ESTUDIO DE LAS CONDICIONES DE REACCIÓN EN LA SÍNTESIS DE NANOTUBOS DE CARBONO DE UNA PARED (SWNT), POR DESPROPORCIONAMIENTO CATALITICO DE *CO*, A PARTIR DE $CoMo/SiO_2$

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Trabajo de Grado presentado como requisito para optar al título de Ingeniero Químico

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A Dios por darme fuerza, disciplina, salud y bienestar

A mis padres Hernando y Enith por su amor y apoyo

A mis hermanos Adriana y José Alejandro

A mis abuelos Hernando, Cecilia y Luisa

A mi familia, mi novia Andrea y a mis seres queridos

Hernando Delgado Gamboa

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Agradezco sinceramente a mi papá Hernando, mi mamá Enith, mis hermanos Adriana y José Alejandro por el amor y apoyo desde siempre, a mi familia, a mi novia Andrea por su amor, comprensión y a todos mis seres queridos.

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A la Universidad de Oklahoma y a quienes fueron mis profesores, especialmente al Dr. Daniel Resasco por permitirme ser parte de su grupo de investigación, a Giulio Lolli por guiarme a través de la investigación. A la Oficina Internacional de OU y todo su equipo por hacer más fácil mi estadía en Norman de principio a fin.

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A todos… muchísimas gracias!

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RESUMEN

TÍTULO:
ESTUDIO DE LAS CONDICIONES DE REACCIÓN EN LA SÍNTESIS DE NANOTUBOS DE CARBONO DE UNA PARED (SWNT), POR DESPROPORCIONAMIENTO CATALÍTICO DE *CO*, EN CATALIZADOR DE *CoMo/SiO₂* [*]

AUTOR:
Hernando Delgado Gamboa [**]

PALABRAS CLAVE:
Nanotubos de Carbono de Una Pared (SWNT), CoMoCAT, nanotecnología, Raman, catálisis

DESCRIPCIÓN:
Los Nanotubos de Carbono de Una Pared (SWNT) son nuevos y prometedores materiales con nanoestructura los cuales han sido de interés en diferentes áreas en nanotecnología debido a su uso como "bloques estructurales". Sus propiedades mecánicas y electrónicas los hacen únicos y abren un amplio rango de aplicaciones.

El propósito de esta investigación fue mejorar la calidad de los SWNT producidos por el método de CoMoCAT a partir del desproporcionamiento del CO utilizando catalizador de CoMo y SiO_2 como soporte, estudiando el efecto de las condiciones de operación mas importantes del proceso tales como la temperatura de reducción del catalizador, y la temperatura y presión de reacción. La técnica usada para la caracterización de los SWNT es espectroscopia Raman.

La síntesis se lleva a cabo en un reactor de lecho fluidizado. Primero, el catalizador se reduce con H_2 en un rango de temperatura de 400-650°C a 1 atm, después se calienta con He a 10°C/min hasta una temperatura entre 650-850°C y una presión de entre 1-3 atm, cambiando luego el flujo a CO para comenzar el crecimiento de SWNT. Cuando la muestra esta ya enfriada y almacenada, la caracterización con espectroscopia Raman se lleva a cabo y las mediciones de calidad son obtenidas de los espectros de Raman. A continuación los resultados son analizados. La calidad de los SWNT así como la selectividad del catalizador hacia los SWNT se ve mejorada a las condiciones encontradas; temperatura de reducción 500°C, 750°C y 40 psi de CO para la temperatura y presión de crecimiento. La sinterización del catalizador se evita al trabajar a la temperatura y presión mencionadas.

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[*] Trabajo de Grado
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ABSTRACT

TITLE:
STUDY OF THE REACTION CONDITIONS IN THE SYNTHESIS OF SINGLE-WALLED CARBON NANOTUBES (SWNT), BY CATALYTIC DISPROPORTIONATION OF *CO*, ON *CoMo/SiO$_2$* CATALYST. [*]

AUTHOR:
Hernando Delgado Gamboa[**]

KEYWORDS:
Single-Walled Carbon Nanotubes, CoMoCAT, nanotechnology, Raman, catalysis.

DESCRIPTION:
Single-Walled Carbon Nanotubes (SWNT) are promising new materials with nanostructure that have been of interest in different research areas in nanotechnology due to their usage as building blocks. Their mechanical and electrical properties make them unique and open a broad range of applications.

The purpose of this research was to enhance the quality of SWNT produced by the CoMoCAT method from CO disproportionation with CoMo catalyst supported on SiO_2, by means of studying the effect of the most important operating conditions of the process such as catalyst's reduction temperature, and reaction's temperature and pressure. Raman spectroscopy is the technique used for the characterization of SWNT.

The synthesis is conducted in a fluidized bed reactor. First, the catalyst is reduced *in situ* with H_2 at a temperature range of 400-650°C at 1 atm, then heated up with He at 10°C/min up to a temperature ranging 650-850°C and pressure from 1-3 atm, then switching to CO flow to start SWNT growth. When the sample is cooled down and stored, Raman spectroscopy characterization takes place and measurements of quality are obtained from the Raman spectrums. Afterward, these results are analyzed.

SWNT quality as well as the catalyst selectivity toward SWNT is enhanced at the conditions found; 500°C for the reduction temperature, 750°C for growth temperature and 40 psi of CO for pressure of growth. Sintering of the catalyst is avoided by working at the temperature and pressure mentioned.

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[*] Work of Degree

[**] The University of Oklahoma, Chemical Engineering Department, PhD. Daniel E. Resasco.

CHAPTER 1. Introduction

The present thesis is the result of an academic semester of work at The University of Oklahoma, Norman Campus, Department of Chemical, Biological and Materials Engineering in the research group specialized in the synthesis, characterization, functionalization, and utilization of Single-Walled Carbon Nanotubes (SWNT) whose director and leader is PhD. Daniel E. Resasco, who supervised and tutored the present work in the company of PhD. Giulio Lolli.

Single-Walled Carbon Nanotubes are a relatively new kind of material that attracts great research interest due to their unique properties that their nanostructure implies which make them have a broad variety of usages in many different fields of science, technology, engineering, medicine, computing, etc. Such usages benefit mankind development in diverse ways that are being object of research in different groups around the world at universities and companies that have envisioned the actual and potential contribution of carbon nanotubes, specially the SWNTs.

Single-Walled Carbon Nanotubes can play an important role in medicine, as nanostructures or nanoshells smaller than cells that could carry substances as proteins or medication and release them at the exact part of the body needing this substance. Nanotubes have to be functionalized in order to be biocompatible with the living body.

According to this, products containing Single-Walled Carbon Nanotubes should be developed but an issue that hinders the use of this material and its mass production and commercialization that has been the motivation of not only the present research but a matter of study lately in this research group, is the high costs for its production. These high costs are related to the conditions under which this material is synthesized.

At the present time, many synthesis techniques for carbon nanotubes have been discovered and studied, and are under constant development aiming more economic procedures and scale up. Basically, there are three main techniques: arc discharge, laser ablation and chemical vapour deposition (CVD)[1]. These techniques produce material of different characteristics, not always producing carbon nanotubes. Undesired forms of carbon are produced besides carbon nanotubes as well as different kinds of nanotubes such as Multi-Walled Carbon Nanotubes and Single-Walled Carbon Nanotubes.

Between the three mentioned techniques, CVD is the only one that produces more nanotubes than other forms of carbon compared to the other two synthesis techniques, although with low quality[2]. Additionally, this technique is the easiest to scale up which makes it more attractive for economical production and commercialization.

CVD comprises different procedures for nanotubes production such as Plasma enhanced CVD, Aerogel-supported CVD, and CoMoCAT process[3-5] among others. However, the one used in this work is the CoMoCAT process as it has been matter of study at the University of Oklahoma ever since its discovery by PhD. Daniel Resasco and its group[6]. In this work a low Co:Mo ratio was used and the catalyst was supported on silica gel (SiO_2) with CO flow as the source of carbon.

Finally, the purpose of this research was to upgrade the product quality of the CoMoCAT process by finding the best operating conditions at which Single-Walled Carbon Nanotubes are synthesized. Simultaneously, improvement of catalyst selectivity toward the production of SWNT was acquired. The characterization of the product was measured with Raman resonance spectroscopy whose spectrums reveal the nanotubes' presence, quality and properties.

CHAPTER 2. Conceptual

2.7 Carbon Nanotubes

Carbon Nanotubes are recently discovered allotropes of carbon as well as diamond and graphite. They were discovered in 1991 by Sumio Iijima and coworkers[7], and after that, carbon nanotubes have been a matter of study of many researchers in the world.

These allotropes of carbon are basically cylindrical macro-molecules constituted only by carbon with unique properties. They are members of the fullerene family because their structure is similar to that of the fullerenes, which include different shapes, like spherical (buckyballs), cones, tubes etc. Their size is in the order of nanometers in diameter and could be many microns in length resulting in very high aspect ratios (length/diameter) of around 10^4 and thus they're considered to be nearly one-dimensional structures. Carbon nanotubes can be divided into two main sections: the sidewalls and the end caps. The end caps are spherical sections of fullerenes, while the sidewalls resemble a graphite sheet rolled into a cylinder.

The chemical structure of ideal (i.e. no defects present) carbon nanotubes consists only of sp^2 orbital hybridization on carbon-carbon bonds, as present on graphite bonds. Whereas, the type of C-C bonding on the defects formed eventually on carbon nanotubes correspond to sp^3 orbital hybridization, similar to the diamond bonds. [8]

These defects are present in the carbon nanotubes structure whenever there are pentagons or heptagons instead of hexagons in the sidewall of the tubes; this is generated by rearrangement of the bonds and causes different types of deformations in the geometry of the tubes, such as enlargement or reduction of diameter, change in the direction of the tube axis, bends, etc.

New structures can be created by inducing defects such as junctions, Y-branches or T-branches that will have new properties. Examples of defects are shown in figure.2.1

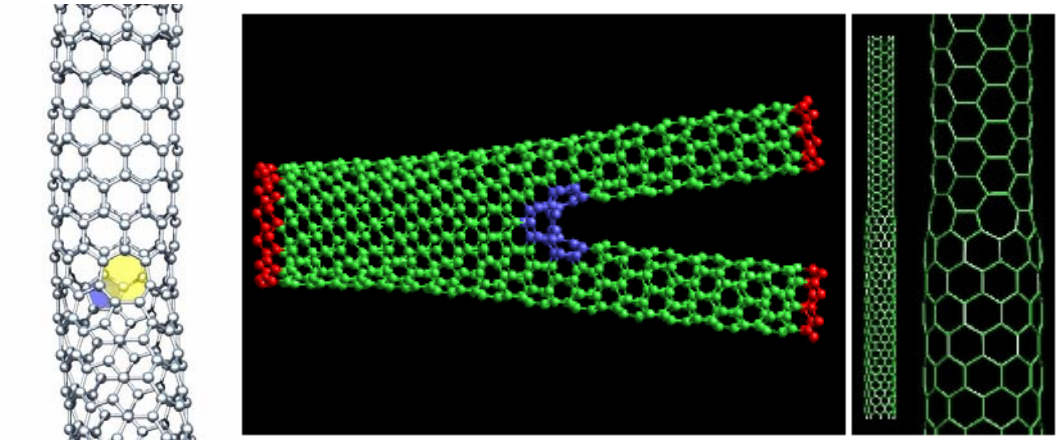


Figure 2.3. Examples of defects in SWNTs. Left; presence of a heptagon and a pentagon. Center; a Y-branch caused by defects. Right; a change in diameter, there are pentagons and heptagons present in all the defects. [9, 10]

2.8 Single-Walled Carbon Nanotubes (SWNT)

There are basically two types of carbon nanotubes:

1 Single-Walled Carbon Nanotubes (SWNT)

2 Multi-Walled Carbon Nanotubes (MWNT)

The SWNT structure can be conceptualized as a graphite sheet (graphene) of one atom of thickness, rolled up into a perfect cylinder with very small diameter, about 1 nm, and several microns in length. SWNT can be conducting or semiconducting depending on the way graphene is rolled up, i.e., properties change accordingly with the chirality of the tube. The chirality of a SWNT is defined by a pair of indices (n,m) that specify the chiral vector, C_h ($C_h = \boldsymbol{n}a_1 + \boldsymbol{m}a_2$); n and m are integers that stand for the number of unit vectors a_1, a_2 in the honeycomb crystal lattice of graphene. The length of the chiral vector equals the circumference of the SWNT and the axis of the nanotube is perpendicular to the chiral vector.

In Figure 2.2., the SWNT cylinder is formed when the AB' border is attached to parallel OB.[11]

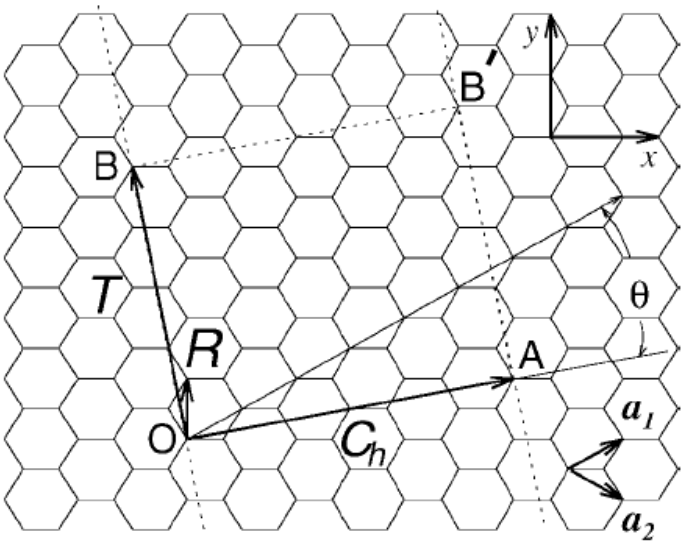


Figure 2.4. Graphene's honeycomb crystal lattice. *OA* is the chiral vector, θ is the chiral angle.

When $m = 0$ or $\theta = 0°$, the nanotubes are called "zigzag" ($n,0$). If $n = m$ or $\theta = 30°$, the nanotubes are called "armchair" (n,n). Or else, they are called "chiral" when $0° < \theta < 30°$.

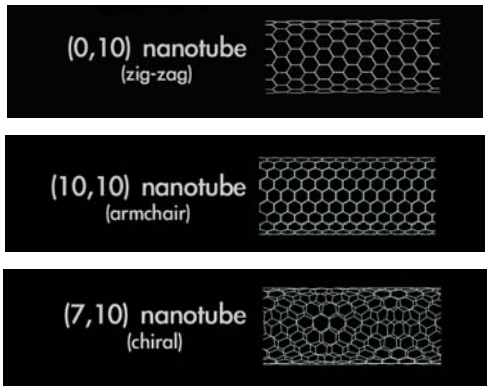


Figure 2.3. Basic types of SWNT.[12]

The (n,m) map in figure 2.4., helps to illustrate the types of SWNT that can be produced. It shows the *zigzag* family and the *armchair* family plus many possible chiral tubes.

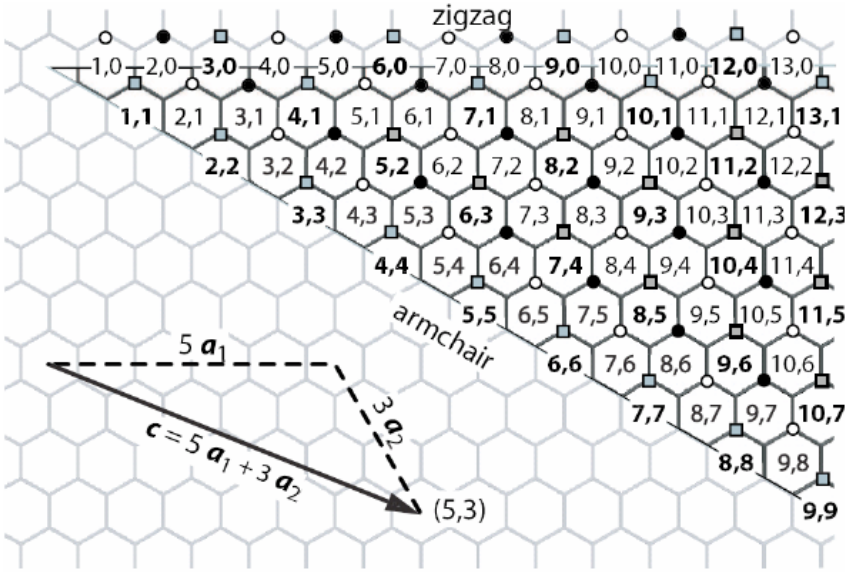


Figure 2.4. ***(n,m)*** **map.** [13]

2.9 Multi-Walled Carbon Nanotubes (MWNT)

This kind of nanotube is a variant of the SWNTs. They can be present in the synthesis product of SWNTs as an undesired formation of carbon. MWNTs do not have as much value as SWNTs since they don't share the same exceptional properties of the single-walled. However, in the family of MWNT exist Double-Walled Carbon Nanotubes (DWNT) which have similar morphology and properties compared to SWNT and their chemical resistance is superior.

MWNT's structure can be conceptualized by thinking of multiple graphite layers wrapped up on themselves in the shape of a cylinder. There are two models that represent the configuration of MWNT; the Russian Doll model and the Parchment model. The Russian Doll consists of various SWNTs concentrically rolled. In the Parchment model a MWNT is a graphite sheet rolled up into itself, similar to a newspaper rolled [8]. The MWNT differ a lot from SWNT in their length and diameter. MWNT are of greater diameter.

2.10 Carbon Nanotubes Properties

The one-dimensional structure of SWNT provides them with unique chemical, electrical, thermal among other properties.

2.10.1 Chemical Reactivity

The carbon nanotubes chemical reactivity is due to the *pi* orbital mismatch given by the tube curvature. Thus, the smaller diameter a carbon nanotube has, the more reactive it is. [14]

2.10.2 Electrical Conductivity

Depending on its chirality (*n*,*m*) a carbon nanotube can be conducting (metallic) or semiconducting. If the difference between its indices is multiple of 3 ($n - m = 3i$; i= integer), and additionally when n=m, then the nanotube is metallic, in the opposite case the nanotube is semiconducting. Accordingly, all armchair tubes are metallic. The length of the tube does not affect its resistance to conduction. Compared to silver and copper, metallic carbon nanotubes the electrical current density is about 1000 times greater. [8, 14, 15]

2.10.3 Thermal Conductivity

Nanotubes are very good thermal conductors all along the tube, and good insulators crossways to the tube axis. Carbon nanotubes could conduct up to 6000 W/m.K while copper's thermal conductivity coefficient is 385 W/m.K. [8]

2.10.4 Optical Activity

Chiral carbon nanotubes loose their optical activity with increasing length.[14]

2.10.5 Mechanical Strength

The strength and rigidity of carbon nanotubes is remarkable, because of this material's tensile strength and elastic modulus (Young modulus) values. In the axial direction, the Young modulus has very large values. These properties are due to the

C-C covalent sp^2 bonds throughout the graphene lattice. On the other hand, carbon nanotube density is very low for a solid (1.3-1.4 g/cm^3), resulting in an excellent material with potential use in composite materials useful for construction of new structures.

Under compression carbon nanotubes tend to collapse forming buckles and changing from sp^2 to sp^3 at some locations. While under tensile strength they deform plastically. [8, 14]

2.10.6 Defects

The presence of defects in the nanotubes causes changes in their properties as well as defects in any material. On carbon nanotubes the presence of defects is manifested when there are pentagons and heptagons by rearrangement of the bonds. The electrical conductivity is affected in the defective zone as well as the thermal conductivity. The tensile strength diminishes in the affected area as happens in a chain. [8]

2.11 SWNT Synthesis

There are many different techniques for the synthesis of Single-Walled Carbon Nanotubes, which are under constant study in order to make them more economically feasible for commercial production. The known techniques are arc discharge, laser ablation, chemical vapour deposition (CVD), catalytic combustion and ion bombardment plus each one's variants. The most significant variation on each technique is the presence or absence of catalysts, which has a definite effect on the type of nanotube that is produced. More explicitly, SWNTs are the major products when catalyst is present, while MWNTs are the major products resulting when non-catalytic synthesis is practiced[2, 16].

2.11.1 Chemical Vapour Deposition (CVD)

A very promising technique for commercial production of SWNTs is Chemical Vapour Deposition (CVD) which leads higher yields over the other techniques. This method consists of two steps: catalyst preparation and nanotubes growth [17].

On the CVD, carbon is obtained usually from gaseous forms of carbon such as methane, carbon monoxide and acetylene. The carbon containing gas is put in the gas phase and is past through an energy source used to split the molecule and release carbon into an atomic and active state. Then carbon diffuses through the substrate containing the metal catalyst (usually a first row transition metal; Co, Ni or Fe) at a temperature range of 650-900°C [2, 17]. A variation of the CVD is the CoMoCAT process.

2.11.2 CoMoCAT Process

In this process, [3-5, 18, 19] SWNTs are produced by catalytic disproportionation of carbon monoxide ($CO \Leftrightarrow C + CO_2$). A formulation of Cobalt and Molybdenum composes the catalyst on a given support, (usually Silica Gel). The Co-Mo formulation prevents sintering of Co, so catalyst selectivity is increased and undesired forms of carbon are not synthesized. The function of Co is the activation of CO [20].

The catalyst is first calcined and then pretreated with H_2 at around 400 – 600 °C, then it reaches the operation temperature by flowing He past the reactor. After calcination Mo is well-dispersed forming small clusters of Mo^{+6}, while Co forms a cobalt-molybdate-like structure at low Co:Mo ratios, or forms a Co_3O_4 phase at high Co:Mo ratios. After the reduction step with H_2 the cobalt-molybdate-like remains as Co_2C well-dispersed ions and the non-interacting phase is reduced to metallic Co, which might lead to undesired formations of C. Thus, lower Co:Mo ratios increase the catalyst selectivity toward SWNT [18, 21].

The reaction temperatures are between 700 – 950°C at pressure around the atmospheric. Throughout the reaction step, Co is gradually reduced by gaseous CO from its oxidized state to the metallic form creating small metal clusters where SWNTs are to be grown. Molybdenum passes to the carbidic form and stabilizes, as well as it disperses Cobalt as Co^{+2} preventing its reduction and also Mo helps as a moderator of the rearrangement of C by acting as a carbon sink. The CoMoCAT process will be explained further on the experimental chapter [18, 21].

2.12 Characterization of SWNT by Raman Resonance Spectroscopy

The samples were to be characterized in order to attain the characteristics of SWNT that will eventually help for the quality examination and further analysis of the samples and the conditions under study. Furthermore, Raman spectroscopy is the technique that will reveal if the samples contain SWNT by straightforward recognition of their characteristic bands on the spectrums and their ratios, which are explained next.

Raman spectra of carbon nanotubes have different bands which represent specific features of the carbon nanotubes [22, 23]. The Radial Breathing Mode (RBM) is the most significant characteristic on the Raman spectrum of Single-Walled Carbon Nanotubes because it provides information of the diameter and chirality of the tubes on the sample. It is located between 100 and 250 cm^{-1} [23, 24]. For the purpose of this research this feature was not considered for the quality analysis, although it is present in all SWNT spectrums taken which confirms that the product contains SWNT.

The bands induced by sp^2 hybridization are the G and D* band, although not equally; graphitic-like formations have sp^2 hybridization, and all carbon links form hexagons resembling an aromatic-rings network. The High Energy Mode (HEM) or G-band represents the stretching mode of the C-C bonds on graphene, along the tube axis and the circumferential direction[25]; it is centered in between 1400 and 1700 cm^{-1}[23,

24]. In this way, the G-band is induced also by graphitic-like carbon as well as SWNTs. The G-band bears information about the electronic properties and is a measure of the sp^2 carbon. This band is characteristics of SWNT but also present on MWNT Raman spectrums.

The D*-band is a second-order overtone mode and it is not induced by defects, its location is between 2500 and 2600 cm^{-1}. This band's intensity is inherent of carbon nanotubes independently to the presence of defects. [26]

The D-band corresponds to defective or diamond-like carbon located in the 1330-1360 cm^{-1} range of the spectra[23, 24]; the defective bonds on SWNTs have sp^3 hybridization, which are present in the tubes caps, MWNTs, and places where there are pentagons or heptagons. On MWNT this band reaches high values, contrary to SWNT of high quality. The 1-D/G or 1-D/D* is a measurement of the amount of defects on the sample, but also indicates the presence of SWNT when these ratios reach high values. On figure 2.5., a SWNT Raman spectrum illustrates the bands.

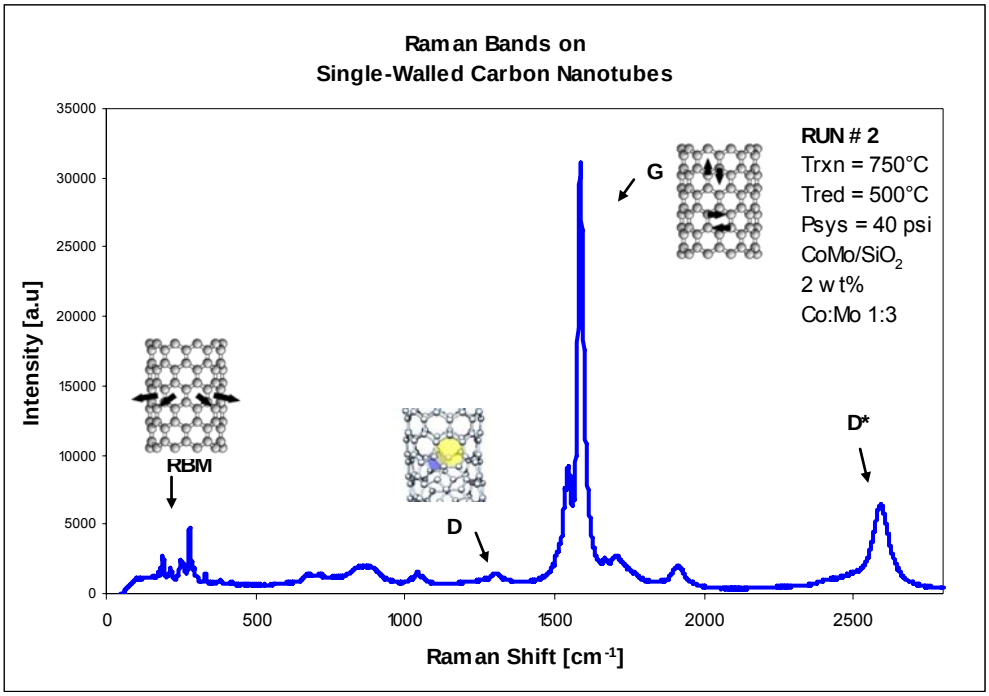


Figure 2.5. Raman bands on SWNT

On figure 2.6., typical Multi-Walled Carbon Nanotubes Raman spectra are present. It's noticeable the absence of the RBM on these spectra, opposite to SWNT Raman spectra.

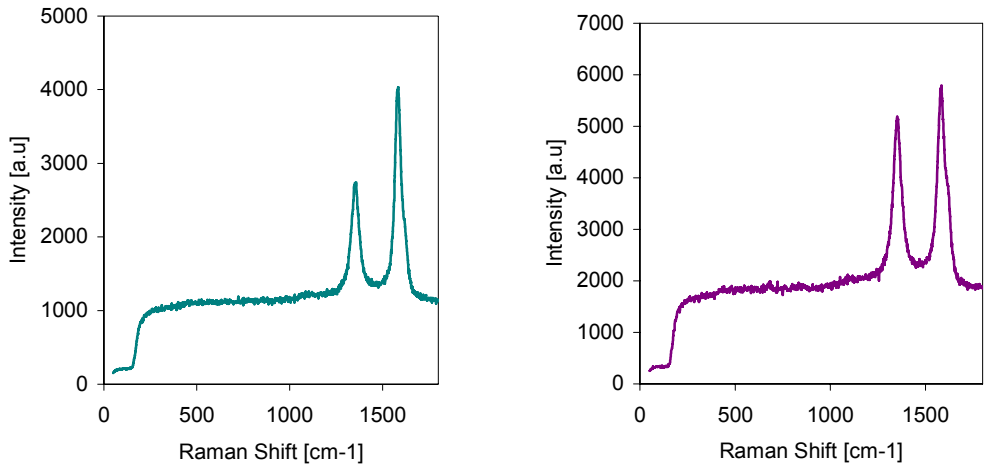


Figure 2.6. Raman spectra of MWNT [27]

In conclusion, as stated before, the objective of this research was to find the best operating conditions on the synthesis of SWNT by the CoMoCAT process in order to produce SWNT of best quality by means of the study of the variables and characterization of the samples proving the presence of SWNT on the products and giving measurements of their quality. Thus, a contribution to knowledge is made through the results of the present work.

CHAPTER 3. Experimental

The methodology of this work, in order to study the effect of reduction temperature, conditions of reaction such as temperature and pressure, on Single-Walled Carbon Nanotubes (SWNT) quality, was to proceed changing one of these three variables at a time while the other two remained constant, taking as a reference point the conditions of production of 500 ºC as temperature of reduction[5], 750 ºC and 14 psi as reaction temperature and pressure respectively. At the same time the catalyst formulation used throughout all the experiments was always the same and the flow rates of Helium (He), Carbon Monoxide (CO) and Hydrogen (H_2) were kept constant as well, at 500 sccm (standard cubic centimeters per minute) for He and H_2 and 1000 sccm for CO for all the runs using a Porter Instrument Company Inc., four-channel mass flow controller [19].

A routine had to be followed from loading the reactor with catalyst to cooling off, sample storage and characterization. The only things that are going to change are the conditions mentioned before and thus the procedures needed to reach these conditions, like the temperature controller setup and the flow rates of the gas streams. Each time a run is performed, a summary of the procedure has to be registered on the reactor log to facilitate the control of the research and for further consultation.

3.4 Catalyst Preparation

In order to produce Single-Walled Carbon Nanotubes employing the CoMoCAT process[3, 4] by means of catalytic decomposition of CO as the source of Carbon, Cobalt-Molybdenum catalyst supported on dry synthetic and precipitated silica (SiO_2) was used [5].

There could be many different formulations of the CoMo catalyst, depending on the ratio between these two transition metals (Co:Mo) and the amount of total metals

(CoMo) per unit mass of catalyst support used (SiO_2). Among all the possible families of CoMo catalysts, it was advised to use for this research an already proven high selectivity CoMo/SiO_2 formulation towards the production of SWNT [5]. The formulation used contained a total metals loading of 2 wt% supported on SiO_2 and a Co to Mo molar ratio of 1:3. This catalyst was used in all the runs and consequently the catalysts were prepared using the same corresponding amounts of Cobalt and Molybdenum precursors, water and silica.

Preparation of the catalyst at the stated formulation was done by incipient wetness coimpregnation of an aqueous solution of Cobalt and Molybdenum precursors, prepared with 335.7 mg of Cobalt Nitrate ($Co(NH_3)_2.6H_2O$) and 611.0 mg of Ammonium Heptamolybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$) plus 22 ml of water on 20 g of SiO_2 (Dry HiSil 210)[3, 5] drop by drop in a ceramic mortar making sure the silica pores were impregnated with this pink colored aqueous solution. This requires considerable time since the catalyst has to be well absorbed by the support.

Subsequently, the impregnated material suffered a thermal treatment by taking it to a convection oven to be dried at a temperature around 110 ºC for 12 hours overnight, then calcined at 500 ºC for 3 hours in static air and finally cooled under vacuum in a desiccator.[3]

3.2 Single-Walled Carbon Nanotubes Growth

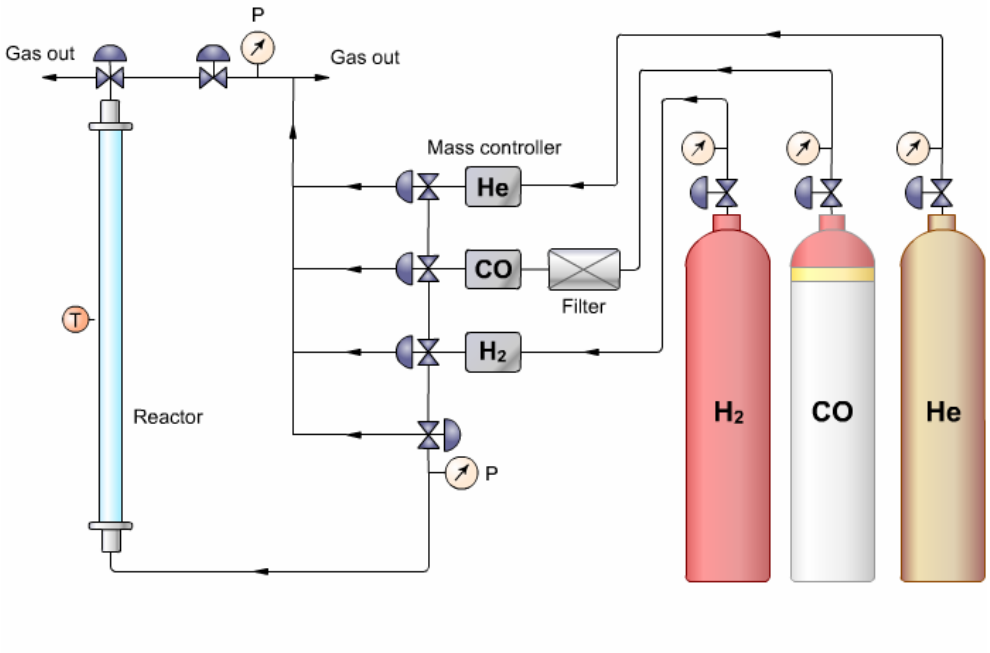
As mentioned before, in order to study the effect of reduction temperature and reaction conditions on SWNTs quality and find the values where better nanotubes are produced, a general procedure is to be followed. However for each condition there is a different procedure. Thus, for the temperature of reduction of the catalyst the experiments were done as follows: from 400 ºC through 650 ºC at a reaction temperature of 750 ºC and pressure of 14 psi. For the reaction temperature the conditions were 500 ºC and 14 psi for the reduction temperature and reaction pressure and temperatures where varied in between 650-850 ºC. Finally for the growth

pressure the values were between 14-80 psi, and 500 ºC and 750 ºC as reduction and reaction temperatures.

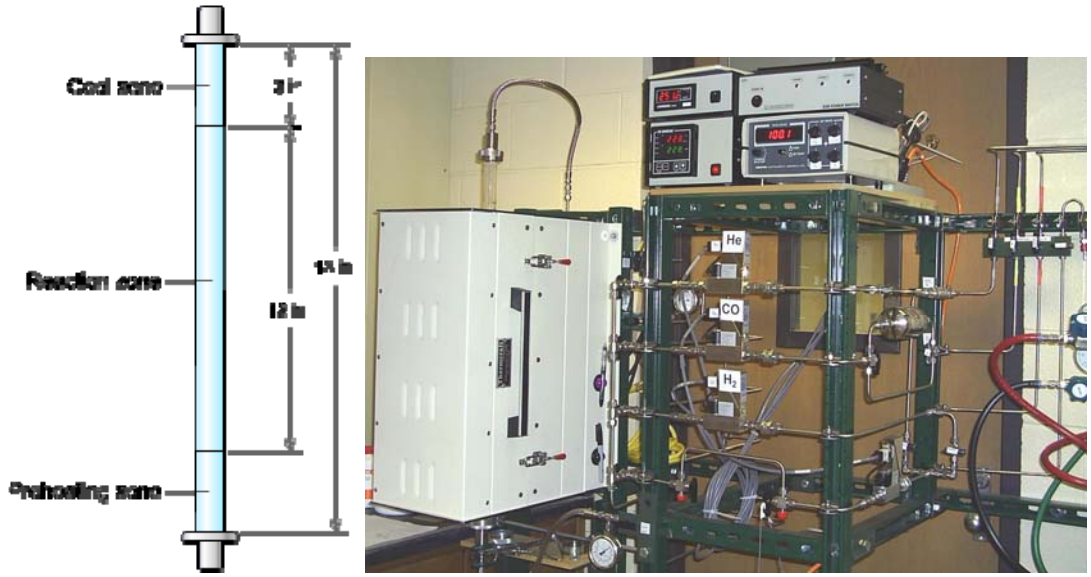
3.2.1 Reactor Setup

The synthesis of the Single-Walled Carbon Nanotubes was conducted in a vertically oriented fluidized bed quartz tube reactor of 1 in. inside diameter and 30 in. long. The reactor had two quartz porous disks that kept the fluidized catalyst powder in the main reaction zone and let the gases flow through the length of the reactor.

To achieve constant temperature, the reactor was located at the interior of an electric Thermocraft furnace that provides heat to the reactor which had three zones: a preheating zone of 3 in., a main and reaction zone of 1 ft. and a cool zone of 3 in., totaling 18 in. An Omega controlling thermocouple is mounted in the middle of the central zone of the furnace, at center of the heated zone and placed next to the external wall of the quartz tube. In order to have a better idea of the assembly, a process flow diagram is illustrated in figure 3.1., and an additional picture presents the real CoMoCAT assembly.



(a)



k

(b) (c)

Figure 3.1. CoMoCAT Reactor assembly. **(a)** Process flow diagram of the CoMoCAT reactor assembly. All the piping is stainless steel. **(b)** Details of the quartz tube reactor. **(c)** Photograph of the real assembly.

Gasses are fed to the system from their gas cylinders as shown in figure 3.1., and run through the lines and reactor due to the pressure gradient between the gas cylinders (higher pressure) and the system. The gasses out of the process exit to the atmosphere. Two pressure gauges are installed: one at the line entering the reactor and the other at the exit of it. CO is passed through a filter before being fed to the process in order to trap impurities eventually formed by CO with the inside walls of the containing cylinder. All the valves work by changing the direction of the flow generally either in the direction of the reactor or straight to the atmosphere, except the valve that controls the pressure in the exit of the reactor next to a bypass valve. These valves are manipulated when switching substances through the synthesis protocol.

3.2.2 Temperature Controller Setup

The temperature setup depends on the conditions at which the process will be held. A temperature ramp of 10 °C/min was used to reach the reduction temperature and subsequently the reaction temperature.

3.2.3 Catalyst Loading

For the production of SWNTs about 2 grams of calcined CoMo catalyst were loaded in each run. This catalyst was weighed in a standard digital balance and then poured down into the reactor from the top and remained at the reacting zone of the quartz tube. After loading the catalyst a safety quartz grid was placed on the top of the reacting part of the tube. Above of the grid a plug of quartz wool is put so that none solid material produced nor catalyst abandon the reacting zone until it is unloaded.

3.2.4 Running the Reactor

Initially, a leak test has to be done after loading the catalyst and adjusting tightly the inlet and outlet gas hoses. The pressure is raised up to 20 psi, the feed and exit valves are closed and after 5 minutes the pressure has to be the same for the leak test to be satisfactory, that is, no gas escapes are present in the system and it is ready to run.

3.2.4.1 Catalyst *in situ* Prereduction with H_2

For the *in situ* prereduction of the catalyst step the pressure is set to be the atmospheric (14 psi) while Hydrogen starts flowing and temperature increases to reach the reduction temperature and it is held for 30 minutes. The prereduction step is very important in the performance of the catalyst ever since it activates the catalyst for further reaction and nanotubes growth [18, 20].

3.2.4.2 SWNT Growth

Next to the prereduction step, Hydrogen gas flow is switched to Helium in order to purge the reactor for 5 minutes at the same temperature, then it’s heated up to the reaction temperature at the same temperature ramp and kept constant for 5 minutes in order to let the temperature stabilize, while pressure is manually and gradually set to the one desired. Right after that, Carbon Monoxide is introduced to the system replacing Helium and keeping the temperature for one hour for SWNT growth. Finally, CO flow is switched to He flow and cooling off starts from reaction

temperature stopping at room temperature. In figure 3.2 the process is represented showing the changes in temperature and gases with time in minutes. The temperature ramp is 10 °C/min as mentioned before. The reaction temperature and reduction temperature vary according to the conditions of the experiment chosen.

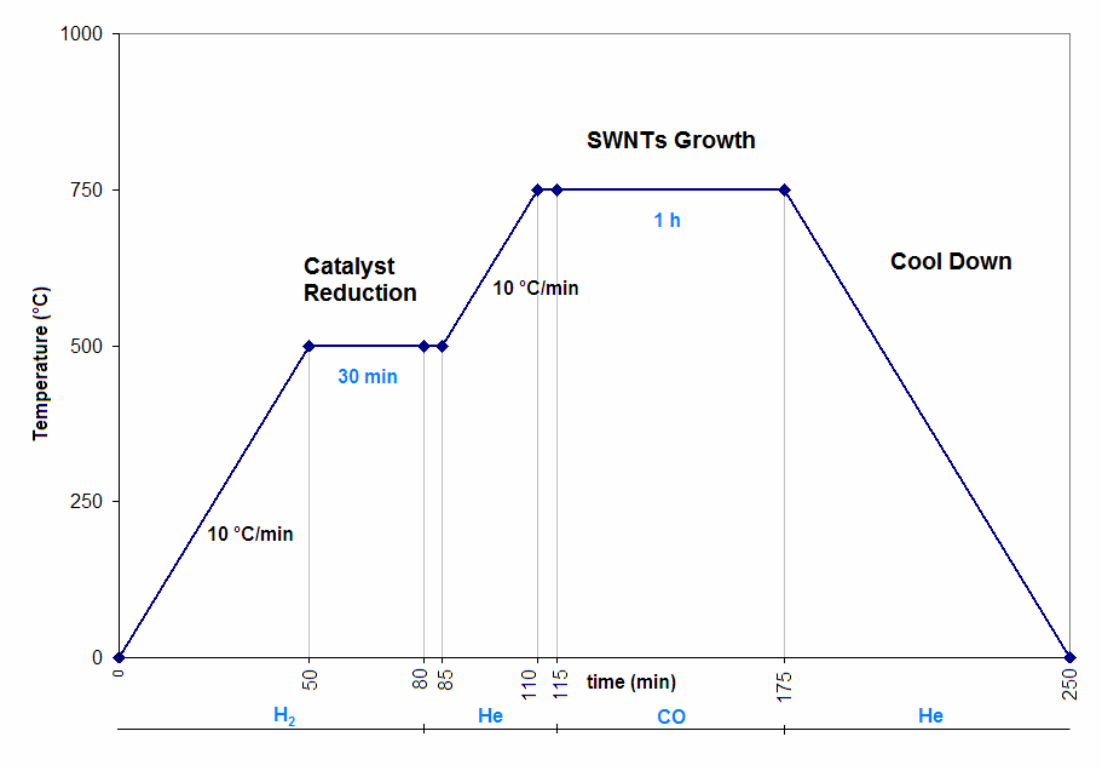


Figure 3.2 Process scheme; Temperature vs. time and gas flow.

3.2.5 Sample Storage

As soon as the reactor finally cools down to room temperature, it's safe to proceed with the storage of the batch. The outlet cap of the reactor is unscrewed, the grid and the quartz wool are removed and the sample is poured into a plastic flask which has to be labeled with the name of the run and the conditions under which the sample was created. During the loading and unloading of the reactor appropriate safety garment, lab robe, goggles, mask and gloves, are imperative.

3.3 Characterization of the Samples

The characterization technique used for all the runs was Raman resonance spectroscopy. The carbon nanotubes' Raman spectrum has significant bands which give information about the structure of the sample that allow the characterization and measurement of the quality of each sample[18, 22], thus, leading to identify what conditions produce nanotubes of best quality and to notice the presence of SWNT on the sample.

3.3.1 Raman Resonance Spectroscopy

All SWNT samples grown with the CoMo catalyst based method (CoMoCAT) were characterized using resonance Raman spectroscopy. The Raman spectra were obtained on a Jovin Yvon-Horiba Lab Ram 600, exciting the samples with a visible laser of constant power of 10 mW at a constant laser excitation wavelength around 500 nm.

For each sample there were from two to three Raman runs varying the scanning time in seconds, and the filter used for the laser beam. The Raman shift region scanned was from 0 to 3000 cm^{-1} where the RBM, D, G and D* bands appear and thus provide fundamental information about the structure of the sample and identification of SWNT. [22, 23]

CHAPTER 4. Results and Analysis

After passing all samples by Raman spectroscopy, each spectrum was used to obtain the most relevant and specific information regarding the characteristics of the SWNT containing samples. Information that reveal the presence of SWNT on a given sample and the quality of such nanotubes.

The information acquired from the Raman spectrums is the intensity of bands or peaks between some specific frequencies associated to SWNTs such as the RBM, G, D and D* bands. Each band represents specific Carbon vibrational modes which some are induced by only SWNT, and others also by graphitic-like carbon, or defective diamond-like carbon formations.

On a SWNT sample of high quality, that is, with a great amount of SWNTs on it, the G-band intensity is the greatest on the spectrum, but this one is present on the MWNT spectrum as well. However, this is one of the two quality parameters taken into account for the analysis of the results in this research. The second quality parameter corresponds to the 1-D/D* ratio [26], which is a qualitative relationship of the amount of undesired forms of carbon vs. SWNTs on the sample. The greater this ratio is, the more SWNT of high quality were produced, that is, SWNT on the sample are less defective.

When these quality parameters are calculated for each sample, a comparison has to be done, by plotting the intensity and the band ratio versus the condition that was varied, either reduction temperature, reaction temperature or system pressure, while the other variables were kept constant at the standard conditions of operation. For this purpose, the most representative samples were used in order to get reproducible results and, in this way, make accurate analysis and come up with solid conclusions and recommendations.

4.5 Selection Between 1-D/G and 1-D/D* as Parameters of Quality

For measurement of the defect concentration or quality of samples containing Single-Walled Carbon Nanotubes it has been of common use the determination of a relation of the intensities of the D-band and the G-band (1 – D/G) from the Raman spectrum of any given sample[24]. The D/G intensity ratio is used to estimate the defect concentration which expressed as 1–D/G gives an accurate and clear approximation of the presence of SWNTs, and as a quality criteria as above mentioned. [26]

Although this criteria works for this purpose, it has been investigated that the G-band is as well somehow defect-induced and therefore might not provide the most exact information about the sample quality. According to this, an alternative and suitable criterion has been demonstrated and proposed to be used for estimating the defects concentration on a carbon-nanotube-containing sample, making use of the second-order overtone mode of the D-band, called D*-mode or D*-band. [26]

For this research a comparison between 1-D/G vs. 1-D/D* was done by varying the temperature of reaction with the intention of finding which ratio showed more sensitivity to changes on a production variable.

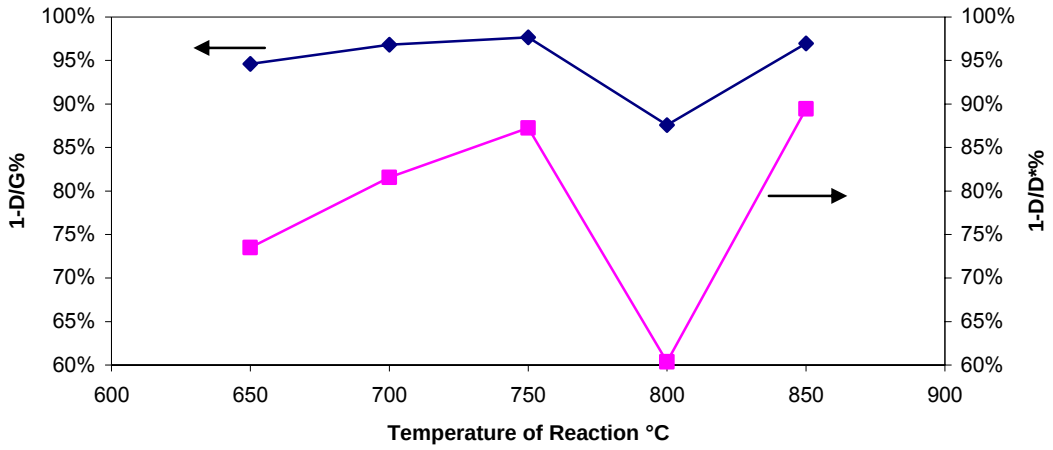


Figure 4.1. Comparison between 1-D/G and 1-D/D* with changes on temperature of reaction.

Figure 4.1., shows the comparison between the two quality parameters at different temperatures of reaction for the SWNTs, where the rhombus points are the 1-D/G and the squares are 1-D/D* vs. Temperature of Reaction in degrees Centigrade.

The graph shows that the 1-D/D* values change more dramatically than the 1-D/G ones for each value of temperature of reaction. Consequently, it can be inferred from this comparison that the 1-D/D* criterion is the most sensitive to changes on a given variable of production of SWNTs.

Accordingly, this band intensity relation has been chosen as a quality criterion in addition to the intensity of the G-band, for the characterization of the SWNT samples resulting from an assortment of runs on the CoMoCAT reactor.

4.6 Effect of Catalyst Reduction Temperature on SWNT Quality

In order to study the effect of the temperature of reduction of the CoMo Catalyst towards SWNT quality, a series of runs were done changing only the temperature of reduction above and below 500 °C at 750 °C and 14 psig of temperature and pressure of reaction respectively.

Run N°	Tred °C	Trxn °C	P psig
6	400	750	14
32	450		
5	500		
37	600		
41	650		

Table 4.4. Catalyst's reduction temperatures and reaction conditions.

Raman spectra at different reduction temperatures are shown in figure 4.2., without the RBM. The results from these series of experiments are shown below in figure 4.3., relating the temperature of reduction with the intensity of the G-band and the 1-D/D* parameters of quality.

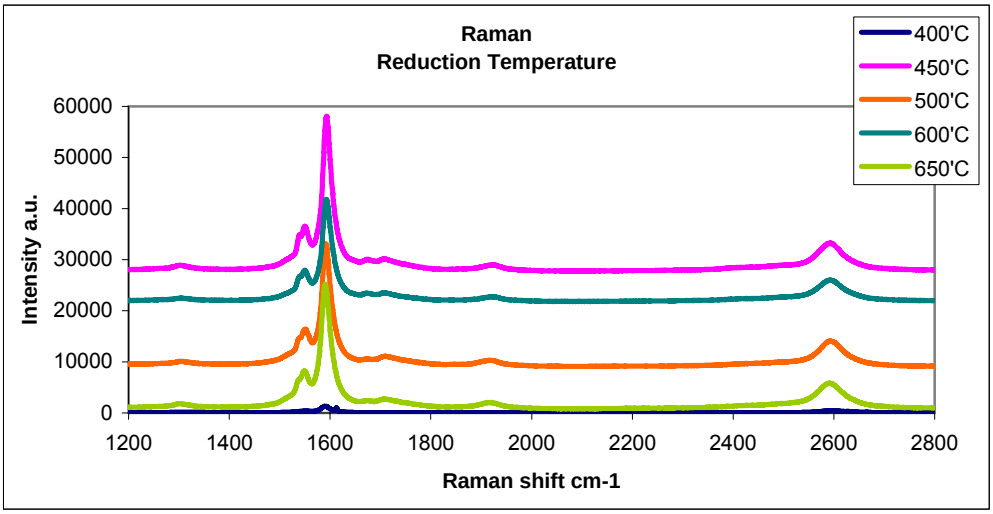


Figure 4.2. Raman spectra at different reduction temperatures

The D, G and D*-bands can be appreciated. For the high G-bands it can be seen that SWNT were present on the samples. The complete individual spectra for all the runs can be found on the Appendix.

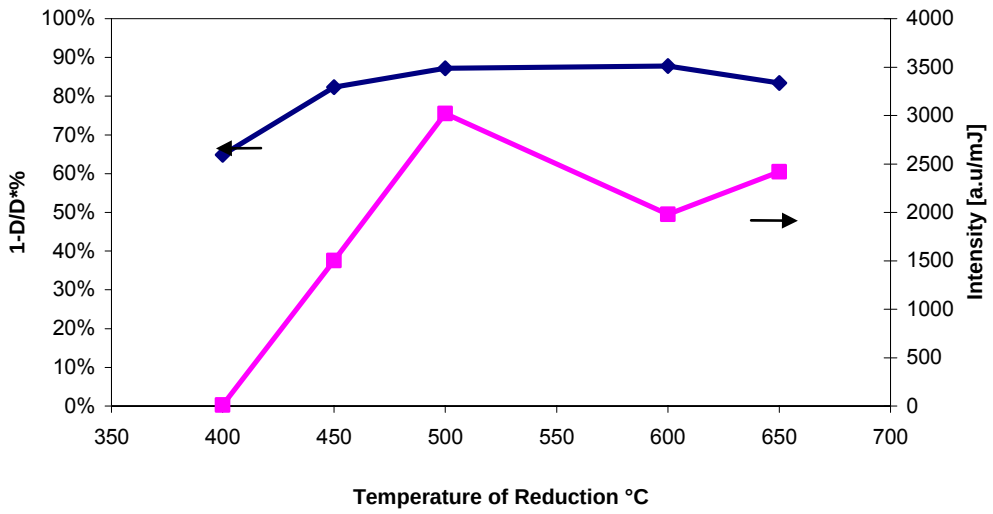


Figure 4.3. Effect of reduction temperature on SWNT quality

It can be seen that the 1-D/D* ratio behaves somehow smoother than the values of intensity, certainly keeping a similar trend below 500 °C.

Below 500 °C there's an under-reduction of the catalyst that can be caused by the poor reduction of the catalyst, that is, cobalt is not well dispersed and there might still be lots of oxidized catalyst.[18]

Above 500 °C an over reduction takes place leading to appearance of large metallic Co clusters, which reduce the catalyst selectivity towards the synthesis of SWNT. Instead, undesired forms of carbon such as Multi-Walled Carbon Nanotubes (MWNT), carbon filaments and graphite can be produced.[18] The presence of these forms of carbon is manifested on the trends of the Intensity and 1-D/D* ratio above 500 °C in figure 4.3.

The intensity effect is due to the capacity of some carbon forms of similar structure to SWNT (MWNT, graphite, carbon fibers, etc) to absorb energy at these frequencies of the G-band (~1592 cm^{-1}) plus the presence of few SWNT on these samples. It was mentioned above that the G-band is partly defect induced; understanding defective as formations different to SWNT.

In addition, hydrogen pace through the reactor might be too high so the catalyst won't have enough contact with hydrogen resulting in a poorly reduced catalyst.

Finally, a temperature of 500 °C was found to be the best condition for the reduction of the catalyst, since working at this point and the already stated conditions of reaction gives the most remarkable results on SWNT quality compared to reducing the catalyst at temperatures above and below 500 °C.

4.7 Effect of Reaction Temperature on SWNT Quality

A series of runs were carried out in order to study the effect of changing the reaction temperature on the production of SWNT, experimenting within a range of 650°C to 850 °C, maintaining 500 °C and 14 psig as conditions of reduction temperature and system pressure.

Run N°	Tred °C	Trxn °C	P psig
27	500	650	14
31		700	
5		750	
24		800	
21		850	

Table 4.5. Reaction temperatures and conditions

On figure 4.4 Raman spectra from these experiments are shown at the latter stated condition, to notice SWNT presence. The result of such runs in terms of quality parameters vs. reaction temperature are shown below in figure 4.5.

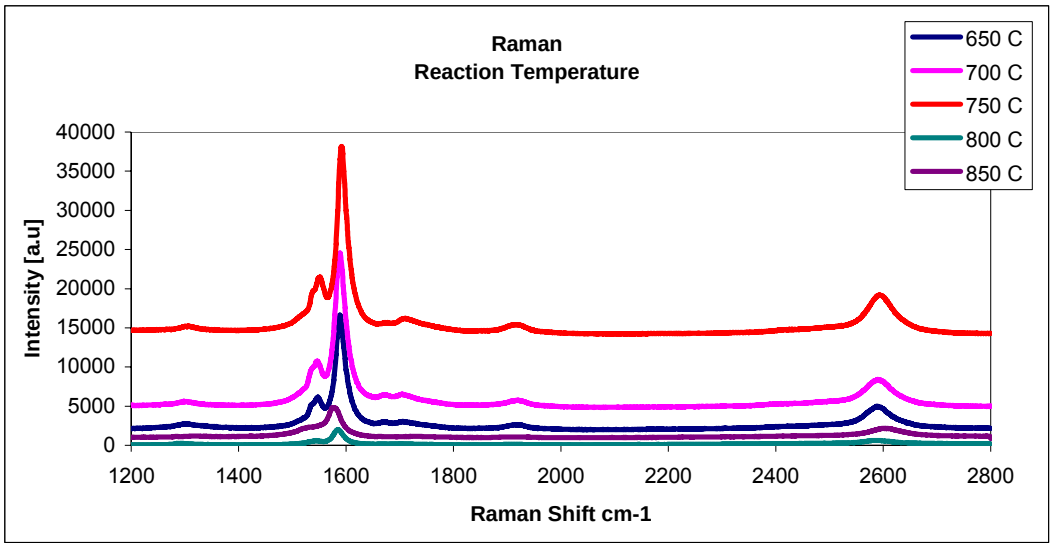


Figure 4.4. Raman spectra at different reaction temperatures

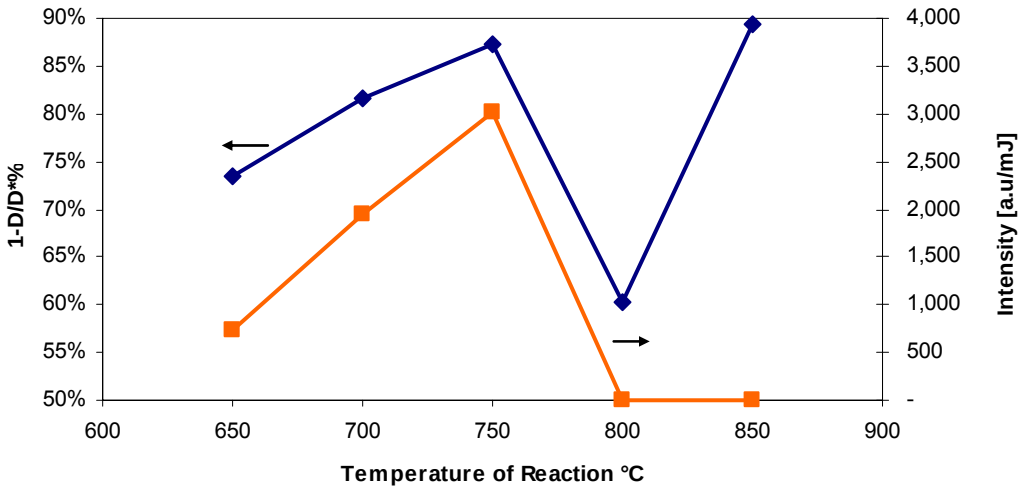


Figure 4.5. Effect of reaction temperature on SWNT quality

It is evident that the temperature of reaction at which better SWNT are produced is that of 750 °C, where the intensity absorbed was the maximum compared to the one absorbed by other samples produced at different temperatures, and also the 1-D/D* ratio has a very significant value, disregarding the value at 850 °C which does not contribute with representative information about SWNT quality.[28]

Both the intensity absorbed and the 1-D/D* ratio decrease at temperatures lower than 750 °C. Throughout this range growth of SWNTs is kinetics limited. This decrease of quality is related to the treatment of the catalyst during the reduction and reaction steps. It has been demonstrated that at low temperatures the amount of SWNT produced is lower.[21] Another explanation is that at low temperatures Co metal clusters are not well dispersed.

Additional important factor is the pace of the gases flowing through the reactor, although pace was kept constant throughout the experiments this variable could be changed and see how it contributes with SWNT production. It might be reduced so the residence time and concentration of CO_2 increase.

Even though best CO_2 conversions are reached at low temperatures because of equilibrium, SWNT's growth does not seem to be benefited within this range. Conversely quality increases when temperature ascends up to 750 ºC.

However at temperatures higher than 750 ºC the CoMo catalyst support, silica gel (SiO_2) starts sintering decreasing catalyst selectivity towards SWNT[28] as well as for carbon causing low carbon yields[5, 18], signifying that fewer or very defective SWNTs were produced at these conditions because of a low retention of carbon. In addition, conversion in equilibrium of CO into C and CO_2 decreases with temperature, which conduces to low carbon yields in the temperature range of 800-850 °C.

Accordingly, the latter explains the significant quality decrease shown on figure 4.5., between the mentioned temperature range, and explains why the 1-D/D* value at the temperature of 850 °C is not a representative measurement of quality. At this condition large amounts of SWNT are not being formed, in fact the overall carbon amount decreases importantly while there's still some defective carbon, so the amount of defects is greater.

4.3.1 Temperature Effect on Reaction's Equilibrium

One of the approaches that can be done in order to understand the process of growth of carbon nanotubes is by analyzing the reaction of disproportionation of gaseous carbon monoxide (CO) that produces solid carbon (C) and gaseous carbon dioxide (CO_2) plus energy.

$$2CO \Leftrightarrow C + CO_2 + \Delta h$$

The conversion in equilibrium for various temperatures at 1 atm in both directions of the reaction is shown in figure 4.6.

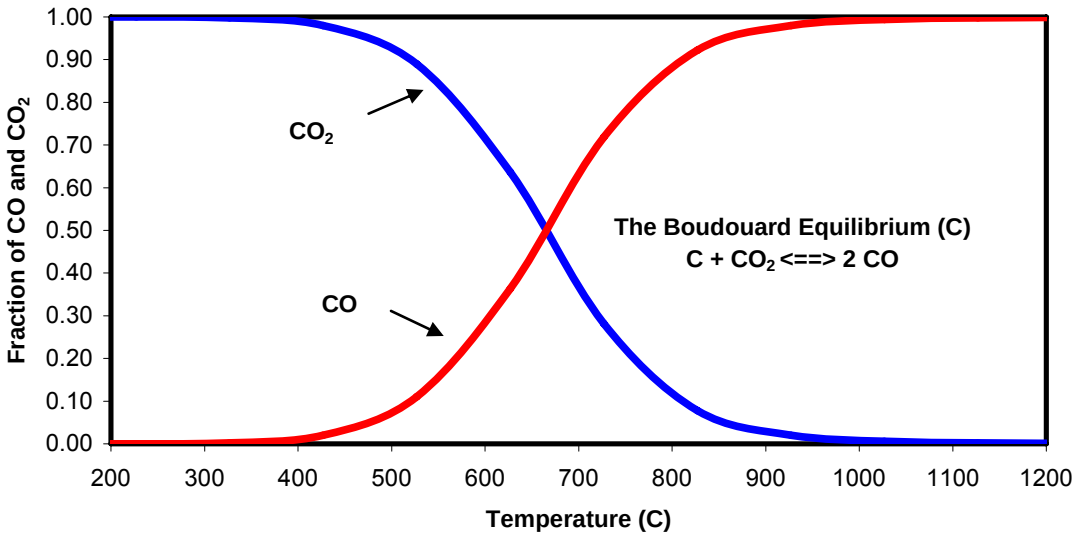


Figure 4.6. Temperature effect on reaction's equilibrium at 1 atm.[29]

Although SWNTs' growth is not solely limited by the reaction kinetics and equilibrium, these effects have to be considered, since for SWNT to be produced, operation conditions must respect nature's restrictions.

The goal in this process is to get CO to decompose so carbon is unchained and ready to be attached to the metal catalyst starting carbon arrangement into SWNT structure mainly.

According to equilibrium, greater conversions of CO_2 are reached at temperatures below 400 ºC but SWNT growth occurs at high temperatures, limiting the CO disproportionation by equilibrium, since it is an exothermic reaction. In the same way, the high temperatures required for SWNT production affect the yield of carbon.

4.4 Effect of Pressure on SWNT Quality

The experiments where organized and developed as follows:

Run N°	Tred °C	Trxn °C	P *psi*
5	500	750	14
2			40
35			60
14			80

Table 4.6. Different system pressures at the conditions listed

On figure 4.7., Raman spectra are shown at different pressures where presence of SWNT can be noticed. The results are shown in figure 4.8., comparing quality parameters as functions of the system pressure in units of pounds per square inch at gauge measurement (psig).

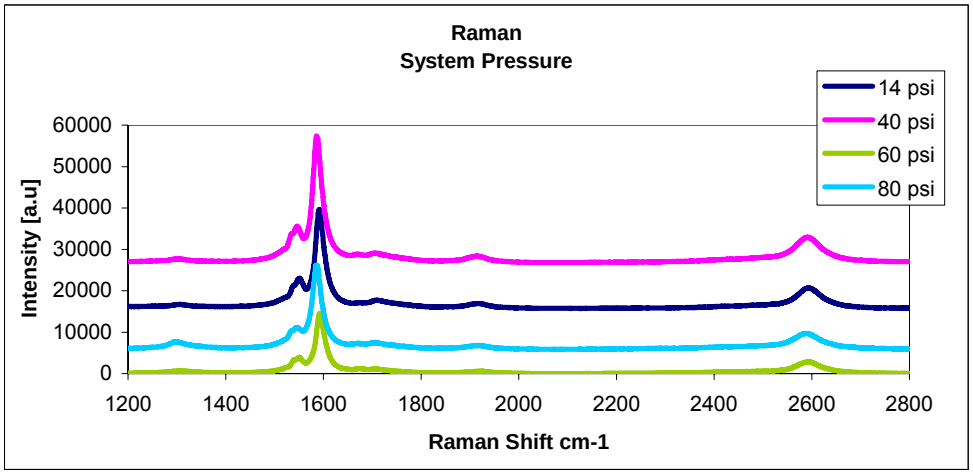


Figure 4.7. Raman spectra at different pressures

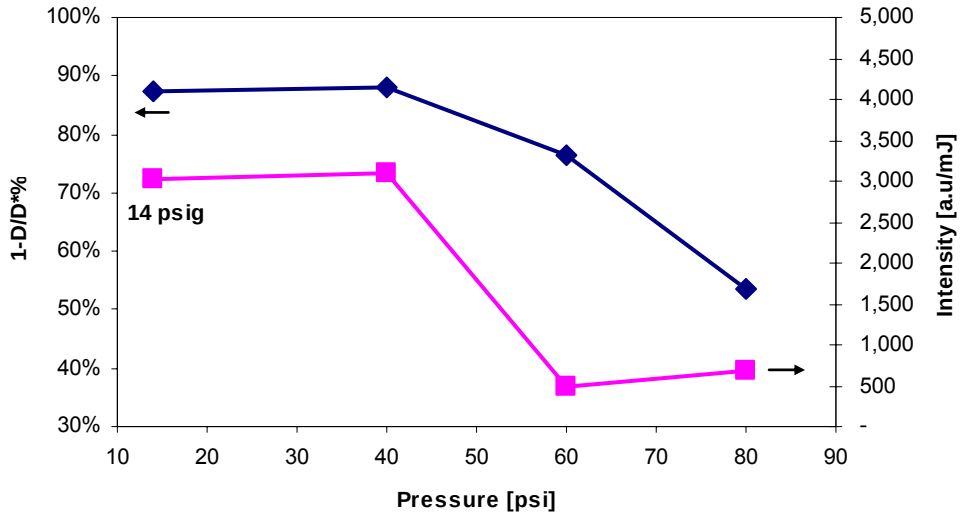


Figure 4.8. Effect of pressure on SWNT quality

In between the range of 14 to 40 psig an increase in quality on both parameters is visible. This is due to the effect pressure has on equilibrium, which can be seen in next subsection's figure 4.9. As pressure increases for an unchanged value of temperature, the equilibrium curve is shifted up being able to achieve superior values of conversion in equilibrium. In addition, pressure affects reaction rate since concentration is higher at higher pressures.

At pressures higher than 40 psig quality diminishes, though greater conversions are reached. The metal catalyst sinters at pressures these high and it's said that the catalyst is being "killed" resulting on lose of selectivity towards SWNT production.[5]

4.4.1 Pressure Effect on Reaction's Equilibrium

Figure 4.9., is a representation of the Bouduard Reaction equilibrium curves at different pressures and temperatures, shown with the intention of appreciating the effect of pressure on equilibrium, and to what extend pressure affects SWNT's quality.

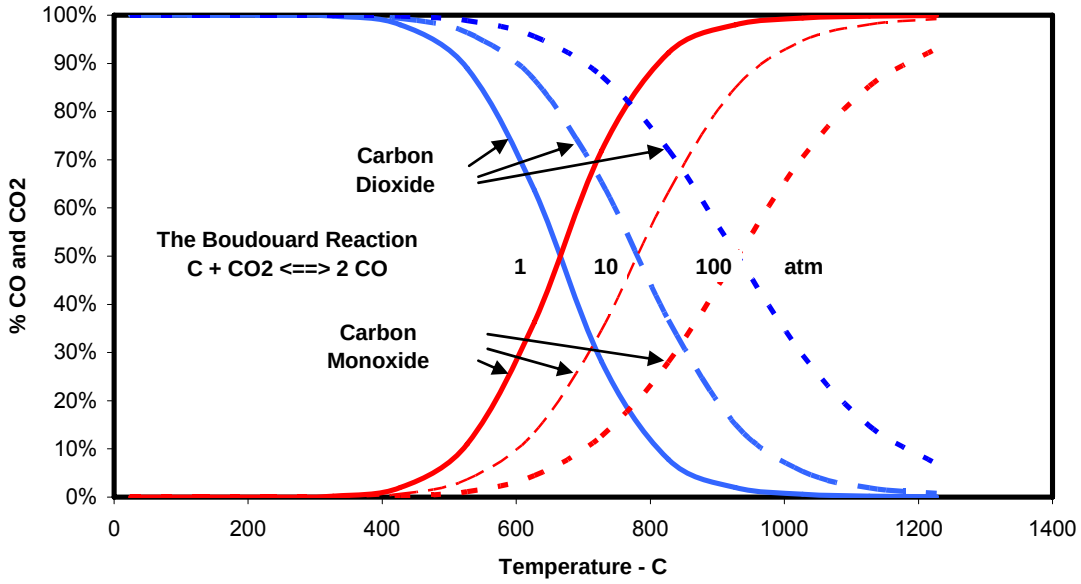


Figure 4.9. Pressure effect on equilibrium.[29]

As pressure increases, greater carbon dioxide conversions can be reached. This affects positively SWNT's growth as can be seen in figure 4.8., but only in the range from 14 to 40 psig as shown on the results, due to sintering of the CoMo catalyst.[5]

CHAPTER 5. Conclusions and Recommendations

5.3 Conclusions

The following conclusions summarize the main findings of the present research:

1. All runs were proven to contain Single-Walled Carbon Nanotubes on their products by means of Raman spectra analysis.

2. The 1-D/D* ratio facilitated the analysis of Single-Walled Carbon Nanotubes samples, synthesized from the disproportionation of CO using bimetallic CoMo catalyst supported on SiO_2 silica gel, by providing accurate information about the quality of SWNT on samples, and as a more sensitive parameter to changes in production conditions compared to the 1-D/G ratio.

3. The temperature of reduction of the $CoMo/SiO_2$ catalyst that resulted on samples with better Single-Walled Carbon Nanotubes was 500 °C.

4. The temperature of reaction for the synthesis of Single-Walled Carbon Nanotubes at which material of the highest quality were produced, is 750 °C.

5. The system pressure in the synthesis of Single-Walled Carbon Nanotubes under which product with a higher quality was obtained compared to other tested system pressures, was 40 psig.

6. Sintering of the CoMo catalyst and its silica gel support reduces the selectivity towards the production of SWNT by resulting in undesired

forms of carbon (MWNT, carbon fibers, graphene) and at the conditions mentioned above this phenomenon does not occur.

7. Samples with SWNT of best quality according to the parameters used and the catalyst selectivity towards SWNT synthesis were the best at a reduction temperature of the catalyst of 500 °C, a reaction temperature of 750 °C, and a system pressure of 40 psig with a Co:Mo ratio of 1:3 supported on SiO_2 Silica Gel with a total metals loading of 2%.

8. The type of selectivity towards SWNT that was sought for in the research regarded the production of samples containing SWNT of high quality versus other carbon formations. Neither the type of selectivity that considers the length of the nanotubes, nor the (n, m) selectivity were purposes of the present research.

9. Although the Radial Breathing Mode (RBM) on SWNT Raman spectra was not taken into account on the analysis of the products, it is a feature of great interest on the spectrum, since its presence implies SWNT identification on the sample.

5.4 Recommendations for Further Study

- ☑ In order to enhance catalyst selectivity toward SWNT synthesis, it is strongly advisable to operate at the conditions mentioned above.

- ☑ Reduce the pace of Hydrogen, and Carbon Monoxide through the reactor in the reduction and reaction steps respectively. This might enhance the reduction of Cobalt and activation of the catalyst and also increment the residence time in the reactor for both species (H_2 and CO), resulting in the reaction step in a possibly higher Carbon yield and greater amount of SWNT in the sample.

- ☑ A deeper characterization of SWNT could be done by studying the Radial Breathing Mode of each sample, so chirality, metallic character, and diameters of SWNTs on the samples can be deduced from the Raman spectra.

- ☑ The effect on SWNT quality of variables different to the ones studied on this work could be considered benefiting high quality SWNT production.

- ☑ Different formulations of $CoMo/SiO_2$ catalyst could be tried, as well as introduction of additional gaseous substances during the reaction step.

- ☑ For information about SWNT quantity and carbon yield Temperature Programmed Oxidation (TPO) technique is recommended.

- ☑ AFM and TEM are powerful techniques helpful in the manipulation and verification of SWNT on any given sample.

- ☑ For deeper study of new CoMo catalysts formulations, characterization can be done by Temperature Programmed Reduction (TPR).

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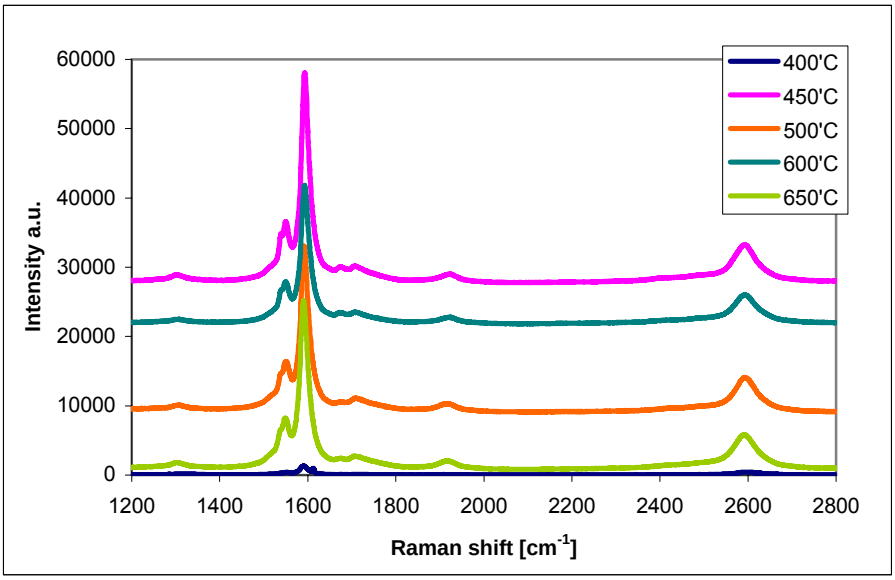
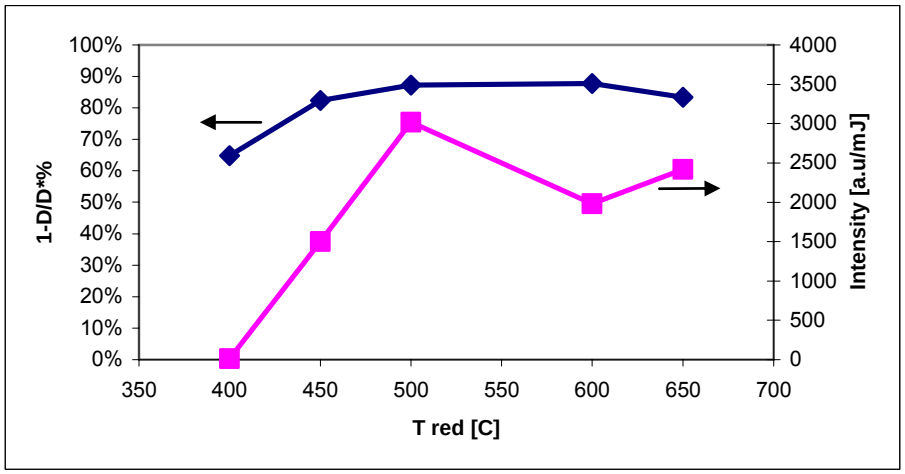
APPENDIX

Appendix 1. Experiments at different reduction temperatures,
with $CoMo/SiO_2$, 2wt% total metals, and Co:Mo of 1:3.



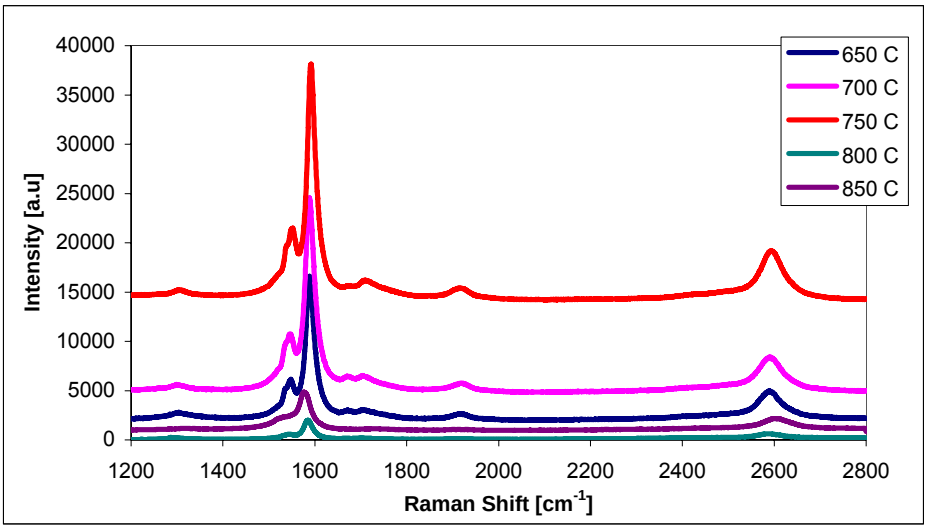
Raman spectra at different reduction temperatures

Intensity Calculations from Raw Data – Reduction Temperature								
Run Nº	**T_{red} °C**	**1-D/D* %**	**Intensity [*a.u*]**	**Filter**	**Fraction**	**time [*sec*]**	**Energy [*mJ*]**	**Intensity [*signal/mJ*]**
6	400	64.83%	1327.89	D1	0.10	120	120	11.07
32	450	82.38%	30044.81	D1	0.10	20	20	1502.24
5	500	87.24%	24149.90	D1	0.10	8	8	3018.74
37	600	87.77%	19811.31	D1	0.10	10	10	1981.13
41	650	83.44%	24177.74	D1	0.10	10	10	2417.77
E = P*t*D; P = 10mW @ T_{rxn} = 750°C and **1atm**								



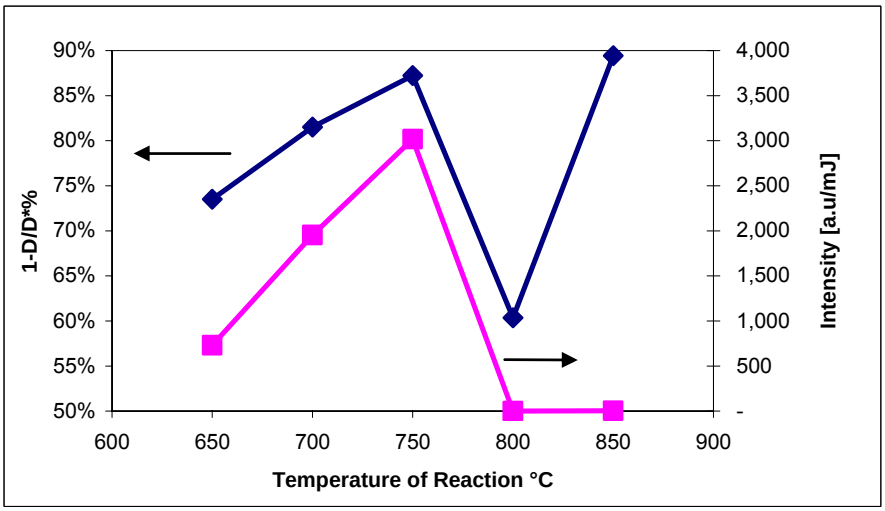
Effect of Reduction Temperature on SWNT's quality

Appendix 2. Experiments at different reaction temperatures, with $CoMo/SiO_2$, 2wt% total metals, and Co:Mo of 1:3.



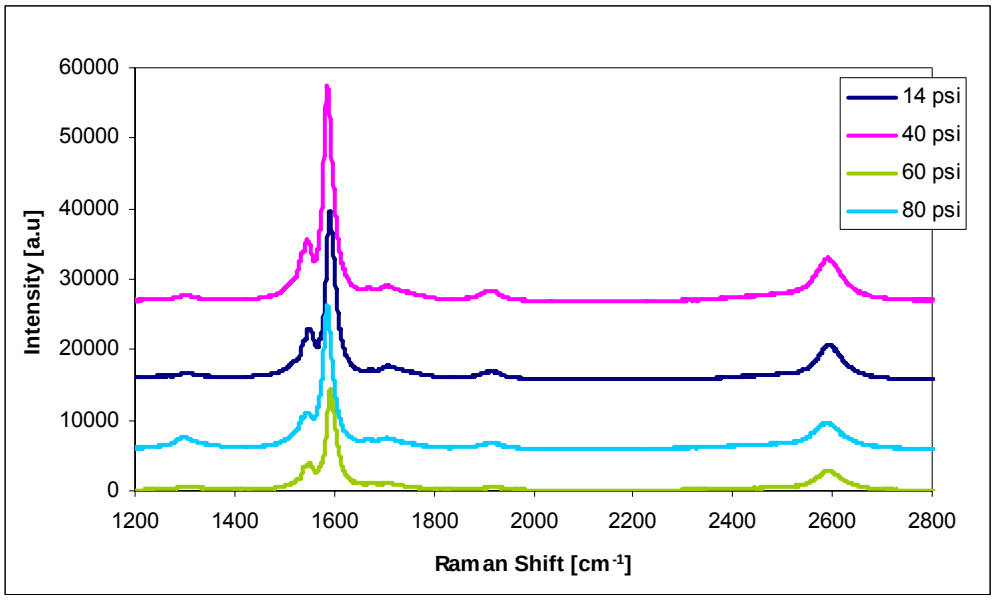
Raman spectra at different reaction temperatures

Intensity Calculations from Raw Data – Reaction Temperature								
Run Nº	**T_{rxn} °C**	**1-D/D* %**	**Intensity [*a.u*]**	**Filter**	**Fraction**	**time [*sec*]**	**Energy [*mJ*]**	**Intensity [*signal/mJ*]**
27	650	73.51	14622.92	D1	0.10	20	20	731.15
31	700	81.54	19551.53	D1	0.10	10	10	1,955.15
5	750	87.24	24149.90	D1	0.10	8	8	3,018.74
24	800	60.36	1993.53	D0	1.00	120	1,200	1.66
21	850	89.43	4468.00	D0	1.00	120	1,200	3.72
E = P*t*D; P = 10mW @ T_{red} = 500°C and **1atm**								



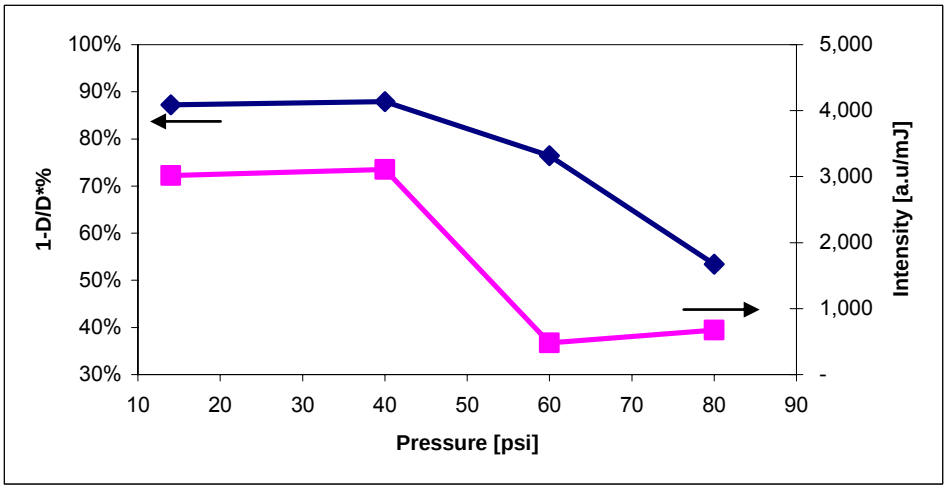
Effect of Reaction Temperature on SWNT's quality

Appendix 3. Experiments at different system pressures, with $CoMo/SiO_2$, 2wt% total metals, and Co:Mo of 1:3.



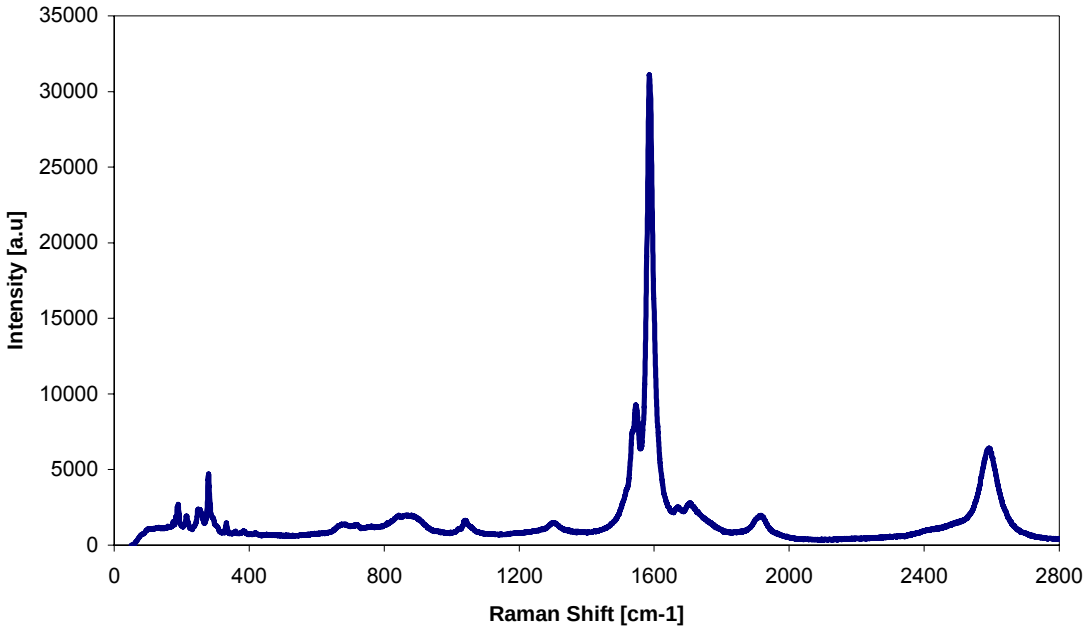
Raman spectra at different pressures

Intensity Calculations from Raw Data – System Pressure								
Run Nº	**P *psi***	**1-D/D* %**	**Intensity [*a.u*]**	**Filter**	**Fraction**	**Time [*sec*]**	**Energy [*mJ*]**	**Intensity [*signal/mJ*]**
5	14	87.24	24149.9	D1	0.1	8	8	3,019
2	40	87.94	31084.7	D1	0.1	10	10	3,108
35	60	76.46	14419.0	D1	0.1	30	30	481
14	80	53.39	20203.0	D1	0.1	30	30	673
E = P*t*D; P = 10mW @ T_{red} = 500°C and **T_{rxn} = 750°C**								

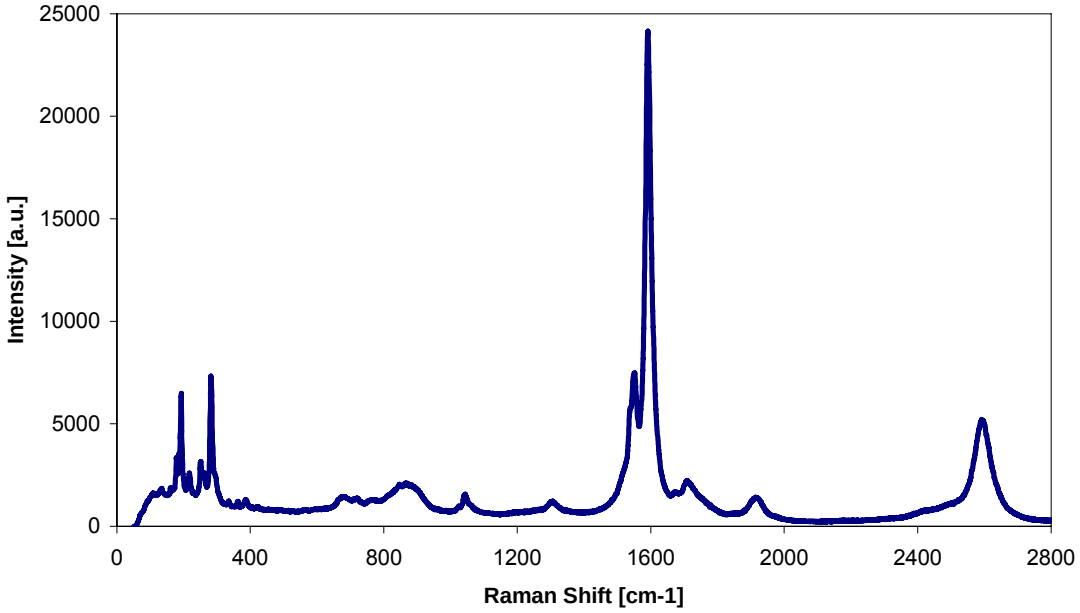


Effect of Pressure on SWNT's quality

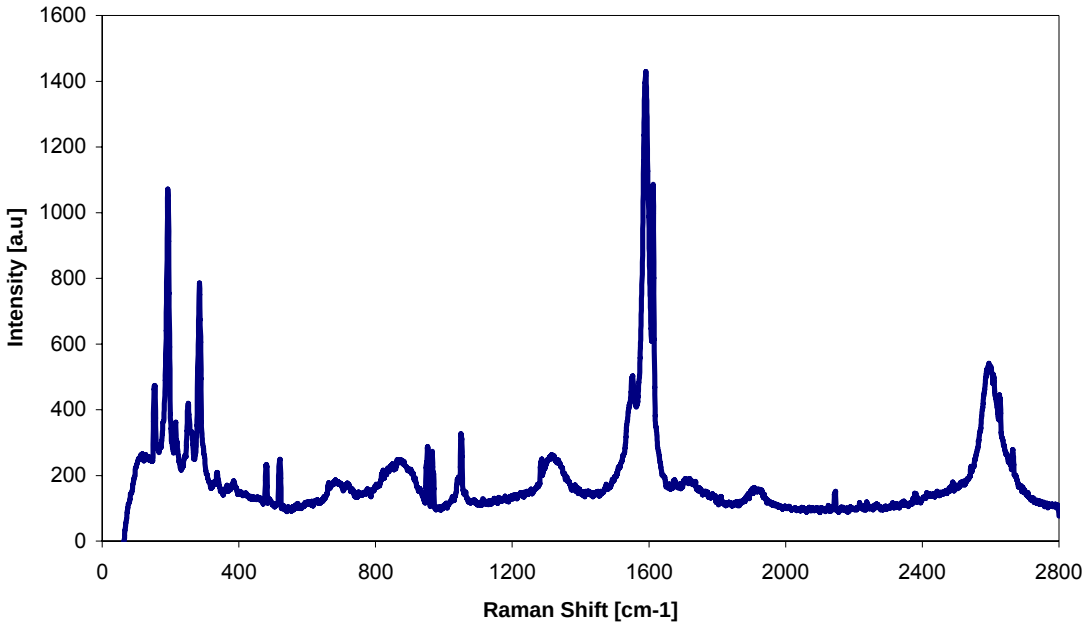
Appendix 4.
Individual Raman spectra
Runs 2, 5, 6, 14, 21, 24, 27, 31, 32, 35, 37 and 41.



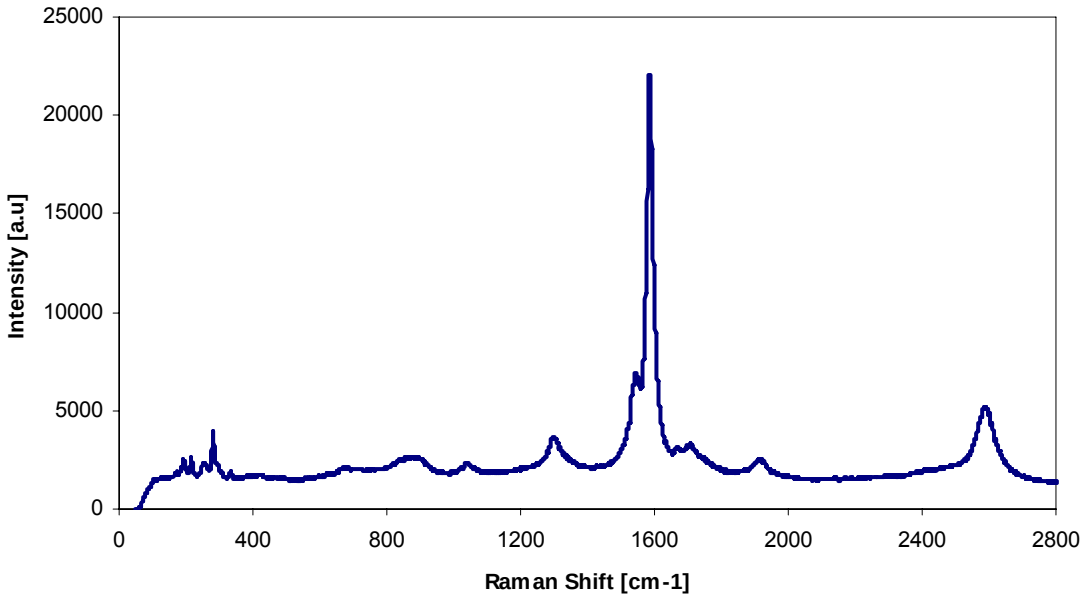
Run 2. Conditions: 750°C, 500°C & 40 psi as reaction temperature, reduction temperature and system pressure.



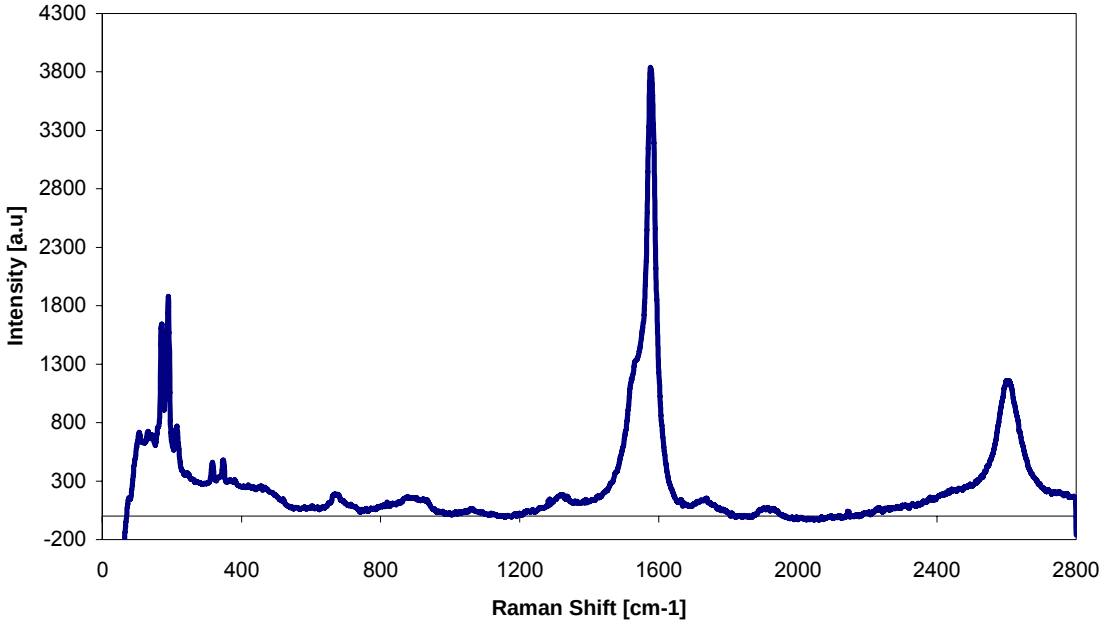
Run 5. Conditions: 750°C, 500°C & 14 psi as reaction temperature, reduction temperature and system pressure.



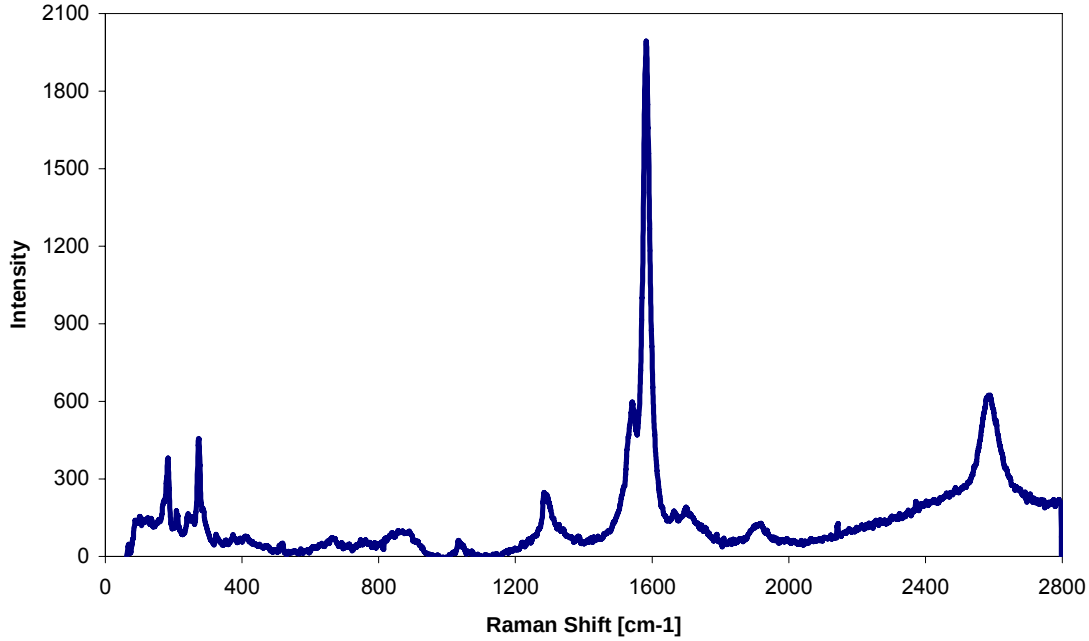
Run 6. Conditions: 750°C, 400°C & 14 psi as reaction temperature, reduction temperature and system pressure. Smoothed trend.



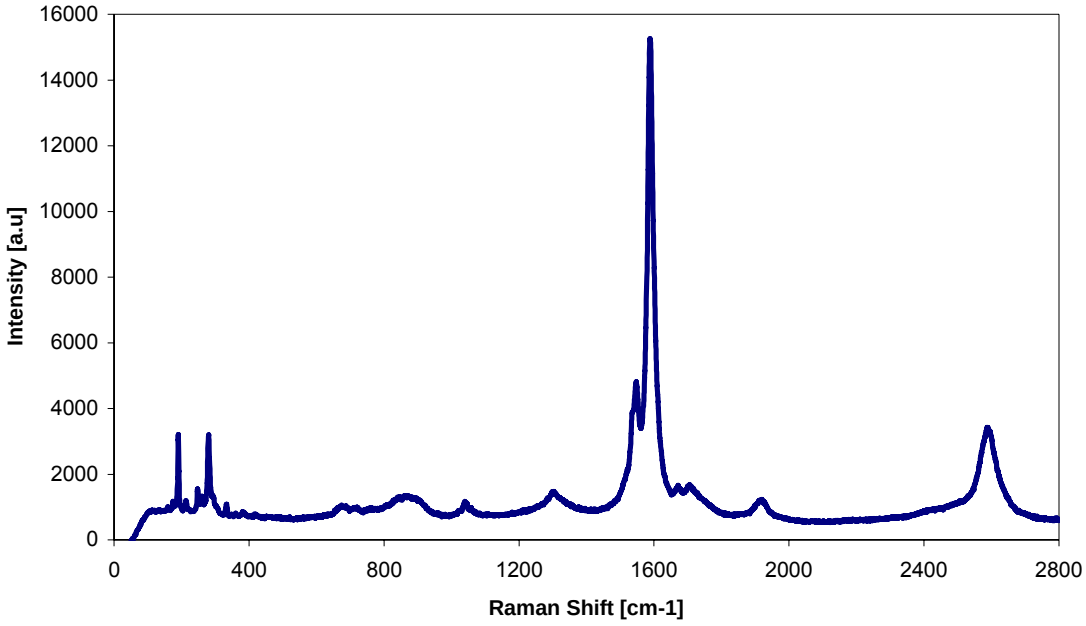
Run 14. Conditions: 750°C, 500°C & 80 psi as reaction temperature, reduction temperature and system pressure



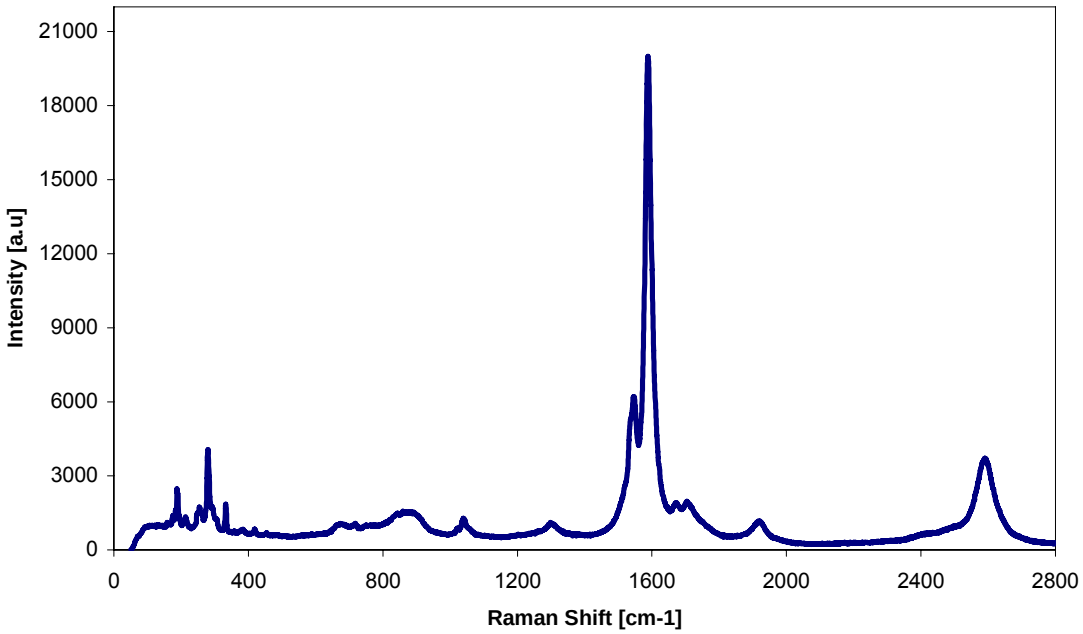
Run 21. Conditions: 850°C, 500°C & 14 psi as reaction temperature, reduction temperature and system pressure. Background removed.



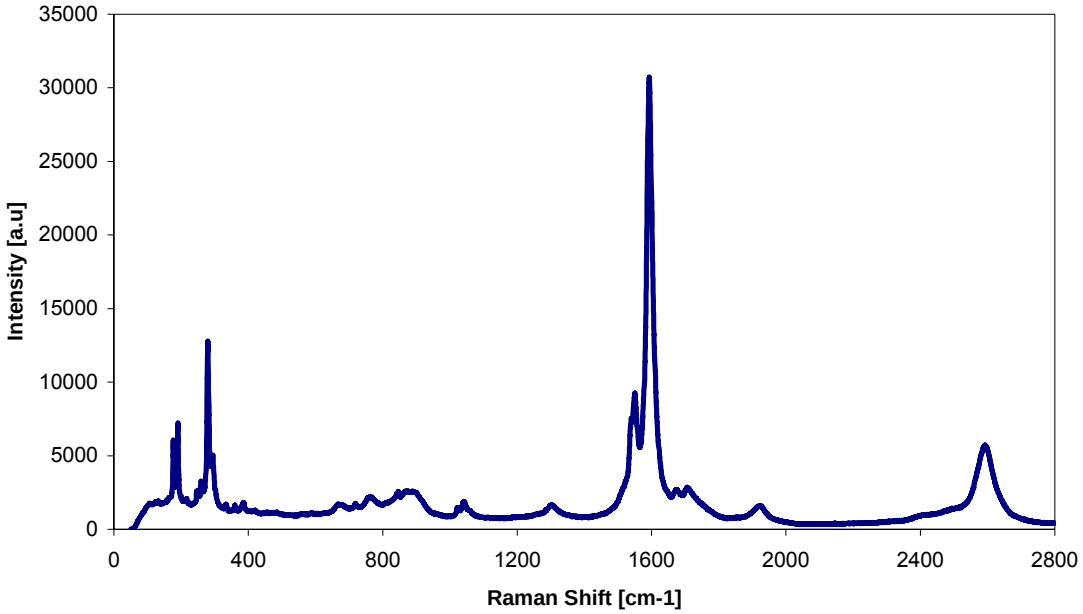
Run 24. Conditions: 800°C, 500°C & 14 psi as reaction temperature, reduction temperature and system pressure. Background removed.



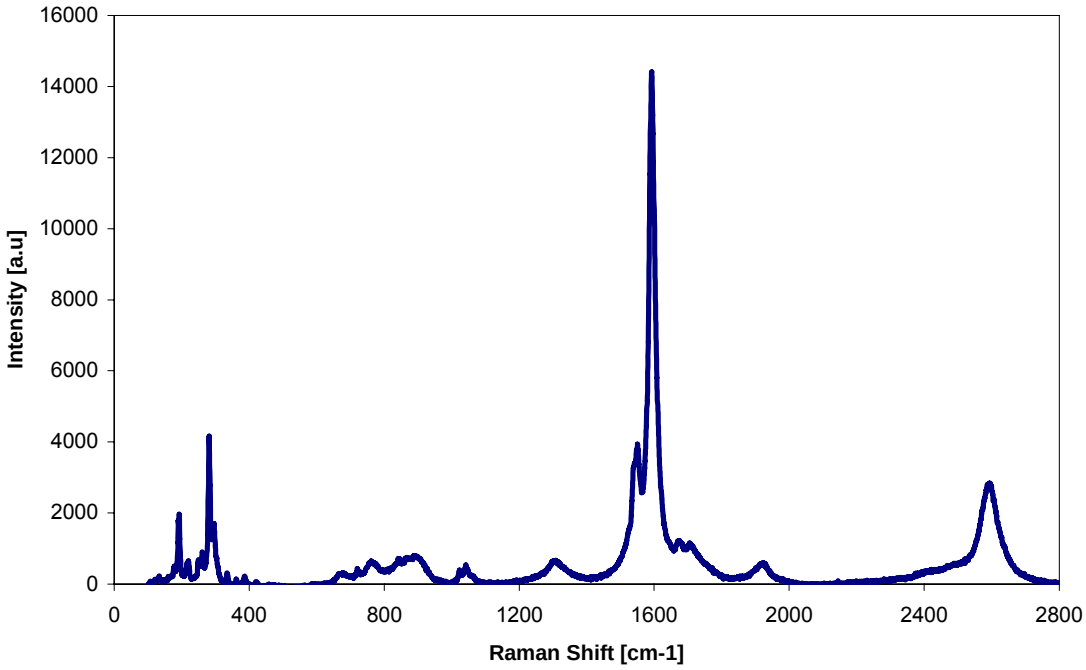
Run 27. Conditions: 650°C, 500°C & 14 psi as reaction temperature, reduction temperature and system pressure.



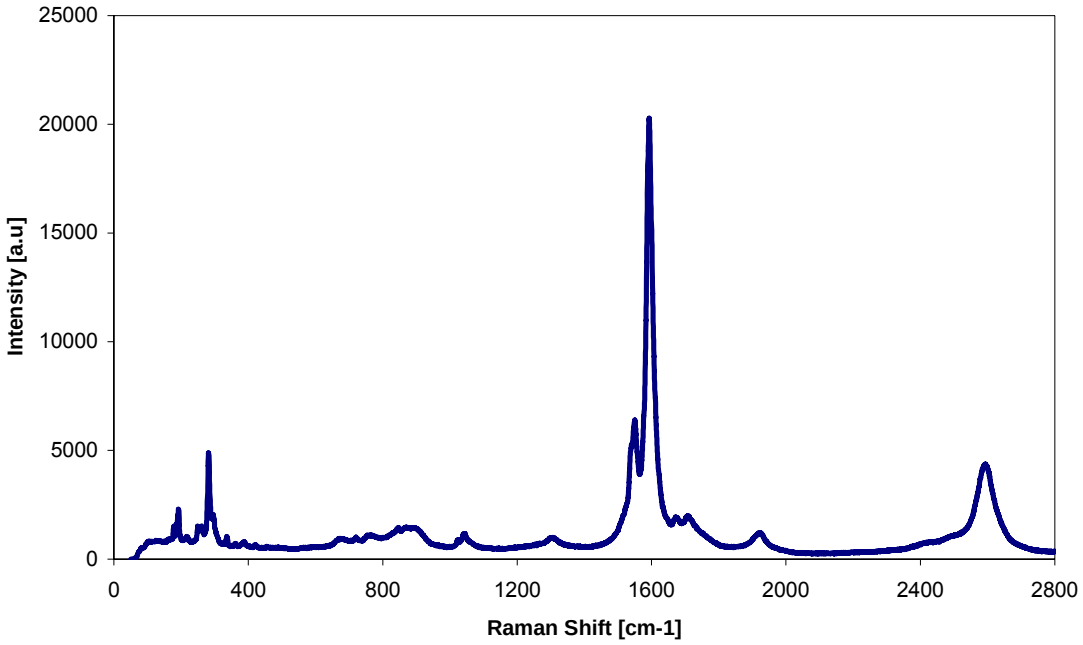
Run 31. Conditions: 700°C, 500°C & 14 psi as reaction temperature, reduction temperature and system pressure.



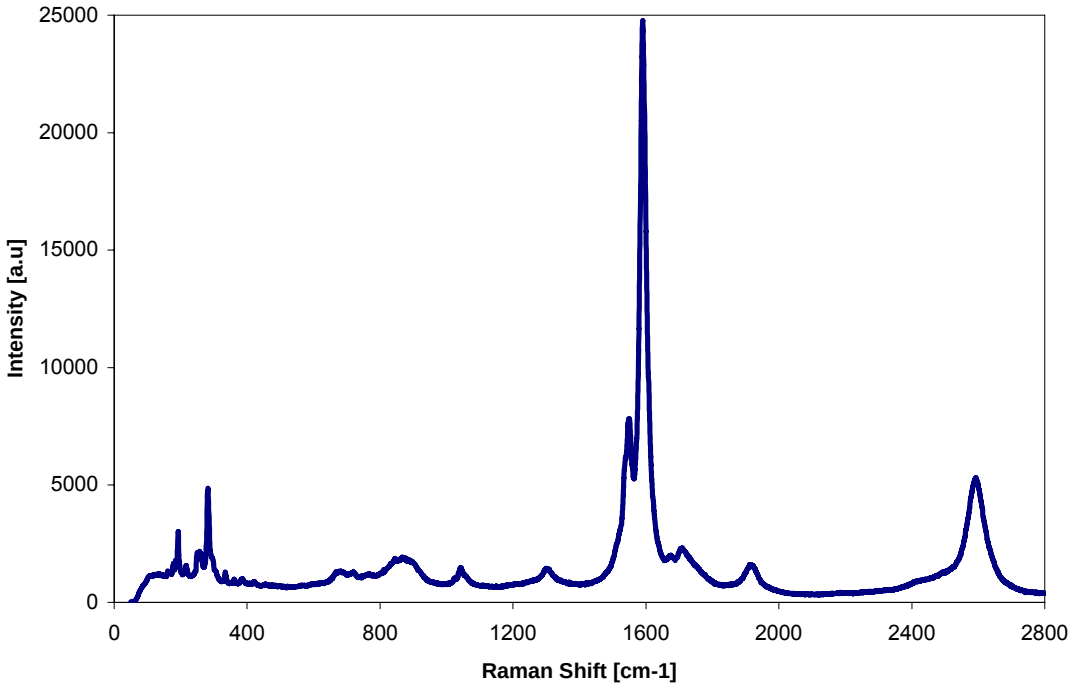
Run 32. Conditions: 750°C, 450°C & 14 psi as reaction temperature, reduction temperature and system pressure.



Run 35. Conditions: 750°C, 500°C & 60 psi as reaction temperature, reduction temperature and system pressure. Background removed.



Run 37. Conditions: 750°C, 600°C & 14 psi as reaction temperature, reduction temperature and system pressure Background removed.



Run 41. Conditions: 750°C, 650°C & 14 psi as reaction temperature, reduction temperature and system pressure. Background removed.