Thermal Runaway in Exothermic Reaction

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1 Introduction

In this project we looked at a simple one dimensional application of the heat equation with a heat generating term. Say a company wants to produce energy by burning biomass from agricultural waste to produce steam, in order to turn turbines that generate electricity. They have to collect the plant fibers and store them until it is brought to the incinerator. If this company want to produce electricity all year long, they will have to store enough plant material until the next crops are harvested. The problem is that plant material such as bagasse, an agricultural waste from sugar cane harvest, will emit a certain amount of energy per volume. It is documented that if the bagasse is not properly stored will spontaneously catch on fire. We wanted to model under what circumstances will the material stay at a constant temperature, where there is no fire, where there is a steady state solution to the heat equation. When there is no solution to the equation, the material keeps heating up, turning into a runaway exothermic reaction.

2 Background

Plants turn carbon dioxide and water into organic matter and oxygen. Organic material per mole has higher potential energy than the surrounding atmosphere. Chloroplasts in plant cells capture units of light energy and use them to do work in the cell. The captured energy gets combined with carbon dioxide and water to make organic molecules that plants use to build their body and excess sugars for storage. Plant material in essence is carbon dioxide and water combined with light energy. The process of plant growth is an endothermic reaction because energy gets absorbed from the surrounding environment. When this happens atoms gets rearranged and new bonds are formed so that the resulting molecule has higher potential energy. Humans and animals then consume organic matter, combine it with oxygen and turn it back into carbon dioxide and water. When human cells arrange the atoms back, they capture the energy as the molecules falls back down to a lower chemical potential energy state, and use it to do work in the cell. Molecules falling back down to a lower energy formation is an exothermic reaction, since energy is emitted into the surroundings.

If the energy company were to store a large volume of organic material for fuel, it is important to minimize the rate at which the material loses it potential energy. They would not want the material to lose all its potential energy at once, which can lead to combustion. In the case of bagasse, a material intended to be used as fuel in a incinerator, they would like to minimize the loss in potential, so that the energy gets released when it is burned to produce the electricity.

One might initially think that large amounts of bagasse bulldozed into a huge pile and stored at ambient temperature, should not result in very much exothermic loss since quite a bit of activation energy is needed to destabilize electron orbitals. But there are many activities in the environment that act as catalysts which lowers the activation energy. Small insects and microorganisms like mold and bacteria from the air will metabolize sugar and plant material, which is a loss in potential. While the material is broken down by metabolism instead of combustion, the end result is the same, the organic molecules consumed get rearranged into a lower energy formation and energy is released into the surroundings. If the bagasse gets piled up too thick, so that not enough heat can make it to the surface, the inside of the pile will heat up over time. When the pile heats up, this again acts like a catalyst as the insects and microbes multiply consuming more material, producing more heat, further decreasing the activation energy. If the pile is very big, given enough time it will catch on fire. This represents a safety hazard and also a loss of energy that could have been converted into electricity. So we are trying to answer the question, how high is too high?

3 Analysis

We assume the bagasse is stored in a long and wide sheet with vertical height of $2L$ in the x direction. This way we simplify the problem so that the temperature at any point in the pile only depends on the height x, so that there is relatively very little surface area towards the length and width directions. If we do not want the pile to heat up over time, we want the change in temperature with respect to time $\frac{\partial U}{\partial t}$ to be 0.

$$\frac{\partial U}{\partial t} = k\frac{\partial^2 U}{\partial x^2} + Qe^{bU} \tag{1}$$

U is the temperature function which only depends on x. Here k is the thermal diffusivity. Q and b control the rate at which the reaction is producing heat. The first term on the RHS of (1) is the heat conduction term, the second term is the heat generating term. Both terms combined gives the change in temperature. If the absolute value of first term is bigger then the absolute value of the second, then the material cools down over time. If the second term is bigger in absolute value, the material will heat up over time. Here we seek a solution to equation (1) when the derivative of U with respect to t is 0. Setting $\frac{\partial U}{\partial t}$ to 0, we use the method of integrating factors to simplify (1). Multiply both sides by U' then integrate both sides results in

$$\frac{1}{2}kU'^2 + \frac{Q}{b}e^{bU} = C \tag{2}$$

We wanted to find for what condition does $U(x)$ exist such that it satisfies the boundary conditions $U'(0) = 0$ and $U(L) = 0$. Here $x = 0$ is the center of the pile and L is the distance from the center. These are symmetric boundary conditions about the x axis. Simplifying then using the method of separation of variables produce

$$\int_U \left(1 - \frac{Q}{bC}e^{bU}\right)^{-\frac{1}{2}} dU = \int_x \left(\frac{2C}{k}\right)^{\frac{1}{2}} dx \tag{3}$$

The RHS of (3) is trivial but for the LHS we need we need to use the method of substitution and set $1 - \frac{Qb}{C}e^{bU} = S$, it can be shown that $dU = -\frac{1}{b(S-1)}$, so the LHS becomes

$$LHS = -\frac{1}{b}\int_S \frac{1}{S^{\frac{1}{2}}(S-1)}dS \tag{4}$$

Now set $S^{\frac{1}{2}} = R$ so that $\partial S = 2RdR$. Now substitute into (4) and LHS becomes

$$LHS = -\frac{2}{b}\int_R \frac{1}{R^2-1}\partial R \tag{5}$$

then the equation becomes

$$-\frac{2}{b}\operatorname{arctanh}(R) = \left(\frac{2C}{k}\right)^{\frac{1}{2}} x + C_1 \tag{6}$$

Undo the substitutions then simplify should result in

$$bU = \ln\left[\frac{bC}{Q}\operatorname{sech}^2\left(-\frac{bC_1}{2} - bx\left(\frac{C}{2k}\right)^{\frac{1}{2}}\right)\right] \tag{7}$$

and solving for $U'(x)$, then applying the boundary condition at $x = 0$ gives

$$U'(0) = \frac{2}{b}\tanh\left[-\frac{bC_1}{2} - b(0)\left(\frac{C}{2k}\right)^{\frac{1}{2}}\right] b\left(\frac{C}{2k}\right)^{\frac{1}{2}} = 0 \tag{8}$$

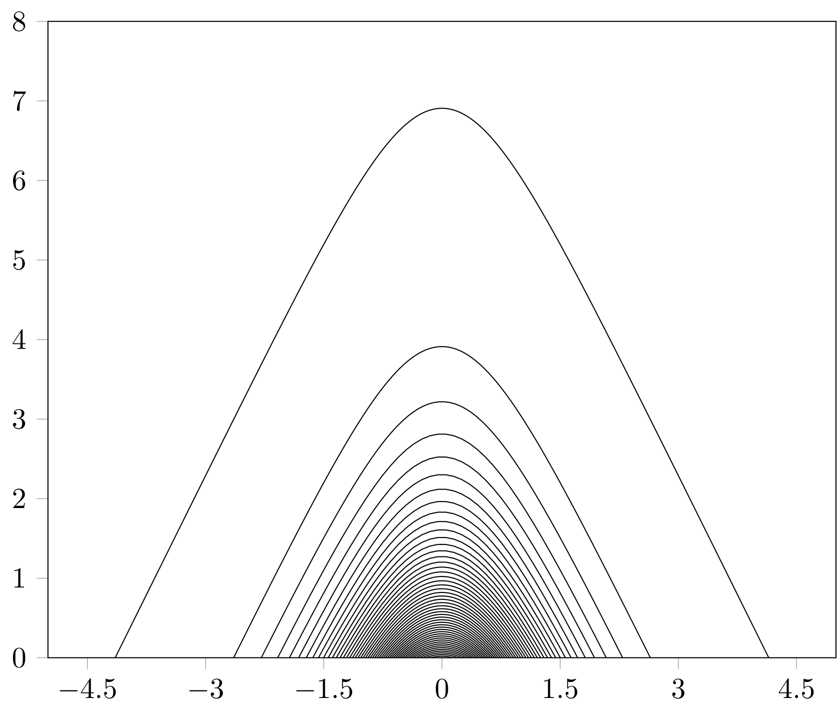
We see that C_1 has to be 0. So now we have U'

$$U'(x) = \tanh\left[-bx\left(\frac{C}{2k}\right)^{\frac{1}{2}}\right]\left(\frac{2C}{k}\right)^{\frac{1}{2}} \tag{9}$$

Now we also have $U(x)$.

$$U(x) = \frac{1}{b}\ln\left[\frac{bC}{Q}\operatorname{sech}^2\left(bx\left(\frac{C}{2k}\right)^{\frac{1}{2}}\right)\right] \tag{10}$$

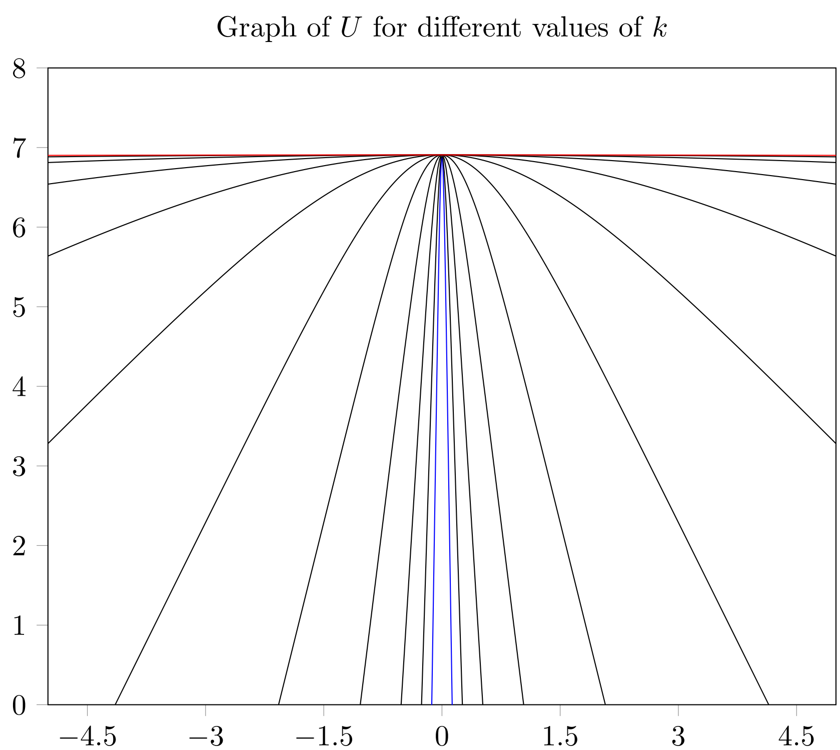
Graph of U for different values of Q



By applying properties of hyperbolic functions, it can be shown that

$$\ln\left[\left(\frac{bC}{Q}\right)^{\frac{1}{2}}+\left(\frac{bC}{Q}-1\right)^{\frac{1}{2}}\right]=bL\left(\frac{C}{2k}\right)^{\frac{1}{2}} \tag{11}$$

Letting b, C, k be constant, we look at what happens to L as we change Q. If Q is relatively small, the LHS of (11) is relatively large, which implies that L on the RHS is large. If Q is relatively large, L is relatively small. As Q moves to close to its max of bC, the LHS will approach 0. This means the L that will satisfy the condition $U(L) = 0$ will get smaller and smaller until it disappears. The graph of $U(x)$ for different values of Q supports this result.



Letting b, C, Q be constant, we look at what happens to L as we change k. When k is large(red), heat easily moves to the surface so the material can be stacked relatively high, so L is large. When k is relatively small, the heat energy encounters resistance as it moves through the material. Since it takes much longer for the heat to get to the surface, L needs to be relatively small(blue). Graph of U for different values of k supports this result.

But we're tasked with finding the solution for a particular L such that is satisfies the boundary condition $U(L) = 0$. Applying the boundary condition $U(L) = 0$ gives

$$0 = \frac{1}{b} \ln \left[\frac{bC}{Q} \operatorname{sech}^2 \left(bL \left(\frac{C}{2k} \right)^{\frac{1}{2}} \right) \right] \tag{12}$$

For a solution to exist it must be true that

$$\left(\frac{Q}{bC} \right)^{\frac{1}{2}} = \operatorname{sech} \left[bL \left(\frac{C}{2k} \right)^{\frac{1}{2}} \right] \tag{13}$$

Now the trick is to apply a clever substitution and let $Z = bL(\frac{C}{2k})^{\frac{1}{2}}$ so that $C = 2K(\frac{Z}{bL})^2$. Substitute into left and right side, then move the Zs to one side gives

$$1 = \frac{2k}{Qb(L)^2} Z^2 \operatorname{sech}^2(Z) \tag{14}$$

therefore

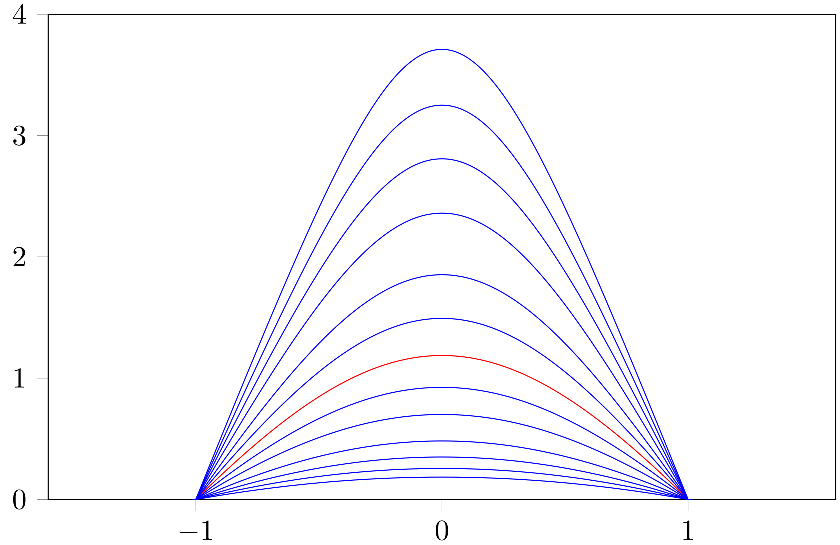
$$L \left(\frac{Qb}{2k} \right)^{\frac{1}{2}} = Z \operatorname{sech}(Z) \tag{15}$$

Since we have symmetric boundary conditions, we focus on the positive values. Looking at graph of $f(z) = Z \operatorname{sech}(Z)$ we see that $f(z)$ has a global max at around 0.6627. For a solution to exist, the LHS of (16) must be less than or equal to the global max of $f(z)$.

$$L \left(\frac{Qb}{2k} \right)^{\frac{1}{2}} \leq 0.6627 \tag{16}$$

By letting b, L, k, Q be constant, we can find a single solution that satisfied $U(L) = 0$ when the LHS of (16) is equal to the global max. We will always find solutions in pairs whenever the LHS (16) is set to less than the global max. There are no solutions when the LHS (16) is more than the global max. As the LHS of (16) approach the global max, the double solutions approach the single solution. Below are graphs of some solutions.

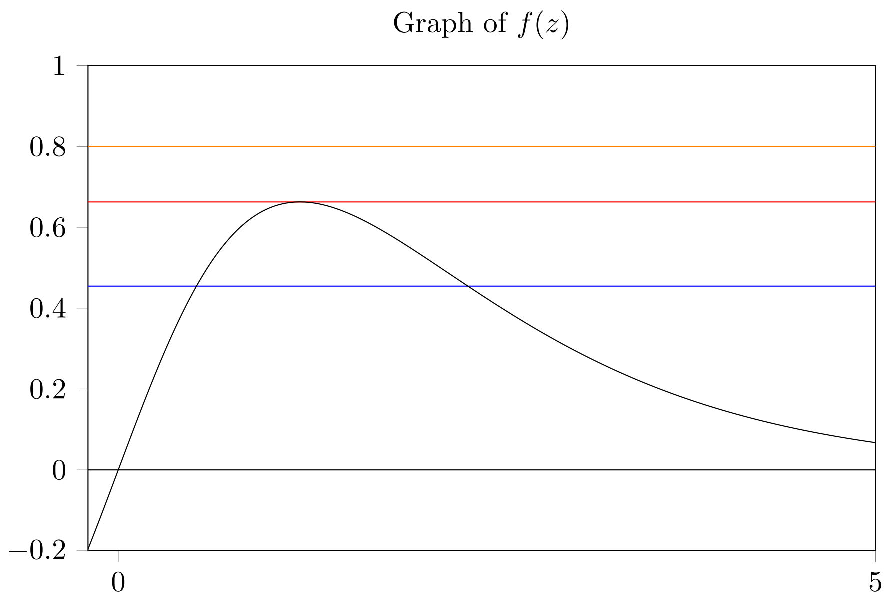
Graph of U for unit L with different values of Q



$Zsech(Z)$	Q	Z_1	Z_2	b	L	k	C_1	C_2
0.6627	0.8783	1.1997	/	1	1	1	3.273	/
0.6532	0.8533	1.037	1.378	1	1	1	2.151	3.798
0.6248	0.7808	0.887	1.578	1	1	1	1.574	4.980
0.568	0.6452	0.723	1.849	1	1	1	1.045	10.66
0.3976	0.3162	0.436	2.542	1	1	1	0.3802	12.93

4 Conclusion

Looking at the graph of $Z\,\mathrm{sech}(Z)$ and some possible values of $L(\frac{Qb}{2k})^{\frac{1}{2}}$, we conclude that there are 3 possible out comes.



The first case, orange line. If Q is too large, no elements of $Z\,\mathrm{sech}(Z)$ can satisfy (16). The second case, red line. The LHS coincide with global max of $Z\,\mathrm{sech}(Z)$ and there is one solution to (16), the global max. The third case, red line. Q is small enough so that two elements in $Z\,\mathrm{sech}(Z)$ satisfy as solution to (16). See "Graph of $f(z)$" and "Graph of U for unit L with different values of Q". From the graphs we conclude that if there is a lot of organic material, there will always be a L that is too big. Any L that takes the LHS of (16) above the global maximum of about 0.6627, will result in runaway exothermic reaction. This will cause the material to lose a significant percentage of its potential energy or even catch on fire over time. Given the physical properties of a material, it should be stored at at a height($2L$) that makes the LHS of (16) a percentage of 0.6627 providing a good margin for safety.