Letter of Response

Dear Professor Hildebrant, Professor Glasser and Head of School,

I have made the following corrections to my dissertation for the degree of Master of Engineering, in accordance with the requirements laid out in the two provided examiners' reports. With each required correction, I have added a note detailing my amendments to satisfy the work required. There are sets of corrections for the two reports, identified here as examiner 1 and examiner 2.

Examiner 1

- **Statement 1:** *"While the description of the relevant scientific methods and approach in the dissertation is largely adequate from the physical and chemical points-of-view, the biological component can be significantly improved. One key misunderstanding/error is the idea that carbon dioxide assimilation during photosynthesis is part of the light-dependent portion of the reaction during biomass assimilation driven by sunlight. This error was stated in several places in the dissertation and this is important to point out since this characteristic may be one reason for inherent irreversibility of the process. Some description of the key 'photo' and 'non-photo' events and relevant enzymes for assimilating the reactants (water and carbon dioxide) and producing the products (oxygen and glucose) would be useful to include in the revised thesis."*
- **Response:** The point regarding carbon dioxide uptake has been duly noted and corrected throughout the dissertation. I have substantially expanded the literature review in sections 1.3.1.2 and 1.3.1.3 in the dissertation to explain the light-dependent and light-independent reactions in greater detail. Discussion with a now greater knowledge of this area has also been added to chapter 3, where it is applicable to comparing theoretical and experimentally measured growth rates, and also in chapter 4, where insight into particular enzymes and

protein complexes allows for recommendations and further research that could be done.

- **Statement 2:** *"Another useful concept to include in the discussion of natural limitations of the photosynthesis reaction is that of the 'action spectrum' for the reaction centers. Due to the characteristic absorption spectrum of photoactive pigments, mainly chlorophyll, only a portion of the photons in the visible spectrum are usable. Thus the irradiance calculations in the theoretical energy available for photosynthesis should take this into account and its effect on the maximal rate of biomass production in plants and algae systems discussed."*

- **Response:** The literature review now includes a section (1.3.1.4) on light absorption and action spectrum, as well as an applicable figure for percentage light absorbance for chlorophyll *a*. Chapter 3 has been revised to take into account the absorption capabilities of this abundantly-occurring pigment by applying the percentage absorbance and reducing the total spectral irradiance and incoming photon density to the absorbable spectral irradiance and photon density for this pigment. By doing this, the new biomass growth rates are calculated, and are substantially lower than those calculated from the total light available in the photosynthetically active radiation spectrum (400 nm to 700 nm.).

- **Statement 3:** *"The discussion of the current dissertation's findings provides a reasonable assessment of their implications on the boundary conditions that may exist for photosynthesis rates in natural systems. That being said, it would be more satisfying if some possible targets/approaches may be suggested as potential candidates that could be tested for improving the efficiency of photosynthesis. For example, a listing of some of the enzymes/proteins involved in either the light-dependent reactions or the 'dark' portion of photosynthesis, and what properties one would need to change them, that can lead to a decrease in entropy of the system as a whole or decrease the light saturation limitation would be very useful."*

- **Response:** As with statement 1, the expanded literature review has brought several points to the discussion in chapters 3 and 4. Of particular concern is the Rubisco enzyme in the light-independent reactions, and the Cytochrome c6f protein complex in the light-dependent reactions. I have made an attempt to analyse how these enzymes currently contribute to decreasing the efficiency of the process, and how they might be improved, by consulting various biochemistry literature.

Examiner 2

- **Statement 1:** *"Need to re-write the abstract with detailed descriptions of findings, e.g., quantum requirements can be reported as numbers, difference in theoretical and experimental values can be quantified, growth rates can be given – this is important for someone interested in the outcome of this work especially when there is a body of literature that uses a microscopic entropy balance."*

- **Response:** I have re-written the abstract to include the theoretical values for quantum requirement and biomass growth rates that were calculated in the dissertation. I have also included the calculated average quantum requirement from the literature sources consulted, so that interest in comparison between the theoretical and measured values can be piqued from reading the abstract.

- **Statement 2:** *"Page 13 – spelling of modelling appears inconsistent"*

- **Response:** This has been corrected. I have standardised spelling to British English throughout the dissertation.

- **Statement 3:** *"Figure 1.3.1. does not have a reference"*

- **Response:** A reference has been added to figure 1.3.1., as well as numerical data for the x and y axes, provided from the reference.

- **Statement 4:** *"In the literature review Andriesse (2001) has been referenced only in Table 1.3.1. However, I believe that it needs a paragraph or so as they have used the microscopic entropy balance and relate growth rates proportional to the square root of the ratio of diffusion to the thermal conductivity. An efficiency term is also derived which could be incorporated/relevant to the macroscopic balance."*

- **Response:** I have added a description of the method employed by Andriesse in the literature review on page 33 in section 1.3.5. This section also provides background for the other measured biomass growth rates utilised for comparison in chapter 3. The efficiency term is indeed useful and has been included and applied in chapter 3 in sections 3.4 to 3.6 to compare theoretical and measured growth rate efficiencies. This is done so by comparing the total light energy available with the light energy converted to biomass chemical energy.

- **Statement 5:** *"A section, perhaps before 2.1.3. should include the ΔS_{rxn} (or $\Delta S_{\text{process}}$) and the calculation of it."*

– **Response:** This derivation has been added in section 2.1.2 on pages 40 to 42 between the derivation and calculation of the change in enthalpy of the process (section 2.1.1) and the change in Gibbs free energy of the process (section 2.1.3). The sequence is logical and this derivation is a valid addition.

– **Statement 6:** *"Page 35 – when $S_{\text{gen}} = 0$ then the entropy balance can be used to evaluate the relationship between QR and wavelength as a function of $\Delta S_{\text{process}}$. It would be interesting to see if this is the same result as those obtained in subsequent sections."*

– **Response:** This relationship is indeed apparent in the subsequent section, section 2.2.3, as equation 2.2.2 demonstrates that the QR is dependent on the wavelength as well as the $\Delta G_{\text{process}}$, or $\Delta S_{\text{process}}$ (either can be used as they are related by $\Delta G_{\text{process}} = \Delta H_{\text{process}} - T\Delta S_{\text{process}}$). I am unsure if there is anything further I can add to this comment, as the observation is apparent within the work.

– **Statement 7:** *"Figure 2.2.4 on page 39 suggests that if you extend the $Q = 0$ line to intersect with $S_{\text{gen}} = 0$ then there is a value for wavelength that allows this (albeit negative (-500 nm?)). However, the entropy balance is violated if both $S_{\text{gen}} = 0$ and $Q = 0$ are imposed – this is because the $\Delta S_{\text{process}}$ is set at the outset of the problem. A discussion on this anomaly would be appropriate."*

– **Response:** I have added additional figure 2.2.5 to the section to indicate the intersection point of the $Q = 0$ *with the* $S_{\text{gen}} = 0$ *line at* -307 nm. Following this I have included a discussion of this anomaly on pages 50 and 51 to indicate what significance this bears to the nature of the overall photosynthesis process. In summary, the process *must* reject heat, regardless of the degree of reversibility.

– **Statement 8:** *"Figure 2.2.4. – it would be appropriate to put the contours of* $Q = 166\,\text{kJ/mol}$ *and* $Q = 238\,\text{kJ/mol}$ *at the two extremes."*

– **Response:** I have added these two contours to figure 2.2.4 to show the intersection points with the x-axis at 400 nm and 700 nm, indicating $S_{\text{gen}} = 0$ at these two points that correspond to their respective heat rejection values, Q.

– **Statement 9:** *"Section 2.3 page 40 can be broken into subsections: 2.3.1 Photon entropy 2.3.2 Limits of operation."*

– **Response:** I have performed the division of section 2.3 into 2.3.1 and 2.3.2 at a suitable point on page 52.

- **Statement 10:** *"Section 2.4 can be broken into subsections: 2.4.1 Model for heat rejection etc. It would be appropriate to bring important results from the appendix here with the picture of the particle and the final result."*
- **Response:** I have broken section 2.4 into subsections 2.4.1, 2.4.2 and 2.4.3. A summarised version of the method, derivation and results from appendix B has now been included in these subsections, so that it can be understood without needing to constantly refer to the appendix.
- **Statement 11:** *"Section 2.4 does not explain alpha and how it is determined."*
- **Response:** Section 2.4 has now been expanded to include more information from the derivation in the appendix, and now includes an explanation of alpha and how it is calculated in sections 2.4.2 and 2.4.3.
- **Statement 12:** *"Chapter 3 does not include the results of Andriesse (2001) who has given some values for CO_2 uptake rates?"*
- **Response:** I have included the carbon dioxide uptake rates mentioned by Andriesse, which are actually provided by Goudriaan and van Laar (1994), in the results of chapter 3, section 3.5, as well as in the literature review in section 1.3.5. The latter is a new section that provides background for the measured biomass growth rates utilised for comparison in chapter 3.
- **Statement 13:** *"A separate conclusion chapter is required that succinctly reiterates the important finds and the relevance to other works from literature and the robustness of macroscopic entropy balance."*
- **Response:** Chapter 4 has been added to the dissertation to serve as a conclusion chapter. It summarises the main results from chapters 2 and 3, and makes recommendations on how to improve the efficiency of photosynthesis, from added detail on the light-dependent and light-independent reactions.
- **Statement 14:** *"Page 64: The density of the algae is considered as that of glucose – I think a weighted average with water and glucose would be more appropriate – not sure how the results are affected?"*
- **Response:** This density has been adjusted to the required weighted average of water and glucose. The results are slightly affected, but not dramatically so as to draw a different conclusion regarding the reasonability of the inner core temperature of a spherical cell. To illustrate, the inner core temperature for a

6 micron cell was slightly above 27 °C, but with the changed density, it is now slightly below 27 °C.

- **Statement 15:** *"Page 66: Not convinced why C1 is zero?"*
- **Response:** I have revised the derivation of the spherical heat generation model and used the spherical centre point condition to explain why C1 is indeed zero. The center of the cell is the hottest point, and as a result, no heat is generated at $r = 0$.

I hope that the corrections and revisions made here are to your satisfaction. I would like to offer my thanks to the two examiners for making valuable contributions and insights into the work I have presented in this dissertation.

Yours sincerely,

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6th September 2011
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