Synthesis of Carbon Nano Materials from Carbohydrate Rich Biogenic Precursors using Chemical Vapor Deposition Method and Optimization of Parameters by Taguchi Optimization Method

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Abstract: **Carbon Nano Materials (CNM) from biogenic carbohydrate rich non-edible precursors such as *Syzygium cumini* (Jamun), *Tamarindus indica* (Imli) and *Litchi chinensis* (Imli) seeds were synthesized by chemical vapour deposition method (CVD). Parameters were optimized by Taguchi optimization method, four parameters such as precursor, temperature, carrier gas and duration and three levels *S. cumini*, *T. indica* and *L. chinensis* as a precursor, Argon (Ar), Nitrogen (N_2) and Hydrogen (H_2) as a carrier gas, 1 hour (hr), 2 hours and 3 hours (hrs) for duration of pyrolysis, 800ºC, 900ºC and 1000ºC for temperature were selected. In the present work, impact of precursor is 35.84% which is the most effective factor than temperature (29.59%) and other parameters such as duration (19.50%) and the least effective factor is carrier gas (15.07%). Impact of parameter on the yield which described by the deviation of signal to noise (S/N) ratio. The result of deviation of S/N ratio shows *T. indica* seed (precursor), 900ºC (temperature), 2 hr (duration) and Ar (carrier gas) are the best parameters. The morphology of CNM is studied by SEM characterization and the nature of synthesized CNM by RAMAN spectroscopy.**

Keywords: **Carbon nano material, Carbohydrate rich non-edible seeds, Pyrolysis, SEM, Taguchi optimization, RAMAN spectroscopy.**

1. Introduction

Using petroleum derived materials as precursor, Carbon nano materials (CNMs) are usually synthesized. As petroleum derived materials are comparatively expensive and also they are at the verge of depletion in the near future. Hence, there is the need to look for other sources of precursors to synthesize CNMs. While following the principle of Green Chemistry, it is desirable that the raw material for any industrial process must be renewable rather than the depleting natural resources. It is one of the prime requirements to explore regenerative materials for synthesis of CNM, however, with high efficiency. Sharon and co-workers [1]-[4] firstly synthesized carbon nano tubes (CNT) from plant-derived precursors and since then there have

been efforts in this direction in different parts of the world. Scientists have been exploring environment-friendly sources of CNMs. Efforts are being made to establish the conditions for growing multi walled carbon nanotube (MWCNTs), single-walled carbon nano tubes (SWCNTs) and vertically aligned MWCNTs using suitable catalytic support by a simple and inexpensive chemical vapour deposition (CVD) techniques. There are different plant derivatives as well as plant parts which have successfully been used for the synthesis of carbon nano materials under pyrolytic conditions (5-9). They also synthesize CNM by a modified tradition sources from vegetable sources [10]-[12]. Almost all plant parts (roots, stem, leaves, seeds etc.) and plant derived products (pinene, latex, oil, juice, camphor) have been used as precursors of CNMs. The choice of precursor is primarily based on wide availability of the plant or plant parts. The next criterion is the percentage of hydrocarbon content (oil or fatty acid, cellulose, polysaccharide, lignin etc.) of the chosen plant precursors. Researchers have also used sugarcane juice, an algae *Euglena*, cotton, fibre, rice straw, corn cob, latex of *Calotropis*, bamboo, and pretreated rice straw as raw materials, however, with promising results. The use of palm oil has yielded aligned CNTs arrays. Spray pyrolysis of biodiesel has yielded well defined multi walled carbon nano tubes [13]. The Carbon Nano Material (CNM) is determined by the nature of precursor. There are several reports with regard to the carbon nano materials being derived from the seeds including Grapes seeds, *T. indica*, Soybean, *Anacardium*, Ritha and Castor [14]-[17].

The aims of the present work are to synthesize carbon nano materials from precursors derived from carbohydrate rich non-edible seeds of plants and parameters were optimized by Taguchi optimization method using CVD process. It has been decided to use various types of carbohydrate rich seeds as Jamun (*Syzygium cumini* (L.) Skeels), Imli (*Tamarindus indica* L.) and Litchi (*Litchi chinensis* Sonn.) to synthesize carbon

nano materials. These seeds contain different amount of carbohydrate, oil and protein constituents, these are rich source of carbon.

2. Materials and Methods

For the synthesis of CNM, the seeds of *S. cumini*, *T. indica* and *L. chinensis* were purchased from local market, CVD furnace was used for pyrolysis.CVD method was used for Pyrolysis of these three type of seeds. The parameters considered were 1) three different gases i.e. Argon (Ar), Nitrogen (N₂), and Hydrogen (H₂) 2) three different temperatures i.e. 800⁰C, 900⁰C and 1000⁰C and 3) duration of pyrolysis 1hr, 2 hrs, and 3 hrs. The seeds were washed with D/W and dried in the muffle furnace at 60⁰C for 6 hrs and the crushed into powder form with the help of mortar and pestle. After crushing, took known amount of precursor into a quartz boat for pyrolysis.
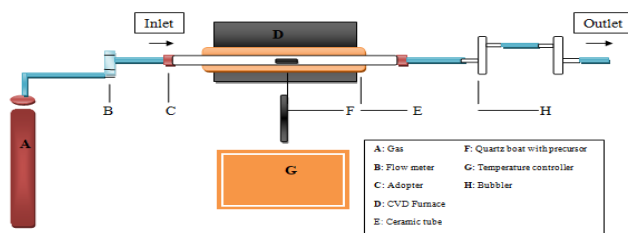

Fig. 1. Schematic diagram of CVD set up

CVD apparatus was used for the synthesis of carbon nano materials from carbohydrate rich non-edible seeds. Known amount of crushed seeds were taken in a quartz boat and placed in the centre of 1 m long quartz tube (inside furnace) that was inserted in the furnace. The carrier gas was flushed into the quartz tube at a higher flow rate (150 ml/min) so as to remove oxygen and the quartz tube was closed. Then the purging of gas was continued at the flow rate (25 ml/min) during pyrolysis. Desired temperatures were set when the temperature reaches 450⁰C - 500⁰C, the biomass starts vaporizing inside the tube and flows along with the carrier gas toward outlet of the tube. By the time the temperature reached 700⁰C the flow rate was gradually decreased and stopped. When it reached at set temperature, it was maintained at that temperature for desired set duration. At high temperature, the hydrocarbons are decomposed and converted into simpler form of carbon. The non-carbonaceous material gets removed along with the carrier gas from the furnace and remnant carbonized carbon material are left in the quartz boat.

A. Standardization of synthesis parameters (Taguchi Optimization of Parameters)

For the present CVD process four parameters, each with three variables were to be tried. Therefore, for the present work, experiment was designed by Taguchi Optimization method [18]. This method is a statistical method developed by Genichi Taghuchi (1950) of Nippon Telephones and Telegraph

Company, Japan for improving the manufactured goods, marketing & advertising, more recently, even applicable for the research field. In this method statistically designed orthogonal arrays (OA) [19]-[20] are being of used to evaluate comparatively smaller number of experiments. It is a simple efficient and systematic approach for the optimization of experimental parameters [21]-[22]. Using Taguchi method one can get information about the most effective parameters controlling the formation of a required product by carrying out only 9 experiments. The Taguchi philosophy of variability reduction is based on the fact that there is a 'best' value for the product. The Taguchi strategy attempts to find the combination of the values of the controllable design variables that minimizes the expected loss over the uncontrollable noise space.

B. Application of Taguchi Optimization for Present work

Four parameters considered for the synthesis of CNM from plant seeds are Carrier Gases, Precursors, Temperatures, and Duration of Pyrolysis. In total, three levels of each parameter were selected (Table 1).

Table 1
Four parameters used for Taguchi Optimization Technique for Carbohydrate-rich non edible seed

S.No.	Parameters	Levels of Parameters		
		Level 1	Level 2	Level 3
1	Gas	Ar	N₂	H₂
2	Temperature (⁰C)	800	900	1000
3	Duration (hr)	1	2	3
4	Precursor (Seeds)	*Syzygium cumini*	*Tamarindus indica*	*Litchi chinensis*

Using above mentioned parameters and its level, L9 orthogonal matrix was designed (Table 2).

Taguchi optimization method is a statistical method [23] in which simple mean of analysis and optimization of complex systems based on the statistical analysis of data are optimized. A special design of orthogonal arrays (OA) is used in Taguchi optimization method to study the entire parameter space with only a small number of experiments. This approach of the statistical analysis is comparatively simple for optimization of experimental designs in order to evaluate performance and quality of the experiments.

Table 2
Arrangement of L9 orthogonal parameters as per Taguchi Optimization Technique for Carbohydrate rich non-edible seeds

Taguchi Level	Gas	Temperature (⁰C)	Duration (hr)	Precursor (Seed)
L1	Ar	800	1	*Syzygium cumini*
L2	Ar	900	2	*Tamarindus indica*
L3	Ar	1000	3	*Litchi chinensis*
L4	N₂	800	2	*Litchi chinensis*
L5	N₂	900	3	*Syzygium cumini*
L6	N₂	1000	1	*Tamarindus indica*
L7	H₂	800	3	*Tamarindus indica*
L8	H₂	900	1	*Litchi chinensis*
L9	H₂	1000	2	*Syzygium cumini*

Statistical analysis of signal to noise (S/N) ratio and an analysis of variance (ANOVA) [24] has to be employed for determining relative importance of various factors. Orthogonal array (OA) analysis is completed by ANOVA and S/N ratio. ANOVA is used to analyze the results of the OA (Orthogonal Arrays) experiment and to determine how much variation each quality (influencing factor) has contributed.

S/N ratio is log function of desired output for optimization, which thereby, helps in data analysis and as well as in prediction of optimal results. An S/N ratio is a key part of the Taguchi optimization method and is often evaluated using a parameter design. Taguchi's S/N ratios are the performance statistics that recommends for selecting the best combination of the design variables. Larger the S/N ratio more robust the design. For the best design, the parameter which gives S/N ratio highest value is considered as the favoured parameter. Thus, to minimize the expected loss, one always finds the combination of the design variables, which maximizes the SN ratio performance statistic.

The S/N is the ratio of the average response of the root mean square variation about the average response. Larger the S/N ratio, smaller the measurement of error because the S/N is the reciprocal of the variance of the measurement error. S/N ratio is used to analyze the test run results because the S/N ratio signifies the mean mean and variation (scatter) of the experimental results.

Calculations for 'Larger the Better': There are three categories of S/N ratios (i) smaller the better, (ii) larger the better and (iii) nominal the best. In the present work target was to get larger quantity of carbon, therefore, "larger the better" is used for calculation using following equation:

$$S/N = -10\log_{10}\left[(1/n)\ \Sigma 1/y_i^2\right] \tag{1}$$

Where *"y_i"* is the mean response calculated as $y = 1/n\ \Sigma y_i$ and n is the number of experiments carried out under similar conditions.

Calculations for Effect of each parameter: To determine the effect of each parameter level (m_i) average value of S/N ratios was calculated for each parameter, using analysis of mean (ANOM). For this calculation, the S/N ratios of each experiment with corresponding parameter levels are calculated using following equation:

$$m_i = (1/n_i)\ \Sigma S/N \tag{2}$$

Where, n_i is the number of experiments repeated with the same parameter levels.

There are two types of average value of S/N ratio is calculated. One is the overall mean S/N ratio calculated from the entire experiments for example from L9 experiment of L9 orthogonal array (i.e. from S/N values given in table). Secondly, average S/N ratio is calculated for each parameter from equation-1. The advantage of the average value of S/N ratio, are considered to be the least effective parameters as compared to

those parameters whose S/N ratios are larger than mean S/N ratio.

The parameters effects, i.e. the contribution of each experimental parameter to the quality characteristic are calculated by the analysis of variance (ANOVA). ANOVA is done by summing of squares (SOS) of variance of all levels of a given parameters. The relations that are used to determine the sum of the squares and the factor effect are given by the following equation:

$$(SOS)\ = \Sigma N_i\ (m_i - \langle m_i \rangle)^2 \tag{3}$$

Where m_i gives the average of the levels contributions for each parameters levels to S/N ratio, $\langle m_i \rangle$ is the average of mi for a given parameter and the coefficient and Ni represents the no. of repeats the experiment is conducted with the same factor level.

SOS is normalized with respect to the degree of freedom (DOF) of the corresponding process parameters.

$$DOF = \text{number of parameter level} - 1 \tag{4}$$

If there are three levels for each parameters then DOF = 3-1 = 2

Some of square (SOS) of variances for all levels for a given parameter are divided by degree of freedom (DOF) of corresponding process parameter to obtain factor of effects (FOE) of various experimental parameters. The equation of calculation of FOE is following:

$$FOE = SOS/[DOF\ x\ (SOS/DOF)] \tag{5}$$

Finally, percentage parameter effect is calculated as following:

$$\text{Parameter effect \%} = 100\ x\ FOE \tag{6}$$

Using L9 orthogonal array nine sets of experiments were carried out. Results were calculated based on equations 1 to 3 mentioned above, nano and micro carbon materials were synthesized by CVD method from different non-edible seeds.

C. Purification of CNM derived from Seeds

Acid-refluxing the sample is an effective measure in reducing the amount of metal particles, amorphous carbon, and raw material based impurities and also for residual functional groups. Various acids such as HCl, HNO_3, H_2SO_4 are commonly used for purification of CNMs. For SEM treatment of our experimental seeds samples, the synthesized CNM was purified utilizing acid reflux with HCl and HNO_3. In the present work, 1.01 gm of crushed CNM produced was weighed and taken in chemical synthetic reactor/ three necked round bottomed flask. In the reaction vessel 100mL Conc. HCl (36.5%) and 100mL Conc. HNO_3 (63%) were added along with the sample and those were refluxed at 110°C for 12 hrs. Then

after, the flask was allowed to cool for 6-8 hrs. The resulting black residual of the reflux process was centrifuged and subsequently the dark liquid was discarded. The powder thus obtained was washed with luke warm double distilled water for several times till the traces of acid was completely removed. The obtained powder was then dried in vacuum oven (24 hours). The sample was now ready for SEM analysis. Obtained CNM was analysed by SEM, and Raman Spectroscopy.

3. Results and Discussions

A. Carbon Nano Materials from carbohydrate rich non-edible seeds

Taguchi optimization method is a statistical method by which experimental parameters are optimized in a small number of experiments. On that basis the orthogonal table was constructed considering different combinations (four possible parameters) with a minimum of three variables of each parameter. We had selected the variable parameters such as carrier gas, temperature, duration and precursors (different type of carbohydrate rich non- edible seeds) and they all are orthogonal to each other. By using Taguchi Optimization technique, an orthogonal table was constructed in which three levels of parameters were used. Therefore, L9 orthogonal table was constructed by using the parameters and their levels as mentioned (Table 2). Pyrolysis was carried out for each set of conditions. Percentage (%) of yield and S/N ratio was calculated for each experimental result by using equation 1. The yields of CNM as well as S/N ratio calculated from each set are also given in table 3. Deviation of S/N ratio was also calculated and factor of effect (FoE) was evaluated.

B. Taguchi optimization on the yield of carbon

So far as yield of carbon from pyrolysis of different seeds are concerned, *Syzygium cumini* and *Litchi chinensis* yielded 22 – 24% carbon, whereas *Tamarindus indica* produced upto 23% carbon. Earlier, Chaudhary *et al.* (2014) derived Carbon nano particles (21% wt./wt.) from *Litchi* seeds, however, as compared to the amount of precursor used. Mopung *et al.* (2015) observed comparatively higher 28.89% of carbon yield the seed of *Tamarindus indica* at a temperature range of 500ºC – 700ºC. Various parameters of pyrolysis do not seem to have much impact on the yield. However, it was observed that out of

three seeds taken *Syzygium cumini* and *Tamarindus indica* yielded higher levels of carbon at lower temperature compared to *Litchi chinensis*. The decrease in CNM yield with increasing temperature could either be due to greater primary decomposition of biomass at higher temperature or through secondary decomposition of carbonaceous materials residues (Ming et. al., 2016). Signal to noise (S/N) ratio of CNM produced under different conditions is plotted in figure 2. The purpose of the proposed work was to find out the best set of parameters for pyrolysis which could give the maximum amount of CNM. For calculation of the S/N ratio "Larger the Better "condition was used. Among three types of carbohydrate rich non-edible seeds *Tamarindus indica* seeds appeared to give the best yield. Following Taguchi optimization, the deviation S/N ratio showed that 900^0C temperature (as applied) and two hours' time of pyrolysis gave the higher yield of CNM. Amongst the three carrier gases applied, Argon was better suited than nitrogen and hydrogen for the yield of CNM. Since hydrogen is a reducing gas, it might have reduced the carbon during secondary decomposition of carbonaceous materials (Li *et al.*, 2017).
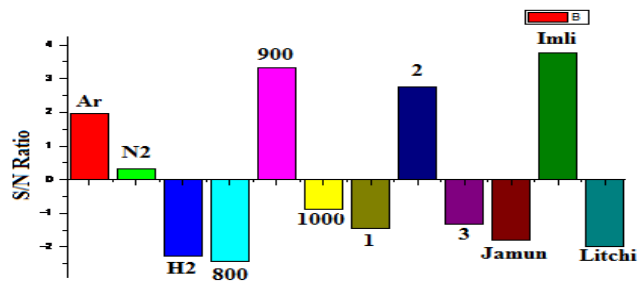

Fig. 2. Schematic representing showing impact of parameter on the CNM synthesis from Carbohydrate rich non-edible seeds (*Syzygium cumini*, *Tamarindus indica*, *Litchi chinensis*), as per Taguchi calculations of S/N ratio

The calculation of percentage impact of each parameter on the production of CNM (Table 4) suggests that precursor (35.84%) has maximum impact on the experimental designing followed by temperature (29.59%) then duration (19.50%) and the least impact is that of carrier gas (15.07%) which was shown in the pie diagram (figure 3). Sharon et al., 2011 [25] working at 800ºC using Argon as carrier gas and pyrolyzing duration of 2 hours showed 15% impact compared to other parameters.

Table 3

Orthogonal array of parameters (Taguchi Optimization technique) set for pyrolysis of *Syzygium cumini, Tamarindus indica and Litchi chinensis* seeds. Yield and S/N ratio of carbon CNM are also shown (Taguchi larger the better)

Taguchi level	Gas	Temperature (^0C)	Duration (hr)	Precursor (Seed)	Precursor wt (gm)	Yield (gm)	Yield after Purification (gm)	% yield	S/N Ratio
L-1	Ar	800	1	*Syzygium cumini*	5	1.354	1.235	24.7	27.85
L-2	Ar	900	2	*Tamarindus indica*	5	0.870	0.680	13.6	22.67
L-3	Ar	1000	3	*Litchi chinensis*	5	1.212	1.166	23.32	27.35
L-4	N₂	800	2	*Litchi chinensis*	5	1.258	1.125	22.5	27.04
L-5	N₂	900	3	*Syzygium cumini*	5	1.108	1.050	21	26.44
L-6	N₂	1000	1	*Tamarindus indica*	5	1.100	1.000	20	26.02
L-7	H₂	800	3	*Tamarindus indica*	5	1.198	1.166	23.32	27.35
L-8	H₂	900	1	*Litchi chinensis*	5	1.256	1.172	23.44	27.40
L-9	H₂	1000	2	*Syzygium cumini*	5	1.335	1.164	23.28	27.34
							Mean S/N Ratio		26.60

Detail of calculation was described in previous chapter.

Histogram of Percentage Factor Effect for different parameters (Fig. 4) showed that precursor had maximum level of impact followed by temperature and duration, however the impact of carrier gas had least impact.
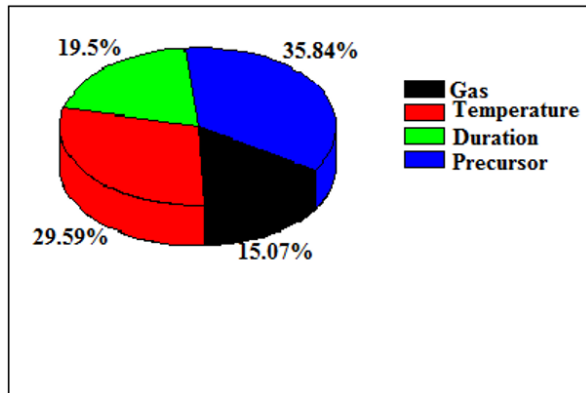

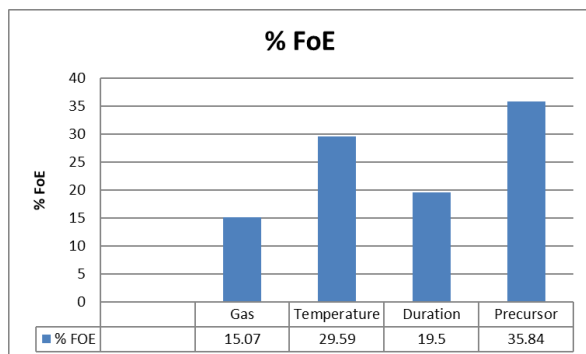Fig. 3. Pie chart showing per cent factor of effects of each parameter

Fig. 4. Histogram of per cent Factor of Effect of different parameters

C. Scanning Electron Microscopy (SEM) micrographs of pyrolised Carbon materials from carbohydrate rich non-edible seeds

Morphological studies of SEM micrograph and observation

of pyrolised different carbohydrate rich non-edible seeds (*Syzygium cumini, Tamarindus indica* and *Litchi chinensis.*) are represented in Table 5.

The SEM micrographs of CNMs (synthesized through CVD of the three precursors: Carbohydrate rich non-edible seeds: *Syzygium cumini, Tamarindus indica* and *Litchi chinensis*) are shown in this table.SEM micrographs are the experiments of different L levels (L1 – L9) as optimized by 'Taguchi method'. The SEM micrograph were obtained from the powder of precursors which revealed plate like structures.

The SEM micrographs of *Syzygium cumini* (L1, L5 and L9 (Table 5)) it was observed that the CNM morphology was multilayered smooth surface plates with porous side and the size range was approx. 30-750 nm. In L1 the size of larger structures were about 150-750 nm and the size of smaller fragments was in the range of 30-100 nm in range. In L5, the size of larger structure was 100-2000 nm and the size of smaller fragments was approx. 50-100 nm. In L9, the length of the larger structure was about 2200 nm and the size of smaller fragments was about 20-100 nm which was impregnated on the larger structures.

On observation and respective comparison of the SEM micrographs of CNM of *Tamarindus indica* (L2, L6 and L7 (Table 5)) it was found that the CNM morphology of L2 was multilayered plate with rough surface and porous sides, the size range was 40-2000 nm. The morphology of L6 showed that the structure with pits (bowl like) contained small fragments of CNM. The pit diameter was about 100 nm, and larger fragments of 2200 nm in size while smaller fragments were of 30-60 nm size. The SEM micrograph of L7 showed that smooth surface plate with multilayered plates. The size of larger fragments was 1500 nm and smaller fragments of 30-100 nm. While working on *T. indica* seed parts, Munusamy *et al.* (2011) [15] found that the decoated *T. indica* seeds were non- porous, whereas the *T. indica* seeds char (TSC) and T-char were of porous structures.
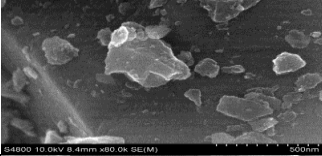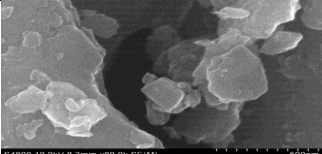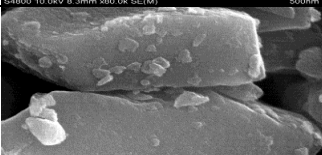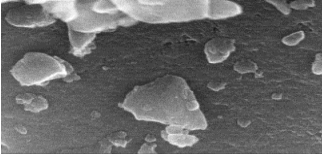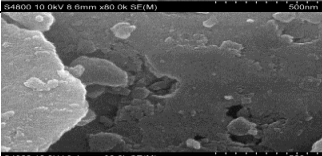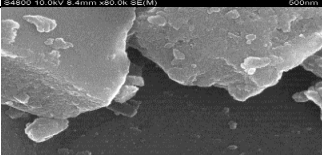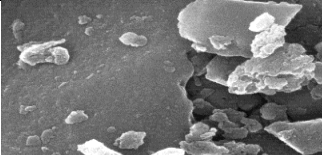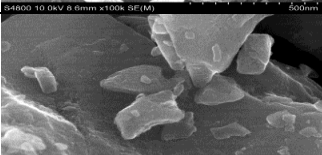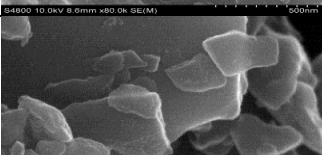
Table 4
Control parameters of the pyrolysis of non-edible seeds *(Syzygium cumini, Tamarindus indica, Litchi chinensis)* and their corresponding S/N ratio

Parameter	Gas			Temperature (^{0}C)			Time duration (hr)			Precursor (seed)		
	Ar	N₂	H₂	800	900	1000	1	2	3	*S. cumini*	*T. indica*	*L. chinensis*
L1	27.85			27.85			27.85			27.85		
L2	22.67				22.67			22.67			22.67	
L3	27.35					27.35			27.35			27.35
L4		27.04		27.04				27.04				27.04
L5		26.44			26.44				26.44	26.44		
L6		26.02				26.02	26.02				26.02	
L7			27.35	27.35					27.35		27.35	
L8			27.40		27.40		27.40					27.40
L9			27.34			27.34		27.34		27.34		
Sum (S/N)	77.87	79.5	82.09	82.24	76.51	80.71	81.27	77.05	81.14	81.63	76.04	81.79s
Deviation S/N	1.95	0.32	-2.27	-2.42	3.31	-0.89	-1.45	2.77	-1.32	-1.81	3.78	-1.97
m$_i$	25.96	26.5	27.36	27.41	25.50	26.90	27.09	25.68	27.05	27.21	25.35	27.26
<m$_i$>	26.60			26.60			26.60			26.60		
m$_i$-<m$_i$>	-0.64	-0.1	0.76	0.81	-1.1	0.3	0.49	-0.92	0.45	0.61	-1.25	0.66
SOS	2.99			5.87			3.87			7.11		
SOS/DOF	1.495			2.935			1.935			3.555		
FoE (%)	15.07			29.59			19.50			35.84		

Table 5
SEM micrographs of carbohydrate rich seeds (*Syzygium cumini*, *Tamarindus indica* and *Litchi chinensis*) in relation to different parameters (carrier gas, temperature and durations) with their corresponding CNM (following Taguchi optimization)

Seed	Parameters Gas–Temp^{0}C-Duration hr-Precursor	SEM Images	CNM Morphology (SEM)
Syzygium cumini	L1 Ar – 800^{0}C – 1 hr – *Syzygium cumini* seed		Multi-layer smooth surface plates with porous sides also small fragments.
	L5 N$_2$ – 900^{0}C – 3 hrs – *Syzygium cumini* seed		Multi-layer smooth surface plates with porous sides also small fragments.
	L9 H$_2$ – 1000^{0}C – 2 hrs – *Syzygium cumini* seed		Multi-layer smooth surface plates with porous sides also small fragments of <100 nm.
Tamarindus indica	L2 Ar – 900^{0}C – 2 hrs –*Tamarindus indica* seed		Multilayer plate with rough surface and porous sides.
	L6 N$_2$ – 1000^{0}C – 1 hr – *Tamarindus indica* seed		Surface with pits (bowl like) containing small fragment of CNM,
	L7 H$_2$ – 800^{0}C – 3 hrs – *Tamarindus indica* seed		Structure with big holes/pores of 100 to 200 nm diameter.
Litchi chinensis	L3 Ar – 1000^{0}C – 3 hrs – *Litchi chinensis* seeds		Smooth surface plates with small fragments.
	L4 N$_2$ – 800^{0}C – 2 hrs - *Litchi chinensis* seed		Smooth surface plates with small fragments.
	L8 H$_2$ – 900^{0}C – 1 hr – *Litchi chinensis* seed		Smooth surface plates with small fragments.

The observation of SEM micrograph of pyrolysed CNM of *Litchi chinensis* seeds (L3, L4 and L8 (Table 5)) had plate like morphology and the length of CNM was about 40-2500 nm in size. The morphology of all the three levels (L3, L4 and L8) of experiment were almost same but with variable of CNM. The larger structure of L3 was about 1500 nm and the smaller fragments of were of 40-200 nm in size. In L4, the larger structures was 2000 nm and the smaller fragments were of 50-250 nm in size. The size of L8 varied from 100-2500 nm. Chaudhary and Bhowmick (2014) [26] observed 40-70nm range of CNPs in aggregated form in Litchi peel.

*D. Result and Inference of Raman spectra of Carbohydrate rich seeds*

Table 6
Raman inference of *Syzygium cumini, Tamarindus indica* and *Litchi chinensis*

| Sample name	Pyrolysing temp	D-band	G-band	I_D/I_G ratio	2D peak
Jamun (L1) *Syzygium cumini*	800^0C	1357	1604	0.874	2915
Jamun (L5) *Syzygium cumini*	900^0C	1366	1607	0.924	2915
Jamun (L9) *Syzygium cumini*	1000^0C	1367	1608	0.945	2919
Tamarind (L7) *Tamarindus indica*	800^0C	1367	1600	0.912	2919
Tamarind (L2) *Tamarindus indica*	900^0C	1365	1600	0.937	2910
Tamarind (L6) *Tamarindus indica*	1000^0C	1364	1601	0.939	2911
Litchi (L4) *Litchi chinensis*	800^0C	1367	1610	0.884	2900
Litchi (L8) *Litchi chinensis*	900^0C	1366	1602	0.945	2920
Litchi (L3) *Litchi chinensis*	1000^0C	1354	1619	0.998	2911

E. Raman spectra of Jamun seeds (Syzygium cumini)

In the Raman spectra of Taguchi optimized *Syzygium cumini* seeds, there was sharp peak of D- band L1 at 1357, L5 at 1366 & L9 at 1367 and G- band of L1 at 1604, L5 at 1607 & L9 at 1608 which revealed the presence of sp^3 and sp^2 carbon with defect (fig 5). In pure diamond this peak remains at 1332 and in pure graphite peak at 1580. The ratio of it it's intensities show the defect in those materials. ID/IG ratio of L1 is 0.874, L5 is 0.924 & L9 is 0. 945.An additional blunt 2D peak revealed at 2915 in L1, at 2915 in L5 & at 2919 in L9 which indicated the graphitic nature of these Carbon nano materials. In above three Raman spectra it was studied that with respect to temperature, as the temperature increased, the ratio of defect in turn increased, it may be due to aggregation of molecules. Similarly, in the case of Hydrogen gas produced more defects than Nitrogen and Argon and with respect to duration of pyrolysis, 2
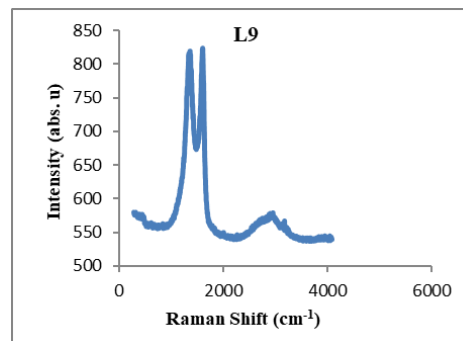
hrs revealed more defect than 3 hrs and 1 hr.
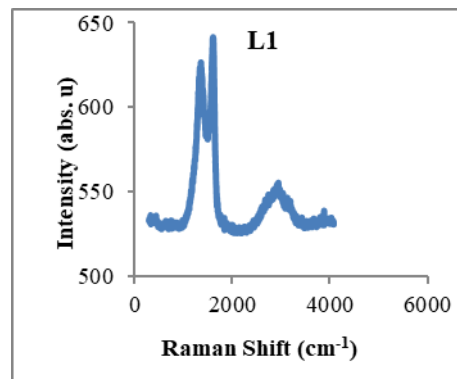
(a) *S. cumini* seed (Ar, 800^0C, 1 hr)
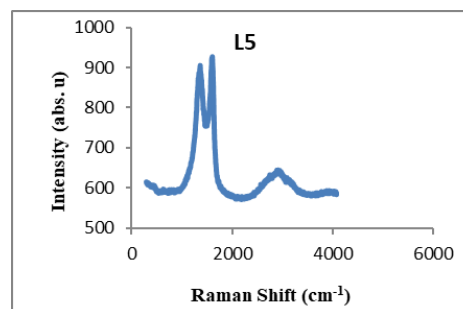
(b) *S. cumini* seed (N_2, 900^0C, 3 hrs)


(c) *S. cumini* seed (H_2, 1000^0C, 2 hrs)

Fig. 5. Raman spectra of L1 (Precursor- *Syzygium cumini* seed, Temp- 800^0C, Gas- Argon, Duration- 1 hr), (B)- Raman spectra of L5 (Precursor- *Syzygium cumini* seed, Temp- 900^0C, Gas- Nitrogen, Duration- 3 hrs), (C)- Raman spectra of L9 (Precursor- *Syzygium cumini* seed, Temp- 1000^0C, Gas- Hydrogen, Duration- 2 hrs)

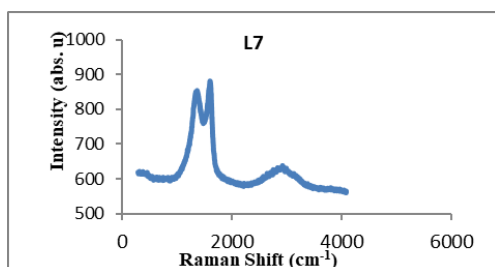*F. Raman Spectra of Tamarindus indica Seed*

In the Raman spectra of Taguchi optimized *Tamarindus indica* (fig. 6) seeds D- band of L2 was at 1365, L6 at 1364 & L7 at 1367 and G- band of L2 at 1600, L6 at 1601 & L7 at 1600 revealing thereby, the presence of sp^3 and sp^2 carbon with defect. The ratio of it its intensities show the defect in these materials. ID/IG ratio of L2 is 0.937, L6 is 0.939 & L7 is 0.912. An additional blunt 2D peak reveals at 2810, in L2, at 2811 in L6 & at 2819 in L7 showed the graphitic nature of those Carbon nano materials.
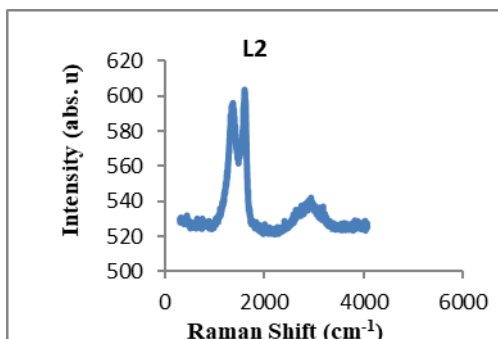
(a) *T. indica* seed (Ar, 900^{0}C, 2 hrs)
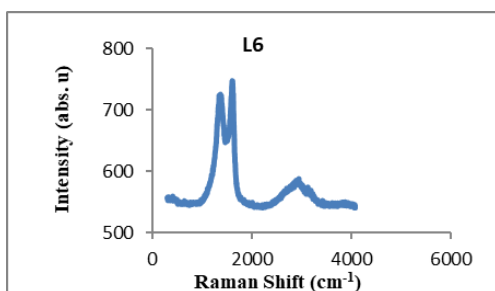
(b) *T. indica* seed (N$_2$, 1000^{0}C, 1 hr)

(c) *T. indica* seed (H$_2$, 800^{0}C, 3 hrs)

Fig. 6. a) Raman spectra of L2 (Precursor- *Tamarindus indica* seed, Temp- 900^{0}C, Gas- Argon, Duration- 2 hrs), b) Raman spectra of L6 (Precursor- *Tamarindus indica* seed, Temp- 1000^{0}C, Gas- Nitrogen, Duration- 1 hr), c) Raman spectra of L7 (Precursor- *Tamarindus indica* seed, Temp- 800^{0}C, Gas- Hydrogen, Duration- 3 hrs).

G. Raman Spectra of Litchi chinensis Seed

In the Raman spectra of Taguchi optimized *Litchi chinensis* seeds (fig. 7) levels show the sharp peak of D- band L3 at 1354, L4 at 1367 & L8 at 1366 and G- band of L3 at 1619, L4 at 1610 & L8 at 1602 due to the presence of sp^3 and sp^2 carbon with defect. The ratio of it its intensities show the defect in these materials. ID/IG ratio of L3 is 0.937, L6 is 0.939 & L7 is 0.912. An additional blunt 2D peak reveals at 2810, in L2, at 2811 in L6 & at 2819 in L7 showing the graphitic nature of those carbon nano materials.

In L3, L4 & L8, the presence of broad peak of 2D peak at 2911, 2900 & 2920 showed samples being graphitic in nature.

Bhardwaj *et al.* (2007) [27] studied on carbon materials of different seeds and found that I$_G$/I$_D$ ratio in soap nut seeds and bamboo fibre had highest value suggesting that it contained more graphitic carbon than disorder carbon atoms.

In the present studies, the analysis of CNMs were done on the basis of D banding, G banding and 2D peaks obtained with this technique and structural information was interpreted (table 6). It was found that the CNMs from carbohydrate rich seeds (*Tamarindus indica*, *Syzygium cumini* and *Litchi chinensis*) produced:
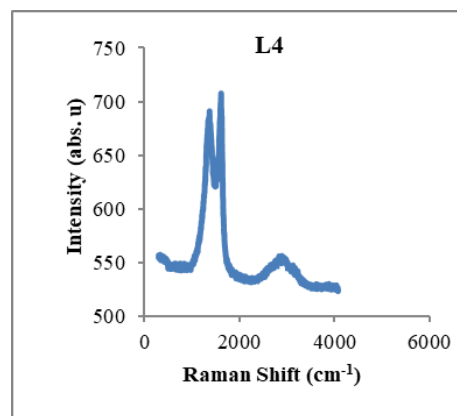
D band – 1354 – 1367 cm-1
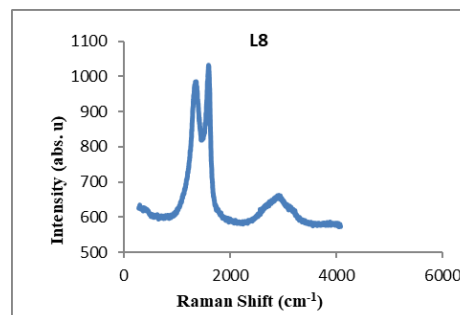G band – 1600 – 1619 cm-1
2D peak – 2900 – 2920 cm-1

On account of the above observation it is sumrised that the CNM synthesized from the aforesaid non-edible seed precursors possessed prevailing graphitic constitution along with some graphene like structure.
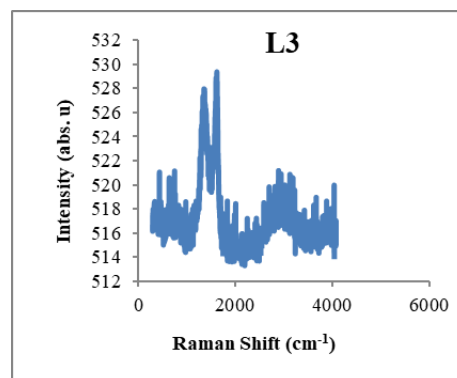
(a) *L. chinensis* seeds (Ar, 1000^{0}C, 3 hrs)

(b) *L. chinensis* seed (N$_2$800^{0}C,2 hrs)

(c) *L. chinensis* seed (H$_2$, 900^{0}C, 1 hr)

Fig. 7. a) Raman spectra of L3 (Precursor- *Litchi chinensis* seed, Temp- 1000^{0}C, Gas-Hydrogen, Duration- 3 hrs), b) Raman spectra of L4 (Precursor- *Litchi chinensis* seed, Temp- 800^{0}C, Gas- Nitrogen, Duration- 2 hrs), c) Raman spectra of L8 (Precursor- *Litchi chinensis* seed, Temp- 900^{0}C, Gas-Hydrogen, Duration- 1 hr)

4. Conclusion

Carbon nano materials (CNM) synthesized from biological precursors carbohydrate rich non-edible seeds (*S. cumini, M. Indica and A. indica*) have been synthesized by CVD method using single zone CVD furnace without using metal catalyst. The process parameters have been optimized for the bulk growth of CNM from these seeds by Taguchi optimization method in which controlling parameters are carbohydrate rich non-edible seeds (*S. cumini, T. Indica and L. chinensis*) as a precursors, temperature (800^0C, 900^0C and 1000^0C), carrier gas (Ar, N_2 and H_2) and duration of pyrolysis (1 hr, 2 hrs and 3 Hrs). This experiment showed that *T.indica* seed as a precursor, 900^0C temperature, Argon as a carrier gas and 2 hrs duration of pyrolysis are the best parameters for the synthesis of CNM in large scale from these precursors. SEM characterization of synthesized CNM shows plates like morphology with smooth and rough surfaces and the size range of obtained CNM was approx 20-2500 nm. Raman spectroscopy reads the interactions of electromagnetic wave with matter and helps us to information regarding molecule structure. In Raman spectroscopy, the intensity of peak is placed on Y-axis ad frequency on X-axis. Frequency depends on the mass of the atoms and the strength of the bonds holding them. Hence sp2 hybridized carbon in >C=C< bond ($1600cm^{-1}$) have higher frequency up to 3000 cm^{-1} while –C-C- bonds have as low as 800 cm^{-1}. The two other parameters in the name of D band is caused by the disorder structure of graphene due to the sp2 hybridized carbon resonance and G bands is caused by the stretching of C-C bonds in graphitic material and is common to all sp2 hybridized carbon. Apart from this, all types of sp2 carbons exhibited a very strong peak in the region/ range -> 2500 – 2800 cm^{-1}. This is Raman signature of graphitic material and is termed 2D band.

Acknowledgement

References

[1] M. Sharon, N. Sundarakoteeswaran, P. D. Kichambre, M. Kumar, Y. Ando, and X. Zhao, "Semiconducting carbon films from a natural source camphor", Diamond and Related Materials, 8, 485-489,1991.
[2] M. Sharon, M. Kumar, P. D. Kichambre, N. R. Avery, and K. J. Black, "Lithium-Ion intercalation into carbons derived from pyrolysis of camphor", Molecular crystal and Liquid crystal, 340, 523-528, 2000.
[3] M. Sharon, D. Pradhan, M. Kumar, Y. Ando, "NanoOctopus: A new form of branching carbon nanofiber", J. Nanoscience and nanotechnology, 3,3, 1-3, 2003.
[4] M. Sharon & M. Sharon, "Carbon Nano Forms and Applications", first ed. McGraw Hill, USA, 2010
[5] M. Kumar and Y. Ando, "Chemical Vapor Deposition of Carbon Nanotubes: A Review on Growth Mechanism and Mass Production", Journal of Nanoscience and Nanotechnology, 10, 3739-3758, 2010.
[6] K. Koziol, B. O. Boskovich, N. Yahya, "Synthesis of Carbon Nanostructures by CVD Method, Carbon and Oxide Nanostructures", Advanced Structural Materials, 5, 23-49, 2010.
[7] C. R. Bhattacharjee and A. Nath, "Chemical Vapour Deposition(CVD) Technique and the Synthesis of Carbon Nanomaterials (CNMs)", J. Of Chemical and Pharmaceutical Research,4(1),706-713,2012.
[8] C. Oncel and Y. Yurum, "Carbon nanotube synthesis via the catalytic CVD method: a review on the effect of reaction parameters", Fullerenes, Nanotubes and Carbon nanostructures,14,17-37,2006.
[9] G. Zhenga, H.Sanob, Y. Uchiyamac, "Parameters Affecting the Structure and Yield of Carbon Nanotubes in CVD Method", Material Science Forum, 544-545,773-776,2007.
[10] M.V.Jayaprakasan, K. Viswanathan and P. P. Pradyumnan, "Nanocarbon Material from Edible Oils: Synthesis and Characterization", Journal of Applied Physics, 3, 6, 51-58, 2013.
[11] P.S.Venkatanarayan, R.Velmurugan and A. Joseph Stanley, "Experimental Characterisation of Catalyst Free Carbon Nanomaterials from Mixed Vegetable and Animal Base Oils through Modified Traditional Process", Journal of Nanomaterials, 2011,1-11,2011.
[12] M. V. Jayaprakasan, K. Viswanathan, P. P. Pradyumnan, "Synthesis of Nanocarbon Powder from Sesame Oil and Its SEM Characterization", International Journal of Scientific and Research Publications,3,5,1-4,2013.
[13] Karthikeyan, S., & Mahalingam, P. (2010). Studies of yield and nature of multi-walled carbon nanotubes synthesized by spray pyrolysis of pine oil at different temperatures. *Int. J. Nanotechnol. Appl*, *4*(3), 189-197.
[14] K. Gergova, N. Petrov, and S. Eser (1994) "Adsorption properties and microstructureof activated carbons produced from agricultural by-products by steam pyrolysis," Carbon. 32, 693-703.
[15] K. Munusamy, R.S. Somani, and H.C. Bajaj (2011); "Carbon for methane uptake," BioResourses 6(1), 537-551.
[16] Sharon, M., Bhardwaj, S., Jaybhaye, S., Sathiyamoorthy, D., Dasgupta, K., & Sharon, M. (2008). Hydrogen adsorption by carbon nanomaterials from natural source. *Asian J Exp Sci*, *22*(2), 75-88.
[17] Gijare, S., Jebin, S., & Sharon, M. (2016). Impact of Catalyst on the Synthesis of Carbon Nano Materials from Castor Seeds by Chemical Vapour Deposition Method. *Advanced Science Letters*, *22*(4), 1003-1007.
[18] S. Tripathi, M. Sharon, Maheshwar, N. N. Maldar, J. Shukla, M.Sharon, "Nanocarbon synthesis using plant oil and differential responses to various parameters optimized using the Taguchi method", Carbon Letters,13,4,210-217,2013.
[19] S. R. Ravella, C. Ganesh, P.R. Shetty and P.J. Hobbs, "The Taguchi Methadology as a Statistical Tool for Biotechnological Applications: A Critical Appraisal," Biotechnology Journal, Vol. 3, No. 4, 2008 pp, 510-523.
[20] H. Gitlow, A. Alan Oppenheim and R. Oppenheim, "Tools and Methods for the Improvement of Quality," Von Hoffman Press Inc., Boston, 1989.
[21] S. Maghsoodloo, G. Ozdemir, V. Jorden and C. H. Husang, "Strengths and Limitations of Taguchi's Contributions to Quality, Manufacturing, and Process Engineering," Journal of Manufacturing System, Vol. 23, No. 2, 2004, pp. 73-126.
[22] R. H. Lochner, "Designing for Quality: An Introduction to the Best of Taguchi and Western Methods of Statistical Method Design," Chapman and Hall, London, 1990.
[23] Taguchi, Genichi. "Robust technology development." *Mechanical Engineering-CIME*, vol. 115, no. 3, Mar. 1993, p. 60+. *Gale Academic OneFile*,
[24] P. Jagdale et al.; "Carbon Nano Material Synthesis from Polyethylene by Chemical Vapour Deposition" *Advances in Materials Physics and Chemistry*, 2012, 2, 1-10.
[25] M Sharon, M. Sharon, G. Kalita & B. Mukherjee (2011). Hydrogen storage by carbon fibers synthesized by pyrolysis of cotton fibers. *Carbon Lett*, *12*, 39-43.
[26] V. Chaudhary, & A. K. Bhowmick (2015). "Green synthesis of fluorescent carbon nanoparticles from lychee (Litchi chinensis) plant." *Korean Journal of Chemical Engineering*, 32(8), 1707-1711.
[27] Bhardwaj, S., Sharon, M., Ishihara, T., Jayabhaye, S., Afre, R., Soga, T., & Sharon, M. (2007). Carbon material from natural sources as an anode in lithium secondary battery. *Carbon letters*, *8*(4), 285-291.