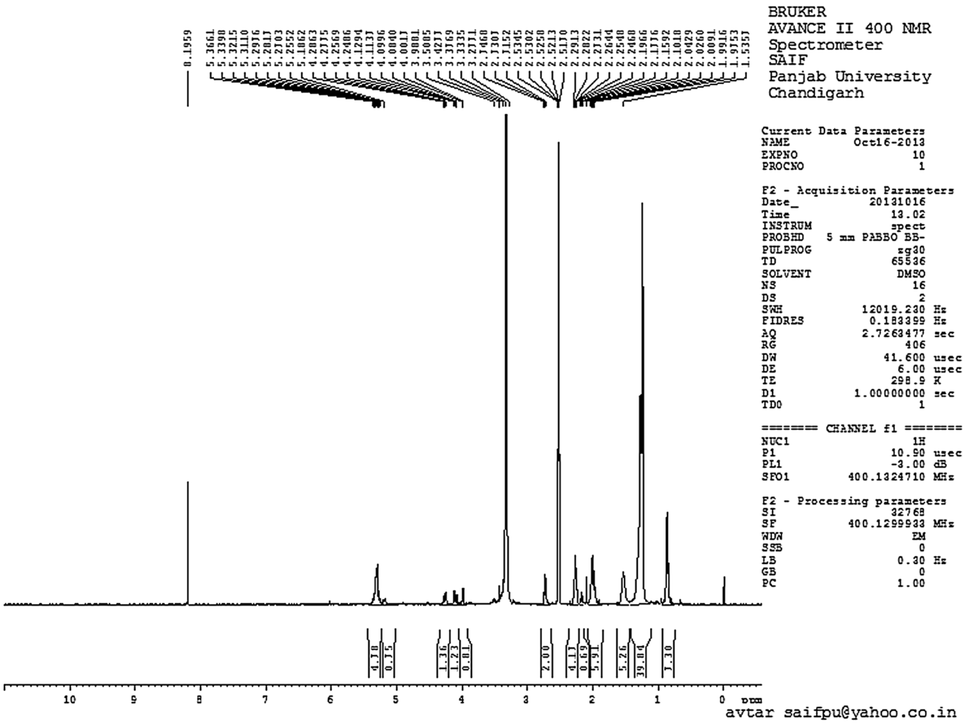

Fig. 5 ^{1}H NMR spectrum of synthesized triglycerides of lauric acid

4 Characterization of CSA Catalyst and Synthesized Medium Chain Triglyceride

4.1 ^{1}H NMR Characterization of Synthesized Triglycerides of Lauric Acid

The use of ^{1}H NMR analysis is convenient and fast in monitoring a reaction, because a small aliquot can be extracted from the batch reaction at any given time and the ^{1}H NMR spectrum analysis provides quantitative information pertaining to the chemical species present in the reaction. The extent of esterification of biodiesel derived raw glycerol was determined by ^{1}H NMR spectroscopy. Purity of triglycerides of lauric acid is further confirmed by the presence of peaks corresponding to triglycerides (5.18–5.36 ppm), diglyceride (3.98–4.28 ppm) and monoglyceride (3.27–3.50 ppm). ^{1}H NMR spectrum of synthesized triglycerides of lauric acid is given in Fig. 5.

4.2 ^{13}C NMR Characterization of Synthesized Triglycerides of Lauric Acid

The progress of esterification of biodiesel derived raw glycerol was also determined by ^{13}C NMR spectroscopy. Purity of triglycerides of lauric acid is confirmed by the presence of peaks corresponding to carbonyl (C=O) functionality in the triglyceride molecule (172.68 ppm). Whereas, peaks corresponding binary mixture of solvent containing DMSO and $CDCl_3$ (38.95–40.20 and 78.41–79.07 ppm respectively). ^{13}C NMR spectrum of synthesized triglycerides of lauric acid is given in Fig. 6.

4.3 FT-IR Characterization of Synthesized Triglycerides of Lauric Acid

FTIR spectrum of triglycerides of lauric acid confirmed the presence of 2,925.57 cm^{-1} (CH_3 stretching), 2,864.54 cm^{-1} (CH_2 stretching), 1,746.61 cm^{-1} (C=O), 1,464.73 cm^{-1} (CH bending), 1,386.76 cm^{-1} (CH rocking) and 1,162.60 cm^{-1} (C–O) respectively. FT-IR spectrum of synthesized triglycerides of lauric acid is given in Fig. 7.

4.4 N_2 Desorption–Adsorption Characterization of CSA Catalyst

BET surface area (S_{BET}) and microporous surface area (S_{micro}) of CSA are 100.7546 and 105.2088 m^2/g respectively. N_2 adsorption–desorption isotherms of CSA has been demonstrated in Fig. 8 and The results of BET surface area and pore volume have been represented in Table 1.

N_2 adsorption–desorption isotherms of CSA was found typically of Type-IV which turned to Type-I feature at lower *p/po* values indicating the presence of both micropore and mesopore. The pore volume of CSA is 0.09376 cm^3/g. The pore size and surface area indicates the

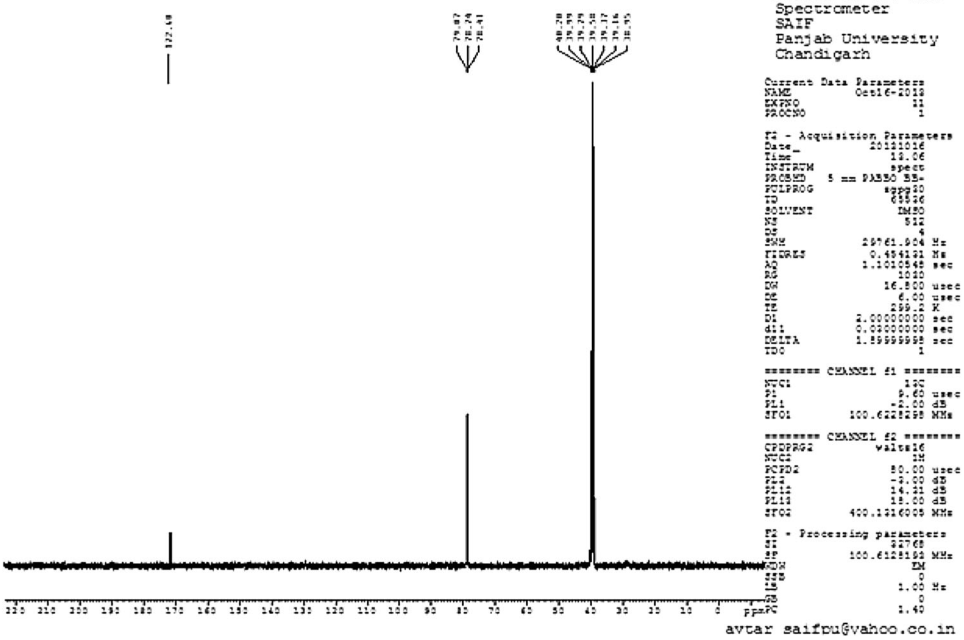

Fig. 6 ^{13}C NMR spectrum of synthesized triglycerides of lauric acid

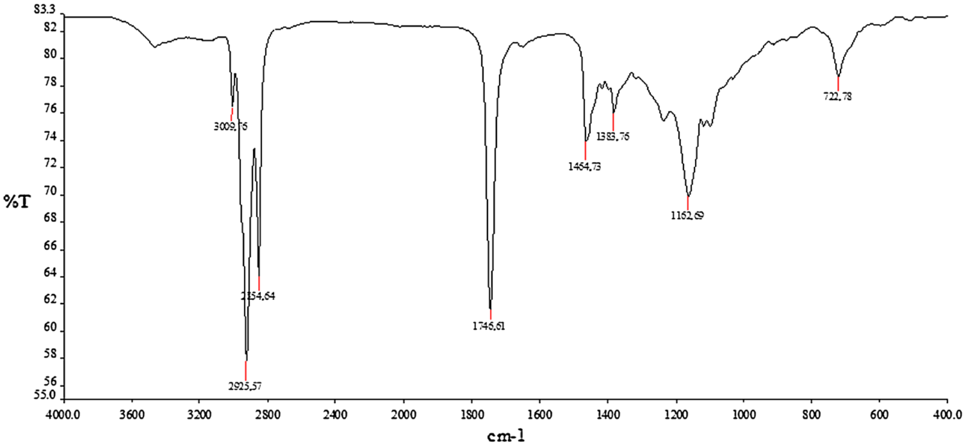

Fig. 7 FT-IR spectrum of synthesized triglycerides of lauric acid

presence of SO_3H groups on the pore surface of cellulose molecules.

5 Regeration and Reusability of CSA Catalyst

In order to reduce cost of triglyceride production, catalyst reusability is most important. Therefore, in this segment CSA catalyst was filtered off from the reaction media and washed at twice with methylene dichloride solvent for removal of impurity traces. Finally washed CSA was place in a tray dryer at 60 °C for 24 h owing to removal of solvent and activation of acid sites on cellulose entity. The results clearly indicate that the catalyst can be reused for three times without significant loss of activity. It has been found that cellulose retains its structure throughout reaction without any change and also it is clearly proven by spectral characterization of catalyst. Figure 9 demonstrates the FT-IR spectrum of fresh and spent catalyst.

FTIR spectrum of CSA (Fig. 9) is confirmed by the presence of 3,468.13 cm^{-1} (–OH stretching of phenolic –OH), 1,334.78 cm^{-1} (C–O–H bending), 1,153.47 cm^{-1} (SO_2 asymmetric stretching provided by presence of SO_3H group), 1,003.02 cm^{-1} (SO_2 symmetrical stretching), 925.86 cm^{-1} (C–O–C stretching), 763.84 cm^{-1} (C–C

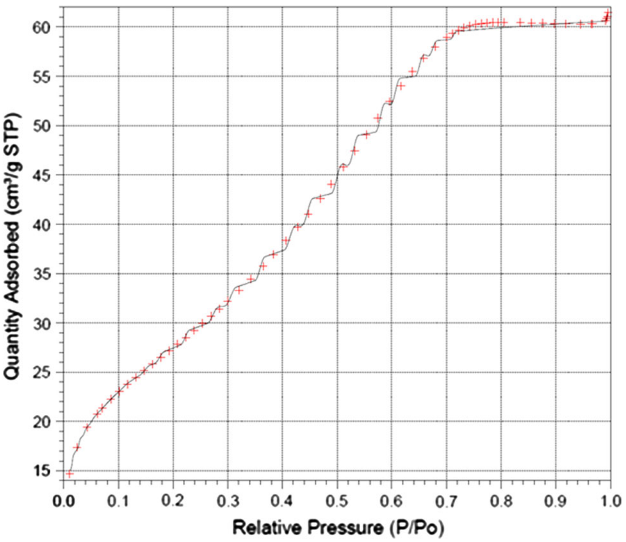

Fig. 8 N_2 adsorption–desorption isotherm of CSA catalyst

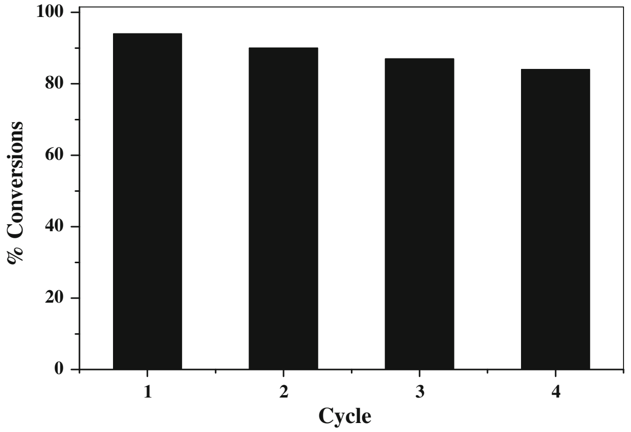

Fig. 10 Effect of catalyst cycle on % conversion of glycerol to triglyceride

stretching) and 709.83, 574.81, 532.37 cm^{-1} (skeleton modes of pyranol ring), respectively.

However, the little decrement in the triglyceride production was observed in subsequent runs. The observed catalyst deactivation could be due to modification of catalyst structure or leaching of active sites at given reaction temperature. The catalyst reusability study is given in Fig. 10.

Table 1 Surface area and pore volume of CSA catalyst

Catalyst	Surface area (m^2/g)		Total	t-plot	DFT pore
	BET S_{BET}	t-plot S_{micro}	PV (cm^3/g) V_{total}	PV (cm^3/g) V_{micro}	size (m^2/g)
SMTSA	100.7546	105.2088	0.09376	−0.003321	43.482

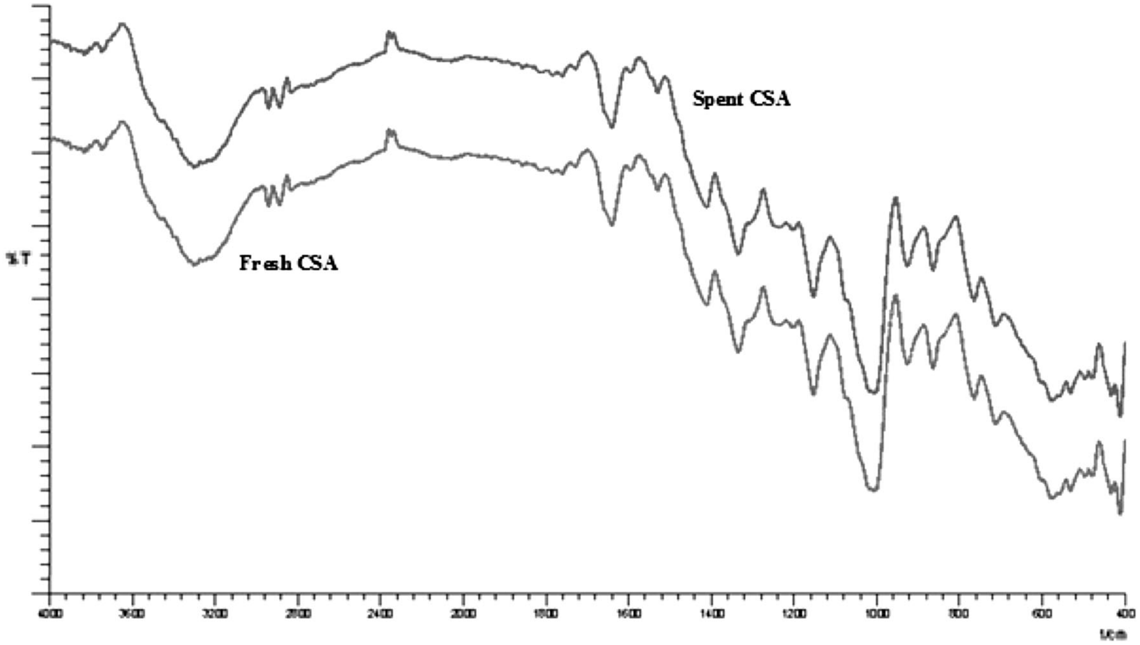

Fig. 9 FT-IR spectrum of fresh and spent CSA catalyst

6 Conclusion

In this study, esterification of biodiesel derived raw glycerol and lauric acid in the presence of CSA, a solid acid catalyst was successfully conducted. During the esterification reaction it has been found that the process was very convenient and efficient. During the experiments, it was found that synthesized catalyst can also be used for three repetitive cycles without significant loss of their activity. Recently, world is facing the problem of disposal of glycerol obtained from biodiesel synthesis as a byproduct and simultaneously they are facing the problem of the abundance of feedstocks for biodiesel synthesis. The purification of crude glycerin from the biodiesel plants is a major issue. Also, the disposal of glycerol by the emerging biodiesel industry is therefore a new engineering challenge in order to make it more competitive with the conventional fossil diesel. This avenue having dual advantages containing (i) raw glycerol can be successfully converted into triglycerides. (ii) Synthesized triglycerides could be used as a feedstock for biodiesel synthesis. This avenue is able to resolve the both challenges. The method offers a marked improvement with its operational simplicity, low reaction time and high yields of pure product. Recently, one of the major deterrent towards widespread commercialization of biodiesel is an abundance of low cost feed stocks. So, by applying such strategies one can easily produce biodiesel in a cost effective manner.

Acknowledgments The authors are very much thankful to the Department of Applied Chemistry, Sardar Vallabhbhai National Institute of Technology (SVNIT), Surat for providing laboratory facilities and financial support for the course of this work. For characterization, we are thankful to Mr. Avtar Singh, SAIF, Punjab University, Chandigarh and Mr. M. H. Malani as well as Mr. M. Rathod from Department of Applied Chemistry, Sardar Vallabhbhai National Institute of Technology (SVNIT), Surat, India are gratefully acknowledged.

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