CHAPTER 4

RESULTS AND DISCUSSION

The preliminary experiments show a range of parameter conditions for the growth of MWNTs and these results were only preliminary and did not necessarily correspond to optimum growth conditions. As the aim of this work was to synthesize well crystalline MWNTs in good yield from renewable natural precursor viz. methyl ester of Madhuca longifolia oil, methyl ester Brassica juncea oil and methyl ester Oryza sativa oil, optimization of the parameters such as reaction temperature, catalyst and flow rate of carbon precursor were carried out. In this part, the results of parameter influence on yield and morphology of MWNTs synthesized from plant based precursor oil were discussed.

4.1 METHYL ESTER OF MADHUCA LONGIFOLIA OIL AS CARBON SOURCE FOR SYNTHESIS OF MWNTS

Much of the research has been carried out on effect of transition metal on growth of CNTs using volatile precursors and very few reported studies which adequately cover the effect of trimetallic combination on growth of CNTs using non volatile precursors. This part of study discusses manipulation of the growth rate, the diameter and the crystallinity of MWNTs by selecting the catalysts.
4.1.1 Effect of Catalyst Composition on Yield and the Morphology of MWNTs Synthesized from methyl ester of *Madhuca longifolia* Oil

In the present work, the effect of catalyst on yield and morphology of Multi-Walled Carbon nanotubes (MWNTs) synthesized from renewable natural precursors using methyl ester of *Madhuca longifolia* oil, by spray pyrolysis method at 650 °C under N₂ atmosphere with a precursor flow rate of 20 mL per hour were studied.

4.1.1.1 Determination of optimum catalyst composition for maximum yield of MWNTs from methyl ester of *Madhuca longifolia* oil

The effect of catalyst composition on yield of MWNTs was studied at 650 °C using methyl ester *Madhuca longifolia* oil as precursor at a flow rate of 20 mL per hour over Fe catalyst supported on silica, Fe-Co catalysts supported on silica and Fe-Co-Mo catalysts supported on silica under nitrogen atmosphere. The Figure 4.1 reveals the dependence of the yield of carbon deposit on catalysts supported on silica. The yield of carbon deposit on Fe catalyst supported on silica was about 34%. But the yield increased greatly (59%) in case of Fe-Co catalysts supported on silica. When Fe-Co-Mo catalysts supported on silica were used, it was almost 68% yield obtained. One of the significant findings emerged from this study is that a trimetallic combination of Fe, Co and Mo catalysts supported on silica leads to higher carbon production rate by decomposition of methyl ester of *Madhuca longifolia* oil than Monometallic (Fe) or Bimetallic (Fe-Co) catalysts at 650 °C.

Several reseaches have reported a similar observation. In the study of synthesis of CNTs by decomposition of acetylene over silica supported transition metals was reported by Willems et al. (2000). Piedigrossu et al. (2000) reported that amount of nanotubes formed over silica
supported Co catalyst depends on content of Cobalt. Kumar et al. (2005) obtained high yield of MWNTs by decomposition of camphor over zeolite supported Fe and Co catalysts. This shows the strong relationship between the catalyst and yield of MWNTs deposit. Jeong et al. (2010) reported based on their study of synthesis of MWNTs from liquefied petroleum gas over alumina supported Fe, Co and Mo catalyst in a fluidized bed reactor that the transition metal act as nuclei for CNTs growth and increased productivity. Perez Mendoza et al. (2005) investigated the influence of Mo on the CVD production of CNTs and reported that the production of high yield of CNTs with low levels of impurities was related to the promoter character of Mo in the reaction.

The result of experiments carried out in this study for synthesis of MWNTs over chosen transition metals supported on silica reveals that Fe was very active in the decomposition of hydrocarbons; however, Co & Mo were necessary for the formation of good Morphology MWNTs.

![Figure 4.1](image_url)  
Yield of MWNTs grown at 650 °C using methyl ester of *Madhuca longifolia* oil as precursor at a flow rate of 20 mL per hour over Fe, Fe-Co, Fe-Co-Mo catalysts supported on silica.
The Fe-Co-Mo catalysts supported on silica combine the advantages and leads to higher growth rate of MWNTs of good Morphology. Also found that small amount of addition of Mo as catalyst along with Fe and Co increased yield. Afre et al. 2006 reported that the peculiarity of these transition metals to catalyse CNT formation via mostly linked to their catalytic activity for the decomposition of carbon compounds, there ability to form carbides and the possibility for carbonate diffuse through and over the metals extremely rapidly.

Hence, the investigator conclude that the increase in yield may be due to collabororative advantages of high catalytic decomposition, effectiveness in growing CNTs and promotional character of Fe, Co and Mo respectively.

4.1.1.2 Effect of Fe catalyst supported on Silica on morphology of MWNTs synthesized from methyl ester of Madhuca longifolia oil

The catalytic vapor deposition of methyl ester of Madhuca longifolia oil over Fe catalyst supported on silica at 650 °C resulted in considerable Morphology of carbon deposit (Figure 4.2). However, as-grown CNTs were of diameter in the range of 55-75 nm with poorly shaped and contains abundant amount of amorphous carbon. Similar results were reported by Li et al. (2008) in their study of co-production of hydrogen and MWNTs from ethanol decomposition over Fe/Al₂O₃ catalyst at 750 °C.
Figure 4.2 SEM micrograph results of MWNTs synthesized at 650 °C using methyl ester of *Madhuca longifolia* oil as precursor at a flow rate of 20 mL per hour over Fe catalyst supported on silica

The HR-TEM micrograph recorded to study diameter and layers of the MWNTs synthesized were shown in Figure 4.3. The influence of the catalyst on morphology of MWNTs was studied through the number of graphene layers, the crystallinity, the inner, and the diameter of the nanotubes measured from HR-TEM images. The HR-TEM images (Figure 4.3) of MWNTs synthesized over Fe catalyst supported on silica shows poor crystallization of walls and a layer of amorphous carbon on outer surface of the tube. The inner and outer diameters of MWNTs are around 14-22 nm and 35-45 nm respectively.
Figure 4.3 HR-TEM micrograph results of MWNTs synthesized at 650 °C using methyl ester of Madhuca longifolia oil as precursor at a flow rate of 20 mL per hour over Fe catalyst supported on silica

The Raman spectrum of carbon deposit contains information about the structure of CNTs. The Raman spectrum recorded for the MWNTs obtained over Fe catalysts supported on silica where shown in Figure 4.4. The spectrum shows G-band at 1572 cm\(^{-1}\) representing the tangential stretching mode of highly oriented pyrolytic graphite and a peak at 1340 cm\(^{-1}\) corresponds to D-band originating from crystalline disorders and lattice imperfections in the curved graphene sheets. The \(I_G/I_D\) value of 1.17 evidences some imperfection in graphitization of MWNTs layers.
The influence of silica supported Fe-Co catalysts on morphology of MWNTs synthesized from methyl ester of Madhuca longifolia oil with a flow rate of 20 mL per hour at 650 °C under nitrogen atmosphere was studied. The representative SEM image of MWNTs synthesized was shown in the Figure 4.5.

According to SEM images, MWNTs formed were very tangle indicating the presence of structural defects responsible for twisting of the tubes. These tubes were found to be relatively thick and covered with a dense outer layer of amorphous carbon and catalyst particle. The diameter of the MWNTs grown was in the range of 40-60 nm. The experimental results were consistent with the literature report of Willems et al. (2000) that Co as a
catalyst active phase is prime importance for obtaining Morphology MWNTs, while the use of Fe can give a higher carbon yield but the product of lower Morphology.

Figure 4.5 SEM micrograph results of MWNTs synthesized at 650 °C using Madhuca longifolia oil as precursor at a flow rate of 20 mL per hour over Fe-Co catalyst supported on silica

The role of the catalyst on diameter and number of layers of MWNTs synthesized was studied by HR-TEM and the result is shown in the Figure 4.6. The tubular nature of CNTs (Figure 4.6) grown over Fe-Co catalysts supported on silica were MWNTs with good in graphitization but thick in size and some portions of tubes covered with a dense outer layer of amorphous carbon. The inner and the outer diameter of the MWNTs were 10-18 and 30-48 nm respectively. The tube consists of fourteen concentric graphitic layers.
The crystalline nature of MWNTs as a function of the catalyst was studied using Raman spectroscopy and the result is depicted in the Figure 4.7. These spectra show G-band at 1580 cm\(^{-1}\) representing the tangential stretching mode of highly oriented pyrolytic graphite and a peak at 1342 cm\(^{-1}\) corresponds to D-band originating from crystalline disorders and lattice imperfections in the curved graphene sheets. The Raman spectrum also exhibits a band at 2684 cm\(^{-1}\) called the D’-band attributed to the overtone of the D band. The value of I\(_G\)/I\(_D\) for the MWNTs grown on Fe-Co catalysts supported on silica was 1.3. It reveals the relative intensity of G-band to D-band increases with incorporation of Co with Fe catalyst.
Figure 4.7  Raman spectra of MWNTs grown at 650 °C using methyl ester of *Madhuca longifolia* oil as precursor at a flow rate of 20 mL per hour over Fe-Co catalysts supported on silica

4.1.1.4 Effect of Fe-Co-Mo catalysts supported on Silica on morphology of MWNTs synthesized from methyl ester of *Madhuca longifolia* oil

The effect of Fe-Co-Mo catalysts supported on silica on morphology of MWNTs synthesized from methyl ester *Madhuca longifolia* oil with a flow rate of 20 mL per hour at 650 °C under nitrogen atmosphere was studied. The representative SEM image of MWNTs synthesized is shown in the Figure 4.8. The SEM image of as-grown carbon deposit over Fe-Co-Mo catalysts supported on silica shows densely populated MWNTs with the diameter in the range of 30-40 nm.
The MWNTs synthesized was characterized using HR-TEM technique to determine and number of layers of MWNTs and the representative image is shown in the Figure 4.9. The HR-TEM image (Figure 4.9) reveals the CNTs grown over Fe-Co-Mo catalysts supported on silica were of MWNTs type. The MWNTs possessed twenty three well crystallized graphite layers with amorphous carbon on their surface. The average inner and the outer diameter of these MWNTs were found to be 12 and 22-36 nm respectively. There was almost no encapsulation of catalyst particles inside the MWNTs grown. The inter layer distance calculated was 0.343 nm.

Zhang et al. (2008) observed that the inner diameter, outer diameter and number of layers of CNTs synthesized over MgO supported Ni and Mo were increased with increasing Mo mole fraction. They suggested the variation in the diameter was ascribed to the catalyst particle size and bimetallic catalyst ratio. Yoeh et al. (2010) in their study of the role of Mo in Co-Mo/MgO for large-scale production of high Morphology CNTs, observed
that CNTs of smallest and narrowest diameter distribution was obtained with 20 wt% of Mo loading. Whereas, Flahaut et al. (2004) stated that the ratio between Co and Mo plays an important role and they proportion of Mo must be kept as low as possible when the synthesis of CNTs with a low number of walls is desired. Cassel et al. (1999) attribute the increase in yield of CNTs by the Fe/Mo catalyst to the role played by Mo catalyst in promoting the aromatization of methane at elevated temperatures. It is important to note that the proportion of nanotubes covered with amorphous carbon is smaller when trimetallic catalyst (Fe-Co-Mo) is used than bimetallic catalyst (Fe-Co). The collaborative effect of Mo was very evident. Mo was required to enhance the activity of oxide catalyst and even distribution of metal particles on substrate (Kitayanan et al. 2000; Cassel et al. 1999).

Figure 4.9  HR-TEM micrograph results of MWNTs Synthesized over Fe-Co-Mo catalysts supported on silica using methyl ester of Madhuca longifolia oil as precursor at a flow rate of 20 mL per hour at 650 °C

In the present study, the investigator obtained best crystallization of graphene walls with inner and outer diameter of 12 and 22-36 nm for the NWMTs synthesized over Fe-Co-Mo catalyst supported on silica. Hence, the
investigator conclude that the combination of Fe, Co and Mo plays an important role and Co incorporation in the catalyst improves the crystalline nature whereas the Mo in low fraction favors formation of less number of walls. The effectiveness of Fe, responsible for high cracking rate and nucleation of CNTs growth, was improved in presence of Co and Mo catalyst. The high crystalline nature of graphene walls was attributed to Co whereas the smaller diameter and narrow tube was ascribed to the combined effect of catalyst which prevents agglomeration of catalyst particles.

Afre et al. (2006) reported that silica supported Fe and Co catalyst produced SWNTs in good Morphology at 700 °C by spray pyrolysis of turpentine oil. Furthermore, synthesis of SWNTs from turpentine oil over silica supported Fe and Co catalyst was reported by Maruyama et al. (2002). In the present study no such formation of SWNTs was evidenced from TEM images. The reason for it may be high cracking rate of precursor and particle size of the catalyst. However, this requires further extensive study for confirmation. Ago et al. (2006) found that the catalytic activity increases in the following order Fe-Mo> Fe> Co> Ni. The addition of Molybdenum to iron catalyst increases the initial methane conversion and prevents the rapid deactivation of the catalyst.

The impact of catalyst on the crystalline nature of MWNTs synthesized was studied through the Raman spectrum recorded for the sample. The Raman spectrum recorded for the carbon deposit obtained on Fe-Co-Mo catalysts supported on silica was shown in Figure 4.10. The characteristic D peak and G-peak were observed at 1347 and 1572 cm\(^{-1}\) respectively. The Raman spectrum also exhibits a band at 2680 cm\(^{-1}\) called the D’-band attributed to the overtone of the D band. Relatively high \(I_G/I_D\) value (1.64) of MWNTs synthesized over Fe-Co-Mo catalysts shows best graphitization of MWNTs obtained over Fe-Co-Mo catalysts.
4.1.2 Effect of Temperature on Yield and the Morphology of MWNTs Synthesized from methyl ester Madhuca longifolia Oil

In this part of research, the effect of temperature viz. 550, 650 and 750 °C on the yield and morphology of MWNTs synthesized using methyl ester Madhuca longifolia oil as carbon precursor for a flow rate of 20 mL per hour over Fe-Co-Mo catalyst supported on silica were discussed under N₂ atmosphere.

4.1.2.1 Optimization of temperature for maximum yield of MWNTs

In this part, optimum reaction temperature for subsequent experiments is determined. The study is carried out at 550, 650 and 750 °C to investigate the effect of temperature on yield of MWNTs over Fe-Co-Mo catalysts supported on silica using methyl ester Madhuca longifolia oil as
precursor at flow rated of 20 mL per hour. The graphical representations of the results obtained are shown in the Figure 4.11.

![Graph showing yield of MWNTs grown at Fe-Co-Mo catalysts supported on silica using methyl ester Madhuca longifolia oil as precursor at a flow rate of 20 mL per hour at 550, 650 and 750 °C]

**Figure 4.11** Yield of MWNTs grown at Fe-Co-Mo catalysts supported on silica using methyl ester *Madhuca longifolia* oil as precursor at a flow rate of 20 mL per hour at 550, 650 and 750 °C

The Figure 4.11 illustrated that low yield of carbon deposit (36%) is produced at 550 °C. Nagaraju et al. (2002) also have stated that there were not observed CNTs at 500 °C by CVD method because the catalyst could not be activated at that temperature. It is found from the Figure 4.11 that carbon yield increased to 68% at 650 °C and again further increase in yield (79%) observed at 750 °C. According to Piao et al. 2002 and Snoeck et al. 1997, the increase in temperature results in an exponential increase of the equilibrium, so the yield rises with increasing temperature, but at high temperature (750 °C) the formation rate of carbon over the catalyst surface might exceed the growth rate of MWNTs thus resulting in termination of growth by
encapsulating the active catalytic particles. Afre et al. (2006) found similar trend in their study of synthesis of CNTs from turpentine oil at different temperatures and reported maximum yield at 700 °C. Zhan et al. (2007) also observed a similar trend in their study of synthesis of CNTs by catalytic decomposition of methane and reported a high yield of MWNTs at 900 °C. This trend is generally observed in the synthesis of CNTs by CVD method. This work suggests that low yield obtained at 550 and 750 °C is possibly due to the fact that the catalyst could not be activated and high rate of pyrolysis followed by encapsulation of catalyst respectively. The high yield obtained at 650 °C in this study is attributed to almost equal rate of pyrolysis of precursor and CNTs growth.

4.1.2.2 Morphology of MWNTs synthesized from methyl ester of Madhuca longifolia oil at 550 °C

The morphology of MWNTs synthesized at 550 °C using methyl ester Madhuca longifolia oil as a precursor with a flow rate of 20 mL per hour over silica supported Fe-Co-Mo catalysts was studied. The representative SEM image of MWNTs synthesized was shown in the Figure 4.12. The MWNTs growth at 550 °C were mostly like noodles shape with diameter in the range of 55-70 nm as shown in SEM image (Figure 4.12). Such an observation was also noted for the synthesis of CNTs using different precursors by several authors Nagaraju et al. (2002), Kumar and Ando et al. (2005) and Ghosh et al. (2007).
Figure 4.12  SEM micrograph results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica using methyl ester of Madhuca longifolia oil as precursor at a flow rate of 20 mL per hour at 550 °C

The HR-TEM micrograph recorded to study diameter and number of layers of the MWNTs synthesized is shown in Figure 4.13. HR-TEM analysis shows a dense rope like tubular carbon nanotubes grown on the surface of chosen catalyst clusters. In this study the investigator found a coexistence of two kinds of CNTs in the sample synthesized at 550 °C. The first one corresponds to MWNTs of small outer diameter around 30-50 nm and the second one is constituted of diameter around 12-16 nm. Yeoh et al. (2009) reported a similar result for the synthesis of high purity MWNTs over Co-Mo/MgO catalyst by catalytic CVD of methane, confirming the formation of CNTs. Whereas, Morancais et al. (2007) observed a mixture of smaller and larger diameter CNTs in the sample synthesized using ethylene at 550 °C in a fluidized bed reactor under Ar atmosphere.
Figure 4.13 HR-TEM micrograph results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica using methyl ester of Madhuca longifolia oil as precursor at a flow rate of 20 mL per hour at 550 °C

The crystalline nature of the sample synthesized was studied using Raman spectrum depicted in Figure 4.14. The Raman spectral study of the as-grown samples shows the presence of all the characteristics bands for the MWNTs viz. The D-band (1300-1330 cm\(^{-1}\)) associated with the defects and impurities, the G-band (1500-1600 cm\(^{-1}\)) corresponds to tangential stretching (\(E_{2g}\)) mode of highly oriented graphitic layer (Dresselhaus et al. 2002; Belin et al. 2005). In this study, the D and G peaks were observed at about 1351 cm\(^{-1}\) and 1578 cm\(^{-1}\) for the samples synthesized at 550 °C. the intensity ratio values of the G and D band, ie \(I_G/I_D\) value 1.26 provides an important information relative to the purity and structural Morphology of the nanotubes that the MWNTs were made up of defective layers ad adhesion of amorphous carbon on the sides of walls.
4.1.2.3 Morphology of MWNTs synthesized from methyl ester Madhuca longifolia oil at 650 °C

The temperature (650 °C) influence on morphology of MWNTs synthesized from methyl ester of Madhuca longifolia oil with a flow rate of 20 mL per hour under nitrogen atmosphere over silica supported Fe-Co-Mo catalysts was studied. The representative SEM image of MWNTs synthesized was shown in the Figure 4.8 a nice growth of MWNTs with diameter of 30-40 nm as shown in Figure 4.8 was observed at 650 °C.

The diameter and number of layers of MWNTs synthesized was studied by HR-TEM and the results are shown in the Figure 4.9 the HR-TEM image clearly shows well graphitized layers of MWNTs with inner and outer diameter in the range of 12 and 22-36 nm respectively, grown from catalytic decomposition of Madhuca longifolia oil at 650 °C. The selectivity towards MWNTs formation was observed in the best optimized condition of the
present study at 650 °C amorphous carbon and catalyst particles were rarely seen in the HR-TEM image of the sample.

It can be observed from HR-TEM image that the nanotubes formed are of multi-walled type composed of around twenty eight walls and most graphene layers grow perpendicularly to the growth axis of the tubes.

The average outer diameter of the nanotube ranges from 22-36 nm and inner diameter is about 12 nm. This observation may be attributed to the presence of oxygen in the precursor molecule which may act as oxidizing agent for removal of amorphous carbon as stated by Ghose et al. (2007) in producing SWNTs from eucalyptus oil. Hsieh et al. (2009) in their study of growth of CNTs from acetylene over Ni alumina catalyst in a fluidized bed reactor observed a similar result. HR-TEM study of the present work shows that the inter layer space of the synthesized MWNTs is 0.343 nm which corresponds to inter layer space of graphene sheets in a graphite structure (Kelly et al. 1981).

The crystalline nature of MWNTs as a function of temperature was studied using Raman spectroscopy and the result is shown in the Figure 4.10. In this study, the D and G peaks were observed at about 1347 cm$^{-1}$ and 1572 cm$^{-1}$ for the samples prepared at 650 °C as shown in Figure 4.10. The Raman spectrum also exhibits a band at 2680 cm$^{-1}$ called the D′-band attributed to the overtone of the D band. The $I_G/I_D$ ration calculated from the peak area was 1.64. This high value further evidences the well graphitization of the MWNTs synthesized.

**4.1.2.4 Morphology of MWNTs synthesized from Madhuca longifolia oil at 750 °C**

The effect of temperature on morphology of MWNTs synthesized at 750 °C using *Madhuca longifolia* oil as a precursor with a flow rate of 20 mL per hour over silica supported Fe-Co-Mo catalysts was studied. The
SEM image of MWNTs synthesized was shown in the Figure 4.15. The carbon nanotube with diameter of 60-70 nm was observed for the as-grown sample at 750 °C (Figure 4.15). The results are in good accordance with the reports of Li et al. (2002) that the increasing diameter of MWNTs at higher temperature may be due to agglomeration of catalyst particles at that temperature.

![SEM micrograph results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica using Madhuca longifolia oil as precursor at a flow rate of 20 mL per hour at 750 °C](image)

Figure 4.15 SEM micrograph results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica using Madhuca longifolia oil as precursor at a flow rate of 20 mL per hour at 750 °C

The representative HR-TEM image of MWNTs synthesized, shown in Figure 4.16 was used to study the influence of temperature on diameter and number of layers of MWNTs.

The carbon deposit obtained at 750 °C were found to be consist of MWNTs of diameter 30-70 nm with around sixty three graphitic layers and adhere amorphous carbon. This observation agrees with experimental results reported by several authors. Afre et al. (2006) in their studies of synthesis of CNTs by spray pyrolysis of turpentine oil at different temperatures reported that with increasing temperature to 700 °C, the amount of amorphous carbon...
was reduced and MWNTs with increased number of graphene walls formed. Ghosh et al. (2007) reported that decomposition of eucalyptus oil using ferrocene at 700 °C was insufficient for growth of MWNTs and at 800 °C MWNTs were formed. Further, they reported that MWNTs with abundant amount of amorphous carbon were formed at 900 °C.

![HR-TEM micrograph results of MWNTs synthesized over Fe-CO-Mo catalysts supported on silica using Madhuca longifolia oil as precursor at a flow rate of 20 mL per hour at 750 °C](image)

Figure 4.16 HR-TEM micrograph results of MWNTs synthesized over Fe-CO-Mo catalysts supported on silica using Madhuca longifolia oil as precursor at a flow rate of 20 mL per hour at 750 °C

The crystalline nature of the product synthesized at 750 °C was studied using Raman spectrum recorded (Figure 4.17). The spectrum shows D peak at 1352 cm\(^{-1}\) and G peak at 1591 cm\(^{-1}\) as shown in Figure 4.17. A similar peaks was observed by Afre et al. (2006) in their study of synthesis of CNTs from turpentine oil at different temperatures and reported that the frequency shift of the D and G peak perhaps due to defects in the tube such as pentagons, curvature etc. the \(I_D/I_G\) value of one indicates comparatively poor crystallization of graphene layers synthesized at 750 °C.
In general, higher temperature initiates pyrolysis of carbon source in vapor state which results in formation of amorphous carbon and structural defects. Even though high reaction temperature apparently favors higher pyrolysis rate, the growth of nanotubes with a bigger diameter happens due to agglomeration of catalyst particles which are usually observed in catalytically growth CNTs.

In the present study, the $I_G/I_D$ ratio rises rapidly from 1.26 to 1.64 when reaction temperature varied from 550 to 650 °C. A further increase in temperature from 650 to 750 °C results in a rapid drop in the $I_G/I_D$ ratio to 1.10. This trend is generally observed in synthesis of CNTs (Kwok et al. 2010; Hornyak et al. 2002; puretzky et al. 2005; Chakraborty et al. 2006). Among the chosen experimental temperatures, the highest $I_G/I_D$ ratio observed for 650 °C. This indicates the highest Morphology and purity of samples formed at 650 °C. Bachmatiuk et al. (2008) reported synthesis of high Morphology MWNTs at 650 °C using ethanol and cyclohexanol by CVD method. Dresselhaus et al. (2002) reported that a decreasing $I_G/I_D$ value corresponds to a higher proportion of sp$^3$ like carbon, originates from disorder in the sp$^2$ hybridized carbon. The lower $I_G/I_D$ value of one for MWNTs synthesized at 750 °C indicates lattice distortion in the curved graphene sheets, tube ends etc. The absence of peaks below 300 cm$^{-1}$ in Raman spectrum of the carbon deposits obtained in this study reveals the absence of SWNTs (Afre et al. 2006).

The present study indicates, under the experimental conditions, carbon nanotubes with good morphology cannot be grown effectively at low (550 °C) and high (750 °C) temperatures, while smaller diameter carbon nanotubes in high yield are formed at 650 °C. This part of study shows that temperature influences the growth and morphology of MWNTs to large extent and 650 °C was found to be optimum temperature for the growth of good
Morphology MWNTs in high yield from the chosen *Madhuca longifolia* oil under the experimental conditions.

![Raman spectra of MWNTs grown on Fe-Co-Mo catalyst supported on silica using *Madhuca longifolia* oil as precursor at a flow rate of 20 mL per hour at 750 °C](image)

**Figure 4.17** Raman spectra of MWNTs grown on Fe-Co-Mo catalyst supported on silica using *Madhuca longifolia* oil as precursor at a flow rate of 20 mL per hour at 750 °C

### 4.1.3 Effect of Precursor Flow Rate on the Synthesis of MWNTs from *Madhuca longifolia* oil

Preliminary experiments conducted with different flow rate of precursor keeping other parameters constant shows the 10 to 30 mL per hour flow rate is suitable for MWNTs synthesis. These results are only preliminary and do not necessarily correspond to optimum growth conditions. Furthermore, the aim of this work is to synthesize well crystalline MWNTs in good yield from renewable natural precursor of *Madhuca longifolia* oil. Therefore, in this part, the effect of precursor flow rate on yield and morphology of MWNTs synthesized from renewable natural precursors over silica supported Fe-Co-Mo catalysts at 650 °C is studied.
This part of work illustrates the effect of *Madhuca longifolia* oil flow rate on the properties of MWNTs grown on Fe-Co-Mo catalyst supported on silica at 650 °C under nitrogen atmosphere. The MWNTs are synthesized using *Madhuca longifolia* oil as precursor at three different flow rates viz. 10, 20 and 30 mL per hour by spray pyrolysis method over Fe-Co-Mo catalysts supported on silica at 650 °C and the results of characterization of the products are discussed with reference to yield and morphology of MWNTs.

### 4.1.3.1 Determination of optimum precursor Flow Rate for maximum yield of MWNTs

In this part, determination of optimum precursor flow rate is fixed for subsequent experiments. This study is carried out at different flow rate of precursor to investigate the influence on yield of MWNTs over Fe-Co-Mo catalysts supported on silica at reaction temperature of 650 °C. The graphical representation of results obtained is shown in the Figure 4.18.

The Figure 4.18 shows that an increase of precursor flow rate from 10 mL per hour to 20 mL per hour increase the yield of MWNTs from 51% to 68%. Further increase of flow rate to 30 mL per hour leads to reduction in yield (35%). Several authors have reported similar observations for the synthesis of carbon nanotubes. Zhan et al. (2007) demonstrated that methane conversion is almost constant for CH$_4$ flow rate between 70 and 100 mL per minute, but starts to drop for more than 100 mL per minute. Kumar & Ando (2005) reported that high yield of MWNTs with least amorphous carbon were formed from 0.2-0.4 g camphor pyrolysed over 0.04-0.08 g zeolite at 700 °C. Shaijumon et al. (2005) stated that the weight of the carbon deposit passed through a maximum as a function of acetylene gas flow rate. They also stated that the yield of CNTs was affected by the deactivation of catalyst particles at higher flow rate of precursor due to the formation of the
carbon coated particles which further decreases the pyrolysis of acetylene. Therefore, the higher yield obtained for the precursor flow of 20 mL per hour may be attributed to the effective pyrolysis of the precursor at this experimental condition.

Figure 4.18  Yield of MWNTs grown on Fe- Co-Mo catalysts supported on silica at 650 °C using *Madhuca longifolia* oil as precursor at a flow rate of 10 mL, 20 mL and 30 mL per hour

4.1.3.2  Morphology of MWNTs synthesized with precursor flow rate of 10 mL per hour

The morphology of MWNTs synthesized using *Madhuca longifolia* oil as a precursor with a flow rate of 10 mL per hour over silica supported Fe-Co-Mo catalysts at 650 °C is studied. The representative SEM image of MWNTs synthesized is shown in the Figure 4.19. The Figure shows the MWNTs formed are of 58-68 nm in diameter with branch like structure. Formation of such a structure indicates the defects in the graphene layer. The defects in the MWNTs formed at this flow rate may be due to lower rate of decomposition of precursor owing to lower vapor pressure of precursor.
Figure 4.19 SEM micrograph Results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica at 650 °C using Madhuca longifolia oil as precursor at a flow rate of 10 mL per hour

The representative HRTEM micrograph recorded to study diameter and number of layers of the MWNTs synthesized is shown in Figure 4.20. It is observed from the Figure 4.20 that the MWNTs formed with inner and outer diameter of 20 and 60-68 nm respectively. Madhuca longifolia oil at a flow rate of 10 mL per hour produced MWNTs of poor Morphology and graphitization with three different diameter range grown is evident from HRTEM image shown in Figure 4.20.
The crystalline nature of graphitic layers of MWNTs is studied using Raman spectrum recorded for the carbon deposit (Figure 4.21). The G-band attributed to crystalline nature of graphitic layers is observed at 1568 cm\(^{-1}\) and D-band assigned to the defects in the layers is observed at 1353 cm\(^{-1}\). The \(I_G/I_D\) ratio calculated is 1.14. This indicated that the MWNTs formed are of moderate graphitization.
4.1.3.3 Morphology of MWNTs synthesized with precursor Flow Rate of 20 mL per hour

The influence of precursor flow rate on morphology of MWNTs synthesized over silica supported Fe-Co-Mo catalysts at 650 °C is studied. The representative SEM image of MWNTs synthesized is shown in the Figure 4.8. At the flow rate of 20 mL per hour, the MWNTs formed are straight and the diameter in the range of 30-40 nm (Figure 4.8). This shows the continuous growth of MWNTs at this precursor flow rate. The fact can be attributed to high rate of decomposition of precursor with increased vapor pressure of precursor.

The MWNTs synthesized is characterized using HRTEM technique to determine diameter and number of layers of MWNTs. The results are shown in the Figure 4.9. The HRTEM image shows the evidences of well crystallization of MWNTs formed at a precursor flow rate of 20 mL per hour.
The inner and outer diameter of the synthesized MWNTs are about 12 and 22-36 nm and consist of twenty eight graphene layers with inter layer distance of 0.34 nm. It is also found that the outer layer of MWNTs was not covered with amorphous carbon and inner and outer diameter of MWNTs is uniform over entire length of the tube. The MWNTs synthesized under this experimental condition is found with no encapsulated catalyst particle.

The crystalline nature of MWNTs as a function of precursor flow rate is studied using Raman spectroscopy and the result is shown in the Figure 4.10. The characteristic D and G peaks are observed at 1347 and 1572 cm$^{-1}$ respectively. The Raman spectrum also exhibits a band at 2680 cm$^{-1}$ called the D’-band attributed to the overtone of the D band. The $I_G/I_D$ ratio of 1.64 for the peaks shows that MWNTs consist of well graphitized graphene layers.

4.1.3.4 Morphology of MWNTs synthesized with precursor Flow Rate of 30 mL per hour

The effect of precursor flow rate on morphology of MWNTs synthesized at 650 °C over silica supported Fe-Co-Mo catalysts is studied. The morphology of MWNTs synthesized is characterrized using SEM technique and representative image is shown in the Figure 4.22.

The increase in precursor flow rate to 30 mL per hour has resulted in amorphous carbon and MWNTs of diameter in the range of 60-80 nm with encapsulated catalyst particle as shown in Figure 4.22. This may be due to higher rate of decomposition of precursor.
Figure 4.22 SEM micrograph Results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica at 650 °C using methyl ester of *Madhuca longifolia* oil as precursor at a flow rate of 30 mL per hour

Shaijumon et al. (2005) stated that at higher acetylene flow rates, the rate of nanotubes growth is lower than that of pyrolytic decomposition which would have resulted in the formation of amorphous carbon. Furthermore, Esconjauregui et al. (2009) stated that the catalyst irrespective of the catalyst metal deactivates as the partial pressure of any of the carbon source was increased, probably due to catalyst encapsulation by amorphous carbon or graphitic layers. The results obtained in this study with high boiling natural precursor viz. methyl ester of *Madhuca longifolia* oil agree with literature reports.

The representative HRTEM image use to study the influence of precursor flow rate on diameter and number of layers of MWNTs synthesized is shown in Figure 4.23. The Figure 4.23 shows the defective structure of MWNTs synthesized using precursor flow rate of 30mL per hour. The tube
diameter is relatively thicker in the range of 45-80 nm with amorphous carbon at the outer wall of the tube. Fonseca et al. (1998) reported that the outer diameter of nanotubes increases when the C₂H₂ conversion rate increases. They reasoned that when the C₂H₂ flow rate per catalytic site is higher, the number of nanotube layers is also higher resulting in thicker nanotubes. A similar observation in the synthesis of MWNTs at different flow rates of precursors was reported by Piedigrossio et al. (2000) and ghosh et al. (2007). Piedigrossio et al. (2000) stated, at the optimum acetylene content in the gas mixture nearly 90% of acetylene is converted into carbon. At higher acetylene flow rate, the rate of nanotubes growth was lower than that of pyrolytic decomposition which resulted in the formation of amorphous carbon. Ghosh et al. (2007) also reported a similar trend that higher flow rate produced a lot of amorphous carbon and lower flow rate produced mainly MWNTs.

![HRTEM micrograph Results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica at 650 °C using methyl ester of Madhuca longifolia oil as precursor at a flow rate of 30 mL per hour](image)

Figure 4.23  HRTEM micrograph Results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica at 650 °C using methyl ester of Madhuca longifolia oil as precursor at a flow rate of 30 mL per hour
The sample synthesized is characterized using Raman spectroscopy to evaluate the crystalline nature of MWNTs formed and the result is depicted in Figure 4.24. The Raman spectral analysis provides information about the structure of MWNTs through the characteristic D and G peaks. The appearance of D and G peaks at 1346 and 1581 cm$^{-1}$ respectively with $I_G/I_D$ value of 1.19 indicates the formation of MWNTs with defective graphitic layers. This thesis work suggests that maintaining the precursor flow rate at appropriate level is necessary to obtain the desired Morphology of MWNTs.

4.2 METHYL ESTER OF *BRASSICA JUNCEA* OIL AS CARBON SOURCE FOR SYNTHESIS OF MWNTS

4.2.1 Effect of Catalyst on Yield and the Morphology of MWNTs Synthesized from methyl ester of *Brassica juncea* oil

Much of the research has been carried out on effect of transition metals as catalyst on growth of CNTs using volatile precursors. The transition metal or combination of transition metals is found to control the formation of...
MWNTs. The detailed study of effect of trimetallic combinations on the growth of carbon nanostructures using non-volatile precursor has not to the best of investigator knowledge been published. The effect of trimetallic combinations as catalyst on growth of MWNTs by spray pyrolysis of non volatile precursors was not reported. Choosing the three types of catalyst viz. Fe, Fe-Co and Fe-Co-Mo catalysts supported on silica, the manipulation of the growth rate, the diameter and the crystallinity of MWNTs synthesized form methyl ester of *Brassica juncea* oil were discussed.

### 4.2.1.1 Determination of optimum catalyst composition for maximum yield of MWNTs from methyl ester of *Brassica juncea* oil

The effect of catalyst composition on yield of MWNTs was studied at 650 °C using methyl ester of *Brassica juncea* oil as precursor at a flow rate 20 mL per hour over Fe catalyst supported on silica under nitrogen atmosphere, Fe-Co catalysts supported on silica and Fe-Co-Mo catalysts supported on silica. The Figure 4.25 reveals the dependence of the yield of carbon deposits on chosen catalysts viz. Fe, Fe-Co and Fe-Co-Mo catalysts supported on silica. The yield on Fe catalyst supported on silica was about 41%. Whereas, the yield increased greatly about 73% in case of Fe-Co catalyst supported on silica. Several studies have revealed that Fe was very active in the decomposition of hydrocarbons; however, Co was necessary for the formation of MWNTs of good Morphology. It has conclusively been shown by Kumar et al. (2005) that Fe and Co catalysts combine the advantages and leads to higher growth rate of MWNTs of good Morphology. It is of interest to note that almost 89% yield was observed with Fe-Co-Mo catalysts supported on silica. A similar observation was reported by willems et al. (2000) in their study of synthesis of CNTs by decomposition of acetylene over silica supported transition metals. Mendoza et al. (2005) investigated that the role of Mo in CNTs synthesis and concluded that high yield of CNTs with low levels of impurities was related to be promoter
character of Mo in the reaction. Jeong et al. (2010) investigated the impact of Fe-Co-Mo catalysts supported on alumina for the growth of CNTs and concluded the impact of Fe-Co-Mo catalysts supported on alumina for the growth of CNTs and concluded that the catalysts favors increased carbon deposit through better nucleation of CNTs growth. A strong relationship between the catalyst and yield of MWNTs deposit was observed in this study. The increase in yield may be due to collaborative advantages of high catalytic decomposition, effectiveness in growing CNTs and promotional character of Fe, Co and Mo respectively.

![Graph](image.png)

**Figure 4.25** Yield of MWNTs grown at 650 °C using methyl ester of *Brassica juncea* oil as precursor at a flow rate of 20 mL per hour over Fe, Fe-Co and Fe-Co-Mo catalysts supported on silica

### 4.2.1.2 Effect of Fe catalyst supported on Silica on morphology of MWNTs synthesized from methyl ester of *Brassica juncea* oil

In this part, the effect of Fe catalyst supported on silica on the morphology of MWNTs synthesized from methyl ester of *Brassica juncea* oil as precursor at a flow rate of 20 mL per hour at 650 °C under nitrogen
atmosphere was studied. The representative SEM image of MWNTs synthesized using the catalyst is shown in the Figure 4.26. The spray pyrolysis of methyl ester of *Brassica juncea* oil over Fe catalyst supported on silica at 650 °C resulted in average Morphology MWNTs of diameter in the range 35-70 nm (Figure 4.26) and also contain somewhat less amount of amorphous carbon. Similar results were reported by Li et al. (2008). In their report on study of co-production of hydrogen and MWNTs from ethanol decomposition over Fe/Al₂O₃ catalyst at 750 °C concluded that there were almost no CNTs formed on Fe/Al₂O₃ besides amorphous carbon.

![SEM micrograph results of MWNTs synthesized at 650 °C using methyl ester of *Brassica juncea* oil as precursor at a flow rate of 20 mL per hour over Fe catalyst supported on silica](image)

The HR-TEM image, recorded with a view to examine the role of the catalyst on diameter and number of layers of MWNTs synthesized is shown in the Figure 4.27. The influence of the catalyst on morphology of as-grown MWNTs were studied through the number of graphene layers, the
crystallinity, the inner, and the outer diameter of the nanotubes measured from HR-TEM images. The HR-TEM image (Figure 4.27) of MWNTs synthesized over Fe catalyst supported on silica shows a layer of amorphous carbon on the outer surface of MWNTs. The inner and outer diameter of MWNTs was 10 and 20-30 nm respectively.

![HR-TEM micrograph results of MWNTs synthesized at 650 °C using *Brassica juncea* oil as precursor at a flow rate of 20 mL per hour over Fe catalyst supported on silica](image)

Figure 4.27 HR-TEM micrograph results of MWNTs synthesized at 650 °C using *Brassica juncea* oil as precursor at a flow rate of 20 mL per hour over Fe catalyst supported on silica

The crystalline nature of the sample synthesized using the catalyst was studied using Raman Spectroscopy. The Raman spectrum analysis, provide information about the structure of CNTs, through G-band originating from crystalline disorders and lattice imperfections in the curved grapheme sheets. The Raman spectrum of carbon deposit obtained over Fe-Co catalyst supported on silica was shown in Figure 4.28. The characteristic peaks for MWNTs, D-band and G-band were observed at 1340 cm⁻¹ and 1572 cm⁻¹ respectively. The Raman spectrum also exhibits a band at 2685 cm⁻¹ called the
D’-band attributed to the overtone of the D band. The $I_G/I_D$ ratio calculated was 1.16. These values indicate that the carbon deposit grown over Fe catalyst supported on silica was MWNTs constituted with defective graphitic layers.

Figure 4.28  Raman spectra of MWNTs grown at 650 °C using methyl ester of *Brassica juncea* oil as precursor at a flow rate of 20 mL per hour over Fe catalyst supported on silica

4.2.1.3  Effect of Fe-Co Catalysts Supported on Silica on Morphology of MWNTs Synthesized from methyl ester of *Brassica juncea* oil

The influence of Fe-Co catalysts supported on silica on morphology of MWNTs synthesized at 650 °C using methyl ester of *Brassica juncea* oil at a flow rate of 20 mL per hour was studied. The representative SEM image of MWNTs synthesized using the catalyst is shown in the Figure 4.29. According to the SEM image, MWNTs synthesized over Fe catalyst supported on silica were very tangle indicating the presence of structural defects responsible for twisting of the tubes. These tubes were found to be
relatively thick and uniform diameter walls covered with amorphous carbon & catalyst. The diameter of the MWNTs grown was in the range of 55-65 nm. The experimental results were consistent with the literature report of Willems et al. (2000) that Co as a catalyst is important for obtaining morphology MWNTs, while the use of Fe can give a higher carbon yield but the product of lower morphology.

![SEM micrograph results of MWNTs synthesized at 650 °C using methyl ester of Brassica juncea oil as precursor at a flow rate of 20 mL per hour Fe-Co catalyst supported on silica](image)

Figure 4.29  SEM micrograph results of MWNTs synthesized at 650 °C using methyl ester of Brassica juncea oil as precursor at a flow rate of 20 mL per hour Fe-Co catalyst supported on silica

The role of catalyst on diameter and number of layers of MWNTs synthesized from methyl ester Brassica juncea oil was studied using HR-TEM and the result is shown in the Figure 4.30. The MWNTs grown over Fe-Co catalyst supported on silica were good in graphitization but thin in size and without any outer layer of amorphous carbon (Figure 4.30). The inner and the outer diameter of the MWNTs were 10 and 22-30 nm respectively. The tube consists of sixteen concentric graphitic layers. The HR-TEM image shown in Figure 4.30 reveals the MWNTs grown over Fe-Co catalyst
supported on silica possessed well crystallized graphene layers with almost no amorphous carbon on their surface. There was almost no encapsulation of catalyst particles inside the MWNTs grown. The interlayer distance calculated was 0.342 nm.

Figure 4.30 HR-TEM micrograph results of MWNTs synthesized at 650 °C using methyl ester of Brassica juncea oil as precursor at a flow rate of 20 mL per hour over Fe-Co catalysts supported on silica

The Raman spectrum shows the impact of the catalyst on crystalline nature of the MWNTs synthesized. The Raman spectrum of carbon deposit obtained over Fe-Co catalyst supported on silica was shown in Figure 4.31 and the $I_G/I_D$ ratio calculated was 1.38. The relatively higher $I_G/I_D$ ratio of MWNTs grown over Fe-Co catalysts supported on silica than Fe catalyst supported on silica indicates that the best graphitized MWNTs were grown with incorporation of Co in the catalyst.
4.2.1.4 Effect of Fe-Co-Mo catalysts supported on Silica on morphology of MWNTs synthesized from methyl ester of *Brassica juncea* oil

The role of Fe-Co-Mo catalysts supported on silica on morphology of MWNTs synthesized from methyl ester of *Brassica juncea* oil at a flow rate of 20 mL per hour at 650 °C was studied. The morphology of MWNTs synthesized was characterized by SEM and the representative image is shown in the Figure 4.32. The SEM image (Figure 4.32) of carbon deposit over Fe-Co-Mo catalyst supported on silica shows densely populated good Morphology MWNTs. The as-grown MWNTs has the diameter in the range of 35-45 nm which is relatively narrower than MWNTs obtained over Fe-Co catalysts supported on silica.
Figure 4.32 SEM micrograph results of MWNTs synthesized over Fe-Co-Mo Catalysts supported on silica using *Brassica juncea* oil as precursor at a flow rate of 20 mL per hour at 650 °C

The MWNTs synthesized was characterized using HR-TEM technique to determine and number of layers of MWNTs and the representative image is shown in the Figure 4.33. The outer diameter of MWNTs was in the range of 15-38 nm. It is important to note from the Figure 4.33 that MWNTs grown over Fe-Co-Mo catalyst consist of around twenty eight graphitic with narrow inner diameter (9 nm) and less amorphous carbon. The fact can be attributed to the collaborative effect of Mo catalyst. The collaborative effect of Mo has been identified as an important contributing factor for the growth of MWNTs by several authors. Zhang et al. (2008) observed that the inner diameter, the outer diameter and the number of layers of CNTs synthesized over MgO supported Ni and Mo were increased with increasing Mo mole fraction.
Figure 4.33 HR-TEM micrograph results of MWNTs synthesized over Fe-Co-Mo catalyst supported on silica using methyl ester of *Brassica juncea* oil as precursor at a flow rate of 20 mL per hour at 650 °C

They suggested the variation in the diameter was ascribed to the catalyst particle size and bimetallic catalyst ratio. Yoeh et al. (2010), in their study of the role of Mo in Co-Mo/MgO for large-scale production of high Morphology CNTs, observed that CNTs of smallest and narrowest diameter distribution was obtained with 20 wt% of Mo loading. Flahaut et al. (2004) studied effect of the ratio between Co and Mo for CNTs growth and reported that the production of Mo must be kept as low as possible when the synthesis of CNTs with a low number of walls is desired. Cassel et al. (1999) attribute the increase in yield of CNTs by the Fe/Mo catalyst to the role played by Mo catalyst in promoting the aromatization of methane at elevated temperatures. The collaborative effect of Mo was very evident. Furthermore to this Kitayanan et al. (2000) and Cassel et al. (1999) pointed out that Mo was required to enhance the activity of oxide catalyst and even distribution of metal particles on substrate.
It is important to note in the present study that the proportion of nanotubes covered with amorphous carbon is smaller when trimetallic catalyst (Fe-Co-Mo catalyst supported on silica) is used than bimetallic catalyst (Fe-Co catalyst supported on silica).

The crystalline nature of MWNTs was studied using Raman spectroscopy and the result is shown in the Figure 4.34. The spectrum shows G-band at 1573 cm\(^{-1}\) representing the tangential stretching mode of highly oriented pyrolytic graphite and a peak at 1349 cm\(^{-1}\) corresponds to D-band originating from crystalline disorders and lattice imperfections in the curved graphene sheets. The Raman spectrum also exhibits a band at 2690 cm\(^{-1}\) called the D’-band attributed to the overtone of the D band. The higher I\(_G\)/I\(_D\) value of 1.91 compared to the value obtained for the sample synthesized over Fe-Co or Fe catalysts evidences the perfection in graphitization of layers of MWNTs grown over Fe-Co-Mo catalysts.

![Figure 4.34 Raman spectra of MWNTs grown on Fe-Co-Mo catalyst supported on silica at 650 ˚C using methyl ester of Brassica juncea oil as precursor at a flow rate of 20 mL per hour](image)

Figure 4.34 Raman spectra of MWNTs grown on Fe-Co-Mo catalyst supported on silica at 650 ˚C using methyl ester of Brassica juncea oil as precursor at a flow rate of 20 mL per hour
The incorporation of Mo as catalyst favors formation of narrower MWNTs. Herrera et al. (2001) observed a similar behavior for the CNTs growth with Co, Mo/MgO catalyst and stated that high Morphology thin-walled CNTs were obtained on addition of small yield of Mo along with catalyst material. Jeong et al. (2010) also reported that the CNTs grown on Fe, Co and Mo/Al₂O₃ catalyst using fluidized bed reactor exhibited a higher degree of crystalline perfection. The \( I_D/I_G \) value of the MWNTs prepared in this study over Fe-Co-Mo catalyst supported on silica was considerably lower than those reported in the literature \( (I_D/I_G = 0.7-1.3) \) for CCVD grown MWNTS. It revel the good Morphology of MWNTs synthesized using Fe-Co-Mo catalyst supported on silica. Kumar et al. (2005) reported MWNTs formation from camphor by decomposition on a high silica zeolite support impregnated with Fe-Co catalyst. They evidenced formation of SWNTs along with MWNTs through RBM band, representing the \( A_{1g} \) symmetry of the tube, in the range 181-259 nm. According to Rao et al. (1997) SWNTs show a sholder like appearance at 1571 cm\(^{-1}\) reflecting the splitting of G-band, a characteristic peak due to quantum confinement effects. Absence of RBM band and peak due to quantum confinement effects in Raman spectrum of the carbon deposits obtained in this study revel absence of SWNTs. The results that the composition of catalyst particle plays an important role in governing the crystallinity of CNTs, but further extensive studies are necessary to provide definite evidence for property of collaborative effect of catalysts.

The investigator obtained best crystallization of graphene with inner and outer diameter of 9 and 15-38 nm for the MWNTs synthesized over Fe-Co-Mo catalyst supported on silica. Hence, the investigator concluded that the combination of Fe, Co and Mo plays an important role and Co incorporation in the catalyst improves the crystallinity whereas the Mo in low
fraction favors formation of thin MWNTs. The effectiveness of Fe, responsible for high cracking rate and nucleation of CNTs growth, was improved in presence of Co and Mo catalyst. The high crystalline nature of graphene walls was attributed to Co where as the smaller diameter was ascribed to the collaborative effect of Mo catalyst which prevents agglomeration of catalyst particles.

4.2.2 Effect of Temperature on the Yield and Morphology of MWNTs Synthesized from methyl ester of Brassica juncea Oil

A second series of experiments were carried out with a view of establishing the influence of temperature viz. 550, 650 and 750 °C on synthesis of MWNTs from methyl ester of Brassica juncea oil at a flow rate of 20 mL per hour Fe-Co-Mo catalysts supported on silica under N₂ atmosphere.

This part of study deals with optimum reaction temperature to be fixed for subsequent experiments. The effect of temperature on yield of MWNTs from vapor phase decomposition of methyl ester of Brassica juncea oil at a flow rate of 20 mL per hour over Fe-Co-Mo catalysts supported on silica was studied.

4.2.2.1 Optimization of temperature for maximum yield of MWNTs

This part of study deals with the optimization of reaction temperature for subsequent experiments. The effect of temperature on the yield of MWNTs from vapor phase decomposition of methyl ester of Brassica juncea oil at a flow rate of 20 mL per hour over Fe-Co-Mo catalysts supported on silica is studied. The results are depicted in the Figure 4.35.
In the presence study, the low yield of carbon deposit (43%) is produced at 550 °C. Noticeably high yield (89%) of carbon deposit is observed for the reaction temperature 650 °C. Further increase in temperature to 750 °C results in a decrease in the yield (51%). Zhan et al. (2007) observed a similar trend in their study of synthesis of CNTs by catalytic decomposition of methane and reported a high yield of MWNTs at 900 °C. This trend is generally observed in the synthesis of CNTs by CVD method. It is clear that low yield of carbon deposit obtained at 550 and 750 °C. This work suggests the non-activation of catalysts and high rate of pyrolysis followed by encapsulation of catalysts as reasons for the low yield at 550 °C and 750 °C respectively. The high yield obtained at 650 °C in this study is attributed to activation of catalyst and almost equal rate of pyrolysis of precursor and CNTs growth.

Figure 4.35  Yield of MWNTs grown on Fe-Co-Mo catalyst Supported on silica using methyl ester of Brassica juncea oil as precursor at a flow rate of 20 mL per hour at 550, 650 and 750 °C

In the presence study, the low yield of carbon deposit (43%) is produced at 550 °C. Noticeably high yield (89%) of carbon deposit is observed for the reaction temperature 650 °C. Further increase in temperature to 750 °C results in a decrease in the yield (51%). Zhan et al. (2007) observed a similar trend in their study of synthesis of CNTs by catalytic decomposition of methane and reported a high yield of MWNTs at 900 °C. This trend is generally observed in the synthesis of CNTs by CVD method. It is clear that low yield of carbon deposit obtained at 550 and 750 °C. This work suggests the non-activation of catalysts and high rate of pyrolysis followed by encapsulation of catalysts as reasons for the low yield at 550 °C and 750 °C respectively. The high yield obtained at 650 °C in this study is attributed to activation of catalyst and almost equal rate of pyrolysis of precursor and CNTs growth.
4.2.2.2 Morphology of MWNTs synthesized from methyl ester of Brassica juncea oil at 550 °C

In this part, the effect of temperature on the morphology of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica using Brassica juncea oil as precursor at a flow rate of 20 mL per hour was studied. The representative SEM image of MWNTs synthesized at this temperature is shown in the Figure 4.36. The SEM image (Figure 4.36) indicated the existence of MWNTs with diameter of 40-70 nm. A similar result were reported in literature (Afre et al. 2006; Ghosh et al. 2007)

The representative HR-TEM image recorded with a view to examine the role of temperature on diameter and number of layers of MWNTs synthesized is shown in the Figure 4.37. It can be observed from HR-TEM image (Figure 4.37) that the nanotubes formed are of multi-walled type composed of bamboo structure in some portion of the tube with poor structure and also graphene layers were not clearly visible. The average outer diameter of the nanotubes ranges from 40-65 nm and inner diameter is about 14 nm. Such an observation may be attributed to the low activation of the catalyst at 550 °C.

Hsieh et al. (2009) in their study of growth of CNTs from acetylene over Ni/alumina catalyst in a fluidized bed reactor observed a similar result. HR-TEM study of the present work shows that the inter layer space of the synthesized MWNTs is 0.34 nm which corresponds to inter layer space of graphene sheets in a graphite structure (Kelly et al. 1981). Raman Spectrum was recorded to find out the crystalline nature of the sample synthesized. The Raman spectrum obtained for the sample is shown in the Figure 4.38. The spectrum showed the characteristic D-peak at 1345 cm⁻¹ and G-peak at 1567 cm⁻¹, which evidenced the formation of graphitic structure. The \( \frac{I_G}{I_D} \) value of 1.20 indicated that the MWNTs grown at 550 °C do not contain well crystalline graphitic layers.
Figure 4.36 SEM micrograph results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica using methyl ester of Brassica juncea oil as precursor at a flow rate of 20 mL per hour at 550 °C

Figure 4.37 HR-TEM micrograph results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica using methyl ester of Brassica juncea oil as precursor at a flow rate of 20 mL per hour at 550 °C
Figure 4.38 Raman spectra of MWNTs grown Fe-Co-Mo catalysts supported on silica using methyl ester of *Brassica juncea* oil as precursor at a flow rate of 20 mL per hour at 550 °C

4.2.2.3 Morphology of MWNTs synthesized from methyl ester of *Brassica juncea* oil at 650 °C

The influence of temperature on morphology of MWNTs synthesized over silica supported Fe-Co-Mo catalyst using methyl ester of *Brassica juncea* oil at flow rate of 20 mL per hour was studied. The representative SEM image of MWNTs synthesized at 650 °C is shown in the Figure 4.32. The growth of entangle MWNTs with diameter in the range of 20-40 nm was evident from the SEM image shown in Figure 4.32.

The diameter and number of layers of MWNTs synthesized was observed using HR-TEM shown in Figure 4.33. The well crystalline graphitic layers of MWNTs grown at 650 °C were evident from the HR-TEM image shown in Figure 4.33. The inner and outer diameter of MWNTs synthesized was in the range of 10 and 20-40 nm respectively. A number of graphitic layers of the MWNTs were found to be around thirty six, HR-TEM study of...
the present work shows that the inter layer space of the synthesized MWNTs is 0.34 nm which corresponds to inter layer space of graphene sheets in a graphite structure (Kelly et al. 1981; Hsieh et al. 2009) in their study of growth of CNTs from acetylene over Ni/alumina catalyst in fluidized bed reactor observed a similar result.

The selectivity towards MWNTs formation was observed in the best optimized condition of the present study at 650 °C and amorphous carbon and catalyst particles are rarely seen. This observation may be attributed to the presence of oxygen in the precursor molecule which may act as oxidizing agent for removal of amorphous carbon as stated by Ghose et al. (2007) in producing SWNTs from eucalyptus oil.

The Raman spectrum depicted in Figure 4.34 shows the impact of the temperature on crystalline nature of the MWNTs synthesized. The D and G peaks were observed at about 1348 cm\(^{-1}\) and 1573 cm\(^{-1}\) for the MWNTs grown at 650 °C. The Raman spectrum also exhibits a band at 2687 cm\(^{-1}\) called the D'-band attributed to the overtone of the D band The I_G/I_D value calculated for the peaks was 1.92. This indicated that well graphitized MWNTs were grown at 650 °C.

4.2.2.4 Morphology of MWNTs synthesized from methyl ester of *Brassica juncea* oil at 750°C

The morphology of MWNTs synthesized at 750 °C over silica supported Fe-Co-Mo catalysts using methyl ester of *Brassica juncea* oil at a flow rate of 20 mL per hour under nitrogen atmosphere was studied.
Figure 4.39  SEM micrograph results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica using methyl ester of Brassica juncea oil as precursor at a flow rate of 20 mL per hour at 750 °C

The SEM image showing the morphology of MWNTs grown at 750 °C was depicted in the Figure 4.39. Though the MWNTs grown were rather straight, the diameter of the MWNTs was found to be around 50-60 nm.

The influence of temperature on diameter and number of layer of MWNTs was observed using HR-TEM and the results were shown in Figure 4.40. The diameter of the MWNTs was around 30-40 nm while the inner diameter was about 10 nm. The number of graphitic layer calculated was around ninety. This observation agrees with the literature reports (Afre et al. 2006). The larger diameter of MWNTs synthesized at 750 °C may be attributed to the agglomeration of catalyst particles at this temperature.
The Raman spectrum shown in Figure 4.41 illustrates the crystalline nature of the MWNTs synthesized at this temperature. The D- peak and the G- peak were observed at 1343 cm\(^{-1}\) and 1579 cm\(^{-1}\) respectively for the MWNTs grown at 750 °C. The Raman spectrum also exhibits a band at 2684 cm\(^{-1}\) called the D’-band attributed to the overtone of the D band. The \(I_G/I_D\) ratio calculated was 1.16. A drop in \(I_G/I_D\) ratio for MWNTs grown at 750 °C was observed comparing to \(I_G/I_D\) ratio for MWNTS grown at 650 °C. Dresslhaus et al. (2002) obtained a similar result and reported that a decreasing \(I_G/I_D\) ratio corresponds to a higher proportion of Sp\(^3\) like carbon originates from disorder in the Sp\(^2\) hybridized graphitic layers. Therefore, the authors suggests that the decrease in \(I_G/I_D\) ratio for MWNTs grown at 750 °C may be attributed to the defects in graphitic layers and amorphous carbon adhere on the walls of MWNTs.
Figure 4.41  Raman spectra of MWNTs grown on Fe-Co-Mo catalysts supported on silica using methyl ester of *Brassica juncea* oil as precursor at a flow rate of 20 mL per hour at 750 °C

4.2.3  Effect of Flow Rate on the Synthesis of MWNTs from methyl ester of *Brassica juncea* Oil

In this part, the effect of precursor flow rate on synthesis of MWNTs using methyl ester of *Brassica juncea* oil by spray pyrolysis method is discussed. The precursor oil is sprayed at different flow rate viz. 10, 20 and 30 mL per hour over Fe-Co-Mo catalysts supported on silica at 650 °C to synthesis MWNTs. The as-grown MWNTs are characterized by SEM, TEM and Raman spectroscopy techniques and based on that the effect of precursor flow rate on the yield and morphology of MWNTs produced is discussed.

4.2.3.1 Determination of optimum precursor flow rate for maximum yield of MWNTs

This party of study deals with determination of optimum precursor flow rate for synthesize of MWNTs using *Brassica juncea* oil. The investigation is carried out at different flow rate of *Brassica juncea* oil to find the influence on yield of MWNTs over silica supported Fe-Co-Mo catalysts at
reaction temperature of 650 °C. The result shows 46% yield of MWNTs when *Brassica juncea* oil sprayed at the precursor flow rate of 10 mL per hour over Fe-Co-Mo catalysts supported on silica at 650 °C. An increase in yield (89%) was observed for the precursor flow rate of 20 mL per hour. The precursor flow rate of 30 mL per hour results in 58% yield of MWNTs. A similar trend has been observed by Kumar & Ando (2003b). They synthesized MWNTs with optimum flow rate of camphor as carbon precursor and stated that yield drastically decreases on both ends of the optimum precursor flow rate. For this observation, they reasoned the rate of decomposition of precursor at the reaction zone. The investigator favors a similar reason for the observation that lower precursor flow (10 mL per hour) of *Brassica juncea* oil at the reaction zone results in low yield owing to lower rate of decomposition; while higher precursor flow rate (30 mL per hour) results in the low yield due to encapsulation of catalyst particle by carbon material produced through rapid decomposition of precursor.

Figure 4.42  Yield of MWNTs grown on Fe-Co-Mo catalysts supported on silica at 650 °C using methyl ester of *Brassica juncea* oil as precursor at a flow rate of 10 mL, 20 mL and 30 mL per hour
At optimum precursor flow rate of 20 mL per hour, the growth rate of MWNTs and the rate of decomposition of precursor may be equal, so that continuous growth of MWNTs occurs and thus higher yield of MWNTs is observed.

### 4.2.3.2 Morphology of MWNTs synthesized with precursor flow rate of 10 mL per hour

The morphology of MWNTs synthesized using methyl ester of *Brassica juncea* oil as a precursor with a flow rate of 10 mL per hour over silica supported Fe-Co-Mo catalysts at 650 °C under nitrogen atmosphere is studied. Figure 4.43 represent the SEM image of MWNTs. The Figure 4.43 shows MWNTs with a diameter in the range of 70-90 nm at a flow rate of 10mL per hour over Fe-Co-Mo catalyst supported on silica at reaction temperature of 650 °C.

![SEM micrograph of MWNTs](image)

**Figure 4.43** SEM micrograph Results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica at 650 °C using methyl ester of *Brassica juncea* oil as precursor at a flow rate of 10 mL per hour
The representative HRTEM micrograph shown in Figure 4.44 illustrates the diameter and number of layers of the MWNTs synthesized. The Figure 4.44 shows the HRTEM image of the sample synthesized for precursor flow rate of 10 mL per hour. It is found from the figure that the inner and outer diameter were 10 and 35-45 nm. The Figure 4.43 also indicates that the MWNTs tend to be curlier and surrounded or interspersed with a lot visible amorphous carbon material with catalysts.

Figure 4.44 HR-TEM micrograph Results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica at 650 °C using methyl ester of *Brassica juncea* oil as precursor at a flow rate of 10 mL per hour
Figure 4.45  Raman spectra of MWNTs grown on Fe-Co-Mo catalysts supported on silica at 650 °C using methyl ester of Brassica juncea oil as precursor at a flow rate of 10 mL per hour

The crystalline nature of the sample studied using Raman spectroscopy. The Figure 4.45 shows Raman spectra for the samples synthesized with precursor flow rate of 10 mL per hour. The G band at 1573 cm\(^{-1}\) is attributed to well crystallize carbon structure, while the D band at 1352 cm\(^{-1}\) is attributed to defects in the structure. The low value (1.12) of relative intensity of the G and D band (\(I_G/I_D\)) obtained for the MWNTs synthesized with precursor flow rate of 10 mL per hour shows the poorly crystallized MWNTs formation. This may be due to the low concentration of precursor in the reaction zone.

4.2.3.3  Morphology of MWNTs synthesized with precursor flow rate of 20 mL per hour

The effect precursor flow rate on morphology MWNTS synthesized over silica supported on Fe-Co-Mo catalysts at 650 °C is studied. The representative SEM image of MWNTs synthesized is shown in the Figure 4.32. The Figure 4.32 indicates that MWNTs formed were with
diameter in the range 20-40 nm. The diameter and number of layers of the MWNTs is studied using HRTEM technique. A HRTEM images (Figure 4.33) of sample prepared using methyl ester of *Brassica juncea* oil as carbon precursor at a flow rate of 20 mL per hour over Fe-Co-Mo catalysts supported on silica at the reaction temperature of 650 °C clearly shows the well graphitized layers of a typical MWNTs with uniform inner (10 nm) and outer diameter (20-40 nm). The HRTEM image also reveals that encapsulated catalyst or amorphous carbon is rarely seen in the sample. The image indicates that the MWNTs are composed of around thirty six walls and layers grow perpendicular to the growth axis of the tube. The crystalline nature of MWNTs as a function of precursor flow rate is studied using Raman spectroscopy. The Figure 4.34 shows the Raman spectra recorded for the samples synthesized with precursor flow rate of 20 mL per hour. Increase in $I_G/I_D$ value (1.92) for the sample synthesized with precursor flow rate of 20 mL per hour shows good graphitization of graphene layers of MWNTs.

### 4.2.3.4 Morphology of MWNTs synthesized with precursor flow rate of 30 mL per hour

The morphology of MWNTs synthesized with precursor flow rate of 30 mL per hour at 650 °C over silica supported Fe-Co-Mo catalysts is studied. The SEM image recorded for the sample synthesized is shown in the Figure 4.46.

However, an increase of precursor flow rate to 30 mL per hour produces largely amorphous carbon and small yield of metal encapsulated in MWNTs of size around 70-90 nm (Figure 4.46). On a close look, the image in Figure 4.46 shows the presence of heavier material impurities other than carbon as a spot. It is likely due to encapsulation of catalyst particle. Bai et al. (2003) found a similar observation in their studies with benzene as precursor and stated that the mole ratio between the catalyst and carbon precursor strongly affected the nature of carbon product. They also stated that at higher
concentration of benzene, carbon nanofibers were formed and at moderate concentration MWNTs were favored.

Figure 4.46 SEM micrograph Results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica at 650 °C using methyl ester of *Brassica juncea* oil as precursor at a flow rate of 30 mL per hour

The MWNTs synthesized is characterized using HRTEM to reveal the influence of precursor flow rate on diameter and number of layers of MWNTs and the representative image is shown in Figure 4.47. The representative HRTEM image (Figure 4.47) of carbon deposit obtained with flow rate to 30 mL per hour at the reaction temperature of 650 °C shows accumulation of less amorphous carbon and small Yield of metal incorporated MWNTs of size around 60 nm. Jen et al. (2005) found a similar observation in a study where carbon spheres synthesized from hydrocarbon in the form of liquid using the pyrolysis technique and reported that as the flow rate of hydrocarbon increases, the diameter of the carbon sphere increases.
Figure 4.47 HR-TEM micrograph Results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica at 650 °C using methyl ester of Brassica juncea oil as precursor at a flow rate of 30 mL per hour

The Raman spectroscopic technique is used to evaluate the crystalline nature of MWNTs formed and the result is depicted in Figure 4.48. The Figure 4.49 shows the Raman spectra recorded for the samples synthesized with precursors flow rate of 30 mL per hour. The decreases in $I_G/I_D$ value (1.17) for the sample prepared with precursor flow rate of 30 mL per hour indicates more defects in as-grown sample. The defects in MWNTs can be attributed to increase of precursor concentration in the reaction zone and encapsulation of catalyst particles. An increase of precursor concentration in the reaction zone leads to increase in decomposition of precursor over catalysts. Above the critical concentration of precursor, rate of decomposition of precursor exceeds rate of diffusion of carbon into the catalyst particle and thus encapsulation of metal particles occurs.
Figure 4.48  Raman spectra of MWNTs grown on Fe-Co-Mo catalysts supported on silica at 650 °C using methyl ester of *Brassica juncea* oil as precursor at a flow rate of 30 mL per hour

4.3 METHYL ESTER OF *ORYZA SATIVA* OIL AS CARBON SOURCE FOR SYNTHESIS OF MWNTS

4.3.1 Effect of Catalyst on Yield and the Morphology of MWNTs Synthesized from methyl ester of *Oryza sativa* Oil

A study on effect of chosen transition metals (Fe, Co and Mo) as catalyst on growth of MWNTs using methyl ester of *Oryza sativa* oil by spray pyrolysis method was carried out in this part. Choosing the catalyst combination, the growth rate, the diameter and the crystallinity of MWNTs synthesized from methyl ester of *Oryza sativa* oil were discussed.

4.3.1.1 Determination of optimum catalyst composition for maximum yield of MWNTs from methyl ester of *Oryza sativa* oil

The effect of catalyst composition on yield of MWNTs was studied at 650 °C using *Oryza sativa* oil as precursor at a flow rate of 20 mL per hour over Fe catalyst supported on silica under nitrogen atmosphere. The
Figure 4.49 reveals that the catalyst influences on the yield of carbon deposit. The yield of carbon deposit obtained using Fe catalyst supported on silica was about 52%. The yield increased to about 96% with Fe-Co catalyst supported on silica. When Fe-Co-Mo catalyst supported on silica was used, it was almost 103% yield obtained. Willems et al. (2000) found similar observation in synthesis of CNTs by decomposition of acetylene over silica supported transition metals. Mendoza et al. (2005) investigated the influence of Mo on the CVD production of CNTs and reported that the production of high yield of CNTs with low levels of impurities was related to the promoted character of Mo in the reaction.

A similar observation was reported by Jeong et al. (2010) that alumina supported Fe, Co and Mo catalyst act as nuclei for CNTs growth and increases the productivity. Kumar et al. (2005) obtained high yield of MWNTs by decomposition of camphor over zeolite supported Fe and Co catalysts. A strong relationship between the catalyst and yield of MWNTs deposit was observed in their study. The general conclusion arrived was Fe metal supported on silica was very active in the decomposition of hydrocarbons, however Mo was necessary for the formation of MWNTs of good Morphology. Silica supported Fe and Mo catalyst combine the advantages and leads to higher growth rate of MWNTs of good Morphology. In the present study, it is interesting to note that a bi-metallic combination of Fe-Mo catalyst supported on silica leads to high yields of MWNTs by decomposition of *Oryza sativa* oil at 650 °C. Hence, the investigator conclude that the increase in yield may be due to synergetic advantages of high catalytic decomposition, effectiveness in growing CNTs and promotional character of Fe, Co and Mo respectively. It is consistent with the observations of Jeong et al. (2010) and Kumar et al. (2005).
4.3.1.2  Effect of Fe catalyst supported on silica on morphology of MWNTs synthesized from methyl ester of *Oryza sativa* oil

In this part, the effect of silica supported Fe catalyst on the morphology of MWNTs synthesized at 650 °C from methyl ester of *Oryza sativa* oil with a flow rate of 20 mL per hour was studied. The representative SEM images of MWNTs synthesized using the catalyst is shown in the Figure 4.50.

The Figure 4.50 indicated low Morphology MWNTs of diameter in the range of 60-72 nm with abundant amount of amorphous carbon were grown using methyl ester of *Oryza sativa* oil over Fe catalyst supported on silica at 650 °C by spray pyrolysis method. Li et al. (2008) also reported very...
low yield of CNTs during the co-production of hydrogen and MWNTs from ethanol decomposition over Fe/Al₂O₃ catalyst at 750 °C.

Figure 4.50  SEM micrograph results of MWNTs synthesized at 650 °C using methyl ester of *Oryza sativa* oil as precursor at a flow rate of 20 mL per hour over Fe catalyst supported on silica

The HR-TEM results of experiments conducted with a view to examine the role of the catalyst on diameter and number of layers of MWNTs synthesized is shown in the Figure 4.51. The influence of the catalyst on morphology of as-grown MWNTs were studied through the number of graphene layers, the crystallinity, the inner, and the outer diameter of the nanotubes measured from HR-TEM images. The HR-TEM image (Figure 4.51) of MWNTs synthesized over Fe-Co catalyst supported on silica shows a layer of amorphous carbon on the outer surface of MWNTs structures. The inner and outer diameter of MWNTs structures were 11 and 20-30 nm respectively. The catalysts were entrapped with in poorly graphitized MWNTs structure.
Figure 4.51 HR-TEM micrograph results of MWNTs synthesized at 650 °C using methyl ester of Oryza sativa oil as precursor at a flow rate of 20 mL per hour over Fe catalyst supported on silica

The impact of the catalyst on the crystalline nature of MWNTs synthesized was studied using Raman spectroscopy. The result is shown in the Figure 4.52. The spectrum shows G-band at 1572 cm$^{-1}$ representing the tangential stretching mode of highly oriented graphite and peak at 1344 cm$^{-1}$ corresponds to D-band originating from crystalline disorders and lattice imperfections in the curved graphene sheets. The Raman spectrum also exhibits a band at 2681 cm$^{-1}$ called the D’-band attributed to the overtone of the D band. According to the Figures 4.52, the value of I_G/I_D for the MWNTs grown on Fe catalyst supported on silica was 1.19.
4.3.1.3 Effect of Fe-Co catalysts supported on silica on morphology of MWNTs synthesized from methyl ester of *Oryza sativa* oil

The influence of silica supported Fe-Co catalysts on morphology of MWNTs synthesized from methyl ester of *Oryza sativa* oil at a flow rate of 20 mL per hour at 650 °C was studied. The representative SEM image of MWNTs synthesized is shown in the Figure 4.53. Experiments were conducted using the Fe-Co catalyst supported on silica at 650 °C and thus formed carbon deposit was analyzed using SEM (Figure 4.53). According to this SEM image, MWNTs synthesized were short and tangle indicating the presence of structural defects responsible for twisting of the tubes. The SEM image evidences reasonably thin MWNTs of diameter in the range of 50-70 nm. The experimental results were consistent with the literature report of Willems et al. (2000) that Co as a catalyst is important for obtaining Morphology MWNTs, while the use of Fe can give a higher carbon yield but the product of lower Morphology.

Figure 4.52 Raman spectra of MWNTs grown at 650 °C using methyl ester of *Oryza sativa* oil as precursor at a flow rate of 20 mL per hour over Fe catalyst supported on silica
The effect of the catalyst on diameter and number of layers of MWNTs synthesized was studied using HR-TEM image shown in Figure 4.54.

Figure 4.53 SEM micrograph results of MWNTs synthesized at 650 ºC using methyl ester of *Oryza sativa* oil as precursor at a flow rate of 20 mL per hour over Fe-Co catalysts supported on silica

The Figure 4.54 shows that the tubular nature of MWNTs grown over Fe-Co catalyst supported on silica were spiral in shape, thick in size and covered with a dense outer layer of amorphous carbon. The inner and the outer diameter of the MWNTs were 10 and 35-46 nm respectively. The tube may consist of around eighty graphitic layers.
Figure 4.54  HR-TEM micrograph results of MWNTs synthesized at 650 °C using methyl ester of *Oryza sativa* oil as precursor at a flow rate of 20 mL per hour over Fe-Co catalysts supported on silica.

Figure 4.55  Raman spectra of MWNTs grown at 650 °C using methyl ester of *Oryza sativa* oil as precursor at a flow rate of 20 mL per hour over Fe-Co catalysts supported on silica.
The impact of the catalyst on crystalline nature of MWNTs synthesized was studied using Raman spectroscopy and result is shown in Figure 4.55. According to the Figure 4.55, the D-peak and G-peak were observed at 1348 cm\(^{-1}\) and 1578 cm\(^{-1}\) respectively. The Raman spectrum also exhibits a band at 2680 cm\(^{-1}\) called the D’-band attributed to the overtone of the D band. The value of \(I_G/I_D\) for the MWNTs grown Fe-Co catalyst supported on silica was 1.26, which is higher than \(I_G/I_D\) ration for MWNTs grown over Fe catalyst. This indicated that catalysts with Co produced MWNTs with better graphitization.

4.3.1.4 Effect of Fe-Co-Mo catalysts supported on Silica on morphology of MWNTs synthesized from methyl ester of *Oryza sativa* oil

The effect of silica supported Fe-Co-Mo catalysts on morphology of MWNTs synthesized from methyl ester of *Oryza sativa* oil at a flow rate of 20 mL per hour at 650 °C was studied. The representative SEM image of MWNTs synthesized is shown in the Figure 4.56. It is intriguing to note that densely populated good morphology of MWNTs (Figure 4.56) were formed over Fe-Co-Mo catalyst using methyl ester of *Oryza sativa* oil at 650 °C. The as-grown MWNTs have the diameter in the range of 40-60 nm which is relatively thinner MWNTs than that obtained over Fe-Co catalyst.

The diameter and number of layers of MWNTs synthesized was studied using HR-TEM technique and the representative image is shown in the Figure 4.57. The Figure 4.57 reveals the HR-TEM image of MWNTs having good crystallized graphite layers without encapsulated catalyst particles on tube wall grown over Fe-Co-Mo catalyst supported on silica and tube core and wall clearly visible. The average inner and the outer diameter of
these MWNTs were found to be 8 and 18-24 nm respectively. The inner layer distance calculated was 0.342 nm.

![SEM micrograph results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica using methyl ester of Oryza sativa oil as precursor at a flow rate of 20 mL hour at 650 °C](image)

Yoeh et al. (2010), in their study of the role of Mo in Co-Mo/MgO for large scale production of high morphology CNTs, observed that CNTs of smallest and narrowest diameter distribution was obtained with 20 wt% of Mo loading. Flahaut et al. (2004) stated that the ratio between Co and Mo plays an important role and the proportion of Mo must be kept as low as possible when the synthesis of CNTs with a low number of walls is desired. Cassel et al. (1999) attribute the increase in yield of CNTs by the Fe/Mo catalyst to the role played by Mo catalyst in promoting the aromatization of methane at elevated temperatures. It is important to note the reports of Kitayanan et al. (2000) and Cassel et al. (1999) that the proportion of nanotubes covered with amorphous carbon was smaller when trimetallic catalyst (Fe-Co-Mo) was used than
bimetallic catalyst support and moreover Mo was required to enhance the activity of oxide catalyst and even distribution of metal particles on substrate.

Figure 4.57  HR-TEM micrograph results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica using methyl ester of *Oryza sativa* oil as precursor at a flow rate of 20 mL hour at 650 °C

The structural morphology of MWNTs as a function of catalyst was studied using Raman spectroscopy and the result is shown in the Figure 4.58. According to the Figure 4.58, the value of $I_G/I_D$ for the MWNTs grown on Fe-Co-Mo catalyst supported on silica was 2.51. The incorporation of Mo as a catalyst favors formation of narrower MWNTs. Herrera et al. (2001) observed a similar behavior for the CNTs growth with Co, Mo/MgO catalyst and stated that high morphology thin-walled CNTs were obtained on addition of small Yield of Mo along with catalyst material. Jeong et al. (2010) also reported that the CNTs grown on Fe, Co and Mo/Al$_2$O$_3$ catalyst using fluidized bed reactor exhibited a higher degree of crystalline perfection. The $I_D/I_G$ value of the MWNTs prepared over Fe-Co-Mo catalyst supported on silica was considerably lower than those reported in the literature ($I_D/I_G = 0.7-1.3$) for
CCVD grown MWNTS (Kwok et al. 2005) revealed the good Morphology of MWNTs produced using Fe-Co-Mo catalyst supported on silica. Kumar et al. (2005) reported MWNTs formation from camphor by decomposition on a high silica zeolite support impregnated with Fe-Co catalyst. According to their report formation of SWNTs along with MWNTs was confirmed through RBM band, representing the $A_{1g}$ symmetry of the tube, in the range 181-259 nm. According to Rao et al. (1997) SWNTs show a shoulder like appearance at 1571 cm$^{-1}$ reflecting the splitting of G-band, a characteristic peak due to quantum confinement effects. Absence of RBM band and shoulder like appearance in G-band in Raman spectrum of the samples show absence of SWNTs. The results are consistent with the HR-TEM results (Lee at al 2002). The above results suggest that the composition of catalyst particle play an important role in governing the crystallinity and length of MWNTs. Hence, by optimizing these conditions a better product can be synthesized using appropriate proportion of catalytic supporting material. However, further extensive studies are necessary to provide a definite evidence for collaborative effect of catalysts.

This is consistent with the observations of Kitiyanan et al. (2000) and Cassel et al. (1999) hence the investigator concludes that the catalyst improves the crystallinity whereas the Mo in low fraction favors formation of thin and lengthy MWNTs. The effectiveness of Fe, responsible for high cracking rate and nucleation of CNTs growth, was improved in presence of Co and Mo catalyst. The high crystallinity of graphene walls was attributed to Co where as the smaller diameter was ascribed to the collaborative effect of Mo catalyst which prevents agglomeration of catalyst particles.
4.3.2 Effect of Temperature on the Morphology and Yield of MWNTs Synthesized from methyl ester of *Oryza sativa* Oil

A third series of experiments were carried out with a view of establishing the influence of temperature viz. 550, 650 and 750 °C on synthesis of MWNTs from methyl ester of *Oryza sativa* oil at a flow rate of 20 mL per hour over Fe-Co-Mo catalysts supported on silica under nitrogen atmosphere.

4.3.2.1 Optimization of temperature for maximum yield of MWNTs

Optimum temperature to be fixed for subsequent experiments was discussed in this part of study. The temperature influence on yield of MWNTs over Fe-Co-Mo catalysts supported on silica using methyl ester of *Oryza sativa* oil as precursor at a flow rate of 20 mL per hour was studied. The results obtained are illustrated in Figure 4.59. The low yield of MWNTs
(48%) obtained at 550 °C is attributed to the low cracking efficiency of catalyst at this temperature and the lower thermal energy of precursor oil vapor. At 650 °C, the yield obtained was 103% and this may be attributed to the high thermal energy of the precursor vapor which is highly sufficient to induce cracking of the precursor molecule. It is evident from the Figure 4.59 that among the chosen temperature conditions (550, 650 and 750 °C) the highest yield (103%) is obtained at 650 °C. The amorphous carbon generated by thermal cracking of precursor at 750 °C deposited as layer on the surface of catalyst. The yield obtained for temperature condition may be attributed to thermal energy of precursor vapors which favors high rate of cracking on the catalyst. As rate of formation of carbon on the catalyst exceeds the rate of dissolution of it into the catalyst, an encapsulation of catalyst particle by graphitized carbon occurs. Thus nucleation and the growth of MWNTs on the catalyst are reduced. This is comparable to the observation of Kumar & Ando (2005), Nagaraju et al. (2002) and Zhan et al. (2007).

![Graph showing yield of MWNTs grown on Fe-Co-Mo catalyst Supported on silica using methyl ester of Oryza sativa oil as precursor at a flow rate of 20 mL per hour at 550, 650 and 750 °C.]

**Figure 4.59** Yield of MWNTs grown on Fe-Co-Mo catalyst Supported on silica using methyl ester of *Oryza sativa* oil as precursor at a flow rate of 20 mL per hour at 550, 650 and 750 °C.
4.3.2.2 Morphology of MWNTs synthesized from methyl ester of *Oryza sativa* oil at 550 °C

The temperature influence on morphology of MWNTs synthesized over silica supported Fe-Co-Mo catalyst from methyl ester of *Oryza sativa* oil with a flow rate of 20 mL per hour was studied at 550 °C. The SEM image of MWNTs synthesized at this temperature was shown in the Figure 4.60. The SEM image (Figure 4.60) shows short MWNTs of diameter in the range of 60-80 nm. Such a MWNTs growth may be due to low rate of cracking of precursor molecule at 550 °C temperature.

![SEM micrograph](image)

**Figure 4.60** SEM micrograph results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica using methyl ester of *Oryza sativa* oil as precursor at a flow of 20 mL per hour at 550 °C

The sample synthesized was characterized with HR-TEM with a view to examine the influence of temperature on diameter and number of layers of MWNTs synthesized. The HR-TEM image recorded was shown in the Figure 4.61.
Large diameter (65 nm), thick fiber like structured MWNTs with defective layers enclosing catalyst was formed at 550 °C. The formation of MWNTs with this morphology may be ascribed to low thermal energy of precursor molecule and low catalytic activity.

Figure 4.61 HR-TEM micrograph results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica using methyl ester of Oryza sativa oil as precursor at effect of 20 mL per hour at 550 °C

The crystalline nature of MWNTs synthesized at 550 °C was analyzed using Raman spectrum recorded for the sample (Figure 4.62). The $I_G/I_D$ ratio reveal the degree of graphitization. The $I_G/I_D$ ratio of MWNTs samples synthesized at 550 °C shown in Figure 4.62 reveals the temperature dependence of degree of graphitization of MWNTs. The study on effect of temperature on degree of graphitization reveals that MWNTs synthesized at 550 °C show low graphitization ($I_G/I_D$ ratio 1.32).
4.3.2.3 Morphology of MWNTs synthesized from methyl ester of *Oryza sativa* oil at 650 °C

Morphology of MWNTs synthesized from methyl ester of *Oryza sativa* oil at a flow rate of 20 mL per hour over Fe-Co-Mo catalysts supported on silica at 650 °C was studied. The representative SEM image of MWNTs synthesized is shown in the Figure 4.56. Formation of lengthy and un-uniform thickness of MWNTs with a diameter of 40-60 nm grown at 650 °C was attributed to the optimum thermal energy of precursor molecule and activation of catalyst which favors the high rate of cracking of precursor molecule on catalyst particle.

Effect of the temperature on diameter and number of layers of MWNTs synthesized was studied using HR-TEM image in Figure 4.57. The MWNTs grown at 650 °C has moderate graphitizing of grapheme layers of around 18-24 nm thick tube entrapping catalyst particles. The reaction
temperature 650 °C is an optimum temperature for the synthesis of lengthy MWNTs but with entrapped catalyst particles. This observation may be attributed to higher rate of cracking of precursor molecule than the dissolution of amorphous carbon into the catalyst particle.

Impact of the temperature on crystalline nature of MWNTs synthesized was studied using Raman spectroscopy and result is shown in Figure 4.58. The characteristic D-peak and G-peak were observed at 1352 cm$^{-1}$ and 1581 cm$^{-1}$ respectively. The Raman spectrum also exhibits a band at 2681 cm$^{-1}$ called the D’-band attributed to the overtone of the D band. The $I_G/I_D$ rate of MWNTs sample synthesized at 650 °C reveals the temperature dependence of degree of graphitization of MWNTs. A moderately crystalline MWNTs synthesized at 650 °C was evident from the $I_G/I_D$ value 2.51 obtained for the sample.

4.3.2.4 Morphology of MWNTs synthesized from methyl ester of *Oryza sativa* oil at 750 °C

The influence of temperature on morphology of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica using methyl ester of *Oryza sativa* oil at a flow rate of 20 mL per hour was studied. The SEM image of MWNTs synthesized at this temperature is shown in the Figure 4.63.

At 750 °C, the precursor molecule begins to undergo thermal cracking which leads to the formation of amorphous carbon and also the catalyst particle tends to form agglomeration at this temperature. Thus MWNTs with large diameter (80-90 nm) and more of amorphous carbon were formed at reaction temperature of 750 °C.
On the basis of HR-TEM result shown in Figure 4.64, the diameter and number of layers of MWNTs synthesized was studied. It was observed that the inner and outer diameter of MWNTs synthesized at 750 °C were 8 and 40-55 nm. At 750 °C, the encapsulated catalysts may begin to assimilate the surrounded carbon layers and facilitate the growth of MWNTs, thus long and well graphitized MWNTs were observed. Extensive HR-TEM investigations of the carbon deposit obtained in these experimental conditions did not reveal SWNTs formation.

Figure 4.65 shows the Raman spectra which illustrate the crystalline nature of MWNTs synthesized at this temperature. The $I_G/I_D$ ratio of MWNTs samples synthesized at 750 °C shown in Figures 4.65 reveals the temperature dependence of degree of graphitization of MWNTs. The highest $I_G/I_D$ value (1.62) observed for the sample synthesized at 750 °C comparing to the values of samples synthesized at 550 and 650 °C indicated the well graphitized of MWNTs synthesized at 750 °C. The absence of RBM peak in the Raman spectrum of samples shows absence of SWNTs in these samples.

Figure 4.63 SEM micrograph results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica using methyl ester of *Oryza sativa* oil as precursor at a flow rate of 20 mL hour at 750 °C
Figure 4.64  HR-TEM micrograph results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica using methyl ester of Oryza sativa oil as precursor at a flow rate of 20 mL hour at 750 °C

Figure 4.65  Raman spectra of MWNTs grown on Fe-Co-Mo catalysts supported on silica using methyl ester of Oryza sativa oil as precursor at a flow rate of 20 mL hour at 750 °C
4.3.3 Effect of flow rate on the synthesis of MWNTs from methyl ester of *Oryza sativa* oil

This part of the work illustrates the results of experiments carried out to determine the significant impact of flow rate on the yield and diameter of the product synthesized. Methyl ester of *Oryza sativa* oil is used for synthesis of carbon nano structures by spray pyrolysis method. The oil is sprayed at different flow rate (10 mL, 20 mL and 30 mL per hour) over Fe-Co-Mo catalyst supported on silica at 650 °C for the synthesis of carbon nanostructures. The as-grown nanostructures are characterized by SEM, HRTEM, and Raman spectroscopy techniques and the results are discussed.

4.3.3.1 Determination of optimum precursor flow rate for maximum yield of MWNTs

The optimum precursor flow rate to attain maximum yield of MWNTs is determined through series of experiments. The study is carried out with different flow rate of precursor to investigate the influence on yield of MWNTs over silica supported Fe-Co-Mo catalysts at reaction temperature of 650 °C. The graphical representation of results obtained is shown in the Figure 4.66. The Figure 4.66 shows the plot of the mass percentage of MWNTs synthesized versus the precursor flow rate. A low yield (47%) of carbon nano structures is observed with *Oryza sativa* oil at a flow rate of 10 mL per hour over Fe-Co-Mo catalysts supported on silica at 650 °C. A highly improved yield (103%) of carbon nanostructure is observed for the precursor flow rate of 20 mL per hour at 650 °C. The precursor flow rate of 30 mL per hour in a similar reaction condition produces low yield of MWNTs (55%). Similar observations for the synthesis of CNTs by varying precursor flow rate were reported by Andrew et al. (2006) and Shaijumon et al. (2005). Andrew
et al. (2006) reported MWNTs yield of anywhere between 8% and 11% using camphor and camphor analogs. Furthermore, Shaijumon et al. (2005) reported the MWNTs yield in the range of 11-27% using acetylene as carbon precursor and stated that the concentration of precursor in the reaction zone is an important factor for the growth of carbon nanotube; the yield might have considerably reduced at low as well as high precursor concentration.

Figure 4.66  Yield of MWNTs grown on Fe-Co-Mo catalysts supported on silica at 650 °C using methyl ester of *Oryza sativa* oil as precursor at a flow rate of 10 mL, 20 mL and 30mL per hour

4.3.3.2  Morphology of MWNTs synthesized with precursor flow rate of 10 mL per hour

The morphology of MWNTs synthesized using methyl ester of *Oryza sativa* oil as a precursor with a flow rate of 10 mL per hour over silica supported Fe-Co-Mo catalysts at 650 °C is studied. Figure 4.67 shows the SEM image of MWNTs sample grown for methyl ester of *Oryza sativa* oil
flow rate 10 mL per hour. The MWNTs are found to be irregularly shaped with diameter in the range of 55-60 nm. The reason for the observation may be attributed to insufficient precursor concentration at the reaction zone to generate carbon through pyrolysis.

Figure 4.67 SEM micrograph Results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica at 650 °C using methyl ester of *Oryza sativa* oil as precursor at a flow rate of 10 mL per hour

The HRTEM micrograph of the sample synthesized with precursor flow rate of 10 mL per hour over Fe-Co-Mo catalysts at 650 °C is shown in Figure 4.68. The image shows the irregularly shaped MWNTs with encapsulated catalyst particles. The MWNTs formed with poor graphitization for 10 mL per hour precursor flow rate, may be due to low concentration of precursor molecule at the reaction zone.
Figure 4.68  HRTEM micrograph Results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica at 650° C using methyl ester of *Oryza sativa* oil as precursor at a flow rate of 10 mL per hour

The structural Morphology of the sample synthesized is studied using Rama spectroscopy and the spectrum recorded is depicted in Figure 4.69. The low value of $I_G/I_D$ ratio (1.46) indicates the poorly graphitized MWNTs formation as shown in Figure 4.69 for precursor flow rate of 10 mL per hour. This may be due to insufficient precursor concentration at the reaction zone for pyrolysis and subsequent MWNTs formation.
4.3.3.3 Morphology of MWNTs synthesized with precursor flow rate of 20 mL per hour

The effect of precursor flow rate on morphology of MWNTs synthesized over silica supported Fe-Co-Mo catalysts at 650 °C is studied. The representative SEM image of MWNTs synthesized is shown in the Figure 4.56. The increase in flow rate of the precursor oil to 20 mL per hour resulted in formation of MWNTs with thickness of around 40-60 nm. This may be attributed to the effective decomposition of sufficient precursor concentration.

The MWNTs synthesized is characterized using HRTEM technique to determine diameter and number of layers of MWNTs. The HRTEM images MWNTs sample synthesized with 20 mL per hour flow rate of methyl ester of Oryza sativa oil over Fe-Co-Mo catalysts supported on silica at a reaction temperature of 650 °C is shown in Figure 4.57. The MWNTs has inner and...
outer diameter in the range of 8 nm & 18-24 nm. The HRTEM image (Figure 4.57) indicates the metal particles, seen as a dark spot on the image, are trapped in the inner hollow region of MWNTs.

The structural Morphology of MWNTs as a function of precursor flow rate was studied using Raman spectroscopy and the result is shown in the Figure 4.58. The characteristic D and G peaks are observed at 1352 and 1581 cm\(^{-1}\) respectively. The \(I_G/I_D\) value of 2.51 for sample prepared with 20 mL per hour flow rate indicates that the MWNTs have defective structures and moderate crystallization of graphene layers. This supports the HRTEM results.

4.3.3.4 Morphology of MWNTs synthesized with precursor flow rate of 30 mL per hour

The morphology of MWNTs synthesized with a precursor flow rate of 30 mL per hour at 650 °C over silica supported Fe-Co-Mo catalysts is studied. The morphology of MWNTs synthesized is characterized using SEM technique and the representative image is shown in the Figure 4.70. The precursor flow rate of 30 mL per hour resulted in randomly short shaped carbon nanostructured with diameter in the range 50-60 nm. Such a formation may be due to cause of higher precursor concentration at the reaction zone.
The HRTEM analysis of MWNTs synthesized is carried out to study the influence of precursor flow rate on diameter and number of layers of MWNTs and the representative image is shown in Figure 4.71. The observed MWNTs are in the range of 45 nm thick with inner diameter of 11 nm. The number of graphitic walls is around twenty. Apart from the MWNTs catalyst particles encapsulated coil-like nanostructure is formed when precursor flow rate is increased to 30 mL per hour. A similar observation was reported by Kang et al. (2008). Amorphous carbon formation in large yield for precursor flow rate of 30 mL per hour may be due to rapid decomposition of precursor material. Higher precursor concentration at the reaction zone favors high rate of cracking and thus formation of catalyst particles encapsulated coil-like nanostructure.
Figure 4.71 HRTEM micrograph Results of MWNTs synthesized over Fe-Co-Mo catalysts supported on silica at 650 °C using methyl ester of *Oryza sativa* oil as precursor at a flow rate of 30 mL per hour.

The sample synthesized is characterized using Raman spectroscopy to evaluate the crystalline nature of MWNTs formed and the spectrum recorded is depicted in Figure 4.72. The characteristic D and G peaks are observed at 1351 and 1576 cm\(^{-1}\) respectively. The Raman spectrum also exhibits a band at 2689 cm\(^{-1}\) called the D’-band attributed to the overtone of the D band. The \(I_G/I_D\) value of 1.42 for the sample synthesized with precursor flow rate of 30 mL per hour shows the poor graphitization of graphene layers of MWNTs (Figure 4.71).
Figure 4.72  Raman spectra of MWNTs grown on Fe-Co-Mo catalysts supported on silica at 650 °C using Oryza sativa oil as precursor at a flow rate of 30 mL per hour

The investigator suggests in general, as stated by Esconjauregui et al. (2009), that irrespective of the metal catalyst, the catalyst deactivates as the partial pressure of any of the carbon source is increased, probably due to catalyst encapsulation by amorphous carbon or graphitic layers.

4.4 COMPARATIVE ASSESSMENT OF MWNTS SYNTHESIZED FROM THE CHOSEN PRECURSORS

In this part, the properties of MWNTs synthesized from the chosen precursors viz. methyl ester of Madhuca longifola oil, methyl ester of Brassica juncea oil and methyl ester of Oryza sativa oil under the selected experimental conditions are compared to ascertain the potential of carbon source as a natural precursor for CNTs synthesis. It may not be appropriate to compare the MWNTS synthesized from different verity carbon sources as the researchers do follow a wide range of experimental conditions and material
property. As the conditions other than precursor properties kept identical in this study for the synthesis of MWNTs using the chosen precursors, an effort is put to compare and explain the potential of the chosen carbon source as precursor under the experimental conditions. As the synthesis of MWNTs from natural liquid precursor is at the early stage of research, the author confines to the yield and morphology of MWNTs synthesized using the chosen precursor oils for assessment of the potential of the oils as carbon precursor. Comparison of the quantity of carbon deposit obtained using the chosen precursor under identical experimental conditions, reveals that methyl ester of Oryza sativa oil produced large quantity of carbon deposit. The carbon deposit obtained by pyrolysis of precursor oil consists of catalyst-support, MWNTs and an amorphous carbon. The potential of precursor assessed based on the MWNTs content in the carbon deposit is appropriate in view of the envisaged objective of this study.

Linear hydrocarbons such as methane, ethylene, acetylene, thermally decompose into atomic carbons or linear dimers/trimers of carbon, and generally produce straight hollow CNTs. On the other hand, cyclic hydrocarbons such as benzene, xylene, cyclohexane, fullerene, produce relatively curved/hunched CNTs with the tube walls often bridged inside (Nerushev et al. 2003; Morjan et al. 2004). Andrews et al. (2006) showed the relationship between the boiling point of the precursor and the quality of the tube. These authors found that precursors of higher boiling point improve the quality of the tubes produced and the fact attributed to the low vapor pressure of carbon precursor.

Besides, using the raman or HRTEM to study the crystallinity of MWNTs. One can also analyze the Selected Area Electron Diffraction (SAED) patterns. The corresponding SAED pattern (Figures 4.73 to 4.75) shows the common reflections of MWNTs obtained from methyl ester of Madhuca
longifolia oil (Figure 4.73), methyl ester of Brassica juncea oil (Figure 4.74) and methyl ester of Oryza sativa oil (Figure 4.75). The more intensive peak 002 planes can be attributed to the formation of graphite carbon.

The selected area diffraction (SAD) pattern obtained by HRTEM is shown figure (Figures 4.73 to 4.75) for the methyl ester of Madhuca longifolia oil, methyl ester of Brassica juncea oil and methyl ester of Oryza sativa oil respectively. The diffuse circle in the SAED micrograph are due to the amorphous carbon film on the copper grid. The prominent sharp rings are due to the concentric graphitic planes of MWCNTs.

The crystallographic property of CNTs was studied by X-ray diffraction as shown in the Figure (Figures 4.76 to 4.78). Typical diffraction peaks at 2θ values in the range of 24-27°, 43.5-45.5° & 77-78° can be indexed to the (002), (101), (110) diffraction planes of hexagonal graphite. This result is consistent with the previous reports and it is remarkably similar to the pattern of graphite (stamatin et al. 2007). The very sharp and higher intensity of peak at 2θ of 26.164° (d_{002} spacing of 0.343 nm) for the MWNTs confirms the presence of more crystalline and graphite structure.

The XRD spectrum of as-synthesized MWCNTs was recorded with 2-theta (2θ) between 10 °C to 80 °C. Figure 4.76 shows the XRD diffraction pattern of MWCNTs synthesized at 650 °C using methyl ester of Madhuca longifolia oil as precursor at a flow rate of 20 mL per hour over Fe-Co-Mo catalysts supported on silica with two major peaks at 24.8° and 43.5° corresponds to C(002) and C(101) respectively are identified.

Figure 4.77 shows the XRD diffraction pattern of MWCNTs synthesized at 650 °C using methyl ester of Oryza sativa oil as precursor at a
flow rate of 20 mL per hour over Fe-Co-Mo catalysts supported on silica having two major intense peak at 25.8° and 44.5° corresponds to C(002) and C(101).

Obviously Figure 4.78 shows the XRD diffraction pattern of MWCNTs synthesized at 650 °C using methyl ester of *Brassica juncea* oil as precursor at a flow rate of 20 mL per hour over Fe-Co-Mo catalysts supported on silica have three peaks at 25.4°, 43.8° and 77° corresponds to C(002), C(101) and C(110). The small peak at 77° corresponds to C(110) suggests presence of Fe3C in the as-synthesized sample. The metal carbides act as active catalysts in the formation of tubular structure of graphitic carbon (Pitamber Mahanandia et al. 2011).

In view of the perspective of green chemistry, the investigator attempts to explore regenerative materials for CNT synthesis with high efficiency. Spray pyrolysis of methyl ester of *Oryza sativa* oil over Fe-Co-Mo catalysts supported on silica results in the formation of MWNTs filled with magnetic nanoparticles, which may find potential applications in magnetic recording, biomedical and environmental protection. methyl ester of *Oryza sativa* oil produces MWNTs along with amorphous carbon under the experimental conditions over Fe-Co-Mo catalysts supported on silica. This research work brings out the successful synthesis of well-graphitized MWNTs using botanical-plant based high vaporizing liquid, methyl ester of *Oryza sativa* oil over Fe-Co-Mo catalysts supported on silica by spray pyrolysis method. The optimum reaction conditions for synthesis of MWNTs using methyl ester of *Oryza sativa* oil over Fe-Co-Mo catalysts supported on silica were 650 °C and precursor flow rate of 20 mL per hour.
Figure 4.73 SAED pattern of MWNTs synthesized at 650 °C using methyl ester of *Madhuca longifolia* oil as precursor at a flow rate of 20 mL per hour over Fe-Co-Mo catalysts supported on silica

Figure 4.74 SAED pattern of MWNTs synthesized at 650 °C using methyl ester of *Brassica juncea* oil as precursor at a flow rate of 20 mL per hour over Fe-Co-Mo catalysts supported on silica
Figure 4.75  SAED pattern of MWNTs synthesized at 650 °C using methyl ester of *Oryza sativa* oil as precursor at a flow rate of 20 mL per hour over Fe-Co-Mo catalysts supported on silica.

Figure 4.76  XRD pattern of MWNTs synthesized at 650 °C using methyl ester of *Madhuca longifolia* oil as precursor at a flow rate of 20 mL per hour over Fe-Co-Mo catalysts supported on silica.
Figure 4.77  XRD pattern of MWNTs synthesized at 650 °C using methyl ester of *Brassica Juncea* oil as precursor at a flow rate of 20 mL per hour over Fe-Co-Mo catalysts supported on silica

Figure 4.78  XRD pattern of MWNTs synthesized at 650 °C using methyl ester of *Oryza sativa* oil as precursor at a flow rate of 20 mL per hour over Fe-Co-Mo catalysts supported on silica
4.5 GROWTH MECHANISM OF MWNTs

The mechanism of CNT nucleation and growth is one of the challenging and complex topics in current scientific research. Various growth models based on the experimental and quantitative studies have been proposed. Occurrence of the following consecutive steps during CNT nucleation and growth is well-established (Brukh & Mitra 2006).

1. Carbon species formation by decomposition of precursor over the catalyst
2. Diffusion of carbon species through the catalyst particle
3. Saturation of carbon species on catalyst nanoparticle
4. Precipitation of the carbon in the form of CNTs

The first step involves the formation of carbon species by catalytic vapor deposition of vapors of the precursor material over the catalyst. In the second step, the diffusion of carbon species through the catalyst particle takes place. The catalyst surface may exert a diffusion barrier. It is still unclear whether carbon species diffuse on the catalyst surface (Hofmann et al. 2005), or through the catalyst bulk (Brukh & Mitra 2006) or whether the surface and diffusion compete. The widely accepted growth model suggests a bulk diffusion of carbon species into the metal particels Ducati et al. (2004). The third step is the precipitation of the carbon in the form of CNTs from the saturated catalyst particle. Considering this mechanism with our experimental results a possible growth mechanism of MWNTs is explained.
Figure 4.79 HRTEM images of as-grown CNTs sample synthesized under constant reaction temperature of $650 \, ^\circ C$ using *Oryza sativa* oil at a flow rate of 20 mL per hour: indicates the reshaping of catalyst particle.

Figure 4.80 HRTEM images of as-grown CNTs sample synthesized under constant reaction temperature of $650 \, ^\circ C$ using methyl ester of *Oryza sativa* oil at a flow rate of 20 mL per hour: indicates metal particle at the tip of tube.
Even though the parameters such as precursor flow rate, effect of temperature and catalyst composition are important for the formation of carbon nanotube in vapor phase decomposition process, the results of this study shows the role of carbon precursor in the formation of carbon nanotube is more significant. Hence, the composition of precursor oil, structure, decomposition temperature and nature of bonding in the molecule have to be considered as important factors for explaining the mechanism of carbon nanotube formation. The major component of methyl ester of Madhuca longifolia oil, methyl ester of Brassica juncea oil and methyl ester of Oryza sativa oil is straight chain Hydrocarbon structure (Tables 3.2 to 3.4). Important factors, which influence the decomposition of molecule, are its structure and the nature of bonding. Hence, the methyl ester of oryza sativa oil with linear carbon chain structure decomposes easily to produce carbon nanotubes. Kumar & Ando (2003a) proposed a mechanism for the growth of MWNTs free from encapsulated metal particles and amorphous carbon based on the cyclic structure of the camphor molecule and presence of oxygen in the molecule. The increase in methyl ester of Madhuca longifolia oil flow rate increases carbon nanotube growth. However, methyl ester of Madhuca longifolia oil flow rate beyond the optimum level, induces the encapsulation of catalyst particles and amorphous carbon formation. The reason for the observation is attributed to the higher decomposition rate of methyl ester of Madhuca longifolia oil than the rate of diffusion of carbon into the catalyst particles. The methyl ester Oryza sativa oil is found to be an efficient precursor for the MWNTS synthesis because of its low decomposition temperature, appropriate carbon content, production of hydrogen gas in-situ through decomposition of precursor oil and presence of oxygen in its molecular structure and higher percentage of Linoleic and Oleic acid. Several authors have reported the role of molecular structure of carbon precursor, the reduction property of hydrogen gas in activating catalyst and the oxidizing property of oxygen in removing amorphous carbon in improving the purity of
carbon nanotubes. Biris et al. (2008) reported significant improvement in purity of carbon nanotube with increased hydrogen gas into the carbon source gas. Kumar & Ando (2003a) stated that during pyrolysis the oxygen atom in the molecule helps in oxidizing (in-situ) amorphous carbon. Even though, the methyl ester of Brassica juncea oil possesses similar properties. It is hypothesized that the molecular structure of the major component of it enables easy encapsulation of catalyst particle and no growth of well-graphitized carbon nanotubes.

The influence of temperature envisaged in all the three steps involved in the growth of carbon nanotube. Increase in temperature increases rate of decomposition of precursor in the first step, thus more amount of carbon particles are produced. However, the amount of carbon produced alone cannot be the sufficient condition for the growth of carbon nanotubes as most of the precursor molecules decomposed in the vapor phase lead to amorphous carbon formation. Liu et al. (2010) stated that a too high temperature (900 °C or higher) would induce a higher decomposition rate in carbon source, resulting in the coverage of substrate by a thick carbon layer in a short time and thus no carbon nanotubes. Effecting cracking of precursor by the catalyst occur at high activated condition, which occurs at highly temperature. Increase in temperature increase catalytic cracking efficiency, thus more amount of carbon is produced over the surface of the catalyst. The generation of carbon over the catalyst surface alone not the sufficient condition of the CNTs formation, as it has to be diffused in the catalyst particle and crystallized as graphitic layer on saturation. The carbon can easily diffuse into the catalyst particle, if the catalyst is in liquid state. Higher temperature favors the catalyst to attain semi-solid state, which enables the carbon to diffuse through it easily. The flow nature of semi-solid catalyst at optimum temperature is reasoned for envisaged hallow structure carbon nanotubes formation.
Catalytic centers on catalyst particle act as nucleation sites for the growth of MWNTs was well-known (Lee & park 2003). The precursor vapor decomposed on surface of the catalyst particle produces carbon. According to Sinclair et al. (2002), as the reactivity between the catalyst and the carbon and the carbon exceeds the threshold value, carbon atom lose their mobility in the solid solution, forming metal carbides. These meta-stable Fe and Co carbides decompose and produced carbon which dissolves in these metal particles. The dissolved carbon diffuses through the metal particles and then precipitates in the form crystalline graphene layer on saturation. This carburized surface act as a barrier for further carbon transfer from the gas phase to the bulk of the catalyst since carbon diffusion is slower through metal carbides (Ozturk et al. 1982). The saturated metal carbides have lower melting point and they are fluid like during the growth process (chakraborthy et al. 2005). If the rate of precursor decomposition and the rate of diffusion of carbon are equal, then the metal rises through a capillary action and tube growth occurs. The fact that the long carbon nanotubes observed have their catalyst particles partially exposed indicates that the direct contact of catalyst surface with carbon precursor id essential for continuous CNT growth.

This is consistent with growth mechanism proposed by Rodriguez (1993). In case decomposition rate exceeds the diffusion rate, more of carbon produced forms a thick carbide layer over the surface of metal, which act as a barrier for further carbon transfer from the gas phase to the bulk of the catalyst. However, the thick carbide layer crystallizes out as graphene layer, which encapsulate the metal particle. A catalyst particle fully encapsulated by layer of graphene sheets prevented from uptake of carbon and CNT growth stops resulting in short MWCNTs.

The catalyst particles undergoes several mechanical reshaping (Figure 4.79) during tip growth of multi-walled nanotubes (Hoffman et al. 2007;
Helveg et al. 2004). This gives the impression that the catalyst is in the liquid state during reaction. The catalyst particle seen inside and at the tip of tube could be the solidified from of the liquid phase metal particle. Thus, the growth process is by the vapor-liquid-solid (VLS) mechanism (Kukovitsky et al. 2000) the CNTs grow with either a tip growth mode or a base growth mode. Base growth mode is suggested when the catalyst particle remain attached to the support, while tip growth happens when the catalyst lifts of the support material. These growth modes depends on the contact forces or adhesion forces between the catalyst and supporting material (Leonhardt et al. 2006), while a weak contact favor tips-growth mechanism, a strong interaction promotes base growth (Bower et al. 2000). These catalysts have lifted off the support material and elongated due to the flow nature and stress induced by the carbon surrounding the catalyst. Catalyst seen at tip of CNTs (Figure 4.80) indicate tip growth mode.