Optimization of cellulose nanofibrils carbon aerogel fabrication using response surface methodology

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Abstract:

This research investigated the simultaneous effects of processing parameters in the making of carbon aerogel from cellulose nanofibrils (NFC). Variables such as peak temperature and heating rate at different levels were systematically investigated with the goal of parameter optimization using response surface methodology (RSM). A face-centered central composite design (CCF) was used to evaluate the feasible range of process conditions where the levels of peak temperature and heating rate were varied at levels ranging from 230 °C to 320 °C. Results indicated that the quadratic model developed for the response surface was adequate for the prediction of optimal parameters. Response surface predictions were developed to explore the integrated and feasible operating space. Optimum conditions were: 300 °C peak temperature and a heating rate of 8.00 °C/min. The carbon aerogel achieved approximately 90.10 g/g of the normalized oil absorption capacity despite a weight reduction percentage of 82%.

Keywords: Carbon aerogel, cellulose nanofibrils, oil absorption, optimization, response surface methodology (RSM)

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Introduction:

Oil recovery from oil spills using absorbent materials has recently attracted extensive scientific and practical interest. Among numerous materials, absorbents from natural precursors are of the most interest. Despite the fact that conventional nature absorbent materials are widely used for large-scale oil spill cleanup, the hydrophilic nature of these materials drastically hampers the oil absorption efficiency. As a result, new absorption materials with hydrophobic properties are of great interest. Examples include carbon foams, graphene aerogel, carbon nanotube aerogel, carbon fiber aerogel, and carbon microbelts aerogel [1-7].

Nanocellulose is a promising new material not only because it is a bio-based, sustainable, nontoxic, abundant, and renewable resource; but it also has unique intrinsic properties [8-11]. In particular, cellulose nanofibrils (NFC) consists of long, flexible fibers cleaved from the hierarchy of plant or wood cellulose by mechanical processes [12-14]. Among these superior properties, thermal stability is of great interest [15]. Since the development of the carbon structures from this potential green alternative, numerous promising applications are in development, ranging from electrochemical energy storage, hydrogen storage, to super capacitors etc. [16-18]. The mechanism and the structure-properties relationships of carbonaceous material have been studied [19-21]. For cellulose material, the carbonization is mainly dominated by two reactions including degradation and depolymerization [22]. In addition, heating temperature, and heating rate during carbonation have been demonstrated as key factors that influence the mechanical properties [23]. However, the effect of these two parameters on the porous and adsorption properties is limited. Our previous study successfully developed a super-light, hydrophobic carbon aerogel with highly oil absorption properties using microfibril cellulose as the raw material [24]. We demonstrated a green synthesis approach involves freeze-drying and carbonization process to achieve 3D porous network structure and hydrophobic properties. In addition, in order to achieve maximum oil absorption capacity and increase the final carbon yield, research attention is focused on two factors: 'peak temperature' and 'heating rate' during carbonization.

There are some disadvantages of studying the influence of the factor on the response one-factor at a time, e.g., it is time consuming involving many experiments and does not

allow for the examination of interaction effects. Design of experiments (DOE) is a tool that allows for parameter optimization, especially in cases where many factors are involved and varied simultaneously. Among the different methods of experimental design, Response Surface Methodology (RSM) is an effective statistical modeling tool. It can be used in studies including biochemical systems, biotechnology, nanotechnology, etc. [25]. RSM allows for: expanded inference; the study of interactions; and parameter optimization. RSM is considered a formal experimental design technique that maximizes inference while minimizing the number of experimental runs.

The research focus of this study was to estimate the effect of key factors on the response of oil absorption and weight reduction, and to determine the optimal values for processing carbon aerogel. This approach quantified the relationship between NFC aerogel carbonization processing conditions and carbon aerogel's physical properties. The RSM used two variables, 'peak temperature' and 'heating rate' on the oil absorption capacity and final weight reduction of carbon aerogel. In addition, physical properties, internal morphology, and thermal properties of carbon aerogel were investigated.

Material and methods:

Material:

Cellulose nanofibrils with a solid content of 5% were obtained from commercial sources (University of Maine, USA). Cross-linker KymeneTM resin was commercially available (Ashland Hercules Inc., USA).

Preparation of NFC aerogel and carbon aerogel:

NFC suspension with concentration of 1.5 wt% and cross linker resin (5 wt% of dry NFC) was mixed and poured into open-ended copper pipes (1.50 inch in length and 0.81 inch in diameter) and sealed with aluminum foil. The samples were then placed into liquid nitrogen for one minute for rapidly freezing, following which the aluminum foil was removed and the samples were freeze-dried in a vacuum lyophilizer (Labconco, Inc., Kansas City, MO) at -51 °C for three days. Ultralight sponge-like aerogel was obtained. Samples were oven-heated at 120 °C for 3 hours to promote cross-linking in order to form a three-dimensional network. Carbonized on NFC aerogel was carried out under flowing nitrogen (20 ml/min) using a tube furnace (Thermo Scientific) by heating the

sample from room temperature to 180 °C with a heating rate of 10 °C/min, followed by increasing the temperature from 180 to 230 °C at a rate of 5 °C/min, and increasing the temperature from 230 to 320 °C at different heating rates ranging from 0.20 to 5 °C/min. Finally, samples were further heat treated by increasing the temperature from 320 °C to peak temperatures of 400 °C, 700 °C and 1000 °C respectively at a rate of 5 °C/min in nitrogen and holding for 15 min. Samples were then cooled to room temperature.

Oil sorption experiments

Oil absorption experiments were carried out using paraffin oil (BP PLC gas station). Carbon aerogel sponges were weighed first and immersed into oil. After the immersion, the sponge was taken out, drained for 30 seconds to wipe away the excess oil, and immediately transferred to a tarred pan. Sample was measured by weight and this process was repeated until carbon aerogels reached sorption saturation. The oil absorption capacity could be defined as the ratio between the weight of absorbed carbon aerogel and the weight of dried carbon aerogel.

Structure characterization of NFC aerogel and carbon aerogel

The inner structures of NFC aerogel and carbon aerogel were imaged using scanning electron microscopy (SEM, Zeiss Auriga SEM/FIB crossbeam workstation). NFC aerogel was coated with a thin layer of gold to provide conductivity and to protect the sample from electron beam damage. The ultrastructure of the carbon aerogel was characterized by transmission electron microscopy (TEM, Zeiss Libra 200 MC). Carbonized aerogel was ground into powder and dispersed into distilled water. TEM samples were prepared by depositing suspension drops (0.001% w/v in water) on amorphous lacey carbon-coated electron microscope grids and were then allowed to dry. The TEM was operated at a 200 kV accelerating voltage. Thermal stability and carbonization yield were determined using thermogravimetric analyzers (TGA; Perkin–Elmer 7 series; Perkin–Elmer Cetus Instruments, Norwalk, CT). The heating program was set up exactly the same to mimic the carbonization process.

Experimental design:

A face-centered central composite design (CCF), where the red stars are at the center of each face of the factorial space, was employed for the designed experiment of this research. Fig. 1 illustrates the diagram of CCF designs for two factors. The CCF provides predictions over the entire design space. Effects of two factors, namely 'peak temperature' and 'heating rate' on two responses of oil absorption and weight reduction respectively were evaluated. There were three levels for each factor as shown in Table 1. The levels were determined based on previous knowledge and screening experiments.

The number of experiments required for the 2^2 full factorial CCF experiments were calculated according to the equation $(N=2^k+2k+nc)$, where k represents the number of factors, 2^k is the number of factorial points, $2k$ stands for the axial points (star points) on the face, while nc means the number of replicates at the center point, in this case $n=2$. The design had a total of 20 runs including 8 factorial points, 8 axial points (star points) and 4 replicates at the center points.

Fig. 1 Graphic representation of two-factor face-centered central composite designs

Table 1 Independent variables and their values for oil absorption capacity

Factor	Level		
	Low	Center	High
Peak temperature (°C)	400	700	1000
Heating rate (°C/min)	0.20	2	10

Statistical analysis

The relationship between the variables and each response Y could be described as a second-degree polynomial quadratic equation:

$$Y = b_0 + \sum_{i=1}^k b_i x_i + \sum_{i=1}^k b_{ii} x_i^2 + \sum_{i=1, j=i+1}^k b_{ij} x_i x_j + \varepsilon \quad (1)$$

where b_0 is the constant value, b_i is the regression coefficients of the individual linear effect, b_{ii} is the quadratic effect and b_{ij} is the interaction between the variables; k is the number of factors studied ($k=2$ in this case).

Statistical analysis including ANOVA and prediction of regression coefficients, response surface and contour plots were developed in JMP software (version10, SAS Institute; Cary, NC, USA). The coefficients with small p -value less than 0.05 were considered to be statistically significant effect.

Results and discussion:

Observation of structure and physical properties

The inner structure of both NFC aerogel and carbon aerogel heat-treated at 1000 °C was imaged using scanning electron microscopy (SEM), and the ultrastructure of carbon aerogel was investigated using TEM (Fig. 2). Both aerogel and carbon aerogel are composed of a three-dimensional network structure with interconnected microfibrils. It is the 3D porous network structure that makes the derived carbon aerogel possessing an ultralow density. Effects of heating temperature and heating rate on physical properties of NFC aerogel and carbon aerogel were evaluated and compared. From the bright-filed TEM image in Fig. 2 (c) and line profile (d), it is clearly and easily observed that carbon aerogel heat-treated at 1000°C is mainly composited of stacks of ribbon-like graphitic layers with a calculated spacing of 0.37 nm. The graphite ribbons orientated randomly and tangled in a complicated manner. In the contrast, graphite structure was barely

observed in carbon aerogel heat-treated at 700 °C and 400 °C, respectively. Results also provided information that the bulk density of NFC aerogel was 0.02 g/cm³ and it decreased to 0.01 g/cm³ after carbonization at various temperatures. Fig. 2 (e) presents an image of NFC aerogel sitting on the flower, visually indicates the ultralight properties. Fig. 2 (f) shows the photograph of water droplet supported on the carbon aerogel, indicating its hydrophobicity. It is believed that hydrophilic functional groups such as C=O, C-O, -OH and C-O-C existed in NFC aerogel could be largely removed during carbonization, leading to the reverse of wetting properties[24].

Fig. 2 SEM images of (a) NFC aerogel, (b) carbon aerogel heat treated at 1000 °C, (c) TEM images of graphite domain in the structure of carbon aerogel heat treated at 1000°C, (d) line profile of graphite domain from the same sample, (e) NFC aerogel sitting on the flower and (f) carbon aerogel holding a water droplet on the surface

Factor optimization by response surface methodology

The central composite design and the observed dependent variables data are summarized in Table 2. The variable coded as ‘-’ and ‘+’ represent the ‘low’ and ‘high’ levels of the studied variables, ‘0’ represents the center point of the design, letters ‘a’ and ‘A’ represent the axial points of the design. The oil absorption capacity ranged from 71.94 to 94.18 g/g at design point of “11” and “2”, respectively. The weight reduction

189 ranged from 66.12 to 87.89%, at design points of “2” and “17”, respectively. Generally,
190 cellulose carbonization is a complex process that usually involves dehydration and
191 depolymerization [22]. Ideally, the carbon yield of NFC is 44.40% according to the
192 molecular stoichiometry $(C_6H_{10}O_5)_n$. However, the depolymerization of the
193 macromolecular chains during carbonization usually happens with the formation of
194 carbon monoxide, and carbon dioxide, aldehydes, organic acid, and tars, which takes
195 away more carbons, leading to a low carbon yield. It has been shown that heating rate
196 plays an important role on the char yield during carbonization [26]. A fast heating rate
197 can create small volatile fragments in cellulose structure, leading to a major mass loss
198 when increasing the temperature. Usually, a slow heating rate of a few °C /min is
199 suggested in order to increase carbon yield. The cellulose structure will experience a
200 series of changes when heating temperature is increased. The structure of the carbon
201 residual has a tendency to become well-ordered during the heat treatment when
202 temperatures range from 400 °C to 900 °C. Graphitization usually starts when the heat
203 treatment exceeds 900 °C. Based on previous studies on cellulose carbonization, the
204 heating temperature is believed to be an important factor that affects carbon yield and
205 may also have influence on the oil absorption capacity [22].

Table 2 Second-order central composite on face design, experimental data for three-level-two factors response surface analysis

Serial number	Pattern	Independent variable		Response variable	
		Peak Temperature (°C)	Heating rate (°C /min)	Oil absorption capacity Q_s (g/g)	Weight reduction (%)
1	—	400	0.2	90.69	73.58
2	—	400	0.2	94.18	66.12
3	a0	400	2	89.18	84.87
4	a0	400	2	83.61	82.41
5	—+	400	10	82.49	84.29
6	—+	400	10	87.95	80.62
7	0a	700	0.2	78.65	87.05
8	0a	700	0.2	74.53	85.29
9	00	700	2	76.93	85.72
10	00	700	2	77.52	87.53
11	00	700	2	71.94	83.38
12	00	700	2	74.1	80.91
13	0A	700	10	72.8	87.60
14	0A	700	10	70.44	84.52
15	+—	1000	0.2	74.11	73.43
16	+—	1000	0.2	74.97	73.93
17	A0	1000	2	68.23	87.89
18	A0	1000	2	76.13	84.45
19	++	1000	10	73.31	85.47
20	++	1000	10	74.86	87.13

The statistical analysis results of the optimization experimentation for two variables

The goodness of fit analysis was employed to estimate how well the statistical models describe the experimental data. The coefficient of determination R-squared closes to 1 indicates a good goodness of fit. The actual by predicted plot is shown in Fig 3, where there was a strong correlation between predicted and actual oil absorption capacities ($R^2=0.88$). Relatively low $R^2=0.60$ was observed for response of carbon aerogel weight reduction. The observed results demonstrate that both responses of oil absorption capacity and weight reduction are affected by experiment factors.

The response model for oil absorption capacity is:

$$Y = 71.38 - 0.023(A - 700) - 0.43(B - 5.1) + 10^{-3}(A - 700)(B - 5.1) + 10^{-4}(A - 700)^2 + 0.15(B - 5.1)^2 \quad (2)$$

where Y is the response variable of normalized oil absorption capacity, A and B are the ‘peak temperature’ and ‘heating rate,’ respectively.

The response model for weight reduction is:

$$W = 93.39 + 0.0058(A - 700) + 0.86(B - 5.1) + 10^{-4}(A - 700)(B - 5.1) - 10^{-5}(A - 700)^2 - 0.4(B - 5.1)^2 \quad (3)$$

where W is the response variable of carbon aerogel weight reduction, A and B are the ‘peak temperature’ and ‘heating rate’, respectively.

Fig. 3 Goodness-of fit of training data set (a) between predicted values obtained via partial least squares fitting and experimentally measured oil absorption capacity values, (b) between predicted values obtained and experimentally measured weight reduction; validation data set (c) between predicted values obtained via partial least squares fitting and experimentally measured oil absorption capacity values and (d) between predicted values obtained and experimentally measured weight reduction

The analysis of variance for the second-order regression equation is summarized in

Table 3. The F value¹ for model of normalized oil absorption capacity (21.06) was 10 times greater than the critical F value (2.96), suggesting a statistical significance. However, the F value for model of weight reduction (4.23) was greater than critical F value but less than 3-5 times greater, indicating a fairly low significance of model [27]. The significance of each coefficient is evaluated by individual p value. The lower the p value, more significant of the variable. In the model for normalized oil absorption capacity, regression analysis revealed that the liner model terms, which are peak temperature, heating rate, and the quadratic model terms peak tem^2 made important contribution to the whole model with p values smaller than 0.05. The order of the terms regarding to the significant are: peak temperature ($p < 0.0001$), peak tem^2 ($p = 0.0005$) and heating rate ($p = 0.0245$). Carbon aerogel's volume was associated with oil absorption capacity. The volume was estimated to be 3.7 mm³, 2.16 mm³ and 2.51 mm³ corresponding to carbon aerogel heat-treated at 400 °C, 700 °C and 1000 °C, respectively. It seems volume shrinkage is small at low heating temperature while large at high temperature. Similar result was also reported by Tang et al, that a plot was drawn describing the shrinkage percentage as a function of heating temperature [19].

Similarly, in the model for weight reduction, regression analysis revealed that the liner model term, heating rate and the quadratic model terms, peak tem^2 and heating rate² were significant with p values smaller than 0.05. The order of the terms regarding to the significant is: heating rate ($p = 0.0052$), heating rate² ($p = 0.0184$) and peak tem^2 ($p = 0.0489$). There was no significant interaction parameter contribute to the model given high p values shown in Table 3. Carbonization temperature exhibited a negative effect on the char yield, consistent with the tendency found by previous studies available in the literature [20]. The carbon yield is apparently sensitive to the heating rate, provided by the fact that slowing heating rate dramatically increase the carbon yield in early research [28].

¹ Fischer variance values (F value), denoted as the model mean square divided by the error mean square, were 21.06 and 4.23 for two models respectively. F values calculated from ANOVA regression were compared with critical F value, which is $F_{0.05, 5, 14} = 2.96$ for both models, where 0.05 is the false-rejection probability, 5 is the degree of freedom of regression and 14 is the degree of freedom of residual error.

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Table 3 Analysis of Variance (ANOVA) for response surface quadratic model

Source	Degree of freedom (df)	Sum of squares	Mean squares	F Ratio	Prob>F
Response: normalized oil absorption capacity (g/g)					
Model	5	883.92	176.79	21.06	<0.0001*
Peak temperature	1	539.58	539.58	64.29	<0.0001*
Heating rate	1	53.27	53.27	6.34	0.0245*
Peak tem* Heating rate	1	19.38	19.38	2.31	0.1509
Peak tem ²	1	170.84	170.84	20.36	0.0005*
Heating rate ²	1	19.56	19.56	2.33	0.1491
Residual	14	117.50	8.39	-	-
Lack of fit	3	16.80	5.60	0.61	0.6213
Pure error	1	100.70	9.15	-	-
Total	19	1001.42			
Response: weight reduction (%)					
Model	5	407.13	81.42	4.23	0.0147*
Peak temperature	1	33.81	33.81	1.76	0.2056
Heating rate	1	210.23	210.23	10.96	0.0052*
Peak tem* Heating rate	1	0.14	0.14	0.01	0.9324
Peak tem ²	1	89.28	89.28	4.65	0.0489*
Heating rate ²	1	136.40	136.40	7.11	0.0184*
Residual	14	268.66	19.19	-	-
Lack of fit	3	192.70	64.23	9.30	0.0024*
Pure error	11	75.95	6.90	-	-
Total	19	675.76			

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Table 4 Estimated regression coefficients for normalized oil absorption capacity and weight reduction

Term	Estimate	Std Error	t Ratio	Prob> t	Lower 95%	Upper 95%
Normalized oil absorption (g/g)						
Intercept	71.37	2.06	34.51	<0.0001	66.94	75.81
Peak tem	-6.90	0.86	-0.80	<0.0001	-8.75	-5.05
Peak tem ²	6.05	1.34	4.51	0.0005	3.17	8.93
Heating rate	-2.10	0.84	-2.52	0.0245	-3.90	-0.31
Weight reduction (%)						
Intercept	93.36	3.13	29.85	<0.0001		
Heating rate	4.19	1.26	3.31	0.0052	1.47	6.90
Heating rate ²	-9.69	3.63	-2.67	0.0184	-17.49	-1.89
Peak tem ²	-4.37	2.02	-2.16	0.0489	-8.72	-0.02

Optimization of normalized oil absorption capacity / weight reduction of carbon aerogel and model validation

The response surfaces of the interaction effects by the combination of two test variables are plotted to define the optimal processing conditions (Fig. 4). The heating rate and peak temperature had a negative impact on the normalized oil absorption capacity. The low heating temperature tended to lead to an increase of normalized oil absorption capacity. The response surface revealed that maximum oil absorption capacity achieved to 91.57 (g/g) at peak temperature of 400 °C with heating rate of 0.20 °C/min. A possible explanation of the phenomenon is that low pyrolysis temperature and low heating rate could results to large sample volume. Volume of carbon aerogel processed under three peak temperatures was compared and 400 °C heat-treated sample maintained larger volume. Research on cellulose carbonization proved and claimed that dehydration is the dominant reaction under low heating temperature [22]. The elimination of hydroxyl groups induces double bonds, conjugated double bonds, consequently helps to maintain the cellulose structure more stable and less accessible to thermal cleavage. Heating the aerogel up to 400 °C only makes the sample experiencing the early stage of carbonization, where thermal cleavage and scission are taken place. The volume of the sample is fairly maintained at such low temperature. With the increasing of the heating temperature, more well ordered stacking graphene sheets were formed through re-polymerization with the releasing of gases and loose of non-carbon element, resulting to a condensed and close packed aromatic structure, consequently the volume shrinkage [22].

Our previous research has demonstrated that macropores and the open pore structure make the carbon aerogel to be efficient as oil absorbent [24]. Larger volume would provide more open voids and drastically increase the oil absorption capacity.

The weight reduction of carbon aerogel affected by combination of peak temperature and heating rate is plotted. Contour plot generated by the predictive model is shown in Fig. 4(d). The interaction effect is obvious on the response. An increase of heating temperature with heating rate up to the optimum point increased the weight reduction to its maximum number, while further increase in heating temperature with heating rate reversed the trend. In fact, the decrease of weight reduction on the contour plot is achieved by decreasing in heating temperature below 700 °C or increasing in heating temperature above 700 °C, and increasing in heating rate above 6 °C/min or decreasing in heating rate below 6 °C/min. Again, the explanation for this is that the formed intermediates oxidation components have the tendency to be taken away in the form of H₂O, CO, and CO₂, when increasing the temperature to 700 °C or 1000 °C. A lower weight reduction is expected. The contour plot is used to find the feasible region for optimized process. Each contour with number marked on stands for a particular height of the corresponding response surface. It can be seen in Fig. 4 that at a low heating temperature with heating rate less than 6 °C /min, decreasing heating rate reduced the weight reduction of carbon aerogel. On the other hand, when heating rate was over 6 °C /min, increasing heating rate reduced the weight reduction. A fast heating rate, for example 10 °C /min, will cause “thermal inertia” effect, which results to less reaction time to trigger decomposition.

Fig. 4 (a) response surface plot and (b) contour profile representing the interaction between the variables affecting the normalized oil absorption capacity by oil density; (c) response surface plot and (d) contour profile representing the interaction between the variables affecting carbon yield after carbonization.

The optimization prediction plots shown in Fig. 5 (a) refers to prediction profile of optimum conditions for carbon aerogel. Graphic desirability traces for variable heat temperature showed that decreasing heating temperature would achieve low weight reduction and high oil absorption capacity. However, in order to achieve hydrophobic properties for the resulted product, heating temperature over 300 °C is necessary to ensure thermal scission and removal of none carbon element in form of H₂O, CO₂, and CO. In addition, heating rate in the range of 6 °C/min to 10 °C/min is more acceptable in accordance with low energy input and high efficiency.

The overlaid contour plot is shown in Fig. 5 (b) with red contours revealing the weight reduction and blue ones revealing oil absorption capacity. It is useful to visually identify the feasible variables for multiple responses. Area highlighted by green dash lines mapped out in overlaid contour plots instructs the operation levels for the feasible

region for desired response in reality, in this case, a relatively high oil absorption capacity and low weight reduction. In this particular case, area highlighted by green dash line is more preferred and should be considered as a feasible operation region. As a result, one of the optimum condition for making carbon aerogel is observed at peak temperature=300 °C and heating rate =8 °C/min, with an acceptable desirability value of 0.55 for all responses.

Fig. 5 (a) Optimization prediction plots and (b) overlaid contour plot for normalized oil absorption capacity (g/g) and weight reduction (%)

Additional experiments runs were performed by randomly selecting combined operation parameters. NFC aerogel samples were carbonized under these selected conditions as summarized in Table 5. In this research, eight data points were collected for

model validation, which accounts for 28% of the whole data set. Root mean square error (RMSE) and coefficient of determination R-squared were used for assessing the fit of regression model. The experimental and predicated response for normalized oil absorption is plotted in Fig. 3 (c). The coefficient of determination R-squared (R^2) for validation was calculated to be 0.58, smaller than that calculated from training data ($R^2=0.88$). The root mean square error value (RMSE) was 2.44 for validation data set, very similar to the value for training data set (RMSE=2.90). These results indicate that the constructed quadratic model is adequate for predicting the normalized oil absorption capacity. On the other hand, from the plot of experimental and predicated response for weight reduction in Fig. 3 (d), the R squared value was calculated to be 0.42, smaller than the value calculated from training data set ($R^2=0.60$). The root mean square error value (RMSE) was 1.83 for validation data set, smaller than the value for training data set (RMSE=4.38). Results also indicate that the constructed quadratic model has the ability to predict the weight reduction. Model fitted for normalized oil absorption has a better prediction than that for weight reduction.

Table 5. Comparison of model predicted and experimental values of normalized oil absorption and weight reduction (validation data set)

Run order	Peak temperature (°C)	Heating rate (°C/min)	Normalized oil absorption (g/g)		Normalized weight reduction (%)	
			Experimental	Predicted	Experimental	Predicted
1	350	6	75.42	86.83	81.53	85.95
2	400	8	75.06	83.50	83.59	86.30
3	400	8	74.43	83.50	81.62	86.30
4	450	3	70.36	83.40	85.27	85.40
5	450	3	68.57	83.40	80.97	85.40
6	500	8	67.95	78.10	84.78	89.30
7	500	6	67.26	78.20	84.68	90.70
8	550	4	69.17	77.20	86.03	90.00

Thermal stability analysis

To explain the discrepancy of oil absorption capacity and weight reduction from carbon aerogel, carbonization process was further investigated by TGA analysis. Fig. 6 illustrates the relationship between temperature and weight/derivative weight percentage of carbon aerogel. The curve shape is consistent with the TGA analysis performed on

cellulose [26]. One should notice that a rapid weight loss step occurs in the range of 230 °C to 320 °C for NFC aerogel. The extrapolated onset temperatures, denoted as the temperature at which the weight loss begins, of carbon aerogel were estimated to be 259 °C, 303 °C and 309 °C respectively corresponding to the heating rate of 0.20 °C/min, 2 °C/min and 10 °C/min. When performing carbonization on aerogel sample at low temperature, such as below 400 °C, carbon yield of CNF carbonized with low heating rate is significantly increased compared to that of high heating rates. The effect of heating rate during rapid mass loss (230 to 320°C) process on the char yield at 1000 °C was compared. The trends highlighted in the insert of Fig. 6 (a) showed that heating rate had a positive effect on the residual carbon yield. Char yield of carbonized aerogel exhibited highest number of 12.60% with heating rate of 10 °C/min, while this number decreased with the decrease of heating rate. The degradation temperatures of NFC aerogel were calculated to appear at 302.30 °C when samples are heat-treated at low heating rate and appeared at 351 to 354 °C when samples were heat-treated at high heating rate. Apparently, for NFC sample with heating rate of 0.20 °C/min, maxima in the rate of mass change occurred at 302 °C and 360 °C, however, their peak intensities were the lowest among all other curves. Decomposition is triggered by temperature and started earlier with low heating rate. Thermal cleavage and thermal scission mainly occur in the temperature range of 240 to 400 °C, whereby heating rate is various. Low heating rate could provide sufficient reaction time to allow the heat dissipating into material, thus leading to more loss of carbon atom in forms of CO and CO₂. In the contrast, high heating rate caused by temperature overshoot has a great potential to lead to “thermal inertia” effect, consequently shift the onset and degradation temperatures to the right side.

Fig. 6 Thermogravimetric analysis (TGA) showing the effect of heating rate during temperature rising from 230 to 320 °C on carbon residual yield at 1000 °C (a) TGA curve and (b) DTG curve

Conclusion

In summary, this research investigated the carbonization process of aerogel derived from cellulose nanofibrils. We demonstrated that there exist the linkage between carbonization operating process variables (peak temperature and heating temperature) and the carbon aerogel performance (normalized oil absorption capacity, weight reduction). The carbon aerogel making process has been successfully optimized by adopting a statistical strategy of response surface methodology, in this case, faced

centered central composite design (CCF). It was found that independent variables had significant linear and quadratic effect on dependent variables. The optimum operating conditions have been referred as peak temperature= 300 °C and heating rate=8.00 °C/min considering low energy input and high efficiency. The desirability for all responses reach to 0.55 and it is acceptable. Compare to conventional single factor optimization methods, which are time consuming and expensive with vague and misleading information, Design of Experiment (DOE) method performed in this research and the resulted model provide integrated and accurate results to systematically and effectively predict the response through various independent variables.

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Graphical Abstract