THIS IS NOT A SCIENTIFIC PAPER!!!

# Calculation of IBU additions after flame out

**Introduction**
Recently I been having a fair amount of success making big hoppy beers via cube hopping and flame out additions, but I have been struggling to predict the amount of bitterness I was going to end up with. As I found myself adding more and more hops in these times this became even more important. This article outlines the process I went though to find a method which could be used to estimate IBU contributions from hop additions after flame out.

Being a no-chill brewer, I began to get frustrated with the hand wavy guesstimation that was used with IBU calculation when no chilling. Currently there is no real accepted method for compensating for the slow chilling and the effect on IBU. Some people recommend just add 10-20 min to your hop additions when calculating IBU, some say do nothing and others use whirlpool calculations. What about cube hopping and later cube additions? What happens when I whirlpool and let the trub settle before cubing? Whirlpooling with lid on or lid off? These were to many unanswered questions. I began thinking about what was actually happening and began reading.

Most software available use some form of IBU calculation that uses a constant temperature (100C). These can not be used once we turn off the heat source as we begin to cool the wort. This is because isomerisation of alpha acids is dependent on temperature as well as time(and a bunch of other stuff) and these equations do not account for that. Now we also add the extra complication that everybody's system is different and will have a different cooling rate.

I realised that we need equations that include temperature as well as time. I thought surely some smart cookie has already done this and began to search around.  Well it turned out that they have… kinda.

The equations just needed some tweaking and reworking to account for changing temperatures (what we brewers want).

**The Reading**
The rest of this article is mainly based on the work in these two papers. I will try to keep it as simple as possible and use as little scientific jargon as I can (keep in mind that it might not always be possible and there is maths involved).

1) Malowicki, M. G.; Shellhammer, T. H. Isomerization and
degradation kinetics of hop (Humulus lupulus) acids in a model
wort-boiling system. J. Agric. Food Chem. 2005, 53, 4434–4439.

2)
JASKULA, B. KAFARSKI, P AERTS,G. COOMAN, L. A Kinetic Study on the Isomerization of Hop r-Acids  J. Agric. Food Chem. 2008, 56, 6408–6415

With some additional reading from a bunch of other papers.

**Utilisation**
When it comes to estimating IBUs as a brewer we really only care about how much utilisation we are going to get from the hops we add. Utilisation is how much of the alpha acids (the bittering component of hops) we add to the beer/wort actually ends up as iso-alpha acids. So I am mainly going to focus on how to calculate this utilisation for time as well as temperature.

The Jaskula et al paper listed [2] tested utilisation against different temperatures (80C, 90C and 100C) and times. They came up with an equation that estimated alpha acid utilisation based on temperature and time. For those that know about chemistry, you might be familiar with Arrhenius behaviour. This paper demonstrated that apha-acid isomerization follows this Arrhenius behaviour with both temperature and time.

**WARNING MATHS!!! FEEL FREE TO SKIP**
$ln(1 - [iso-\alpha-acid_t]/[\alpha-acid_0]) = -kt$ ( equ 1)
where, $[iso-\alpha-acid_t]$ is the current iso-alpha concentration, $\alpha-acid_0$ is the initial alpha acid concentration, t is time in seconds and k is the rate constant that varies with temperature.
(from [2])

rearranging to see utilisation more clearly
$U = 1 - e^{-kt}$ (equ 2) ,
where U(utilisation) = $[iso-\alpha-acid_t]/[\alpha-acid_0]$

and
$k = Ae^{-E/RT}$ (equ 3)
where A is the pre-exponential factor, E is the free energy of activation, R is the gas constant (8.3 J/K/mol) and T is absolute temperature (K).
(from [2])

This paper solved k (equ 3) for varying temperatures and produced some general equations for k.
Basically for k, $A = 3.13 * 10^9$ and $E/R = 11661$
(from [2])

**Changing temperature and rate of utilisation**

The problem with this equation (equ 2) is that it will give you U for a given time and temperature but it assumes that the temperature was held constant the whole time . In the case of flameout/no chill/whirlpool we are dealing with a changing temperature.

If instead of looking at the utilisation we can look the rate of utilisation. This tells us how our utilisation will be changing over time.

The rate of utilisation is simply the derivative of utilisation with respect to time.
$\frac{dU}{dt} = ke^{-kt}$ (equ 4)
where $\frac{dU}{dt}$ is the derivative of U with respect to time.

**Replacing temperature (T)  with time (t)**
If we know our rate of cooling or how or system cools after flame out we can derive an equation for temperature with respect to time. Thus enabling us to replace T in the equation for k with a function of time (t).

This required me to figure out how my system cooled.


# Experiment time
The next step was to work out the rate of cooling of my system. I conducted two cooling experiments

Experiment 1 Lid on cooling
I brought ~ 27L of water to the boil in my kettle and let it get to a good rolling boil for ~5 min. Then I switched off the heat and put on the lid. I then recorded the temperature every 5 min. It took 2hr 15min to get down to 80C at which point I had had enough and stop recording.

Cooling with lid on kettle
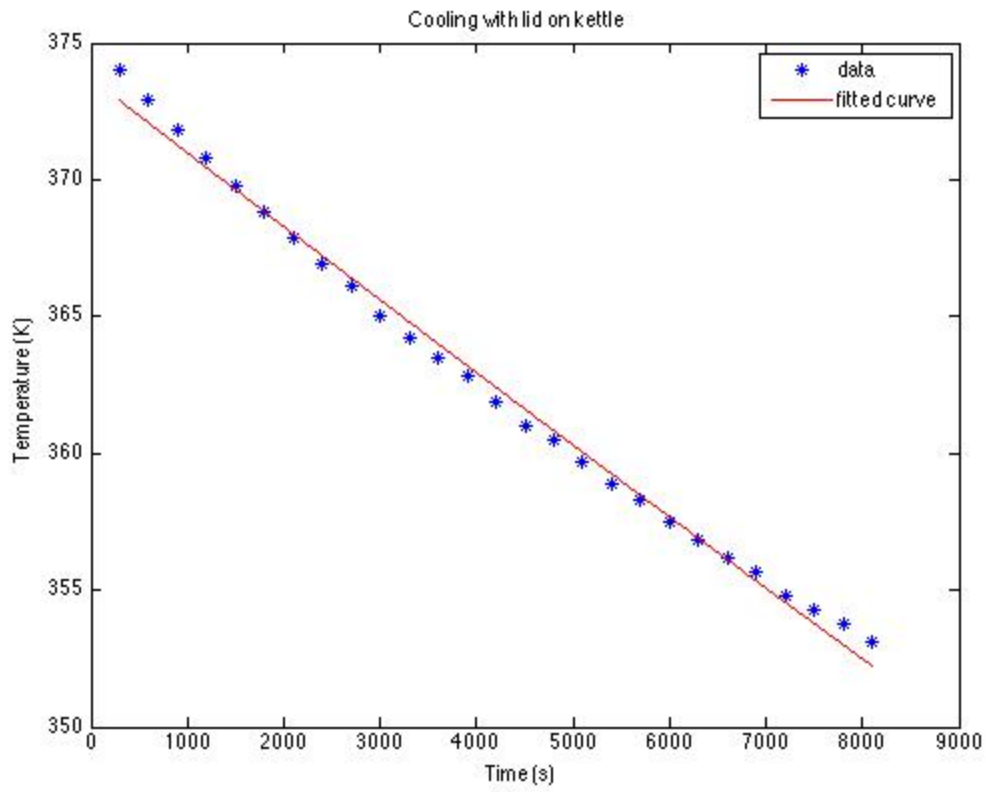
Experiment 2: Lid off cooling
After I finished experiment 1 I brought the kettle back up to a rolling boil and left the lid off and extractor fan above on. I then took measurement every 5 min. This took 30 min to get down to 80C.



Cooling with lid off kettle
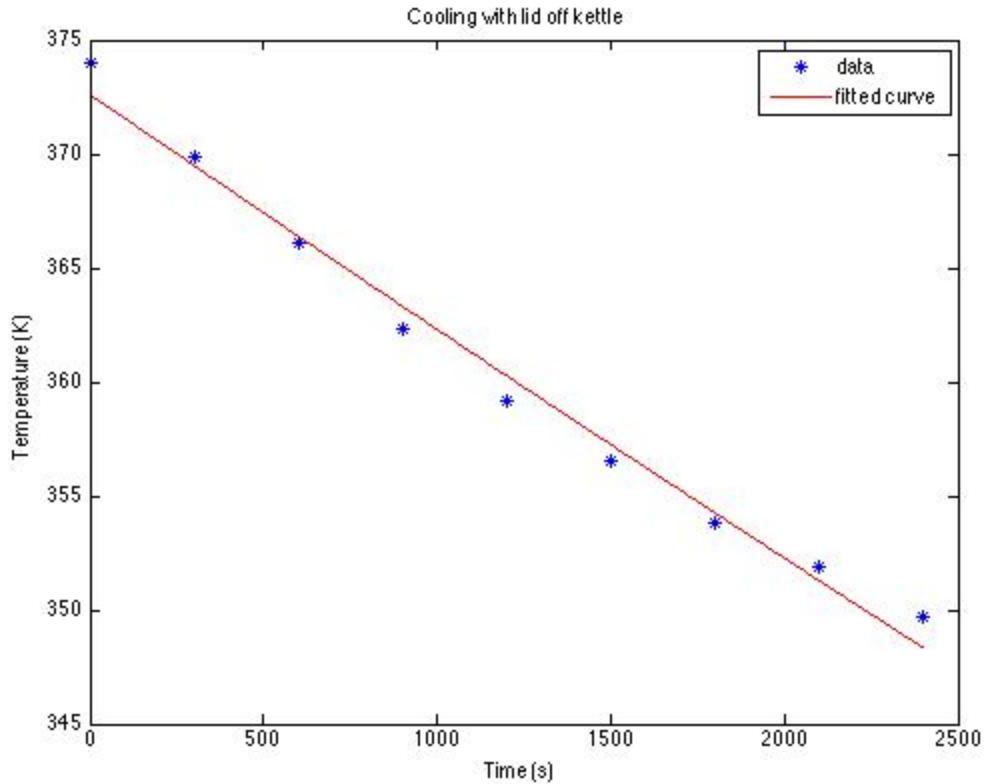
I was amazed at the difference in the cooling rates between leaving the lid on and having the lid off. The lid off was colling at ~4+ times the rate. I also think leaving the extractor fan above the kettle on has increased the rate of cooling. There may also have been slightly less water in the kettle since I did boil for 5 min but this should not have made much of a difference.

**MORE MATHS**
Temperature seemed to be following exponential cooling rate.
$T = Ce^{-Dt}$ (equ 5)
where C and D are constants, T is temperature (K) and t is time(s).
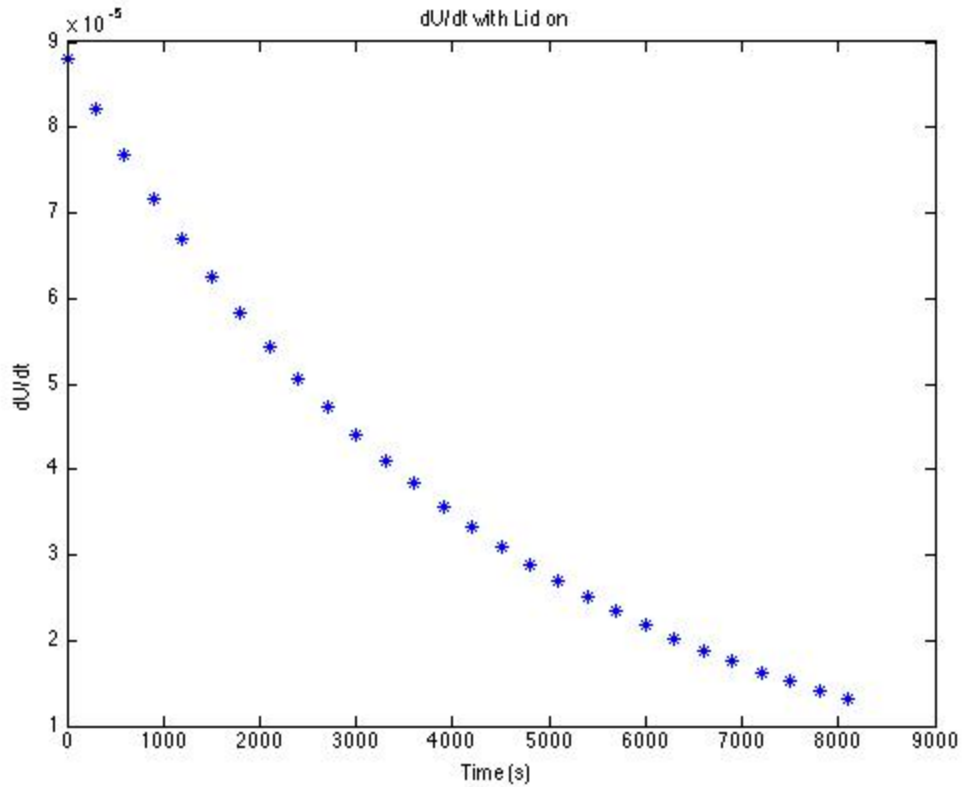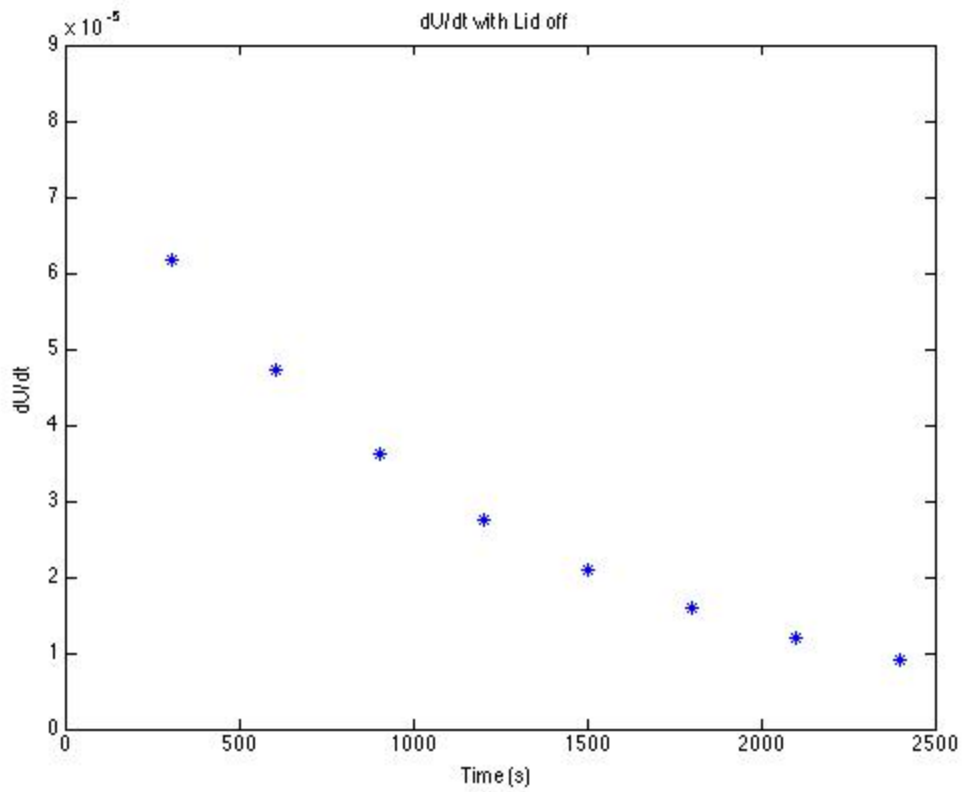I used matlab to fit the data.
For experiment 1(lid on)
C = 373.7236
D = -7.3069*10^-6

For experiment 2

C = 372.6305
D = -2.8059*10^-5

Now that we have found equations for how the temperature (T) (equ 5) changes with time (t) we can find how our rate of utilisation ($\frac{dU}{dt}$) varies with time. By plugging all the numbers in and replacing T (equ 5) in the equations we can calculate $\frac{dU}{dt}$ (equ 4) .

dU/dt with Lid off

By using our equations for temperature  (equ 5) given the time we can find change in U (dU/dt) for each second  (equ 4). Then by finding the area under the dU/dt curve (or integrating) we should get the total utilisation (U).

Area of dU/dt with Lid on
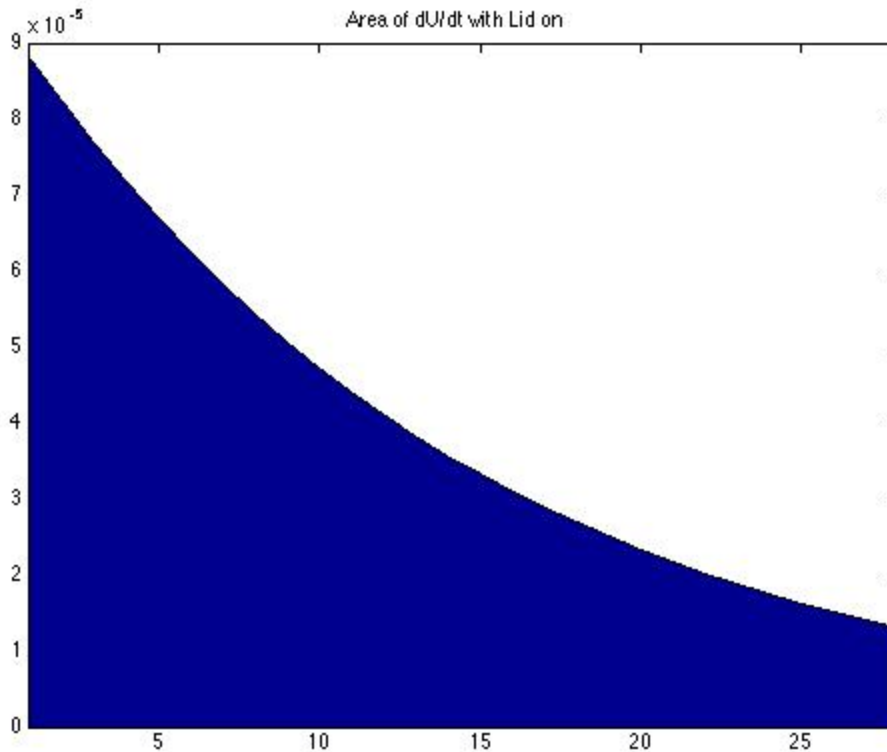
**Utilisation for both cooling rates**
The results are quite surprising.
For lid on
U = 32.18%
and lid off
U = 7.98%

There is quite a startling difference but it should not be that surprising given the difference in cooling rate. This means that a no chill, flame out addition left to cool with the lid on will contribute similar amount of IBU as a 60min addition. While lid off was similar to a 10-15min addition. However when you think about how the 'lid on' was still above 80C after 2 hr maybe it is not that surprising how many IBUs were added in the lid on situation.

**Checking against current utilisation estimates**
To make sure I had not made a mistake and was actually calculating something in the realms of reality, I checked the equation for a constant boiling temperature (100C). That is, I calculated utilisation for when T was held at 100C for various times. Just as the equations will work for a changing temperature, they will also work for a fixed temperature.

| Time | U (Calculated) | U (Rager) | U (Tinseth) | U (Paper 2 (2)) |
|------|----------------|-----------|-------------|-----------------|
| 10   | 5.14%          | 6.7%      | 10.4%       | 4.4%            |
| 30   | 14.65%         | 17.1%     | 22%         | 13%             |
| 60   | 27.16%         | 30.8%     | 28.6%       | 27.9%           |

The calculated U agrees mostly with the U from [2]. This is hardly surprising since this was the data used to find the constants in the equation. It is also fairly agreeable with the other established methods of calculating IBU (Rager and Tinseth). You can see that this equation is actually a conservative estimate of IBU as it gives slightly lower results than other methods. Overall it looks like my results might actually mean something.

**Finding a practical cooling rate for my brew system**
Now to generate something useful I needed to get the cooling equation for how my system would perform during an actual brew. Since I no chill I use a cube to cool the wort in. After 1 test brew it became apparent that my cube was cooling faster than 'lid on' but slower than 'lid off'. I had assumed that the cube and lid on would be pretty similar. In order to get an equation for how my system will perform during an actual brew, I needed to combine the cooling rates of 'lid off' and my cube to simulate how my system would cool before, during and after being added to the cube

This lead me to re-run the cooling experiment in a cube and find the cooling equation for it. Once again I brought 27lt up to a rolling boil in my kettle then drained to my cube. I found that it took ~5min to drain the kettle to the cube and the cooling in this time was the same as 'lid off' (wort was at 96C once the cube was full). Then put the cube one the garage floor (as I normally do with a brew) and took temperature readings of my cube every 10 min (could not be bothered with the 5 mins). I used this data to find my cooling equation for the cube. It turned out that the cube was cooling at roughly twice the rate of the 'lid on' and half the rate of 'lid off'.

I used this data to come up with a plan for how I would cool my wort each brew. I decided I would leave my wort with the lid off for 15min before adding to the cube. This would mean I would be transferring the wort to the cube at ~90C (still as safe temperature I think). During this time I can do any type of hop additions I want (hop burst etc).
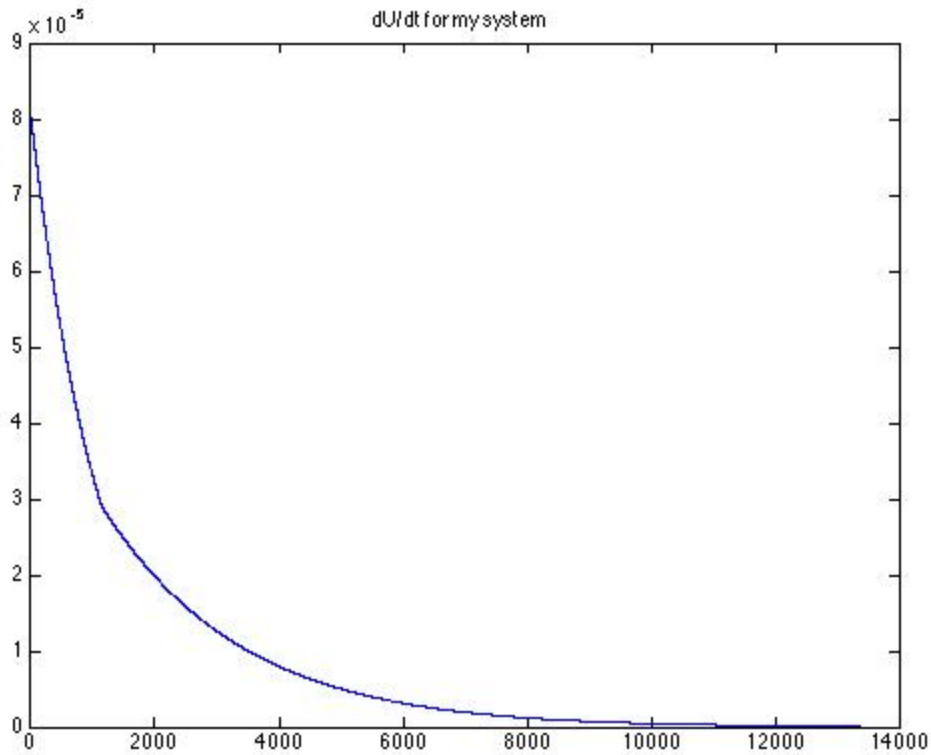
dU/dt for my system

Above is the graph of dU/dt for my system with 15min of 'lid off' cooling before adding to the cube. You can see the kink in the graph is where the wort is cubed. This is because the rate of utilisation is dropping faster while the lid is of before being added to the cube.

**Testing the formula on an actual brew**
To test the formula I decided to brew a beer that would test the formula as mush as possible. After all, the real test is whether the formula is useful enough predict IBUs in the final beer. I elected to brew a beer with a big hoppy flavour and aroma from late additions. This is the kind of beer that no chillers have been struggling with or thought unable to brew. I brewed a 'West coast IPA' style beer. Below is the hopping schedule.

# Hops

| Amount | Variety | Type | AA | Use | Time | IBU |
|--------|---------|------|------|-----------------------|--------|-------|
| 15 g | Columbus | Pellet | 13.9 | Boil | 60 min | 18.73 |
| 35 g | Columbus | Pellet | 13.9 | Whirlpool at 76 °C | 60 min | 4.3 |
| 20 g | galaxy | Pellet | 14.5 | Whirlpool at 76 °C | 60 min | 2.23 |

| 15 g | Nelson Sauvin | Pellet | 12 | Whirlpool at 76 °C | 60 min | 1.59 |
|---|---|---|---|---|---|---|
| 15 g | Columbus | Pellet | 13.9 | Whirlpool at 90 °C | 15 min | 6.34 |
| 10 g | galaxy | Pellet | 14.5 | Whirlpool at 90 °C | 15 min | 4.41 |
| 5 g | Nelson Sauvin | Pellet | 12 | Whirlpool at 90 °C | 15 min | 1.82 |
| 15 g | Columbus | Pellet | 13.9 | Whirlpool at 95 °C | 7.5 min | 7.94 |
| 10 g | galaxy | Pellet | 14.5 | Whirlpool at 95 °C | 7.5 min | 5.52 |
| 5 g | Nelson Sauvin | Pellet | 12 | Whirlpool at 95 °C | 7.5 min | 2.28 |
| 15 g | Columbus | Pellet | 13.9 | Whirlpool at 100 °C | 0 min | 10.35 |
| 15 g | galaxy | Pellet | 14.5 | Whirlpool at 100 °C | 0 min | 10.79 |

The whirlpool times are the time the addition was made to the wort after flame out. You can see they are listed in the reverse order for when they are added(sorry). I was able to calculate a utilisation for each hop addition using the utilisation formulas for my system that I derived and enter it as a whirlpool addition in the software to get an estimate of IBU. This came to a total IBU of ~76.

| Time after flame out (min) | Wort Temperature (C) | Calculated Utilisation (%) |
|---|---|---|
| 0 | 100C | 12.9 |
| 7.5 | 94.9 | 9.9 |
| 15 | 90.3 | 7.9 |
| 60 | 75.9 | 2.3 |
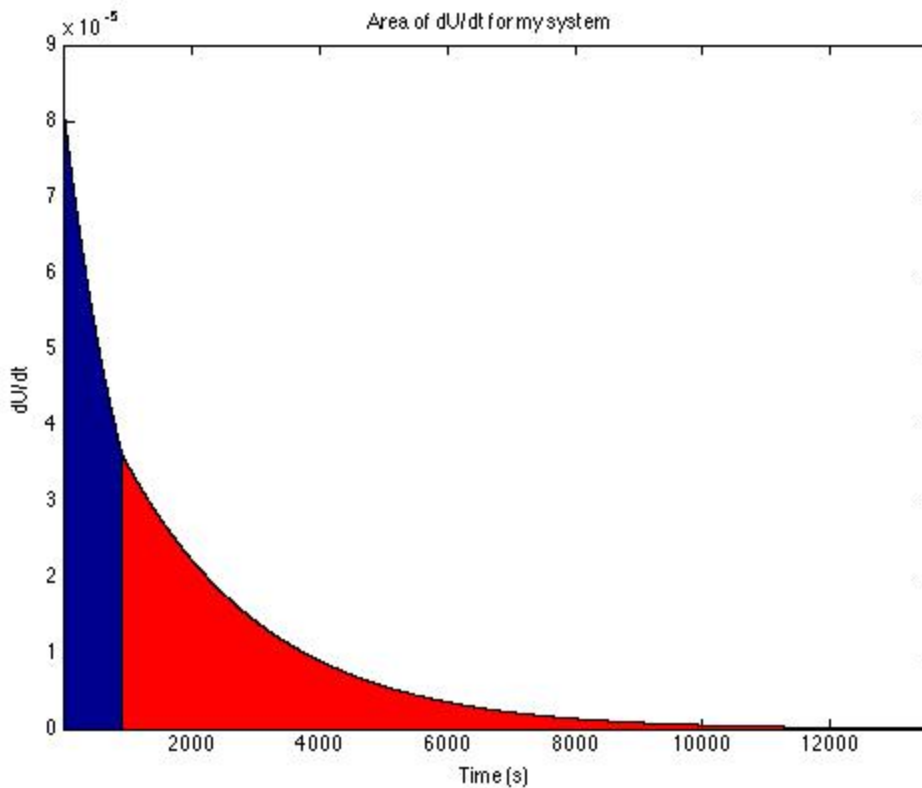
*Rate of utilisation graph and areas for 0 min (100C flame out) (blue + red) and 15 min (~90C)(red) hop additions.*

In the above graph you can see a hop addition added at flame out will have a utilisation of the whole area under the graph (blue + red). Where the 15 minute (900 seconds) addition will have the red area utilisation.

Unfortunately this brew is still in the fermenter and I can not tell you how it tastes yet.

**Examples of system rates of utilisation**
To give people a better idea of how utilisations from different systems and cooling techniques differs I made a few examples.

**No chill straight to cube**
This is the utilisation estimate for a flameout addition when the wort is transferred to a cube straight after flameout, without a hop stand or whirlpool.

dU/dt for my system
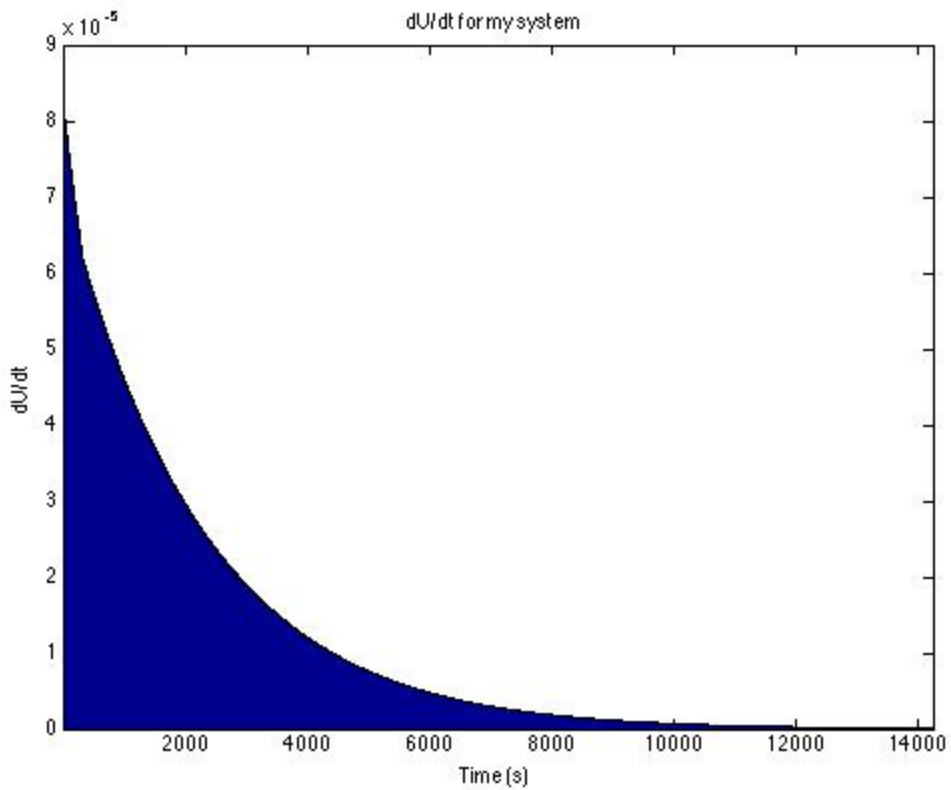
U= 15.9% This utilisation is similar to a 25 min boil addition.

### 15 Minute whirlpool with lid on then chill
This is the utilisation estimate for a flameout addition when the wort is left with the lid on for 15 minutes (900 seconds )before fast chilling often referred to as a hop stand or whirlpool.

dU/dt for my system
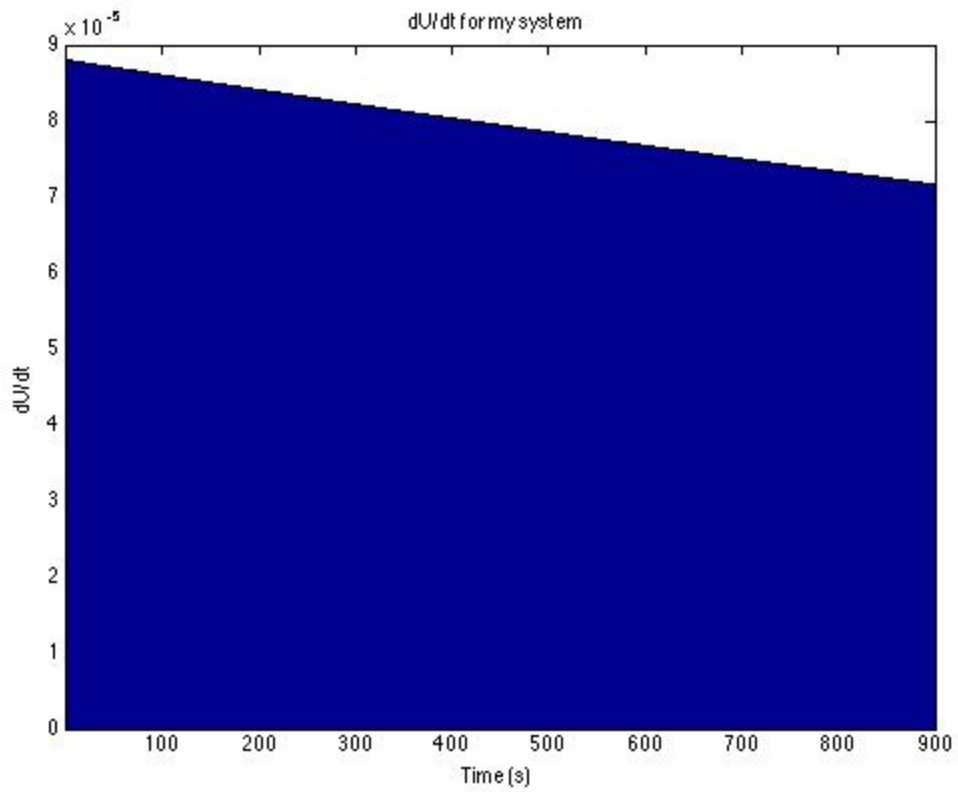
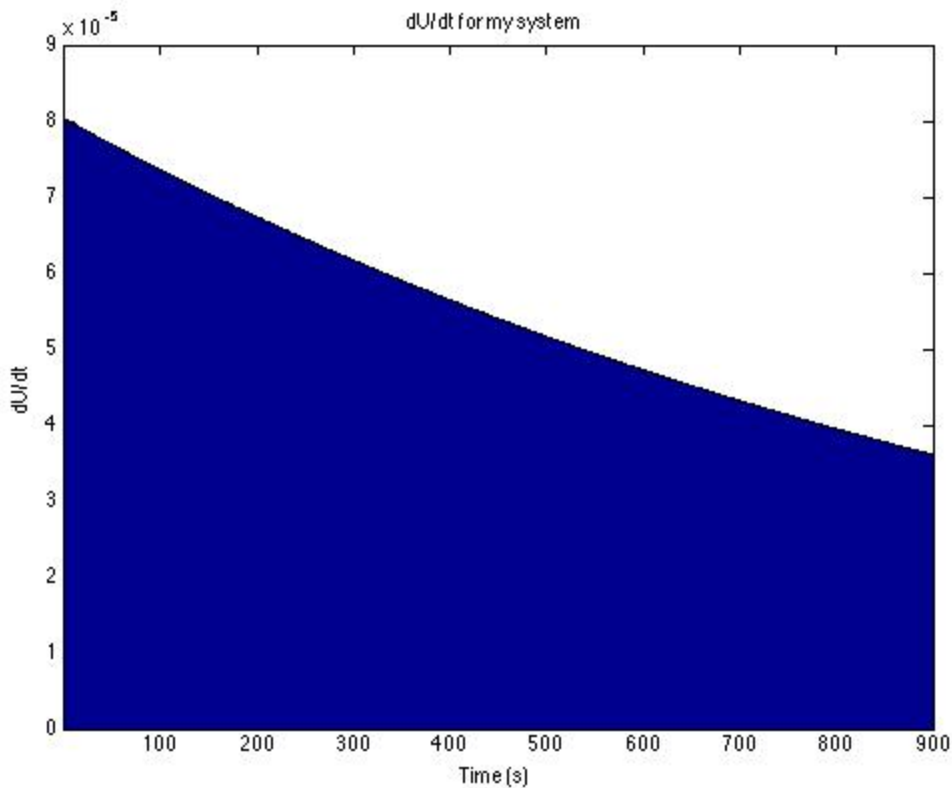U = 7.2%.

## 15 Minute whirlpool with lid off then chill

This is the utilisation estimate for a flameout addition when the wort is left with the lid off for 15 minutes (900 seconds )before fast chilling often referred to as a hop stand or whirlpool.

$U = 5\%$.

**Conclusions**
Most brewing software lets you input whirlpool additions but it asks for the utilisation. Using this method we can get an estimate of this utilisation from hop additions during a hop stand/whirlpool. No chill brewers can also add their flameout/cube hops as whirlpool additions in their software and get an IBU contribution estimate.

As a no chill brewer, I know now I am going to be letting my no chill wort cool with the lid off for about 15 min (90C) before cubing. During this time I can make hop additions and have an idea how how much bitterness I am actually going to get.

If this method is somewhat correct, it may give you some sort of understanding of the bitterness levels to expect it will not tell you anything about the aroma or flavours. Just because a flame out hop addition on a no chill system can give you a similar IBU contribution as a ~15 min boil addition when chilling does not mean they have the same flavour or aroma contribution. That is something that people are going to have to figure out with experimentation.

I think the most important thing to take away from this article is how important it is knowing your system and the massive impacts your methods for no chilling/whirlpooling can have in the final product (your delicious beer).

You should be able to figure out your rate of cooling and make some sort of adjustment. If not hopefully I have at least given you a good idea of how your system will be cooling and some sort of IBU contribution you might be getting from your hop additions after flame out.

**Further Stuff**
1) If there is enough interest I might make a tool/spreadsheet(I have not really thought about it much) that people can enter their cooling equation and hop additions to get an estimate of utilisation. You could then plug this into your normal brew software.

2) I would like to test this against some real world data. I don't have acess to the equipment needed but I am considering contacting someone from a  university and seeing it anyone is interested in this work and may want to produce a proper paper on it.

3) If this formula works I would also like to include a wort gravity factor in it and possibly iso-alpha degradation.

4) Please be constructive with criticism.

**Limitations**

1) The equations demonstrated do not factor iso-alpha degradation.

The first paper listed [1] does account for degradation of iso-alpha acids. Some of you are probably aware already (I was not) not only are alpha acids isomerised but iso-acids are degraded. This means that the ios-acids are converted to something else. The higher the temp the faster it all this happens. As it happens temperatures below 100C (as in whirlpool and no chill) this happens relatively slowly.

This paper does exactly what I had been looking for.  However on closer inspection it is obvious that the 5.2 pH acetate solution that they use is fairly different than our beer wort as they get max utilisations of 60%+ which is much higher than we see as brewers. eg. 1 hr boil at 100C yielded a utilisation of ~47% where the software that I use predicts utilisation of a wort of 47 OG to have a utilisation of 28-31% depending on the method selected.

Luckily the rate of degradation of iso-alpha acids is lower the lower the temperature. It appears that in the temperatures and time frames we are interested utilisation can still be modelled by a single exponential pattern. This seems to be what was done in [2].

Ideally i would like to run the experiments that [2] did with the methods of [1] how ever I don't have access to the equipment. Hopefully it does not matter anyway.

2) This method is highly dependent on how accurate your cooling equation is and the accuracy of the equation of the rate constant k. There are methods to fit curves to data in excel spreadsheets but I am not familiar with them (I use Matlab).

3) There may be a temperature that isomerisation no longer occurs rather than it just taking longer and longer. I have seen figures of 80C and 75C quoted as the limits of isomerisation. Clearly isomerisation does still occur at 80C, [2] proved this. It may just be that isomerisation is happening so slowly that people choose to ignore it. I was unable to find an papers discussing this.

4) This formula does not account for OG, which I think is pretty important.

**Disclaimer**
1) IBUs are affected by almost everything we do as a brewer (OG, temperature, time, pH, pitch rate amount of trub etc). No matter how good our formulas are they will only be an estimation. These methods  have outlined are really only an estimation of an estimation.

2) I am not a chemist or food scientist, however I am a research scientist in another completely unrelated field. I am not part of a lab that has access to HPLC equipment, just a curious bloke with a thermometer, access to research journal articles and some Mathlab skills.

3) This was something I put together relatively quickly in my spare time. I am human and have probably made some mistakes. I have not done rigorous checking yet.

4) This is an informal article, not a scientific paper and I have structured it as such. I have tried to make it more readable and easier to understand (I may have failed miserably).

5) My spelling and grammar can be atrocious.

6) I might be an idiot and the whole thing might be wrong.