

## Continuous and Non-Continuous Stirring Patterns For The Reactive Mixing Process of Glycerin

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### Abstract

In this study, the behavior of glycerin nitration reactive mixing employing continuous and non-continuous stirring patterns was investigated. The changes in nitration of glycerin were observed by means of a color change technique based on a fast nitration reaction arising from continuous stirring patterns (RUN 1 and 2) and non-continuous stirring patterns (RUN 3 and 4). Nitration process was identified from thermal behavior measured by a temperature sensor throughout the mixing process up to the formation of nitroglycerin. The results showed that the four stirring patterns (RUN 1, 2, 3, and 4) affected both the mixing time and duration of the glycerin nitration process. The temperatures in the glycerin nitration reaction were changed and increased drastically in all RUN's. These results explicitly demonstrate the different thermal behavior in the mixing performance that was stimulated by the continuous and non-continuous stirring patterns. The stirring pattern of non-continuous flows during the glycerin nitration process, RUN 3 generates the shortest reaction time and RUN 4 generates the earliest initial reaction time.

**Keywords:** continuous stirring, non-continuous stirring, reactive mixing, glycerin nitration.

### Introduction

The success of many processes in a wide range of field such as chemistry, industry and others depends on the effectiveness and efficiency of a variety of stirring and mixing processes. Stirring (agitation) is the motion brought to bear in a certain way on a material or materials in a vessel where the movement usually has a circular pattern. Mixing is the random spreading of a material or materials into another material or materials and vice versa. Applications of some characteristics of mixing are shown in

references [1-22, 29-31]. In the previous study, on how best to understand mixing processes in turbulent flows, ironically, were only understood in a statistical sense. Similarly, detailed analysis of the mechanisms of the actual mixing process in deterministic laminar flows is nearly absent from literature.

Studies into mixing with reactive fluids are rare, probably due to the dangers involved with such materials. Generally, research has been done numerically or by simulation. However, this study employed an experimental design, the fluid used was glycerin which was mixed with nitric acid ( $\text{HNO}_3$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) as a catalyst to produce nitroglycerin and water ( $\text{H}_2\text{O}$ ). Nitroglycerin (NG), or glycerol trinitrate, is a compound formed by the nitration of glycerol and has the molecular name of 1, 2, 3-propane triol trinitrate,  $\text{C}_3\text{H}_5(\text{ONO}_2)_3$  as its chemical formula and a molecular weight of 227 gram/mole. At 25 °C this compound has a mass of 1,591 gram/cm<sup>3</sup>. Nitroglycerin has several important uses including medicine to reduce pain and to prevent angina pectoris attacks, as an explosive and as rocket fuel. However, Nitroglycerin has many important uses in various industries but, it is extremely sensitive to sudden impact and heat and its manufacture is extremely dangerous which occurs very rapidly and exothermically. In this process temperatures rise quickly and if not properly controlled have the potential of causing explosions [3, 4, 23, 24, and 32], and many accidents have occurred in its manufacturing process, highlighting the importance of optimum control in the glycerin nitration process.

The process of mixing is based upon various mechanisms from agitation for sparging to static flow manipulation. Agitation in a tank equipped with a stirrer is a very common, yet, one of the biggest problems is obtaining suitable experiment instruments for studying macro fluids. Tanks with mixers usually have an impeller installed in their centers, an optional baffle, spargers, a coil and a tube. The modeling of such a tank requires consideration of several aspects. Firstly, a vital consideration in selecting suitable experiment equipment is that they must have a specific domain, in this case the volume of liquid in the tank, which becomes a more specific variable with certain fluid compositions and how it is placed in a tank with a mixer. Secondly, any movement of a rod in the tank must be done in a special way and this special treatment has a beneficial effect on the stirring and mixing process. Stirring is the method to mechanically induce surface tension in the material, whereas mixing is the process of diffusing a substance through material's surface [25-27].

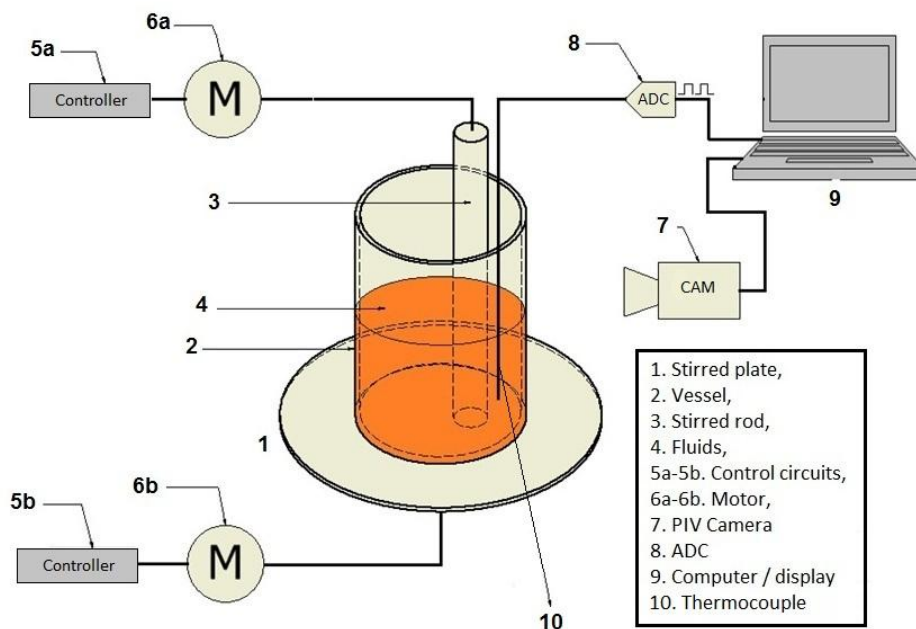
In any chemical process, the main problem is how to measure or visualize the mixing and flow systems. The interaction between fluid mechanics and chemical reactions is extremely interesting due to its effects on mass transfer and the transport phenomenon. The stirring rods and rotating vessels were employed to generate chaotic mixing and chaotic mixing is used as the driving force of mass transfer at high and low viscosities to achieve homogeneity in the entire domain. Chaotic mixing can provide enough energy to trigger termination of the chemical bond, which causes chemical reactions. Therefore, in order to determine the characteristics of fluid flow in reactive mixing systems, this study focused on investigating the reactive mixing behavior of nitroglycerin process stimulated by continuous and non-continuous stirring patterns.

**Materials and Methods**

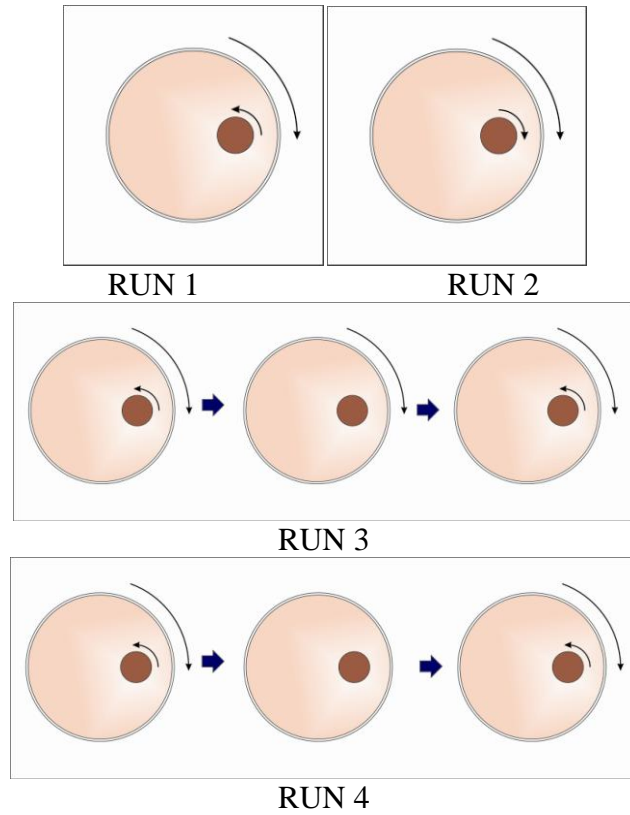
The experimental set up is presented in Figure 1. The glycerin was mixed with nitric acid in a glass vessel in proportions of 1 : 3. The glass vessel was on a revolving plate with a mixing rod placed in it. Both the plate and the rod were revolved in various directions. There were 4 revolution patterns: the first was RUN 1, the vessel revolved clockwise (30 rpm) and the rod revolved counterclockwise (30 rpm); the second, RUN 2, the vessel and the rod revolved clockwise (30 rpm); the third, RUN 3, the tank revolved clockwise continuously (30 rpm) and the rod was revolved counterclockwise for 1 minute (30 rpm) and then stopped for 1 minute and restarted again, and so on; the fourth, RUN 4, the tank was revolved clockwise (30 rpm) and the rod was revolved counterclockwise (30 rpm) for 2 minute and then both were stopped for 1 minute and then repeatedly restarted and stopped at 1 minute intervals until the experiment was completed. These patterns are presented in Figure 2.

The geometry of the flow domain is characterized by two dimensionless parameters: the ratio of the radius of the rod and the cylindrical tank  $R_2/R_1$ , and the dimensionless eccentricity  $e = \epsilon / R_1$ . The geometrical parameters ( $\epsilon$ ) are set to  $R_2/R_1$ . A sketch of the mixer studied is presented in Figure 3.

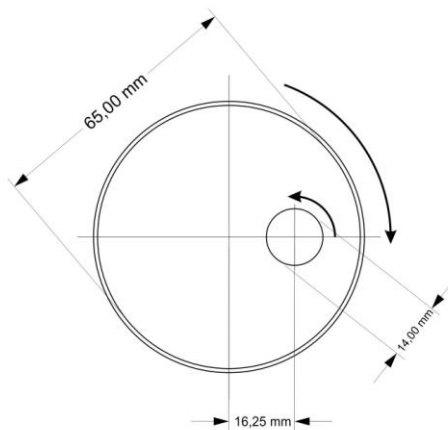
The revolution of glycerin nitration was observed by a color change technique [12] based on fast nitration reaction under four motion patterns of stirring rod and rotating vessel (RUN 1, 2, 3, and 4). Nitration reaction behavior was identified by measuring fluid temperature using thermocouple throughout the mixing process up to the formation of the nitroglycerin.



**Figure 1:** The Experimental Setup



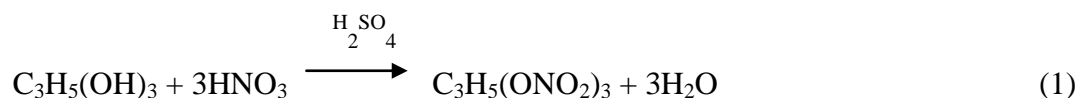
**Figure 2:** The Revolutions Patterns of The Stirring Rod and Rotating Vessel (RUN 1, 2, 3, 4)



**Figure 3:** Sketch of The Mixer

## Results and Discussion

The elemental reaction of producing nitroglycerin is the etherification reaction of glycerin and nitric acid. This chemical reaction can be expressed as:



In this reaction, the mixed feed acid contains both  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . The reagent  $\text{H}_2\text{SO}_4$  acts as a dehydrating agent (Ren, 1994). Therefore, only the  $\text{HNO}_3$  participates in this reaction.

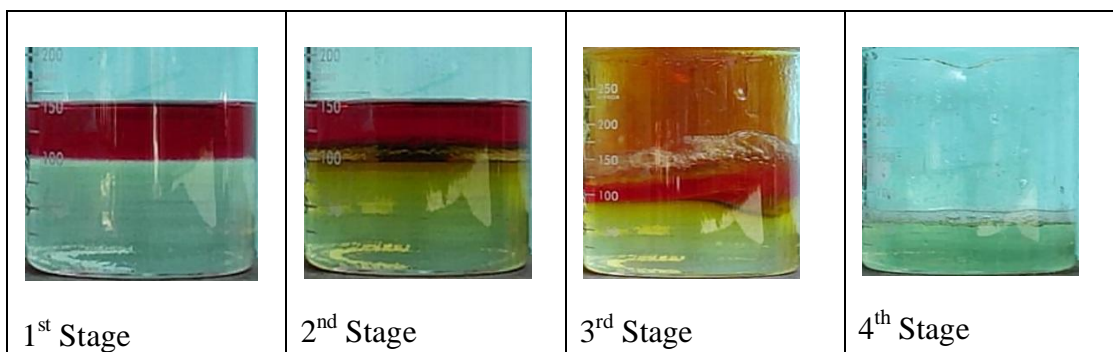
The nitroglycerin formation process in the rotating vessel with stirring rod consisted of four stages. The first stage was the mixing of glycerin and nitric acid. The second stage was the reaction of glycerin and nitric acid shown by the color changes in the fluid mixture. The third stage, the subsequent reactions between glycerin and nitric acid, was indicated by change from fluid into gas (vapor/smoke). The fourth stage was the end of the nitroglycerin process as indicated by the formation of nitroglycerin and gas bubbles. The four stages of the nitroglycerin formation process in rotating vessel with stirring rod are presented in Figure 4.

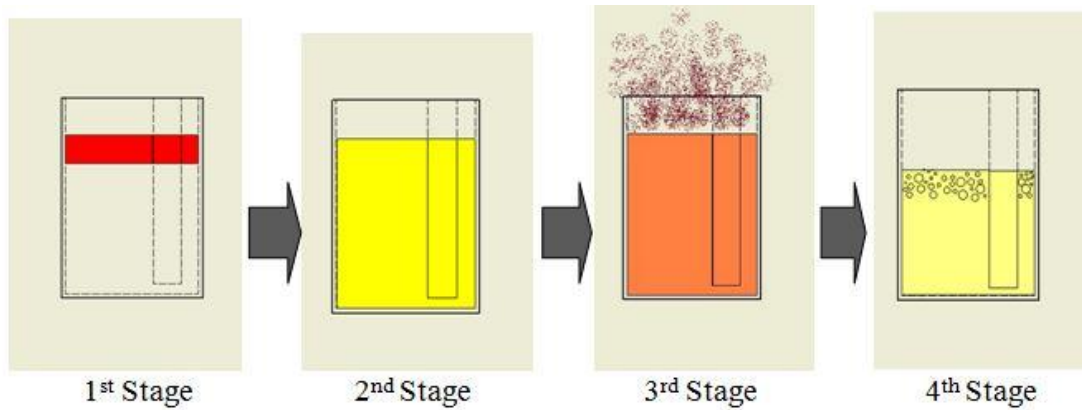
The mixing stage (1<sup>st</sup> stage) was the mixing period of the glycerin and nitric acid. The two fluids are separated due to differences in density. They are slowly mixed by the rotations of the vessel and stirring rod. This period lasted until the upper layer glycerin became increasingly thin until finally the mixture color changed to bright red.

The color change stage (2<sup>nd</sup> stage) was the period of the color mixture change, from bright red to golden yellow, indicating the presence of a chemical reaction between the glycerin and the nitric acid.

The 3<sup>rd</sup> stage, the phase change was the period where the next reaction occurred and physical state changed from fluid to gas. This was indicated by the first appearance of a vapor which at first was light brown until it became dark brown. In this period, there was also the phenomenon of the fluid boiling.

The formation of nitroglycerin and bubbles stage (4<sup>th</sup> stage) was the end of nitroglycerin process. Gas bubbles were formed from the exothermic reaction of nitroglycerin, the nitroglycerin produced was light yellow.

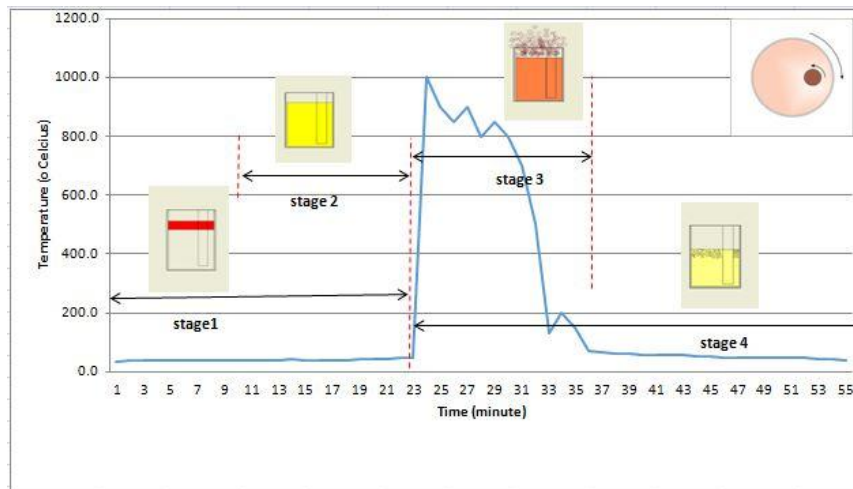




**Figure 4:** Illustration of The Four Stages in Nitroglycerin Process

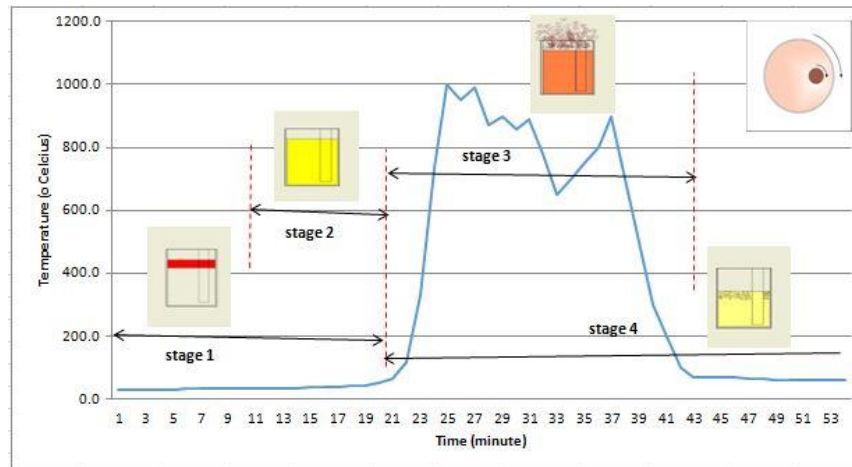
Fluid treatment was studied based on phase change time occurring in the glycerin mixing. Phase change time periods were identified from the image and thermocouple signal for each RUN's.

Model perturbations/revolutions affecting nitration process, Figures 5-8, show the changes in temperature at certain mixing times.



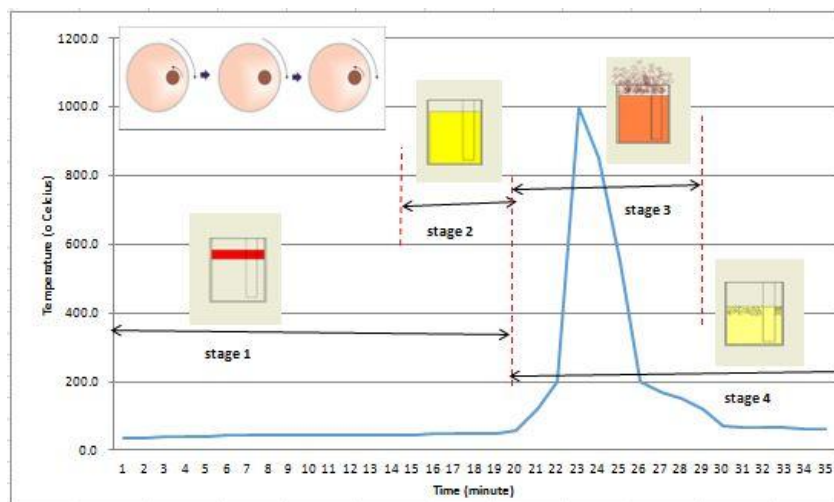
**Figure 5:** Stage and Temperature vs Time at RUN 1

Figure 5 shows the stage and temperature evolution for RUN 1. The temperature increased slowly to 20°C for 23 minutes. After 23 minutes, the temperature rose rapidly in a matter of seconds, and in the 24<sup>th</sup> minute reached the maximum (1000°C) that the sensor could detect. These high temperatures lasted for 13 minutes (above 100° to over 1000°C), after which they declined to below 100°C. After more than 30 minutes, the temperature finally dropped below 100°C and returned to room temperature (31°C).



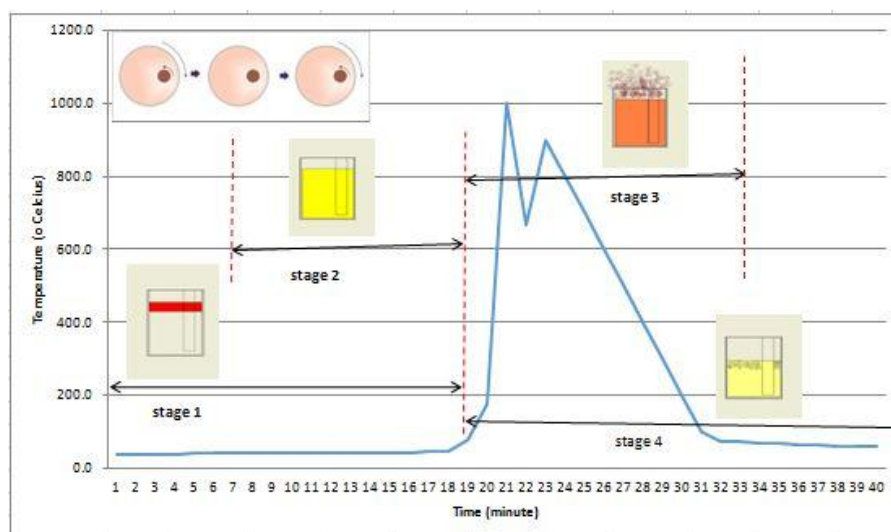
**Figure 6:** Stage and Temperature vs Time at RUN 2

Figure 6 shows the stage and temperature evolution for RUN 2. The temperature increased slowly to 30°C for 21 minutes. After that, the temperature increased quickly to high degree of Celsius for 22 minute after which they dropped below 100°C. After more than 30 minutes, the temperature was below 100°C before finally going back to room temperature (31°C).



**Figure 7:** Stage and Temperature vs Time at RUN 3

Figure 7 shows stage and temperature evolution for RUN 3. The temperature increased slowly to 25°C for 20 minutes. After 20 minutes, the temperature went up quickly and in the 23<sup>th</sup> minute reached the maximum temperature. These high temperatures occurred for approximately 9 minutes (above 100° to over 1000°C), after which they declined to below 100°C. After more than 30 minutes, the temperature was below under 100°C then finally dropped to room temperature (31°C).



**Figure 8:** Stage and Temperature vs Time at RUN 4

Figure 8 shows the stage and temperature evolution for RUN 4. The temperature increased slowly to 40°C for 19 minutes. After 19 minutes, the temperature rose rapidly to high degree of Celsius for 12 minute after which they dropped below 100°C. After more than 30 minutes, the temperature was below 100°C before finally going back to room temperature (31°C).

If the curves 1<sup>st</sup> to 4<sup>th</sup> in Fig. 5-8 are compared, certain phenomena can be observed. In the first stage, the nitroglycerin reaction mechanism, namely in the mixing stage, whereby the glycerin layer above the nitric acid layer was mixed with sulfuric acid due to the agitation of the vessel and rotating rod, the temperature behavior occurred linearly and increased from room temperature up to temperatures between 20 to 40 °C over an average of 20 minutes for each treatment, the highest temperature (40°C) occurred in RUN 4, then 30°C in RUN 2 and in RUN 3 at 25°C, and 20° C in RUN 1.

In the second period of the nitration process, namely the stage of color change, where the fluid mixture changed from clear light yellow, to dark yellow, to light brown and finally to dark brown, the temperature behavior was quite extreme, increasing from 40°C to 1000°C. In RUN 1, the temperature increased rapidly in less than 1 minute, in RUN 2 less than 3 minutes and in RUNs 3 and 4 the temperature rose in less than 2 minutes. The second stage was the beginning of the exothermic reaction. When compared to all other treatments, the onset of the temperature of the exothermic reaction was most rapid in RUN 4 followed by RUN 3, RUN 2, and then RUN 1.

In the third period, the nitroglycerin reaction mechanism was followed by formation of smoke, where the brown smoke that initially formed in a thin layer eventually become thick and dense. In this period, there was also the phenomenon of the fluid boiling. The temperature behavior was quite extreme in this stage, and increased rapidly up to 1000°C which lasted for a few minutes. The longest period of high temperatures occurred in RUN 2 (22 mins), and then RUN 1 (13 mins), then RUN 4 (12 mins), and the shortest was in RUN 3 (9 mins).



In the fourth period, namely, the formation of nitroglycerin and gas bubbles, where gas bubbles formed from the exothermic reaction of nitroglycerin, and the temperature decreased slowly until it reached room temperature again. All treatments (RUNs 1, 2, 3, and 4), took more than 30 minutes to return to room temperatures.

In a stirring vessel, stirring generates variations in the flow pattern of the system causing the fluid to circulate within the vessel. The first stirring pattern was called RUN 1, vessel and rod rotated in opposite directions. In the second mixing pattern, RUN 2, vessel and rod rotated in the same direction. The third mixing pattern, RUN 3, vessel and rod rotated anticlockwise and stirring stopped from time. In the fourth stirring pattern, RUN 4, vessel and rod rotated counterclockwise and the vessel and rod stopped, then rotated again. Varying flow patterns (chaotic flows) affect the internal energy of the system. In this experiment, the change in internal energy of the system was observed through temperature and time changes that occurred during the reaction.

For chaotic flows, two types of temporal modulation are considered for the stirring protocols: a continuous one and a non-continuous one [11]. In this experiment, the continuous stirring protocols represented by RUN 1 and 2, while the non-continuous protocols represented by RUN 3 and 4. The results of this treatments difference was found that the initial exothermic reaction is faster for non-continuous protocols (RUN 3 and 4) compared to the continuous protocols (RUN 1 and 2). Likewise, for a long time reaction, shorter time for the exothermic reaction is at a non-continuous protocols (RUN 3 and 4) when compared with continuous protocols (RUN 1 and 2).

During a chemical reaction, energy is transformed from one form to another and chemical bonds are broken and new one formed, these changes can be observed through changes in color, smell, sound, and temperature. The energy is required to break the chemical bonds, and when atoms form new bond arrangements they generate heat. In exothermic reactions, the amount of energy needed to form a new bond is greater than the amount of energy used to break the bonds, so that the overall reaction produces heat, and this is what happens when glycerin is mixed with nitric acid. Exothermic reaction occurs because the product (nitroglycerin) has lower energy content in its chemical bonds than the reactants (glycerin + nitric acid). This is an ideal situation because one law of thermodynamics states that all reactants and products are trying to minimize their energy.

Chemical reaction rate changes the amount of reactants into products in a unit of time, but the speed of the chemical reaction is not part of the equation of chemical equilibrium and the way to determine the speed of a chemical reaction is to do the experiment itself. In a reaction, the reaction rate could change. At the beginning, the amount of reactant is still sufficient for the reaction to run quickly, but as the reaction proceeds, some reactants turn into products and as these products do not react further, so the reaction rate is reduced. In the end, when all the reactants turn into products, the reaction terminates.

The reaction will go faster in the presence of collisions, first collisions will occur on the surfaces in contact, so the high surface area to volume ratio will accelerate the reaction [11, 12, 25, 33, 34]. In the non-continuous stirring protocol (RUN 3 and RUN 4), the mixing was triggered by the presence of wider tangent surface area. Then the number of collisions are larger than those in RUN 1 and RUN 2. This causes a faster

chemical reaction in non-continuous stirring protocols (RUN 3 and RUN 4) compared with continuous stirring protocols (RUN 1 and RUN 2).

Energy changes arising from mechanical sources work directly aligned with the system. In this experiment, the source of an important change in the internal energy came from the heat given to or taken from the trajectory of a chemical reaction by varying the mixing flow pattern. It was found in this study that the patterns of non-continuous chaotic flows generate shorter reaction time (in RUN 3) and earlier initial reaction time (in RUN 4).

## Conclusion

The mixing time for dissolving fixed amounts of glycerin in fixed amounts of nitric acid were measured and compared to those from several different revolutions/flow patterns. It was found that the mixing time and the rate of exothermic reaction of glycerin nitration had been influenced by the revolutions patterns of both the rod and vessel. The results showed that the four stirring patterns (RUN 1, 2, 3, and 4) affected both the mixing time and duration of the glycerin nitration process. The temperatures in the glycerin nitration reaction were changed and increased drastically in all RUN's. These results explicitly demonstrate the different thermal behavior in the mixing performance that was stimulated by the continuous and non-continuous stirring patterns. The stirring pattern of non-continuous flow during the glycerin nitration process, RUN 3 generates the shortest reaction time and RUN 4 generates the earliest initial reaction time.

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