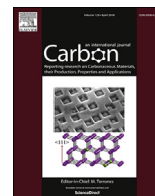




Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Microwave synthesis of carbon onions in fractal aggregates using heavy oil as a precursor

Mohamed Adam^{a,*}, Abarasi Hart^b, Lee A. Stevens^a, Joseph Wood^b, John P. Robinson^a, Sean P. Rigby^a

^a Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD, UK

^b School of Chemical Engineering, University of Birmingham, Birmingham, B15 2TT, UK

ARTICLE INFO

Article history:

Received 19 June 2018

Received in revised form

22 July 2018

Accepted 28 July 2018

Available online xxx

ABSTRACT

In this work we report a method for preparing carbon onions through microwave heating of heavy oil. It was shown that microwave heating of heavy oil mixed with a carbon catalyst at 300 W leads to the growth of a several-centimetre long fractal carbon structure in just 60 s. Scanning electron microscopy (SEM) images showed that the structure is predominantly made of networks of small particles with diameters ranging from tens to hundreds of nanometres. High-resolution transmission electron microscopy (HRTEM) images revealed the presence of disordered graphitic structures, including carbon onions with diameters as small as 30 nm. This was supported by the Raman spectroscopy which showed typical spectra for carbon onions with disordered graphitic structure. CO₂ gas sorption results revealed a specific surface area of up to 164 m²/g. The carbon onions are believed to form through pyrolysis of the oil into light hydrocarbons followed by nucleation and growth of concentric graphitic layers. The carbon tree, subsequently, grew through aggregation of the carbon onions and further deposition of pyrolytic carbon, with the electric field configuration favoured the longitudinal growth of thin branches. This study demonstrates that carbon onions can be prepared from cheap unrefined liquid precursors.

© 2018 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The past three decades have seen important discoveries in the synthesis and applications of carbon nanostructures. This was initiated by the discovery of C₆₀ Fullerene which was first reported by Kroto et al. [1], followed by carbon nanotubes reported by Iijima [2]. Carbon onions (or onion-like carbon) were discovered earlier by Iijima [3], however, they were first described by Ugarte [4] who prepared carbon onions by exposing amorphous carbon particles to a high-intensity electron beam. Carbon onions are identified by their spherical or polyhedral shape with concentric disordered graphitic shells/layers. They can have a diameter ranging from 5 to 100 nm [5]. Their significance comes from their unique electric and dielectric properties as well as their nanoscopic size and high surface area, making them attractive candidates for applications such as electrochemical energy storage [5,6], electromagnetic shielding and heating [7], catalysis [8], solid lubricants [9], and composite

materials [10].

Besides electron beam irradiation, carbon onions can be prepared by other methods among which the most widely used are electric arc discharge, thermal annealing and flame pyrolysis. In the electric arc discharge method, a DC current is passed through a graphite rod (anode) placed in an inert atmosphere. The high temperature generated by the arc discharge evaporates the graphite generating carbon neutrals and ions which deposit on the surface of the cathode, forming the carbon onions [11]. Flame pyrolysis involves burning a simple hydrocarbon such as acetylene in an oxygen-deficient environment. Combustion produces the heat required for the hydrocarbon decomposition. Carbon onions then grow out of the decomposition products [12]. In the thermal annealing method, sp³-hybridised carbon nanoparticles such as nanodiamonds are heated in an inert atmosphere leading to sp³-sp² transformation (graphitisation). sp³-sp² transformation of nanodiamonds happens in the temperature range between ~600 and ≥1700 °C [5,13]. Thermal annealing of nanodiamonds has recently received attention due to its ability to produce carbon onions with well-defined particle size, however the nanodiamond raw materials needed for the process are expensive.

* Corresponding author.

E-mail address: Mohamed.Adam@nottingham.ac.uk (M. Adam).

In this work we report a method for preparing carbon onions using microwave energy as the heating method and crude heavy oil as the precursor. Microwave heating is a selective and volumetric heating technique. Heating is achieved instantaneously as a result of the interaction of the electromagnetic field with the material at the molecular level. This allows targeting of microwave absorbers without the need to preheat the entire environment. It also allows for rapid heating because the process is not restricted by the temperature gradient and the heat transfer coefficients as in the cases of conventional conductive and convective heating methods.

The microwave heating technique has been previously used for preparing carbon nanostructures such as carbon nanotubes [14] carbon fibres [15–17], carbon filaments [18] and carbon nanodots [19]. It has also been used for preparing carbon onions, however this was either from a pre-processed amorphous carbon [20] or refined hydrocarbons [21] rather than direct synthesis from the crude material.

The present study demonstrates that carbon onions can be prepared from a cheap, unrefined precursor. Crude heavy oil with properties similar to the one used in the present study costs around 38 US dollar per bbl [22]. This corresponds to only ~0.28 US dollar per kg carbon assuming 89% carbon content and specific gravity of 0.97 [23] compared to ~2500 US dollar per kg for nanodiamonds [5]. Crude heavy oil is also cheaper than the refined hydrocarbons like acetylene and methane, which are commonly used as precursors for preparing carbon onions [24]. The present study also shows the formation of a several-centimetres long fractal structure, which is thought to grow through aggregation of carbon onions and further deposition of pyrolytic carbon.

One of the possible industrial applications of this fractal growth of carbon tree within a heavy oil medium is in the downhole microwave-assisted thermal recovery and upgrading of heavy oil. The growth of carbon trees would act as an in-situ production of a microwave susceptor within the oil reservoir which can improve the efficiency and effectiveness of electromagnetic-to-thermal energy conversion. This work is a proof-of-concept study in which the formation and growth mechanisms of the carbon structures within the oil medium will be discussed in detail and linked to the microwave heating effect.

2. Experimental

The experimental setup involved heating heavy oil mixed with a carbon catalyst in a Discover-SP microwave heating apparatus (CEM Corporation, USA). Fig. 1 shows a schematic of the microwave heating system. It includes a 35 mL quartz tube placed in a microwave heating cavity.

The system is equipped with a magnetic stirrer and an IR thermometer directed towards the bottom of the quartz tube. The system is set to hold an internal pressure of up to 20 bar before it vents automatically. The heavy oil used in this study was supplied by Touchstone Exploration Inc. Canada. The properties of the oil, which was produced through Toe-to-Heel Air Injection (THAI) technology, are listed in Table 1. During the experiments, typically, 10 g of the THAI oil was mixed with 0.5 g carbon catalyst in the quartz tube. The carbon catalyst was a 50:50 w/w mixture of activated carbon and NiO-MoO₃/γ-Al₂O₃. The purpose of the catalyst was the catalytic upgrading of the heavy oil. Details of the catalyst preparation steps can be found in the supplementary information document. The quartz tube was purged with nitrogen before being covered with a PTFE/silicone septa cap. The heating system was then assembled as shown in Fig. 1.

The formed solid was filtered using a 37 μm wire mesh. The solid was then washed with xylene, followed by isopropanol before drying in an electric oven at 105 °C. Elemental analysis was carried out using a LECO CHN628 elemental analyser (LECO Corporation, USA), which showed 94.7 ± 2.5% C, 2.0 ± 0.5% H, and 0.62 ± 0.24% N; all weight percentages. The solid carbon was then characterised using different techniques including high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), Raman Spectroscopy and gas sorption. HRTEM was performed on a JEOL 2100F FEG-TEM (JEOL Ltd., Japan) operated at 200 kV. For TEM analysis the samples were first ground using a mortar and pestle. The powders were then dispersed in isopropanol before sprinkling them onto the carbon TEM grid for investigation. SEM microscopy was performed on a JEOL 7100F FEG-SEM microscope (JEOL Ltd., Japan) operated at 10 kV. The samples were mounted on steel sample holders with adhesive carbon tape. Two types of sample were used for SEM microscopy: powder sample ground with a mortar and pestle and unground branches taken from the bottom part (root) of the formed solid. Prior to SEM imaging, the samples were coated with Iridium in a Quorum Q150T ES coater (Quorum Technologies Ltd., UK). Raman spectra were recorded using a LabRAM HR spectrometer (Horiba-Jobin-Yvon) with a laser wavelength of 532 nm, operating at a power of approximately 0.3 mW.

Gas sorption analysis was carried out using a Micromeritics ASAP 2420 instrument (Micromeritics Instrument Corp., USA). Prior to the analysis, the samples were outgassed at 120 °C for 15 h under vacuum conditions. N₂ sorption isotherms were carried out at –196 °C from 0.001 to 0.998 relative pressure (P/P₀). In addition, CO₂ adsorption isotherms were carried out at 0 °C from 0.012 × 10^{–3} to 0.034 relative pressure to investigate signs of activated diffusion or narrow micropores inhibiting N₂ adsorption. Brunauer–Emmett–Teller (BET) and Dubinin–Raduskevich (D-R) models were used for calculating the surface area and pore volume. The Calculations were performed using an interactive data analysis software, MicroActive V 4.03.01 (Micromeritics Instrument Corp.,

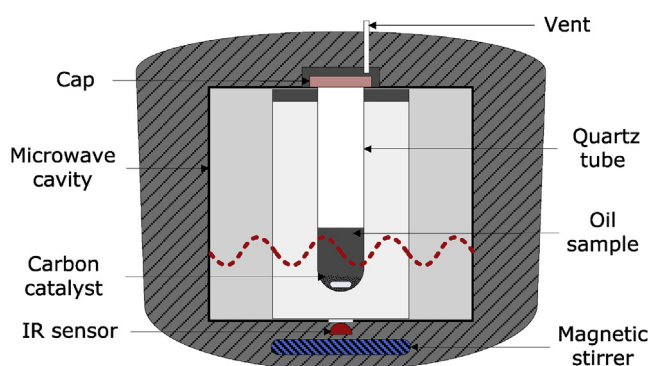


Fig. 1. Schematic of the microwave heating apparatus. (A colour version of this figure can be viewed online.)

Table 1
Characteristics of the THAI oil used in this study.

Property	Value ^a
Specific gravity at 20 °C	0.971
Viscosity at 20 °C (cP)	1360
Sulphur content (wt. %)	3.2
Composition (wt. %)	
Saturates	32.34 ± 0.34
Aromatics	33.19 ± 1.77
Resins	15.86 ± 0.44
Asphaltenes	7.91 ± 0.40

^a These data were taken from previously published work [25].

USA).

The dielectric properties of the formed solids were measured in a cylindrical cavity using the cavity perturbation technique. The dielectric properties define the material's interaction with the electromagnetic field. The dielectric constant is related to the ability of a material to be polarised and store electromagnetic energy, whilst the loss factor determines the ability of a material to convert electromagnetic energy into heat. The loss tangent, which is the ratio of the loss factor to the dielectric constant, is a measure of the efficiency of energy conversion [26]. Details of the dielectric measurement system can be found elsewhere [25]. Ground samples were loaded into a 3 mm i.d quartz tube supported on porous glass fibre. The tube was purged with nitrogen flowing at 5 mL/min to avoid oxidation at high temperatures. The dielectric measurements were performed at different temperatures starting from 20 up to 1100 °C. The dielectric properties of pulverised solids are affected by the packing density of the solid as it considers the voids as part of the material. The measured dielectric properties were therefore corrected using the Landau-Lifshitz-Looyenga's formula following the method reported by Nelson [27] which considers the powder as a solid-air mixture.

3. Results and discussion

Fig. 2 shows typical power, temperature and pressure profile during microwave heating of the heavy oil. The oil was first heated at 50 W for 5 min followed by 150 W for 2 min. The aim of this low-power heating period was to gradually increase the temperature of the oil to around 100 °C to reduce its viscosity and improve mixing. There was no evidence of solid formation during this low-power preheating period. The power was then increased to 300 W. A sharp pressure increase can be seen in Fig. 2 30 s into the high-power heating region, indicating the start of solid carbon formation. This sharp increase in pressure can be attributed to the formation of volatiles following the pyrolysis and gasification of the oil around the solid carbon formed.

Fig. 3 shows images of the products obtained after heating the oil for 60 s in the high-power region. A several-centimetre long fractal structure with tree-like shape was formed. The bottom part, which will be called the 'root', is mostly concentrated around the oil interface with part of it completely immersed in the oil. The top part of the carbon tree, which will be called the 'stem', emerges from the root section above the oil level. The root has a fibrous macro-structure with thin branches, whereas the stem section consists of one or more members with more than 1.0 mm thickness.

Fig. 4 indicates a relationship between the quantity of the solid

formed and the maximum pressure reached during heating. This supports what has been proposed earlier in this section that the increase in the internal pressure during microwave heating is caused by the pyrolysis and gasification of the oil around the carbon formed. The weight of the catalyst collected after filtration, washing and drying was within ± 0.01 g of the initial mass, whereas up to 0.13 g solid carbon was formed during microwave heating as shown in Fig. 4. This confirms that the solid carbon formed during microwave heating came from the oil and not from the solid catalyst.

3.1. Morphology and nanostructure

The morphology and nanostructure of the carbon tree was studied using SEM and HRTEM. Fig. 5 displays SEM images for samples taken from the root and stem sections of the carbon tree. More SEM images can be found in Figures S1–S3 in the supplementary information document. The SEM images show a fractal structure of particle with sizes ranging from tens to hundreds of nanometres. It was observed that the size of the particles in the stem section of the carbon tree is, in general, larger than those in the root section.

SEM images for uncrushed branches taken from the root section of the carbon tree are displayed in Fig. 6. It can be seen that the entire structure is predominantly made of networks of small particles of the order of tens to hundreds of nanometres.

Fig. 7 shows HRTEM images obtained for samples taken from the root and stem sections of the carbon tree. The HRTEM images reveal the presence of disordered graphitic structures including carbon onions with diameters as small as 30 nm (Fig. 7 (a) and (b)), as well as curved concentric graphitic structures with radius of curvature larger than 100 nm (Fig. 7 (c)). Evidence for these graphitic layers can be seen in the SEM images in Fig. 5 (c) and in Figures S1 and S2 in the supplementary information document. The interlayer spacing between the disordered graphitic layers was calculated by processing the HRTEM images using image processing software, ImageJ 1.48v (NIH, USA). The processed images together with examples of the calculated interlayer spacing can be found in Fig. S5 in the supplementary information document. The interlayer spacing in the carbon onions was found to be in the range 0.27–0.30 nm. For the larger curved graphitic structures, interlayer spacing in the range 0.38–0.44 nm were detected. Highly ordered planar graphite has an interlayer spacing of ~ 0.34 nm [28,29]. However, the spacing is affected by the degree of ordering and the diameter of curvature [29,30] which explains the wide range of interlayer spacing observed in the present study.

3.2. Raman spectroscopy

Fig. 8 shows normalised Raman spectra for samples taken from the root and stem parts of the carbon tree. Both are typical spectra for disordered graphitic structures with two predominant peaks; one at ~ 1596 cm^{-1} while the other is at ~ 1345 cm^{-1} . The former corresponds to the G-mode which arises from the vibration in the planar graphitic layers between the sp^2 carbon atoms. The latter corresponds to the D-mode (disordered mode) which is related to the breathing of hexagonal carbon rings with defects [31,32]. The G-mode of planar graphite is usually located at ~ 1582 cm^{-1} . However, non-planar graphitic structures usually experience a shift in the signal position due to bond bending caused by shell curvature [31]. These Raman spectra support the HRTEM results (Fig. 7) that the solid carbon consists, mainly, of carbon onions with disordered graphite structures.

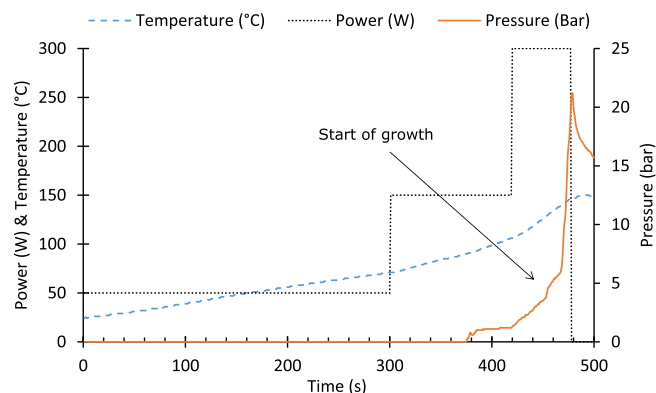


Fig. 2. Typical power, temperature and pressure profiles during the microwave heating experiments. (A colour version of this figure can be viewed online.)

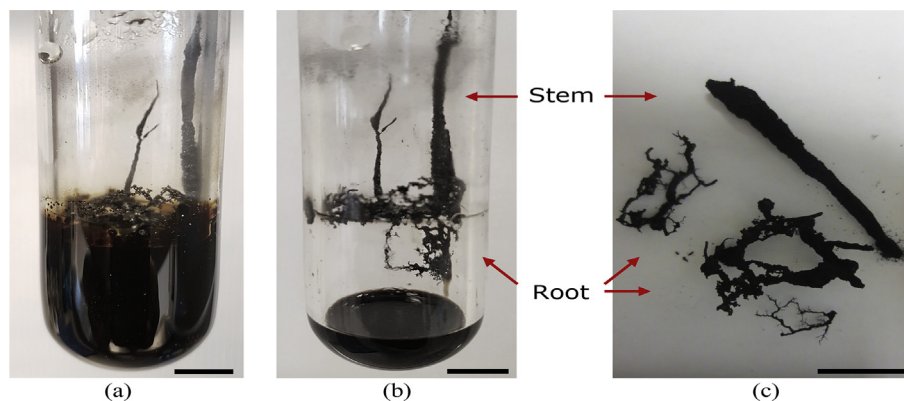


Fig. 3. The tree-like solid produced after microwave heating of heavy oil for 60 s in the high-power region: (a) the formed solid and the oil directly after the experiment; (b) the solid after decanting part of the oil; (c) collected solid after washing and drying. (A colour version of this figure can be viewed online.)

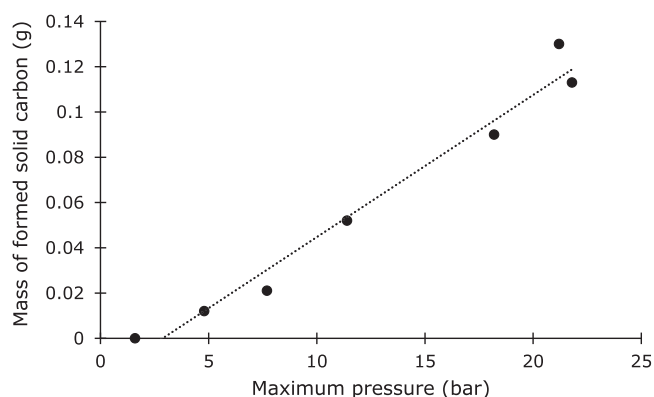


Fig. 4. Weight of the solid carbon formed during microwave heating as a function of the maximum pressure.

3.3. Surface area

Gas sorption experiments were first run with N_2 at $-196^\circ C$. The isotherms obtained can be found in [Figures S6](#) in the supplementary information document. The BET surface area calculated from the N_2 isotherms was only 1.7 and $7.6\text{ m}^2/\text{g}$ for the stem and root sections of the carbon tree, respectively. However, CO_2 sorption at $0^\circ C$ revealed the presence of micropores which added significantly to the surface area. The CO_2 sorption isotherms can be found in [Figures S7](#) in the supplementary information document. [Table 2](#) shows the specific surface area and pore volume calculated from CO_2 adsorption isotherms at $0^\circ C$ using Dubinin-Radushkevich (D-R) method. The D-R method is considered a more reliable tool for obtaining the surface area and pore volume of microporous materials compared to the more widely used, BET method [33–35]. The significantly higher surface areas obtained from CO_2 adsorption at $0^\circ C$ compared to those from N_2 adsorption at $-196^\circ C$ indicates that most of the pores are micropores. Due to the low critical temperature of N_2 , its sorption isotherms are carried out at low temperatures and low relative pressures. However, at low temperature and very low pressures the rate of gas diffusion into micropores is extremely slow, which restricts equilibration and results in an underestimated surface area [34]. Evidence for this restricted diffusion and equilibration can be seen in the low-pressure hysteresis in the N_2 isotherms ([Figure S6](#) in the supplementary information document). CO_2 has a higher critical temperature compared to N_2 , and thus its sorption isotherms can be carried out at higher

temperatures and higher relative pressures which improves the diffusion rate into micropores and accelerates equilibration.

It can be seen from [Table 2](#) that the root section of the carbon tree has significantly greater surface area and pore volume than those of the stem part. This can be related to the presence of particles with smaller sizes in the root section as observed in the SEM images.

The average diameter of the particles could be estimated from the specific surface area by assuming spherical particles whose full surface is available for gas adsorption:

$$d = \frac{6}{\rho S} \quad (1)$$

where d , S and ρ are the average diameter (m), specific surface area (m^2/g) and the density of the particles (kg/m^3) respectively. Assuming the particles are mostly carbon onions whose specific gravity is 1.9 [5], and substituting for the surface area from the values listed in [Table 2](#) gives average particle diameters of 19.2 and 39 nm for the root and stem sections, respectively. However, the smallest diameter detected in the SEM and HRTEM were ~ 50 nm and ~ 30 nm respectively. This indicates that there are other adsorption sites beyond just a smooth external surface. Previous studies on carbon onions suggested that the higher surface area calculated from gas sorption compared to that obtained from electron microscopy is caused by the surface roughness creating additional adsorption sites [36].

Previously, Zeiger, et al. [13] showed that carbon onions prepared through thermal annealing of nanodiamonds with 5–15 nm diameter could have a specific surface area of up to $493\text{ m}^2/\text{g}$. This higher specific surface area compared to the $164\text{ m}^2/\text{g}$ seen in the present study is because of the smaller particle size produced through thermal annealing. Future studies to investigate the effect of the processing parameters on the size of the formed particles as a way to improve the surface area. Additionally, the surface area in the current study was obtained for samples taken from the bulk products. The surface area can, therefore, be improved also by either minimising the fraction of the other carbon structures within the bulk product or separating the formed carbon onions from the other carbon structures.

3.4. Formation and growth mechanism

This study revealed the formation of two unique features during microwave processing of heavy oil. The first is the disordered graphitic structures, specifically carbon onions, at the nano-scale.

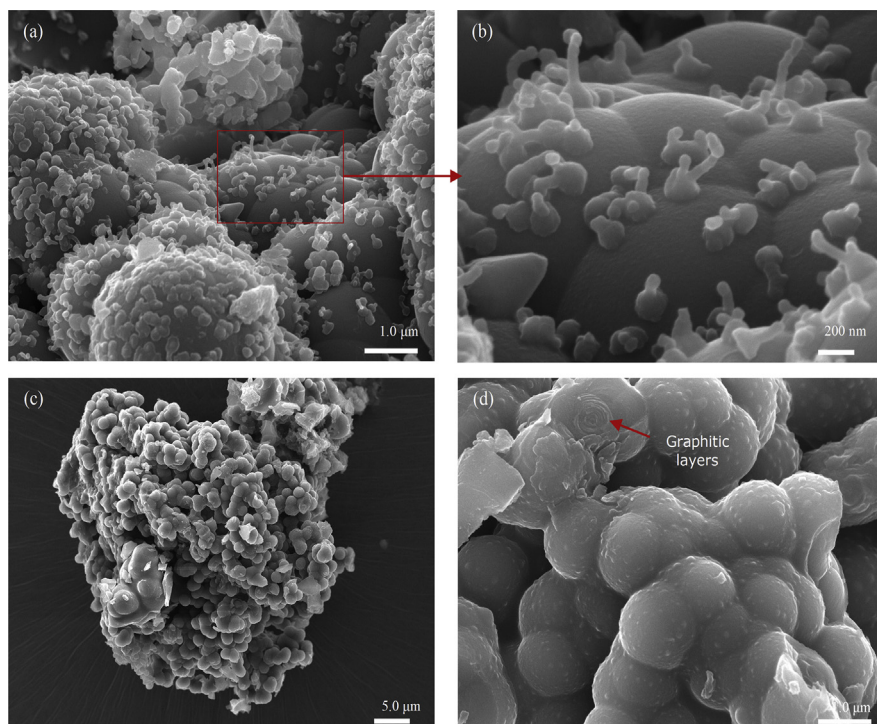


Fig. 5. SEM images of crushed sample taken: (a) & (b) from the “root” section; (c) & (d) from the stem section of the carbon tree. (A colour version of this figure can be viewed online.)

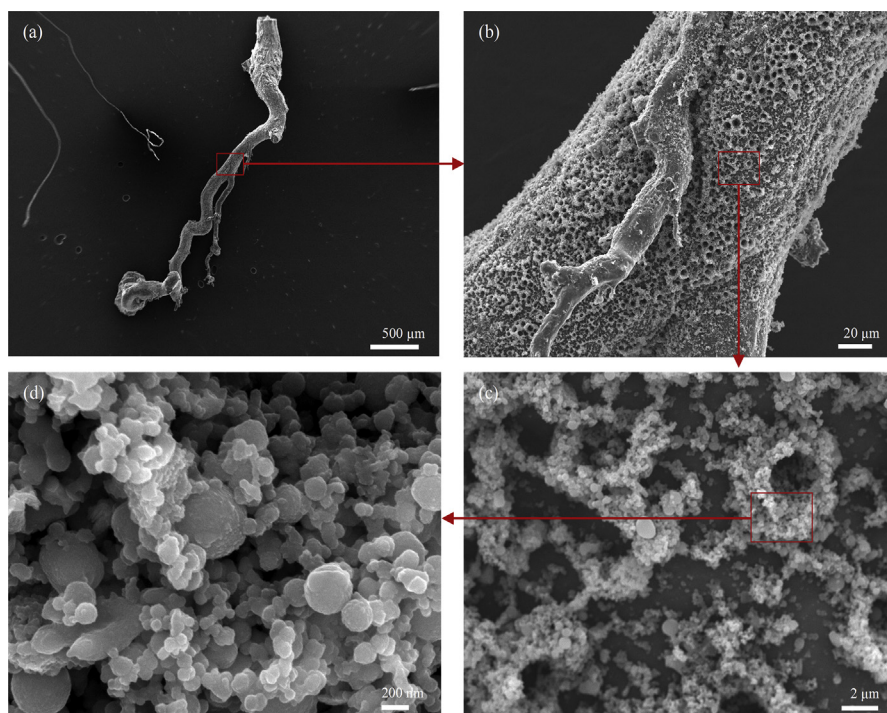


Fig. 6. SEM images for sample taken from the “root” section. (A colour version of this figure can be viewed online.)

The second is the fractal structures and the growth of a carbon tree at the micro- and macro-scale. In this section we present our understanding of the formation mechanism of these features, and link this to the microwave heating effect.

3.4.1. Nano-scale features

Previous studies of carbon onion synthesis suggested different formation mechanisms for different synthesis methods. One of the early published attempts to understand the formation mechanism of carbon onions was the work reported by Saito [11] which was

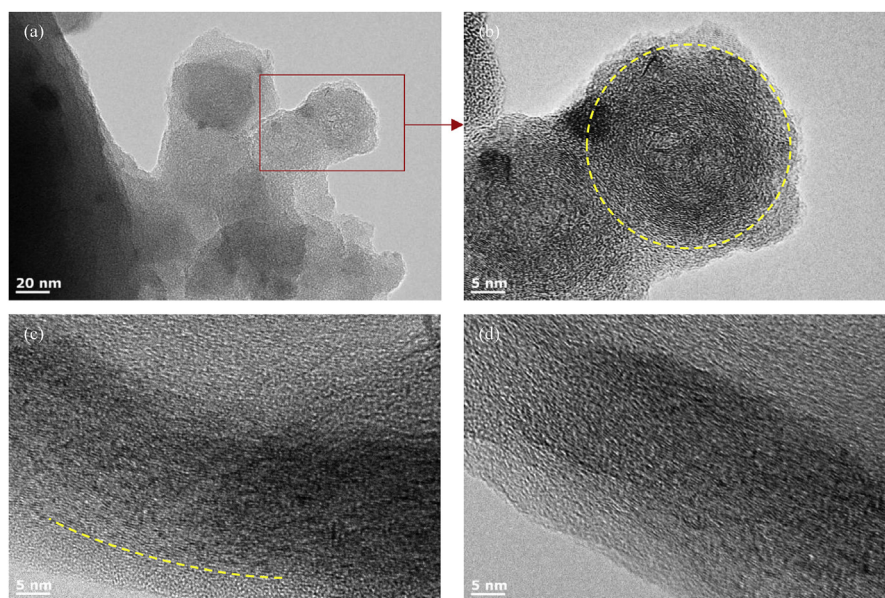


Fig. 7. HRTEM images of sample taken: (a) & (b) from the root section showing onion-like carbon structures with ~30 nm diameter; (c) & (d) from the stem section showing graphitic structures with higher radii of curvature as in (c) or no obvious curvature as in (d). (A colour version of this figure can be viewed online.)

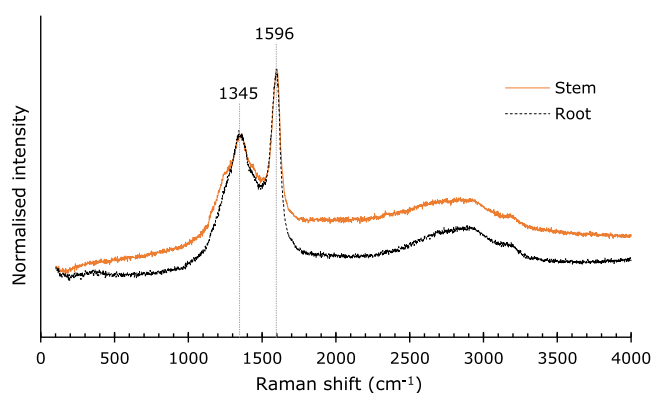


Fig. 8. Raman spectra of samples taken from the stem and root sections of the carbon tree produced. (A colour version of this figure can be viewed online.)

Table 2

Specific surface area and pore volume calculated from CO₂ adsorption isotherms at 0 °C using Dubinin-Radushkevich (D-R) model.

	Stem	Root
D-R micropore volume (cm ³ /g)	0.033	0.066
D-R micropore surface area (m ² /g)	81.3	164.4

based on the arc discharge synthesis method. It was suggested that carbon neutrals (C and C₂) and ions, evaporated from the graphite in the anode, deposit and coagulate on the surface of the cathode forming small clusters which grow up to form larger particles. The structure of these particles at this stage were believed to be amorphous with high structural fluidity due to the high temperature. As new carbon particles start to grow surrounding the previously grown particles, graphitisation starts to take place in the previously grown particles beginning from the external layers and progressing towards the centre following the direction of cooling. Thermal annealing is another synthesis method with a distinctive formation mechanism. The sp³-sp² transformation and graphitic

shells formation during the thermal annealing involves desorption of the functional groups and reconstruction of the dangling bonds and amorphous carbon. Graphitisation is believed to progress from the outer layers of the nanoparticle towards the inside [5]. This suggested mechanism was supported by experimental results which involved comparing the nanostructure of carbon onions prepared from nanodiamonds at different temperatures [5,13].

The similarity between the arc discharge and thermal annealing mechanisms is the outside-to-inside formation of the graphitic layers starting from an amorphous structure. The main difference is that in the arc discharge method the amorphous structure is an intermediate state formed during the process. Vander Wal and Tomasek [12] suggested a fundamentally different mechanism for the formation and growth of carbon onions. Their suggested mechanism was based on observations from carbon onion synthesis through thermal pyrolysis using different hydrocarbons in conditions similar to flame pyrolysis. They dismissed the hypothesis of the formation of intermediate amorphous carbon (carbonisation) prior to the sp³-sp² transition (graphitisation) on the ground that the temperature and the heating time during the flame pyrolysis were not sufficient for significant structural changes once the carbonisation takes place. Instead, they proposed a mechanism that involves decomposition/pyrolysis of the hydrocarbon precursor into their basic C₂ fragments, followed by nucleation and surface growth. They suggested that these steps may overlap during the process.

We propose that the onion-like structures in the present study were formed through the pyrolysis, nucleation, and surface-growth mechanism. The process starts when a carbon catalyst at a hot-spot, i.e. an area of high electric field intensity, heats to a higher temperature than the rest of the catalyst particle. The loss factor of carbon materials is known to increase with temperature. Thus, the loss factor at the hot-spot increases above that of the surroundings, leading to higher temperatures and further increase in loss factor – a phenomenon known as thermal runaway. At high temperatures when the heat flow exceeds the critical heat flux, a gas/vapour film is created around the overheated carbon catalyst. The high temperature also decomposes the oil into lighter hydrocarbons, including C₂ fragments which are needed for the nucleation and

growth of the carbon onions [12,37]. The nucleation and growth, as described by Vander Wal and Tomasek [12], take place in this gas/vapour film. The grown carbon onion particles then deposit on the surface of the carbon catalyst. Further deposition of pyrolytic carbon structures could take place, increasing the size of the deposited particles [38,39].

3.4.2. Macro-scale features

The carbon tree is suggested to grow through aggregation of the carbon onions and further deposition of pyrolytic carbon. Like the carbon catalyst, the deposited carbons are good microwave absorbers and, as can be seen in Fig. 9, their loss tangent is significantly higher than that of the THAI oil, particularly at high temperatures. This allows the deposited carbons to be selectively heated to high temperature and to maintain a gas/vapour film around them where the pyrolysis, nucleation, growth and aggregation of carbon onions can continue to take place as illustrated by Fig. 10.

The growth of the carbon tree can extend to the gas/vapour phase above the liquid level. In this case, the C_2 fragments needed for the nucleation and growth could come from the products of pyrolysis in the liquid or from the pyrolysis in the vapour phase.

The electric field distribution may play a role in determining the shape and growth direction of the carbon tree branches. Fig. 11 shows examples of the electric field distribution around a 2 mm i.d. rod with dielectric properties equivalent to those of the carbon tree at an intermediate temperature, 500 °C, simulated using COMSOL Multiphysics® v5.3. The details of the simulation parameters can be found in the supplementary information document. Fig. 11 (a) shows that when the rod axis is parallel to the direction of the electric field, hot spots with high electric field intensity appear at the longitudinal ends of the rod. These hot-spots would create a good environment for the formation of carbon onions. Such configuration favours the longitudinal growth and, thus, explains the vertical growth of the stem part of the carbon tree. However, a different configuration is observed when the rod axis is perpendicular to the direction of the electric field as can be seen in Fig. 11 (b). In this case, the electric field intensity around the rod circumference in the radial direction is, in general, higher than it is at the longitudinal ends. Hot-spots may appear in the corners as displayed in Fig. 11 (b). This configuration may be responsible for the

branched growth in the root part of the carbon tree.

3.5. Opportunities and potential industrial applications

Carbon onions have been considered as attractive candidates for many applications due to their unique electrical and dielectric properties together with their high surface area. The surface area of the carbon onions obtained in the present study is smaller than that of carbon onions produced through thermal annealing of nanodiamonds in previous studies. However, the surface area could be increased if the processing parameters can be adjusted to control the size of the particles formed.

It has been shown that carbon onions could be prepared rapidly and at low bulk temperatures form a cheap liquid precursor, exploiting the selective and volumetric nature of microwave heating. Carbon onions in the present study were prepared within a timescale of only 60 s. In contrast, thermal annealing of nanodiamonds is usually achieved in a timescale in the order of hours [5,13]. The selective heating nature of microwaves allowed the process to be carried out in low bulk temperatures as microwave heating is directly targeted at the carbon catalyst and, later, the deposited carbon with no need to excessively preheat their surroundings. The bulk temperature measured at the end of the microwave processing in the current study was only ~150 °C (Fig. 2). Processing under such mild conditions could bring technical and economic advantages when considering scaling-up. This microwave synthesis technique allows, in principle, for higher carbon conversion compared to other pyrolysis-based techniques such as flame pyrolysis in which a significant fraction of the carbon precursor is burnt to generate the heat required to keep the temperature at the pyrolysis/decomposition temperature. The yield achieved in this study was limited by the size of the reactor and the maximum pressure it can handle. However, with an improved reactor design higher yields are possible.

One of the potential industrial applications for the fractal growth of the microwave-absorbing carbon tree within a heavy oil medium is in the microwave-assisted thermal recovery and upgrading of heavy oil. The benefits of using microwave heating for downhole applications is that the electromagnetic field can penetrate the rock matrix, allowing heating to take place a significant distance away from the electromagnetic source. The fractal growth of carbon trees would act as an in-situ production of a microwave susceptor within the oil reservoir which can improve the efficiency of the electromagnetic-to-thermal energy conversion.

4. Conclusions

This study showed that microwave heating of heavy oil mixed with carbon catalyst leads to the fractal growth of several-centimetre long carbon trees, with branched roots and one or more stems emerging from the oil. A relationship was observed between the quantity of the solid formed and the maximum pressure reached during heating. The increase in the internal pressure during microwave heating was attributed to the pyrolysis and gasification of the oil around the formed carbon. The morphology and nanostructure of the solid carbon formed were characterised with SEM and HRTEM. The SEM images showed that the structure is largely made of networks of small particles with diameters of the order of tens to hundreds of nanometres. The HRTEM images revealed the presence of disordered graphitic structures including carbon onions with diameters as small as 30 nm as well as curved concentric graphitic structures with a radius of curvature larger than 100 nm. This was confirmed by the Raman spectra which showed two predominant peaks at ~1596 cm^{-1} and ~1345 cm^{-1} , a typical spectrum for carbon onions

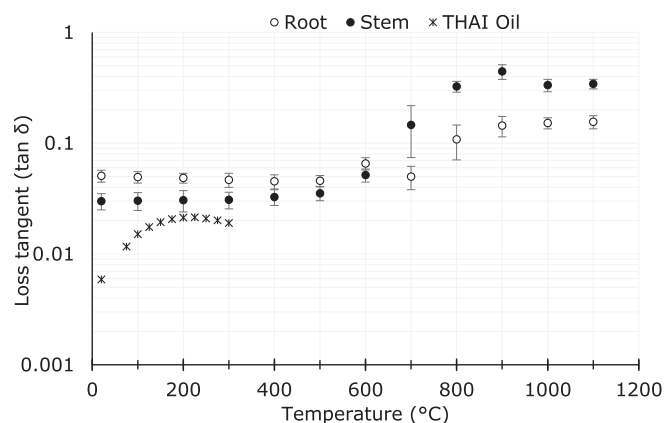


Fig. 9. Dielectric loss tangent of solid carbon taken from different parts of the carbon tree as a function of temperature at 2.47 GHz. The density was corrected using Landau-Lifshitz-Looyenga's formula using carbon onions' density of 1.9 g/cm³. The graph also includes the dielectric properties of the THAI oil which was replotted from a previous work [25]. The dielectric constant and loss factor can be found in Figure S8 in the Supplementary information document.

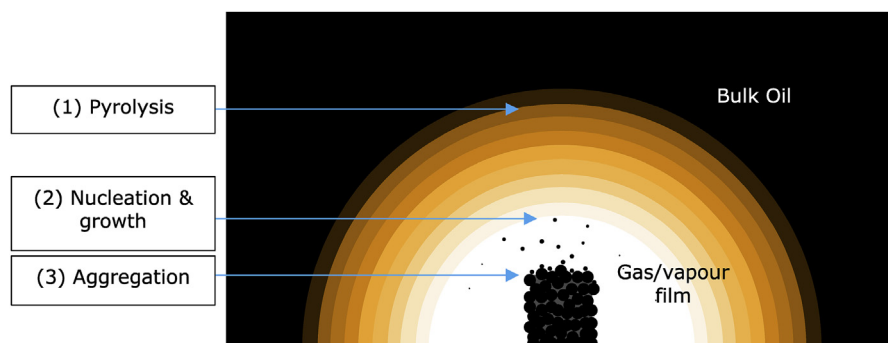


Fig. 10. The suggested mechanism for the formation and growth of the carbon onion tree under microwave heating. (A colour version of this figure can be viewed online.)

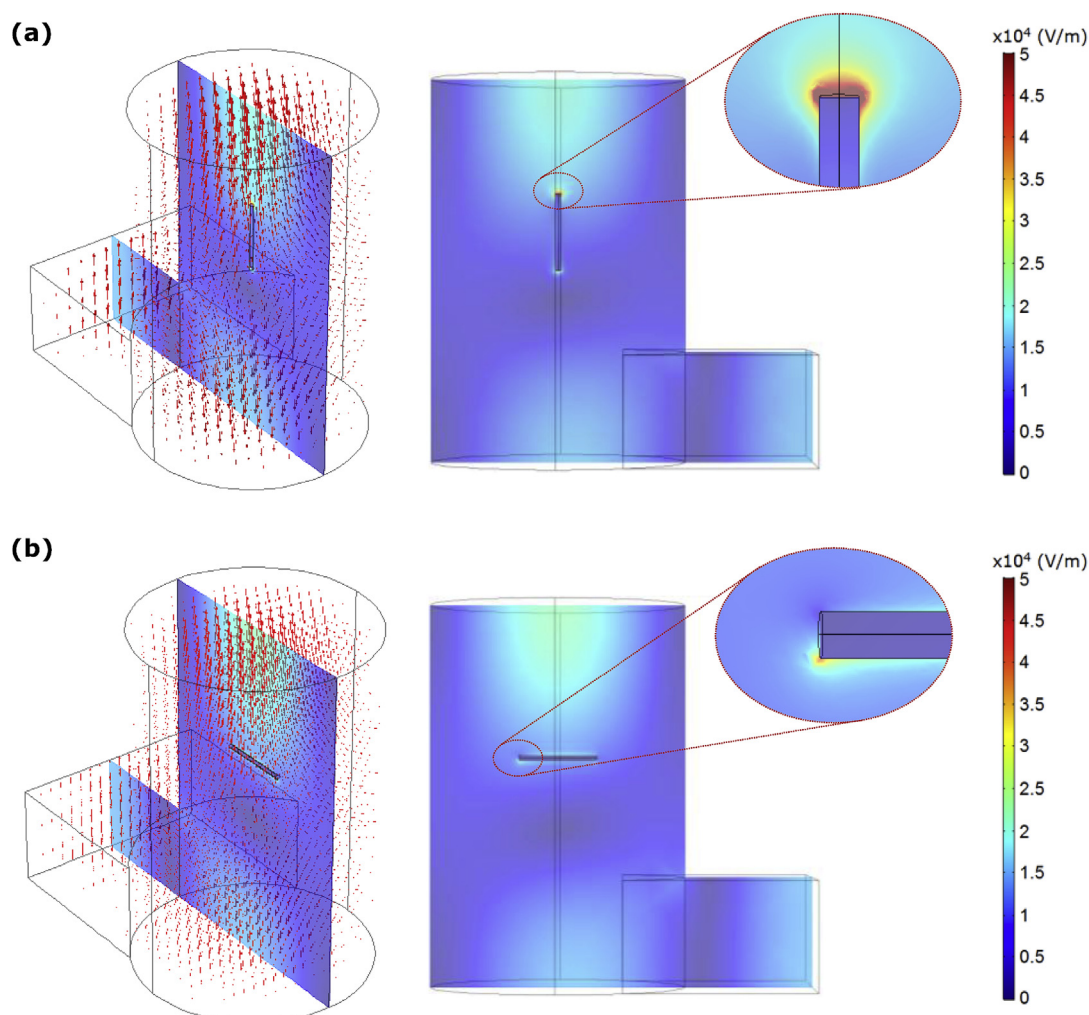


Fig. 11. Simulated electric field intensity around a 2 mm rod with dielectric properties equivalent to carbon onion at 500 °C at different rod orientations: (a) parallel; (b) perpendicular to the direction of the electric field. The red arrows refer to the direction of the electric field. (A colour version of this figure can be viewed online.)

with disordered graphitic structures.

CO₂ gas sorption results gave a surface area of 81 m²/g and 164 m²/g for the stem and root parts of the carbon tree respectively. This variation was attributed to the smaller particle sizes seen in the root compared to those in the stem. The surface area could be further increased if the processing parameters can be adjusted to control the size of the particles formed.

It is proposed that the carbon onions were formed through

pyrolysis of the heavy oil into lighter hydrocarbons, including C₂ fragments, followed by nucleation and surface growth of the concentric graphitic layers. The carbon tree is thought to grow through the aggregation of carbon onions and further deposition of pyrolytic carbon, with the electric field configuration supporting the longitudinal growth of the branches when the branch axis is parallel to the direction of the electric field.

This study demonstrates that carbon onions can be prepared

rapidly from a cheap unrefined precursor such as heavy oil, exploiting the selective and volumetric features of microwave heating. Future studies to investigate methods to improve the yield and quality of the produced carbon onions. The effect of the different processing parameters such as the applied power and heating time on the size and quality of the produced carbon onions to be studied. This would allow for optimising the process to produce onions with the required size and properties. Future work is to study, also, the effect of the chemical and physical properties of the oil precursor on the nanostructure of the produced carbon onions. More work is needed for a deeper understanding of the effect of the electric field distribution inside the microwave heating cavity on the micro- and macro-structure of the carbon tree as well as its direction of growth.

Acknowledgements

This work was supported by the Engineering and Physical Sciences Research Council [grant number EP/N032985/1]. The authors would like to thank Petrobank Energy and Resources, Ltd. (now Touchstone Exploration Inc.), Canada for supplying the oils used in this study. We would like also to thank Graham Rance, Michael Fay, Nicola Weston, Elisabeth Steer, and Christine Granger-Boulby from the Nanoscale and Microscale Research Centre (nmRC) for their assistance with imaging and Raman Spectroscopy. The assistance of Will Meredith from the Cleaner Fossil Energy and Carbon Capture Technologies Research Group with the elemental analysis is also appreciated.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.carbon.2018.07.066>.

References

- [1] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, C₆₀: buckminsterfullerene, *Nature* 318 (1985) 162, 11/14/online.
- [2] S. Iijima, Helical microtubules of graphitic carbon, *Nature* 354 (1991) 56, 11/07/online.
- [3] S. Iijima, Direct observation of the tetrahedral bonding in graphitized carbon black by high resolution electron microscopy, *J. Cryst. Growth* 50 (1980) 675–683, 11/01/1980.
- [4] D. Ugarte, Curling and closure of graphitic networks under electron-beam irradiation, *Nature* 359 (1992) 707, 10/22/online.
- [5] M. Zeiger, N. Jackel, V.N. Mochalin, V. Presser, Review: carbon onions for electrochemical energy storage, *J. Mater. Chem.* 4 (2016) 3172–3196.
- [6] M. Zhang, N. Zhao, J. Sha, E. Liu, C. Shi, J. Li, et al., Synthesis of novel carbon nano-chains and their application as supercapacitors, *J. Mater. Chem.* 2 (2014) 16268–16275.
- [7] P.P. Kuzhir, A.G. Paddubskaya, S.A. Maksimenko, V.L. Kuznetsov, S. Moseenkov, A.I. Romanenko, et al., Carbon onion composites for EMC applications, *IEEE Trans. Electromagn. C.* 54 (2012) 6–16.
- [8] Y. Lin, X. Pan, W. Qi, B. Zhang, D.S. Su, Nitrogen-doped onion-like carbon: a novel and efficient metal-free catalyst for epoxidation reaction, *J. Mater. Chem.* 2 (2014) 12475–12483.
- [9] A. Hirata, M. Igarashi, T. Kaito, Study on solid lubricant properties of carbon onions produced by heat treatment of diamond clusters or particles, *Tribol. Int.* 37 (2004) 899–905, 11/01/2004.
- [10] S. Suarez, L. Reinert, M. Zeiger, P. Miska, S. Grandthyll, F. Müller, et al., In-situ nanodiamond to carbon onion transformation in metal matrix composites, *Carbon* 129 (2018) 631–636, 04/01/2018.
- [11] Y. Saito, Nanoparticles and filled nanocapsules, *Carbon* 33 (1995) 979–988, 01/01/1995.
- [12] R.L. Vander Wal, A.J. Tomasek, Soot nanostructure: dependence upon synthesis conditions, *Combust. Flame* 136 (2004) 129–140, 01/01/2004.
- [13] M. Zeiger, N. Jackel, M. Aslan, D. Weingarth, V. Presser, Understanding structure and porosity of nanodiamond-derived carbon onions, *Carbon* 84 (2015) 584–598, 04/01/2015.
- [14] Y. Kang, X. Yu, M. Kota, H.S. Park, Carbon nanotubes branched on three-dimensional, nitrogen-incorporated reduced graphene oxide/iron oxide hybrid architectures for lithium ion battery anode, *J. Alloy. Comp.* 726 (2017) 88–94, 12/05/2017.
- [15] J.-z. Zou, X.-r. Zeng, X.-b. Xiong, H.-l. Tang, L. Li, Q. Liu, et al., Preparation of vapor grown carbon fibers by microwave pyrolysis chemical vapor deposition, *Carbon* 45 (2007) 828–832, 04/01/2007.
- [16] D. Fu, X. Zeng, F. Deng, H. Sheng, J. Zou, Growth of oriented vapor grown carbon fibers on pyrolytic carbon films without catalyst, *J. Mater. Sci.* 45 (2009) 570, November 25.
- [17] A.M. Schwenke, S. Hoepfner, U.S. Schubert, Microwave synthesis of carbon nanofibers - the influence of MW irradiation power, time, and the amount of catalyst, *J. Mater. Chem.* 3 (2015) 23778–23787.
- [18] B. Fidalgo, Y. Fernández, L. Zubizarreta, A. Arenillas, A. Domínguez, J.J. Pis, et al., Growth of nanofilaments on carbon-based materials from microwave-assisted decomposition of CH₄, *Appl. Surf. Sci.* 254 (2008) 3553–3557, 03/30/2008.
- [19] F. Nakul, A.H. Aimon, B.W. Nuryadin, F. Iskandar, Preliminary study of heat supply during carbon nanodots synthesis by microwave-assisted method, *J. Phys. Conf.* 739 (2016) 012045.
- [20] V. Asokan, V. Venkatachalapathy, K. Rajavel, D.N. Madsen, Microwave irradiation on carbon black: studies on the transformation of particles into nanoballs, nano-sticks and nano-onion like structures, *J. Phys. Chem. Solid.* 99 (2016) 173–181, 12/01/2016.
- [21] R. Bajpai, L. Rapoport, K. Amsalem, H.D. Wagner, Rapid growth of onion-like carbon nanospheres in a microwave oven, *CrystEngComm* 18 (2016) 230–239.
- [22] Alberta Government, Economic dashboard, Oil Prices (2018), 09 April, <http://economicdashboard.alberta.ca/OilPrice>.
- [23] A. Hart, M. Greaves, J. Wood, A comparative study of fixed-bed and dispersed catalytic upgrading of heavy crude oil using-CAPRI, *Chem. Eng. J.* 282 (2015) 213–223, 12/15/2015.
- [24] H. Kuo Chu, Recent progress in the preparation and application of carbon nanocapsules, *J. Phys. Appl. Phys.* 43 (2010), 374001.
- [25] Y. Zhang, M. Adam, A. Hart, J. Wood, S.P. Rigby, J.P. Robinson, Impact of oil composition on microwave heating behavior of heavy oils, *Energy Fuel.* 32 (2018) 1592–1599, 02/15 2018.
- [26] D.M.P. Mingos, Microwave syntheses of inorganic materials, *Adv. Mater.* 5 (1993) 857–859.
- [27] S.O. Nelson, Density-permittivity relationships for powdered and granular materials, Instrumentation and Measurement, *IEEE Transactions on* 54 (2005) 2033–2040.
- [28] Q. Zou, Y.G. Li, B. Lv, M.Z. Wang, L.H. Zou, Y.C. Zhao, Transformation of onion-like carbon from nanodiamond by annealing, *Inorg. Mater.* 46 (2010) 127–131, February 01.
- [29] O.V. Kharisova, B.I. Kharisov, Variations of interlayer spacing in carbon nanotubes, *RSC Adv.* 4 (2014) 30807–30815.
- [30] M. Endo, K. Takeuchi, T. Hiraoka, T. Furuta, T. Kasai, X. Sun, et al., Stacking nature of graphene layers in carbon nanotubes and nanofibers, *J. Phys. Chem. Solid.* 58 (1997) 1707–1712, 11/01/1997.
- [31] M. Choucair, J.A. Stride, The gram-scale synthesis of carbon onions, *Carbon* 50 (2012) 1109–1115, 03/01/2012.
- [32] F. Tuinstra, J.L. Koenig, Raman spectrum of graphite, *J. Chem. Phys.* 53 (1970) 1126–1130.
- [33] C.U. Pittman, W. Jiang, Z.R. Yue, C.A. Leon y Leon, Surface area and pore size distribution of microporous carbon fibers prepared by electrochemical oxidation, *Carbon* 37 (1999) 85–96, 01/01/1999.
- [34] M. Thommes, K.A. Cychoz, A.V. Neimark, Chapter 4-advanced physical adsorption characterization of nanoporous carbons a2-tascón, in: M.D. Juan (Ed.), *Novel Carbon Adsorbents*, Elsevier, Oxford, 2012, pp. 107–145.
- [35] T.A. Centeno, F. Stoeckli, The assessment of surface areas in porous carbons by two model-independent techniques, the DR equation and DFT, *Carbon* 48 (2010) 2478–2486, 08/01/2010.
- [36] N. Sano, H. Wang, I. Alexandrou, M. Chhowalla, K.B.K. Teo, G.A.J. Amaratunga, et al., Properties of carbon onions produced by an arc discharge in water, *J. Appl. Phys.* 92 (2002) 2783–2788.
- [37] M. Frenklach, On surface growth mechanism of soot particles, *Symposium (International) on Combustion* 26 (1996) 2285–2293, 01/01/1996.
- [38] Z. Fan, R. Tan, K. He, M. Zhang, W. Peng, Q. Huang, Low temperature growth of catalyst-free carbon micro-trees, *J. Mater. Sci.* 50 (2015) 13–20, January 01.
- [39] P.M. Ajayan, J.M. Nugent, R.W. Siegel, B. Wei, P. Kohler-Redlich, Growth of carbon micro-trees, *Nature* 404 (2000) 243, 03/16/online.