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Mini-project report

A Novel Commercial Heat Source Based on the Chemical Dehydration of Carbohydrates

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Abstract

In support of the University's aim to further develop thermochemical hydrogen production processes, the dehydration of carbohydrates using sulphuric acid was investigated. The heat of reaction of sucrose and starch with various concentrations of acid was measured, and the end-products monitored. It was discovered that the quantity of Heat per gram of starch exceeded that of sucrose, although the reaction with sucrose yielded a better quality carbon final product. Based on the data gathered so far, it would be difficult to say if the heat of the reaction would be sufficient to drive energy generation processes. Further work would be recommended to determine the heat of reaction at the elevated temperatures and pressures indicated in the industrial process proposal.

1. Introduction

Due to the decline in proven reserves of fossil fuels [1-2] and increasing levels of greenhouse gases,[3-4] novel ways to generate energy are currently being considered and explored. One such idea is the dehydration of sucrose by sulphuric acid, patented by Statix Industries,[5] to be used as a novel commercial heat source. It has been proposed that the heat evolved from the process could generate electricity via a conventional steam turbine; the University is also interested in utilising this heat for thermochemical hydrogen production processes. A valuable by-product of the dehydration reaction is carbon nano-particles, which can be sold on the open market as a soil improver, coke replacement material, and colorant for use in plastics, toners and tyres. Indeed, the sequestering of atmospheric carbon dioxide in sugar beet crops, and its subsequent conversion to a marketable product, is one of the main selling-points of Statix Industries' process. Although the reaction is well-known, experimental data for the dehydration of sucrose by sulphuric acid is limited and more research is required to answer some of the fundamental questions of the process.

The idea behind the Statix Process [5] is that it can take advantage of two established chemical processes – photosynthesis and dehydration. Sugar beet is grown, preferably on unutilised or marginal land, and the crop processed to produce a refined sugar solution (approximately 66% by weight). The advantages to using a sugar solution in preference to crystallised sugar are twofold: the dehydration process and reactor respond more favourably [6] to use of a sugar solution; and elevated CO₂ emissions are avoided, as further refining to crystallised sugar is unnecessary. The sugar solution is injected into the Statix reactor with concentrated sulphuric acid at 450 °C and 5 bar. The excess heat is absorbed into a salt jacket surrounding the reaction vessel and the molten salt can be used, for example, to produce steam to generate electricity. The products of the dehydration reaction are water and elemental carbon and, ideally, the hot sulphuric acid should be distilled from the carbon slurry for re-use. Although there are issues arising from the production of sulphuric acid, much of this reagent has already been recovered [6] and recycled from the steel-making process. As industry leaders now endeavour to make decisions that are more environmentally appropriate,[7] recycling the acid removes the need for neutralisation and disposal, which in turn reduces water consumption and generates a valuable product. It can be argued, therefore, that responsibility for CO₂ emissions from sulphuric acid production lies with the steel-making industry as part of their manufacturing process.

Due to the project being at its very early stages of development, the questions behind this proposal are many. Perhaps the most fundamental question is whether the heat from the dehydration of sucrose is sufficient to meet the needs of downstream energy generation processes. In an initial attempt to address this question, experiments were run to measure the heat evolved during the reaction, using different concentrations of sulphuric acid and different forms of carbohydrates. The ultimate aim of this mini-project was to develop a robust experimental method and gain an understanding of the reaction and the thermodynamics of the system. The experimental results could then be used at a later date in computer simulations of the process as a whole.

2. Experimental

The basic apparatus consisted of a Dewar flask containing water (500 mL) and a magnetic flea; a stoppered round-bottomed flask was held in place inside the Dewar flask by a tight-fitting polystyrene lid. A digital datalogger thermometer was also suspended in the Dewar flask. A carbohydrate (sucrose or starch) was reacted with sulphuric acid in the round-bottomed flask by adding one reactant to the other after a 30-minute period of equilibration; the reactants were briefly stirred before replacing the stopper. The temperature of the water in the Dewar flask was monitored prior to adding the second reactant; the water temperature was recorded at 5-minute intervals until the reaction was complete and the temperature had settled. A table of experiments and observations can be seen in Results and Discussion, below.

A disadvantage of the apparatus used was that it was not possible to stir both the water and the reaction simultaneously, as the magnetic fleas were attracted on either side of the reaction vessel. In order to stir both components of the reaction, it would be necessary to obtain a mechanical stirrer for the reaction vessel while using a magnetic flea to stir the water. It would be advisable to address this problem before the reaction of starch and sulphuric acid was further explored.

3. Results and Discussion

Table 1. List of Heat of Reaction experiments.

Exp't Number	1 st Reactant, Quantity	2 nd Reactant, Quantity	Comments and Observations
1	Sucrose, 10.0832 g	Conc. H ₂ SO ₄ , 40 mL	Product was black slurry.
2	Conc. H ₂ SO ₄ , 40 mL	Sucrose, 10.0450 g	Product was black slurry with some black solid.
3	Sucrose, 66 wt % aq. Solution (from 10.0272 g solid)	Conc. H ₂ SO ₄ , 15 mL	Reactant quantities in line with Statix Industries' proposal of 1 kg/h of 66 wt % of sucrose solution and 1 L/h of acid. Product was solid carbon cake.
4	H ₂ O, 5 mL	Conc. H ₂ SO ₄ , 15 mL	Blank – to obtain heat of hydration for Exp't 3.
5	Starch, 66 wt % aq. Solution (from 9.9949 g solid)	Conc. H ₂ SO ₄ , 15 mL	Starting starch solution was not a mobile slurry; impossible to stir on addition of acid. Product was black slurry with white, unreacted starch at centre.
6	Starch, 50 wt % aq. Solution (from 10.0170 g solid)	Conc. H ₂ SO ₄ , 20 mL	Starch solution was difficult to stir on addition of acid. Product was black slurry with white, unreacted starch at centre.
7	Starch, 33 wt % aq. Solution (from 5.2744 g solid)	Conc. H ₂ SO ₄ , 15 mL	Product was black slurry with some black solid; no unreacted starch remaining.
8	H ₂ O, 10 mL	Conc. H ₂ SO ₄ , 15 mL	Blank – to obtain heat of hydration for Exp't 7.
9	Sucrose, 66 wt % aq. Solution (from 10.0090 g solid)	95 vol % H ₂ SO ₄ , 15 mL	Product was solid carbon cake with some black slurry remaining.
10	Sucrose, 66 wt % aq. Solution (from 10.0942 g solid)	90 vol % H ₂ SO ₄ , 15 mL	Product was black slurry with some black solid.
11	Sucrose, 66 wt % aq. Solution (from 10.0086 g solid)	85 vol % H ₂ SO ₄ , 15 mL	Product was black slurry with no carbon solid.

The increase in temperature of 500 mL of water was used to calculate the quantity of Heat obtained from the reaction of 1 g of carbohydrate with sulphuric acid. The temperature increase was taken as the temperature at the end of reaction, minus the value following equilibration and prior to addition of the acid. The end of

reaction was deemed to be 1 h 15 min for the samples in solution and 2 h 30 min for the solid samples, as the solid samples took longer to react. To determine the Heat (J) of each carbohydrate, ΔT was calculated as the temperature increase less the value measured in the blank experiment (if applicable); the Specific Heat Capacity of water at 25 °C ($c_p = 4.1801 \text{ J/g K}$) was used.[8-9] The total Heat released for each experiment (i.e. carbohydrate plus water) was also calculated; equations used for both sucrose and starch can be seen in Appendix 6.1.

3.1 Sucrose

Table 2. Results from Heat of Reaction experiments for Sucrose.

Exp't No.	Sample Wt (g)	Sample Type	H ₂ O in Sample (mL)	H ₂ SO ₄ Conc'n	Temp Increase (°C)	Mean Temp (°C)	Total Heat (J)	Heat from Sucrose (Jg ⁻¹)
1	10.0832	Solid	0	Conc.	2.1	23.6	4389.1	435.3
2	10.0450	Solid	0	Conc.	2.7	23.2	5643.1	561.8
3	10.0272	66 wt% aq.	5	Conc.	5.9	26.1	12331.3	708.7
4	Blank	N/A	5	Conc.	2.5	22.9	5225.1	N/A
9	10.0090	66 wt% aq.	5	95 vol%	4.2	24.2	8778.2	355.0
10	10.0942	66 wt% aq.	5	90 vol%	1.8	23.1	3762.1	N/D
11	10.0086	66 wt% aq.	5	85 vol%	1.5	22.5	3135.1	N/D

With reference to the above table, and to the graph in Appendix 6.2, it can be seen that the most significant temperature increase comes from the reaction of 66 wt % aqueous sucrose solution with concentrated H₂SO₄. In order to determine how much of this came from the water, a blank experiment was run with water and conc. H₂SO₄, omitting the sucrose sample. Due to time constraints, the blank experiments were not run with lower concentrations of acid; it was, therefore, not possible to determine the quantity of Heat arising from Experiments 10 and 11 as the temperature increase was lower than the value obtained for the blank experiment. Consequently, the quantity of Heat quoted for Experiment 9 is an approximation. The reaction of the solutions progressed more quickly than the solids, inferring that the carbohydrate had greater availability for the dehydration reaction to take place. The end of the reaction was, therefore, much easier to determine, due to the sharper curve of the plotted data.

It was also observed that the final product varied depending on the starting materials: solid sucrose and concentrated acid yielded a fine, black slurry; 66 wt % aqueous sucrose solution with concentrated acid yielded a solid carbon cake. Reacting 66 wt % aqueous sucrose solution with less concentrated acids produced a mixture of solids and slurry. (See experimental observations in Section 2, above.) This, in combination with the temperature data, suggests that more water is lost as steam as the concentration of the acid increases, leading to a drier product. In practise, the starting materials can be tailored to give the desired form of carbon final product. This information may prove useful when planning the reaction on a large scale, when efficient removal of the product from the reaction vessel should be considered.

3.2 Starch

Table 3. Results from Heat of Reaction experiments for Starch. For graph, see Appendix 6.3.

Exp't No.	Sample Wt (g)	Sample Type	H ₂ O in Sample (mL)	H ₂ SO ₄ Conc'n	Temp Increase (°C)	Mean Temp (°C)	Total Heat (J)	Heat from Starch (Jg ⁻¹)
5	9.9949	66 wt% aq.	5	Conc.	3.3	21.9	6897.2	167.3
6	10.0170	50 wt% aq.	10	Conc.	4.9	25.0	10241.2	313.0
7	5.2744	33 wt% aq.	10	Conc.	5.4	24.2	11286.3	792.5
8	Blank	N/A	10	Conc.	3.4	23.0	7106.2	N/A

Once a robust method had been developed for sucrose (using a 66 wt % aq. solution), it was decided that the method should be tried with an alternative carbohydrate; however, the same method did not prove to be robust when using starch. Due to its different properties, 5 mL of water was not enough to mobilise the starch into a slurry, which resulted in the reaction not going to completion. While a 50 wt % starch solution was more mobile, there was not enough water present to maintain availability of the starch for the acid to fully react with the carbohydrate. The dehydration reaction did go to completion when using a 33 wt % starch solution, yielding a final product of fine black slurry with very little carbon solid. Despite the problems encountered with the experimental method for starch, the results show potential for further investigation. When compared to sucrose (see Appendix 6.4), the 33 wt % starch solution did not show as great a temperature increase as the 66 wt % sucrose solution; however, when this temperature increase is converted into a Heat per gram value, the potential energy from starch is greater than from sucrose. This indicates that the starch method is worthy of further investigation and may be optimised by stirring, such that a stronger starch solution may be used.

3.3 Sulphuric Acid

The percent sulphuric acid concentration values quoted in the experimental refer to volume/volume dilutions of a laboratory stock solution with water. The precise mole percent value of the stock solution and, therefore, dilutions was not known. The four solutions were titrated against 0.1 M NaOH to determine the molarity (for calculation, see Appendix 6.1). The mole percent concentrations can be seen in the table below.

Table 4. Concentration of Sulphuric Acid Solutions.

Solution	Sample Weight (g)	Titre (mL)	Concentration (M)	Concentration (mol %)	Concentration (wt %)
Conc. H ₂ SO ₄	0.0322	6.288	17.9	88.2	97.6
95 vol %	0.0332	6.098	16.8	74.7	94.2
90 vol %	0.0234	4.130	16.2	68.6	92.2
85 vol %	0.0299	4.855	14.9	56.9	87.8

The partial vapour pressures of aqueous sulphuric acid at 20 °C were plotted in Excel using data taken from Perry's Chemical Engineers' Handbook [10] (see Appendix 6.5 for graph). The graph shows that above the theoretical concentration of concentrated sulphuric acid (18.4 M)[11] the acid decomposes to SO₃, which is characterised by an increase in vapour pressure at high concentrations of H₂SO₄. This means that the maximum concentration of acid that could be used at 20 °C is approximately 18.4 M (95.3 mol %). The concentrated sulphuric acid used in the experiments was determined to be 17.9 M, rather than 18.4 M, so there would be an opportunity to conduct the experiments with a slightly more concentrated acid.

4. Conclusions and Future Work

At this very early stage in the project, it is difficult to reach a firm conclusion regarding the value of the experimental data shown in Section 3. That said, the experiments did produce meaningful results and demonstrated that the dehydration reaction generates a measurable amount of heat as well as a carbon end-product. The results show that, while starch contains a greater amount of heat per gram, the final product is inferior to that produced from sucrose. This is an issue that will need to be considered when scaling up the reaction for industry – which is most important, the evolution of heat or the quality of the carbon end-product? Of course, upon further research, it may be possible to optimise the experimental method for starch. The main problem with starch was its tendency to coagulate into a gelatinous solid, making full availability of starch molecules to the acid unlikely. This problem could be addressed by stirring; the apparatus used in these experiments made stirring impossible, and a rig set up with a mechanical stirrer that could overcome the sticky nature of the starch could prove more successful.

Further work for this project should include some experimentation at the temperature and pressure proposed by Statix Industries. However, to attain a temperature of 450 °C and 5 bar pressure while measuring the heat

of the dehydration reaction is not trivial. A modified bomb calorimeter could be utilised, but there are numerous problems to be overcome:

- The sample cannot be ignited; a discrete compartment would be required to hold the acid separately from the carbohydrate until the bomb was pressurised and ready for measurement;
- Tipping the bomb in order to pour the acid into the carbohydrate may invalidate the data-handling software settings;
- Standard bomb calorimeters are not normally designed to reach temperatures of 450 °C; could the calorimeter be combined with a furnace to reach the required temperature and pressure?
- Standard laboratory heating equipment will reach 450 °C but without the facility to pressurise to 5 bar.

Given that these hurdles could be overcome, much more information regarding the industrial reaction process would be obtained. This should include data on the rate and the heat of the reaction at elevated temperatures, and the physical form of the carbon end-product. Further research should also yield data regarding the reactions undergone by sulphuric acid, with particular emphasis on the opportunity for reusing the acid, or the feasibility of employing a continuous process. With reference to the original aim of the project – to determine whether the heat from the dehydration of sucrose was sufficient to meet the needs of downstream energy generation processes – it is not yet possible to judge. From the experiments completed at room temperature, it is clear that a notable amount of energy is available, but how this would translate to a high temperature and pressure reaction is, as yet, unknown.

Computational simulations using the data may provide projections of how the reaction would proceed in an industrial capacity, and decisions can then be made as to the worth of further laboratory research. In addition, a full lifecycle analysis of the process would provide valuable data on carbon sequestration, emissions and offsetting, as well as its financial viability. Although this process cannot be viewed as an independent heat source, it is a good example of the modern cradle-to-cradle concept, which aims to generate energy from other industries' waste products. This innovative way of thinking, especially when coupled with the promising results obtained from this initial investigation, certainly makes a good case for further research into this novel source of heat.

5. References

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6. Appendices

6.1 *Calculations*

Heat (Jg^{-1}):

$$c_p = \frac{q}{m \times \Delta T}$$

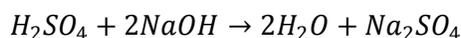
$$q = 4.1801 \frac{J}{gK} \times 500g \times (Temp\ Increase - Blank^*)$$

$$q \div sample\ weight\ (g) = Heat\ (J)\ per\ gram$$

*Blank value not subtracted when calculating Total Heat.

Concentration of sulphuric acid from titration data:

$$Moles\ of\ NaOH = titre\ mL \times \frac{1\ L}{1000\ mL} \times \frac{0.1\ mol\ NaOH}{L}$$



Therefore: 1 mol $H_2SO_4 \approx 2$ mol NaOH

$$Moles\ of\ H_2SO_4 = moles\ of\ NaOH \times \frac{1\ mol\ H_2SO_4}{2\ mol\ NaOH}$$

$$Sample\ vol\ L = \frac{sample\ wt\ g}{density\ gL^{-1}}$$

Density of H_2SO_4 at 25 °C = 1833.1 $g\ L^{-1}$

$$Molarity\ H_2SO_4 = \frac{mol\ H_2SO_4}{sample\ vol\ L}$$

$$Mass\ (g)H_2SO_4\ in\ 1\ L = Molarity \times MW$$

$$Vol\ (L)H_2SO_4\ in\ 1\ L = \frac{Mass\ (g)H_2SO_4\ in\ 1\ L}{Density\ g\ L^{-1}}$$

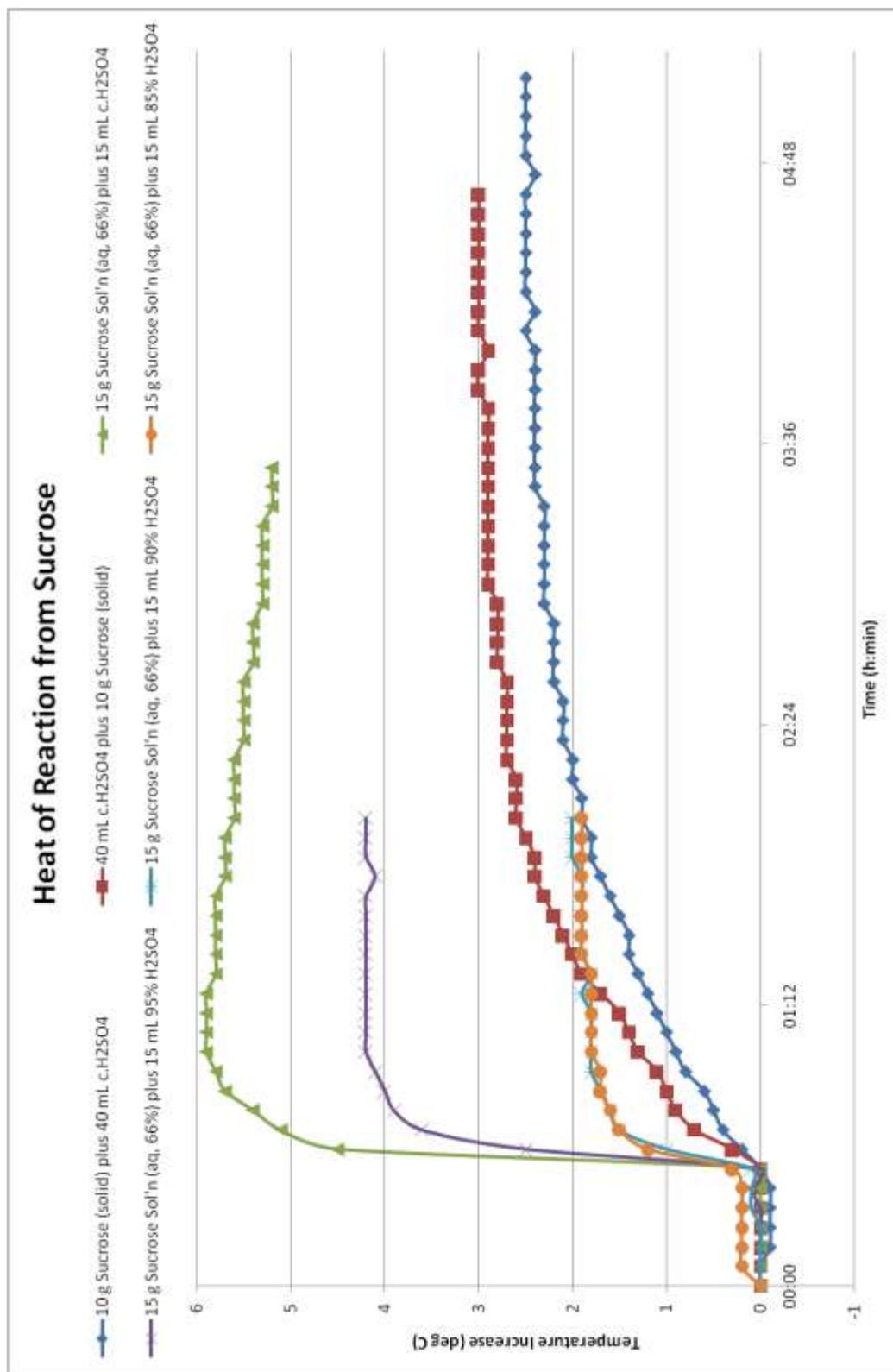
$$Vol\ H_2O = 1\ L - Vol\ (L)H_2SO_4\ in\ 1\ L \equiv Mass\ H_2O\ (g)\ in\ 1\ L$$

$$Molarity\ H_2O = \frac{mass\ H_2O\ g}{MW}$$

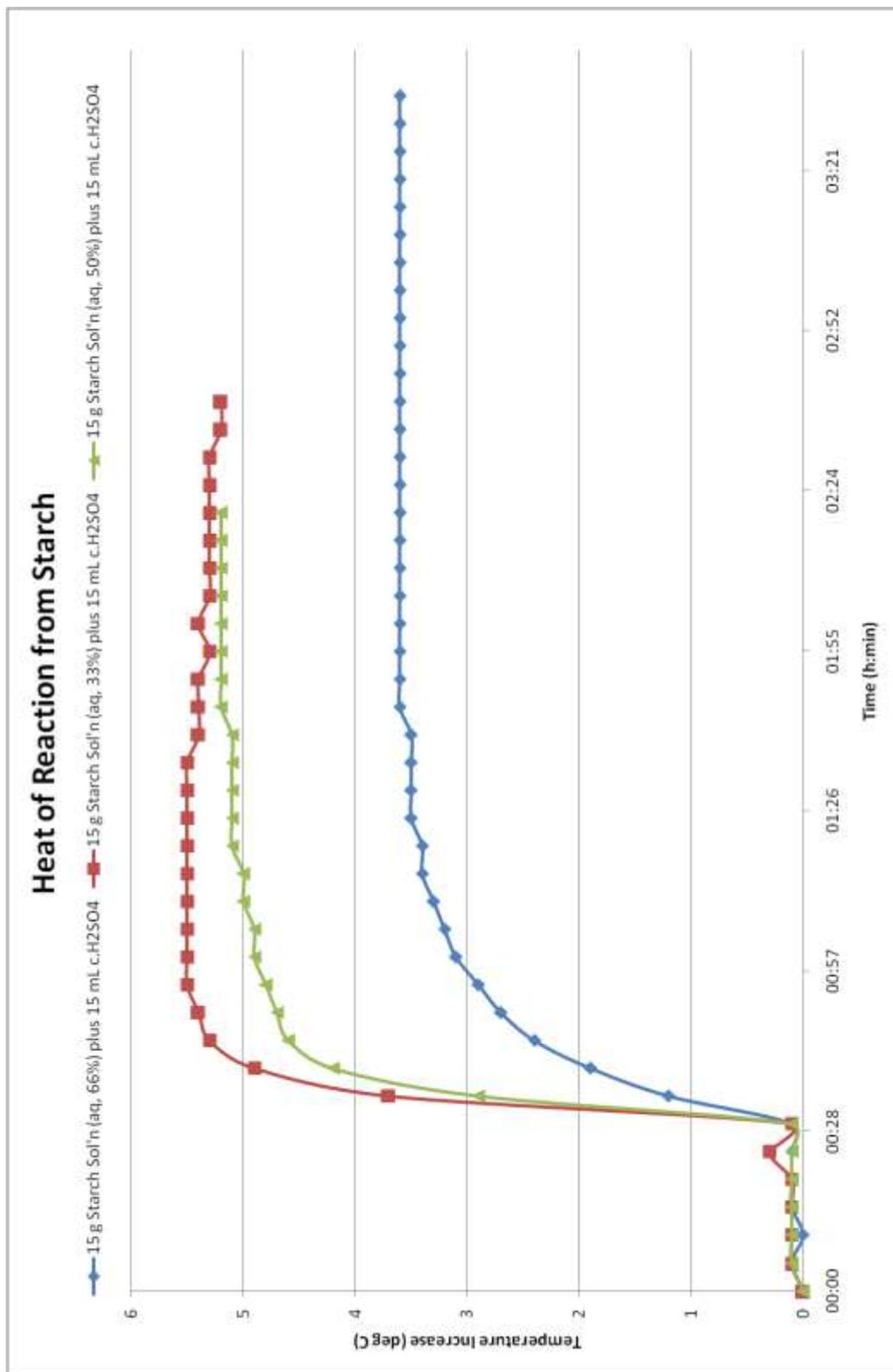
$$mol\ \% H_2SO_4 = \frac{Molarity\ H_2SO_4}{Molarity\ H_2SO_4 + Molarity\ H_2O} \times 100$$

$$wt\ \% H_2SO_4 = \frac{Mass\ (g)H_2SO_4\ in\ 1\ L}{Mass\ (g)H_2SO_4\ in\ 1\ L + Mass\ H_2O\ (g)\ in\ 1\ L} \times 100$$

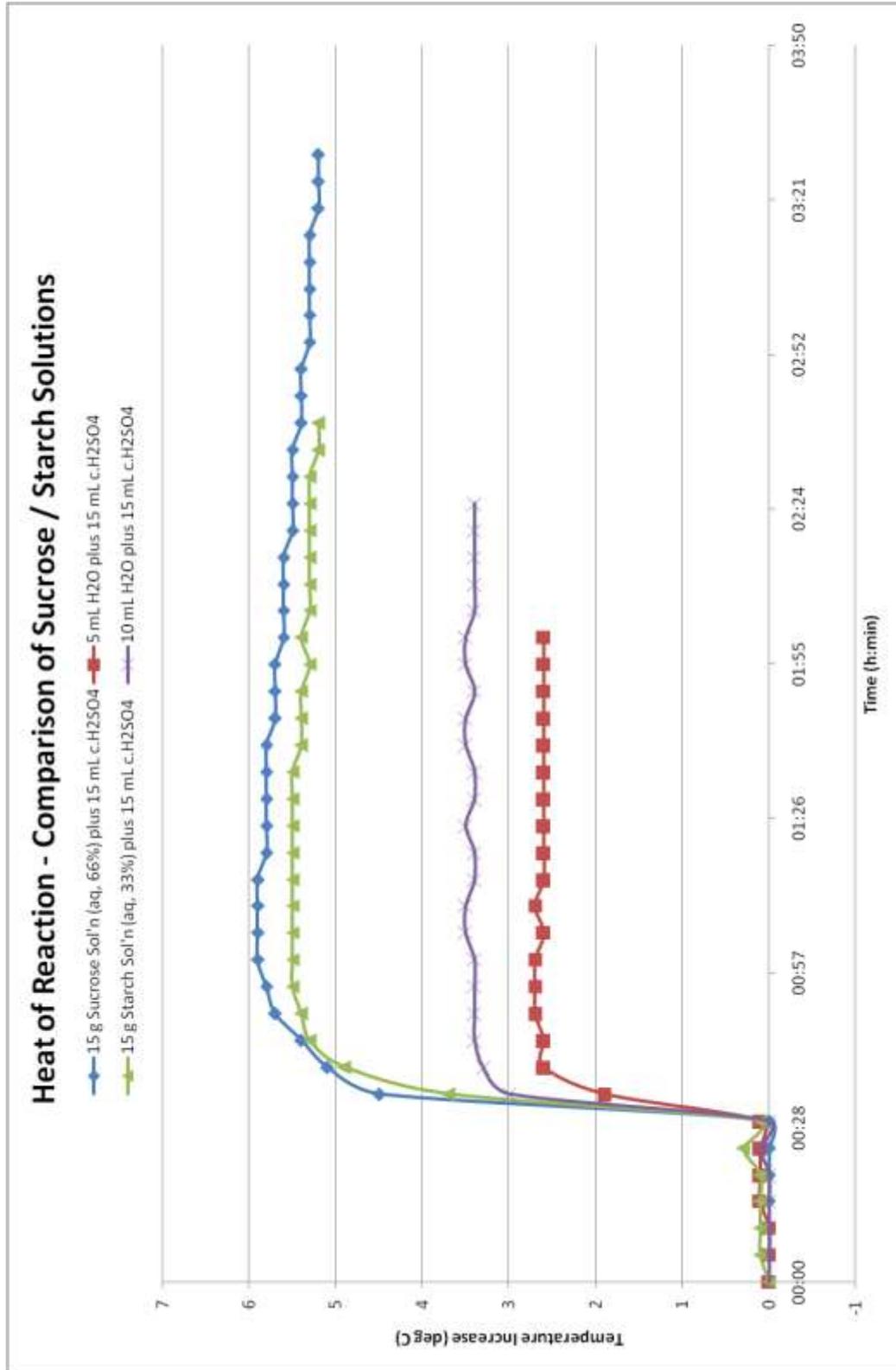
6.2 Heat of Reaction from Sucrose



6.3 Heat of Reaction from Starch



6.4 Heat of Reaction – Comparison of Sucrose / Starch Solutions



6.5 Partial Vapour Pressures of Aqueous Sulphuric Acid

