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Author: Pritishma Lakhe Devon Kulhanek Wanmei Sun Bin Zhang Micah J. Green M. Sam Mannan

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Calorimetry of Explosive Thermal Decomposition of Graphite Oxide

Pritishma Lakhe[1], Devon Kulhanek[2], Wanmei Sun[2], Bin Zhang[1], Micah J. Green[2,*] and M. Sam Mannan[1]

[1]Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843, USA
[2]Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843, USA

[*]Corresponding author: Micah J. Green, Tel: +1 979 862 1588; Fax: +1 979 458 1493; E-mail: micah.green@tamu.edu; Mailing address: 3122 TAMU Room 200, College Station, TX 77843

Abstract

Graphite oxide (GO) has shown immense potential in energy storage and composite filler applications, and large-scale production of GO is of increasing commercial and academic interest. However, prior studies show that GO has the potential to undergo explosive decomposition. In this study, advanced Reactive System Screening Tool was used to track the temperature and pressure of the explosive decomposition of GO. The data showed that the explosive decomposition temperature of GO strongly depends on sample size. The temperature and pressure generation are on the order of 1000s of °C per minute and 1000s of psig per minute respectively for less than a gram of material. Therefore, the rapid decomposition of bulk GO can lead to catastrophic consequences. The paper further compared the thermal stability of GO from different sources and found that the GO surface area has significant effects on GO stability. Finally, the Frank-Kamenetskii model was used to predict the critical mass necessary for GO to undergo explosive decomposition, the model predicted the mass within a factor of experimental data. The results of this study are beneficial in assessing and predicting the hazards of bulk GO during storage and handling.

Keywords: Graphite oxide, energetic material, thermal hazard, nanomaterials, explosive decomposition

1. Introduction

Industrial and academic interest in graphene has grown substantially since its discovery in 2004 [1–3]. Graphene has a high thermal and electrical conductivity and therefore, it is used in applications such as conductors, energy storage devices, batteries, sensors, and others [4–7]. Because of the promising development in graphene-based applications, interest in scaling-up graphene is also increasing.

Current methods to produce graphene such as exfoliation and chemical vapor decomposition are not economical [8]. However, one method to mass-produce graphene-like material economically and consistently is via the graphite oxide (GO) route. The GO route has gained prominence in recent years because it has shown potential for bulk production at high yield [9]. There are several GO synthesis routes, and the modified Hummers method is the most popular [10, 11]. This route involves the oxidation of graphite into graphite oxide and exfoliation using a sonicator to produce graphene oxide. Finally, graphene oxide is reduced thermally or chemically to decrease oxygen content. The reduced GO produces a graphene-like material referred to as "reduced graphene oxide (rGO)".

Since GO's isolation in the 1850s, the energetic nature of GO has been well documented [12–14]. Energetic materials, in general, can decompose violently if they are improperly stored or handled [15]. Two of the most recent examples of such incidents are the West Fertilizer Company explosion in West, Texas [16, 17] and the Tianjin explosion in China [18, 19], both involving ammonium nitrate. The literature in the area of GO energetics has highlighted its potential to violently decompose [4, 9, 20–23]. In fact, Rodriguez *et al.* showed that when GO is heated, it decomposes in three stages: (1) the endothermic stage with evolution of water vapor at 80 °C; (2) the exothermic stage where GO decomposes to CO_2, CO, and H_2O at 200 -240 °C, (this step is also known as thermal reduction of GO); (3) the internal combustion of GO in presence of air at temperatures above 530 °C [14]. Therefore, it is crucial to understand the hazards associated with bulk GO to avoid any potential safety incident during storage and handling of the material.

Kim *et al.* showed that local heating of GO can trigger rapid decomposition throughout the sample mass. Such rapid decomposition of GO resulted in large volume expansion and produced low-density rGO. Sample heating, exposure to flame, or even a camera flash can trigger this rapid decomposition of solid GO [20]. The paper by Krishnan *et al.* also reported that when GO was heated on a hotplate, it underwent explosive decomposition within a few seconds releasing H_2O and CO_2 and the initial GO produced a "puff of black plume of r-GO." [21]

Qiu *et al.* compared GO decomposition enthalpy to industrially known energetic materials to provide a perspective of GO energetic behavior. GO decomposition enthalpy is between 1400 - 1700 J/g, comparable to benzoyl peroxide at 1602 J/g and trinitrotoluene at 2305 J/g [22]. Additionally, in 2016, Qiu *et al.* concluded that the explosive thermal decomposition of GO is a function of mass because at higher masses the reaction rate is higher than the heat transfer rate to the surrounding environment [23]. The excess heat from reaction will lead to local self-heating and thermal runaway of the sample. The authors determined thermo-kinetic data such as reaction order and activation energy using Differential Scanning Calorimetry (DSC). The thermo-kinetic data were used to numerically solve for the critical temperature at which GO decomposes explosively in non-adiabatic conditions for a given mass. However, this numerical prediction needs to be validated with experimental data; which is discussed in detail below.

All the prior thermo-kinetic analysis of GO decomposition reported in the literature were performed using micro-calorimeters such as DSC which use few milligrams of material. DSC is a quick screening method to determine thermal hazard of materials early in the process. When the mass of a material increases, the thermal hazard of the material may also change. Although the intrinsic-kinetic properties remain the same, increasing size introduces uncertainty due to the heterogeneity of the material, hotspots, and decreased surface-area-to-volume ratio [24]. Therefore, the data from DSC may not necessarily predict the behavior of GO at large scale accurately.

In this study, the pseudo-adiabatic calorimeter called Advanced Reaction System Screening Tool (ARSST) to study the thermal behavior of GO between 0.2 g to 0.5 g. Using the data from ARSST, the trend of detected "onset" temperature, T_{onset} with the mathematical model proposed by Qiu *et al.* are compared and T_{onset} of commercially available GO synthesized using the modified Hummers method is compared to the laboratory synthesized GO. Most importantly, pressure release rate during GO decomposition are quantified in this study, which has not been reported in literature to date. The effect of surface area of GO is also studied by changing the drying method to determine the critical mass necessary for GO to decompose explosively. Finally, the critical mass predicted by the Frank Kamenetskii model is compared to experimental results. The results from this study are beneficial in assessing the hazards of bulk GO during storage and handling.

2. Method and Experimental Setup

2.1. Graphite Oxide Preparation

Graphite oxide was prepared using a modified Hummers Method without pretreatment of the graphite [25]. Graphite was obtained from Bay Carbon Inc. Potassium permanganate, hydrogen peroxide, and 95-98 % sulfuric acid was obtained from Sigma Aldrich. The graphite oxide solution was washed 3 times with 10 % HCl to remove salt byproducts. 37 % HCl was obtained from Sigma Aldrich and mixed with distilled water to create the washing acid. The solution washed with distilled water until the pH was neutral at 4.5. The sample was either dried under vacuum in an oven at 40 °C for 24 hours or freeze-dried (Vitris Benchtop Freeze Dryer) for approximately 72 hours to yield a dry GO powder.

2.2. Thermal Decomposition Analysis

Thermal analysis of GO was conducted in the Advanced Reactive System Screening Tool (ARSST) manufactured by Fauske and Associates, Burr Ridge, IL. The ARSST is an open test cell capable of handling chemical system for temperature as high as 500 °C and pressure up to 500 psig. Therefore, ARSST is ideal to conduct experiments for up to a few grams of energetic material. The GO sample was heated at a constant rate of approximately 6 °C/min. The sample cell is a glass test cell with a volume of 10 ml, which is placed inside a stainless-steel vessel of volume 350 ml. A thermocouple and pressure transducer tracked the dynamic temperature and pressure changes during the decomposition process. The pressure transducer was located outside the glass test cell in 350 ml vessel and for each test the thermocouple touched the sample mass.

It should be noted that the data collection rate for ARSST is every 30 s or sooner if it detects a temperature chance of 2 °C or a pressure change of 2 psi. The decomposition reaction occurs rapidly as seen in Figure S1. Therefore, there is a possibility the data collection is not fast enough to truly capture the temperature and pressure generation rates.

2.3. Characterization

2.3.1. Thermogravimetric Analysis

The water in GO sample and mass loss due to GO decomposition were measured using a Q50 thermogravimetric analyzer (TGA) from TA Instruments, New Castle, DE. The measurements were done in a nitrogen environment. The sample was heated from room temperature to 250 °C at a constant value of 5 °C/min and held at the isothermal condition for 30 minutes at 110 °C. The final GO mass was measured after cooling to 50 °C.

2.3.2. Surface Area Analysis

The surface area of GO was determined using Brunauer-Emmett-Teller (BET) theory. The measurements were carried out in Micrometric ASAP2010 system. The samples were pre-treated under vacuum for 12 hours at 70 °C.

2.3.3. Elemental Analysis

The oxygen content and metal impurities in GO samples were determined using Fast Neutron Activation Analysis (FNAA) technique. In this technique, the atoms in the material are converted into radioactive atoms. When the radioactive atoms decay, they emit unique radiation that identifies the atom. This method can provide qualitative and quantitative analysis of elements present in a sample [26]. All the testing was done in the Elemental Analysis Lab at Texas A&M University, College Station, TX.

2.3.4. Thermal Conductivity Measurement

The thermal conductivity of graphite oxide was measured using a TPS 2500S hot disc thermal constants analyzer from Thermtest Inc., Canada. A Kapton sensor of 2 mm radius was used for the analysis. A heating power of 8 mW was applied for 10 seconds to the sample at room temperature of 20.1 °C. An average thermal conductivity value after 4 tests were used for the analysis.

3. Results and Discussion

3.1. Thermal Decomposition of GO

In this study, GO was synthesized using the modified Hummers method and dried in a vacuum oven at 40 °C for 24 hours. The thermal stability experiments were conducted in an ARSST with GO mass at least two to three orders of magnitude higher than previously reported sample sizes. The explosive decomposition of GO is marked by a rapid increase in temperature and pressure of the sample. The T_{onset} is defined as the temperature at which the system (ARSST) detects a rapid increase in temperature and pressure. The T_{onset} for the ARSST system in this study is the temperature at which the second derivative of dT/ dt with time is greater than 3 $°C/min^2$. In a perfect scenario, the dT/dt^2 should be 0 $°C/min^2$ up to the explosive decomposition, however due to noise in heating rate and thermocouple data, the threshold value of 3 $°C/min^2$ was chosen to avoid false "onset" detection due to external heating. A detailed explanation is shown in the supplementary information (SI).

Figure 1a shows a negative correlation between T_{onset} with increasing GO mass. The mass was varied from 0.2 g to 0.5 g and noticed T_{onset} decreased from 144 ± 8 °C to 128 ± 6 °C respectively. The experiments were repeated four times for each data point to account for uncertainty in the measurement. The correlation

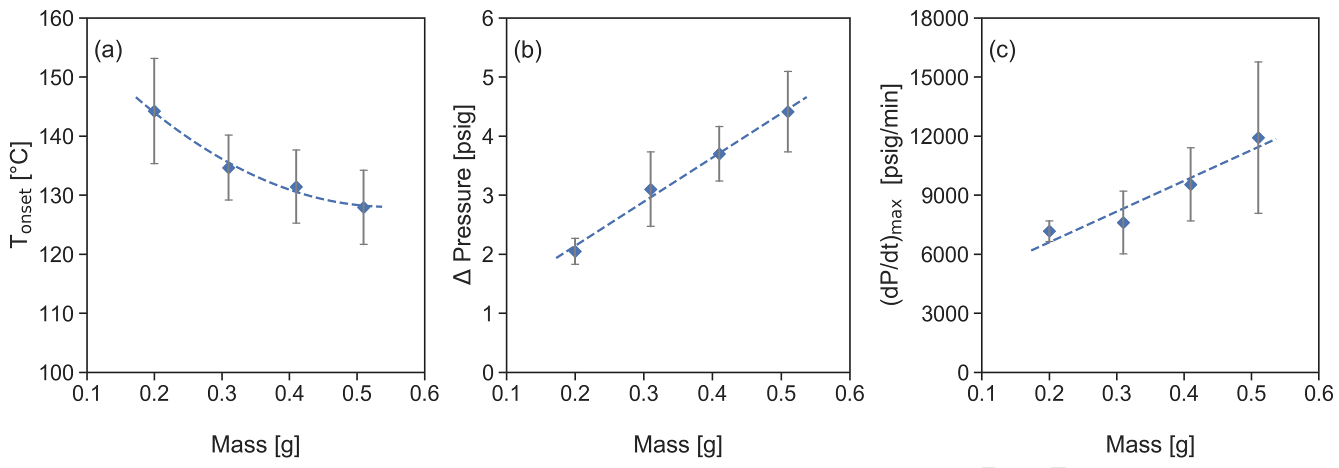

Figure 1: Experimental data for thermal decomposition of GO synthesized using the modified Hummers method. The GO was dried in vacuum oven. (a) Shows T_{onset} with varying GO mass. T_{onset} is defined as the temperature at which GO decomposed explosively. (b) Shows pressure generated due to non-condensable gasses generated during GO decomposition. (c) Shows the maximum pressure generation rate during GO decomposition with varying GO mass.

between T_{onset}, ΔP and dP/dt with varying mass are statistically significant. The details on the statistical test is shown in SI. Based on the experimental result, the rate of change of T_{onset} with increasing mass was -18 °C/g. The negative correlation between T_{onset} with a mass of GO is consistent with the theory: as the mass of GO increases, the rate of reaction increases producing heat and releasing gaseous products. Due to the limited heat transfer from the material to the environment, the excess heat feeds into the reaction, thus making the reaction proceed rapidly resulting in explosive decomposition of the material.

A previous study solved the differential energy balance shown in Equation 1 to numerically obtain T_{onset} for varying mass when the surface area (S) and heat transfer coefficient (h) is known [23].

$$\mathrm{mC_p}\frac{\mathrm{dT}}{\mathrm{dt}} = -\mathrm{m}\Delta\mathrm{H}\frac{\mathrm{dx}}{\mathrm{dt}} - \mathrm{hS}(\mathrm{T}-\mathrm{T_o}) \tag{1}$$

The rate of reaction dx/dt in Equation 1 was calculated using the Arrhenius equation, m is the mass of reactant, C_p is heat capacity, ΔH is heat of reaction, and T_o is the temperature of the surrounding. The graphical solution to Equation 1 reproduced from Qiu *et al.* is available in SI (Figure S3). The slopes predicting the T_{onset} were generated by solving Equation 1 for a range of hS. The resulting slopes are shown in Table 1 along with experimental result from the current study.

Table 1: Change in T_{onset} with increasing GO mass

Determination technique	hS [W/K]	slope
Model [23]	0.0013	-0.925 °C/g
	0.049	-10.85 °C/g
	0.49	-12.21 °C/g
Experiment (this study)	0.019	-18.00 °C/g

The result indicates stronger dependency of T_{onset} with mass than previously predicted. The maximum hS for the study was 0.019 W/K. The detected T_{onset} for the ARSST system and mass dependency is stronger because the model assumes homogeneous solid with uniform temperature distribution. However, the heat transfer in bulk GO is non-uniform and the probability of hotspots in higher. In addition, the system for this study is pseudo-adiabatic and the heat transfer to the surrounding is minimum. Therefore, the self-heating of GO is accelerating the explosive thermal decomposition of GO in the system.

Furthermore, as we increase the mass increases, pressure after GO decomposition should also increase. Figure 1b shows that pressure generated due to GO decomposition increases linearly with GO mass. In fact, pressure increased at a rate of 7.44 psig/g. As we increase the mass, we expect to see an increase in pressure after GO decomposition. The amount of pressure generated at the end of GO decomposition corresponds to 40 wt% mass loss of initial GO. This result agrees with mass data from Thermogravimetric Analysis (TGA) and literature [21].

Previous literature in the area of thermal stability of GO made no attempt to quantify the pressure generation rate during rapid decomposition of GO. This study quantified the pressure release rate and Figure 1c shows the maximum pressure release rate during explosive decomposition. The maximum pressure release rate is thousands of psig per minute and this rate is for material less than a gram. Based on these data, if large quantities of GO stored in a closed container decomposes suddenly, the effect of pressure generation could be catastrophic depending on the quantity of GO and the size and container it is store in.

3.2. Thermal Decomposition of Commercial GO

Further, the explosive decomposition of two commercially available GO was compared with that of GO synthesized in the laboratory. All three GO were prepared using the modified Hummers method, however, the exact parameters used to synthesize commercial GO are not available, especially for the washing step. The commercial GO were bought from Graphenea, Spain and The Sixth Element Inc, China, labelled commercial GO-A and commercial GO-B respectively. The commercial GO-A was supplied in a powder form and the initial water content was 19 wt %, therefore, the GO was dried under vacuum at 40 °C for 4 hours. Similarly, the commercial GO-B was supplied as a wet powder in 55 ± 5 wt% water. The GO was dried under vacuum for 24 hours at 40 °C. The thermal decomposition data for GO synthesized in the lab is shown in Figure 2a and Figure 2b, commercial GO-A is shown in Figure 2c and Figure 2d, and the thermal decomposition data for commercial GO-B is shown in Figure 2e and Figure 2f. For a sample mass of 0.50 g, the T_{onset} for commercial GO-A was 116 ± 1 °C, for commercial GO-B was 100 ± 2 °C compared to the T_{onset} for GO synthesized in the lab at 128 ± 6 °C. The T_{onset} of commercial GO-B is lowest as shown in Table 2. In order to understand the cause of the difference in T_{onset} of the GO, a detailed analysis of the materials was done, and the result is tabulated in Table 2.

The presence of potassium salt impurity was monitored because it is the most common impurity present in GO and there are a few literature studying the effect of metal salt impurities on the decomposition of GO at temperatures between 100 °C - 200 °C. Yuan *et al.* reported potassium salt impurities in GO increase the heat release during thermal decomposition of GO but the authors do not mention if the potassium content effects the decomposition temperature [27]. However, Qiu *et al.* reported that the presence of potassium salt impurity only effects the combustion of rGO in air at temperature over 500 °C. They further concluded that increasing hydroxyl ion (or pH) before drying decreases the thermal stability of GO, thus lowering the T_{onset} of GO and not the presence potassium salt impurities [23]. In their study, the Δ pH of 10 showed change in onset by 50 °C. The analysis of the commercial GO and GO produced in laboratory shown in Table 2 indicates that GO synthesized in laboratory has less than 110 ppm potassium salt impurity and

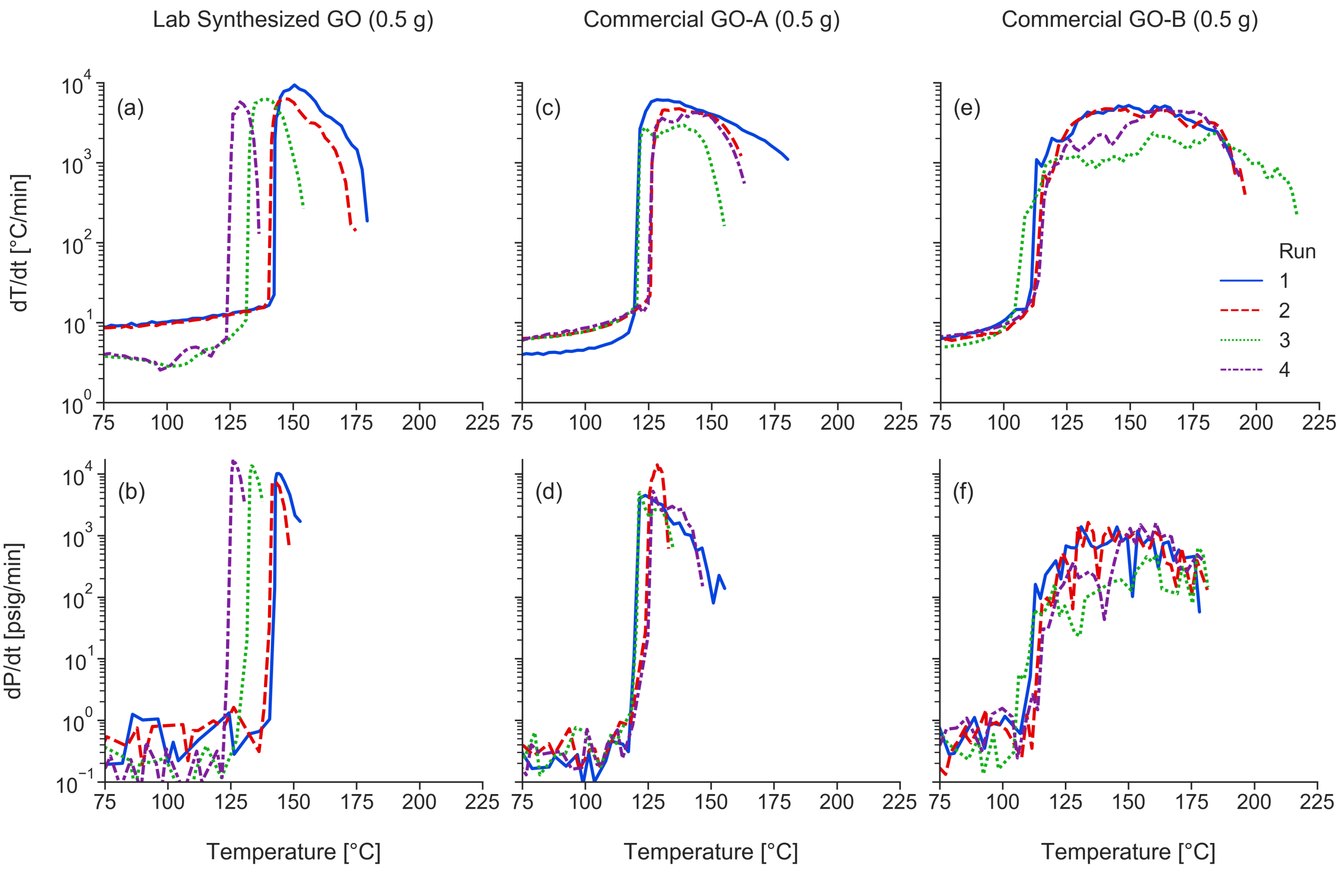

Figure 2: Experimental data for thermal decomposition of GO synthesized using modified Hummers method and commercial GO. The 4 runs are repeated experiments for 0.5 g each. (a) and (b) are for GO synthesized in lab and, (c) and (d) are for commercial GO-1 and (e) and (f) are for commercial GO-2. The average heating rate of 6 °C/min was applied for all the tests. Explosive decomposition was seen for all GO with temperature increase rate of 1000s °C/min (Figures a, c, and e). The pressure increase rate for GO synthesized in lab and commercial GO-A (b and d) is 10 times higher than the commercial GO-B (f).

higher pH compared to commercial GO-B. The oxygen and water content in all the samples are comparable. Based on literature, higher pH of GO synthesized in laboratory should have lower onset, but the opposite is observed in the experiment. Nonetheless, it is important to note that the difference in pH between the GO synthesized in laboratory and commercial GO-B (Δ pH = 1.5) is significantly less compared to pH difference studied in literature (Δ pH = 10), therefore, the effect of pH on the samples studied in this work is not dominant. It should be noted; the pH of commercial GO-A should not be measured because the material was supplied as solid powder.

Therefore, the surface area of bulk GO has more significant effects on T_{onset} than impurities such as potassium salt or the pH of the material. As shown by BET surface area analysis, GO synthesized in the lab has a surface area (SA) almost twice larger than commercial GO-A and fifteen times larger than commercial GO-B. The lower surface area limits the materials capability to transfer heat to the surrounding environment. For any material to undergo runaway thermal decomposition, the rate of reaction needs to be higher than the rate of heat transfer to the surroundings. Thus, in case of commercial GO, the lower

Table 2: Comparison between GO synthesized in lab and commercial GO

Variable Measured	GO synthesized in lab	Commercial GO-A	Commercial GO-B
T_{onset} at 0.5 g GO	128 ± 6 °C	116 ± 1 °C	100 ± 2 °C
Potassium Salt Content	< 110 ppm	583 ± 22 ppm	9 ± 1 wt%
Oxygen Content	37 ± 2 wt%	47 ± 3 wt%	39 ± 3 wt%
Water Content	12 wt%	12 wt%	10 wt%
pH	4.5	Not applicable (solid sample)	3.0
BET Surface Area	12.2 m^2/g	7.0 m^2/g	0.8 m^2/g
Oxygen Content after decomposition	< 10 wt%	23 ± 2 wt%	26 ± 10 wt %

SA decreases the thermal stability of the material.

In addition, the maximum pressure increase rate for GO synthesized in the lab (Figure 2b) and commercial GO-A (Figure 2d) is 10 times higher than for commercial GO-B (Figure 2f). The difference is due to the degree of reduction of GO. The oxygen content analysis of the residual material after the decomposition - also known as reduced Graphite Oxide (rGO) - showed no detectable oxygen content for GO synthesized in lab whereas for commercial GO-B the oxygen content was 26 ± 10 wt%. Therefore, the GO synthesized in the lab and commercial GO-A released most of its oxygen as CO or CO_2 as confirmed in the pressure increase rate, and commercial GO-B released only 35 % of its original oxygen content after decomposition.

The analysis thus far was done for dry GO powder. However, GO are often commercially shipped as a wet powder. The commercial GO-B procured for this study was delivered as a wet powder in 55 wt% water. It is noteworthy that in 3 of the 4 tests of the wet GO also underwent explosive decomposition. The rate of temperature and pressure increase for wet GO was in 100s of °C and psig per min, respectively. These rates are significantly lower compared to its dry counterparts. However, the thermal hazard of GO is present even in solution form and caution must be taken while drying GO. Detailed graphs for wet GO are available in Figure S3.

3.3. Determination of Critical Mass of GO

Explosive decomposition of a sample occurs when the rate of heat generated by the decomposition reaction is higher than the rate of heat dissipated into the surrounding environment. For small quantities of GO mass, heat transfer to the surrounding is faster than the heat generated by the decomposition reaction and explosive decomposition is not seen. However, above a certain critical mass, heat dissipation to the surrounding is not fast enough, and the material shows explosive decomposition behavior. Oven-dried GO is compact, with high bulk density and low specific surface area, hence the critical mass necessary for it to undergo explosive decomposition is less than 5 milligrams [22].

The freeze-drying method was used to produce a porous GO with higher surface area (19 m^2/g). The freeze-drying method produces a highly porous dry material because there is no capillary-induced aggregation in the material. Visually, the freeze-dried GO (GO-FD) appears fluffy compared to vacuum oven-dried material.

For a porous material with high surface area, the critical mass at which the material decomposes will be

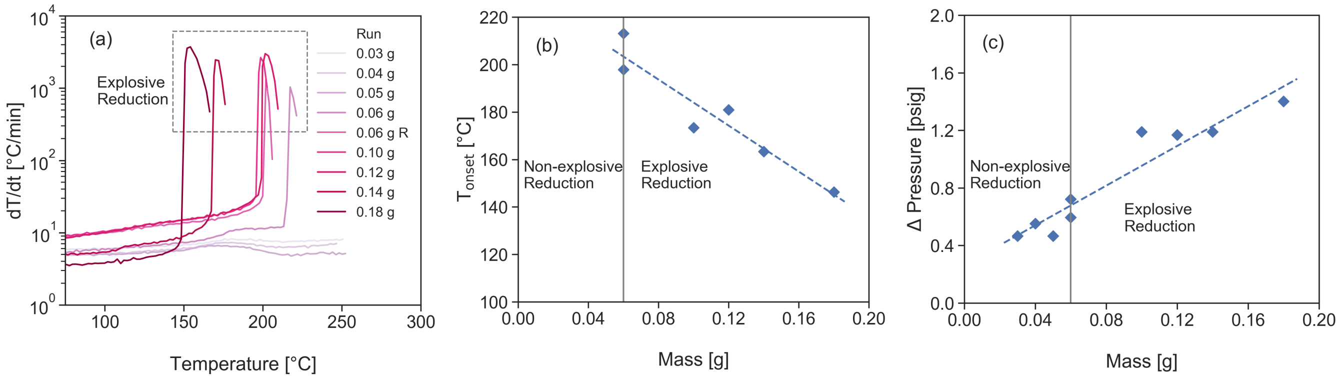

Figure 3: Experimental data for thermal decomposition of freeze-dried GO (GO-FD) synthesized using modified Hummers method. (a) Shows the rate of temperature increase with temperature. An abrupt increase in temperature as seen in tests 60 mg and above indicates explosive decomposition of the material. The GO-FD was heated at an average heating rate of 6 °C/min. The critical mass necessary for freeze-dried GO-FD to undergo explosive decomposition is 60 mg in a spherical vessel of 1.34 cm radius. (b) Shows the T_{onset} with varying mass of GO-FD. (c) Shows the pressure generate at the end of experiment. The T_{onset} and pressure generated for GO-FD is consistence with the previous experiments.

higher than for a material with a low surface area. The experiments were carried out in an ARSST with constant heating of 6 °C/min. For GO-FD, the critical mass was observed to be 60mg. GO-FD masses greater than 60 mg underwent explosive decomposition, which is shown by an abrupt increase in pressure and temperature in Figure 3a. Figure 3b and Figure 3c show the correlation between GO-FD mass and T_{onset} and pressure generated, respectively. The T_{onset} and pressure trends for GO-FD agree with the trends seen in Figure 1 for oven-dried GO.

3.4. Frank Kamenetskii Model

In this section, the experimental critical mass of GO necessary for explosive decomposition is compared to the critical mass of GO predicted by thermal explosion theory and models available in the literature. A commonly used model to describe thermal decomposition for homogeneous solids is the Frank Kamenetskii (FK) model. The FK approach assumes a non-homogenous system and assumes the temperature difference between the center of the solid and its surface is the most critical factor for determining explosiveness [28]. In ideal cases, the FK parameter δ combines critical parameters such as reactant geometry, reaction kinetics, heat transfer, and temperature into a single equation to determine critical conditions necessary for explosive decomposition of the material [29–31].

$$\delta = \rho \frac{q}{\lambda} \frac{E_a}{RT_f^2} d^2 A e^{\left(\frac{-E_a}{RT_f}\right)} \tag{2}$$

where ρ is the density, q is the specific heat of reaction, λ is thermal conductivity, E_a is the activation energy, R is the gas constant, d is the characteristic linear dimension in meters, A is the exponential factor, and T_f is the temperature of the vessel. In the experiment, the material was constantly heated using an external heater, therefore T_{kis} (the temperature at which the reaction rate is the maximum) given by Kissinger's equation (Equation 3) was used instead of T_f. The heating rate is denoted by b [32]. A heating rate of 6

°C/min used in the model is consistent with the experimental procedure in Section 3.3.

$$\left(\frac{\mathrm{E_a}}{\mathrm{RT_{kis}^2}}\right)=\frac{\mathrm{A}}{\mathrm{b}}\mathrm{e}^{\left(\frac{-\mathrm{E_a}}{\mathrm{RT_{kis}}}\right)} \tag{3}$$

The FK approximation assumes energy conservation equation in poorly conducting solids with a distributed internal temperature and no resistance to heat transfer at the surface [33]. However, the FK model neglects reactant consumption and assumes activation energy is large. Babushok *et al.* proposed a correction to the FK parameter to account for reactant consumption as shown in the equation below [34].

$$\delta(1-\varepsilon)\{1-2.946(1+2\varepsilon)\left(\frac{\mathrm{n}}{\Theta_\mathrm{T}}\right)^{\frac{2}{3}}+\frac{4}{9}(1+6\varepsilon)\frac{\mathrm{n}}{\Theta_\mathrm{T}}\ln(\Theta_\mathrm{T})\}=\mathrm{C} \tag{4}$$

where

$$\varepsilon=\frac{\mathrm{RT_f}}{\mathrm{E_a}} \tag{5a}$$

$$\Theta_\mathrm{T}=\frac{\mathrm{E_a}}{\mathrm{RT_f^2}}\frac{\mathrm{q}}{\mathrm{C_p}} \tag{5b}$$

Here, C is the geometry factor for the critical condition, which for a sphere is 3.32, n is the reaction order, and $\mathrm{C_p}$ is the heat capacity. This model is most accurate for finite values of activation energy but not for low activation energies [35]. Sanchez *et al.* further worked on the model proposed by Babushok *et al.* to get an accurate numerical model for evaluation of a critical condition with a low activation energy for thermal explosion. The equation is shown below and was validated for $\mathrm{Ba(TFA)_2}$ and $\mathrm{Y(TFA)_2}$ systems by the authors [36].

$$\delta(1-\varepsilon)\{1-2.25(1+3.76\varepsilon)\left(\frac{\mathrm{n}}{\Theta_\mathrm{T}}\right)^{\frac{2}{3}}\}=\mathrm{C} \tag{6}$$

Equation 6 is used to calculate critical density necessary for GO to undergo thermal decomposition with increasing radius of a sphere as shown in Figure 4. Because the ARSST experiments were carried out in an open test cell, the rapid volume expansion of GO during explosive decomposition resulted in mass loss of GO from the test cell. Consequently, the experimental data could not be used to determine the thermokinetic parameters of the reaction. Instead the kinetic parameters for decomposition in the model such as activation energy and frequency factor were used from literature [23].

The model predicted the critical density necessary for thermal decomposition of GO-FD to be 9.63 $\mathrm{kg/m^3}$ for a sphere of radius 1.34 cm, which corresponds to the critical mass of 0.1 g which is the first point in the graph in Figure 4. However, experimentally the explosive decomposition of GO-FD was seen at 0.06 g for a sphere of radius 1.34 cm. The difference in model and experimental result could be a result of the thermal conductivity value used. A thermal conductivity value of 0.44 W/mK was obtained experimentally using hot disc method for GO paste and used in the simulation. In reality, the thermal conductivity will be lower than 0.44 W/mK because the model does not account for sample porosity or void fraction of freeze-dried GO in Section 3.3. Increasing void fraction in the GO mass will decrease the thermal conductivity

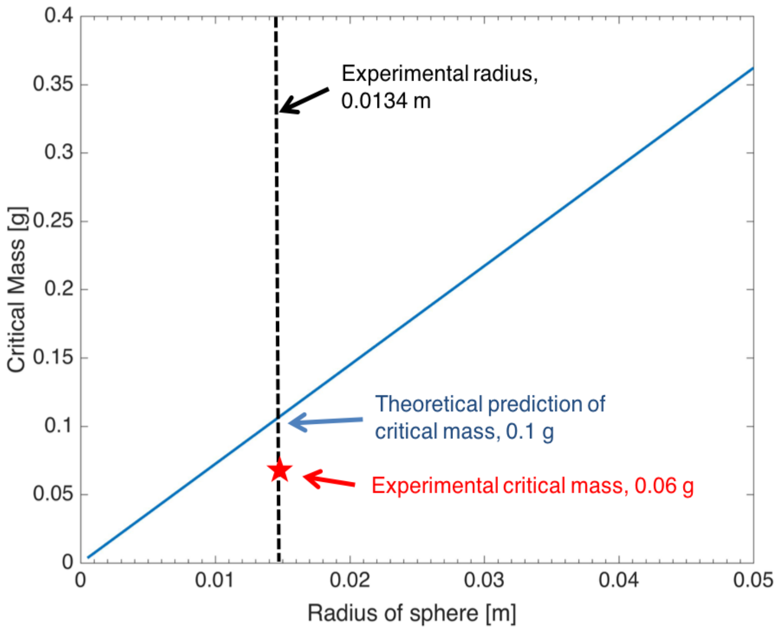

Figure 4: This figure shows the critical density and critical mass predicted by solving the modified Frank Kamenetskii's equation (Equation 6). The blue line in the graph shows the critical density necessary for GO-FD to undergo explosive decomposition. The black dotted line in the graph represents the corresponding critical mass in a spherical container. The critical density of 9.63 kg/m^3, which corresponds to critical mass of 0.097 g for 0.013 m radius is comparable to experimental critical mass of 0.060 g for same 0.013 m radius.

of the material. Lower thermal conductivity will decrease the sample's ability to dissipate the heat to the surrounding environment, therefore, explosive decomposition is observed at a lower mass. Thus, if lower thermal conductivity is account for in the model, the critical sample mass predicted will decrease and further align with the experimental data.

Therefore, the result from the FK model is comparable to the experimental results. The remaining data points in Figure 4 show the predicted critical mass of GO necessary for GO to undergo explosive decomposition in a spherical container. The model assumes the spherical vessel is completely filled with GO. This information is valuable to GO manufacturers to determine the safe transport and storage size for bulk GO. Hence, if the GO morphology and decomposition kinetics are known, the model can predict the critical density and thus the critical mass necessary for the GO to decompose explosively.

4. Conclusions

As seen in this study, dry GO with a mass of 0.5 g can release 1000s of psig pressure per minute during its explosive decomposition. The experiments also suggest that bulk GO explosive decomposition can occur at temperatures close to those used in common drying processes *i.e.,* <150 °C. Furthermore, the decomposition temperature or T$_{onset}$ is negatively correlated with GO mass at a rate of -18 °C/g for this study.

Similarly, a comparison of decomposition of GO from different sources shows that the surface area of GO determines whether it decomposes explosively or not. If the surface area is low, upon heating the rate of reaction dominates the rate of heat dissipation to the surrounding, initiating runaway scenarios or explosive decomposition.

Moreover, high surface area GO was obtained by changing the drying method from oven drying to freeze-drying. In a spherical container of radius 1.34 cm, freeze-dried GO decomposed explosively at a critical mass of 60 mg. The experimental results were compared with the Frank Kamenetskii model, and the model predicted the critical mass to be 100 mg. The discrepancy in the result is due to the high porosity of the sample used in the experiment, which reduces the thermal conductivity of the material, and caused the experimental results to be lower than the prediction.

Finally, precautions should be taken when handling bulk GO in both industry and laboratory settings, especially if the material will be stored in a closed container. The decomposition results of this study can further be used in conducting a risk assessment of bulk GO during storage and transportation by industry interested in producing and shipping bulk quantities of GO.

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6. Declaration of Interest

None

References

[1] M. Segal, "Selling graphene by the ton," *Nature nanotechnology*, vol. 4, no. 10, p. 612, 2009.

[2] S. Ahn, J. Sung, H. Kim, and Y. Sung, "Emerging analysis on the preparation and application of graphene by bibliometry," *J Material Sci Eng*, vol. 4, no. 192, pp. 2169–0022, 2015.

[3] I. P. O. Informatics Team, "Graphene - the worldwide patent landscape in 2015," UK Intellectual Property Office, Cardiff Road, Newport, NP 10 8QQ United Kingdom, Tech. Rep., March 2015.

[4] D. Li and R. B. Kaner, "Graphene-based materials," *Science*, vol. 320, no. 5880, pp. 1170–1171, 2008. [Online]. Available: http://science.sciencemag.org/content/320/5880/1170

[5] Y. Wang, Z. Shi, Y. Huang, Y. Ma, C. Wang, M. Chen, and Y. Chen, "Supercapacitor devices based on graphene materials," *The Journal of Physical Chemistry C*, vol. 113, no. 30, pp. 13 103–13 107, 2009.

[6] D. A. Brownson, D. K. Kampouris, and C. E. Banks, “An overview of graphene in energy production and storage applications,” *Journal of Power Sources*, vol. 196, no. 11, pp. 4873–4885, 2011.

[7] T. Wang, D. Huang, Z. Yang, S. Xu, G. He, X. Li, N. Hu, G. Yin, D. He, and L. Zhang, “A review on graphene-based gas/vapor sensors with unique properties and potential applications,” *Nano-Micro Letters*, vol. 8, no. 2, pp. 95–119, 2016.

[8] Y. Li and N. Chopra, “Progress in large-scale production of graphene. part 1: chemical methods,” *Jom*, vol. 67, no. 1, pp. 34–43, 2015.

[9] S. Pei and H.-M. Cheng, “The reduction of graphene oxide,” *Carbon*, vol. 50, no. 9, pp. 3210 – 3228, 2012, festschrift dedicated to Peter A. Thrower, Editor-in-Chief, 1972 - 2012. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0008622311008967

[10] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, and J. M. Tour, “Improved synthesis of graphene oxide,” *ACS nano*, vol. 4, no. 8, pp. 4806–4814, 2010.

[11] J. Chen, B. Yao, C. Li, and G. Shi, “An improved hummers method for eco-friendly synthesis of graphene oxide,” *Carbon*, vol. 64, pp. 225–229, 2013.

[12] B. C. Brodie, “On the atomic weight of graphite,” *Philosophical Transactions of the Royal Society of London*, vol. 149, pp. 249–259, 1859.

[13] R. Croft, “Lamellar compounds of graphite,” *Quarterly Reviews, Chemical Society*, vol. 14, no. 1, pp. 1–45, 1960.

[14] A. M. Rodriguez and P. V. Jiménez, “Thermal decomposition of the graphite oxidation products,” *Thermochimica acta*, vol. 78, no. 1-3, pp. 113–122, 1984.

[15] [Online]. Available: http://www.csb.gov/investigations/completed-investigations/

[16] D. M. Laboureur, Z. Han, B. Z. Harding, A. Pineda, W. C. Pittman, C. Rosas, J. Jiang, and M. S. Mannan, “Case study and lessons learned from the ammonium nitrate explosion at the west fertilizer facility,” *Journal of hazardous materials*, vol. 308, pp. 164–172, 2016.

[17] CBS, “West fertilizer company fire and explosion,” U. S. Chemical Safety and Hazard Investigation Board, Tech. Rep., 2016.

[18] G. Fu, J. Wang, and M. Yan, “Anatomy of tianjin port fire and explosion: Process and causes,” *Process Safety Progress*, vol. 35, no. 3, pp. 216–220, 2016.

[19] B. Zhao, “Facts and lessons related to the explosion accident in tianjin port, china,” *Natural Hazards*, vol. 84, no. 1, pp. 707–713, 2016.

[20] F. Kim, J. Luo, R. Cruz-Silva, L. J. Cote, K. Sohn, and J. Huang, “Self-propagating domino-like reactions in oxidized graphite,” *Advanced Functional Materials*, vol. 20, no. 17, pp. 2867–2873, 2010.

[21] D. Krishnan, F. Kim, J. Luo, R. Cruz-Silva, L. J. Cote, H. D. Jang, and J. Huang, “Energetic graphene oxide: challenges and opportunities,” *Nano today*, vol. 7, no. 2, pp. 137–152, 2012.

[22] Y. Qiu, F. Guo, R. Hurt, and I. Külaots, “Explosive thermal reduction of graphene oxide-based materials: Mechanism and safety implications,” *Carbon*, vol. 72, pp. 215 – 223, 2014. [Online]. Available: http://www.sciencedirect.com/science/article/pii/S0008622314001274

[23] Y. Qiu, F. Collin, R. H. Hurt, and I. Külaots, "Thermochemistry and kinetics of graphite oxide exothermic decomposition for safety in large-scale storage and processing," *Carbon*, vol. 96, pp. 20–28, 2016.

[24] G. Maschio, J. Feliu, J. Ligthart, I. Ferrara, and C. Bassani, "The use of adiabatic calorimetry for the process analysis and safety evaluation in free radical polymerization," *Journal of thermal analysis and calorimetry*, vol. 58, no. 1, pp. 201–214, 1999.

[25] W. S. Hummers Jr and R. E. Offeman, "Preparation of graphitic oxide," *Journal of the american chemical society*, vol. 80, no. 6, pp. 1339–1339, 1958.

[26] [Online]. Available: http://eal.tamu.edu/neutron-activation-analysis.php

[27] B. Yuan, L. Song, K. M. Liew, and Y. Hu, "Mechanism for increased thermal instability and fire risk of graphite oxide containing metal salts," *Materials Letters*, vol. 167, pp. 197–200, 2016.

[28] A. R. Shouman, "A review of one aspect of the thermal-explosion theory," *Journal of engineering mathematics*, vol. 56, no. 2, pp. 179–184, 2006.

[29] D. A. Frank-Kamenetskii, *Diffusion and heat transfer in chemical kinetics.* Plenum Press, 1969.

[30] W. Gill, A. Donaldson, and A. R. Shouman, "The frank-kamenetskii problem revisited. part i. boundary conditions of first kind," *Combustion and Flame*, vol. 36, pp. 217–232, 1979.

[31] T. Boddington, P. Gray, and D. Harvey, "Thermal theory of spontaneous ignition: criticality in bodies of arbitrary shape," *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, vol. 270, no. 1207, pp. 467–506, 1971.

[32] H. E. Kissinger, "Reaction kinetics in differential thermal analysis," *Analytical chemistry*, vol. 29, no. 11, pp. 1702–1706, 1957.

[33] P. F. Beever and J. F. Griffiths, "Scaling rules for prediction of thermal runaway," in *International Symposium on Runaway Reactions.* AIChE, 1989, pp. 1–20.

[34] V. Babushok, V. Goldshtein, and V. Sobolev, "Critical conditions for thermal explosion with reactant consumption," *Combustion science and technology*, vol. 70, no. 1-3, pp. 81–89, 1990.

[35] D. Sánchez-Rodríguez, J. Farjas, and P. Roura, "The critical conditions for thermal explosion in a system heated at a constant rate," *Combustion and Flame*, vol. 186, pp. 211–219, 2017.

[36] D. Sánchez-Rodriguez, J. Farjas, and P. Roura, "The critical condition for thermal explosion in an isoperibolic system," *AIChE Journal*, 2017.

Calorimetry of Explosive Thermal Decomposition of Graphite Oxide

Pritishma Lakhe[1], Devon Kulhanek[2], Wanmei Sun[2], Bin Zhang[1], Micah J. Green[2,*] and M. Sam Mannan[1]

[1]Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843, USA

[2]Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843, USA

[*]Corresponding author: Micah J. Green, Tel: +1 979 862 1588; Fax: +1 979 458 1493; E-mail: micah.green@tamu.edu; Mailing address: 3122 TAMU Room 200, College Station, TX 77843

Highlights

1. GO can explosively decompose at normal drying temperatures.
2. During thermal decomposition of GO, pressure generation rate can be greater than 1000s pisg/min.
3. Surface area of GO determines the critical mass necessary for GO to decompose.
4. Frank - Kamenetskii parameter can be used to predict the critical mass for GO to decompose.