Chapter 3

SODIUM ALUMINATE PREPARED FROM WASTE ALUMINUM SOURCE AS A HETEROGENEOUS CATALYST FOR THE TRANSESTERIFICATION OF JATROPHA OIL

Waste aluminium foil is utilized as the precursor material for the preparation of sodium aluminate and is employed as a heterogeneous catalyst in the transesterification reaction of Jatropha *curcas* oil.
3.1 INTRODUCTION

Sodium aluminates are class of compounds formed from alumina and the oxide of sodium. Sodium aluminate is commercially obtained as a solid or in solution form. It exists in anhydrous as well as hydrated forms. The pure anhydrous sodium aluminate is a white crystalline solid having variable formulas given as NaAlO$_2$, Na$_2$O·Al$_2$O$_3$ or Na$_2$Al$_2$O$_4$ and the hydrated form is represented as NaAl(OH)$_4$. The structures of hydrated and anhydrous forms are entirely different. Anhydrous sodium aluminate, NaAlO$_2$, has a three-dimensional network structure in which AlO$_4$ tetrahedra are linked with each other in the corners. But, the hydrated form has a layer structure containing AlO$_4$ tetrahedra joined to form rings. Sodium ions as well as water molecules present in the layers shows hydrogen bonding with O atoms in the AlO$_4$ tetrahedra [1].

![Structure of sodium aluminate](image)

Figure 3.1. Structure of sodium aluminate [2]

The molar mass of NaAlO$_2$ is 82.978 g/mol. NaAlO$_2$ is water soluble and shows strong basicity in water and is insoluble in alcohol [1,3]. Sodium aluminate is an excellent candidate known for many years for versatile
applications. [4-6]. Some of the important uses and applications [7-9] are picturised in figure 3.2.

Figure 3.2. Uses and applications of sodium aluminate

The Bayer Process utilizes sodium aluminate for the extraction and purification of gibbsite from bauxite ores [10]. Khachatryan described the preparation of aluminium oxide by thermal dissociation of aluminum hydroxide obtained by precipitation, with formalin, from sodium aluminate [11]. Lluis et al. suggested an economically feasible alternative process for the production of hydrogen using sodium aluminate solutions. There is an improvement in the rate and yield of hydrogen production when compared with pure NaOH solution [12]. NaAlO₂ is used as a solid base catalyst in the one-pot synthesis of glycidol [13]. Sodium aluminate is also used as a heterogeneous catalyst in the transesterification reaction for the production of biodiesel [14,15]. The literature review on aluminate catalysed biodiesel production is given in chapter 1 section 1.9.1.
The commercial preparation of sodium aluminate is from bauxite using soda ash or by the dissolution of bauxite in NaOH [16]. In the present study, we have used waste aluminium foils as the precursor material for the preparation of sodium aluminate. Aluminium foil is used because of its cost effective nature, easy availability and high solubility in strong bases leading to the formation of aluminates [17].

3.2 EXPERIMENTAL

3.2.1 Catalyst Preparation

2.7 g of used aluminium foil (chopped into small pieces) was added slowly with stirring to a 0.5 M NaOH solution and kept at 90 °C. The solution was then evaporated slowly with stirring to get a solid product. The resultant product was kept in a hot air oven overnight at 90 °C and then calcined at 650
°C for 3 h in a muffle furnace. The obtained catalyst was characterized using different analytical techniques.

Different catalytic systems were also prepared by varying the Na:Al molar ratios such as 30:70, 35:65, 40:60 and 50:50. The systems were designated as $SA_m:n$, where, ‘SA’ stands for sodium aluminate and ‘m:n’ indicates the molar ratio of Na with Al in the catalyst system.

![Figure 3.4. Photographs of different catalyst systems](image)

The catalytic activity of the catalyst systems were investigated in the transesterification reaction of *Jatropha curcas* oil with methanol. The detailed procedures for the transesterification reaction, biodiesel analysis, reusability studies and determination of fuel properties are mentioned in chapter 2.

### 3.3 RESULTS AND DISCUSSION

In the present study, waste aluminium foil was used for the first time in the preparation of sodium aluminate following an easy and low cost method in which aluminium was converted to sodium aluminate, NaAlO$_2$, using NaOH. The catalyst preparation was done by a simple procedure where waste aluminium was added to NaOH solution and the mixture was then subjected to heat treatment. The developed catalyst was found to be highly efficient for the
production of biodiesel from jatropha oil. The reaction parameters were varied to find out the suitable conditions for the transesterification reaction. The catalyst showed heterogeneity in methanol and was found to be reusable.

### 3.3.1 Characterization Studies

The catalyst systems were characterized using different techniques to investigate the active phase responsible for catalysis.

#### 3.3.1.1 XRD Analysis

The XRD patterns of all the prepared catalysts are shown in figure 3.5. The characteristic peaks at 2θ values of 20.8°, 23.5°, 30.3°, 33.7°, 34.6°, 39.8°, 41.9°, 45.4°, 46.0°, 48.3°, 54.5, 58.0°, 60.9°, 63.1°, and 65.8° correspond to diffraction from the (101), (110), (102), (200), (112), (211), (103), (113), (212), (220), (310), (302), (312), (204) and (214) lattice planes respectively of gamma-NaAlO₂ with tetragonal crystal structure ((JCPDS Card No.. 00-019-1179). In addition, peaks at 2θ values of 37.5°, 51.6°, 68.8°, 73.8°, 76.0° and 78.2° corresponds to reflections from the (201), (230), (322), (411), (332) and (341) lattice planes respectively of pure NaAlO₂ with orthorhombic crystal structure ((JCPDS Card No. 01-083-0316). Some of the peaks of pure NaAlO₂ may be merged with the gamma-NaAlO₂ diffraction peaks.
Figure 3.5. XRD Patterns of prepared catalyst systems

The chemical reaction taking place during the formation of sodium aluminate is represented by the equation (1) as,

$$2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \rightarrow 2\text{NaAlO}_2 + 3\text{H}_2 \quad \ldots \quad (1)$$
3.3.1.2 FTIR Spectral Analysis

FTIR spectral analysis supports the formation of NaAlO₂ (Figure 3.6).

![FTIR Spectrum of different systems](image)

Figure 3.6. FTIR Spectrum of different systems

The vibration bands observed at 570 cm⁻¹, 738 cm⁻¹ and 1034 cm⁻¹ were probably attributed to absorption peak of Al–O vibration [18,19,20]. A broad absorption peak of O–H stretching vibration is observed at 3450 cm⁻¹ and a minor absorption peak of O–H bending vibration is observed at about 1652 cm⁻¹ that are assigned to H₂O molecule absorbed from air [18]. The band around 809 cm⁻¹ is due to stretching vibration of tetrahedral Al⁴⁺ [21]. The material displayed a peak at 1430 cm⁻¹ indicating the presence of carbonate.
which may be aroused due to the adsorption of gaseous carbon dioxide on the basic sites of the catalyst [22].

Thus, XRD pattern and FTIR spectra of the catalyst supports the existence of the catalyst in the crystalline NaAlO$_2$ state. The initial transesterification reaction studies showed that the catalyst, SA50:50 is highly active compared to other systems. So SA50:50 was further characterised by ICP-AES, FESEM and TEM analysis. Elemental analysis of the catalyst was performed to understand the percentage of Na and Al in the catalyst. The percentage of Na was found to be slightly higher with a Na/Al ratio of 1.4. But in the XRD pattern there is no extra peak corresponding to NaOH or Na$_2$O indicating the efficient dispersion of Na in the matrix of NaAlO$_2$.

### 3.3.1.3 FESEM and TEM Analysis

The surface morphology of sodium aluminate was investigated by FESEM. The material displayed highly porous uniform structure throughout the surface. The inter particle agglomeration resulted in the formation of macropores as evident from the FESEM photograph shown in figure 3.7(a) & (b). Many macroporous basic materials were reported to be effective heterogeneous catalysts for the transesterification of oils [23-25]. TEM images also revealed the porous interconnected network of the catalyst.
3.3.2 Catalytic Activity Studies

The activity of the catalysts was investigated in the transesterification of jatropha oil. A number of experiments were conducted to investigate the influence of reaction variables on the FAME yield. At first, the activity of different catalyst systems were evaluated inorder to find out the best catalyst that gives highest oil conversion compared to other systems; results obtained are given in table 3.1. From the results, it is observed that the catalyst, SA50:50 showed a maximum conversion of 100% under the selected reaction conditions. The FAME contents obtained over other catalysts are not fuel
grade (> 96.5%). The catalyst, SA50:50 was selected for the further optimisation studies on the investigation of different parameters on the FAME yield.

Table 3.1. Catalytic activity comparison

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Na:Al molar ratio</th>
<th>Catalyst system</th>
<th>FAME content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30:70</td>
<td>SA30:70</td>
<td>87.54</td>
</tr>
<tr>
<td>2</td>
<td>35:65</td>
<td>SA35:65</td>
<td>89.90</td>
</tr>
<tr>
<td>3</td>
<td>40:60</td>
<td>SA40:60</td>
<td>95.32</td>
</tr>
<tr>
<td>4</td>
<td>50:50</td>
<td>SA50:50</td>
<td>100</td>
</tr>
</tbody>
</table>

Reaction conditions: Methanol to oil molar ratio of 12:1, catalyst weight of 4 wt%, temperature 65 °C and a reaction time of 1 h

3.3.2.1 Effect of Reaction Temperature

The effect of reaction temperature on the FAME content was investigated and the results are shown in figure 3.8. It can be seen that temperature had a positive effect on FAME yield where the FAME content increases with increase in the reaction temperature and a maximum yield of 100 % was obtained at 65 °C. The FAME content reached the international standard specification as per ASTM D6751 and EN 14214 even at a reaction temperature of 55 °C for 1 h reaction. The enhanced activity with increase in the reaction temperature can be explained as the increased miscibility of oil and methanol leading to improved reactants’ interaction. The decreased viscosity of oil with increase in the temperature can result in better mixing of the reaction mixture [26].
Figure 3.8. Effect of reaction temperature on the FAME content with the following reaction conditions: methanol to oil molar ratio of 12:1, catalyst weight of 4 wt% and a reaction time of 1 h.

3.3.2.2 Effect of Catalyst Weight

The availability of active catalyst sites got augmented with increase in catalyst dosage and resulted in better performance with increase in catalyst weight [27]. The catalyst weight is varied from 1 to 5 wt% of oil and it is observed that the FAME yield increased with increase in the amount of catalyst. The FAME yield reached 100% at a catalyst weight of 4 w% (Figure 3.9) and thus it is selected for further experiments.
Figure 3.9. Effect of catalyst weight on the FAME content with the following reaction conditions: methanol to oil molar ratio of 12:1, temperature of 55 °C and a reaction time of 1 h.

3.3.2.3 Effect of Reaction Time

Figure 3.10 displayed the influence of time on the reaction and it can be seen that as the reaction time increases, the FAME content also got increased and maximum FAME content of 100% is attained at reaction time of 1 h. Thereafter it remained the same.

Figure 3.10. Effect of reaction time on the FAME content with the following reaction conditions: methanol to oil molar ratio of 12:1, catalyst weight of 4 wt% and reaction temperature of 55 °C
3.3.2.4 Effect of Methanol to Oil Molar Ratio

Excess methanol was usually used for the transesterification reactions, which act as a solvent for the reaction. The use of extra methanol was also intended for arresting the reversible reaction [28]. But the use of methanol in excess demands the need of distillation for the recovery of methanol at the end and adds the energy requirement of the entire process. So a medium amount of methanol as a solvent is always recommended. However most of the heterogeneous catalyzed processes demand the use of a high methanol to oil molar ratio of 12:1 onwards for the effective reaction under mild conditions [29]. Wan et al had used commercial sodium aluminate, NaAlO₂ for the transesterification of soybean oil and they also found 12:1 as the suitable methanol to oil molar ratio under the selected reaction conditions [30]. But the maximum yield obtained in their study was 93.9%, which is below the minimum FAME content specified by EN standards. We have analysed the influence of methanol in the transesterification of jatropha oil over sodium aluminate catalyst of present investigation and it is found that for 1 h reaction, the FAME yield reached the international standard specifications even at a low methanol to oil molar ratios of 6:1 at 55 °C. The FAME yield was 81.4% at the molar ratio of 3:1 which increased with further increase in the methanol content. In order to get maximum FAME content of 100%, we have selected the best methanol to oil molar ratio as 12:1. The results indicate that slight excess of methanol has an impressive effect on the reaction and yielded high FAME content at a comparatively low excess of methanol. This result is promising (Figure 3.11) since it makes the entire process of biodiesel production more economical. Ilgen had reported a methanol to oil molar ratio
of 6:1 as the best molar ratio in the transesterification of canola oil over marble based catalyst [31].

Figure 3.11. Effect of the methanol to oil molar ratio on the FAME content with the following reaction conditions: catalyst amount of 4 wt%, temperature of 55 °C and a reaction time of 1 h.

3.3.3 Reusability and Leaching Studies

The reusability of the catalyst was investigated by repeating the experiments with the used catalyst and the catalyst showed admirable activity till 3 repeated runs. The results are shown in Figure 3.12. The reaction mixture after the first cycle was analysed to know the leaching of the catalyst to the reaction mixture. It was found that only a very small amount of the catalyst is leached out to the liquid medium. From the ICP-AES analysis, it was observed that the percentage leaching of Na was found to be 0.5 wt% of the catalyst and that of Al was found to be 0.2 wt% of the catalyst which is negligibly small that can be eliminated during the washing of biodiesel with water.
Figure 3.12. Reusability results with the following reaction conditions: methanol to oil molar ratio of 12:1, catalyst amount of 4 wt%, temperature of 55 °C and a reaction time of 1 h.

The regenerated catalyst after 3rd run is analyzed by FTIR spectral measurements and the FTIR spectrum of fresh and the used catalyst is shown in figure 3.13. It is clearly observed that the catalyst structure remained unaffected after the repeated catalytic reactions which suggest the stability of the catalyst in the reaction medium.

Figure 3.13. FTIR spectra of fresh and used catalyst.
3.3.4 Fuel Properties of Biodiesel

Some of the fuel properties of the prepared biodiesel were determined according to the standard procedures described in chapter 2 and the values are given in table 3.2. The measured fuel properties lie in the range of standard values as given by ASTM and EN international standards. The results indicated that the prepared biodiesel can be used as a substitute fuel for petrodiesel [32,33].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Test Methods</th>
<th>Unit</th>
<th>Limits (EN 14214)</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester content</td>
<td>EN 14103</td>
<td>wt%</td>
<td>96.5 min</td>
<td>100</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>EN 14105</td>
<td>wt%</td>
<td>0.02 max</td>
<td>0.00</td>
</tr>
<tr>
<td>Monoglyceride</td>
<td>EN 14214</td>
<td>wt%</td>
<td>0.8</td>
<td>0.0</td>
</tr>
<tr>
<td>Diglyceride</td>
<td>EN 14214</td>
<td>wt%</td>
<td>0.20</td>
<td>0.00</td>
</tr>
<tr>
<td>Total glycerol</td>
<td>EN 14105</td>
<td>wt%</td>
<td>0.25 max</td>
<td>0.00</td>
</tr>
<tr>
<td>Acid value</td>
<td>EN 14104</td>
<td>mg KOH/g</td>
<td>0.50 max</td>
<td>0.15</td>
</tr>
<tr>
<td>Water content</td>
<td>EN ISO 12937</td>
<td>mg/kg</td>
<td>500 max</td>
<td>0</td>
</tr>
<tr>
<td>Viscosity</td>
<td>EN 445</td>
<td>mm²/s</td>
<td>1.96-6.0</td>
<td>3.84</td>
</tr>
<tr>
<td>Density</td>
<td>EN ISO 3675</td>
<td>g/m³</td>
<td>860-900</td>
<td>872</td>
</tr>
</tbody>
</table>

*Reaction conditions: Methanol to oil molar ratio of 12:1, catalyst amount of 4 wt%, temperature of 55 °C and a reaction time of 1 h

3.4 CONCLUSIONS

Highly efficient catalyst derived from waste aluminium foils is effectively used for biodiesel production from jatropha oil. The material is found to be
highly crystalline NaAlO$_2$ as evident from the XRD and FTIR spectral analyses. The material displayed a uniform surface morphology with the presence of macropores in the catalyst matrix as revealed from FESEM and TEM images. The transesterification of jatropha oil occurred under mild reaction conditions and the FAME content reached more than 99% even at a low methanol to oil molar ratio of 6:1 within a short duration of 1 h reaction at 55 °C. The catalyst is found to be reusable without much loss in activity till 3 repeated cycles.

REFERENCES


Chapter 4

LITHIUM SILICATE CATALYZED PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL WITH STATISTICAL OPTIMISATION OF REACTION PARAMETERS

Lithium silicate is used as a heterogeneous catalyst for the transesterification reaction of waste cooking oil and the reaction parameters involved in the process are optimised by response surface methodology.
4.1 INTRODUCTION

Heterogeneous catalysts that can efficiently replace the use of homogeneous catalysts in the transesterification reaction are of great interest for the production of biodiesel. As already reviewed in chapter 1, different types of solid acid and solid base catalysts have been reported in the transesterification of triglyceride feedstocks. Heterogeneous catalysts based on lithium shows better performance in biodiesel production [1]. There are many reports on heterogeneous catalysts based on lithium for the transesterification reaction to produce biodiesel. Wang et al. had reported the use of commercial Li₂CO₃ as a heterogeneous catalyst in the transesterification of soybean oil [2]. LiOH modified Montmorillonite K 10 was used as a solid base catalyst for the transesterification reaction of methyl laurate with glycerol [3]. Lithium nitrate incorporated CaO catalyst was used in the transesterification of glyceryl tributyrate with methanol for the production of methyl butanoate [4]. A nanocatalyst is prepared by the impregnation of lithium ion on the CaO support and is employed in the transesterification of cotton seed oil [5]. Magnesium oxide supported lithium containing solid base catalyst is tested in the transesterification of mutton fat to produce biodiesel [6]. Lithium zirconate nanomaterials show excellent catalytic activity in the transesterification of tributyrin [7]. Li/ZnO catalyst is used in the soybean oil transesterification [8]. Li₂TiO₃ and LiAlO₂ were also tested in biodiesel production [9, 10].

Among the lithium based catalysts, lithium silicates are one of the best suited and highly active heterogeneous catalysts for the biodiesel production [11-13]. Lithium silicate is not only used as a heterogeneous catalyst, but also
has several other important roles in different fields. Some of the important applications of lithium silicate are depicted below [14-17].

![Applications of lithium silicate](image)

**Figure 4.1. Applications of lithium silicate**

Different methods such as solid state reaction, hydrothermal method, sol-gel method, etc. are reported for the preparation of lithium silicate [18-20]. The literature regarding the use of lithium silicate as a heterogeneous catalyst in the transesterification reaction is described in chapter 1 section 1.9.2.1. All these reports utilized conventional optimisation strategy for the optimisation of different reaction parameters that affects the FAME content. As evident from the literature data, normally, the methanol to oil molar ratio, weight of the catalyst, reaction time, as well as the temperature of the reaction mixture is the variable reaction parameters affecting the yield of biodiesel. The conventional one-to-one optimization strategy for all these parameters in obtaining a suitable condition with the maximum yield make the optimization of biodiesel production process over various heterogeneous catalysts highly tedious.
necessitating the development of alternate strategies for parameter optimization. [21]. In the present work, we preferred to use the Response Surface Methodology (RSM), the statistical optimization technique for the present lithium silicate heterogeneous catalysed biodiesel production process. RSM is a widely used mathematical-cum-statistical technique being employed for the optimization, modeling and analysis of the yield of biodiesel [22-25]. The Box Behnken Design (BBD) is one of the most common designs in optimization studies, which in combination with RSM technique was applied here for the optimization of different variables so as to attain the maximum efficiency in the lithium silicate catalysed process of the production of biodiesel [26, 27].

4.2 EXPERIMENTAL

4.2.1 Catalyst Preparation

![Preparation of catalyst](image)

Figure 4.2. Preparation of catalyst
The catalysts were prepared by incipient wet impregnation method using aqueous solution of LiNO₃. Impregnation was done over SiO₂ support at varying Li: Si molar ratios. The mixture was then stirred using a mechanical stirrer with an rpm of 800 at 90 °C for 6 h where the contents got dried after 6 h. The dried mixture was then kept in a hot air oven at 90 °C for overnight. Calcination was done at 650 °C for 3 h to obtain the lithium silicate catalyst. Methanol washing was given for the catalyst after refluxing with methanol at 65 °C for 1 h to remove the methanol soluble fraction so as to ensure heterogeneity in the reaction the catalyst was then filtered, dried and activated at the calcination temperature for 1 h.

Different catalytic systems were also prepared by varying the Li: Si molar ratios such as 10:90, 20:80, 30:70, 40:60, 50:50 and 66.66:33.33. The systems were designated as Li:Si(m:n). Where, m:n indicates the molar ratio of Li:Si in the catalyst. For simplicity, Li:Si(66.66:33.33) is further designated as Li:Si(2:1).

![Figure 4.3. Different catalyst systems prepared](image-url)
4.2.2 Experimental Design for Transesterification and Statistical Analysis by RSM

Box-Behnken Design (BBD), the experimental design selected for the present study, helps in understanding the effects of the four different reaction parameters on the FAME content in the transesterification of waste cooking oil over lithium silicate catalyst, Li:Si(2:1). The design of experiment for the transesterification of waste cooking oil was established using the software Minitab version 14 (Minitab USA) [28]. The optimization of different reaction parameters that affects the methyl ester yield during the transesterification process was done by applying the principles of RSM. BBD was used along with RSM to understand the existence of interactions among the variables and the responses. The model used here was for deducing a mathematical correlation between different independent variables on the FAME content.

The reaction parameters chosen for the design of experiments were temperature, catalyst weight, reaction time and methanol: oil molar ratio. Stirring speed was kept constant as 500 rpm in all the experimental trials and the reactions were conducted at atmospheric pressure. The levels and range of the four variables are selected based on the literature reports [29-31], properties of reactants and the preliminary studies that were carried out in the laboratory. The three levels, *i.e.*, high (+1), medium (0) and low (-1), values of reaction variables are illustrated in table 4.1.
Table 4.1. Experimental range and levels of the independent variables used in the study.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Range and levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol: oil molar ratio</td>
<td>9:1</td>
</tr>
<tr>
<td></td>
<td>12:1</td>
</tr>
<tr>
<td></td>
<td>15:1</td>
</tr>
<tr>
<td>Catalyst amount (wt%)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>7</td>
</tr>
<tr>
<td>Reaction time (h)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Reaction temperature (°C)</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>65</td>
</tr>
</tbody>
</table>

The biodiesel conversion at room temperature was negligible over the present catalyst. Therefore it was not taken as the lower temperature limit. 15:1 was selected as the maximum methanol to oil molar ratio because, this is the point at which maximum conversion of 100% is obtained. 9:1 was selected as the lower limit since below this limit only a small amount of FAME was obtained. Similar is the case for the selection of catalyst weight as well as reaction time.

Based on these high, medium and low values, 27 experimental trials were assigned. All the trials were carried out in duplicate and the results were analyzed by fitting the data to a second order polynomial Eq. (1).

\[
Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j, \quad i < j \rightarrow (1)
\]

Where, \( Y \) represents the response variable; \( \beta_0 \) is the interception coefficient; \( \beta_i \) is the coefficient of the linear effect; \( \beta_{ii} \) is the coefficient of quadratic effect; \( \beta_{ij} \) is the coefficient of interaction effect when \( i < j \), and \( k \) is the numbers of variables involved in the experiment. Regression analysis of the data was
carried out by using the same software by fitting it to the second order polynomial Eq. (1) and thus evaluates the significance of the model by statistical analysis.

The validity of quadratic model was checked by carrying out four different experiments as predicted by the point prediction software, Minitab 14. The influence of the catalyst in the production of biodiesel by the way of RSM mediated optimization was compared with the obtained values. The value of regression and correlation coefficients can indicate the significance and validity of the model for this optimization.

4.3 RESULTS AND DISCUSSION

In the present study, statistical optimization of reaction variables for biodiesel production over lithium silicate catalyst was carried out successfully. To determine the desired loading of LiNO₃ over SiO₂, so as to obtain the best catalyst, a series of catalysts were prepared by varying the Li:Si molar ratios. The systems were characterized to evaluate its properties responsible for catalysis.

4.3.1 TPD of CO₂ Analysis

The basicity of the prepared systems was investigated using temperature programmed desorption (TPD) of CO₂ since lithium silicate is a base catalyst used in biodiesel production. The total basicity measurements carried out by TPD of CO₂ for all catalysts are summarized in table 4.2 and the CO₂-TPD profiles are given in figure 4.4.
The peaks present around room temperature (RT) to 200 °C are assigned to desorption of CO₂ physisorbed or adsorbed on weakly basic sites. The peaks around 200 °C to 400 °C are ascribed to desorption of CO₂ adsorbed on moderately basic sites. The peaks above 400 °C are assigned to CO₂ adsorbed on strongly basic sites. The basicity measurements indicate that silica possesses negligible basicity, and basicity is enhanced upon lithium loading. As the amount of lithium increases, the total basicity also increases and reaches a maximum value of 0.3679 mmol g⁻¹ in the case of Li:Si(2:1) catalyst.

Figure 4.4. TPD of CO₂ profiles on the support and lithium silicate catalysts
Table 4.2. TPD-CO$_2$ results of the catalysts

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Catalyst system</th>
<th>Weak (RT-200 °C)</th>
<th>Medium (200 °C-400 °C)</th>
<th>Strong (400 °C-700 °C)</th>
<th>Total (RT-700 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SiO$_2$</td>
<td>0.0000</td>
<td>0.0</td>
<td>0.0036</td>
<td>0.0036</td>
</tr>
<tr>
<td>2</td>
<td>Li:Si(10:90)</td>
<td>0.0000</td>
<td>0.0002</td>
<td>0.0000</td>
<td>0.0060</td>
</tr>
<tr>
<td>3</td>
<td>Li:Si(20:80)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.012</td>
<td>0.0120</td>
</tr>
<tr>
<td>4</td>
<td>Li:Si(30:70)</td>
<td>0.0000</td>
<td>0.0006</td>
<td>0.0129</td>
<td>0.0135</td>
</tr>
<tr>
<td>5</td>
<td>Li:Si(40:60)</td>
<td>0.0009</td>
<td>0.011</td>
<td>0.0305</td>
<td>0.0424</td>
</tr>
<tr>
<td>6</td>
<td>Li:Si(50:50)</td>
<td>0.0037</td>
<td>0.1989</td>
<td>0.0471</td>
<td>0.2497</td>
</tr>
<tr>
<td>7</td>
<td>Li:Si(5:2)</td>
<td>0.0000</td>
<td>0.2493</td>
<td>0.1186</td>
<td>0.3679</td>
</tr>
</tbody>
</table>

4.3.2 Effect of Li:Si Molar Ratio on the FAME Content

An initial activity study is conducted over different catalysts to find the most efficient system for the biodiesel production. The reaction conditions chosen were based on previous reports and experiments conducted in the laboratory. The obtained FAME content for each reaction is given in table 4.3.

Table 4.3. Effect of Li:Si molar ratio on the FAME content

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Catalyst system</th>
<th>Li:Si molar ratio</th>
<th>FAME content [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li:Si(10:90)</td>
<td>10:90</td>
<td>14.62</td>
</tr>
<tr>
<td>2</td>
<td>Li:Si(20:80)</td>
<td>20:80</td>
<td>23.64</td>
</tr>
<tr>
<td>3</td>
<td>Li:Si(30:70)</td>
<td>30:70</td>
<td>55.19</td>
</tr>
<tr>
<td>4</td>
<td>Li:Si(40:60)</td>
<td>40:60</td>
<td>80.03</td>
</tr>
<tr>
<td>5</td>
<td>Li:Si(50:50)</td>
<td>50:50</td>
<td>99.98</td>
</tr>
</tbody>
</table>
It is found that, the activity of different systems was in good correlation with basicity data obtained from TPD of CO$_2$. In the case of Li:Si(50:50), a conversion of 99.98 % was obtained. But this catalyst was not much reusable, and the activity dropped to 85.6 % in the second cycle itself. Since the international standard specification (EN 14214) of FAME content is 96.5 %, the catalyst was not found to be suitable for biodiesel production. At a Li:Si molar ratio of 2:1, the catalyst was found to be effectively reusable yielding 98.5 % FAME in the second cycle. Hence, the system with Li:Si molar ratio of 2:1 was chosen for further optimization studies. The increase in the Li:Si molar ratio leads to the formation of a catalyst with a more stable structure which may be reason for the reusability. The reactions over other catalyst systems yielded lower FAME content, some amount of mono and diglycerides are also formed. The active catalyst, Li:Si(2:1) was further characterized using SEM, ICP-AES and TEM analyses so as to investigate the structural and textural properties of the system to correlate with its catalytic activity.

4.3.3 FTIR Spectral Analysis

The identification of different functional groups present in the catalysts as well as in silica is done by the FTIR spectral analysis (Figure 4.5). In the spectra, the broad band centered at 3560 cm$^{-1}$ corresponds to the stretching vibration of -OH groups from adsorbed water [32]; the bands located at 962 cm$^{-1}$ and 906 cm$^{-1}$ were due to the asymmetric stretching vibration of Si–O-H silanol groups and bending vibration of O–Si–H, respectively; and also, bands
of O–Si–O and Si–O–Si bridges are seen around 800 cm\(^{-1}\) [33]. The absorption peaks in the spectra of silica at about 794 cm\(^{-1}\) and 1100 cm\(^{-1}\) corresponds to the O-Si-O stretching vibration [34]. The absorption band at about 1623 cm\(^{-1}\) corresponds to the bending vibration of water molecules that are bound to the catalyst surface [35, 36]. The absorption bands that originated as a result of Li-O bond vibration are at about 445-611 cm\(^{-1}\) in the lithium silicate samples [32]. The absorption bands corresponding to Li-OH vibration and Si-O-Li vibration are at 855 cm\(^{-1}\) and 965 cm\(^{-1}\) respectively, in the spectra of lithium silicates [32]. The O-Si-O stretching vibration observed at 1100 cm\(^{-1}\) and 794 cm\(^{-1}\) in SiO\(_2\) [32] is shifted to 1060 cm\(^{-1}\) and 785 cm\(^{-1}\) in the FTIR spectrum of the Li:Si(2:1) catalyst. This may be due to the interaction between Lithium and silica.

Figure 4.5. FTIR spectra of the silica and lithium silicate catalysts
4.3.4 XRD Analysis

The crystalline nature of the catalysts was investigated by X-ray diffraction analysis (Figure 4.6). The characteristic peaks at 2θ values of about 18.9°, 26.9°, 33.2°, 38.7°, 43.2°, 51.9°, 55.2° and 59.1° corresponds to the diffraction from (020), (111), (130), (131), (221), (132), (241) and (330) crystal planes of Li₂SiO₃ [37-40]. Weak diffraction from Li₂Si₂O₅ phase was also observed at 2θ value corresponding to 22.2° [39].

![Figure 4.6. XRD patterns of silica and lithium silicate catalysts](image)

Figure 4.6. XRD patterns of silica and lithium silicate catalysts
The chemical reaction for the formation of major crystalline phase \((\text{Li}_2\text{SiO}_3)\) of the catalyst can be written as,

\[
2\text{LiNO}_3 + \text{SiO}_2 \rightarrow \text{Li}_2\text{SiO}_3 + \text{NO}_2
\]

### 4.3.5 SEM and TEM Analysis

The surface morphology of Li:Si(2:1) was investigated using SEM analysis.

![SEM, TEM and high resolution TEM photographs of silicon dioxide [(a), (c) and (e)], lithium silicate [(b), (d) and (f)]](image)

Figure 4.7. SEM, TEM and high resolution TEM photographs of silicon dioxide [(a), (c) and (e)], lithium silicate [(b), (d) and (f)]
The SEM images of pure SiO$_2$ and the developed lithium silicate are shown in Figure 4.7. From the Figure 4.7a, it is clear that SiO$_2$ exhibits a flake like morphology. A drastic change in the morphology is observed for silica upon incorporation of lithium (Figure 4.7b). Similar to other biodiesel catalysts reported, here also the catalyst showed a macroporous morphology throughout the surface, which could enhance the production of biodiesel. Several researchers reported the usage of macroporous catalysts in the transesterification reaction for producing biodiesel with high yield [41-43]. TEM images and high resolution TEM photographs of silica and Li:Si(2:1) are shown in Figure 4.7(c) & (e) and (d) & (f) respectively, which further confirms the porous nature of the synthesized catalyst.

4.3.6 ICP-AES Analysis

The ICP-AES analysis of Li:Si(2:1), the best catalyst, was carried out to determine the composition of the catalyst, and the results reveal that the Li:Si ratio is 2:1, which supports the existence of the catalyst in the form of Li$_2$SiO$_3$ as suggested from x-ray diffraction analysis. Analysis of the undissolved portion confirmed the existence of SiO$_2$ in the sample and the total Li:Si molar ratio of the catalyst is found to be 1:1 indicating the dispersion of Li$_2$SiO$_3$, the active phase of the material, over SiO$_2$ support.

4.3.7 Statistical Optimization of Reaction Parameters

Based on the preliminary experiments, different reaction parameters were selected for the transesterification reaction. Initially, the transesterification reaction was carried out with used cooking oil under the
reaction conditions of catalyst weight of 6 wt%, methanol to oil molar ratio 15:1, reaction temperature 65 °C and reaction time 1 h. We obtained fuel grade biodiesel under these conditions. But, the FAME content was only 96.93%. To obtain better yields, the reaction time was increased to 2 h. At this condition, the maximum FAME content of 100% was obtained. The FAME content remained as 100% at a reaction time of 3 h, as expected. Thus, 2 h is taken as the medium value of reaction time and 3 h as the higher reaction time. This is to obtain higher FAME content under low catalyst weight, reaction temperature and methanol to oil molar ratio.

Temperature, methanol to oil molar ratio, and weight of the catalyst are the other prominent variables affecting the transesterification process for the biodiesel production. All these variables were subjected to BBD analysis, followed by RSM to find the optimum conditions in maximizing the production of biodiesel; accordingly, a set of 27 experiments was performed (Table 4.4). The results, which were analyzed by the analysis of variance (ANOVA), showed that the predicted and experimental values for FAME content did not show significant difference, and thus accuracy of the model is confirmed. A second order polynomial equation was fitted to the optimization of biodiesel production, which resulted in the following regression equation.

\[
Y = -338 + 5.67 X_1 + 86.7 X_2 + 11.4 X_3 + 26.5 X_4 - 0.0372 X_1^2 - 2.91 X_2^2 - 0.357 X_3^2 - 2.92 X_4^2 - 0.353 X_1 X_2 - 0.0584 X_1 X_3 + 0.058 X_1 X_4 - 2.601 X_2 X_3 - 3.00 X_2 X_4 + 1.257 X_3 X_4
\]

Where, \(Y\) = (FAME content), \(X_1\) = (reaction temperature), \(X_2\) = (reaction time), \(X_3\) = (methanol to oil molar ratio), and \(X_4\) = (catalyst weight). Based on the results, the model was used to generate response surfaces for the analysis of the variable effects on the production of biodiesel. The response surface and
contour plots generated using the above equation are depicted in Figure 4.8 and Figure 4.9, respectively.

Table 4.4. Experimental trials according to Box- Behnken Design for optimizing lithium silicate catalyzed transesterification

<table>
<thead>
<tr>
<th>Run Order</th>
<th>Temperature [°C]</th>
<th>Time [h]</th>
<th>Methanol to oil molar ratio</th>
<th>Catalyst weight [wt%]</th>
<th>Observed FAME [%]</th>
<th>Expected FAME [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>55</td>
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<td>83.89</td>
<td>76.54</td>
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<td>2</td>
<td>12</td>
<td>7</td>
<td>99.3</td>
<td>99.07</td>
</tr>
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<td>12</td>
<td>6</td>
<td>95.79</td>
<td>96.24</td>
</tr>
<tr>
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<td>55</td>
<td>1</td>
<td>12</td>
<td>7</td>
<td>96.55</td>
<td>90.8</td>
</tr>
<tr>
<td>6</td>
<td>55</td>
<td>2</td>
<td>15</td>
<td>5</td>
<td>83.04</td>
<td>88.47</td>
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<td>45</td>
<td>1</td>
<td>12</td>
<td>6</td>
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<td>74.57</td>
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<tr>
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<td>2</td>
<td>12</td>
<td>6</td>
<td>96.1</td>
<td>96.24</td>
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<td>55</td>
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<td>15</td>
<td>7</td>
<td>99.27</td>
<td>100</td>
</tr>
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<td>1</td>
<td>9</td>
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<td>62.72</td>
<td>70.03</td>
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<td>15</td>
<td>6</td>
<td>98.56</td>
<td>97.43</td>
</tr>
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<td>9</td>
<td>6</td>
<td>97.05</td>
<td>90.28</td>
</tr>
<tr>
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<td>65</td>
<td>2</td>
<td>15</td>
<td>6</td>
<td>100</td>
<td>98.57</td>
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<td>12</td>
<td>5</td>
<td>99.06</td>
<td>96.04</td>
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<td>91.84</td>
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<td>2</td>
<td>12</td>
<td>5</td>
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<td>81.29</td>
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<td>55</td>
<td>2</td>
<td>9</td>
<td>7</td>
<td>83.03</td>
<td>84.21</td>
</tr>
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<td>18</td>
<td>55</td>
<td>3</td>
<td>12</td>
<td>7</td>
<td>99.74</td>
<td>97.57</td>
</tr>
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<td>19</td>
<td>55</td>
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<td>12</td>
<td>5</td>
<td>83.87</td>
<td>77.26</td>
</tr>
<tr>
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<td>55</td>
<td>2</td>
<td>12</td>
<td>6</td>
<td>96.85</td>
<td>96.24</td>
</tr>
<tr>
<td>21</td>
<td>45</td>
<td>2</td>
<td>12</td>
<td>7</td>
<td>85.01</td>
<td>87.67</td>
</tr>
</tbody>
</table>
Chapter 4

4.3.7.1 Analysis of Variance

The significance, precision and fitness of the model for this optimization process were determined from the ANOVA table (Table 4.5) which is given by the software Minitab. The linear, square and the interaction effects of the four different reaction parameters on the FAME content were given by the ANOVA table. The p-values and F-values of these parameters suggest the significance of the variables for this model. The lower P-values (<0.05) of the temperature, catalyst weight, methanol to oil molar ratio and reaction time indicates the significance of the model. Also, the model predicted an R² value of 82.4 % which suggests the suitability of the model for use in optimization of the lithium silicate catalysed biodiesel production.

Table 4.5. Analysis of variance for the second order polynomial model for optimization of biodiesel production over lithium silicate

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>14</td>
<td>1904.50</td>
<td>136.036</td>
<td>4.02</td>
<td>0.010</td>
</tr>
<tr>
<td>Linear</td>
<td>4</td>
<td>1392.38</td>
<td>348.095</td>
<td>10.28</td>
<td>0.001</td>
</tr>
<tr>
<td>Temp</td>
<td>1</td>
<td>314.68</td>
<td>314.675</td>
<td>9.29</td>
<td>0.010</td>
</tr>
<tr>
<td>Time</td>
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<td>489.86</td>
<td>489.857</td>
<td>14.47</td>
<td>0.003</td>
</tr>
<tr>
<td>mol ratio</td>
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<td>417.366</td>
<td>12.33</td>
<td>0.004</td>
</tr>
<tr>
<td>cat wt</td>
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<td>170.48</td>
<td>170.479</td>
<td>5.04</td>
<td>0.044</td>
</tr>
</tbody>
</table>
4.3.7.2 Validity of the Model

To evaluate the validity of the model, four random experimental trials as predicted by the software were performed (Table 4.6). In all these experiments, the expected and observed FAME content values were in good agreement. The correlation coefficient was calculated as 0.95. Since the correlation coefficient is close to unity, the model is significant for the optimization of lithium silicate catalyzed biodiesel production. The optimum conditions predicted for the production of biodiesel are: reaction temperature 55 °C, methanol to oil molar ratio 15:1, catalyst weight 7 wt%, and reaction
time 2.5 h. Thus, from the results on the optimisation of reaction variables, it is well evident that we could establish the preparation of a highly effective catalyst for biodiesel production.

Table 4.6. Validation experimental trials

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Temperature [°C]</th>
<th>Time [h]</th>
<th>Methanol/oil molar ratio</th>
<th>Catalyst weight [wt%]</th>
<th>Expected FAME [%]</th>
<th>Observed FAME [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>55</td>
<td>2.5</td>
<td>15</td>
<td>7</td>
<td>99.27</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>45</td>
<td>2.5</td>
<td>12</td>
<td>6</td>
<td>91.78</td>
<td>90.05</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>2.5</td>
<td>15</td>
<td>6</td>
<td>95.8</td>
<td>96.43</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>2</td>
<td>9</td>
<td>6</td>
<td>89.73</td>
<td>91.06</td>
</tr>
</tbody>
</table>

4.3.7.3 Surface and Contour Plots

Normally, the independent analysis of reaction parameters is difficult due to the interaction effects between the variables. The regression equation gives the interaction effect which is graphically presented in the form of contour plots (Figure 4.8). The distribution of FAME content with respect to different reaction parameters can be obtained in this case. The contour area gives the FAME content under the suggested experimental conditions. In all the contour plots, the relation between two different parameters were shown while the other parameters are kept at the medium values (a temperature of 55 °C, reaction time of 2 h, the methanol to oil molar ratio of 12:1 and a catalyst concentration of 6 wt%). The elliptical shape of the plots refers to the significance of the plotted parameters on the FAME content [44].
Figure 4.8. Contour plots showing the distribution of FAME content w.r.t catalyst weight, methanol to oil molar ratio, reaction temperature and reaction time.

The response surface plots showing the effects of different parameters on the FAME content in the transesterification of waste cooking oil over lithium silicate are given in Figure 4.9. It consists of a set of six different plots. In Figure 4.9(a), the interaction effect of catalyst weight and molar ratio on the FAME content is depicted while the other two parameters, reaction time and reaction temperature were kept constant as same before, respectively. It is
observed that the FAME content increases with increase in both catalyst weight and methanol to oil molar ratio. Also, it reaches a maximum value of 100 % in the medium values of catalyst weight and methanol to oil molar ratio. In Figure 4.9(b), the effects of reactant’s molar ratio and reaction time on the FAME content are plotted. The FAME content increases with increase in reaction time; at lower reaction time of 1 h, the FAME content is only about 70 %. This increases with time and at 3 h, maximum biodiesel conversion is obtained at which the lower methanol to oil molar ratio of 9:1 is suggested for the maximum conversion. Figure 4.9(c) explains the effects of catalyst weight and reaction time on the FAME content. From the graph, the FAME content increases with increase in catalyst weight and reaction time. Figure 4.9(d) represents the response surface plots to understand the influence of molar ratio and temperature on the FAME content. The increase in temperature had a positive effect in the transesterification reaction, which increased the biodiesel yield. The FAME content increased with increase in methanol to oil molar ratio. Figure 4.9(e) explains the variation of FAME content with change in the catalyst weight and temperature. A mutual effect is observed for the two parameters on the FAME content. Increase in both catalyst weight and temperature increases the yield of biodiesel produced. Figure 4.9(f) describes the impact of reaction time and temperature on the FAME content. The higher the reaction temperature, the higher will be the FAME content. Increase in reaction time also favors the FAME content.
Figure 4.9. The Surface plots showing the effects of different parameters on the biodiesel production over lithium silicate

4.3.8 Comparison of Catalytic Activity

The catalytic activity of the catalyst, Li:Si(2:1) under the optimum reaction conditions suggested by the RSM technique was compared with the reported data over other heterogeneous catalysts, and the results are presented in Table 4.7.
Table 4.7. Comparison of the transesterification activity and the optimum reaction conditions given by RSM in the biodiesel production by different heterogeneous catalysts with the present work

<table>
<thead>
<tr>
<th>Catalyst system</th>
<th>FAME content/Conversion yield [%]</th>
<th>Methanol to oil molar ratio</th>
<th>Time [h]</th>
<th>Catalyst amount [wt%]</th>
<th>Temperature [°C]</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(NO\textsubscript{3})\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>94</td>
<td>65:1</td>
<td>3</td>
<td>10</td>
<td>65</td>
<td>[45]</td>
</tr>
<tr>
<td>CaO- MgO mixed oxide Sr/ZrO\textsubscript{2}</td>
<td>93.55</td>
<td>38.67:1</td>
<td>3.44</td>
<td>3.7</td>
<td>115.87</td>
<td>[46]</td>
</tr>
<tr>
<td>Montmorillonite KSF Sulfated zirconia</td>
<td>79.6</td>
<td>8:1</td>
<td>3</td>
<td>3</td>
<td>190</td>
<td>[48]</td>
</tr>
<tr>
<td>CaO/Al\textsubscript{2}O\textsubscript{3}</td>
<td>98.64</td>
<td>12.14:1</td>
<td>5</td>
<td>5.97</td>
<td>64.29</td>
<td>[50]</td>
</tr>
<tr>
<td>Na\textsubscript{2}O/NaX</td>
<td>99.3</td>
<td>6:1</td>
<td>6</td>
<td>10</td>
<td>60</td>
<td>[51]</td>
</tr>
<tr>
<td>Sr\textsubscript{3}Al\textsubscript{2}O\textsubscript{6}</td>
<td>95.7</td>
<td>25:1</td>
<td>1.1</td>
<td>1.3</td>
<td>60</td>
<td>[52]</td>
</tr>
<tr>
<td>Li:Si(2:1)</td>
<td>100</td>
<td>15:1</td>
<td>2.5</td>
<td>7</td>
<td>55</td>
<td>Present work</td>
</tr>
</tbody>
</table>

Also, the catalytic activity results of lithium based catalysts comparing the operating conditions, efficiency of the process, catalyst, etc. is tabulated and given in Table 4.8. The lower reaction temperature and lower reaction time at reasonable methanol to oil molar ratio with high FAME content is the highlight of the present work compared to other studies reported for biodiesel production.
Table 4.8. Lithium based heterogeneous catalysts for the transesterification reaction

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Catalyst</th>
<th>FAME yield/content/co conversion (%)</th>
<th>Optimum reaction conditions</th>
<th>Reference</th>
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<tbody>
<tr>
<td>1</td>
<td>Li$_2$CO$_3$</td>
<td>97.2</td>
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<td>[2]</td>
</tr>
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<td>2</td>
<td>Lithium silicate</td>
<td>86.7</td>
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<td>3</td>
<td>Li$_4$SiO$_4$</td>
<td>98.8</td>
<td>1, 12:1, 65, 3</td>
<td>[12]</td>
</tr>
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<td>Lithium orthosilicate</td>
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<td>6, 18:1, 65, 2</td>
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<td>[34]</td>
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<td>32.8, 24:1, 65, 3</td>
<td>[53]</td>
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<td>7, 15:1, 55, 2.5</td>
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</tbody>
</table>

4.3.9 Fuel Properties of Biodiesel

The fuel properties of the biodiesel prepared over lithium silicate catalyst under the predicted optimum reaction conditions were determined, and it was found that the biodiesel meets the standard specifications of ASTM D6751 and EN 14214 (Table 4.9). Thus, the catalyst was found to be highly effective and was suitable for the industrial scale up.
Table 4.9. Fuel properties of biodiesel obtained under optimum reaction conditions* using lithium silicate as catalyst.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Test Methods</th>
<th>Unit</th>
<th>Limits (EN 14214)</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester content</td>
<td>EN 14103</td>
<td>wt.%</td>
<td>96.5 min</td>
<td>100</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>EN 14105</td>
<td>wt.%</td>
<td>0.02 max</td>
<td>0.00</td>
</tr>
<tr>
<td>Monoglyceride</td>
<td>EN 14214</td>
<td>wt.%</td>
<td>0.8</td>
<td>0.00</td>
</tr>
<tr>
<td>Triglyceride</td>
<td>EN 14214</td>
<td>wt.%</td>
<td>0.20</td>
<td>0.00</td>
</tr>
<tr>
<td>Total glycerol</td>
<td>EN 14105</td>
<td>wt.%</td>
<td>0.25 max</td>
<td>0.00</td>
</tr>
<tr>
<td>Acid value</td>
<td>EN 14104</td>
<td>mg KOH/g</td>
<td>0.50 max</td>
<td>0.10</td>
</tr>
<tr>
<td>Water content</td>
<td>EN ISO 12937</td>
<td>mg/kg</td>
<td>500 max</td>
<td>0.00</td>
</tr>
<tr>
<td>Viscosity</td>
<td>D445</td>
<td>mm²/s</td>
<td>1.96-6.0</td>
<td>3.82</td>
</tr>
<tr>
<td>Density</td>
<td>EN ISO 3675</td>
<td>g/m³</td>
<td>860-900</td>
<td>868</td>
</tr>
</tbody>
</table>

* 15:1 methanol-to-oil molar ratio, 7 wt% catalyst, 55 °C reaction temperature and 2.5 h reaction time.

4.3.10 Reusability Studies

After the reaction, under the optimum reaction conditions, the catalyst was recovered from the reaction mixture and washed several times with methanol. The catalyst was then dried at 90 °C, activated at 650 °C for 1 h, and reused for the biodiesel production. The catalyst was stable up to three cycles yielding a FAME content of 96.9 % in the 3rd cycle and the catalytic activity was dropped to 86.8 % at the 5th cycle (Figure 4.10).
4.3.11 Characterization Studies of Reused Catalyst

FTIR spectral analysis of the catalyst after the third run was carried out to understand the nature of the catalyst after the repeated cycles of reaction. The catalyst structure remains unaltered even after the reuse, as it is evident from the FTIR spectrum of the reused sample (Figure 4.11).
4.4 CONCLUSIONS

We have tested the applicability of the principles of Box Behnken Design and Response Surface Methodology for the optimization of different reaction parameters in the production of biodiesel using lithium silicate as the heterogeneous catalyst. 100 % yield of biodiesel was obtained under the suggested optimum reaction conditions of methanol to oil molar ratio of 15:1, catalyst amount of 7 wt% of oil, temperature of 55 °C and reaction time of 2.5 h, model predicted a FAME yield of 99.27 %. The methyl ester products obtained under the optimized mild reaction conditions were analyzed, and it is confirmed that its fuel properties met the specification of biodiesel as mentioned in the international standards, indicating its applicability as a diesel fuel substitute. The catalyst was found to be effectively reusable leading to the formation of fuel grade biodiesel at a low reaction temperature of 55 °C till three repeated cycles.

REFERENCES

Lithium Silicate Catalyzed Biodiesel Production via Statistical Optimization


Lithium Silicate Catalyzed Biodiesel Production via Statistical Optimization


Ceria is employed as a support material for the preparation of a novel heterogeneous catalyst, Na/CeO$_2$ which shows excellent catalytic activity in the transesterification reaction of waste cooking oil
5.1 INTRODUCTION

Cerium is the most abundant (66.5 ppm) rare earth element in the earth crust and is the most reactive element among the rare earth metals except europium. In most of the cases, cerium occurs in minerals in the form of oxides. Cerium dioxide (ceria, CeO$_2$) is an inorganic rare earth metal oxide containing cerium and oxygen. In the case of all other rare earths, the dioxide is not the stable phase. Cerium is the unique rare earth element with a stable dioxide phase [1].

![Figure 5.1. Cubic fluorite structure of ceria](image)

The electronic structure of ceria is variable in nature because cerium exhibits dual valance states and hence has dual electronic configuration. The valance states of cerium changes from 3 to 4 because the energy of valence electrons is same as that of the energy of the inner 4f level electrons. The crystal structure of ceria is assumed to be cubic fluorite (Figure 1) with a space group of $Fm\bar{3}m$ with the lattice parameter of 5.411 Å [2,3]. In perfect ceria, the oxygen ions have a formal charge of -2 and the cerium ions have a formal charge of +4. In ceria, Ce$^{4+}$ ions form a cubic close packing arrangement and
occupies in the corners and faces of the cube. The cerium ion is surrounded by 8 oxygen ions in the cube which are occupied in the tetrahedral sites. The oxygen ion is surrounded by four cerium ions in a tetrahedral arrangement. i.e., the body center positions of all the small cubes are occupied by oxide ions and the alternate corners are occupied by Ce$^{4+}$ ions. The octahedral sites remain vacant.

5.1.1 Properties of Ceria

There are abundant properties for ceria [4-8] and some of the most important properties that are beneficial in catalysis are pictured (Figure 5.2) and briefly mentioned below.

Figure 5.2. Properties of ceria

Ceria has an intrinsic property of receiving and releasing oxygen and thus acts as a three way catalyst [9]. Ceria can easily release the oxygen from its crystal lattice which creates defects in the lattice resulting in oxygen vacancies which are responsible for its high oxide ion conductivity. [10]. Having high oxygen storage capacity (OSC), it can mediate reduction through the uptake of
oxygen and oxidation through the release of oxygen. The excellent redox property of ceria makes it as a promising catalyst in industry [11,12]. Ceria has high thermal stability, which is one of the important aspects while considering the three way catalysis and the stability can be improved by combination with other metal oxides [13].

5.1.2 Catalytic Applications

It is an extensively studied material for heterogeneous catalysis [14]. Pure ceria as well as ceria supported systems are used in different catalytic applications [15]. Ceria based catalysts are widely investigated in the soot oxidation reactions. Pure ceria and doped ceria catalysts, due to their higher redox activity are very active [16,17]. Vanadium supported on ceria-zirconia mixed oxide is used as a solid catalyst in the transesterification of diethylmalonate using \(n\)-butanol [18]. In addition, \(\text{CeO}_2\) is widely used in many organic transformations [19-31].

The catalytic activity of \(\text{CeO}_2\) based materials is greatly influenced by the synthetic procedure since the size, shape, surface area, morphology, etc. of the developed catalyst depends on the mode of preparation [32]. In the literature, different methods such as sol-gel, co-precipitation, impregnation, hydrothermal, microwave technique, etc. are reported for the preparation of pure and doped \(\text{CeO}_2\) systems [33,34]. Most of these methods need the requirement of several conditions such as maintenance of fixed pH and temperature, constant stirring rate, etc. Also, the preparation may require multiple steps, making the entire process a tedious one. Ceria based systems have been also studied as promising solid catalysts for biodiesel production [35-39] and is briefly reviewed in chapter 1 section 1.9.3.
In the present study, Na loaded CeO$_2$ catalyst was prepared from CeO$_2$ and NaOH and it showed excellent activity and reusability in the transesterification of waste cooking oil with methanol for the preparation of biodiesel. We used a simple, green and easily performable method of solid state mixing of precursors and further heat treatment for CeO$_2$ support preparation [26]. The effectiveness of the support preparation method was analysed by comparison of the activity with other Na/CeO$_2$ catalysts prepared using two other CeO$_2$ support materials.

5.2 EXPERIMENTAL

5.2.1 Preparation of CeO$_2$ Supports

5.2.1.1 Solid State Mixing

![Figure 5.3. Scheme for the preparation of CeO$_2$](image)

Support material was prepared based on a reported procedure [26]. Citric acid and cerium nitrate were taken in a fixed weight ratio (1:1) and grinded to
make a paste. It was then transferred to a beaker and kept it at a temperature of 60 °C for 1 h with frequent stirring. The mixture was aged overnight and calcined at 600 °C for 3 h to get the CeO₂ support (CeO₂).

**5.2.1.2 Direct Thermal Decomposition**

Direct thermal decomposition of nitrate precursor was also employed for the CeO₂ support material preparation. Weighed amount of cerium nitrate was transferred to a china dish and calcined in a muffle furnace at 600 °C for 3 h to get the CeO₂ powder (CeO₂T).

![Figure 5.4. Scheme for the preparation of CeO₂T](image)

**5.2.1.3 Hydrothermal Method**

10 g cerium nitrate was added to 200 ml of isopropanol taken in an RB flask and stirred for 3 h in an oil bath at a temperature of 85 °C. First, the color of the solution was yellow, after some time it became a white coloured sol. The resultant sol was added to distilled water to obtain a clear solution. 1:1 NH₃ solution was added drop wise, until the pH reaches 9. The resultant mixture was then treated hydrothermally at 180 °C overnight. The obtained
precipitate was filtered and washed with deionized water and is dried in the oven at 60 °C for overnight and calcined at 500 °C for 3 h to get the CeO$_2$ powder (CeO$_2$HT).

5.2.2 Preparation of Na Loaded CeO$_2$ Catalysts

NaOH is incorporated into the CeO$_2$ support by impregnation method. In a typical procedure, NaOH was added to 200 ml distilled water and was heated to 60 °C with stirring. CeO$_2$ was added to it for obtaining a NaOH:CeO$_2$ weight ratio of 3:1 and the resultant suspension was stirred while heating. The mixture was then dried at 90 °C for overnight and calcined at 650 °C for 3 h. Methanol washing was given for the material to ensure heterogeneity in the reaction by separating the unbounded NaOH. The Na loaded CeO$_2$ was dried and activated at 650 °C for 1 h to get the Na/CeO$_2$ catalyst.

Catalyst systems were also prepared by changing the NaOH/CeO$_2$ weight ratio as 1:1 and 2:1 that are designated as 1Na/CeO$_2$ and 2Na/CeO$_2$. 

Figure 5.5. Scheme for the preparation of CeO$_2$HT
respectively. In a similar manner, Na loaded CeO₂ catalysts (Na/CeO₂T and Na/CeO₂HT) were prepared by using CeO₂ produced from direct thermal decomposition and hydrothermal methods respectively (NaOH to CeO₂ weight ratio 3:1).

Figure 5.6. Photographs of the CeO₂ based materials of the present study

The catalytic activity of the catalyst systems were investigated in the transesterification reaction of waste cooking oil with methanol. The detailed procedures for the transesterification reaction, biodiesel analysis, reusability studies and determination of fuel properties are mentioned in chapter 2.

5.3 RESULTS AND DISCUSSION

The prepared Na loaded CeO₂ catalyst systems were characterized by different techniques inorder to find out the textural, spectral and morphological features so as to find out the active phase responsible for catalysis. The catalytic activity of the all the catalysts was tested in the transesterification reaction of waste cooking oil using methanol. The effects of different reaction parameters such as methanol to oil molar ratios, reaction time, amount of catalyst and reaction temperatures that affects the transesterification reaction
were investigated using Na/CeO₂ to find out the suitable reaction conditions to attain the highest oil conversion.

5.3.1 Catalyst Characterization

5.3.1.1 XRD Analysis

![XRD patterns of ceria and Na loaded ceria systems](image)

Figure 5.7. XRD patterns of ceria and Na loaded ceria systems

XRD was used to identify the crystal structure as well as to find out the active phases present in the material. The XRD patterns of CeO₂ and Na loaded CeO₂ are shown in figure 5.7. It is clear that the ceria systems exhibited all of the major peaks of CeO₂ at 2θ values of 28.3°, 32.8°, 47.2° and 56.2° indicating the cubic fluorite structure [40-42]. No characteristic diffraction
peaks from other cerium species can be detected in the samples. Some new peaks are formed at 20 values of 36.2°, 37.7°, 40.1°, 41.2°, 43.7° and 45° as a result of incorporation of sodium hydroxide. These peaks correspond to the crystalline Na₂CO₃. Na₂CO₃ is highly unstable at a temperature of 650 °C and will decompose in to sodium oxide and carbon dioxide during the calcination process. However, the XRD patterns of synthesized catalytic systems showed the peaks corresponding to crystalline phase of Na₂CO₃ and which may due to the formation of Na₂CO₃ on the surface of support during the analysis as a result of adsorption of CO₂ in the atmosphere over the sodium oxide loaded on CeO₂ because of strong basicity of Na₂O [43]. The increase in the intensity of the diffraction band corresponding to Na₂CO₃ with increased amount of NaOH incorporation suggests increase in the basicity of the systems.

The active phase of the catalyst, i.e., Na₂O, may be formed during calcination of the NaOH impregnated CeO₂, which is then effectively dispersed over the support as represented below.

\[
2\text{NaOH} + \text{CeO}_2 \overset{\Delta}{\rightarrow} \text{Na}_2\text{O/CeO}_2 + \text{H}_2\text{O} \quad \text{(1)}
\]

5.3.1.2 FTIR Spectral Analysis

The FTIR spectra of CeO₂ and Na loaded CeO₂ systems are shown in figure 5.8. In CeO₂, a broad band is seen around 3447 cm⁻¹, corresponding to the adsorbed water molecules as well as surface hydroxyl groups [44]. The bands around 1627 cm⁻¹ correspond to H₂O bending vibration and that around 1375 cm⁻¹ is because of Ce–OH stretching vibration [45]. All the systems showed a well resolved sharp band around 553 cm⁻¹, which is attributed to the stretching vibration of Ce–O bond in the fluorite like structure of CeO₂ [46].
The FTIR spectrum of Na loaded CeO$_2$ system shows the absorption bands of carbonates in addition to the peaks of ceria. The bands around 2968 cm$^{-1}$, 2478 cm$^{-1}$ and 1692 cm$^{-1}$ correspond to Na$_2$CO$_3$ [47]. The symmetric stretching vibration of the carbonate ion at about 1045 cm$^{-1}$, its out-of-plane bending vibration at 854 cm$^{-1}$, the asymmetric stretching at 1457 cm$^{-1}$ and the in-plane bending vibration about 700 cm$^{-1}$ are also observed [48]. Presence of strong bands of carbonates indicates the high basicity of the systems since carbonates arises from the absorption of atmospheric CO$_2$ on the basic sites of the materials. Those peaks were absent in the unmodified CeO$_2$.

Figure 5.8. FTIR spectra of ceria and Na loaded ceria systems
5.3.1.3 TPD of CO₂ Analysis

TPD of CO₂ analysis of the Na loaded catalysts prepared from three different CeO₂ supports is investigated for comparing their basicities so as to correlate with the catalytic activity. The TPD of CO₂ profiles of CeO₂ and Na loaded ceria systems are shown in figure 5.9.

![Figure 5.9. TPD of CO₂ profiles of CeO₂ and Na loaded ceria systems](image)

The total basicity is calculated and data is given in table 3.1. It is observed that in the case of Na/CeO₂ system, there is no contribution towards basicity from the weak and medium basic sites. The total basicity is resulted only from the strong basic sites of the catalyst. CeO₂ shows low basicity of 0.5638 mmolg⁻¹ in comparison with Na/CeO₂, which shows a total basicity of 3.8618
mmolg$^{-1}$. The basicity data of other two catalysts; Na/CeO$_2$T and Na/CeO$_2$HT were found to be low in comparison with Na/CeO$_2$.

Table 5.1. TPD-CO$_2$ results of the support and catalysts

<table>
<thead>
<tr>
<th>Catalyst system</th>
<th>Basicity Distribution (mmolg$^{-1}$)</th>
<th>Total Basicity (RT - 900 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weak (RT-200 °C)</td>
<td>Medium (200 °C-400 °C)</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>0.0363</td>
<td>0.1083</td>
</tr>
<tr>
<td>Na/CeO$_2$T</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Na/CeO$_2$</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Na/CeO$_2$HT</td>
<td>0.0000</td>
<td>0.0006</td>
</tr>
</tbody>
</table>

5.3.1.4 SEM Analysis

Figure 5.10. SEM images of ceria and Na loaded ceria systems
SEM analysis of the samples is also done to understand the morphology, one of the factors influencing the catalytic activity. The SEM images of the supports and different catalysts are shown in figure 5.10. The surface morphologies of all the supports are different. The incorporation of NaOH also results in a change in morphology. The main CeO₂ support of present investigation has a porous flake-like morphology which can incorporate more amount of NaOH, than the other ceria systems, leading to an enhancement in the basicity of Na/CeO₂ and can highly contribute to the catalytic activity compared to other systems. CeO₂T and CeO₂HT systems show lumps of agglomerated particles. Flake-like morphology is displayed by all the Na incorporated catalysts.

**5.3.1.5 TEM Analysis**

The particle size and shape of CeO₂ and Na/CeO₂ catalyst can be clearly identified from the TEM analysis. From the TEM images (figure 5.11), it can be seen that both CeO₂ and Na/CeO₂ nanoparticles showed irregular shape and the Na/CeO₂ particles are somewhat bigger than that observed in CeO₂ sample. The increase in the size may be a resultant of the surface coverage of the support material with Na species. The SAED patterns of CeO₂ (Figure 5.11c) as well as Na/CeO₂ (Figure 5.11f) are shown in figure 5.11. Both the samples exhibited a polycrystalline nature as evident from the SAED patterns. CeO₂ was confirmed to exist in its cubic fluorite structure from the diffraction patterns ((111) plane having a d-spacing of about 0.31 nm and (210) plane with a d spacing of 0.19 nm). The Na/CeO₂ catalyst contains both peaks corresponding to cubic fluorite CeO₂ as well as that of Na₂CO₃ (corresponds to...
(121) plane having a d-spacing of about 0.23 nm and (212) plane with a d spacing of 0.24 nm).

![Figure 5.11. TEM Photographs of CeO2 (a & b) and Na/CeO2 (d & c)](image)

5.3.2 Catalytic Activity Studies

Transesterification of waste cooking oil with methanol is carried out over the catalyst systems. At first, the activities of the ceria systems were checked
and it was observed that the ceria supports prepared from three different methods exhibit only very low activity towards the transesterification reaction, i.e., CeO₂ – 2.38 %, CeO₂T -1.27 % and CeO₂HT -3.28 %.

5.3.2.1 Effect of Support Preparation Method

In order to understand the effect of preparation method of ceria in its use as a support material, the activity of the three catalysts, Na/CeO₂, Na/CeO₂T and Na/CeO₂HT were checked initially in the transesterification reaction. Among these systems, the Na/CeO₂ showed the highest activity; the data is presented in the table 5.2.

Table 5.2. Transesterification reaction results over different catalyst systems

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Catalyst system</th>
<th>FAME content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na/CeO₂</td>
<td>97.76</td>
</tr>
<tr>
<td>2</td>
<td>Na/CeO₂T</td>
<td>77.46</td>
</tr>
<tr>
<td>3</td>
<td>Na/CeO₂HT</td>
<td>82.54</td>
</tr>
</tbody>
</table>

Reaction conditions: 65 °C, 6 wt% of catalyst, methanol to oil molar ratio 12:1, 2 h reaction

This may be due to the porous nature of the ceria support which can thus incorporate more amount of NaOH into it resulting in high basicity and catalytic efficiency. The initial reactions are carried out 65 °C using 6 wt% of catalyst at a methanol to oil molar ratio of 12:1 for 2 h reaction. It is evident that the catalyst prepared using CeO₂ support synthesized via solid state mixing displayed the highest activity.

5.3.2.2 Influence of NaOH Loading

The influence of NaOH loading on CeO₂ in the transesterification reaction is also investigated. The FAME content increases with increase in the amount
of NaOH loading and reaches the maximum value of 100 % under the conditions of catalyst weight 6 wt%, methanol to oil molar ratio 15:1, reaction temperature 65 °C for 2 h reaction (figure 5.12) over Na/CeO₂ with a NaOH:CeO₂ weight ratio of 3:1. A reusability upto three cycles was also shown by the Na/CeO₂ catalyst producing fuel grade biodiesel (>96.5 %). So, this system is selected as the best catalyst for further studies for analyzing the influence of reaction parameters on biodiesel yield.

Figure 5.12. Influence of NaOH/CeO₂ weight ratio on the FAME content under the reaction conditions of catalyst weight 6 wt%, methanol to oil molar ratio 15:1, reaction temperature 65 °C and reaction time 2 h.

5.3.2.3 Effect of Calcination Temperature and Calcination Time

The calcination temperature of the catalyst in the preparation is varied from 500 °C to 700 °C with an interval of 50 °C and the calcination time is changed from 1 h to 4 h. The time for calcination was fixed as 3h (Figure 5.13a) and the calcination temperature chosen was 650 °C (Figure 5.13b). It was found that initially, the FAME content showed a positive trend towards the calcination temperature and calcination time. The best calcination temperature and
calcination time chosen for the study was 650 °C and 3 h respectively since maximum conversion was obtained at these conditions. The activity results of the catalyst at different calcination temperatures and calcination time are given in figure 5.13.

![Figure 5.13](image)

Figure 5.13. Effect of calcination temperature and calcination time on the FAME content under the reaction conditions of catalyst weight 6 wt%, methanol to oil molar ratio 15:1, reaction temperature 65 °C and reaction time of 2 h

### 5.3.2.4 Effect of Catalyst Weight

The weight percentage of the catalyst in the reaction is changed from 1 wt% to 7 wt% (Figure 5.14) and it can be seen that the catalytic activity is strongly influenced by the amount of catalyst. As the catalyst weight increased, the number of active sites available for catalysis were also increased. These results showed an increase in the FAME content with catalyst loading that reached a maximum value of 100% at a catalyst weight of 6wt%.
5.3.2.5 Effect of Reaction Temperature

To study the effect of reaction temperature (Figure 5.15) on the transesterification, reactions were performed at different temperatures.

Figure 5.14. Effect of catalyst weight on the conversion of waste cooking oil under the reaction conditions of methanol to oil molar ratio 15:1, reaction temperature 65 °C for 2 h reaction

Figure 5.15. Effect of reaction temperature on the transesterification of waste cooking oil under the reaction conditions of catalyst weight 6 wt%, methanol to oil molar ratio 15:1 for 2 h reaction
In most of the studies, the reflux temperature of methanol (65 °C) is selected as the best temperature for attaining maximum FAME [49-52]. Here also, the FAME content reached its maximum value of 100 % at a temperature of 65 °C.

5.3.2.6 Effect of Methanol to Oil Molar Ratio

The stoichiometric methanol to oil molar ratio of 3:1 is needed for transesterification of triglycerides [53].

Figure 5.16. Effect of methanol to oil molar ratio on the conversion of waste cooking oil under the reaction conditions of catalyst weight 6 wt%, reaction temperature 65 °C for 2 h reaction time

But, due to the reversible nature of the reaction, this amount is not sufficient to complete the reaction. A higher molar ratio is required to drive the reaction to completion at a fast rate [52,54]; in addition, excess methanol can act as a solvent for the reaction. Therefore, the methanol to oil molar ratio is changed from 3:1 to 15:1 (figure 5.16) for this study and it is observed that the FAME content increased from 26.2 % to 100 %. Almost linear increase of
FAME content was shown from 3 to 12 ratio obtaining up to 98.18 %. Thereafter, with a slight increase full conversion is observed at a methanol to oil molar ratio of 15:1 and hence it is chosen as the best methanol to oil molar ratio for further studies.

### 5.3.2.7 Effect of Reaction Time

The reaction time was varied from 0.5 h to 2 h (figure 5.17) and it was observed that the biodiesel meets the fuel grade quality after 1.5 h while the full conversion of waste cooking oil was observed at a reaction time of 2 h.

![Figure 5.17. Effect of reaction time on the FAME content under the reaction conditions of catalyst weight 6 wt%, methanol to oil molar ratio 15:1 and reaction temperature 65 °C](image)

5.3.3 Reusability Studies

The FAME content obtained in repeated cycles of reaction is shown in figure 5.18. Up to three cycles, biodiesel with more than 96.5% FAME yield is obtained. But thereafter the activity of the catalyst is decreased and the FAME content dropped to 87.24 % in the 4th cycle. The result indicated that the
Na/CeO$_2$ catalyst have a good potential for use in the large-scale biodiesel production process due to its excellent catalytic efficiency even in repeated cycles.

Figure 5.18. Reusability studies of the Na/CeO$_2$ catalyst under the reaction conditions of catalyst weight 6 wt%, methanol : oil molar ratio 15:1, reaction temperature 65 °C for 2 h reaction

The retention of the characteristic vibration bands in the catalyst after the repeated cycles of reaction was analyzed by FTIR spectral analysis. The FTIR spectra of the fresh catalyst and the catalyst after 5$^{th}$ cycle are shown in figure 5.19. The spectra show the retainment of all the characteristics peaks of carbonate and ceria suggesting the stability of the catalyst after repeated runs. The slight reduction in the area of carbonate peaks may be a resultant of the loss of some of the active sodium species which lead to a reduction in the basicity of the catalysts. This can be the reason for the decrease in activity from the 4$^{th}$ cycle onwards.
5.3.4 Fuel Properties of Biodiesel

The quality of the biodiesel having FAME content of 100 % produced under the best reaction conditions of catalyst weight 6 wt %, temperature 65 °C, time 2 h and methanol to oil molar ratio of 15:1 is checked for determining the fuel properties of biodiesel and comparing them with the international standard values as specified by ASTM and EN standards [55] (Table 5.3). The values lies in the range of standard values suggesting the suitability of using the present biodiesel sample as an alternate fuel for petroleum based fuels in the diesel engines.
**Table 5.3. Fuel properties of prepared biodiesel using Na/CeO₂ catalyst under the selected reaction condition**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Test Methods</th>
<th>Unit</th>
<th>Limits (EN 14214)</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester content</td>
<td>EN 14103</td>
<td>wt%</td>
<td>96.5 min</td>
<td>100</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>EN 14105</td>
<td>wt%</td>
<td>0.02 max</td>
<td>0.00</td>
</tr>
<tr>
<td>Monoglyceride</td>
<td>EN 14214</td>
<td>wt%</td>
<td>0.8</td>
<td>0.0</td>
</tr>
<tr>
<td>Diglyceride</td>
<td>EN 14214</td>
<td>wt%</td>
<td>0.20</td>
<td>0.00</td>
</tr>
<tr>
<td>Total glycerol</td>
<td>EN14105</td>
<td>wt%</td>
<td>0.25 max</td>
<td>0.00</td>
</tr>
<tr>
<td>Acid value</td>
<td>EN 14104</td>
<td>mg KOH/g</td>
<td>0.50 max</td>
<td>0.25</td>
</tr>
<tr>
<td>Water content</td>
<td>EN ISO 12937</td>
<td>mg/kg</td>
<td>500 max</td>
<td>0</td>
</tr>
<tr>
<td>Viscosity</td>
<td>D445</td>
<td>mm²/s</td>
<td>1.96-6.0</td>
<td>3.48</td>
</tr>
<tr>
<td>Density</td>
<td>EN ISO 3675</td>
<td>g/m³</td>
<td>860-900</td>
<td>862</td>
</tr>
</tbody>
</table>

*Reaction conditions: 15:1 methanol to oil molar ratio, 6 wt% catalyst, 65 °C reaction temperature and 2 h reaction time.

**5.4 CONCLUSIONS**

Na loaded CeO₂ catalysts have been successfully synthesized and its catalytic performance in the transesterification reaction of triglycerides from waste cooking oil has been investigated. The preparation method of ceria support and the active catalyst is simple and thus easily scalable. The high FAME content of 100% under the selected reaction conditions of catalyst weight 6 wt %, temperature 65 °C, reaction time 2 h and methanol to oil molar ratio of 15:1 indicates the high activity of the developed catalyst material. The catalyst can be easily separated from the reaction mixture and can be reused three times with only a slight reduction in catalytic activity. CeO₂ prepared via
solid state mixing and further heat treatment is found to be the best support for Na species incorporation.

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Chapter 6

HIGHLY REUSABLE NOVEL SODIUM TITANATE NANOTUBE CATALYST FOR BIODIESEL PRODUCTION

Porous titania is prepared by a facile method and is utilized as a precursor material for the preparation of sodium titanate nanotube which shows excellent catalytic activity in the transesterification reaction of waste cooking oil.

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Sree Neelakanta Govt. Sanskrit College, Pattambi
6.1 INTRODUCTION

The use of surfactants during the preparation of materials can result in porous morphology thereby increasing the diffusion of more reactants into the catalyst surface to take part in the reaction thereby increasing the catalytic activity [1]. In the present work, sodium titanate is prepared from TiO₂ and NaOH via wet impregnation method. TiO₂ is prepared via sol gel method with the presence of poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (P123) as the surfactant. P123 assisted synthesis of TiO₂ had been already reported, but in most of the studies, several organic solvents are employed [2,3]. In this work, we had prepared the precursor, TiO₂ in the presence P123 using water as the solvent. The catalytic activity of the developed sodium titanate catalyst is studied by employing it as a solid base catalyst in the transesterification reaction of waste cooking oil (WCO) with methanol. The different reaction parameters affecting the FAME content were varied for attaining better results. The TiO₂ prepared in the absence of P123 is also used in sodium titanate preparation for comparison of catalytic activity. In the next three sections, a brief mention is given about TiO₂, titanates and sodium titanate to get an idea about the catalyst material of present investigation.

The earth crust contains the metal titanium and it is the element in the 9th position. Titanium is mainly produced from ilmenite ore and has the ability to interact with oxygen forming titanium dioxide (TiO₂) which is also known as titania [4]. For the commercial production of titania, two methods are reported. The sulfate process and chloride process. Titanium Pigment Corporation and the Titan Company introduced the sulfate process in 1961 and the chloride
process by DuPont in 1951[5]. The three crystalline polymorphs of titania are rutile, anatase, and brookite (Figure 6.1). Among the three forms, rutile is the stable and most common form and the other two are stable metaphases. All the three forms are naturally occurring and consist of TiO$_6$ octahedra. Phase transition from brookite to anatase and then to rutile was observed with increase in the temperature [6]. Only difference in their structures lies in the arrangement of the TiO$_2$ octahedra in the three dimensional network structures [7].

![Figure 6.1. Crystal structure of titania for a) rutile b) brookite c) anatase [8]](image)

The important uses of titania include the degradation of pollutants [9], as implant materials [10], as photocatalyst [11], as electrode in dye-sensitized solar cell [12], as gas sensor [13], etc. It provides whiteness and opacity to products such as paints, plastics, papers, inks, foods, and toothpastes [14]. It is used in cosmetic and skin care products and in sunblock, where it helps to protect the skin from ultraviolet light [15].
6.1.1 Titanates

Titania forms compounds with other metals known as titanates that are defined as any titanium containing anion. The properties and structural features of these titanates are strongly influenced by the preparation method and the conditions [16]. These nanomaterials have received much attention due to their remarkable properties and technological importance. They are used widely for different applications such as, solar cells, photocatalysts, absorbents, catalytic support, gas sensors and particulate filters [17].

6.1.2 Catalytic Applications of Titanates

Alkali metal titanates of general formula $A_2O_nTiO_2$ ($3 \leq n \leq 8$ where, $A=$ K, Na, Li), are of great interest as photocatalysts [18]. Sodium and potassium silicon titanates are used for the preparation of industrially important catalysts that are used in the hydrogenation of pyrene and hydrodesulfurization of dibenzothiophene [19]. Different titanate systems are used in the transesterification reaction for the production of biodiesel [20]. The adsorption and photocatalytic performance of the titanate catalysts was tested using the rhodamine dye [21]. The photocatalytic degradation of methylene blue under ultraviolet radiation has been reported with titanate nanotubes [22]. CO methanation was done over nickel catalysts supported on calcium titanate [23]. Selective catalytic reduction of NOx by NH3 is carried over using iron titanate [24]. Titanate containing ruthenium nanoparticles are employed in the ammonia decomposition reaction [25]. The layered titanates are reported as photocatalysts for the decomposition of methylene blue [26]. Cobalt titanate was used for the oxidation of lignin model compound using $H_2O_2$ [27].
Photocatalytic degradation of methyl orange under ultraviolet light was done in the presence of bismuth titanate [28].

6.1.3 Sodium Titanate

Sodium titanates are compounds with a titanate structure containing sodium ion. Depending upon the Na:Ti molar ratio used in the preparation, they form structures like Na$_2$TiO$_3$, Na$_2$Ti$_3$O$_7$, Na$_2$Ti$_6$O$_7$, etc. [29]. Sodium titanate is found to have an important role as an ion exchanger in treating the pollutants thereby for the removal of environmental pollutants [30]. Bo et al. reported the mechanical bending property of Na$_2$Ti$_3$O$_7$ titanate nanowires [31]. Sodium titanates have found great role in batteries [32], as fuel-cell electrolytes [33], as catalysts and for the treatment of liquid wastes that are produced from different industries [34]. Also, it is used as functional material or as substrate for a broad range of applications [35].

Different types of sodium titanate nanostructures like nanotubes, nanowires, nanobelts, nanoribbons, etc. are reported in the literature [36]. The method of preparation is one of the important factors that can lead to the formation of different morphologies and it can also change the internal structures. Several methods such as hydrothermal method, sol-gel method, fusion method, etc. are used for the synthesis of sodium titanates [37,38]. A number of researchers reported the preparation of sodium titanate using TiO$_2$ and NaOH by different methods [39,40]. The reports on the catalytic application of sodium titanate in the transesterification reaction for the production of biodiesel are described in chapter 1 section 1.9.4.
In the present study, we have used sodium titanate in the transesterification reaction of WCO. The catalysts were characterized by different techniques and the reusability of the catalysts were also investigated to check the suitability of the sodium titanate nanotube of present investigation as an effective heterogeneous catalyst in biodiesel production.

6.2 EXPERIMENTAL

6.2.1 Material Preparation

6.2.1.1 Preparation of Titania

The TiO$_2$ support was prepared using sol-gel method. To 222.5 ml of distilled water, 1.6 ml of con.HNO$_3$ was added and stirred for 5 minutes. To this solution, 18.5 ml titanium isopropoxide was added drop by drop with
constant stirring. The resultant suspension was stirred overnight to obtain the transparent TiO$_2$ sol. 0.3 g poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (P123) was dissolved in 300 ml water and added in a dropwise manner to the stirred TiO$_2$ sol kept at 80 °C. The sol is then evaporated to dryness and the mixture is again dried in an oven at a temperature of 80 °C for overnight and is powdered. The powder is calcined at 350 °C for 2 h and the catalyst system is labeled as TiO$_2$-P123. Titania is also prepared without using the surfactant P123, following the above procedure and the system is labeled as TiO$_2$.

### 6.2.1.2 Preparation of Sodium Titanate

Sodium hydroxide is incorporated to TiO$_2$-P123 to produce a solid base catalyst by wet impregnation method according to the procedure described by Hernández-Hipólito et al. [37] with a slight modification. A definite amount (about 6 g) of sodium hydroxide is dissolved in 200 ml of water and weighed amount (1 g) of TiO$_2$-P123 powder is added to this solution. The resultant suspension is stirred at a temperature of 60 °C for overnight and is evaporated to dryness and then the product obtained is dried at 90 °C for overnight. It was then calcined at a temperature of 650 °C for 3 h. The powdered catalyst is washed with methanol so as to remove any unbound species including excess NaOH. It is then dried and activated at the calcination temperature for 1 h. The obtained sodium titanate is labeled as NT-P123. Sodium titanate is also prepared in a similar manner from TiO$_2$ synthesized without using P123 and the catalyst is labeled as NT. Methanol washing was given for the catalyst after refluxing with methanol at 65 °C for 1 h to remove the methanol soluble...
fraction so as to ensure heterogeneity in the reaction the catalyst was then filtered, dried and activated at the calcination temperature for 1 h.

![Photographs of different catalyst systems](image)

Figure 6.3. Photographs of different catalyst systems

The catalytic activity of the catalyst systems were investigated in the transesterification reaction of waste cooking oil with methanol. The detailed procedures for the transesterification reaction, biodiesel analysis, reusability studies and determination of fuel properties are mentioned in chapter 2.

### 6.3 RESULTS AND DISCUSSION

A facile synthetic methodology was proposed for the preparation of sodium titanate from titania and NaOH and its catalytic application is evaluated in the biodiesel production by the transesterification reaction of waste cooking oil with methanol. Here, a nonionic surfactant, P123 is employed for the preparation of titania via sol-gel method. The characterization studies revealed the composition of the material as well as the active sites responsible for catalysis. The catalyst showed excellent activity and reusability in biodiesel production under mild reaction conditions.
6.3.1 Characterization of Prepared Systems

Different characterization techniques are employed to determine the composition, structure as well as the morphology of the prepared catalysts.

6.3.1.1 FTIR Spectral Analysis

Figure 6.4. FTIR spectra of titania (TiO$_2$ & TiO$_2$-P123) and sodium titanate (NT & NT-P123) systems

The FTIR spectra recorded for all the systems are depicted in figure 6.4. In the case of titania systems (TiO$_2$ and TiO$_2$-P123), the broad peak observed
around 500 cm\(^{-1}\) corresponds to the Ti-O stretching vibration in anatase [41]. The peak centered around 1640 cm\(^{-1}\) corresponds to –OH bending vibrations of adsorbed water molecules [42]. In sodium titanate systems (NT and NT-P123), the absorption peak seen at 505 cm\(^{-1}\) correspond to the Ti-O stretching vibrations [43, 44]. The bands centered around 3450 cm\(^{-1}\) correspond to the stretching vibrations of the adsorbed water [45]. The peak present at 916 cm\(^{-1}\) corresponds to Ti–O bonds in TiO\(_6\) octahedra and the peak centered around 996 cm\(^{-1}\) is due to the bending vibrations of Ti–OH non-bridging bonds in the sodium titanate [46]. A characteristic peak is observed at 875 cm\(^{-1}\), corresponding to the Na–O bending vibration of the Na–O–Ti bond in sodium titanates [47]. According to the literature, sharp peaks are observed for Na-O bond vibrations around 1440 cm\(^{-1}\) [47]. The vibration of carbonate expected around 1443 cm\(^{-1}\) as a result of adsorption of CO\(_2\) [48] by sodium titanate may be merged with the Na-O bonding vibrations.

6.3.1.2 XRD Analysis

The crystalline phases present in the catalyst systems are studied by X-ray diffraction analysis. Figure 6.5 shows XRD patterns of all the synthesized samples. The diffraction patterns of titania systems (TiO\(_2\) and TiO\(_2\)-P123) shows characteristic peaks of anatase structure of titanium dioxide with broad diffraction bands at 2\(\theta\) values of about of 25.4°, 37.8°, 48.0°, 54.2 ° (JCPDS: No. 21-1272) and that of rutile at 27.4° [49,50]. In the XRD pattern of NT-P123, two phases, i.e., Na\(_2\)Ti\(_3\)O\(_7\) and Na\(_2\)Ti\(_6\)O\(_{13}\) are observed [51]. The diffraction peak observed at 2\(\theta\) value of 12° corresponds to the characteristic peak of titanate structures which is very weak in NT [52]. The peaks of anatase
TiO₂ are also present in the NT-P123 catalyst showing that titania is not completely transformed into sodium titanate. NT shows some of the peaks corresponding to Na₂Ti₆O₁₃ phase but with very low intensity. NT is mostly amorphous in nature with feeble diffraction from anatase, rutile and sodium titanate phases. Thus, from the XRD analysis, it is confirmed that the NT-P123 catalyst forms a stable crystalline sodium titanate structure.

Figure 6.5. XRD patterns of titania (TiO₂ & TiO₂-P123) and sodium titanate (NT & NT-P123) systems

The chemical reaction representing the formation of major crystalline phases of the catalyst is given in equation (1) and (2) as,
6.3.1.3 SEM Analysis

The surface morphology of all the systems was investigated with scanning electron microscope and the SEM images are shown in figure 6.6. The titania systems (TiO$_2$ & TiO$_2$-P123) showed aggregated particles. TiO$_2$-P123 is composed of small aggregates when compared with TiO$_2$. In the case of sodium titanate systems (NT & NT-P123), particles are seen as clusters or aggregates of a rod like morphology.

![SEM images of titania and sodium titanate systems](image)

Figure 6.6. SEM images of titania (TiO$_2$-P123 & TiO$_2$) and sodium titanate (NT-P123 & NT) systems
From the preliminary studies on transesterification, it was found that the catalyst, NT-P123 shows excellent activity as well as reusability. NT-P123 is thus further characterized by ICP-AES and TEM analyses inorder to clearly understand the structure that leads to high catalytic activity.

6.3.1.4 ICP-AES Elemental Analysis

The ICP-AES analysis of NT-P123 was done inorder to determine the percentage of Na and Ti present in the catalyst. The weight percentage of Na and Ti is found to be 35.96 % and 10.67 % respectively which shows the existence of catalyst with a Na: Ti mole ratio of 7:1. The excess Na present in the catalyst may be effectively dispersed over the sodium titanate nanotubes as evident from the absence of peaks corresponding to the oxides/carbonates of sodium in the XRD pattern.

6.3.1.5 TEM Analysis

The TEM photographs of TiO$_2$-P123 and NT-P123 are shown in figure 6.7. Titania nanoparticles show spherical morphology with porous texture and the size of the particles falls in the range of 3-10 nm. It also displayed a polycrystalline nature as seen from SAED patterns. The bunches of rods can be seen in sodium titanate catalyst which at high resolution looks like a porous nanorod. This porous structure may be highly effective in binding excess Na species in the catalyst so as to increase its total basicity and thus the catalytic efficiency.
Figure 6.7. TEM photographs of TiO$_2$-P123 and NT-P123 systems

The selected area electron diffraction (SAED) patterns of TiO$_2$-P123 and NT-P123 further reveals the crystalline nature of the samples and shows good agreement with the structure reported from the X-ray diffraction patterns. The TiO$_2$-P123 sample shows broad peaks which can be indexed to the (101), (004), (200) and (211) reflections, and they correspond to the well crystalline anatase phases. In the case of NT-P123, there are three planes with separations of 0.30, 0.35 and 0.21nm correspond to the interplanar distances of the (-311), (-111) and (004) respectively. Out of this the first two planes correspond to the Na$_2$Ti$_6$O$_{13}$ phase and the (004) plane corresponds to anatase titania showing the presence of titania in the sodium titanate catalyst. These values also matches with the interplanar distances in Na$_2$Ti$_3$O$_7$ corresponding to (-202) and (012) planes [49-52].
6.3.2 Catalytic Activity Studies

Initially, the transesterification of WCO was performed over four different catalyst systems (TiO$_2$-P123, NT-P123, TiO$_2$ and NT) using methanol at randomly selected reaction conditions and the results are shown in the table 6.1. Both the sodium titanate catalysts are able to reach 100% conversion within 1.5 h of reaction. The activity of TiO$_2$ and TiO$_2$-P123 is negligible under the same reaction conditions.

Table 6.1. Observed FAME content in the transesterification reaction over four different catalyst systems

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Catalyst</th>
<th>FAME Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NT-P123</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>NT</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>TiO$_2$-P123</td>
<td>10.7</td>
</tr>
<tr>
<td>4</td>
<td>TiO$_2$</td>
<td>8.7</td>
</tr>
</tbody>
</table>

Reaction conditions: waste cooking oil 5 g, reaction temperature 65 °C, catalyst weight 4 wt%, methanol to oil molar ratio 15:1 for 1.5 h reaction

The reusability of the catalyst, NT-P123 is excellent in comparison with NT catalyst and thus NT-P123 is chosen for further studies. The effect of different reaction parameters on the transesterification reaction over NT-P123 is studied and the best reaction condition at which maximum FAME content is obtained is determined.

6.3.2.1 Effect of Methanol to Oil Molar Ratio

Methanol to oil molar ratio is one of the most important parameters that affects the yield of methyl esters [52]. Since the transesterification of
triglyceride is a reversible reaction, excess of methanol shifts the equilibrium towards the direction of mono ester formation [53]. Literature studies revealed that in order to shift the equilibrium towards forward direction, use of high molar ratios of alcohol to oil even such as 45:1 and 60:1, etc. is required [54,55]. In order to understand the influence of methanol to oil molar ratio on the FAME content, the transesterification reaction is carried out at varying methanol to oil molar ratio (3:1 - 18:1) over 4 wt% catalyst amount, reaction temperature 65 °C and reaction time 1.5 h. The increase in alcohol to oil molar ratios from 3:1 to 18:1 resulted in a significant effect on the ester yield. The yield of methyl esters increased from 75.34 % to 100 % from methanol to oil molar ratio of 15:1 onwards. The excess methanol used in the reaction can be collected by distillation and can be reused. Fuel grade biodiesel is obtained at a methanol to oil molar ratio of 6:1 onwards.

![Figure 6.8. FAME content versus methanol to oil molar ratio](image)

Figure 6.8. FAME content versus methanol to oil molar ratio
6.3.2.2 Effect of Catalyst Loading

Catalyst amount plays an important role in the transesterification reaction [56]. To determine the effect of catalyst weight on the reaction rate, different amounts of catalysts (1-6 wt% with respect to the weight of oil) were used in the transesterification at a methanol to waste cooking oil molar ratio of 15:1 at 65 °C for 1.5 h reaction. Increase in catalyst loading from 1 to 2 wt% showed a hike in the initial activity; producing fuel grade biodiesel with a FAME content of >96.5 %. From 4 wt% onwards, 100 % FAME content was achieved. Thus, 4 wt% of catalyst was selected for further studies.

![Figure 6.9. FAME content versus amount of catalyst](image)

6.3.2.3 Effect of Reaction Time

The suited lowest reaction time for the production of fuel grade biodiesel was determined by performing reaction at varying reaction time in the range of 0.25 h – 2 h with an interval of 0.25 h under the reaction conditions of methanol to oil molar ratio 15:1, temperature 65 °C and catalyst weight 4 wt%. The experimental results, reported in Figure 6.10 indicated that the conversion
increased steadily with the reaction time and reached 100 % FAME content at 1.5 h which thereafter remained constant.

Figure 6.10. FAME content versus reaction time

6.3.2.4 Effect of Reaction Temperature

In order to know the effect of reaction temperature on the FAME yield, the waste oil transesterification reaction was conducted at different temperatures starting from room temperature (RT) (35 °C) to 65 °C under the selected reaction conditions of methanol to oil molar ratio of 15:1, reaction time of 1.5 h and 4 wt % catalyst amount (Figure 6.11). The low rate of reaction in the range RT–50 °C could possibly be due to the high viscosity of the oil at lower temperatures, resulting in poor mixing between oil–methanol–catalyst phases [57]. When the transesterification reaction was performed at 55 °C, fuel grade biodiesel was obtained having a FAME content of 98.01 %. 100 % conversion of oil was obtained at a higher temperature of 65 °C. Thus from the above studies, the most suited conditions of biodiesel production over NT-P123 was
found to be catalyst amount 4 wt%, reaction temperature 65 °C, methanol to oil molar ratio 15:1 and reaction time 1.5 h.

Figure 6.11. FAME content versus reaction temperature

6.3.2.5 Catalyst Reusability

The catalyst reusability is an important issue for the heterogeneous catalysed production processes [58]. To study the recyclability of the catalyst, the solid catalyst was recovered by filtration and washed thoroughly with methanol for removal of surface adsorbed compounds, followed by activation at 650 °C for 1 h. The recovered catalyst was then subjected to further transesterification reactions. The reusability test is carried out at the selected reaction conditions of 4 wt% catalyst weight, 15:1 methanol to oil molar ratio, 65 °C temperature and 1.5 h reaction time. NT gave fuel grade biodiesel only upto two cycles. In the third cycle, the FAME content is reduced to 80.12 %. Over NT-P123, no loss in activity was detected even after five recycles demonstrating the efficiency of the catalyst. The catalytic activity of NT-P123 was reduced to 97.12 % in the 6th cycle (Figure 6.12). The formation of stable
sodium titanate structure without any leaching of the active species may be the reason for the excellent catalytic activity and the high reusability of the NT-P123 catalyst.

![Figure 6.12. Reusability results of the catalyst under the reaction conditions of 15:1 methanol to oil molar ratio, 4 wt% catalyst, 65 °C reaction temperature and 1.5 h reaction time.](image)

Figure 6.12. Reusability results of the catalyst under the reaction conditions of 15:1 methanol to oil molar ratio, 4 wt% catalyst, 65 °C reaction temperature and 1.5 h reaction time.

The structure of the catalyst after the 8th cycle of reaction is analysed by FTIR spectroscopy (Figure 6.13) and it is found that the catalyst structure is slightly affected eventhough the basic functional groups present in the catalyst remained the same. The intensity of peak of Na-O/carbonate vibration observed around 1443 cm\(^{-1}\) is reduced which may be due to the reduced basicity associated with leaching of basic sites after repeated cycles leading to decreased activity from 7th cycle onwards. The peak intensities varied to a notable extent indicating some deformation to the structure.
For biodiesel to be used in diesel engines, the fuel must meet various specifications stated in biodiesel standard, mainly United States biodiesel standard ASTM D6751 and European biodiesel standard EN 14214 [59,60]. Some of the fuel properties of prepared biodiesel from waste cooking oil using NT-P123 catalyst under the selected reaction conditions were summarized in table 6.2 along with a comparison to the recommended biodiesel international standards specifications of EN 14121 and ASTM D6751. The results revealed comparable fuel properties of biodiesel with the standard values which affirm the suitability of present waste cooking oil as a biodiesel feedstock where the reaction is performed in the presence of sodium titanate as a transesterification catalyst.
Table 6.2. Fuel properties of biodiesel obtained under selected reaction conditions*

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Test Methods</th>
<th>Unit</th>
<th>Limits (EN 14214)</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester content</td>
<td>EN 14103</td>
<td>wt.%</td>
<td>96.5 min</td>
<td>100</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>EN 14105</td>
<td>wt.%</td>
<td>0.02 max</td>
<td>0.00</td>
</tr>
<tr>
<td>Monoglyceride</td>
<td>EN 14105</td>
<td>wt.%</td>
<td>0.8</td>
<td>0.0</td>
</tr>
<tr>
<td>Triglyceride</td>
<td>EN 14105</td>
<td>wt.%</td>
<td>0.20</td>
<td>0.00</td>
</tr>
<tr>
<td>Total glycerol</td>
<td>EN 14105</td>
<td>wt.%</td>
<td>0.25 max</td>
<td>0.00</td>
</tr>
<tr>
<td>Acid value</td>
<td>EN 14104</td>
<td>mg KOH/g</td>
<td>0.50 max</td>
<td>0.20</td>
</tr>
<tr>
<td>Water content</td>
<td>EN ISO 12937</td>
<td>mg/kg</td>
<td>500 max</td>
<td>0</td>
</tr>
<tr>
<td>Viscosity</td>
<td>D445</td>
<td>mm²/s</td>
<td>1.96-6.0</td>
<td>3.51</td>
</tr>
<tr>
<td>Density</td>
<td>EN ISO 3675</td>
<td>g/ m³</td>
<td>860-900</td>
<td>872</td>
</tr>
</tbody>
</table>

*Reaction conditions: 15:1 methanol: oil molar ratio, 4 wt% catalyst, 65 °C reaction temperature and 1.5 h reaction time.

6.4 CONCLUSIONS

Sodium titanate solid base catalyst is prepared by impregnating sodium hydroxide to porous titania. The phase transition from anatase to sodium titanate is evident from various characterisation results. Morphological changes are also observed and sodium titanate displays porous nanorod like structure. The prepared catalysts are used in transesterification of waste cooking oil with methanol to produce biodiesel. The reason for the excellent performance of sodium titanate nanotube may be due to its porous nature. Also, since the preparation is started from TiO₂ with porous morphology, it could incorporate more amount of NaOH for the formation of excess sodium incorporated sodium titanate phase. The maximum FAME content of 100 % is obtained at
Porous Sodium Titanate Nanotube Catalyst for Biodiesel Production

methanol to oil molar ratio of 15:1, catalyst amount of 4 wt%, reaction temperature of 65 °C in 1.5 h. The catalyst maintained sustained activity till five cycles of repeated use and the biodiesel produced exhibited excellent fuel properties.

REFERENCES
SODIUM SILICATE HETEROGENEOUS CATALYST FOR BIODIESEL PRODUCTION FROM WASTE COOKING OIL

Sodium silicate was prepared by a simple method of impregnation and was used in the transesterification reaction of waste cooking oil in which the parameter optimization was done by applying response surface methodology.

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7.1 INTRODUCTION

Alkali and alkaline earth metal incorporated silica based heterogeneous catalysts are well studied in biodiesel production [1,2]. Sodium silicates are inorganic compounds that are formed from $\text{Na}_2\text{O}$ and $\text{SiO}_2$ [3]. Different crystalline forms such as $\text{Na}_2\text{Si}_2\text{O}_5$, $\text{Na}_2\text{SiO}_3$, $\text{Na}_4\text{SiO}_4$, etc. are the reported sodium silicates [4]. Sodium silicate is also used as a starting material for the preparation of zeolites such as $\gamma$-zeolite [5], NaY zeolite [6] and NaX zeolite [7]. Due to the presence of $\text{Na}_2\text{O}$, it is found to be highly basic and hence is widely investigated in the transesterification reaction [8]. It is also used for the conversion of glycerol to lactic acid [9]. The complete mechanisms for the transesterification reaction catalysed by sodium silicate were not well studied and not still clear. Guo et al. in their study reported a possible mechanism for the soybean oil transesterification with methanol [10] which is similar to the homogeneous base catalysed mechanism of transesterification reaction [11]. Chapter 1 gives a brief review on sodium silicate catalysed biodiesel production in the section 1.9.2.2.

In most of the reports on sodium silicate catalysed biodiesel productions commercial sodium silicate catalysts are employed [12-16]. Efforts have been made continuously on the preparation of sodium silicate catalysts which can show better catalytic activity in biodiesel production. $\text{Na}_2\text{Si}_2\text{O}_5$ is prepared from $\text{NaOH}$ and tetraethylorthosilicate by the sol gel method showing excellent catalytic efficiency in biodiesel production [17]. But, the catalyst precursor is expensive and preparation involves the use of ethanol as a solvent. The sodium silicate prepared from less expensive precursors by simple
methods is of great importance in the transesterification process. In the present work, simple method of impregnation was employed for the preparation of sodium silicate from silicon dioxide and NaOH. Optimization of reaction parameters is one of the crucial factors in the biodiesel production process since it provides the best condition at which the maximum conversion is obtained [18-22]. Traditional optimisation approach is involved in many of these sodium silicate catalysed transesterification processes [12-17]. Two studies deals about the statistical optimisation of reaction parameters on sodium silicate catalysed biodiesel production process [23,24]. Table 7.1 shows activity of sodium silicate catalysts that are reported in biodiesel production from different feedstocks.

Table 7.1. Activity of sodium silicate catalysts in the transesterification reaction

<table>
<thead>
<tr>
<th>Reaction conditions [Methanol: oil molar ratio, catalyst weight, temperature and time of reaction]</th>
<th>Oil source</th>
<th>FAME yield/Content (%)</th>
<th>Reusability data</th>
</tr>
</thead>
<tbody>
<tr>
<td>15:1, 6 wt%, 65 °C, 45 min</td>
<td>Jatropha curcas oil</td>
<td>99</td>
<td>91.11 %, 5 cycles</td>
</tr>
<tr>
<td>9:1, 3 wt%, 60 °C, 1 h</td>
<td>Rapeseed oil</td>
<td>99.6</td>
<td>92 %, 6 cycles</td>
</tr>
<tr>
<td>7.5:1, 3 wt%, 60 °C, 1 h</td>
<td>soybean oil</td>
<td>100</td>
<td>94 %, 5 cycles</td>
</tr>
<tr>
<td>6:1, 5 %, 65 °C, 100 min</td>
<td>Cottonseed oil</td>
<td>97.6</td>
<td>Not mentioned</td>
</tr>
<tr>
<td>400 W microwave power, 11:1, 4 wt%, 5 min</td>
<td>Rapeseed oil</td>
<td>95.8</td>
<td>72.0 %</td>
</tr>
<tr>
<td>6:1, 2.5 %, 64 °C, 240 min</td>
<td>Jatropha curcas oil</td>
<td>92.8</td>
<td>5 cycles</td>
</tr>
<tr>
<td></td>
<td>Waste cooking oil</td>
<td>57.92</td>
<td>Not mentioned</td>
</tr>
</tbody>
</table>
Present study aims the statistical optimisation of sodium silicate catalysed biodiesel production by response surface methodology (RSM). We have obtained fuel grade biodiesel with high FAME content of 99.97% under the optimized reaction conditions. Also, the sodium silicate catalyst is reusable till three cycles yielding biodiesel with fuel quality. The fuel properties of the biodiesel lies in the range of standard values as given by ASTM and EN international standard specifications.

**7.2 EXPERIMENTAL SECTION**

**7.2.1 Catalyst Preparation**

![](image)

Figure 7.1. Scheme for the preparation of catalyst

NaOH solution (4 g in 200 ml water) and SiO₂ (6 g) mixture was stirred with heating at 90 °C and then evaporated to dryness. The dried product was kept overnight in an air oven at 90 °C. It was then calcined at 550 °C for 5 h to
get sodium silicate. Methanol washing was given for the catalyst after refluxing with methanol at 65 °C for 1 h to remove the methanol soluble fraction so as to ensure heterogeneity in the reaction the catalyst was then filtered, dried and activated at the calcination temperature for 1 h.

Different catalysts were prepared by varying the Na:Si molar ratio as 20:80, 30:70 40:60 and 50:50 and the catalysts are designated as 20:80NS, 30:70NS, 40:60NS and 50:50NS.

![Figure 7.2. Photographs of different catalyst systems prepared](image)

7.3 RESULTS AND DISCUSSION

In the present work, we have prepared sodium silicate and its catalytic activity is studied in the transesterification reaction for the production of biodiesel. The catalyst is characterized by different techniques inorder to find out the active phase responsible for its catalytic activity. The preparation of sodium silicate from silica and NaOH is done by impregnation method. The
effect of different reaction parameters such as the amount of catalyst, methanol to oil molar ratio, reaction period and reaction temperature that affects the fatty acid methyl ester (FAME) content of the biodiesel was investigated by response surface methodology (RSM).

7.3.1 Characterization of Catalysts

Different characterisation techniques are adopted to characterize the catalysts and so as to determine the composition, morphology as well as the active phase responsible for catalysis.

7.3.1.1 FTIR Spectral Analysis

The nature of the catalysts was evaluated by FTIR spectral analysis by investigating the characteristic vibration bands. Figure 7.3 shows the FTIR spectra of SiO2 as well as all the prepared catalyst systems. In the spectrum of SiO2, band present at around 1100 cm\(^{-1}\) is due to the asymmetric stretching vibration of the Si-O bond of the SiO\(_4^{2-}\) tetrahedra and the bands in the range of 900-500 cm\(^{-1}\) are due to the symmetric stretching vibrations of the Si-O-Si bond [25]. The band present around 469 cm\(^{-1}\) is due to the Si-O bending vibration of the SiO\(_4^{2-}\) tetrahedron [26]. In the sodium silicates, the band present at 612 cm\(^{-1}\) corresponds to the Na–O bond vibration suggesting the formation of sodium silicate [24]. The spectra showed an absorption band at 1020 cm\(^{-1}\), which could be attributed to the Si–O–Na stretching. The bands present at 1652 cm\(^{-1}\) and 3450 cm\(^{-1}\) are due to the bending and stretching vibrations of adsorbed water molecules in sodium silicate [27]. The band around 1413 cm\(^{-1}\) indicates the presence of carbonates formed by the
adsorption of atmospheric CO₂ on the basic sites and is found to have maximum intensity in 50:50NS.

Figure 7.3. FTIR spectra of SiO₂ and different catalyst systems

7.3.1.2 XRD Analysis

Figure 7.4 shows the XRD patterns of silica as well as sodium silicate catalyst systems. The catalysts 20:80NS and 30:70NS consists of mainly the peaks of silica (marked as *). When we increase the amount of NaOH, some of
the peaks of silica disappear and there is an additional formation of sodium silicate crystalline phase as observed from the XRD pattern of the 40:60NS catalyst onwards.

Figure 7.4. XRD patterns of SiO$_2$ and different catalyst systems

The XRD pattern of the 50:50NS catalyst shows the peaks of silica as well as sodium silicate. The peaks present around at 20 values of 16.9°, 25.1°, 29.6°,
34.9°, 37.4°, 48.2°, 52.3° and 65.9° correspond to the Na$_2$SiO$_3$ phase of the sodium silicate [16,17,23]. Thus, the XRD analysis indicated the active sodium silicate phase of the catalyst as Na$_2$SiO$_3$. Excess SiO$_2$ present in the sample may be acting as a support material to bind Na$_2$SiO$_3$.

The chemical equation representing the formation of major crystalline phase of the catalyst is given in equation (1) as,

\[ 4\text{NaOH} + 2\text{SiO}_2 \rightarrow 2\text{Na}_2\text{SiO}_3 + 2\text{H}_2\text{O} \quad (1) \]

**7.3.2 Initial studies on Transesterification Reaction**

At first, the transesterification was carried out in a randomly selected condition using all the catalyst systems inorder to determine the best ratio of Na:Si (Table 7.2). The reaction conditions chosen for the study are, catalyst amount 6 wt%, methanol to oil molar ratio 15:1, temperature 65 °C and reaction time 75 min. The fatty acid methyl ester (FAME) content increases with increase in the amount of NaOH and attains the fuel grade value of 99.97% over 50:50 NS, where the Na:Si molar ratio is 50:50.

<table>
<thead>
<tr>
<th>Sl. no</th>
<th>Na/Si molar ratio</th>
<th>FAME content [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0:100</td>
<td>7.83</td>
</tr>
<tr>
<td>2</td>
<td>20:80</td>
<td>20.04</td>
</tr>
<tr>
<td>3</td>
<td>30:70</td>
<td>30.10</td>
</tr>
<tr>
<td>4</td>
<td>40:60</td>
<td>64.35</td>
</tr>
<tr>
<td>5</td>
<td>50:50</td>
<td>99.97</td>
</tr>
<tr>
<td>6</td>
<td>60:40</td>
<td>100</td>
</tr>
</tbody>
</table>
50:50NS catalyst is further characterized in detail by ICP-AES, TPD of CO$_2$ analysis, SEM and TEM analyses inorder to determine the elemental composition, basicity as well as its morphology which are the important things that affects the activity of a catalyst. The ICP-AES analysis revealed the percentage of sodium and silicon present in the catalyst. From the results, the Na:Si molar ratio of the catalyst is confirmed as 1:1.

7.3.2.1 TPD of CO$_2$ Analysis

The basicity of the catalyst is determined from the TPD of CO$_2$ and the profiles are given in figure 7.5. From the results, it is clear that the catalyst is highly basic showing a total basicity of 0.4634 mmolg$^{-1}$ compared to SiO$_2$ which is having a very low basicity of 0.0036 mmolg$^{-1}$.

![Figure 7.5. TPD of CO$_2$ profiles of SiO$_2$ and 50:50NS catalysts](image)
7.3.2.2 SEM Analysis

Surface morphology, which is one of the important factors affecting the catalytic activity is analysed by SEM.

![SEM photographs of SiO2 (a & c) and 50:50NS (b & d) systems](image)

The SEM images of SiO2 and 50:50NS catalyst are shown in Figure 7.6(a & c) and Figure 7.6(b & d) respectively. Porous morphology is observed in the case of 50:50NS catalyst whereas agglomerated morphology is found in SiO2. Similar type of SEM images is reported for sodium silicate catalyst by Long et al. which is highly active in the transesterification of rapeseed and Jatropha oils [17].
7.3.2.3 TEM Analysis

Catalyst having macroporous morphology showed excellent activity in the transesterification reaction [28].

Figure 7.7. TEM images of SiO$_2$ (a & c) and 50:50NS (b & d) systems

Several researchers reported the use of macroporous catalysts for biodiesel production [29,30]. Here the catalyst, 50:50NS exhibits a macroporous morphology which was evident from the TEM images shown in figure 7.7. The higher basicity and the macroporous nature may be the reasons for the
excellent catalytic activity of the present catalyst in the transesterification reaction.

7.3.3 Catalytic Activity Studies

The catalyst systems are used for the transesterification reaction of WCO with methanol to produce biodiesel. The catalyst was activated at the calcination temperature for 1 h before its use in the reaction.

7.3.3.1 Effect of Calcination Temperature and Calcination Time of the Catalyst

The calcination temperature of the 50:50NS catalyst was varied from 250 to 650 °C at an interval of 100 °C. The transesterification is carried over these catalysts under the selected reaction conditions of catalyst amount 6 wt%, methanol to oil molar ratio 15:1, reaction temperature 65 °C, catalyst calcination time of 5 h and reaction time 75 min. It was found that as the calcination temperature increased, the catalytic activity of the catalyst also got increased (Table 7.3). The biodiesel obtained for the catalyst calcined at a temperature of 550 °C meets the fuel grade specifications. So, it was selected as the best lowest calcination temperature. The calcination time was varied in between 1 h to 6 h at 550 °C and the transesterification reaction was performed over these catalysts under the reaction conditions of catalyst amount 6 wt%, methanol to oil molar ratio 15:1, temperature 65 °C and reaction time 75 min. It was observed that as the time of calcination increased, the activity of the catalyst also got increased (Table 7.3). The biodiesel met the fuel grade
specifications from 4 h onwards. But, the maximum conversion was obtained at a calcination time of 5 h and thus it was chosen for further studies.

Table 7.3. Impact of calcination temperature and calcination time on the FAME content

<table>
<thead>
<tr>
<th>Calcination temperature (°C)</th>
<th>FAME content [%]</th>
<th>Calcination time (h)</th>
<th>FAME content [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>30.00</td>
<td>1</td>
<td>65.34</td>
</tr>
<tr>
<td>350</td>
<td>43.81</td>
<td>2</td>
<td>74.47</td>
</tr>
<tr>
<td>450</td>
<td>83.74</td>
<td>3</td>
<td>90.23</td>
</tr>
<tr>
<td>550</td>
<td>99.97</td>
<td>4</td>
<td>99.97</td>
</tr>
<tr>
<td>650</td>
<td>100</td>
<td>5</td>
<td>100</td>
</tr>
</tbody>
</table>

7.3.4 RSM Studies on Biodiesel Production

Here, we have used the statistical technique of response surface methodology for the optimisation of reaction variables in biodiesel production. Among the different designs in RSM, Box–Behnken design was employed for the present study to investigate the operating conditions of transesterification reaction to obtain a high conversion to biodiesel. The studied factors that have pronounced influence in the transesterification reaction are methanol to oil molar ratio, reaction time, reaction temperature and catalyst amount. The other variables such as stirring speed and pressure were kept constant for the studies as 400 rpm and atmospheric pressure respectively. The relationship between response (FAME content) and four reaction variables were evaluated using RSM. The designing of experiments and their evaluation were performed using the software, Minitab version 14 (Minitab USA). The catalyst with Na:Si
molar ratio of 50:50 calcined at a temperature of 550 °C for 5 h is selected for RSM studies for the optimisation of different reaction parameters such as catalyst amount, methanol to oil molar ratio, temperature and reaction time.

7.3.4.1 Experimental Design

The reaction variables and selected level of each factor is represented in figure 7.8.

![Diagram showing reaction parameters](image)

Figure 7.8. The range of reaction parameters in the Box–Behnken design

Preliminary studies were conducted to observe the effect of catalyst dosage on the production of biodiesel from WCO. Based on the values of FAME content obtained for each catalyst weight, the range of catalyst dosage (3–5 wt%) was selected. Similar studies were also conducted to observe the effect of reaction time, temperature and methanol to oil molar ratio on the transesterification process. The range selected for the reaction are time 45 min –75 min, temperature 45 °C-65 °C and methanol to oil molar ratio 6:1–12:1.

The software analysed the range of parameters and generated a set of 27 experimental trials (Table 7.4). The experiments are carried out in the

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laboratory in duplicates and the results are tabulated as experimental FAME. The software analysed the data based on a second order polynomial equation (equation 1) and predicted the values of FAME content for each trial which is given as the predicted FAME (Table 7.4).

\[
Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j, \quad i \neq j \quad \rightarrow (1)
\]

In the equation (1), Y represents the response variable; \( \beta_0 \) is the interception coefficient; \( \beta_i \) is the coefficient of the linear effect; \( \beta_{ii} \) is the coefficient of quadratic effect; \( \beta_{ij} \) is the coefficient of interaction effect when \( i < j \); and \( k \) is the numbers of involved variables.

Table 7.4. Experimental conditions, observed FAME content and predicted FAME content according to Box–Behnken design

<table>
<thead>
<tr>
<th>Run order</th>
<th>Temperature (˚C)</th>
<th>Molar ratio</th>
<th>Catalyst weight (wt %)</th>
<th>Time (min)</th>
<th>Experimental FAME content (%)</th>
<th>Predicted FAME content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>55</td>
<td>12</td>
<td>5</td>
<td>60</td>
<td>87.50</td>
<td>89.64</td>
</tr>
<tr>
<td>2</td>
<td>55</td>
<td>9</td>
<td>5</td>
<td>75</td>
<td>85.32</td>
<td>86.15</td>
</tr>
<tr>
<td>3</td>
<td>55</td>
<td>6</td>
<td>3</td>
<td>60</td>
<td>66.80</td>
<td>56.82</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>9</td>
<td>4</td>
<td>45</td>
<td>26.86</td>
<td>27.23</td>
</tr>
<tr>
<td>5</td>
<td>65</td>
<td>9</td>
<td>4</td>
<td>45</td>
<td>38.56</td>
<td>37.34</td>
</tr>
<tr>
<td>6</td>
<td>55</td>
<td>9</td>
<td>3</td>
<td>75</td>
<td>70.28</td>
<td>76.87</td>
</tr>
<tr>
<td>7</td>
<td>45</td>
<td>12</td>
<td>4</td>
<td>60</td>
<td>34.36</td>
<td>35.56</td>
</tr>
<tr>
<td>8</td>
<td>65</td>
<td>9</td>
<td>5</td>
<td>60</td>
<td>57.47</td>
<td>63.80</td>
</tr>
<tr>
<td>9</td>
<td>55</td>
<td>9</td>
<td>3</td>
<td>45</td>
<td>43.64</td>
<td>46.32</td>
</tr>
<tr>
<td>10</td>
<td>65</td>
<td>9</td>
<td>4</td>
<td>75</td>
<td>79.68</td>
<td>71.47</td>
</tr>
<tr>
<td>11</td>
<td>55</td>
<td>12</td>
<td>4</td>
<td>45</td>
<td>64.15</td>
<td>63.56</td>
</tr>
</tbody>
</table>
**7.3.4.2 Statistical Analysis**

In the present study, the response variable, the FAME content was established by the following equation,

\[
\text{FAME} = -956 + 32.35 \text{ Temperature} - 4.6 \text{ Molar ratio} + 35.4 \text{ catalyst wt} + 0.49 \text{ Time} - 0.3279 \text{ Temperature}^2 - 0.592 \text{ Molar ratio}^2 - 6.29 \text{ catalyst wt}^2 - 0.0133 \text{ Time}^2 + 0.095 \text{ Temperature} \times \text{ Molar ratio} + 0.415 \text{ Temperature} \times \text{ catalyst wt} + 0.0380 \text{ Temperature} \times \text{ Time} + 1.81 \text{ Molar ratio} \times \text{ catalyst wt} + 0.0901 \text{ Molar ratio} \times \text{ Time} - 0.261 \text{ catalyst wt} \times \text{ Time}
\]
The results show that there is a good agreement between the model and the experimental data [31]. The plot representing experimental FAME content versus predicted FAME content is shown in figure 7.9. The coefficient of determination ($R^2$) reflects the variability of the dependent variable which is explained by its relationship with the independent variables. In general, a high $R^2$ value indicates that the model accounts for higher variability of the data and thus, the data points will lie closer to the regression line which confirms the closeness of the two values with a minimum standard deviation. In other words, a high $R^2$ value indicates that there is good fit between the model and experimental data [32]. The $R^2$ and adjusted $R^2$ are determined as 0.9586 and 0.9103 respectively having values close to unity with a slight difference between the values. This observation also confirms the significance of the model. The $R^2$ value for the predicted FAME content which is a measure of how good the model predicts values for the response is 0.7614 which is greater than 0.75 proposing the significance of the model [33].

![Observed versus predicted FAME content](image)

**Figure 7.9.** Observed versus predicted FAME content
7.3.4.2.1 Analysis of Variance

Analysis of variance (ANOVA) is carried out to determine the significance and fitness of the model as well as to know the effects of significant individual terms and their interaction on the selected responses. The ANOVA results are tabulated in Table 7.5. The regression model has an F-value of 19.84 and a p-value less than 0.05, which indicates that the model is significant. Here, the p-value represents the probability of error, and it is used to check the significance of each regression coefficient. The p-value of each coefficient should be less than 0.05 for the model to be significant [34]. In the present study, the lower p-values (< 0.05) and higher F-value of all the independent variables shows the significance and suitability of the model for the present optimisation studies using the sodium silicate catalyst. The lack of fit is also determined for the quadratic regression model. The p-value of the lack of fit parameter is greater than 0.05 which indicates a good fit between the quadratic regression model and experimental data and thus the model can sufficiently describe the relationship between the dependent variable (i.e. the FAME content) and the independent variables [35].

Table 7.5. Analysis of variance

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>14</td>
<td>11256.8</td>
<td>804.06</td>
<td>19.84</td>
<td>0.000</td>
</tr>
<tr>
<td>Linear</td>
<td>4</td>
<td>4557.3</td>
<td>1139.32</td>
<td>28.11</td>
<td>0.000</td>
</tr>
<tr>
<td>Temperature (X₈)</td>
<td>1</td>
<td>1388.7</td>
<td>1388.69</td>
<td>34.26</td>
<td>0.000</td>
</tr>
<tr>
<td>Molar ratio (X₉)</td>
<td>1</td>
<td>741.7</td>
<td>741.67</td>
<td>18.30</td>
<td>0.001</td>
</tr>
<tr>
<td>Catalyst wt (X₆)</td>
<td>1</td>
<td>877.4</td>
<td>877.40</td>
<td>21.65</td>
<td>0.001</td>
</tr>
</tbody>
</table>
### Chapter 7

#### 7.3.4.2.2 Pareto Chart

Figure 7.10 represents a Pareto chart, which graphically shows the significance of each coefficient in the polynomial equation. The coefficient with greater t-value contributes more to the significance of the model [32]. As demonstrated in the figure, square term for reaction temperature ($X_1$) is the most significant term that contributes to biodiesel yield with t-value = 11.9, followed by the linear term of reaction time ($X_4$) having a t-value = 6.18. The other parameters also strongly influence the FAME content because they have also have higher t-values. So, all the reaction parameters have significant effect.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time ($X_4$)</td>
<td>1</td>
<td>1549.5</td>
<td>1549.50</td>
<td>38.23</td>
<td>0.000</td>
</tr>
<tr>
<td>Square</td>
<td>4</td>
<td>6223.1</td>
<td>1555.77</td>
<td>38.39</td>
<td>0.000</td>
</tr>
<tr>
<td>Temperature*Temperature</td>
<td>1</td>
<td>5735.5</td>
<td>5735.48</td>
<td>141.51</td>
<td>0.000</td>
</tr>
<tr>
<td>Molar ratio*Molar ratio</td>
<td>1</td>
<td>151.3</td>
<td>151.35</td>
<td>3.73</td>
<td>0.077</td>
</tr>
<tr>
<td>catalyst wt*catalyst wt</td>
<td>1</td>
<td>211.2</td>
<td>211.23</td>
<td>5.21</td>
<td>0.041</td>
</tr>
<tr>
<td>Time*Time</td>
<td>1</td>
<td>47.4</td>
<td>47.43</td>
<td>1.17</td>
<td>0.301</td>
</tr>
<tr>
<td>2-Way Interaction</td>
<td>6</td>
<td>476.4</td>
<td>79.40</td>
<td>1.96</td>
<td>0.151</td>
</tr>
<tr>
<td>Temperature*Molar ratio</td>
<td>1</td>
<td>32.5</td>
<td>32.55</td>
<td>0.80</td>
<td>0.388</td>
</tr>
<tr>
<td>Temperature*catalyst wt</td>
<td>1</td>
<td>69.0</td>
<td>68.97</td>
<td>1.70</td>
<td>0.217</td>
</tr>
<tr>
<td>Temperature*Time</td>
<td>1</td>
<td>130.1</td>
<td>130.07</td>
<td>3.21</td>
<td>0.098</td>
</tr>
<tr>
<td>Molar ratio*catalyst wt</td>
<td>1</td>
<td>117.8</td>
<td>117.83</td>
<td>2.91</td>
<td>0.114</td>
</tr>
<tr>
<td>Molar ratio*Time</td>
<td>1</td>
<td>65.8</td>
<td>65.77</td>
<td>1.62</td>
<td>0.227</td>
</tr>
<tr>
<td>catalyst wt*Time</td>
<td>1</td>
<td>61.2</td>
<td>61.23</td>
<td>1.51</td>
<td>0.243</td>
</tr>
<tr>
<td>Error</td>
<td>12</td>
<td>486.4</td>
<td>40.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack-of-Fit</td>
<td>10</td>
<td>486.4</td>
<td>48.64</td>
<td>0.08</td>
<td>0.02</td>
</tr>
<tr>
<td>Pure Error</td>
<td>2</td>
<td>0.0</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>26</td>
<td>11743.1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
on the response variable and hence are regarded as the significant variables of biodiesel yield.

![Figure 7.10. Pareto chart](image)

### 7.3.4.2.3 Response surface and contour plots

The model is plotted as a three-dimensional surface representing the response (FAME content) as a function of two factors within the experimental range considered in the center level of the other factor. The response surfaces and contour plots showing the interaction between reaction parameters with the response variable are shown in figure 7.11 and figure 7.12 respectively.
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Figure 7.11. Surface plots on FAME yield

It is observed that the FAME content is higher when methanol to oil molar ratio is in its highest level. The reaction temperature also exerted significant influence on the reaction in giving higher FAME content. The FAME content is higher in the case of experiments carried out at a reaction temperature of 65 °C. Similarly, an increase in the amount of catalyst enhances the FAME contents in a linear fashion. The reaction time also has a positive effect on the transesterification reaction in giving higher FAME content. From the figures, the optimal conditions estimated by the model equation for the transesterification reaction of waste cooking oil over sodium silicate are as follows: catalyst weight 5 wt%, reaction temperature 65 °C, methanol to oil
molar ratio 12:1 and reaction time 60 min at which a FAME content of 99.97% is obtained. The theoretical FAME content predicted under the above conditions was 98.45%.

Figure 7.12. Contour plots

7.3.5 Validation of the model

The validity of the model is determined by random selection of four different experimental trials and by determining the statistical correlation between the experimental and predicted FAME content (Table 7.6). The correlation coefficient is found to be 0.97, which is very close to unity suggesting the significance of the model for the optimisation studies [36].
Table 7.6. Validation experiments

<table>
<thead>
<tr>
<th>Temp [°C]</th>
<th>Time [min]</th>
<th>Methanol/oil molar ratio</th>
<th>Catalyst weight [wt%]</th>
<th>Expected FAME [%]</th>
<th>Observed FAME [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>60</td>
<td>12:1</td>
<td>4</td>
<td>98.81</td>
<td>98.5</td>
</tr>
<tr>
<td>45</td>
<td>75</td>
<td>9:1</td>
<td>5</td>
<td>87.11</td>
<td>89.46</td>
</tr>
<tr>
<td>50</td>
<td>60</td>
<td>6:1</td>
<td>4</td>
<td>96.90</td>
<td>95.8</td>
</tr>
<tr>
<td>60</td>
<td>45</td>
<td>9:1</td>
<td>3</td>
<td>50.67</td>
<td>42.78</td>
</tr>
</tbody>
</table>

7.3.6 Fuel Properties of Biodiesel

Some of the important fuel properties of prepared biodiesel are determined by the standard methods and the results obtained are given in the table 7.7.

Table 7.7. Fuel properties of biodiesel

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Test Method</th>
<th>Unit</th>
<th>Limit (EN 14214)</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester content</td>
<td>EN 14103</td>
<td>% m/m</td>
<td>96.5 min</td>
<td>99.97</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>EN 14105</td>
<td>% m/m</td>
<td>0.02 max</td>
<td>0.00</td>
</tr>
<tr>
<td>Diglyceride</td>
<td>EN 14105</td>
<td>% m/m</td>
<td>0.2 max</td>
<td>0.0</td>
</tr>
<tr>
<td>Monoglyceride</td>
<td>EN 14105</td>
<td>% m/m</td>
<td>0.8 max</td>
<td>0.0</td>
</tr>
<tr>
<td>Triglyceride</td>
<td>EN 14105</td>
<td>% m/m</td>
<td>0.2 max</td>
<td>0.03</td>
</tr>
<tr>
<td>Total glycerol</td>
<td>EN 14105</td>
<td>% m/m</td>
<td>0.25 max</td>
<td>0.00</td>
</tr>
<tr>
<td>Acid value</td>
<td>EN 14104</td>
<td>mgKOH/g</td>
<td>0.50 max</td>
<td>0.23</td>
</tr>
<tr>
<td>Water content</td>
<td>EN ISO 12937</td>
<td>mg/kg</td>
<td>500 max</td>
<td>0</td>
</tr>
<tr>
<td>Density</td>
<td>EN ISO 3675</td>
<td>Kg/m³</td>
<td>860–900</td>
<td>872</td>
</tr>
<tr>
<td>Viscosity</td>
<td>EN ISO 3104</td>
<td>mm²/s</td>
<td>3.5–5.0</td>
<td>4.1</td>
</tr>
</tbody>
</table>

The values of all the fuel properties are in the range of standard values as given by ASTM D6751 and EN 14214 international standard specifications [37-40]. This indicates that biodiesel prepared over sodium silicate catalyst of...
present investigation under the optimum reaction condition can be used as a fuel substitute of petrodiesel fuel.

7.3.7 Catalyst Reusability Studies

The reusability of the catalyst was checked by carrying out the transesterification reaction under the optimum condition obtained from the RSM studies using the catalyst which is separated from the reaction mixture after the reaction. The catalyst was activated at 550 °C for 1 h before each cycle of reaction and the results are presented in figure 7.13. The catalyst can be repeatedly used for three cycles producing fuel grade biodiesel and in the fourth cycle, the FAME content is dropped to 82.34 %.

![Figure 7.13. Reusability results of the catalyst under the optimum reaction conditions of catalyst weight 5 wt%, methanol to oil molar ratio 12:1, temperature 65 °C and reaction time 60 min.](image)

The catalyst structure after the 6th cycle of reaction is analysed by FTIR spectroscopy and the FTIR spectra of the fresh catalyst and the catalyst after 6th cycle is shown in figure 7.14. In the FTIR spectra, no detectable difference
is observed in the vibration bands of the as prepared and used samples indicating the stability of the catalyst after repeated cycles of reaction.

Figure 7.14. FTIR spectra of the fresh and used 50NS catalysts

7.4 CONCLUSIONS

Present study reports the preparation of sodium silicate from silica and NaOH by the impregnation method followed by calcination at 550 °C for 5 h and the successful evaluation of its use as a heterogeneous catalyst in the transesterification of waste cooking oil with methanol. The optimization of the effect of various reaction parameters on the reaction efficiency of biodiesel production is done using response surface methodology. A FAME content of 99.97 % is resulted under the optimum conditions of methanol to oil molar ratio 12:1, catalyst weight 5 wt%, temperature 65 °C and reaction time 60 min which is suggested by the model. The methyl ester produced was analyzed, and it was confirmed that the fuel properties met the specification of biodiesel as specified in ASTM D6751 and EN 14214 standards. The reusability studies of the catalyst showed that the catalyst can be effectively used for three repeated
runs producing fuel grade biodiesel and after the third run, the catalytic activity of the catalyst decreases.

REFERENCES


Chapter 8

SUMMARY AND CONCLUSIONS
8.1 SUMMARY

Waste cooking oil as well as *Jatropha curcas* oil are the widely used non-edible oil feedstock used for the production of biodiesel by the transesterification reaction using methanol. The waste cooking oil is a pollutant and hence its effective utilization for the production of an alternate fuel, biodiesel has its own importance. The waste cooking oil is available in plenty from the various restaurants. So, it is a cheap source for biodiesel production. Use of non-edible oil in biodiesel production has the additional advantage of reclaim of barren land. Thus *Jatropha curcas* oil mediated biodiesel production is not causing any competition with food uses or with agricultural area. The effective transformation of these oils into biodiesel is achieved in the presence of catalysts. Here, we had prepared five different sets of heterogeneous catalysts from different precursor materials and the transesterification reactions of oils with methanol were performed over these catalysts. Highly active homogeneous catalysts are readily available in the market which is widely used in the transesterification reaction in industrial scale operations, but they have many disadvantages. Hence as an alternate, many heterogeneous catalysts are developed. We have used eco-friendly and reusable heterogeneous catalysts. Here, all the heterogeneous catalysts are prepared in a cost effective manner via simple methods and the prepared systems are characterized by different analytical techniques inorder to understand the structure, crystalline phase, nature and composition. Studies are also conducted to understand the influence of different reaction parameters on the transesterification reaction. The reusability of the catalysts and fuel properties of biodiesel are also analyzed to
determine the heterogeneity of the reaction as well as to know the fuel quality of the prepared biodiesel respectively.

Present study mainly deals with the preparation, characterization and catalytic activity studies of alkali metal incorporated heterogeneous catalysts in the transesterification reaction of non-edible oils for the production of biodiesel. Different catalysts of present investigation includes sodium aluminate, lithium silicate, Na loaded CeO$_2$ catalysts, sodium titanate and sodium silicate. The thesis is structured into 8 chapters including the summary and conclusion chapter. The summary of each chapter and the conclusion obtained are mentioned in brief in the following sections.

Chapter 1 describes the literature review on biodiesel and the catalysts used in biodiesel production with a special emphasis to heterogeneous catalysts. The need and significance of alternate energy resources is briefly narrated. Also, the advantages of biodiesel over other alternate fuels making it as a superb candidate for the energy related purposes is clearly visible from the discussions. Biodiesel properties, its preparation methods and analysis are also included. The superiority of heterogeneous catalysts over homogeneous catalysts in biodiesel production is mentioned in the chapter. It is evident from the review that basic solid catalysts are superior in biodiesel production. Finally, a review on catalysts in the production of biodiesel and the literature regarding the use of the different heterogeneous catalysts including similar systems of present study, i.e. sodium aluminates, lithium silicates, CeO$_2$ based catalysts, sodium titanates and sodium silicates in the transesterification reaction are also described there in detail.
Chapter 2 deals the experimental section. This chapter gives the details of materials used throughout the study. Also, the various analytical techniques adopted in the present study for the catalyst characterization as well as biodiesel analysis are clearly described in the chapter. The working principle and the details of instruments used for the analyses are briefly explained. A general procedure for the purification of biodiesel feedstock, transesterification reaction and reusability studies are given in the chapter. The quality of biodiesel is usually assessed from its fuel properties and therefore the determination of fuel properties is important while dealing with biodiesel. Hence the chapter also discussed the general procedures adopted in the present study for finding out the biodiesel fuel properties.

Chapter 3 discusses the preparation, characterization and application of sodium aluminate in the transesterification of Jatropha curcas oil for biodiesel production. In the introduction section of the chapter, structure, uses and catalytic applications of sodium aluminate is briefly mentioned. Then, the preparation of sodium aluminate catalyst is mentioned with a schematic representation. We had published the first time use of waste aluminium foils in the preparation of sodium aluminate. With the help of different characterisation results we could correlate the active phase, texture and morphology with the catalytic activity. The best catalyst was found to be highly crystalline NaAlO$_2$ as evident from the XRD and FTIR spectral analyses. The catalytic activities in the transesterification reaction are studied and the reaction parameters are varied to find out the suitable condition to attain maximum FAME content. The transesterification of jatropha oil occurred under mild reaction conditions and the FAME content reached more than 96.5% even at a low methanol to oil
molar ratio of 6:1 within a short duration of 1 h reaction at 55 °C. The catalyst was found to be reusable without much loss in activity till 3 repeated cycles. The fuel properties of the produced biodiesel are analyzed to understand the applicability of its use as a substitute fuel for petrodiesel.

In the chapter 4, the preparation, characterization and catalytic application of lithium silicate in the transesterification reaction of waste cooking (WCO) oil for the production of biodiesel is narrated. The chapter gives a brief introduction to lithium silicate, its uses and applications. Simple method of impregnation was performed for the material preparation and the catalyst was analyzed using different techniques. Here, Box-Behnken Design coupled with Response Surface Methodology is employed to optimize the process parameters required for the production of biodiesel from WCO over lithium silicate as catalyst. The statistical studies confirmed the significance of the model in the optimisation of biodiesel production. The fuel properties of biodiesel obtained under the suggested optimum reaction conditions met the specifications as mentioned in the international standards. Catalyst heterogeneity and low reaction temperature are the major attractions of the present biodiesel preparation strategy.

Chapter 5 deals with the preparation of novel ceria based catalysts, its characterization studies and application of these catalysts in the biodiesel production. The chapter gives an introduction to ceria and its structure. The uses, properties as well as its catalytic applications are also mentioned. Ceria support is prepared via a facile route and NaOH is incorporated to the ceria by impregnation method to prepare the solid base catalyst. To the best of our knowledge, Na loaded CeO$_2$ catalysts are used for biodiesel production for the
first time. The catalytic activity of the ceria systems are investigated in the transesterification reaction of waste cooking oil with methanol. A comparative study with catalyst derived from CeO$_2$ prepared via different methods is also included in this chapter inorder to investigate the effect of preparation method of the support material in the catalyst properties and catalytic activity. FAME content of 100% was achieved when the transesterification was carried out under mild reaction conditions over Na/CeO$_2$ catalyst when the support was prepared by solid state mixing of its precursor cerium nitrate with citric acid followed by heat treatment. The reusability studies of the catalyst were carried out to assess the stability in the reaction. The fuel properties were analysed and compared with the values given by international standards.

In the chapter 6, the preparation and characterization of novel sodium titanate catalyst and its catalytic application in biodiesel production is described. The chapter gives a brief introduction to titania and its catalytic applications. Then, the reports on titanates and its catalytic applications were mentioned. A brief mention of sodium titanate is also given. In this work, a highly reusable sodium titanate catalyst with porous nanotubular morphology is developed from porous titania and NaOH for its catalytic application in biodiesel production by the transesterification reaction of WCO with methanol. Here, in comparison with other reported procedures, titania sol is prepared in the presence of a nonionic surfactant in aqueous solution thereby avoiding the use of toxic and harmful organic solvents in catalyst development. The porous titania incorporated more NaOH for the production of highly basic heterogeneous catalyst. The catalyst is characterized by different techniques inorder to understand the crystalline structure, phase and morphology which
are the key factors in determining the catalytic activity. The porous sodium titanate nanotube showed excellent catalytic activity and reusability compared to sodium titanate catalyst developed using TiO$_2$ prepared in the absence of surfactant. The fuel properties of the biodiesel was determined and are compared with the international standard values.

Chapter 7 deals with the preparation of sodium silicate, its characterization studies and application of these catalysts in the biodiesel production. The chapter gives brief introduction to sodium silicate and the transesterification reaction over reported sodium silicate catalysts. In this work, we have performed the preparation of sodium silicate from commercial silica and NaOH by the impregnation method for the first time. We have successfully evaluated its catalytic efficiency in the transesterification of waste cooking oil with methanol by the RSM studies. The reusability of the catalyst as well as the fuel properties of the biodiesel are also investigated and the results are promising.

Chapter 8 summarizes results of the present work on the development, characterization and transesterification reaction of alkali metal incorporated heterogeneous catalysts and concludes the thesis.

8.2 CONCLUSIONS

In the present investigations, we had developed 5 different sets of highly active, reusable and eco-friendly heterogeneous catalysts from different precursors/supports and alkali metal sources. The developed alkali metal incorporated catalysts are characterized by different analytical techniques for investigating the structure, morphology as well as the active phases that are
responsible for catalysis. The prepared heterogeneous catalysts are used in the transesterification reaction for the production of biodiesel from non-edible oil feedstock. The reaction conditions affecting the performance of the catalysts were studied and found out the best suited conditions over each set of catalyst systems. The fuel properties of the prepared biodiesel samples under the selected reaction conditions over the best catalyst in each set is analysed by different procedures and it is found that the fuel properties of the prepared biodiesel samples lies in the range of values mentioned by ASTM and EN international standards suggesting the suitability of its use as a petro-diesel fuel substitute. The reusability studies of the best heterogeneous catalyst from each set of systems are carried out inorder to investigate the reusability as well as the heterogeneous nature of the prepared catalysts. All the prepared catalysts are reusable and can be used in the repeated cycles of reactions which accounts its importance compared to many reported catalysts in biodiesel production.

8.3 FUTURE OUTLOOK

Biodiesel can solve many of the issues regarding the energy crisis. Present investigation has its own significance for the near future, because it promises the low cost production of biodiesel from non-edible vegetable oils. Another important aspect is that, the developed heterogeneous catalysts showed excellent catalytic activity and has the advantages for the commercial production. The present study can be extended to the use of other non-edible vegetable oils as well as animal fats for the production of biodiesel.
List of Publications


List of Presentations

1. **Sudha Kochiyil Cherikkallinmel** and Binitha N Narayanan, Catalytic activity of calcium impregnated silica in the waste cooking oil methanolysis, International conference on Emerging frontiers in chemical Sciences, Department of Chemistry, Farook College, September 2017.


3. **Sudha Kochiyil Cherikkallinmel** and Binitha N Narayanan Synthesis of Biodiesel from waste cooking oil with silica-supported KOH based catalysts, Department of Chemistry, M.E.S.K.V.M. College, Valancheri, December 2015.
