Basic Environmental Engineering and Pollution Abatement Professor Prasenjit Mondal Department of Chemical Engineering Indian Institute of Technology Roorkee Lecture 20 Tutorial 4

Hello everyone, now, we will have a tutorial session and in this class we will solve some numerical problems based on our last four classes.

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Problem 1
1 gram of a MSW sample is heated at 105 °C for 24 h and the weight of the dried material is found as 0.9 g, which is further heated in a furnace at 950 °C for 7 min in absence of air by putting the lid of the crucible. The weight loss is found as 0.3 g. The remaining material is cooled with lid cover. When the temperature reaches to ambient temperature, its lid is opened and it is further heated in an oven at 750 °C for half an hour in presence of oxygen. After cooling the material , the residual mass of the material is found as 0.14 g. Determine the moisture content, volatile matter, ash and fixed carbon of the waste.
Solution Initial mass = 1 g Moisture content = (1-0.9)*100 = 10 % VM content = (0.3)*100 = 30 % Ash content = (0.14)*100 = 14 % Fixed carbon = 100-10-30-14 = 46 %

Problem number 1, statement is 1 g of a MSW sample is heated at 105 °C for 24 hour and the weight of the dried material is found as 0.9 g, which is further heated in a furnace is at 950 °C for 7 minutes in absence of air by putting the lid of the crucible. The weight loss is found as 0.3 g. The remaining material is cooled with lid cover, when the temperature reaches to ambient temperature, its lid is open and it is further heated in an oven at 750 °C for half an hour in presence of oxygen. After cooling the material the residual mass of the material is found as 0.14 g. Determine the moisture content volatile matter, ash and fixed carbon of the waste.

So, this problem is a case of proximate analysis and we can solve it as per our discussion in the previous class. So, here we have

Initial mass = 1 g Moisture content = (1-0.9)*100 = 10 %VM content = (0.3)*100 = 30 %Ash content = (0.14)*100 = 14 %

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So, problem number 2, The statement is an industrial waste water is tested for measuring BOD₅ value, the wastewater is diluted 100 times with dilution water before it is used in the test. The DO of one real and blank sample are determined, which is 10 ppm. Other two BOD bottles filled with real and blank samples are incubated for 5 days at 20 °C. After 5 days the DO value of the real and blank samples are found as 3 ppm and 9.5 ppm respectively. Calculate the BOD5 of the original waste water sample. If 5 ml of microbial seeds are used in the preparation of 300 ml dilution water, how the BOD value will differ.

So, this is the problem based on the determination of BOD. So, we have the formula.

$$BOD_{5}\left(\frac{mg}{L}\right) = D * [[(DO)_{t=0} - (DO)_{t=5}]_{sample} - [(DO)_{t=0} - (DO)_{t=5}]_{Blank}]$$

where D is the dilution factor.

In the present case

D = 100

 $(DO)_{t=0} = 10$ ppm for both real sample and blank test bottles

 $(DO)_{t=5}$ for real sample test bottle = 3 ppm

 $(DO)_{t=5}$ for blank test bottle = 9.7 ppm

Therefore, BOD₅ (in ppm) = 100[(10-3) - (10-9.7)] = 670 ppm

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For seeded dilution 287 + 3 = 3 t	ر س
BOD_5 (in mg/L) = D*[[(DO)_{t=0} - (DO)_{t=5}] - [(DO)_{t=0} - (DO)_{t=5}]*f]	ę
Sample Blank	
Where D [*] = dilution factor	
f = ratio of seed volume in dilution solution to seed volume in BOD test on seed, normally f is near to 1	
Seed volume in 300 ml dilution water = 5 ml	
For 100 time dilution 3 ml of real waste water sample is added with 297 ml of dilution water to prepare real/test sample	
Therefore volume of seeds in real/test sample (297*5)/300 mi	
Hence, f = (5*300)/(5*297)= 1.01 Thus, BOD = 100[(10-3)-(10-9.7)*1.01)] =669.1 pp	m

For seeded dilution

$$BOD_{5}\left(\frac{mg}{L}\right) = D * [[(DO)_{t=0} - (DO)_{t=5}]_{sample} - [(DO)_{t=0} - (DO)_{t=5}]_{Blank}] * f$$

Where D^* = dilution factor, f = ratio of seed volume in dilution solution to seed volume in BOD test on seed, normally f is near to 1

Seed volume in 300 ml dilution water = 5 ml

For 100-time dilution 3 ml of real waste water sample is added with 297 ml of dilution water to prepare real/test sample

Therefore, volume of seeds in real/test sample (297*5)/300 ml

Hence,
$$f = (5*300)/(5*297) = 1.01$$

Thus,

BOD = 100[(10-3) -(10-9.7) *1.01)] =669.1 ppm.

Problem 3
2 g of a dried agricultural waste is leached with benzene and ethanol mixture (2:1 v/v) at ~ 60
$^{\circ}$ C for 3 h. After leaching, the residue is dried in a hot air oven at 105 $^{\circ}$ C to a constant weight
of 1.8 g. This dried material is put in a flask containing 150 ml of (N/2) NaOH solution. The
mixture is boiled for 3.5 h with recycled distilled water. After this the residue is washed with
distilled water till all the sodium ions are removed and dried to a constant weight of 1.3 g.
Determine the extractives and hemicelluloses content of this waste on dry basis. If moisture
content of the waste is 15 %, determine these values with respect to original sample.
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Problem number 3, The statement is 2 g of a dried agricultural waste is leached to it benzene and ethanol mixture 2:1 volume by volume at 60 degrees centigrade for 3 hour. After leaching the residue is dried in a hot air oven at 105 degrees centigrade to a constant rate of 1.8 g. These dried material is put in a flask containing 150 ml of N by 2 NaOH solution. The mixture is boiled for 3.5 hour with recycled distilled water. After this the residue is washed with distilled water till all the sodium ions are removed and dried to a constant weight of 1.3 g. Determine the extractives and hemicelluloses content of this waste on dry basis. If moisture content of the waste is 15%, determine these values with respect to original sample.

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Basis: Dry sample
Initial weight (M_o) = 2 g
Weight after extractives = M_1 = 1.8 g \sim
Weight after hemicellulose separation = M_2 = 1.3 g
Extractive content = $(M_0 - M_1)^* 100/M_0 = (2 - 1.8)^* 100/2 = 10\%$
Hemicellulose content = $(M_1-M_2)*100/M_0 = (1.8-1.3)*100/2 = 25\%$
With respect to original waste material the extractives and hemicelulose contents are
Extractive content = (85/100) *10 % = 8.5 %
Hemicellulose content = (85/100) *25 % = 21.25 %

Basis: Dry sample

Initial weight $(M_o) = 2 g$

Weight after extractives = $M_1 = 1.8$ g

Weight after hemicellulose separation = $M_2 = 1.3$ g

Extractive content = $(M_0-M_1)*100/M_0 = (2-1.8)*100/2 = 10$ %

Hemicellulose content = $(M_1-M_2)*100/M_0 = (1.8-1.3)*100/2 = 25 \%$

With respect to original waste material the extractives and hemicelulose contents are

Extractive content = (85/100) *10 % = 8.5 %

Hemicellulose content = (85/100) *25 % = 21.25 %

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Problem 4	
COD analysis of a waste water sample is K-dichromate solution as reducing age ammonium sulphate. 100 ml of waste ammonium sulphate are 50 ml and 75 ml Determine the COD of the sample. Assum	carried out through chemical method using (N/10) nt. Excess dichromate is titrated against ferrous water sample is used. The titter value of ferrous I for original sample and blank sample respectively. The there is no interfering element in the sample.
Solution COD = 8000(b-s)*n/sample volume = 8000(75-50)*0.1/100 = 200 mg/l	where <i>b</i> is the volume of FAS used in the blank sample, <i>s</i> is the volume of FAS in the original sample, and <i>n</i> is the normality of FAS.
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Next problem 4. COD analysis of a waste water sample is carried out through chemical method using N/10 potassium dichromate solution as reducing agent. Excess dichromate is titrated against ferrous ammonium sulfate 100 ml of waste water sample is used. The titer value of ferrous ammonium sulfate are 50 ml and 75 ml for original sample and blank sample respectively. Determine the COD of the sample. Assume there is no interfering element in the sample.

So, this is a problem of COD analysis. And for this we have the formula

COD = 8000(b-s)*n/sample volume

where *b* is the volume of FAS used in the blank sample, and *s* is the volume of FAS in the original sample, and *n* is the normality of FAS.

= 8000(75-50)*0.1/100

= 200 mg/l

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Problem 5	
1.5 g of a solid waste is kept in the bomb of a calorimeter. The initial and final temperatu water in bucket are 23 and 28 $^{\circ}$ C respectively. The bucket wash is titrated against Na ₂ CO ₃ and the titer value is 2.5 ml. Sulphur content in the solid waste is 2 %. Parr 45C: Cr wire is used to ignite the waste sample and 4 cm of the wire is fused. The water equivof the calorimeter is 2402 cal per °C. Hydrogen content of the waste is 8 %. Calculate the and LHV of the solid waste.	res of N/10 10 Ni- √alent 2 HHV

Problem number 5. statement is 1.5 g of a solid waste is kept in the bomb of a calorimeter. The initial and final temperatures of water in bucket are 23 and 28 °C respectively. The bucket wash is titrated against N/10 Na₂CO₃ and the titer value is 2.9 ml. Sulfur content in the solid waste is 2 %. Parr 45C10 NiCr wire is used to ignite the waste sample and 4 cm of the wire is fused. The water equivalent of the calorimeter is 2402 calorie per °C. Hydrogen content of the waste is 8 %. Calculate the HHV and LHV of the solid waste.

So this is the problem related to determination of heating value. And we will discuss and we will solve it. So, to understand this, we will have some discussion on the principles of the determination of heating value.

Say to determine the heating value initially small amount of material say 1 g is taken in a bomb calorimeter and it is combusted and the heat released during the combustion is taken up by some water and the temperature rise in the water and the bomb calorimeter material is measured. That means the heat given up by the material due to the combustion is taken up by the water and the bomb material. So, this is the principle and by that way, we by measuring

the temperature difference, we can calculate how much heat is released during the combustion of unit mass of the solid waste and we can determine the heating value.

And that heating value in this case is high heating value, because in this case, the small amount of material is used and excess oxygen is provided for complete combustion and then the flue gas which is generated that is again cooled down because although local temperature is very high, but the volume of the heated gas is very less and outside water volume is more.

So, almost all heat is transferred to the water and into the bomb material and there is slight temperature gain. So, we are assuming that since the temperature is below 100 °C, so, all moisture produced during the combustion of the material is already converted to water. So, the amount of heat which we are getting or we are able to recover that is the total heat or the high heating value we are getting through this instrument.

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So, this is the photograph of the bomb calorimeter. So, here the crucible the weighted amount of material is put here. So, say around 1 g, so after that this is put into this bomb and after putting it here the lid is tightened and then from this, we have some connection vulnerable here we can send oxygen and pressurize it.

After that, then we put it inside this water and in this water bucket we put some water around 2-liter water and then this is put inside this calorimeter and where this some hiding arrangement is there. So, when the material is that there is some filament. So, these two ends we have left for electrical connection, so, an electrician will be provided. So, this filament will be burned and the material will catch fire.

So, when this material will catch fire combustion will take place and heat will release and that heat will be distributed to this bomb material bomb well to the water inside this bucket and this temperature will be measured by this temperature measurement device. So, this is the principle which is followed in the bomb calorimeter.

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Now, we will see by the experiment which I have mentioned here, so, after putting it inside will start firing. So, initially the temperature of this calorimeter will increase and it will attain a constant value. So, there will be some differential temperature we can get, it will be coming into equilibrium within a few minutes, and then we will be getting that ΔT value.

So, we will be calculating ms Θ . So, that is equal to mass*specific heat* Δ T. So, that will be the heat taken by the water body and this this on bomb. So, that we will be following to measure the heat released by the combusted material.

So, after this experiment, the following data should be available at the completion of test in an adiabatic calorimeter that is T_a temperature at time of firing, corrected for thermometer scale error. So, we have to correct if there is any error in the thermometer measurement and T_f is the final maximum temperature again some correction is needed or nowadays we can get ΔT also differential thermometer is also available.

And in this case, the heat which we get during the heat which is really released here it is transmitted to the water and by ΔT change we calculate the heat taken up by this, but which heat is taken up by this water and the bomb material that is not exactly produced during the combustion reactions only. It had some contribution which are not from this combustion of this, but from other sources also what are those sources one is this crucible which we are using that will also be burned and it will also release some amount of energy number one, if there is any sulfur the SOx will be produced.

So, that SOx again inside these bomb and water vapor will be condensed. So, that will give up sulfuric acid production. So, that will also add some amount of heat to the total heat which will be taken up by the water and acids, some nitrogen nitric acid can be formed and that some amount of heat is also generated due to the formation of this acid. And we need to correct this contribution to calculate the exact heating value of the material.

So, if we see that C_1 , C_2 , C_3 another parameter we will get. What are those parameters? C_1 is the milliliters of standard alkali solution used in acid titration. So, to determine the value or contribution of the heat generated during acid formation for that after completion of this bomb calorimeter test will be open the lid and then we will depressurized it and then we will open the lid and then take the material out and then this bomb calorimeter wall will be washed and then that washed will be containing the acids which was deposited on the wall and that will be titrated against the alkalis solution.

So, that what is the ml of a milliliters of standard alkali solution used for acid titration that we can generate to the experiment and C_2 is the percentage of sulfur in the sample we can determine and C_3 is the centimeter of fused wire consumed in firing. So before starting what

is the length of fused wire we are using and after experiment, what is the length of the fused wire unburned so that difference of the burnt or used. So heat has been released from that.

So, that heat we have to consider for error correction and M is the mass of the sample in grams. How much amount of material we are using that we can also calculate. So, these data will be able to generate.

Now, if you see after the combustion heat is generated H_1 . And this is taken up by the water and the bomb material. So, if we have m mass of water than $m_w S_w \Delta T$ (heat taken up by this water) + $M_B S_B \Delta T$. So, this is a heat taken up H_2 , H_3 that is water and the bomb material, so, that we can get total heat taken up that is equal to $\Delta T(m_w * S_w + M_B \text{ into } S_B)$.

So, for a particular bomb calorimeter this material are fixed, there material of construction their sides are fixed and this bomb is also fixed their volume are also fixed. So, these two terms are constant. So, that is nothing but W that is called that water equivalent.

So, this is the heat taken up and what is the heat released by this material we have M gram of material, so, $M^*H = \Delta T^*W$, but as we mentioned that this is not exactly the amount of heat which was generated during the combustion, it also adds something so, we have to subtract those because of this your E₁ error correction E₂, E₃, E₁ is from this due to the C₁, E₂ is due to the C₂ and E₃ is due to the C₃. So, by doing these correction we can calculate the actual heat which was generated during the combustion.

So, high heating value $H = (\Delta T_w - E_1 - E_2 - E_3)/M$, here M is the mass of the material taken in a bomb calorimeter. So, this is the process we follow and by using this formula, we can calculate the heating value, but now, the W, how can we get the value of W. W value can be measured using the same calorimeter and using a known substance now the substance will be known.

So, we know the heating value of these substance. So this is the calibration of the equipment we can say, since this we use a known material and combust it and in that case, we know how much ΔH is there how much heating value is there. So, we will be putting this formula we will be calculating E₁, E₂, E₃, M, since in that case will we get the getting the value $\Delta T * w$. So, we can also get the value of W= (HM + E₁ + E₂ + E₃)/ ΔT .

So, that way also you can calculate the value of the W and this is done prior to the applications of the bomb calorimeter and performing the same experiment using a known compound whose heating value is known to us like say benzene is used.

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Ther	Thermochemical corrections :		
E ₁ =	E_1 = correction in calories for heat of formation of nitric acid (HNO ₃)		
:	C1 calories, if 0.0709	N Sodium carbonate wa	s used for the acid titration
E2=	correction in calories	for heat of formation of	f sulfuric acid
	= (13.7)(C ₂)(M) calorie	S	
E ₃ = correction in calories for heat of combustion of fuse wire			
=	$(2.3)(C_3)$ when using F	Parr 45C10 nickel-chrom	ium fuse wire, or
-	$(2.7)(C_3)$ when using	34 B. & S. gage iron fuse	wire
=	0 when using 34 gage	e or finer platinum wire	W can be determined by
Gro	ss heat of Combustion.	$Hg = \frac{T * W - E_1 - E_2 - E_3}{M}$	standardizing the calorimeter using a compound whose heat of combustion is known
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So, how we will calculate the gross heating value then, this formula just we have discussed and how we will calculate the E_1 , E_2 , E_3 that we have to know. So,

 E_1 = correction in calories for heat of formation of nitric acid just to I have mentioned that is equal to C_1 calories.

= C1 calories, if 0.0709N Sodium carbonate was used for the acid titration

 E_2 = correction in calories for heat of formation of sulfuric acid

 $= (13.7) (C_2)(M)$ calories

E₃= correction in calories for heat of combustion of fuse wire

 $= (2.3) (C_3)$ when using Parr 45C10 nickel-chromium fuse wire, or

= (2.7) (C₃) when using 34 B. & S. gage iron fuse wire

= 0 when using 34 gage or finer platinum wire

So, these values will be provided by the supplier of the bomb calorimeter. So, now, knowing all those things we can calculate the Hg values knowing the value of W. So, W can be

determined by standardizing the calorimeter using a compound whose heat of combustion is known basically, benzene is used.

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	Standardization procedure
	• The procedure for the standardization test is exactly the same as for testing a fuel sample. A pellet of benzoic acid weighing not less than 0.9 nor more than 1.25 grams is added. The energy equivalent of the calorimeter is determined by:
	$W = \frac{H * M + E_1 + E_3}{T}$
	W = energy equivalent of the calorimeter in calories per degree celsius
	H = heat of combustion of the standard benzoic acid sample in calories per gram
	M = mass of the standard benzoic acid sample in grams
	T = net corrected temperature rise in degree C
	E ₁ = correction for heat of formation of nitric acid in calories
	E_3 = correction for heat of combustion of the firing wire in calories
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So, this is the standardization procedure we have mentioned. So, that is W is the energy equivalent of the calorimeter in calories per degree Celsius. So, these are the different methods we have already discussed normally 0.9 or 1.2 within this the benzoic acid is used for the determination of W value.

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Solution	Data given	
$Hg = (T^*W - E_1 - E_2 - E_3)/M$		M = 1.5 gram
Therefore,		$C_1 = 2.5 \text{ m/} c_2 = 2\%$ $C_2 = 2\%$ $C_3 = 4 \text{ cm}$
E ₁ = (2.5 ml)(1 cal/ml) = 2.5 ca	al;	$T = 28 - 23 = 5 \circ C$
$E_2 = (13.7)(C_2)(m)$ calories = 1	.3.7*2*1.5 = 41.1 Cal	
$E_3 = = (2.3)(C_3) = (2.3 \text{ cal/cm})$	(4 cm) = 9.2 cal	
Hg = (5*2402 - 2.5- 41.1 - 9.2	2)/1.5 = 7971 Cal /gram	
Hn= 0.555927*[1.8Hg -91.23	H] in KCal/Kg = 0. <u>555</u> 92 = 7570.59	7 [1.8*7971 -91.23* <u>8]</u> KCal/Kg
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Now, let us see in our problem statement, what are the values. So, as par as our problem statement, we know that high heating value will

 $W = (H*M + E_1 + E_2)/T$

And in this case, the M is equal to 1.5 gram, and C_1 that is 2.5 ml standard alkali is required and C_2 2% sulfur and

 $C_3 = 4$ centimeter of fuse wire

$$T = 28 - 23 = 5 \ ^{\circ}C$$

W = 2402 calorie/ $^{\circ}C$

 $E_1 = (2.5 \text{ ml})(1 \text{ cal/ml}) = 2.5 \text{ cal};$

 $E_2 = (13.7)(C_2)(m)$ calories = 13.7*2*1.5 = 41.1 Cal

 $E_3 = = (2.3)(C_3) = (2.3 \text{ cal/cm}) (4 \text{ cm}) = 9.2 \text{ cal}$

Hg = (5*2402 - 2.5 - 41.1 - 9.2)/1.5 = 7971 Cal /gram

So, net or low calorific value Hn will be having by some empirical relationship we have discussed in the previous class.

Hn= 0.555927*[1.8Hg -91.23H] in KCal/Kg

=0.555927 [1.8*7971 -91.23*8] = 7570.59 KCal/Kg

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And then problem number 6. So, the statement is to determine the water equivalent of a bomb calorimeter 1.1651 g benzoic acid sample, high heating value 6318 cal/g was used. The experiment produced a net corrected temperature rise of 3.077 °C. The acid titration required 11.9 ml standard alkali and 8 cm of parr 45C10 nickel-chromium fuse wire was consumed in the firing. Determine the water equivalent of the bomb calorie meter. So, I just discussed.

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Therefore,	
E ₁ = (11.9 ml)(1 cal/ml) = 11.9 cal;	
$E_2 = (13.7)(C_2)(m)$ calories = 0 as C_2 is 0	
E ₃ = =(2.3)(C ₃) = (2.3 cal/cm) (8 cm) = 18.4 cal	
We know that	
$W = (H*M + E_1 + E_2 + E_3)/T$	
W_{-} (6318)(1.1651) + 11.9 + 18.4	
3.077 - 2402.1 cal per deg e	
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		Problem 6
To determi sample (H temperatur cm of Parr water equiv	he the water equivalent of HV 6318 cal/g) was use e rise of 3.077° C. The acio 45C10 nickel-chromium fus alent of the bomb calorim	of a bomb calorimeter 1.1651 gram benzoic acid d. The experiment produced a net corrected d titration required 11.9 ml of standard alkali and 8 se wire was consumed in the firing. Determine the eter.
Solution:		-
Given data	H = 6318 cal/gram 🧹	
	M = 1.1651 gram 🦯	
	C ₁ = 11.9 ml	T = 3.077° C
	C ₂ = 0	
	$C_3 = 8 \text{ cm}$	
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So, water equivalent we can calculate by this formula

 $W = (H^*M + E_1 + E_2 + E_3)/T$

Now, in this case H is given, M is given C_1 is given, C_2 is very important, because we are taking pure benzene. So, we are using benzoic acid. So, benzoic does not have any sulfur, so, sulfur content is equal to 0 or C_2 equal to 0. So, E_2 will also be 0 and C_3 is 8 cm and T is 3.077 °C.

Therefore,

 $E_1 = (11.9 \text{ ml})(1 \text{ cal/ml}) = 11.9 \text{ cal};$

 $E_2 = (13.7)(C_2)(m)$ calories = 0 as C_2 is 0

 $E_3 = = (2.3)(C_3) = (2.3 \text{ cal/cm}) (8 \text{ cm}) = 18.4 \text{ cal}$

 $W = [(6318*1.1651) + 11.9 + 18.4]/3.077 = = 2402.1 \text{ cal/}^{\circ}C$

Thank you very much for your patience.