Chapter 5
Catalytic Action of CuAlS$_2$ Micro-Particles and Nanoparticles in Cellulose Pyrolysis
5.1. INTRODUCTION

The human civilization from the start has intended to control and regulate the different sources of energy available on earth. Of the various available energy sources on earth, the fossil fuel has been one of the largest energy sources to human from time immemorial. With the progress of human civilization, the efficacy of energy increased. The increase in the energy demand led to environmental impact. The non renewable energy sources started depleting and large energy generation led to environmental hazard. So researchers tried to minimize the hazard and optimize the energy extract. In the fossil fuel category, biomasses comprise sources such as wood, agricultural crops cultivated for energy purpose, forest and agricultural residues. Biomass contains stored chemical energy, originally derived from the sun energy.

The controlled thermochemical conversion process is one of the basic ways of converting biomass into fuels. The conversion process in the presence of atmospheric oxygen is known as biomass gasification. While the conversion process taking place in inert atmosphere is known as biomass pyrolysis. The dry biomass consists of 88% to 99.9% organic compounds like cellulose, hemicellulose and lignin. In them, the cellulose is the major constituent contributing about 40-45%. Thus in energy extraction by biomass gasification or pyrolysis, cellulose is the main constituent. To augment gasification or pyrolysis process, catalysts play an important role. Catalysts in nano forms have been found to be more effective than bulk form [1, 2]. Thus the authors thought to study the catalytic effect of copper aluminium disulphide (CuAlS$_2$).

In this paper the authors studied the catalytic action of CuAlS$_2$ micro-particles and nanoparticles on cellulose pyrolysis. The study was performed by analysing the recorded simultaneous thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves. The CuAlS$_2$ micro-particles were synthesized by heating precursors at high temperature in an evacuated ampoule. Literature shows that CuAlS$_2$ nanoparticles have been synthesized by different techniques, such as nanoparticles by facile heat arrested method [3], nanocrystals by colloidal route [4], nanocrystals by ball milling [5], nanowires by the direct polyl method [6], nanorods by wet chemical method
[7], etc. Among all these synthesis methods, the wet chemical method is the most convenient, less expensive and easy to tailor the chemistry of the nanoparticles. Thus the author synthesized CuAlS$_2$ nanoparticles by the wet chemical method.

The as-synthesized CuAlS$_2$ micro-particles and nanoparticles were comprehensively characterized for, stoichiometry, structure, surface morphology and thermal stability. After complete characterizations, the micro-particles and nanoparticles were used as catalyst in cellulose pyrolysis. The obtained results are discussed in details.

5.2. EXPERIMENTAL PROCEDURE

5.2.1. SYNTHESIS OF CuAlS$_2$ MICRO-PARTICLES

In CuAlS$_2$ micro-particles synthesis, copper (99.999%), aluminium (99.97%) and sulphur (99.999%) [Johnson-Mathey Chemicals Ltd., UK] powders were taken in stoichiometric proportions and sealed in an evacuated (~10$^{-6}$ torr) pre-cleaned quartz ampoule. The powders were thoroughly mixed by rigorous physical shaking of the sealed ampoule and the sealed powder was spread evenly all throughout the ampoule. The ampoule was then loaded in the two-zone horizontal furnace. The temperature of the ampoule was raised to 1000°C with the slow heating rate of 0.3°C·min$^{-1}$ and maintained at this temperature for 72 hours. Slow heating is required to avoid explosion due to generation of high sulphur pressure with temperature. After that the temperature was brought down to ambient temperature. The synthesized compound was unloaded from the ampoule. The compound was homogenized by grinding with agate mortar to yield CuAlS$_2$ micro-particles. The as synthesized CuAlS$_2$ micro-particles were characterized before use as catalyst in cellulose pyrolysis. The micro size CuAlS$_2$ particles were used for the catalytic studies by sieving the grounded powder.

5.2.2. SYNTHESIS OF CuAlS$_2$ NANOPARTICLES

The CuAlS$_2$ nanoparticles were synthesized by simple wet chemical technique. Cupric chloride (CuCl$_2$•2H$_2$O) [S D Fine-Chem. Ltd., Mumbai, India], triethanolamine (TEA)
(C₆H₁₅NO₃) [Sisco Chem. Pvt. Ltd., Mumbai, India], aluminium chloride (AlCl₃•6H₂O) [Oxford Laboratory, Mumbai, India], ammonia liquid (NH₃) [Chiti-Chem Corporation, Vadodara, India], sodium hydroxide pellets (NaOH) [Loba Chemie, Mumbai, India] and thiourea (NH₂CSNH₂) [Chiti-Chem Corporation, Vadodara, India] were used for the synthesis of CuAlS₂ nanoparticles.

In the synthesis of CuAlS₂ nanoparticles by wet chemical method, initially 10 ml of 0.5M copper (II) chloride (CuCl₂•2H₂O) solution was mixed with 5 ml of 3.7M TEA solution in a 100ml clean glass beaker under continuous stirring for 5 minute. The CuCl₂•2H₂O acts as precursor for Cu and TEA acted as complexing agent to slow down the release of the metal ions resulting in slow precipitation of the compound by ion-ion reaction and to prevent the agglomeration. Then in the above solution, 16 ml of 7.6M NH₃ solution was added and stirred for 5 minute. In continuous stirring, 10 ml of 0.5M aluminium chloride (AlCl₃•6H₂O) solution was added and stirred for 5 minutes. Then 10 ml of 2.5M NaOH solution was mixed under continuous stirring. The stirring was continued for another 5 minute. Finally under continuous stirring, 10 ml of 1.0M thiourea solution was mixed and stirred for 5 minute. At last, 38 ml of deionised water was added to make the final solution 100 ml. The final solution of 100 ml slowly turned greenish-black in colour, the precipitates generated get settled at the bottom of the beaker. After 4 hrs the final solution was filtered out to get nanoparticles yield. The obtained nanoparticles were washed with distilled water and methanol for several times. After multiple wash, they were dried in oven at 50°C for 24 hrs to obtained nanoparticles yield. The reaction mechanism of CuAlS₂ nanoparticles synthesis is as below:

\[
\text{CuCl}_2 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} + \text{TEA} \rightarrow [\text{Cu(TEA)}]^{+2} + 2\text{NaCl} + 2\text{OH}^- + 2\text{H}_2\text{O} \\
\text{AlCl}_3 \cdot 6\text{H}_2\text{O} + 3\text{NaOH} + 3\text{NH}_3 \rightarrow [\text{Al(NH}_3)_3]^{+3} + 3\text{NaCl} + 6\text{H}_2\text{O} + 3\text{OH}^- \\
2(\text{NH}_2)_2\text{CS} + 2\text{OH}^- \rightarrow 2\text{C}_2\text{H}_2\text{N}_2 + 2\text{H}_2\text{O} + 2\text{HS}^- \\
2\text{HS}^- + 2\text{OH}^- \rightarrow 2\text{S}^- + 2\text{H}_2\text{O} \\
[Cu(TEA)]^{+2} + [\text{Al(NH}_3)_3]^{+3} + 2\text{S}^- + 3\text{H}_2\text{O} \rightarrow \text{CuAlS}_2 \downarrow + \text{TEA} + 3\text{NH}_4\text{OH}
\]
5.2.3. BASE MATERIAL

Cellulose (microcrystalline powder, Alfa Aesar, Heysham, UK) was directly market procured and used without any treatment for the study of catalytic activity of CuAlS₂ micro-particles and nanoparticles in cellulose pyrolysis.

5.2.4. CHARACTERIZATIONS

The stoichiometric composition of the as-synthesized CuAlS₂ micro-particles and nanoparticles were done by the energy dispersive analysis of X-rays (EDAX) attached to LEO 1430 VP scanning electron microscope. The X-ray diffraction (XRD) pattern was recorded on Philips Xpert MPD X-ray diffractometer in the 2θ range of 0-100° using CuKα radiation (λ = 1.5405 Å) employing the scanning rate of 10° min⁻¹. The crystal structure, lattice parameters and phase were determined from the XRD patterns. The crystallite size and crystallinity of the as synthesized CuAlS₂ micro- and nanoparticles were determined by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) patterns, respectively. The TEM images and SAED patterns of as synthesized CuAlS₂ micro- and nanoparticles were recorded using Philips, Tecnai 20 transmission electron microscope. The thermal analysis data were recorded from ambient temperature to 1223K for as-synthesized CuAlS₂ micro- and nanoparticles. The catalytic effect of CuAlS₂ micro-particles and nanoparticles on cellulose pyrolysis was recorded from ambient temperature to 931K. All the thermal measurements were done at a heating rate of 10 °C·min⁻¹ in inert N₂ atmosphere at a flow rate of 100 mL·min⁻¹ using Seiko SII-EXSTAR TG/DTA-7200.

5.2.5. CATALYTIC ACTIVITY

The catalytic activity of as-synthesized CuAlS₂ micro-particles and nanoparticles on market procured cellulose pyrolysis was done by recording simultaneous thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) curves employing thermal analyzer, Seiko SII-EXSTAR TG/DTA-7200. The TG, DTG and DTA curves were recorded for pure cellulose and cellulose mixed with 10%, 5% and 2.5% of
CuAlS$_2$ micro-particles and nanoparticles as catalysts. The cellulose samples containing catalyst were freshly prepared by rigorous physical mixing of as-synthesized CuAlS$_2$ micro- and nanoparticles with market procured cellulose.

5.3. RESULTS AND DISCUSSION

5.3.1. ENERGY DISPERSIVE ANALYSIS OF X-RAY (EDAX) ANALYSIS

The chemical compositions of the as synthesized CuAlS$_2$ micro-particles and nanoparticles were determined by EDAX technique. The obtained spectra are shown in Figure 1(a) and Figure 1(b) respectively, which reveals that synthesized micro-particles and nanoparticles, contains only Cu, Al and S elements. The observed weight % of the elements with standard values is tabulated in Table 1. The values clearly states that the synthesized micro-particles are copper rich and nanoparticles are sulfur rich. No extra peaks were observed in the EDAX spectra stating that the synthesized CuAlS$_2$ micro-particles and nanoparticles are free from impurities or contaminants.

<table>
<thead>
<tr>
<th>Elements</th>
<th>EDAX Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Standard</td>
</tr>
<tr>
<td></td>
<td>Micro-particles</td>
</tr>
<tr>
<td>Cu</td>
<td>41.09</td>
</tr>
<tr>
<td>Al</td>
<td>17.44</td>
</tr>
<tr>
<td>S</td>
<td>41.47</td>
</tr>
</tbody>
</table>

Table 1: EDAX data of CuAlS$_2$ micro-particles and nanoparticles.
Figure 1: EDAX spectra of as synthesized CuAlS$_2$ (a) micro-particles and (b) nanoparticles.
5.3.2. STRUCTURAL ANALYSIS

The Figure 2(a) shows the XRD pattern of as synthesized CuAlS$_2$ micro-particles and nanoparticles. The micro-particles XRD peaks are sharp, stating the entire particles to be crystalline in nature. The nanoparticles XRD peaks are broad stating crystallite size to be small. The obtained XRD patterns were analyzed by powder-X software. It was observed that both, the CuAlS$_2$ micro-particles and nanoparticles possess tetragonal structure. The observed lattice parameters are tabulate in Table 2, the parameters are in good agreement with the standard data, JCPDS File No. 25-0014. The average crystallite size of CuAlS$_2$ micro-particles and nanoparticles determined from X-ray line broadening using the Debye-Scherrer’s formula and Hall-Williamson plot [8] are tabulated in Table 2. The values of the residual strain obtained from Hall-Williamson plots, Figure 2(b), indicate presence of tensile strain in CuAlS$_2$ micro-particles and compressive strain in case of CuAlS$_2$ nanoparticles.

![Figure 2: (a) X-ray diffraction patterns of as synthesized CuAlS$_2$ micro-particles and nanoparticles.](image-url)
Figure 2: (b) Hall-Williamson plots of as synthesized CuAlS$_2$ micro-particles and nanoparticles.

Table 2: XRD parameters.

<table>
<thead>
<tr>
<th>CuAlS$_2$</th>
<th>Lattice parameters / JCPDS 25-0014</th>
<th>Crystallite size (nm)</th>
<th>Strain ($\times 10^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro-particles</td>
<td>a = b (Å) / 5.325 / 5.325</td>
<td>c (Å) / 10.39 / 10.39</td>
<td>Debye-Scherrer’s / 50.15</td>
</tr>
<tr>
<td>Nanoparticles</td>
<td>a = b (Å) / 5.325 / 5.325</td>
<td>c (Å) / 10.32 / 10.39</td>
<td>Crystallite size (nm) / 7.64</td>
</tr>
</tbody>
</table>
5.3.3. SCANNING ELECTRON MICROSCOPY

The SEM images of as synthesized CuAlS$_2$ micro-particles and nanoparticles are shown in Figure 3: (a, b) In case of CuAlS$_2$ micro-particles, the particles are irregular in shape while in case of nanoparticles; the particles are spherical in shape and are evenly distributed.

![SEM images of CuAlS$_2$ (a) micro-particles and (b) nanoparticles.](image)

**Figure 3:** SEM images of CuAlS$_2$ (a) micro-particles and (b) nanoparticles.
5.3.4. TRANSMISSION ELECTRON MICROSCOPY AND SELECTED AREA ELECTRON DIFFRACTION ANALYSIS

The samples for the TEM and SAED analysis were prepared by ultrasonically dispersing CuAlS$_2$ micro-particles and nanoparticles in methanol just prior to loading for analysis. The particles size determined from the TEM image of the CuAlS$_2$ micro-particles, Figure 4(a), states that the size of the particles vary in μm range. While the average particles size, Figure 4(b), in case of CuAlS$_2$ nanoparticles were ~ 10 nm. The SAED patterns are shown in Figure 4(a) for micro-particles, it clearly show spot patterns stating crystalline nature. Figure 4(b) shows SAED pattern for nanoparticles, which show rings pattern confirming polycrystalline nature of the samples. The rings formed by connecting spots of CuAlS$_2$ micro-particles SAED pattern were indexed as (112), (211), (220), (204), (312), (116), (400) and (332). The indexed planes are in good agreement with the XRD planes of the CuAlS$_2$ micro-particles.

![Figure 4: (a) TEM image and SAED pattern of as synthesized CuAlS$_2$ micro-particles](image-url)
The CuAlS$_2$ nanoparticles rings were indexed as (112), (200), (220) and (116). The indexed planes are in good agreement with the XRD planes of CuAlS$_2$ nanoparticles. Both the SAED analysis stated the structure to be tetragonal.

5.3.5. THERMAL ANALYSIS

Before studying the catalytic effect of CuAlS$_2$ micro-particles and nanoparticles on cellulose pyrolysis, the thermal analysis of CuAlS$_2$ micro-particles and nanoparticles were undertaken. The thermal curves, TG, DTG and DTA were recorded for both CuAlS$_2$ micro-particles and nanoparticles in inert N$_2$ atmosphere, Figure 5(a-c) respectively. All the thermal curves were recorded in the temperature range of ambient temperature to 1227K keeping the rate of heating as 10°C·min$^{-1}$. In the analyzed temperature range, the TG curve, Figure 5(a), reveals that the total weight loss in case of micro-particles is 6.89% and it decomposes by three steps, while the total weight loss in case of nanoparticles is 53.37%
and it decomposes by five steps. Thus the TG curve reveals that the weight loss in case of as synthesized nanoparticles is more in comparison to micro-particles. The TG also showed that the weight loss starting temperature in case of CuAlS$_2$ nanoparticles is $\sim$303 K and in case of CuAlS$_2$ micro-particles it is $\sim$400 K. Thus the weight loss and starting temperature seen from the TG analysis establishes that the CuAlS$_2$ micro-particles are more stable than CuAlS$_2$ nanoparticles.

Figure 5: (a) TG (b) DTG and (c) DTA curves of as synthesized CuAlS$_2$ micro-particles and nanoparticles.
Figure 6: The Coats-Redfern plots for the decomposition of CuAlS$_2$ (a) micro-particles and (b) nanoparticles.
The DTG curves, Figure 5(b), shows three sharp peaks in case of CuAlS$_2$ micro-particles and five sharp peaks in case of CuAlS$_2$ nanoparticles. The numbers of peaks are in complete agreement with the number of weight loss steps observed in TG curves. Thus DTG analysis corroborates the TG analysis.

The DTA curves, Figure 5(c), of as synthesized CuAlS$_2$ micro-particles and nanoparticles lies below zero level stating the decomposition to be endothermic. The DTA curves of the CuAlS$_2$ micro-particles and nanoparticles also clearly show different rates of decrease. In case of CuAlS$_2$ nanoparticles, the DTA rate of decrease is sharp compared to micro-particles. The fast decrease in DTA curve of CuAlS$_2$ nanoparticles is due to large weight loss, as observed in TG curve. Both observations clearly states that CuAlS$_2$ nanoparticles decomposes faster than CuAlS$_2$ micro-particles. These results state that the CuAlS$_2$ micro-particles are more stable then corresponding nanoparticles. The results of DTA substantiate the results of the analysis of TG and DTG curves.

The weight increase seen in CuAlS$_2$ nanoparticles at 890K may be due to decomposition of the compound. With decomposition of the compound it reacts with nitrogen of the inert atmosphere [9] and gains weight which is reflected in the TG curve. The decomposition of CuAlS$_2$ nanoparticles at around 890K is substantiated by the DTA increase seen above 890K. This means heat is released from the sample compound, possible only when decomposition is taking place.

The activation energy values were calculated from TG curves having three steps for micro-particles and five steps for nanoparticles employing standard Coats-Redfern (C-R) method [10]. The C-R plots of both the CuAlS$_2$ micro-particles and nanoparticles are shown in Figure 6(a) and 6(b) respectively. The C-R method was employed since it is a standard method and simple to use with data obtained from the TG curve. Other thermal parameters such as, activation enthalpy ($\Delta H$), activation entropy ($\Delta S$) and Gibbs free energy change ($\Delta G$) for both CuAlS$_2$ micro-particles and nanoparticles were evaluated using TG data by below equations [11]. The evaluated parameters are tabulated in Table 3.

$$\Delta H = E_a - RT$$  \hspace{1cm} (1)
\[ \Delta S = 2.303 \, R \log \left( \frac{A h}{kT} \right) \tag{2} \]

\[ \Delta G = \Delta H - T \Delta S \tag{3} \]

Here, \( E_a \) is the activation energy, \( A \) is Arrhenius constant, \( k \) is Boltzmann constant, \( h \) is Planck’s constant and \( T \) is temperature of DTG peak between decomposition steps.

**Table 3:** Kinetic and thermal parameters for micro-particles and nanoparticles of \( \text{CuAlS}_2 \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Steps</th>
<th>Temp. range (K)</th>
<th>Weight Loss %</th>
<th>DTG Peak (K)</th>
<th>Activation energy ( (E_a) ) (kJ-mol(^{-1}))</th>
<th>Pre-exponential Factor ( (Z) )(min(^{-1}))</th>
<th>( \Delta S ) (J.K(^{-1})mole(^{-1}))</th>
<th>( \Delta H ) (kJ-mol(^{-1}))</th>
<th>( \Delta G ) (kJ-mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CuAlS}_2 ) micro-particles</td>
<td>I</td>
<td>400-572</td>
<td>1.69</td>
<td>470.01</td>
<td>175.52</td>
<td>6.66 x 10(^{30})</td>
<td>307.34</td>
<td>171.61</td>
<td>27.16</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>573-823</td>
<td>2.21</td>
<td>687.23</td>
<td>276.11</td>
<td>2.78 x 10(^{32})</td>
<td>335.21</td>
<td>270.40</td>
<td>40.03</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>824-1227</td>
<td>2.99</td>
<td>1049.00</td>
<td>182.17</td>
<td>3.68 x 10(^{20})</td>
<td>104.29</td>
<td>173.45</td>
<td>64.05</td>
</tr>
<tr>
<td>( \text{CuAlS}_2 ) nanoparticles</td>
<td>I</td>
<td>303-430</td>
<td>9.88</td>
<td>339.47</td>
<td>56.47</td>
<td>5.93 x 10(^{18})</td>
<td>79.36</td>
<td>53.65</td>
<td>26.71</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>431-770</td>
<td>29.06</td>
<td>606.2</td>
<td>57.79</td>
<td>5.55 x 10(^{15})</td>
<td>16.56</td>
<td>52.75</td>
<td>42.71</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>771-870</td>
<td>-3.61</td>
<td>816.48</td>
<td>265.33</td>
<td>2.78 x 10(^{28})</td>
<td>257.21</td>
<td>258.54</td>
<td>48.53</td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>871-1020</td>
<td>9.07</td>
<td>927.48</td>
<td>235.28</td>
<td>5.62 x 10(^{24})</td>
<td>185.42</td>
<td>227.57</td>
<td>55.60</td>
</tr>
<tr>
<td></td>
<td>V</td>
<td>1021-1227</td>
<td>8.29</td>
<td>1115.07</td>
<td>401.66</td>
<td>6.10 x 10(^{30})</td>
<td>299.43</td>
<td>392.39</td>
<td>58.51</td>
</tr>
</tbody>
</table>

According to Table 3, the positive value of \( \Delta H \) in both \( \text{CuAlS}_2 \) micro-particles and nanoparticles suggest that heat is being absorbed by the sample leading to dissociation endorsed by the typical endothermic nature reflected in the entire temperature range of the DTA curve. In the temperature range from ambient temperature to nearly 800 K, the entropy values of as synthesized micro-particles are much higher in comparison to nanoparticles. This means the disorder in micro-particles is more than nanoparticles. But increasing disorder does not lead to decomposition of micro-particles as less weight loss is observed in this temperature range of TG curve. In case of \( \text{CuAlS}_2 \) nanoparticles, the entropy value is less compared to micro-particles, stating that more ordering is taking place in nanoparticles.
compared to micro-particles. This behaviour of nanoparticles is common, because nanoparticles are formed of cluster from the atoms or molecules without any structure. As energy is received due to heating, ordering and attainment of structure takes place leading to less entropy values.

5.3.6. CATALYTIC EFFECT OF CuAlS$_2$ IN THERMAL DECOMPOSITION OF CELLULOSE

The catalytic effect of CuAlS$_2$ micro-particles and nanoparticles on cellulose pyrolysis was studied by recording the simultaneous TG, DTG and DTA curves. Just before recording the thermographs the CuAlS$_2$ micro-particles and nanoparticles were physically thoroughly mixed with cellulose and loaded for thermal analysis. In all the thermal analysis, the total sample loading weight was kept constant as 5 mg.
Figure 7: (a) TG (b) DTG and (c) DTA curves of pure cellulose and cellulose mixed with 10%, 5% and 2.5% CuAlS₂ micro-particles and nanoparticles each.
The thermographs were recorded for the pure cellulose and cellulose mixed with catalyst CuAlS$_2$ micro-particles and nanoparticles, Figure 7. Three concentrations of CuAlS$_2$ micro-particles and nanoparticles each were taken as catalyst. The concentration of the catalyst CuAlS$_2$ micro-particles and nanoparticles taken for thermal catalytic study were 10%, 5% and 2.5%.

The TG curves, Figure 7(a), clearly states that pure cellulose is stable from ambient temperature to 568K. In this temperature range 8% weight loss is observed. This weight loss may be due to evaporation of trapped moisture from the pure cellulose. Between, 569K – 660K the decomposition of cellulose takes place. This decomposition is being reflected by the maximum weight loss seen in this temperature range. The weight loss in this temperature range is 80%.

The nature of the TG curves of cellulose mixed with 10%, 5% and 2.5% CuAlS$_2$ micro-particles are nearly same as that of pure cellulose. Minor deviation is seen at high temperatures in case of cellulose mixed with 10% and 5% CuAlS$_2$ micro-particles. The weight loss in both, the cellulose mixed with 10% and 5% CuAlS$_2$ micro-particles is slightly less than the pure cellulose. Whereas in case of cellulose mixed with 2.5% CuAlS$_2$ micro-particles, the weight loss is nearly same as that of pure cellulose. The weight loss deviation in case of cellulose mixed with 10% and 5% CuAlS$_2$ micro-particles can be explained as; the heat provided to these samples gets absorbed mostly by the catalyst then by the cellulose. The absorption of heat by catalyst CuAlS$_2$ micro-particles is more because of its high concentration. Due to less heat available for cellulose to decompose, the weight loss due to cellulose decomposition is less observed leading to less weight loss than pure cellulose.

The TG curves of 10%, 5% and 2.5% CuAlS$_2$ nanoparticles mixed cellulose showed early start of decomposition. The decomposition starting temperature for all the concentrations of CuAlS$_2$ nanoparticles mixed cellulose is 480K. This decomposition starting temperature is nearly 90K lower than the pure cellulose and for all concentrations of CuAlS$_2$ micro-particles mixed with cellulose. The other observation is that the temperature range of decomposition of cellulose mixed with CuAlS$_2$ nanoparticles has extended behaviour (481K – 670K) compared to pure cellulose and cellulose mixed with CuAlS$_2$ micro-particles (569K – 660K).
Also the weight loss in case of cellulose mixed with CuAlS\textsubscript{2} nanoparticles is 70\%. This weight loss value of nearly 70\% is less than the weight loss value of nearly 80\% observed in case of pure cellulose and cellulose mixed with CuAlS\textsubscript{2} micro-particles (all concentrations).

The above observations from the TG curves for the pure cellulose, cellulose mixed with CuAlS\textsubscript{2} micro-particles and nanoparticles are clearly reflected in the simultaneously recorded DTG and DTA curves. The DTG has one peak clearly corroborates the one step decomposition for all the samples as seen in TG curves. The DTG peaks of all the samples lie in their respective temperature range in which the decomposition has taken place in TG curves, thus confirming the TG observations.

In case of DTA, all samples showed small exothermic nature at the start of temperature followed by the entire curve lie below the base line all throughout the entire temperature range stating them to be endothermic. With the initial small exothermic nature all DTA curves show linear decrease upto 575K. Above 575K there is an endothermic peak. This endothermic peak ranges between temperatures 575K to 640K. The initial exothermic nature may be due to heat released owing to reaction of cellulose with entrapped water. Latter endothermic nature may be due to weight loss observed in the TG. The weight loss means heat is absorbed by the samples leading to decomposition and evaporation of the decomposed components. The absorption of heat leading to decomposition of all samples is the reason of endothermic nature of DTA. Other than the DTA curve lying below base line, a DTA endothermic peak is observed in case of all the seven samples. The endothermic peaks lies at the temperatures corresponding to the maximum weight loss observed in TG. The behaviour of DTA curves after the endothermic peaks is of increasing nature. The DTA observation clearly states that at the endothermic peaks, the decomposition of samples takes place and after the start of decomposition the DTA increase states that further decomposition leads to release of energy which is reflected in the increasing nature of the DTA curve. The DTA curve increase after start of decomposition means complete structural change taking place in the temperature range.
The thermal analysis and specifically the TG analysis clearly states that CuAlS$_2$ nanoparticles are better catalyst for cellulose pyrolysis compared to CuAlS$_2$ micro-particles. The analysis also showed that the concentration change (10%, 5% and 2.5%) of CuAlS$_2$ nanoparticles as catalyst has no effect on the decomposition starting temperature in cellulose pyrolysis.

The kinetic and thermal parameters calculated from the thermographs by employing Coats-Redfern (C-R) method, Figure 8, are tabulated in Table 4. It is clearly seen that the activation energy and activation enthalpy value is highest for pure cellulose decomposition and lowest for decomposition of cellulose mixed with CuAlS$_2$ nanoparticles for all concentrations. The activation energy and activation enthalpy values for cellulose mixed with CuAlS$_2$ micro-particles lies between pure cellulose and cellulose mixed with CuAlS$_2$ nanoparticles but their values are near to the pure cellulose values.
Figure 8: Coates-Redfern plots for the decomposition of (a) cellulose (b) cellulose mixed with CuAlS$_2$ micro-particles and (c) cellulose mixed with CuAlS$_2$ nanoparticles.
Table 4: Kinetic and thermal parameters obtained for cellulose decomposition without and with different percentage of CuAlS$_2$ catalyst.

<table>
<thead>
<tr>
<th>Cellulose</th>
<th>Decomp. Temp. Range (K)</th>
<th>Weight Loss %</th>
<th>DTA Peak (K)</th>
<th>DTG Peak (K)</th>
<th>Activation energy ($E_a$) (kJ·mol$^{-1}$)</th>
<th>Pre-exponential Factor ($Z$) (min$^{-1}$)</th>
<th>$\Delta S^*$ (J·K$^{-1}$·mol$^{-1}$)</th>
<th>$\Delta H^*$ (kJ·mol$^{-1}$)</th>
<th>$\Delta G^*$ (kJ·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Cellulose</td>
<td>569-660</td>
<td>80.30</td>
<td>609.54</td>
<td>612.23</td>
<td>219.04</td>
<td>$1.12 \times 10^{30}$</td>
<td>290.35</td>
<td>213.95</td>
<td>36.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micro-particles</td>
<td>569-660</td>
<td>71.88</td>
<td>606.42</td>
<td>608.19</td>
<td>199.78</td>
<td>$3.01 \times 10^{28}$</td>
<td>260.32</td>
<td>194.73</td>
<td>36.40</td>
</tr>
<tr>
<td></td>
<td>481-670</td>
<td>69.13</td>
<td>589.68</td>
<td>593.83</td>
<td>114.59</td>
<td>$1.17 \times 10^{21}$</td>
<td>118.62</td>
<td>109.65</td>
<td>39.21</td>
</tr>
<tr>
<td>Nano-particles</td>
<td>569-660</td>
<td>73.73</td>
<td>606.05</td>
<td>610.52</td>
<td>215.76</td>
<td>$7.35 \times 10^{29}$</td>
<td>286.85</td>
<td>210.69</td>
<td>35.56</td>
</tr>
<tr>
<td></td>
<td>481-670</td>
<td>70.47</td>
<td>583.08</td>
<td>594.70</td>
<td>117.75</td>
<td>$2.45 \times 10^{21}$</td>
<td>124.79</td>
<td>112.81</td>
<td>38.59</td>
</tr>
<tr>
<td>10%</td>
<td>569-660</td>
<td>76.20</td>
<td>606.13</td>
<td>610.89</td>
<td>217.10</td>
<td>$9.83 \times 10^{29}$</td>
<td>289.25</td>
<td>212.02</td>
<td>35.32</td>
</tr>
<tr>
<td></td>
<td>481-670</td>
<td>75.74</td>
<td>586.96</td>
<td>595.14</td>
<td>123.08</td>
<td>$7.41 \times 10^{21}$</td>
<td>133.98</td>
<td>118.13</td>
<td>38.40</td>
</tr>
<tr>
<td>5%</td>
<td>569-660</td>
<td>76.20</td>
<td>606.13</td>
<td>610.89</td>
<td>217.10</td>
<td>$9.83 \times 10^{29}$</td>
<td>289.25</td>
<td>212.02</td>
<td>35.32</td>
</tr>
<tr>
<td></td>
<td>481-670</td>
<td>75.74</td>
<td>586.96</td>
<td>595.14</td>
<td>123.08</td>
<td>$7.41 \times 10^{21}$</td>
<td>133.98</td>
<td>118.13</td>
<td>38.40</td>
</tr>
<tr>
<td>2.5%</td>
<td>569-660</td>
<td>76.20</td>
<td>606.13</td>
<td>610.89</td>
<td>217.10</td>
<td>$9.83 \times 10^{29}$</td>
<td>289.25</td>
<td>212.02</td>
<td>35.32</td>
</tr>
<tr>
<td></td>
<td>481-670</td>
<td>75.74</td>
<td>586.96</td>
<td>595.14</td>
<td>123.08</td>
<td>$7.41 \times 10^{21}$</td>
<td>133.98</td>
<td>118.13</td>
<td>38.40</td>
</tr>
</tbody>
</table>
The activation enthalpy ($\Delta H$) value is positive in all the thermal decomposition, stating the decomposition to be endothermic. This endothermic nature is also reflected in the DTA curve, Figure 7 (c), in which the curve lies almost below zero base line except an initial exothermic nature. The activation energy and activation enthalpy values are lowest in case of CuAlS$_2$ nanoparticles, stating it to be the best catalyst in comparison to CuAlS$_2$ micro-particles in all percentage mixture for cellulose pyrolysis. These results support the results obtained from the TG analysis.

The above cellulose pyrolysis mechanism with and without added CuAlS$_2$ catalyst can be understood as follows. In the case of pure cellulose with increase in pyrolysis temperature, initially moisture inside the cellulose gets evaporated. Later on, the already dried portions of the particles, in the neighbourhood of the heated surface, undergo thermal degradation and devolatilization to form an active substance. When the pyrolysis temperature is further increased, the thermal decomposition of cellulose components begins to occur, and the volatile species gradually evolved out from the cellulose particle surface leading to absolute degradation.

In the presence of CuAlS$_2$ nanoparticles, which enhance the devolatilization of cellulose and also thermal degradation, through formation of weak bonds between volatiles and the catalyst which caused other bonds in the volatile molecules to be stretched and weakened, ultimately to enhance the release of final gas products. The catalyst accelerates primary and secondary decomposition reactions of cellulose leading to pyrolysis to occur at a lower temperature. In particular, CuAlS$_2$ nanoparticles with a large external surface area to volume ratio than that of CuAlS$_2$ micro-particles disperses better in the cellulose substrate for a closer and more uniform contact between cellulose and catalyst particles, which finally promotes the overall decomposition of cellulose.

**5.4. CONCLUSIONS**

The study of catalytic activity of as-synthesized CuAlS$_2$ micro-particles and nanoparticles on market purchased cellulose pyrolysis was done by recording simultaneous TG, DTG and
DTA curves. The CuAlS$_2$ micro-particles were synthesized by high temperature heating method in an evacuated quartz ampoule. The CuAlS$_2$ nanoparticles were synthesized at ambient temperature by the simple wet chemical technique. Prior to pyrolysis study, as-synthesized CuAlS$_2$ micro-particles and nanoparticles were comprehensively characterized. The EDAX analysis showed that the synthesized micro-particles are copper rich, whereas nanoparticles are sulfur rich. Both of the particles do not have impurity or contaminants. The XRD confirmed that the CuAlS$_2$ micro-particles and nanoparticles possess tetragonal structure. The determined lattice parameters of both the particles were in good agreement with the reported data. The average crystallite sizes of CuAlS$_2$ micro-particles and nanoparticles determined from X-ray line broadening using the Debye-Scherrer’s formula and Hall-Williamson plot showed that the crystallite size of micro-particles lies in the range of $\mu$m and nanoparticles size is in nanometer. The values of the residual strain obtained from Hall-Williamson plots, indicates presence of tensile strain in CuAlS$_2$ micro-particles and compressive strain in case of CuAlS$_2$ nanoparticles. The particles size determined from the TEM image of the CuAlS$_2$ micro-particles lies in $\mu$m range and nanoparticles average size came out to be $\sim$ 10 nm. The thermal analysis of CuAlS$_2$ micro-particles and nanoparticles in the temperature range of ambient temperature to 1227 K exhibited that CuAlS$_2$ micro-particles decomposes by three steps with 6.89% weight loss and nanoparticles decomposes by five steps with 53.37% weight loss. The thermal curves clearly show that the weight loss starts early in case of CuAlS$_2$ nanoparticles ($\sim$303 K) than CuAlS$_2$ micro-particles ($\sim$400 K). Thus with less weight loss and high decomposition starting temperature the CuAlS$_2$ micro-particles are more stable than nanoparticles. The catalytic study of CuAlS$_2$ micro-particles and nanoparticles in cellulose pyrolysis was done in the temperature range of ambient temperature to 923 K. The thermal analysis of simultaneously recorded TG, DTA and DTG curves clearly states that CuAlS$_2$ nanoparticles are better catalyst than micro-particles.
REFERENCES:


