Biological Treatment Of petroleum Waste Water

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ABSTRACT:

The waste water from petroleum industries contains high organic matter content , oil and grease , dissolved solids and turbidity . The petroleum waste water normally treated in a plant comprising of primary ,secondary and tertiary treatment . The high organic loading needs to be treated in biological treatment step. Biological treatment can be suspended growth or attached growth type. The anaerobic treatment have advantages such as reduction in sludge content , many investigators have investigated biological treatment of petroleum refinery waste water.

Key Words : Biological treatment, Material and Energy Balance , waste water

1-Introduction :

Pollution of water occurs when one or more substances that will modify the water in negative fashion are discharged in it. These substances can cause problems for people, animal sand also for the environment(1). Wastewater can be defined as the flow of used water discharged, from homes, businesses industries, commercial activities and institutions .Wastewater treatment is the process of purification of wastewater from impurities, suspended substances, pollutants and organic matter to become reusable (non-human) or to be disposed of in the waterways without causing contamination(1).

2-Wastewater and petroleum wastewater :

The refineries were classified into either hydro-skimming unit, which include a crude distillation unit, a desulphurising unit and a reforming unit, or a complex unit, which include a catalytic cracking unit with the hydro-skimming refinery. In addition, Petrochemical plants were sometimes incorporated within the refinery complex. In general, the pollutants in wastewater can be divided into organic matter, inorganic matters which include nitrogen, phosphorus, ammonia and iron chlorides as well as heavy metals.

The organic compounds and ammonia nitrogen considered the principal chemical characteristics of environmental concern in wastewater. The chemical oxygen demand (COD) and 5-day biochemical oxygen demand (BOD_5) are used as parameters to describe organic matter in wastewater(2).

3- Petroleum wastewater generation in refineries:-

Transforming crude oil into useful products such as Gasoline and kerosene was achieved by the numerous refinery configurations. During these processes, the petroleum wastewater was generated in the units such as Hydro-cracking, Hydro-cracker flare, Hydro-skimming, Hydro-skimmer flare, sourwater, Condensate, Condensate flare and the desalter. Normal-alkanes (C_{10}-C_{21}), aromatics, and polycyclic hydrocarbons(3).

4- Current petroleum wastewater treatment techniques :-

The petroleum wastewater treatments are classified into three types; physical, chemical and biological. However, the treatment required a typical application of the integrated system due to the complexity of characteristics of petroleum wastewater. Thus, the conventional treatment methods need multistage process treatment. The first stage consisted of pre-treatment, which includes mechanical and physicochemical treatments followed by the second stage which is the advanced treatment of the pretreated wastewater. the techniques and methods for petroleum wastewater treatment included physical, chemical, biological treatment processing(3).

- Physical treatment :-
- Chemical treatment :-
- Biological treatment :-

4.1Biological treatment methods[4]:-

- Aerobic biological processes -
- Anaerobic biological process:-

5- Process description:

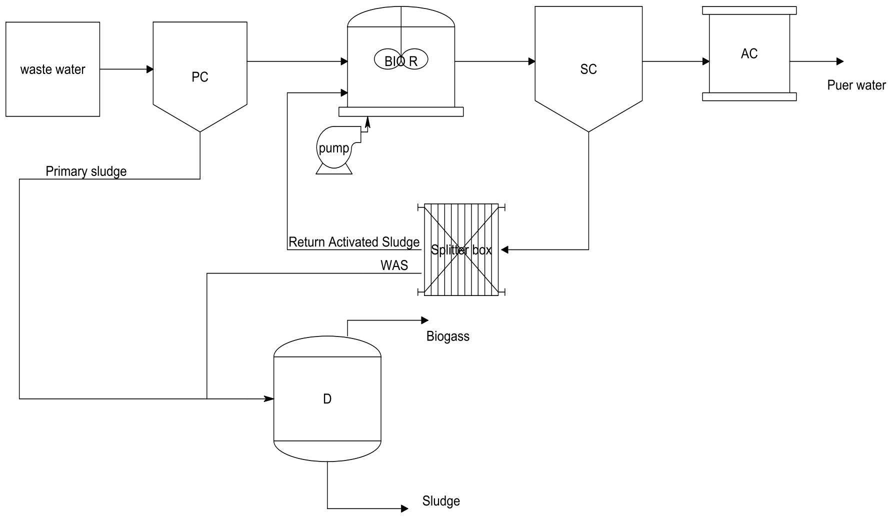


Figure (1)Process Flow Sheet

Table(1) list of equipment in the Process Flow Diagram

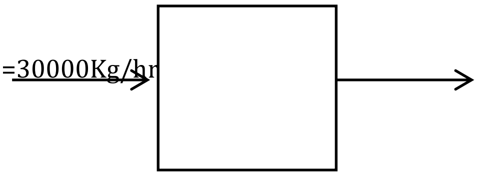
Abbreviation equipment	Equipment
PC	Primary clarifiers
BIO R	Bioreactors
SC	Secondary clarifiers
AC	Activated Carbon
WAS	waste-activated sludge
D	Digesters

6-Material Balance :

- A mass balance also called a Material Balance is an application of conservation of mass to the analysis of physical systems[5]. By accounting for a material entering and leaving a system, mass flows can be identified which might have been unknown, or difficult to measure without this technique. The exact conservation law used in the analysis of the system depends upon the context of the problem but all revolve around the mass conservation, i.e. that matter cannot disappear or be created spontaneous

- Quantity of materials entering = amount of materials outsideof materials entering = amount of materials outside

6-1 Material Balance at wastewater tank:-

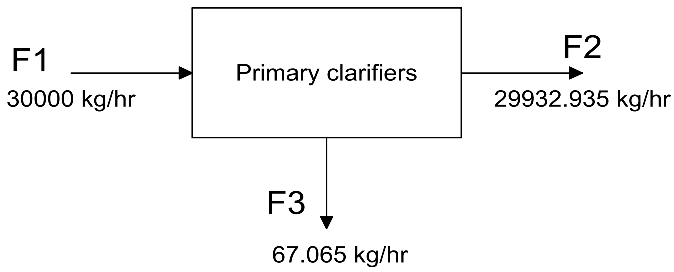


F=30000Kg/hr F1=30000Kg/hr

Input=output

F=F1

6-2 **Material Balance at primary clarifiers:-**



Table(2) The organic materials were removed in the proportions shown in the table below [4]

Component	Percentage in removal %
Oil	90
Tss	95
Bod	95
COD	95
PHENOL	85

Table(3) : Overall and Component Material Balance on Multi component primary clarifiers

Unit	Stream f1 input		Stream f2 output		Stream f3 output	
Component	W%	Kg/hr	W%	Kg/hr	W%	Kg/hr
Oil	0.022	6.6	0.0022	0.66	8.857	5.94
Tss	0.175	5.25	0.0087	0.2625	7.436	4.9875
Bod	0.02	6	0.001	0.3	8.499	5.7
COD	0.045	13.5	0.00225	0.675	19.123	12.825
PHENOL	0.016	4.8	0.00240	0.72	6.083	4.08
WATER	99.87	29963.85	99.9	29930.31	50	33.532
TOTAL	100	30000	100	29932.935	100	67.065

Over all material balance:-

F1=F2+F3

30000=F2+67.065

F2=29932.935 kg/hr

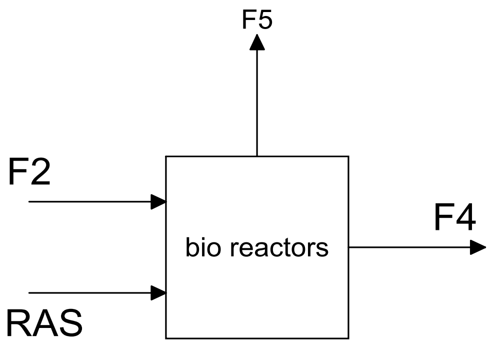
Error=0

6-3 Material balance bio reactors:-

Determine the amount of reflux(5):

RAS=0.75*F2+0.25* Bacteria*(1-XA)

=0.75*29932.93+0.25*2.61*(1-0.9)



RAS=22449.7

$8COHNS+4O_2+ 1/3N+bacteria \rightarrow 3CO_2+1/3NH_3+C_5H_7NO_2+other\ end\ product$

Table (4) stoichiometric calculations follows

Component	Mole	Change(90%)	Remaining
COHNS	0.0349	0.03141	0.00349
O_2	0.12	0.12	0
CO_2	0	0.094	0.094
H_2O	1662.79	0	1662.79
NH_3	0	0.01	0.01
$C_5H_7NO_2$	0	0.03141	0.03141
Bacteria	0.0349	0.0394	0
N	0.01	0.01	0
other end products	0	0.0349	0.0349

Table (5) Overall and Component input Material Balance on Multi component bio reactors

Component	**Stream F2 IN**		
	Mole	**Kg/hr**	**W%**
OIL	0.0088	0.66	0.0012
TSS	0.0035	0.2625	0.0005

BOD	0.004	0.3	0.00057
COD	0.009	0.675	0.0012
PHENOL	0.0096	0.72	0.0013
N	0.01	0.14	0.00026
O_2	0.12	3.84	0.0073
Bacteria	0.0349	2.61	0.0049
H_2O	1662.79	29930.31	57.13
RAS	-	22449.7	42.85
TOTAL		**52389.49**	**100**

Table (6) Overall and Component output 1 Material Balance on Multi component bio reactors:

Component	**Stream F4 out1**		
	Mole	**Kg/hr**	**W%**
OIL	0.0088	0.594	0.0011
TSS	0.0035	0.236	0.00045
BOD	0.004	0.27	0.00051
COD	0.009	0.607	0.00115
PHENOL	0.0096	0.648	0.00123
H_2O	1662.79	29930.31	57.136
RAS	-	22449.7	42.85
other end products	0.0349	0.89	0.0016
TOTAL		52383.25	100

Table (7) Overall and Component output 1 Material Balance on Multi component bio reactors:

Component	**Stream F4 out2**		
	Mole	**Kg/hr**	**W%**
Co_2	0.94	3.88	95.80
Nh_3	0.01	0.17	4.19
TOTAL		4.05	100

F2=52389.49 kg/hr

RAS=22449.7 Kg/hr

F4=52383.52 Kg/hr

F5=4.05 Kg/hr

Erorr=0.003

6-4 Material balance at secondary clarifiers:-

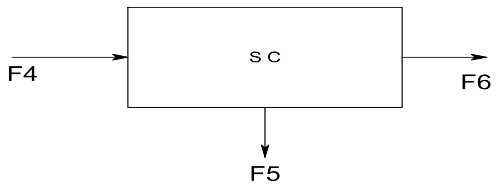


Table (8) The organic materials were removed in the proportions shown in the table below [5]

Component	Percentage in removal %
OIL	94
TSS	97.6
BOD	94.4
COD	93.4
PHENOL	65

Table (9) : Overall and Component Material Balance on Multi component secondary clarifiers

Unit	Stream F4 in		Stream F7 out		Stream F6 out	
Component	**W%**	**Kg/hr**	**W%**	**Kg/hr**	**W%**	**Kg/hr**
OIL	0.0011	0.594	0.0024	0.5583	0.00011	0.0366
TSS	0.00045	0.236	0.001	0.230	0.000018	0.0056
BOD	0.00051	0.27	0.00113	0.2548	0.000050	0.0151
COD	0.00115	0.607	0.00252	0.566	0.000133	0.04
PHENOL	0.00123	0.648	0.0018	0.42	0.00075	0.226
H_2O	57.136	29930.31	-	-	99.99	29930.31
RAS	42.85	22449.7	99.9	22449.7		
other end products	0.0016	0.89	0.0039	0.89		
TOTAL	100	52383.25	100	22452.61		29930.632

F4=52383.25 Kg/hr

F6=29930.632 Kg/hr

F7=22452.61 Kg/hr

Error=0.00001

6-5 Material balance at splitter:-

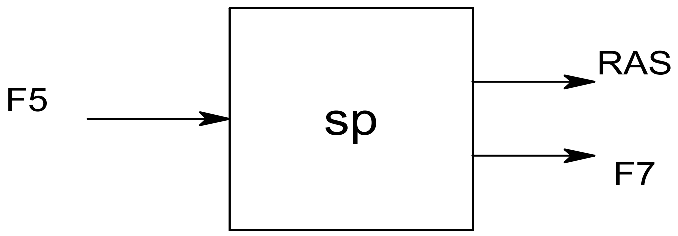


Table (10) : Overall and Component Material Balance on Multi component splitter

Unit	Stream F7 in		Stream F8 out1		Stream RAS out2	
Component	**W%**	**Kg/hr**	**W%**	**Kg/hr**	**W%**	**Kg/hr**
OIL	0.0024	0.5583	19.1	0.5583	-	-
TSS	0.001	0.230	7.9	0.230	-	-
BOD	0.00113	0.2548	8.75	0.2548	-	-
COD	0.00252	0.566	19.4	0.566	-	-
PHENOL	0.0018	0.42	14.43	0.42	100	
RAS	99.9	22449.7	-	-		22449.7
other end products	0.0039	0.89	30.59	0.89		
TOTAL		22452.61	100	2.91	100	22449.7

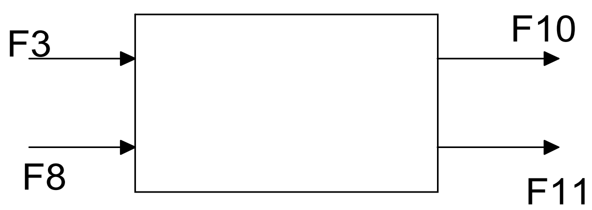
F7=22452.61 Kg/hr

RAS OUT=22449.7 Kg/hr

F8=2.91 Kg/hr

Error=0

6-6 Material balance at digester :-



F8+F3=2.91+67.065=69.975 kg/hr

1 kg → 0.2 kg bio gas

69.975 —x→

X=13.99 kg/hr (biogas)

Sludge=69.975-13.99

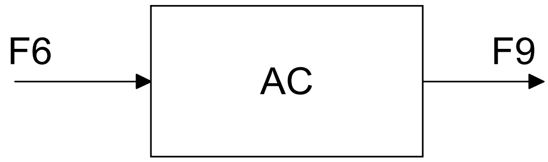
=55.98 kg/hr

F10=13.99Kg/hr

F11=55.98Kg/hr

Error=0.0007

6-7 Material balance at Activated Carbon:-



Filter percentage 65%

Table (11) : Overall and input Component Material Balance on Multi component Activated Carbon

Component	Stream F6IN	
	Kg/hr	W%
OIL	0.0366	0.0001
TSS	0.0056	0.0000187
BOD	0.0151	0.000050
COD	0.04	0.000133
PHENOL	0.226	0.00075
H_2O	29930.31	99.99
Total	29930.632	100

Table (12) : Overall and output Component Material Balance on Multi component

Component	Stream F9 Out	
	Kg/hr	W%
OIL	0.0023	0.0000076
TSS	0.0036	0.00012
BOD	0.0098	0.000032
COD	0.026	0.000086
PHENOL	0.146	0.000487
H_2O	29930.31	99.99
Total	29930.497	100

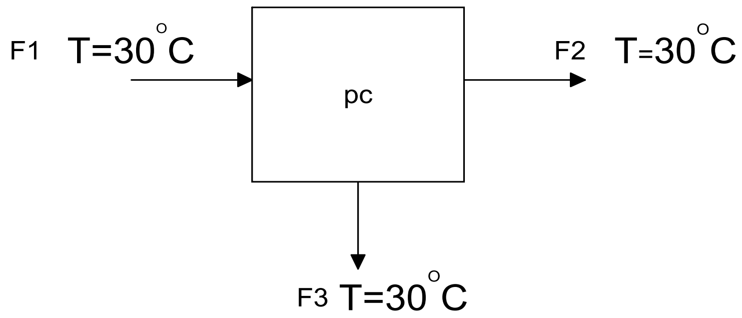
F6=29930.632Kg/hr

F9=29930.497Kg/hr

7-Energy Balance:

Energy can be considered to be separately conserved in all but nuclear processes .The conservation of energy, however, differs from that of mass in that energy can be generated (or consumed) in a chemical process. Material can change form, new molecular species can be formed by chemical reaction, but the total mass flow into a process unit must be equal to the flow out at the steady state(5).

7-1 Energy Balance at primary clarifiers:-



Generally:-

Q=MCPT

Where:-

Q=quantity of heat (kj/hr).

M=mass flow rate (kg/hr).

CP=specific heat (kj/kg.c)

Table(13) Input energy balance at primary clarifiers :-

Stream F1input			
Component	**Mass in kg/hr**	**Cp_i**	**Cp_i*m_i**
OIL	6.6	2.09	13.794
TSS	5.25	2.8	14.7
BOD	6	0.916	5.496
COD	13.5	0.916	12.366
PHENOL	4.8	1.43	6.864
H_2O	29963.85	4.18	125248.83
TOTAL	30000		125303.05

$Qin=(\sum_i cp_i*m_i)*T$

=125302.05*30=3759061.5 kj/hr

Table(14) output energy balance at primary clarifiers :-

Stream F2 output 1			
Component	**Mass in kg/hr**	**Cp_i**	**Cp_i*m_i**
OIL	0.66	2.09	1.3794
TSS	0.2625	2.8	0.735
BOD	0.3	0.916	0.2748
COD	0.675	0.916	0.6183
PHENOL	0.72	1.43	1.0296
H_2O	29930.318	4.18	125108.72
TOTAL	29932.935		125112.76

Table(15) output energy balance at primary clarifiers:-

Stream F3 output 2			
component	**Mass in kg/hr**	**Cp_i**	**Cp_i*m_i**
OIL	5.94	2.09	12.14
TSS	4.9875	2.8	13.965
BOD	5.7	0.916	5.2212
COD	12.825	0.916	11.747
PHENOL	4.08	1.43	5.83
H_2O	33.532	4.18	140.16
TOTAL	67.065		189.33

$Q_{out}=(\sum_i cp_i*m_i)*T$

Q(F2)=125112.76*30

=3753382.8 Kj/hr

Q(F3)=189.33*30

=5679.9 Kj/hr

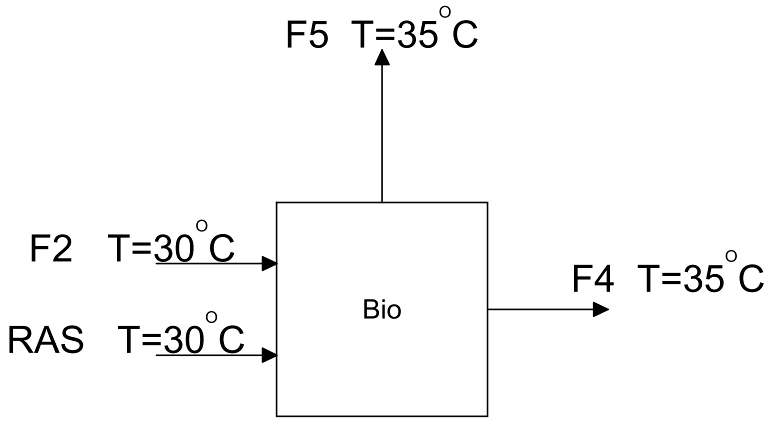
Q_{out}=Q(F2)+Q(F3)=3753382.8+5679.9

Q_{out}=3759062.7 kj/hr

Load=Q_{out}-Q_{in}=3759062.7-3759061.5

Load=1.2 kj/hr

7-2 Energy Balance at Bioreactor:-



Table(16) Input energy balance on bioreactor :-

Stream F2 input1			
Component	**Mass in kg/hr**	**Cp_i**	**Cp_i*m_i**
OIL	0.66	2.09	1.379
TSS	0.2625	2.8	0.735
BOD	0.3	0.916	0.2748
COD	0.675	0.916	0.6183
PHENOL	0.72	1.43	1.0296
H_2O	29930.31	4.18	125108.69
N	0.14	1.0395	0.145
O_2	3.84	0.916	3.517
Bactera	2.61	1.3	3.393
TOTAL	2993.51		125119.77
Stream RAS input 2			
RAS	22449.7	1.24	28059.88

$Q_{in}=(\sum_i cp_i*m_i)*T$

=125119.77*30=3753593.1kj/hr

Q_{in}(RAS)=28059.88*30=841796.4Kj/hr

Qin=Q(F2)+Q(RAS)

=3753593.1+841796.4

=4595389.5Kj/h

Table(17) output energy balance at bioreactor :-

		Stream F4 output1	
Component	**Mass in kg/hr**	**Cp_i kj/kg.c**	**Cp_i*m_i**
OIL	0.594	1.73	1.02
TSS	0.236	2.6	0.613
BOD	0.27	0.9	0.243
COD	0.607	0.9	0.546
PHENOL	0.648	1.2	0.77
H_2O	29930.31	3.47	103858.17
RAS	22449.7	1.24	27837.62
OTHER END	0.89	0.00695	0.0061
TOTAL STREAM F4	52383.25		131698.96
Stream F5 output2			
Co_2	3.88	0.85	3.298
NH_3	0.17	4.2	0.714
TOTAL	4.05		4.012

$Q_{out}=(\sum_i cp_i*m_i)*T$

Q(F4)=131702.39*35=4609463.88 kj/hr

Q(F5)=4.012*35=140.42 Kj/hr

Q_{out}=Q(F4)+Q(F5)=4609463.88+140.42

=4609604.30 kj/hr

Load= Q_{out}- Q_{in} =4609604.30-4595389.5

Load of reaction =14214.8 kj/hr

7-3 Energy Balance at secondary clarifiers:-

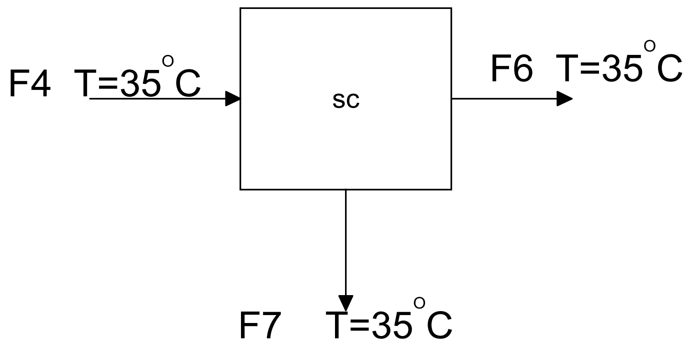


Table (18) input energy balance at secondary clarifiers:-

Stream F4 input			
Component	Mass in kg/hr	Cp_i kj/kg.c	Cp_i*m_i
OIL	0.594	1.73	1.02
TSS	0.236	2.6	0.613
BOD	0.27	0.9	0.243
COD	0.607	0.9	0.546
PHENOL	0.648	1.2	0.77
H_2O	29930.31	3.47	103858.17
RAS	22449.7	1.24	27837.62
OTHER END	0.89	0.00695	0.0061
TOTAL STREAM F4	52383.25		131698.96

$Q_{in}=(\sum_i cp_i*m_i)*T$

$Q_{in}=131698.96*35=4609463.88$ kj/hr

Table(19) output energy balance at secondary clarifiers:-

Stream F6 output 1			
Component	Mass in kg/hr	Cp_i kj/kg.c	Cp_i*m_i
OIL	0.0356	1.73	0.0615
TSS	0.0056	2.6	0.014
BOD	0.0151	0.9	0.0135
COD	0.04	0.9	0.036
PHENOL	0.226	1.2	0.271
H_2O	29930.31	3.47	103858.17
TOTAL	29930.632		103858.56
Stream F7 output 2			
OIL	0.5583	1.73	0.965
TSS	0. 230	2.6	0.598
BOD	0.2548	0.9	0.229
COD	0.566	0.9	0.509
PHENOL	0.42	1.2	0.504
RAS	22449.7	1.24	27837.62
OTHER END	0.89	0.00695	0.0061
TOTAL	22452.61		27840.43

$Q_{out}=(\sum_i cp_i*m_i)*T$

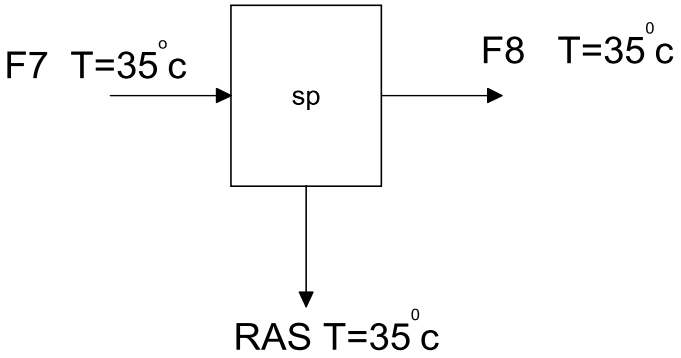
Q(F6)=103858.56*35=3635049.6 kj/hr

Q(F7)=27840.43*35=974415.05 kj/hr

Q_{out}=Q(F6)+Q(F7)=4609464.6 kj/hr

Load=Q_{out}-Q_{in}=o.77 kj/hr

7-4 Energy Balance at splitter:-



Table(20) input energy balance at splitter

Stream F7 input			
Component	**Mass in kg/hr**	**Cp_i kj/kg.c**	**Cp_i*m_i**
OIL	0.5583	1.73	0.965
TSS	0. 230	2.6	0.598
BOD	0.2548	0.9	0.229
COD	0.566	0.9	0.509
PHENOL	0.42	1.2	0.504
RAS	22449.7	1.24	27837.62
OTHER END	0.89	0.00695	0.0061
TOTAL	22452.61		27840.43

$Q_{in}=(\sum_i cp_i*m_i)*T$

Q_{in}=27840.43*35=974415.05 kj/hr

Table(21) output energy balance at plitter

Stream F8 output1			
Component	**Mass in kg/hr**	**Cp_i kj/kg.c**	**Cp_i*m_i**
OIL	0.5583	1.73	0.965
TSS	0.230	2.6	0.598
BOD	0.2548	0.9	0.229

COD	0.566	0.9	0.509
PHENOL	0.42	1.2	0.504
OTHER END	0.89	0.00695	0.0061
TOTAL	2.91		2.811
Stream output 2			
Component	**Mass in kg/hr**	**Cp_i kj/kg.c**	**Cp_i*m_i**
RAS	22449.7	1.24	27837.62
TOTAL	22449.7		27837.62

$Q_{out}=(\sum_i cp_i*m_i)*T$

Q(F8)=2.811*35=98.385 Kj/hr

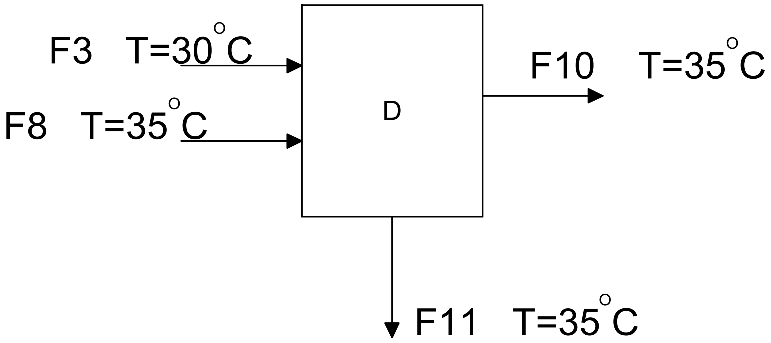
Q(RAS)=27837.62*35=974316.7 Kj/hr

Q_{out}=Q(F8)+Q(RAS)=98.385+974316.7 Kj/hr

=974415.085 kj/hr

Load=$Q_{out}-Q_{in}$=0.035Kj/hr

7-5 Energy Balance at Digester:-



Table(22) input energy balance at digester

Stream F3 input1			
Component	Mass in kg/hr	Cp_i	Cp_i*m_i
OIL	5.94	2.09	12.14
TSS	4.9875	2.8	13.965
BOD	5.7	0.916	5.2212
COD	12.825	0.916	11.747
PHENOL	4.08	1.43	5.83
H_2O	33.532	4.18	140.16
TOTAL	67.065		189.32

Stream F8 input2			
Component	**Mass in kg/hr**	**Cp_i kj/kg.c**	**Cp_i*m_i**
OIL	0.5583	1.73	0.965
TSS	0.230	2.6	0.598
BOD	0.2548	0.9	0.229
COD	0.566	0.9	0.509
PHENOL	0.42	1.2	0.504
OTHER END	0.89	0.00695	0.0061
TOTAL	2.91		2.811

$Q_{in}=(\sum_i cp_i*m_i)*T$

Q(F3)=189.32*30=5679.6 Kj/hr

Q(F8)=2.811*35=98.385 Kj/hr

Q_{in}= Q(F3)+ Q(F8)=5777.9 kj/hr

Table(23) output energy balance at digester

Stream F10 output1			
Component	**Mass in kg/hr**	**Cp_i kj/kg.c**	**Cp_i*m_i**
BIOGAS	13.99	2.2	30.778
Stream F11 output2			
SLUDGE	55.98	4.18	233.99

$Q_{out}=(\sum_i cp_i*m_i)*T$

Q_{out}(F10)=30.778*35=1077.23 Kj/hr

Q_{out}(F11)=233.99*35=8189.65 Kj/h

Q_{out}=Q(F10)+Q(F11)=9266.88 Kj/hr

Load=Q_{out}-Q_{in}=3488.9 kj/hr

7-6 Energy Balance at Actived Carbon:-

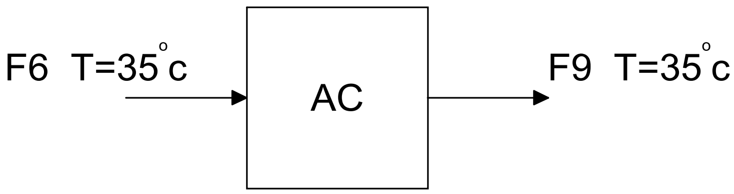


Table (24)input energy balance at Actived carbon

Stream F6 input			
Component	Mass in kg/hr	Cp_i kj/kg.c	Cp_i*m_i
OIL	0.0356	1.73	0.0615
TSS	0.0056	2.6	0.014
BOD	0.0151	0.9	0.0135
COD	0.04	0.9	0.036
PHENOL	0.226	1.2	0.271
H_2O	29930.31	3.47	103858.17
TOTAL	29930.632		103858.56

$Q_{in}=(\sum_i cp_i*m_i)*T$

$Q_{in}=103858.56*35=3635049.6$ kj/hr

Table(25)output energy balance at Actived carbon

Stream F9 output			
Component	**Mass in kg/hr**	**Cp_i kj/kg.c**	**Cp_i*m_i**
OIL	0.0023	1.73	0.0039
TSS	0.0036	2.6	0.0093
BOD	0.0098	0.9	0.0088
COD	0.026	0.9	0.0234
PHENOL	0.146	1.2	0.1752
H_2O	29930.31	3.47	103858.17
TOTAL	29930.497		103858.39

$Q_{out}=(\sum_i cp_i*m_i)*T$

$=103858.39*35=3635043.65$ kj/hr

Load= $Q_{out}-Q_{in}=3635043.65-3635049.6=-5.95$ kj/hr

8- Conclusions

The water drainage with activated sludge using a reactor in the phase of biological processing carried out by bacteria in the presence of oxygen, which produces clean water and less harmful products plus energy and so we can benefit from the treated water in hygiene and for the purposes of agriculture and irrigation of land and others.

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