

A systematic study of multi-layer graphene formation from hydrocarbon
explosions: insights on temperature effects, syngas, and nitrogen-doping

by

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M.Sc., Tribhuvan University, Nepal, 2017

AN ABSTRACT OF A DISSERTATION

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Department of Physics
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Abstract

A systematic study on the formation and characterization of carbon formed during the explosion of various hydrocarbon precursors is presented. The carbon formed was a powder at higher precursor oxygen content and an aerosol gel at lower oxygen where the carbon yield was larger. The carbon formed linearly decreased with the O/C ratio, with some residual carbon at O/C greater than 1. The explosion temperature was measured by a spectrometer that detected black body, Planck radiation from the incandescent carbon, the analysis of which indicated temperatures in the range 1900–3100 K. The peak explosion temperature was found to increase with the oxygen-carbon (O/C) ratio. These findings were supported to some extent by theoretical calculations of the adiabatic flame temperature at constant volume based on the anticipated chemical reactions occurring during the explosion. The carbon collected was characterized by Raman, X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), etc. HRTEM and Raman analyses indicated the presence of a threshold temperature of around 2100 K that separated two product types for all hydrocarbons: amorphous soot at temperatures less than 2100 K and multi-layer graphene at temperatures greater than 2100 K. The resulting graphene exhibited a turbostratic structure. The layers are stacked more randomly or misaligned, leading to a less structured and more disordered configuration, consisting of 6–30 layers depending on the O/C ratio and precursor used. Additionally, the explosion process yielded syngas as a byproduct gas for all hydrocarbons, with methane—producing only syngas.

Nitrogen-doped graphene was produced using the explosion process using pyridine ($\text{C}_5\text{H}_5\text{N}$) as a precursor and introducing nitrogen-bearing gas during the explosion of acetylene and ethylene. X-ray photoelectron spectroscopy (XPS) analysis of the resulting carbon confirmed the presence of nitrogen, with the atomic percentage ranging from 0.6% to 3.4%, depending on the precursor material.

Fine powder dispersion was conducted in 4 L and 17 L transparent plastic chambers using various powder dispersers. This dispersion system was then implemented in a 17 L aluminum chamber equipped with an ignition system to investigate the explosion of different powder samples. The experiments revealed incomplete combustion with longer burn times, and no graphene was produced.

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Dedication

To all who have inspired me to become who I am today!

Chapter 1

Introduction

The term ‘graphene’ was introduced by Hanns-Peter Boehm in 1961–1962 for the hypothetical single-layer structure of graphite [1]. After that, several groups tried to make free-standing single-layer graphene (SLG), but none were successful. Finally, in 2004, Andre Geim and Konstantin Novoselov at the University of Manchester fully isolated the SLG by micromechanical cleavage of graphite with an ordinary adhesive tape [2]. They conducted extensive studies on the properties of graphene and uncovered its exceptional characteristics [2–5]. This groundbreaking achievement by Geim and Novoselov generated a wave of global interest and hype around the potential applications of graphene.

Graphene is made up of a single layer of carbon atoms arranged in a hexagonal lattice [5]. Carbon atoms in graphene form a strong in-plane sp^2 covalent bond, which gives graphene mechanical strength [6]. The out-of-plane π electrons hybridize, forming two half-filled bands of free-moving electrons responsible for excellent electronic properties [4–7].

In addition to excellent electronic properties, graphene is highly conductive and flexible, and it absorbs only 2.3% of visible light [8, 9]. This makes graphene attractive in portable electronics, semiconductors, transparent conductors, and as a material for solar cells [10]. Also, graphene is impermeable to most gases and liquids [11]. Because of this, graphene can be used for the filtration and desalination of water and as a protective coating. Graphene has numerous other applications like energy storage, composite materials, lubrications, batteries,

sensors, etc [12]. Graphene has enormous potential with an application in all fields; it is truly a material that can change the world.

Although single-layer graphene is ‘ideal’ graphene, multi-layered graphene also keeps the properties of SLG. The graphene council [13] and European Chemical Agency (ECHA) [14] state that graphene properties hold up to 34 carbon layers. Depending upon the applications, the need for graphene also varies. For example, applications such as computer chips, transistors, transparent conductors, etc., use SLG [10, 12]. And multi-layer graphene flakes are used in composite fillers, conductive coatings, lubrications, batteries, supercapacitors, etc [12]. The lack of high-quality graphene on an industrial scale limits the use of graphene to exploit its unique properties.

One of the most common methods for producing graphene, chemical vapor deposition (CVD) [15, 16], requires expensive equipment and a controlled environment. While CVD has shown promise for high-quality graphene production, scaling up the process while maintaining high quality and yield has proven challenging [17]. Liquid-phase exfoliation of graphite to produce graphene [18, 19] has the potential for large-scale production. However, certain methods, like Hummer’s method, suffer from low yields and poor control over the size and quality of the graphene. Furthermore, this method can have a negative environmental impact due to the use of dangerous chemicals and the generation of waste products [20].

We have developed a unique method for synthesizing multi-layer graphene nanosheets [21–24]. This method involves a controlled explosion of gaseous hydrocarbon in a multi-liter chamber. Our process is scalable, cost-effective, and produces high-quality multi-layer graphene with no requirement for post-purification of the prepared sample. The gas chromatography shows we have carbon monoxide (CO) and hydrogen (H_2), commonly known as syngas, as a byproduct gas of the reaction. Syngas has a different commercial value in the energy world.

During an explosion, the temperature inside the chamber is greater than a normal flame temperature (2000 K), and as a result, thus formed sooty carbon changed into multi-layer graphene. Earlier work from our group also demonstrated that high temperature is key for graphene synthesis. The work of Choi et al. [25] supports this hypothesis. They used

an acetylene flame that produced normal soot. When irradiated with a CW CO₂ kilowatt laser, the flame temperature jumped from 2100 K to 3000 K. Thus, formed soot changed to “shell-shape carbon nanoparticles” composed of graphenic-like curved layers. Other work by Pawlyta et al. [26] showed the change in morphology of commercial carbon blacks from a round, ball-like shape to a few-layer graphitized structure at an elevated temperature (2800 °C). The resulting change in the morphology of the carbon supports our hypothesis that the high temperature (> 2100 K) during the explosion is the fundamental cause of the graphenic nature of the carbon produced.

This work aims to conduct extensive testing of the high-temperature graphene synthesis hypothesis. The approach involves utilizing liquid aromatic hydrocarbons (benzene, toluene, xylenes) and aliphatic hydrocarbon (ethylene) as hydrocarbon precursors in the explosion synthesis. The focus will also be on reducing the temperature of an acetylene mixture to the open flame temperature limit (approximately 2000 K) using a lower oxygen content and introducing ammonia to dilute the acetylene and oxygen mixture. The main objective is to observe if the previously formed graphene transforms into soot at a lower temperature.

Furthermore, the study intends to employ the explosion synthesis method to produce various other nanomaterials, each possessing unique properties and applications. These materials include nitrogen-doped graphene, metal-doped graphene, and syngas, a mixture of CO and H₂. The research also aims to explore the potential of discovering additional nanomaterials with distinctive properties during the process.

Characterization of the carbon produced from all hydrocarbons has shown that the morphology of carbon produced changes with the oxygen-carbon ratio and the peak explosion temperature during an explosion. Soot is formed at lower oxygen content and temperature, and multi-layer graphene is formed at higher O/C ratios and temperatures. Detailed results on individual hydrocarbons will be discussed in the following chapters.

The arrangement of the chapters in this thesis is as follows. Chapter 2 begins with a brief description of the hydrocarbon precursors used in the study, the experimental procedure, the data collection and analysis procedure, and the scientific tools used to characterize the sample. Chapter 3 will present the extensive work done on aromatic hydrocarbons. The

work on acetylene and ethylene is discussed in Chapter 4. Chapter 5 discusses a thorough investigation of syngas, a mixture of CO and H₂ produced as a byproduct gas during graphene manufacturing. The work on the synthesis of nitrogen-doped graphene will be covered in Chapter 6. Chapter 7 gives a brief description of the work done on the powder explosions. The findings and prospective future work to fully understand the explosion synthesis process are summarized in Chapter 8, which also explores the practical uses of the graphene sample created in this study.

Chapter 2

Experimental method and characterization techniques

2.1 Brief description of hydrocarbon precursors used in this study

Benzene (C_6H_6), toluene (C_7H_8), and xylenes (C_8H_{10}) are the aromatic hydrocarbons used in this study. These hydrocarbons are highly flammable and readily burn in the presence of oxygen, producing free carbon [27]. Moreover, they have a low boiling point and can easily transform into vapor when heated during an explosion. Additionally, the hexagonal ring structure of these hydrocarbons is akin to that of graphene [28]. Figure 2.1 shows the molecular structure of aromatic hydrocarbon precursors.

Acetylene (C_2H_2), ethylene (C_2H_4), and methane (CH_4) were chosen as the aliphatic hydrocarbons for this study. These precursors have a wide flammability range, facilitating the generation of free carbon through fuel-rich reactions. Furthermore, these precursors are easily obtainable and cost-effective, making them suitable for potential scale-up.

The precursors used to produce nitrogen-doped graphene were pyridine ($\text{C}_5\text{H}_5\text{N}$), acetonitrile (CH_3CN), and ethylenediamine ($\text{C}_2\text{H}_4(\text{NH}_2)_2$). These precursors are nitrogen-rich,

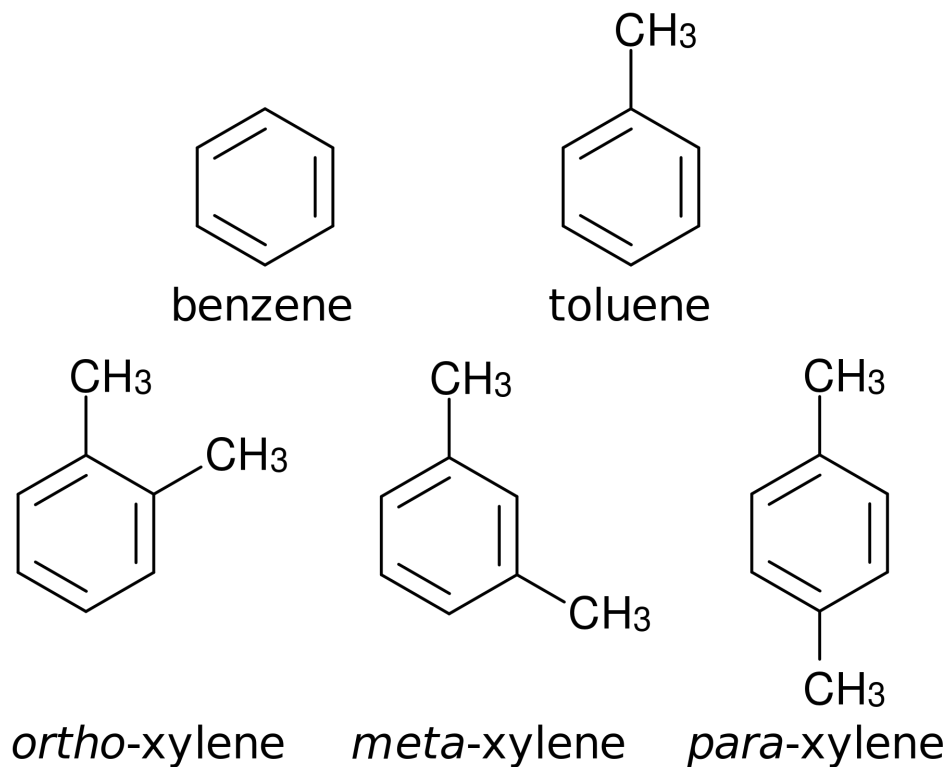


Figure 2.1: Molecular structure of benzene, toluene and xylenes.

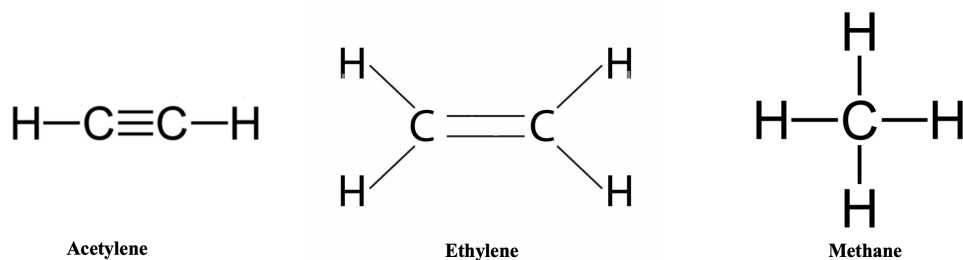


Figure 2.2: Molecular structure of the aliphatic hydrocarbons used in this study.

highly flammable in the presence of an oxidizer. They are readily available, making them desirable for nitrogen-doped graphene synthesis. Additionally, ammonia (NH_3) was introduced into the acetylene and oxygen mixture to yield nitrogen-doped graphene.

The primary oxidizer employed in this study was oxygen (O_2). Furthermore, nitrous oxide (N_2O) was utilized to investigate the role of the oxidizer and to produce nitrogen-doped graphene.

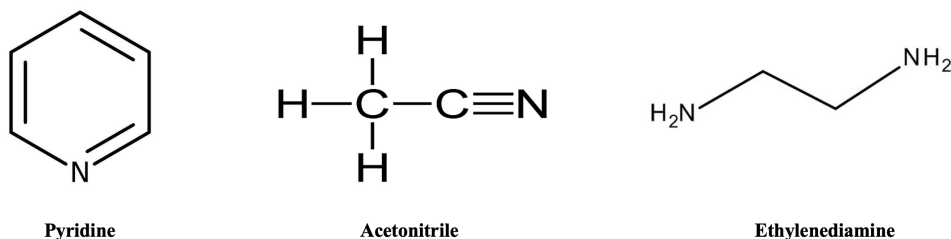


Figure 2.3: Molecular structure of hydrocarbon precursors used in the production of nitrogen-doped graphene.

All these hydrocarbons are highly flammable and have health hazards if inhaled. So the experiment was conducted by ensuring the use of appropriate personal protective equipment (PPE). All liquid and gaseous hydrocarbons were stored in a separate room, well-ventilated, and deprived of oxidizer for safety reasons.

2.2 Explosion process, data collection, and analysis procedure

Figure 2.4 shows a picture of an explosion chamber, a 17 L cylinder with an internal height of 37 cm and diameter of 24 cm made of 2.54 cm thick aluminum. In a typical explosion, the chamber was evacuated to 0.03 atm, filled to 1 atm absolute pressure with different oxygen and hydrocarbon molar ratios, and ignited. There are three methods of ignition used during the explosion. The first method involves an electromotive spark plug and a Tesla coil. The second method utilizes a pair of electrodes and a step-up transformer to provide high voltage, approximately 10000 V. The third method involves an electric matchstick. An electric matchstick contains explosives at its tip and is designed to ignite when exposed to standard wall voltage. Upon ignition, it produces a substantial flash that spreads throughout the chamber. In contrast, the spark generated by a spark plug remains confined primarily to its tip. A valved port is on top of the chamber to collect gas after an explosion. Three quartz windows are in the chamber's circumference for optical access to the interior. A

fiber optic at one quartz window collects light from an explosion flash. It transmits that to an Ocean Optics spectrometer, later used to calculate the temperature using Planck’s blackbody radiation law [29]. More about temperature measurement in section 3.3.1 On the top of the chamber is a plugin for a piezoelectric crystal to collect pressure impulse data and a pressure gauge to measure the fill and overpressure before and after an explosion, respectively. During the experimentation process, the chamber was heated to a temperature range of 343–353 K to evaporate the liquid hydrocarbons, while the explosion took place at room temperature for gaseous hydrocarbons. Following a successful explosion, a small amount of over-pressurized gas was collected in a Tedlar sample bag for gas analysis. The remaining gas was safely released into a fume hood. Next, the chamber was allowed to cool down to room temperature, and the lid was removed to collect the sample. The sample’s mass and approximate mass yield were measured. Afterward, the chamber was cleaned using acetone to prepare it for the next explosion. Additional characterizations were performed as per the requirements and needs of the explosion materials. A detailed explanation of the instrumentation and characterization techniques will be provided in the next section.

2.3 Raman spectroscopy

Raman spectroscopy is a spectroscopic technique used to determine the vibrational modes of molecules and materials from which molecules and materials can be identified. The technique is based on the inelastic scattering of monochromatic light [30]. When light is shined into a molecule, the photon induces a polarization on the molecular electron cloud, which leads the molecule to a higher energy state with the photon’s energy transferred to a molecule. Because of that, the electrons are excited to a higher energy state called a “virtual state.” The virtual state is unstable, and the photon is immediately re-emitted as scattered light. The most scattered light is at the same wavelength as the initial light source; this is called Rayleigh scattering and does not provide useful information. However, Raman scattering occurs on approximately 1 in 10 million photons. If the electron cloud gains energy from the photon during scattering, the scattered photon loses energy, called the Stokes–Raman

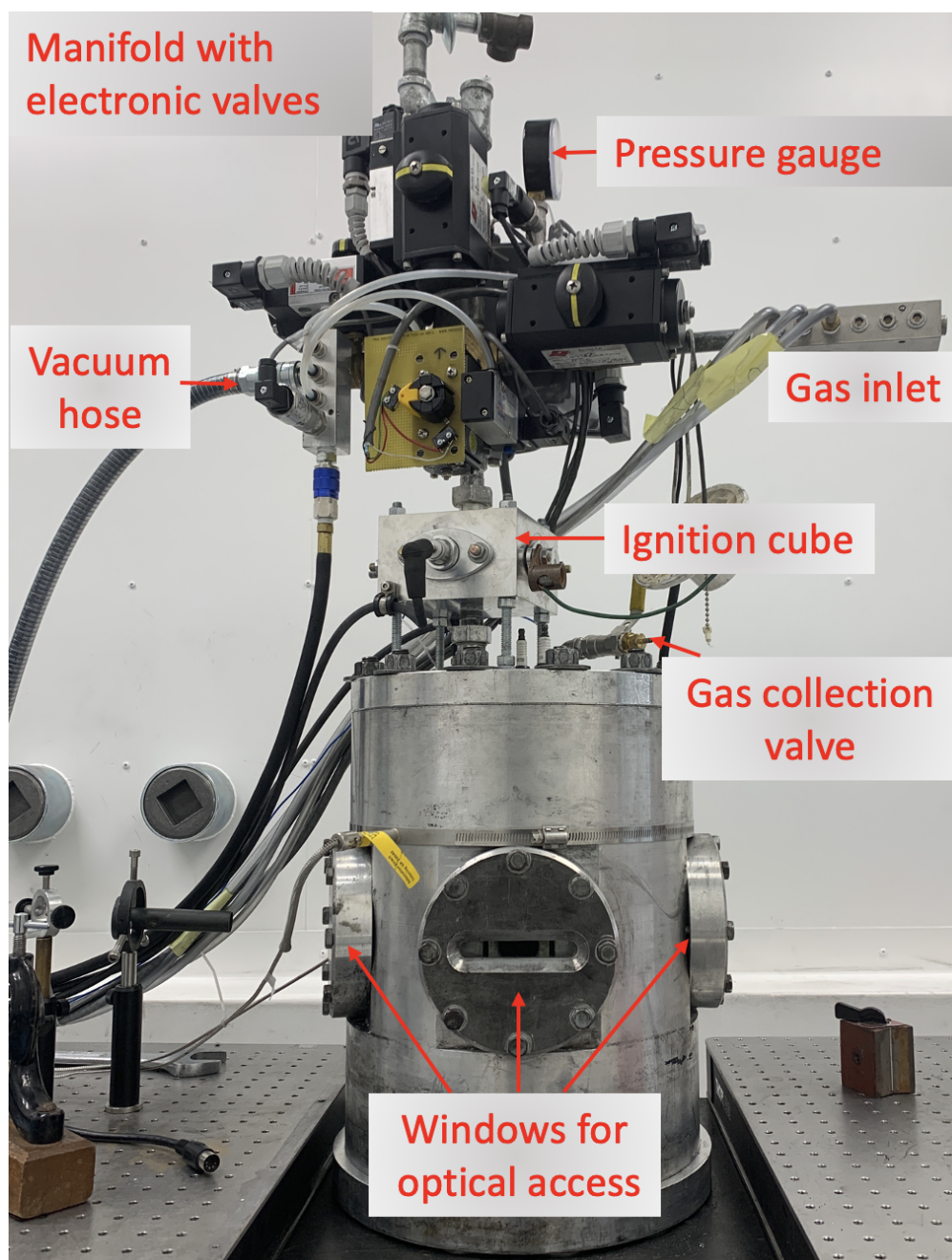


Figure 2.4: 17 L explosion chamber. The accessories of the chamber are labeled with red text and arrows.

scattering. On the opposite, if an electron cloud loses energy and the scattered photon gains energy, it is called anti-Stokes Raman scattering. Both Stokes and anti-Stokes are equally favorable processes. Because most molecules are in the ground vibrational level, Stokes scattering is a statistically more probable process than anti-Stokes. As a result, the Stokes

Raman scattering is always more intense than the anti-Stokes, so Stokes–Raman scattering is measured in Raman spectroscopy.

Raman is one of the most important measurements to characterize carbon materials. In the Raman spectrum of graphene, the D, G, and 2D bands are prominent features that provide valuable information about graphene’s structural properties [26, 31–33]. These bands arise from different vibrational modes and electronic transitions within the carbon lattice [32, 33].

The D band is located at a lower wavenumber (typically around 1340–1350 cm^{-1} and is associated with defects, disorder, and structural imperfections in the graphene lattice. It arises due to the breathing mode of sp^2 carbon atoms in a hexagonal lattice. When the lattice contains defects or disorder, such as vacancies or grain boundaries, this mode becomes Raman active, leading to the appearance of the D band. The D band intensity is often used to indicate the degree of disorder in graphene, as higher defect concentrations result in a more prominent D band peak.

The G band is located at a higher wavenumber (around 1580 cm^{-1}) and is the most prominent feature in the Raman spectrum of graphene. It arises due to the E_{2g} phonon mode, which involves in-plane bond stretching of the sp^2 carbon atoms in the graphene lattice. The G band is a characteristic signature of sp^2 carbon-carbon bonds and indicates the overall graphitic nature and quality of graphene.

The 2D Band is positioned at a higher wavenumber than the G band (around 2700 cm^{-1}) and is unique to graphene and other two-dimensional materials. It arises due to the second-order double resonance process and is associated with a two-phonon process that involves two in-plane optical phonons with opposite momentum. The 2D Band is highly sensitive to the number of graphene layers. In monolayer graphene, the 2D Band is a single sharp peak, but in multi-layer graphene, additional peaks can be observed due to interlayer coupling effects.

All the graphene samples produced in this study exhibit a disordered or imperfect atomic arrangement in their layers, commonly known as turbostratic graphene layers. In traditional layered graphene, layers are arranged in Bernal (ABA) and Rhombohedral (ABC) stacking

[34]. However, in turbostratic graphene, the layers are stacked more randomly or misaligned, leading to a less structured and more disordered configuration [34]. Despite its imperfect structure, turbostratic graphene retains some remarkable properties, making it a subject of interest for various nanotechnology and materials science applications.

Raman spectroscopy analyses were conducted in two different devices, Thermo Fisher Scientific DXR Raman (532 nm, laser power = 10 mW, 10X magnification) and using an Invia Reflex Renishaw micro spectrometer equipped with an argon laser ($\lambda = 532$ nm, laser power = 1 mW). We used a 100X objective (NA = 0.90). The author performed the measurements using these instruments.

2.4 X-Ray powder diffraction

X-ray crystallography is a technique to determine a crystal's atomic and molecular structure [35]. Crystal atoms scatter incident X-rays primarily through interaction with the atoms' electrons. This phenomenon is known as elastic scattering. A regular array of scattering electrons produces a regular array of spherical waves. In most directions, these waves cancel each other out through destructive interference. However, they add constructively in a few specific directions, as determined by Bragg's law: $2d\sin\theta = n\lambda$, where n is any integer λ is the wavelength of the X-ray, d is the distance between diffracting planes, and θ is the glancing angle.

X-rays are used to produce the diffraction pattern because their wavelength, λ , is the same order of magnitude as the spacing, d , between planes in a crystal. The diffraction peak depends upon numerous factors; for example, a more crystalline sample has more prominent diffraction peaks. Typical X-ray diffraction is recorded as 2θ (angle between incident and scattered X-rays). From the peak position and the full width at half maximum (FWHM) of diffraction peaks, we can obtain information like the lattice parameters, the average spacing between layers, crystallite size, their orientation, and the crystal structure of an unknown substance.

Like Raman, XRD can differentiate other carbon forms from graphite based on the diffrac-

tion peak position and shape [36]. All samples in this study were measured with D8 Advance Diffractometer Bruker with $\text{CuK}\alpha$ source of 0.154 nm and exhibit asymmetric (sharp increase at a lower angle side and gradual decrease at a higher angle side) of the (100) and (110) diffraction peaks in the XRD spectrum, which is also known as Warren effect.

2.5 Brunauer–Emmett–Teller (BET) specific surface area (SSA) measurement

The BET is a technique to measure the SSA of porous solid materials using the nitrogen (N_2) adsorption-desorption technique [37]. The analysis method includes passing the known amount of pure N_2 gas into the sample tube and recording the volume of gas adsorbed at different relative pressure P/P_0 (saturation pressure compared to the equilibrium pressure). Throughout the analysis, the sample tube is at liquid N_2 bath 77 K. Before analysis, the samples were vacuum degassed at 350 °C for 10 hours to remove the moisture and free the pores. After finishing the measurement, we will get a complete isotherm of adsorbed volume versus relative pressure.

The inbuilt software then calculates the SSA using the monolayer region of the isotherm and the BET equations. The monolayer adsorption pressure ranges between 0.05–0.3 for most carbon-related materials [37]. We can get other information from the BET measurement, like the pore volume, pore size distribution, and mean pore size. The pores play a crucial role in determining the total surface area of the nanoparticles, which are categorized based on their size into micro, meso, and macro pores. Micro pores are generally less than 2 nanometers in size, while meso pores are in the range of 2 to 50 nanometers. These pores are found within the internal structure of nanoparticles and contribute significantly to their specific surface area. Macro pores are relatively larger, typically larger than 50 nanometers in diameter. These pores are present on the external surface of nanoparticles and are responsible for gas penetration into the interior of the particles during the BET measurement.

All carbon samples in this work were measured using Quantachrome Autosorb iQ with

an N₂ bath at 77 K.

2.6 Transmission electron microscopy (TEM)

TEM is an imaging technique used to observe a sample at the nanoscale level. It relies on a stream of electrons emitted from a source, passes through a sample, and is detected. TEM provides information about the structural morphology of the sample, crystal structure, and the number of layering in a layered sample. Like Raman, TEM can also distinguish soot and layered graphene.

High-resolution TEM was performed at the Microscopy and Analytica Imaging Research Resource Laboratory (MAI) at the University of Kansas. Measurements were performed on a Hitachi H-8100 (200 keV) on copper grids. Measurements were also taken with a CM-100 (100 keV) TEM instrument here at K-State.

2.7 X-ray photoelectron spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a surface-sensitive analytical technique used to determine materials' elemental composition and chemical state. It provides valuable information about the elements present in a sample and their oxidation states by analyzing the energies of photoelectrons emitted from the sample's surface. When X-rays of sufficient energy are directed at a material, they can cause the ejection of electrons from the atoms' innermost energy levels (core levels) in the sample. This process is known as the photoelectric effect. The ejected photoelectrons carry information about the energy levels of the core electrons and are characteristic of the element from which they originate. A specialized instrument called an XPS spectrometer is used to detect and analyze the emitted photoelectrons. The XPS data is presented as a spectrum of electron counts (intensity) as a function of binding energy.

Each element in the sample contributes to the spectrum with characteristic peaks corresponding to different core levels. We can identify the elements present by analyzing the peak

positions and intensities and gain insights into their chemical states. In the XPS spectrum of graphene, the peaks labeled as C1s, N1s, and O1s correspond to the core-level photoelectron peaks of carbon (C), nitrogen (N), and oxygen (O) atoms, respectively, present in the graphene sample. These peaks provide valuable information about the elemental composition and chemical states of these elements in the material

C1s Peak:

- The C1s peak represents the photoelectrons emitted from the 1s core level of carbon atoms in the graphene lattice.
- The position (binding energy) and shape of the C1s peak can provide information about the different carbon species present in the sample, such as sp² hybridized carbon atoms in the graphene lattice or other carbon-containing functional groups.
- In the case of graphene, the C1s peak is typically used to identify the graphitic carbon species and can give insights into the material's quality and level of graphitization.

N1s Peak:

- The N1s peak corresponds to the photoelectrons emitted from the sample's 1s core level of nitrogen atoms.
- If the graphene sample is functionalized with nitrogen-containing groups, such as nitrogen-doped graphene, the N1s peak will appear at a characteristic binding energy, reflecting the chemical state of nitrogen in the material.

O1s Peak:

- The O1s peak represents the photoelectrons emitted from the 1s core level of oxygen atoms in the graphene sample.
- Oxygen can be present in graphene in different forms, such as oxide groups (e.g., C=O) or hydroxyl groups (e.g., -OH), which can be identified and characterized based on the position of the O1s peak in the XPS spectrum.

XPS analysis of all samples in this study was done in the Surface and Material Characterization Facility, University of Nebraska-Lincoln.

2.8 Other characterization tools

Thermogravimetric analysis (TGA) was done in Shimadzu TGA-50 Analyzer to determine the thermal stability of carbon samples. During the measurement, the sample was heated from 25 to 600 °C at the rate of 10 °C/min in a nitrogen atmosphere. Fourier transform infrared spectroscopy (FTIR) analysis and gas chromatography (GC) was done to measure the component of product gases in Agilent Cary 630 FTIR spectrometer and gas chromatograph model 310 configured with a traditional 4-filament Thermal Conductivity Detector that can heat to 275 °C, respectively. Dynamic light scattering (DLS) was used to measure the primary particle size, shape, and size distribution of the carbon sample. Carbon samples were dispersed in dimethylformamide (DMF) and measured using a 532 nm laser and ALV 5000 correlator.

Chapter 3

Aromatic hydrocarbons

This chapter will explore the experiments conducted on liquid aromatic hydrocarbons and the subsequent characterization of the resulting carbons. It will cover a paper submitted to the journal Carbon Trends.

3.1 Introduction

Graphene is a single layer of carbon atoms arranged in a hexagonal honeycomb lattice. It has excellent mechanical, electrical, thermal, and optical properties [38]. Because of these outstanding properties, it has the potential for many technological uses. The extraordinary characteristics of graphene originate from the 2p orbitals, which form the π bond that delocalizes over the sheet of graphene [39]. Although Single Layer Graphene (SLG) is ‘ideal’ graphene, few-layered graphene also keeps the properties of SLG. According to the ISO standard, “few-layer graphene” is 3–10 carbon layers [40]. Moreover, the Graphene Council states that the characteristics of graphene are retained in structures comprising as many as 34 carbon layers [13]. Depending upon the applications, the type of graphene also varies. For example, pristine SLG is used in applications such as computer chips, transistors, transparent conductors, etc. [10, 12]. Few-layer and multi-layer graphene flakes have an application in mixing with composite fillers, lubrication, conductive coatings, batteries,

supercapacitors, etc.[10, 12]. The lack of high-quality graphene on an industrial scale limits the use of graphene to exploit its unique properties. The primary methods for the bulk production of graphene are chemical vapor deposition (CVD) and exfoliation of graphite using the Hummers’ method [12, 41, 42]. Although the CVD method produces high-quality graphene, the need for a high-temperature furnace, a controlled environment for graphene growth, and difficulty in removing grown graphene from the substrate make up-scaling this process expensive and challenging [17]. Producing graphene from graphite to graphene using Hummers’ method followed by reduction requires many harsh chemicals (hydrazine), and undesirable byproducts are formed along with graphene [20]. So, it is not environmentally friendly.

We have developed a unique method for synthesizing multi-layer graphene nanosheets [21–24]. This method involves a controlled explosion of gaseous hydrocarbon in a multi-liter chamber, resulting in high-quality multi-layer graphene. Explosion synthesis is based on the notion that high-temperature conditions are crucial for forming graphene. Previous work by our team revealed that a critical factor for synthesizing graphene is a high temperature of 3000 K [21, 23]. In a separate study, Kim and colleagues used a laser-enhanced acetylene diffusion flame to generate a distinctive graphene-like carbon called “shell soot” at 3200 K [25]. More recently, rapid joule heating [43] has been utilized to create high-temperature conditions that can produce graphene.

Our explosion process is scalable, cost-effective, and eliminates the need for post-synthesis purification. Gaur et al. and Syed et al. have demonstrated in their recent research that the multi-layer explosion graphene can be utilized to manufacture micro-supercapacitors [44] and serve as a cathode catalyst for lithium-oxygen batteries (LOBs) [45]. The work presented here will focus on producing multi-layer graphene via the explosion of aromatic hydrocarbons at varying oxygen-to-carbon ratios. Additionally, the impact of the peak explosion temperature on the morphology of the resultant carbon sample will be examined.

3.2 Materials and Methods

3.2.1 Hydrocarbons precursors

The precursor materials, namely benzene, toluene, and xylenes were obtained from Acros Organics with a purity of 99.9%, while oxygen, with a purity of over 99%, was purchased from Matheson gas.

3.2.2 Experimental chamber

The experiment was conducted in a 17-liter cylinder made of 2.54 cm thick aluminum, with a height of 37 cm and an internal diameter of 24 cm. Additional details regarding the chamber and its setup can be found in our previous work [21–24, 46].

3.2.3 Explosion method and data collection

During the experimental process, an electrical heating tape was wrapped around the chamber to heat it to a temperature of around 343–353 K. In a typical explosion, the preheated chamber was evacuated to 0.03 atm and filled with liquid hydrocarbons. The pressure change in the pressure gauge monitored the evaporation of liquid hydrocarbons. The rest of the chamber was filled with oxygen at up to 1 atm absolute pressure and ignited using an electrode at the chamber’s center. The explosion resulted in the formation of solid carbon particles due to the high pressure and temperature generated by the fuel-rich mixture. During the explosion, the incandescent light emitted from the hot carbon aerosol was collected through an optical fiber placed at one window of the chamber and transmitted to an Ocean Optics FX spectrometer in the range of 200–1000 nm. The spectrum so obtained was used to calculate the peak explosion temperature by fitting the Planck black body radiation law [29]. After the explosion, the over-pressurized gas in the chamber was collected in a Tedlar sample bag for gas analysis, while the remaining gas was vented into a fume hood. Once the explosion was completed, the chamber was allowed to cool down to room temperature, and the lid was removed to collect the sample. The sample mass and approximate volume were

measured, and the chamber was cleaned with acetone to prepare for subsequent explosions.

3.2.4 Materials characterization

The product collected after the explosion was a powder at high precursor gases O/C (≥ 1) and fluffy aerosol gel at low O/C (< 1) [47–49]. The yield decreases as oxygen content increases because more oxygen is available for carbon to form CO and CO₂. Table 3.1 shows the carbon mass produced, mass yield percentage, and peak explosion temperature for different hydrocarbon precursors and O/C ratios. The explosion temperature was calculated by fitting Plank’s blackbody radiation law on the collected spectra and found to be in the range 2000–2500 K. The carbon materials collected from the chamber were characterized in a number of ways. An Agilent Cary 630 FTIR spectrometer was used for Fourier Transform Infrared Spectroscopy (FTIR) analysis of the gaseous products. A Gas Chromatograph (Buck 310, Buck Scientific, East Norwalk, CT) was used for the gas analysis, which is equipped with a traditional 4-filament Thermal Conductivity Detector that can heat up to 275 °C. Raman spectra of all carbon samples were recorded using a DXR Raman microscope with a 532 nm (2.33 eV) laser. Quantichrome Autosorp iQ using liquid N₂ at 77 K was used to measure the Brunauer–Emmett–Teller (BET) specific surface areas (SSA). Prior to BET analysis, the sample was vacuum degassed at 350 °C for 10 hours. The SSA and pore size distribution were obtained from the linear region of adsorption-desorption isotherm using the BET equation. X-Ray Powder Diffraction (XRD) was carried out using a D8 ADVANCE diffractometer (Bruker, 0.154 nm). The powdered samples were uniformly placed in a plastic disc, and the data were collected using a step scan mode with a step size of 0.05 and a counting time of 1.6 s at each step. A comparison was made with graphite from Acros Organics. Shimadzu TGA–50 Analyzer was used to conduct Thermogravimetric Analysis (TGA) to determine the thermal stability of carbon samples. During the analysis, the sample was heated from 25 to 600 °C at 10 °C/min in a nitrogen atmosphere. High-resolution TEM characterization was performed at the University of Kansas’s Microscopy and Analytica Imaging Research Resource Laboratory (MAI) using Hitachi H-8100 (200 keV) on copper grids.

Precursors	O/C	Mass (g)	Yield(%)	Peak Temperature (K)
Benzene	0.8	3.12	23.7	2100
	0.96	0.75	6.6	2500
	1.2	0.02	0.2	N/A
Toluene	0.63	5.42	31.4	2100
	0.9	1.1	8.4	2400
	1.22	0.2	0.01	N/A
Xylenes	0.6	4.36	28.4	2000
	0.85	2.12	18.4	2100
	1.4	0.4	0.5	2440

Table 3.1: Mass, mass yield (%) and the peak explosion temperature for benzene, toluene, and xylenes precursors at different O/C ratios.

3.3 Results and Discussion

3.3.1 Temperature measurement during explosion

Spectroscopy is a non-intrusive technique that allows measuring high temperatures like those generated during explosions. The measurement technique is based on Planck's black body radiation law, which gives the spectral energy density $B(\lambda, T)$ as a function of wavelength λ that depends only on the body's temperature.

$$B(\lambda, T) = \frac{2hc^2}{\lambda^5} \left(\frac{1}{e^{\frac{hc}{\lambda kT}} - 1} \right) \quad (3.1)$$

Where h is the Planck's constant, c is the speed of light and k is the Boltzmann constant. Applying Wein's approximation, $hc \gg \lambda kT$, yields

$$B(\lambda, T) = \frac{2hc^2}{\lambda^5} e^{\frac{-hc}{\lambda kT}} \quad (3.2)$$

Now from the spectral energy density ratio at two wavelengths, λ_1 and λ_2 , separated by hundreds of nm, to avoid local spectral biases and molecular interference and rearranging the terms. We will get the temperature (T),

$$T = \frac{\frac{hc}{k} \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right)}{\ln \left(\frac{B_1}{B_2} \left(\frac{\lambda_1}{\lambda_2} \right)^5 \right)} \quad (3.3)$$

An optical fiber at one window of the chamber collects light during an explosion. It transmits that to the spectrometer. The light collection integration time can vary from 20 μs to 10 ms, with a 1.8 ms buffer time between each shuttered integration time. We calculated the peak explosion temperature from these spectra using the Planck’s black body radiation described above. Figure 3.1 shows a typical example of the spectrum of the light emitted as a function of time during an explosion, along with two Planck’s black body curves at $T = 2100\text{ K}$. The radiation intensity is smaller at the beginning because there is no carbon in the chamber. As carbon forms, the blackbody radiation from the incandescent carbon will increase. As time passes, carbon particles agglomerate into fractal aggregates that can form a gel, stick to the chamber wall, and settle at the bottom of the chamber, and cool off, all leading to a decrease in intensity. Each intensity curve is the average of the rapidly changing temperatures in the chamber over a time interval of 10 ms. At higher wavelengths, the spectrometer gets noisier making analysis difficult. Table 3.1 shows the peak explosion temperature of all hydrocarbons at different O/C ratios. At higher O/C ratios, the peak explosion temperature is higher due to the availability of more oxygen for the reaction, which makes the reaction more energetic. The explosion radiation collected from benzene and toluene at ($\text{O/C} > 1$) shows numerous emission peaks due to low or no carbon yield. Therefore, Plank’s black body radiation cannot be applied to get the explosion temperature, and such instances are marked as “N/A” in Table 3.1.

3.3.2 Gas chromatography (GC) and Fourier transform infrared spectroscopy (FTIR)

Figure 3.2 displays the FTIR and GC analyses conducted on a gaseous toluene product. According to the FTIR analysis, residual hydrocarbon is present in the gaseous product, along with hydrogen, carbon monoxide, carbon dioxide, and water vapor. Meanwhile, the GC analysis shows that the predominant gaseous products are a mixture of hydrogen and carbon monoxide, with a minor amount of carbon dioxide and water. Table 3.2 summarizes the GC findings for the product gas obtained from benzene and toluene explosion.

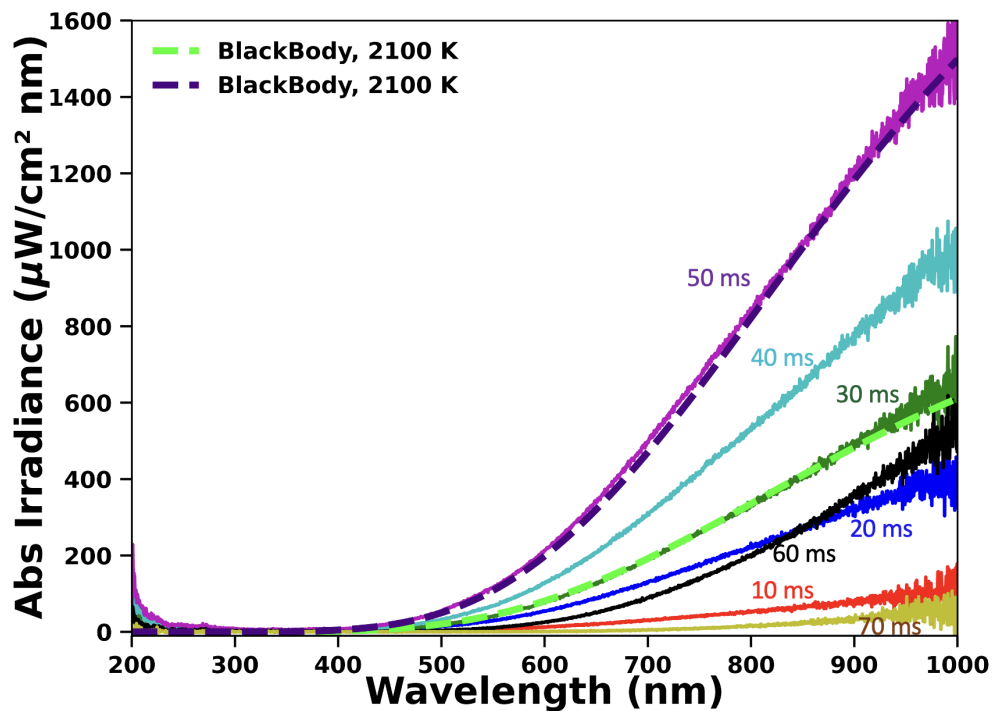


Figure 3.1: Blackbody spectra from an explosion of toluene at $O/C = 0.63$ mixture collected via the spectrometer along with two Blackbody curves at $T = 2100$ K for the direct comparison.

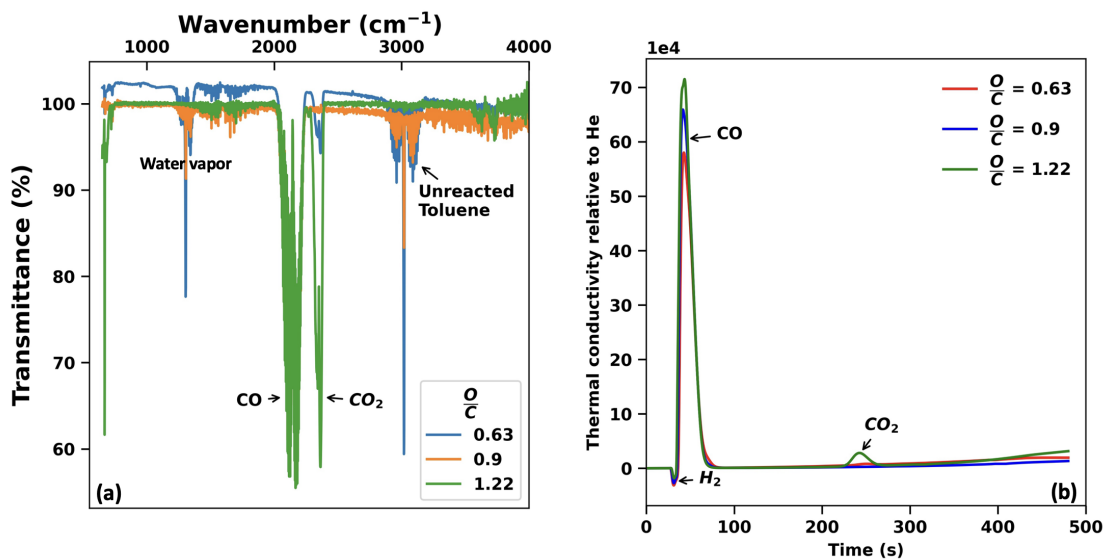


Figure 3.2: (a) FTIR of gaseous products and (b) GC analysis of the gaseous products from toluene at different O/C ratios, respectively.

Precursors	O/C	Measured gaseous products		
		H ₂ (%)	CO (%)	CO ₂ (%)
Benzene	0.8	39.5	55.1	0
	0.96	33.6	58.7	0
	1.3	30.6	59.7	6.9
Toluene	0.63	41.3	51.8	< 1
	0.9	35.9	59.9	0
	1.22	28.6	65.7	< 1

Table 3.2: Measured gaseous products from aromatic hydrocarbon explosions.

3.3.3 High-resolution transmission electron microscopy (HRTEM)

The prepared carbon samples' morphology and microstructure were investigated using HRTEM. Figure 3.3 and Figure 3.4 shows the HRTEM images of benzene and toluene precursor carbon samples. When the explosion temperature $T \leq 2100$ K (Figure 3.3a–c and Figure 3.4a–c), the primary particles are 20–30 nm round ball-like in shape and comprise of small graphitic domains commonly known as Basic Structural Units (BSUs) [50, 51]. These structures are arranged concentrically like onions. This structure is mostly similar to the soot [52]. However, at peak explosion temperature higher than 2400 K (Figure 3.3d–f and Figure 3.4d–f), the particles became graphitized and exhibit a layered structure with a size of 30–40 nm. This structure is consistent with folded sheets of multi-layer graphene. We hypothesize that the high temperature during explosion aided in the graphitization of small carbon nanoparticles into a layered structure.

Figure 3.5 shows the TEM image of the carbon sample from xylenes. Samples a–c at $O/C = 0.59$, and the peak explosion temperature was 2100 K, whereas d–f at $O/C = 1.4$ had a peak explosion temperature of 2440 K. Despite an increase in peak explosion temperature, the carbon produced from xylenes is soot. The primary particles are spherical 20–80 nm in size and lack layered structure.

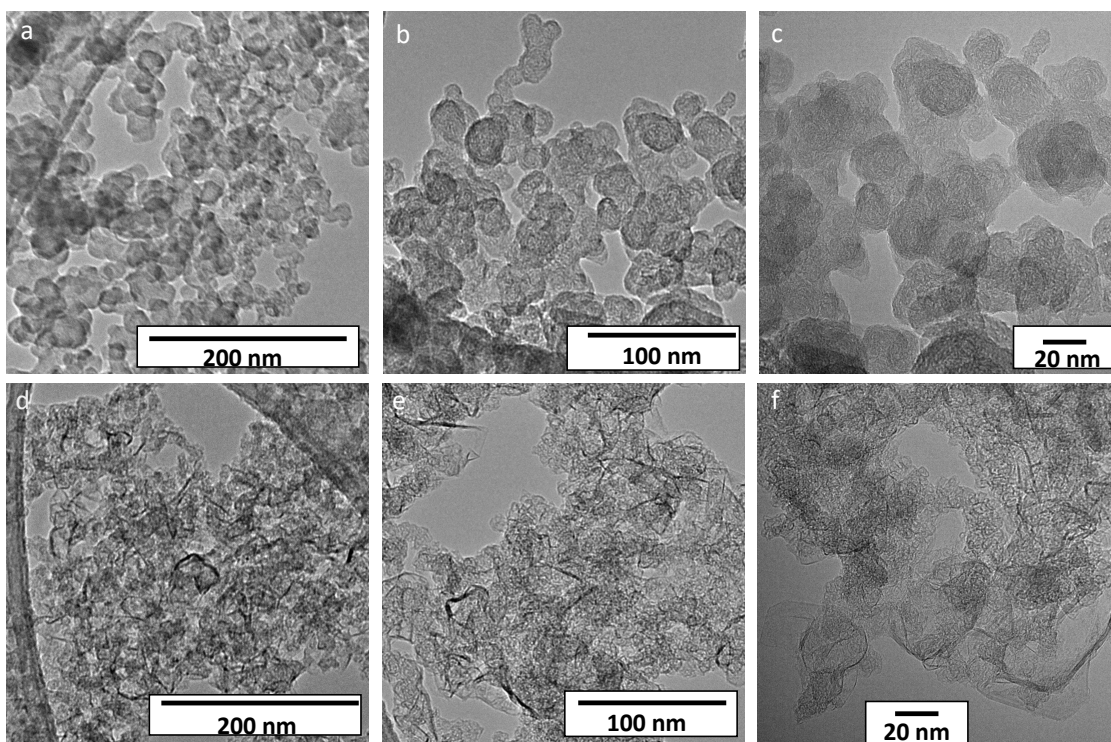


Figure 3.3: HRTEM of benzene carbon. Images (a–c) at an O/C of 0.8 and a temperature (T) below 2100 K. Primary particles are round ball-like shaped, resembling soot. Whereas images (d–f) at an O/C of 0.96 and a temperature above 2400 K. The primary particles are multi-layer, folded sheets of graphene.

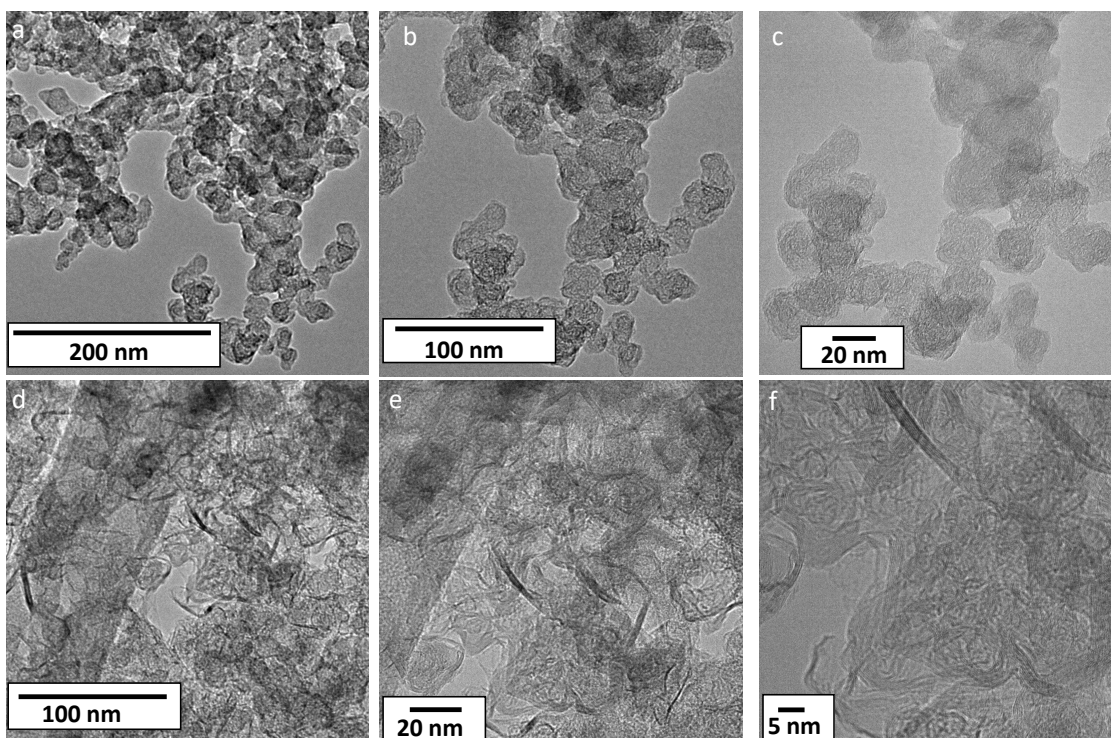


Figure 3.4: HRTEM of toluene carbon. Images (a–c) at an O/C of 0.8 and a temperature (T) below 2100 K. Primary particles are round ball-like shaped, resembling soot. Whereas images (d–f) at an O/C of 0.96 and a temperature above 2400 K. The primary particles are multi-layer, folded sheets of graphene.

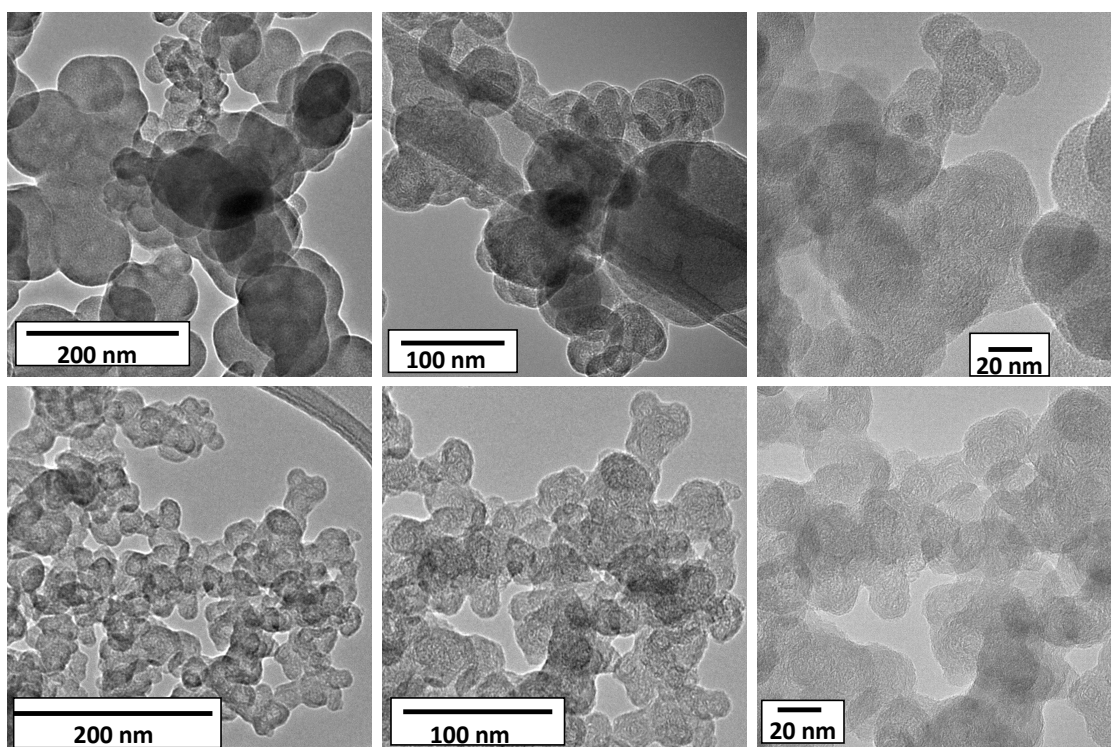


Figure 3.5: HRTEM of xylenes carbon. Images (a–c) at an O/C of 0.59 and a temperature (T) below 2100 K, while images (d–f) at an O/C of 1.4 and a temperature above 2400 K. Carbon sample at both O/C ratio and temperature is a round ball-like particle linked together in a chain-like structure resembling soot.

3.3.4 X-ray powder diffraction

The X-Ray Powder Diffraction (XRD) spectrum of all the carbon samples is shown in Figure 3.6. The Graphite from Acros Organics was also measured for the direct comparison. All samples exhibit a strong (002) peak at around 24.5–25° indicating the presence of a multi-layer structure [36]. The lower diffraction angle and the larger full width at half maximum (FWHM) of (002) peak than that of graphite is due to a small crystallite size [53]. The asymmetric nature of (100) and (110) peaks and the absence of (101) peaks suggest the existence of turbostratic graphene layers as implied by the Warren effect [54, 55]. The d-spacing (d) was determined using Bragg’s law (Eq. 3.4), and the crystallite size was obtained using the Scherrer equation (Eq. 3.5). By dividing the crystallite size (τ) by d-spacing (d), the number of layers was determined. Table 3.3 presents the values of the (002) peak’s position, its full width at half maximum (FWHM), the d-spacing, the crystallite size (τ), and the number of layers for all carbon samples. The number of layers for the soot sample is marked as “N/A” because it does not possess a layered morphology. The d-spacing of all carbon samples is larger than graphite ($2\theta = 26.4^\circ$ and $d = 0.336$ nm).

Bragg’s Law:

$$2d\sin\theta = n\lambda \quad (3.4)$$

Scherrer’s equation:

$$\tau = K\lambda/(\beta\cos\theta) \quad (3.5)$$

In equations 3.4 and 3.5, d is the interlayer spacing, K is a dimensionless shape factor = 0.89 for carbon, λ is the X-ray wavelength = 0.154 nm, θ is the (002) peak position, also called Bragg angle, β is the full width at half max of (002) peak and τ is the mean size of the crystallite domains.

The carbon sample from xylenes shows a narrower (002) diffraction peak, which occurs at higher 2θ values than the benzene and toluene carbons due to larger primary particles. These larger particles are also observable in the high-resolution transmission electron microscopy

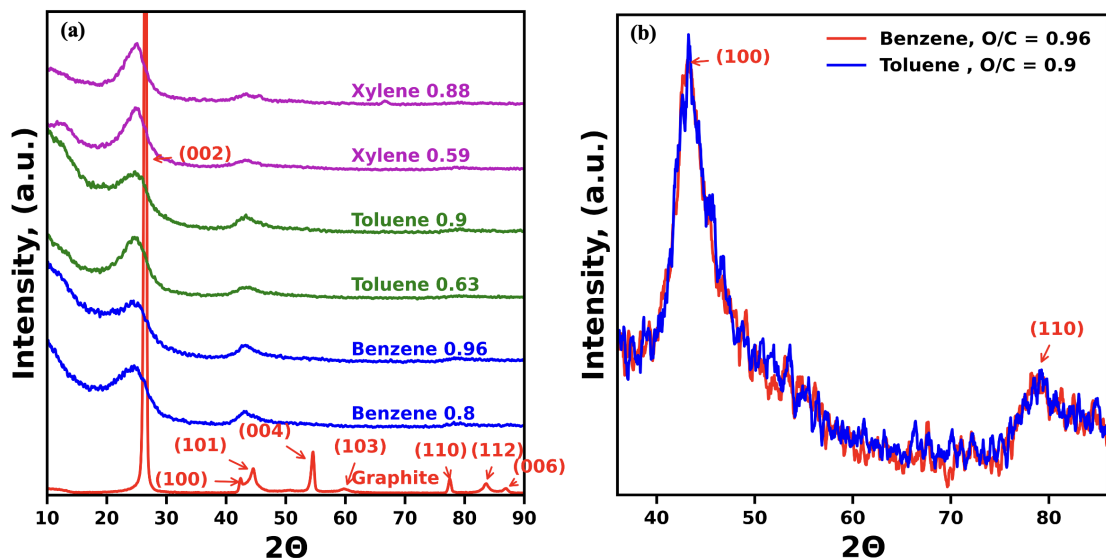


Figure 3.6: (a) XRD spectrum of all carbon samples compared with graphite. The (002) peak of carbon samples are scaled to be the same, (b) asymmetric (100) and (110) peaks show the Warren effect to imply the turbostratic nature of graphene samples.

Precursors	O/C	(002) peak position (2θ)	d-spacing (nm)	Crystallite size (τ) nm	Number of layers
Benzene	0.8	24.4	0.362	1.9	N/A
	0.96	24.7	0.363	2.3	6
Toluene	0.63	24.8	0.359	2.2	N/A
	0.9	24.6	0.362	2.3	6
Xylenes	0.6	24.9	0.357	2.3	N/A
	0.85	25	0.356	2.5	N/A
	1.4	25	0.356	2.5	N/A

Table 3.3: (002) peak position, d-spacing, crystallite size, and number of layers of different precursors carbon samples.

(HRTEM) images (Figure 3.5) and are reflected in the lower BET-specific surface area value (Table 3.4).

3.3.5 Raman spectroscopic analysis

Raman spectroscopy is the main characterization technique for materials closely related to graphene. Pristine single-layered graphene has a characteristic Raman spectrum that includes a G band at approximately 1580 cm^{-1} and a 2D band between 2660 and 2700 cm^{-1}

[33]. The G peak corresponds to the E_{2g} phonons of C sp^2 atoms. The Raman spectrum of graphite and multilayer graphene consists of D, G, and 2D, respectively. The D peak is a breathing mode of A_{1g} symmetry involving phonons near the K zone boundary and becomes active only in the presence of disorder. The 2D peak is the D-peak overtone. Both the D and 2D bands exhibit dispersive behavior, with their frequencies changing as a function of the energy of the incident laser [32, 33]. The intensity ratio of the D and G band, I_D/I_G , measures the degree of disorder and the average size of the sp^2 domains. The presence of a 2D peak in the Raman spectrum distinguishes graphene from the soot [56]. The position and the shape of the 2D peak can be used to differentiate between single, bilayer, and a few-layered graphene and graphite [32, 33]. The 2D peak for single-layer graphene can be represented by a single Lorentzian peak. As the number of layers increases, the 2D peak broadens and shifts to a higher wavenumber. In addition, it can be fitted into multiple Lorentzian [33]. Fig 3.7a,b shows the Raman spectra of different precursor carbon samples at different O/C ratios. We used Raman spectroscopy to assess the quality of the carbon samples at different O/C ratios and peak explosion temperatures. For carbon samples at $T < 2100$ K (benzene at O/C = 0.8 and toluene at O/C = 0.63), Figure 3.7a, b shows a small 2D band and overlapping D and G bands, indicating the sample was soot [56]. Contrarily, the carbon sample at $T > 2400$ K had a large 2D band. The valley between the D and G bands has decreased, indicating a multi-layer graphene nature. The position of D, G, and 2D bands at $1335\text{--}1340\text{ cm}^{-1}$, $1575\text{--}1582\text{ cm}^{-1}$, and $2665\text{--}2670\text{ cm}^{-1}$, respectively, is consistent with the literature [32, 33]. The large D band in our sample is due to the edge defects, which are numerous due to the nanometer-size primary particles. Raman analysis of xylenes carbon shows no visible 2D band at around 2670 cm^{-1} and the D and G bands overlap, resembling the spectra of soot [56].

Despite the multi-layer structure strongly evident in the HRTEM, the 2D Raman band of carbon sample for benzene at O/C = 0.96 and toluene O/C = 0.9 is a single Lorentzian similar to that observed in single-layer CVD graphene [57]. The reason for this is the lack of interaction or weak interaction between the stacked graphene layers, known as turbostratic (or misaligned) graphene. The two Raman peaks at around 1880 cm^{-1} and 2010 cm^{-1} ,

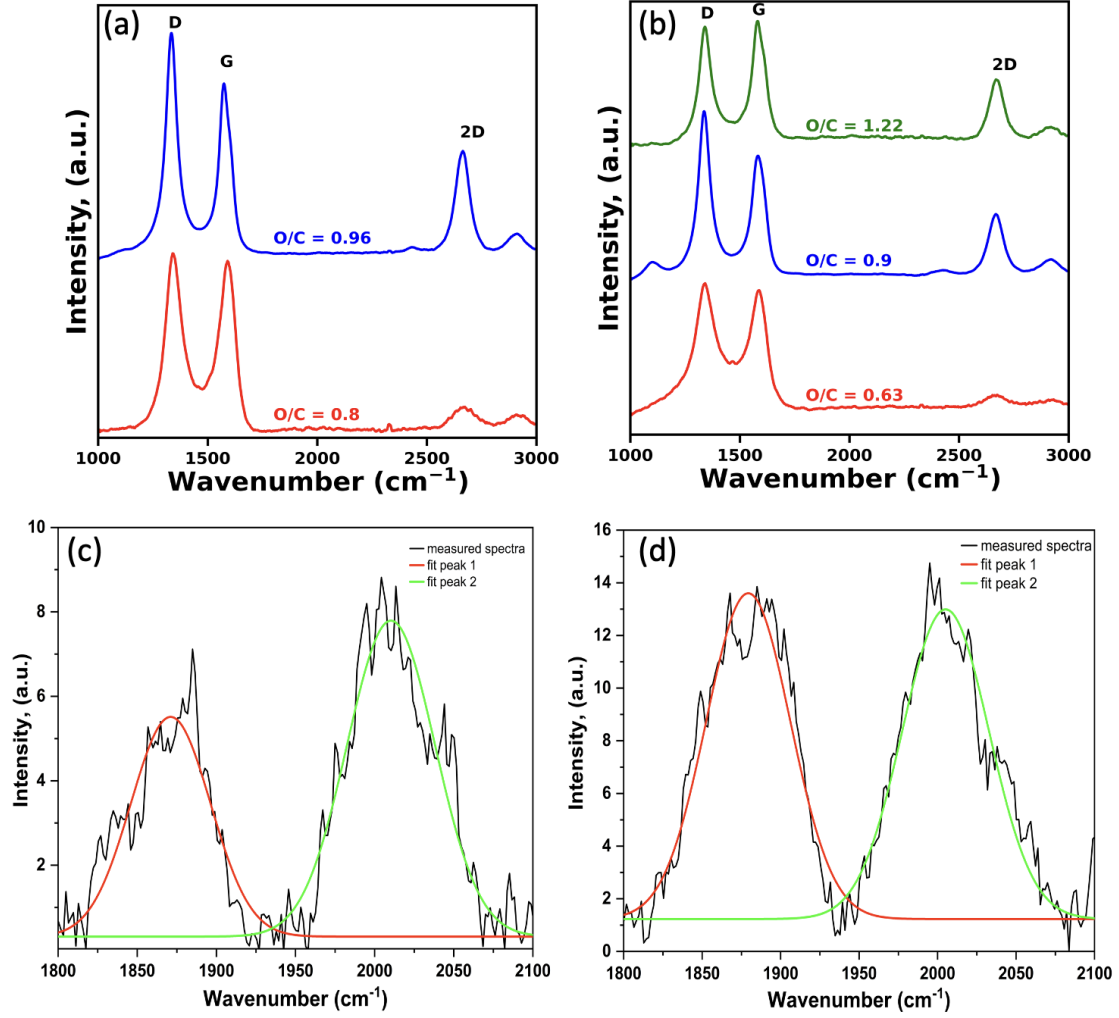


Figure 3.7: (a) Combined Raman spectra of all carbon samples and graphite for a direct comparison. G peak intensities are scaled to be the same. (b) 2D peak of benzene and toluene that produced graphene compared with the 2D peak of graphite. We can observe a significant peak shift. (c) Turbostratic peak of benzene, O/C = 0.96, and (d) Turbostratic peak of toluene, O/C = 0.9

(Figures 3.7c and 3.7d), further confirm the turbostratic nature of our (benzene O/C = 0.96 and toluene O/C = 0.9) samples [43].

3.3.6 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) shown in Figure 3.8 demonstrates that our samples are thermally stable up to 600 °C. No significant mass change indicates our sample could be pure carbon without any volatile impurities.

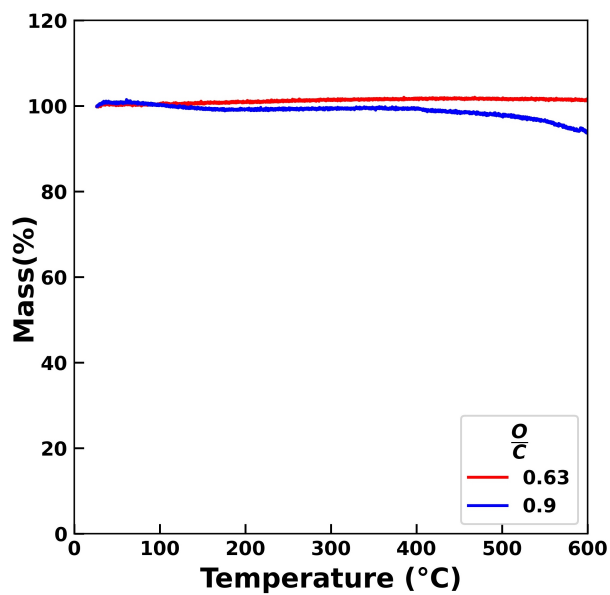


Figure 3.8: TGA of toluene Carbon at O/C = 0.63 and 0.9.

3.3.7 BET-specific surface area

Figure 3.9 shows the N_2 adsorption-desorption isotherm and the pore size distribution of two different carbon samples. The pores in solid materials are classified into three different categories: macroporous (> 50 nm), mesoporous (2–50 nm), and microporous (< 2 nm). The knee at lower pressure indicates the presence of micropores in the sample [37]. The hysteresis loop at higher pressure shows the presence of mesopores [37]. Table 3.4 summarizes the specific surface area (SSA) of all carbon samples at different O/C ratios. The higher SSA of the graphene sample compared to the soot sample could be due to the more exposed surface for gas adsorption because of their layered structure.

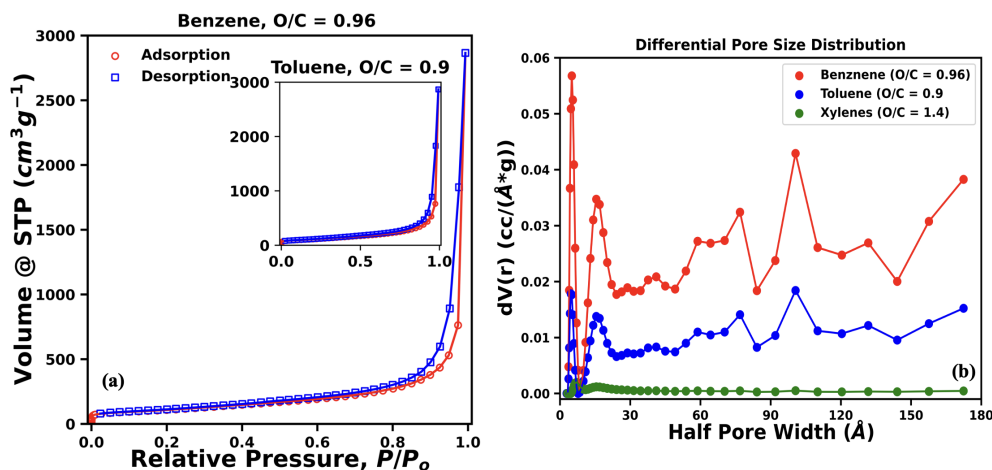


Figure 3.9: (a) Adsorption-Desorption isotherm of benzene carbon with toluene as inset, (b) differential pore size distribution of benzene and toluene carbons.

Precursors	O/C	Specific Surface Area (m^2/g)
Benzene	0.8	191
	0.96	391
Toluene	0.63	160
	0.9	385
Xylenes	0.6	32
	0.85	54
	1.4	32

Table 3.4: BET-specific surface area of benzene, toluene and xylenes carbon at different O/C ratios.

3.3.8 Graphene formation mechanisms

The immediate product of our explosion reaction is soot. The current understanding of the soot formation mechanism involves a chain reaction of resonance stabilized radical (RSR) via acetylene (C_2H_2) or vinyl (C_2H_3) addition, leading to the generation of larger RSRs. At suitable flame conditions, ca. 2000 K, a variety of hydrocarbons such as radicals, stable PAH, and unsaturated aliphatic species can cluster with RSRs, forming incipient particles. These incipient RSR moieties, with sizes ranging from 1–6 nm, undergo particle growth via clustering of hydrocarbons by radical chain reaction (CHRCR) to fully grown soot particles of size 10 to 50 nm [58].

In our experiment with three different aromatic hydrocarbons, benzene, toluene, and xylenes, with zero, one, and two methyl (CH_3) groups attached to the benzene ring, respectively, we observed two different temperature ranges and two different sample morphologies. The first one is when $T < 2100$ K, which is in the range of open flame temperatures, and the product of all these reactions is soot. The second is above 2400 K, which is higher than the open flame temperature, and leads to the production of multi-layer graphene flakes for benzene and toluene but not for the xylenes. The carbon formed with xylenes, which has two methyl groups attached to its aromatic ring, is soot at all temperatures. Based on these observations, we hypothesize that the high temperature during the reaction and the lower H/C ratio of precursor hydrocarbons, benzene, and toluene, are the key factors responsible for graphene formation. The first law of thermodynamics explains the high temperature observed in our explosions. The first law of thermodynamics can be written as

$$Q = \Delta U + P\Delta V \tag{3.6}$$

In Eq. 3.6 Q is the heat created by the combustion reaction, ΔU is the change in internal energy of the gas, P is the pressure and ΔV is the change in the gas volume. At constant pressure, e.g., an open flame,

$$Q = nC_v\Delta T_p + P\Delta V, \tag{3.7}$$

where n is the number of moles, C_v is the heat capacity at constant volume, and ΔT_p is the change in temperature during a constant pressure reaction. However, our chambers are constant volume, then.

$$Q = nC_v\Delta T_p \quad (3.8)$$

where ΔT_v is the change in temperature during a constant volume reaction. The heat Q generated by the chemical reaction is the same at constant P or V . Then comparison of Eqs. 3.7 and 3.8 show that $\Delta T_v > \Delta T_p$. The constant volume chamber produces no mechanical work so that all the heat makes the system hotter. With this argument, for a diatomic gas, one can show that $\Delta T_v = (7/5)\Delta T_p$.

We propose that at this higher temperature, the amorphous soot formed in the chamber is converted (graphitized) to graphene. This crystal domain growth at high temperature has been seen in other studies [26, 59, 60]. For example, Weisenberger et al. [59] and Pawlyta et al. [26], heat-treated commercial, amorphous carbon black at a temperature above 2400 °C. This caused the sample to crystalize to a graphite-like structure. Abrahamson et al. [60] used a CW CO₂ laser to anneal amorphous carbon black at 2600 °C. This process resulted in a morphological transformation from soot to a graphitized layered structure.

This constant volume, higher temperature, soot crystallization mechanism also explains our previous work describing multi-layer graphene produced from acetylene (C₂H₂) and ethylene (C₂H₄) at higher explosion temperatures [22, 24]. However, it does not explain the non-crystalized, amorphous soot formed from the xylenes precursor at similar high temperature. Nor does it explain our unpublished observation [22, 24] that despite a higher explosion temperature of over 2500 K, propane (C₃H₈) only led to soot formation. Based on these observations, we can conclude empirically that too many methyl groups impede the formation of graphene during the explosion process. The reason for this remains for future research.

3.4 Conclusion

The results of this study demonstrate that fuel-rich mixtures of aromatic hydrocarbons with oxygen can be subjected to an explosion in a multi-liter chamber to yield graphene, with some limitations. Specifically, benzene and toluene generated soot at lower explosion temperatures, 2100 K, and multi-layer graphene at higher temperatures, 2400 K, while xylenes did not yield graphene even under the same high explosion temperatures. This correlation to create soot rather than graphene with increasing methyl groups was found with aliphatic fuels as well. Further investigation is necessary to determine the underlying factors responsible for this trend.

Analysis of the produced carbon using various techniques, including Raman, TEM, and XRD, revealed the formation of two distinct carbon types: soot and multi-layer graphene. The resulting graphene is a fractal aggregate aerosol gel [49]. The monomers of this gel have approximately six weakly associated, disordered turbostratic graphene layers and a 20–40 nm lateral size. The graphene produced is thermally stable up to 600 degrees Celsius, making it suitable for high-temperature applications. Notably, the specific surface area of the graphenes produced with these aromatic precursors were as much as a factor of two larger than those we produced with aliphatics [21, 23]. The high specific surface area and high porosity of the graphene suggest its potential as a promising candidate for electrochemical applications [61, 62]. We hypothesized that the high explosion temperature during the constant volume reaction is the primary reason for forming graphene rather than soot.

The findings of this research are vital in understanding the explosion synthesis of graphene, with the possibility of far-reaching effects in developing new materials using this method.

3.5 Acknowledgements

The authors gratefully acknowledge financial support from Hydrograph Clean Power Inc. We also thank Dr. Prem Thapa Chettri, from the University of Kansas, for the TEM measurements.

Chapter 4

Other gaseous hydrocarbons

This chapter focuses on the morphology of carbon samples from acetylene and ethylene precursors. Previous work from our group [21, 23] was focused on the explosion at $\text{O}_2/\text{C}_2\text{H}_2 > 0.25$. This is an extension of that work in the low oxygen regime, i.e., $\text{O}_2/\text{C}_2\text{H}_2 < 0.25$ and 100% acetylene.

4.1 Acetylene

4.1.1 100% acetylene using an electromotive spark plug

During the experiment, the explosion chamber was evacuated to 0.03 atm. In order to decrease the residual air left due to an imperfect vacuum, the chamber was filled with acetylene (C_2H_2) and vacuumed again. Subsequently, the chamber was once again filled with C_2H_2 and ignited using an electromotive spark plug at the top of the chamber. Despite the attempt, the mixture did not ignite. Efforts were made to ignite the mixture at higher pressures of 1.25, 1.5, and 1.75 atm, but these attempts were unsuccessful as well. Although pure acetylene did not ignite at room temperature and higher pressures, a minute amount of carbon was formed at the tip of the spark plug. We hypothesized that the ignition energy was insufficient to ignite the entire mixture, resulting in only the acetylene near the spark plug's tip being burned. Figure 4.1 shows the spark plug after ignition and the Raman

spectra of the collected carbon. The small 2D band and the overlapping D and G bands in Raman spectra indicate the carbon formed is soot [56].

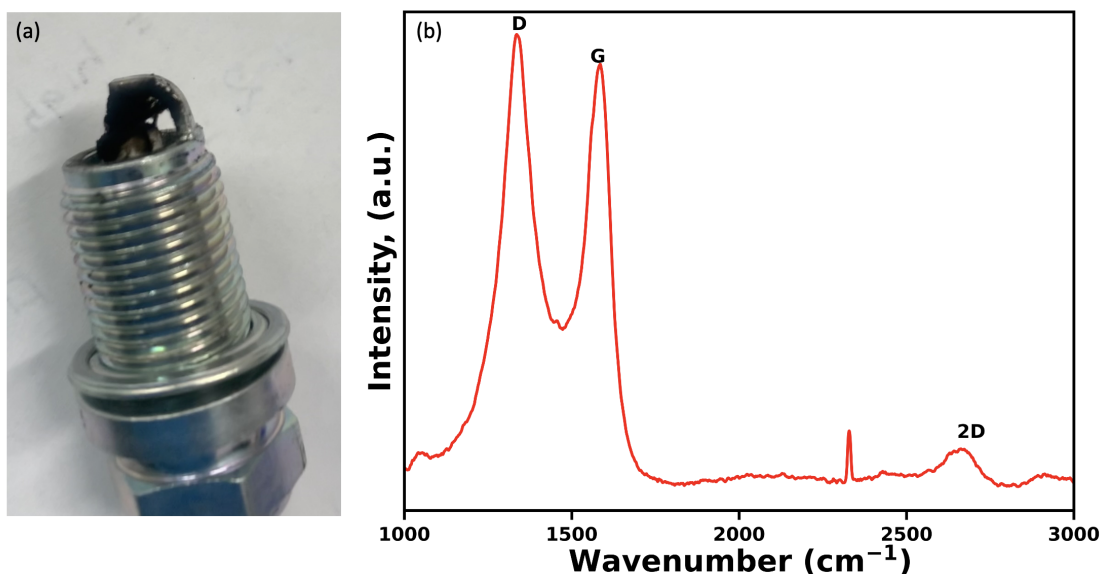


Figure 4.1: (a) Spark plug with carbon at the tip, (b) Raman spectra of carbon from the spark tip. The Raman shows a tiny 2D band and a significant overlap of the 2D band, a characteristic of soot.

4.1.2 100% and lower O/C acetylene using an electric matchstick

We changed the ignition source from a spark plug to an electric matchstick to increase the ignition energy. An electric matchstick contains explosives at its tip and is designed to ignite when exposed to standard wall voltage. Upon ignition, it produces a substantial flash that spreads throughout the chamber. In contrast, the spark generated by a spark plug remains confined primarily to its tip. During the experiment, the pre-evacuated chamber was filled with the different oxygen-to-acetylene mixtures and ignited using an electric matchstick. The electric matchstick was fired using wall voltage. The oxygen-to-carbon ratios studied were 0 (100% acetylene), 0.05, 0.1, 0.15, and 0.2. Black and fluffy carbon material in the form of aerosol gel was collected after each explosion. Figure 4.2 shows the image of the flowmeter, experimental chamber, matchstick, and carbon formed after an explosion.

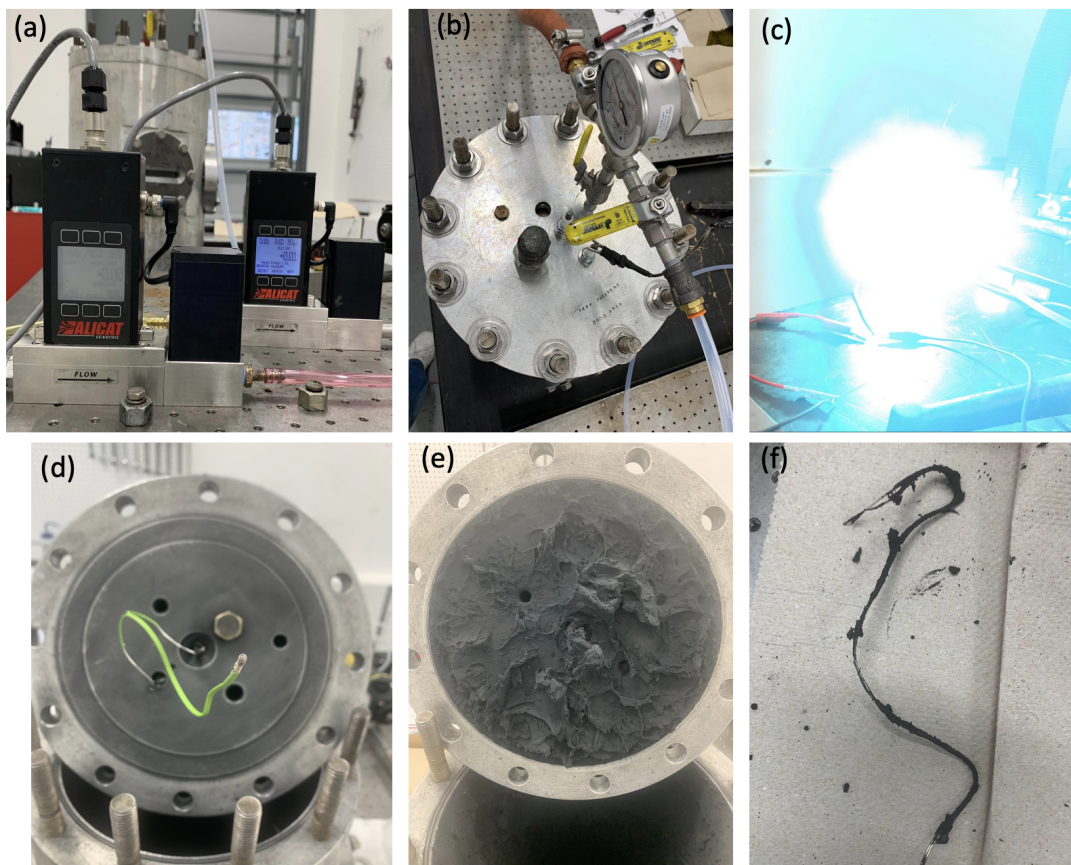


Figure 4.2: (a) Electronic flow meter, (b) experimental chamber setup, (c) fully fired electric matchstick, (d) electric matchstick setup inside the chamber lid, (e) chamber lid with fluffy black carbon formed after an explosion, and (f) remain of the matchstick (not burned completely during an explosion).

4.1.3 Acetylene and oxygen (O/C from 0.25–0.75)

This O/C ratio range and the low O/C we discussed in section 4.1.2 combine to form a complete description of the acetylene precursor. The necessary data for some of the O/C ratios in this range is used from the work of Justin Wright with his permission. The carbon produced from each explosion was collected, and the chamber was cleaned using a paper towel and acetone for subsequent explosions. The collected carbon sample was weighed to determine the mass yield. The peak temperature of the explosion was calculated by analyzing the spectra obtained during the explosion using Planck’s black body radiation. Figure 4.3a, b shows the sample spectra collected at $\text{O}_2/\text{C}_2\text{H}_2 = 0.6$, and Figure 4.3c shows the temperature at different O/C ratios. The peak temperature was measured in the 2400–

3100 K range, increasing with O/C. The maximum value was recorded at O/C = 0.7. During the low O/C acetylene explosion, the data acquisition control system, which was used to record data in previous experiments, was unavailable. As a result, we lack temperature data in this particular range. Table 4.1 shows the precursor ratio, the sample collected, and the mass yield of the carbon sample from the acetylene explosion. The mass yield decreases with increasing O/C. Also, the visual appearance of the carbon formed changes from black fluffy aerosol gel to grey powder at higher O/C. The yield at 100% acetylene is slightly lower, probably because all acetylene did not react completely. Further characterizations like Raman, XRD, BET, and TEM were done to fully understand the morphology of the carbon formed during an explosion.

O/C	C ₂ H ₂ (L)	O ₂ (L)	Sample collected (g)	Yield (%)
0	17	0.58	2.67	87
0.05	16.2	0.8	2.09	95
0.1	15.45	1.55	1.74	90
0.15	14.78	2.22	1.41	85
0.2	14.16	2.84	1.27	81
0.25	14.16	2.84	8.76	68
0.3	14.16	2.84	8.14	65
0.35	14.16	2.84	6.97	58
0.4	14.16	2.84	6.68	58
0.45	14.16	2.84	5.65	51
0.5	14.16	2.84	4.84	45
0.6	14.16	2.84	3.33	33
0.75	14.16	2.84	1.76	19

Table 4.1: Precursor fill ratio, carbon mass collected, mass yield of carbon samples from acetylene explosion. The mass yield of carbon samples decreased linearly with O/C ratios, with the exception of 100% acetylene. This trend aligns with our findings, indicating that at higher oxygen content, carbon monoxide and carbon dioxide are produced at the cost of carbon, resulting in lower mass yields of carbon in the samples.

The Raman of the carbon from acetylene is shown in Figure 4.4 and graphite is also measured for direct comparison. The Raman spectra display the three bands, the D, G, and 2D bands. The 2D band of the acetylene sample is observed at a lower frequency of around 2670 cm⁻¹ compared to graphite at approximately 2715 cm⁻¹ [33]. Furthermore, the shape of the 2D band changes from a combination of multiple Gaussian to a single Gaussian, which

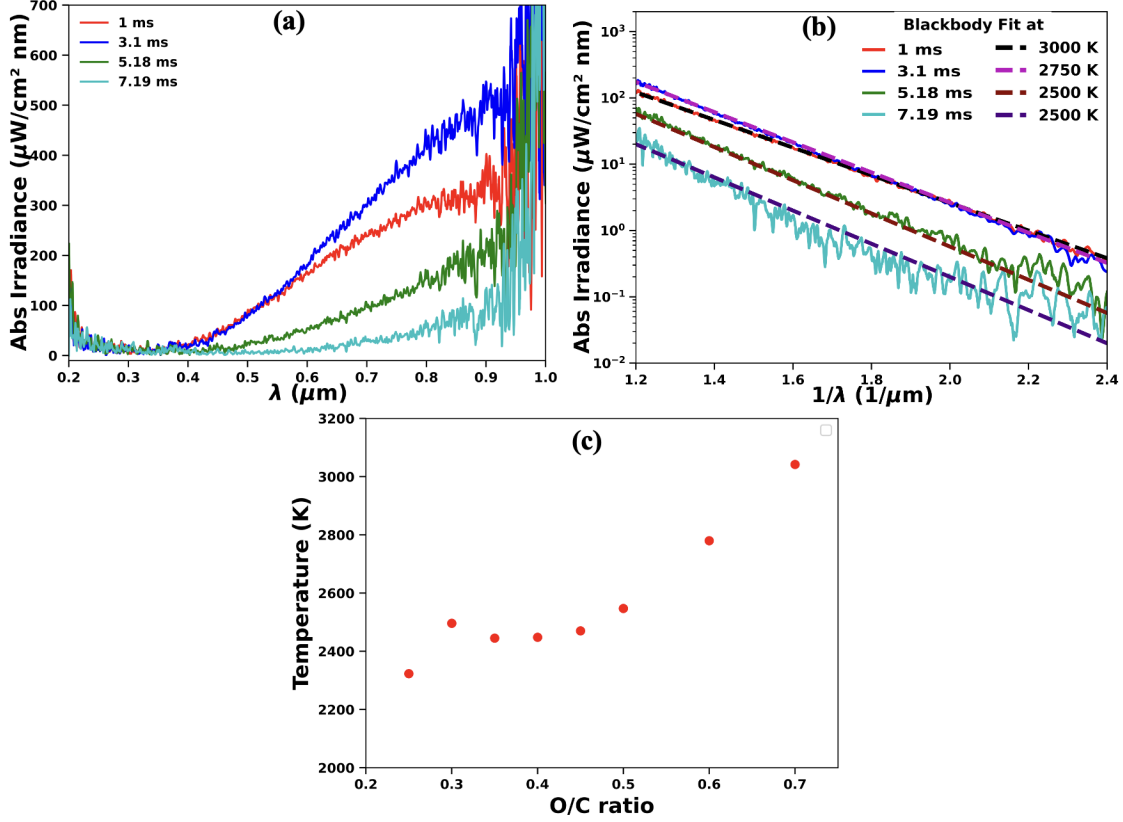


Figure 4.3: (a) Blackbody spectra from an explosion of O/C = 0.6 mixture collected via the spectrometer. The four lines increase in time with $\Delta t \sim 2.1$ ms between each line. (b) Linearized blackbody with four blackbody temperatures (dashed lines). (c) The peak explosion temperature from acetylene explosion at different O/C ratios. The peak explosion temperature increases with the O/C ratio.

is a distinct indicator of few-layer graphene [32, 33]. The presence of the D band suggests that the sample is nano-sized and has numerous defects. Increasing the O/C ratio results in an increase in the peak intensity ratio, I_D/I_G , which reaches its maximum value at O/C = 0.2. The intensity of the D band decreases from O/C = 0.25, and it remains constant after 0.5. The lower value of I_{2D}/I_G for O/C ratios less than 0.25 implies inferior graphene quality. Overall, the Raman spectra suggest that all samples are multi-layer graphene, with the highest defect density and smallest particle size observed at O/C = 0.2. Graphene quality is lower for O/C ratios less than 0.25, whereas ratios greater than 0.5 lead to a highly crystalline structure with a larger primary particle.

Figure 4.5 displays the X-Ray powder diffraction spectrum of all acetylene carbon. All

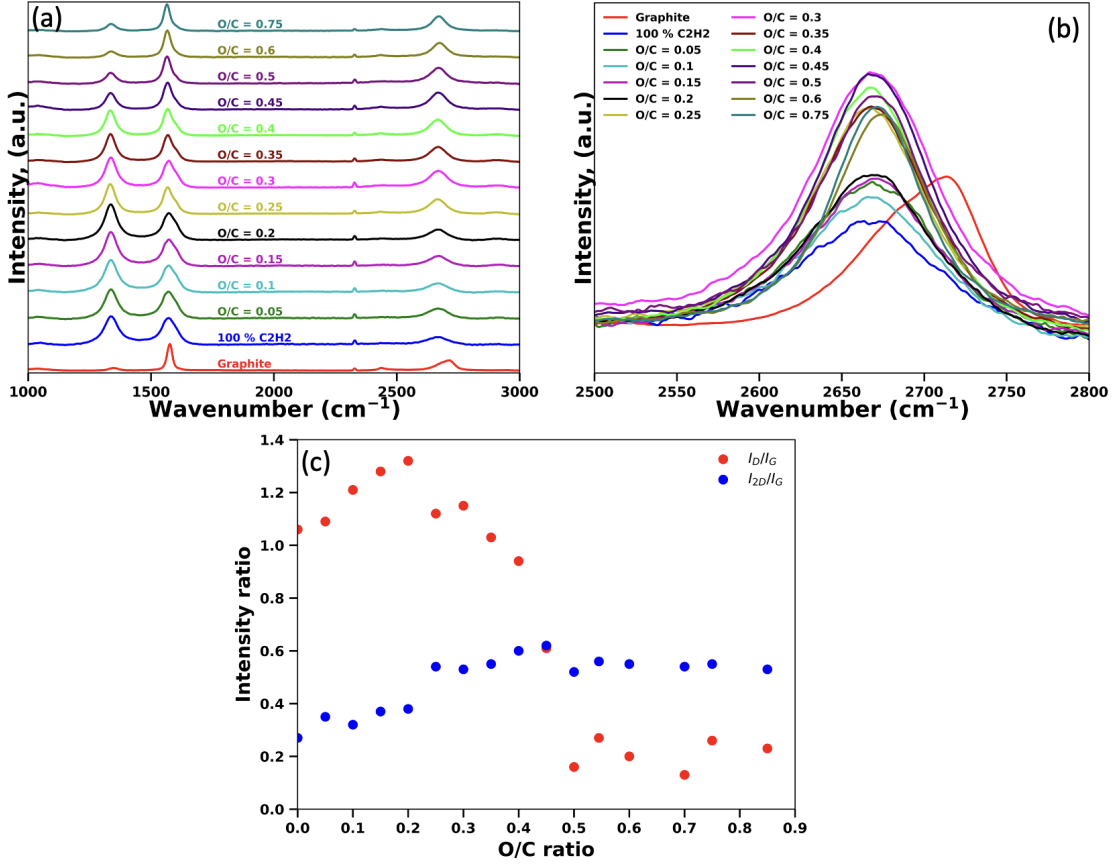


Figure 4.4: Complete Raman spectra of acetylene carbon, (a) Raman spectra compared with graphite, (b) 2D peak of all the carbon samples plotted along with graphite to see the shift in the band, and (c) intensity ratio of D, G, and 2D band for all acetylene carbon.

O/C ratio carbon samples exhibit a strong (002) diffraction peak, indicating the presence of a layered graphitic domain [53]. The asymmetric nature of the (100) and (110) peaks due to the Warren effect and the absence of the (101) peak suggests that the graphitic domains are turbostratically arranged with each other [54, 55]. Moreover, the diffraction peaks are more intense and narrower when O/C is greater than 0.5, implying strong ordering and a larger crystallite size. The (002) band is centered around $2\theta = 25.45^\circ$ for $O/C < 0.45$ and 25.8° for $O/C \geq 0.5$, yielding the interplanar spacing of $d = 0.351$ nm and 0.346 nm, respectively. These d-spacing values are larger than graphite's d-spacing ($2\theta = 26.4^\circ$ and d-spacing = 0.337 nm), indicating that the graphene layers are weakly interacting. Additionally, Table 4.2 provides a detailed calculation of the crystallite size (τ) and the number of layers in the carbon sample computed using the Scherrer equation.

Scherrer's equation is:

$$B(\tau) = \frac{K\lambda}{\beta \cos \theta} \quad (4.1)$$

where K is a dimensionless shape factor = 0.89 for carbon, λ is the x-ray wavelength = 0.154 nm, θ is the (002) peak position, also called Bragg's angle, β is the full width at half max of (002) peak and τ is the mean size of crystallite domains. Interpreting τ as the vertical height, we found the number of layers = $\frac{\tau}{d}$.

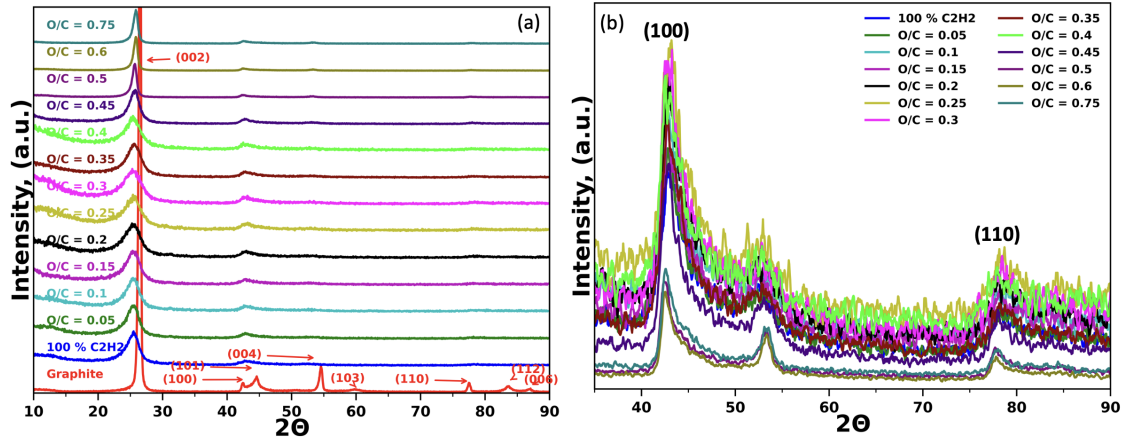


Figure 4.5: XRD of acetylene carbon samples prepared at different O/C ratios compared with graphite. The graphene spectra are normalized to have (002) peak intensity = 1, (a) combined XRD spectrum of all samples and graphite, (b) asymmetric (100) and (110) peaks to show the turbostratic nature of the carbon samples.

Figure 4.6, 4.7 and 4.8 shows the TEM images of carbon samples from acetylene at different O/C ratios. The sample at 100% acetylene and O/C = 0.05 shows the mixed morphology, soot, and graphene. As the O/C ratio increases, the quantity of soot in the sample reduces. The complete transformation from soot to graphene occurs at O/C = 0.1. For O/C ratios greater than 0.15, the sample consists entirely of multi-layer graphene. The next transition happens at O/C = 0.5, as seen in Figure 4.8d. An O/C ratio greater than or equal to 0.5 is called a “high O/C.” The graphene sample in this range has higher crystallinity and larger particle size (Table 4.2). Figure 4.8d shows the high-resolution TEM image of graphene at O/C = 0.5. The primary particles are 50–100 nm in size.

O/C	(002) peak position (2θ)	d-spacing (nm)	Crystallite size (τ) nm	Number of layers
0	25.45	0.350	3.58	10
0.05	25.45	0.350	3.58	10
0.1	25.45	0.350	3.45	9
0.15	25.45	0.350	3.16	8
0.2	25.45	0.35	2.92	8
0.25	25.45	0.35	2.78	8
0.3	25.45	0.35	2.55	7
0.35	25.55	0.349	3.18	9
0.4	25.4	0.351	3.07	9
0.45	25.7	0.347	4.43	13
0.5	25.7	0.347	10.08	29
0.6	25.86	0.345	10.76	31
0.7	25.8	0.345	10.35	30
0.75	25.75	0.346	9.49	28

Table 4.2: (002) peak position, d-spacing, crystallite size, and number of layers of acetylene carbon samples. All samples have d-spacing larger than graphite ($d = 0.337$ nm), indicating turbostratic graphene layers. The O/C greater than 0.5 has a larger crystallite size and a higher number of graphene layers.

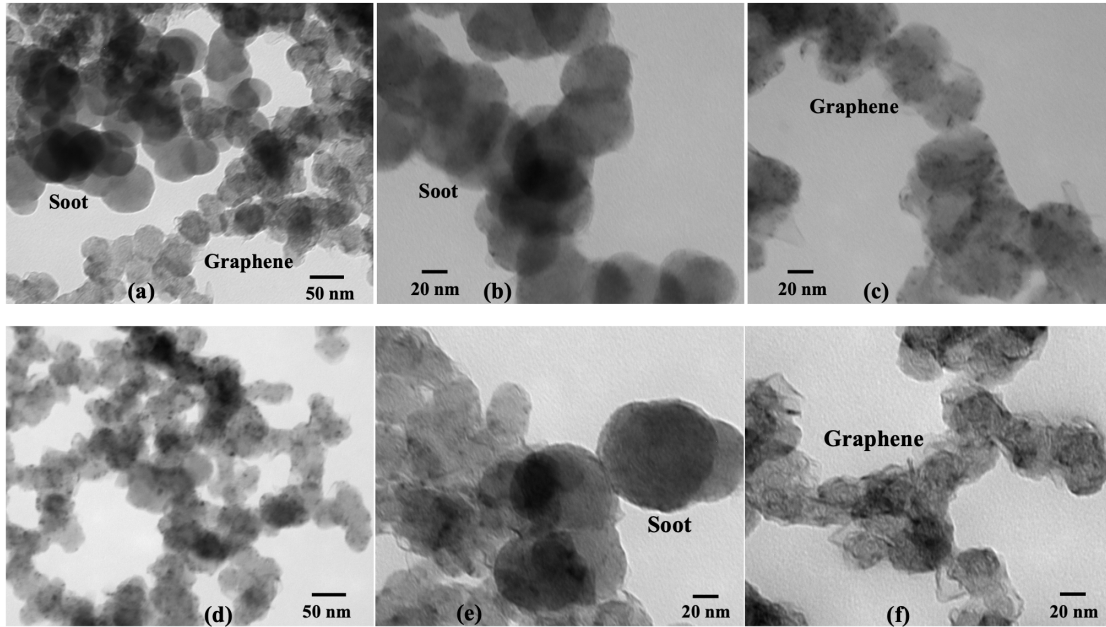


Figure 4.6: (a), (b) and (c) TEM images of carbon sample from 100% acetylene and (d), (e) and (f) at O/C = 0.05. Images show mixed carbon: graphene and soot are formed. Some particles are 20–90 nm round ball-like particles linked together in a chain-like structure resembling soot, while others are multi-layered, folded sheet structures characteristic of graphene. These findings are consistent with our observations that lower oxygen content favors soot formation.

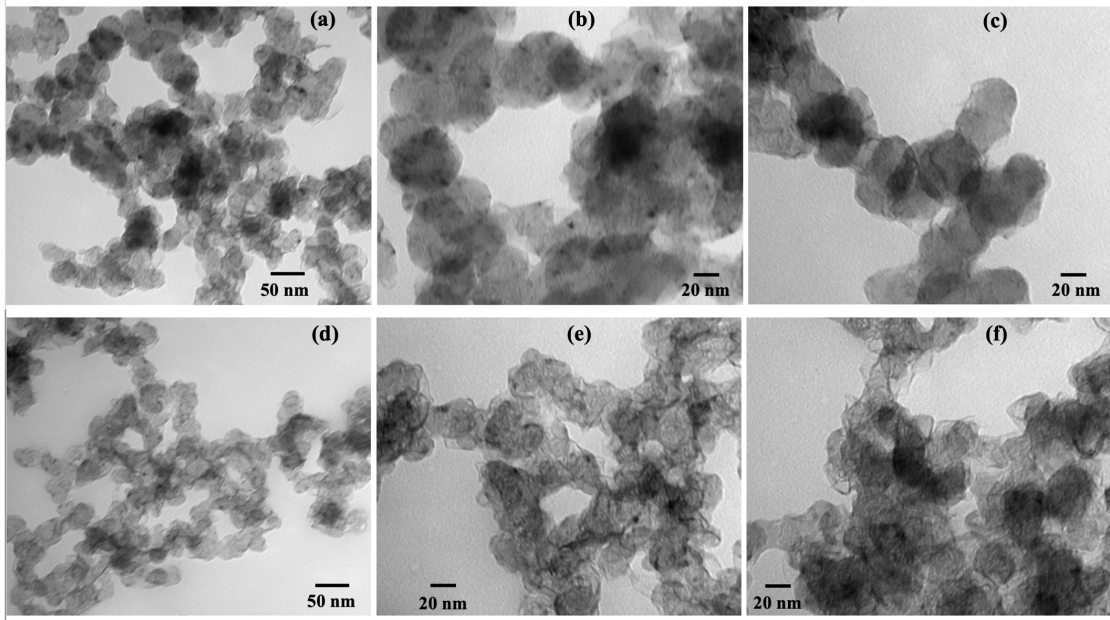


Figure 4.7: (a), (b) and (c) TEM images of carbon sample acetylene at $O/C = 0.1$ and (d), (e) and (f) at $O/C = 0.15$. The images show that the soot disappears. Only multi-graphene with folded sheet structures is present. These findings corroborate our observations, indicating that the increasing oxygen content favors graphene formation.

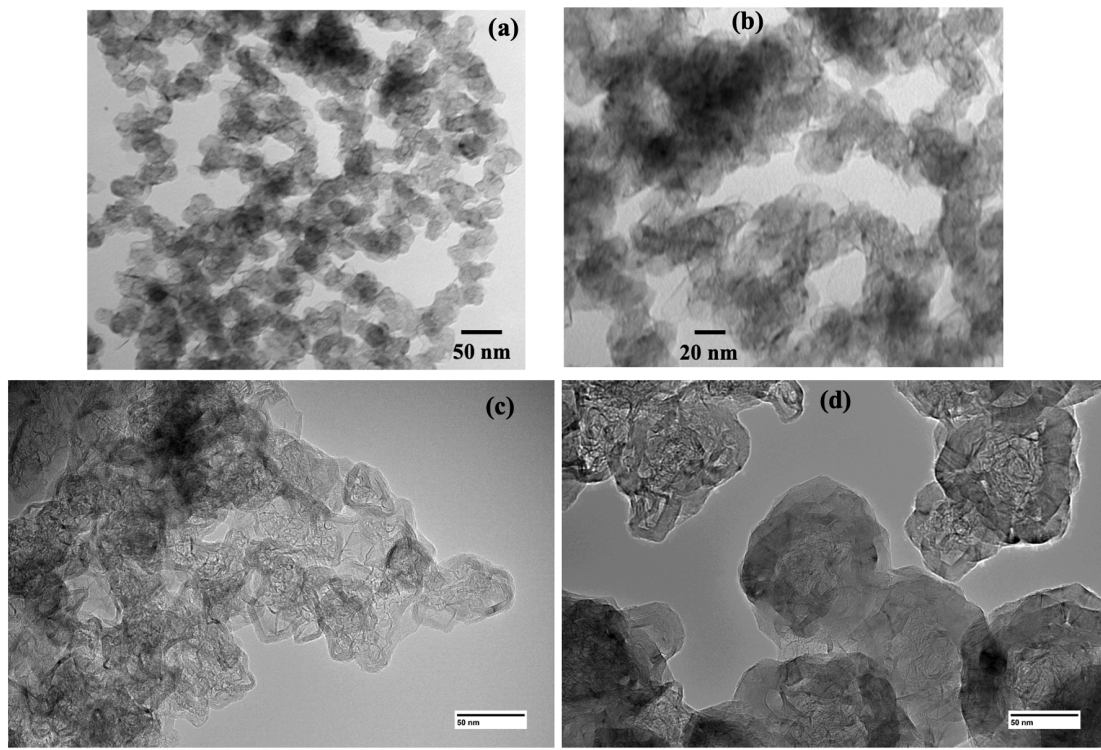


Figure 4.8: (a), (b) TEM images of carbon sample acetylene at $O/C = 0.2$. (c) at $O/C = 0.3$ and (d) at $O/C = 0.5$. All samples exhibit folded sheet multi-layer graphene structures. The samples at $O/C = 0.2$ and 0.3 display smaller primary particles and fewer layers, whereas the sample at $O/C = 0.5$ demonstrates larger primary particles, higher crystallinity, and a greater number of layers.

Figure 4.9 shows the Brunauer–Emmett–Teller (BET) specific surface area (SSA) of the acetylene carbon at different O/C ratios. The SSA increases as the O/C ratio rises, reaching its highest point at $O/C = 0.25$, and subsequently decreases. The peak SSA value observed at $O/C = 0.25$ can be attributed to the smaller size of the particles and their layered morphology. In contrast, lower O/C ratios result in a smaller SSA value, likely due to the presence of soot alongside graphene in the carbon sample. This can be observed in TEM images (Figure 4.6). The presence of spherical soot particles reduces the exposed surface area available for gas adsorption. A significant decline in the SSA value occurs for O/C ratios equal to or greater than 0.5, which can be attributed to the larger primary particles and a higher number of layers. This is supported by observations from Raman spectroscopy, XRD, and TEM (Figure 4.8 and Table 4.2).

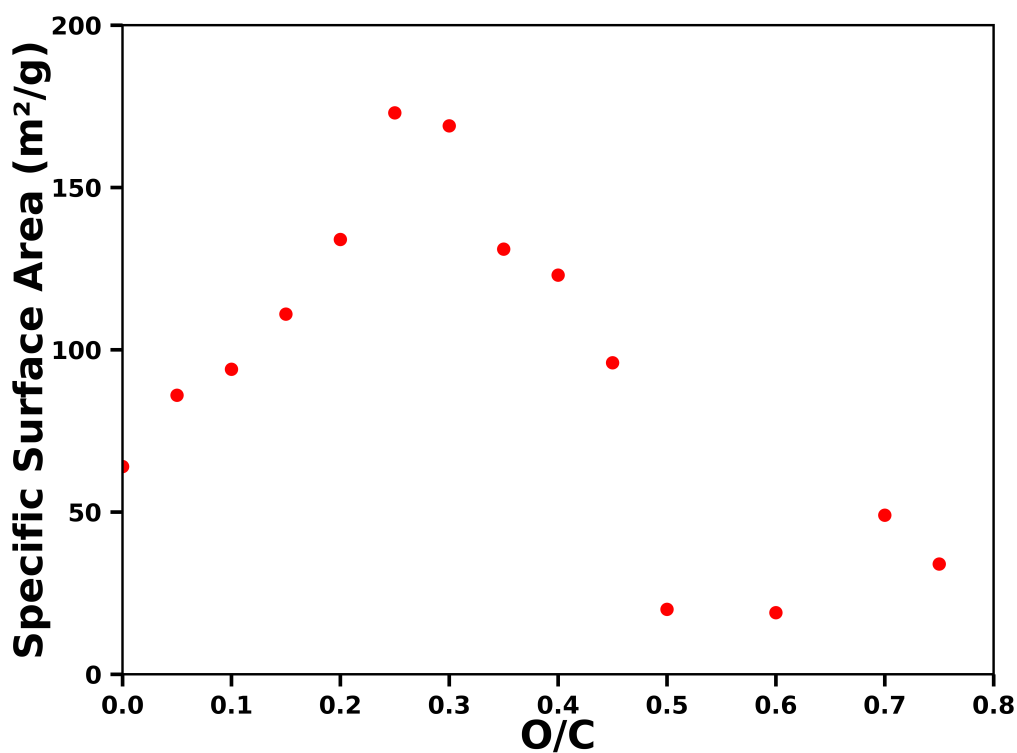


Figure 4.9: SSA of acetylene carbon vs. O/C ratio: Initially, as O/C increases, SSA rises, but at higher O/C, SSA decreases. These trends align with graphene TEM images. Lower O/C samples have soot and graphene mix with larger particles, reducing SSA. Increasing O/C leads to smaller particle sizes and increased SSA but at higher O/C, more layers form, increasing mass and decreasing SSA.

4.2 Acetylene, ammonia, and oxygen

In order to produce nitrogen-doped graphene, we introduced ammonia into the acetylene and oxygen explosion. Upon analyzing the spectra data for the peak temperature, we noticed significant decreases in temperature. As a result, we did a comprehensive characterization to determine the percentage of nitrogen doping and examine any potential changes in the morphology of the resulting carbon at lower reaction temperatures. We selected O/C = 0.3 and 0.5 for this experiment because they are our flagship low and high O/C acetylene samples. During an experiment, in addition to acetylene and oxygen, we introduced ammonia at 10%, 20%, and 30% of the total volume.

4.2.1 Experimental methods

After vacuuming the experimental chamber, a mixture of C_2H_2 , O_2 , and NH_3 was introduced and ignited using an electromotive spark plug. However, the O/C = 0.3 + NH_3 mixture did not ignite beyond 20% ammonia. The amounts of precursor used and the samples collected after each explosion are listed in Table 4.3. Although we could not collect data for other temperatures due to the poor timing of the spectrometer and an ignition source, we did record the peak explosion temperature for O/C = 0.5 + 20% NH_3 . Figure 4.10 displays the spectra and temperature of this explosion, which reached a peak temperature of approximately 2200 K, 400 K lower than the temperature without ammonia. Based on this result, we assumed a similar decrease in temperature for 0.3 + NH_3 . The physical appearance of the 0.3 sample did not show much change with and without ammonia, while the 0.5 O/C sample transformed from a greyish powder to a black fluffy aerosol gel with the addition of ammonia. Further characterizations of the collected carbon samples, such as Raman, XRD, TEM, and BET, will be discussed below.

O/C	C ₂ H ₂ (mol)	O ₂ (mol)	NH ₃ (mol)	Sample collected (g)	Yield (%)
0.3	0.46	0.14	0.07	7.05	64
0.3	0.41	0.12	0.14	5.46	55
0.3	0.36	0.11	0.21	N/A	N/A
0.5	0.36	0.18	0.14	3.45	40

Table 4.3: Precursor fill ratio, carbon collected and yield from acetylene, ammonia, and oxygen explosion.

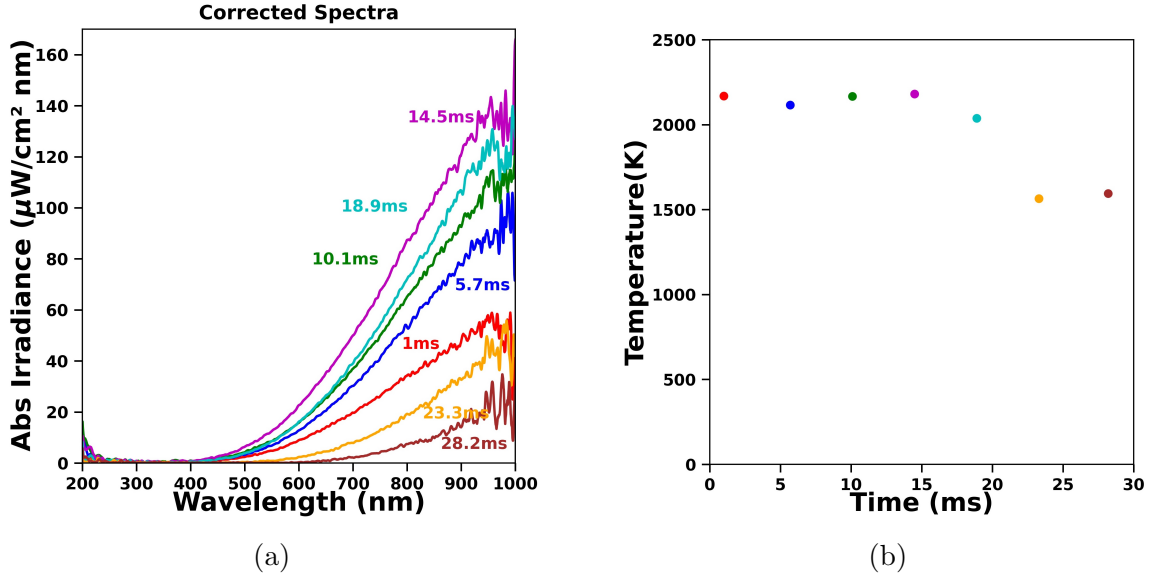


Figure 4.10: (a) Blackbody spectra of O/C = 0.5 + 20% NH₃, (b) peak explosion temperature vs. time, the spectra and the corresponding temperature are denoted by the same color.

4.2.2 TEM

The TEM imaging of the carbon formed is shown in Figure 4.11. The morphology of 0.3 carbon does not change much at 10% NH₃, but at 20% NH₃, the primary particles are now 20–30 nm spherical shaped, resembling soot [63]. So, decreasing peak explosion temperature changes the morphology of carbon samples from multi-layer graphene to soot. Similarly, the O/C = 0.5 carbon changed to a smaller particle with the addition of ammonia. The 0.5 + 20% NH₃ carbon is close to 0.3 with no ammonia rather than 0.5 carbon with no ammonia.

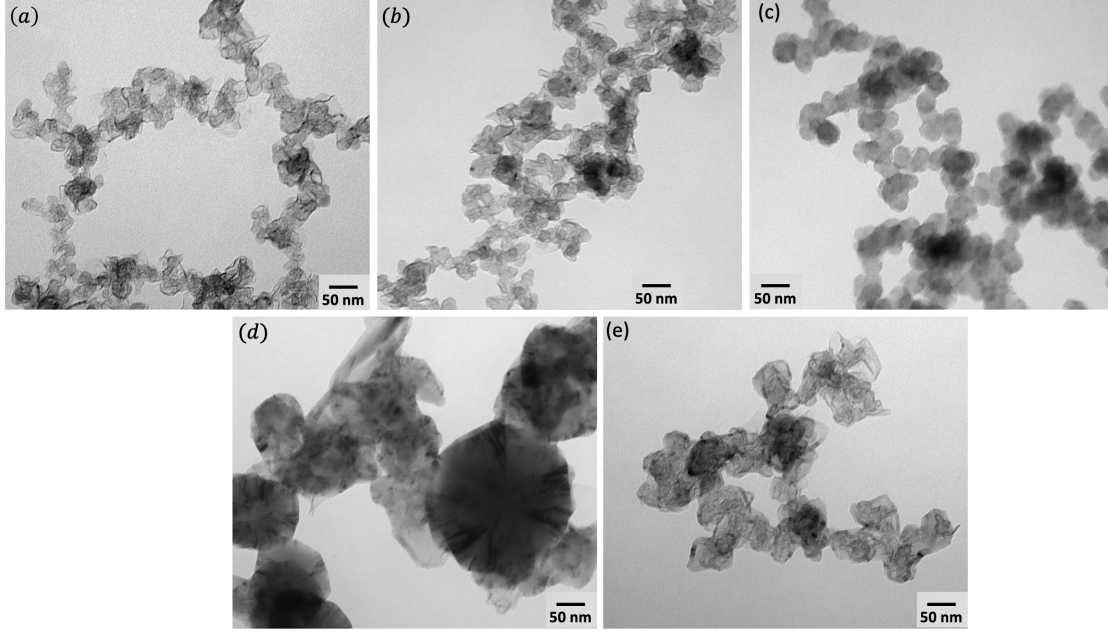


Figure 4.11: TEM images of carbon samples at different O/C ratios and ammonia concentrations are shown: (a) at O/C = 0.3, (b) at O/C = 0.3 + 10% NH₃, and (c) at O/C = 0.3 + 20% NH₃. At 10% ammonia, the sample displays folded multi-layer graphene. With 20% ammonia, it transforms into round ball-like soot. Images (d) and (e) show carbon at O/C = 0.5 and 0.5 + 20% ammonia, respectively. Primary particles change from larger, more layered structures to smaller, fewer layers. At 20% ammonia, O/C = 0.3 mixture forms soot due to decreased temperature, while O/C = 0.5 forms a sample similar to O/C = 0.3 without ammonia.

4.2.3 Raman

Raman spectra of the carbon formed are shown in figure 4.12. For the 0.3 O/C sample, adding ammonia changed the shape of the D, G, and 2D bands. With increasing ammonia, the intensity of the 2D band at 2670 cm⁻¹ decreases and eventually vanishes; also, the D and G bands overlap, which means the sample is soot [56]. For the 0.5 O/C sample, adding ammonia has a minor shift in the G peak location and a larger FWHM in the G peak. The peak ratio I_D/I_G has significantly increased, approaching 0.3 O/C samples with added ammonia, which signifies a higher degree of disorder and the presence of amorphous carbon [64].

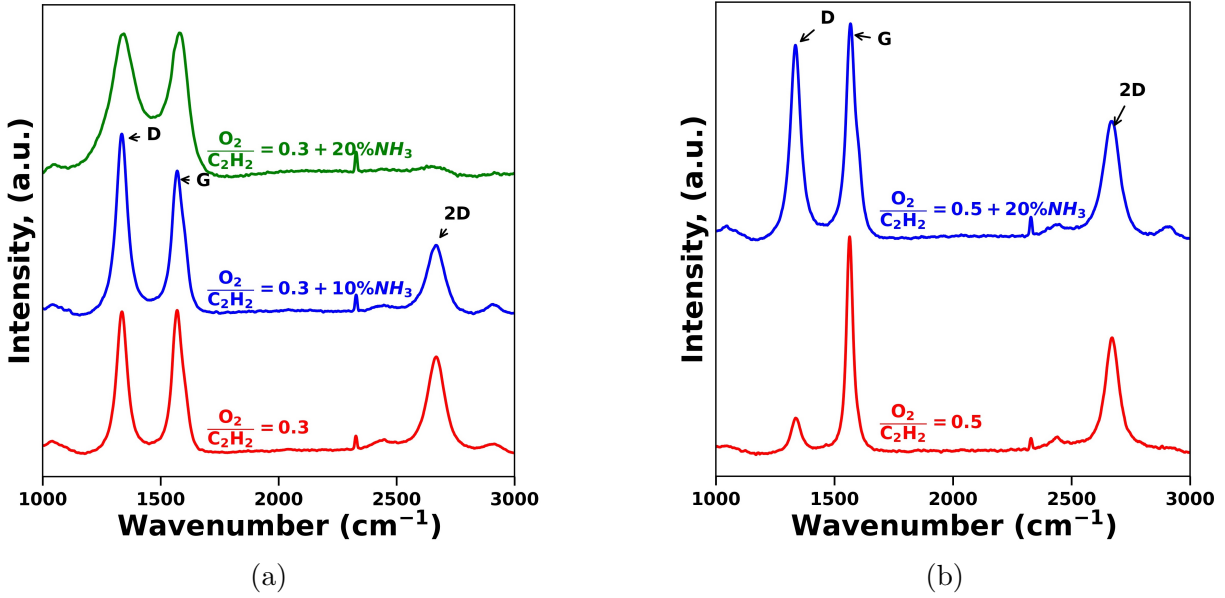


Figure 4.12: (a) Raman comparison of 0.3 samples with and without ammonia, (b) Raman comparison of 0.5 samples with and without ammonia. All graphs are scaled to have the same G peak intensity. At 20% ammonia, the 2D band of the 0.3 sample vanishes, and the overlap of the D and G bands increases, indicating the graphene-to-soot transition.

4.2.4 X-ray powder diffraction

Figure 4.13 shows the XRD of the ammonia added to the acetylene carbon samples. The 0.3 O/C + 20% NH₃ carbon appears slightly less crystalline than the original sample, with the (002) peak shifted to lower 2θ and increased FWHM. The 0.3 O/C + 10% NH₃ samples appear similar to the 0.3 O/C sample within experimental error. Adding 20% NH₃ to the 0.5 O/C, the carbon formed changed from the high O/C to low O/C properties with a broader (002) diffraction peak.

4.2.5 BET-specific surface area

The BET-specific surface area values reflect the morphology change observed in TEM, Raman, and XRD. When 20% ammonia is added to the 0.5 sample, the surface area increases from 20 m²/g to 110 m²/g. Additionally, the sample transforms from a grey powder composed of 50–100 nm primary particles to a black and fluffy aerosol gel consisting of primary particles sized 30–50 nm. Similarly, in the case of the 0.3 sample, the surface area decreases

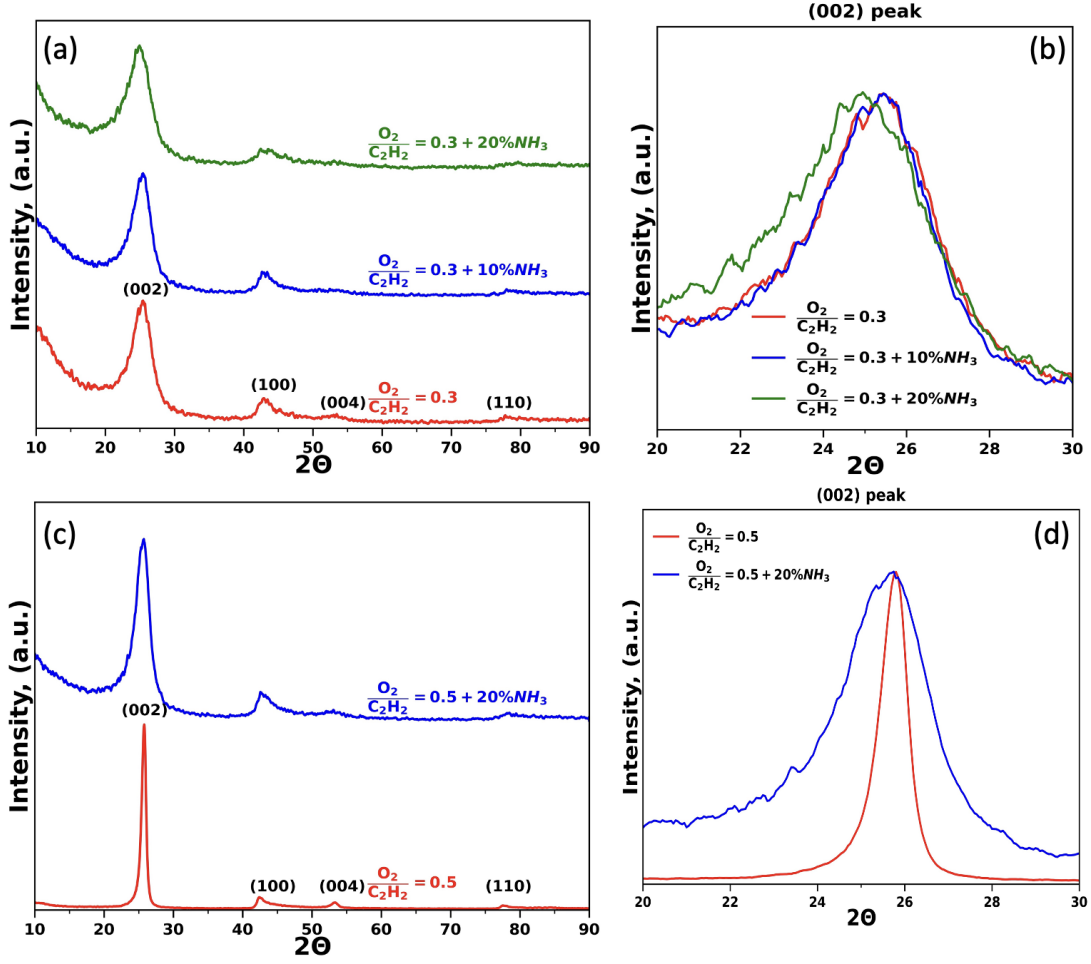


Figure 4.13: XRD of ammonia plus acetylene carbon samples, (a) 0.3 O/C sample with various % ammonia, (b) comparison of 0.3 O/C (002) diffraction peak, (c) 0.5 + 20% NH_3 , (d) comparison of 0.5 O/C (002) diffraction peak.

from $170 \text{ m}^2/\text{g}$ to approximately $112 \text{ m}^2/\text{g}$ when 20% ammonia is added. This change indicates the multi-layer graphene transitioned into a soot-like material.

4.2.6 X-ray photoelectron spectroscopy (XPS)

The XPS analysis on the carbon sample derived from the reaction of acetylene, ammonia, and oxygen reveals the presence of nitrogen in the carbon. The atomic percentages of nitrogen in the samples are measured as 0.88, 1.08, and 1.49 for compositions of $0.3 + 10\% \text{NH}_3$, $0.3 + 20\% \text{NH}_3$, and $0.5 + 20\% \text{NH}_3$, respectively. The nitrogen content in the carbon increases proportionally with the amount of ammonia utilized. Notably, the higher doping

percentage observed in the $0.5 + 20\%$ NH_3 sample can be attributed to the higher explosion temperature of the 0.5 mixture than the 0.3 mixture. At elevated temperatures, a greater amount of ammonia dissociates, leading to an increased incorporation of nitrogen into the carbon lattice.

4.3 Ethylene and oxygen

Ethylene was studied only from 0.6 to 0.9. This range was used because it was enough to see the intended morphology change in the carbon formed. Another reason is that the flammability limit of C_2H_4 is narrower than C_2H_2 [65]. Table 4.4 shows the precursor fill ratio, carbon collected, yield, and the peak explosion temperature during the explosion. Similarly to acetylene, carbon formed from ethylene is a fluffy aerosol gel at lower O/C and powdery at higher O/C.

The peak explosion temperature of ethylene measured using the fiber optics at the chamber window is 1900–2630 K. The lower temperature corresponds to the lower O/C, and the higher temperature to the higher O/C. The increase in temperature is due to the higher oxygen content in the mixture at the higher O/C. We could not measure the temperature at $\text{O/C} = 1$ because it was not a black body. Only gaseous products are formed at O/C greater than 1.

O/C	$\text{C}_2\text{H}_4(\text{L})$	$\text{O}_2(\text{L})$	Sample collected (g)	Yield (%)	Temperature (K)
0.6	10.65	6.45	3.5	33	1890
0.7	10.06	7.04	2.34	24	2070
0.8	9.58	7.52	1.7	18	2100
0.825	9.37	7.73	1.18	13	2150
0.85	9.25	7.85	0.89	10	2250
0.9	8.99	8.11	0.18	2	2630

Table 4.4: Precursor fill ratio, carbon collected, yield, and the peak explosion temperature from ethylene explosion. The yield decreases as the oxygen content increases, and the peak explosion temperature rises. This occurs because more oxygen is available to the fuel to form exothermic carbon monoxide and carbon dioxide gases.

4.3.1 TEM

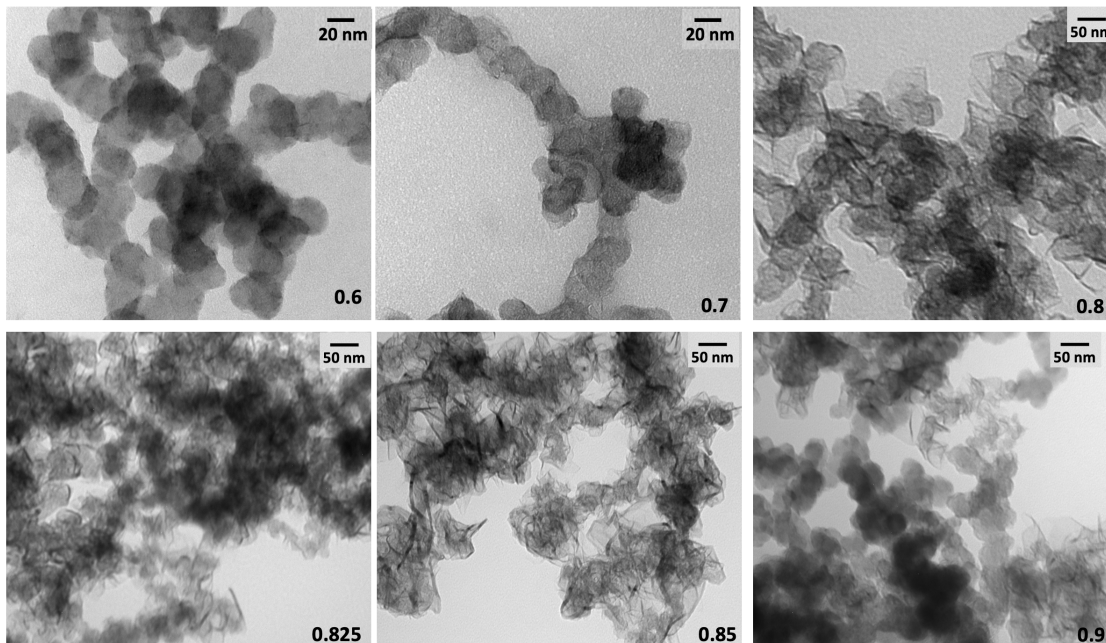


Figure 4.14: TEM images of carbon from ethylene at different O/C ratios. Images (a) and (b) shows 20-30 nm round ball-like particles linked together in a chain-like structure resembling soot. Whereas images (c), (d), (e), and (f) displayed a multi-layered, folded sheet structure characteristic of graphene. These findings align with the peak explosion temperature observed during carbon formation at different O/C ratios. The temperature at O/C = 0.6 and 0.7 were in the open flame range, favoring the soot formation, while the O/C greater than 0.7 corresponds to a higher temperature favorable for graphene formation.

The TEM imaging (Figure 4.14) shows that the carbon morphology depends on the explosion temperature. The carbon formed at O/C = 0.6 and 0.7 has low T and is soot. The primary particles are 20–50 nm and comprise of small graphitic domains commonly known as Basic Structural Units (BSUs) arranged concentrically like onions [50, 51]. The carbon formed at O/C $\geq$ 0.8 has a higher T, and the carbon formed is multi-layer graphene.

4.3.2 Raman spectroscopy

Figure 4.15 depicts the Raman spectra of ethylene carbon that demonstrate the change in morphology. The 0.6 and 0.7 samples exhibit no or a minor 2D band, and the D and G bands overlap, reminiscent of soot [56, 64]. As the O/C ratio reaches $\geq$ 0.8, the 2D band becomes

prominent, and the valley between the D and G bands decreases, resembling multi-layer graphene.

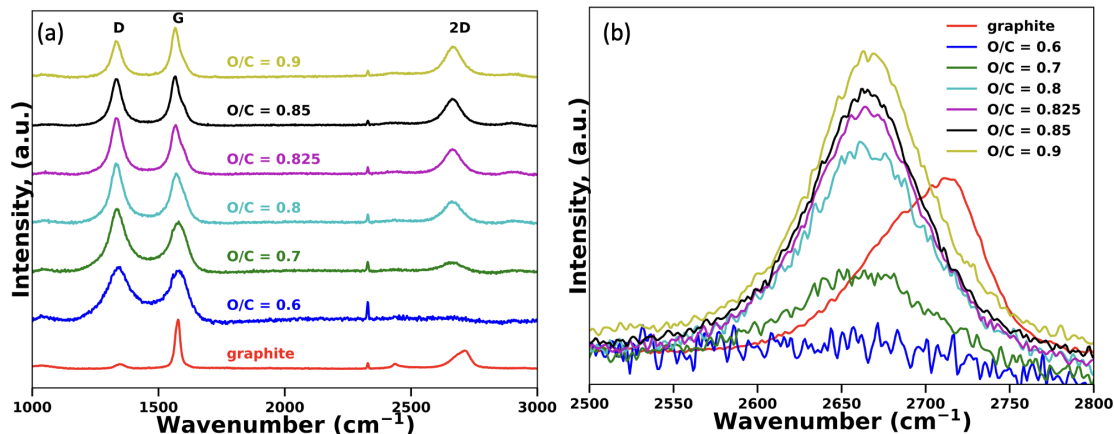


Figure 4.15: Raman of ethylene samples prepared at different O/C ratios compared with graphite. (a) combined Raman spectrum of all samples and graphite, (b) evolution of the 2D peak as a function of O/C ratio and its relative shift compared to graphite.

4.3.3 X-ray powder diffraction

Figure 4.16 illustrates that all carbon samples containing ethylene and oxygen exhibit a strong peak at approximately 25–26° in the XRD spectrum, which indicates the presence of a multilayer structure [36]. The asymmetric nature of the (100) and (110) peaks suggests the existence of a turbostratic graphene layer [54, 55], similar to the acetylene-oxygen samples. The samples with higher O/C ratios (i.e., ≥ 0.8) display a higher signal-to-noise ratio and lower FWHM of the (002) peak, indicating a higher level of crystallinity [53]. Table 4.5 shows the (002) peak’s location, the d-spacing, the crystallite size (τ), and the number of layers. The number of layers for the soot sample is marked as “N/A” because it does not possess a layered morphology.

4.3.4 BET-specific surface area

Figure 4.17 shows the BET-specific surface area of carbon samples from ethylene. Like acetylene, carbon samples derived from ethylene exhibit lower BET-specific surface area

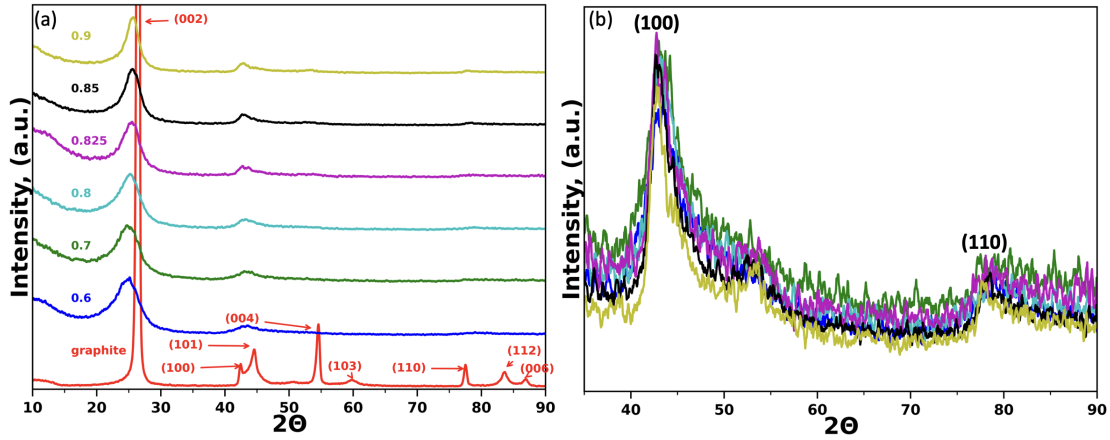


Figure 4.16: XRD of ethylene samples prepared at different O/C ratios compared with graphite. The graphene spectra are normalized to have the same (002) peak intensity, (a) combined XRD spectrum of all samples and graphite, (b) asymmetric (100) and (110) peaks to show the turbostratic nature of the carbon samples.

O/C	(002) peak position (2θ)	d-spacing (nm)	Crystallite size (τ) nm	Number of layers
0.6	25	0.356	1.98	N/A
0.7	25	0.356	2.1	N/A
0.8	25.4	0.351	2.82	8
0.825	25.5	0.349	2.87	8
0.85	25.6	0.348	2.94	9
0.9	25.7	0.347	3.81	11

Table 4.5: (002) peak position, d-spacing, crystallite size and number of layers of ethylene carbon samples.

(SSA) for soot samples. The SSA increases with the O/C ratio, peaking at O/C = 0.825, corresponding to a fluffy aerosol gel of multi-layer graphene. Beyond O/C = 0.825, the SSA decreases slightly as the carbon sample transitions from a fluffy aerosol gel to a powder with larger primary particles and increased graphene layers.

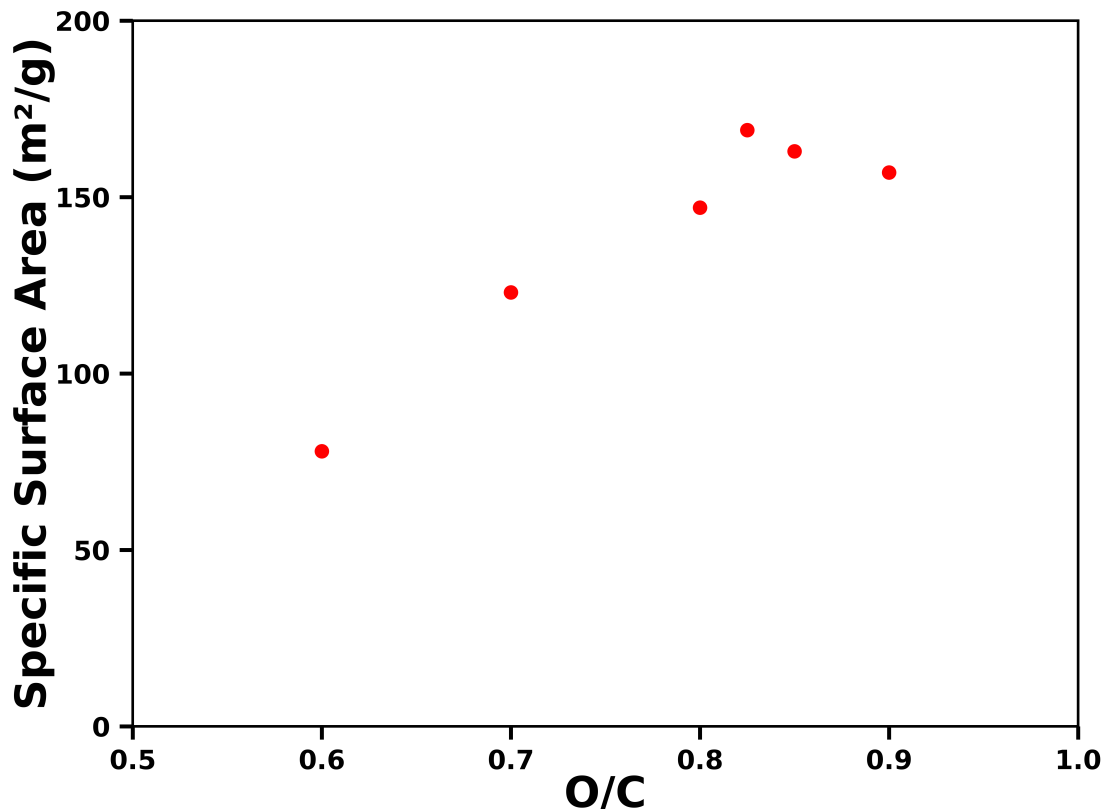


Figure 4.17: BET-specific surface area of carbon sample from ethylene vs. O/C ratio. The SSA of samples with O/C = 0.6 and 0.7 (soot samples) is lower than that of the graphene sample.

4.4 Conclusion

In conclusion, our study on acetylene and ethylene reveals that both precursors exhibit similar trends in the morphology of carbon produced, mass yield, peak explosion temperature, and the specific surface area. The carbon formed is a fluffy aerosol gel at lower O/C and a greyish powder form at higher O/C. The mixture explodes at $O/C > 1$, producing only gaseous products. As the O/C ratio increases, the peak explosion temperature rises due to the increased availability of oxygen for the energetic reaction [66].

In the case of acetylene, the carbon formed at low or no oxygen is a combination of soot and graphene. At an O/C ratio of 0.1, the morphology changes completely from soot to graphene. In the O/C ratio range of 0.1 to 0.45, the carbon sample consists of 6–10 weakly stacked graphene layers. The visual appearance of graphene is black fluffy aerosol gel. As

the O/C ratio exceeds 0.5, both the particle size and the number of graphene layers increase. As a result, the carbon's appearance changes from a black gel to a grey powder.

Adding ammonia to the acetylene and oxygen mixture during the explosion reduces the peak explosion temperature and alters the morphology of the carbon produced. By adding 20% ammonia to the $O/C = 0.5$ mixture, the temperature decreases by around 400 K. Moreover, the carbon changes from grey powder to black fluffy aerosol gel. However, adding 10% ammonia to the $O/C = 0.3$ sample has no effect on the graphene morphology, while adding 20% causes the carbon to transition from graphene to soot.

In the case of ethylene, the carbon produced at an O/C ratio of 0.9 is grey powder, whereas lower O/C ratios yield black and fluffy aerosol gel. Soot is formed at O/C ratios of 0.6 and 0.7, with the transition to graphene taking place at $O/C = 0.8$. Analysis with Raman and TEM techniques shows that carbon produced at peak explosion temperatures below 2100 K is soot, while above 2100 K, it is multi-layer graphene.

Additionally, the by-product gas generated during the explosion is syngas, a mixture of CO and H_2 that has great value in the industry. In the next chapter, we will delve into the properties and applications of syngas in more detail.

Chapter 5

Syngas production from the controlled explosion of hydrocarbons

Rapid urbanization and increasing population have resulted in massive energy demand [67]. The existing energy source (fossil fuels) is nonrenewable, releasing a large amount of CO₂, a greenhouse gas, into the air, causing global warming. Therefore, a new environmentally benign energy source is needed to fulfill the increasing energy demand [67]. Hydrogen and synthetic gas (syngas, a mixture of H₂ and CO) production technology can supply clean fuels and significantly reduces greenhouse gases [68, 69]. Hydrogen and syngas are used as a source of hydrogen for fuel. Other uses include the production of ammonia and methanol via the Fischer-Tropsch process [70].

Three major routes for syngas production are steam reforming of natural gas or liquid hydrocarbons [71], gasification of coal [72], and partial oxidation of hydrocarbons [73, 74]. All these processes are highly endothermic. Steam reforming and Coal gasification process involve subjecting precursor to elevated temperature ($> 700\text{ }^{\circ}\text{C}$) [75]. The existing method of partial oxidation of hydrocarbon requires a reaction temperature above $900\text{ }^{\circ}\text{C}$ and various catalysts, which makes this process expensive and energy intensive.

This chapter will explore a novel method for producing syngas through the explosion of different hydrocarbon precursors. The experimental procedure, analysis, and outcomes will

be thoroughly examined and presented. The reaction was carried out at room temperature and 1 atm absolute pressure. During the reaction, oxygen and fuel were filled into the chamber at different O/C ratios, and the mixture was ignited using an electromotive spark plug. Syngas was formed when methane was used as a fuel, and the combination of syngas and multi-layer graphene was formed with other hydrocarbon precursors.

5.1 Experimental procedure

The experimental chamber is a 17 L cylinder with a height of 37 cm and an internal diameter of 24 cm made of 2.54 cm thick aluminum. Detail about the experimental setup and explosion procedure can be found in Chapter 2. Hydrocarbons used in this experiment are methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), benzene (C_6H_6), toluene (C_7H_8), and xylenes (C_8H_{10}). Product gas composition from different fuels at different O/C ratios is described in detail in the following sections.

5.2 Methane as a fuel

The explosion chamber was vacuumed to ~ -28 ” Hg and then filled with the fuel-rich mixture of methane and oxygen to 1 atm absolute pressure. The ignited was initiated using the spark cube at the top of the chamber. The oxygen-to-carbon ratio varied at 2.2, 2, 1.8, 1.6, and 1.4; all mixtures, except 1.4, exploded. Therefore, we concluded that it is the lower explosion limit of methane. The final chamber pressure after the explosion at 2.2 was less than the ambient pressure, making it impossible to collect any gas. Because of the flammability limit and not enough final pressure in the chamber, we successfully collected gas only with the 1.6, 1.8, and 2.0 mixtures. The oxygen-to-carbon ratio, the initial and final pressures, and the expected moles of gaseous products are shown in Table 5.1.

The product gas was characterized using gas chromatography, shown in Figure 5.2. The GC shows the presence of CO, CO_2 , and some unquantifiable amount of water. Table 5.2 summarizes the amount of gas measured using GC at different O/C. The calculated results

O/C	Reactant moles		Relative overpressure after explsn (atm)	Calculated products			
	CH ₄	O ₂		CO	CO ₂	H ₂ O (liq)	H ₂
2.2	0.33	0.37	0.93	0.27	0.06	0.34	0.32
2	0.35	0.35	1.03	0.33	0.02	0.37	0.37
1.8	0.37	0.33	1.23	0.32	0.05	0.24	0.49
1.6	0.39	0.31	1.39	0.35	0.04	0.19	0.59

Table 5.1: Precursor fill ratio, relative overpressure, and calculated product of methane explosion. At higher O/C, the quantities of carbon monoxide and hydrogen decrease while the amount of water increases. However, the level of carbon dioxide remains relatively consistent throughout this process.

given in Table 5.1 are in good agreement with the measured values.

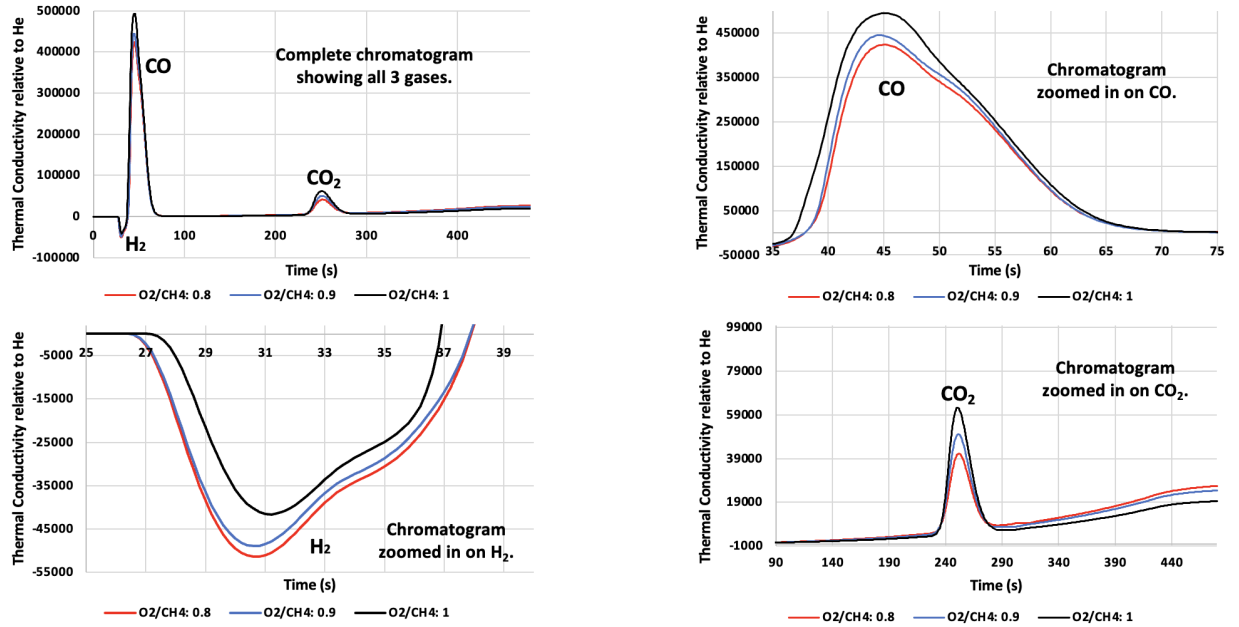


Figure 5.1: GC measurements showing the full chromatogram and closeups of the three detected gas peaks for oxygen-to-fuel = 1.0, 0.9, and 0.8.

5.3 Other hydrocarbons as fuel

Similarly, other hydrocarbons like acetylene, ethylene, benzene, and toluene exploded at different O/C ratios, and the product gas was analyzed using FTIR and GC. The chamber was heated to an elevated temperature (~ 80 °C) for the liquid hydrocarbons to evaporate

O/C	Measured products		
	CO	CO ₂	H ₂
2	0.25	0.034	0.33
1.8	0.26	0.029	0.49
1.6	0.27	0.024	0.58

Table 5.2: Products gas from methane explosion measured by GC. Similar to the expected moles, at higher O/C, the quantities of carbon monoxide and hydrogen decrease while the quantity of carbon dioxide increases.

before ignition. The primary product of these hydrocarbons was few-layer graphene and syngas as a byproduct gas.

5.3.1 Acetylene

Oxygen and acetylene at various O/C ratios were ignited in an explosion chamber. The reaction produced multi-layer graphene and syngas. The graphene formed was in the form of an aerosol gel for $O/C < 0.5$ and a powder form for $O/C \geq 0.5$. The gaseous product was analyzed using FTIR and GC. While GC can detect hydrogen, FTIR cannot detect it due to its zero net dipole moment. Figure 5.2 shows the FTIR spectroscopy of the gaseous product, which shows that some unreacted acetylene is present in the product gas. Other gaseous products formed are methane, carbon monoxide, hydrogen and some water vapor. Figure 5.3 shows the gas chromatography on the product gas, and the results are summarized in Table 5.3.

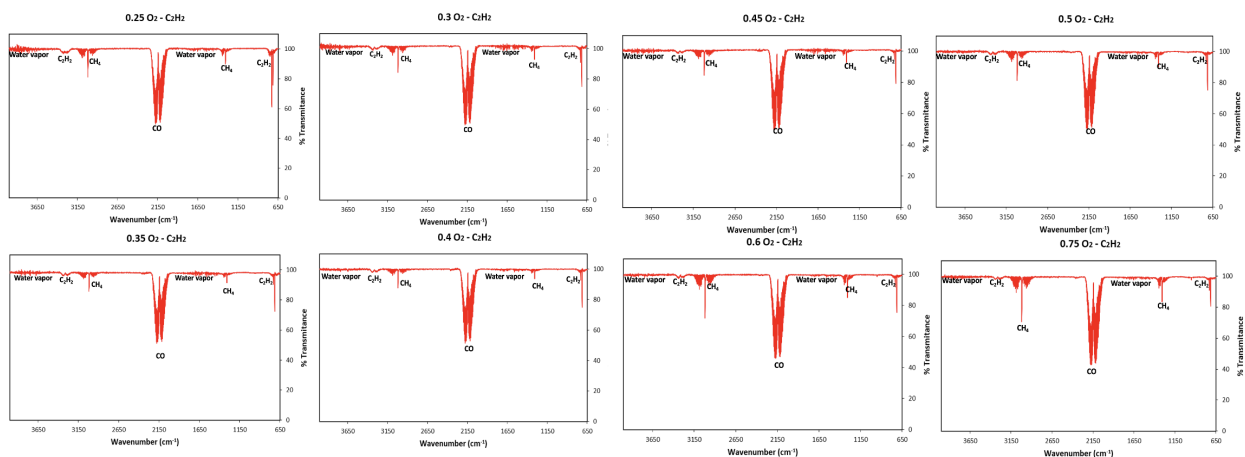


Figure 5.2: FTIR analysis of the gaseous product from acetylene. The graphs are labeled with the respective oxygen-to-carbon ratio.

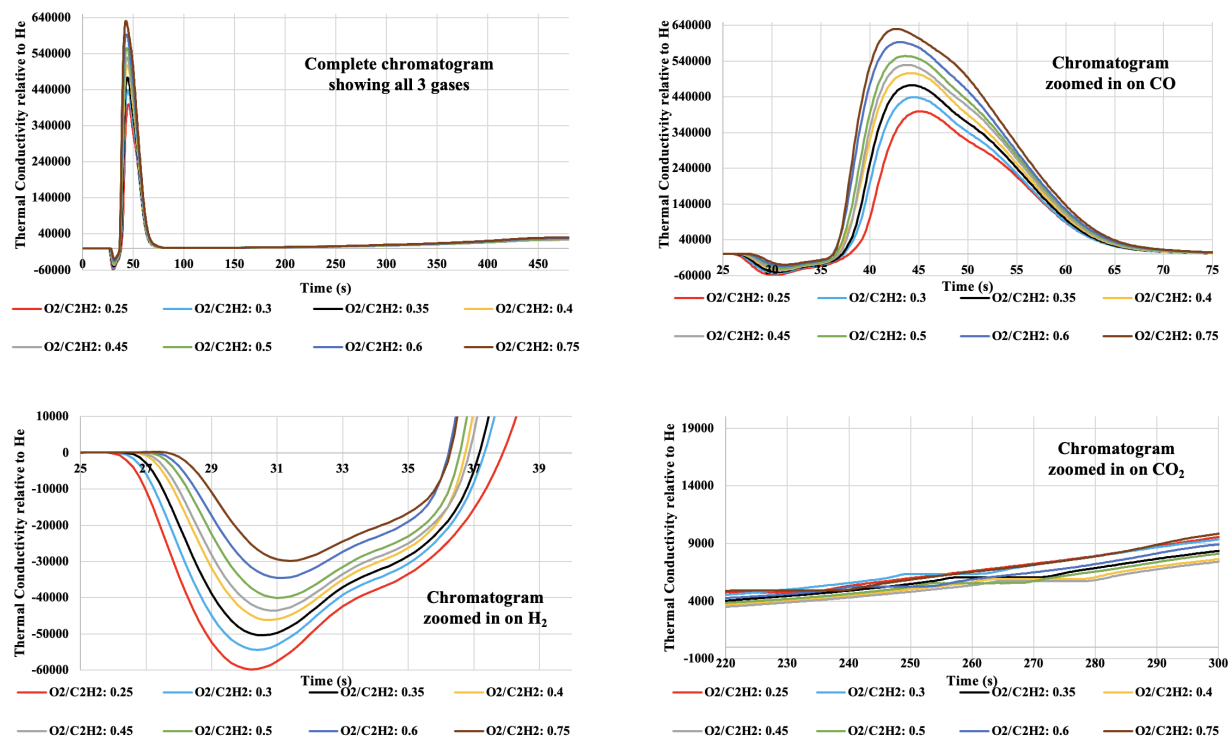


Figure 5.3: GC measurements showing the full chromatogram and closeups of the three detected gas peaks from acetylene explosion.

5.3.2 Ethylene

Oxygen and ethylene at an O/C ratio of 0.8, 0.825, 0.85, and 0.9 were ignited in an explosion chamber. The reaction produced multi-layer graphene and syngas. The gaseous product

O/C	Reactant moles		Measured products (moles)	
	C_2H_2	O_2	CO	H_2
0.25	0.51	0.13	0.22	0.58
0.3	0.49	0.15	0.25	0.53
0.35	0.47	0.16	0.28	0.49
0.4	0.45	0.18	0.32	0.45
0.45	0.43	0.20	0.35	0.44
0.5	0.42	0.21	0.37	0.40
0.6	0.39	0.24	0.42	0.36
0.75	0.36	0.27	0.48	0.33

Table 5.3: Product gas from acetylene explosion measured by GC. At higher O/C, the quantities of carbon monoxide increase and hydrogen decrease. This finding aligns with the lower carbon yield observed in Chapter 4 during the acetylene experiments, which can be attributed to the increased availability of oxygen for the fuel to form carbon monoxide.

was analyzed using FTIR and GC. Figure 5.4 shows the FTIR spectroscopy of the gaseous product. The gaseous products formed are methane, hydrogen, carbon monoxide, and water vapor. Figure 5.5 shows the gas chromatography of the product gas, and the results are summarized in Table 5.4.

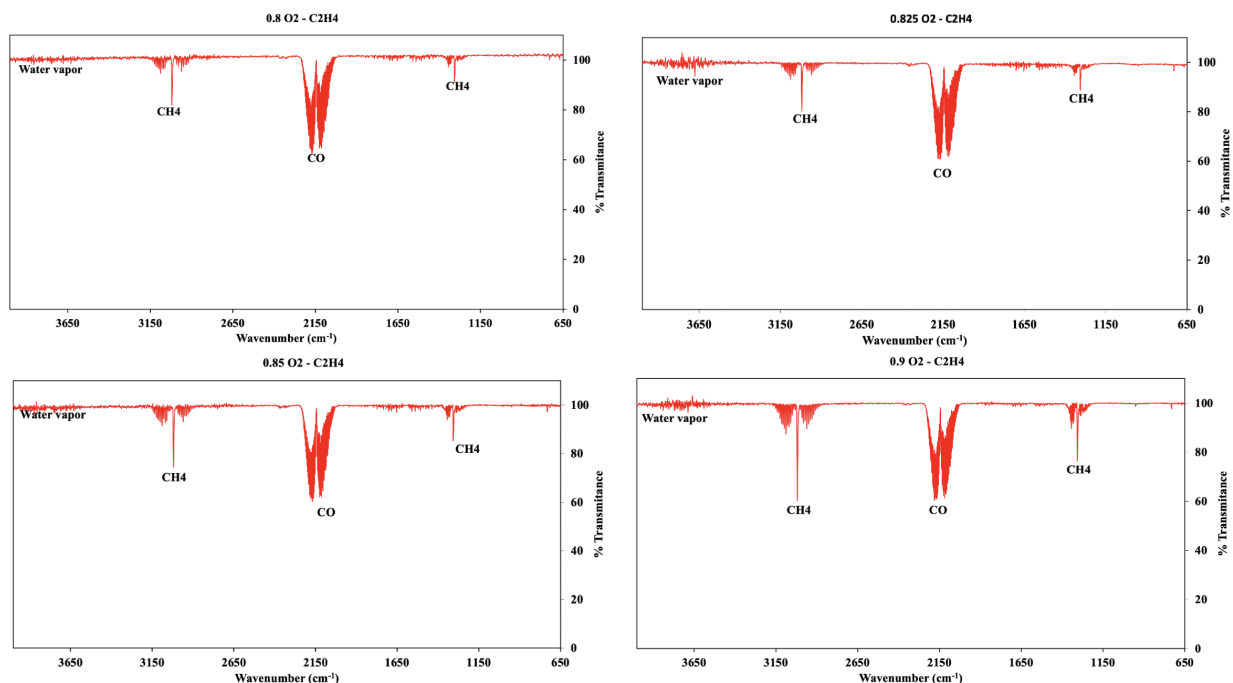


Figure 5.4: FTIR analysis of the gaseous product from ethylene explosion. The graphs are labeled with the respective oxygen-to-carbon ratio.

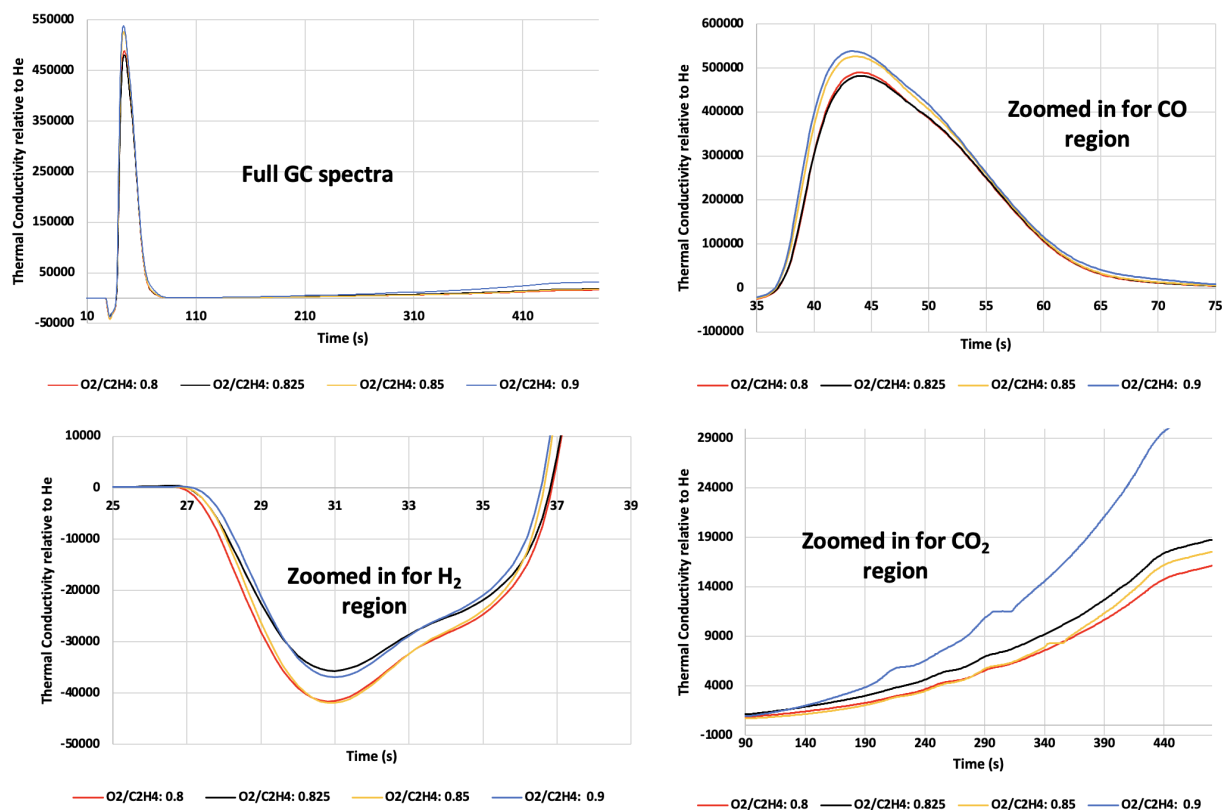


Figure 5.5: GC measurements showing the full chromatogram and closeups of the two detected gas peaks from ethylene explosion.

O/C	Reactant moles		Measured products		
	C_2H_4	O_2	CO	CH_4	H_2
0.8	0.39	0.31	0.62	0.02	0.73
0.825	0.37	0.32	0.63	0.06	0.64
0.85	0.37	0.33	0.64	0.05	0.66
0.9	0.36	0.35	0.66	0.06	0.62

Table 5.4: Product gas from ethylene explosion measured by GC. At higher O/C, the quantities of carbon monoxide increase and hydrogen decrease. This observation is consistent with the lower carbon yield observed in Chapter 4 during the ethylene experiments, which can be attributed to the increased oxygen availability for the fuel to form carbon monoxide.

5.3.3 Aromatic hydrocarbons as a fuel

The fuel-rich mixture of benzene and toluene was ignited in a chamber with oxygen at different O/C ratios. The chamber was heated to an elevated temperature (80 °C) for the liquid hydrocarbons to evaporate before ignition. The primary product of these hydrocarbons was multi-layer graphene and syngas as a byproduct gas. Figure 5.6 and 5.7 shows the FTIR and GC of gaseous product from the benzene explosion. Similarly, Figure 5.8 and 5.9 show the FTIR and GC of gaseous products from the toluene explosion. When the O/C ratio is lower (0.8 for benzene and 0.63 for toluene), unreacted hydrocarbon is left after an explosion. Whereas at higher O/C ratios, the hydrocarbons react entirely. The primary constituents of the gaseous products are carbon monoxide and hydrogen, with an additional presence of carbon dioxide at higher O/C ratios for both benzene and toluene. In addition to these compounds, the gaseous products contain minor amounts of water vapor and methane. Table 5.5 quantifies the amount of gas formed during the explosion reaction.

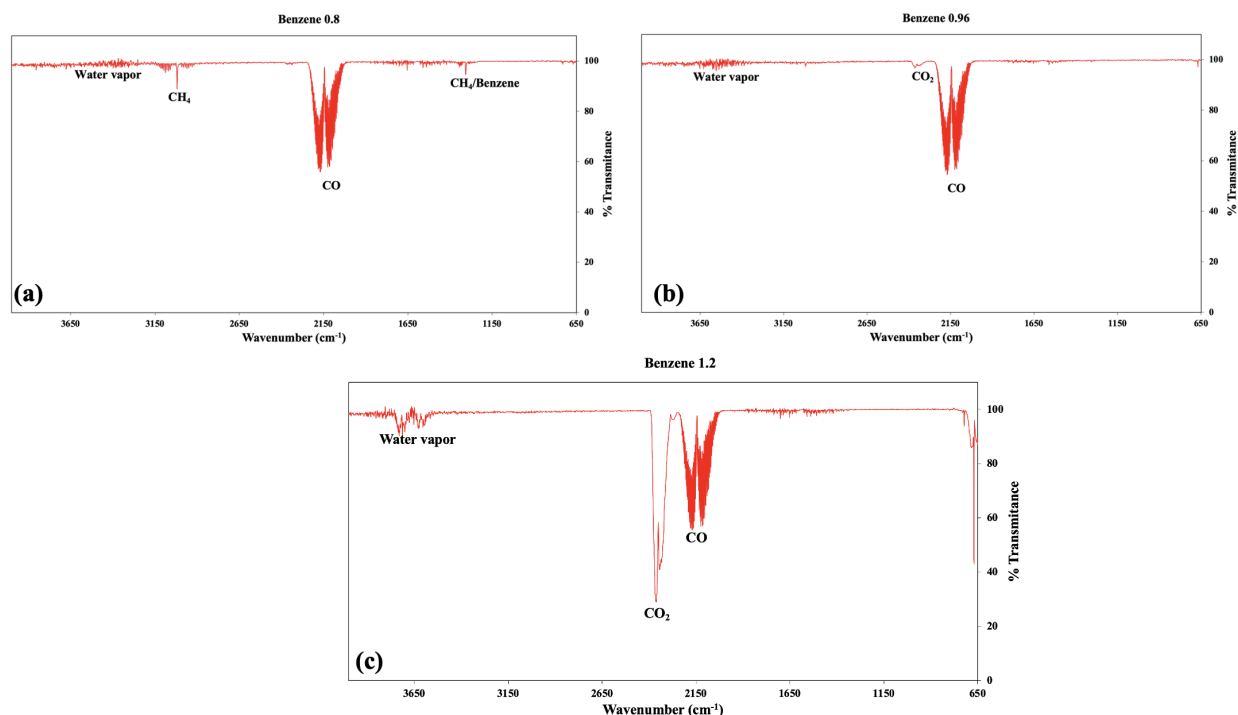


Figure 5.6: FTIR analysis of the gaseous product from benzene explosion. The graphs are labeled with the respective oxygen-to-carbon ratio and detected gas.

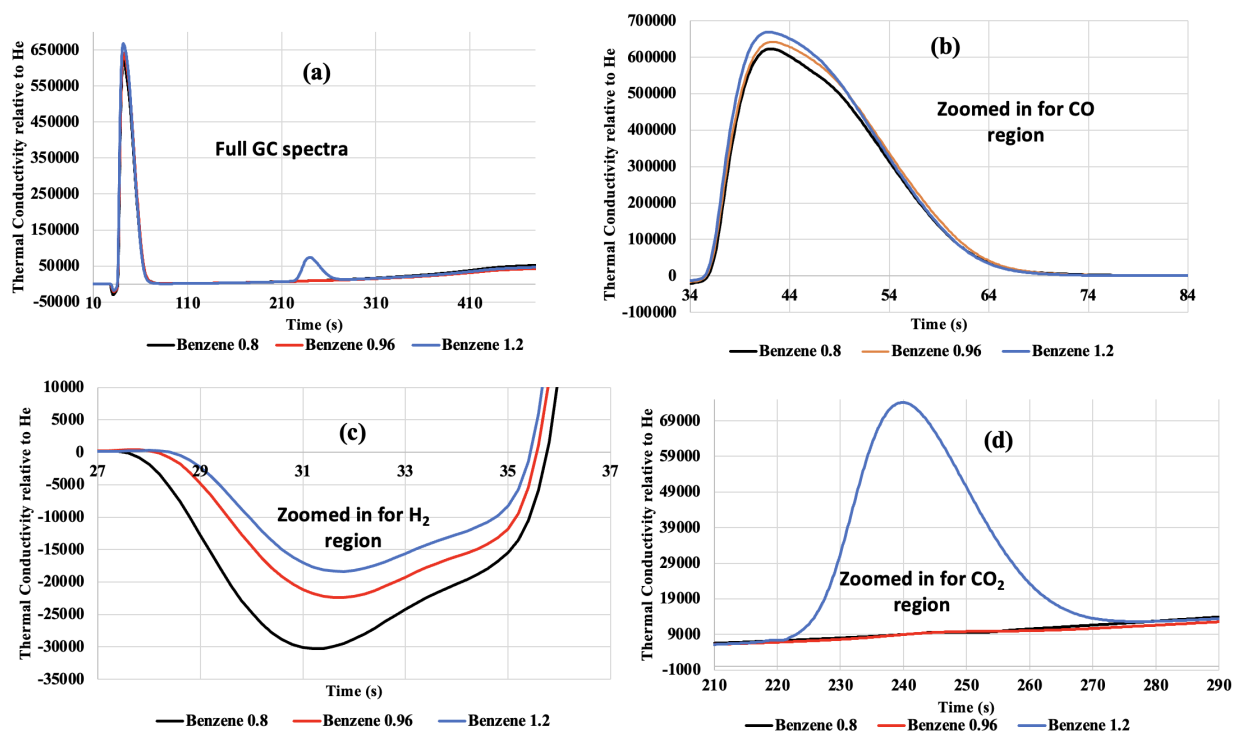


Figure 5.7: GC measurements showing the full chromatogram and closeups of the three detected peaks from the benzene explosion.

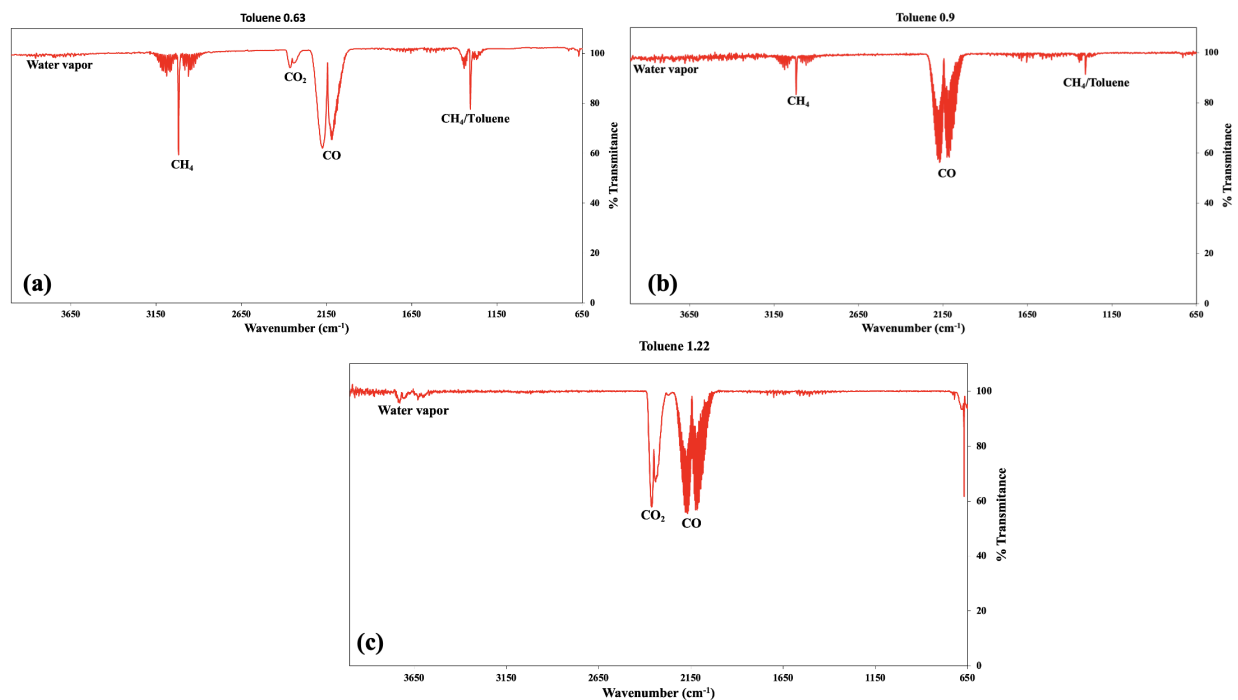


Figure 5.8: FTIR analysis of the gaseous product from toluene explosion. The graphs are labeled with the respective oxygen-to-carbon ratio and detected gas.

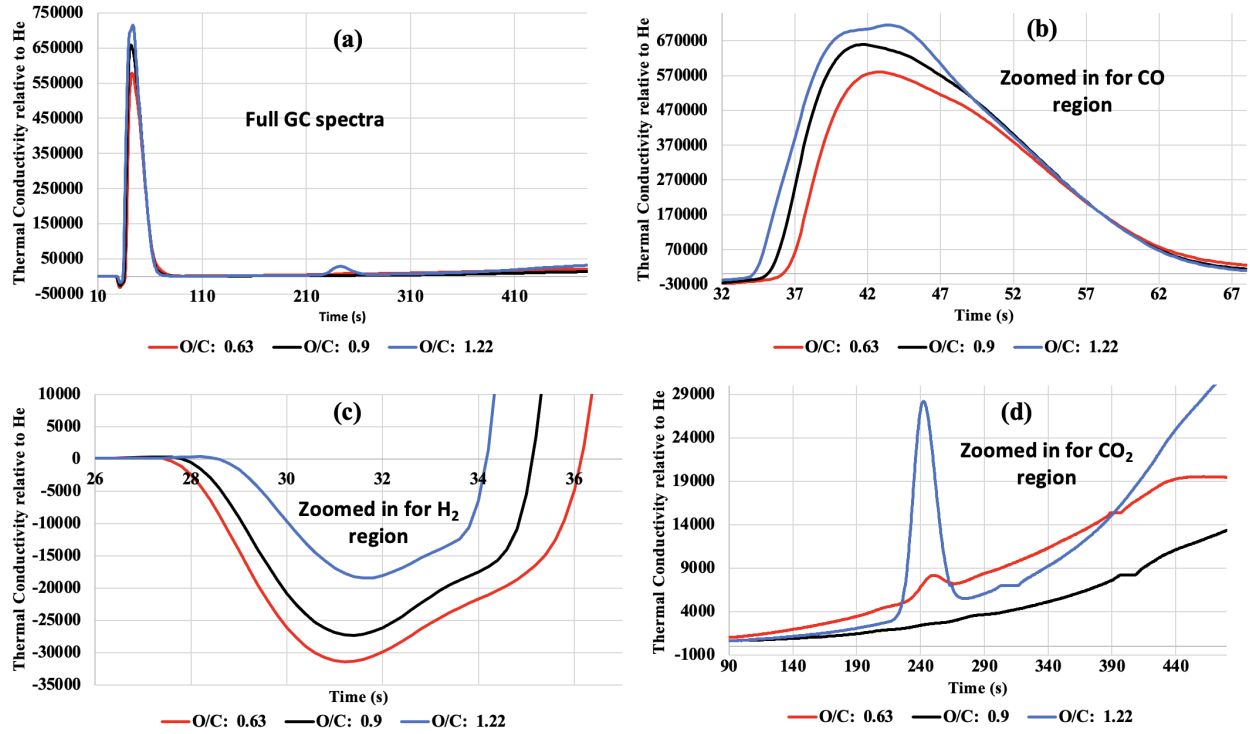


Figure 5.9: GC measurements showing the full chromatogram and closeups of the three detected peaks from toluene explosion.

Precursors	O/C	Measured Products	
		CO	H ₂
Benzene	0.8	0.74	0.53
	0.96	0.70	0.40
	1.2	0.63	0.32
Toluene	0.63	0.79	0.63
	0.9	0.87	0.52
	1.22	0.76	0.33

Table 5.5: product gases measured using GC.

5.4 Conclusion

In summary, we have shown that the fuel-rich mixture of hydrocarbons and oxygen, O₂, can be exploded in a multi-liter chamber to yield syngas. The GC results show that amount of hydrogen decreases at higher O/C and water vapor forms. Out of all fuels, methane, CH₄, is best for producing syngas because no elemental carbon was formed during the reaction. The overall explosion process is energy efficient in the sense that a simple spark is enough to initiate the reaction, and the reaction continues using the energy carried by precursor gases.

In addition to syngas, water and a small fraction of methane, CH_4 , are detected by FTIR with all fuels. Acetylene and ethylene did not produce carbon dioxide (CO_2), whereas other hydrocarbons showed a slight presence of CO_2 . Elemental carbon in the form of multi-layer graphene is also produced from the reaction.

Chapter 6

Nitrogen doped graphene using explosion synthesis

6.1 introduction

Nitrogen doping (N-doping) of graphene is substitutional doping, which introduces nitrogen atoms into the carbon lattice. This method modifies the electronic properties of graphene [76, 77]. Doping nitrogen atoms transforms graphene into an n-type semiconductor accompanied by opening a band gap [76, 78], which allows graphene to develop into a tunable electronic device. Doped graphene also has applications in fuel cells [79]. Nitrogen doping in graphene usually has four different bonding configurations with the carbon lattice, pyridinic N, graphitic N (or quaternary N), pyrrolic N, and N oxides of pyridinic N. In the case of pyridinic N, nitrogen forms bonds with two carbon atoms located at the edges or defect sites of the graphene. Graphitic N, on the other hand, replaces a carbon atom within the hexagonal ring structure. Pyrrolic N forms a five-membered ring when bonded to carbon, while N oxides of pyridinic N involve the nitrogen atom bonding with two carbon atoms and one oxygen atom. All four bonding configurations are shown in Figure 6.1. Nitrogen-doped graphene has different properties compared with pristine graphene. N-doping introduces a more active region on the graphene surfaces, which directly participates in the catalytic re-

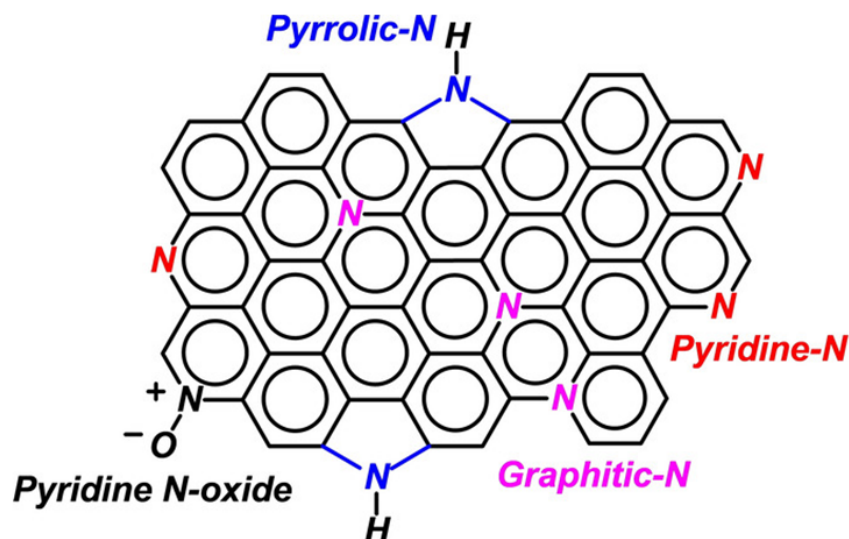


Figure 6.1: Bonding configuration for nitrogen in N-doped graphene.

actions, such as oxygen reduction reactions (ORR) and hydrogen evolution reactions (HER) in electrochemical water splitting [79, 80].

6.2 Experimental methods

The detail about the experimental chamber and the explosion procedure can be found in Chapters 2 and 3. During an explosion, the hydrocarbon precursors and oxygen are ignited in the chamber at different O/C ratios. After a successful explosion, a small portion of the product gas is collected for the FTIR and GC analysis, and the remaining gas is vented safely. The carbon formed during the explosion was collected and subjected to further analysis to examine the morphology of the carbon sample and determine its nitrogen content. The following is a list of precursor materials utilized for producing N-doped graphene.

- i. Pyridine(C_5H_5N) and Oxygen (O_2)
- ii. Pyridine(C_5H_5N), Acetylene (C_2H_2) and Oxygen (O_2)
- iii. Acetylene (C_2H_2) and Nitrous Oxide (N_2O)
- iv. Acetonitrile CH_3CN and Oxygen (O_2)

v. Ethylenediamine ($\text{C}_2\text{H}_8\text{N}$) and Oxygen (O_2)

6.3 Pyridine and oxygen

The explosion of pyridine and oxygen at O/C ratios of 0.5 and 0.8 was carried out in a 17 L explosion chamber. During the process, the explosion chamber was heated to $\sim 70^\circ\text{C}$ to evaporate the liquid pyridine. Table 6.1 shows the mass of the sample collected after an explosion, mass yield (%), and the peak explosion temperature. The peak explosion temperature was determined by fitting Planck's black body radiation law to the spectrum of the incandescent light emitted during the explosion as described in Chapter 3. Similar to other hydrocarbons described in previous Chapters, the mass yield decreases, and the peak explosion temperature (T) increases at a higher O/C ratio.

$\text{C}_5\text{H}_5\text{N}$ (mol)	O_2 (mol)	O/C	Mass collected(g)	Yield (%)	Peak explosion temperature (K)
0.19	0.38	0.8	0.91	8	2440
0.25	0.32	0.5	1.78	12	1980

Table 6.1: Mass, mass yield, and the peak explosion temperature of the carbon samples from pyridine explosion. At higher O/C, the mass yield decreases, and the peak explosion temperature increases. These findings are consistent with our observation that higher oxygen favors more carbon monoxide and a higher temperature.

6.3.1 Raman spectroscopy

Figure 6.2 shows the typical Raman of carbon samples from pyridine. The O/C = 0.5 sample with the peak explosion temperature of 1980 K shows a very small 2D band, indicating a higher amorphous carbon content in the sample [56]. As the O/C ratio increases along with the temperature, the intensity of the 2D band rises, signifying a larger proportion of crystalline carbon. Also, the relative overlap between the D and G bands decreases slightly, implying some morphological change of the carbon from soot to graphene [56].

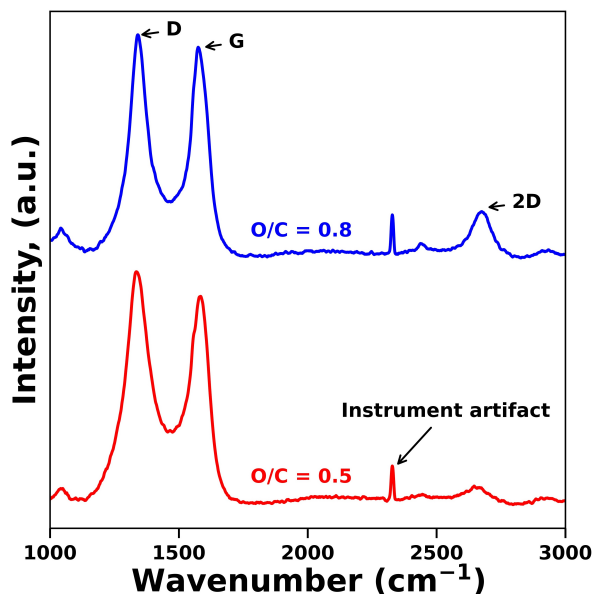


Figure 6.2: Raman spectrum of carbon sample from pyridine at $O/C = 0.5$ and 0.8 . At the higher O/C ratio, the 2D band appeared significantly larger, and the overlap between the D and G bands decreased, indicating a transition from a soot-like structure to a graphene-like structure. These results are in line with our previous findings, suggesting that higher oxygen levels promote the formation of crystalline carbon rather than soot.

6.3.2 X-ray photoelectron spectroscopy (XPS)

XPS analysis was done in the Surface and Material Characterization Facility, University of Nebraska–Lincoln. Figure 6.3 shows the typical XPS results of carbon samples from pyridine. Both samples show the C1s, O1s, and N1s peaks. The N1s peak has four different nitrogen bonding in the binding energy range 398–404 eV, corresponding to pyridinic N (398–398.9 eV), pyrrolic N (399.5–400.4 eV), graphitic N (400.5–402 eV), and pyridinic N oxide at binding energies higher than 402 eV. The C1s peak for both samples is located at 284 eV, corresponding to the graphite-like sp^2 carbon. The O1s peak is observed in both samples, possibly due to physisorbed oxygen on the graphene surface. The higher peak intensity ratio of O1s to C1s in our sample suggests stronger oxygen adsorption ability on the graphene surface, which may suggest a potential application in fuel cells [79]. The peak intensity ratio of N1s and C1s is used to determine the nitrogen content in the sample. Furthermore, elemental analysis of the $O/C = 0.5$ sample was done to verify the nitrogen content in the

sample. Table 6.2 shows nitrogen composition in the pyridine samples.

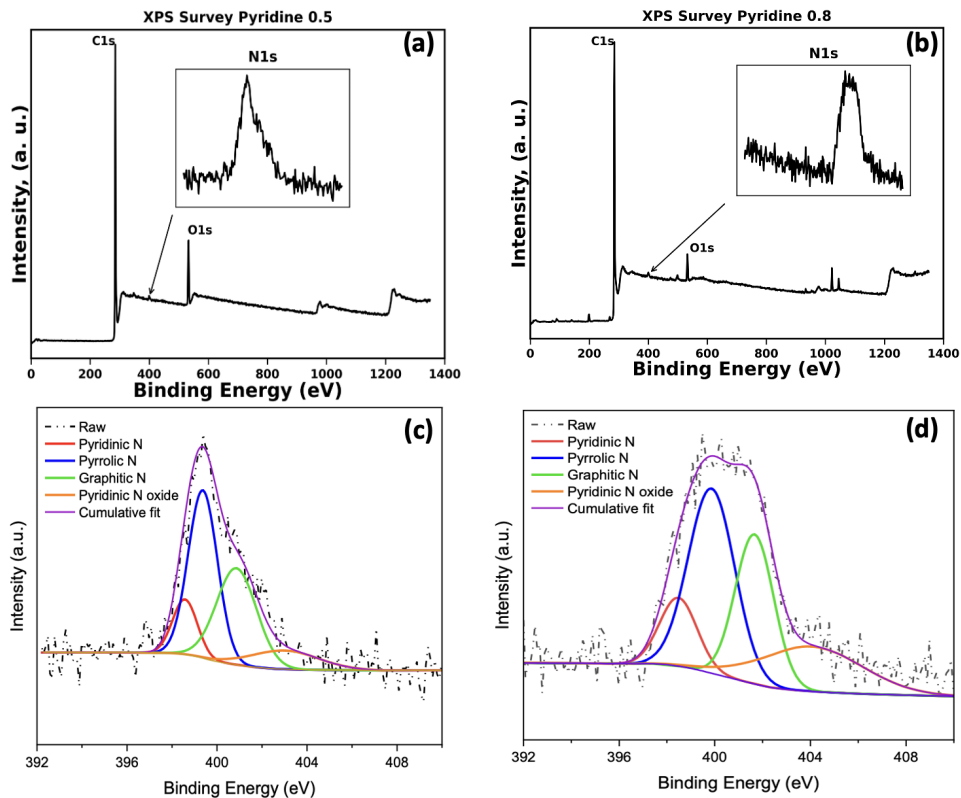


Figure 6.3: a) and (b): The XPS survey spectra of a pyridine sample at $O/C = 0.5$ and 0.8 , respectively. (c) and (d): Four bonding configurations of the nitrogen at $O/C = 0.5$ and 0.8 , respectively.

O/C	Atomic % of N	
	XPS	Elemental Analysis
0.5	1.3	1.41
0.8	1.2	NA

Table 6.2: Nitrogen % composition in the pyridine sample

6.4 Pyridine, acetylene and oxygen

In another experiment to produce nitrogen-doped graphene, pyridine was added as a nitrogen precursor in acetylene and oxygen explosion. The explosion was conducted in a 17-liter aluminum chamber. Initially, the preheated chamber was vacuumed to 0.3 atm and then

filled with 10 ml pyridine. Once the liquid pyridine had completely evaporated, the remaining chamber was filled with acetylene and oxygen at an O/C ratio of 0.3. The final pressure before ignition was 1 atm absolute. The mixture was then ignited using an electromotive spark plug and a Tesla coil. After a successful explosion, carbon formed inside the chamber was collected and further characterized to quantify the amount of nitrogen doping in the carbon sample. Figure 6.4 shows the XPS analysis of the carbon sample from this experiment. O/C = 0.3 was chosen because we produced this sample commercially using our explosion method. The atomic fraction of nitrogen is 0.6%, which is comparatively lower than that of the sample generated from pyridine and oxygen.

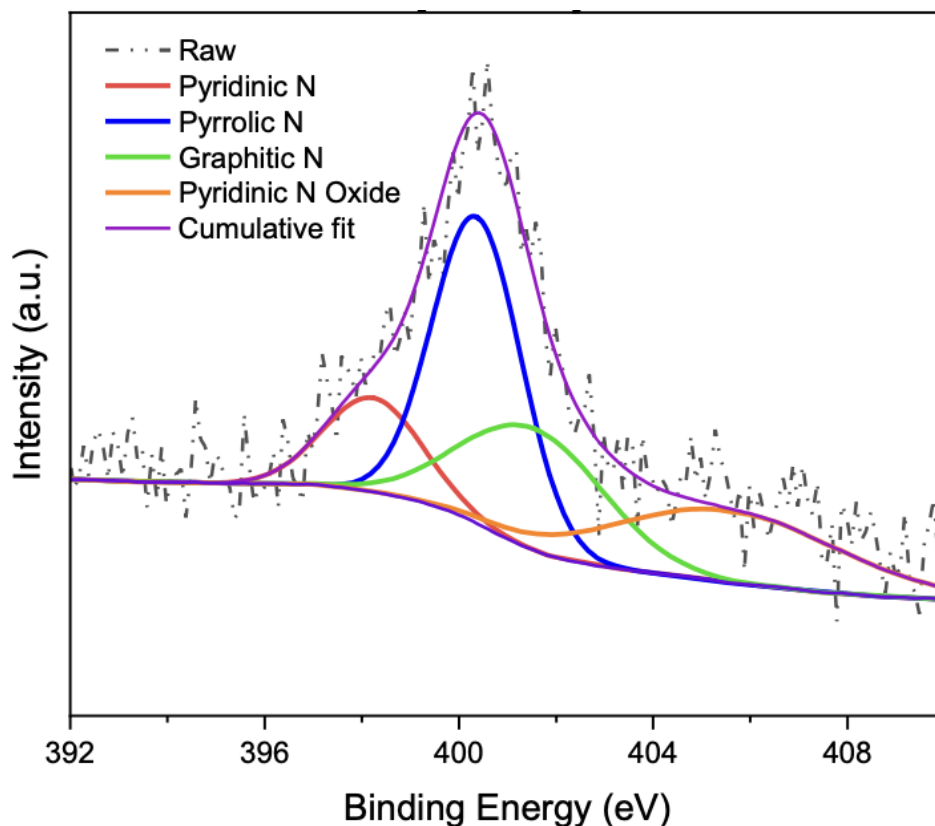


Figure 6.4: XPS spectrum N1s peak of carbon from pyridine, acetylene, and oxygen explosion along with four nitrogen bonding configurations

6.5 Acetylene and nitrous oxide

Other precursors we used were Acetylene (C_2H_2) and Nitrous Oxide (N_2O). The experimental procedure is the same as described for other hydrocarbon precursors. Table 6.3 shows the initial precursor ratio and the experimentally measured parameters during and after the explosion. In addition to the peak pressure and temperature measured during an explosion, gas chromatography, and FTIR was done on the product gas. Other characterizations like TEM, Raman, XRD, and BET are to understand the morphology of the carbon formed. Also, we did the XPS analysis to calculate the amount of nitrogen in the carbon sample.

In addition, to produce nitrogen-doped graphene, we also wanted to study the role of oxidizers in the explosion process. Because of this, we opted to utilize nitrous oxide. A highly effective oxide and a viable substitute for oxygen, serving as both an oxidizer and a nitrogen source. As a result, we conducted thorough examinations of the carbon produced from this mixture.

C_2H_2 (mol)	N_2O (mol)	$\text{N}_2\text{O}/\text{C}_2\text{H}_2$	Mass collected (g)	Yield (%)	Peak explosion pressure (psi)
0.41	0.25	0.6	5.72	57	203
0.39	0.27	0.7	4.93	53	150

Table 6.3: Explosion initial and final measured parameters.

6.5.1 Peak explosion temperature

Figure 6.5 shows the spectra collected from the chamber’s window during the explosion and the temperature calculated after that, as described in Chapter 3. The peak explosion temperature for 0.6 and 0.7 was ~ 2500 K, with the 0.7 sample reaching peak temperature earlier than the 0.6 sample. The temperature measured with these precursors is slightly lower than the acetylene and oxygen at the same molar ratio because of the change in the oxidizer.

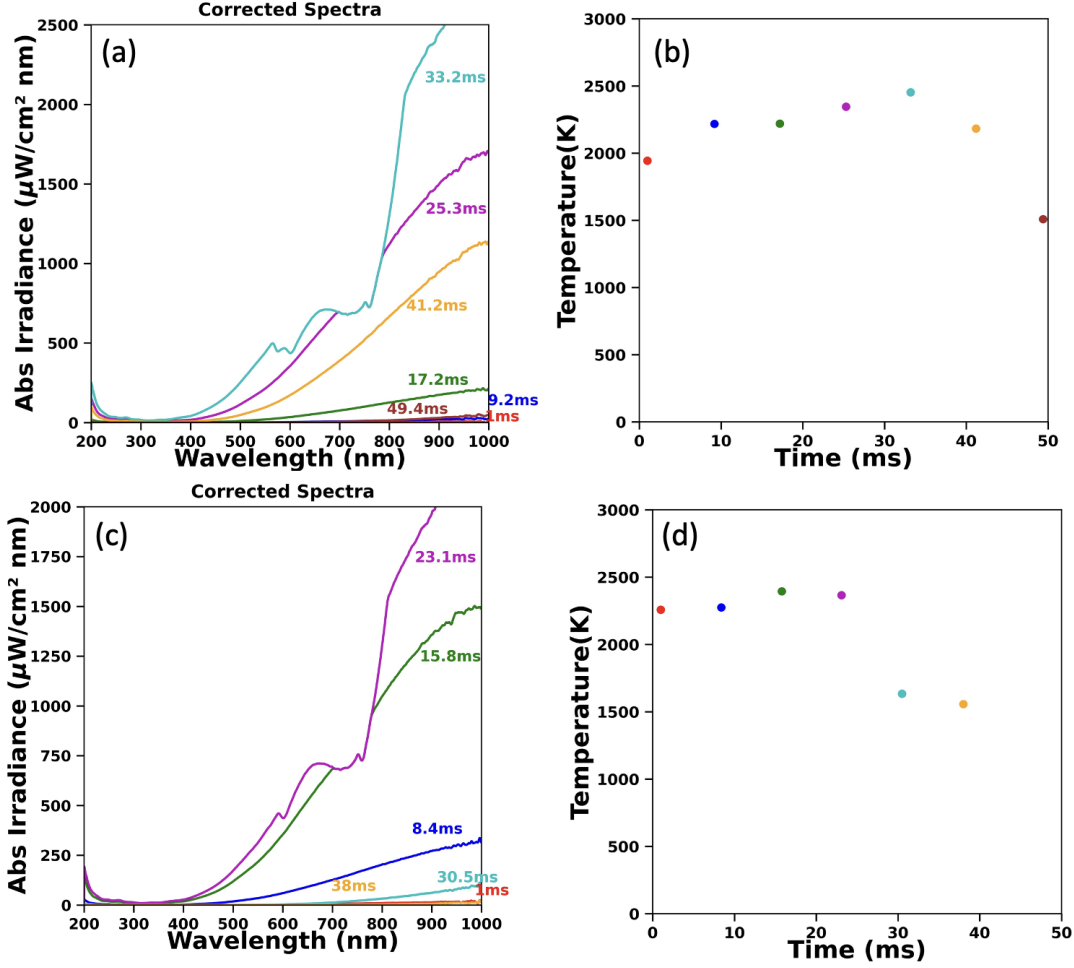


Figure 6.5: (a) Spectra recorded during an explosion of $\text{N}_2\text{O}/\text{C}_2\text{H}_2 = 0.6$, (b) corresponding temperature, and (c) spectra of $\text{N}_2\text{O}/\text{C}_2\text{H}_2 = 0.7$, (d) corresponding temperature, the spectra and the temperature calculated is denoted by the same color.

6.5.2 TEM

The TEM images of the carbon formed from acetylene and nitrous oxide are shown in Figure 6.6. The morphology of carbon formed at both oxidizer-to-fuel ratios is folded sheet of multi-layer graphene.

6.5.3 Raman

Figure 6.7 shows the Raman spectra carbon samples. Acetylene and oxygen at $\text{O}/\text{C} = 0.3$ is plotted alongside for the direct comparison. The slight decrease in the I_D/I_G ratio at higher N_2O content indicates the increase in crystallinity of the graphene produced. A similar effect

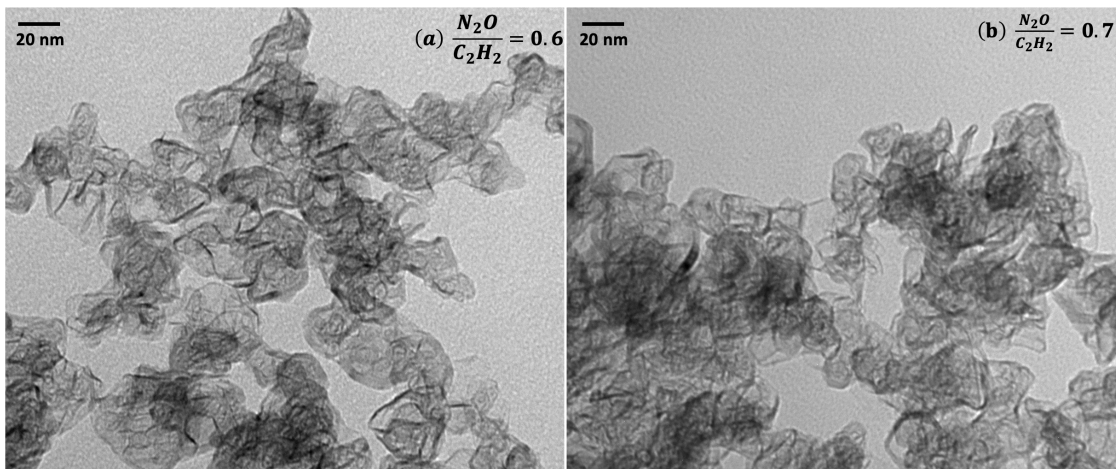


Figure 6.6: TEM images of carbon sample from acetylene and nitrous oxide, (a) at $C_2H_2/N_2O = 0.6$, and (b) $C_2H_2/N_2O = 0.7$. Both samples have a multi-layer graphene morphology and a peak explosion temperature above graphene formation temperature, indicating a high temperature favors graphene formation.

at a higher O/C ratio was observed when oxygen was used as an oxidizer.

6.5.4 X-ray diffraction (XRD)

Figure 6.8 shows the XRD spectrum of carbon from acetylene and nitrous oxide compared with graphene produced from acetylene and oxygen at $O/C = 0.3$. The (002) peak position and d-spacing are the same for all three samples. The asymmetric nature of the (100) and (110) peaks due to the Warren effect [54] and the absence of the (101) peak suggest that the graphene obtained is turbostratic. The number of graphene layers is between 8–9, similar to the graphene from acetylene and oxygen at $O/C = 0.3$.

6.5.5 XPS analysis

Figure 6.9 shows the XPS nitrogen peak analysis of the carbon from acetylene and nitrous oxide. Both O/C ratios show some nitrogen present in the sample. For the 0.6 sample, nitrogen doping is approximately 0.67 atomic percentage, but the N1s peak signal is insufficient for accurate peak fitting. At 0.7, the nitrogen doping in the carbon sample increases to 1.36%, and the peak fitting was done to determine the N bonding configuration. Calculating

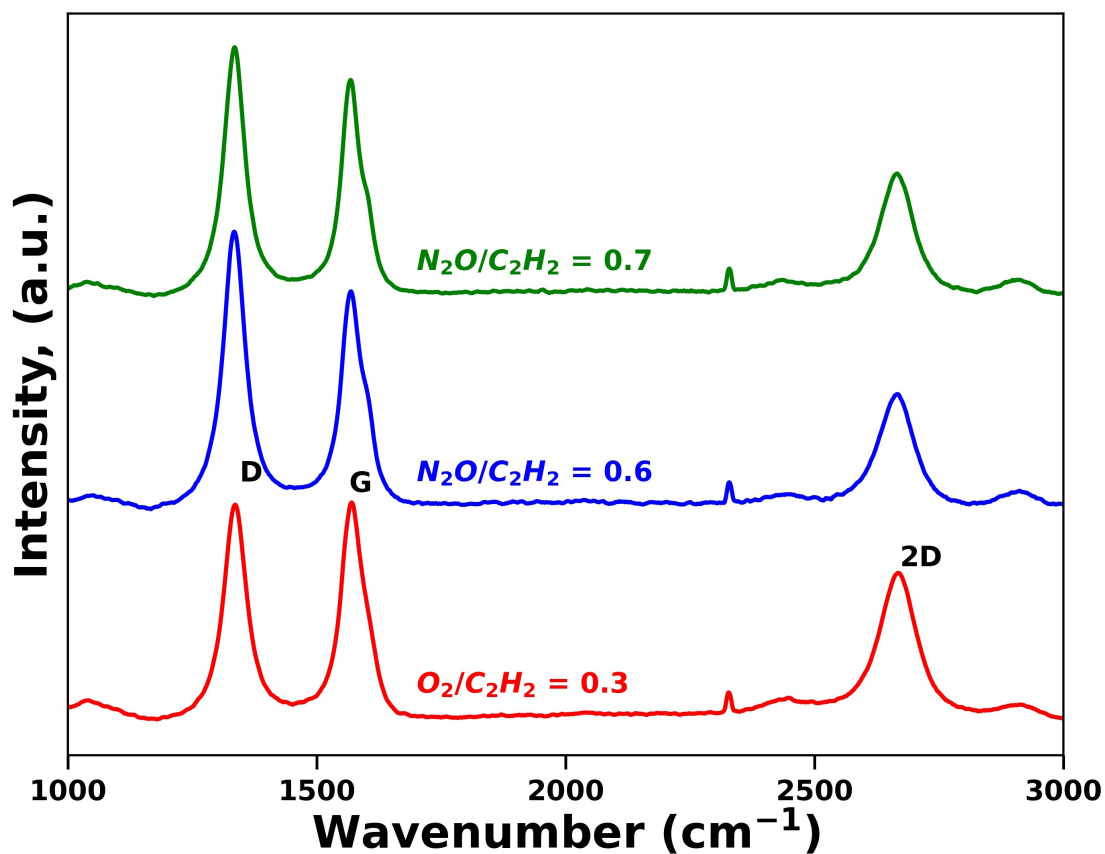


Figure 6.7: Raman spectra of carbon sample from acetylene and nitrous oxide. The Raman spectrum of both samples exhibits the typical features of multi-layer graphene. This result is consistent with our findings that nitrous oxide is another potential oxidizer for graphene formation. Acetylene at $O/C = 0.3$ is also plotted for direct comparison.

the peak area shows that the pyridinic N is 79.8%, and graphitic N is 20.2%.

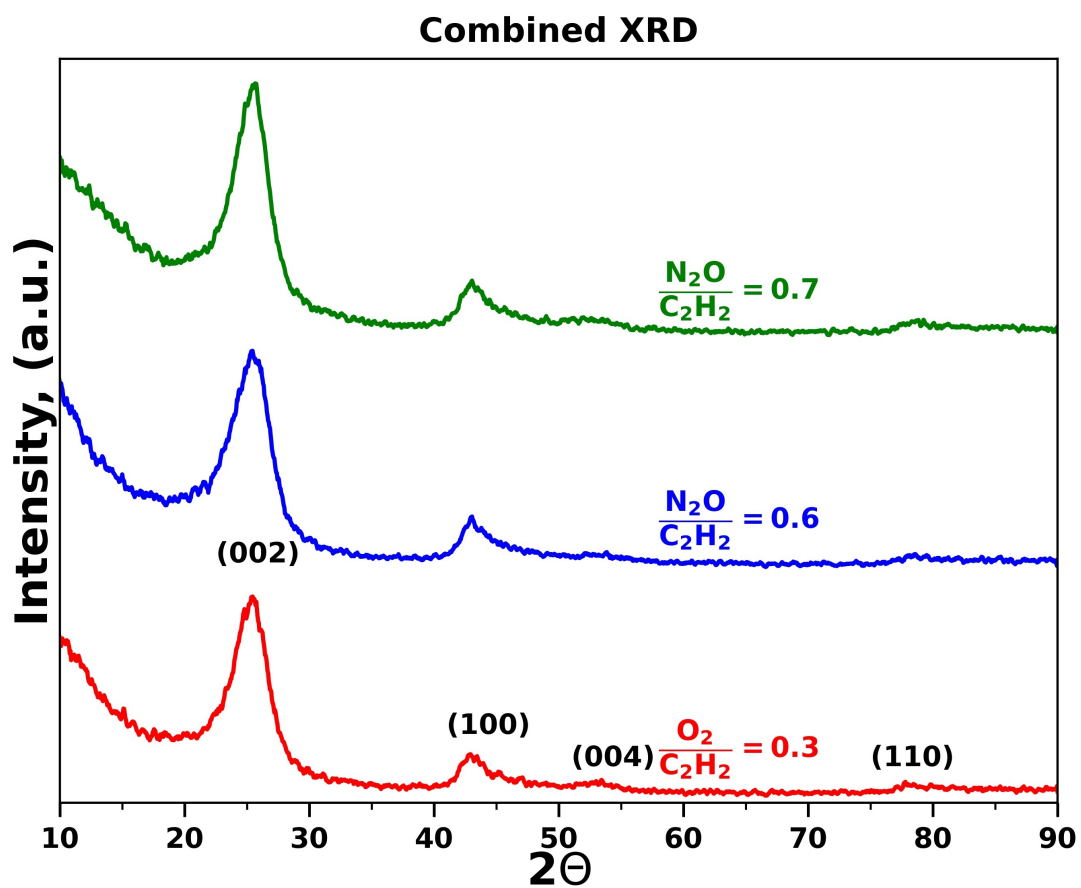


Figure 6.8: XRD spectrum of carbon from acetylene and nitrous oxide mixture compared with the 0.3 acetylene and oxygen graphene.

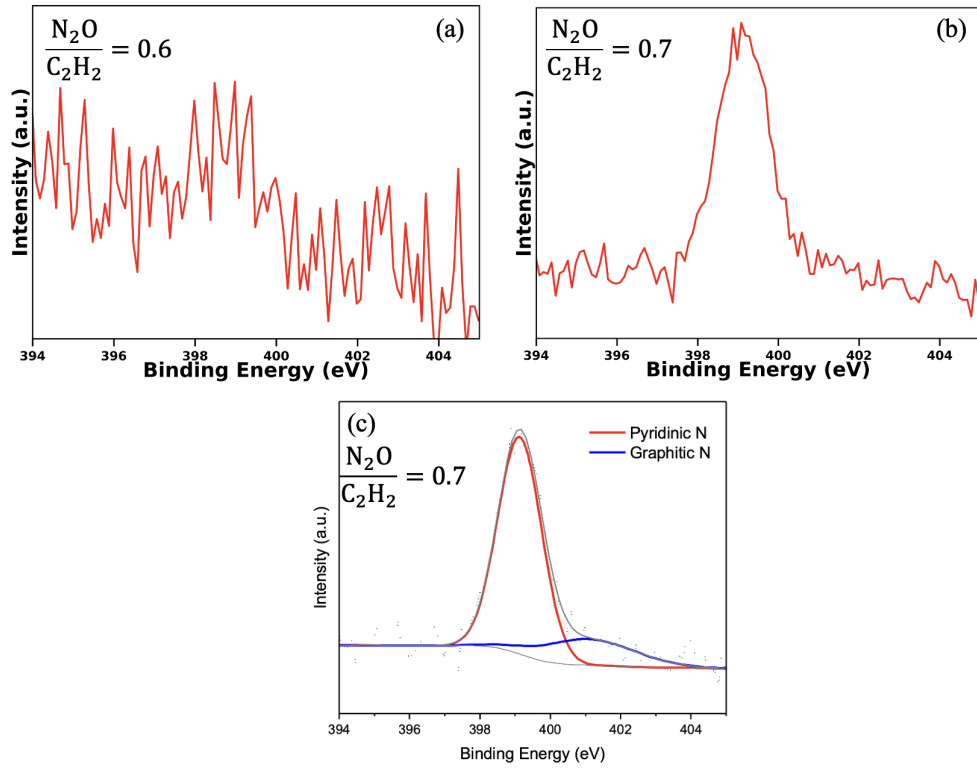


Figure 6.9: XPS spectrum N1s peak from acetylene and nitrous oxide explosion. (a) N1s spectra of carbon sample at $N_2O/C_2H_2 = 0.6$, (b) at $N_2O/C_2H_2 = 0.7$, (c) peak fitting of $N_2O/C_2H_2 = 0.7$ sample with two different nitrogen bonding configurations.

6.6 Ethylene diamine + oxygen and acetonitrile + oxygen

Other precursors used in the nitrogen doping study were ethylene diamine and acetonitrile. When ethylene diamine was used, gaseous products were formed with little solid carbon. After an explosion of ethylenediamine, the chamber looks uniformly coated with black paint. We hypothesized that some solid carbon was produced during the reaction and mixed with water, another reaction product. Despite our efforts, we were unable to obtain a sufficient amount of carbon for testing purposes. On the other hand, the reaction with acetonitrile was successful. We exploded a 15 ml acetonitrile and oxygen mixture in a 17 L explosion chamber, collecting 50 mg carbon. Figure 6.10 displays the XPS analyses of the carbon sample obtained from the acetonitrile explosion.

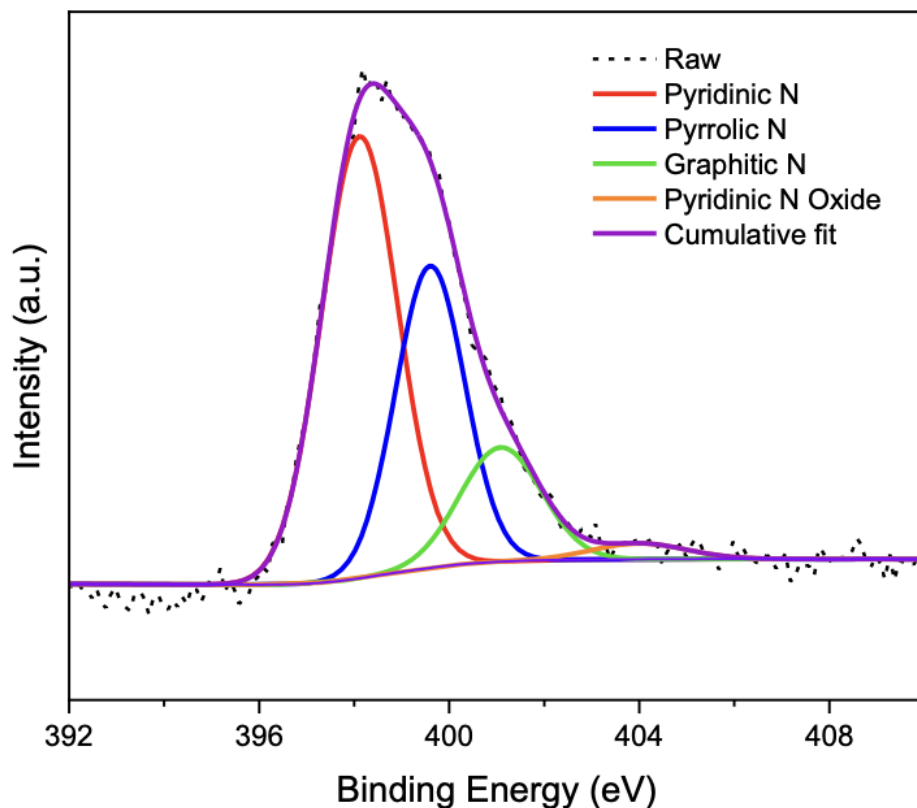


Figure 6.10: XPS spectrum N1s peak of carbon from acetonitrile, and oxygen explosion along with four nitrogen bonding configurations

6.7 Conclusion

A viable process of producing nitrogen-doped graphene using an explosion synthesis is shown. The atomic percentage of nitrogen in the resulting graphene sample ranged from 0.6 to 3.4% (Table 6.4). XPS analysis shown in Table 6.4 revealed the presence of nitrogen in four different bonding configurations in the carbon sample. Pyrrolic nitrogen was found to be the most prominent, except for carbon derived from acetonitrile and the acetylene and nitrous oxide at a fuel-oxidizer ratio of 0.7, which had a majority of pyridinic nitrogen. Raman spectroscopy indicated that the graphene structure remained intact.

N-bonding configuration	Pyridine O/C = 0.5	Pyridine (O/C = 0.8)	N₂O/C₂H₂ = 0.7	C₅H₅N, C₂H₂ and O₂	Acetonitrile
Pyridinic N	0.2	0.1	1	0.1	1.8
Pyrrolic	0.6	0.5	N/A	0.2	1.1
Graphitic N	0.4	0.3	0.36	0.1	0.5
Pyridinic N oxide	0.1	0.3	N/A	0.1	0.1
Total N	1.3	1.2	1.36	0.6	3.4

Table 6.4: Summary of total atomic percentage of nitrogen-doped in the graphene sample from different hydrocarbon precursors broken down into four different bonding configurations.

Moreover, the XPS results obtained from the pyridine and oxygen mixture and the nitrous oxide and acetylene mixture demonstrated increased doping with higher nitrogen precursor. This study introduces nitrous oxide as an alternative oxidizer with a high potential for producing nitrogen-doped graphene with a high yield. Further investigations are necessary, particularly with higher nitrous oxide-acetylene ratios, to elucidate the relationship between doping and oxidizer functionality.

Additionally, this study extends the application of the explosion process beyond graphene synthesis, highlighting its future potential in producing various metal-doped graphene materials. Our collaborators are currently exploring the practical applications of this nitrogen-doped graphene, such as in conductive inks, cathode materials for methanol fuel cells, and electrocatalytic water splitting.

Chapter 7

Powdered particulate explosion study

As described in previous sections of this work, open flames of gaseous and liquid hydrocarbons generate soot. In contrast, explosions of the same hydrocarbons in a chamber with temperatures exceeding ~ 2100 K can produce few-layered graphene. Similarly, fine powders explodes in the presence of an oxidizer and produces soot [81], and we want to see if we can explode dust in a confined chamber in the presence of an oxidizer and produce graphene. To expand this approach, we conducted experiments using particulate precursors and exploded various powders, including agricultural dust, coal fines, graphite, and starches. Creating graphene from agricultural dust could address two issues: providing a straightforward method for making graphene and repurposing problematic waste materials. This chapter will delve into the details of our research on the powder explosion.

7.1 Visualization of powder dispersion in a 4 L chamber

We built a 4 L transparent plastic chamber 30 cm long and 13 cm in diameter, as shown in Figure 7.1. During the dispersion process, we first put some cornstarch powder on top of the mesh at the bottom of the chamber and then vacuum-tightened the chamber. We then slowly vacuum the chamber to ~ 0.03 atmospheres. We took care not to allow any powder

to escape from the holder during the vacuuming process. Finally, the oxygen was injected into the chamber through the bottom, causing the powder to disperse.

Figure 7.1 also presents different disperser designs, and we found that the spiral nozzle resulted less clumping, which we used for further experiments. After achieving satisfactory dispersion in the 4 L chamber, we conducted an explosion in a 17 L aluminum chamber. We used a pair of electrodes at the center of the chamber as an igniter. We partially evacuated the chamber and dispersed the dust with pressurized oxygen during the process. We manually initiated the ignition immediately after closing the inlet valve.

Upon opening the chamber after the explosion, we observed dense gas and some burnt powders in the lid. The gas remained inside the chamber and had a higher density than air, indicating that it was primarily composed of CO₂. We also noticed some clumped cornstarch powder around the chamber, and the bottom had burnt and unburnt powder fractions with burned layers on top, suggesting that the particles ignited while settling.

Recognizing the need for improved ignition and dispersion, we replaced the 4 L dispersion chamber with a larger 17 L transparent plastic chamber and utilized an electric matchstick as a more energetic ignition source. This new chamber precisely matched the dimensions of our explosion chamber, allowing us to better understand the dispersion dynamics within the aluminum chamber during an explosion. Figure 7.2 depicts the 17 L transparent chamber and the setup of the explosion chamber. The dispersion process was similar to that of the 4 L chamber, except that we utilized a larger dust container, a 1/2" diameter and 6" long tube capable of holding up to 30 g of powder. In contrast, the 4 L chamber could only accommodate 5 g of powder.

Furthermore, an electronic inlet valve capable of opening and closing within a few hundred milliseconds was added to the 17 L chamber. Pictures and videos of the dispersion were captured and subsequently analyzed to observe the dispersion and calculate the fall time. The fall velocity was also calculated separately using Stokes' equations and compared to the observed velocity. Table 7.1 summarizes the terminal velocity and residence time of various powders. Snapshots of the chamber during dispersion are shown in Figure 7.3, which clearly indicates that particles begin to settle after 350 ms, and nearly all particles settle

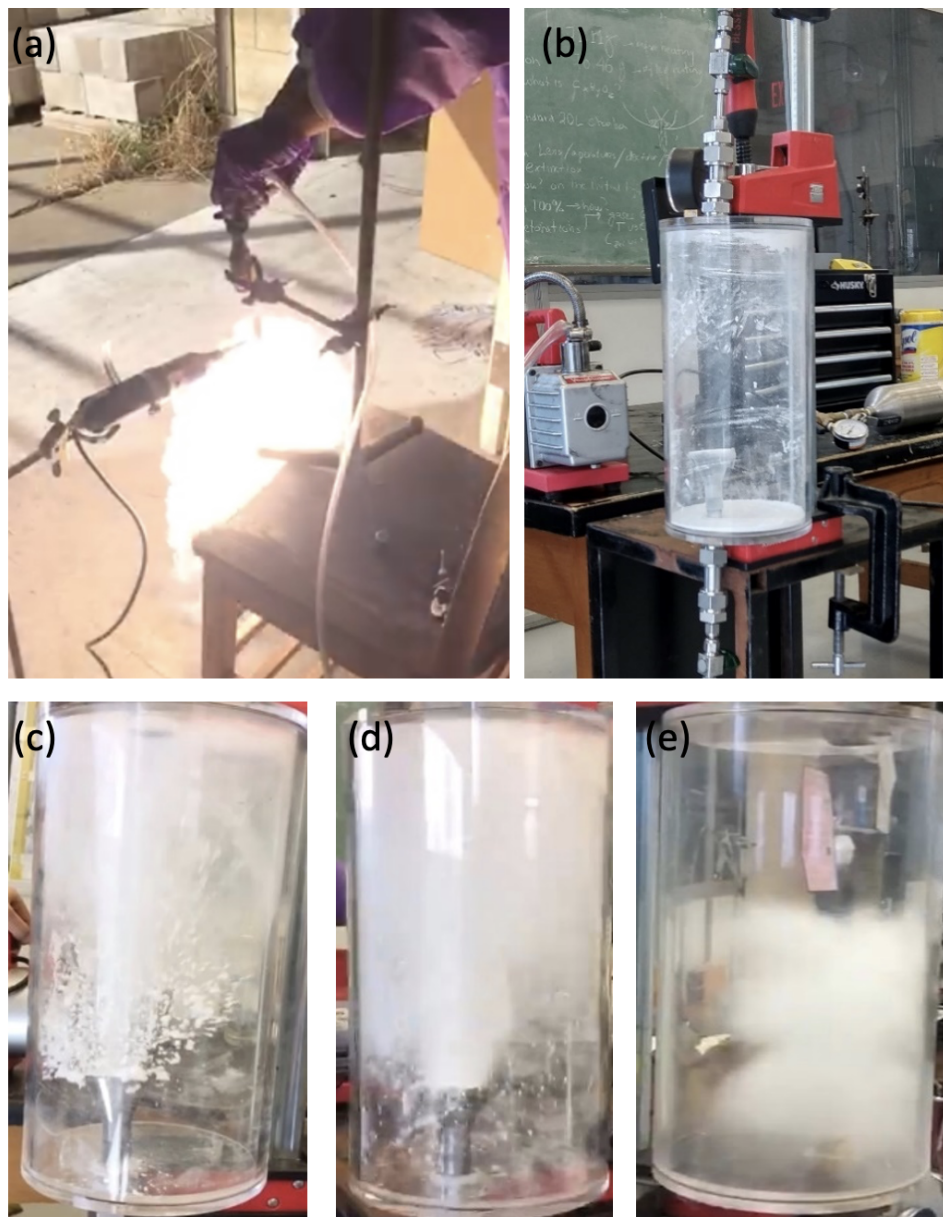


Figure 7.1: (a) Snapshot of dust explosion in the air using spark generated from spark plug as an igniter, (b) 4L transparent chamber used to visualize dust dispersion, (c) dust dispersion using the cone as a disperser, (d) dust dispersion using cone and a mesh on top of the cone, and (e) dust dispersion using spiral nozzle as a disperser.

at the bottom of the chamber after 2–3 seconds. The disparity between the experimentally observed residence time (2–3 seconds) and that predicted by Stokes' law, Table 7.1, could be due to the fact that particles are still clumped during dispersion and are not uniformly dispersed.

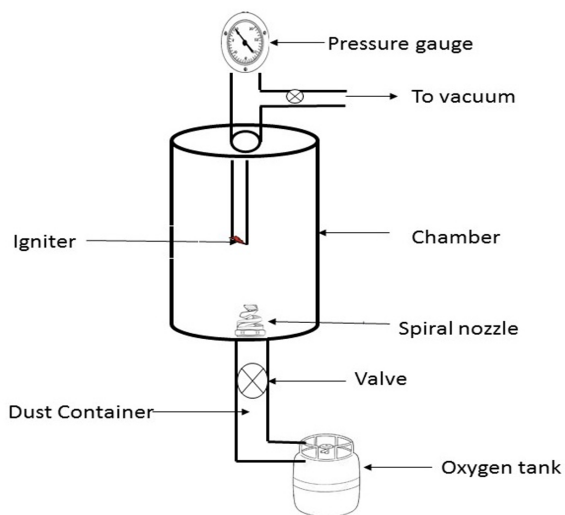


Figure 7.2: (a) 17 L transparent chamber for viewing dispersion, (b) schematic of the explosion set up in a 17 L aluminum chamber.

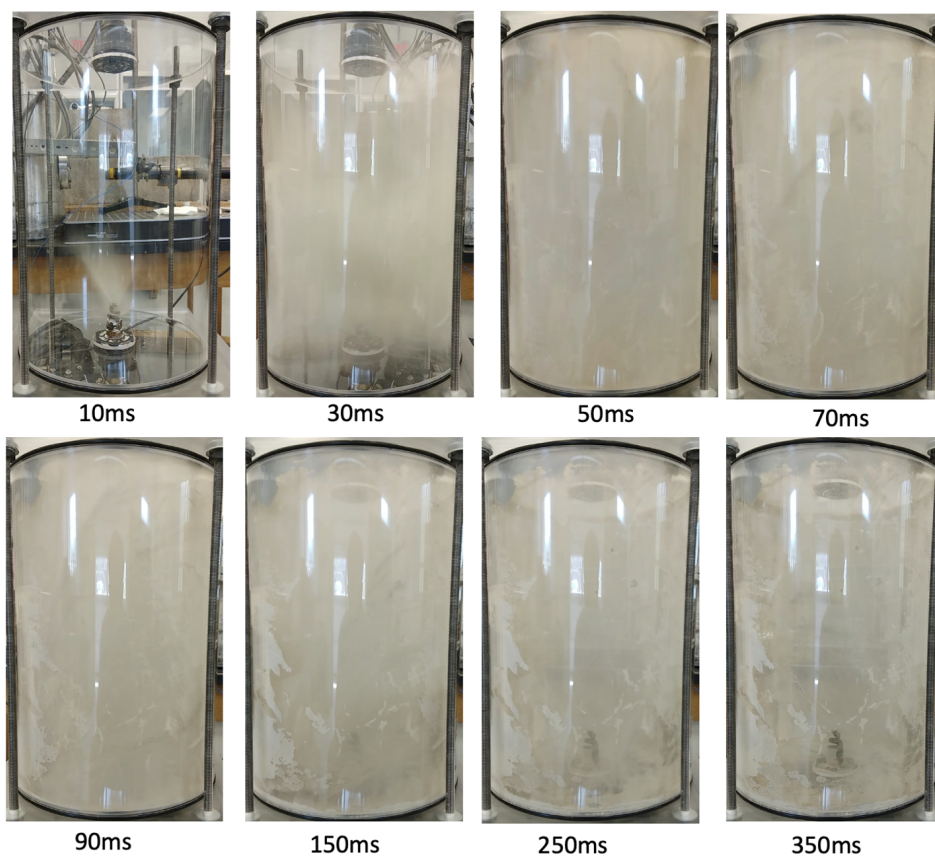


Figure 7.3: Frames of dust dispersion process with dust concentration 880 g/m^3 . Almost all particles settle at the bottom after 350 ms.

Powder	diameter (μm)	density (g/cm^3) [82]	fall velocity (cm/s)	residence time (s)
Cornstarch	20	0.82	0.98	31
Sugar	20	0.80	0.56	45
Coal fines	30	0.64	1.73	17
Graphite	30	0.56	1.51	20
Aluminum	30	0.71	1.92	16

Table 7.1: Fall velocity and the calculated residence time of various particulate precursors.

7.2 Results and Discussion

Figure 7.5 summarizes the different particulate precursors utilized during an explosion, their average particle size, pre- and post-explosion mass, typical burn time, the oxidizer and igniter employed, and any observed changes in powder color following an explosion. Notably, one instance involved graphite, which was not ignited using an electric spark but was easily burned with an electric matchstick. Visual representation of a standard explosion and the chamber after an explosion is depicted in Figure 7.4. When we analyzed the explosion video, we saw a bright white and bluish flash for a short time and a continuous burn with a red flame for longer. Figure 7.4b shows the burnt and unburnt powder fraction after the explosion with a burned layer at the top. This explains why only some powder was burned because most of the powder had already settled at the bottom before burning. So, if we can increase the energy and disperse particles for a longer time, we can burn all the powder in the first blue flash.

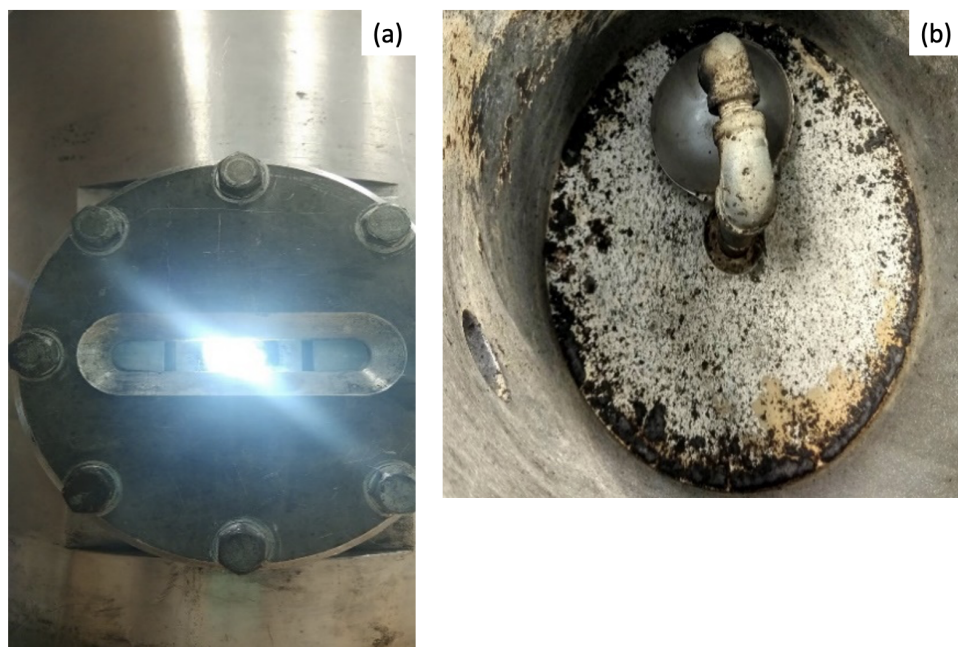


Figure 7.4: (a) Snapshot during an explosion and (b) bottom of the chamber after an explosion. The burnt layer on top of the unburnt layer supports our observation that particles start to burn while settling.

Powder	Size (μm)	Mass before (g)	Mass after (g)	Burning time	Gas used	Igniter	Color after explosion
Graphite	50 - 70	15	10	4.5 s	O ₂	Matchstick	Grey
	20 - 35	15	8.2	2.5 s		Matchstick	Grey
	20 - 35	15		Not burned		Electric spark	
Walnut char	< 10 (majority)	15	8	5.5 s	O ₂	Matchstick	White
		15	4	400 ms	CH ₄ , O ₂		
Agricultural dust	10 - 100	10	2.5	2 s	O ₂	Electric spark	Partial black
		15	5.8	2 s	O ₂	Electric spark	
		20	4.5	2.5 s	O ₂ , H ₂	Electric spark	
		15	1.3	8.5 s	O ₂ , CH ₄	Matchstick	
Sugar	10 - 35	5	~ 0	300 ms	O ₂	Electric spark	Brown
		10	1.8	434 ms			
		15	4	434 ms			
cornstarch	15 - 20	15	3.2	3 s	O ₂ , CH ₄	Electric spark	Partial black
Coal fines	10 - 40	15	6	5 s	O ₂	Matchstick	Further black
Graphene	100 (nm)	4	0.4	1.5 s	O ₂	Electric spark	No change

Figure 7.5: Detail about the particulate precursors before and after an explosion.

7.3 Conclusion

Despite our significant effort, none of the particulate precursors underwent complete combustion during the explosion, and we were unable to extract any valuable material from the powders. Figure 7.5 displays that graphene powder had the highest burn rate, with approximately 90%, while powdered sugar had the shortest burn time. As a result, we ultimately halted this project but plan to revisit it with a better understanding of dispersion and ignition energies. To summarize, we successfully dispersed the powder in a 4 L and 17 L chamber, and observations during the dispersion process showed that the particles settled in just a few hundred milliseconds. The spiral nozzle demonstrated the best performance among the three powder dispersers tested. We subsequently adapted the dispersion system to a 17 L explosion chamber and were able to burn approximately 90% of the powder using an electric matchstick and oxygen. However, we could not achieve complete combustion within a few milliseconds, and the average burn time during an explosion was between 1 to 3 seconds.

Chapter 8

Overall trends

8.1 Product yield during an explosion

Figure 8.1 shows the carbon mass yield versus O/C ratio for each hydrocarbon precursor used in this study. The primary products from a hydrocarbon explosion consist of solid carbon, carbon monoxide, hydrogen, and a minimal quantity of carbon dioxide and water. The generation of solid carbon decreases linearly as the oxygen-to-carbon ratio (O/C) rises, as more oxygen becomes accessible to form carbon monoxide and carbon dioxide. When the O/C ratio is less than 1, carbon dioxide does not form. As the O/C ratio exceeds 1, carbon monoxide production decreases while carbon dioxide formation increases. Likewise, water begins to form, depleting the amount of hydrogen at $O/C > 1$. Also, with aromatic hydrocarbons, when the O/C ratio is greater than 1, a trace amount of carbon is formed. The information on which explosion products forms at different oxygen-fuel ratios from all hydrocarbons and cross-referencing them with the flammability limits [65] of the respective hydrocarbons will assist in selecting the appropriate hydrocarbon for the experiment.

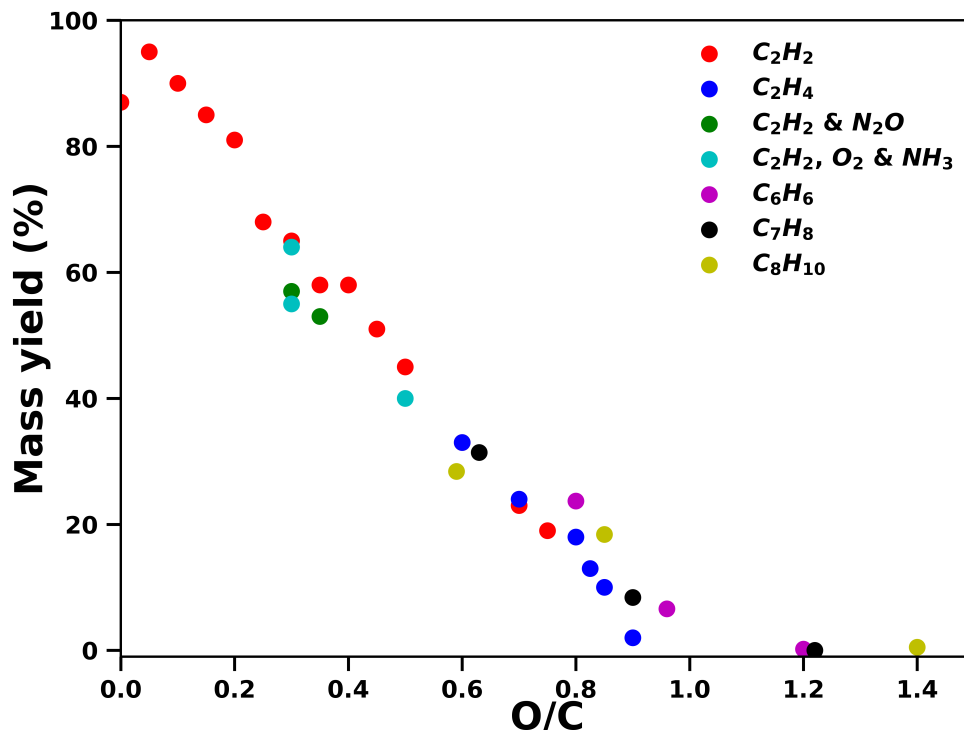


Figure 8.1: Mass yield vs O/C ratio of all hydrocarbon precursors. The mass yield of carbon samples decreased linearly with O/C ratios. This trend aligns with our findings, indicating that at higher oxygen content, carbon monoxide and carbon dioxide are produced at the cost of carbon, resulting in lower carbon samples.

8.2 Peak explosion temperature

Figure 8.2 shows the peak explosion temperature measured using a spectroscopic technique of all hydrocarbons plotted vs. O/C ratio. The measured temperature is in the range of 1800–3100 K, increasing with the O/C ratio. Based on the Raman and TEM characterization results, the temperature of around 2100 K separates the graphene and the soot regime. This result shows that a temperature greater than 2100 K is necessary for obtaining graphene. These results indicate a temperature threshold for the graphene formation exists at which the carbon undergoes significant graphitization and the transition from soot to graphene. Also, we form graphene instead of graphite at this high temperature due to the short time frame of the explosion process. The temperature peaks and quench rapidly within a few ms, as a result of which thus, graphitized graphene sheets do not have the opportunity to stack into the more stable and ordered AB layering of graphite, instead trapping them in a

metastable state known as turbostratic graphene [83]. This change in morphology at high temperatures has been seen in other studies. For example, Luong et al. [43] used rapid joule heating to get the high-temperature condition that produces turbostratic graphene from any carbon-containing precursors.

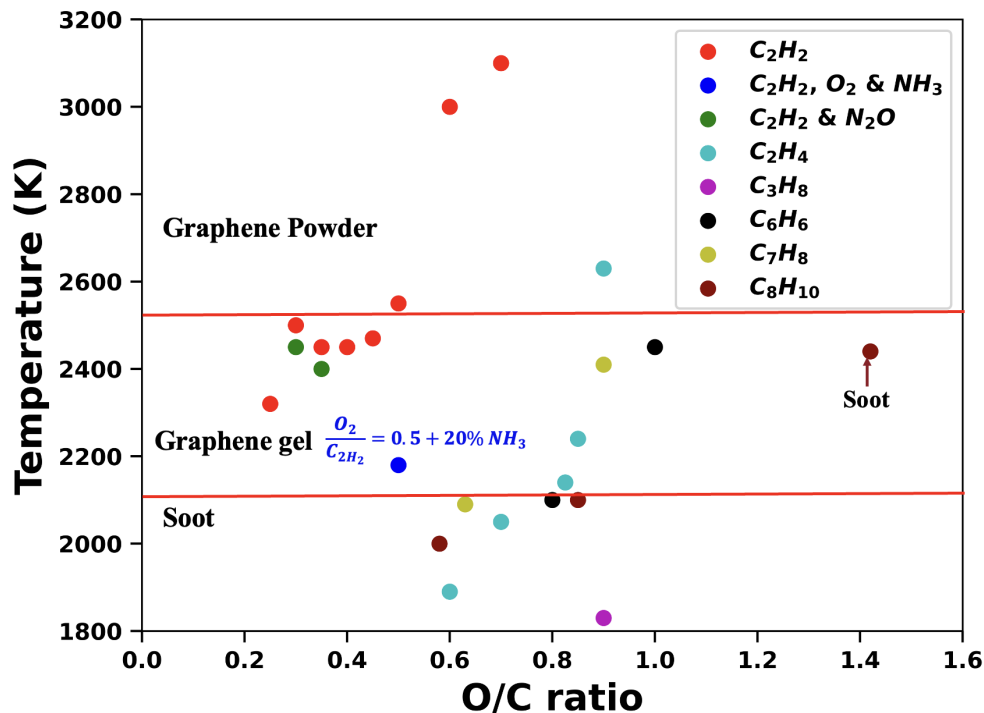


Figure 8.2: Peak explosion temperature of all hydrocarbons. The red line shows three different regimes: soot, graphene gel, and graphene powder. These distinctions are based on Raman and TEM imaging and also from visual observation.

We also attempted to predict the adiabatic flame temperature at constant volume based on the expected chemical reaction that happens with all precursors during an explosion. Predicted chemical reactions are based on the fact that the carbon in the precursor gas goes to either free carbon in the form of graphene, carbon monoxide, and carbon dioxide. Similarly, hydrogen and oxygen in the reactant go to hydrogen gas and water. Applying the first law of thermodynamics enables us to calculate the high temperature that arises during a constant volume explosion, which is adiabatic due to the rapidity of the explosion. The exothermic chemical reaction releases heat, causing the temperature of the products to increase up to a maximum point. This maximum temperature is known as the adiabatic

flame temperature. The first law of Thermodynamics,

$$\Delta U = Q - W = Q - P\Delta V \quad (8.1)$$

In Eq. 8.1 Q is the heat created by the combustion reaction, ΔU is the change in internal energy of the gas, P is the pressure, and ΔV is the change in the gas volume. At constant volume, equation 8.1 becomes,

$$Q = \Delta U \quad (8.2)$$

Using enthalpy and ideal gas law,

$$\begin{aligned} H &= U + PV = U + nRT \\ \Delta H &= \Delta U + \Delta(nRT) \end{aligned} \quad (8.3)$$

Where ΔH is the change in enthalpy of formation, n is the number of moles of gas, R is universal gas constant and ΔT is the change in temperature. From equation 8.2 and 8.3,

$$Q = \Delta H - \Delta(nRT)$$

In adiabatic process,

$$\begin{aligned} Q &= 0 = \Delta H - \Delta(nRT) \\ H_{products}(T_{ad}, P) - H_{reactants}(T_i, P) - R(n_{products}T_{ad} - n_{reactants}T_i) &= 0 \end{aligned} \quad (8.4)$$

Using the enthalpy of formation value for the reactants and products [84] and using Eqn 8.4, we calculated the adiabatic flame temperature (T_{ad}). Figure 8.3 shows the temperature calculated using this method.

As expected, the adiabatic flame temperature rises along with the O/C ratio for all hydrocarbons. An approximate threshold temperature of 2200 K separates the formation of

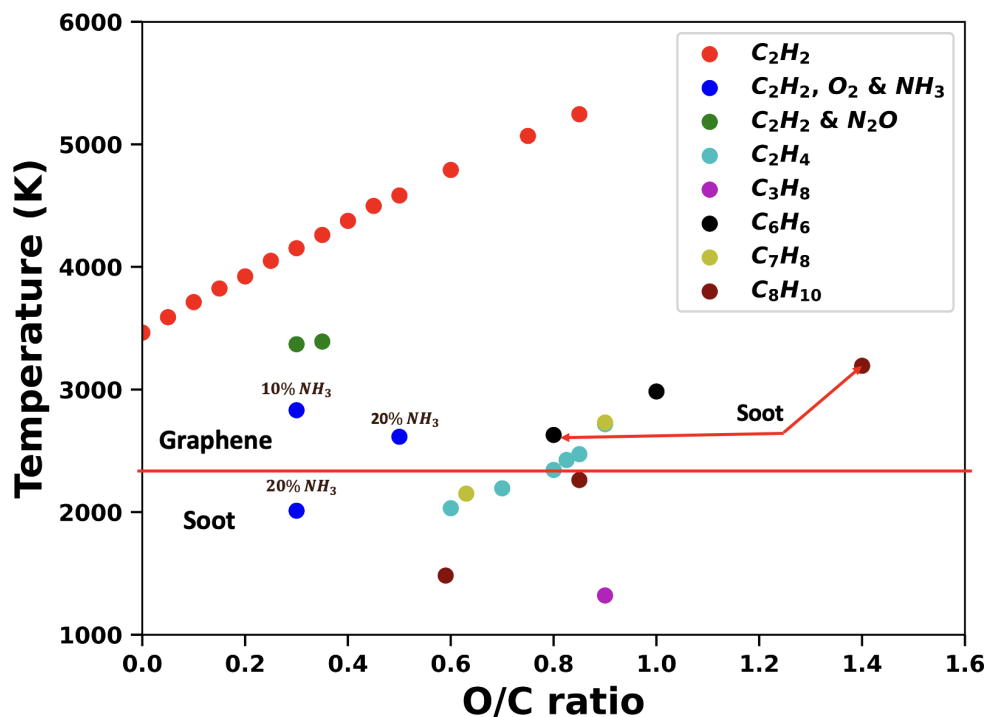


Figure 8.3: Calculated adiabatic flame temperature of all hydrocarbons. The red line shows two different regimes: soot and graphene. These distinctions are based on Raman and TEM imaging and also from visual observation.

soot and graphene, although there are a few exceptions. This differentiation is determined by analyzing Raman and TEM data. Consequently, by considering the anticipated chemical reactions, we can generally forecast the ability of a hydrocarbon precursor to generate graphene even before conducting any experiments.

The calculated adiabatic flame temperature, determined based on predicted chemical reactions, is higher than the temperature measured during an explosion, Figure 8.4. There are two possible explanations for this disparity. Firstly, the calculated temperature assumes the complete conversion of all fuel into carbon, carbon monoxide, hydrogen, water, or carbon dioxide. However, since these reactions are fuel-rich, some fuel remains unreacted, as seen in the FTIR analysis of the gaseous product, leading to a decrease in temperature compared to the calculated value. For example, if we assume 10% of acetylene remains unreacted, the calculated adiabatic flame temperature decreases by 650 ± 50 K from what we measured with the 100% acetylene conversion.

Secondly, the spectrometer used in the measurements has a significant buffer time (1.8 milliseconds between two spectra), which introduces the possibility of consistently missing the peak temperature of the explosion. This accounts for the temperature discrepancy observed in the separate measurements conducted by Nepal et al. [22] and Wright et al. [24], who employed a two-color pyrometer and a spectrometer, respectively, yielding different values for the temperature of the same hydrocarbon explosions.

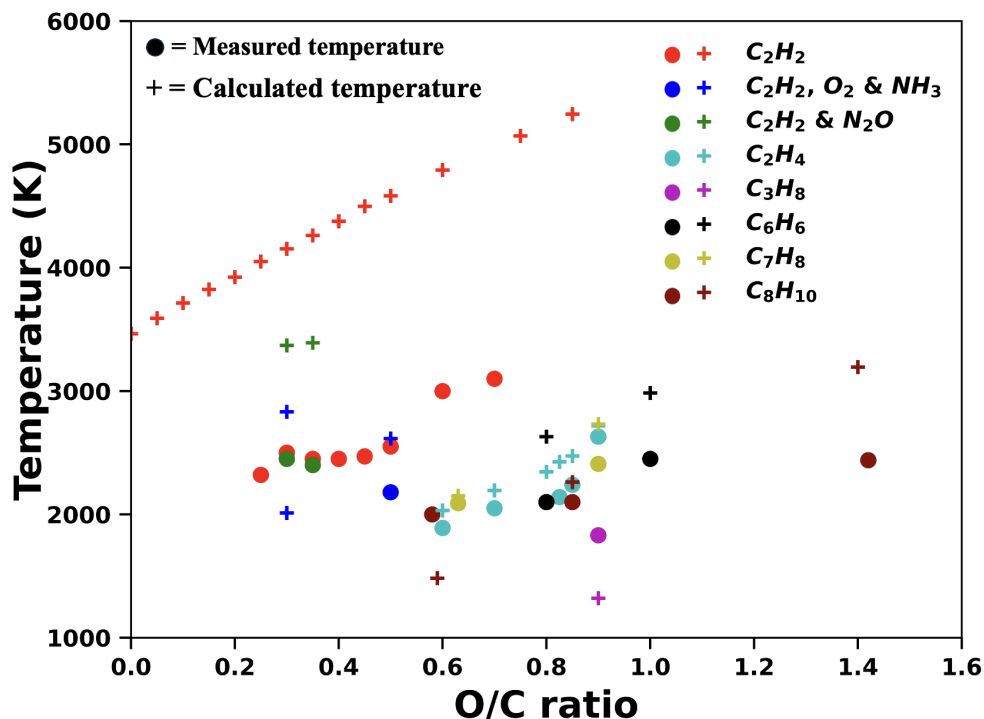


Figure 8.4: The combined graph of the theoretical adiabatic flame temperature (AFT) and the peak explosion temperature measured during an experiment. A solid circle represents the experimentally measured temperature, while a solid plus symbol represents the calculated AFT. The temperatures are labeled with different colors corresponding to different hydrocarbon precursors.

8.3 Characterization trend vs O/C ratio

8.3.1 HRTEM and TEM morphology

Microscopy images in Chapters 3 and 4 show that the carbon formed in this study has two different morphologies: amorphous soot and multi-layer graphene. The carbon formed at a lower O/C ratio from all hydrocarbons is either soot or a mixture of soot and graphene. Whereas at higher O/C, the morphology changes from soot to graphene.

8.3.2 Raman intensity ratios

The distinction between soot and graphite in the Raman spectra is the 2D band, the overlapping of D and G bands [85], which was calculated as described in Figure 8.5b. Graphite has a 2D band at around 2715 cm^{-1} , and the D and G band does not overlap. Whereas soot has no 2D band, and the D and G bands overlap with each other. And the difference between graphite and graphene is the position of the 2D band. In the case of graphene, the 2D band appears at a lower wavenumber at around 2680 cm^{-1} . Figure 8.6 shows the overlap of the D and G bands and the intensity ratios of different Raman bands versus the O/C ratio for all hydrocarbons.

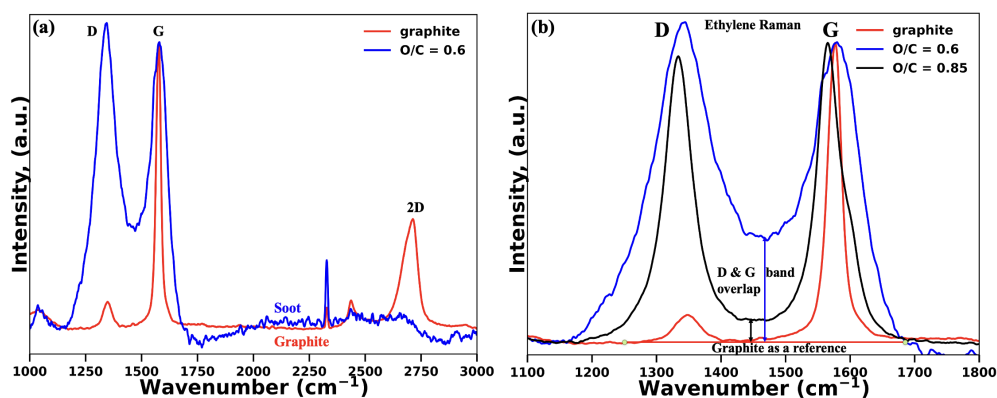


Figure 8.5: Raman spectra of ethylene sample compared with graphite. (a) The complete Raman spectra of O/C = 0.6 (soot) and graphite. Notably, the soot sample has no 2D band. (b) The Raman spectra of graphite, soot, and graphene samples obtained from ethylene were analyzed to determine the relative overlap of the D and G bands. The calculation was performed using the Raman spectra of graphite as a reference.

As the O/C ratio increases, the relative overlap of the D–G band decreases, implying soot to graphene transition, Figure 8.5a. And the intensity ratio, I_D/I_G , of the graphene sample decreases, meaning the graphene is more ordered and crystalline (Figure 8.6). The I_{2D}/I_G ratio for all graphene samples is greater than 0.3, indicating few-layer graphene (Figure 8.6). The 2D band for all graphene samples can be represented by a single Gaussian, which is a characteristic of turbostratic graphene. From Raman, we can infer that all hydrocarbons produce soot at lower O/C, and then the morphology changes to multi-layer graphene at higher O/C. Thus, formed graphene is turbostratic.

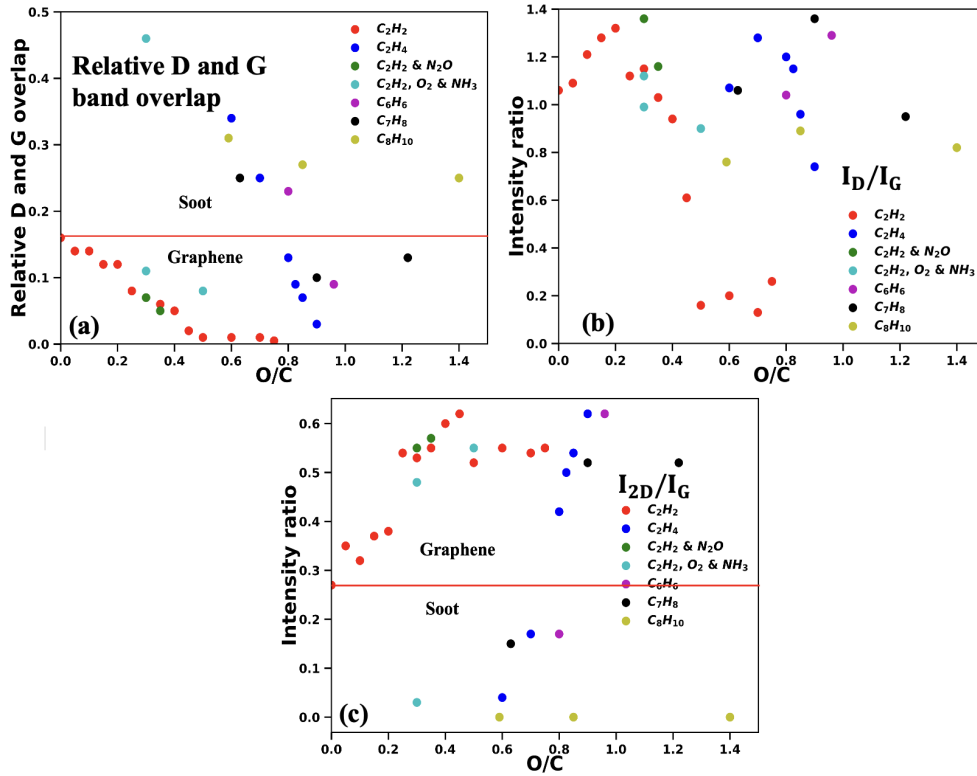


Figure 8.6: Combined Raman analysis of all hydrocarbons. (a) Relative overlap of Raman D and G bands. The soot sample shows a higher relative overlap than the graphene samples. (b) Intensity ratio, I_D/I_G . (c) Intensity ratio, I_{2D}/I_G . Graphene samples has a higher 2D band intensity compared to the soot samples.

8.3.3 XRD FWHM of (002) peak, crystallite size, and the number of layers

Figure 8.7 shows the X-ray diffraction analysis of the carbon produced in this study. The full width at half max (FWHM) and crystallite size are used to determine the carbon samples' crystallinity and crystal size [86]. Acetylene and ethylene samples at high O/C have a lower (002) FWHM value to imply a large crystallite size, indicating a more ordered and higher crystalline sample. Other samples have broader (002) bands indicating the smaller crystallite and the presence of amorphous carbon to some extent.

The d-spacing (d) was determined using Bragg's law (Eqn 3.4), and crystallite size (τ) was obtained using the Scherrer equation (Eqn 3.5). By dividing the crystallite size (τ) by d-spacing (d), the number of layers was determined and found to be between 6–30 layers. A higher O/C sample with a high explosion temperature and larger crystallite size has a higher number of layers, and the lower O/C sample with a lower peak explosion temperature has fewer layers.

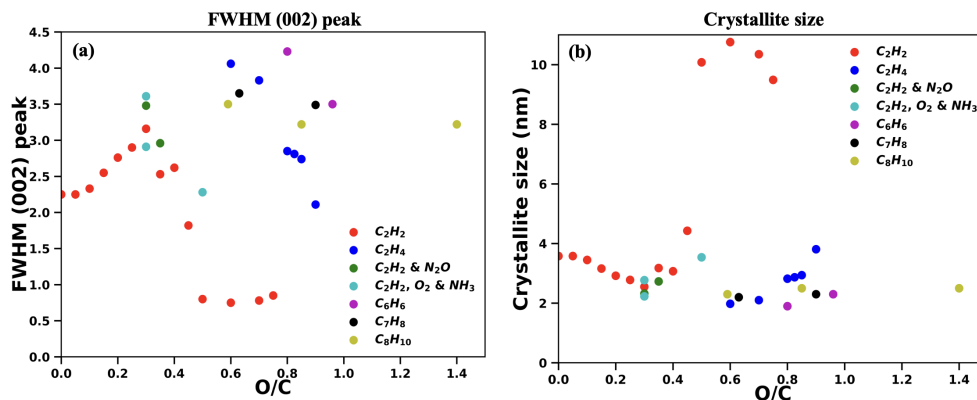


Figure 8.7: X-ray diffraction (XRD) analysis of carbon formed from all hydrocarbon precursors.

8.3.4 BET specific surface area

Figure 8.8 shows the specific surface area (SSA) of various hydrocarbons. The SSA does not exhibit a clear overall trend. However, a lower SSA is observed at lower O/C ratios and with

a sooty sample in each hydrocarbon sample. As the O/C ratio increases, the surface area gradually increases, signifying the transition from soot to graphene. Subsequently, the SSA begins to decrease at higher O/C ratios, where graphene is present in powder form. Notably, the SSA for the benzene and toluene samples is nearly twice that of acetylene and ethylene, primarily due to the smaller size of the primary particles, as evident from TEM imaging.

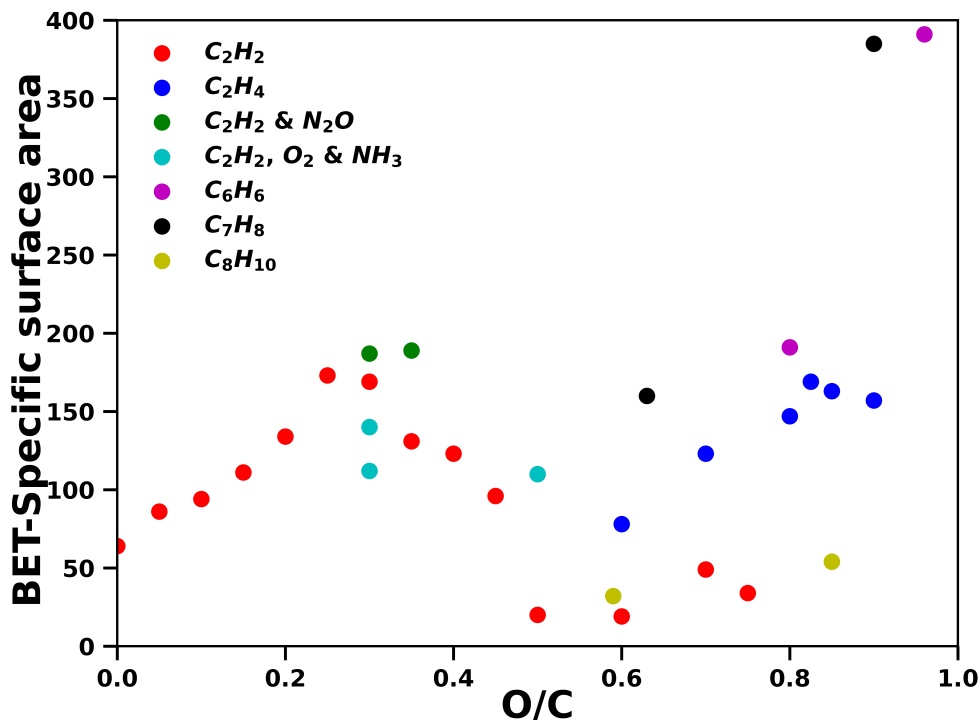


Figure 8.8: Combined BET-specific surface area of all hydrocarbon precursors. The SSA for all hydrocarbons shows an increasing trend with the O/C ratio until reaching a peak, after which it starts to decrease at higher O/C ratios. This trend is consistent with our previous finding that the lower O/C samples tend to be either soot or a mixture of soot and graphene, characterized by larger particles. As the O/C ratio increases, the particles transform into a graphene gel with smaller particle sizes and a layered sheet structure. However, at higher O/C ratios, the particle size increases, leading to a reduction in SSA.

8.4 Necessary condition for the formation of graphene in the explosion process

By conducting a comprehensive experiment involving aliphatic and aromatic hydrocarbons and analyzing the carbon generated during an explosion, we can assert that temperature is a crucial factor in graphene formation. The critical temperature that distinguishes the formation of soot from graphene is approximately 2100 K. This conclusion gains further support from our findings that when 20% ammonia is added to a mixture of 0.3 acetylene-oxygen, the peak explosion temperature drops below 2100 K, resulting in a morphological transition from few-layer graphene to soot. Besides temperature, the structure of the carbon formed also depends, to some extent, on the characteristics of the initial hydrocarbon precursor. Some hydrocarbons can be graphitized (layered graphene structure) at around 2200 °C, while others do not exhibit any signs of graphitic layer structure even at 3000 °C [87].

However, it is important to acknowledge certain limitations regarding the temperature threshold for soot and graphene formation. Despite reaching a peak temperature above 2500 K, xylenes and propane still produce soot. Based on these observations, we can empirically conclude that an excess of methyl groups hinders the formation of graphene during the explosion process. The specific reasons behind this phenomenon remain subjects for future research.

8.5 Practical use of graphene, nitrogen-doped graphene and syngas in the real word

We have successfully demonstrated the utilization of graphene derived from acetylene in micro-supercapacitors [44] and as a cathode catalyst in lithium-oxygen batteries [45]. Additionally, explosive graphene has been effectively modified into reactive graphene using a modified Hummers' method [88]. Our current research focuses on exploring the application of graphene in lubrication to enhance the tribological performance of base oil. Furthermore,

we are incorporating graphene into concrete and plastics to bolster their strength.

Due to the higher specific surface area (SSA) of graphene derived from aromatic hydrocarbons compared to aliphatic, we are conducting a study to employ high SSA graphene in constructing a 3D-printed supercapacitor. Moreover, this graphene variant is promising as a cathode material in battery applications. We are investigating nitrogen-doped graphene as a cathode catalyst for methanol oxidation and oxygen reduction reactions in direct methanol fuel cells (DMFCs). The N-doping process increases the conductivity of graphene by introducing more conducting electrons, and efforts are underway to develop a highly conductive ink using N-doped graphene.

Recognizing hydrogen as a potential next-generation energy source, our team is developing a continuous methane engine that converts methane into syngas.

8.6 Prospective future work to fully understand the explosion synthesis process

Our main aim is to get a comprehensive understanding of the role of hydrocarbons in the explosion synthesis process, which will build a base to choose the right precursors. We aim to investigate the influence of ignition energy on the morphology of the resulting graphene. Our collaboration with the Missouri University of Science and Technology has already generated some initial findings, and we plan to continue this work. Also, we will delve deeper into the study of pure acetylene explosions.

Furthermore, we will enhance our method for synthesizing nitrogen-doped graphene to augment the nitrogen content in the samples. We have already made progress in producing various metal-doped graphene through collaboration with the Chemical Engineering Department at K-State, and we will continue to optimize this project. Additionally, we will explore the practical applications of the samples generated in this research.

8.7 Conclusion

In conclusion, this systematic study focused on the formation and characterization of carbon generated during the explosion of various hydrocarbon precursors. The collected carbon was subjected to various characterization techniques, including Raman spectroscopy, X-ray diffraction (XRD), and high-resolution transmission electron microscopy (HRTEM). The analyses revealed the presence of two product types for all hydrocarbons: amorphous soot and multi-layer graphene. The graphene exhibited a turbostratic structure consisting of 6–30 layers, depending on the O/C ratio and precursor used.

An examination of different precursor mixtures and their explosion temperatures determined that a high temperature greater than 2100 K during constant volume explosion and an unsaturated hydrocarbon with lower hydrogen content is the main reason graphene was formed. The findings of this study were supported to some extent by theoretical calculations of adiabatic flame temperature based on anticipated chemical reactions during the explosion.

The results demonstrated that the carbon formed exhibited different properties depending on the initial oxygen-carbon ratio and the peak temperature. At higher oxygen levels and a higher peak temperature, the carbon appeared as a powder, while at lower oxygen levels and a lower peak temperature, it formed an aerosol gel with a larger carbon yield. The explosion temperature was measured using a spectrometer, revealing temperatures ranging from 1900 to 3100 K, with the peak temperature increasing as the oxygen-carbon (O/C) ratio increased.

The explosion process was extended beyond graphene production to generate syngas and doped graphene. A thorough analysis of the product gas resulting from the explosion revealed that the predominant components were carbon monoxide and hydrogen, commonly known as syngas. Among all hydrocarbons, methane demonstrated superior suitability for syngas production because it did not produce any carbon. The study also delved into the production of nitrogen-doped graphene by introducing nitrogen-bearing gas during the explosion of acetylene and by utilizing pyridine as a hydrocarbon precursor. X-ray photoelectron

spectroscopy (XPS) analysis verified the presence of nitrogen in the resulting carbon, with varying atomic percentages ranging from 0.6% to 3.4%, depending on the precursor material. Moreover, we successfully synthesized titanium-doped graphene through the explosion process, with potential applications currently under exploration.

In addition to characterizing the carbon formed during the explosion, the study investigated fine powder dispersion in different chamber sizes and conducted explosion experiments using various powder samples. The experiments revealed incomplete combustion and longer burn times, highlighting the need for further exploration and optimization to achieve efficient combustion.

Overall, this systematic study contributes to a deeper understanding of graphene formation, its characteristics under different experimental conditions, and the potential for producing nitrogen-doped graphene through controlled explosion processes. The findings have implications for the development of graphene-based materials with tailored properties and highlight areas for future research and improvement in an explosion process.

Bibliography

- [1] Hanns-Peter Boehm. Graphene—how a laboratory curiosity suddenly became extremely interesting. *Angewandte Chemie International Edition*, 49(49):9332–9335, 2010.
- [2] Kostya S Novoselov, Andre K Geim, Sergei V Morozov, De-eng Jiang, Yanshui Zhang, Sergey V Dubonos, Irina V Grigorieva, and Alexandr A Firsov. Electric field effect in atomically thin carbon films. *science*, 306(5696):666–669, 2004. doi: 10.1126/science.1102896.
- [3] Daniel C Elias, Rahul Raveendran Nair, TMG Mohiuddin, SV Morozov, P Blake, MP Halsall, Andrea Carlo Ferrari, DW Boukhvalov, MI Katsnelson, AK Geim, et al. Control of graphene’s properties by reversible hydrogenation: evidence for graphane. *Science*, 323(5914):610–613, 2009.
- [4] AH Castro Neto, Francisco Guinea, Nuno MR Peres, Kostya S Novoselov, and Andre K Geim. The electronic properties of graphene. *Reviews of modern physics*, 81(1):109, 2009. doi: 10.1103/RevModPhys.81.109.
- [5] Andre K Geim and Konstantin S Novoselov. The rise of graphene. *Nature materials*, 6(3):183–191, 2007. doi: 10.1038/nmat1849.
- [6] Changgu Lee, Xiaoding Wei, Jeffrey W Kysar, and James Hone. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *science*, 321(5887):385–388, 2008. doi: 10.1126/science.1157996.
- [7] D Cooper, B D’Anjou, N Ghattamaneni, B Harack, M Hilke, A Horth, et al. Isrn condensed matter. *Phys*, 2012:501686, 2012.
- [8] Andre Konstantin Geim. Graphene: status and prospects. *science*, 324(5934):1530–1534, 2009. doi: 10.1126/science.1158877.

- [9] Jonathan K Wassei and Richard B Kaner. Graphene, a promising transparent conductor. *Materials today*, 13(3):52–59, 2010. doi: 10.1016/S1369-7021(10)70034-1.
- [10] Konstantin S Novoselov, Vladimir I Falko, Luigi Colombo, Pr R Gellert, Matthias Georg Schwab, and Kwanpyo Kim. A roadmap for graphene. *nature*, 490(7419):192–200, 2012. doi: 10.1038/nature11458.
- [11] J Scott Bunch, Scott S Verbridge, Jonathan S Alden, Arend M Van Der Zande, Jeevak M Parpia, Harold G Craighead, and Paul L McEuen. Impermeable atomic membranes from graphene sheets. *Nano letters*, 8(8):2458–2462, 2008. doi: 10.1021/nl801457b.
- [12] Yanwu Zhu, Shanthi Murali, Weiwei Cai, Xuesong Li, Ji Won Suk, Jeffrey R Potts, and Rodney S Ruoff. Graphene and graphene oxide: synthesis, properties, and applications. *Advanced materials*, 22(35):3906–3924, 2010. doi: 10.1002/adma.201001068.
- [13] The Graphene Council. The graphene council classification framework. *The Graphene Council*, page 17, 2022. URL www.thegraphenecouncil.org.
- [14] European Chemical Agency. The reach consortia filing with echa in europe. *ECHA*, 2022. URL <https://echa.europa.eu>.
- [15] Bing Deng, Zhongfan Liu, and Hailin Peng. Toward mass production of cvd graphene films. *Advanced Materials*, 31(9):1800996, 2019. doi: 10.1002/adma.201800996.
- [16] Roberto Munoz and Cristina Gómez-Aleixandre. Review of cvd synthesis of graphene. *Chemical Vapor Deposition*, 19(10-11-12):297–322, 2013. doi: <https://doi.org/10.1002/cvde.201300051>.
- [17] Maryam Saeed, Yousef Alshammari, Shereen A Majeed, and Eissa Al-Nasrallah. Chemical vapour deposition of graphene—synthesis, characterisation, and applications: A review. *Molecules*, 25(17):3856, 2020. doi: 10.3390/molecules25173856.
- [18] Yenny Hernandez, Valeria Nicolosi, Mustafa Lotya, Fiona M Blighe, Zhenyu Sun, Sukanta De, Ignatius T McGovern, Brendan Holland, Michele Byrne, Yurii K Gun’Ko,

- et al. High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature nanotechnology*, 3(9):563–568, 2008. doi: 10.1038/nnano.2008.215.
- [19] Wencheng Du, Xiaoqing Jiang, and Lihua Zhu. From graphite to graphene: direct liquid-phase exfoliation of graphite to produce single-and few-layered pristine graphene. *Journal of Materials Chemistry A*, 1(36):10592–10606, 2013. doi: 10.1039/C3TA12212C.
- [20] Colin Hong An Wong, Zdeněk Sofer, Marie Kubešová, Jan Kučera, Stanislava Matějková, and Martin Pumera. Synthetic routes contaminate graphene materials with a whole spectrum of unanticipated metallic elements. *Proceedings of the National Academy of Sciences*, 111(38):13774–13779, 2014. doi: 10.1073/pnas.1413389111.
- [21] Arjun Nepal, Gajendra P Singh, Bret N Flanders, and C M Sorensen. One-step synthesis of graphene via catalyst-free gas-phase hydrocarbon detonation. *Nanotechnology*, 24(24):245602, 05 2013. doi: 10.1088/0957-4484/24/24/245602. URL <https://doi.org/10.1088/0957-4484/24/24/245602>.
- [22] Arjun Nepal. *GRAPHENE NANOSHEETS PRODUCED VIA CONTROLLED DETONATION OF HYDROCARBONS*. Kansas State University, 2015.
- [23] Justin P. Wright, Shusil Sigdel, Stephen Corkill, Jose Covarrubias, Levon LeBan, Arjun Nepal, Jun Li, Ranjith Divigalpitiya, Stefan H. Bossmann, and Christopher M. Sorensen. Synthesis of turbostratic nanoscale graphene via chamber detonation of oxygen/acetylene mixtures. *Nano Select*, 3(6):1054–1068, 2021. doi: 10.1002/nano.202100305. URL <https://doi.org/10.1002/nano.202100305>.
- [24] Justin P. Wright. *A systematic empirical study on the synthesis of turbostratic nanoscale graphene produced via chamber detonation of gaseous hydrocarbon precursors*. Kansas State University, 2022.
- [25] Young Jeong Kim, Sanghoon Lee, Peter Pikhitsa, and Mansoo Choi. Laser induced transition from soot generation to shell shaped carbon nanoparticles in an acetylene

- flow: aerosol characterization. *Journal of mechanical science and technology*, 22:134–140, 2008. doi: 10.1007/s12206-007-1016-7.
- [26] Mirosława Pawlyta, Jean-Noël Rouzaud, and Stanislaw Duber. Raman microspectroscopy characterization of carbon blacks: Spectral analysis and structural information. *Carbon*, 84:479–490, 2015. doi: 10.1016/j.carbon.2014.12.030.
- [27] Wikipedia. Benzene, 2023. URL <https://en.wikipedia.org/wiki/Benzene>.
- [28] Science Direct Topics. Benzene, 1996. URL <https://www.sciencedirect.com/topics/chemical-engineering/benzene>.
- [29] Arjun Nepal and CM Sorensen. Temperature of detonation of hydrocarbons measured with a two-color pyrometer. *ACTA Scientific Applied Physics*, 2(4):28–33, 2022. URL <https://actascientific.com/ASAP/pdf/ASAP-02-0045.pdf>.
- [30] L.A.K. Staveley. *The Characterization of Chemical Purity: Organic Compounds*. Elsevier Science, 2016. ISBN 9781483279992. URL <https://books.google.com/books?id=DzUXBQAAQBAJ>.
- [31] Andrea Ferrari and Denis Basko. Raman spectroscopy as a versatile tool for studying the properties of graphene. *Nature nanotechnology*, 8:235–46, 04 2013. doi: 10.1038/nnano.2013.46.
- [32] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim. Raman spectrum of graphene and graphene layers. *Phys. Rev. Lett.*, 97:187401, Oct 2006. doi: 10.1103/PhysRevLett.97.187401. URL <https://link.aps.org/doi/10.1103/PhysRevLett.97.187401>.
- [33] L.M. Malard, M.A. Pimenta, G. Dresselhaus, and M.S. Dresselhaus. Raman spectroscopy in graphene. *Physics Reports*, 473(5):51–87, 2009. ISSN 0370-1573. doi: <https://doi.org/10.1016/j.physrep.2009.02.003>. URL <https://www.sciencedirect.com/science/article/pii/S0370157309000520>.

- [34] Joseph A Garlow, Lawrence K Barrett, Lijun Wu, Kim Kisslinger, Yimei Zhu, and Javier F Pulecio. Large-area growth of turbostratic graphene on ni (111) via physical vapor deposition. *Scientific Reports*, 6(1):19804, 2016. doi: 10.1126/sciadv.aat0074.
- [35] Wikipedia. X-ray diffraction, 2023. URL https://en.wikipedia.org/wiki/X-ray_crystallography.
- [36] Andrew K Kercher and Dennis C Nagle. Microstructural evolution during charcoal carbonization by x-ray diffraction analysis. *Carbon*, 41(1):15–27, 2003. doi: 10.1016/S0008-6223(02)00261-0.
- [37] Matthias Thommes, Katsumi Kaneko, Alexander V. Neimark, James P. Olivier, Francisco Rodriguez-Reinoso, Jean Rouquerol, and Kenneth S.W. Sing. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (iupac technical report). *Pure and Applied Chemistry*, 87(9-10):1051–1069, 2015. doi: doi:10.1515/pac-2014-1117. URL <https://doi.org/10.1515/pac-2014-1117>.
- [38] A. K. Geim. Graphene: Status and prospects. *Science*, 324(5934):1530–1534, 2009. doi: 10.1126/science.1158877. URL <https://www.science.org/doi/abs/10.1126/science.1158877>.
- [39] Daniel R Cooper, Benjamin D’Anjou, Nageswara Ghattamaneni, Benjamin Harack, Michael Hilke, Alexandre Horth, Norberto Majlis, Mathieu Massicotte, Leron Vandsburger, Eric Whiteway, et al. Experimental review of graphene. *International Scholarly Research Notices*, 2012, 2012.
- [40] ISO. Iso/ts 80004-13:2017(en), nanotechnologies — vocabulary — part 13: Graphene and related two-dimensional (2d) materials, 2017. URL <https://www.iso.org/obp/ui/#iso:std:iso:ts:80004:-13:ed-1:v1:en>.
- [41] Sungjin Park, Jinho An, Inhwa Jung, Richard D Piner, Sung Jin An, Xuesong Li, Aruna Velamakanni, and Rodney S Ruoff. Colloidal suspensions of highly reduced graphene

- oxide in a wide variety of organic solvents. *Nano letters*, 9(4):1593–1597, 2009. doi: 10.1021/nl803798y.
- [42] Claire Berger, Zhimin Song, Xuebin Li, Xiaosong Wu, Nate Brown, Cécile Naud, Didier Mayou, Tianbo Li, Joanna Hass, Alexei N Marchenkov, et al. Electronic confinement and coherence in patterned epitaxial graphene. *Science*, 312(5777):1191–1196, 2006. doi: 10.1126/science.1125.
- [43] Duy X Luong, Ksenia V Bets, Wala Ali Algozeeb, Michael G Stanford, Carter Kittrell, Weiyin Chen, Rodrigo V Salvatierra, Muqing Ren, Emily A McHugh, Paul A Advincula, et al. Gram-scale bottom-up flash graphene synthesis. *Nature*, 577(7792):647–651, 2020. doi: 10.1038/s41586-020-1938-0.
- [44] Anand PS Gaur, Wenjun Xiang, Arjun Nepal, Justin P Wright, Pingping Chen, Thiba Nagaraja, Shusil Sigdel, Brice LaCroix, Christopher M Sorensen, and Suprem R Das. Graphene aerosol gel ink for printing micro-supercapacitors. *ACS Applied Energy Materials*, 4(8):7632–7641, 2021. doi: 10.1021/acsaem.1c00919.
- [45] Syed Shoaib Hassan Zaidi, Shusil Sigdel, Christopher M. Sorensen, Gibum Kwon, and Xianglin Li. Incorporation of Novel Graphene Nanosheet Materials as Cathode Catalysts in Li–O₂ Battery. *Journal of Electrochemical Energy Conversion and Storage*, 20(2), 03 2023. ISSN 2381-6872. doi: 10.1115/1.4056937. URL <https://doi.org/10.1115/1.4056937>. 020907.
- [46] Christopher Sorensen, Arjun Nepal, and Gajendra Prasad Singh. Process for high-yield production of graphene via detonation of carbon-containing material, September 13 2016. US Patent 9,440,857.
- [47] Rajan Dhaubhadel, Corey S Gerving, Amitabha Chakrabarti, and Christopher M Sorensen. Aerosol gelation: Synthesis of a novel, lightweight, high specific surface area material. *Aerosol science and technology*, 41(8):804–810, 2007. doi: 10.1080/02786820701466291.

- [48] R Dhaubhadel, TP Rieker, A Chakrabarti, and Christopher M Sorensen. Synthesis of silica aerosol gels via controlled detonation. *Aerosol Science and Technology*, 46(5): 596–600, 2012. doi: 10.1080/02786826.2011.651175.
- [49] Wongyo Kim, Christopher M Sorensen, Danny Fry, and Amitabha Chakrabarti. Soot aggregates, superaggregates and gel-like networks in laminar diffusion flames. *Journal of aerosol science*, 37(3):386–401, 2006. doi: 10.1016/j.jaerosci.2005.05.022.
- [50] AGNES Oberlin. Carbonization and graphitization. *Carbon*, 22(6):521–541, 1984.
- [51] Agnès Oberlin. High-resolution tem studies of carbonization and graphitization. In *Chemistry and physics of carbon*, pages 1–143. CRC Press, 2021.
- [52] Tomoji Ishiguro, Yoshiki Takatori, and Kazuhiro Akihama. Microstructure of diesel soot particles probed by electron microscopy: First observation of inner core and outer shell. *Combustion and Flame*, 108(1):231–234, 1997. ISSN 0010-2180. doi: [https://doi.org/10.1016/S0010-2180\(96\)00206-4](https://doi.org/10.1016/S0010-2180(96)00206-4). URL <https://www.sciencedirect.com/science/article/pii/S0010218096002064>.
- [53] ZQ Li, CJ Lu, ZP Xia, Y Zhou, and Z Luo. X-ray diffraction patterns of graphite and turbostratic carbon. *Carbon*, 45(8):1686–1695, 2007. doi: 10.1016/j.carbon.2007.03.038.
- [54] BE Warren. X-ray diffraction in random layer lattices. *Physical Review*, 59(9):693, 1941. doi: 10.1103/PhysRev.59.693.
- [55] Hiroyuki Fujimoto. Theoretical x-ray scattering intensity of carbons with turbostratic stacking and ab stacking structures. *Carbon*, 41(8):1585–1592, 2003. ISSN 0008-6223. doi: [https://doi.org/10.1016/S0008-6223\(03\)00116-7](https://doi.org/10.1016/S0008-6223(03)00116-7). URL <https://www.sciencedirect.com/science/article/pii/S0008622303001167>.
- [56] A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner, and U. Pöschl. Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information. *Carbon*, 43(8):1731–1742, 2005. ISSN 0008-6223. doi: <https://doi.org/10.1016/j.carbon.2005.05.011>.

- org/10.1016/j.carbon.2005.02.018. URL <https://www.sciencedirect.com/science/article/pii/S0008622305001247>.
- [57] L. G. Cançado, A. Reina, J. Kong, and M. S. Dresselhaus. Geometrical approach for the study of G' band in the raman spectrum of monolayer graphene, bilayer graphene, and bulk graphite. *Phys. Rev. B*, 77:245408, 06 2008. doi: 10.1103/PhysRevB.77.245408. URL <https://link.aps.org/doi/10.1103/PhysRevB.77.245408>.
- [58] KO Johansson, MP Head-Gordon, PE Schrader, KR Wilson, and HA Michelsen. Resonance-stabilized hydrocarbon-radical chain reactions may explain soot inception and growth. *Science*, 361(6406):997–1000, 2018. doi: 10.1126/science.aat3417.
- [59] Matthew Weisenberger, Ignacio Martin-Gullon, José Vera-Agullo, Helena Varela-Rizo, César Merino, Rodney Andrews, Dali Qian, and Terry Rantell. The effect of graphitization temperature on the structure of helical-ribbon carbon nanofibers. *Carbon*, 47(9): 2211–2218, 2009. doi: 10.1016/j.carbon.2009.03.070.
- [60] Joseph P Abrahamson, Madhu Singh, Jonathan P Mathews, and Randy L Vander Wal. Pulsed laser annealing of carbon black. *Carbon*, 124:380–390, 2017. doi: 10.1016/j.carbon.2017.08.080.
- [61] Piotr Kamedulski, Malgorzata Skorupska, Pawel Binkowski, Weronika Arendarska, Anna Ilnicka, and Jerzy P Lukaszewicz. High surface area micro-mesoporous graphene for electrochemical applications. *Scientific Reports*, 11(1):1–12, 2021. doi: 10.1038/s41598-021-01154-0.
- [62] Iván Esteve-Adell, María Porcel-Valenzuela, Leire Zubizarreta, Mayte Gil-Agustí, Marta García-Pellicer, and Alfredo Quijano-Lopez. Influence of the specific surface area of graphene nanoplatelets on the capacity of lithium-ion batteries. *Frontiers in Chemistry*, 10:807980, 2022. doi: 10.3389/fchem.2022.807980.
- [63] Randall L Vander Wal. A tem methodology for the study of soot particle struc-

- ture. *Combustion science and technology*, 126(1-6):333–351, 1997. doi: 10.1080/00102209708935680.
- [64] Andrea C Ferrari and John Robertson. Interpretation of raman spectra of disordered and amorphous carbon. *Physical review B*, 61(20):14095, 2000. doi: 10.1103/PhysRevB.61.14095.
- [65] Engineering Tool Box. Gases - explosion and flammability concentration limits, 2023. URL https://www.engineeringtoolbox.com/explosive-concentration-limits-d_423.html.
- [66] Alan Williams and David Barry Smith. Combustion and oxidation of acetylene. *Chemical Reviews*, 70(2):267–293, 1970.
- [67] Patrick J Woolcock and Robert C Brown. A review of cleaning technologies for biomass-derived syngas. *Biomass and bioenergy*, 52:54–84, 2013. doi: 10.1016/j.biombioe.2013.02.036.
- [68] André L Boehman and Olivier Le Corre. Combustion of syngas in internal combustion engines. *Combustion Science and Technology*, 180(6):1193–1206, 2008. doi: 10.1080/00102200801963417.
- [69] Barbara Elvers and Fritz Ullmann. *Ullmann’s encyclopedia of industrial chemistry*, volume 16. Wiley-VCh, 1990.
- [70] Arno de Klerk. Fischer–tropsch process. *Kirk-Othmer Encyclopedia of Chemical Technology*, pages 1–20, 2000.
- [71] Jens R Rostrup-Nielsen. *Catalytic steam reforming*. Springer, 1984.
- [72] MR Beychok. Coal gasification and the phenosolvan process. *Am. Chem. Soc., Div. Fuel Chem., Prepr.:(United States)*, 19(5), 1974.

- [73] SS Bharadwaj and Lanny D Schmidt. Catalytic partial oxidation of natural gas to syngas. *Fuel processing technology*, 42(2-3):109–127, 1995. doi: 10.1016/0378-3820(94)00098-E.
- [74] Sivaprakash Sengodan, Rong Lan, John Humphreys, Dongwei Du, Wei Xu, Huanting Wang, and Shanwen Tao. Advances in reforming and partial oxidation of hydrocarbons for hydrogen production and fuel cell applications. *Renewable and Sustainable Energy Reviews*, 82:761–780, 2018. doi: 10.1016/j.rser.2017.09.071.
- [75] Jie Ren, Jing-Pei Cao, Xiao-Yan Zhao, Fei-Long Yang, and Xian-Yong Wei. Recent advances in syngas production from biomass catalytic gasification: A critical review on reactors, catalysts, catalytic mechanisms and mathematical models. *Renewable and Sustainable Energy Reviews*, 116:109426, 2019. doi: 10.1016/j.rser.2019.109426.
- [76] D Usachov, O Vilkov, A Gruneis, D Haberer, A Fedorov, VK Adamchuk, AB Preobrajenski, P Dudin, A Barinov, M Oehzelt, et al. Nitrogen-doped graphene: efficient growth, structure, and electronic properties. *Nano letters*, 11(12):5401–5407, 2011. doi: 10.1021/nl2031037.
- [77] LS Panchakarla, KS Subrahmanyam, SK Saha, Achutharao Govindaraj, HR Krishnamurthy, UV Waghmare, and CNR Rao. Synthesis, structure, and properties of boron-and nitrogen-doped graphene. *Advanced Materials*, 21(46):4726–4730, 2009. doi: 10.1002/adma.200901285.
- [78] Roshni Yadav and CK Dixit. Synthesis, characterization and prospective applications of nitrogen-doped graphene: A short review. *Journal of Science: Advanced Materials and Devices*, 2(2):141–149, 2017. doi: 10.1016/j.jsamd.2017.05.007.
- [79] Liangti Qu, Yong Liu, Jong-Beom Baek, and Liming Dai. Nitrogen-doped graphene as efficient metal-free electrocatalyst for oxygen reduction in fuel cells. *ACS nano*, 4(3):1321–1326, 2010. doi: 10.1021/nn901850u.

- [80] R Imran Jafri, N 7 Rajalakshmi, and SJJMC Ramaprabhu. Nitrogen doped graphene nanoplatelets as catalyst support for oxygen reduction reaction in proton exchange membrane fuel cell. *Journal of Materials Chemistry*, 20(34):7114–7117, 2010. doi: 10.1039/C0JM00467G.
- [81] R.K. Eckhoff. *Dust Explosions in the Process Industries*. Elsevier Science & Technology Books, 1991. ISBN 9780750611091. URL <https://books.google.com/books?id=UP9wQgAACAAJ>.
- [82] ANVAL VALVES PVT LTD. Bulk density chart, 2023. URL <https://anval.net/resource/material-bulk-density-guide/>.
- [83] Kevin M Wyss, Duy Xuan Luong, and James M Tour. Large-scale syntheses of 2d materials: Flash joule heating and other methods. *Advanced Materials*, 34(8):2106970, 2022. doi: 10.1002/adma.202106970.
- [84] Michael Frenklach, Tom Bowman, and Greg Smith. Gri-mech home page, 2000. URL <http://combustion.berkeley.edu/gri-mech/index.html>.
- [85] Markus Knauer, Manfred E Schuster, Dangsheng Su, Robert Schlögl, Reinhard Niessner, and Natalia P Ivleva. Soot structure and reactivity analysis by raman microspectroscopy, temperature-programmed oxidation, and high-resolution transmission electron microscopy. *The Journal of Physical Chemistry A*, 113(50):13871–13880, 2009. doi: 10.1021/jp905639d.
- [86] Ahmad Monshi, Mohammad Reza Foroughi, Mohammad Reza Monshi, et al. Modified scherrer equation to estimate more accurately nano-crystallite size using xrd. *World journal of nano science and engineering*, 2(3):154–160, 2012. doi: 10.4236/wjnse.2012.23020.
- [87] Rosalind E Franklin. Crystallite growth in graphitizing and non-graphitizing carbons. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 209(1097):196–218, 1951. doi: 10.1098/rspa.1951.0197.

- [88] Stefan Bossmann, Christopher Sorensen, Jose Covarrubias, Madumali Kalubowilage, and Arjun Nepal. Graphene/graphene oxide core/shell particulates and methods of making and using the same, June 17 2020.