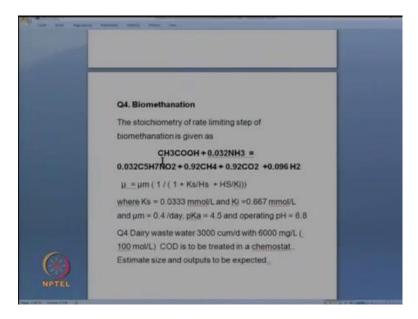
Advanced Chemical Reaction Engineering Prof. H. S. Shankar Department of Chemical Engineering Indian Institute of Technology, Bombay

> Lecture - 37 Illustrative Examples

(Refer Slide Time: 00:26)



Today we will be looking at this biomethanation reaction. Now, what happens in biomethanation is something like this.

(Refer Slide Time: 00:30)

BIOMETHANA TION Insoluble Organics Extra Cellular Enzymes Solubilizes organics volatile Acids by acid producing bacteria (Acetic Gasification by Hethane producing Dacteria (C#4, CO2)

Generally you have insoluble organics say if you going to a let say a dairy industry for example, the waste organics lot of solids are coming. So, insoluble organics they gets digested by extra cellular enzymes in the reaction equipment and become soluble organics. And then volatile acids from in bacteria works on it; it give you a acetic acid; and then gasification by methane producing bacteria it will give you methane and carbon dioxide. So, is the 3 step reaction that is what you see in the biomethanation process.

Stage 1 is solubilization, stage 2 is acid formation, and stage 3 is gasification using methane bacteria. Now, generally we find that it is not a bad assumption to assume that the methane producing step is the slowest step of the reaction. So, is the mostly design therefore is done on the basis of this assumption that methane producing is the slowest step. Although, there are instances where this solubilization is quite slow as a result we may have to take this also into our account. So, as well this problem is concerned we are looking at production of methane using acetic acid as a substrate and that is a chemical reaction that is set up acetic acid.

(Refer Slide Time: 01:55)

STOI CHIOMETRY CH3 COOH + 0.032 NH3 = 0.032 Cs H7 NO2 + 0.92 CH4 + 0.92 CO2 + 0.096 H20

So, this is the chemical representation what is going on acetic acid this is the nitrogen that is present in the environment to give you some bacterial growth; which is this is the chemical representation of bacteria and methane and carbon dioxide ok. So, you notice here the roughly equal quantities of methane and carbon dioxide is produced volume basis; there is lot of literature in biomethanation over the last 30, 40 years many many plans have been set off all over the world. It is a reasonable well known technology; there are many problems with it we will talk about it as we will go along. Now, what is seems to be an appropriate growth function is a let me write down the growth function.

(Refer Slide Time: 02:43)

The growth function is something that we have set up it look something like this mu m mu equal to mu m within brackets 1 by 1 plus K s by H s and H s by K I; this was a propose by Graef and Andrews rules bay back in 1974; there is a lot of material on this what is H s? H s is the an ionized acid. So, this is the an ionized part acetic acid which is the which was is important as far as the a growth function is concerned ok.

The numbers are given K s is given K i is given this form of Graef function we have seen earlier also; this is the form where substrate inhibits the rate of chemical reaction. And, therefore we would like to operate the process at H s value equal to K s times K i square root. So, the best choice of H s which is the substrate which is active as far as the process is concerned is square root H s times K i we can calculate that is from here. So, what you want look at is a very important area dairy waste water just taken 3000 cubic per day 6000 milligram per liter 6000 roughly 100 mile mole is not mole 100 mille mole sorry 100 mile mole per liter is the concentrational acetic acid they will come out of this 3000 milligram per liter sorry 3000, 6000 milligrams per liter ok; it is being treated in a chemostat. Chemostat is our C S T R equivalent of which we are talk about all ready; what you want to do is what just get an idea of the size and what are the outputs that we can expect?

Now, in go around the world you find that dairy waste waters what they would do is that they would first do a biomethenation. And, as you will see as you go around this problem you will see the biomethanation is not able to complete remove or consume this 6000 milligram per liter; it is only able to do part of it. And, the other words the effluents come out of dairy waste water still is vary concentrated from the point of view of discharge. So, you will have to do another step of treatment before it to suitable for discharge. So, we will have to look at that also find out how to handle this kinds of problems.

So, if this is the rate function where mu is mu m times this one; so what is the best choice of H s that we will take? What is that value, tell me?

Student: (Refer Time: 05:34)

What is that please calculate and tell me?

(Refer Slide Time: 05:37)

M I+ Ks HS mmol/L 0.0333 mmor/L s" H+ / HS рн - 6.8

This is the ionization reaction here K a is given K a is given somewhere I think K a is 4.5 and operating P H is 6.8. So, you can find out what is the H s value? So, the H s at which we will operates 0.15; is there with everybody 0.15 root of k 1 k 2 K s K i square root is 0.15; is it all right do we all agree?

(Refer Slide Time: 06:06)

$$(Hs) = \sqrt{K_s K_i}$$
opt
$$\sqrt{(0.0333)(0.667)}$$

$$= 0.15 \text{ mmoL/L}$$

$$\mu = 0.4 \left[\frac{1}{1 + \frac{0.0333}{0.15} + \frac{0.15}{0.667}} \right]$$

$$= 0.27/d.$$

This is what I have got H S optimum I got 0.15. So, as per the data given the best choice mu equal to D correct we must have mu equal to D chemostat mu equal to D. Therefore, dilution rate at which we will operate is 0.27 per day; is it can you please calculate and

tell me whether this mistake in my calculation 0.27 per day is 0.27 is all right? So, what should be we have?

(Refer Slide Time: 06:43)

D= / = 0.27/d V: F/D= 3000 M3/d 0.27/d 11111 m HS= 5 H+/Ka 0.15 104" = 29.9 mmoL

So, our equipment volume should be 3000 divided by 0.27 that is about 11000 cubic meter is what you get no 3000 divided by 0.27 is about 11000; is it all right 11000 is ok. So, what is the now if it is 11000 what is the value of S minus I will get is a 1795, S minus comes from the acetic acid equilibrium here; what is equilibrium is given all the numbers I given yes or no?

(Refer Slide Time: 07:23)

5= 5+ HS 1795+9= 1804 mg/L COD LOSS = $F(S_0-5)$ $6 \rightarrow 0$ 3000 (q-7) =12600 12000 kg/d Kg /01 $Y_{c++/s} = (0.92)\frac{16}{60} = 0$ $Y_{c02/s} = (0.92)\frac{16}{44}$ 0.24 0.67

So, what is the acetic acid that you have started with stills remains un reacted; that is acetic acid that is still remains un reacted 1795 is a S minus; how much is H s can you calculate, what is H s at the end of the process S minus? What is the H s is this correct; if there is a mistake tell me I will correct it 0.15 mile mole per liter 0.15 multiplied by 60 is 9 is it not, it is it all right? See our operating the process as optimum value of H s; H s is optimum is 0.15 mile mole per liter that is what you told me multiplied by 60 is a molecular weight of acetic acid. So, I put it as 9; is it ok?

So, what we saying that we are the process that we are steadying at 6000 and the biomethanation reduces it to 2000; is that clear? So, biomethanation process is able to reduce the organics to a level of 2000 it is not able to reduces it to a level that is suitable to discharge. So, it is 18 and answer is so I have to make some adjustment in these numbers. So, these numbers are not exactly correct; please help me now what is a loss C O D S naught minus of S. So, this is a s not exactly 6; so you tell me the actual numbers please so it is 6 minus 1.8 not 2.

So, this is not exactly 11000 it be slightly less slightly more. So, please tell me these numbers; 12 126.

Student: 12600.

12600; is it k is it all right with everybody? So, what am I saying that so much loss of C O D as 12000.

(Refer Slide Time: 09:12)

STOI CHIOMETRY C H3 COOH + 0.032 NH3 = 0.032 C5 H7 NO2 + 0.92 CH4 + 0.92 CD2 + 0.096 H20

Now, if you look back at our Stoichiometry it says what is it say C O 2 and there roughly in equal volumes. So, in terms of mass basis I will calculated here. So, based on the just look back at this one per every 60 we get 0.92 times methane which is 0.92 point 16 and 0.92 times 44 correct. So, there is Y axis this is Y Y P S and this Y P carbon dioxide; so that is what I have done. So, fraction methane to substrate is 0.24 I get carbon dioxide substrate 0.67 please verify it is 1 6; how did I get 1795.

(Refer Slide Time: 09:54)

D= m = 0.27/d $I = F/D = \frac{3000}{0.27/4} M^{3}/d$ 11 111 5 H+/Ka

So, brilliant question see 29.9 multiplied by...

Student: 60.

60 is it ok all right is it with everybody ok? Now, please tell me if these numbers are correct 0.92 times 16 is 0.24 and then 0.92 44 is 0.67. so, if I ask you what is the methane fraction in biogas; what will you tell me typically weight by weight? Methane fraction 0.24 divided by 0.91 what about that number is. So, you will find in biogas on weight basis the methane is not more than about 26, 27 percent; on volume basis it is equal on weight basis it is only 25, 26 percent is it with everybody 0.24, 0.67 all right ok.

(Refer Slide Time: 10:56)

Methane Production = (12 600) 0.24 = 2025 kg/d (12600) (0.67) = 8000 kg

So, what is the methane production a made a small mistake here. So, you can tell me so it is 600; so this number is how much please tell me? 3025 fine 0.26 is it?

Student: ((Refer Time: 11:12)).

Yes just 2 minutes just 2 minutes there is some important questions are coming please I am just what is mistake I made here please tell me C O D losses 12600 that is this is the acetic acid loss out of that we said this is a fraction; that is why you multiplied by 0.24. What we are saying is for every 60 we are getting p0.92times 16. So, that is the fraction we are talking about it; is that is it with everybody what we are saying. So where are so we have 3000 k g of methane and so many kilo grams of some slight mistake here; what is this number please tell me? 12600 8440 fine. Suppose I ask you what is the thermal value of biogas what will you tell me; what is the thermal value of biogas?

(Refer Slide Time: 12:10)

Methane Fraction In gas = 2880 = 0.26. So CHUis 26.1. in biogas GAS THERMAL VALUE = (0.26)(14000) = 3640 kcal = 4918 Kcd/M3 [NOTE 1 kg Gas = 0.74M3]

So, the methane I calculate here just to put it in the context; methane is about 14000 kilo calories per kilo gram I taken this from the literature. So, biogas is about close to 5000 kilo cal 3600 per k g or per cubic meter you can also calculate that I have done that. So, 3640 is what we get showing that biogases is a lean gas is not a very rich gas it is a lean gas. And, therefore its combustion in a I c engine will require suitable design which people done all ready is very popular around the world; biogas engines are operating very well. And, what is the problem that we face biogas in I c engines? The problem with I c engines is that and this reaction if there is protein generally you produce hydrogen sulfide here. And, that creates problem in the combustion for which in small scale it is not easy to handle, in large scale you can remove the hydrogen sulfide. What we find is by biomethanation gives you biogas; yes it gives you very good thermal value; but it produces a waste water which is not ready for discharge. So, we must look at doing a system design in which the waste water is taken care.

(Refer Slide Time: 13:33)

Effluent = 2000 mg/L Effluent Treatment $D: \frac{1}{B} \frac{\mu_m S}{K_s + S}$ $D = \frac{1}{0.3 \times 10} = \frac{0.5}{10}$ $V = F/D = \frac{6pqo}{0.5}$

And, this waste water we said the fluent that is comes down the biogas is this is 1804 somebody said. So, we said the yesterday that we our systems will have dilution rate of this type correct; where mu m I taken whatever you done yesterday; so this is a kind of number I get. So, the second system which will take care of the waste water is that; it were it has a dilution rate of 0.5 and the system volume of 6000 is it please tell me? This is all right 3000 cubic meter per days coming the dilution rate is 1 by B times mu m s K s and all there have taken yesterdays values or given you yesterday. So, D value is 0.3 is knows 0.5 and this is what I get please tell me this is it is I have taken B as 0.3 mu m as 0.3 per day K s has 10; this is in problem number one same thing we done this yesterday same number. Say B is 0.3 everything is what we have done in yesterday yes or no shall we go forward all right where have we?

So, we have an equipment size of 6000 cubic meters; which is what that treatment of that waste water. And, what is the size of the equipment the biomethanation? What was biomethanation size we got 11000. So, you can say 11000 plus 6000 17000 cubic meter have we used off. Now, let us look at the real problem?

(Refer Slide Time: 15:11)

COD LOSS (3000) = 0 Oxygen Supply Needed @1Kgoz KWH POWER PRODUCTION 00×0.3 (OR Soka 147

The real problem is here see what happens is that is this correct total C O D loss that in this in this is the biogas; is this correct what I have written 2000 nah it is 2000. See we have to remove, see we have to what comes out off the biogas plant is a 2000 milligrams per liter 3000 cubic meters. So, the total amount of C O D that we have to treat in the fluent treatment plant are the E T P they call; is this is this correct? Let me repeat what comes out of the biogas plant is 1804 1.084. So, this is slightly less; so is 540 k g per day ok.

So, what comes out of the biogas plant comes at 1804 I have written 1.80 k g per cubic meter 3000 cubic meter 5400 k g per day has be handle in your E T P plant correct; is this what we have say I am coming to then I am coming to that ok. Now, how much oxygen is required to treat to oxidized 5400 k g of oxygen demand; if it is typically glucose 1 is to 1 is reasonable number. So, to be able to process 5400 hundred k g; so you will required 5400 k g of oxygen. Now, you can ask how this numbers comes from; of course this number comes from practice if you go to a any waste treatment plant they will tell you that every kilogram of oxygen demand you roughly require 1 kilo water of n h v. That means you aeration equipment the amount of energy that you must put in; so that you know it is sort of bubbles through this is about 1 kilo a tar a every kilogram of oxygen you have to supply; is this clear?

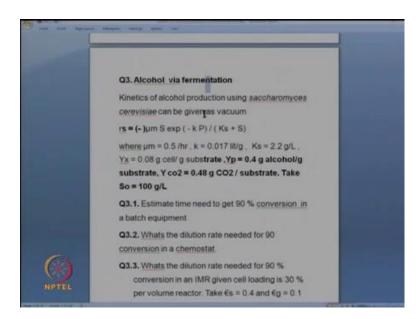
So, if you have 5400 kilo I mean kilograms of oxygen to be supplied you will required 5400 kilo tower of electricity. So, how many kilograms of methane did you produce? 3024. So, to produce see what we do in this one that we burned, we burned methane and then converting into electricity. So, your 3024 k g a methane burning and then generally efficiency between 0.3 to 0.2 in that range. In the other words 20 to 30 percent typically 20to 23 percent of the thermal energies converted to electricity. So, I will just estimated these numbers are not correct numbers are not correct; please tell me now 3024 14000 by 860; what is a number correct if it is 0.3 what is it? If it is 0.2 what is it?

Student: 14768.

14768; I will write 770; if it is 0.2? So, what we are saying is that if you burned this you can get so much of electricity; if it is a 30 percent efficiency so much; if it is 20 percent efficiency so much. Generally you would find that I c engines efficiency is a quite good. So, you have get something in this range. So, I will get by 860 see kilo calories a kilo tars conversion see 860 kilocalories equal to 1 kilo tar this is something that I have learnt in my school. So, what we are trying to say here is that see in E T P you consume so much and you generate so much. So, there is a slight power surplus, this is power surplus which is use to various other purposes; is it clear? So, when you have biogas plant you have some surplus energy you can use a various other purposes; part is a reason why biogas is a very popular in varies places is that it does give you some power surplus; very good question that is lets go back to that question. Where are we; we calculate its C O D loss in the E T P plant it is converted into carbon dioxide; in both cases there is a loss of carbon. In 1 case the carbon is given comes to you as methane, in another case the carbon comes to as carbon dioxide; is it clear?

Now, the important point to recognize here is that in many places you will find when they do this power production using gas the wasted energy which is the exhaust from the engine in many of these dairies they need lot of hot water. Because dairy requires lot of washing to be done in varies places. Therefore, they are able to use that energy to generate hot water. And, because of that thermal efficiency of the process because they are able to recover lot of heat from the waste heat, thermal efficiency is the very high. And, other words many of these dairies they are able to integrate biogas, waste water treatment and therefore that waste water they are able to converted into hot water and use it for various kinds of washing. So, it integrates very nicely in terms of thermal, in terms of say protecting the environment and so on. So, it is very popular around the world; if you can effort the investment on the biogas plant, investment in the waste treatment both are very large energy intensive investment intensive activity.

(Refer Slide Time: 21:01)



The second exercise see alcohol fermentation are status in this country.

(Refer Slide Time: 21:09)

FERMENTATION ALCOHOL $G |_{12} = 2C + 50 + 2C0_{2}$

Of course all the alcohol in this country is produce from sugarcane molasses. And, in many parts in the world particularly the world the warmer religious in the world it is from sugarcane molasses. Now, this data that I have taken is a rated which the substrate gets consume is given by this function mu m S k minus k P and all that; these numbers by enlarge whole for sugarcane molasses. And, these numbers 0.17 all these effects are quite. Now, what happens in a sugar industry is that the molasses comes to you as 50 percent sugar 44, 45 sometimes 48 percent; 48 percent means 400 to 500 grams per liter as hexose sugar.

Now, industry what they will do is that they will dilute this to about 10 percent; they will dilute this from 500 or 450 grams per liter to 100 grams per liter. The question is fermentation alcohol industries typically dilute molasses 200 grams per liter why? Now, you will you will realize that let me write this Stoichiometry here C 6 H 1 2 0 6 giving you twice C 2 H 5 O H plus twice C 0 2; this is 180, this is 92; this is 88. And, other words strictly anaerobic conversion hexose sugar to alcohol is actually roughly 49, 51 percent roughly say 50; is that clear?

Now, if you start with 1 gram of sugar you will get half a gram of alcohol. Now, if it is if you start this as 100 grams per liter then you should get 50 grams per liter of alcohol correct; is that clear? If you a started with 500 grams per liter you would have got 250 grams per liter of alcohol. Therefore, the amount of water you have to remove in this case it is only 4 times you know 250 to and you have to only remove per every k g of alcohol you have to remove 250 k m in 750 k g of water; here you will have to remove 950 k g of water. Just see the difference if you could have used 500 grams per liter sugar you have removing 750 k g of water per every k g of alcohol; here you are using per every 50 you are removing 950. So, 1 to 19 here it is 1 to 3 you can see the advantage if you can use a higher concentration; is that clear?

Alcohol industries they do not use 500 grams per liter they use 100 grams per liter; they are willing to scarifies this advantage why? Because energy cost of distillation is very high we all know that but in spite of the energy cost is so high they diluted to 100 grams per liter and not worth with 500 grams per liter. So, question is why; is a is a question clear to all of you why do we dilute molasses? Say it again; molasses is available in a sugar industry typically 500 grams per liter as hexose sugar.

Now, this is diluted to 100 grams per liter hexose sugar prior to fermentation question is why? What I am trying to explain here is that if they could have work with 500 grams

per liter they would have go 250 grams per liter of alcohol. Therefore, per every 250 grams they have to evaporate 750 grams of water; 1, 2, 3 per every k g 3 k g of water has to be evaporated. But if they do this they have to remove 5 to 95 so 1 to 19 the amount of water to be removed in this case is per every k g 19 k g of water has to be remove; while here it is only 3 k g. So, there is such great advantage in distillation when you can use 500 but they only use 100; the question is why? The answer is there are many answers many reasons why they do this; first reason is that molasses come is extremely viscous; it is so viscous it is not easy to pump at all. If you want to pump molasses you will have to dilute; that is the first reason.

Secondly, molasses contains lost of suspended solids which comes from the process; see what we do is that we have criticize the sugar. So, we are just rejecting what we are not able to recover correct. So, it has lot of suspended solids and to be able to remove the suspended solids you have to reduce the viscosity. So, that is another reason why they dilute. The third reason they dilutes this that this is negative effect of alcohol accumulation in the process which inhibits the rate of chemical reaction was called product inhibition. With all these factors combined make it essential for them to diluted to a level which they can work with; is that clear that is why they dilute. Third is this reason that alcohol accumulation in the process inhibits the rate of chemical reaction because is this minus k P can look at this; this reason this minus k P effect is so that that makes it worth. So, that is why they would dilute thank you my friend k let us go forward now.

Now, let us quickly calculate; let us say we have the typical size of alcohol distilleries in brazil is very big but ours is only forty tones per day is typical; and biggest would be a little larger. So, if you looking at 40 tons per day alcohol factory.

(Refer Slide Time: 27:28)

Alcohol: 40 TON D F (5 - 5) 0.4 = 40000/24 0)(04) = 111 P = (5,-5) YP/S = (100-10) 0.4 36 Kg/ M

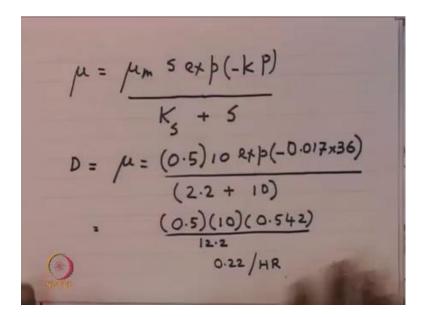
So, just made some calculation a 40 tons per day alcohol factory; how much should be this 40 tons per day; is this correct? This see whether what is this calculation is correct 40 thousand k g per day divided by 24 and then this is the S naught is 100; S is 10. So, we are taking around the 90 percent conversion; so I put is 90 ok. And, you can see here Y P is 0.4 only 40 percent of alcohol is we get 48 percent is carbon dioxide you see; is it all right? And, then remaining 40 and then this is 48; what happens is remaining? This is 8 it is going I squares on only 8 percent is sell. So, 96 still 4 percent is unaccounted; there are other products of formed in fermentation you know let little bit of glycerol and other product of forms that is why the data is not there.

So, what is f equal to 46 is this correct 46; 46 cubic meter per hour. So, what is the concentration alcohol in solution, what is the concentration of alcohol in solution? 36 k g per cubic meter is 3.6 percent, 3.6 percent is the alcohol in solution. So, in other words if we start with 1 k g you will get 36 percent is alcohol the rest is going to carbon dioxide. See you can see here 8 percent is sell 48 percent is carbon dioxide and there are some side reactions like glycerol and all that which takes a way little bit. So, what the useful alcohol is only 40 percent not much more in that. And, please recognize 90 percent conversion of hexose sugar are also not very common you know; the reason is this inhibition makes it quite difficult to handle; as a alcohol accumulate this inhibition becomes worst. So, you will find a process a very good factory in India would be 80 to 83 percent not much more than that.

So, we are looking at here we getting 36 per 36 k g per cubic meter; but in actuality we are not looking at much more then about 30, 29, 30 like that; that is what is the common. So, the amount of energy that is required to recover the alcohol is very large. So, for 36 means you have to remove 9, 960 k g of water has to remove to be able to concentrate this. So, this is a serious problem with the problem with alcohol fermentation lies really in the chemical reaction equipment; we have been able to figure out what is the way to take it forward.

Now, an interesting work got done in ((Refer Time: 30:41)) 1970 is very old research; they spent a lot of time trying to see whether this problem that we are facing here very lean concentration of alcohol. And, very high energy cost of recovery; can we do something about it 1970's 1980's it till goes on. And, then varies kinds of answers have been given. Let me quickly run through that because it is context is the important. But before that let us finish of it.

(Refer Slide Time: 31:14)



What is the dilution rate at which we must operate the plant? What is the dilution rate; mu m mu m is 0.5 S is 10 is it right S is 10 yes or no? S is 10and K is minus point 0.017 P is 30 things; 0.22 is correct 525 seen all right. So, what is the size of the equipment? Suppose you have producing 40 tons per day a alcohol what is the size of the equipment that you will have?

(Refer Slide Time: 31:50)

 $F = 46 M^{3} / D H R$ D = 0.22/hr 206 Productivity = DP = (0.22) (36)

Size of the equipment is what I have got here about 200 cubic meter per hour per hour. Now, this is the term see what is the productivities alcohol D times P is about 8 k g per cubic meter per hour or 8 gm per liter per hour; is it clear what we are saying? And, this is what makes the whole technology little inviolable because per unit volume of equipment you are not producing very much in 7.9 k g per cubic meter per hour. Now, if you look at the reality of alcohol production in India what you find is situation is much worse. Because this is for a continuous process; why there is no shut down time you know filling and empty which is very substantial amount of times required to fill and remove. And, then in between also you have to clean equipment and so on; you will find because is the fact that the see here our residents time is about 5 hours correct. But you will find there the actual filling time and then cleaning time etcetera it becomes 18 hours ok.

So, this what we are getting a 7.9 actually more like a 2 or 3 grams per liter per hour is what we achieve in a commercial process; is this point clear to all of you. And, all the problem arises from the fact that we have got the chemical reaction technology right; the real we that engineering of that reaction is were the problem is; that is why all these problems are coming.

Therefore, just look at what was done. So, people have looked at what can we do I mean from the point of view of reactor design is there anything we can do; is that clear is the

problem create to all of you? See you have just done a calculation for continuous process we said that its productivity is 7.9 correct based on the fact that we have produce 36 k g per cubic meter and our dilution rate is 0.22. And, therefore our productivity is 7.9; if you have run a batch process then the actual residence time would have been not 5 hours more like 18 hours, 20 hours sometimes even more.

So, you are getting much much lower productivity in the batch equipments that you see operating in this country. Continuous fermentations are not very common around the world not very common there only may few factories. If I ask you why; why is it that continuous fermentations are not very common people prepare a batch? What would be a our answer, why is it that people prepare to do alcoholic fermentation in a batch; why would they prepare batch? In fact you would see if you go to places like Madhya Pradesh and Uttar Pradesh and all that there are much smaller distilleries 5 kilo liters per day, 5, 2 kilo liters per day small plants are running you see. And, therefore the productivities are much much lower.

And, therefore many of these alcohol they are not going for pharmaceutical not controlled by government varies issues are there in a in the commercial sector. But the problem is that this productivities are very very low and there are not good answers yet. So, let us drew you what does being happening in this fermentation technology alternatives for alcohol.

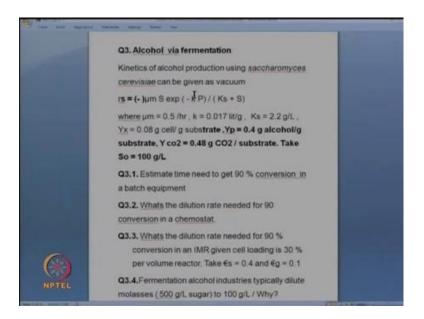
(Refer Slide Time: 35:19)

Fermentation Alcohol Reactor Alternatives Batch 1. 2. chemostat Immobilized cell Reactor 3 4. Vacuum Fermentation

A very nice book I mean a P H D thesis 1971 Berkley it is in our library; it is only about 120, 130 pages. And, they have just looked at batch, chemostats, I immobilize cell reactor, vacuum fermentation and some combinations also; they have looked at to see whether we can get around this problem of very poor productivity of the reaction equipment; what they have done is that see this batch reactor correct. Now, if we have to overcome this problem; what do what can we do? See this inhibition due to product if you want to knock out this problem what can we do? Productivity is low but we want to somehow get rate of this alcohol; you have to remove the product; how do you remove a product? So, they said let us do vacuum. So, what happen if you do a fermentation and the vacuum? So, you have an equipment which is operating something like 30 millimeters 30, 35 millimeters of mercury ok; what would happened to alcohol; it will go into the vapor phase, alcohol water would also go into the vapor phase.

So, what will be the net effect of that as for as product in the in the broth in solution concentration will come down correct. And, other words as the fermentation proceeds alcohol in the broth would go into the vapor phase we continuously remove it because it is under vacuum. Therefore, the reaction keep going forward. So, continuous fermentation essentially helps you knock out this effect. So, that reaction is able to proceed in the forward direction and give you a much higher level of substrate conversion; this has been proven in the laboratory for 1980's lot of research is there which shows it is a very interesting technology from the point of view of driving the sugar tools nearly complete conversion. But a huge problem came many try to commercialize this.

(Refer Slide Time: 37:47)

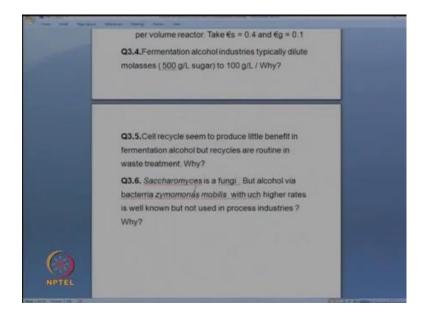


So, what happened was this gas phase which contains the alcohol and water which at a pressure of 30 millimeters of mercury; if it has to be in a taken to the next stage of the process you have to compress it. So, you have to compress from 30 mm to atmospheric pressure. So, suddenly it can be release into the atmosphere into a tank which contains alcohol. So, you have to compress from 30 mm to one atmosphere that compression is a huge cost; you have spent money in a creating vacuum; vacuum also cost money correct there is a energy costing vacuum. You need power to compress the product to atmospheric pressure. So, energy cost of production become very large. Therefore, while in our technology of it seem very attractive; it would able to drive the reaction to completion you see. And, therefore since here able to drives the reaction to completion much higher concentration of s ok.

See the your s need not be 100 grams per liter, it can be 500 grams per liter; it can be anything there is no great problem. So, you have an advantage of very highly concentrated alcohol I mean it is from 3 percent you go to something like 16, 17 percent; because there is a lot of alcohol water vapor in the gas phase. So, you do not get very high concentration 20 percent you will get. So, to that extent you can say on a energy cost of distillation. But the net result was that the energy cost of vacuum operation, energy cost of compression was so large that the benefits of using the much higher s was not satisfactory.

So, after may be about 10, 15 years of a lot of research it had to given up. In fact the last I mean chapter of this theses I mean sort of says very very surprisingly it is says that may be 5000 years ago the understood this; that is what it says you know that technology of last so many thousands of years we are not been able to fundamentally bring about the improvement in the alcohol fermentation technology; that is what it says. That is very interesting to observe they we still do not seem to have an answer to alcohol fermentation; not yet. Now, something more interesting also has happened that means draw attention to that.

(Refer Slide Time: 40:19)



See if we see it says you can read here saccharomyces is the is the organism that is used all over the world. Saccharomyces is a fungi they work well under acetic P H. So, the P H of fermentation is about 4.2, 4.3 and the P H adjustment is done by alcohol ok.

But in 1970's the figure out that is a this fungi works very slowly the we should change about to bacteria; this particular bacteria zymomonas it accurse in a naturally in certain fermentations in a particularly in some of the farm and juice it occurs. So, they isolated and all that and then they have try to commercialize a process using zymomonas as the bacteria for fermentation.

And, there are several laboratory extremely in even pilot plants in which this has been tried out and it is a excellent; performance is excellent. The reason is zymomonas bacteria they rated which is able to do the fermentation is much much superior to fungi bacteria works faster than fungi. So, the something went wrong, what went wrong? What went wrong was the bacteria works best at neutral P H. And, when you want to do anything neutral P H which means you have sugar solution all nutrients already and it is neutral P H they invention by several competing organisms become very high. Therefore, if to be able to operate a bacterial fermentation for alcohol requires that molasses be sterilized; while if you do with it saccharomyces at P H of 4.2 the competition from other organisms are very low.

So, alcoholic fermentation do go through sterilization if you use fungi. But if you use bacteria you have to sterilize. So, the energy cost of sterilization and cooling it to ambient temperature and so on prohibitive. So, while the technology worked very well economics did not favor it is adoption. So, it this is also fail and there is lot of research in 1980's which says that you know this can be done but it is also not very satisfactory. I went to a factory I will not name a factory in 1970's; they said no no no we have got a great idea we have go do this; they said they will do sell recycle. What is the ideal cell recycle r x is mu times x correct; higher the cell concentration higher the cell reaction rate.

So, they said I have got a great answer to this problem. So, they invested on what is called as a centrifuge in those days and then did this process and it failed. So, process did not work; so they were wondering what they hell went wrong in our most fundamentally wrong mu r x is equal to mu x must be wrong then correct; they put more cells into the system. But the process failed; how do you explain this you understand what I am saying you have a process in which you have recycle the cells. So, cell concentration is several times more than you normally operate but the process does not quite give you the result that you expect; you got 36 you got 38 now; it is not anything very different. So, what seems to gone wrong is interestingly see when you run a process particularly and say batch process or generally about batch process 20, 22 hours 26 hours; as the product accumulate the bacteria is starts to some sort of denature the enzyme starts to it starts to die basically. So, you have lot of cells in the output but many of them are not viable cells.

So, when you do a centrifuge and recycle you are recycling cells all right but the viability of those cells to recycles are very very small. So, essentially because of viabilities are very small it did not give you any great result. And, the other words pure culture fermentation see alcohol is a pure culture fermentation; where you recycle you have to be sure there what you recycle is all viable. But in the in the environment of fermentation of 24, 26 hours many of those cells die; it does not survive. And, that is part of the reason why it is the recycle has not been very successful.

But interestingly recycles are very very common in waste treatment. See in pure culture it is not very successful but in waste treatment if you do not recycle your process will fail; you understand what I am saying how do you explain that? Why we recycle in a in a waste treatment plant but we do not have great benefits in recycling in a pure culture fermentation? The answer is in pure culture the product accumulation seems to have very very bad effect on the organism; while in places like waste treatment it is poly culture; where there is predator pray interaction. And., therefore predator ensures that the pray is always active because the predator wants to eat correct.

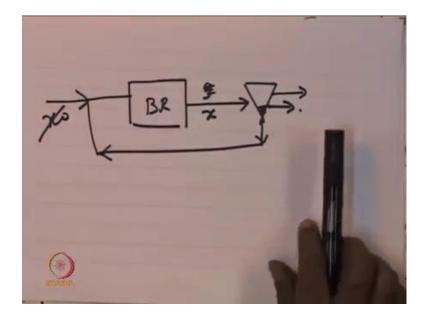
So, this predator pray relationship ensures that all organisms are active. So, waste treatment recycles are critical to success of a process but in pure culture recycle is actually not very useful. So, recycle see this people have try recycle in pure culture like alcoholic fermentation it is not very successful. The reason is not successful because during the process of fermentation of 18, 20 hours viability of many of this organisms starts to go down. Therefore, when you try to separate this organism after the fermentation 18, 20 hours and recycle the viable cells in that recycle stream is not very large. And, therefore it does not benefit you.

But in waste treatment what happens it is a poly cultural there are hundreds of organisms working; and they all work to feed on the waste that is existing. So, the predator pray relationship ensures there is very highly active environment is established; that is why recycles are crucial for success of waste treatment and recycles are not very useful in pure culture.

In waste treatment the predator pray relationship ensures that all organisms are always active; in the waste treatment environment will have spends some time on ecology which you will do when we meet; we will talk about ecology shortly in the next class. So, we will explain that but ecology is what is crucial to success of what we call as natural processes. All natural process you need ecology ok this sort of completes this part. So,

we will go to the most interesting part of which is natural selection. How recycle affect predator pray relationship.

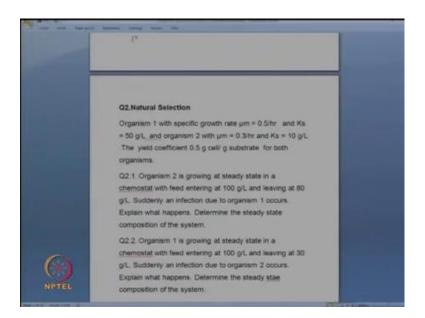
(Refer Slide Time: 47:32)



Let me draw once again we had a bio reactor they then we had we put this back correct. Now, what happens here in the bio reactor there is lot of growth. And, this growth is because of what with this lot of nutrients available, lot of food available. And, therefore it grows; therefore you have starting with x naught which is very small. So, there is a lot of cell growth here x which your concentrative here; and this cell growth is because of the poly culture. So, that means this environment the multiplicity organism present they selected what is most useful to this environment correct. And, that you have concentrated here; that means you have done concentration of the most useful organism for your process which you are putting back. But in a alcoholic fermentation you are started with pure culture; and that pure culture in this environment it was as it is no ecology. Therefore, it is getting affected because of the accumulation of the new coming toxicity or the products. And, that is why it is start to die when you do this it starts to die; because so much of toxicity is there it will die it is clear to all of us.

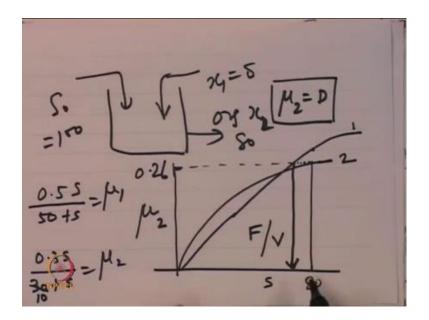
Poly culture is what nature is all about and predator pray is what ensures highly active population; this is a very beautiful example of natural selection. See Darwin talked about natural selection you have read in biology that natural selection it what happens in the natural environment.

(Refer Slide Time: 49:25)



This is an example where I illustrate you how this natural selection actually happens; you can do this numbers to realize how beautifully it works. The example is here there is a chemostat in which this organism is growing; it says it is got specific growth rate mu m is so much and all that. And, then this chemostat is working and as it when it is working suddenly there is a infections that happens; what is happening that you have this chemostat.

(Refer Slide Time: 49:51)



And, then it is coming in and going out S naught is 100 and it will going out at 80. So, organism 1; this is organism 1 x 1 is it correct organism 1 growing, organism 2 is growing, organism 2 is growing. At an instant when there steady state is establish organism 1 infects the process this what it says is the problem statement clear to all of you. Your chemostat is running S naught equal to 100 and 80 is coming out therefore x 2 is growing. So, you running a process in which x 2 is growing and when they x 2 growth is a steady state suddenly a infection occurs ok.

Infection means what somewhere from where this x 1 has coming some delta value of x 1 has coming; our question is what will happened to the process; is this question clear to all of us? The growth rates of both the organisms all those data is given here mu m is given k s everything is given here; is this clear? So, let us say suppose you make a plot of mu is a growth rate o verses. And, let us say this is what this is organism 2 is it right; organism 2 it is growing. Now, it says organism 1 is only 0.5 S by 50 plus S this is mu 1 correct and this 0.3 S divided by 30 plus S this is mu 2 is that clear; 10 is it this is 10 is it ok.

Now, tell me I mean what is our understanding of chemostats? Our understanding of chemostat is a D equal to mu; that means when steady state is establish when steady state is establish D was equal to mu or in other words mu 2 was equal to D when steady state was establish; do we agree? What is mu 2 do we know mu 2 80 grams per liter is given. So, if you plot mu 2 verses S let us say this is a curve this is 80 correct. And, then corresponding to that what is the we can find out yes or no; is this clear to all of us?

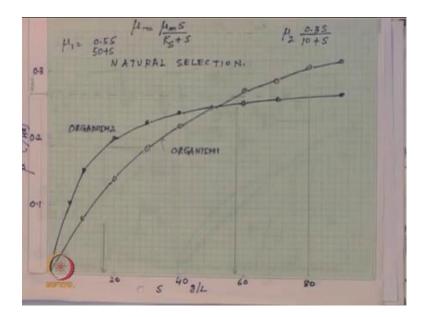
Now, we say it is there is a infection due to organism ` we should plot this I plotted that I will show you in a minute; that curve looks something like this, this is organism 1 you will plot shortly. So, this is how organism 1 looks like. Now, what will happen you please tell me we looking at this curve; what will happen is this question clear to all of us? We have a steady state of organism 2 what is mu equal to can you please calculate and tell me; how much is it?

Student: 0.26.

0.26. So, it is running at 0.26 per hour is the dilution rate at which is working. Hence, that instant organism 1 has come in. Now, what is this specific growth rate of organism 1 corresponding to 80 it is higher than 2 is it not; it somewhere here yes or no organism 1

it will grow faster than 2. So, it is here so what will happen in the process substrate it organism 1 will compete for the same substrate; both will start eating what is our steady state d must be equal to mu is our steady state correct d must be equal to mu is our steady state. So, what will happened to the process now? D will become; what is D? D is F by V does D change our wall setting is not change correct. So, F by V has not change when D is not changed; if D is not changed what will happened to the process? Organism 1 it will grow correct what happens to 2 it will reduce; then what eventually what will happened process? Do 2 will get washed out; you can see here that S will keep coming down and then this will be the steady state value of s is it not it. In the steady state value S organism 2 will be knocked out organism; well 1 is would have would be growing and the value of S will reduce from 80 to some lower value.

(Refer Slide Time: 54:20)



See, I plotted at here so you can see here it comes in a 80 to about 54 some some smaller value; is that clear is the phenomena clear what I am trying to bring out see natural selection happens every minute in the natural environment. We are talking about bio diversity and all that today but the importance is write here ok that simply by adjusting your dilution rate you have selected a different organism. For example, it is important to realize and if you go to any you know nay river which is starting; as you can see as the velocity of the river changes the ecology changes; the whole ecology changes because dilution rates so different. And, therefore the organism that can sustain will be also keep on changing. And, this is a illustration of that; is that clear to all of you? Why is that

organism 1 this is organism this is organism 2 is knocked out and organism 1 starts to grow you can see here yeah it is. Finally, at steady state there is only 1 organism which is organism 2 is knocked out and organism 1starts to growing.

Steady state there is only 1 organism; we having a chemostat in which our dilution rate is fixed. Now, organism this infection has taken place that infection has taken place. Therefore, eventually what would happened eventually we said D must be equal to mu; because that is a representation of steady state. And, our this graph says there is only 1 point of intersection correct; at that point of intersection D can only be equal to mu 1correct and mu 2 has to get out organism 2 have no chance of surviving in that environment.

What am I saying is that I am running my process D equal to 0.266; under that environment when this infection accurse organism 2 will have to get out; is this clear, is this clear to all of you? Can now see how in the natural environment this happens at every minute. So, that is why you see the organism that is populating an environment really depends upon the share rate of the environment. See, if you look at just yourself diarrhea for example, what is diarrhea; what is our what is our system doing? It is increasing the dilution rate to knock out the organism; diarrhea is an example where it is it is a phenomena of increasing the dilution rate. So, there is knocks out the organisms; it is a natural response to getting rate of the organism; there is what happens in the natural environment is this clear, is that phenomena clear to all of you?

So, you can repeat this there is second part is same exercise is repeated saying that if on this side. For example, what I am trying to put a cross is different organism; for example in the second in this exercise what I said is there organism 1 growing at 30 not 80 at 30. And, suddenly this infection accurse here the selection is for the opposite organism; you know we can see here here when you are starting a 30, 30 see here you can see here that the organism what is what is selected is organism 2; 1 is knocked out. The important point here is to recognize that the environment determines if this substrate concentration changes at different organism is selected; see the way nature is organized you see this it is this organization that we must understand properly to understand the importance of diversity.

Natural environment is much bigger what I am saying is much bigger. So, this phenomena explains how things happen in the natural world. Now, the question that we want to answer is how long does it take for the steady state to get establish? We know that steady state one organism get knocked out but how long does it take; can we tell how long does it take, can we write the differential equations to tell how long does it take? Let us write the differential equation you can solve it at home; let us write the differential equation.

(Refer Slide Time: 59:01)

$$\begin{array}{c} \begin{array}{c} Q2!\\ F_{\chi_{10}}-F_{\chi_{1}} & 10^{\circ} \\ \hline & J_{\cdot} \int_{-8^{\circ}} \\ F_{\chi_{20}}-F_{\chi_{2}} + \left[\mu_{2} \chi_{2} \right]^{\vee} \\ \hline & \frac{d_{\cdot} V_{\chi_{2}}}{dt} \\ \hline & F_{\chi_{20}}-F_{\chi_{2}} + \left[\mu_{2} \chi_{2} \right]^{\vee} \\ \hline & \frac{d_{\cdot} V_{\chi_{2}}}{dt} \\ \hline & F_{\chi_{10}}-F_{\chi_{1}} + \left(\mu_{1} \chi_{1} \right)_{\nu} \\ \hline & \frac{d_{\cdot} v_{\chi_{1}}}{dt} \\ \hline & F_{\chi_{10}}-F_{\chi_{1}} + \left(\mu_{1} \chi_{1} \right)_{\nu} \\ \hline & \frac{d_{\cdot} v_{\chi_{1}}}{dt} \\ \hline & F_{\chi_{10}}-F_{\chi_{1}} + \left(\mu_{1} \chi_{1} \right)_{\nu} \\ \hline & \frac{d_{\cdot} v_{\chi_{1}}}{dt} \\ \hline & \int_{8^{\circ}} \\ F_{\chi_{10}}-F_{\chi_{1}} = \left[08/L \right] \\ \hline & Y_{\chi_{1}} = \delta \left(0.00019 \right) \\ \end{array}$$

So, I will write for organism 1; first one is organism 2 is it not it I will write for 2 is it all right yes or no? Why have I knock this out; there is no the infection is momentary, it has infection is not coming continuously it is momentary. So, let me write for the there are 2 ways infection can occur; one that you continuously put in the infection let me write I will come back in a minute.

```
Student: ((Refer Time: 1:00:04))
```

I am taking Y to be the same for both; is this ok or material balance; this is our material balance this is what you have written material balance is correct; these we have knocked out this terms. Now, in problem this in 2.1 what are the initial conditions, what is the initial condition for this problem? It is at steady state that means steady state value is what 80 grams per liter is the value of steady state. That means, at this point when this happens S naught is 80 what is x 2 and it going out at 80. I am talking about question 2.1

is coming at hundred going out at 80. So, what is a cell mass? 100 minus of 80 is 20 you will coefficient this point five 10 grams per liter is cell mass ok ; yes or no do you all agree is 10 grams per liter 10 mass. Now, at this instant of time this is 0 time an infection occurs what is the value of x 1? Let us say some delta some some 0.001 grams. So, much has entered so that the density has become 0.001 grams per liter x 1; so much of x 1 has entered is this clear? It is a momentarily now can you solve this problem now; initial condition is fully specified; is it clear what we are saying can you solve this differential equation? because initial conditions fully specified x 2 is known what is that not x this is S is 80 S naught is always 100 is it clear S naught is 100, S is 80 at the time of infection; x 1 became 0 0 1.

Now, instead of 0 0 1 you can put 0.1 you can vary that number when I say how long does it takes it depends upon the magnitude the inflection; if it is small it will take a long time if it is large the steady state the new steady state would be reached quickly; is this clear? Can you solve this problem and find out how long it takes for the new steady state to be achieved yes or no? So, similarly for q 2.2 also you can do the same thing what is the initial condition for 2.2.

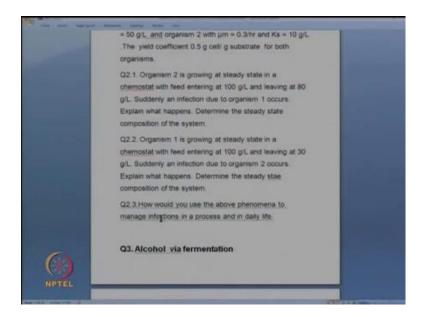
(Refer Slide Time: 1:02:41)

358/2

Our question initial condition for 2.2 S naught is this is 2.2 S naught is 100, S is 30 correct. And, what is x 1 is 100 minus of 30 70 is it is 35 grams per liter. And, x 2 is let us say point 0 0 1 gram per liter this is the infection ok. So, this is t equal to 0; when the

infection is just occurred. Similarly, this is t equal to 0 when the infection is just occurred 0 plus. So, you can solve forward march is it can we solve can we finish this problem now; is it is it yes or no? Now, the question is I want to ask you is this is the most important question.

(Refer Slide Time: 1:03:25)



So, how do we use the above phenomena to manage the infections in a process; after all infections are something that happens to us it happens to a process if it is a biological process; how do we manage these infections? What is that you and I have learned having known this phenomena; we have learn this phenomena now showing that if you change the dilution rate; you can knock out the organisms. Essentially what we are saying is that if there is infection you have to change the dilution rate in an appropriate direction to knock out the organism correct. So, we have learned that now that if you want to knock out an organism you change your dilution rate. So, that particular organism just knocked out. In fact industry what they do they do lot of washing it is essentially do it this only correct; it is increasing the dilution rate to knock out the organism.

So, if you are talking about the pure culture you know fermentations; if you want to knock out the organism that is the infected the process you will have to change the dilution rate. And, that all that substrate will have to go into your waste treatment plant; you see this is the problem of biology that you have to except huge amount of waste that

has to going to waste treatment plant. But that is something that you have to except there is an infection or I will stop that.