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BORATE AUTOCASTING: KINETICS MODEL AND EFFECT OF CARBON DIOXIDE ON REACTION RATE

by

Ali Zuhair Fadhel

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Ali Zuhair Fadhel

BORATE AUTOCAUSTICIZING: KINETICS MODEL AND EFFECT OF CARBON DIOXIDE ON REACTION RATE

Ali Zuhair Fadhel, M.S.

Western Michigan University, 2007

Borate autocausticizing is a promising approach to the operational and environmental improvement of Kraft pulping and its chemical recovery. Its advantages include partial or total elimination of the lime cycle, pulp strength improvement, and energy savings. Borate autocausticizing involves the use of an amphoteric salt, sodium metaborate, to de-carbonize sodium carbonate and produces trisodium borate, the reaction occurs at high temperatures. Tran and Cameron (1999) suggest that the reaction follows the path below.

$$NaBO_2 + Na_2CO_3 \longrightarrow Na_3BO_3 + CO_2$$

This thesis systematically analyzes the reaction kinetics of borate autocausticizing. The uniqueness of this research is the usage of a thermo-gravimetric analysis to study the kinetics of the borate/carbonate reaction. The weight loss data generated by the TGA are used to monitor the concentration of the reactants; the data are analyzed using the differential method/excess method for batch reactor o obtain a kinetic expression for the reaction. The equimolar reaction produces bisodium borate and has an overall order of 2.5 at 700 ^{0}C. The reaction produces trisodium borate when the metaborate to carbonate molar ratio is 0.1-0.2, the order of sodium metaborate is 1.5 at 700 ^{0}C. In addition, the reaction conversion reduces in the presence of CO_2 at 850 ^{0}C.

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INTRODUCTION AND BACKGROUND

Paper plays a vital and meaningful role in all areas of human activity; it is used to record, communicate and store information. Paper is also used in wrapping, packaging and structural applications. The traditional definition of paper, in relation to its manufacturing process, is a felted sheet that is formed on a fine screen from fibers that are suspended in water. Also, pulp is defined as the fibrous material in the paper manufacturing process [1]. The paper making process consists of many steps and processes starting with logging of trees and ending with the final product as shown in Figure 1. The pulping part of the process demonstrated in Figure 1 is chemical pulping; chemicals and heat are used to convert the wood into the fibrous mass. The details of chemical pulping are discussed in further details later in this section. The figure shows the basic units of an integrated mill; which both pulp manufacturing and paper making exist in the same mill.

Pulping is the process through which the bonds of the fibers within the wood or other fibrous raw material are systematically broken. This process reduces the fibrous raw material (mainly wood) into a fibrous mass. Pulping is divided into many categories including mechanical and chemical pulping.

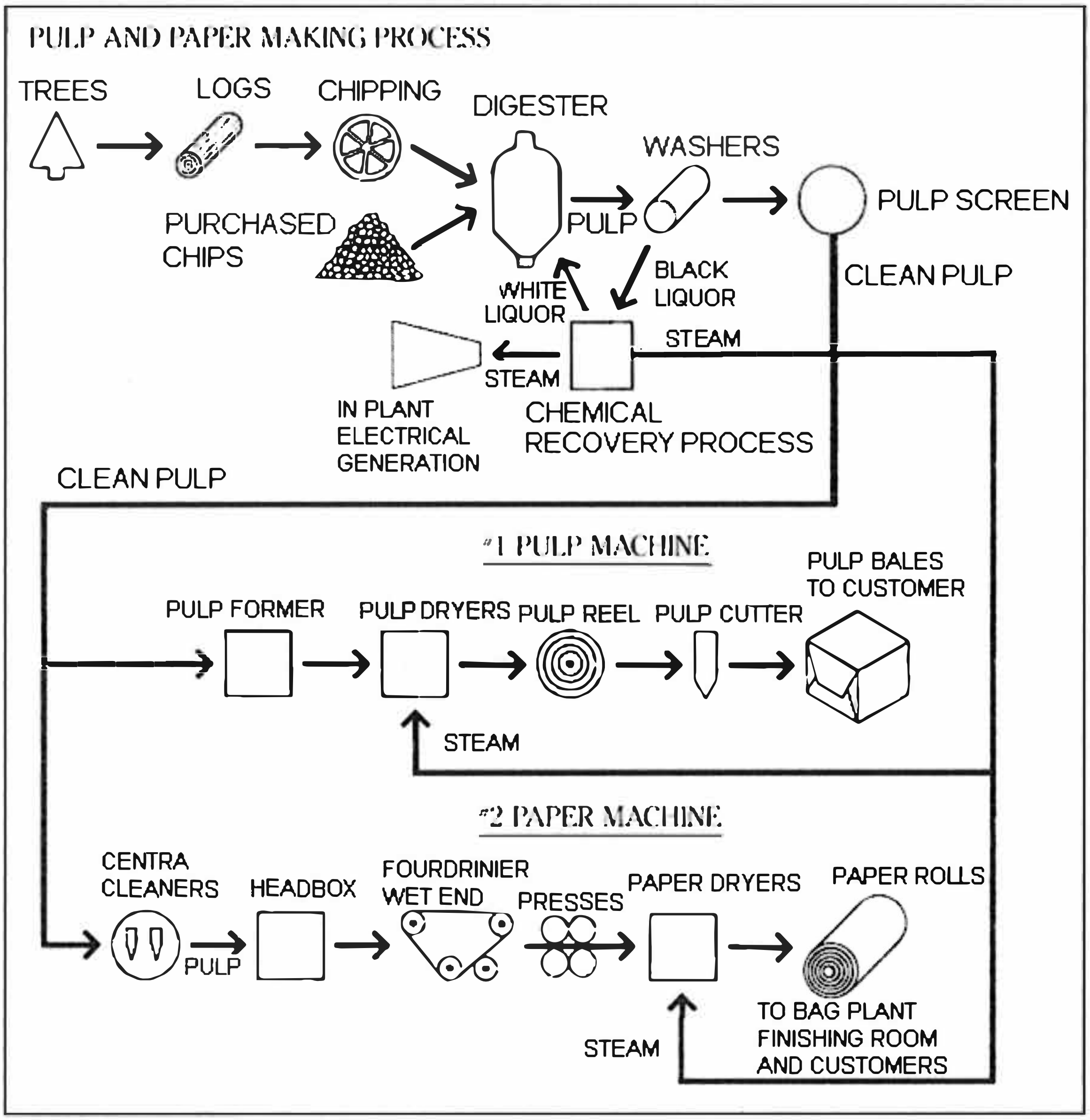


Figure 1. Schematic of the Pulp and Paper Making Process [2].

In chemical pulping, aqueous solutions and the appropriate chemicals are used at high temperature and pressure to degrade and dissolve away the lignin leaving the cellulose and hemicelluloses in the form of fibers [1]. Examples of the chemical pulping process are Kraft, sulfite and soda pulping. Chemical pulping dominates about 70% of the North American pulping operation and Kraft pulping occupies represents 95% of the chemical pulping processes.

Mechanical pulping is carried out through mechanical energy. Examples of the process are stone groundwood, refiner mechanical pulp and thermomechanical pulp; mechanical pulping processes enjoy a high yield (about 90%) of short, impure, weak and unstable fibers. On the other hand, chemical pulping employs chemicals and heat to produce long, strong and stable fibers with a yield of about 50%. The focus of this thesis is related to the pulping process, specifically the Kraft (chemical) cooking of the pulp.

Kraft Pulping

The Kraft pulping process started as the soda process, which was first patented in 1854 and was recognized as the first chemical delignification process. The soda process used a strong alkaline solution of sodium hydroxide. Two years later, in 1865, a patent that covered the process of chemical recovery, which involved the incineration of the spent soda liquor for the recovery of the alkali, was introduced to the soda process. The first successful mill implementation of the soda process took place in 1866.

A tremendous improvement in the soda process was achieved when C.F. Dahl developed the Kraft or Sulfate process. Dahl introduced sodium sulfate (saltcake) into the recovery furnace; a cheaper process with accelerated delignification was achieved. Dahl obtained a patent for his findings in 1885 and the process was implemented in Sweden a year later. The name Kraft, which is the German word for strength, was assigned to the process due to the fact that the product paper enjoyed superior strength properties.

However, the Kraft process produced paper that was considerably darker in color when compared to the dominant pulping process then, the sulfite process. The development of the bleaching process in the 1930s and 1940s by Howard Raspon enabled the Kraft process to achieve pulp with brightness comparable to the sulfite pulp.

A flow diagram for the modern pulp process is shown in Figure 2. The chips and the white liquor, which contains the cooking chemicals (sodium hydroxide and sodium sulfide) are fed to the digester. The digester can be operated in batch or continuous fashions. In batch Kraft pulping, the chips are fed to the cooker and liquor is added until the chips are covered, liquor heating starts by forced circulation through a heat exchanger. Batch cooking takes about 3 hours, an hour for liquor heating to 170 ^{0}C followed by two hours of cooking at this temperature.

In continuous Kraft pulping, the chips are fed to the cooker after being preheated while passing through a steaming vessel to purge air and noncondensables. The first zone of the continuous cooker is operated at 120 ^{0}C (intermediate temperature), which facilitates a uniform penetration of the chemicals into the chips. As the cooking is continued, the mixture is heated to the cooking temperature of 170 ^{0}C by circulating the cooking liquor through a heat exchanger or by steam injection [3].

Once cooking is completed, the spent liquor is extracted in a low pressure tank. The flash steam from the blow tank is then used in the steaming vessel. Brown stock washing is the step that follows the spent liquor extraction. In this step, the liquor and the cooked pulp are separated and the pulp is screened and cleaned. This step concludes the processing and cooking of the pulp in the Kraft process. The remaining blocks belong to the chemical recovery of the pulping chemicals. It must be noted that the chemical recovery system is of great importance to the Kraft pulping, it is the process by which the Kraft process survived the competition since it was established.

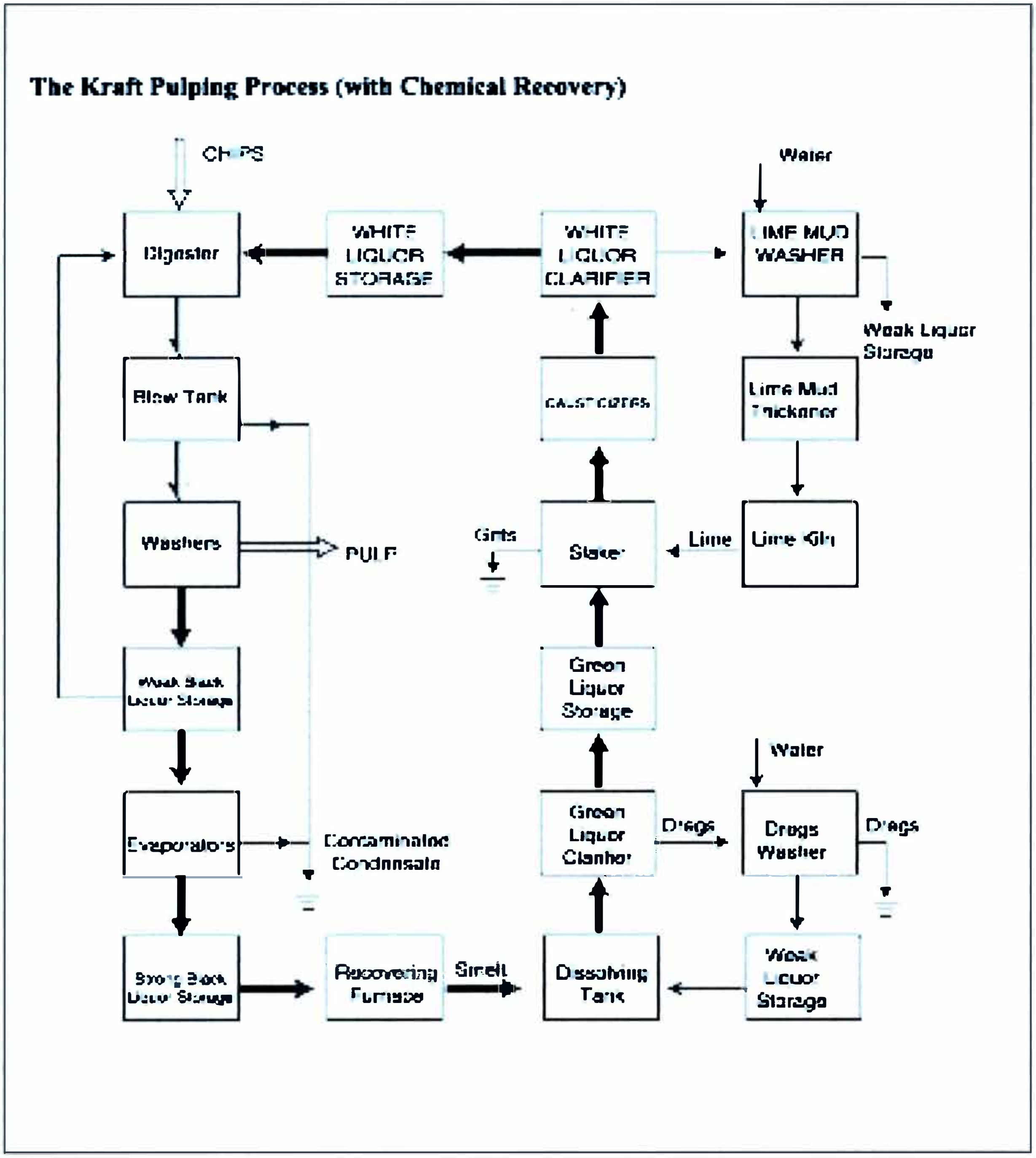


Figure 2. Flow Diagram of the Kraft Pulping Process [3].

The chemical recovery process starts with collecting the weak black liquor (about 15% solids) and ends with producing the white liquor which is used for the next cooking cycle.

The weak black liquor is collected from the brown stock washing and then concentrated to about 70% solids through the use of multiple-effects evaporators. The concentrated liquor is then incinerated in the recovery furnace, organic compounds oxidize to give off energy while inorganics are reduced and form a smelt at the bottom of the recovery furnace. Figure 3 shows the dominant chemical reactions in the recovery boiler. As shown in the figure, the smelt contains sodium sulfide (Na_2S) and sodium oxide (Na_2O). Reactions with oxygen, CO, and CO_2 and other products from the oxidation zone and reduction zone take place to produce sodium carbonate and sodium sulfate. The smelt is transferred from the furnace to the dissolving tank to form the green liquor. The name green liquor is assigned to this liquor due to its green color.

The green liquor, consisting mainly of sodium carbonate and sodium sulfide, is clarified to remove dregs (carbon and inorganics). The clarified green liquor is then mixed with reburned lime at high temperature and violent agitation in the slaker. The lime (CaO) is converted to calcium hydroxide (known as milk-of-lime), as shown in reaction 1. This marks the beginning of the causticizing process.The calcium hydroxide reacts with the sodium carbonate to form sodium hydroxide, the cooking chemical, as shown in reaction 2.

$$CaO + H_2O \longrightarrow Ca(OH)_2 + HEAT \qquad (1)$$

$$Ca(OH)_2 + Na_2CO_3 \longrightarrow 2NaOH + CaCO_3 \qquad (2)$$

The slaking and causticizing reactions start in the slaker, which is a vented atmospheric tank. Further mixing of the reactants is carried out for a period of 2 hours in mixing tanks to assure completion of the causticizing reaction. The resulting solution is named the "white liquor". The white liquor is clarified and the settled calcium carbonate mud is transferred to be washed, filtered, and reburned. The process of collecting the calcium carbonate mud and burning it to form calcium oxide is known as the calcium cycle.

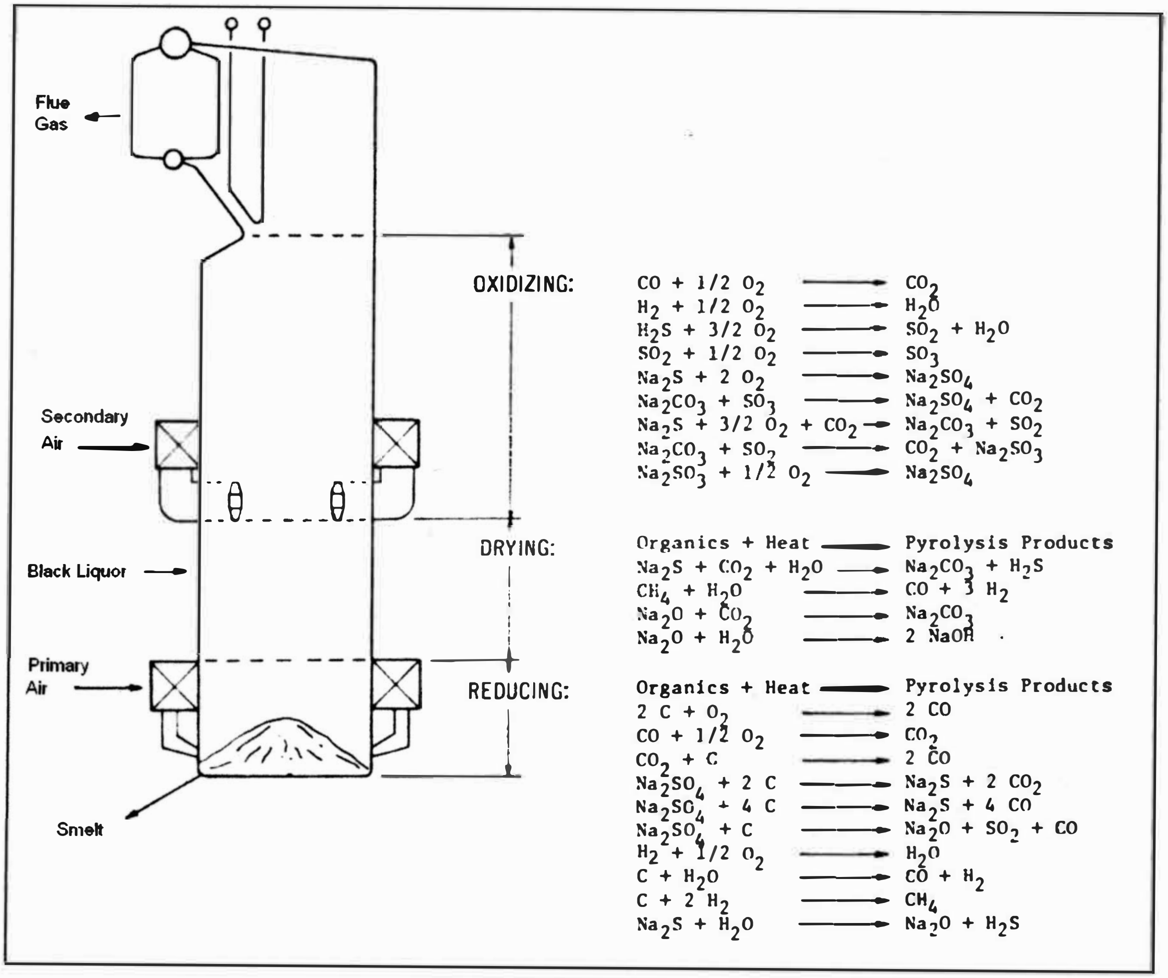


Figure 3. Combustion Zones in the Kraft Recovery Boiler [4].

Although the process of Kraft chemical recovery has many advantages, i.e. reliable technology, efficient chemical recovery and good thermal efficiency, efforts have been taken in the last 60 years to develop and improve this technology. These efforts are driven by the high capital cost and large scale equipment.

A promising approach is the use of borate to generate caustic within the sodium cycle (autocausticizing). The borate acts on the sodium carbonate and decarbonizes it (by driving the CO_2 out), the product (trisodium borate) reacts with water to form caustic. This process has the potential of eliminating the calcium cycle totally or partially. Borate causticizing could lower the capital cost, operation cost and expansion cost for the Kraft mills; these are some of the incentives for the study, development and implementation of this process [4].

Borate Autocausticizing

Borate autocausticizing is considered as a non-conventional causticizing process. The process is based on the use of an amphoteric salt, sodium metaborate, to de-carbonate sodium carbonate [5]. Also, sodium metaborate has many applications including adhesives, textile processing, detergents and cleaners, and corrosion inhibition [6].

Borate was recognized to form caustic with a high enough pH to be utilized in the pulping process by Janson. However, the stoichiometry and kinetics were not sufficiently understood until Tran, Mao, Cameron and Blair investigated the process and corrected the stoichiometries [7]. The investigation suggests that the reaction has many possible paths. However, the data and conclusions indicate that the dominant path leads to the formation of trisodium borate and carbon dioxide as shown in reaction 3 [8].

$$NaBO_2 + Na_2CO_3 \longleftrightarrow Na_3BO_3 + CO_2 \qquad (3)$$

$$Na_3BO_3 + H_2O \longrightarrow 2NaOH + NaBO_2 \qquad (4)$$

As proposed by the authors, reaction 3 is carried out in the recovery boiler. The product of the borate autocausticizing, trisodium borate, is then mixed with water in the green liquor mixing tank to yield sodium hydroxide, the causticizing solution, and sodium metaborate as shown in reaction 4. Figures 4 and 5 demonstrate the Kraft cooking cycle without autocausticizing (conventional) and with partial borate autocausticizing, respectively [11]. Figure 4 is represents the steps shown in Figure 2 in a different way. Figure 5 reflects the presence of sodium metaborate and boron ion at the different stages of the process when borate autocausticizing is utilized; process changes are required for the implementation of borate causticizing in Kraft pulping.

Borate autocausticizing could potentially eliminate the conventional causticizing and calcining process if fully utilized. This presents a significant potential for savings on capital investments, raw material cost, energy cost, equipment maintenances cost and production cost. Also, this technology could enable mills that are limited by their pulping capacity to expand their production without further investments [9].

In addition, borate autocausticizing improves pulping efficiency by about 2 % [9]. Although the improvement is incremental, the cost saving are sufficient since pulp represents a high cost in the paper making process. Furthermore, this technology is an item on the "2020 Agenda" [10]. The Department of Energy, National Science Foundation, Forest Services, Department of Agriculture and academia have formed a partnership and the "2020 Agenda"; they have considered autocausticizing as one of the technologies capable of increasing energy efficiency, reducing environment deterioration and improving the industry profits. The energy savings result from the partial elimination of the lime cycle; modern mills consume fossil fuel mainly to operate the lime kiln [11].

Borate effects on the pulp and black liquor properties have been studied. From the pulp point of view, the conclusions were in favor of the borate presence in Kraft pulping; the borate improves the fiber strength and reduces its viscosity [12]. This effect results in stronger pulp, stronger paper and easily pumpable solution, which reduces energy consumption of the pumping systems. On the other hand, borate presence increases the black liquor boiling point and viscosity. The latter could be offset by the great advantages and cost savings offered by borate autocausticizing.

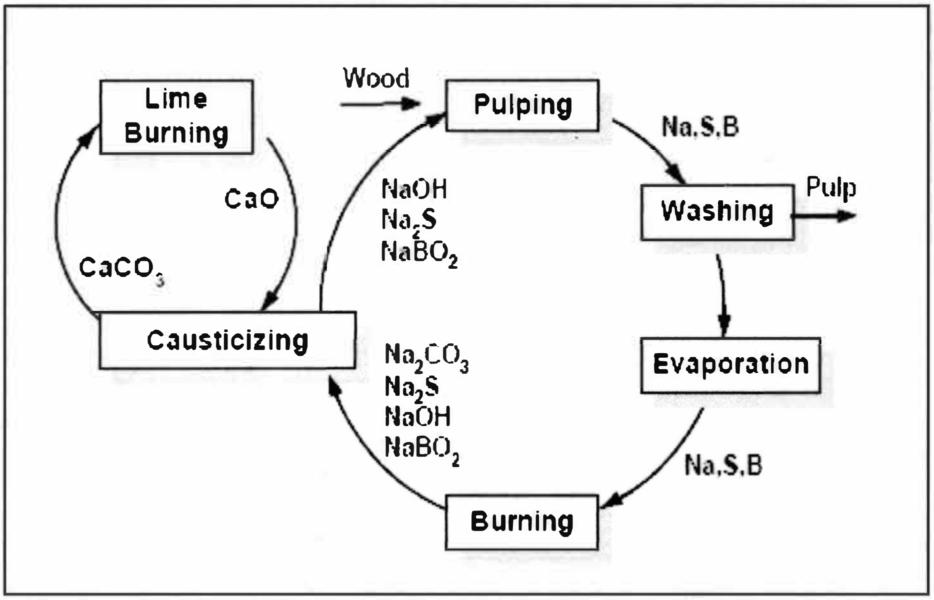


Figure 4. Conventional Kraft Pulping [11].

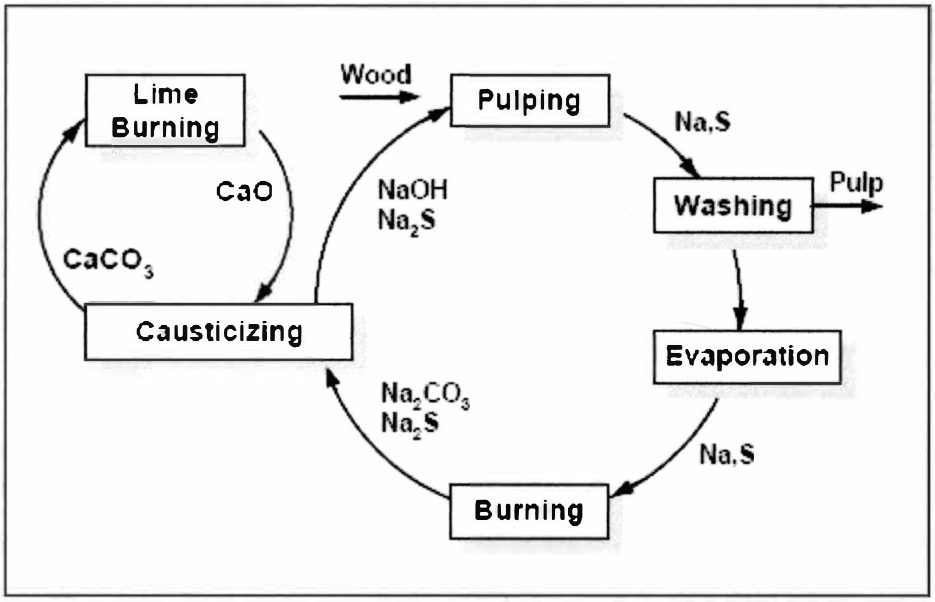


Figure 5. Kraft Pulping with Partial Borate Autocausticizing [11].

Moreover, borate benefits the technology of Black Liquor Gasification (BLG) [13]. BLG aims at utilizing the black liquor to generate power since it has the advantage of high power-to-heat ratio; the process also serves environmental and safety issues in the process of black liquor recovery. The drawback of BLG, in the conventional Kraft pulping, is the increased causticizing demand since it forms sodium carbonate instead of sodium sulfide; sodium sulfide forms in the smelt in the recovery boiler. Borate autocausticizing could solve this problem; its presence in the gasifier would favor the formation of sodium metaborate (which then mixes with water to form sodium hydroxide) and carbon dioxide since sodium metaborate does not react with sodium sulfide.

OBJECTIVES AND EXPERIMENTAL DESIGN

Statement of the Problem

As discussed above, borate autocausticizing has a great potential for improving the process of Kraft pulping in terms of economical and operational perspectives. However, it has been shown that the metaborate/carbonate reaction rate is hindered by the presence of carbon dioxide [8]. This is among the reasons why borate autocausticizing is not widely used in the process of paper making. We plan to thermogravimetricly analyze the kinetics of borate autocausticizing process with particular emphasis on the effects of carbon dioxide.

Objectives

The focus of this thesis is the Kraft recovery process. This research is aimed at a systematic study of the kinetics of borate autocausticizing using a Thermogravimetric Analyzer (TGA). The usage of TGA confers uniqueness to this thesis, when compared to the other studies that have been carried out to understand and quantify the rate of sodium metaborate reaction with sodium carbonate. Basically, the objectives of this thesis can be summarized as following:

(1) Investigate and apply the use of the Thermogravimetric Analyzer (TGA) in the study of borate autocausticizing reaction kinetics.

(2) Generate reaction rate data for a kinetic model of the borate autocausticizing reaction and investigate the effects of carbon dioxide on the reaction rate.

Methods

The design of the experiments will be based on a kinetics model since the investigation involves generating a kinetic expression for the reaction and studying its reversibility in the presence of carbon dioxide. The reaction kinetics are assumed to follow Arrhenius' law for the following reasons:

- The reaction is temperature dependent [8].
- The reaction is elementary; it follows the stoichiometry [8].

Arrhenius' kinetic model is shown in equation 5 [14] and the expected irreversible and reversible reaction rates are shown in equations 6 and 7, respectively [8]. The rate data will be generated using the TGA as weight loss per minute for different temperatures, different stoichiometric ratios of reactants, and different carbon dioxide concentrations in the purge gas. It will be assumed that the weight loss is strictly carbon dioxide [15].

$$k = k_0 e^{\Delta E/RT} \tag{5}$$

$$d[CO_2]/dt = k\,[NaBO_2]^m[Na_2CO_3]^n \tag{6}$$

$$d[CO_2]/dt = k\,[NaBO_2]^m[Na_2CO_3]^n - k'[CO_2]^x[Na_3BO_3]^y \tag{7}$$

Where;

k, k'	reaction rate constants
k_0	is the pre-exponential factor
m, n, x, y	order of the reaction with respect to the individual reactants
ΔE	is the activation energy
R	is the universal gas constant
T	is the absolute temperature

The proposed kinetic model by Tran and Cameron (1999) follows Arrhenius' equation and equation 6 with m and n equal to 1. The values of the pre-exponential factor and activation energy are 2580 ± 400 L/mol-sec and 35 ± 2.5 kcal/mol, respectively, in the experimental temperature range of 1000-1200 K (727 – 927 ^{0}C).

The kinetics analysis will be based on an Arrhenius' type correlation of equation 6. The reversibility of the reaction will be removed by purging the reactor with nitrogen gas and hence, preventing the presence of any carbon dioxide in the reactor atmosphere. The kinetics of the reaction are analyzed using the Differential Method for batch reactor [16]. The overall order of the irreversible reaction (m+n) is obtained by using equal concentrations of the reactants, sodium metaborate and sodium carbonate ($[NaBO_2] = [Na_2CO_3]$), and running the reaction isothermally. The initial concentration of the sodium metaborate in the molten salts mixture, which is the reactant that is monitored in the experiment, is determined by the weight of the mixture recorded by the TGA, which is then converted to molar concentration as discussed later. A concentration-time curve ($[NaBO_2]$ = function (time)) is then fitted with a 4th or 5th degree polynomial using Microsoft Excel®. The derivative of the concentration-time curve yields the rate of the reaction, $-d[NaBO_2]/dt$ or $d[CO_2]/dt$.

The order of the reaction is determined by plotting the natural logarithm of the rate (the derivative of concentration-time function) against that of the concentration to represent Equation 8.c, which is a straight line function. In the case of equal reactant concentrations, the slope of the line equals the overall order of the reaction and the y-intercept equals the rate constant "k".

$$d[CO_2]/dt = k\ [NaBO_2]^m[Na_2CO_3]^n \quad (6)$$

$$\text{Ln}\ (d[CO_2]/dt) = \text{Ln}(k) + \text{Ln}([NaBO_2]^m) + \text{Ln}([Na_2CO_3]^n) \quad (8.a)$$

$$\text{Ln}\ (d[CO_2]/dt) = \text{Ln}(k) + m*\text{Ln}([NaBO_2]) + n*\text{Ln}([Na_2CO_3]) \quad (8.b)$$

Since; $[NaBO_2] = [Na_2CO_3]$

$$\text{Ln}\ (d[CO_2]/dt) = \text{Ln}(k) + (m+n)*\text{Ln}([NaBO_2]) \quad (8.c)$$

The individual reactants orders are determined using the excess method [16]. A large amount of sodium carbonate is supplied to react with sodium metaborate isothermally. The moles of sodium carbonate are assumed to stay constant during the reaction and therefore, the rate is a function of sodium metaborate concentration only. The linear fit of the natural logarithm of the derivative of sodium metaborate consumption rate versus the natural logarithm of sodium metaborate concentration ($[NaBO_2]$) has a slope equal to "m", as shown below.

$$d[CO_2]/dt = k\ [NaBO_2]^m[Na_2CO_3]^n \quad (6)$$

$$d[CO_2]/dt = k_1\ [NaBO_2]^m \quad (6.a)$$

where, $k_1 = k\ [Na_2CO_3]^n = \text{constant}$

$$\text{Ln}\ (d[CO_2]/dt) = \text{Ln}(k_1) + \text{Ln}([NaBO_2]^m) \quad (8.d)$$

$$\text{Ln}\ (d[CO_2]/dt) = \text{Ln}(k_1) + m*\text{Ln}([NaBO_2]) \quad (8.e)$$

The pre-exponential factor and the activation energy are calculated using the Equation 5. The natural logarithm of the rate constant "k" at different reaction temperatures is plotted against the inverse of the absolute temperature. The slope of the line has a value of Ln (k_0) and the slope represents $\Delta E/R$.

In conclusion, the experiments conducted to obtain the kinetics data involve using three different mixture molar ratios ($[NaBO_2]/[Na_2CO_3]$) of 1, 0.2 and 0.1 and running the reaction at three different isothermal reaction temperatures of 700, 850, 950 ^{0}C. The molar ratios will be varied by varying the weight of the metaborate salt in the salt mixture as discussed later. In addition, the carbon dioxide effect on the reaction rate is studied by feeding carbon dioxide in the purge gas, which is usually 100% nitrogen, from a cylinder.

The previous discussion covered the theoretical basis for the kinetics analysis of the reaction. The next paragraphs will discuss in details the application of TGA generated data to such analysis. The Thermogravimetric Analyzer (TGA), shown in Figure 6, measures the weight change and plots it as function of temperature or time. The TGA can run experiments in temperatures as high as 1000 ^{0}C, which makes it suitable for the purpose of this thesis. The reactants, in the form of salts, are mixed and heated to the desired temperature and a set time. Meanwhile, readings of weight, temperature and time are recorded electronically.

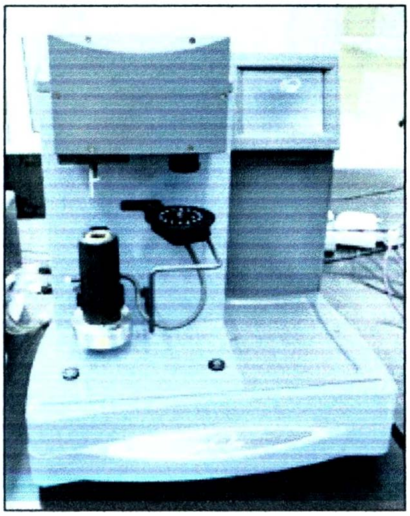


Figure 6. ThermoGravimetric Analyzer TA Q500

For our experiment, premixing of the salts is recommended to ensure intimate contact. Sodium carbonate and hydrated sodium metaborate are dissolved in distilled

(DI) water and the solution is then heated to evaporate the mixing water. Both the salts are soluble in water at temperature below boiling (water boiling temperature is 100 ^{0}C). The salts mixture is then placed in a dryer at around 120 ^{0}C for more than 24 hours, the dry salts are ground using a mortar and pestle.

To run an experiment, the ground salt is loaded in the platinum TGA tray and an experimental procedure is set. The TGA control program allows setting different heating rates (^{0}C/min), durations of reaction temperature (isotherms) and experiment termination criteria.

The results obtained from the ThermoGravimetric Analyzer (TGA) were displayed and exported into Microsoft Excel ® using a specialized program, The Universal Analysis Program. The TGA data includes the weight of specimen in milligrams (mg) , the experiment elapsed time in minutes, the reactor temperature in degrees Celsius (^{0}C), the samples chamber (reactor) purge gas flow rate in milliliters per minute (ml/min), and the balance purge gas flow rate in ml/min.

The Universal Analysis software has the capability of differentiating the data with respect to time or temperature. We obtained the differential data of weight of sample with respect to time, as shown in Figure 7, which is used as a guide to mark the initiation of the reaction. The beginning of the reaction is accompanied by the increase of the derivative of the weight with respect to time indicating the beginning of sodium carbonate de-carbonization and formation of trisodium borate. The weight change of the mixture after the point of reaction initiation is about 15%, which is consistent with the findings published by Tran and Cameron (1999). For mixtures with sodium metaborate to sodium carbonate ratio of 1, the dehydration weight loss is about 7.5%.

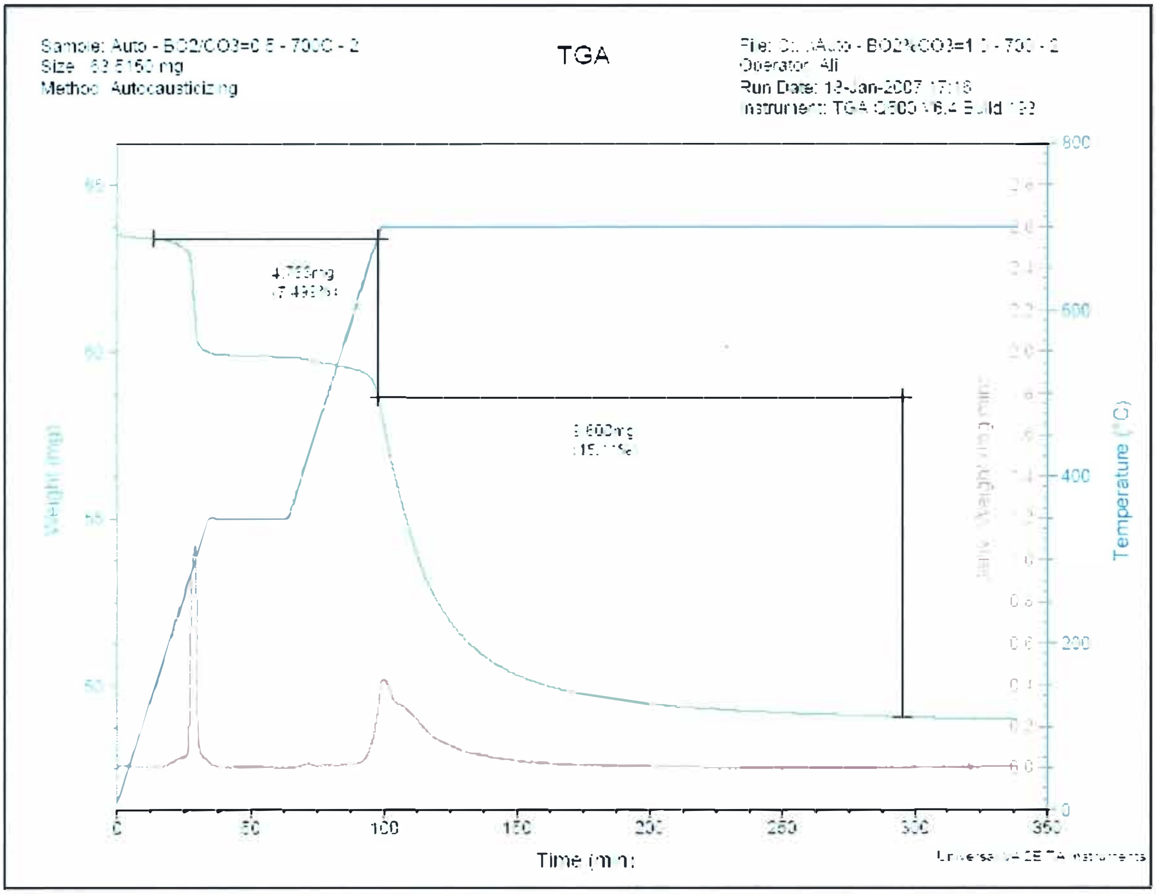


Figure 7. TGA Data for Equimolar Autocausticizing Reaction – 700 ^{0}C.

The first peak of the weight derivative corresponds to the dehydration of the salts, as shown in Equation 9. The second peak of the weight derivative, occurring at about 700 ^{0}C, indicates the beginning of the autocausticizing reaction.

$$NaBO_2.4H_2O + Na_2CO_3 \longleftrightarrow Na_3BO_3 + CO_2\uparrow + H_2O\uparrow \qquad (9)$$

Microsoft Excel ® is used to analyze the data obtained from the Universal Analysis program. The weight of the molten salts obtained from the TGA is converted to molar concentrations in moles per liter (mol/L) using the mix molar weight, the specific gravity of mixture as well as material balance techniques. An example of mixture molecular weight calculation for a sample with sodium metaborate to sodium carbonate molar ratio ($NaBO_2/Na_2CO_3$) of 1/5 or 0.2 is shown below. Similar methods are used to obtain the molecular weights of samples with sodium metaborate to sodium carbonate ratios of 1 and 0.1.

1 mole mixture = 1 mole $NaBO_2$ + 5 moles Na_2CO_3

1 mole mixture = 1 x 65.7995 g/mole $NaBO_2$ + 5 x 105.998 g/mole Na_2CO_3

1 mole mixture = 595.7895 gram

The initial number of moles of sodium metaborate (at time = 0 or t_0) is obtained by dividing the salts' weight at the point of reaction initiation by the molecular weight. The moles are then divided by the mix volume, which is obtained by dividing the weight of salts by the density of the molten mix. The specific gravity of the molten mixture equals 1.9 [17] and is assumed to stay constant during the course of the reaction.

The concentration of sodium metaborate at any time "t" during the reaction period equals the number of moles of carbon dioxide emitted subtracted from the initial concentration of sodium metaborate. The moles of carbon dioxide emitted can be calculated by the weight difference of the mix at any time interval ($t-t_0$) divided by the molecular weight of carbon dioxide. The modeled reaction time is 3600 seconds (1 hours) from the time the reactor reaches the isothermal reaction temperature. The weight curve reaches a plateau within this reaction time period.

RESULTS AND DISCUSSION

A summary table for each reaction was generated; the tables and graphs are shown in the appendices. Table 1 shows an example for a reaction at 700 ^{0}C and $NaBO_2/Na_2CO_3$ moles ratio of 1, this ratio will be referred to as "ratio" in parts of this section. The time of reaction and sample weight are obtained from the TGA data, the weight of reactants at the beginning of the reaction (at highest value for the differential of weight and time curve) is used to calculate the number of moles of sodium borate at time zero, as discussed earlier. The sodium metaborate concentration at different times is calculated by deducting the amount of carbon dioxide moles emitted from the metaborate initial concentration. The conversion at target temperature accounts of the reaction occurring during the temperature ramp. Also, the conversion at target temperature after 1 hour measures the completeness of the reaction at the isothermal reaction temperature after the specified time period. These conversion calculations are based on the stoichiometry shown in reaction 3 where the product is trisodium borate, one mole sodium metaborate produces one mole carbon dioxide.

The sodium metaborate concentration, referred to as "C_A" in parts of this discussion, is plotted against time and the curve is fitted with a 4th degree polynomial, shown in Figure 8. The concentration-time function is differentiated with respect to time to yield the rate equation, $-dC_A/dt$ in terms of time "t". A linear plot of the natural logarithm of the rate equation and the concentration of sodium metaborate is used to obtain the order of the reaction and the reaction rate constant "k". Figure 9 shows the linear fit for the kinetics of reaction 9 at 700 ^{0}C, two experiments were carried out at the same conditions and are presented in the figure.

Table 1. Rate Data for Autocausticizing Reaction at 700 ^{0}C and $NaBO_2/Na_2CO_3$ = 1.0.

$NaBO_2$ Initial Concentration [C_A] (mmol)	0.3546
Sample Weight at Target Temperature (mg)	60.92031
Moles CO_2 Emitted until target temperature (mmol)	0
[C_A] at Target Temperature (mmol)	0.3546
[C_A] at Target Temperature after 3600s (mmol)	0.1693
Conversion after 1h at target temperature (%)	52.25
Conversion at target temperature (%)	0

Ratio = 1 - 700 C - S.G. = 1.9

Time	**Sample Weight**	**$NaBO_2$**	**[$NaBO_2$]**	**- dC_A/dt**	**Ln ($-dC_A/dt$)**	**Ln (C_A)**
Seconds	**mg**	**mmol**	**mol/L**	**mol/L.s**		
0	60.91	0.3544	11.11	0.005100	-5.279	2.407
300	58.50	0.2998	9.78	0.004030	-5.514	2.281
600	56.77	0.2605	8.76	0.003197	-5.746	2.170
900	55.64	0.2349	8.06	0.002569	-5.964	2.087
1200	54.85	0.2168	7.55	0.002114	-6.159	2.021
1500	54.26	0.2036	7.16	0.001800	-6.320	1.969
1800	53.84	0.1940	6.88	0.001594	-6.442	1.928
2100	53.53	0.1870	6.67	0.001463	-6.527	1.897
2400	53.35	0.1818	6.50	0.001375	-6.589	1.872
2700	53.13	0.1777	6.39	0.001298	-6.647	1.854
3000	52.98	0.1744	6.28	0.001200	-6.725	1.838
3300	52.76	0.1716	6.21	0.001048	-6.861	1.826
3600	52.76	0.1693	6.13	0.000809	-7.120	1.813

From Figure 9 we can conclude that reaction 9 has an overall order of 2.5. One observation was that the overall conversion of the reaction was about 50%. To isolate the individual order of the reactants, borate and carbonate, the excess method is employed. The ratios of moles of Sodium Borate to Sodium Carbonate are 0.2 and 0.1; these ratios truly supply an excess amount of carbonate and validate the assumption that the concentration of carbonate remains almost unchanged during the course of the reaction.

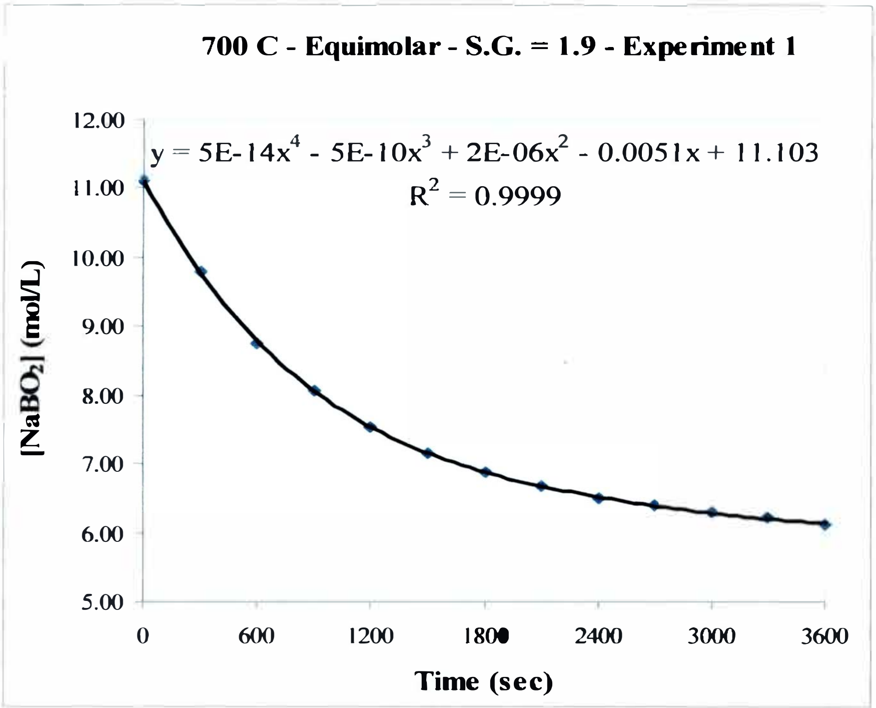


Figure 8. Concentration - Time Plot for Equimolar Autocausticizing Reaction - 700 ^{0}C.

The method followed in the above analysis was used to analyze data for autocausticizing experiments with molar ratios of 0.2 and 0.1 at 700 ^{0}C. Figures 10 and 11 show the kinetic equation fit for the experiments, the y-intercepts of the lines are different from the one with ratio of 1 because it incorporates the concentration of the excess reactant in its value.

The conclusion of this part of the study is that the order of reaction with respect to the limiting reactant, the sodium metaborate or “A”, is approximately 1.5. In the reaction with molar ratios of 0.1 and 0.2, the overall conversion was more than 80%.

The results of these experiments are slightly different than published data. The difference could result from the natural decomposition of sodium carbonate, which starts at around 400 ^{0}C [18]. Also, previous research indicates that 1 mole sodium metaborate generates between 1 to 1.3 moles carbon dioxide [19], probably due to sodium carbonate decomposition.

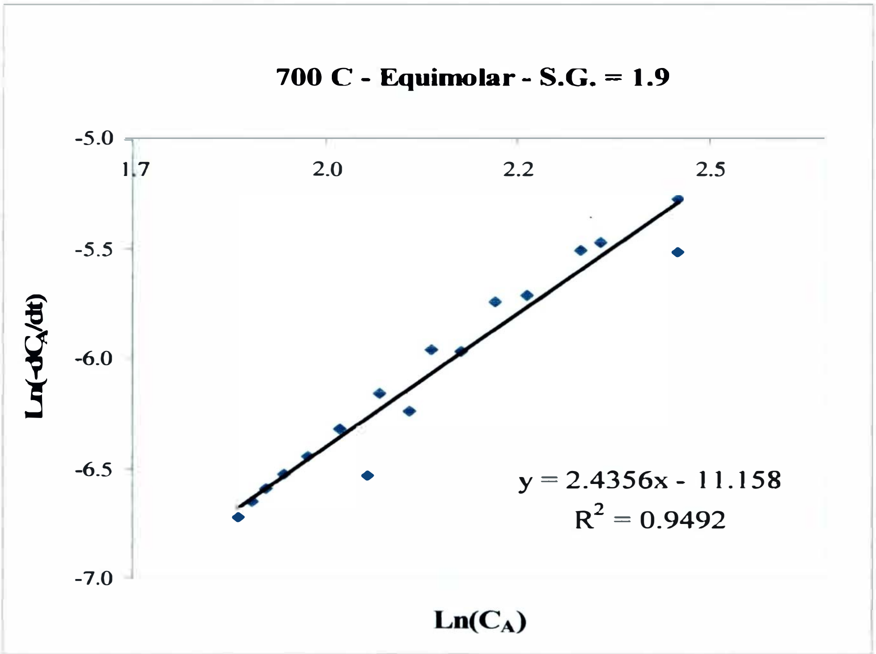


Figure 9. Kinetic Equation Fit for Equimolar Autocausticizing Reaction - 700 ^{0}C.

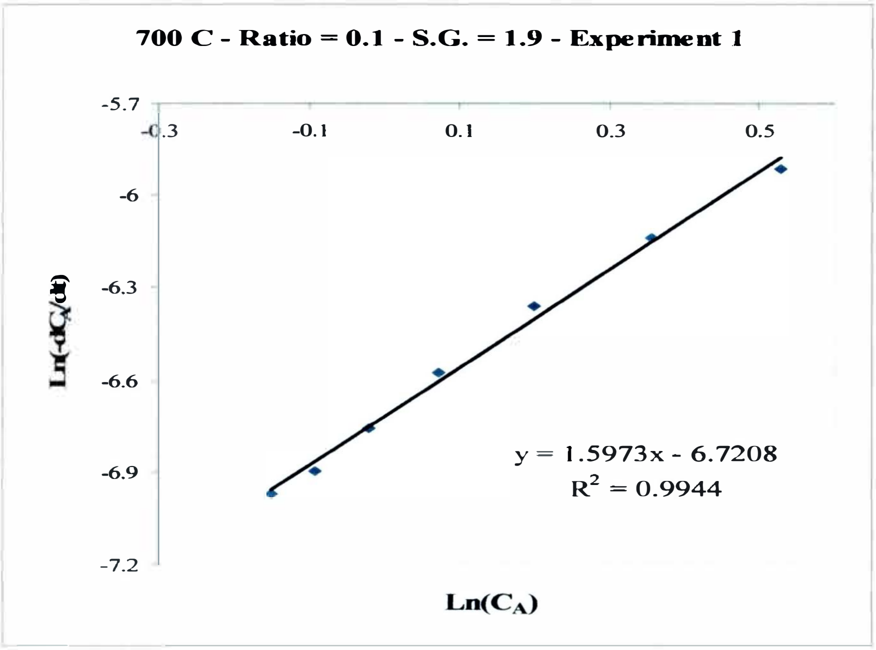


Figure 10. Kinetics Equation Fit for Autocausticizing Reaction with Reactants Ratio of 0.1 at 700 ^{0}C – Experiment 1.

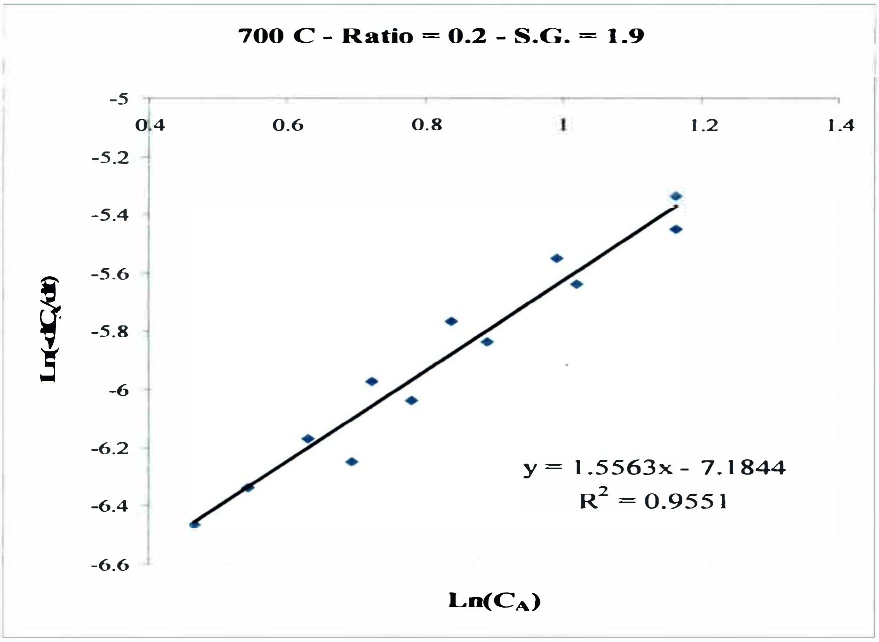


Figure 11. Kinetics Equation Fit for Autocausticizing Reaction with Reactants Ratio of 0.2 at 700 ^{0}C.

The second temperature that the reaction was studied at is 850 ^{0}C. The differential method for the kinetics rate evaluation and excess method, discussed above, were also used in this analysis. Concentration-time plots as well as kinetic equation fits were utilized to obtain the order of the reaction at this temperature. Figure 12 shows the time-concentration polynomial fit and Figure 13 shows the kinetic equation linear fit for the autocausticizing reaction at 850 ^{0}C.

The order of the reaction for the two experiments that were carried out at this temperature, which is represented by the slope of the line in Figure 13, is 18. The steep concentration drop at this temperature, in Figure 12, is a clear indicator of this high rate of de-carbonization. This observation was noted in previous research, a sharp increase in carbon dioxide generation rate was observed at such temperature. The salts mixture reaches its pooled melting point, which is accompanied by stress release due to thermal expansion. This facilitates the movement of the molecules and results in a higher reaction rate.

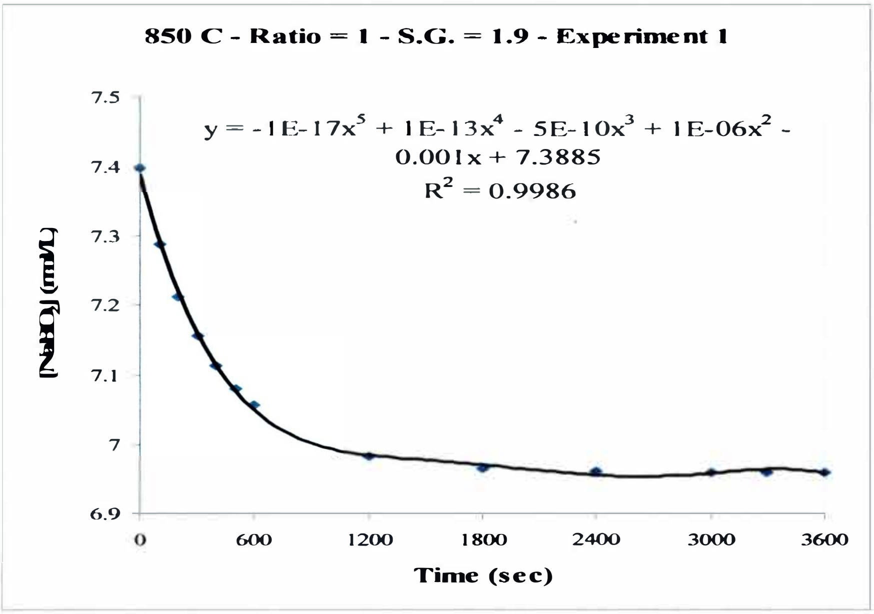


Figure 12. Concentration - Time Plot for Equimolar Autocausticizing Reaction - 850 ^{0}C.

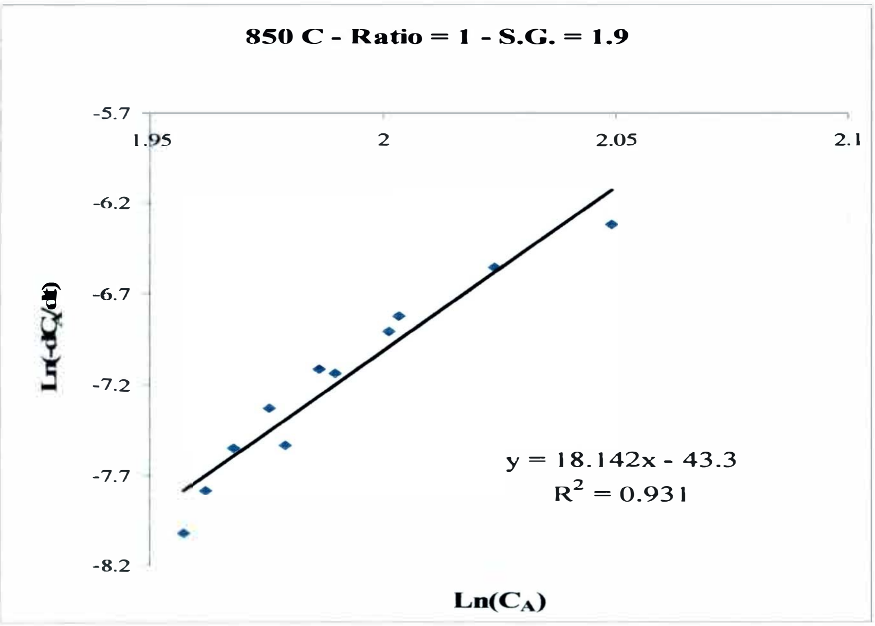


Figure 13. Kinetic Equation Fit for Equimolar Autocausticizing Reaction - 850 ^{0}C.

Also, this high order of reaction could result from an error in the order estimation due to the fact that only about 5-10% conversion took place at 850 ^{0}C; most of the reaction took place during the temperature ramp. In spite of the fact that the reaction reached completion (the concentration plateaus), the overall conversion of the reaction was about 50% only.

Reactions for mixtures with excess sodium carbonate (sodium metaborate to sodium carbonate ratios of 0.1 and 0.2) were also carried out at 850 ^{0}C. The results were inconclusive because the sodium metaborate conversions were almost 100%, as indicated by the conversion at target temperature calculations in Tables 2 and 3, at the time the reactor reached the target temperature of 850 ^{0}C. The reaction reached completion during the temperature ramp.

Table 2. Summary Table for Autocausticizing Reaction with Ratio of 0.1 - 850 ^{0}C.

Ratio = 0.1 - 850 C - S.G. = 1.9 - Experiment 2	
$NaBO_2$ Initial Concentration [C_A] (mmol)	0.05703
Sample Weight at Target Temperature (mg)	61.62
Moles CO_2 Emitted until target temperature (mmol)	0.05870
[C_A] at Target Temperature (mmol)	-0.00167
[C_A] at Target Temperature after 3600s (mmol)	-0.03077
Conversion after 1h at target temperature (%)	154.0
Conversion at target temperature (%)	102.9

The third temperature the reaction was studied at is 950 ^{0}C. Figure 14 shows an example of a concentration-time curve; the concentration profile looks rather linear without any similarity to what we observed in previous experiments at 700 ^{0}C and 850 ^{0}C. This behavior can be explained by the fact that only about 2-6% conversion was obtained at the isothermal stage of the experiment, which probably resulted from sodium carbonate decomposition. We conclude that the reaction was finished during the temperature ramp and little to no conversion took place at 950 ^{0}C. Also, the overall conversion of the reaction was about 50%.

Table 3. Summary Table for Autocausticizing Reaction with Ratio of 0.2 - 850 ^{0}C.

Ratio = 0.2 - 850 C - S.G. = 1.9 - Experiment 1	
$NaBO_2$ Initial Concentration [C_A] (mmol)	0.07969
Sample Weight at Target Temperature (mg)	44.21
Moles CO_2 Emitted until target temperature (mmol)	0.07439
[C_A] at Target Temperature (mmol)	0.00530
[C_A] at Target Temperature after 3600s (mmol)	-0.02731
Conversion after 1h at target temperature (%)	615.1
Conversion at target temperature (%)	93.35

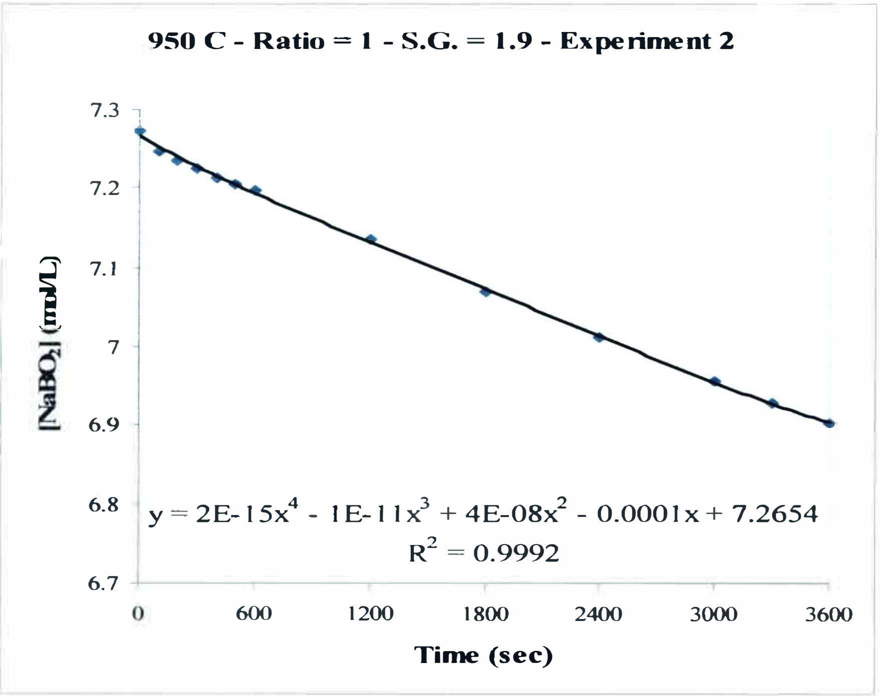


Figure 14. Concentration - Time Plot for Equimolar Autocausticizing Reaction - 950 ^{0}C.

A phase diagram for sodium oxide and borate (the reacting ions of the system) is used to analyze the reaction. The phase diagram analysis indicates that for mixtures with molar ratio of 1.0 (38% sodium metaborate by weight), a phase change is taking place between 700 ^{0}C and 850 ^{0}C, as shown in Figure 15 – points C and F. At point C (molar ratio of 1.0 and 700 ^{0}C reaction temperature), the reaction system is at the borderline of a semi-molten phase (some crystals are present), the system reaches a total liquid state at temperatures higher than 700 ^{0}C. We suspect that this phase change could impact the order of the reaction causing a significant different in the order between the two temperatures. Another reason for this tremendous increase in the rate of carbon dioxide formation could result from errors in the estimation of the rate due to sodium carbonate decomposition, sodium carbonate has low stability at temperatures greater than 840 ^{0}C [20].

The phase diagram analysis for this part suggests that, for mixtures with molar ratio of 0.2 (sodium metaborate weight percent of 11), there is a possibility of phase change. The conditions are at the borderline as indicated by point E. This explains the large difference in conversion percentages between the two reactions, as shown in Tables 2 and 3.

The phase diagram also suggests that for a molar ratio of 1.0 (38% weight percent sodium metaborate), the product of the reaction is bisodium borate and not trisodium borate. The stoichiometry for the bisodium borate product is shown in equation 10. For each mole carbon dioxide emitted, two moles sodium metaborate are emitted, which explains the 50% overall conversion for reactions with molar ratio of 1.0. With the stoichiometry shown in equation 10, the overall conversion is about 100% for reactions with molar ratio of 1.0

$$2NaBO_2 + Na_2CO_3 \longleftrightarrow Na_2B_4O_5 + CO_2 \qquad (10)$$

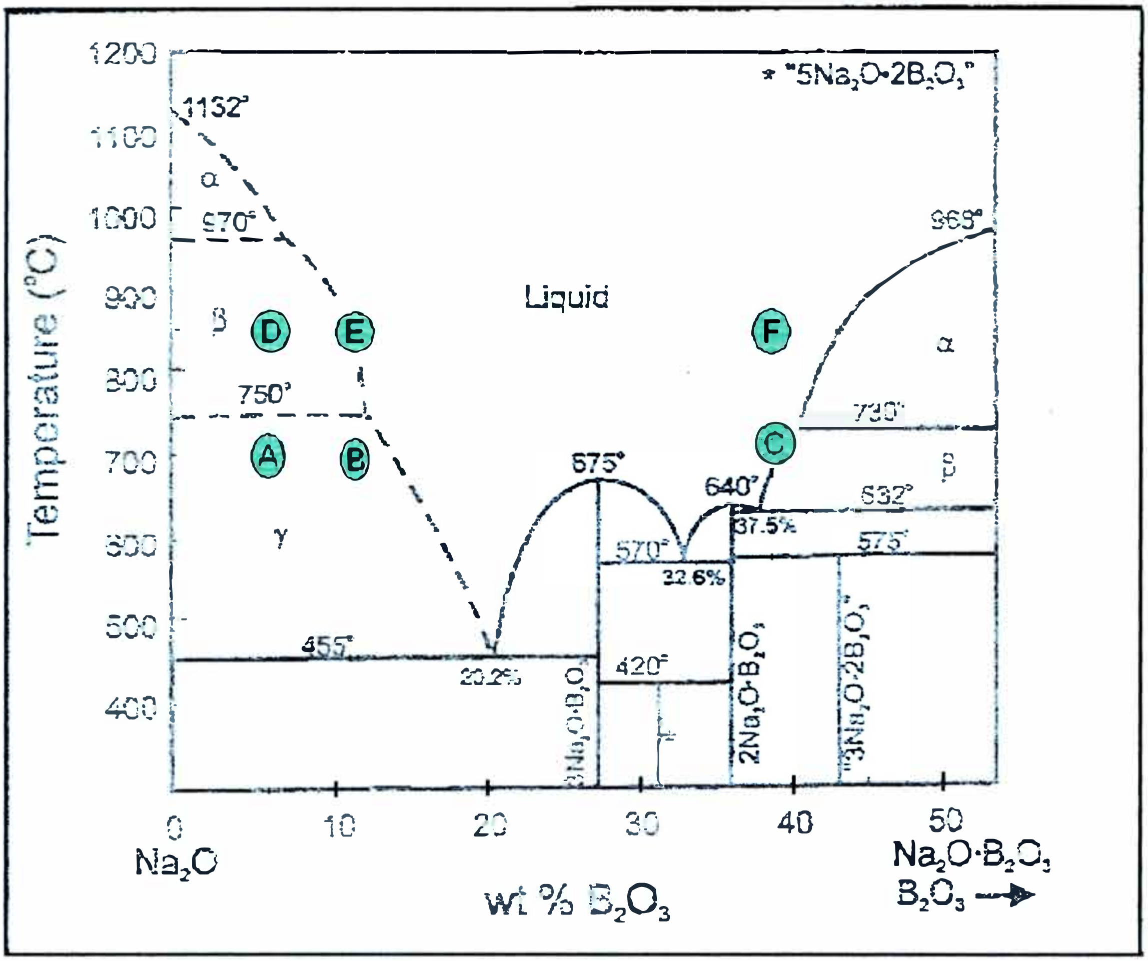


Figure 15. Phase Equilibrium Diagram for the $Na_2O.Na_2O.B_2O_3$ System [8].

The pre-exponential constant and activation energy for reactions with molar ratio of 1.0 are calculated using the Arrhenius' Law. The reaction constant "k" is obtained at two close temperatures, 700 and 695 °C, since the order of the reaction changes when the temperature change is large. The natural log of "k" is plotted against the inverse of the absolute reaction temperatures, as shown in Figure 16. The exponential of the y-intercept of the line equals the pre-exponential constant "k_0" and the slope of the line equals ΔE/R. From the figure, the activation energy (ΔE) equals 19 kcal/mol and "k_0"equals 0.000 567 $L^{1.5}/mol^{1.5}.s$

The difference in activation from the published data result from the difference in reactor size and absence of agitation in our experiments, the scale of TGA experiments is in milligrams (sample size between 30 and 100 mg or 0.000 03 and 0.000 1 kg) compared to 0.1-5.5 kg in previous experiments [17].

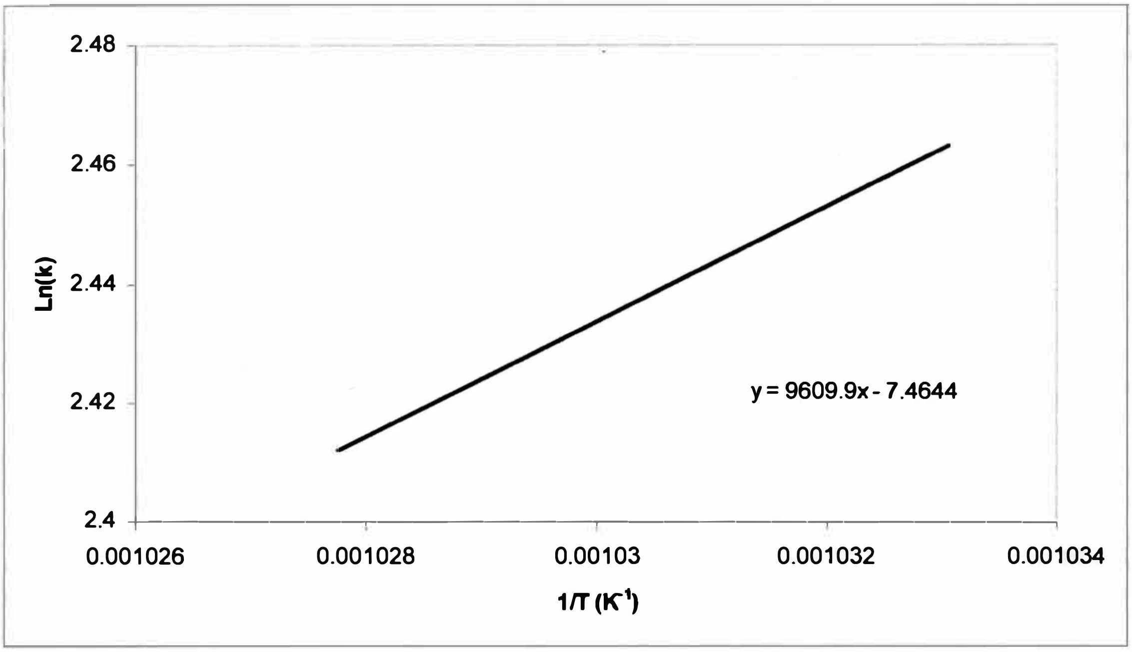


Figure 16. Arrhenius Law Plot for Autocausticizing Reaction with Molar Ratio of 1.0 and Temperature Range of 695-700 ^{0}C.

The effect of carbon dioxide presence in the reactor atmosphere on the autocausticizing reaction was also studied. The percent weight change of the molten salts is measured and compared at different volume percentages of carbon dioxide in the purge gas. Figure 17 shows the TGA results for an experiment carried out at 700 ^{0}C and molar ratio of 1.0 in 5 % volume CO_2 atmosphere. Comparing this figure with Figure 7 (100% nitrogen purge), the only weight loss occurring here is due to dehydration of the salts mixture, which equals about 7%. There is no reaction occurring at 700 ^{0}C when the purge gas contains as little as 5% carbon dioxide by volume. This indicates the strong reversibility of the reaction.

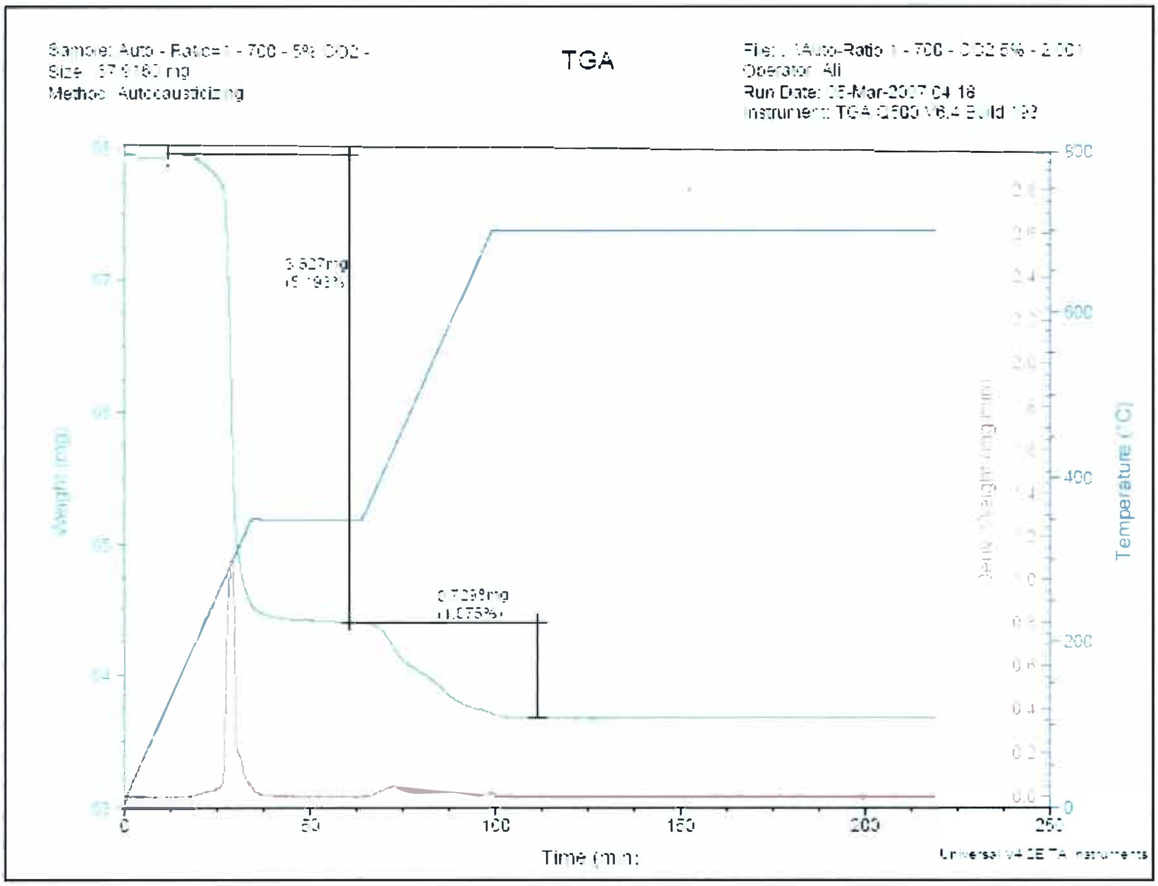


Figure 17. TGA Results for Equimolar Autocausticizing Reaction – 700 ^{0}C and 5% Volume CO_2 in Purge Gas.

The effect of carbon dioxide on the reaction conversion is also studied at 850 ^{0}C. The weight change percentages of the reaction are compared at different carbon dioxide percentages. The results are presented in Figures 18 and 19 for salt mixtures with molar ratios of 1 and 0.1, respectively. The percent weight change drops significantly due to the presence of carbon dioxide in the purge gas even at small percentages. This indicates the importance of sweeping the reactor, or the smelt bed in practice, to maintain a high rate of autocausticizing.

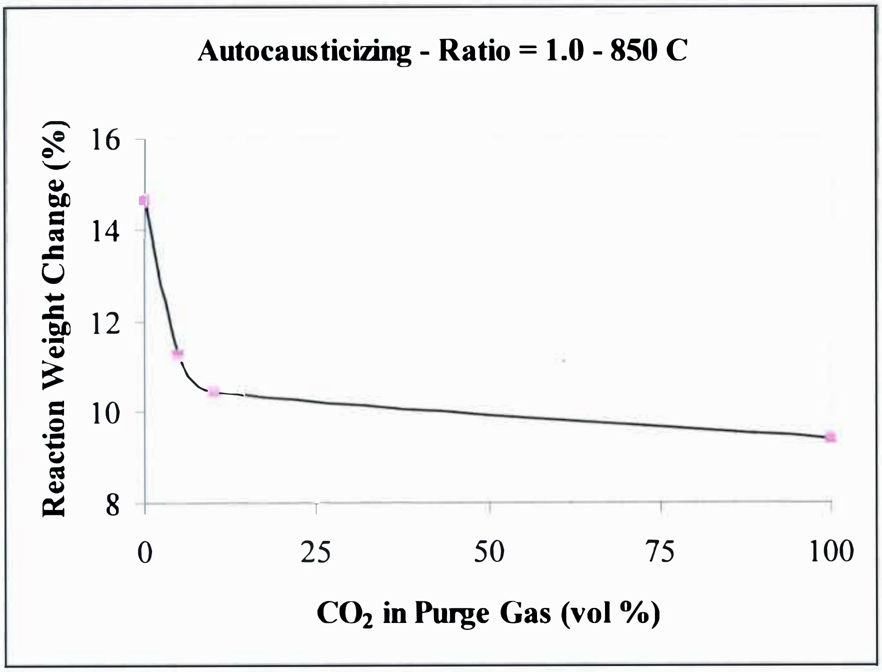


Figure 18. Effect of CO_2 Presence in the Purge Gas on Autocausticizing Reaction - Molar Ratio = 1.0.

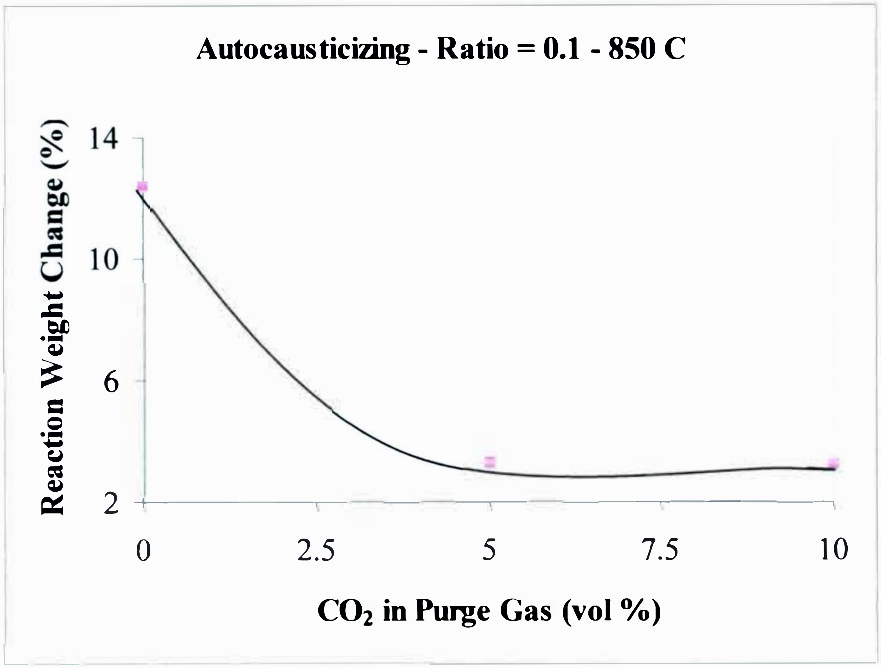


Figure 19. Effect of CO_2 Presence in the Purge Gas on Autocausticizing Reaction – Molar Ratio = 0.1.

CONCLUSIONS

The ThermoGravimetric Analyzer (TGA) is used to study the kinetics of borate autocausticizing at different temperatures and different stoichiometry ratios. The weight loss data from the TGA are converted to concentrations, the derivative of weight with respect to time is used as an indicator to mark the initiation of the reaction. The Differential Method for batch reactor is used to interpret the weight loss data and create a kinetic expression for the reaction.

At 700 ^{0}C, borate autocausticizing has an overall order of 2.5, the order of the reaction increases tremendously at 850 ^{0}C, possibly due to a phase change in the product as well as sodium carbonate decomposition at this temperature. The order of the reaction with respect to sodium metaborate, when molar ratios are 0.1 and 0.2, is 1.5. The phase diagram of the reaction system suggests that the product of the reaction is bisodium borate when the molar ratio is 1.0 and trisodium borate when the molar ratio is 0.1 and 0.2. The activation energy of the reaction with molar concentration of 1.0 is calculated for a temperature range of 695-700 ^{0}C and is found to be around $\Delta E = 19$ kcal/mol.

The reversibility of the reaction in the presence of carbon dioxide is confirmed by feeding carbon dioxide in the reactor purge gas, which is usually pure nitrogen. The conversion of the reaction is strongly affected by the presence of carbon dioxide in the reaction atmosphere even at small percentages.

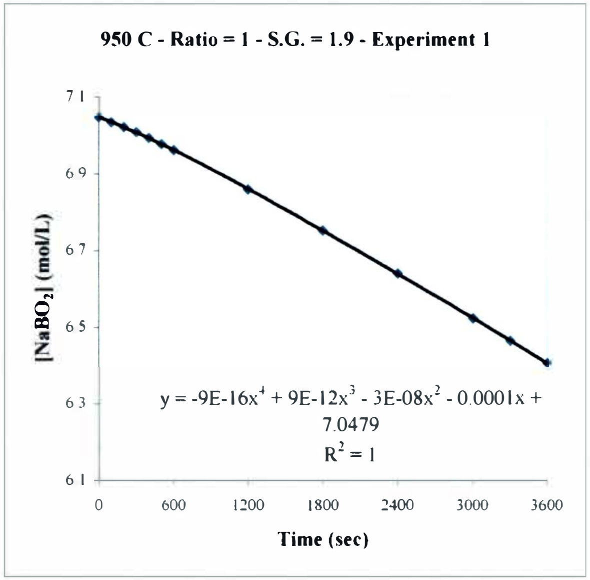
Appendix A

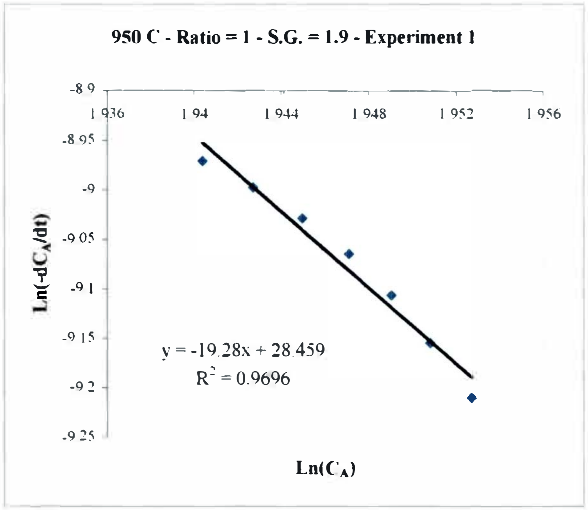
Borate Autocausticizing Reaction Rate Data
Molar Ratio = 1.0 – 700 ^{0}C

$NaBO_2$ Initial Concentration [C_A] (mmol)	0.2201
Sample Weight at Target Temperature (mg)	33.58
Moles CO_2 Emitted until target temperature (mmol)	0.0961
[C_A] at Target Temperature (mmol)	0.1240
[C_A] at Target Temperature after 3600s (mmol)	0.1108
Conversion after 1h at target temperature (%)	49.68
Conversion at target temperature (%)	43.67

Ratio = 1 - 950 C - S.G. = 1.9 - Experiment 1

Time	Sample Weight	$NaBO_2$	[$NaBO_2$]	- dC_A/dt	Ln(-dC_A/dt)	Ln (C_A)
Seconds	mg	mmol	mol/L	mol/L.s		
0	33.58137	0.1240	7.048	0.0001000	-9.210	1.953
100	33.56903	0.1237	7.034	0.0001057	-9.155	1.951
200	33.5576	0.1234	7.022	0.0001109	-9.106	1.949
300	33.54508	0.1231	7.008	0.0001157	-9.065	1.947
400	33.53139	0.1228	6.993	0.0001199	-9.029	1.945
500	33.51693	0.1225	6.978	0.0001237	-8.998	1.943
600	33.502	0.1222	6.961	0.0001271	-8.971	1.940
1200	33.40839	0.1200	6.859	0.0001393	-8.879	1.926
1800	33.3109	0.1178	6.752	0.0001415	-8.863	1.910
2400	33.20935	0.1155	6.640	0.0001382	-8.886	1.893
3000	33.1049	0.1131	6.525	0.0001342	-8.916	1.876
3300	33.0522	0.1119	6.466	0.0001333	-8.923	1.867
3600	32.99977	0.1108	6.407	0.0001340	-8.917	1.857

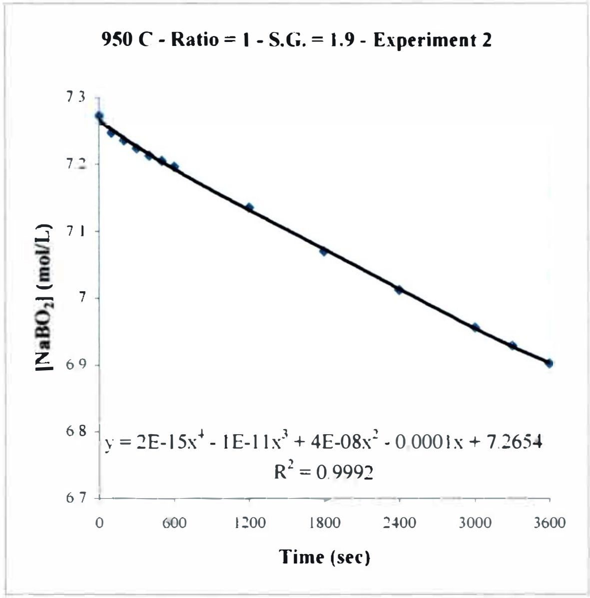


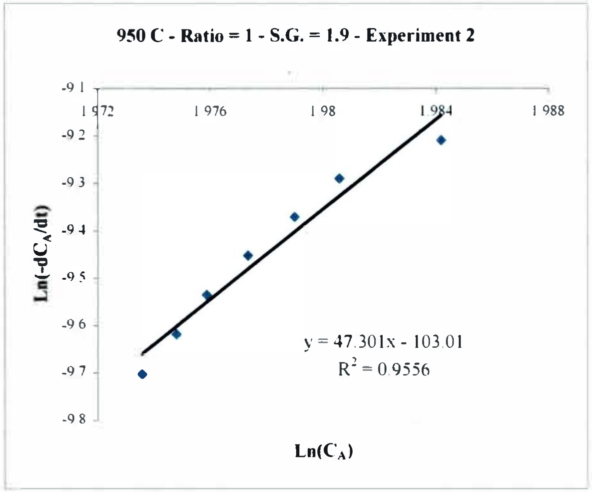


$NaBO_2$ Initial Concentration $[C_A]$ (mmol)	0.2217
Sample Weight at Target Temperature (mg)	34.04
Moles CO_2 Emitted until target temperature (mmol)	0.09203
$[C_A]$ at Target Temperature (mmol)	0.1297
$[C_A]$ at Target Temperature after 3600s (mmol)	0.1218
Conversion after 1h at target temperature (%)	45.05
Conversion at target temperature (%)	41.51

Ratio = 1 - 950 C - S.G. = 1.9 - Experiment 2

Time	Sample Weight	$NaBO_2$	$[NaBO_2]$	$-dC_A/dt$	$Ln(-dC_A/dt)$	$Ln(C_A)$
Seconds	mg	mmol	mol/L	mol/L.s		
0	34.0421	0.12970	7.273	0.0001000	-9.210	1.984
100	34.01754	0.12914	7.247	0.0000923	-9.291	1.981
200	34.00671	0.12889	7.235	0.0000851	-9.371	1.979
300	33.99553	0.12864	7.224	0.0000785	-9.453	1.977
400	33.98551	0.12841	7.213	0.0000723	-9.535	1.976
500	33.97825	0.12824	7.205	0.0000665	-9.618	1.975
600	33.96989	0.12805	7.196	0.0000611	-9.703	1.974
1200	33.91296	0.12676	7.135	0.0000334	-10.308	1.965
1800	33.85176	0.12537	7.070	0.0000065	-11.937	1.956
2400	33.798	0.12415	7.012	-0.0000298	#NUM!	1.948
3000	33.74614	0.12297	6.956	-0.0000860	#NUM!	1.940
3300	33.72104	0.12240	6.929	-0.0001248	#NUM!	1.936
3600	33.6963	0.12184	6.902	-0.0001724	#NUM!	1.932


950 C - Ratio = 1 - S.G. = 1.9 - Experiment 2


950 C - Ratio = 1 - S.G. = 1.9 - Experiment 2

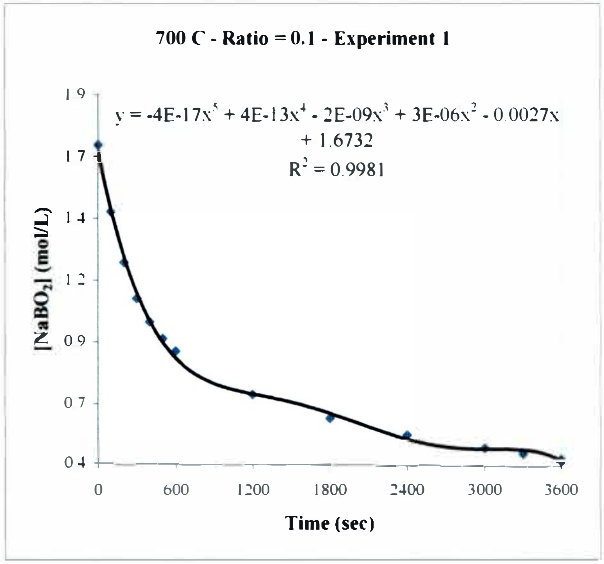
Appendix B

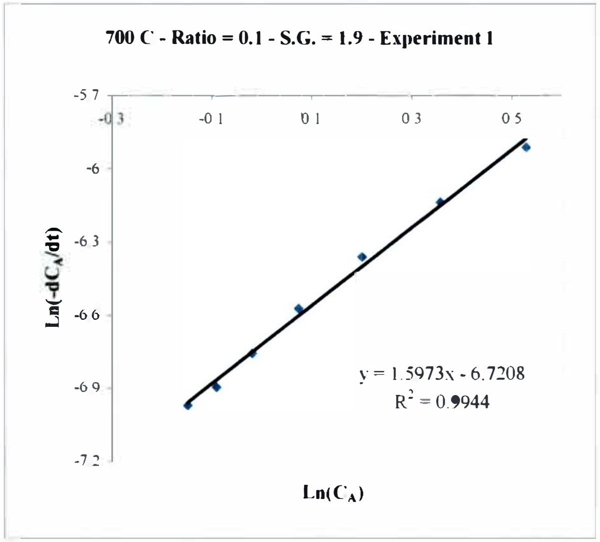
Borate Autocausticizing Reaction Rate Data
Molar Ratio = 0.1 and 0.2 – 700 ^{0}C

Dry Sample Wt (mg) @ 350 C	97.13
$NaBO_2$ Initial Concentration $[C_A]$ (mmol)	0.08460
Sample Weight at Target Temperature (mg)	95.23
Moles CO_2 Emitted until target temperature (mmol)	0.0
$[C_A]$ at Target Temperature (mmol)	0.08460
$[C_A]$ at Target Temperature after 3600s (mmol)	0.02041
Conversion after 1h at target temperature (%)	75.87
Conversion at target temperature (%)	0

Ratio = 0.1 - 700 C - S.G. = 1.9 - Experiment 1

Time	Sample Weight	$NaBO_2$	$[NaBO_2]$	$-dC_A/dt$	$Ln(-dC_A/dt)$	$Ln(C_A)$
Seconds	mg	mmol	mol/L	mol/L.s		
0	95.23	0.08460	1.696	0.00270	-5.915	0.528
100	94.63	0.07077	1.428	0.00216	-6.138	0.356
200	94.17	0.06025	1.221	0.00173	-6.361	0.200
300	93.85	0.05291	1.076	0.00140	-6.572	0.073
400	93.64	0.04813	0.981	0.00116	-6.757	-0.019
500	93.49	0.04474	0.914	0.00101	-6.895	-0.090
600	93.37	0.04217	0.862	0.00094	-6.969	-0.148
1200	92.99	0.03344	0.686	0.00179	-6.326	-0.376
1800	92.78	0.02868	0.590	0.00411	-5.495	-0.528
2400	92.63	0.02531	0.522	0.00738	-4.909	-0.651
3000	92.52	0.02264	0.467	0.01170	-4.448	-0.761
3300	92.46	0.02146	0.443	0.01446	-4.236	-0.814
3600	92.42	0.02041	0.422	0.01780	-4.028	-0.864

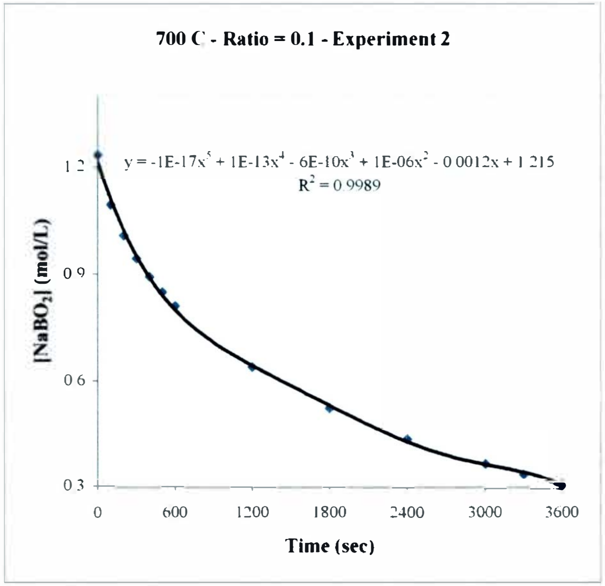


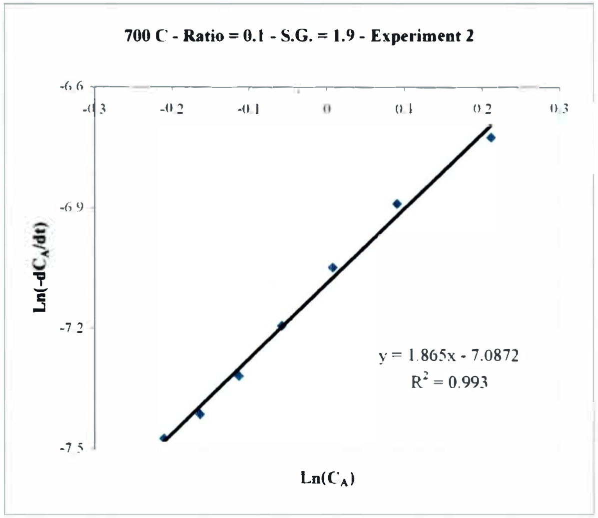


Dry Sample Wt (mg) @ 350 C	42.21
$NaBO_2$ Initial Concentration [C_A] (mmol)	0.03647
Sample Weight at Target Temperature (mg)	40.61
Moles CO_2 Emitted until target temperature (mmol)	0.01023
[C_A] at Target Temperature (mmol)	0.02624
[C_A] at Target Temperature after 3600s (mmol)	0.00645
Conversion after 1h at target temperature (%)	82.33
Conversion at target temperature (%)	28.05

Ratio = 0.1 - 700 C - S.G. = 1.9 - Experiment 2

Time	Sample Weight	$NaBO_2$	[$NaBO_2$]	- dC_A/dt	Ln(-dC_A/dt)	Ln (C_A)
Seconds	mg	mmol	mol/L	mol/L.s		
0	40.61	0.02624	1.234	0.001200	-6.725	0.210
100	40.47	0.02319	1.094	0.001018	-6.890	0.089
200	40.39	0.02130	1.007	0.000869	-7.048	0.007
300	40.33	0.01993	0.943	0.000752	-7.193	-0.058
400	40.28	0.01882	0.892	0.000664	-7.318	-0.114
500	40.24	0.01788	0.848	0.000603	-7.413	-0.164
600	40.20	0.01705	0.810	0.000568	-7.473	-0.211
1200	40.04	0.01339	0.639	0.000804	-7.125	-0.449
1800	39.93	0.01095	0.524	0.001624	-6.423	-0.647
2400	39.85	0.00911	0.436	0.002897	-5.844	-0.829
3000	39.79	0.00766	0.367	0.004650	-5.371	-1.001
3300	39.76	0.00702	0.337	0.005757	-5.157	-1.088
3600	39.74	0.00645	0.310	0.007064	-4.953	-1.172

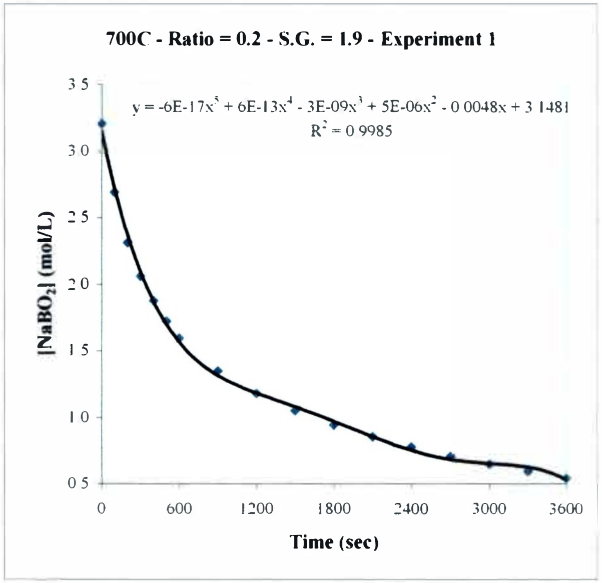

700 C - Ratio = 0.1 - Experiment 2


700 C - Ratio = 0.1 - S.G. = 1.9 - Experiment 2

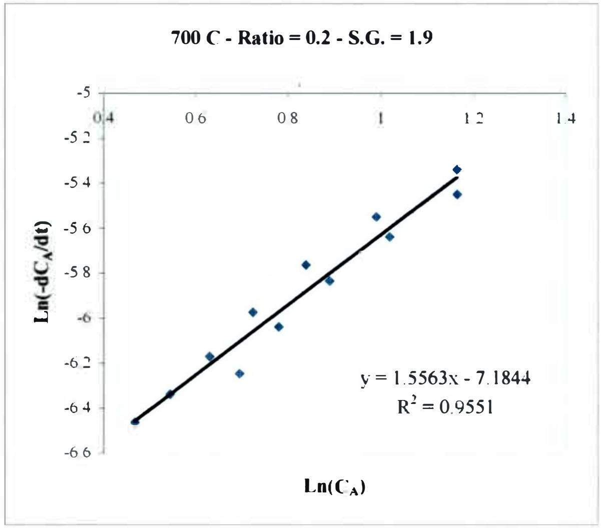
$NaBO_2$ Initial Concentration $[C_A]$ (mmol)	0.09148
Sample Weight at Target Temperature (mg)	54.51
Moles CO_2 Emitted until target temperature (mmol)	0
$[C_A]$ at Target Temperature (mmol)	0.09148
$[C_A]$ at Target Temperature after 3600s (mmol)	0.01453
Conversion after 1h at target temperature (%)	84.12
Conversion at target temperature (%)	0

Ratio = 0.2 - 700 C - S.G. = 1.9 - Experiment 1

Time	**Sample Weight**	**$NaBO_2$**	**$[NaBO_2]$**	**$-dC_A/dt$**	**$Ln(-dC_A/dt)$**	**$Ln(C_A)$**
Seconds	**mg**	**mmol**	**mol/L**	**mol/L.s**		
0	54.51	0.09148	3.204	0.004800	-5.339	1.164
100	53.82	0.07587	2.691	0.003888	-5.550	0.990
200	53.32	0.06462	2.313	0.003141	-5.763	0.839
300	53.00	0.05723	2.061	0.002548	-5.973	0.723
400	52.76	0.05188	1.877	0.002094	-6.169	0.630
500	52.57	0.04743	1.722	0.001769	-6.337	0.544
600	52.41	0.04382	1.596	0.001560	-6.463	0.468
900	52.10	0.03682	1.349	0.001537	-6.478	0.300
1200	51.89	0.03212	1.182	0.002235	-6.104	0.167
1500	51.73	0.02851	1.052	0.003469	-5.664	0.051
1800	51.60	0.02553	0.945	0.005112	-5.276	-0.057
2100	51.50	0.02306	0.855	0.007098	-4.948	-0.157
2400	51.40	0.02094	0.778	0.009416	-4.665	-0.251
2700	51.32	0.01908	0.710	0.012114	-4.413	-0.343
3000	51.25	0.01741	0.648	0.015300	-4.180	-0.433
3300	51.18	0.01590	0.593	0.019139	-3.956	-0.522
3600	51.12	0.01453	0.542	0.023854	-3.736	-0.612



700C - Ratio = 0.2 - S.G. = 1.9 - Experiment 1

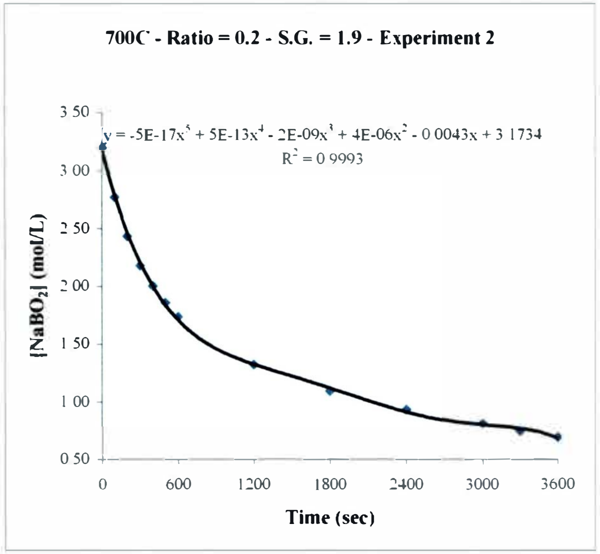


700 C - Ratio = 0.2 - S.G. = 1.9

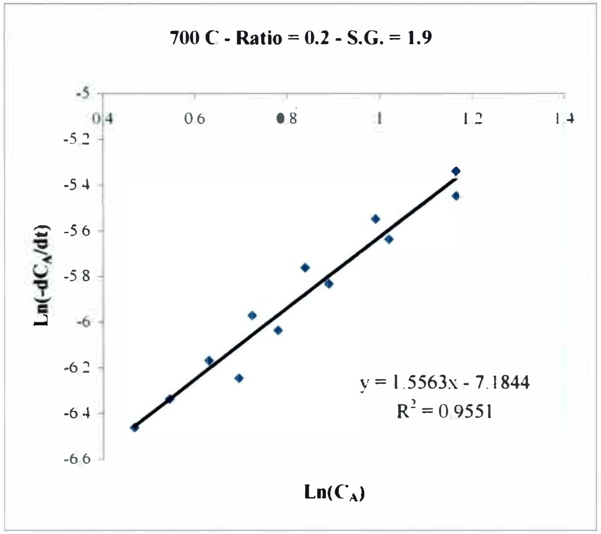
$NaBO_2$ Initial Concentration $[C_A]$ (mmol)	0
Sample Weight at Target Temperature (mg)	65.31
Moles CO_2 Emitted until target temperature (mmol)	
$[C_A]$ at Target Temperature (mmol)	0.1096
$[C_A]$ at Target Temperature after 3600s (mmol)	0.0220
Conversion after 1h at target temperature (%)	79.91
Conversion at target temperature (%)	

Ratio = 0.2 - 700 C - S.G. = 1.9 - Experiment 2

Time	**Sample Weight**	**$NaBO_2$**	**$[NaBO_2]$**	**$-dC_A/dt$**	**$Ln(-dC_A/dt)$**	**$Ln(C_A)$**
Seconds	**mg**	**mmol**	**mol/L**	**mol/L.s**		
0	65.31	0.1096	3.204	0.004300	-5.449	1.164
100	64.62	0.0938	2.770	0.003558	-5.639	1.019
200	64.09	0.0817	2.434	0.002924	-5.835	0.890
300	63.69	0.0728	2.181	0.002388	-6.037	0.780
400	63.42	0.0665	2.002	0.001938	-6.246	0.694
500	63.20	0.0616	1.859	0.001566	-6.459	0.620
600	63.01	0.0574	1.738	0.001260	-6.676	0.553
1200	62.39	0.0433	1.324	0.000402	-7.818	0.281
1800	62.06	0.0356	1.094	0.000300	-8.110	0.090
2400	61.82	0.0302	0.934	0.000306	-8.091	-0.069
3000	61.64	0.0261	0.808	0.000550	-7.506	-0.213
3300	61.54	0.0240	0.743	0.001014	-6.894	-0.297
3600	61.47	0.0223	0.692	0.001938	-6.246	-0.369



700C - Ratio = 0.2 - S.G. = 1.9 - Experiment 2



700 C - Ratio = 0.2 - S.G. = 1.9

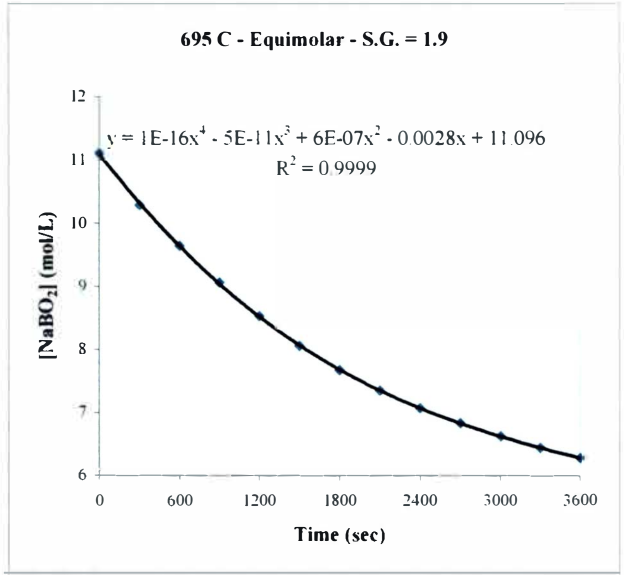
Appendix C

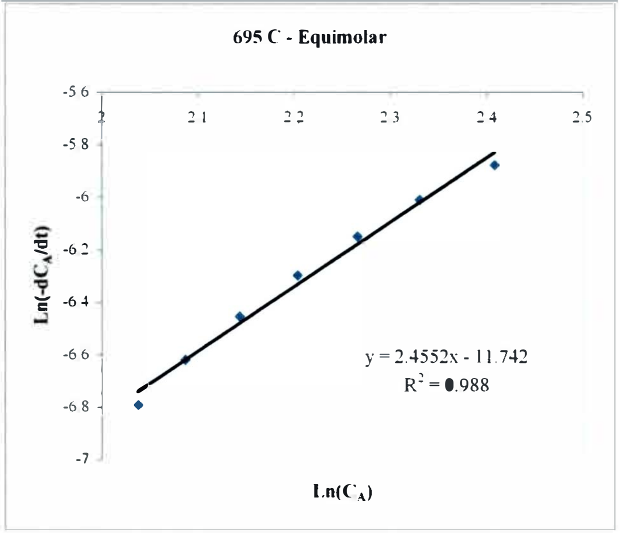
Borate Autocausticizing Reaction Rate Data - Activation Energy Calculation

$NaBO_2$ Initial Concentration $[C_A]$ (mmol)	0.5110
Sample Weight at Target Temperature (mg)	87.79
Moles CO_2 Emitted until target temperature (mmol)	0
$[C_A]$ at Target Temperature (mmol)	0.5110
$[C_A]$ at Target Temperature after 3600s (mmol)	0.2513
Conversion after 1h at target temperature (%)	50.81
Conversion at target temperature (%)	0.000

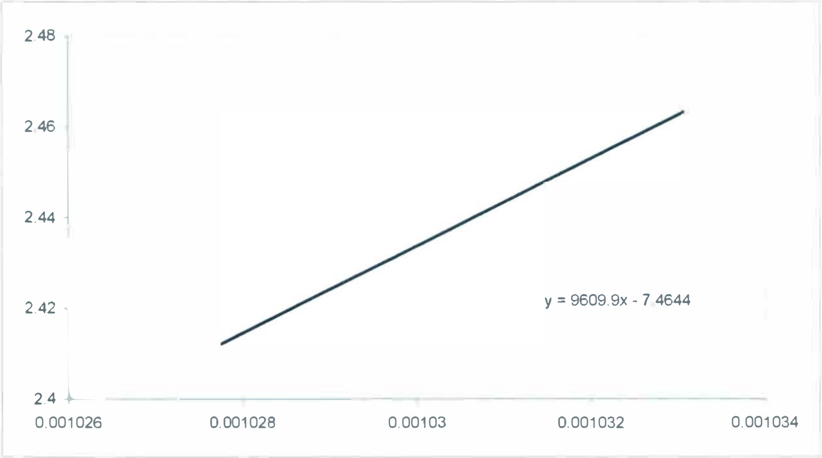
Ratio = 1 - 695 C - S.G. = 1.9

Time	Sample Weight	$NaBO_2$	$[NaBO_2]$	$-dC_A/dt$	$Ln(-dC_A/dt)$	$Ln(C_A)$
Seconds	mg	mmol	mol/L	mol/L.s		
0	87.79	0.5110	11.11	0.002800	-5.878	2.408
300	85.59	0.4610	10.28	0.002453	-6.010	2.330
600	83.96	0.4239	9.64	0.002134	-6.150	2.266
900	82.54	0.3917	9.06	0.001841	-6.297	2.204
1200	81.28	0.3630	8.53	0.001575	-6.453	2.143
1500	80.20	0.3385	8.06	0.001336	-6.618	2.087
1800	79.33	0.3188	7.67	0.001124	-6.791	2.037
2100	78.62	0.3026	7.35	0.000938	-6.972	1.994
2400	78.02	0.2891	7.07	0.000778	-7.158	1.956
2700	77.52	0.2775	6.83	0.000646	-7.345	1.922
3000	77.08	0.2676	6.63	0.000539	-7.525	1.891
3300	76.70	0.2589	6.44	0.000459	-7.686	1.863
3600	76.36	0.2513	6.28	0.000405	-7.811	1.838





k	T	1/T	ln(k)	ko	E/R	E
(L/mol.s)	^{0}C	1/K		L/mol.s		kcal/mol
11.158	700	0.001027749	2.412157	1737.148	9609.9	19.0949
11.742	695	0.001033058	2.463172			



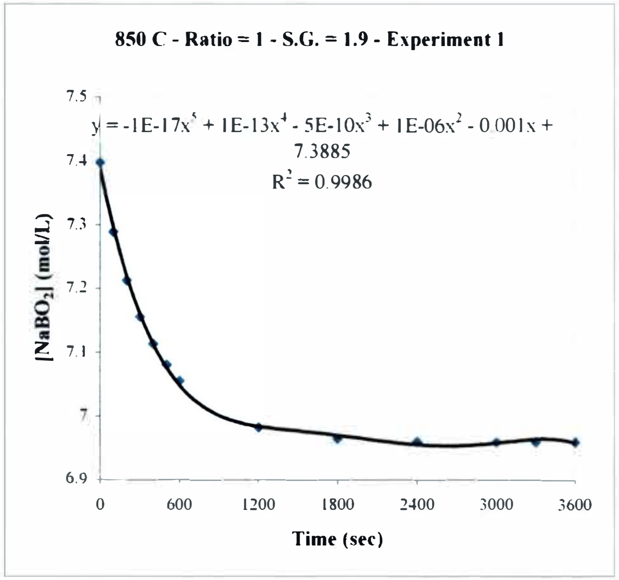
Appendix D

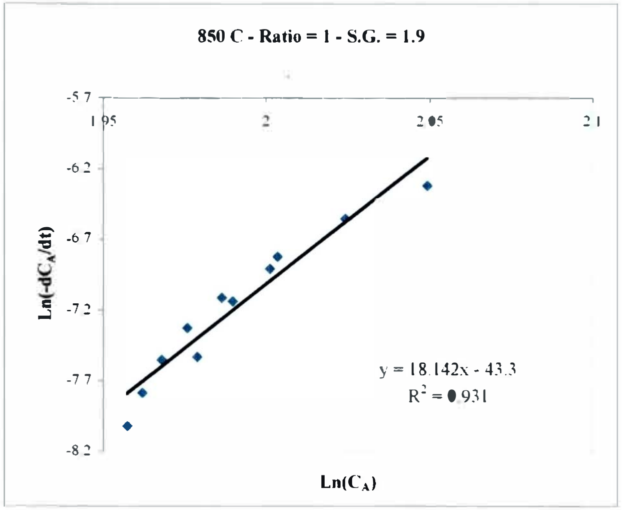
Borate Autocausticizing Reaction Rate Data
Molar Ratio = 1.0 – 850 ^{0}C

$NaBO_2$ Initial Concentration $[C_A]$ (mmol)	0.2834
Sample Weight at Target Temperature (mg)	43.67
Moles CO_2 Emitted until target temperature (mmol)	0.1142
$[C_A]$ at Target Temperature (mmol)	0.1692
$[C_A]$ at Target Temperature after 3600s (mmol)	0.1573
Conversion after 1h at target temperature (%)	44.51
Conversion at target temperature (%)	40.30

Ratio = 1 - 850 C - S.G. = 1.9 - Experiment 1

Time	Sample Weight	$NaBO_2$	$[NaBO_2]$	$-dC_A/dt$	$Ln(-dC_A/dt)$	$Ln(C_A)$
Seconds	mg	mmol	mol/L	mol/L.s		
0	43.67	0.1692	7.397	0.001000	-6.908	2.001
100	43.54	0.1662	7.289	0.000815	-7.113	1.986
200	43.45	0.1642	7.213	0.000657	-7.328	1.976
300	43.38	0.1626	7.156	0.000525	-7.553	1.968
400	43.33	0.1614	7.113	0.000416	-7.786	1.962
500	43.29	0.1606	7.080	0.000328	-8.022	1.957
600	43.26	0.1599	7.055	0.000260	-8.255	1.954
1200	43.17	0.1579	6.983	0.000172	-8.665	1.943
1800	43.15	0.1574	6.964	0.000452	-7.702	1.941
2400	43.15	0.1573	6.960	0.000969	-6.939	1.940
3000	43.14	0.1573	6.959	0.001750	-6.348	1.940
3300	43.14	0.1573	6.959	0.002290	-6.079	1.940
3600	43.14	0.1573	6.959	0.002976	-5.817	1.940

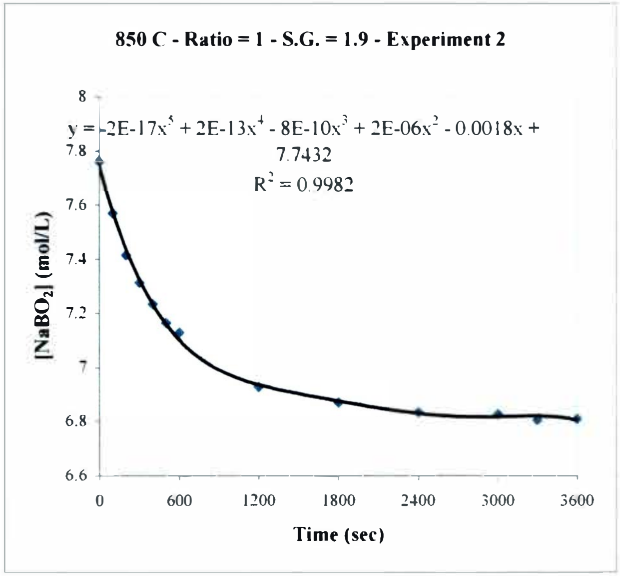


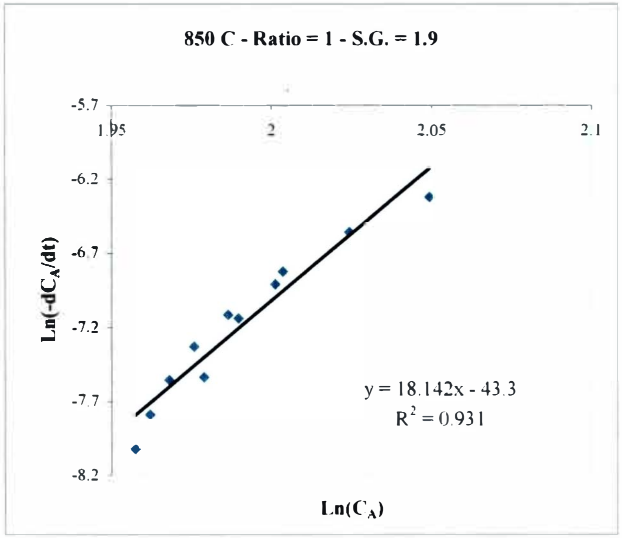


$NaBO_2$ Initial Concentration $[C_A]$ (mmol)	0.2317
Sample Weight at Target Temperature (mg)	36.06
Moles CO_2 Emitted until target temperature (mmol)	0.08508
$[C_A]$ at Target Temperature (mmol)	0.14658
$[C_A]$ at Target Temperature after 3600s (mmol)	0.12528
Conversion after 1h at target temperature (%)	45.92
Conversion at target temperature (%)	36.73

Ratio = 1 - 850 C - S.G. = 1.9 - Experiment 2

Time	Sample Weight	$NaBO_2$	$[NaBO_2]$	$-dC_A/dt$	$Ln(-dC_A/dt)$	$Ln(C_A)$
Seconds	mg	mmol	mol/L	mol/L.s		
0	36.06	0.1466	7.761	0.001800	-6.320	2.049
100	35.86	0.1422	7.569	0.001423	-6.555	2.024
200	35.71	0.1387	7.415	0.001090	-6.822	2.004
300	35.61	0.1364	7.313	0.000795	-7.137	1.990
400	35.53	0.1347	7.235	0.000535	-7.533	1.979
500	35.46	0.1331	7.165	0.000306	-8.091	1.969
600	35.43	0.1323	7.130	0.000104	-9.170	1.964
1200	35.23	0.1279	6.929	-0.000719	#NUM!	1.936
1800	35.18	0.1266	6.871	-0.001240	#NUM!	1.927
2400	35.14	0.1258	6.835	-0.001717	#NUM!	1.922
3000	35.13	0.1257	6.827	-0.002100	#NUM!	1.921
3300	35.11	0.1252	6.806	-0.002154	#NUM!	1.918
3600	35.12	0.1253	6.810	-0.002025	#NUM!	1.918





Appendix E

Borate Autocausticizing Reaction Rate Data
Molar Ratio = 0.1 and 0.2 – 850 ^{0}C

Ratio = 0.1 - 850 C - S.G. = 1.9 - Experiment 1	
$NaBO_2$ Initial Concentration [C_A] (mmol)	0.03892
Sample Weight at Target Temperature (mg)	41.79
Moles CO_2 Emitted until target temperature (mmol)	0.04621
[C_A] at Target Temperature (mmol)	-0.00729
[C_A] at Target Temperature after 3600s (mmol)	-0.02954
Conversion after 1h at target temperature (%)	175.9
Conversion at target temperature (%)	118.7

Ratio = 0.1 - 850 C - S.G. = 1.9 - Experiment 2	
$NaBO_2$ Initial Concentration [C_A] (mmol)	0.05703
Sample Weight at Target Temperature (mg)	61.62
Moles CO_2 Emitted until target temperature (mmol)	0.05870
[C_A] at Target Temperature (mmol)	-0.00167
[C_A] at Target Temperature after 3600s (mmol)	-0.03077
Conversion after 1h at target temperature (%)	154.0
Conversion at target temperature (%)	102.9

Ratio = 0.2 - 850 C - S.G. = 1.9 - Experiment 1	
$NaBO_2$ Initial Concentration [C_A] (mmol)	0.07969
Sample Weight at Target Temperature (mg)	44.21
Moles CO_2 Emitted until target temperature (mmol)	0.07439
[C_A] at Target Temperature (mmol)	0.00530
[C_A] at Target Temperature after 3600s (mmol)	-0.02731
Conversion after 1h at target temperature (%)	615.1
Conversion at target temperature (%)	93.35

Ratio = 0.2 - 850 C - S.G. = 1.9 - Experiment 1	
$NaBO_2$ Initial Concentration [C_A] (mmol)	0.1099
Sample Weight at Target Temperature (mg)	61.06
Moles CO_2 Emitted until target temperature (mmol)	0.1007
[C_A] at Target Temperature (mmol)	0.0092
[C_A] at Target Temperature after 3600s (mmol)	-0.0348
Conversion after 1h at target temperature (%)	476.7
Conversion at target temperature (%)	91.60

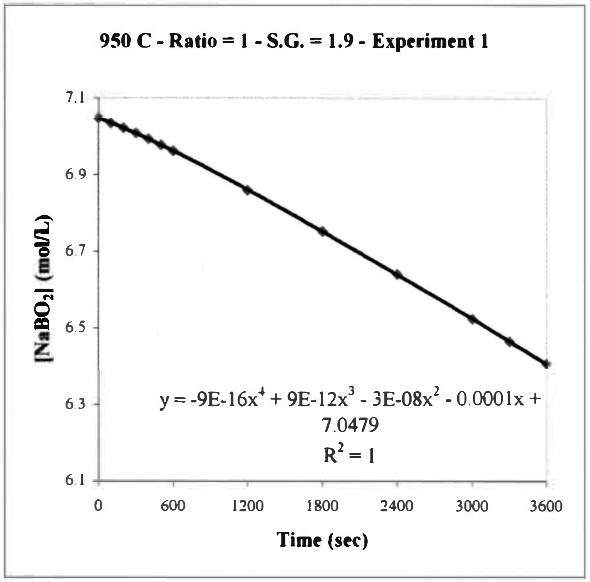
Appendix F

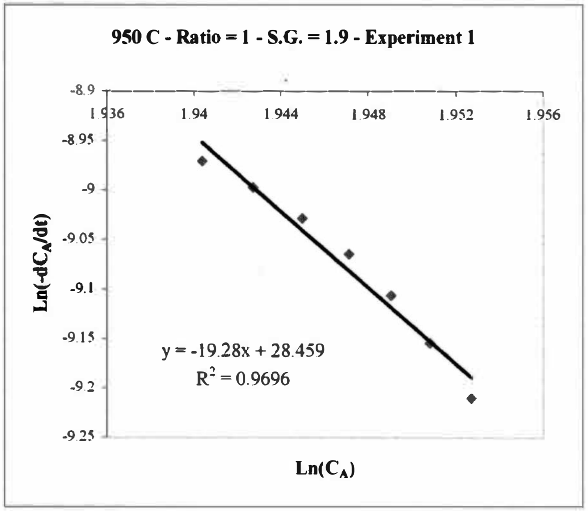
Borate Autocausticizing Reaction Rate Data
Molar Ratio = 1.0 – 950 ^{0}C

$NaBO_2$ Initial Concentration [C_A] (mmol)	0.2201
Sample Weight at Target Temperature (mg)	33.58
Moles CO_2 Emitted until target temperature (mmol)	0.0961
[C_A] at Target Temperature (mmol)	0.1240
[C_A] at Target Temperature after 3600s (mmol)	0.1108
Conversion after 1h at target temperature (%)	49.68
Conversion at target temperature (%)	43.67

Ratio = 1 - 950 C - S.G. = 1.9 - Experiment 1

Time	**Sample Weight**	**$NaBO_2$**	**[$NaBO_2$]**	**- dC_A/dt**	**Ln(-dC_A/dt)**	**Ln (C_A)**
Seconds	**mg**	**mmol**	**mol/L**	**mol/L.s**		
0	33.58137	0.1240	7.048	0.0001000	-9.210	1.953
100	33.56903	0.1237	7.034	0.0001057	-9.155	1.951
200	33.5576	0.1234	7.022	0.0001109	-9.106	1.949
300	33.54508	0.1231	7.008	0.0001157	-9.065	1.947
400	33.53139	0.1228	6.993	0.0001199	-9.029	1.945
500	33.51693	0.1225	6.978	0.0001237	-8.998	1.943
600	33.502	0.1222	6.961	0.0001271	-8.971	1.940
1200	33.40839	0.1200	6.859	0.0001393	-8.879	1.926
1800	33.3109	0.1178	6.752	0.0001415	-8.863	1.910
2400	33.20935	0.1155	6.640	0.0001382	-8.886	1.893
3000	33.1049	0.1131	6.525	0.0001342	-8.916	1.876
3300	33.0522	0.1119	6.466	0.0001333	-8.923	1.867
3600	32.99977	0.1108	6.407	0.0001340	-8.917	1.857

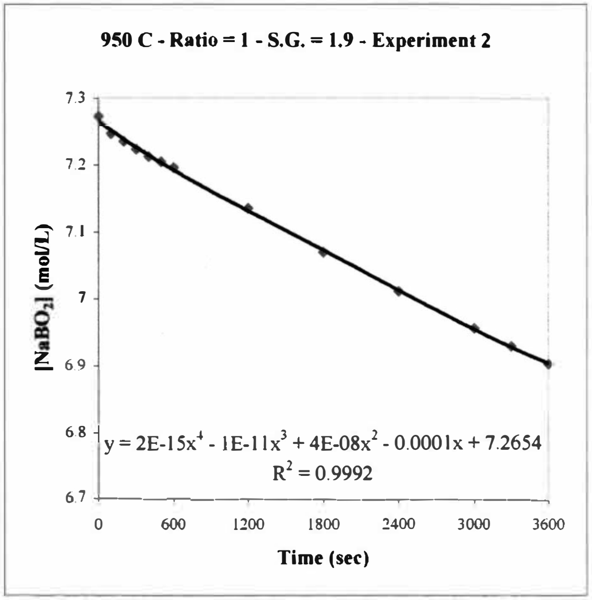

950 C - Ratio = 1 - S.G. = 1.9 - Experiment 1

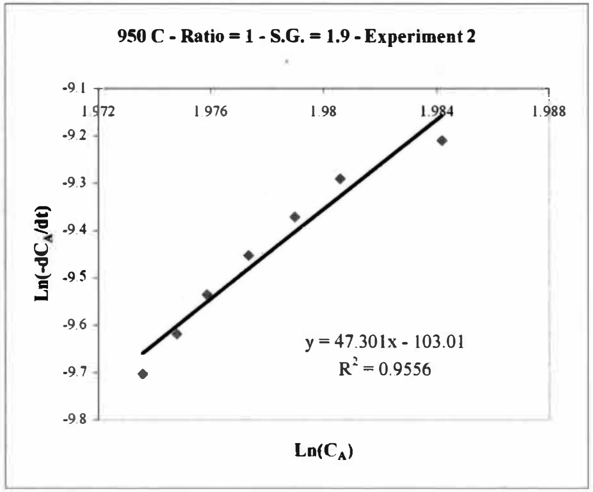

950 C - Ratio = 1 - S.G. = 1.9 - Experiment 1

$NaBO_2$ Initial Concentration $[C_A]$ (mmol)	0.2217
Sample Weight at Target Temperature (mg)	34.04
Moles CO_2 Emitted until target temperature (mmol)	0.09203
$[C_A]$ at Target Temperature (mmol)	0.1297
$[C_A]$ at Target Temperature after 3600s (mmol)	0.1218
Conversion after 1h at target temperature (%)	45.05
Conversion at target temperature (%)	41.51

Ratio = 1 - 950 C - S.G. = 1.9 - Experiment 2

Time	Sample Weight	$NaBO_2$	$[NaBO_2]$	$- dC_A/dt$	$Ln(-dC_A/dt)$	$Ln (C_A)$
Seconds	mg	mmol	mol/L	mol/L.s		
0	34.0421	0.12970	7.273	0.0001000	-9.210	1.984
100	34.01754	0.12914	7.247	0.0000923	-9.291	1.981
200	34.00671	0.12889	7.235	0.0000851	-9.371	1.979
300	33.99553	0.12864	7.224	0.0000785	-9.453	1.977
400	33.98551	0.12841	7.213	0.0000723	-9.535	1.976
500	33.97825	0.12824	7.205	0.0000665	-9.618	1.975
600	33.96989	0.12805	7.196	0.0000611	-9.703	1.974
1200	33.91296	0.12676	7.135	0.0000334	-10.308	1.965
1800	33.85176	0.12537	7.070	0.0000065	-11.937	1.956
2400	33.798	0.12415	7.012	-0.0000298	#NUM!	1.948
3000	33.74614	0.12297	6.956	-0.0000860	#NUM!	1.940
3300	33.72104	0.12240	6.929	-0.0001248	#NUM!	1.936
3600	33.6963	0.12184	6.902	-0.0001724	#NUM!	1.932





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