CHAPTER 3

RESULT AND DISCUSSION

3.1. LIPID EXTRACTION FROM *ADENANTHERA PAVONINA* SEED

The most important factors troubling superheated solvent extraction were particular to be a selection of solvent, extraction temperature, solvent flow rate, mean size of the particle and extraction time, each of them at three different levels varying from 70 to 110 °C, 0.25 to 0.75 mm, and 0.5 to 1.5 L/hr, respectively with respect to different time period up to 120 min. Subsequently, the extraction pressure was kept as to 15 bars to guarantee methanol, chloroform and n-hexane in liquid circumstances at the extraction temperatures.

3.1.1. Effect of different solvent system on extraction

Preference of the solvent system for the extraction of oil from *Adenanthera pavonina* seed is an essential factor. Selection of the solvent for oil extraction at the preliminary action would permit cost-effective invention without further expense required for the purification of the product. Moreover, the preferred solvent must have good extraction ability and stumpy viscosity to augment the free transmission. A professional extraction procedure requires the diffusion of fluid into the solid. An organic solvent have a superior solubility with oil. Additionally it has been used to humiliate the particle cell walls and to liquefy the oil to augment the oil yield. The effect of different solvent systems on saga seed oil extraction yield is shown in Fig.3.1. Hexane is widely used for
oil extraction due to the low slippery residual effects, high stability, low boiling point and diminutive corrosiveness. Different solvents such as Hexane (H), Chloroform (C), mixture of Chloroform with Methanol (C:M) and mixture of Chloroform and Methanol with Hexane (C:M:H) were taken as in terms of volume ratio and they had been selected based on types of lipid present in the seed such as polar and non polar lipids at 15 bar pressure, 70 °C temperatures and 1 lph of solvents flow. From this investigation, it was observed that the highest oil extraction yield was achieved as 25.3 wt% from *Adenanthera Pavonina* using the most valuable solvent mixture of 2:1:3 volume ratio of Chloroform: Methanol: Hexane. For further studies, this mixed solvent system was used for oil extraction from *Adenanthera pavonina* seed.

![Fig. 3.1. Effect of different solvent system of Hexane (H), Chloroform (C), mixture of Chloroform with Methanol (C:M) and mixture of Chloroform and Methanol with Hexane (C:M:H) on extraction.](image-url)
3.1.2. Effect of temperature on extraction

Temperature for saga seed oil extraction was examined for the reason that the optimistic consequence of temperature on distribution of solutes in extraction processes, it may perhaps to carry out superheated solvent extraction process at the higher permeable temperature. The temperature effect was evaluated in between 70 to 110 °C with mean particle size of 0.50 mm, solvent flow rate of 1 L/hr and 2 hr of extraction time at 15 bar pressure. The extraction yield is shown in Fig. 3.2. From this figure, it was observed that the extraction efficiency was found to be increased generally with increasing temperature.

![Graph showing effect of temperature on extraction yield](image)

**Fig. 3.2.** Effect of temperature on oil extraction at 1.0 L/hr of solvent flow, 0.5 mm of mean particle size and 3:2:1 volume ratio of Hexane, Chloroform and Methanol.

The resulted collective yield values obtained as 19.4, 24.3 and 25.1 wt% at 70, 90 and 110 °C, respectively. Clear yellow saga seed oil was obtained
at 70 and 90 °C, slight brownish color was acquired at 110 °C due to the effect of degradation of essential components at the superior temperatures. Additionally, it is accounted that extreme heating gives rise to create free fatty acids from triacylglycerols during the extraction operation (Luque et al 2005). Based on the mentioned specific statement to prevent any unwanted changes in seed oil quality, the further tentative investigations were carried out at 90 °C.

3.1.3. **Effect of mean size of the particle on extraction**

The mean particle size is found to be an essential constraint for the extraction of oil from the biomass. The smaller dimension of biomass leads to greater in the interfacial area between the solid and liquid.

![Graph showing the effect of mean particle size on oil extraction](image)

**Fig. 3.3.** Effect of mean particle size on oil extraction at 90 °C temperature, 1.0 L/hr of solvent flow and 3:2:1 volume ratio of Hexane, Chloroform and Methanol.
Hence, the increase in interfacial area enhances the oil extraction yield. The mean size of the seed particles were varied as 0.25, 0.5, and 0.75 mm. The mean size of the seed particles on the extraction of saga seed oil as collective effectiveness at 90 °C temperature, 15 bar pressure, 1 L/hr flow rate, and up to 120 min extraction time has been shown in Fig. 3.3. The extraction efficiencies were found to be 26.2, 23.8 and 19.3 wt% for 0.25, 0.50, and 0.75 mm, respectively.

From the Fig. 3.3, it was observed that the cumulative extraction yield was progressively improved from 19.3 wt% to 26.2 wt% with reduction in mean particle size from 0.75 mm to 0.25 mm. Further reduction of the mean particle size, did not show any improvement in oil extraction. This shows that the highest lipid extraction yield of 26.2 wt% was achieved with the seed mean particle size of 0.25 mm. It is well acknowledged that the rate of mixed solvent extraction is controlled by the mean particle size of the seed. The worst extraction rate is endorsed because of the higher mean particle size. However, the higher particle size creates complexity for the solvents to penetrate into the core of the seed to leach the lipid. It is taken in mind that the particle size is not only enhanced the extraction rate, but also raises the lipid extraction yield. Han et al. (2009) mentioned that the most important cause for escalating oil yield was due to shrink in particle size, which in turn enhance the specific surface area of the oilseed interacting with the solvent. For further investigation, to have higher efficiencies, the most favourable value for the mean particle size was decided as 0.25 mm.

3.1.4. Effect of solvents flow on extraction

The outcome of mixed solvent flow rate contained by 0.5–1.5 L/hr on extraction yield of Adenanthera pavonina seed oil at 90 °C temperature, 15
bar pressure, 0.25 mm particle size, and up to 120 min extraction time is shown in Fig. 3.4. The consequential values were 16.3, 26.2 and 23.4 wt% at 0.5, 1.0 and 1.5 L/hr respectively. From this investigation, the extraction rate of saga seed oil was escalating too fast from the flow rate of 0.5 to 1.0 L/hr. The extraction yield was found to be increased with increasing flow rate, this is due to the mass of saga seed oil moves from the surface of the small solid particles into the solvent phase synchronized for the most part of the extraction process and escalating the solvent flow rate resulted in faster mass transfer. Moreover, the increasing flow rate from 1.0 to 1.5 L/hr causes low yield due to the low diffusivity at higher solvent flow rate trend to reduce the contact time between solid and liquid. In solid–liquid interaction, the rate of diffusion is time dependent. As per the Knudsen diffusion statement the parameters such as time, temperature and pressure are mainly considered for diffusion in solid. The time duration needs to contact between solid and liquid at higher flow of solvent is less. However, the yield was found as less at 1.5 L/hr when compared with 1 L/hr of solvent flow. Longer extraction times, slower extraction rate with immense amount of final extracts and 1.0 L/hr solvent flow rate were selected as the most favourable values.
Fig. 3.4. Effect of solvent flow on oil extraction at 90 °C temperature, 0.25 mm of mean particle size and 3:2:1 volume ratio of Hexane, Chloroform and Methanol.

3.1.5. Comparing with conventional method

The *Adenanthera pavonina* seed oil extraction yield was found to be 26.2 wt% and 19.7 wt% for superheated mixed solvent extraction and Soxhlet extraction, respectively. The maximum value was achieved for the superheated mixed solvent extraction and the tiniest value was for the Soxhlet extraction method. From the result, superheated extraction technique was found to be more efficient when compared with Soxhlet extraction method with respect to the quantity of oil extracted and time required for extraction technique. Therefore, superheated extraction for higher scale of oil extraction from *Adenanthera pavonina* seed will be pertinent.
3.1.6. Characterization of saga seed oil

The composition of fatty acid was highly founded (by Gas Chromatography) as linoleic acid 49.8%, oleic acid 22.4%, hexadecanoic acid 7.2%, gadoleic acid 6.4% and remains 14.2% (Table 3.1) and quantified in terms of relative percentage.

**Table 3.1. Fatty acid composition identified in the oil of *Adenanthera pavonina***

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Fatty acids</th>
<th>Carbon atom</th>
<th>Formula</th>
<th>Relative %</th>
<th>SHE</th>
<th>Soxhlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Hexadecanoic acid</td>
<td>C16:0</td>
<td>C_{16}H_{32}O_{2}</td>
<td>7.2</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Heptadecanoic acid</td>
<td>C17:0</td>
<td>C_{17}H_{34}O_{2}</td>
<td>1.4</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Stearic acid</td>
<td>C18:0</td>
<td>C_{18}H_{36}O_{2}</td>
<td>2.1</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Oleic acid</td>
<td>C18:1 Cis</td>
<td>C_{18}H_{34}O_{2}</td>
<td>22.4</td>
<td>22.8</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Elaidic acid</td>
<td>C18:1 <em>Trans</em></td>
<td>C_{18}H_{34}O_{2}</td>
<td>0.3</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Linoleic acid</td>
<td>C18:2</td>
<td>C_{18}H_{32}O_{2}</td>
<td>49.8</td>
<td>50.3</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>cis-10-Nonadecenoic acid</td>
<td>C19:1</td>
<td>C_{19}H_{36}O_{2}</td>
<td>1.2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>Arachidic acid</td>
<td>C20:0</td>
<td>C_{20}H_{40}O_{2}</td>
<td>0.9</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>Gadoleic acid</td>
<td>C20:1</td>
<td>C_{20}H_{38}O_{2}</td>
<td>6.4</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>Behenic acid</td>
<td>C22:0</td>
<td>C_{22}H_{44}O_{2}</td>
<td>0.3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>Erucic acid</td>
<td>C22:1</td>
<td>C_{22}H_{42}O_{2}</td>
<td>1.9</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>12.</td>
<td>Lignoceric acid</td>
<td>C24:0</td>
<td>C_{24}H_{48}O_{2}</td>
<td>3.2</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>13.</td>
<td>Nervonic acid</td>
<td>C24:1</td>
<td>C_{24}H_{46}O_{2}</td>
<td>1.7</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>14.</td>
<td>Hexacosanoic acid</td>
<td>C26:0</td>
<td>C_{26}H_{52}O_{2}</td>
<td>0.3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>15.</td>
<td>Unknown</td>
<td>-</td>
<td>-</td>
<td>0.8</td>
<td>3.6</td>
<td></td>
</tr>
</tbody>
</table>

**Total fatty acids** 99.9% 99.8%
From this fatty acid profile, it was observed that the unsaturated fatty acids (USFAs) were found to be high as 83.7% when compared with saturated fatty acids (SFAs) as 15.4%. Properties of *Adenanthera pavonina* such as molecular weight, acid value, iodine value, saponification value, and free fatty acid (FFA) were determined (Table 3.2). The natural lipid and phospholipids present in saga seed oil were found as 86.2 wt% and 13.8 wt% respectively and were analysed by thin layer chromatography.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Units</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight of fatty acids</td>
<td>g/mol.</td>
<td>285.86</td>
</tr>
<tr>
<td>Molecular weight if triglyceride</td>
<td>g/mol.</td>
<td>895.63</td>
</tr>
<tr>
<td>Density</td>
<td>g/cc.</td>
<td>0.916</td>
</tr>
<tr>
<td>Acid value</td>
<td>mg of KOH/g</td>
<td>8.6</td>
</tr>
<tr>
<td>Iodine value</td>
<td>-</td>
<td>89.1</td>
</tr>
<tr>
<td>Saponification value</td>
<td>mg of KOH/g</td>
<td>182.3</td>
</tr>
<tr>
<td>Free fatty acid (FFA)</td>
<td>wt%</td>
<td>4.3</td>
</tr>
<tr>
<td>Saturate fatty acids (SFAs)</td>
<td>Relative %</td>
<td>15.4</td>
</tr>
<tr>
<td>Unsaturated fatty acids (USFAs)</td>
<td>Relative %</td>
<td>85.7</td>
</tr>
</tbody>
</table>

### 3.1.7. Extraction Kinetics

Separation kinetic is essential to replicate the mass transfer process and mechanism. Consequently, the major objective of this study is to examine the oil extraction kinetics and thermodynamic properties of extraction rate constant, activation energy, frequency factor, and activation enthalpy, activation entropy and activation Gibbs free energy from *Adenanthera pavonina* seed. The different temperature (70, 90 and 110 °C) effect was selected in this study from the previous research investigation (Ramachandran
et al 2014). The other parameters conditions were chosen as 0.25 mm of mean particle size, 3:2:1 volume ratio of Hexane, chloroform with methanol and 1 L hr-1 of solvent flow velocity at 15 bar of system pressure.

Semi batch extraction was executed at various time intervals between 0 to 120 min in a 25 gm biomass loading system. The *Adenanthera pavonina* seed oil yield percentage at different temperature with respect to various time intervals are shown in Table 3.3. From these results, the maximum amount of oil yield was achieved as 26.2 wt% of seeds at 363 K, in 120 min.

**Table 3.3.** Percentage yield of Adenanthera pavonina seed oil at different temperature

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>70 ºC</th>
<th>90 ºC</th>
<th>110 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (wt%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>3</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>40</td>
<td>7</td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td>60</td>
<td>12</td>
<td>16</td>
<td>19</td>
</tr>
<tr>
<td>80</td>
<td>14</td>
<td>19</td>
<td>22</td>
</tr>
<tr>
<td>100</td>
<td>17</td>
<td>23</td>
<td>24.5</td>
</tr>
<tr>
<td>120</td>
<td>19.4</td>
<td>24.3</td>
<td>25.1</td>
</tr>
</tbody>
</table>

Rate equation for extraction of oil from *Adenanthera pavonina* seed can be written as:

\[
dY/dt = kY^n
\]

\[
(3.1)
\]

Where Y – Extracted oil yield (percentage), t – extraction time period (min), k - the rate constant (min\(^{-1}\)) and n - order of reaction.
In view of the facts that, oil yield percentage was found to be increased with increase in extraction time and the values for dY/dt have a positive sign (Widyan & Shyoukh 2002). Using the values from Table 3.4, differential method was applied (Laidler 1987). From the plots of ln (dY/dt) versus ln Y (Fig.3.5), fitted datum was found as linear by means of equation 3.1. The order of kinetics was found as first order by the values of n acquired from the slopes of the straight lines and the reaction rate constants (k) were obtained. Rate constants determined from the plots were found to be increases with increase in temperature. This is obtained due to the improvement in the diffusivity of the solvent to enhance the rate of extraction. Consequently, the rate of reaction is often found to depend powerfully on temperature.

**Table 3.4.** Reaction rate constant (k) at different temperature

<table>
<thead>
<tr>
<th>T (K)</th>
<th>k (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>343</td>
<td>0.0019753</td>
</tr>
<tr>
<td>363</td>
<td>0.0022347</td>
</tr>
<tr>
<td>383</td>
<td>0.0022969</td>
</tr>
</tbody>
</table>

Thus the lipid extraction kinetics from *Adenanthera pavonina* seed can be demonstrated by the subsequent equation obtained after integrating of Equation 3.1 as:

\[ Y_t = Y_i e^{kt} \]  \(.......... \) (3.2)
Fig.3.5. A plot of ln $dY/dt$ versus ln Y at 70 °C, 90 °C and 110 °C for *Adenanthera pavonina* seed oil.

Where $Y_t$ is the percentage of extracted oil at time $t$ and $Y_u$ is the percentage of un-extracted oil content at time $t$ is equal to zero. Karlovic et al (1986) examined the temperature effect on the oil extraction kinetics from corn germ flakes primed by a dry degeneration process. Augment of temperature improves the capacity of solvents to liquefy the oil due to the thermal energy can conquered the cohesive and adhesive interactions (Suganya & Renganathan 2012).

Activation energy was calculated using Arrhenius Equation. The relation between rate constant versus extraction temperature can be described by the Arrhenius equation. It can be written as:

$$k = A e^{-E_a/RT} \quad \text{......... (3.3)}$$

Where, $k$ - reaction rate constant (min$^{-1}$), $A$ - frequency factor or Arrhenius constant (sec$^{-1}$), $E_a$ - the activation energy (kJ mol$^{-1}$), $R$ - the...
universal gas constant (J mol$^{-1}$ K$^{-1}$) and T - the absolute temperature (K). A plot of ln$k$ versus $1/T$ offers a straight line whose slope represents the activation energy of Adenanthera pavonina oil extraction and $-E_a/R$ is shown in Fig. 3.6 (Topallar & Gecgel 2000). As a result, the activation energy ($E_a$) was calculated as 4.16 kJ mol$^{-1}$ and friction factor was calculated as $5.48 \times 10^{-4}$ sec$^{-1}$. The same type of result was previously reported by Sepidar et al (2009) for the extraction oil from Jatropha curcas (Amin et al 2010).

![Graph showing ln$k$ versus $1/T$](image)

**Fig. 3.6** A plot of ln$k$ versus $1/T$ for Adenanthera pavonina seed oil.

The activation thermodynamic parameters of enthalpy, entropy and free energy were designed according to transition state theory (Laidler 1987), the following equations are given as:

\[
\Delta H^\circ = E_a - RT \\
A = \frac{RT}{hN} (A e^{(\Delta H^\circ/RT)})
\]

\[
......... (3.4) \\
......... (3.5)
\]
\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{......... (3.6)} \]

Where, \( N \) is the Avogadro’s number, \( h \) is the Planck constant, \( \Delta H^\circ \) is the activation enthalpy, \( \Delta S^\circ \) is the activation entropy and \( \Delta G^\circ \) is the activation Gibbs free energy. The activation thermodynamic parameters at different temperature are shown in Table 3.5.

**Table 3.5.** Activation thermodynamic properties of saga seed oil extraction at various temperatures.

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( \Delta H^\circ ) (J mol(^{-1}))</th>
<th>( \Delta S^\circ ) (J mol(^{-1})K(^{-1}))</th>
<th>( \Delta G^\circ ) (J mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>343</td>
<td>1310.697</td>
<td>-310.00</td>
<td>107641.2</td>
</tr>
<tr>
<td>363</td>
<td>1144.407</td>
<td>-308.78</td>
<td>113230.8</td>
</tr>
<tr>
<td>383</td>
<td>978.1169</td>
<td>-308.39</td>
<td>119094.1</td>
</tr>
</tbody>
</table>

Thermodynamic parameters (\( \Delta H \), \( \Delta S \), and \( \Delta G \)) for the extraction of *Adenanthera pavonina* oil using mixed solvent were estimated by the following equations:

\[ K = \left( \frac{Y_t}{Y_u} \right) \quad \text{......... (3.7)} \]

\[ \ln K = -\frac{\Delta H}{R} \frac{1}{T} + \frac{\Delta S}{R} = -\frac{\Delta G}{R} \frac{1}{T} \quad \text{......... (3.8)} \]

Where \( K \) is the equilibrium constant, \( Y_t \) is the percentage yield of oil at temperature \( T \), \( Y_u \) is the percentage unextracted oil, \( \Delta H \) is the enthalpy change, \( \Delta S \) is the entropy change, and \( \Delta G \) is the change in free energy or Gibb’s energy.
A plot of ln $K_e$ versus $1/T$ (Figure 3.7) should give a straight line whose slope represents the enthalpy change of extraction, $-\Delta H$. Thus, the enthalpy change was calculated to be $\Delta H = 11.476$ kJ mol$^{-1}$ for *Adenanthera pavonina* seed oil extraction.

The $\Delta H$ value obtained was indicating the physicochemical nature of the oil extraction process. Other thermodynamic parameters ($\Delta S$ and $\Delta G$) and the equilibrium constant values for extraction at 120 min are included in Table 3.6 for each temperature. According to these results, the positive value of enthalpy indicates that the process is endothermic and requires energy. In addition, the negative value of $\Delta G$ ($\Delta G < 0$) at 363 K indicates that there is a decrease in the free energy. The extraction process of *Adenanthera Pavonina* oil using mixed solvent at 363 K is a non spontaneous process.

**Table 3.6.** Thermodynamic properties of extraction process of *Adenanthera Pavonina*.

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$K_e$</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/mol K)</th>
<th>$\Delta G$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>343</td>
<td>6.27</td>
<td>11.476</td>
<td>48.72</td>
<td>-5.23</td>
</tr>
<tr>
<td>363</td>
<td>7.98</td>
<td>11.476</td>
<td>48.88</td>
<td>-6.28</td>
</tr>
<tr>
<td>383</td>
<td>9.53</td>
<td>11.476</td>
<td>48.71</td>
<td>-7.18</td>
</tr>
</tbody>
</table>

The system initially consists of the *Adenanthera Pavonina* seeds and mixed solvent, whereas the extracted oil molecules from the *Adenanthera Pavonina* seeds during the process increases the entropy of the mixture in the course of the extraction. The positive value of entropy change ($\Delta S > 0$) at 363 K indicates that the process is irreversible.
Fig. 3.7 A plot of ln $K_e$ versus $1/T$ for *Adenanthera pavonina* seed oil.

From these investigations, the superheated extraction using mixed solvent for *Adenanthera Pavonina* was found to be more effective than other conventional techniques. Saga seed oil extraction process obeys the first order kinetics. The activation energy of lipid extraction was $E_a = 4.16 \text{ kJ mol}^{-1}$ and the activation thermodynamic properties of $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$ at 90 °C were designed as 1.14 kJ mol$^{-1}$, -308.78 J mol$^{-1}$K$^{-1}$ and 113.23 kJ mol$^{-1}$, respectively. The extraction time of 120 min at 90 °C with hexane, chloroform and methanol as a mixed solvent extraction corresponds to less energy and less cost requirement. The enthalpy value was found to be $\Delta H = 11.476 \text{ kJmol}^{-1}$, and the other thermodynamic parameters at 90 °C were calculated as $\Delta S = 48.88 \text{ Jmol}^{-1}\text{K}^{-1}$ and $\Delta G = -6.27 \text{ kJmol}^{-1}$. 
3.2. BIODIESEL PRODUCTION FROM *Adenanthera pavonina* USING CaHPW$_{12}$O$_{40}$/SiO$_2$ AS A HETEROGENEOUS ACID CATALYST

In this division, calcium salt of tungstophoric acid catalyst supported on silica was synthesised by two step impregnation techniques. This prepared material was used as a heterogeneous catalyst to catalyze the *Adenanthera pavonina* seed oil by transesterification reaction for biodiesel production. Characterization of catalyst, the reaction studies and reusability of catalyst were investigated.

3.2.1. Characterization of catalyst

Fourier Transform Infrared (FTIR) spectroscopy was used to verify the presence of HPW and structural integrity of prepared Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ catalyst at molecular level. The typical bands of HPW Keggin anions can be clearly observed as follows: $v_{as}$ (W–O–W) at 797 cm$^{-1}$, $v_{as}$ (W–O–W) at 898 cm$^{-1}$, $v_{as}$ (W=O) at 982 cm$^{-1}$ and $v_{as}$ (P–O) at 1080 cm$^{-1}$, where e, c, t and i stand for the specific positions of different oxygen atoms in Keggin structure, such as edge-shared, corner, terminal and internal, respectively (Shanhui Zhu et al 2013; Kian Fei et al 2011). Fig. 3.8(a) presents FTIR spectra of samples of silica supported calcium salt of tungstophoric acid. Even the samples with lower amounts of HPW, the characteristic bands of the Keggin anion are shown from 700 to 1100 cm$^{-1}$. Band in the region of 1200–1000 cm$^{-1}$ and the absorption peak at 471 cm$^{-1}$ are assigned to asymmetric stretching and bending vibration of Si–O–Si, respectively. This is indicating the whole retention of Keggin structure on the prepared Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ catalyst by impregnation process.
**Fig. 3.8 (a)** FTIR spectra of SiO$_2$, H$_3$PW$_{12}$O$_{40}$, CaHPW$_{12}$O$_{40}$ and Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ catalyst.

The XRD patterns of these samples are shown in Fig. 3.8(b). The characteristic peaks of bulk HPW were observed at 2$\theta$ of 20.6, 25.4 and 30.4. There were apparent characteristic peaks of HPW on H$_3$PW$_{12}$O$_{40}$, CaHPW$_{12}$O$_{40}$ and CaHPW$_{12}$O$_{40}$/SiO$_2$ catalysts. It meant that all the samples maintained the structure of HPW. When the more calcium-salts introduced to HPW, the
weaker diffraction of HPW displayed. It indicated that the calcium-salts had an influence on the crystal structure of HPW. After immobilization of calcium tungstophosphate on silica carrier, the diffraction peaks of the sample became very weak.

![Fig. 3.8 (b) XDR of H₃PW₁₂O₄₀, CaHPW₁₂O₄₀ and Ca(HPW₁₂O₄₀)/SiO₂ catalyst.](image)

Thermogravimetric analysis result of CaHPW/SiO₂ is shown in Fig. 3.8(c), it was seen that CaHPW/SiO₂ catalyst as synthesized has gone through two weight loss stages with the increase in testing temperature. The first weight loss stage before 200 °C was associated with the elimination of some hydration water and physically absorbed water derived from silica and heteropolyacid salt and the second loss stage in the region of 200–500 °C corresponded to the loss of constitutional water and the beginning of decomposition of heteropolyacid salt’s Keggin structure. When the catalyst CaHPW/SiO₂ was calcined above
500 °C, no appreciable weight loss was observed in the TGA pattern, which indicated that Keggin anions have been transformed into oxides $P_2O_5$ and $WO_3$.

![TGA Pattern](image)

**Fig. 3.8 (c)** TGA (Thermogravimetric analysis) of Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ catalyst.

**Fig. 3.9 (a)** and (b) demonstrates the $N_2$ adsorption–desorption isotherms and BJH pore size distribution of Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ catalyst. From Fig. 3.9, isotherms exhibit the typical IV type adsorption isotherms among hysteresis loop and this typical isotherm indicates the mesoporous materials. A prickly variation equivalent to the capillary condensation surrounded by uniform mesopores was observed in the relative pressure varying between 0.05–0.25, which indicates that the Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ obtained after impregnation using tungstophoric acid solution still have typical mesoporous structure. Consequently, it can be concluded that there is no evidence to influence the introduction of $H^+$ ions on mesoporous structure of Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ samples. The BET surface area, BJH pore size and pore volume of Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ were found as 44.067 m$^2$/g, 48.5 Å and 0.041 cm$^3$/g, respectively.
Fig. 3.9 (a) N$_2$ adsorption–desorption isotherms of Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ catalyst

Fig. 3.9 (b) BJH pore size distribution of Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ catalyst
Fig. 3.10(a), shows the EDX analysis and confirms that the presence of elements as P, W and Ca in the catalysts with the silica peak. The EDX analyses show that the Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ catalysts have been synthesized successfully step by step.

![Energy dispersive X-ray (EDX) analysis](image)

**Fig. 3.10 (a)** Energy dispersive X-ray (EDX) analysis

From the Fig. 3.10(b), the cylindrical and spherical shapes can be seen in the Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ catalyst. The SEM image shows that the silica surface is well covered by Calcium salt of tungstophoric, which is reliable with a sharp decrease in BET surface area of the silica after successful impregnation of catalyst. The calcium nitrate exhibited a loose irregular network structure. The presence of pores became larger when the Ca(NO$_3$)$_2$ was treated with tungstophoric solution. The larger amounts of pores and larger pore size would increase the accessibility of HPW into the Calcium bulk, which would give a higher concentration of covalent bonded Calcium with an HPW group. The prepared acid catalyst has granular nano size and mesoporous structure. From
the FTIR, it was observed that the arrangement of Keggin anion were not distorted with the replacement of calcium for the protons of heteropolyacids. Acid-Base titration method was used for the determination of H⁺ content of the catalyst by titrating with NaOH. The value of H⁺ content was obtained as 0.029%.

![SEM image of Ca(HPW₁₂O₄₀)/SiO₂](Fig. 3.10 (b) SEM image of Ca(HPW₁₂O₄₀)/SiO₂)

3.2.2. **Biodiesel characterization**

¹H NMR spectra of methyl ester were analysed using a Bruker 500 MHz Avance 3 device with CDCl₃ as solvent and TMS (tetra methyl silane) as an internal standard. Fig. 3.11 represents, ¹H-NMR spectra of *Adenanthera Pavonina* biodiesel. An attribute gesture produced from the protons of methylene group neighbouring to the ester group of a molecule in TG (a-CH₂) was eluted at 2.3 ppm and the protons in the methoxy cluster of the methyl ester
were detected at 3.66 ppm. The conversion of biodiesel was executed based on these attribute proton signals in the NMR spectra. The conversion of the methyl ester from Saga seed oil was determined as 97.4 wt%.

![Fig. 3.11](image)

**Fig. 3.11** $^1$H-NMR Spectra of *Adenanthera pavonina* Biodiesel.

### 3.2.3. Reaction Studies

#### 3.2.3.1. Comparison of catalysts

In this study, transesterification reaction was carried out with different catalysts of HPW, HPW/SiO$_2$, CaHPW/SiO$_2$ and CaPW/SiO$_2$ under the same reaction condition. The conversions of these catalytic processes were compared. The transesterification reaction was carried out with the temperature of 65 °C, 1
wt.% of catalyst, the molar ratio of methanol and mixed waste vegetable oil as 20:1 and reaction time up to 30 min. The conversion of triglyceride with respect to different catalyst result was shown in Table 3.7. The conversion of triglyceride with the addition of catalyst was found to be much higher in HPW > HPW/SiO₂, CaHPW/SiO₂ and CaPW/SiO₂ was very low due to the lower acid site density. However, compared with HPW and HPW/SiO₂ the conversion was little low for CaHPW/SiO₂ due to the reduction acid strength, but the reusability of catalyst was very high for CaHPW/SiO₂. Based on the higher stability and reusability, the CaHPW/SiO₂ catalyst was selected for further reaction studies.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (wt%)</th>
<th>Reproducibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPW</td>
<td>92.45</td>
<td>1 run ± 5 wt%</td>
</tr>
<tr>
<td>HPW/SiO₂</td>
<td>91.62</td>
<td>4 runs ± 5 wt%</td>
</tr>
<tr>
<td>CaHPW/SiO₂</td>
<td>90.76</td>
<td>&gt;10 runs ± 4 wt%</td>
</tr>
<tr>
<td>CaPW/SiO₂</td>
<td>64.30</td>
<td>-</td>
</tr>
</tbody>
</table>

### 3.2.3.2. Effects of temperature on transesterification reaction

The triglyceride primarily wants to improve the active of their relevant carbonyl functions to start the reaction. The lengthy alkyl cuffs in a triglyceride molecule can interfere with the activation of the carboxylic group. The activation of the triglyceride is very complex. In order to support the methanol nucleophilic attack on the triglyceride, a reasonably high reaction temperature is essential to activate this carbonyl group. Thus, the research were conducted at different temperature using Ca(HPW₁₂O₄₀) acid catalyst with silica support. The conversion of triglycerides is shown in Fig. 3.12(a). From this Fig. 3.12(a), it was observed that the conversion of triglycerides was found
to be augmented with increase in reaction temperature. The highest conversion of triglycerides was achieved at 65 °C. The highest conversion of triglyceride was obtained as 96 wt.% after reaching 20 min of reaction time with 1 wt.% of catalyst loading. Hence, the reaction temperature was selected as 65 °C which is called as methanol reflux temperature.

Fig. 3. 12 (a) Effect of temperature with respect to time at different temperature with constant parameters of 40 kHz sonication frequency, 20:1 mole ratio of methanol to oil and 1 wt% of Ca(HPW\text{12}O_{40})/SiO\text{2} catalyst

3.2.3.3. Effects of catalyst loading on transesterification reaction

The catalyst quantity used in reactions affects the reaction rate drastically though it doesn’t alter the equilibrium conversion for reversible reactions. Once, catalyst are having more activity, less amount of the catalyst is
required. In order to scrutinize the activity of Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ acid catalyst, a variety of mass ratios of catalyst to oil were used in transesterification reaction of *Adenanthera pavonina* seed oil with methanol. Reactions were carried at constant parameters of methanol reflux temperature (65 °C), 40 kHz of sonication frequency and 20:1 molar ratio of methanol to oil. Fig. 3.12(b) shows the effect of mass ratio of Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ acid catalyst to oil on the reaction. For Ca(HPW$_{12}$O$_{40}$)/SiO$_2$, 96.8% conversion was obtained at 20 min when 0.5 wt% of catalyst was used.

![Fig. 3.12 (b) Effect of Catalyst loading with constant parameters of 40 kHz sonication frequency, methanol reflux temperature and 20:1 molar ratio of methanol to oil.](image)

When the catalyst amount was used as 0.25 wt% and 0.75 wt%, the reaction rates were found to be less with the comparison of 0.5 wt%. The conversion of triglycerides was found to be increased with increasing the amount of catalyst from 0.25 wt% to 0.5 wt%. On the other hand insufficient amount of catalyst leads to the incomplete conversion of triglycerides into fatty
acid methyl esters. Same time further increase of 0.5 to 0.75 wt% proved to have negative impact of end product conversion due to the addition of excess amount of catalyst react with triglycerides to form more water. The excess of water content may affect the catalyst activity.

3.2.3.4. Effects of oil-methanol ratio on transesterification reaction

![Graph showing effect of methanol to oil ratio on transesterification reaction](image)

Fig. 3.12 (c) Effect of Methanol to Oil molar ratio with constant parameters of 40 kHz sonication frequency, methanol reflux temperature and 0.5 wt% of Ca(HPW\textsubscript{12}O\textsubscript{40})/SiO\textsubscript{2} catalyst.

The molar relative amount of alcohol to Adenanthera pavonina oil is one of the most significant factors that influences the conversion of triglyceride to methyl ester. As per the stoichiometric response, 3 moles of methanol are required per mole of triglyceride. In practical, the molar relative amount of methanol should be more than the stoichiometric ratio to drive the transesterification reaction to achieve complete conversion (Ramachandran et al
In this examination, the effect of molar ratio of methanol to *Adenanthera pavonina* oil was investigated with different molar ratios of 12:1, 16:1 and 20:1. Each reaction was run at methanol reflux temperature with 0.5 wt% of Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ acid catalyst and 40 kHz sonication frequency. The changes in conversion of triglyceride are shown in Fig. 3.12(c). The conversion of triglyceride was observed as 97.4% at the 16:1 molar ratio of methanol to *Adenanthera pavonina* oil with 20 min reaction time. The conversion of triglyceride was found to be increased with increase in molar ratio from 12:1 to 16:1. Further increase in molar ratio from 16:1 to 20:1 leads to decrease in the conversion of triglyceride. This is due to the presence of mass transfer limitation during the transesterification reaction.

### 3.2.3.5. Effects of catalyst reusability on transesterification reaction

One of the most significant properties of heterogeneous acid catalysts is the stability and the ability to be recycled. The reusability and lifetime of Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ acid catalyst were observed at methanol reflux temperature for 15 cycles. In all the cycles, the reaction parameters and the quantity of the reactants were kept constant. Once the reaction was completed, the reaction mixture was centrifuged and the solid catalyst was separated. This separated catalyst was reused for the next cyclic run. Fig. 3.12(d) shows the reusability behaviour of Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ acid catalyst. The result indicated that Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ have better stability and durability for the first 10 cyclic runs. The biodiesel yield was observed as 96.5% at 10$^{th}$ cycles when 0.5 wt% of Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ was used. A slight decrease in conversion of triglyceride was observed after 10 cycles. The conversion dropped to around 92% at the15th cycle. Both the catalyst and properties loss could be the reason for slight decrease in biodiesel conversion. It is possible that the catalyst could be lost by leaching and during the transfer of catalyst between the cycles.
Fig. 3.12 (d) Effect of reusability of catalyst at constant parameters of 40 kHz sonication frequency, methanol reflux temperature, 0.5 wt% of Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ catalyst, 16:1 mole ratio of methanol to oil and 15 min reaction time.

3.2.4. Reaction kinetics

- Calculation of Rate Constant, Activation Energy and Pre-exponential Factor.

Plots of ($X_A/1 - X_A$) versus (t) are shown in Fig. 3.13. Rate constant was calculated using the Fig. 3.13. Activation energy was calculated through the Arrhenius equation (E.q. 3.3).

$$-\frac{d(A)}{dt} = k(A)^2$$  \hspace{1cm} \ldots \ldots (3.9)
Fig. 3.13. A plot of $X_A/(1-X_A)$ versus $t$ at 45 °C, 55 °C and 65 °C for transesterification of *Adenanthera pavonina* seed oil.

Therefore, plots of $\ln k$ versus $1/T$ are shown in Fig. 3.14. Activation energy ($E_a$) and pre-exponential or frequency factor were calculated using Fig. 3.14 to be 63.24 kJ/mol and $2.15 \times 10^{12}$ sec$^{-1}$, respectively. Based on the proposed kinetic model, the kinetic parameters for this catalyst were determined. The experiments demonstrate that the reactions followed second-order kinetics. The proposed kinetic model describes the experimental results well and the rate constants follow the Arrhenius equation.

Activation energy is defined as the minimum energy required starting a chemical reaction. The activation energy of a reaction is usually denoted by $E_a$ and given in units of kilojoules per mole. The pre-exponential factor is the pre-exponential constant in the Arrhenius equation and empirical relationship between temperature and rate coefficient.
Calculation of Activation thermodynamic properties

The activation enthalpy ($\Delta H^\ddagger$), entropy ($\Delta S^\ddagger$) and the Gibb’s free energy of activation ($\Delta G^\ddagger$) were determined for all temperatures by the thermodynamics fundamental equations (E.q. 3.4, 3.5 and 3.6), respectively. The thermodynamic activation properties for transesterification of *Adenanthera pavonina* at different temperature were shown in Table 3.8. Thermodynamic activation parameters, enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) of the reaction evaluated based on activation transition theory showed the following values of 60.43 kJ mol$^{-1}$ and $-9.84$ J K$^{-1}$ mol$^{-1}$, respectively. Gibb’s free energy of activation ($\Delta G^\ddagger$) was found to be 63.75 kJ mol$^{-1}$ at optimized temperature of 65 °C. Indicated nonspontaneous, endergonic and endothermic characteristics, because of the values of $\Delta G^\ddagger$ and $\Delta H^\ddagger$ were positive and $\Delta S^\ddagger$ was negative.
Table 3.8. Activation thermodynamic properties of saga seed oil transesterification reaction at various temperatures.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Delta H^\ddagger$ (J mol$^{-1}$)</th>
<th>$\Delta S^\ddagger$ (J mol$^{-1}$K$^{-1}$)</th>
<th>$\Delta G^\ddagger$ (J mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>318</td>
<td>60596.08</td>
<td>-9.33</td>
<td>63562.75</td>
</tr>
<tr>
<td>328</td>
<td>60512.93</td>
<td>-9.59</td>
<td>63657.33</td>
</tr>
<tr>
<td>338</td>
<td>60429.78</td>
<td>-9.84</td>
<td>63754.45</td>
</tr>
</tbody>
</table>

Values of $\Delta S^\ddagger$ ($\Delta S^\ddagger < 0$) may arise as result of association mechanism, which means that the reactant species joined to each other to form over transition states along the reaction. Thus, the transition state structure is more ordered than the reactants in the ground state. Therefore, there is negative activation entropy. Meanwhile, $\Delta H^\ddagger$ values ($\Delta H^\ddagger > 0$) indicate that the process is endothermic. An external power source is needed to raise the energy level and transform the reactants to their transition state. Values of $\Delta G^\ddagger$ ($\Delta G^\ddagger > 0$) can be attributed to high energy level in the transition state rather than to the reacting species.

Other thermodynamic parameters determination

Thermodynamic Parameters of $\Delta S$ and $\Delta H$ were calculated based on the definition of Gibbs energy free using Eq.3.8 and using linear plot of ln $K_e$ versus ln $1/T$ (Fig. 3.15). Values of $\Delta S$ and $\Delta H$ were calculated as 10.37 kJ/mol and 45.85 kJ/mol.K, respectively.
Fig. 3.15. A plot of $\ln K_e$ versus $1/T$ for Transesterification of *Adenanthera pavonina* seed oil.

From the results (Table 3.9) of the thermodynamic parameters it was found that the transesterification reaction was an endothermic reaction and the reaction rate was found to be increased with increasing temperature. Moreover, enthalpy and entropy change were not affected by methanol concentration due to the excess addition.

Table 3.9. Calculated values of thermodynamic parameters

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$K_e$</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/mol K)</th>
<th>$\Delta G$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>318</td>
<td>4.87</td>
<td>10.37</td>
<td>45.84</td>
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<td>328</td>
<td>5.67</td>
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<td>45.84</td>
<td>-4.73</td>
</tr>
<tr>
<td>338</td>
<td>6.13</td>
<td>10.37</td>
<td>45.84</td>
<td>-5.09</td>
</tr>
</tbody>
</table>
3.3. BIODIESEL PRODUCTION FROM *Adenanthera pavonina* USING SrHPW$_{12}$O$_{40}$/SiO$_2$ AS A HETEROGENEOUS ACID CATALYST

In summary, tungstophoric acid is a promising solid catalyst for biodiesel production via transesterification of vegetable oils with methanol. However, the reaction rate is relatively higher but the reusability of tungstophoric is difficult due to the higher solubility in methanol and leaching highly occurs during the reaction. Using Sr(HPW$_{12}$O$_{40}$)/SiO$_2$ nano-sized particle is one way to improve the catalytic reusability and activity since the nano size leads to a relatively large surface area. Little work has been done to study the effect of the reaction temperature on the catalytic activity of nano powder Sr(HPW$_{12}$O$_{40}$)/SiO$_2$ on transesterification of vegetable oil with methanol. In this present work, the catalytic activity and stability of nano powder Sr(HPW$_{12}$O$_{40}$)/SiO$_2$ in transesterification of *Adenanthera pavonina* oil with methanol at elevated reaction temperatures has been investigated. Effects of various reaction conditions, such as the reaction temperature, the methanol/oil molar ratio, the catalyst amount, and the reaction time, on biodiesel yield have also been investigated under ultrasonic irradiation condition. Recycling experiments have been conducted in order to examine the stability and reusability of catalysts. The kinetics and the thermodynamic properties have been evaluated with respect to the temperature effects.

3.3.1. Characterization of Sr(HPW$_{12}$O$_{40}$)/SiO$_2$ catalyst

The physical properties value such as surface area, pore volume and pore size are presented in Table 3.10. As the SrTPA loading increases, surface area decreases relative to the support (Silica). The decrease in the surface area may be ascribed to the fact that as the SrTPA species enters the mesopores of
silica, there is filling of the pores and surface coverage. Decrease in the surface area is first indication of chemical interaction between SrTPA and silica.

### Table 3.10. Physical properties of Sr(HPW\textsubscript{12}O\textsubscript{40})/SiO\textsubscript{2}

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values with Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Surface area</td>
<td>52.043 m\textsuperscript{2}/g</td>
</tr>
<tr>
<td>2. Pore volume</td>
<td>58.1 Å</td>
</tr>
<tr>
<td>3. Pore size</td>
<td>0.048 cm\textsuperscript{3}/g</td>
</tr>
</tbody>
</table>

The N\textsubscript{2} adsorption-desorption isotherms of pure SrTPA/SiO\textsubscript{2} are of type IV according to the IUPAC classification and exhibited a H1 hysteresis loop was shown in Fig. 3.16 (a) and (b).

*Fig. 3.16 (a) N\textsubscript{2} adsorption–desorption isotherms of Sr(HPW\textsubscript{12}O\textsubscript{40})/SiO\textsubscript{2} catalyst*

A sharp increase in the isotherm between relative partial pressures 0.2 and 0.4 during adsorption and desorption indicates capillary condensation
of N\textsubscript{2} in the mesopores, which is characteristic of mesoporous materials. Also, considerable adsorption amounts indicate that there is a considerable volume of nanospaces even after the introduction of SrTPA species.

![Fig. 3.16 (b) N\textsubscript{2} adsorption-desorption isotherms of Sr(HPW\textsubscript{12}O\textsubscript{40})/SiO\textsubscript{2} catalyst](image)

The position of the inflection point is related to the diameter of the mesopores, and the sharpness of the step designates the uniformity of the mesopore size distribution. In addition, a narrow pore size distribution was observed for the SrTPA/SiO\textsubscript{2}, indicating long range order over large scales. Slight broadening may be due to the introduction of SrTPA inside the pores of silica. The decrease in pore volume in catalyst is due to presence of SrTPA inside the channels of Silica.

A FT-IR spectrum of Silica shows a broad band around 1100 corresponding to asymmetric stretching of Si-O-Si (Fig. 3.17 (a)). The bands at 1100 to 1200 and 458 cm\textsuperscript{-1} are due to symmetric vibrations of Si-O-Si and
bending vibrations of Si-O, respectively. The obtained bands are in good agreement with the reported literature (Yijun and Shuijin 2008).

Fig. 3.17 (a) FTIR spectra of SiO$_2$, H$_3$PW$_{12}$O$_{40}$, CaHPW$_{12}$O$_{40}$ and Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ catalyst.

The typical bands for TPA (Kozhevnikov et al 1996) at 982 cm$^{-1}$ corresponding to $V_{as}$ vibration of W = O$_d$ (terminal oxygen linked to a lone tungsten atom), and 897 cm$^{-1}$ for stretching vibrations of W-O$_b$-W (corner sharing oxygen’s of two different triads of tungsten atom) are clearly observed in SrTPA/SiO$_2$. Appearance of these fingerprint bands strongly indicate that the
primary structure of TPA is completely retained even after impregnation on the support. The absence of vibration band at 1080 cm⁻¹ ($V_s$ stretching of P-O) in TPA may be due to superimposition on the bands of SiO₂.

The XRD patterns of these samples are shown in Fig. 3.17(b). The characteristic peaks of bulk HPW were observed at 2θ of 20.6, 22.4 and 30.4. There were apparent characteristic peaks of HPW on $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{CaHPW}_{12}\text{O}_{40}$ and $\text{CaHPW}_{12}\text{O}_{40}/\text{SiO}_2$ catalysts. It meant that all the samples maintained the structure of HPW. When the more calcium-salts introduced to HPW, the weaker diffraction of HPW displayed. It indicated that the calcium-salts had an influence on the crystal structure of HPW. After immobilization of calcium tungstophosphate on silica carrier, the diffraction peaks of the sample became very weak.

![Fig. 3.17 (b) XDR of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, Sr$\text{HPW}_{12}\text{O}_{40}$ and Sr(HPW$_{12}$O$_{40}$)/SiO$_2$ catalyst.](image-url)
Thermogravimetric analysis result of SrHPW/SiO$_2$ is shown in Fig. 3.17(c), it was seen that SrHPW/SiO$_2$ catalyst as synthesized has gone through two weight loss stages with the increase in testing temperature.

**Fig. 3.17 (c)** TGA (Thermogravimetric analysis) of Ca(HPW$_{12}$O$_{40}$)/SiO$_2$ catalyst.

The first weight loss stage before 200 °C was associated with the elimination of some hydration water and physically absorbed water derived from silica and heteropolyacid salt and the second loss stage in the region of 200–500 °C corresponded to the loss of constitutional water and the beginning of decomposition of heteropolyacid salt’s Keggin structure. When the catalyst SrHPW/SiO$_2$ was calcined above 540 °C, weight loss was observed in the SrHPW/SiO$_2$ pattern, which indicates the presence of strontium degradation.
Fig. 3.18(a) Energy dispersive X-ray (EDX) analysis of SrTPA/SiO₂.

Fig. 3.18(a), shows the EDX analysis and confirms that the presence of elements as P, W and Ca in the catalysts with the silica peak. The EDX analyses show that the Sr(HPW₁₂O₄₀)/SiO₂ catalysts have been synthesized successfully step by step. The analyzed values were almost equivalent to the predicted values (Table 3.11).

**Table 3.11.** Compression of analytical and predicted elemental values of Sr(HPW₁₂O₄₀)/SiO₂.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Mass percent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
</tr>
<tr>
<td>O</td>
<td>24.49</td>
</tr>
<tr>
<td>P</td>
<td>0.95</td>
</tr>
<tr>
<td>Si</td>
<td>4.28</td>
</tr>
<tr>
<td>Sr</td>
<td>2.68</td>
</tr>
<tr>
<td>W</td>
<td>67.56</td>
</tr>
</tbody>
</table>

From the Fig. 3.18(b), the spherical shapes with un-uniform size of the particles can be seen in the Sr(HPW₁₂O₄₀)/SiO₂ catalyst. The SEM image shows that the silica surface is well covered by Calcium salt of tungstophoric,
which is reliable with a sharp decrease in BET surface area of the silica after successful impregnation of catalyst. The calcium nitrate exhibited a loose irregular network structure.

![SEM image of Sr(HPW$_{12}$O$_{40}$)/SiO$_2$.](image)

**Fig. 3.18 (b) SEM image of Sr(HPW$_{12}$O$_{40}$)/SiO$_2$.**

The presence of pores became larger when the Sr(NO$_3$)$_2$ was treated with tungstophoric solution. The larger amounts of pores and larger pore size would increase the accessibility of HPW into the Calcium bulk, which would give a higher concentration of covalent bonded Calcium with an HPW group. The prepared acid catalyst has granular nano size and mesoporous structure. From the FTIR, it was observed that the arrangement of Keggin anion were not distorted with the replacement of calcium for the protons of heteropolyacids. Acid-Base titration method was used for the determination of H$^+$ content of the catalyst by titrating with NaOH. The value of H$^+$ content was obtained as 0.029%.
3.3.2. Biodiesel characterization

IH-NMR spectra of *Adenanthera Pavonina* biodiesel are shown in Fig. 3.19. An attribute gesture produced from the protons of methylene group neighbouring to the ester group of a molecule in TG (a-CH2) was eluted at 2.3 ppm and the protons in the methoxy cluster of the methyl ester were detected at 3.66 ppm. The conversion of biodiesel was executed based on these attribute proton signals in the NMR spectra. The conversion of the methyl ester from Saga seed oil was determined as 95.6 wt%.

![H-NMR Spectra of Adenanthera pavonina Biodiesel using SrTPA/SiO2 catalyst.](image)

Fig. 3.19 $^1$H-NMR Spectra of *Adenanthera pavonina* Biodiesel using SrTPA/SiO2 catalyst.
3.3.3. Reaction Studies on SrTPA/SiO$_2$

Present reaction studies were investigated for transesterification of Adenanthera pavonina seed oil catalyzed by silica supported SrHPW$_{12}$O$_{40}$ with methanol. The different parameters effect was performed such as temperature, methanol-oil molar ration, catalyst quantity and reusability of SrTPA/SiO$_2$ catalyst. These reaction conditions were designed under ultrasonication effect.

3.3.3.1. Temperature effect on transesterification

_Adenanthera pavonina_ oil initially needs to activate their respective carbonyl functions to start the reaction. The long alkyl chains in a triglyceride molecule can interfere with the activation of its carboxylic group. The activation of the triglyceride is very difficult. In order to favor the methanol nucleophilic attack on the triglyceride, a comparatively high reaction temperature is needed to activate this carbonyl group. Thus, the experiments using the SrTPA/SiO$_2$ acid catalyst were conducted at 45, 55 and 65 °C. The conversion of triglyceride is shown in Fig. 3.20a. From the Fig. 3.20a, it was observed that the conversion of triglyceride was found to be increased with increase in reaction temperature. The equilibrium conversion of triglyceride was found to be almost reached by 30 min. The highest conversion of triglyceride was obtained as 95.8 wt.% after reaching 30 min reaction time at 65°C. At high temperature above 65 °C and long reaction time the triglyceride will required pressurised reactor system and the pressurised reaction only possible in a continuous process to get proper mixing of reactants with catalyst to some extent (Shu et al., 2009). Hence, the reaction temperature was selected as 65 °C.
Fig. 3.20a. Effect of reaction temperature on biodiesel production at 1wt% of catalyst, 20:1 molar ratio of methanol to oil under sonication of 40 kHz frequency.

3.3.3.2. Effect of Methanol-Oil molar ratio

The excess amount of methanol needs to force the reaction towards the formation of methyl esters (Yee et al., 2011). From Fig. 3.20b, it was observed that the conversion of triglyceride was found to increase with increase in the molar ratio of methanol and oil from 12:1 to 16:1 and then decreased with increase in the molar ratio of methanol and oil above 16:1. The increased molar ratio will increase the transesterification reaction and produce more water. However, the production of more water will reduce the rate of the transesterification reaction. From the above analysis, it was observed that the molar ratio of 16:1 was found to be an optimum ratio for the maximum conversion of triglyceride. Phan and Phan (2008) also found a similar trend in their work. The conversion of waste cooking oil was reported as 88 wt.% for a
methanol and mixed oil molar ratio of 8:1. This gradually decreased to 82 wt.% when the molar ratio was increased to 12:1 for the reaction period of 80 min.

![Graph](b.png)

**Fig. 3.20b.** Effect of methanol to oil molar ratio on biodiesel production at 65 °C with 1wt% of catalyst under sonication of 40 kHz frequency.

### 3.3.3.3. Effect of SrTPA/SiO$_2$ catalyst loading

The amount of catalyst was also affecting the rate of reaction. The higher catalyst loading is required to increase the availability of active sites (Yee et al., 2011). The SrHPW$_{12}$O$_{40}$/SiO$_2$ acid catalyst was used to study the effect of catalyst loading (0.5, 0.75 and 1 wt.%) with reaction temperature of 65 °C and molar ratio of methanol/mixed oil as 16:1. The conversion result is shown in Fig. 3.20c. The conversion of triglyceride was found to be increased with increase in the catalyst loading from 0.5 to 0.75 wt.% and then decreased with increase in the catalyst loading above 0.75 wt.%. The conversion of triglyceride was found to be maximum at 0.75 wt.% of catalyst loading when
compared to 1 and 0.25 wt.% of catalyst loading. This may be due to the formation of more water produced at higher catalyst loading. So the excess of water content may affect the catalyst and transesterification reaction. Qiu et al. (2011) also observed similar results, when the catalyst amount increased from 2.0% to 6.0%, the biodiesel production yield was increased from 71.09% to 98.03%. However, with further increase in the catalyst amount reduced the biodiesel yield.

**Fig. 3.20c.** Effect of catalyst of SrTPA/SiO$_2$ loading on biodiesel production at 65 °C with 16:1 molar ratio of methanol to oil under sonication of 40 kHz frequency.

### 3.3.3.4. Reusability effect of catalyst on transesterification

The catalyst reusability is one of main key factor to be considered to minimize the biodiesel production cost. In this present investigation, the catalyst was recycled to test its activity as well as stability. After the completion of transesterification reaction the catalyst was recovered from the reaction
mixture by filtration. The recovered catalyst was charged for the subsequent runs without any further pre-treatment such as washing and calcination. After each run, the catalyst was collected quantitatively and the same procedure was carried out to recover the catalyst after each cycle. The reusability investigation test was shown in Fig. 3.20d. From this investigation, observed that there were no appreciable changes in % conversion of *Adenanthera pavonina* seed oil using regenerated SrHPW$_{12}$O$_{40}$/SiO$_2$ catalyst up to fifteen transesterification reaction cycles.

![Fig. 3.20d](image)

**Fig. 3.20d.** Effect of reusability of catalyst SrTPA/SiO$_2$ on biodiesel production at 65 °C with 16:1 molar ratio of methanol to oil and 0.75 wt% of catalyst under sonication of 40 kHz frequency.

### 3.3.4. Kinetics

The kinetics parameters of transesterification reaction were investigated by subjecting conversion of triglycerides at temperatures of 45, 55 and 65 °C. Then, rate constants (k) were determined applying the values of
conversion ($X_A$) versus time ($t$), where slope and intercept of the line represent the values of $kC_{A0}$ at each temperature.

A plot of $X_A/(1-X_A)$ versus $t$ at different temperature was shown in Fig. 3.21, it can be observed that temperature increase leads to larger line slope, increasing the rate constant ($k$) value and showing the temperature dependence on the transesterification process. The calculated $k$ values and $R^2$ values were shown in Table Table 3.12.

![Graph showing the relationship between $X_A/(1-X_A)$ and time at different temperatures](image)

**Fig. 3.21.** A Plot of $X_A/(1-X_A)$ versus $t$ at different temperature.

**Table 3.12.** Rate constant ($k$) and Determination Coefficient ($R^2$).

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>$k$ (ml/mol.sec)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>70.53</td>
<td>0.9507</td>
</tr>
<tr>
<td>55</td>
<td>150.74</td>
<td>0.9376</td>
</tr>
<tr>
<td>65</td>
<td>273.43</td>
<td>0.9389</td>
</tr>
</tbody>
</table>
The quantitative relationship between assays temperature, rate constant and activation energy can be expressed by Arrhenius equation. According to this equation, the graphical representation of ln k versus 1/T (K⁻¹) gives a straight line with slope and intercept of −Ea/R and ln A (Fig. 3.22), which enables the determination of activation energy (Ea) as 60.6 kJ/mol and pre-exponential factor (A) as 6.47 x 10¹¹ sec⁻¹, respectively.

![Graph](image)

**Fig. 3.22.** A plot of ln(k) versus 1/T.

### 3.3.5. Thermodynamic properties

The thermodynamic activation parameters (ΔH°, ΔS° and ΔG°) for Adenanthera pavonina oil transesterification reaction were calculated using an equation (E.q. 3.4, 3.5 and 3.6) according to transition state theory. These activation thermodynamic parameters are shown in Table 3.13 for each temperature.
Table 3.13. The thermodynamic activation parameters for saga seed oil transesterification reaction at various temperatures.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Delta H^\ddagger$ (J mol$^{-1}$)</th>
<th>$\Delta S^\ddagger$ (J mol$^{-1}$K$^{-1}$)</th>
<th>$\Delta G^\ddagger$ (J mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>318</td>
<td>57957.89</td>
<td>-19.339</td>
<td>64107.94</td>
</tr>
<tr>
<td>328</td>
<td>57874.74</td>
<td>-19.597</td>
<td>64302.64</td>
</tr>
<tr>
<td>338</td>
<td>57791.6</td>
<td>-19.847</td>
<td>64499.86</td>
</tr>
</tbody>
</table>

These values indicate that the transesterification reaction are nonspontaneous, endergonic and endothermic characteristics, because the values of $\Delta G^\ddagger$ and $\Delta H^\ddagger$ were positive and $\Delta S^\ddagger$ was negative.

The thermodynamic parameters of $\Delta H$, $\Delta S$ and $\Delta G$ for the transesterification of saga seed oil can be estimated using the equation 3.8. At equilibrium, none of the oil reaction changes with time.

The plot of $\ln K_e$ versus $1/T$ (Fig. 3.23) gives a straight line with the slope representing the enthalpy change of transesterification reaction and the intercept representing the entropy change. The enthalpy change and entropy change was calculated as $\Delta H = 10.37$ kJ/mol and $\Delta S = 45.85$ J/mol K for saga seed transesterification reaction, respectively. The $\Delta H$ value obtained indicated the physicochemical nature of the transesterification process. The positive value for enthalpy indicates that the oil transesterification process is endothermic and requires energy input during the process.
Fig. 3.23. A plot of ln$K_e$ versus $1/T$.

Table 3.14. Calculated values of thermodynamic parameters

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>$K_e$</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/mol K)</th>
<th>$\Delta G$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>318</td>
<td>4.867</td>
<td>10.366</td>
<td>45.845</td>
<td>-4.184</td>
</tr>
<tr>
<td>328</td>
<td>5.667</td>
<td>10.366</td>
<td>45.845</td>
<td>-4.731</td>
</tr>
<tr>
<td>338</td>
<td>6.133</td>
<td>10.366</td>
<td>45.845</td>
<td>-5.097</td>
</tr>
</tbody>
</table>

Other thermodynamic parameter $\Delta G$ and the equilibrium constant values for transesterification reaction are given in Table 3.14 for each temperature. An increase in the entropy change and a decrease in the free energy indicate that the process is spontaneously forward. The positive value of entropy change ($\Delta S > 0$) at $T \geq 65$°C indicates that the process is irreversible. Thus, the transesterification process at the lower temperature is not suitable for saga seed oil, because the equilibrium constant is very low at the temperature lower than 55 °C as shown in Table 3.14.
3.3.6. Properties of Biodiesel

Table 3.15. Properties of biodiesel from Adenanthera pavonina using CaHPW/SiO$_2$ and SrHPW/SiO$_2$ catalysts with ASTM and EN standards.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Obtained Biodiesel</th>
<th>Diesel</th>
<th>Biodiesel ASTM D975</th>
<th>Biodiesel ASTM D6751</th>
<th>Biodiesel EN 14214</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaTPA/SiO$_2$</td>
<td>SrTMAP/SiO$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (Kg L$^{-1}$)</td>
<td>0.86</td>
<td>0.87</td>
<td>0.85</td>
<td>0.82-0.90</td>
<td>0.86-0.90</td>
</tr>
<tr>
<td>Kinematic viscosity (mm$^2$ s$^{-1}$) at 40°C</td>
<td>4.3</td>
<td>4.5</td>
<td>2.6</td>
<td>1.9-6.0</td>
<td>3.5-5.0</td>
</tr>
<tr>
<td>Flash point °C</td>
<td>134</td>
<td>137</td>
<td>68</td>
<td>130 min</td>
<td>120 min</td>
</tr>
<tr>
<td>Cloud point °C</td>
<td>2</td>
<td>3</td>
<td>-15 to 5</td>
<td>-3 to 12</td>
<td>-</td>
</tr>
<tr>
<td>Pour point °C</td>
<td>-2.5</td>
<td>-2</td>
<td>-35 to -15</td>
<td>-15 to 10</td>
<td>-</td>
</tr>
<tr>
<td>Cetane number</td>
<td>53</td>
<td>52</td>
<td>48</td>
<td>47 min</td>
<td>51 min</td>
</tr>
<tr>
<td>Water content (wt %)</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.05 max</td>
<td>0.05 max</td>
</tr>
<tr>
<td>Ash content (wt %)</td>
<td>0.005</td>
<td>0.005</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The properties of biodiesels are shown in Table 3.15, and also compared the properties of biodiesel with conventional diesel, ASTM D6751 and EN 14214. However, the properties of biodiesel such as density, kinematic viscosity, flash point, cloud point, pour point, cold filter plugging point, cetane number, water content and ash content have comparable with conventional diesel and met the limits of the biodiesel standard of ASTM D6751 and EN 14214 (Table 3.15).
3.4. BIOFUEL ADDITIVES PRODUCTION FROM BYPRODUCT OF GLYCEROL USING CaHPW_{12}O_{40}/SiO_{2} AS A HETEROGENEOUS ACID CATALYST

In this division, calcium salt of tungstophoric acid catalyst supported on silica was used as a heterogeneous catalyst to catalyze the acetylation reaction using byproduct of glycerol as a reactant to get biofuel additives as product and the process parameters were optimized.

3.4.1. Comparison of catalytic and non catalytic processes

In this experimental study, acetylation reactions were carried out for both catalytic and non catalytic process under the same parameter condition. The conversion of these two processes has been studied.

![Comparison of catalytic and non catalytic processes](image)

**Fig. 3.24.** Comparison of the catalytic and non catalytic acetylation process on glycerol conversion and selectivity of MG, DG & TG at 120 °C, 2 wt% of catalyst, 9:1 M ratio of Acetic acid to glycerol up to 30 min under sonication.
This acetylation comparison study was carried out with the use of 2 wt% of silica supported calcium salt of tungstophoric acid as a catalyst, the temperature of 120 °C, 9:1 molar ratio of Acetic acid to glycerol and reaction time up to 30 min under the ultrasonication process condition (40 kHz). The conversion of glycerol with respect to the reaction time was shown in Fig. 3.24. The conversion of glycerol with the use of Ca(HPW₁₂O₄₀)/SiO₂ catalyst was found to be significantly more than that of non-catalytic process.

3.4.2. Effect of reaction time on glycerol acetylation

The reaction profile over Ca(HPW₁₂O₄₀)/SiO₂ acid catalyst with different reaction time was observed and the effects are shown in Fig. 3.25. The conversion of glycerol was attained very high even at 8th min to get monoacrylglycerol and the overall conversion was found within 15th min.

Fig. 3.25. Effect of reaction time on glycerol conversion and selectivity of MG, DG and TG at 120 °C with 2 wt% of catalyst and 9:1 M ratio of Acetic acid to glycerol under sonication.
At the initial start of the acetylation reaction, the selectivity in the direction of formation of monoacylglycerol reaction was prolonged in the forward direction of diacyl and triacylglycerol formation at the expense of monoacylglycerol. The selectivity for diacyl and triacylglycerol formation increased with increase in time was essential due to the additional acetylation of monoacyl. The glycerol conversion is nearly completed within the reaction time period of 15 min. Consequently, the reaction time was selected as 15 min.

3.4.3. Effect of reaction temperature on glycerol acetylation

Crude glycerol, in the beginning wants to stimulate their particular carbonyl functions to initiate the reaction. The conversion effect of glycerol is shown in Fig. 3.26. From this investigation, it was observed that the conversion of glycerol was found to be increased with increase in reaction temperature.

Fig. 3.26. Effect of reaction temperature on glycerol conversion and selectivity of MG, DG and TG with 2 wt% of catalyst, 9:1 M ratio of Acetic acid to glycerol and 15 min of reaction time under sonication.
The Monoacylglycerol formation was leading at lowest reaction temperature. As the reaction temperature was increased from 50 to 120 °C, an identical augmentation in conversion was observed from 42.5% to 98.6%. The selectivity towards diacyl and triacylglycerol was predominant in the temperature range of 50 to 120 °C. The equilibrium conversion was attained at 120 °C after 15 min of reaction time period and 9:1 molar ratio of Acetic acid to glycerol with 2 wt% of Ca(HPW_{12}O_{40})/SiO_{2} under sonication. Hereafter, 120 °C was preferred as the process temperature for further reaction studies.

### 3.4.4. Effect of catalyst loading on glycerol acetylation

The quantity of catalyst loading was increasing the rate of reaction. The superior catalyst addition was essential to augment the availability of active sites to enhance the reaction rate.

![Fig. 3.27](image_url)

**Fig. 3.27.** Effect of catalyst loading on glycerol conversion and selectivity of MG, DG and TG at 120 °C with 9:1 M ratio of Acetic acid to glycerol and 15 min of reaction time under sonication.
The effects of catalyst loading was investigated by varying the quantity of silica supported calcium salt of tungstophoric acid (Ca(HPW\textsubscript{12}O\textsubscript{40})/SiO\textsubscript{2}) catalyst in the range of 0 to 2 wt% at 120 °C of reaction temperature, 20 min of reaction time and 9:1 molar ratio of acetic acid to glycerol under sonication of 40 kHz frequency. The result is shown in Fig. 3.27. From this investigation, the result was found that the glycerol conversion and selectivity of mono, di and triacylglycerol found to be increased from 23, 15, 6 and 2 wt% to 98.6, 43.9, 29.4 and 25.3 wt% with increase in catalyst quantity of 0 to 1.5 wt%. Further increase in the addition of Ca(HPW\textsubscript{12}O\textsubscript{40})/SiO\textsubscript{2} catalyst did not show much improvement in the conversion. Suitable catalyst quantity was selected as 1.5 wt% for the next studies.

3.4.5. Effect of molar ratio of glycerol to acetic acid on acetylation reaction

![Graph](image)

**Fig. 3.28.** Effect of molar ratio of Glycerol to Acetic acid on glycerol conversion and selectivity of MG, DG and TG at 120 °C with 1.5 wt% of catalyst and 15 min of reaction time under sonication.
Conversion of glycerol and selectivity of mono, di and triacylglycerol during acetylation of raw glycerol depends on molar ratio of glycerol to acetic acid. The effect of glycerol to acetic acid molar ratio on glycerol acetylation reaction from the range of 1:3 to 1:9 was considered and the results were shown in Fig. 3.28. The glycerol conversion was slightly varied with a change in molar ratio of glycerol to acetic acid. The conversion of glycerol was found to be enhanced with increase in the ratio of glycerol to acetic acid and maximum conversion was attained as 98.6 wt% at a ratio of 1:6. The conversion was not changed above the molar ratio of 1:6. Conversely, the selectivity’s are differed with increase in glycerol to acetic acid molar ratio. High monoacylglycerol was formed at lower molar ratio and its selectivity trim down with increase in molar ratio of glycerol to acetic acid. In addition, di and triacylglycerol was found to be increased with increase in acetic acid concentration.

3.4.6. Biofuel additives characterization

Samples were withdrawn periodically at different time intervals and analyzed by gas chromatography (GC) followed by Mass Spectrometry (MS). The conversion of glycerol and the selectivities are calculated as follows. The GC-MS results of biofuel additives conversion for CaHPW/SiO₂ catalyst are shown in Fig. 3.29.

\[
\text{The conversion of glycerol} = \frac{\text{Number of glycerol mols reacted}}{\text{Total number of glycerol mols taken}}
\]  
(3.9)

\[
\text{Selectivity} = \frac{\text{No of moles of desired product}}{\text{Total no of moles of all products}}
\]  
(3.10)
Fig. 3.29. GC-MS of Acetylated glycerol using CaHPW/SiO\textsubscript{2} catalyst.
3.5. BIOFUEL ADDITIVES PRODUCTION FROM BYPRODUCT OF GLYCEROL USING SrHPW\textsubscript{12}O\textsubscript{40}/SiO\textsubscript{2} AS A HETEROGENEOUS ACID CATALYST

In this Section, SrTPA/SiO\textsubscript{2} catalyst was used as a heterogeneous catalyst to catalyze the byproduct of glycerol by acetylation reaction for biofuel additives production and the reaction studies were investigated.

3.5.1. Effect of reaction time on glycerol acetylation

Different experiments were examined in order to evaluate the effect of reaction time. The reaction time varied from 0 to 30 min and the outcomes are shown in Fig. 3.30.

![Fig. 3.30. Effect of reaction time on glycerol conversion and selectivity of MG, DG and TG at 120 °C with 2 wt\% of catalyst and 9:1 M ratio of Acetic acid to glycerol under sonication.](image-url)
As expected in the beginning of the acetylation reaction, the selectivity towards monoacetin was high. However, as the reaction continued the selectivity towards diacetin and triacetin increased due to the expense of monoacetin. This increase in selectivity to diacetin and triacetin over time was mainly corresponded to the further acetylation of monoacetin, as the glycerol conversion were being completed from 0 to 15 min. Therefore, SrTPA/SiO$_2$ was highly selective catalyst for producing monoacetin in lower reaction times.

3.5.2. **Effect of reaction temperature on glycerol acetylation**

![Graph showing the effect of reaction temperature on glycerol conversion and selectivity](image)

**Fig. 3.31.** Effect of reaction temperature on glycerol conversion and selectivity of MG, DG and TG with 2 wt% of catalyst, 9:1 M ratio of Acetic acid to glycerol and 15 min of reaction time under sonication.

The effect of reaction temperature was examined and the results are shown in Fig. 3.31. Glycerol conversion and selectivity depend on both the nature of the catalyst and the temperature of the acetylation reaction. The conversion of glycerol increased slightly with an increase in the acetylation reaction temperature. That should be due to the fact that as the reaction
temperature increased from 50 to 120 °C, the formation of diacetin and triacetin was predominant, whereas the monoacetin production was preferred in lower reaction temperatures. Similar selectivity’s and activities were achieved by using dodecatungstophosphoric acid, immobilized into silica matrix at 120 °C (Chimienti et al 2001).

3.5.3. **Effect of catalyst loading on glycerol acetylation**

The quantity of catalyst loading was distressing the rate of reaction. The superior catalyst shipments were essential to augment the availability of active sites to enhance the reaction rate.

![Graph showing effect of catalyst loading on glycerol conversion and selectivity](image)

**Fig. 3.32.** Effect of catalyst loading on glycerol conversion and selectivity of MG, DG and TG at 120 °C with 9:1 M ratio of Acetic acid to glycerol and 15 min of reaction time under sonication.

The effects of catalyst loading was investigated by varying the quantity of silica supported calcium salt of tungstophoric acid (Sr(HPW₁₂O₄₀)/SiO₂) catalyst in the range of 0 to 2 wt% at 120 °C of reaction
temperature, 20 min of reaction time, 9:1 molar ratio of acetic acid to glycerol under sonication of 40 kHz frequency. The result was shown in Fig. 3.32. From this investigation, the result was found that the glycerol conversion and selectivity of mono, di and triacylglycerol increased from 23, 15, 6 and 2 wt% to 99.2, 42.0, 31.2 and 26.0 wt% with increase in catalyst quantity of 0 to 1.5 wt%. Further increase in the addition of Sr(HPW_{12}O_{40})/SiO_{2} catalyst did not shows much improvement in the conversion. Suitable catalyst quantity selected as 1.5 wt% for the next studies.

3.5.4. Effect of glycerol to acetic acid molar ratio on glycerol acetylation

Fig. 3.33. Effect of molar ratio of Glycerol to Acetic acid on glycerol conversion and selectivity of MG, DG and TG at 120 °C with 1.5 wt% of catalyst and 15 min of reaction time under sonication.

Conversion of glycerol and selectivity of mono, di and triacylglycerol during acetylation of raw glycerol moreover depend on molar ratio of glycerol to acetic acid. The effect of glycerol to acetic acid molar ratio
on glycerol acetylation reaction from the range of 1:3 to 1:9 was considered and the results were shown in Fig. 3.33. The glycerol conversion was slightly varied with a change in molar ratio of glycerol to acetic acid. The conversion of glycerol was found to be enhanced with increase in the ratio of glycerol to acetic acid and maximum conversion was attained as 99.2 wt% at a ratio of 1:6. The conversion was not changed above the molar ratio of 1:6. Conversely, the selectivity’s are differed with increase in glycerol to acetic acid molar ratio. High monoacylglycerol was formed at lower molar ratio and its selectivity trim down with increase in molar ratio of glycerol to acetic acid. In addition, di and triacylglycerol was found to be increased with increase in acetic acid concentration.

3.5.5. **Biofuel additives characterization**

Samples were withdrawn periodically at different time intervals and analyzed by gas chromatography (GC) followed by Mass Spectrometry (MS). The GC-MS results of biofuel additives conversion for CaHPW/SiO₂ catalyst are shown in Fig. 3.34. The overall conversion and selectivities were calculated by using equation 3.9 and 3.10, respectively.

![Fig. 3.34. GC-MS of Acetylated glycerol using SrHPW/SiO₂ catalyst.](image)