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**A Green Approach for the production of biodiesel from fatty acids of corn  
deodorizer distillate**

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**Abstract**

A novel alginic acid derived tin catalyst, tin alginate (Sn-Alg), was successfully synthesized, characterized and applied for methyl esterification. Initially, amount of catalyst, methanol to fatty acid ratio and reaction time were optimized using oleic acid standard for esterification. The best reaction conditions were found to be 4 % catalyst amount, 1:12 oleic acid to methanol mole ratio and 2 hours reaction time with 98.7 % fatty acid methyl ester recovery. Capability of Sn-Alg beads to esterify fatty acids of corn deodorizer distillate was evaluated by high recovery (97.6%), obtained after 8 cycles with reprocessed catalyst under optimized parameters. Results of present study indicated that on the basis of environmental pollution, reusability, avoiding use of potassium or sodium hydroxides or sulphuric or phosphoric acids, ease of catalyst separation, solid Sn-Alg catalyst has a great potential for biodiesel production from high free fatty acid deodorizer distillates.

**Keywords:** Tin alginate; Oleic acid; Corn deodorizer distillate; Biodiesel

## 1. Introduction:

As the world starts to accept the gales of changes towards green energy, biofuel stands at the frontline of this ideology. Biodiesel, a part of biofuel is rapidly evolving as a sustainable attractive alternative source of petroleum fuel due to its environment friendly, renewable and green properties.<sup>1</sup> Biodiesel is low carbon exhaust emission neutral fuel that can be prepared by either transesterification of triglycerides (the main component of vegetable oils or animal fats) or esterification of free fatty acids (FFAs) with a short chain alcohol (mainly methanol).<sup>2</sup> In recent years, biodiesel gained progressively more attention as it is considered to be one of the best promising remedy to offset negative environmental effects resulting from overconsumption of non-sustainable fossil fuels.<sup>3</sup> Currently, more than 95% of the world biodiesel is mainly prepared from commercially available vegetable oils such as soybean, rapeseed, sunflower and palm consequently leading to alleviate food versus fuel dispute.<sup>4</sup> As the demand for vegetable oils for food supply has increased enormously due to growing population, it is incredible to justify the use of these oils for biodiesel production. Furthermore, these oils could be more expensive to use as fuel.<sup>5</sup>

Hence, the contribution of non-edible plant oil and the use of waste vegetable oil have been found to be promising for biodiesel production. That is an effective way to resolve the issue between food supply and fuel besides reduction of raw material cost<sup>6</sup>. Meanwhile, substantial attention has been specified to the other cheaper feedstocks such as vegetable oil palm oil fatty acid distillates (POFAD) and vegetable oil deodorizer distillate (VODD).<sup>7, 8</sup>

Deodorizer distillate (DD) is the waste that produced during the deodorization process of vegetable oils. Mainly it contains free fatty acids (FFAs; 30–60% w/w), sterols, sterol esters (10–

30%, w/w), Hydrocarbons (10–30%, w/w, mainly squalene), and glycerides (10–20%, w/w, mainly mono- and diglycerides), as well as several other minor substances. Due to its high content of free fatty acids this product could be used as an excellent cheaper source for biodiesel.<sup>9</sup> Conventionally, homogeneous acid and basic catalysts (such as H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, NaOH, KOH, etc.) are most frequently used for the preparation of biodiesel, however, these kinds of catalytic system suffer from many drawbacks such as environmental pollution, generates much waste water during product washing, long reaction time, difficulty in separation and purification of target product, and equipment corrosion that severely hampers the commercialization of the relevant process.<sup>7, 10</sup> In view of the difficulties faced with homogeneous catalysts, research for the development of heterogeneous catalysts was escalated in many academic and industrial laboratories.<sup>11-13</sup> These types of catalysts offer several distinctive advantages related to the simplicity of continuous production methods over batch methods. The development of solid catalyst with cheap and reusable materials has a great potential in this specific research area.<sup>13</sup>

Trakarnpruk et al.<sup>14</sup> has reported the research on biodiesel production from palm fatty acids distillate (PFAD) containing 93% of FFAs using two catalyst systems i.e. Tungstophosphoric acid and Cs-salt Immobilized-Silica. Comparatively, Tungstophosphoric acid was reported a good catalyst with 96.7 % recovery of FAME conversion at 85 °C in 15 hours reaction time, 12:1 molar ratio of methanol to PFAD and 15 wt% catalysts. Boey et al.<sup>15</sup> used Ferric Alginate beads as a solid acid catalyst for the esterification of lauric acid with methanol using response surface methodology for optimization. The optimized parameters (3 hr reaction time, 15:1 methanol to PFAD molar ratio) were used for esterification of PFAD which bring about 88.8 % methyl esters conversion. Algalic acid derived, aluminum-alginate solid acid

catalyst was synthesized by Qiuyun et al.<sup>10</sup> exhibited high catalytic activity, with a 92.6% conversion of methyl oleate in the presence of 4 % of the catalyst dosage upon refluxing for 3 h of methanol and acid mixed in a molar ratio of 10:1.

Based on aforementioned literature information, we prepared a novel tin-alginate catalyst from cost-effective and risk-free sodium alginate polymer, which was used for the esterification reaction of oleic acid with methanol for optimization and afterward applied for esterification of corn deodorizer distillates (CDD). Finally, the reusability of Sn-Alg was evaluated.

## 2. Material and Methods

### 2.1. Chemicals

Oleic acid (99%) was obtained from Fluka, tin chloride ( $\text{SnCl}_2$ ). $2\text{H}_2\text{O}$  and sodium alginate was supplied by Sigma-Aldrich Chemie GmbH (USA). Whereas methanol, n-hexane were provided by Fisher Chemical. Anhydrous sodium sulfate (99%) was purchased from Sigma-Aldrich Corporation (USA). All the chemicals used were of analytical grade. The chromatographic methyl ester standard, methyl heptadecanoate was supplied by Sigma-Aldrich Chemie GmbH (USA). Deodorizer distillate samples were obtained from Zade edible oil refining industries (Konya, Turkey).

### 2.2. Preparation of tin-alginate beads for esterification

Tin-alginate (Sn-Alg) beads were prepared according to the literature information.<sup>15</sup> About, 4 g of sodium alginate was added to 200 mL of distilled water (heated to 60°C), stirred the content until a clear viscous solution was obtained. The solution was then allowed to cool at room temperature. Then, the viscous solution was added drop-wise using a Pasteur pipette into 0.1 mol L<sup>-1</sup> solution of ( $\text{SnCl}_2$ ). $2\text{H}_2\text{O}$  at room temperature (28–30 °C). The Sn-Alg beads formed

were left for 2 hours to equilibrate it in the  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  solution. Finally the beads were washed and dried in an oven at  $60\text{ }^\circ\text{C}$  for 2 days.

### 2.3. Characterization

The amount of Sn metal in the Sn–Alg beads was evaluated by using a Perkin Elmer SCIEX Inductively Coupled Plasma Mass Spectrometer (ICP-MS) with ELAN DRC-e technology (USA) through calibration model of standard metal. The chemical composition of the prepared Sn–Alg solid acid catalyst was characterized by scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) detector EVO-LS 10 (Carl Zeiss, Germany), X-ray diffraction (XRD) on Bruker Advance D8 XRD, Germany model using  $\text{CuK}\alpha$  radiation ( $\alpha=1.5417\text{Å}$ ). Functional group characterization of Sn–Alg beads were done on a Vertex 70 (Bruker, Germany) model armed with Platinum ATR Diamond accessory. Thermostability of the synthesized Sn–Alg catalyst was performed with 5–9 mg sample on the SETARAM thermo gravimetric analyzer (Setsys Evolution, France). Analysis temperature was ranged from  $25\text{--}1000\text{ }^\circ\text{C}$  at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ , under oxygen atmosphere with a gas flow rate of  $20\text{ mL}/\text{min}$ . Acidic strength of the Sn–Alg beads was verified using  $0.1\text{ g}$  of dried beads put in  $5\text{ mL}$  of anhydrous methanol and one drop of  $0.1\%$  Hammett indicator (crystal violet, bromophenol blue, methyl red and neutral red) then left it to equilibrate for 2 hours. Any changes in color are noted.<sup>7</sup>

### 2.4. Esterification of corn deodorizer distillate (CDD)

Based on the optimized results,  $2.5\text{ g}$  of corn deodorizer distillate (CDD) was subjected for esterification reaction at  $60\text{ }^\circ\text{C}$  for 2 hours with Sn–Alg beads. The initial acid value of CDD was determined using the AOCS Cd 3d-63 method.<sup>16</sup> The main fatty acid composition of CDD

was found to be 16.17% palmitic acid, 2.05% Palmitelaidic acid, 0.32% Palmitoleic acid, 5.37%; stearic acid, 30.93%; elaidic acid, 0.74%; oleic acid, 42.12%; linoleic acid, 2.17% and linolenic acid 0.14%.

## 2.5. Esterification reaction

An appropriate amount of oleic acid, methanol and Sn–Alg catalyst were added in a round bottom flask and refluxed under optimized conditions. For comparison oleic acid and methanol was also refluxed without the addition of Sn-Alg catalyst under the similar conditions. Then small aliquots of sample were withdrawn from the reaction mixture for esterification efficiency determination through their acid value by titration. The conversion of FFA was calculated based on the following Eq.(1).<sup>10</sup>

$$\text{FFA Conversion (\%)} = \frac{\text{Initial Acid Value} - \text{Final Acid Value}}{\text{Initial Acid Value}} \times 100 \quad (1)$$

To confirm the good reproducibility of reaction the esterification experiments were conducted three times.

## 2.6. Gas chromatographic analysis

Gas chromatography apparatus (Agilent Technologies, 7890A GC System) equipped with a flame ionization detector (FID) was used for the methyl oleate determination. Standard materials and samples of CDD were also analyzed by a gas chromatography-mass spectroscopy system. The GC-MS analysis for FAMES was performed on Agilent 6890 N gas chromatography instrument coupled with an Agilent MS-5975 inert XL mass selective detector and an Agilent



autosampler 7683-B injector (Agilent Technologies, Little Fall, NY, USA). For the identification of methyl esters, confirmation of results of GC-FID, and to identify peaks of unknown compounds GC-MS was used a supportive technique. The content of fatty acid methyl esters (FAME) in samples was determined by succeeding the European regulation procedure EN 14103 with a high cyanopropyl-containing polysiloxane HP-88 GC capillary column (100 m x 0.25 mm ID x 0.25  $\mu\text{m}$  film thickness) using methyl heptadecanoate as an internal standard. FAMEs content was calculated by use of the Eq.(2).<sup>17</sup>

$$C = \frac{\sum A - A_{IS}}{A_{IS}} \times \frac{C_{IS} \times V_{IS}}{m} \times 100\% \quad (2)$$

Whereas;  $IS$  = Internal Standard (methyl heptadecanoate)

$\sum A$  = Total Peak area of FAME;  $\sum A_{IS}$  = Total Peak area of Internal Standard

$C_{IS}$  = Concentration of Internal Standard;  $V_{IS}$  = Volume of Internal Standard

$m$  = Mass of Sample

### 3. Result and discussion

#### 3.1. Characterization of Sn–Alg catalyst

Alginate is a copolymer composed of alternating blocks of unbranched binary copolymers of  $\beta$ -D-mannuronic and  $\alpha$ -L-guluronic acid through 1, 4-linkage. When sodium salt of alginic acid was put into  $(\text{SnCl}_2) \cdot 2\text{H}_2\text{O}$  solution, gelatin like spherical white small globules were formed instantly due to the fast cross-linking process between alginate and tin ions. According to Ruiz et al.<sup>18</sup>, when divalent cations interact ionically with blocks of  $\beta$ -D-

mannuronic and  $\alpha$ -L-guluronic acid residues, resulting in the formation of a three-dimensional network, which is usually described by the “egg-box” model.<sup>19</sup>

The Sn-Alg bead was washed off with deionized water to remove sodium chloride which is formed as side product. The catalyst was stabilized in the presence of alginate crosslinking which prevented it from hydrolysis.<sup>15</sup>

The result obtained for the detection of Sn metal through ICP-MS explained that amount of Sn was found to be  $0.266 \pm 0.005$  g per g of catalyst beads. The acid strength of Sn-Alg beads lies in the range between pH 1 and pH 3. This demonstrated that the Sn-Alg beads are strongly acidic and is most applicable for esterification reaction.

Scanning electron micrograph images of the Sn-Alg beads are shown in Supplementary Figure 1, which shows clear surface morphology. It was found that Sn-Alg beads had displayed a core-shell structure with smooth surface. The mean size of the dry beads was measured and found to be 1270 nm.

### 3.2. X-ray diffraction analysis

According to the literature sodium alginate does not have any prominent peaks for the polymers as predictable from polysaccharides.<sup>15</sup> The X-ray diffraction pattern of a Sn-Alg beads are represented in Figure 1 which shows two intense peaks of Sn metal at  $2\theta$  values of around  $31.5^\circ$  and  $45.1^\circ$  angles with other several broad signals of Sn metal cross linked with hydroxyl group of algalic acid located at  $2\theta$  values of  $27.3^\circ$ ,  $33.2^\circ$ ,  $36.5^\circ$ ,  $51.5^\circ$ ,  $51.5^\circ$  and  $66.2^\circ$ . The results of XRD are comparable with the reported values.<sup>20, 21</sup> Sn(II) forms metal carboxylate bonds with alginate molecules during the ion exchange interaction. Sn(II) ion in the  $\text{SnCl}_2$  solution is exchanged with Na ion from the sodium alginate solution. The Sn(II) ion forms

bonds with the carboxylate groups of alginate molecules. The chloride ion will form bonds with sodium ions and are then washed off. In Figure 1, labelled SnO represents the signals of Sn cross linked with hydroxyl group of algalic acid. It is not tin oxide and the catalytic effect is due to the Sn-Alg beads.

**(Insert Figure 1 here)**

### 3.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) is an analytical technique that measures the volatilization of a sample by recording mass loss as a function of temperature. Various studies have been investigated the distinctive effects of different metals on thermal stability of alginate polymer<sup>19</sup>. Figure 2 shows the distinctive TG–DTG thermogram of Sn–Alg beads operated under oxidative conditions. The TG–DTG thermogram of Sn–Alg beads closely analogous to the TG–DTG curves of Fe (III) alginate and calcium alginate thermogram reported by Boey et al.<sup>15</sup> and Knog et al.<sup>22</sup>, respectively.

**(Insert Figure. 2 here)**

The weight loss starts to begin around 50–150 °C due to the dehydration of sample. Weight loss around 149–380 °C is due to early degradation of alginate polymer and the succeeding both weight losses approximately 380–560 °C and 560–895 °C are due to additional putrefaction of alginate polymer.<sup>23</sup> From thermogravimetric profile of Sn–Alg it is very clear that the catalyst beads remain pristine deprived of any decomposition at the refluxing temperature (65°C) of methyl alcohol.

### 3.4. FT-IR studies

FT-IR analysis of alginate standard and Sn-Alg beads are presented in Figure 3 (a) and 3 (b), respectively. The cross linking interaction between Sn (II) and alginate was investigated by FT-IR functional groups analysis. The main peaks of sodium alginate are observed at 3225, 1594, 1402 and 1024  $\text{cm}^{-1}$ , which are assigned to  $\nu\text{O-H}$ ,  $\nu_s \text{C=O}$ ,  $\nu_{as} \text{C=O}$ , and  $\nu\text{C-O}$  groups, respectively. The broad band of hydroxyl group observed around 3225  $\text{cm}^{-1}$  in the sodium alginate and Sn-Alg beads spectra can be accredited to the cumulative effect of large number of O-H groups present in the alginate polymer. The shifting of O-H broad bands to higher frequency from 3225 to 3360  $\text{cm}^{-1}$  is also observed that is caused by the hydrogen bonds subsiding strength due to the presence of Sn (II) in the sample. The distinctive absorption band in Figure 3a at nearly 1594  $\text{cm}^{-1}$  and 1402  $\text{cm}^{-1}$  exhibited by symmetric ( $\nu_s$ ) and asymmetric ( $\nu_{as}$ ) stretching vibration of free carboxylate group ( $-\text{COOH}$ ). Conversely, by the addition of Sn(II) solution in the alginate sample the free carboxylate group ( $-\text{COOH}$ ) band 1594  $\text{cm}^{-1}$  and 1402  $\text{cm}^{-1}$  shifted towards higher frequencies 1621  $\text{cm}^{-1}$  and 1407  $\text{cm}^{-1}$  due to the cross linking interaction of Sn(II) ion with the carboxylate group of alginate polymer.<sup>24,15</sup>

**(Insert Figure. 4 here)**

Cozzi et al.<sup>25</sup> revealed that a strong band appeared at 1726  $\text{cm}^{-1}$  is due to the Stretching vibration of the free carbonyl group. This band is clearly seen in Sn-Alg beads though it was totally absent in sodium alginate spectrum. Comparing spectrum of alginate and Sn-Alg beads another noticeable large absorption bands around 500–700  $\text{cm}^{-1}$  in Sn-Alg beads are ascribed to the Sn-O bond stretching vibrations as reported by Wu et al.<sup>26</sup>

### 3.5. Optimization of esterification reaction catalyzed by Sn–Alg beads

#### 3.5.1. Effect of methanol/oleic acid molar ratio on methyl oleate conversion

From a theoretical perspective, one mole of methanol required to esterify one mole of free fatty acids as the esterification process is a reversible process, therefore an excess of methanol must be needed to move the reaction towards the formation of methyl ester.<sup>10, 27</sup> The impact of oleic acid to methanol molar ratio was investigated in the range of 1:6 to 1:25 on the methyl oleate conversion in the presence of 4% weight of Sn–Alg catalyst for 2 hours. As it is seen in Supplimentary Figure 2a, the FFA conversion linearly increases with the increase in methanol to oil molar ratio. Le Chatelier's principle play main role to explain the trend of increase in conversion rate of methyl oleate. By increasing the amount of methanol, the tendency of equilibrium shifted towards the right side which favors more methyl oleate formation. The highest conversion 98.5% was achieved at 1:12 oleic acid / methanol molar ratio. Actually the increase in molar ratio of methanol to fatty acid stimulates well mixing between catalyst and reactants which improves the mass transfer rate and ultimately resulting in a higher conversion. However, a decrease in % conversion was observed when the molar ratio of oleic acid/ methanol exceeds than 1:12 to 1:25. This possibly might be due to the dilution effect that was caused by adding more amount of methanol.<sup>10</sup>

#### 3.5.2. Optimization of Sn–Alg catalyst amount on oleic acid conversion

A range of catalyst concentration was studied by changing the catalyst amount from 1% to 20% based on the mass of oleic acid (Supplimentary Figure 2b). The maximum conversion of oleic acid into methyl oleate was reached to 98.7% with 4% Sn–Alg catalyst. However, no significant increase in the conversion was observed after 4% catalyst loading. Subsequently, 4% catalyst was preferred for the further optimization studies. Compared to our study Qiuyun et al.<sup>10</sup>

described that, 92.6% conversion of oleic acid was achieved with 4% amount of aluminum alginate solid acid (Al-SA) catalyst. However after three repetitive esterification process the efficiency of Al-SA was reduced to 47.1%. In view of above discussion newly synthesized Sn-Alg catalyst is more reactive towards the esterification process. The activity of Sn-Alg catalyst is probably due to Sn (II) metal ion that attached on the surface of alginic acid together act as a lewis acid that activate the carbonyl carbon which is accountable for nucleophilic attack by methanol, thus it makes an increase conversion of oleic acid<sup>12</sup>.

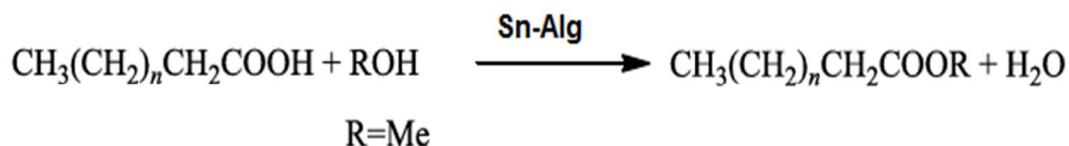
### 3.5.3. Effect of reaction time on oleic acid conversion

The progress of FFA conversion with respect to the time was also studied (Supplimentry Figure 2c). It can be seen as the reaction progresses exceed 2 hours, the conversion reached to maximum point of 98% afterward the reaction reached a plateau as there are no significant changes in the methyl esters yield and the products accomplished a near-equilibrium composition. This information demonstrates that very high catalytic reactivity of Sn-Alg is for an esterification reaction. Hence the optimal reaction time used for all esterification process was 2 hours.

### 3.6. FAME production from FFA content of CDD using Sn-Alg catalyst

The most effective alginic acid derived Sn-Alg catalyst after optimization studies was tried for the conversion of waste CDD containing a high amount of FFAs (86.3 wt%), in the presence of methanol, into fatty acid methyl esters that produce biodiesel through simultaneous esterification and transesterification. The initial acid value of CDD was found to be  $166.32 \pm 2.0$  mg KOH/g. Esterification of CDD with optimized 12:1 methanol to CDD molar ratio, 4% mass

ratio of Sn–Alg catalyst to CDD at a 65°C for 2 hours gave more than  $96.8 \pm 0.8\%$  production of biodiesel.



In general, biodiesel is considered to be an environmental friendly fuel which is biodegradable, free from toxic components and not produce poisonous exhaust gases such as sulfur oxide or aromatic compounds.<sup>28</sup> Efficacious application of the optimized reaction conditions using Sn–Alg beads for esterification of CDD and obtaining tremendous production of methyl esters confirmed that Sn–Alg beads is appropriate to be used as a heterogeneous solid acid catalyst for converting FFA CDD into biodiesel. Due to antimicrobial activity, Sn-Alg catalyst has little corrosiveness activity. Moreover, ease of separation and reuse of solid catalyst make it more economical. This process is very simple with negligible environmental issues.

Figure 4a, shows the typical FAME chromatogram of CDD obtained with Sn–Alg catalyzed esterification reaction and (b) with alkali catalyst (KOH) saponification. Difference of the Figure 4a and 4b indicates that Sn–Alg is reactive enough for converting FFAs comparative to corrosive alkali.

**(Insert Figure. 4 here)**

Some properties of produced biodiesel such as viscosity, acid value, density and cetane number are presented in Table 1, and compared with standard values of American Society for Testing and Materials (ASTM). All values are in good agreement with the standard specification of biodiesel. However the higher cetane number was found in the prepared CDD than ASTM

standards for biodiesel that specifies good ignition quality of biofuel. The higher cetane numbers of the biodiesel can decrease the NO<sub>x</sub> emissions and also contributes the absence of aromatic compounds from the biodiesels exhaust.<sup>29</sup>

**(Insert Table. 1 here)**

### **3.7. Reusability of Sn–Alg catalyst**

Stability and reusability of the catalyst are essential to bring down the cost of biodiesel production. Therefore, successive experiments were performed to inspect the stability and reusability of Sn–Alg catalyst catalysts after collecting catalyst beads from reaction mixture and reprocessed them for further esterification reaction. Catalyst was reused without any additional pretreatments like washing or drying. About 97.6% biodiesel was obtained up to 8 times with reprocessed catalyst from CDD as clearly displayed in Figure 5. However, a slight decrease in the conversion efficiency was observed after 8 cycles of esterification reaction. According to Boey et al.<sup>15</sup> this diminutive effect is possibly due to the repetitive heating and agitation of the beads due to esterification reaction. In comparison to literature<sup>10</sup>, the Sn–Alg catalyst is stable enough to be reprocessed several times easily handled recovered and there is no regeneration step necessary to renovate the acid capability of the catalyst, hence decreasing the cost of catalyst production and therefore the cost of biodiesel production.

**(Insert Figure 5 here)**



#### 4. Conclusions

A newly synthesized Sn–Alg catalyst exhibited greater catalytic activity for the esterification of large amount of FFAs from waste material like CDD. Around 96.8 % FFAs converted into a worthwhile FAME product under the best reaction conditions; 4 % catalyst amount, 1:12 oleic acid to methanol mole ratio and 2 hours reaction time at a fixed temperature 65°C. Biodiesel is considered to be an environmental friendly fuel. For the preparation of biodiesel, commonly homogeneous catalysts like KOH, NaOH, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> are used. But many problems like environmental pollution, trouble in separation of catalyst and purification biodiesel, and corrosion of equipment are associated with these catalysts. Therefore, green approach was applied by using Sn-Alg solid catalyst to convert waste corn oil deodorizer distillate to biodiesel. Moreover, the prepared Sn–Alg catalyst can be easily separated from the product by simply filtration, without any washing with high purity product.

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#### Conflict of Interest

The authors declare that they don't have any conflict of interest.

**References.**

- 1 W.N.N. Wan Omar, N.A. Saidina Amin, *Biomass and bioenergy*. 2011, 35, 1329-1338.
- 2 Q. Shu, J. Gao, Z. Nawaz, Y. Liao, D. Wang, J. Wang, *Appl. Energy*. 2010, 87, 2589-2596.
- 3 T.-H. Đặng, B.-H. Chen, *Fuel Process. Technol.*, 2013, 109, 7-12.
- 4 M. Balat, *Energy Convers. Manage.*, 2011, 52, 1479-1492.
- 5 A.B. Chhetri, M.S. Tango, S.M. Budge, K.C. Watts, M.R. Islam, *Int. J. Mol. Sci.*, 2008, 9, 169-180.
- 6 M.R. Uddin, K. Ferdous, M.R. Uddin, M.R. Khan, M. Islam, *Chem. Eng. & Sci.*, 2013, 1, 22-26.
- 7 P.-L. Boey, S. Ganesan, G.P. Maniam, M. Khairuddean, J. Efendi, *Energy Convers. Manage.*, 2013, 65, 392-396.
- 8 L. Wang, W. Du, D. Liu, L. Li, N. Dai, *J. Mol. Catal. B: Enzym.* 2006, 43, 29-32.
- 9 S. Naz, S.T.H. Sherazi, F.N. Talpur, S.A. Mahesar, H. Kara, *J. AOAC Int.*, 2012, 95, 1570-1573.
- 10 Z. Qiuyun, L. Hu, Q. Wenting, L. Xiaofang, Z. Yuping, X. Wei, Y. Song, *China Pet. Process. Pe.*, 2013, 15, 19-24.
- 11 X. Liu, H. He, Y. Wang, S. Zhu, *Catal. Commun.*, 2007, 8, 1107-1111.
- 12 A.B. Ferreira, A. Lemos Cardoso, M.J. da Silva, International Scholarly Research Network ISRN *Renew. Energ.*, 2012., Article ID 142857, 13 pages  
doi:10.5402/2012/142857
- 13 C.V. McNeff, L.C. McNeff, B. Yan, D.T. Nowlan, M. Rasmussen, A.E. Gyberg, B.J. Krohn, R.L. Fedie, T.R. Hoye, *Appl. Catal. A.*, 2008, 343 39-48.
- 14 W. Trakarnpruk, *Walailak J. Sci. & Tech.*, 2012, 9, 37-47.

- 15 P.-L. Boey, S. Ganesan, G.P. Maniam, M. Khairuddean, S.-E. Lee, *Appl. Catal. A: General*, 2012, 433,12-17.
- 16 American Oil Chemists' Society, AOCs Official Method Cd 8d-63 In Official Methods and Recommended Practices of the AOCs; Firestone, D., ed.; AOCs: Champaign, USA, 1973.
- 17 F. Gasparini, J.R.d.O. Lima, Y.A. Ghani, R.R. Hatanaka, R. Sequinel, D.L. Flumignan, J.E. de Oliveira, *Bioenergy Technol., World Renewable Energy Conference, Sweden* 2011, 101–10.
- 18 M. Ruiz, C. Tobalina, H. Demey-Cedeño, J.A. Barron-Zambrano, A.M. Sastre, *React. Funct. Polym.*, 2013, 73, 653-657.
- 19 J. Rowbotham, P. Dyer, H. Greenwell, D. Selby, M. Theodorou, *Interface Focus*. 2013, 3, 20120046. <http://dx.doi.org/10.1098/rsfs.2012.0046>
- 20 S. Sladkevich, J. Gun, P. Prihodchenko, V. Gutkin, A. Mikhaylov, V. Novotortsev, J. Zhu, D. Yang, H. Hng, Y. Tay, *Nanotechnology*. 2012, 23, 485-601.
- 21 J.Y. Gong, S.R. Guo, H.S. Qian, W.H. Xu, S.H. Yu, *J. Mater. Chem.*, 2009, 19, 1037-1042.
- 22 Q. Kong, B. Wang, Q. Ji, Y. Xia, Z. Guo, J. Yu, *Chin. J. Polym. Sci.*, 2009, 27, 807-812.
- 23 J. Soares, J. Santos, G. Chierice, E. Cavalheiro, *Eclética Química*. 2004, 29, 57-64.
- 24 M. Al-Remawi, *J. Appl. Sci.*, 2012, 12, 727-735.
- 25 D. Cozzi, P.G. Desideri, L. Lepri, G. Ciantelli, *J. Chromatogr. A.*, 1968, 35, 396-404.
- 26 D. Wu, J. Zhao, L. Zhang, Q. Wu, Y. Yang, *Hydrometallurgy*. 2010, 101, 76-83.
- 27 S. Gan, H.K. Ng, C.W. Ooi, N.O. Motala, M.A.F. Ismail, *Bioresour. Technol.*, 2010, 101, 7338-7343.

28 T. G. W. Zillillah, Z. Li, *Green Chem.*, 2012, 14, 3077-3086.

29 K. A. Antonopoulos, D. C. Rakopoulos, D. T. Hountalas, E. G. Giakoumis, *Energy Conversion and Management*, 2006, 47, 3272-3287.

### Figure and Table Captions

Figure 1. The X-ray diffraction pattern of a Sn–Alg beads

Figure 2. TG–DTG thermogram of Sn–Alg beads operated under oxidative conditions.

Figure 3. FT–IR analysis of alginate standard (3a) and Sn–Alg beads (3b)

Figure 4. Typical FAME GC chromatograms of CDD obtained by catalyzed esterification reaction with Sn–Alg (Figure 4a); with alkali catalyst (KOH) saponification (Figure 4b).

Figure 5. Reusability of Sn–Alg catalyst. About 97.6% biodiesel was obtained up to 8 times with reprocessed catalyst from CDD.

Table 1. Important properties of synthesized biodiesel (FAME) compared with standard values of American Society for testing and materials (ASTM).

Fig. 1.

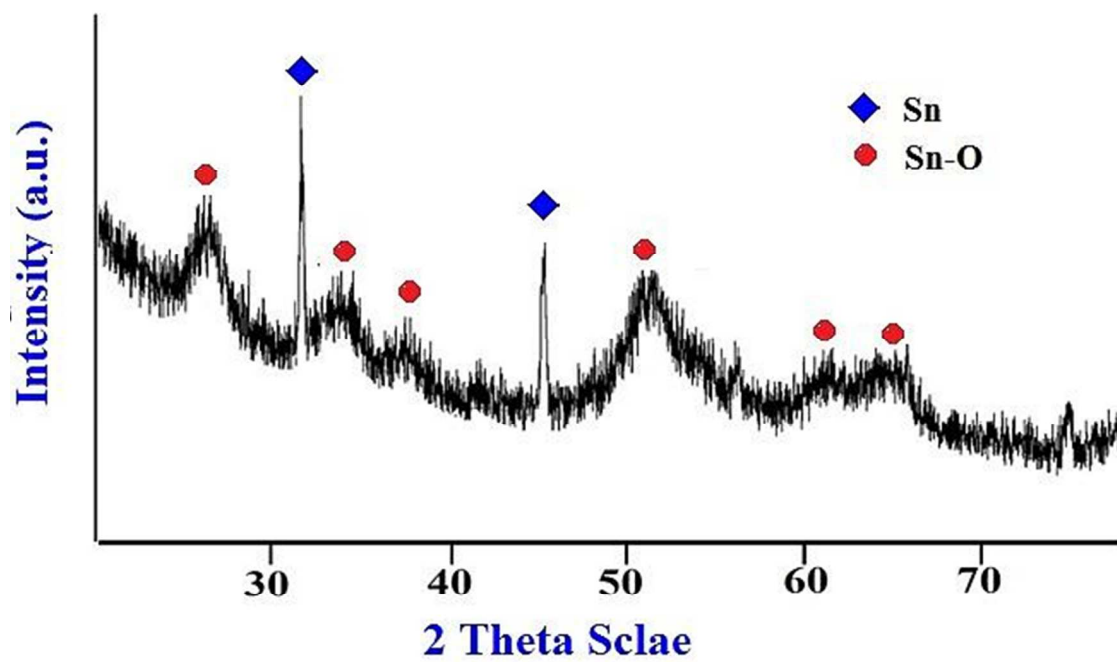


Fig. 2.

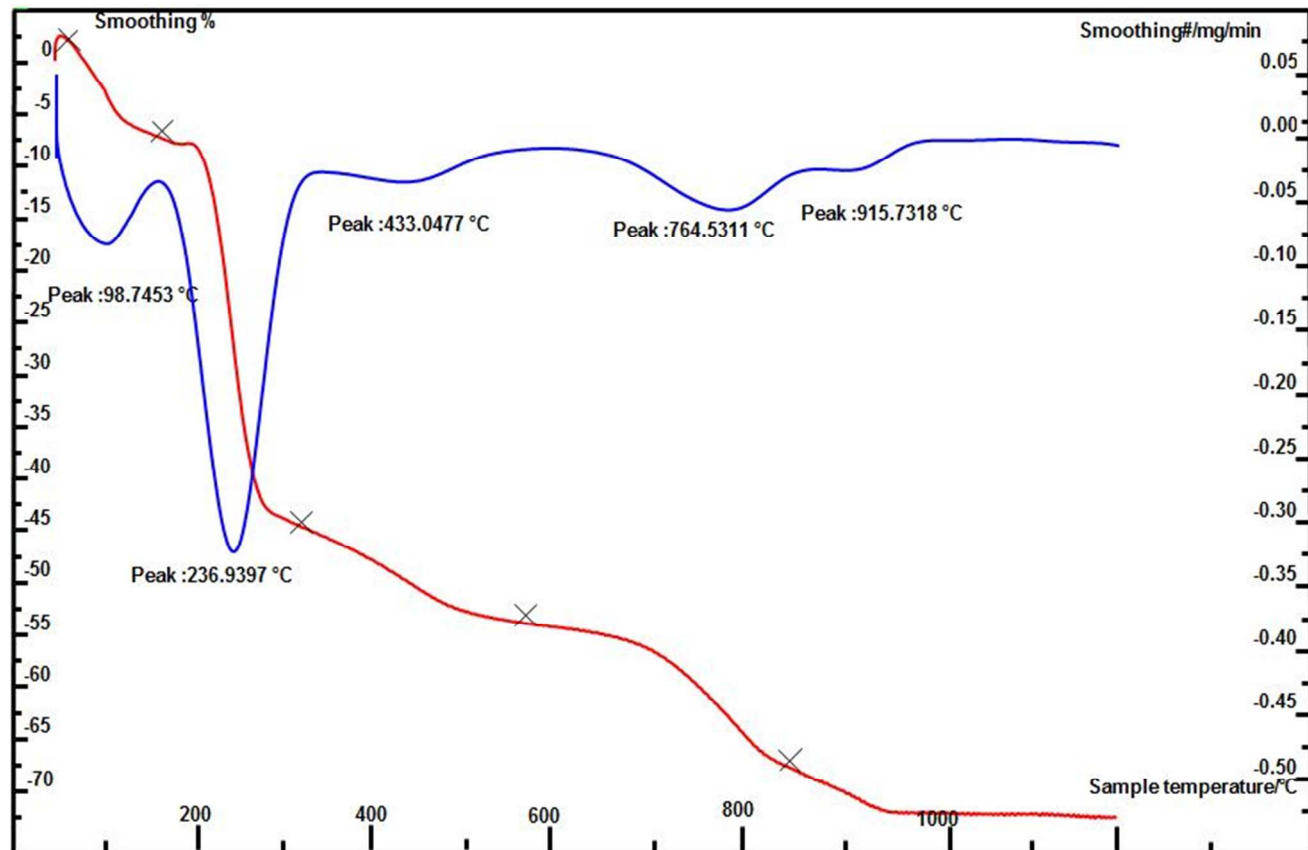


Fig. 3.

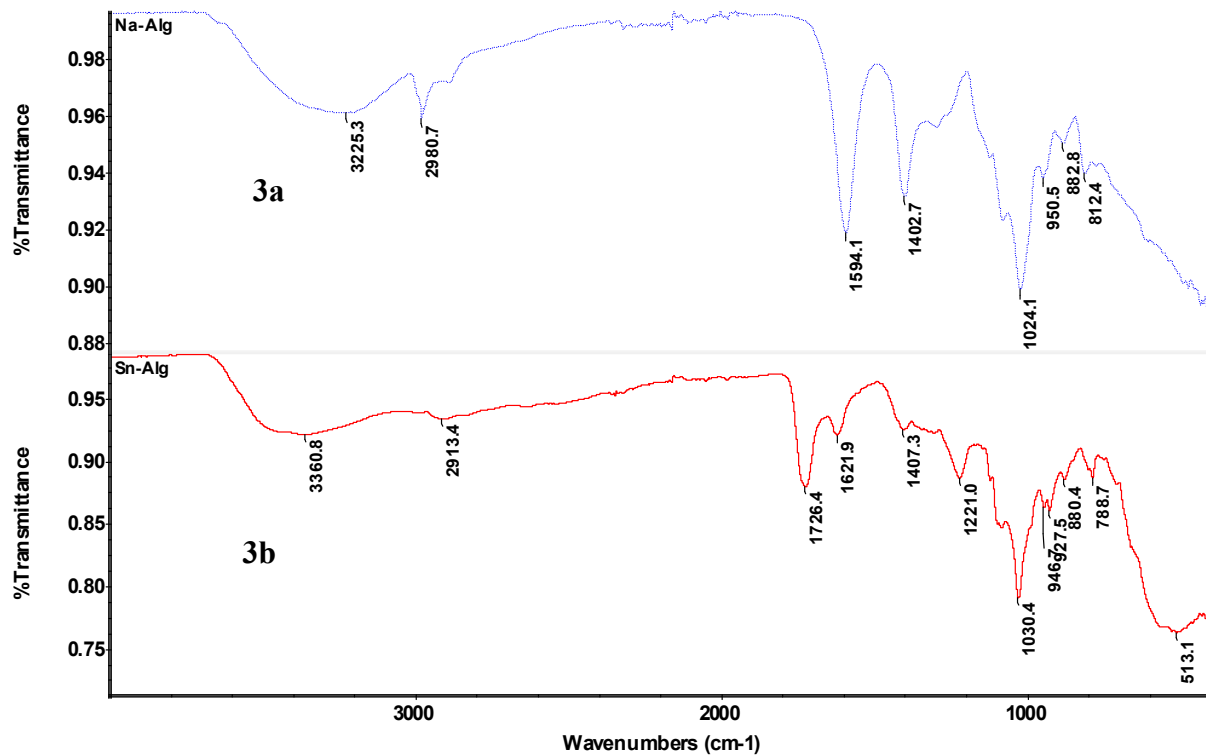




Fig.4

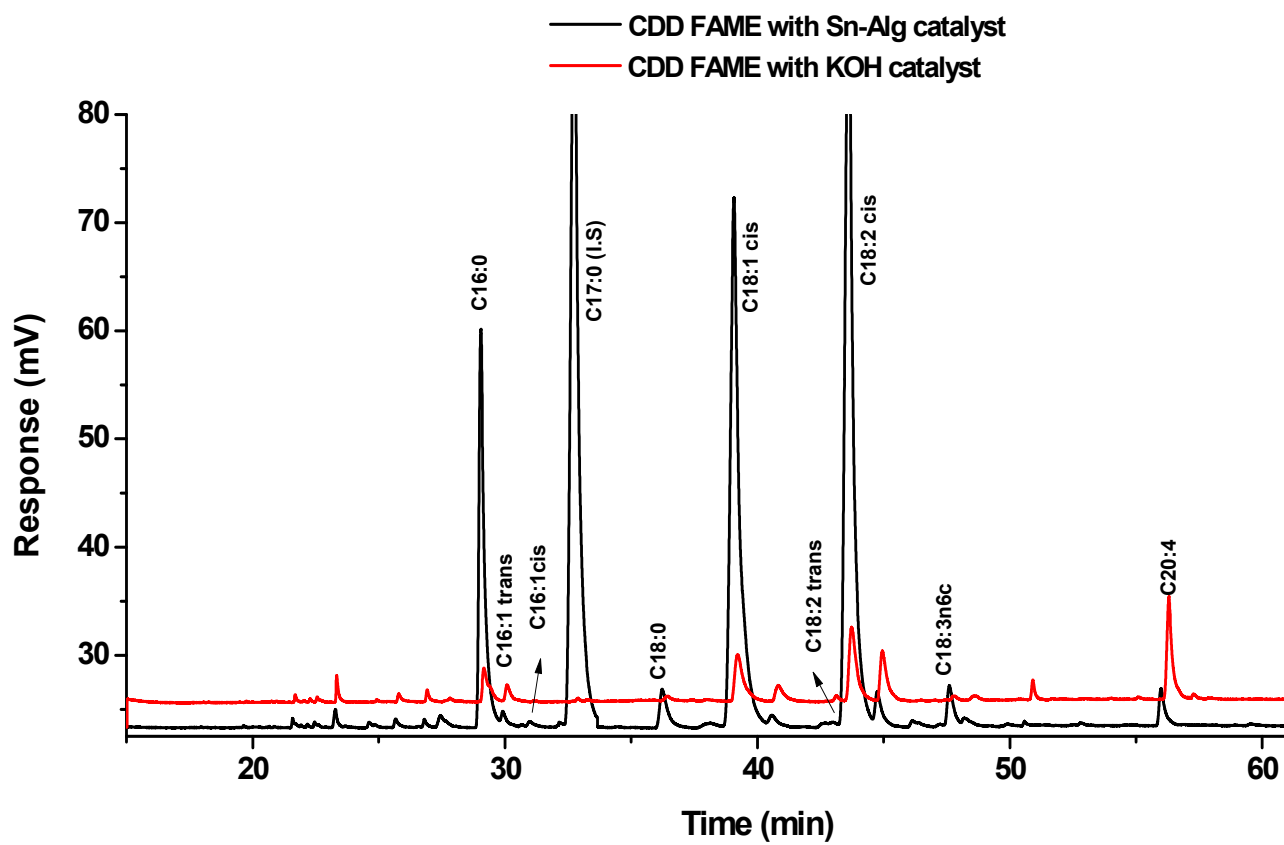


Fig. 5

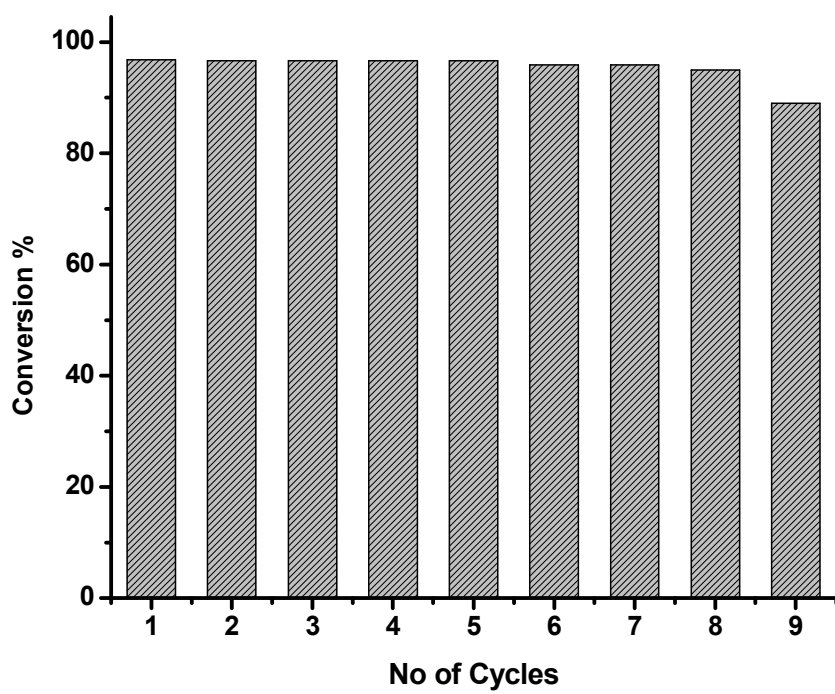


Table 1 Properties of synthesized biodiesel (FAME).

Properties	Waste CDD	FAME of CDD	ASTM 6751-11a Values	Biodiesel standard Testing Method
Density (g/cm <sup>3</sup> )	0.97	0.85	0.86-0.90	ASTM D4052
Viscosity mm <sup>2</sup> /sec at 40 °C	36.25	3.12	1.9 - 6.0	ASTM D 445
Acid value (mg KOH/g)	166.32	0.5-0.7	0.5 max	ASTM D 664
Cetane number	38.33	54.18	47min	ASTM D 613