CHAPTER VI

Transesterification of soybean oil with Lewis-acid catalysts

VI.1 Introduction

Acid-catalyzed transesterification process has been widely studied and reported. Although the acid-catalyzed reaction is much slower than the base-catalyzed one,\textsuperscript{1,2} the former is more suitable for oils with relatively high free fatty acid contents.\textsuperscript{3,4}

![Scheme VI.1: Mechanism of a) Bronsted acid and b) Lewis acid-catalyzed transesterification of vegetable oils](image)

where R', R'' and R''' are carbon chains of the fatty acids

Scheme VI.1: Mechanism of a) Bronsted acid and b) Lewis acid-catalyzed transesterification of vegetable oils
The mechanism of acid-catalyzed transesterification of vegetable oils is shown in Scheme VI.1. The transformation of the other two ester functionalities also proceeds in the same way. The mechanism suggests that the reaction should be carried out in the absence of water in order to avoid the formation of carboxylic acids which reduces the yield of alkyl esters.

### VI.2 Results and Discussion

In our endeavour to find cost-effective acidic catalytic systems, transesterification of soybean oil to FAME was carried out using a few Lewis acid catalysts which were easily available in the laboratory. Except In(OTf)$_3$ which is an expensive catalyst, all others viz. SnCl$_2$.H$_2$O, CoCl$_2$.H$_2$O, FeCl$_3$, FeCl$_3$.6H$_2$O and SnCl$_4$.5H$_2$O were not that costly.

Table VI.1: Catalyst screening under MW

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Catalyst</th>
<th>Time (min)</th>
<th>Yield (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SnCl$_2$.2H$_2$O</td>
<td>5</td>
<td>No Reaction</td>
</tr>
<tr>
<td>2</td>
<td>SnCl$_4$.5H$_2$O</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>CoCl$_2$.6H$_2$O</td>
<td>5</td>
<td>No Reaction</td>
</tr>
<tr>
<td>4</td>
<td>FeCl$_3$</td>
<td>3</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>FeCl$_3$.6H$_2$O</td>
<td>3</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td>In(OTf)$_3$</td>
<td>5</td>
<td>No Reaction</td>
</tr>
</tbody>
</table>

Six metal-based Lewis acid catalysts were screened for their activity, and the results are shown in Table VI.1. From the table, it is seen that hydrated SnCl$_2$, which has been previously reported to be a good catalyst for both esterification and transesterification,$^5,6,7,8,9,10,11$ gives no result under microwave irradiation. However, hydrated SnCl$_4$ gives 30% yield in 5 minutes. This result is not unexpected as the strength of Lewis acids in general increases with increase in nuclear charge of the central atom as well as with increase in the number and electronegativity of the atoms attached to the central metal atom.$^{12}$ Although CoCl$_2$.6H$_2$O catalyzes esterification of oleic acid and oleyl alcohol at elevated temperatures,$^{13}$ it fails to transesterify soybean oil under microwave irradiation. Fe(III) salts have been reported earlier to be good catalysts for esterification as well as transesterification reactions. Fe$_2$(SO$_4$)$_3$ has been
used to esterify free fatty acids in waste cooking oil as a pre-treatment step for biodiesel production.\textsuperscript{14} Another catalyst, iron(III) β-diketonate has been used in the transesterification, but not in biodiesel production.\textsuperscript{15} FeCl\textsubscript{3} and other Fe(III) salts are generally stronger hard Lewis acids. But they behave as Bronsted acids in presence of alcohols when the metal coordinates with the hetero atom of the proton donor, thus significantly increasing the H\textsuperscript{+} donating tendency of the alcohol (Fig.VI.1 and VI.2). These properties make Fe(III) salts excellent catalysts for activation of carbonyl compounds.\textsuperscript{15,16} In this study also this is evident as both FeCl\textsubscript{3} (anhydrous) and FeCl\textsubscript{3}.6H\textsubscript{2}O (hydrated) catalyze the transesterification reaction quite efficiently giving respectively 90% and 95% yields in 3 minutes, the hydrated salt being slightly better. Indium trifluoromethanesulfonate, In(OTf)\textsubscript{3} which is considered to be a very good Lewis acid catalyst,\textsuperscript{17} has also been employed for transesterification in this study but it failed to catalyse the reaction under microwave irradiation.

\begin{center}
\textbf{Fig.VI.1: Lewis acid assisted Bronsted acid catalyst}
\end{center}

\begin{center}
\textbf{Fig.VI.2: Fe(III) chloride coordinating to O-atom of methanol assisting release of a H\textsuperscript{+}}
\end{center}

After ascertaining FeCl\textsubscript{3}.6H\textsubscript{2}O to be the best catalyst under microwave irradiation, microwave power was optimized. Three power settings were considered, the minimum being 350W where 90% product yield was recorded in 5 minutes. Increasing the power to 420W increased the yield to 95% in 5 minutes. Further increasing the power to 560W did not affect the yield but reduced the reaction time to 3 minutes. Hence, the best reaction condition under microwave irradiation for transesterification of vegetable oils
under microwave irradiation is 20 wt.% of FeCl$_3$·6H$_2$O as catalyst at 560W power (Table VI.2).

<table>
<thead>
<tr>
<th>S.No.</th>
<th>MW power</th>
<th>Time (min)</th>
<th>Yield (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>350 W</td>
<td>5</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>420 W</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>560 W</td>
<td>3</td>
<td>95</td>
</tr>
</tbody>
</table>

The efficacy of the catalysts was also examined at ambient temperature as well as under reflux. The room temperature during all the experiments was around 32 °C. It was interesting to note that none of the Lewis acids did show their activity at room temperature even after 24 hours of stirring. This shows that Lewis acid catalyzed transesterification reactions require high activation energy which may be provided in the form of thermal or microwave heating. Also, proper mixing of the methanol and triglyceride phases does not take place at ambient temperature, and this goes against enabling the catalyst, which is more soluble in methanol, to reach the triglyceride for reaction.

Table VI.3: Screening of catalysts at RT and under reflux

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Catalyst</th>
<th>RT (32 °C)</th>
<th>Reflux (70 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Time (h)</td>
<td>Yield (%)</td>
</tr>
<tr>
<td>1</td>
<td>FeCl$_3$</td>
<td>24</td>
<td>No Reaction</td>
</tr>
<tr>
<td>2</td>
<td>FeCl$_3$·6H$_2$O</td>
<td>24</td>
<td>No Reaction</td>
</tr>
<tr>
<td>3</td>
<td>SnCl$_4$·5H$_2$O</td>
<td>24</td>
<td>No Reaction</td>
</tr>
<tr>
<td>4</td>
<td>In(OTf)$_3$</td>
<td>24</td>
<td>No Reaction</td>
</tr>
</tbody>
</table>

The same catalysts were further tested for their activity in refluxing methanol. As was expected the reactions were successful with all the catalysts albeit different yields. Anhydrous FeCl$_3$ showed the best activity giving 90% yield in 10 hours whereas In(OTf)$_3$ the least activity with only 21% product yield in 24 hours. Hydrated FeCl$_3$ also did show good activity with 91% yield in 15 hours. Although both anhydrous and hydrated FeCl$_3$ afforded similar amount of product, the anhydrous salt is considered better under reflux conditions as it takes lesser time.
VI.3 Conclusion

From the above experiments it may be concluded that FeCl₃ salts are quite active and efficient catalysts for transesterification reactions under reflux and microwave irradiation but inactive at ambient temperature. The hexahydrate salt works better under microwave irradiation whereas the anhydrous salt acts better under reflux.

VI.4 Experimental Section

VI.4.1 Materials

Methanol used was of HPLC grade purchased from Rankem India. Commercially available soybean oil was bought and purified before use. Stannous chloride dihydrate (SnCl₂.2H₂O) was procured from Qualigens while stannic chloride pentahydrate (SnCl₄.5H₂O) was procured from Sigma Aldrich. Anhydrous ferric chloride (FeCl₃) was purchased from Rankem whereas ferric chloride hexahydrate (FeCl₃.6H₂O) was purchased from Sigma Aldrich. Cobaltous chloride (CoCl₂.6H₂O) was bought from CDH and indium trifluoromethanesulfonate was bought from Sigma Aldrich. ¹H NMR spectra were recorded on Bruker 300 MHz NMR spectrometer. Microwave experiments were carried out in a Catalyst™ Systems Scientific Microwave Reactor.

VI.4.2 Method

Transesterification was first carried out under microwave irradiation with the Lewis acids given in the Table VI.1. A mixture of oil (500 mg), methanol (10 mL/g of purified oil, 5 mL) and catalyst (20 wt% of oil, 100 mg) was taken in a 50 mL two-necked microwave vessel and refluxed under 560W microwave irradiation power with magnetic stirring for 5 minutes. After that the product mixture was partitioned between water and petroleum ether (3 x 15 mL). The combined organic phase was washed with brine, dried over anhydrous Na₂SO₄ and the solvent was removed under vacuum to yield the crude product. The crude product was purified by column chromatography over silica gel (60-120 mesh) using a mixture of petroleum ether and ethyl acetate (25:1) as the eluent.

Transesterification of soybean oil at room temperature (RT) was also carried out with the same set of catalysts except the ones that did not undergo any reaction under MW irradiation. A mixture of oil (500 mg), methanol (10 mL/g of purified oil, 5 mL) and
catalyst (20 wt% of oil, 100 mg) was stirred magnetically in a 50 mL round bottom flask at room temperature. Reaction was monitored by TLC. Even after continuing the reaction for 24 hours no indication of product formation was seen on TLC, indicating that no reaction takes place at room temperature.

The same set of catalysts was examined again for transesterification under reflux condition. A mixture of oil (500 mg), methanol (10 mL/g of purified oil, 5 mL) and catalyst (20 wt% of oil, 100 mg) was stirred magnetically in a round bottom flask at refluxing temperature. Reaction was monitored by TLC. After completion of the reaction, the product mixture was extracted with petroleum ether and the combined filtrate was partitioned between water and petroleum ether. The organic phase was washed with brine, dried over anhydrous Na₂SO₄ and the solvent was removed under vacuum to yield the crude product which was then purified by column chromatography over silica gel (60-120 mesh) using a mixture of petroleum ether and ethyl acetate (25:1) as the eluent.
REFERENCES


