SHIELD!: A Self-Heating Natural Mosquito Repellent System

A new perspective.

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Introduction

The purpose of the project is to evaluate the effectiveness of using a high-energy reaction and a high concentration of the Nepetalactone and evaluate the effect of shrinking repellent size on the product effective time before replacement is needed. Nepetalactone is the active ingredient in the repellent. Some quick background about nepetalactone:

Nepetalactone is the main component of Nepeta Cataria commonly known as Catnip. Catnip has been used in ancient time as a medicine, as a flavor for food, and in tea. The lethal dosage for nepetalactone is 1300mg/kg[2].

Shield! Was previously designed to be portable, and used a calcium oxide and water reaction to generate heat that aids the diffusion of the repellent. This previous design yielded a maximum temperature of 50^{o}C for the repellent at which the diffusivity is 0.0438cm^2/s and the interfacial concentration is 0.0173mol/m^3. The new design has a maximum temperature of 60^{0}C for the repellent at the diffusivity is 0.0459cm^2/s and the interfacial concentration is 0.029mol/m^3.

The new design uses the reaction between calcium hydride and water to produce heat. This reaction is known to be fast and produces ~229kJ per mole of calcium hydride reacted. The effect of shrinking repellent size was considered to gauge product effectiveness and life span.

Shield! was scaled up ~473% to accommodate high repellent concentration. Due to this scale, the cost of production went up and product cost to consumers must be increased as well. The economics of the new design is presented with only base case scenario which is meeting 50% of the market demand. The same demand curve for the smaller size Shield! was utilize to come up with base case scenario. With this scenario, the selling price for Shield! will be set at $16 for the reusable container and $1.50 for the recharge canister. The net present worth after 10 years is $71M with a payback time of 3 years. This shows with the bigger size Shield!, the project is still profitable. It is also effective for 1.5 hours after which replacement is needed for further protection.

Modeling the Reaction

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2 + Heat \quad \Delta H = -228.71\frac{KJ}{mol}$$

The above reaction is first order with respect to calcium hydride[1] . Water concentration does not affect reaction rate as it is present in 25% excess. The kinetics of the reaction was determined by using hydrogen production rate data to back calculate the concentration of the calcium hydride in the system. Using the integral method and assuming a first order kinetics, the rate constant was calculated to be ~0.569 min^{-1}. The high rate constant shows that the reaction is relatively fast. As a result, hydrogen production will end relatively fast too. And the effect of hydrogen release on the repellent diffusion is therefore negligible. This statement is true since the diffusivity of nepetalactone in hydrogen was estimated to be $\sim 1.56 * 10^{-16} cm^2/s$. Intuitively, the hot hydrogen could volatize the repellent leading to higher initial concentration as observed when modeled in COMSOL. Also, the hydrogen will aid the dispersion of the of already volatized repellent particles which is also limited by the production rate. Using a mixture of alcohol and water can prolong hydrogen production[1]. This approach was not considered due to concerns of alcohol intoxication. The reaction of calcium hydride and water is exothermic and generates ~228.71kJ/mol. For this application, I am using approximately 0.113 mole of calcium hydride which will generate ~ 25.8 kJ of heat. This is enough to raise the repellent temperature to 60^oC and keep there for more than 30 minutes.

Material Balance:

For the material balance, a batch reactor was assumed and the following shows how the model was developed.

$$A + 2B \rightarrow C + 2D$$

$Where$

$$A = CaH_2;\ \ B = H_2O;\ \ C = Ca(OH)_2;\ \ D = H_2$$

Balance on C:

$$\frac{dN_c}{dt} = r_c V \quad (1)$$

Table 1: Stoichiometric table of Calcium Hydride reaction

Component	In	Δ	Out
A	N_{AO}	$-XN_{AO}$	$N_A = N_{AO}(1-X)$
B	N_{Bo}	$-XN_{AO}$	$N_B = N_{Bo} - XN_{AO}$
C	0	XN_{A0}	$N_C = XN_{A0}$
D	0	$2XN_{A0}$	$N_D = 2XN_{A0}$

From the stoichiometric table

$$N_c = XN_{A0} \quad (2)$$

$$\frac{d(XN_{A0})}{dt} = r_c V \quad (3)$$

Using relative rate law

$$r_c = kC_A = \frac{kN_A}{V} \quad (4)$$

Sub into equation 3

$$\frac{d(XN_{A0})}{dt} = kN_A \quad (5)$$

Simplifying and applying stoichiometric table relation

$$\frac{dX}{dt} = k\frac{N_A}{N_{A0}} = k(1-X) \quad (6)$$

$$\frac{dX}{1-X} = kdt \quad (7)$$

Integrating the equation 7 and solving for X:

$$X = 1 - \exp(-kt) \quad (8)$$

The above equation shows how the conversion changes over time. From this I can also calculate the extent of reaction at any given time.

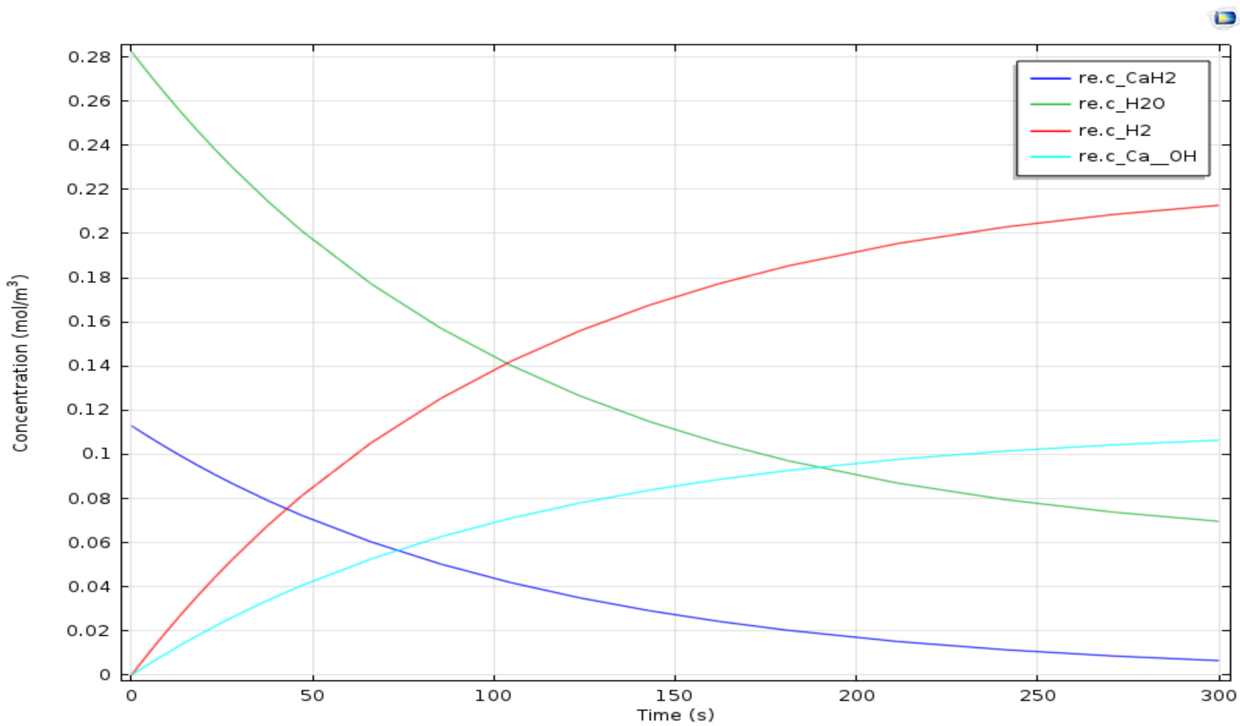

Figure 1: Concentration profile

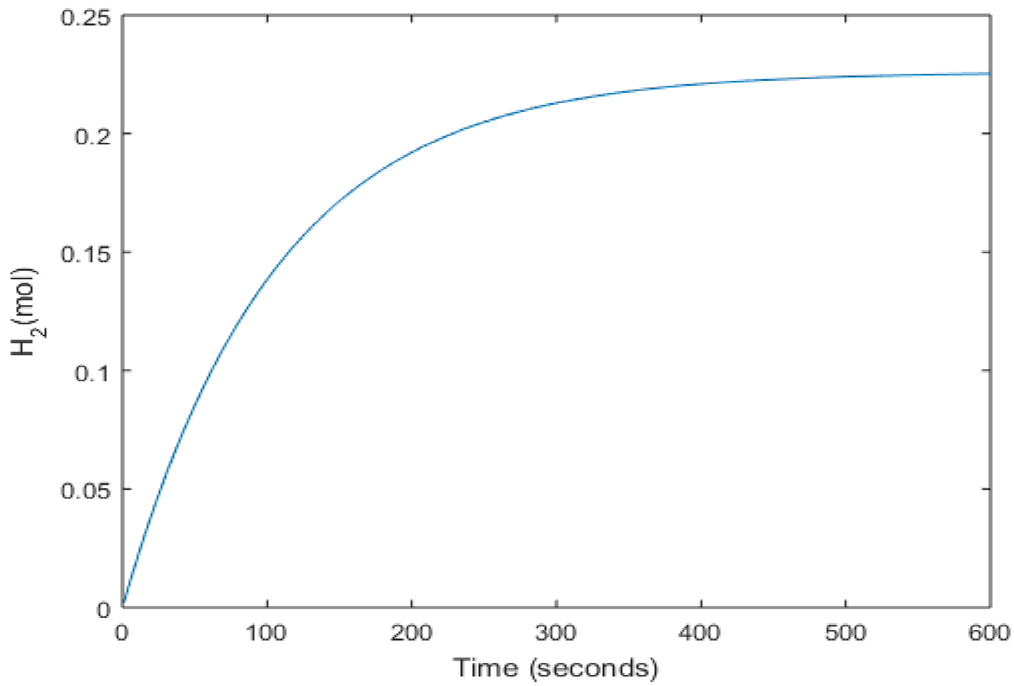

Figure 2:Hydrogen production

Energy Balance:

The amount of heat generated at any given time can be calculated using the following equation

$$Q = \xi(t) * \Delta H_{rxn}$$

$$\xi(t) = X * N_{A0} = N_{A0}[1 - \exp(-k * t)]$$

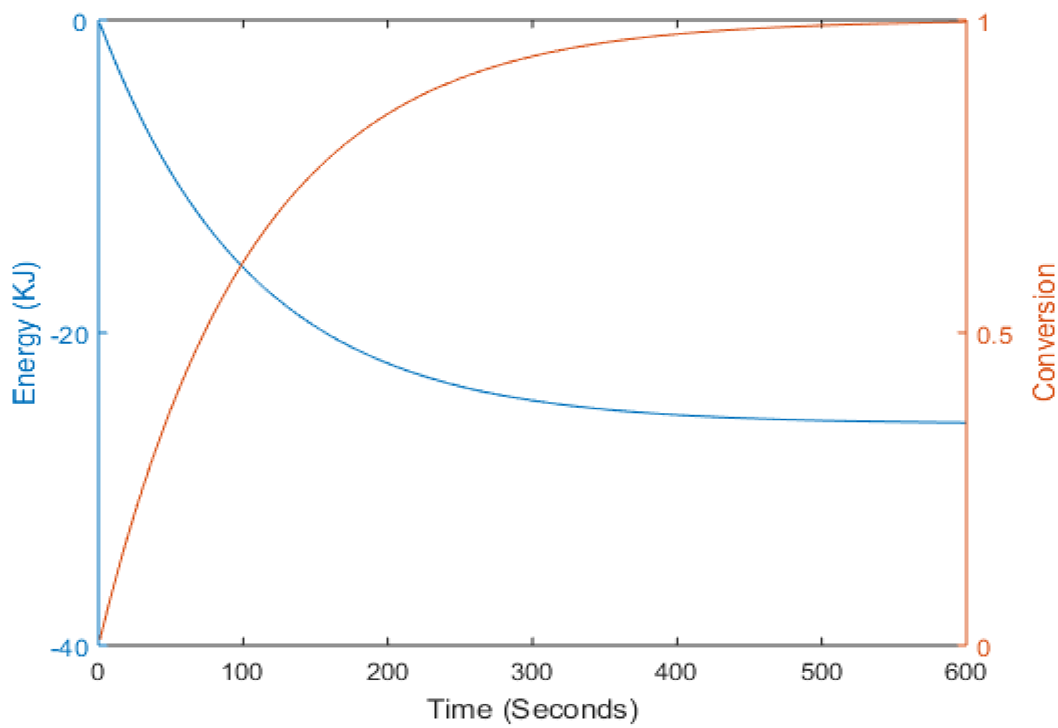

Figure 3: Energy generated from the reaction and conversion plotted against time

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Heat transfer model

The study of the effects of heat on the self-heating repellent system is an important aspect of the design of the product as it will help determine how much energy is required to increase the temperature of the repellent, how long it will take to activate the repellent and how long the repellent will sustain a temperature at which it will effectively diffuse into the atmosphere. The design of the product was modelled in COMSOL Multiphysics using the heat transfer modules provided by the software along with thermodynamic properties obtained from scientific handbooks such as Perry's Chemical Engineers handbook. The product was modelled as a 2D axisymmetric component to decrease computation time taken by COMSOL. The major assumption made while modeling the product in COMSOL is that there is no loss of heat from the surface area of the product as it is well insulated. Other assumptions made in modeling the product is listed in the appendix.

To simplify computation, the product was modelled as a solid in COMSOL. The time dependent heat transfer for solids was modelled using equation 9.

$$\rho Cp\,\frac{\delta T}{\delta t} + \rho Cp\boldsymbol{u} * \nabla T = \nabla * (K\,\nabla T) + Q \; (9)$$

For the surface area of the well-insulated stainless steel container, the stationary heat equation displayed in equation 10 is used as it assumes that the heat lost through the surface area is negligible and there is no heat lost from those boundaries.

$$-\boldsymbol{n} * (-k\nabla T) = 0 \; (10)$$

A heat transfer in fluid element was added to account for the transfer of heat from the top of the repellent to the atmosphere. The equation used by COMSOL to compute this is displayed in equation 11.

$$\rho Cp\,\frac{\delta T}{\delta t} + \rho Cp\boldsymbol{u} * \nabla T = \nabla * (K\,\nabla T) + Q + Qvd + Qp \; (11)$$

To obtain an accurate model of the product, it was essential to consider the phase change that occurs within the paraffin wax. To account for the phase change, the latent heat of melting of the phase change material is considered and is modeled using the heat transfer with phase change feature in the software.

The material properties change as the material changes phase therefore it is important to incorporate a step function which will exchange the material properties of the liquid and solid paraffin wax as the transitional temperature for the phase change is reached; in this case, at 70 ^{0}C. The equation used to account for the phase change by COMSOL is the same as equation 11. However, when dealing with phase change, some thermodynamic properties need to be modified. The modification implemented are displayed below:

$$\rho = \theta\rho_{\mathrm{phase1}} + (1-\theta)\rho_{\mathrm{phase2}} \quad (12)$$

$$\mathrm{Cp} = \frac{1}{\rho}\left(\theta\rho_{\mathrm{phase1}}\mathrm{Cp}_{\mathrm{phase1}} + (1-\theta)\rho_{\mathrm{phase2}}\mathrm{Cp}_{\mathrm{phase2}}\right) + \mathrm{L}\frac{\delta\alpha,\mathrm{m}}{\delta\mathrm{T}} \quad (13)$$

$$\mathrm{k} = \theta\mathrm{k}_{\mathrm{phase1}} + (1-\theta)\mathrm{k}_{\mathrm{phase2}} \quad (14)$$

$$\alpha_m = \frac{(1-\theta)\rho_{phase2} - \theta\rho_{phase1}}{2 * \theta\rho_{phase1} + (1-\theta)\rho_{phase1}} \quad (15)$$

Lastly, a heat source is implemented in COMSOL. The heat source comes from the reaction between calcium hydride and water which is modeled in MATLAB. Data relating the amount of energy released with respect to time is imported from MATLAB to COMSOL through the interpolation function and can be used as a heat source from the reaction layer of the product.

Heat Transfer Results:

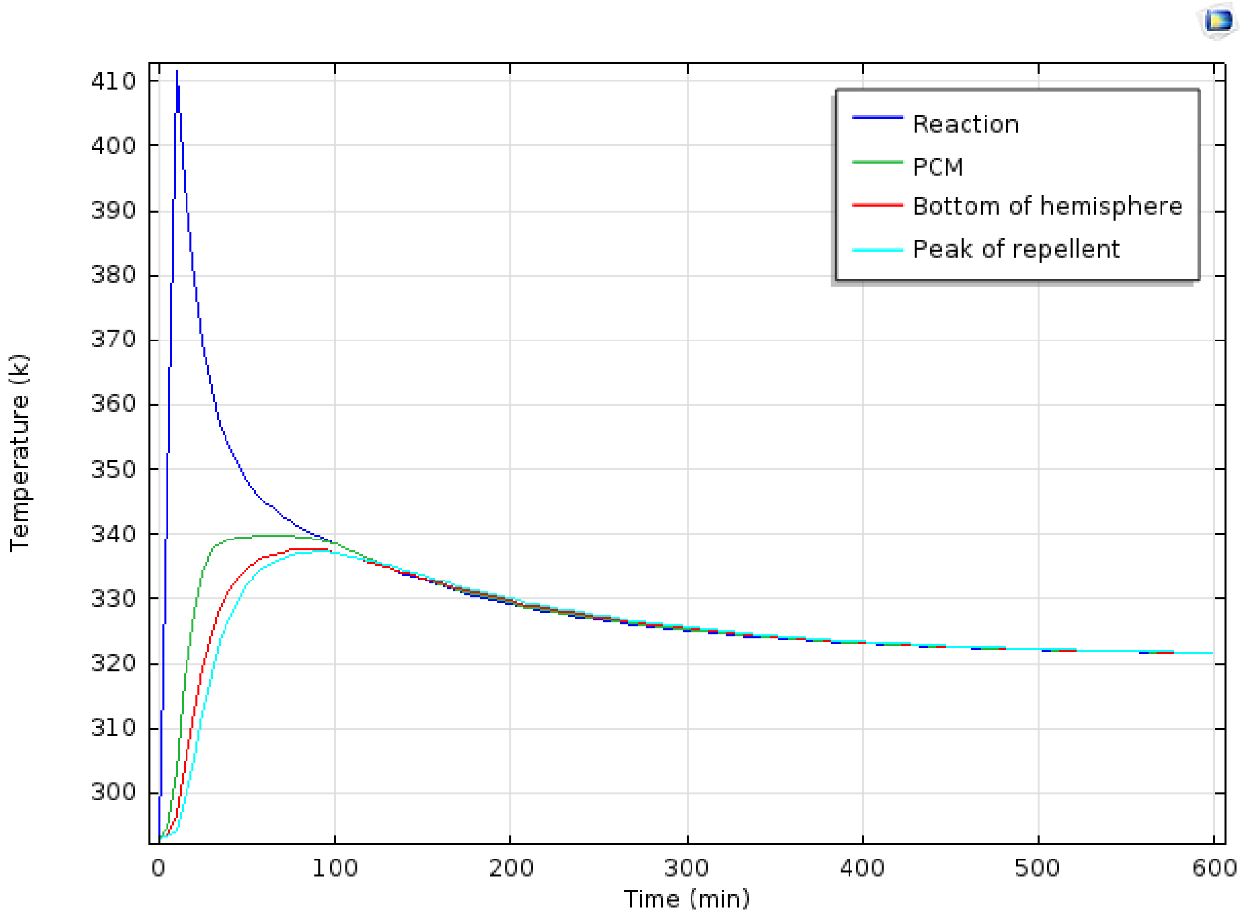

Figure 4: Temperature profile

Mass Transfer Modeling: Steady State Diffusion

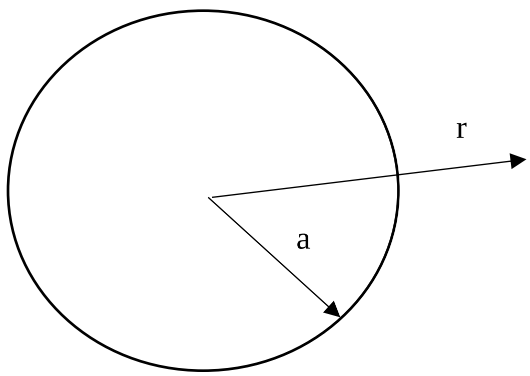

Figure 5:Schematic of the system where a is the specified radius of the system

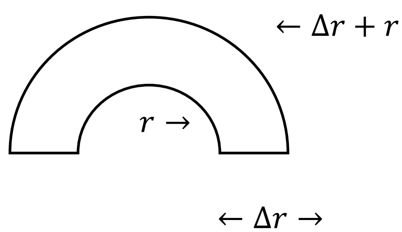

Figure 6: Differential volume element

Steady state diffusion was performed to obtain a model that relate the radius of the repellent to time. This way, the effect of shrinking repellent size can be modelled in the unsteady state diffusion.

The mass balance around the differential volume reduces to

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 N_{A,r}\right) = 0 \quad (14)$$

Further simplifications:

$$\frac{\partial}{\partial r}\left(r^2 N_{A,r}\right) = 0 \quad (15)$$

Fick's Law:

$$N_{A\,r} = C_{A,r}v^* - D_{AB}\frac{dC_A}{dr} \quad (16)$$

Applying assumption 2 – 3, Fick's Law simplifies to:

$$N_{A\,r} = -D_{AB}\frac{dC_A}{dr} \quad (17)$$

Substitute into equation and integrate twice to obtain

$$C_A(r) = \frac{C_1}{D_{AB}}\frac{1}{r} + C_2 \quad (18)$$

Boundary conditions:

$BC1: r = a$ $\qquad C_A = C_{AI} = \frac{p_A}{RT}$ (Ideal Gas assumption)

$BC2: r = \infty$ $\qquad C_A = 0$

Applying the boundary conditions:

$$C_A(r) = C_{AI} * \frac{a}{r} \quad (19)$$

Flux:

$$N_{Ar} = D_{AB} * C_{AI} * \frac{a}{r^2} \quad (20)$$

Mass release rate:

$$W = N_{Ar}(a) * SA \; (21)$$

$$W = D_{AB} * C_{AI} * \frac{1}{a} * 2\pi a^2 \quad (22)$$

$$W = D_{AB} * C_{AI} * 2\pi a \quad (23)$$

If the mass release rate is relatively small, I can use a mass balance on the hemisphere to deduce the rate of change of its size with time.

$$\frac{d}{dt}\left(\frac{2}{3}\pi a^3 \rho\right) = -2\pi r^2 * N_{A,r} * M_N \quad (24)$$

$$2\pi a^2 \rho \frac{da}{dt} = -2\pi r^2 * D_{AB} * C_{AI} * \frac{a}{r^2} * M_N \quad (25)$$

$$2\pi a^2 \rho \frac{da}{dt} = -2\pi * D_{AB} * C_{AI} * a * M_N \quad (26)$$

$$a \frac{da}{dt} = -D_{AB} C_{AI} * M_N \quad (27)$$

Separate and integrate:

$$a^2(t) = \frac{-D_{AB} * C_{AI} * M_N * t}{\rho_N} + a_0^2 \quad (28)$$

Non-Steady State Diffusion:

Mass balance on the differential volume for spherical coordinate yields

$$\frac{\partial C_A}{\partial t} + \left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 N_{A,r}\right) + \frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}\left(N_{A,\theta}\sin\theta\right) + \frac{1}{r\sin\theta}\frac{\partial N_{A,\phi}}{\partial \phi}\right] - R_A = 0 \quad (29)$$

Applying assumptions 6, the equation simplifies to

$$-\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 N_{A,r}\right) = \frac{\partial C_A}{\partial t} \quad (30)$$

Fick's Law:

$$N_{A\,r} = -D_{AB}\frac{\partial C_A}{\partial r} + C_{A,r} v_1^* \quad (31)$$

Substitute into equation 31 to obtain

$$\frac{\partial C_A}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\, D_{AB}\frac{\partial C_A}{\partial r} - C_{A,r} v_r^*\right) \quad (32)$$

Boundary conditions:

$initial\ condition$: $\quad t = 0 \quad\quad C(r,0) = 0$

$BC1: r = \sqrt{\frac{-D_{AB} * C_{AI} * M_N * t}{\rho_N} + a_0^2} \quad (shrinking\ radius\ from\ SS\ balance);$

$C_A = C_{AI} = \frac{p_A}{RT}$ (Ideal Gas assumption)

$BC2: r = \infty \qquad C_A = 0$

Using the above relations, a MATLAB routine was written to solve the partial differential equation. Solving the partial differential equation, I can obtain a concentration profile as function of time and position.

Before solving the above equations, I needed to estimate the diffusivity of the repellent to be able to model the temperature dependence of the diffusivity. The kinetic theory of gases approach for binary mixture was used to predict the diffusivity. To use the kinetic theory, the Lennard-Jones parameter needs to be estimated. Lydersen group contribution method was used to estimate the critical volume of Nepetalactone which was then used to estimate the Lennard-Jones parameters found in the kinetic theory equation.

Once these parameters were estimated, the kinetic theory can be applied directly to obtain the diffusivity of nepetalactone in air.

Estimating Diffusivity:

Kinetic theory of gases equation[#]

$$D_{AB} = \frac{2}{3}\left(\frac{k}{\pi}\right)^{\frac{3}{2}} N^{\frac{1}{2}} T^{\frac{3}{2}} \frac{\left(\frac{1}{2M_A} + \frac{1}{2M_B}\right)^{\frac{1}{2}}}{P\left(\frac{\sigma_A + \sigma_B}{2}\right)^2} \quad (33)$$

Estimating Lennard-Jones Parameter

$$\sigma = 0.841 V_c^{\frac{1}{3}} \quad (34)$$

$$V_c: critical\ volume\ [=] cm^3/mol$$

Estimating Vc using group Lydersen Method:

$$V_c = 40 + \sum \Delta \mathrm{V_L} \quad (35)$$

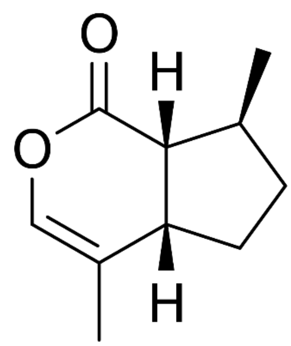

Figure 7: Structure of Nepetalactone

Table 2: Group contributions for critical volume

Groups	ΔV_L
>C=O (ring)	50
>CH- (ring) X 3	46 X 3
-CH2 (ring) X 2	44.5 X 2
>C= (ring)	37
=CH- (ring)	37
-O- (ring)	8
-CH3 X 2	55 X 2

Using the Lydersen method, the critical volume was found to be $509cm^3$. This volume was then used to estimate the Lennard-Jones parameter for diffusivity calculation.

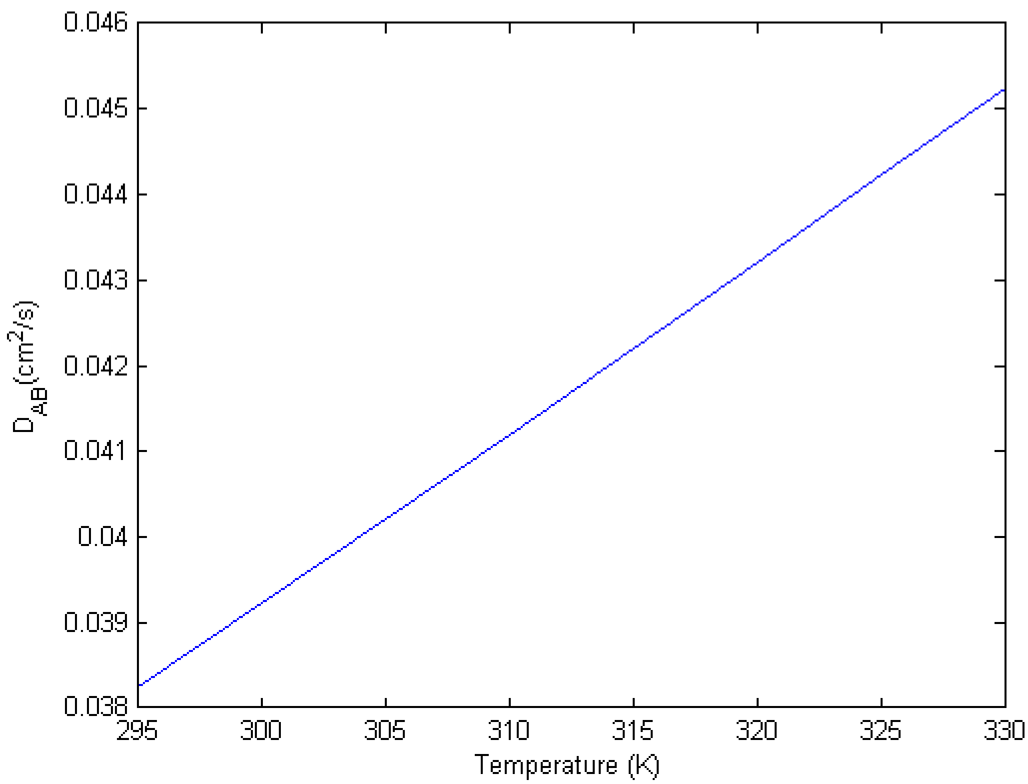

Figure 8: Diffusivity as function of temperature

The figure above shows the diffusivity at different temperatures. The diffusivity changes linearly with temperature. The consequence is that the higher the increase in temperature caused by the reaction section the more repellent that will be released. Based on the new design and modeling in COMSOL, the repellent only reaches a maximum temperature of ~60°C. At this temperature, the diffusivity of the repellent is ~ $0.0459cm^2/s$.

Using this diffusivity, the first principle model equation was then solved. The following concentration profiles were obtained.

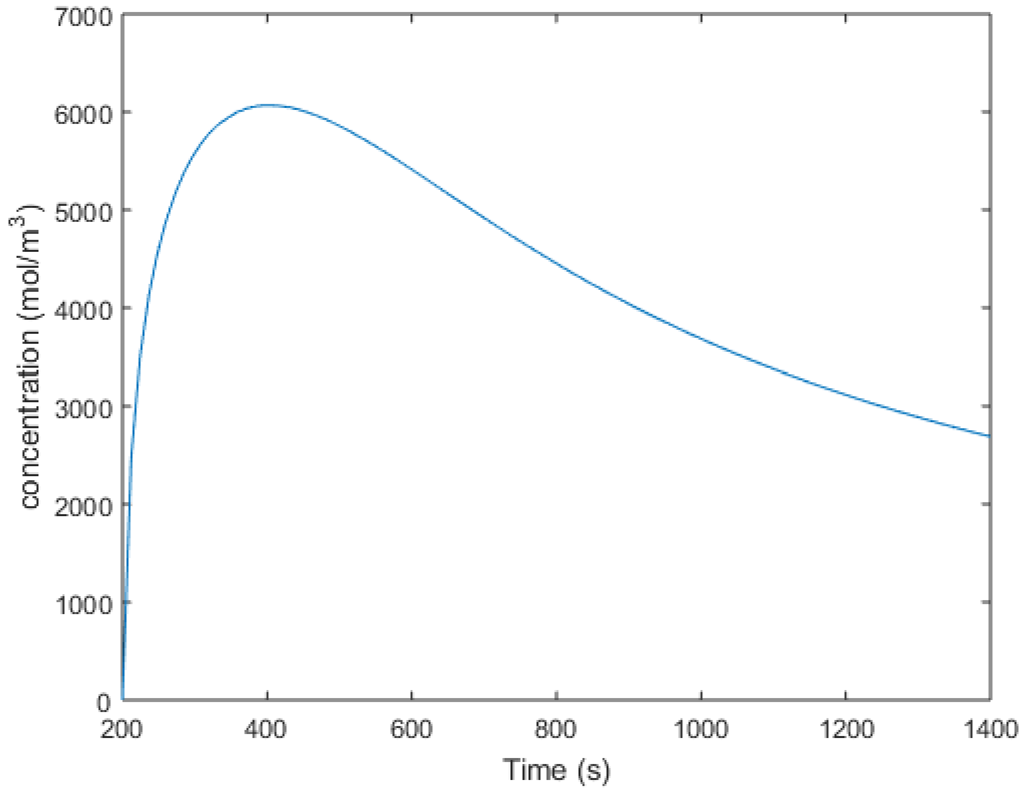

Figure 9:interfacial concentration variation with time

The above plot shows how the interfacial concentration of the repellent changes as function of time. As can be observed from the figure, the maximum concentration is reach after 7 minutes before it starts to decrease due to shrinking repellent size.

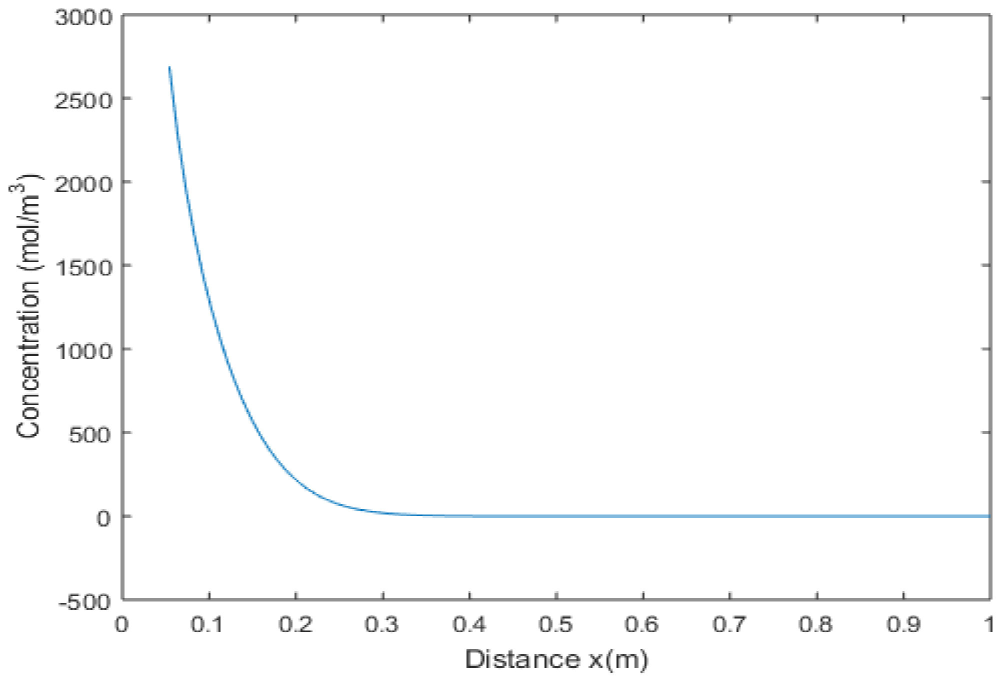

Figure 10: Concentration profile from the interface to 1m away after 23 minutes

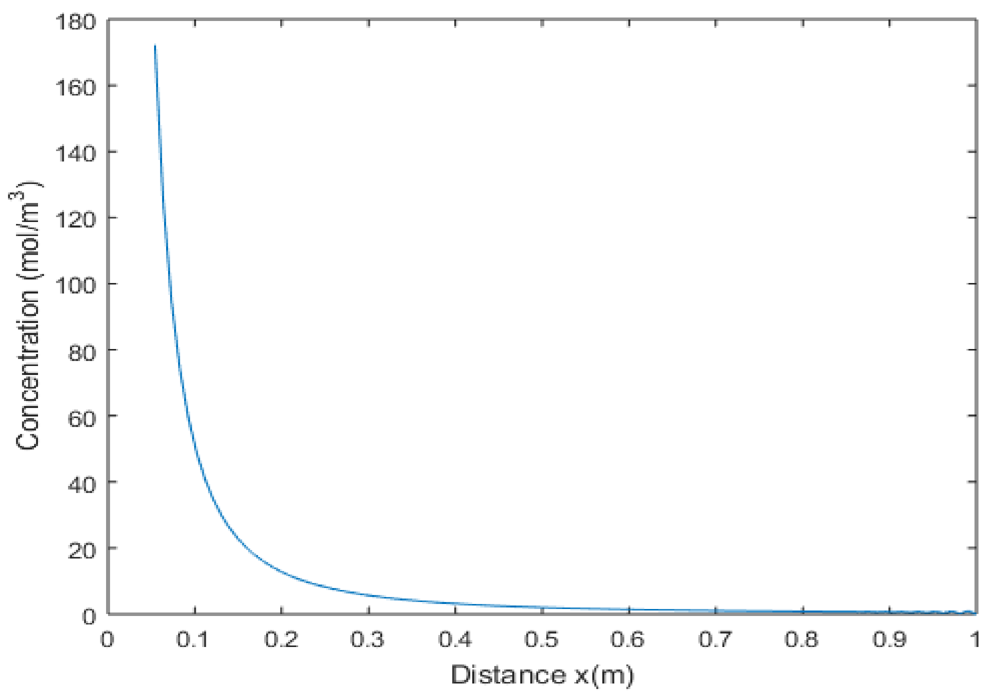

Figure 11: Concentration profile from the interface to 1m away after 23 minutes with wind speed of 0.01m/s.

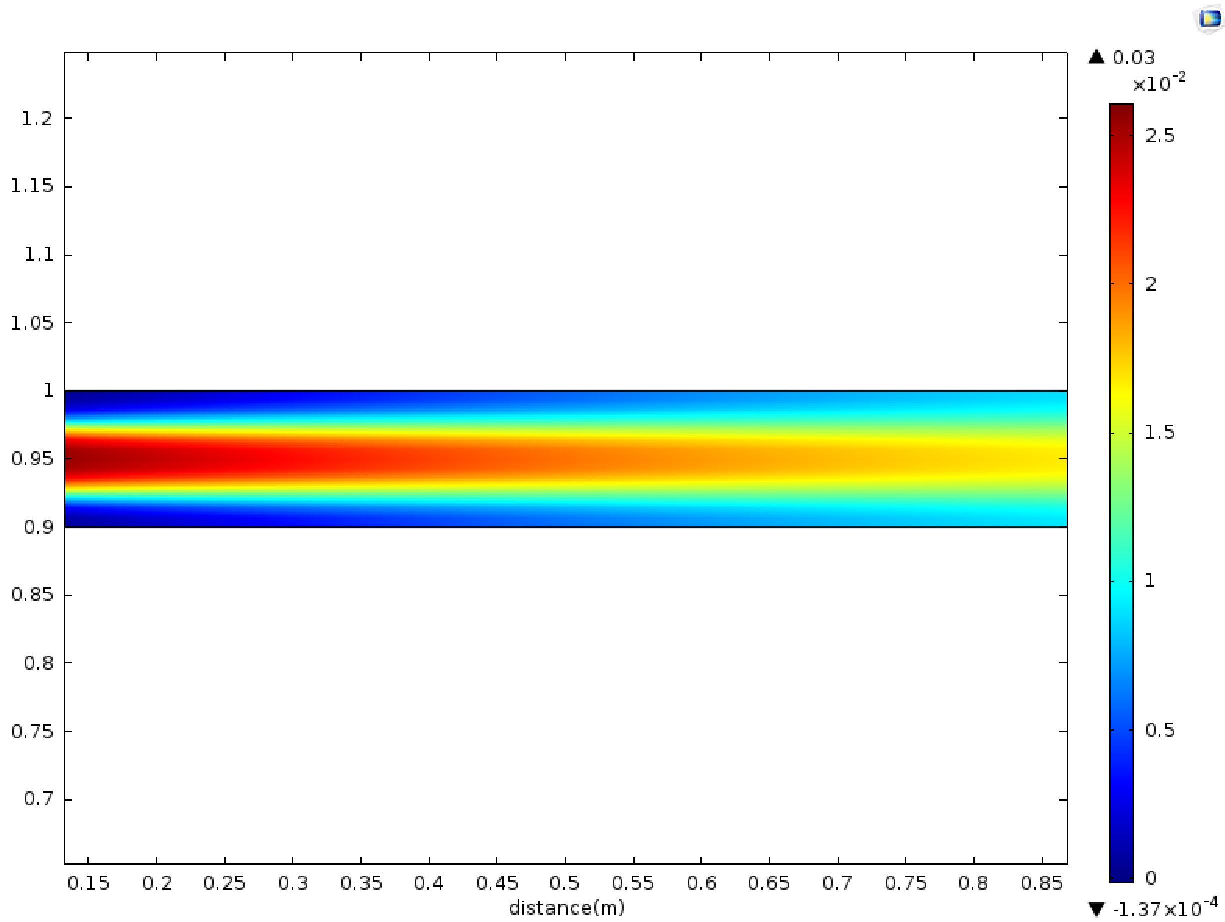

Figure 12: Concentration profile with hydrogen production

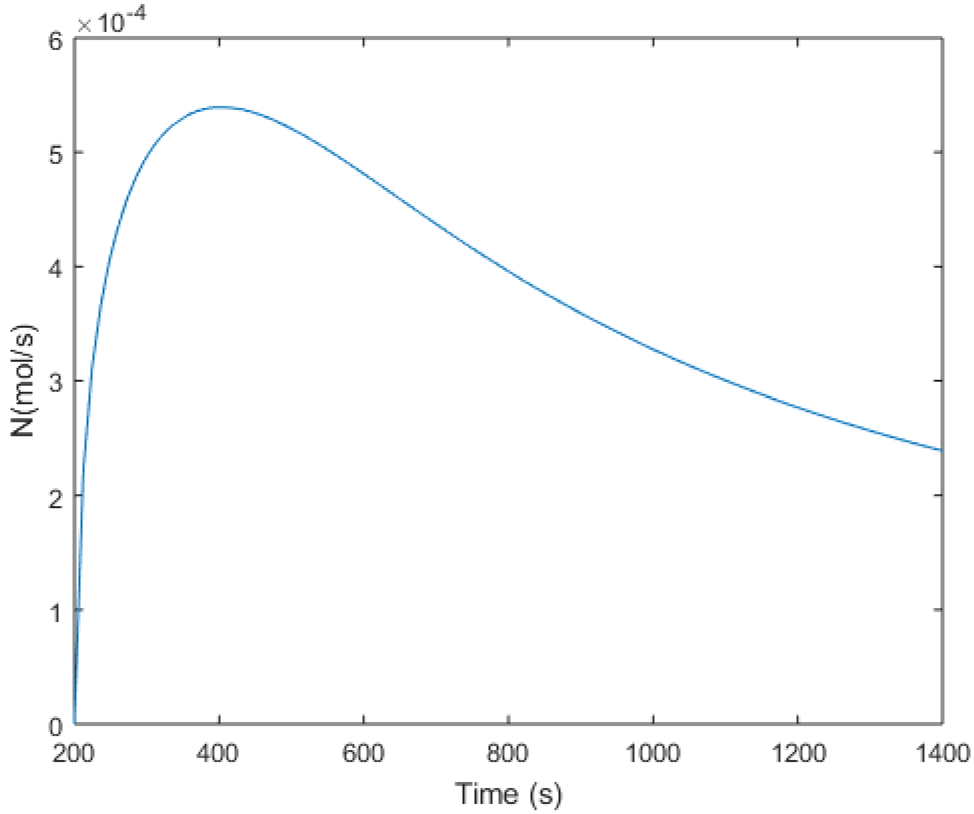

Figure 13: Mass release rate

The mass release rate can be calculated by doing a numerical differentiation on the concentration profile data obtained from solving the first principle model then multiplying the result by the surface area of the hemisphere. Once the mass release rate is estimated, the time it takes for the repellent to run out can then be estimated.

Economics:

Using a percentage estimate method, the cost of production is assumed to scale linearly with cost of the old design by a factor of 4.73. This number is gotten by calculating how much the radius of the hemisphere was scaled. The previous radius was 0.01143m and new radius is 0.0541m which is a scale up of ~473%. The cash flow diagram is presented below.

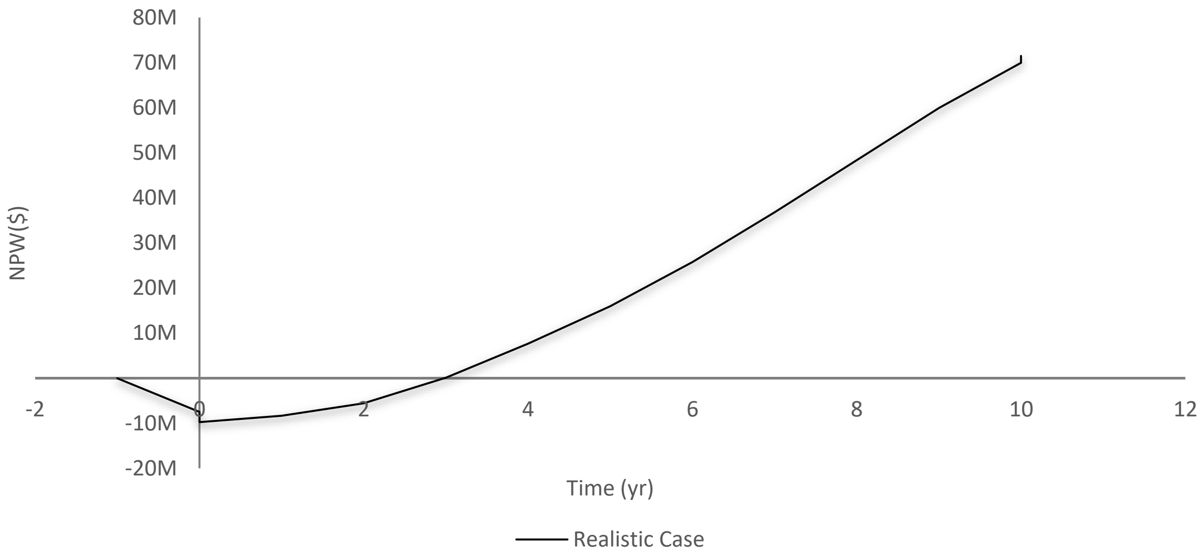

Figure 14: NPW

Table 3: Investment

FCI	$ 7.5M
WC	$ 1.5M
SE	$ 622K
DCFRR	76%

Conclusions and Recommendations

The main purpose of this individual project was to model the effect of decreasing repellent size, and the use of a high energy reaction on a scaled up version of Shield!. It was found that the repellent will have a lower life time of 1.5 hours than the 6 hours previously calculated for the smaller version. This is due to shrinkage of the repellent. Nevertheless, the product is still profitable with an NPW of 71M after 10 years and payback time of 3 years. This project is recommended for serious investors.

Acknowledgements

- I will like to thank Aaron Driscoll for his help and guidance.
- I will also like to thank Ahmet Manisali for his help with mass transfer.
- I will also like to acknowledge Dr. Sunol, and Kyle Cogswell for their feedback.

References:

[1]"Energy Sources, Part A: Recovery, Utilization, and Environmental Effects." *Taylor and Francis Online*. N.p., 5 Jan. 2016. Web. 29 Apr. 2017.

[2] "Catnip Uses, Benefits & Dosage - Drugs.com Herbal Database." *Drugs.com*. Drugs.com, n.d. Web. 29 Apr. 2017.

Appendix:

List of Technical Assumptions

Heat Transfer

1. Well insulated stainless steel container therefore heat transfer through the sides and bottom of the container can be neglected.
2. Ambient pressure remains constant within the reaction space
3. Excess water present therefore reaction is first order with respect to calcium oxide.
4. Heat transfer through radiation is neglected internally and externally
5. Chemical reaction in canister bag goes to completion
6. Density, heat capacity and thermal conductivity of all materials except phase change material are independent of temperature and remain constant
7. Change in volume of phase change material during transition between phases is minute and can be neglected
8. Initial temperature value of all materials are ambient temperature
9. The average reaction rate constant over a time period of 80 minutes is utilized and is assumed to be constant for duration reaction.
10. Repellent diffuses into atmosphere until depletion
11. Material properties for Calcium oxide and water mix are additive

Mass Transfer

1. The sphere contains a pure component A; therefore, we need to consider the mass transport process only in the surrounding fluid.

2. The fluid is unbounded in extent and quiescent. It contains only the diffusing species A and a non-diffusing species B.
3. The motion arising from diffusion can be neglected. This requires that either the mixture in the fluid be dilute in species A, consisting primarily of the non-diffusing species B, or that the rate of mass transport be small.
4. The problem is spherically symmetric. This means that in a spherical polar coordinate system there are no gradients in the polar angular coordinate, or in the azimuthal angular coordinate.
5. There are no chemical reactions.
6. Ideal gas mixture
7. Internal diffusion is negligible
8. Temperature at the interface is constant and equal to the temperature of the liquid phase.
9. After an initial transient, steady state is assumed to prevail. This implies that the change in size of the sphere due to mass transfer occurs on a time scale that is very large compared with the time scale for the diffusion process for a given radius of the sphere to reach steady state.