## Thermal Operations In Food Process Engineering: Theory And Applications Prof. Tridib Kumar Goswami Department of Agricultural and Food Engineering Indian Institute of Technology, Kharagpur

## Lecture – 54 Thermal Death Reaction Kinetics

Good morning. We have done a lot of heat transfer, heat transfer analysis from various angles right from the basic to a very complicated of NTU for heat exchangers we have done right. Now let us look into because we are coming to the end of the course, only few lectures are left. So, we should also look into some of the applications right. There are many major applications for food and other in all industries because heat transfer is one of the basic in most of the industries; I do not see in all industries, but in most of the industries thermal is a part, a non-thermal is any industry oriented work non thermal it may not be so much, but thermal is always associated.

And of course, in such a short course around say 30 in 60 lectures, it is just not possible to cover everything in detail right from the basic. So, that is why I decided that if the basic is strong, then you can handle any situation anything which you will come across right.



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So, let us do today on this that lecture number 54 this Thermal Death Reaction Kinetics or thermal death time things like that right so; obviously, the word thermal and death is associated with microbes right.

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So, microbes whose death kinetics; obviously, we are not going to do the kinetics of the death, but definitely we shall handle something related to the thermal where temperature at least is associated right. So, if temperature is associated we have come across by this time how to handle different temperatures or transfer of heat through those these we have come across. So, to look into that; let us look some think like that sterilization right. The word itself sterilization tells that the product is absent from the microbes sterile right.

Obviously the word sterile and sterilization they are not identical; had it been identical then there would not have been two words, but sterile usually is associated with the non-vegetative earlier vegetative cells are all destroyed whether it is pathogenic or nonpathogenic whatever there all destroyed, but in sterilization it is all the organisms which are destroyed. But common concept is that all the organisms are destroyed means there is no organism right, but mathematically it is not possible to bring it to 0. It is never possible to bring it to 0 why and how that is what is our point of concern right.

So, let us look into that. Sterilization which is a first order reaction; obviously, if you ask me again need to go into the detail of the reaction orders; first order kinetics, second order kinetics, 0<sup>th</sup> order kinetics those I am third order kinetics I am we are not going to do that the first order is the very simple one right.

So, the rate of the reaction in each moment is proportional to the amount of the microbes still to be degraded. If N be the if N is to indicate the number of microorganism present in the system at any given moment the variation of this number as the function of chosen time t of exposure to the selected sterilization temperature that can be written as dN dt right dN dt = -k N where N denotes the number of organisms present in the system at any given moment and t is the time of exposure how much time it is exposed to that environment right.

So, this dN = -k N, why minus because as the time is progressing the number is decreasing that is why it is negative that everywhere we have seen in heat transfer also we have seen that minus k dt dx right. So, they are also we have seen as the x is a progressing temperature is decreasing right. So, that is the same thing here also number is decreasing as the time is progressing that is why negative and k is a proportionality constant right for k is a constant which is typical of the species and conditions of the chosen microorganisms.

Obviously, this k is not fixed or a constant it depends on the species organism which you have taken as well the environmental conditions all put together that k is a constant right. This seems to be obvious for dry sterilization because dry sterilization means you are by some means you are heating where there is no moisture; it is all dry heat which we called dry heat right, but less rigorous for steam sterilization.

So, if you are using steam as the medium for sterilization this may not all good right in which is a water vapor molecules also seem to take part in the reaction like reaction means in this the this is in degradation of the numbers. Actually this bimolecular reaction is of the first order since the steam is present in high excess, all the reaction long and its concentration may be regarded as constant. The above expression can be developed as dN / N that dN / N = -k dt this is rearranged and rewritten as dN / N = -k dt.

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By converting from base e or this is dN /dt right. So, by converting base e or that is called Naperian logarithms which are less practical in this specific case to the base 10 logarithms, the following is obtained that is  $\log N = -k t$  where -k t plus of course, constant  $\log N = -k t$  plus the constant where k is that this k = K / 2.303 right 2.303. Due to the shift from the base e logarithm to the base 10 with this change of k to k / 2.303 is required this is small k.

If you remember earlier it was capital K. So, that capital K is impressed by small k with K /2.303 because we shifted from 1 N to this log 10 base right this is 2. At some 0, the following is also true at time t = 0 N is N<sub>0</sub> and log N<sub>0</sub> is equal to constant right. Therefore, log N = - k t + log N<sub>0</sub> that is that N<sub>0</sub> or constant value right. So, this can be rearranged that log N /N<sub>0</sub> = - k t or we can again rewrite it as N / N<sub>0</sub> = 10<sup>-kt</sup> where again k small is equals to capital K / 2.303 where capital K was related to that N right.

So,  $N_0$  is the initial number of microorganism, N is the number of microorganism after the exposure time, t t is the elapsed exposure period or which can be told as the elapsed time for sterilization time and k is small k is the reaction rate constant which depends on the space species and conditions of the microorganism taken or chosen.

Hence, it can be calculated that the required it can be calculated that the time required to reduce the microorganism concentration to any preset value is the function of its initial concentration that is what we see that the time required this. That is this the time required

to reduce the microorganism concentrations from a preset value preset value is  $N_0$  is the function of its initial you know preset value means whatever you want to do that is N not  $N_0$  is a function of the initial concentration right initial concentration is this. This is the preset one right. So, this N which you want to and this is a function of which was originally present right.

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So, from these we can now look at the sterilization reaction is therefore, either and all or nothing process nor a potential barrier process as we used to think off right because, we said that N /  $N_0$  right. So, this is the set value which you want to correct and it can never be 0 is a function of N 0 that is whatever was the initial. For that a new term has been introduced as called D-value or decimal reduction time.

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The D-value is defined as the decimal or decadal decimal or decades from that decadal one decade is 10 right. So, decadal or decimal reduction or decay whatever we call time that is it is the time required at the specified temperature t to reduce the microbial population being considered by one logarithmic cycle or value. That is from 100% to 10% of the initial value right. This is that 100% to 10 % of the initial value right.

So, it is 0.9 z value or temperature coefficient another terminology is that the z value is defined as the temperature coefficient of microbial destruction that is as the number of degrees of temperature which causes a tenfold variation of D or more generally of this sterilization rate.

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So, we defined two terminologies. One is D and other is z value and if we look at for different value of z and F for typical microorganisms for different microorganisms, we see that if it is the microorganism that is clostridium, botulinum is one whose  $D_{121}$  is 10° right. Whereas, Giobacillus stereo stearothermophilus right that value is 2  $D_{121}$  and z value is 6 bacillus subtilis whose  $D_{121}$  value is 0.5 in minutes whereas, z value is 10 °C bacillus megaterium D value is 0.04.

Whereas, z value is 7 and clostridium sporogenes is 0.8 to 1.5 whereas, z value is 13 °C and clostridium histolyticum is 0.01 d value whereas, z value is 10 °C

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So, with all these it is apparent that depending on the microorganisms the value of d or z are varying right both D and z are functions of the microorganisms and the environment because here we have said it is  $D_{121}$  it could have been any other right. So,  $D_{110}$  that would have different z value or  $D_{131}$  that would have another z value which says that as we said in the beginning that depending on the species that is which one we are taking or depending on the environment dictates by this that this 121 corresponds to what pressure and what pressure of steam etcetera that will dictate this and then the z value also changes right. So, this is a unique thing which you have learnt.

Now so,  $f_0$  or equivalent exposure time another parameter we are bringing in where D value is a function of the exposure time, T in saturated that is condensing why because if this is a steam heat transfer we have already done.

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AVERAGE VALUE OF D AND	z FOR SOME TYPICAL MIC	ROORGANISMS	
Microorganism	D <sub>121</sub> (minutes)	z (°C)	
Clostridium botulinum	0.2	10	
Geobacillus stearothermophilus	2.0	6	
Bacillus subtilis	0.5	10	
Bacillus megaterium	0.04	7	
Clostridium sporogenes	0.8 - 1.4	13	
Clostridium histolyticum	0.01	10	
Fo or EQIVALENT EXPOSURE TIME:- LW D-value is a function of the exposure temperature T in			
saturated, (i.e. condensing) steam conditions for each			
different microorganism; $D = D(T)$ . On the basis of the			
definition of coefficient z it has al	so to be: $D(T - z) = DT X$	10.	

So, if this is this is steam so, when it is giving away its latent heat of condensation. So, from the steam vapor it becomes liquid water at the same temperature  $100 \,^{\circ}$ C.

And this is what we have we know is condensation. We have found out what is the condensation heat transfer coefficient etcetera right condensing vapor heat transfer coefficient etcetera. Steam conditions for each different microorganisms are different. So, that is why D is a function of  $D_T$ . So, on the basis on the basis of the definition of coefficient z it has also to be D is function of  $D_T - z = D_T \times 10$ .

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)	With the obvious condition that D which satisfies this relationship is: D value at the temperature T <sub>0</sub> for a giv Let us now calculate the time int temperature T <sub>0</sub> the same reduction actual exposure temperature T, co interval 't'. It has obviously to be: $\frac{dN}{dt} = -kN$ and the definition of D $\int_{0}^{0} \frac{d_0}{d_0} = \int_{0}^{1} \frac{d}{d_0}$	= $D_0$ if $T = T_0$ , the mathematical function = $D_0 X 10^{\frac{T_0 - T}{Z}}$ (A) where $D_0$ is the D ren microorganism. terval required to obtain at a constant of a microbial population obtained at the population obtained at the ontinuously variable over a certain time and from the relation $\frac{dN_{T_0}}{N} = \int_0^t \frac{dN_T}{N}$ value
1	<u>, a e</u> .	

So, we can say that the obvious condition that  $D = D_0$ . If T becomes  $T_0$  then the mathematical function which satisfies this relationship is  $D = D_0 \times 10^{(T0 - T)/z}$  right. So, if  $D = D_0$  when T is  $T_0$ , this situation mathematically satisfied from the is satisfied from the relation that  $D = D_0 \times 10^{(T0 - T)/z}$  right.  $D_0$  is the D value at the temperature  $T_0$  for a given microorganism.

So, now let us now calculate the time interval required to obtain at a constant temperature  $T_0$ , the same reduction of a microbial population obtained at the actual exposure time T right; obtained at the actual time exposure not time sorry temperature T right. Just by looking at this T then I thought that I mispronounced and it should be pronunciation should be t, but temperature what temperature continuously which is continuously variable over a certain time interval of small T.

It has; obviously, to be like this that integration between 0 to  $T_0 D N$  at  $T_0 / N t= 0$  to T D N T/ N value right. So, D N  $T_0$  over N between 0 to  $T_0$  value integration is equals to 0 to T D N T / N value right. So, this means that 0 to  $T_0 D T_0$  right 0 to  $T_0 D T_0 / D_0 = 0$  to T D T / D right. So, this is rewritten in this form that D of  $T_0$  over D<sub>0</sub> between 0 to  $T_0$  and 0 to T D T / D which we have already seen earlier right.

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	D-value is variable with the actual exposure temperature and is given by expression (A), but D <sub>0</sub> is $t_0 = \int_0^{\infty} \int_0^{\infty} \int_0^{\infty} \dots (B)$ constant, so we can write: It is thus possible to calculate the lethal effect of the exposure of a microbial population to a variable temperature T by relating it to a hypothetical sterilization performed at a constant temperature T <sub>0</sub> for the time t <sub>0</sub> . If the constant reference temperature is assumed equal to 121.11 °C (250 °F) and the z-value equal to 10, the equivalent time given by expression (B) is named F <sub>0</sub> : $F_0 = \int_0^t 10^{\frac{T-121.11}{10}} dt \dots (C)$
9	6 2 3 C 6 2 1

So, from this we can say that D value is variable with the actual exposure time temperature and is given by the expression say a which was earlier shown that

temperature a expression was shown earlier right. This we can say here. So, this was here that  $b = D_0 \times 10^{(T0-T)/z}$  that is true for this temperature for this expression right.

So, we can write that D value is a variable with the actual with the actual exposure temperature and is given by the expression a, but  $D_0$  e is as  $T_0 = 0$  to T D  $10^{(T - T0)/z}$  to dT right. So, this is for relation B and  $D_0$  is a constant. So, we can write that it is we can write that  $T_0$  is 0 to T  $10^{(T - T0)/z}$  to dT. So, it is thus possible to calculate the lethal effect of the exposure of microbial population to a variable temperature T by relating it to a hypothetical sterilization performed at a constant temperature  $T_0$  for the time small  $T_0$ .

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\*\*\*\*\*  $T - T_0 dt$ D-value is variable with the actual exposure temperature and is given by expression (A), but  $D_0$  is a  $t_0 = |10|^Z$ ...(B) constant, so we can write: It is thus possible to calculate the lethal effect of the exposure of a microbial population to a variable temperature T by relating it to a hypothetical sterilization performed at a constant temperature To for the time to . If the constant reference temperature is assumed equal to 121.11 °C (250 °E) and the z-value equal to 10, the equivalent time given by T - 121.11 dtexpression (B) is named F<sub>0</sub>:  $F_{0} = \int 10^{-10}$ 

If the constant reference temperature is assumed equal to 121.11 °C corresponding to say 250 Fahrenheit. This 250 Fahrenheit converted to 121.11 °C because conversion of degree Fahrenheit to degree centigrade is that decimal association right. And, the z value equal to 10, the equivalent time is given by this expression B right and this is named as F 0. So,  $F_0$  is equals to 0 to T 10<sup>(T-121.11) /10</sup> times dT here only that T<sub>0</sub>, we have taken as 121.11 correct for the  $F_0$ .

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So,  $F_0$  is the equivalent exposure time at 121.11 °C of the actual exposure time at a variable temperature calculated for an ideal mechanism with a temperature coefficient of destruction equal to 10 °C.  $F_0$  means the equivalent amount of time in minutes at 121 °C or 2 250 Fahrenheit which has been delivered to a product by the sterilization process. If we assume that if we assume a sterilization lasting 15 minutes constantly at 121 °C, we then obtain  $F_0 = 15 \times 10^{(121-121)/10}$ . So, this becomes 1.

So, it is 15. So, 15 minutes which is according to the definition of  $F_0$  right. So, and that is if that then from there we can also say that there is a lethal rate there is a term called lethal rate. Due to the exponential expression of the calculation of  $F_0$  so, calculation of  $F_0$ is not immediate tables have. Therefore, been developed which list the so, called lethal rates that is the equivalence coefficient allowing to compare the exposure at the temperature T to the exposure of for this same time at 121 °C. Lethal rates may also be regarded the  $F_0$  values for single unit time right.

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So, we can see it from this that this is the table where we can say that the lethal rates are like that for different temperatures right. It is assumed that at z = 10 °C. Therefore, F<sub>0</sub> values are calculated by its rigorous definition at 121.11 °C corresponding to 250 °C right and these are those values. So, here we see ninety then plus 0 is this when a 0.1, 0.2 like that up to 0.9 the values are there. So, rigorous 90 to 130° the lethal rate values are given right.

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So, if that be true, then we can say that in condition of saturated steam for reference temperature of 121.11 °C, z is 20 °C and for the temperature values between 90 to 130 °C with intervals of 0.1 °C is like this right.

So, we have seen what is the z value and similarly another one; z values are assumed and 12 as z values are assumed as variable between 7 and 12 and different equivalent times at 121 °C are calculated on such a basis it is in interesting to notice how much the variation of z value considerably influences the lethal rates when T varies T varies. Now sterile which is free from viable microorganisms which I said earlier and sterilization any physical or chemical process which destroys all life forms with special regard to microorganisms including bacteria and sportiness forms right.

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So, with this perhaps we come to the close of the thermal death time or death rate whatever we call. We have not shown you specifically the different rates right or the temperatures, only we have said about the temperatures and time right. So, that temperature you can bring yeah with the pressures like add to 1 atmosphere pressure g it is 121.11 degree centigrade ok.

Thank you.