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Steam Assisted Flare Stack Capital Costing

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In industrial plants, flare stacks primarily serve the purpose of burning flammable gases released by safety valves during unplanned over-pressurization of plant equipment. They are also used during plant start-up and shutdown, maintenance, testing and emergency purposes.

The following article covers preliminary costing of a flare stack system based on Sec 3.2 of US EPA guidelines.

Cost Estimation General Notes

The total capital investment (TCI) includes,

- Equipment Costs (EC) of the flare itself
- Cost of auxiliary equipment
- Monitoring equipment & Instrumentation
- Cost of Taxes and freight
- All direct and indirect costs

The capital cost depends on the degrees of sophistication required and the number of appurtenances selected such as KO drums, seals, controls, ladders and platforms. The basic support structure of the flare, the size and height, and the auxiliary equipment are the controlling factors in the cost of the flare.

The capital investment will also depend on the availability of utilities such as steam, natural gas, and instrument air. The total capital investment is a battery limit cost estimate and does not include the provisions for bringing utilities, services, roads on site, backup facilities, real estate, the R&D and piping and instrumentation interconnections that may be required in the process generating waste gas [2].

The costing method presented in this article is based on a new plant installation with no retrofit costs involved, such as demolition. The expected cost accuracy of the mentioned costs is $\pm 30\%$. The cost correlations presented here is restricted to flare tip diameters ranging 1 inch to 60 inches and flare stack height from 30 feet to 500 feet. The material of construction is carbon steel.

This is except when it is standard practice to use other construction materials other than carbon steel, as is the case with burner tips.

Equipment Costs

The flare costs for the tower type are [2],

Self Supporting Group

$$C_F = [93.6 + 10.97d_j + 0.899h]^2 \quad (1)$$

Guy-Supported Group

$$C_F = [124 + 10.42d_j + 0.564h]^2 \quad (2)$$

Derrick-Supported Group

$$C_F = [91.7 + 3.26d_j + 1.968h]^2 \quad (3)$$

where,

C_F = Flare costs in 2017 USD

d_j = Flare Tip Diameter [in]

h = Flare stack height [ft] (min 30 ft)

Each of these costs includes flare tower, supports, burner tips, pilots, utilities (steam, natural gas, LPG), piping from base, utility metering and control, liquid seal, gas seal, and galvanized caged ladders and platforms as required. Costs are based on carbon steel, construction, except for upper four feet and burner tip, which are based on stainless steel [SS 310] construction.

The equipment costs for the flare do not include monitoring equipment costs that may be needed to demonstrate compliance with applicable operating limits for flares [2]. However, the key monitoring equipment may include,

- Pilot Flame monitor
- Gas Chromatograph
- Hydrogen analyzer
- Calorimeter
- Flare Gas Flow monitor
- Steam Fine controls/Metering
- Air Fine controls/Metering

The lower heating value [LHV] is based on the calorimeter based on flare gas composition. Other monitoring equipment maybe required depending on the flare application. For e.g., new flares at a petroleum refinery may also additionally require sulphur monitoring provisions for the flare vent gas for regulatory compliances [2]

For purposes of capital estimation, it is assumed that the transfer line / vent stream will be the same diameter as the flare tip. The length of the vent stream is considered to be 100 ft as a minimum. The costs associated with vent stream piping is as follows [2],

$$C_P = 183 \times \left[\frac{L_{vent}}{100} \right] \times D_{vent}^{1.21} ; 1" < D_{vent} < 24 \quad (4)$$

$$C_P = 200 \times \left[\frac{L_{vent}}{100} \right] \times D_{vent}^{1.07} ; 30" < D_{vent} < 60" \quad (5)$$

where,

C_P = Vent Stream Piping Cost [USD in 2017]

L_{vent} = Length of pipe run [ft] [100 ft min]

D_{vent} = Vent stream line diameter [in]

The piping costs [C_P] includes costs for straight run, Sch 40 carbon steel pipes only.

The cost for knock-out drum is expressed as,

$$C_K = 20.5 \times [D \times WT \times (L + 0.812D)]^{0.737} \quad (6)$$

where,

C_K = KO Drum Cost [USD in 2017]

L = KO Drum height [in]

D = Flare tip diameter [in]

WT = KO Drum thickness [in]

The liquid seal costs are included in the flare equipment costs.

For flares with routine flow, a flame arrestor may be required rather than a liquid seal. The costs for the flame arrestor (applicable for flares with a diameter of 24" or less) are estimated as follows [2],

$$C_S = 39.15d_j^2 + 3592 \quad (7)$$

where,

C_S = Flame arrestor cost [USD in 2017]

d_j = Flare tip diameter [in]

The costs for flare gas recovery system [FGRS], if applicable is estimated based on design capacity.

$$C_{FGRS} = 731.3 \times Q_{cap} \quad (8)$$

$$Q_{cap} = q_m \times DF \quad (9)$$

where,

C_{FGRS} = Cost of FGRS [USD in 2017]

Q_{cap} = Design FGRS capacity of system [scfm]

DF = Design Factor [-]

The design factor (DF) depends on the number of compressors. With one compressor, DF = 1.3, with two compressors, DF = 1.2, with three compressors, DF = 0.6, with four compressors, DF = 0.3. Additionally, utilities costs [C_U] have to be included.

The flare equipment cost (EC) is then computed as a sum of all the above costs as,

$$EC = C_F + C_M + C_K + C_P + C_S + C_{FGRS} + C_U \quad (10)$$

The purchased equipment costs (PEC) are equal to EC plus factor for ancillary instrumentation (i.e., 10% for control room instruments, 3% sales tax, 5% for freight)

$$PEC = EC[1 + 0.1 + 0.2 + 0.05] = 1.18 \times EC \quad (11)$$

Installation Costs

Installation Costs are of two types

– Direct Installation Costs [DC]

– Indirect Installation Costs [IC]

Installation costs cover foundations and supports, equipment handling and erection, piping, insulation, painting, and electrical. Indirect installation costs cover engineering, construction and field expenses, contractor fees, start-up, and performance testing. These direct and indirect installation costs are generally estimated as a factor of the PEC.

Other direct costs include site preparation and building installation costs, as needed. Depending on the site conditions, the installation costs for a given flare could deviate significantly from costs generated by these average factors [2].

In general, the costs presented assume that steam is available at the facility either as purchased steam or steam produced from an existing facility boiler. If additional steam generation facilities were required to supply steam for a new steam-assisted flare, these costs can be accounted for under the site preparation term. If buildings are needed to house controls or monitoring equipment, these costs can be accounted for under the building cost term [2].

Total Capital Investment [TCI] Costs

The TCI cost is obtained by summing the purchased equipment cost (PEC), the direct installation costs, and the indirect installation costs and adding costs for contingencies.

Contingency costs are typically estimated as a factor of the total direct costs and installation costs and are typically between 5% and 15% of the total direct and indirect costs; a contingency factor (CF) of 0.1 [10%] can be used as a practical value.

$$TCI = [(1.89 \times PEC) + SP + Bldg] \times [1 + CF] \quad (12)$$

where,

PEC = Purchased equipment cost [USD]

SP = Painting costs [USD]

Bldg = Buildings cost [USD]

CF = Contingency factor [USD]

Direct Annual Costs

Direct annual costs include labor (operating and supervisory), maintenance (labor and materials), natural gas, steam, and electricity. Unless the flare is to be dedicated to one vent stream and specific on-line operating factors are known, costs should be calculated based on a continuous operation of 8,760 hrs/y and expressed on an annual basis. Flares serving multiple process units typically run continuously for several years between maintenance shutdowns [2].

Operating labor for most industrial applications is estimated at 630 hours annually. A completely manual system could easily require 1,000 hours. Conversely, 130 hours has been estimated for flares to control vented storage tank emissions at unmanned oil production sites.

A standard supervision ratio of 0.15 should be assumed. Maintenance labor is estimated at 0.5 hours per 8-hour shift for applications without a flare gas recovery system, or the same as operating labor for unmanned sites. Maintenance labor is estimated at 1 hour per 8-hour shift for applications with a flare gas recovery system. Maintenance materials costs are assumed to equal maintenance labour costs [2].

Indirect Annual Costs

The indirect (fixed) annual costs include overhead, capital recovery, general and administrative charges, property taxes, and insurance. The system capital recovery cost (CRC) is based on an estimated 15-year equipment life. For a 15-year life and an interest rate of 5%, the capital recovery factor is 0.0963.

Current Case Study - Cost Estimation

From the flare stack design estimations, the flare stack height is 86 ft, suggesting a guy-wired configuration. The parameters for cost estimation are as follows,

Table 1. Flare Stack and KO Drum Parameters

Parameter	Value	Unit
Flare Tip Diameter [d_i]	12	Inch
Height of Flare Stack [H]	86	ft
Vent Stream Piping Dia [D_{vent}]	12	Inch
Vent Stream Piping [L_{vent}]	100	Ft
Flare Configuration	Guy-Wire Support	
KO Drum Diameter [D]	70.9	Inch
KO Drum Height [L]	212.6	Inch
KO Drum Wall Thickness [WT]	0.37	inch

The fuel gas recovery system data is as follows,

Table 2. FGRS Data

Parameter	Value	Unit
Fuel Gas Recovery System [FGRS]	Yes	-
Number of Compressors [N_{Total}]	2	-
FGRS Design Factor [DF]	1.2	-
Total Operating Hours of Flare [T]	100	hrs/y
Flare Gas Vol Flow Rate [q_m]	6,944	scfm
Design flow of FGRS [Q_{FGRS}]	8,333	scfm
No of Compressors running for full gas recovery [N_{op}]	1.667	-

The FGRS system data is as follows,

Table 3. Other Fuel Data

Annual Purge Gas Requirement		
Annual Operational Hours [t_{purge}]	8,760	hrs/y
Annual Pilot Gas Requirement		
Annual Operational Hours [t_{pilot}]	8,760	hrs/y
Avg Pilot Gas Consumption [Q _{pilot}]	70	scf/h
Auxiliary Gas [LPG] Requirements		
Annual Operational Hours [t_{aux}]	100	hrs/y
Auxiliary Gas Flow Rate [To increase LHV] [Q _{aux}]	2,632	scfm
Annual Auxiliary Gas [LPG] Offset [Savings]		
Annual Operational Hours [t_{pilot}]	100	hrs/y
LHV of Flare gas [LHV _{flare}]	282	btu/scf
LHV of auxiliary fuel [LHV _{aux}]	2,641	btu/scf
Annual Steam Requirements		
Annual Operational Hours [t_{steam}]	100	hrs/y
Steam assisted flow rate [S]	322	lb/h

The cost data chosen for the year 2017 is shown below. For the current case study, cost estimation is performed for Year 2024.

Table 4. Cost Data

Parameter	Value	Unit
Base Year	2017	-
Desired US Dollar Year	May 2024	-
CEPCI Value - Base Year 2017	567.5	-
CEPCI Value - Year 2024 May	800.2	-
Annual Interest Rate	5	%
Equipment Life [n]	15	yrs
Capital Recovery Factor [CRF]	0.0963	-

The equipment costs for flare monitoring systems are as follows [2],

Table 5. Equipment Costs for Flare monitoring [2]

Monitoring System	C_m Cost [USD]
Pilot Flame Monitor	4,100
Gas Chromatograph	131,000
Hydrogen Analyzer	36,900
Calorimeter	77,300
Flare Gas Flow Monitor	58,000
Steam Fine Controls/Metering	58,700
Air Fine Controls/Metering	49,600

The utilities costs are,

Table 6. Utilities Cost [2]

Utilities	Price [C_u]	Cost [USD]
Steam ($Cost_{steam}$)	7.70	USD/1000 lb
Natural Gas ($Cost_{fuel}$)	4.14	USD/ Mscf
LPG ($Cost_{LPG}$)	9.00	USD/ Mscf
Electricity ($Cost_{Elec}$)	0.0688	USD / kWh
Operator Labour Rate [L]	29.63	USD/h
Maintenance Labor Rate [L_{maint}]	25.12	USD/h
No of operator labour hours annually [t_{labour}]	630	hrs/y
Number of Maintenance Labor Hours per Shift	1.00	hrs/shift

For the current case study, a fuel gas recovery system (FGRS) is considered with two compressors [DF = 1.2]. The annual operational hours are 8,760 hrs/y.

The average pilot gas consumption is 70 scf/h. The total operational hours of the flare are 100 hrs/y. Estimating the various consumption rates,

Fuel Gas Recovery System Consumption

The design flow rate of the FGRS is,

$$Q_{FGRS} = 1.2 \times 6944 \text{ scfm} = 8,333 \text{ scfm} \quad (13)$$

The number of compressors running for full gas recovery is,

$$N_{op} = \frac{6944 \times 2}{8333} = 1.667 \quad (14)$$

The total compressor electricity consumption [E_{FGRS}] is,

$$E_{FGRS} = \frac{1.667}{2} \times (75 \times 0.00144 \times 8,333) \times 0.746 \times 100 = 55,950 \text{ kWh/y} \quad (15)$$

Annual Purge Gas Consumption

The purge gas consumption is,

$$F_{pu} = 0.04 \times \left[\frac{\pi d_j^2}{4} \right] \times \left(\frac{3600}{1000} \right) \times t_{purge} \quad (16)$$

where,

F_{pu} = Annual flare purge gas volume [Mscf/y]

d_j = Flare tip diameter [in]

t_{pu} = Total time flare was in operation (typically assume 8,760 hrs/y)

0.04 = Conservative min gas velocity [ft/s]

144 = Conversion from ft² to in²

3600 = Conversion from sec to hrs

1000 = Conversion scf to Mscf

$$F_{pu} = 0.04 \times \left[\frac{\pi \times 12^2}{4 \times 144} \right] \times \left(\frac{3600}{1000} \right) \times 8760 \quad (17)$$

$$F_{pu} = 991 \text{ Mscf/y} \quad (18)$$

Annual Pilot Gas Consumption

To estimate the pilot gas consumption [F_{pilot}], the number of burners is estimated first followed by pilot gas consumption as,

$$F_{pu} = Q_{pilot} \times N \times t_{pilot} \times 10^{-3} \quad (19)$$

where,

F_{pilot} = Annual pilot gas volume [Mscf/y]

Q_{pilot} = Avg pilot gas consumption based on pilot burner design (scf/h). If actual pilot gas consumption is not available from the manufacturer, a default value of 70 scf/h for an energy efficient pilot burner can be chosen

t_{purge} = Total time flare was in operation (typically assume 8,760 hrs/y)

N = Number of pilot burners [-]

10^{-3} = Conversion factor from scf to Mscf

The number of pilot burners can be taken as,

Table 7. Number of Pilot burners [2]

Flare Tip Diameter	No of Pilot Burners
[inches]	[-]
1 in to 10 in	1
12 in to 24 in	2
30 in to 60 in	3
> 60 inches	4

For the flare tip diameter of 12 inches, the number of pilot burners is taken as 2. The annual pilot gas consumption is therefore,

$$F_{pu} = 70 \times 2 \times 8760 \times 10^{-3} = 1,226 \text{ Mscf/y} \quad (20)$$

Annual Auxiliary Gas Consumption

The auxiliary gas consumption [F_{aux}] is,

$$F_{aux} = Q_{aux} \times t_{aux} \times 60 \times 10^{-3} \quad (21)$$

where,

F_{aux} = Annual auxiliary gas volume [Mscf/y]

Q_{aux} = Auxiliary gas flow rate [scfm]

t_{aux} = Total time flare was in operation (assume same as the flare operational hours)

$$F_{aux} = 2,632 \times 100 \times 60 \times 10^{-3} \quad (22)$$

$$F_{aux} = 15,795 \text{ Mscf/y} \quad (23)$$

Annual Steam Consumption

The annual steam consumption [F_{steam}] is,

$$F_{steam} = S \times t_{steam} \quad (24)$$

where,

S = Steam flow rate [lb/h]

t_{steam} = Total time flare was in operation (assume same as the flare operational hours)

$$F_{aux} = 322 \times 100 = 32,200 \text{ lb/y} \quad (25)$$

Annual Auxiliary Gas Offset [Savings]

Flare gas recovery is generally used when the recovered gas can be used for beneficial purposes such as process heaters / boilers. In these cases, the recovered gas can be used to determine the amount of auxiliary gas purchases that can be offset. The number of operational hours is taken as the annual number of hours the auxiliary gas is used.

$$F_{offset} = Q_{rec} \times \frac{LHV_{flare}}{LHV_{aux}} \quad (26)$$

where,

F_{offset} = Annual volume of auxiliary gas purchases [Mscf/y]

Q_{rec} = Annual volume of flare gas recovered [Mscf]

LHV_{flare} = LHV flare gas [Btu/scf]

LHV_{aux} = LHV auxiliary gas [Btu/scf]

$$F_{offset} = \frac{60 \times 100}{1000} \times 2632 \times \frac{282}{2641} = 1,685 \text{ Mscf/y} \quad (27)$$

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Total Capital Investment [TCI]

Equipment Cost

The equipment costs are calculated as shown in the following table, Table 8. Equipment Costs

Equipment	Value	Cost [USD]
Flare Cost [C_F]	$C_F = \left[[124 + 10.42d_j + 0.564h]^2 \right] \times \left[\frac{CEPCI_{2024}}{CEPCI_{2017}} \right]$ $C_F = [124 + (10.42 \times 12) + (0.564 \times 86)]^2 \times \left[\frac{800.2}{567.5} \right]$	\$124,835
Vent Stream Piping [C_p]	$C_p = 183 \times \left[\frac{L_{vent}}{100} \right] \times D_{vent}^{1.21} \times \left[\frac{CEPCI_{2024}}{CEPCI_{2017}} \right] \text{ for } 1" < D_{vent} < 24$ $C_p = 183 \times \left[\frac{100}{100} \right] \times 12^2 \times \left[\frac{800.2}{567.5} \right] \text{ for } 1" < D_{vent} < 24$	\$5,218
Knock-out Drum [C_k]	$C_K = 20.5 \times [D \times WT \times (L + 0.812D)]^{0.737} \times \left[\frac{CEPCI_{2024}}{CEPCI_{2017}} \right]$ $C_K = 20.5 \times [70.9 \times 0.37 \times (212.6 + (0.812 \times 70.9))]^{0.737} \times \left[\frac{800.2}{567.5} \right]$	\$19,889
Flare Seal/Flare Arrestor [C_s]	$C_S = [39.15d_j^2 + 3592] \times \left[\frac{CEPCI_{2024}}{CEPCI_{2017}} \right]$ $C_S = [(39.15 \times 12^2) + 3592] \times \left[\frac{800.2}{567.5} \right]$	\$13,014
Flare Gas Recovery [C_{FGR}]	$C_{FGRS} = 731.3 \times Q_{cap} \times \left[\frac{CEPCI_{2024}}{CEPCI_{2017}} \right]$ $C_{FGRS} = 731.3 \times 8,333 \times \left[\frac{800.2}{567.5} \right]$	\$8,592,988
Monitoring Equipment [C_M]	$C_M = 4,100 + 131,000 + 36,900 + 77,300 + 58,000 + 58,700 + 49,600$	\$415,600
Utility Costs [C_U]	$C_U = 250,000$	\$250,000
Total Equipment Costs [A]		\$9,421,544
Instrumentation	$0.1 \times A = 0.1 \times 9,421,544$	\$942,154

Sales Tax	$0.03 \times A = 0.03 \times 9,421,544$	\$282,646
Freight	$0.05 \times A = 0.05 \times 9,421,544$	\$471,077
Total Purchased Equipment Cost [B]		\$11,117,422

Direct Installation Costs

The direct installation costs are calculated as shown in the following table,

Table 9. Direct Installation Costs

Equipment	Value	Cost [USD]
Foundations & Support	$0.12 \times B = 0.12 \times 11,117,422$	\$1,334,091
Handling & Erection	$0.40 \times B = 0.40 \times 11,117,422$	\$4,446,969
Electrical	$0.01 \times B = 0.40 \times 11,117,422$	\$111,174
Piping	$0.02 \times B = 0.40 \times 11,117,422$	\$222,348
Insulation	$0.01 \times B = 0.01 \times 11,117,422$	\$111,174
Direct Installation Costs [DIC]		\$6,225,756
Painting [SP]		\$250,000
Buildings [Bldg]		\$1,000,000
Total Direct Installation Costs [DC]		\$18,593,178

Indirect Installation Costs

The indirect installation costs are calculated as shown in the following table,

Table 10. Indirect Installation Costs

Equipment	Value	Cost [USD]
Engineering	$0.1 \times B = 0.10 \times 11,117,422$	\$1,111,742
Construction & Field Expenses	$0.1 \times B = 0.10 \times 11,117,422$	\$1,111,742
Contractor Fees	$0.1 \times B = 0.10 \times 11,117,422$	\$1,111,742
Startup	$0.01 \times B = 0.01 \times 11,117,422$	\$111,742
Insulation	$0.01 \times B = 0.01 \times 11,117,422$	\$111,742
Total Indirect Installation Costs [IC]		\$3,557,575
Contingency Factor [CF]	10%	
Contingency Cost [CC]	$0.10 \times [DC + IC] = 0.1 \times [18,593,178 + 3,557,575]$	\$2,215,075
Total Capital Investment [TCI] - 2024		\$24,365,828

Direct Annual Costs

The direct annual costs are calculated as shown in the following table,

Table 11. Direct Annual Costs

Equipment	Value	Cost [USD]
Operator Labour Costs	$L_{maintenance} \times t_{labour} = 25.12 \times 630$	\$15,826
Supervisor Labour Costs	$15\% \times \text{Operator Labour Costs} = 0.15 \times 15,826$	\$2,374
Maintenance Costs		
Maintenance Labour	$\frac{1 \frac{hr}{shift} \times L_{maintenance} \times 100 \text{ hrs}}{8 \text{ hrs per shift}} = \frac{1 \times 25.12 \times 100}{8}$	\$314
Materials	$100\% \times \text{Maintenance Labour} = 1 \times 314$	\$314
Annual Electricity Cost [C_E]	$C_E = E_{FGRS} \times \text{Cost}_{Elec} = 55,950 \times 0.0688$	\$3,849
Annual Purge Gas Cost [C_{purge}]	$C_{purge} = E_{purge} \times \text{Cost}_{purge} = 991 \times 4.14$	\$4,102
Annual Pilot Gas Cost [C_{pilot}]	$C_{pilot} = E_{pilot} \times \text{Cost}_{pilot} = 1,226 \times 4.14$	\$5,077
Annual Auxiliary Fuel Cost [C_{aux}]	$C_{aux} = E_{aux} \times \text{Cost}_{aux} = 15,795 \times 9$	\$65,391
Annual Fuel Offset from recovered Fuel Gas [C_{rec}]	$C_{rec} = -F_{offset} \times \text{Cost}_{aux} = -1,685 \times 4.14$	-\$6,974
Annual Steam Cost [C_{steam}]	$C_{steam} = F_{steam} \times \text{Cost}_{steam} = 32,209 \times 7.70$	\$248
Direct Annual Costs [DAC]		\$90,521

Indirect Annual Costs

The indirect annual costs are calculated as shown in the following table,

Table 12. Indirect Annual Costs

Equipment	Value	Cost [USD]
Overhead [O]	$[60\% \times \text{Labour costs}] + \text{Maintenance Costs}$ $[60\% \times (15826 + 2374)] + 314 + 314$	\$11,548
Administrative Charges [AC]	$2\% \times TCI = 0.02 \times 24,365,828$	\$487,317
Property Taxes [PT]	$1\% \times TCI = 0.01 \times 24,365,828$	\$243,658
Insurance [I]	$1\% \times TCI = 0.01 \times 24,365,828$	\$243,658
Capital Recovery Factor [CRF]	$CRF = \frac{i \times (1 + i)^n}{(1 + i)^n - 1} = \frac{0.05 \times (1 + 0.05)^{15}}{(1 + 0.05)^{15} - 1}$	0.0963
Capital Recovery [CR] = CRF x TCI	$CR = CRF \times TCI = 0.0963 \times 24,365,828$	\$2,347,460
Indirect Annual Costs [IAC]		\$3,333,640
Total Annual Indirect Costs [TAC] = DAC + IAC		\$3,424,161

Appendix A – Cost Estimation

Capital Costing of Flare System									
Fuel Gas Recovery System					Capital Costs				
Flare Gas Recovery System					Equipment Costs				
Flare Tip Diameter [d _t]	12	inches			Flare Cost [C _f]	124,835	USD		
Height of Flare Stack [h]	86	ft			Vent Stream Piping [C _v]	5,218	USD		
Vent Stream Piping Diameter [D _{vent}]	12	inches			Knock-out Drum [C _k]	19,889	USD		
Vent Stream Piping [F _{vent}]	100	ft			Flare Seal / Flare Arrestor [C _s]	13,014	USD		
Flare Configuration	Govt-Who Support				Flare Gas Recovery [C _{gr}]	8,592,988	USD		
Is it Permissible?	Permissible				Monitoring Equipment [C _m]	415,600	USD		
KO Drum Diameter [D]	70.9	inches			Utility Costs [C _u]	250,000	USD		
KO Drum Height [L]	212.6	inches			Total Equipment Costs [A]	9,421,544	USD		
KO Drum Wall Thickness [WT]	0.37	inches			Instrumentation [0.1 x A]	942,154	USD		
Cost Data					Sales Tax [0.03 x A]	285,646	USD		
Base Year	2017				Freight [0.05 x A]	471,077	USD		
Desired US Dollar Year	2024 May				Total Purchased Equipment Cost [B]	11,117,422	USD		
CEPCI Value - Base Year 2017	567.5				Direct Installation Costs				
CEPCI Value - Desired Year 2024 May	800.2				Foundations & Supports [0.12 x B]	1,334,091	USD		
Annual Interest Rate	5	%			Handling & Erection [0.40 x B]	4,446,969	USD		
Equipment Life [n]	15	years			Electrical [0.01 x B]	111,174	USD		
Capital Recovery Factor [CRF]	0.0963				Piping [0.02 x B]	222,348	USD		
Utilities Cost [Base Year 2017]					Insulation [0.01 x B]	111,174	USD		
Steam [Cost _{steam}]	7.70	USD / 1000 lb			Direct Installation Costs [DIC]	6,225,756	USD		
Natural Gas [Cost _{nat}]	4.14	USD/Mscf			Painting [B]	250,000	USD		
LPG [Cost _{lpg}]	9.00	USD/Mscf			Buildings [Bdg]	1,000,000	USD		
Electricity [Cost _{elec}]	0.0688	USD/kWh			Total Direct Installation Costs [DC]	18,593,178	USD		
Operator Labor Rate [L]	29.63	USD/hr			Indirect Installation Costs				
Maintenance Labor Rate [L _{maintenance}]	630	hrs/yr			Engineering [0.1 x B]	1,111,742	USD		
Number of Operator Labour hours annually [F _{annual}]	1.00	hrs/shift			Construction & Field Expenses [0.1 x B]	1,111,742	USD		
Number of Maintenance Labor Hours per Shift					Contractor Fees [0.1 x B]	1,111,742	USD		
Monitoring Equipment Cost [Base Year 2017]					Startup [0.01 x B]	111,174	USD		
Monitoring System	Is it Required??	Cost [USD]			Insulation [0.01 x B]	111,174	USD		
Pilot Flame Monitor [USD]	Yes	41,100			Total Indirect Installation Costs [IC]	3,557,575	USD		
Gas Chromatograph [USD]	Yes	131,000			Contingency Factor [CF]	10	%		
Hydrogen Analyzer [USD]	Yes	36,900			Contingency Cost [C]	2,215,075	USD		
Calorimeter [USD]	Yes	77,200			Total Capital Investment [TCI] - 2024 May	24,365,828	USD		
Flare Gas Flow Monitor [USD]	Yes	58,000							
Steam Flow Controls/Metering [USD]	Yes	58,700							
Air Flow Controls/Metering [USD]	Yes	49,600							
Total [USD]		415,600							

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Asset Integrity Management in Transfer and Stockpiling Sector

Dr. Marcio Wagner da Silva

One of the major challenges to managing stockpiling area is to deal with very big assets like kilometers of pipelines, hundreds of storage tanks, and pumps which in contrast with the refining processing assets do not have planned shutdown windows. Under this scenario, the main way to ensure the process safety requirements as well as the adequate performance with minimum production losses is to ensure an adequate asset integrity plan aiming to maximize the operating lifecycle of the assets balancing the maintenance costs and process safety risks, mainly related to hydrocarbon contention losses.

To achieve this goal, it's fundamental that the stockpiling manager carried out a closer integration with the equipment inspection area. Despite the existence of the equipment inspection team which is technically responsible for the integrity of the whole refinery asset integrity, it's important to understand which only the operation personnel have the adequate knowledge of the process characteristics which can demand more attention in the care of the processing assets like salt deposition, dead legs, process fluids with higher corrosion rates, etc. Furthermore, the operating personnel have adequate knowledge of the consequences of contention loss and process safety accidents in the operating assets, mainly in hydrocarbon storage tanks.

In other words, as previously described in the section about the relationship between operation and maintenance teams, it's fundamental to reach a confidence and mutual cooperation relationship between the stockpiling operation and the equipment inspection teams. Of course, this is true for all operation areas of the refinery, but due to the characteristics of the stockpiling assets this is even more relevant to the stockpiling area.

The main threat to the asset integrity of stockpiling assets (mainly pipelines and storage tanks) is the corrosion process. Unfortunately, the corrosion is a common and deep concern to the crude oil refining industry which needs to be adequately managed aiming to ensure a sustainable management based on the three Ps of sustainability tripod: People, Planet, and Profit which need to be prioritized in this order aiming to prioritize the life and environment in detriment of the business if necessary. As previously mentioned, asset management is a pillar to the process safety policy in stockpiling operations, and the corrosion threat needs to be adequately managed through the assertive asset integrity plan.

The Corrosion Threat – A Brief Review

Corrosion process can be defined as the degradation of metal properties like mechanical resistance, being the metal converted to a non-metallic state by a chemical or electrochemical action. The most common corrosion process is the aqueous corrosion which demands the presence of water, and the corrosion process is based on electrochemical reactions.

The corrosion reactions involve basically anodes (the corroded metal), cathodes, known as electrodes, and electrolytes which are the solution through the ions are transported from the anode to the cathode. It's important to quote that the electrodes can be two different metals or distinct areas of the same metal. During the corrosion process, two reactions occur: anodic reactions in the anode which is characterized

by electron loss and the cathodic reaction which involves the reduction of the electrolyte ions which consumes the electrons released in the anode. Figure 1 presents the basic concept of electrochemical corrosion.

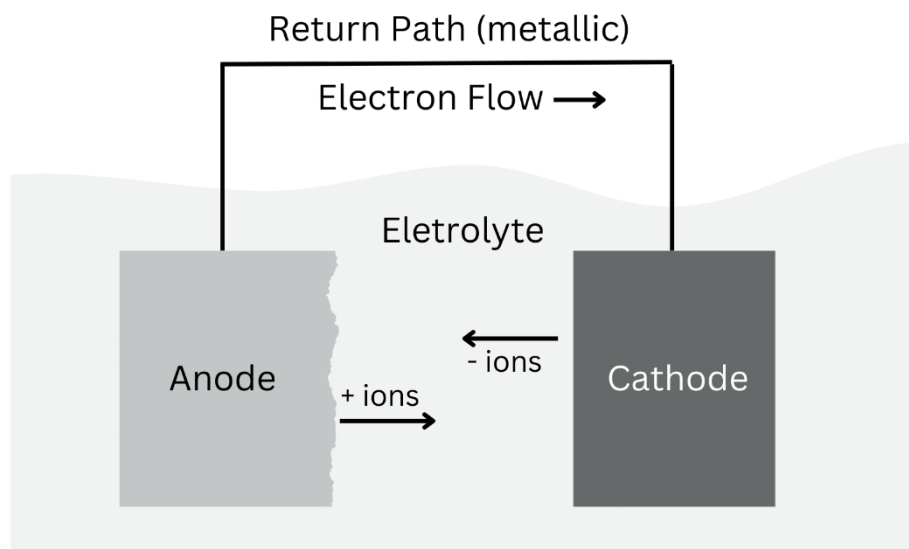
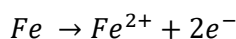
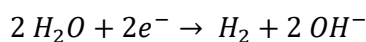
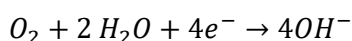


Figure 1 – Typical Electrochemical Cell

Considering the iron corrosion as example, when the iron is corroded is produced positively charged ion in the anodic reaction as presented below:



The electrons produced from the reaction move through the metal to another location where they are in turn consumed in a reaction that produces hydroxyl ions. The reaction depends on the nature of the electrolyte, but typically is one of the following:



The reactions represented above are referred to as cathodic reactions. Movement of the ions through the electrolyte completes the electrical circuit. The iron ions typically react with the water and/or oxygen to form a corrosion deposit of rust or some other iron oxide, but, in some cases, they may react with carbon dioxide or hydrogen sulfide to form iron carbonate or iron sulfide.

Corrosion Classification and Forms

The corrosion process can be classified based on several factors like electrolyte, corrosion product, mechanical factors, etc. Figure 2 summarizes the classification of the corrosion processes.

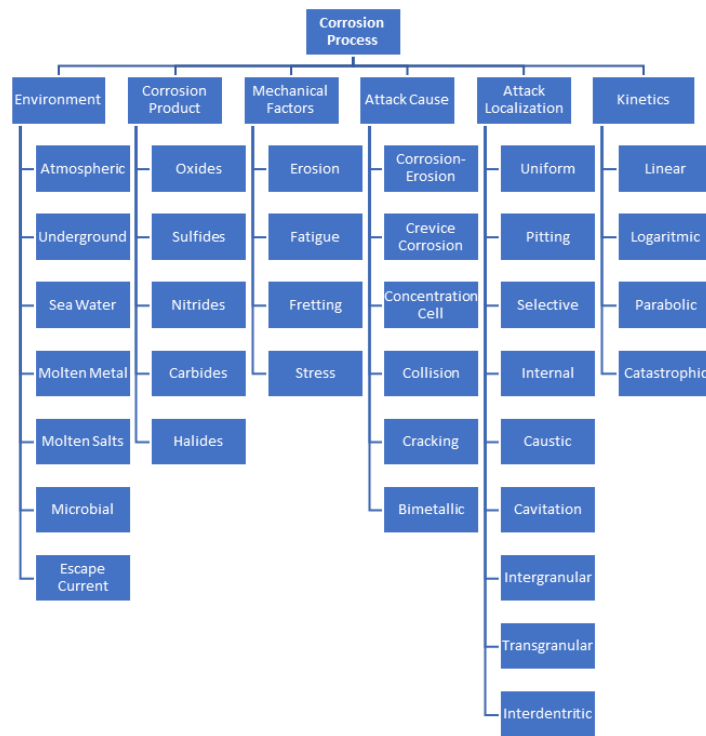


Figure 2 – Classification of the Corrosion Process

Corrosion can occur in different ways, and its classification can be made based on the appearance of the corroded metal.

Corrosive processes of an electrochemical nature present identical mechanisms because they will always consist of anodic and cathodic areas, between an electron current and an ion current circulate. However, the loss of mass and mode of attack on the material occurs in different ways.

Uniform corrosion - consists of the attack of the entire metal surface in contact with the corrosive medium with the consequent decrease in thickness.

This type of corrosion generally occurs due to micro piles of local action and is probably the most common type of corrosion, especially in corrosive processes of structures exposed to the atmosphere and other media that result in a uniform action on the metal surface.

Uniform corrosion is a form of wear that is easier to monitor, especially when it comes to internal corrosion in equipment or installations, considering that the loss of thickness is approximately the same across the entire metal surface.

However, it is an important type of corrosion from a wear point of view and can lead the equipment or installation to significant failures, limiting its useful life. Other types of corrosive attack where there is a preferential location for corrosion to occur, resulting in a localized loss of thickness, are called localized corrosion.

Crevice corrosion - Crevices are subject to the formation of piles of differential aeration and differential ionic concentration. When the medium is liquid, piles of differential ionic concentration preferably occur and when the medium is gaseous, piles of differential aeration tend to occur.

Crevice normally occur in welded joints with overlapping sheets, in riveted joints, in flanged connections, in threaded connections, in coverings with screwed sheets, among other situations that generate gaps. In any case, gaps should be avoided or eliminated as they are preferential regions for corrosion.

Pitting corrosion - Pitting corrosion is a form of localized corrosion that consists of the formation of cavities of small and reasonable depth. It occurs at certain points on the surface while the rest can remain practically without corrosive attack.

It is a type of corrosion very characteristic of metallic materials that form protective films (passivable metals like stainless steels) and generally results from the action of the active-passive island at the points where the passive layer is ruptured. It is a type of corrosion that is more difficult to monitor when it occurs inside equipment and installations since controlling the loss of thickness does not characterize the wear observed.

In passive materials, the breakdown of passivity generally occurs through the action of so-called halide ions (Cl⁻, Br⁻, I⁻, F⁻) and this localized dissolution of the film generates an active area that, in the face of the remaining passivate, causes very intense corrosion, and localized. An important quantity in this case is the potential for a break in passivity. In fact, what happens is a change in the anode polarization curve.

The presence of halide ions causes changes in the anodic polarization curves, making the break in passivity more likely. Another important aspect is the pit formation mechanism, as failure begins at points of weakness in the passivating film (formation defects) and the pH inside the pit changes substantially in the acidic direction, which makes it difficult to restore the initial passivation. It follows that the small active area formed in front of a large cathodic area causes intense and localized corrosion. A relatively common case of passivating breaking is the stainless steel in the chloride presence which leads to pitting corrosion.

Plate corrosion - This is a type of localized corrosion which is characterized by the plates formation by the corrosion products which progressively detached, exposing the metal to a new attack.

Galvanic corrosion - The galvanic corrosion occurs when a metal is put in contact with a nobler material in the presence of an electrolyte, leading this metal to act as an anode. The galvanic series of metals and alloys is used to predict if this type of corrosion can occur when different metals are put in contact.

Intergranular corrosion (IGC) - The corrosion process occurs in the boundary of material crystallites.

Transgranular corrosion - Transgranular corrosion occurs when a crack does not follow material grain boundaries but travels right across the grain.

Concentration cells corrosion - Concentration cells are a form of galvanic corrosion. Just as two dissimilar metals joined cause corrosion, so do dissimilar condition within the electrolyte. The corrosion occurs when two or more areas of the same metal surface are in contact with electrolytic solutions of different concentrations. The same metal has different electrical properties in the presence of different concentrations of the same electrolyte.

Differential aeration (oxygen concentration cell) and ion concentration (salt concentration cells) create dissimilar polarities (anodic and cathodic areas). Differences in dissolved oxygen concentration led to localized corrosion of metal in hidden areas such as under deposits or in crevices.

Corrosion associated with fluid flow – In fluid flow, corrosive processes can be accelerated due to the association of the mechanical effect with the corrosive action. The main types of corrosion associated with flow are corrosion-erosion, cavitation corrosion and turbulence corrosion. Erosion of a metallic material is the mechanical wear caused by the surface abrasion of a solid, liquid, or gaseous substance, this process is common when the fluid presents solids which can clash with the pipe removing the protective film which is produced during the corrosive process, exposing the metal surface, and accelerating the corrosive process. Figure 3 presents an example of the occurrence of corrosion-erosion in tubulation.

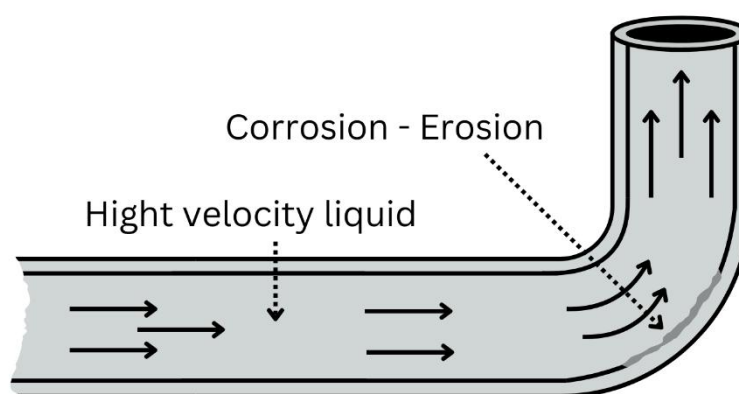


Figure 3 – Corrosion-Erosion phenomena in a tubulation

The corrosion-erosion process is a special concern for the integrity of stockpiling assets. In the off-site design step of a crude oil refinery special attention should be applied to define the maximum velocity in the pipelines aiming to avoid the corrosion-erosion phenomena, mainly for liquids which can contain solids particles which will raise the severity of the issues caused by corrosion-erosion process.

Cavitation corrosion occurs in low pressure regions which leads to the collapse of gas bubbles, during this process the protective film over the material is removed leading to the acceleration of the corrosive process. This process is commonly associated with the pumps operation which is a daily operation in stockpiling areas of crude oil refineries, as well known, the required Net Positive Suction Head (NPSH) should be attended to avoid the cavitation phenomena.

Meeting the required NPSH it's ensured that the fluid has sufficient energy in the pump suction to be kept in the liquid phase, avoiding the vapor formation, and consequently eliminating the cavitation risk.

Selective corrosion - Corrosive processes called selective corrosion are those in which a galvanic couple is formed due to the large difference in oxidation potential between two elements of a metal alloy. The most common types of selective corrosion are graphitic corrosion and dezincification.

Graphitic corrosion: Corrosive process that occurs in gray cast iron and nodular cast iron. Cast iron is normally used for water, sewage, and drainage pipes, among others. Since graphite is a much more cathodic material than iron, the graphite veins, or nodules in cast iron act as a cathodic area while iron acts as an anodic area, transforming into a corrosion product. To minimize graphitic corrosion problems, it is common practice to coat the pipes.

Corrosion by dezincification: Dezincification is the corrosive process observed in zinc alloys, especially brass, used in heat exchangers (coolers, condensers, etc.) and piping for salt water, for example. The corrosion process results in the destruction of zinc (the most anodic material), leaving behind copper and corrosion products. A greater tendency to dezincification is observed in brass with a high zinc content, dezincification can be avoided by heat treating the alloy to solubilize it and by using alloys that contain inhibitory elements such as As (Arsenic) and Sb (Lead).

Corrosion under insulation (CUI) – This is a relatively common corrosion mechanism which is found in the stockpiling assets. As described by the name, this corrosion process is observed in tubulations and equipment like tanks which conduct and storage hot products like asphalt and vacuum residue where the service temperature demands the use of insulation both to keep the internal temperature and protect the operating and maintenance personnel against injuries. The corrosion under insulation occurs when there is a moisture concentration over the insulation in the external surface, the process is most severe in equipment which operates under cyclic conditions once there is a temperature fluctuation leading to the accumulation of moisture in the insulation which are kept in contact with the equipment surface, raising the corrosion rates. Once the equipment surfaces are not generally accessible for visual inspection, the onset of corrosion cannot be easily identified, and in extreme cases, severe corrosion with consequential loss of system integrity can occur leading to production loss and process safety accidents. The API 583 presents the main strategies to deal with corrosion under insulation and fireproofing.

Naphthenic Corrosion – The naphthenic corrosion occurs in processing units that process bottom barrel streams that tends to present high concentration of naphthenic acids and operates under high temperatures. Due to these characteristics, naphthenic corrosion phenomenon is observed in crude oil distillation units and residue upgrading units like delayed coking.

The characteristics of the processed crude oil slate are a determinant factor in the naphthenic corrosion. A very relevant characteristic of oils for refining hardware is naphthenic acidity. Naphthenic acidity is determined based on the amount of KOH required to neutralize 1.0 gram of crude oil, normally a mixture of crude oils is sought in the refinery load so that it does not exceed 0,5 mg KOH/g, above this reference, the bottom sections of the distillation units can undergo a severe corrosive process, leading to shorter periods of operational campaign and higher operating costs in addition to problems associated with integrity and safety. Naphthenic acidity is directly linked to the concentration of oxygenated compounds in the crude oil that tend to be concentrated in the heavier fractions, giving instability and odor to the intermediate currents.

The sulfur content in the crude oil is another key factor in the naphthenic corrosion phenomena. In crude oils with sulfur content higher than 2,0 %, a protective layer of iron sulfide (FeS) is formed in the metal surface that is insoluble, avoiding then the attack by naphthenic acids as presented in Figure 4. In this sense, refiners processing very low sulfur crude oils with high Total Acid Number (TAN) can face severe issues with naphthenic corrosion in their refining hardware.

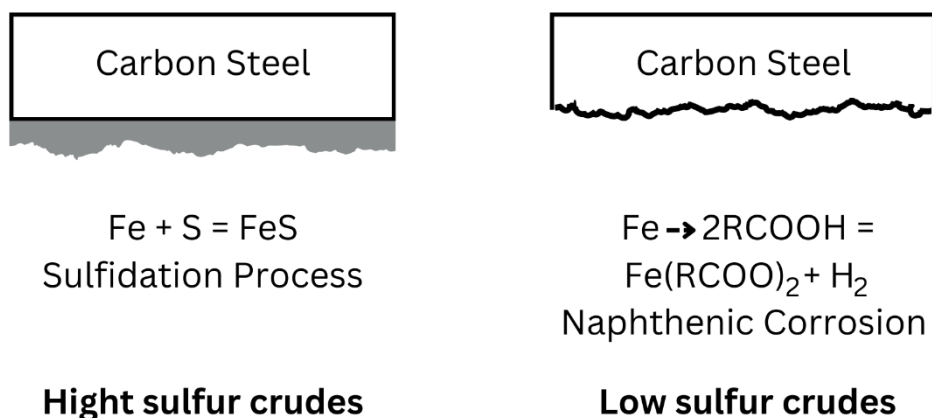
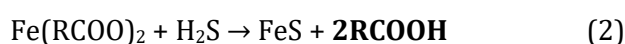


Figure 4 – Naphthenic Corrosion Process

The equation 1 presents the chemical representation of naphthenic corrosion.



According to the literature, above of 400 oC the iron naphthenate (corrosion product) is soluble in hydrocarbons and is attacked by hydrogen sulfide (H_2S) leading to the regeneration of the naphthenic acid, as represented in equation 2.



In crude oil distillation units, the bottom section of atmospheric column and the vacuum distillation column are the most common regions where naphthenic corrosion is observed while in delayed coking units the phenomenon is observed in bottom section of main fractionators column.

The carbon steel, series 300 and 400 stainless steel, and nickel alloys tend to suffer naphthenic corrosion.

Among the actions to control the naphthenic corrosion in the refining hardware is the blending of crude oils aiming to keep the Total Acid Number (TAN) and sulfur content inside the adequate limits. Other alternatives are the injection of neutralizers or corrosion inhibitors in the processing streams and the selection of materials with higher resistance to naphthenic acid attack.

Refiners processing crudes with high acidity and low sulfur normally applies chromium and molybdenum alloys in the bottom sections of crude oil distillation columns and transfer pipes as well as in residue upgrading units. In extreme conditions, it's possible to consider applying stainless steel 317 L that presents high resistance to naphthenic corrosion, this decision needs to consider the higher capital investment due to the high cost of this material.

As inspection and monitoring strategies, ultrasound and X-ray assay are normally applied to identify localized corrosion and thickness loss as well as sacrifice metals coupons to determine the corrosion rates. Naphthenic acid corrosion is not expected to be serious issue for stockpiling assets, but the knowledge of this corrosion mechanism it's important to be considered in possible issues related to the pipelines dedicated to feed or withdraw hydrocarbons for crude oil distillation and delayed coking units.

Corrosion Protection

Unfortunately, the corrosion process is a thermodynamically favorable process. It means that the corrosion process can be controlled but not totally stopped, or in other words, the corrosion process will lead the metals to the less energy intensive state, which is the oxidated compounds, this makes sense if we consider that the metals production is a highly intensive energy process.

Understanding the corrosion process, it's possible to develop and design adequate strategies to control the corrosive processes. The corrosion control strategies can be

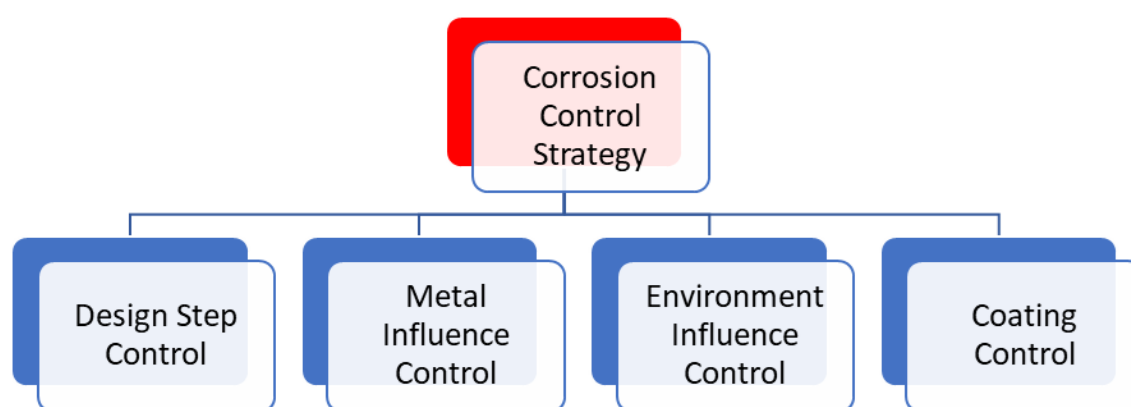


Figure 5 – Classification of Corrosion Control Strategies

During the design phase it's possible to take actions capable of making the assets intrinsically more resistant to the corrosion processes. The most applied strategies to control the corrosion process in the design stage are:

- Adequate material of construction (MOC) selection – Considering the information regarding the process like fluid, contaminants concentration, temperature, etc. it's possible to carry out an adequate materials selection aiming to ensure adequate resistance to the equipment or tubulation at least to avoid premature failures. The main criteria applied to select the materials for processing equipment are the cost, chemical, mechanical, and physical properties and availability;
- Materials compatibility – As described earlier, some materials are incompatible when operating in electrochemical contact leading to galvanic corrosion and this fact should be considered during the design stage or during the maintenance of process equipment once will be led to the insertion of failure point or weakness in the process;

- Changes in the environment conditions – In some cases the corrosion control can be reached changing process variables which will reduce the corrosivity of the environment where the process equipment is operating. Changes in variables like pH, temperature, humidity or flowrate can minimize the severity of the corrosion process and enlarge the range of materials which can be applied to the process;
- Components geometry – Normally, a good process equipment design will avoid crevices and sharp corners once these arrangements will lead to contaminants concentration and tension accumulation over the material which expose the process equipment to crevice and stress corrosion processes, respectively. This point is especially relevant for stockpiling assets which concentrate the most part of tubulations and pipes in the refinery, the design of the tubulations and pipelines should avoid sudden changes in the flow direction to avoid the corrosion-erosion process;

The corrosion control through the metal influence is one of the most applied corrosion control strategies, especially in stockpiling assets. In this strategy, actions are taken in order to raise or reduce the oxidation potential to reach the protection to the metal of the process equipment, this can be reached through the cathodic or anodic protection.

The cathodic protection of a metal can be reached through basically two strategies:

1. Impressed current: An external power source is connected to the structure or process equipment and the anode;
2. Sacrificial anode: In this case, pieces of a metal with high oxidation potential are installed than the process equipment metals aiming to force the equipment shell to be the cathode and forcing the corrosion process to the sacrificial anodes. This strategy is commonly applied to control the corrosion process of the bottom plates of storage tanks, mainly those dedicated to storage crude oil.

In the anodic protection strategy, the metal is lead to a passivity state reducing then the corrosion rates. This can be reached through the formation of a protective layer over the metal composed of metal oxide. It's important to highlight that this protective layer will reduce significantly the corrosion rates, but it's not capable of stopping the corrosion process.

Due to their characteristics, the anodic protection cannot be applied to metals that do not oxidize in the process operation environment and the superficial irregularities over the metal needs to be avoided once will led to failure of the oxide layer, creating the worst scenario of great area of the cathode (passivated metal) and small area of the anode (exposed metal) creating high anodic current intensity which will lead to high corrosion rates. The most common materials where are applied the anodic corrosion protection are stainless steel.

The environment influence control involves the changes in the process environment through process variables manipulation aiming to reduce the corrosion rate and protect the process equipment. Changing variables like temperature, composition, fluid velocity and contaminants concentration it's possible to reduce the corrosion rates and extend the operational lifecycle of process equipment.

Among the composition changes it's possible to quote the example of the passivity broken of the stainless steel under chlorides concentration, reducing the chlorides concentration can be an effective strategy to minimize the corrosion process over stainless steel equipment.

The fluid velocity is another variable which can be managed to control the corrosion process, as mentioned earlier, the corrosion-erosion process is related to the excessive velocity which removes the protective layer of the metal exposing the base metal to the corrosive process as well as the excessive velocity can lead to the cavitation process which will raise the corrosion rates and lead the premature failure of process equipment.

Regarding the temperature, it's possible to change the corrosive behavior of a metal by changing the temperature. An example is the change of the galvanic couple behavior of Zinc (Zn) and Iron (Fe). Under environment temperature the Zinc is anodic in relation to Iron, but when the temperature is raised above to 60 oC the Zinc become cathodic in relation to the Iron. Another effect of the temperature is to reduce the oxygen solubility in the fluid which affects the protective layer formation over the metal, influencing the corrosion rates.

The corrosion control through coating consists of using a coating over the metal to be protected aiming to create a barrier between the corrosive environment and the metal.

The threat of “dead legs”

One of the most important challenges to the asset management in stockpiling area is dealing with the called “dead leg” tubulations. These tubulations or tubulations sections present none of low velocity flowrate (stagnant flow), leading to high corrosion rates.

The stagnant flowrate will lead to an adequate environment where microorganisms can develop colonies and proliferate leading to deposits which will create adequate scenario for high corrosion rates based on deposit corrosion (a type of concentration cells corrosion). Despite the “dead legs” tubulations not present flowrate, these tubulations sections are still connected to the process, leading to a severe risk of hydrocarbon contention loss which can lead to severe process safety accidents.

The “dead legs” threat is a significant concern in the downstream industry both in on-site and off-site (stockpiling assets) of the crude oil refineries. The API 574 and 581 deals with “dead legs” issues and establishes the orientations to minimize the risk of the contention loss due to the “dead legs” corrosion.

Ideally, the “dead legs” issues should be considered in the design step of any industrial facility avoiding tubulation sections with stagnant or low frequency flowrates, but this is very difficult to reach mainly considering long tubulations arrangements like the stockpiling area of crude oil refineries. Despite this fact, it's important to consider this issue during the design step and management of change in stockpiling assets, it's not rare to refinery personnel conduct process changes in stockpiling assets deactivating tubulations and pipeline sections simply blocking the flowrate to the tubulation using a valve or a mechanic device like line blinds which creates “dead legs” and create a new threat to the process. The “dead legs” can be classified in three main categories:

- Permanent “dead legs” – Tubulation sections where never is expected flowrate, in this case it’s recommended to proceed a management of change to eliminate this tubulation section, eliminating the process safety risk;
- Temporary “dead legs” – Tubulation sections temporally without flowrate, in this case an adequate flushing procedure should be conducted to minimize the corrosion risk or involve the equipment inspection team to define the maximum period of time that this section could be kept under this condition;
- Operational “dead legs” – These assets are normally used by the operation teams under specific conditions like shutdown and start-up of processing units or storage tanks, this can be very common in the operation of stockpiling assets in crude oil refineries. In these cases, the best management route is to establish in accordance with the equipment inspection team, the adequate frequency and inspection technique to monitor the corrosion rate and integrity of the tubulation sections.

To avoid this, the management of change in stockpiling assets should always be conducted by a multidisciplinary team led by a process engineer with expertise in the asset as well as inspection engineer aiming to avoid the superficial analysis which can raise the risk of stockpiling assets. One of the key reliability tasks which should be conducted by the stockpiling manager is a deep analysis and identification of “dead legs” in the stockpiling assets aiming to allow an adequate management of these points like suggested in Figure 6.

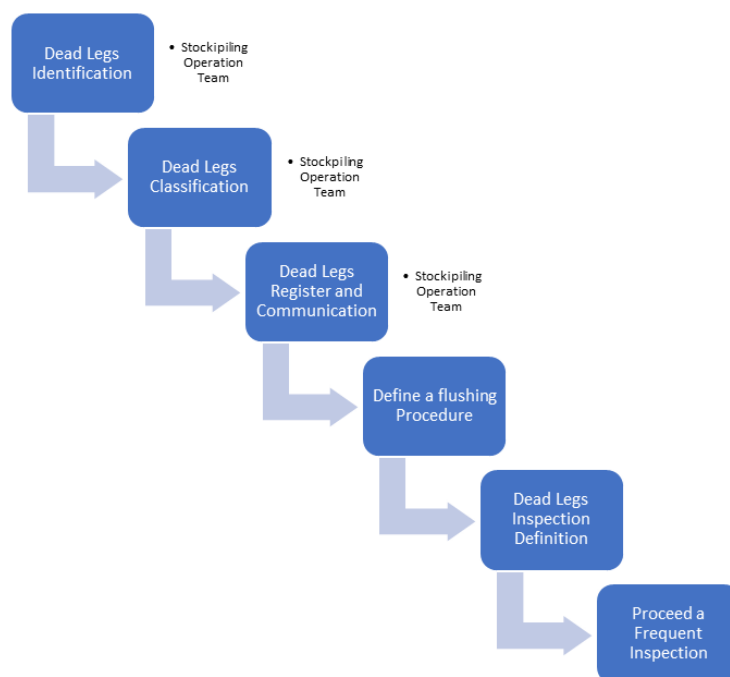


Figure 6 – Proposed strategy to manage “dead legs” in stockpiling assets.

The first step of the “dead legs” management strategy is to identify the “dead legs” tubulations followed by the classification as described above. The “dead legs” classified as permanent should be eliminated (if possible) through an adequate management of change process aiming to eliminate the process safety risk associated with this threat while the another “dead legs” registered and communicated to the equipment inspection and operation teams, for the cases where the flushing procedure is possible, this

procedure can be defined and communicated to the stockpiling team aiming to ensure that the flushing procedure will be carried out under the defined frequency, minimizing the process safety risks associated.

For the “dead legs” where the flushing process is not possible, the equipment inspection team should define an adequate frequency of inspection with adequate technique aiming to determine the corrosion rate and the remaining life of the tubulation as well as define the best strategy to repair the low thickness points.

Corrosion process in storage tanks

Another key question regarding asset integrity of stockpiling assets is related to the corrosion process in storage tanks. Along the history of the crude oil refining history is not rare heard about contention loss events and process safety accidents caused by hydrocarbon leakages from storage tanks.

The most common scenario is the contention loss from hydrocarbon storage tanks due to failure of the bottom provoked by corrosion process, but the corrosion process of the roof is another important concern to refiners once it will allow the contamination of the inventory with raining water leading to quality issues of the derivatives and can cause accidents with the operators which needs to access the tank roof to operating routine tasks like tank gauging verification.

Regarding the roof corrosion process, the main corrosion process present is related to the presence of acid compounds in the vapor space between the liquid surface and the roof, as presented in Figure 7.

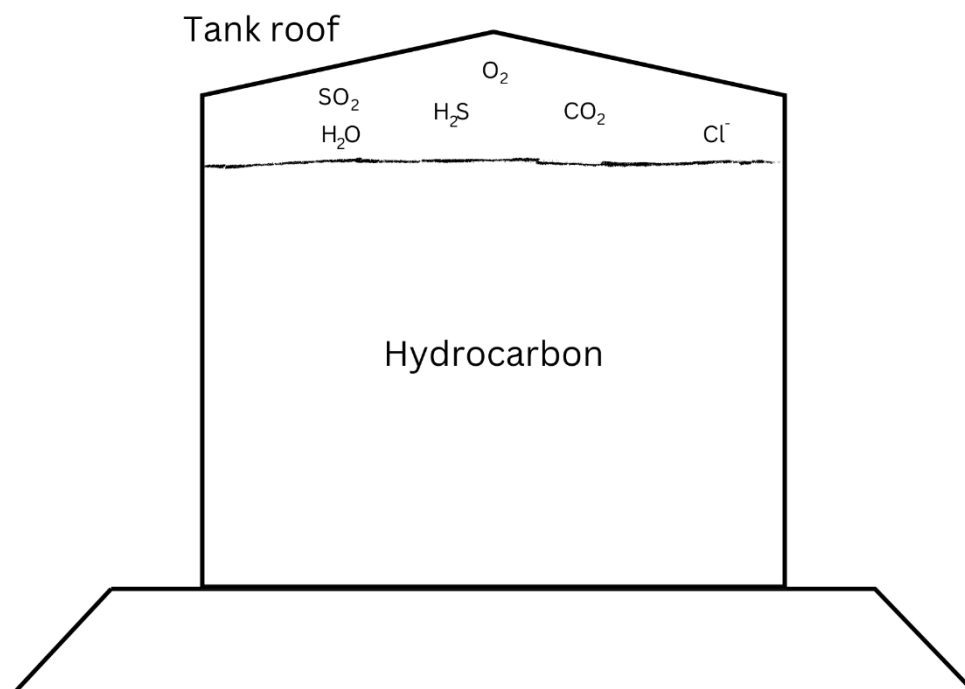


Figure 7 – Corrosion phenomena of hydrocarbon storage tank roof

The composition of the vapor space relies on the stored hydrocarbon but is expected that heavy and high contaminants concentration like fuel oil and heavy sulfur diesel tends to present high sulfur compounds concentration which will raise the corrosion rates of the roof. As present in Figure 7, the most common corrosive compounds present in the vapor space of hydrocarbon storage tanks are CO₂, SO₂, H₂S, Cl⁻, O₂, and H₂O.

The internal environment of the storage tanks favors the corrosion process due to the high relative humidity and temperature (which can reach values above 60 oC). These conditions plus the presence of acid compounds will be led to acid condensation over the roof sheet reducing the pH to values under 3 which will lead to higher localized corrosion rates.

Unfortunately, the roof corrosion process is responsible for a significant reduction in the operating life of storage tanks. Over the years the refiners developed and test some corrosion control techniques like roof coating, special paints and material change aiming to control the corrosion process, the most applied strategy by the refiners for the storage tanks which presents chronic issues regarding the roof corrosion is change the roof sheet material from carbon to stainless steel which presents higher corrosion resistance.

Another alternative to control the roof corrosion process in storage tanks is to use Volatile Corrosion Inhibitors (VCI). These compounds adsorb on the surface of the roof sheet suppressing the corrosion reactions, typical compounds applied as VCI are organic amines and carboxylates.

Regarding the bottom plate corrosion, this is considered the higher risk corrosion process once will be led to an immediate contention loss with significant risk of fire of the storage tank. Nowadays, aiming to mitigate this process safety risk, the most part of the hydrocarbon storage tanks are designed with double bottom plates.

The most common corrosion mechanism in the bottom plates of storage tanks is the localized corrosion which can be pitted or under deposit corrosion associated with microbial action of sulfur reducing bacteria which will lead to sulfuric acid formation which decrease the pH of the region and lead to higher localized corrosion rates. Further the corrosive process, the microbiological corrosion in storage tanks can lead to biofilm precipitation which can provoke quality issues of the derivatives like diesel and gasoline like filter plugging and reduction of the operating life of the tank.

The microbiological corrosion issues of storage tanks became a significant concern for the refiners in the last years due to the change in the derivatives specifications over the years. Nowadays, the necessity to produce very low sulfur derivatives like diesel and gasoline raise the microbiological corrosion risks due to the reduction in the sulfur content which acts like a biocide in higher concentrations as practiced in the past, this scenario tends to be worst in the near future once there is a growing trend to use biomass in coprocessing with fossil raw materials like the HVO (Hydrotreated Vegetable Oil) which will reduce even more the sulfur content and raise the water retention of the final blending.

One of the most effective ways to minimize the corrosion process in the bottom plates of hydrocarbon storage tanks is to minimize the water content in the bottom of the tanks. The first step here is to understand that the stockpiling assets are designed to deal only with the emulsified water which will be separated by decantation in the tanks and then drained, for this reason it's fundamental to ensure that

the storage tanks rely with adequate and reliable draining systems. This is especially true for storage tanks dedicated to storage diesel, gasoline, and naphtha.

The storage tanks in crude oil refineries are normally constructed over a concrete foundation aiming to avoid the contact of the bottom plate with the soil as well as to ensure rigidity to withstand the bottom plates, mainly for high diameter tanks. Despite the strategy to isolate the bottom plate from the soil, it's possible moisture accumulation occurs between the bottom plate and the concrete foundation. This issue can be minimized through an adequate design which uses deflecting plates to seal the gap between the bottom plate and concrete pad, avoiding water accumulation in this region which fatally will lead to corrosion.

A key question related to the integrity of the storage tanks is an adequate evaluation of the conditions of the bottom plates during maintenance shutdowns. The visual inspection of the equipment can help but is not sufficient to ensure adequate identification of corroded and fragility points which will reduce the operating lifecycle of the tank. For improve the accuracy of the tank inspection during the maintenance window the inspection team used to apply nondestructive testing or analysis aiming to identify corroded and low thickness points over the bottom plates, this information is applied to determine the local where the plate should be changed or reinforced, defining the maintenance extent of the storage tank.

One of the most applied nondestructive tests to evaluate the condition of tank floors is the MFL (Magnetic Flux Leakage) which is described in Figure 8.

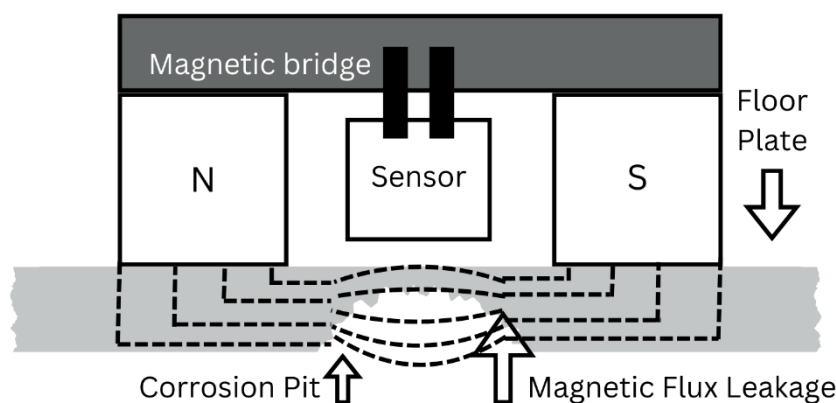


Figure 8 – Basic Principle of the MFL (Magnetic Flux Leakage) Testing

The basic principle behind the MFL testing is to produce a magnetic flux through two poles which is reduced when the flux finds a defect or a low thickness region over the storage tank floor. Using the report produced by the MFL testing the equipment inspection team will define the maintenance scope of the storage tank which can vary from spot repairs to the total substitution of the floor plates of the tank.

For crude oil storage tanks is relatively common to find significant thickness loss of the floor plates during the maintenance windows considering the characteristics of the fluid (high salt and water concentration) which normally leads the inspection team to recommend the total substitution of the floor plates. For crude oil storage tanks another key inspection factor is the condition of the sacrifice anodes which are installed in the floor plates to ensure the protection through cathodic protection method, if the sacrifice anodes are found in poor condition it's fundamental to substitute the pieces and the tanks should never put under operation without these devices under the risk to accelerate the corrosion process which will lead to content loss and process safety accidents.

The corrosion of above ground storage tanks bottom is one of the main concerns to the stockpiling operation team and asset integrity personnel. The main objective to manage the corrosion rate in the bottom plates is to ensure that the storage tank will reach the next scheduled inspection without loss of containment of the stored hydrocarbons.

The key factors to define the strategy of corrosion control in the bottom of the storage tanks are:

- Foundation type;
- Bottom type (double or single);
- Tank pad

The use of double bottom is a widespread practice in the refining industry aiming to control the leakage risks associated with hydrocarbon containment losses due to corrosion process.

Tank pad selection is another relevant topic which can help in the corrosion control of the storage tanks bottom, contamination of the tank pad with corrosive electrolytes like water will raise the corrosion rates. The most common corrosion pad applied in the crude oil refineries is the concrete due to the simplicity and effectiveness, despite these advantages the concrete pad can make hard to monitoring and control the corrosion process, to overcome this challenge some refiners adopt the strategy to inject Volatile Corrosion Inhibitors (VCI) between the bottom plates and the tank pad aiming to avoid or minimize the risk to reach a corrosive environment in this region.

As previously mentioned, define an adequate strategy to control the corrosion process is crucial in the asset management of stockpiling assets, especially the above ground storage tanks. The most common strategies applied to control the corrosion process in the bottom of storage tanks are the cathodic protection method and the VCI application as previously mentioned.

The cathodic protection is applied in the storage tanks bottom using sacrificial anodes, impressed current or both. As previously described, the protection is reached by forcing the bottom plates of the tank to act as the cathode in the electrochemical cell, forcing the corrosion process to the sacrificial anode for example. The API 651 presents the details for the design of cathodic protection for above ground storage tanks.

Although it may seem obvious, the cathodic protection system of storage tanks should be considered a critical system to the asset integrity of the stockpiling assets of a crude oil refinery and demands specific maintenance plans.

As mentioned above, it's fundamental to build a good relation and partnership between the stockpiling operation, maintenance and inspection teams aiming to build adequate asset integrity policies to the stockpiling operations. Figure 9 presents a proposed model to ensure an adequate asset integrity policy for stockpiling assets.

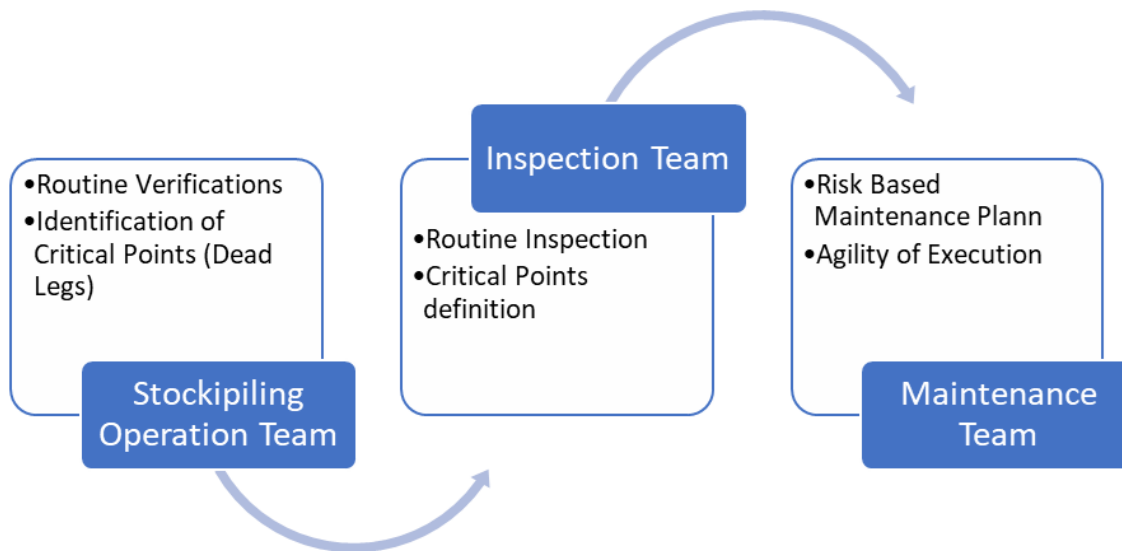


Figure 9 – Asset Integrity Policy Model for Stockpiling Assets

It's important to understand that the stockpiling assets normally do not have defined maintenance shutdowns like the processing units and the failure of stockpiling assets tends to have a more delayed impact over the refinery production planning than the processing units assets leading to a trend of stockpiling assets losing priority in the daily maintenance schedule. This scenario can lead to a quick degradation of integrity of these assets, mainly the storage tanks.

As presented in Figure 8, the synergy between the stockpiling operation, equipment inspection, and maintenance teams is fundamental to ensure the integrity of the stockpiling assets.

The equipment inspection should be based on risk analysis considering the historical inspection of the equipment, mainly considering fabrication defects, contamination with corrosive agents from the process (chloride, ammonium salts, etc.), and the extension of the last maintenance and inspection. Postpone a scheduled inspection of a storage tank, for example, should be avoided and if necessary, needs to be carried out after a deep analysis of multidisciplinary team aiming to ensure that all factors and risks were considered and mitigated.

As described through this chapter, the adequate management of stockpiling assets is a hard and challenging task for the refiners. Considering the impact of the failure and unavailability of these assets over the refining business, especially the storage tanks, an adequate management process of stockpiling assets should be a priority for the refinery management teams and needs to be one of the pillars of the strategic planning of the crude oil refineries.

Considering their characteristics, capital costs involved in the maintenance, and impact over the refinery production planning, the storage tanks demand the creation of a special group which will focus permanently on scheduling, planning, execute, and monitoring the maintenance of storage tanks. This group should be composed of a multidisciplinary team involving at least the following areas: stockpiling operation, static equipment maintenance, equipment inspection, engineering, HSE (Health, Safety, and Environment), remaining maintenance disciplines, production planning, optimization, etc. Figure 10 presents a proposal of composition and role definition for the storage tanks maintenance team of a typical crude oil refinery.

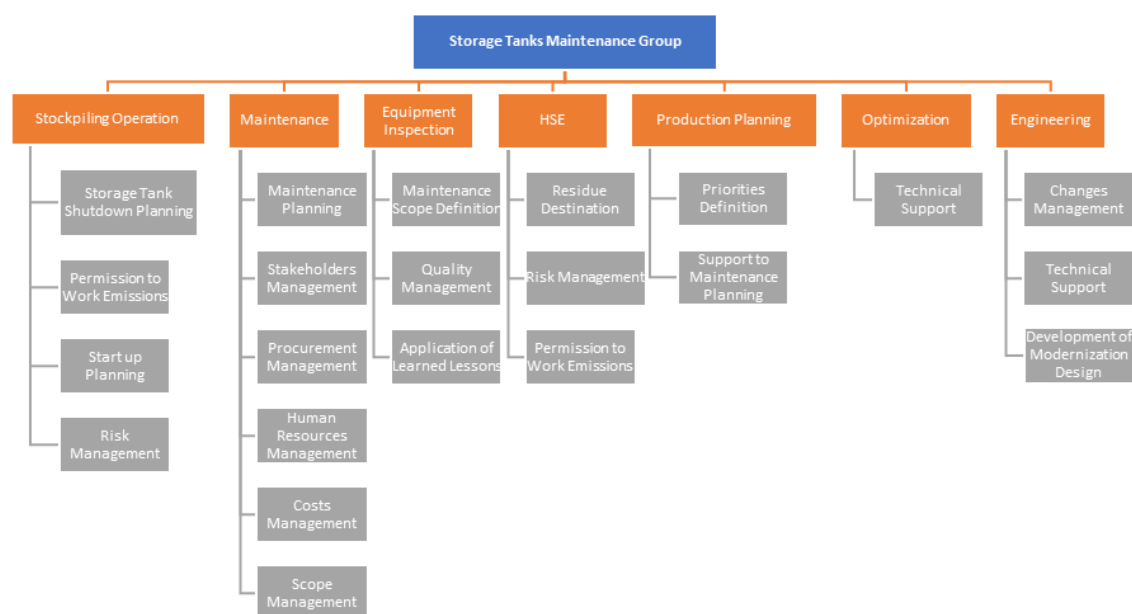


Figure 10 – Proposed composition and roles of the storage tanks maintenance group of a typical crude oil refinery

The composition proposed in Figure 10 is only a suggestion which can be customized according to the characteristics of each refinery. It's fundamental to define adequately the storage tanks maintenance scheduling aiming to avoid accumulation of storage tanks under maintenance due to the impact over the refinery production planning and the difficulties of managing high amount of high complexity and risk maintenance tasks in parallel.

In some cases, the accumulation of storage tanks under end life and the impact of this unavailability over the refinery results can be the driving force to postpone some maintenance of this equipment. As quoted above, this decision needs to be deeply studied and be adequately supported by the inspection team aiming to avoid new accumulation of storage tanks maintenance in the future and, in the worst scenario, process safety accidents caused by asset integrity failures. The decision to postpone an internal inspection of a hydrocarbon storage tank should be only considered after the execution of nondestructive analysis capable of ensuring or at least reducing the failure probability under operation.

The threat of Fluid Hammer in stockpiling assets

Another great threat to the integrity of stockpiling assets is the fluid hammer phenomenon. The fluid hammer is defined as a shock wave produced by a sudden pressure variation inside pipes resulting from

flow variations imposed on the flow of liquids. The most common causes or contributors for fluid hammer occurrence are:

- Sudden opening and closing of valves;
- Failure of protective devices like steam traps;
- Sudden stoppage of dynamics equipment;

These flow characteristics can lead to hydraulic transients where a liquid mass is chocked with the pipeline and accessories causing vibration, noise, and potential failures of the pipes. The following operational systems demand special attention regarding the risks of fluid hammer occurrence:

- Low pressure steam and condensate pipelines (higher probability of condensation);
- Hydrocarbon pipelines with the possibility of two-phase flow (unit load lines);
- Steam pipelines with poor thermal insulation (overload of the steam trap system);
- Pipes subject to sudden pressure variations (e.g. water supply);
- Emergency water supply pipelines;

It's fundamental to always consider that the fluid hammer is not a normal operating condition. The occurrence of this phenomenon is related to failures of design, maintenance and process adjustment and under no circumstances the operating personnel can accept coexist with the fluid hammer occurrence, in some cases, the hydraulic transient can lead to severe contention loss and process safety accident.

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Benchmarking Waste Water Treatment Systems

Karl Kolmetz , Cheah Phaik Sim

Abstract

Engineers today have a dual responsibility. There is the responsibility to produce the chemicals needed for food, medicine, and improvements in life style. Coupled with this need for chemical production is the need to produce these requirements with fewer impacts to the environment.

There are two routes to reduce the impacts to the environment. The first route is to develop processes that produce fewer unwanted by-products, the minimization of waste generation. The second route is the transformation of the unwanted by-products to streams of low environmental impact.

Each chemical plant constructed should include each of the routes. The transformation of the unwanted by-products to streams of low environmental impact is called the Waste Water Treatment System. It can process streams of various compositions and transform them to the desired streams of low environmental impact.

The Waste Water Treatment System has a variety of unit operations. They include gravity separators, mechanical separators, filters, stripper towers, aeration and clarifiers basins, as well as others. The transformation of the by-product streams is based of the effectiveness of each of these unit operations.

Each of these unit operations has three values.

- 1) Industry Standard Design Value
- 2) Actual Design Value and
- 3) Present Operating Value

The difference between the values can be benchmarked to establish areas good operation and areas of opportunities for improvements.

An overview of each of the unit operations of a Waste Water Treatment System will be constructed and industry guidelines will be given for individual unit benchmarking.

Introduction

Many industries use large volumes of water in their manufacturing operations. Industrial Waste Water Treatment Systems treat wastewater from an industrial or manufacturing process such as a cooling tower, food or animal processing plant or any type of manufacturing process that generates wastewater. The Pulp and Paper, Steel, Refining, and Chemical industries account for more than 90% of the water used by industries in North America. ⁽¹⁾

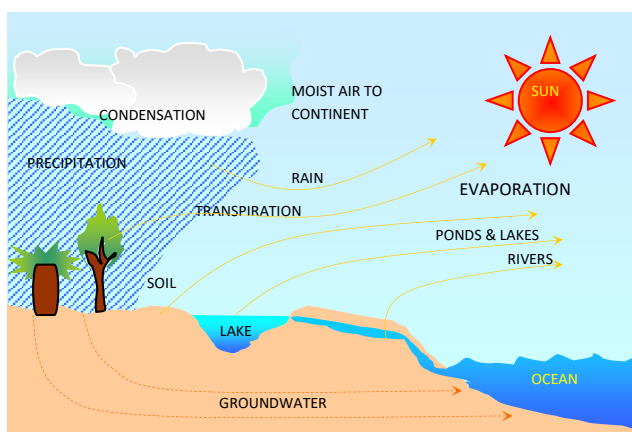


Figure 1- The Water Cycle

The treatment process and equipment is specifically directed to control or remove certain organic or chemical compounds. The flow may or may not contain domestic wastewater and ranges from several hundred to several million GPD. Industrial applications can present challenges that are specific to the plant or process. Maintenance on these systems is always mandatory and contains specific performance parameters.

The amount of organic material that can be discharged safely is defined by the effect of the material on the dissolved oxygen level in the water. Organisms in the water use the organic matter as a food source. In a biochemical reaction, dissolved oxygen is consumed, as the end product of water and carbon dioxide are formed

Atmospheric oxygen can replenish the dissolved oxygen consumption to exceed this re-supply; the dissolved oxygen level drops, leading to the death of fish and other aquatic life.

Under extreme conditions, when the dissolved oxygen concentration reaches zero, the water may turn black and produce odors. Organic compounds are normally measured as chemical oxygen demand (COD) and biochemical oxygen demand (BOD).

Industrial Waste Water Considerations include;

1. Volume of daily flow
2. All biological and chemical characteristics of the wastewater,
3. Including biodegradability, toxic material content and any material covered by specific environmental regulations
4. Regulations of the local health department and federal or state Environmental Protection Agency

The Waste Water Treatment System can be broken down into distinct components. ⁽²⁾

1. Pretreatment Units
2. Primary Treatment
3. Secondary Treatment
4. Tertiary Treatment
5. Sludge Handling (thickening and denaturing)
6. Sludge Disposal

Waste Water Treatment System Overview

Pretreatment Units

Sedimentation - Gravity Separation

Sedimentation is the separation from water of suspended particles that are heavier than water by gravitational settling. The purpose of sedimentation is 1) clarification - to produce clean water, which can be used, recycled or further treated and 2) consolidation - to produce concentrated solids that can be more easily handled and treated.

Most waste treatment system employ a gravity separation step for suspended particle or oil removal. The settling rate of a particle is defined in terms of "free" verses "hindered" settling. A free settling particle's motion is not affected by that of other particles, the vessel's wall, or turbulent currents. A particle has a hindered settling rate if there is any interference from these effects. ⁽²⁾

Table 1 - Effect of Particle Size on Settling

Unit	Size (microns)	Time to fall 1 meter	Settling (m/h)
Gravel	10,000	1 sec	3600
Sand Course	1,000	10 sec	360
Sand Fine	100	125 sec	28
Silt	10	108 min	0.5
Bacteria	1	180 hr	
Colloidal matter	0.1	2 years	
Color Particles	0.001	200 years	

Gravity settling is employed primarily for removal of inorganic suspended solids, such as grit and sand. The equipment employed for gravity separation for waste treatment is normally either a rectangular basin with moving bottom scrapers for solids removal or a circular tank with a rotating bottom scraper.

Rectangular tanks are normally sized to decrease horizontal fluid velocity to approximately 1 foot per minute. Their lengths are three to five times their width and their depths are three to eight feet.

Circular clarifiers are ordinarily sized according to the surface area, because velocity must be reduced below the design particle's terminal velocity. The typical design provides a rise rate of 600-800 gpd/ft².

API Separator

When wastewater contains appreciable amount of hydrocarbons, removal of these contaminants becomes a problem. Oil is commonly lower in density than water; therefore, if it is not emulsified, it can be floated in a separate removal stage or in a dual-purpose vessel that allows sedimentation of solids.

For example, the refining industry uses a rectangular clarifier with a surface skimmer for oil and a bottom rake for solids as standard equipment. Stokes' Law expresses the basic principle governing the separation of oil from water by gravity differential as follows: ⁽⁴⁾

$$v_p = \frac{g(\rho_p - \rho_w)d_p^2}{18\mu}$$

Where:

u_p = particle settling velocity

g = acceleration due to gravity, 9.81 m/s^2

ρ_p = density of particle

ρ_w = density of water

d_p = diameter of particle

μ = dynamic viscosity

Primary Treatment – Flotation

Air Flotation

Where the density differential is not sufficient to separate oil and oil-wetted solids, air flotation may be used to enhance oil removal. In this method, air bubbles are attached to the contaminant particles and thus the apparent density difference between the particles is increased.

Dissolved air flotation (DAF) is a method of introducing air to a side stream or recycle stream at elevated pressures in order to create a super saturated stream. When this stream is introduced into the waste stream, the pressure is reduced to atmospheric, and the air is released as small bubbles. These bubbles attach to contaminants in the waste, decreasing their effective density and aiding in their separation.

The most important operation parameters for contaminant removal by dissolved air flotation are; (1)

- Air pressure
- Recycle or slip stream flow rate
- Influent total suspended solids (TSS) including oil and grease
- Bubble size
- Dispersion

As in gravity settling, air flotation units are designed for a surface-loading rate that is a function of the waste flow and rise velocity of the contaminants floated by air bubbles. The retention time is a function of the tank depth.

DAF units can be rectangular in design but are usually circular, resembling a primary clarifier or thickener. They are often single stage units.

Induced Air Flotation (IAF) is another method of decreasing particle density by attaching air bubbles to the particles, however the method of generating the air bubble differs. A mechanical action is employed to create the air bubbles and their contact with the waste contaminants. The most common methods use high-speed agitators or recycle a slipstream through venturi nozzles to entrain air into the wastewater.

In contrast to DAF units, IAF units are usually rectangular and incorporate four or more air flotation stages in series. The retention time per stage is significantly less than in DAF circular tanks.

As in gravity settling, the diameter of the particle plays an important role in separation. Polyelectrolytes may be used to increase effective particle diameters. Polymers are also used to destabilize oil / water emulsions, thereby allowing the free oil to be separated from the water. Polymers do this by charge neutralization, which destabilizes an oil globule surface and allows it to contact other oil globules and air bubbles. Emulsion breakers, surfactants, or surface-active agents are also used in air flotation to destabilize emulsions and increase the effectiveness of the air bubbles.

Filtration

Filtration is employed in waste treatment whenever suspended solids must be removed. In practice, filtration is most often used to polish wastewater following treatment. In primary waste treatment, filters are often employed to remove oil and suspended solids prior to biological treatment. More commonly, filters are used following biological treatment prior to final discharge or reuse.

Filtration is also widely used as a tertiary treatment for suspended solids removal. The fundamental requirement is that the suspended particles are of sufficient size or capable of being increased in size by flocculation. In cases when it is not possible to flocculate such particles, more advanced techniques such as ultra-filtration is more practical.

Some of the advantages of filtration are as follows: (3)

1. Simple to operate and easy to control
2. Can be used for almost any type of free-flowing liquid stream containing suspended solid particles
3. Relatively cost competitive with regard to sludge dewatering processes
4. Lower energy consumption as compared to others
5. Can be integrated easily with other treatment trains
6. Great potential for recovery as the process will not chemically change the characteristics of the materials treated.

Some of the disadvantages, among others are: (3)

1. Not capable of producing a high purity effluent as both the liquid product and dewatered sludge still contain a certain fraction of the liquid and solid phase
2. Not capable of separating chemical components especially when they are present in the same phase.
3. Not capable of destroying or chemically changing the toxicity of materials
4. Will produce a liquid waste stream that requires further treatment prior to disposal.

Ultra-filtration

Ultra-filtration, by definition, is a membrane filtration process that separates high molecular weight solutes or colloids from a solution or suspension. The process has successfully been applied to both homogeneous solutions and colloidal suspensions that are difficult to separate practically by other techniques.

The types of membrane used for ultra-filtration are similar to reverse osmosis membranes that are made of cellulose acetate and nylon. It has demonstrated unique capabilities in the treatment of industrial wastewaters such as the separation of oil from water, reduction of toxic compounds present in the wastewater and recovery of valuable byproducts. Nevertheless, the process is unattractive to small-scale industries due to high operating and capital costs. (3)

Secondary Treatment - clarification

The Secondary Treatment consists of at least two types of systems. The first is Fixed Film / Media System and the second is Suspended Growth Systems.

The Fixed Film / Media Biological Oxidation System has a media in which the Biological Film is attached to a Media. The Waste Water is slowly passed through the Media and the Biological Film degrades the organics to non-organic products. The fixed film system include Trickling filters, Rotating Biological Contactor (RBC), etc.

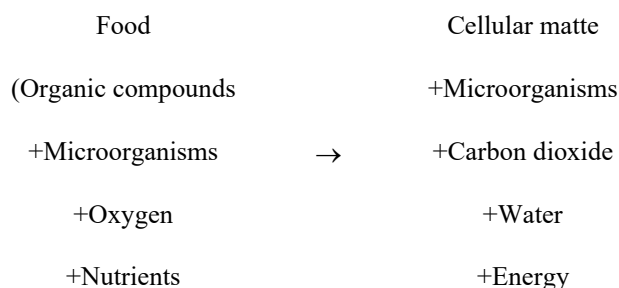
The Suspended Growth Biological Oxidation System includes Stabilization Ponds, Single Pass Aerated Lagoons and Activated Sludge Systems

Biological Oxidation

One of the most common ways to convert soluble organic matter to insoluble matter is through biological oxidation. Soluble organics metabolized by bacteria are converted to carbon dioxide and bacterial floc, which can be settled from solution.

The biodegradable contaminants in water are usually measured in terms of biochemical oxygen demand (BOD). BOD is actually a measure of the oxygen consumed by microorganisms as they assimilate organics.

Bacteria metabolize oxygen along with certain nutrients and trace metals to form cellular matter, energy carbon dioxide, water and more bacteria. This process may be represented in the form of a chemical reaction. (1)



The purity of the water depends on minimizing the amount of organic compounds that remain after secondary treatment. Factors that affect biological oxidation are shown in Table 2. (1)

Table 2 - Factors Affecting Biological Oxidation

Factor	Affect
Food, BOD	To maintain control with efficient BOD removal, the proper amount of food must be supplied
Dissolved Oxygen	Insufficient oxygen levels inhibit BOD removal
pH, toxicants	With time, bacteria adapt to change in conditions. Rapid changes in pH or type of waste organic inhibit the process
Time	The degree of degradations varies with time
Nutrients	Bacteria require trace amounts of nitrogen and phosphorus for cell maintenance.
Temperature	Low Temperature result in slow reaction rates, higher temperature may kill many strains of bacteria

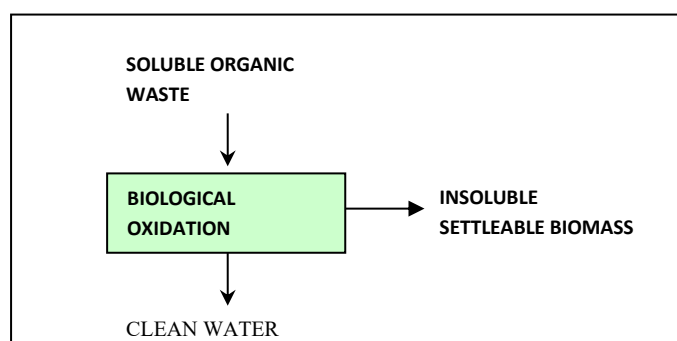


Figure 2 - Biological oxidation converts soluble waste to clean water and insoluble biomass

Fixed Film / Media Systems

Fixed Film / Media Oxidation passed influent wastewater across a substructure laden with fixed biomass. Fixed media allow a biological layer to grow on a substructure continually exposed to raw wastewater. As the layer grows in thickness oxygen transfer to the inter-most layers is impeded. Eventually, some of the layer is removed. This phenomenon is called sloughing. In a continuous process this material is carried to a sedimentation stage, where it is removed.

Media plugging and lack of oxygen transfer are the primary difficulties encountered with fixed media designs. Plugging problems can be alleviated by increase wastewater shear. This is normally accomplished by recycling a portion of the wastewater. The graphical representation of bio-film formations in the fixed film/media system is shown in Figure 3.

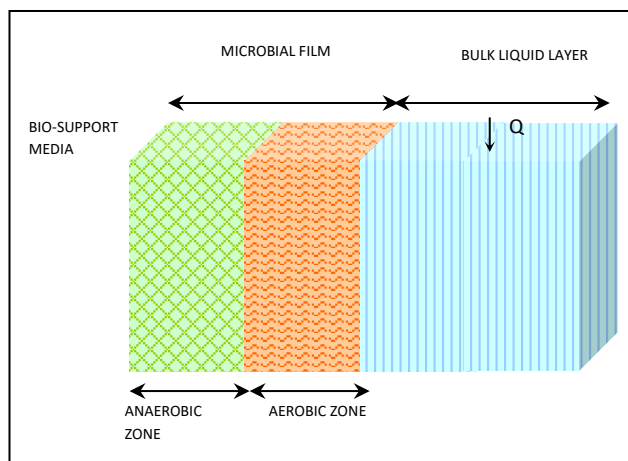


Figure 3 - Volumetric element for Microbial film and Bulk Liquid Layers in the fixed film/media system

Suspended Growth Biological Oxidation Systems

Activated Sludge Systems

Activated sludge system is a biological process that is characterized by the suspension of aerobic microorganisms being maintained in a relatively homogenous state by the mixing or turbulence induced from the aeration process ⁽³⁾.

The microorganisms oxidize the soluble and colloidal organics in the presence of molecular oxygen. In the oxidation process, a part of the organic material is transformed into new cells that subsequently undergo auto-oxidation in the aeration basin. In the conventional activated sludge process, the typical hydraulic retention time (HRT) is in the range of 6 to 10 hours, and the volumetric loading rate (VLR) of the reactor is in the range of 0.32 to 0.64 kg BOD /m³.day.

In the process, the flocs generated from the oxidation process are separated in a clarifier and partly recycled into the aeration basin with some removed for disposal off site or further treatment. The supernatant overflows from the clarifiers as final discharge. The process has been widely used throughout the world as one of the most proven method to treat, not only sewages but also highly toxic industrial wastewaters. Since its invention, the process has been modified to improve its efficiency and reduce the capital and operation costs. ⁽³⁾

The advantages of the activated sludge process are as follows:

- Requires limited space – HRT is 3 to 36 hour range
- MLSS is in the range of 1500 to 10,000 mg/l
- Reliable operator control capability
- Can handle shock loads better with less recovery time required
- Can handle high loaded waste streams
- Excellent solids removal capability

The disadvantages, among others, are as follows:

- Requires highly trained operators
- Requires substantial monitoring
- Requires high operation and maintenance costs
- Sensitive to toxic discharges or load fluctuations
- Generates waste sludge products that are difficult to dewater

The control of contaminate oxidation at high BOD loading requires a bacteria population that is equal to the level of food. The need is the basis for the activated sludge process. In the activated sludge process, reactants, food, and microorganism are mixed in a controlled environment to optimize BOD removal. The process incorporates the return of concentrated microorganisms to the influent waste.

When bacteria are separated from wastewater leaving an aeration basin and reintroduced to the influent, they continue to thrive. The re-circulated bacteria continue to oxidize wastewater contaminants, and if present in sufficient quantity, produce a relatively low BOD effluent water. Because the activated sludge process incorporates the return of concentrated microorganisms, it must include a process for microorganism concentration and removal. This process includes an aeration stage and a sedimentation stage.

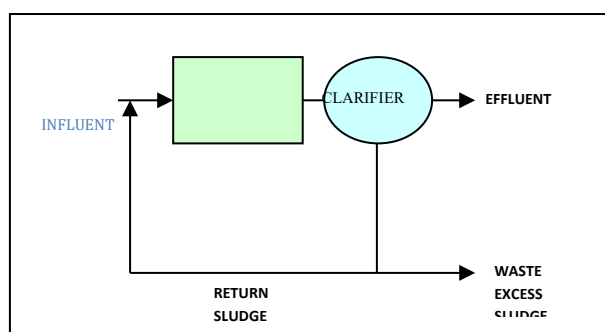


Figure 4 - Activated sludge process returns active biomass to enhance waste removal

The operating parameters that affect the performance of any activated sludge process are BOD, microorganism, dissolved oxygen, retention time, nutrient concentration, and external influences of temperature and pH. In order to understand the various activated sludge designs, it is necessary to examine the relationship between available food and bacteria population.

Initially, excess food is present; therefore the bacteria reproduce in a geometric fashion. This is termed the “log growth phase”. As the population increase and food decrease a plateau is reached in population. From the inflection point on the curve to the plateau, population is increasing but at a decreasing rate. This is called the “declining growth phase”.

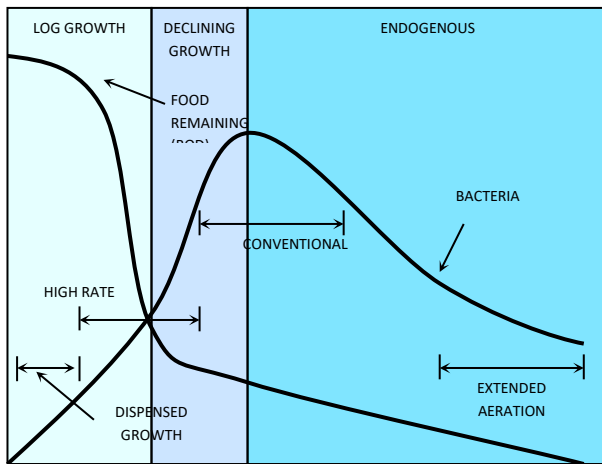


Figure 5 - Model of bacteria population as a function of time and amount of food

Once the plateau is crossed, the bacteria are actively competing for the remaining food. The bacteria begin to metabolize stored materials, and the population decreases. This area of the curve is termed “endogenous respirations”. Eventually, the bacterial population and the DOD are at a minimum.

Because activated sludge is a continuous, steady state process, each plant operates at some specific point on the curve, as determined by the oxidation time provided. The point of operation determines the remaining bacteria population and BOD of the effluent.

Optimization of an activated sludge plant requires the integration of mechanical, operational and chemical approaches for the most practical overall program. Mechanical problems can include excessive hydraulic loading, insufficient aerations, and short-circuiting. Operational problems may include spill and shock loads, pH shocks, failure to maintain correct mixed liquor concentrations, and excessive sludge retention in the clarifier. Because activated sludge depends on microorganism re-circulation, sedimentation is the key stage. The settle ability of the biomass is a crucial factor. As bacteria multiply and generate colonies, they excrete natural biopolymers. These polymers and the slime layer that encapsulates the bacteria influence the flocculation and settling characteristics of the bacteria colonies.

It has been determined empirically that the natural settle ability of bacteria colonies is also a function of their position on the time chart. Newly formed colonies in the log growth phase are relatively non-settle able. At the end of the declining growth phase and the first part of the endogenous phase, natural flocculation is at an optimum. As the endogenous phase continues, colonies break up and floc particles are dispersed, decreasing the biomass settle ability.

Although microbes are eventually able to break down most complex organics and can tolerate very poor environments, they are very intolerant of sudden change in pH, dissolved oxygen and the organic compounds that normally upset an activated sludge system. These upsets normally result in poor BOD removal and excessive carry over of suspended solids (unsettled microorganisms) in the final effluent.

Types Of Activated Sludge Systems ⁽⁴⁾

1. Conventional, plug flow systems

The most common activated sludge design used by municipalities and industry operates in the endogenous phase, in order to produce an acceptable effluent in BOD and TSS levels. Conventional aeration represents a “middle of the road” approach because its capital and operating cost are higher than those of the high rate process, but lower than those of the extended aeration plants. Natural flocculation is at the optimum, so the required sedimentation time for the removal of suspended solids from the effluent is minimized. ⁽¹⁾

Settled wastewater and return activate sludge (RAS) enter the front end of the aeration tank and are mixed by diffused air or mechanical aeration. In early designs, air application was generally uniformed throughout the tank length; however, low DO concentrations usually occurred in the initial passes of the tank. In modern designs, the aeration system is designed to match the oxygen demand along the length of tank by tapering the aeration rates. During the aeration period, adsorption, flocculation, and oxidation of organic matter occur. Activated sludge solids are separated in a secondary settling tank. ⁽⁴⁾

2. Extended Aeration, plug flow systems

Extended aeration plants operate in the endogenous phase, but use longer periods of oxidation to reduce effluent BOD levels. This necessitates higher capital and operating cost (i.e., larger basins and more air). In conjunction with lower BOD, extended aeration produces a relatively high-suspended solids effluent when optimum natural settling ranges are exceeded.

Extended aeration design may be necessary to meet effluent BOD requirements when the influent is relatively concentrated in BOD or the waste are difficult to biodegrade. Because extended aeration operates on the declining side of the biomass population curve, net production of excess solids is minimized. Therefore, savings in sludge handling and disposal cost may offset the higher pant capital and operating cost required for extended aeration. ⁽¹⁾

The extended aeration process is similar to the conventional plug-flow process except that is operates in the endogenous respiration phase of the growth curve, which requires a low organic loading and long aeration time. Because of the long HRT (in the order of 24 to 36 hours), aeration equipment design is controlled by mixing needs and not oxygen demand. The process is used extensively for pre- engineered plants for small communities. Generally, primary clarification is not used. Secondary clarifiers are designed at lower hydraulic loading rates than conventional activated sludge clarifiers to better handle large flow rate variations of small communities. Although the bio-solids are well stabilized, additional bio-solids stabilization is required to permit beneficial reuse. ⁽⁴⁾

3. Complete Mix Systems

The complete mix activated sludge (CMAS) is an application of the flow regime of a continuous flow stirred-tank reactor. Settled wastewater and RAS are introduced typically at several points in the aeration tank. The organic load, MLSS concentration and oxygen demand are uniform throughout the tank. An advantage of the CMAS is the dilution of shock loads that occurs in the treatment of industrial wastewaters. The CMAS is relatively simple to operate but tends to have low organic substrate concentrations that encourage the growth of filamentous bacteria, causing sludge bulking problems.

Process	Aeration Retention Time, hrs	MLSS, ppm	DO ppm	Sludge Recycle %	BOD Loading Lb/mft3	F/M Lb BOD / lb MLVSS	Sludge Production	BOD Removal %
High Rate	0.5-3	300 - 1000	0.5-2	5- 15	2.5	1.5 – 5.0	0.65 – 0.85	75-85
Conventional	6 – 8 (diffused)	1000 – 3000	0.5-2.0	20-30	20-40	0.2-0.5	0.35-0.55	85-90

	9-12 (mechanical)							
Extended Aeration	18-35	3000 - 6000	0.5-2.0	75-100	10-25	0.03-0.15	0.15-0.20	90-95
Step Aeration	3-5	2000 - 3500	0.5-2.0	25-75	40-60	0.2-0.5	0.35-0.55	85-95
Contact Stabilization	3-6	1000 -3000 (aeration) 4000–10000 (contact basin)	0.5-2.0	25-100	60-70	0.2-0.6	0.35-0.55	85-95
Pure Oxygen	1-3	3000-8000	2-6	25-50	100-250	0.25-1.0	0.35-0.55	95-98
Complete Mix	3-5	3000-6000	0.5-2.0	25-100	50-120	0.2-0.6	0.35-0.55	85-95

Table 3 - Activated Sludge Systems ⁽¹⁾

4. Contact Stabilization

Due to the highly efficient absorptive capabilities of activated biomass, the time necessary for biomass to capture the colloidal and soluble BOD is approximately 30 minutes to one hour. Oxidation of fresh food requires the normal aeration time of 4-8 hours. IN the contact stabilization design, relatively quick sorption time reduces aeration tank volume requirements. The influent waste is mixed with return biomass in the initial aeration tank (or contact tank) for 30-90 minutes. The entire flow goes to sedimentation, where the biomass and its captured organics are separated and returned to a re-aeration tank. In the re-aeration tank the wastes under go metabolism at a high biomass population. The system is designed to reduce tank volume by containing the large majority of flow for a short period of time.

This process is not generally as efficient in BOD removal as the conventional plant process, due to mixing limitation in the contact basin. Operating costs are equivalent. Due to the un-stabilized state of the biomass at sedimentation, flocculation is inferior. Suspended solids in the effluent are problematic.

Because this design exposed only a portion of the active biomass to the raw effluent at a time, it is less susceptible to feed variations and toxicants. For this reason it can be beneficial for treatment of industrial wastes. ⁽¹⁾

The contact zone detention time is relatively short (30 to 60 minutes), and the MLSS concentration is lower than in the stabilization zone. Rapid removal of soluble BOD occurs in the contact zone, and colloidal and particulate organics are captured in the activated sludge floc for degradation later in the stabilization zone.

In the stabilization zone, RAS is aerated and the detention time is in the order of 1 to 2 hours to maintain a sufficient SRT (solids retention time) for sludge stabilization. Because the MLSS concentration is so much higher in the stabilization zone, the contact stabilization process requires so much less aeration volume than CMAS or conventional plug flow process for the same SRT. The process was developed for BOD removal and the short contact time limits the amount of soluble BOD degraded and NH₄-N oxidation. ⁽⁴⁾

5. Step Feed

In a plug flow basin, the head of the basin receives the waste in its most concentrated form. Therefore, metabolism and oxygen demand are greatest at that point. As the waste proceeds through the basin, the rate of oxygen uptake (respiration rate) decreases, reflecting the advanced stage of oxidation.

Tapered aeration and step aeration reduce this inherent disadvantage. Tapered aeration provides more oxygen at the head of the basin and slowly reduces oxygen supply to match demand as waste flows through the basin. This results in better control of the oxidation process and reduced air cost.

Step aeration modifies the introduction of influent waste. The basin is divided into several stages, and raw influent is introduced to each stage proportionally. All return microorganisms (sludge) are introduced at the head of the basin. This design reduces aeration time to 3-5 hours, while BOD removal efficiency is maintained. The shorter aeration time reduces capital expenses because a small basin can be used. Operating costs are similar to those of a conventional plant.⁽¹⁾

Flexibility of the operation is one of the important features of this process because the apportionment of the wastewater feed can be changed to suit operating conditions. The concentration of MLSS may be as high as 5000 to 9000 mg/l in the first pass, with lower concentrations in subsequent passes as more influent feed is added. This process has the capability of carrying a higher solids inventory and thus a higher SRT for the same volume as a conventional plug flow process.⁽⁴⁾

6. Oxidation Ditch

Oxidation ditch consists of a ring or oval-shaped channel equipped with mechanical aeration and mixing devices. Screened wastewater enters the channel and is combined with the RAS. The tank configuration and aeration and mixing devices promote unidirectional channel flow, so that the energy used for aeration is sufficient to provide mixing in a system with a relatively long HRT. The aeration/mixing method used creates a velocity from 0.25 – 0.30 m/s in the channel, which is sufficient to keep the activated sludge in suspension. At these channel velocities, the mixed liquor completes a tank circulation in 5 –15 minutes, and the magnitude of the channel flow is such that it can dilute the influent wastewater by a factor of 20-30. As a result, the process kinetics approach that of a CMAS, but with plug flow along the channel.

7. High -Purity Oxygen

A staged enclosed reactor is used in the high-purity oxygen. Three or four stages are generally used and the influent wastewater, RAS and high-purity oxygen are added to the first stage. The oxygen partial pressure in the headspace may range from 40 to 60 percent in the first stage to 20 percent in the last stage. At high oxygen partial pressure, higher volumetric oxygen transfer rates are possible so that pure oxygen systems can have a higher MLSS concentration and operate at a shorter HRT and higher VLR than conventional processes. The rate of oxygen addition is 2 to 3 times greater than CAS. Major advantages for pure oxygen systems are the reduced quantities of off-gas if odor control and VOC control are required.

8. Sequential Batch Reactors (SBR)

The SBR is a fill-and-draw type of reactor system involving a single complete-mix reactor in which all steps of the activated sludge process occur. An SBR goes through a number of cycles per day; a typical cycle may consist: fill, aeration, settle and withdrawal of supernatant. An idle step may also be included to provide flexibility at high flows. Mixed liquor remains in the reactor

during all cycles, thereby eliminating the need for separate secondary clarifiers. The HRT ranges from 18 to 30 hours, based on influent flow rate and tank volume used.

Latest Research in Wastewater Treatment Systems

Recently, biological process has been attracting considerable attention for removing heavy metals from aqueous wastes. Biofilm systems, in particular, are able to retain relatively high biomass concentrations resulting in shorter liquid detention times, better performance stability and higher volumetric removal rates. The efficiency of an expanded bed biofilm reactor in the treatment of waste waters contaminated with heavy metals has been investigated for rubber product manufacturing industry. In the study, it has been found that the process could achieve 60% to 90% removal of Zinc.

Process	Process Influent	BOD	COD	TOC	SS	Oil	Phenol	NH ₃	Sulfide
API Separator	Raw Water	5-40	5-30		10-50	60-99	0-50		
Primary Clarifier	API Effluent	30-60	20-50		50-80	60-95	0-50		
DAF	Separator Effluent	20-70	10-60		50-85	70-85	10-75		
Filter	API Effluent	40-70	20-55		75-95	65-90	5-20		
Secondary Oxidation Pond	API Effluent	40-95	30-65	60	20-70	50-90	60-99	0-15	70-99
Aerated Lagoon	Primary Effluent	75-95	60-85		40-65	70-90	90-99	10-45	95-99
Activated Sludge	Primary Effluent	75-95	60-85		40-65	70-99	90-99	10-45	95-99
Trickling Filter	API Effluent	60-85	30-70		60-85	50-80	70-98	15-90	70-99
Cooling Tower	Primary Effluent	50-95	40-90	10-70	50-85	60-75	75-99	60-95	
Activated Carbon	Primary Effluent	70-95	70-90	50-80	60-90	75-95	90-99	7-33	

Tertiary Filter granular media	Secondary Effluent			50-65	75-95	65-95	5-20		
Activated Carbon	Secondary + Filter Effluent	91-98	86-94	50-80	60-90	70-95	90-99	33-87	

Typical Removal Efficiencies for Oil Refinery Treatment Process (1)

Application of plant-based flocculants can be considered as new in industrial wastewater treatments. Despite its biodegradable characteristics, plant-based flocculants possess an advantage for oxidation and coagulation process. A newly invented plant-based flocculants, namely KN2 has been introduced in the treatment of inking wastewater. Comparison has also been made with other conventional chemical-based flocculants (i.e. PAC, PE, PDMC, etc.) in order to compare their effectiveness in removing pollutants. Application of activated carbon as a polishing media at the final stage shows a drastic declination in COD and BOD values as well as the other parameters.

Dissolved Air Flotation (DAF) using micro-bubbles of size 50µm are used to remove suspended solids, emulsified oils & greases from industrial and municipal waste waters. Micro-sized air bubbles are formed by injection of pressurised recycle water into a flotation tank using special designed nozzles or needle valves. These bubbles will attach to the suspended solids and float them to the surface. The floated sludge can be removed either by overflow or mechanical scraping. Influencing parameters being studied are bubble size, particle size, air pressure for saturated vessel, air saturation system, and efficiency of suspended solids removal. The saturation system consists of an unpacked saturation vessel, an air compressor and the associated control system. The saturation vessel operated at a 4 bars pressure. The results of the study have reported that percentage removal of Suspended Solids, COD, Colour and Turbidity were 90%, 91%, 86% and 90%, respectively. Simulation has been carried out to obtain kinetic data for the parameters under study.

Conclusions

The Waste Water Treatment System has a variety of unit operations. They include gravity separators, mechanical separators, filters, stripper towers, aeration and clarifier basins, as well as others. The transformation of the by-product streams is based of the effectiveness of each of these unit operations.

Each of these unit operations has three values.

- 1) Industry Standard Design Value
- 2) Actual Design Value and
- 3) Present Operating Value

The difference between the values can be benchmarked to establish areas good operation and areas of opportunities for improvements. A review of the individual unit operations should be conducted to maximize the effectiveness of a Waste Water Treatment

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How to design and optimize Bubble Cap Trays

Dr.-Ing. Volker Engel

Tower trays and internals are the heart of all distillation columns. Their design is an essential part of a process engineer's task and determines the process reliability and economy.

This article is the 2nd part of a series on different kinds of trays and internals.

Bubble Cap trays have been used for about 80 years in technical applications and are a very well studied tray type. Nowadays, they are mainly used for handling low liquid loads, as for this field of application there are only few alternatives!

On a distillation tray vapor enters liquid and forms a two phase regime (bubbling, froth, spray). The tray types differ mainly in the way the vapor enters the liquid. For *Bubble Cap Trays* the gas flow path is very different compared to other tray types and is depicted in *Fig. 1*.

Before entering the liquid, the gas ascends in the riser (a), is redirected in the top of the cap (b) (reversal area) and then flows downwards in the cylindrical annular gap (c). Finally, the vapor enters the liquid layer through vertical slots, holes or the skirt of the cap (d).

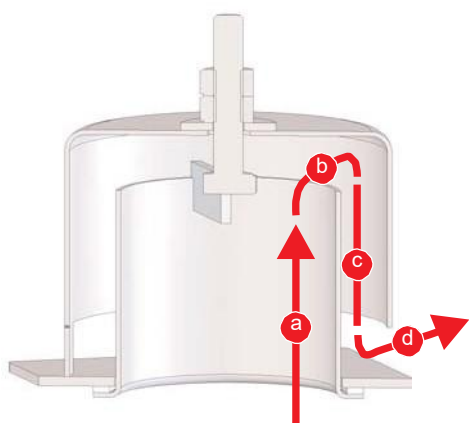


Fig. 1: Gas Flow Path

As long as the riser is higher than the outlet weir and the panels and risers are liquid-tight, the tray is able to handle very small amounts of liquid. This is the main advantage of this tray type and a typical field of application.

The main disadvantages are the relatively high costs for the equipment and a higher pressure drop compared to other tray types.

There are many different types and sizes of bubble caps. Historically, there are cast iron types (still in use!), oval, rectangular and round bubble caps.

Today, new bubble cap trays are usually equipped with bubble caps with an outer cap diameter of 2 inch, 3 inch, 4 inch or 6 inch. As the caps are fabricated by deep drawing, the material thickness is about 1mm. For special materials types or thick materials, the caps are rolled and welded.

There are several types of cap designs (*Fig. 2*).

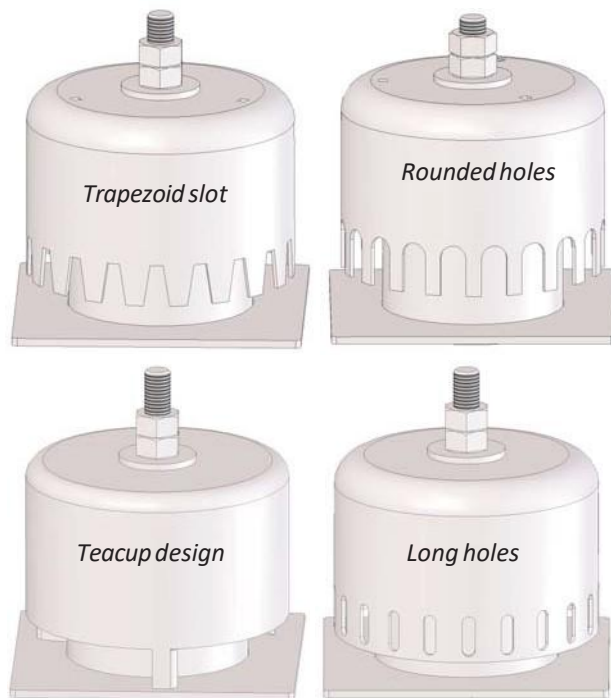


Fig. 2: Bubble Cap Designs

The cap is normally bolted (double nut!) to the riser, sometimes welded, sometimes wedged. (It is not fun to move on the top of bubble caps for maintenance or inspection duty.)

The caps are categorized by the top level of the gas opening and the area of the openings (expressed by a function of the “opened” height of the slots / skirt).

The pitch of the bubble caps is important for the function of the tray: In standard applications it is triangular and expected to be 1.25 .. 1.5 times the cap diameter [HOPPE/MITTELSTRASS 1967].

The risers are welded or pressed in the tray panel or gasketed by pulling the riser flange to the tray panel (*Fig. 3*).

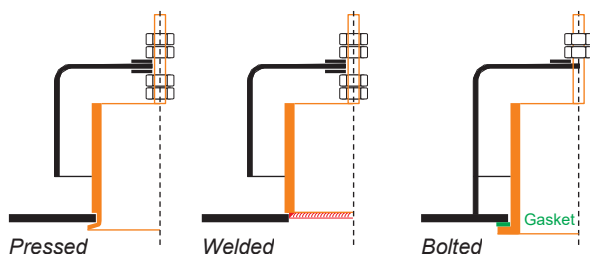


Fig. 3: Fastening of Risers

The values of the riser area, the reversal area, the annular gap as well as the escape area of the bubble cap have to be balanced. As the fabrication possibilities are on the one hand confined by the riser dimension, which is limited by the available pipe dimensions, and on the other hand by the cap, which is restricted to the dimensions of the deep drawing tools, you will have to find a compromise to have almost equal values for all areas.

The relative free area (riser area per active area) is typically about 5 to 10% and the resulting total pressure drop per tray is about 8 to 12mbar. The tray spacing is usually not less than 500mm (for large tower diameters it should be higher due to inspection and maintenance reasons).

The *Operating Area* of a bubble cap tray is defined by different limits. In Fig. 4, a qualitative operation diagram is shown. Please note, that the position and shape of all curves depend on the physical data, the tray and cap geometry and the gas/liquid load. Each curve can be limiting!

The *Operation Point* (Op in Fig. 4) of the design case (as well as the minimum and maximum load) has to stay inside all limiting curves. For stable operation and good efficiency there is a *useful operation area* with narrower limits (e.g. 80%-FFCF and 85%-FFJF curves).

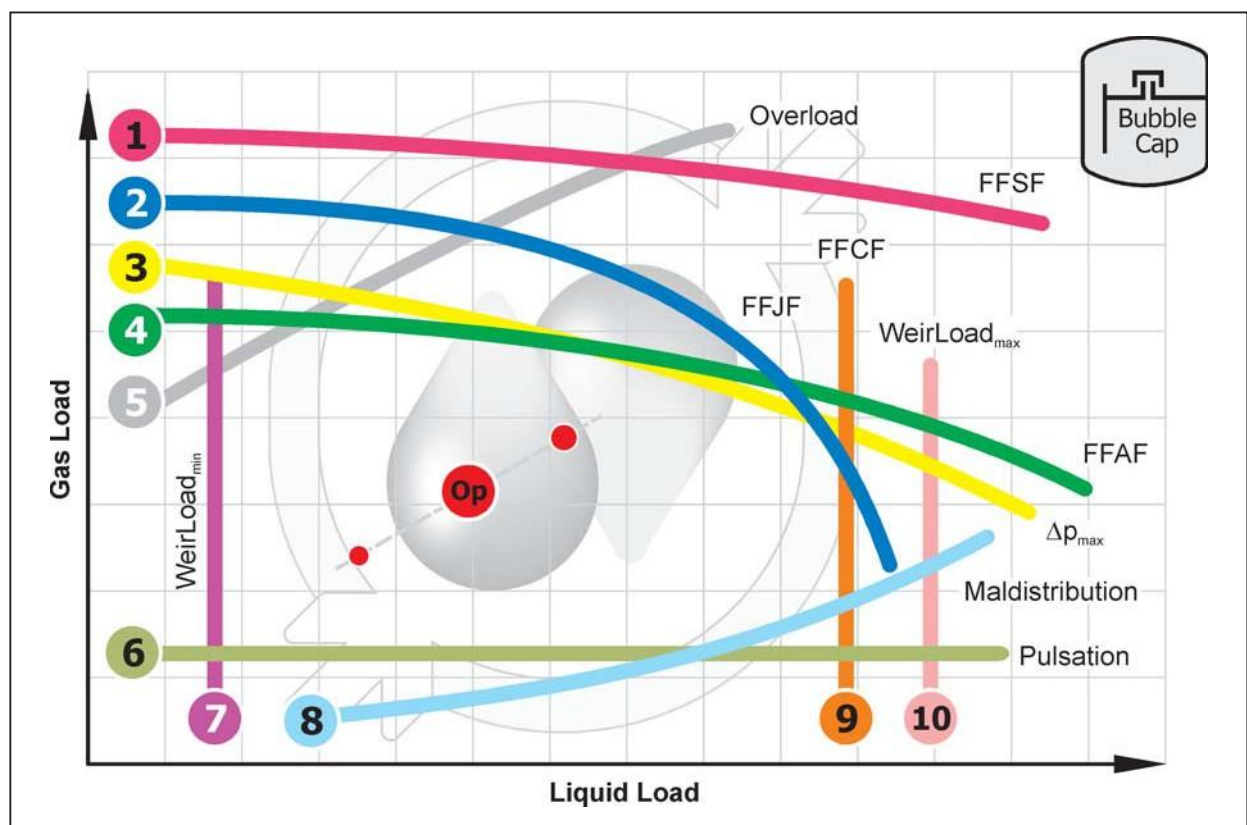


Fig. 4: Qualitative Operation Diagram for Bubble Cap Trays

The first step in analyzing a design is – of course

– calculating all relevant parameters. For a bubble cap tray design there are 10 main parameters shown as curves in *Fig. 4*. These parameters are discussed in this article. There are some additional effects you will have to look at: entrainment, head loss at downcomer exit (clearance), flow regime, downcomer residence time, efficiency, sealing, construction issues, statics, ...

Please note, that all free suppliers' software only show a limited number of these parameters and therefore are not save to use for design, rating and troubleshooting of trays. For save design you should be able to calculate all parameters! (e.g. software TRAYHEART OF WELCHEM)

In the following sections, all 10 main parameter curves of *Fig. 4* are described. Each suggested action for preventing a certain effect may result in fertilizing another. The main task for designing trays is to balance these different and contradicting effects.

1

System Flood FFSF

There is a system limit set by the superficial vapor velocity in the tower. When the vapor velocity exceeds the settling velocity of liquid droplets („Stokes Law Criterion“), vapor lifts and takes much of the liquid with it. A well known model was published by STUPIN AND KISTER 2003.

This flooding effect cannot be reduced by use of other tray types or by increasing tray spacing.

The only way is to enlarge the vapor cross section area (e.g. enlarging tower diameter or reduce downcomer area).

2

Jet Flood FFJF

There are several definitions in literature for the so called *Jet Flood*. Similar definitions are *Entrainment Flood*, *Massive Entrainment*, *Two-Phase Flood* or *Priming*. For practical understanding, Jet Flood describes any liquid carried to the tray above by the gas stream. This leads to a shortcut recycling of the liquid with loss of tray efficiency, additional pressure drop and additional downcomer load. For good tray performance, the Jet Flood value should be less than 75-80%.

You can reduce Jet Flood by

- a) lowering the gas velocity (higher open area, i.e. more bubble caps, higher escape area)
- b) enlarging the tray spacing
- c) lowering the froth height on the tray deck (by reducing weir height or weir crest height)
- d) enlarging the active area (i.e. the gas flow area) by sloping the downcomers

Pressure Drop

3

In most cases there is specified a maximum allowable pressure drop of the tower. You have to ensure that the pressure drop per tray does not exceed a certain value. This leads to a limiting curve within the operation diagram.

To reduce the pressure drop of a design, you can

- a) lower the gas velocity by enlarging the number of bubble caps or change their geometry

- b) lower the froth height on the tray deck (by reducing weir height or weir crest height)
- c) enlarge the active area (with place for more bubble caps) by reducing the downcomer area or sloping the downcomers

Aerated Downcomer Backup FFAF

4

This limiting effect is also known as *Downcomer Backup Flood*. It describes the (aerated) backup of the downcomer due to pressure drop effects. It is important to not mix this up with the

Choke-Flood-effects (ref. to 9).

The level of the liquid in the downcomer is the result of (i) head loss at the clearance, (ii) the liquid height on the outlet deck, (iii) an inlet weir (if present) and (iv) the pressure drop of the tray itself. All these effects can be expressed by "hot liquid height". This resulting level in the downcomer has to compensate these effects! Taking into account the aeration of the liquid in the downcomer, the level has to be less than tray spacing plus weir height.

To reduce a high Aerated Downcomer Backup value you have to

- a) reduce the pressure drop of the tray (ref. to 3)
- b) reduce the head loss of the clearance (use higher clearance height or radius lips or recessed seal pans in case of insufficient sealing)
- c) avoid inlet weirs

Please note, that it is no option to enlarge the downcomer area to reduce this flooding effect!

5

Overload Caps

At high gas loads, the space between the caps is dried - the liquid can't enter this region and is blown to a froth layer above the caps. This is not a recommended and stable regime! The effect is close to the *Blowing effect* of sieve trays (where the liquid layer is "disconnected" from the tray panel and blown upwards).

Therefore, the bottom skirt of the bubble cap should not be used for the gas outlet. (In a teacup design, the skirt should not be blown totally free.)

To prevent overload of caps, you can

- a) adapt the design of the caps (more slots, enlarge width of slots, higher skirt)
- b) enlarge the number of caps

6

Pulsation

The slots of bubble caps are opened by the gas flow. To have a stable operation, the gas has to open all slots of all bubble caps. If there is not enough gas (minimum slot velocity not reached), the bubble caps are pulsating.

To reduce Pulsating you have to

- a) change cap design (less slots, reduce width of slots)
- b) reduce number of bubble caps

7

Minimum Weir Load

The uniform thickness of the two-phase layer is essential for the successful operation of a tray.

To achieve this uniform flow, the tray panels have to be in level and the outlet weir has to be installed accurately.

To compensate small tolerances, the weir crest should be higher than 3mm and the weir load more than $9 \text{ m}^3/\text{m}/\text{h}$. In case of low weir loads you will normally have to consider gasketing the tray to avoid any leakage and loss of liquid.

To ensure these minimum values, you can use

- a) notched weirs
- b) blocked weirs

Gas Maldistribution

8

In all types of trays the liquid must have a driving force to flow from the inlet to the outlet. As long as there is no gas driven flow (as generated by fixed valves or push valves) the hydraulic gradient is the main reason for liquid flow.

Because the bubble caps are obstacles in the liquid flow pass, the hydraulic gradient is significant higher for bubble cap trays than for other trays.

Why might the hydraulic gradient be a problem? At a high hydraulic gradient, the tray will not work properly (*Fig. 5*): At the tray inlet the liquid “closes” the caps. The gas will use less liquid affected bubble caps for passage. This leads to a gas maldistribution and a bad efficiency of the tray. If the liquid head of rows with high gradient gets too high, weeping occurs!

To reduce gas maldistribution you have to

- a) reduce the number of cap rows (e.g. by switching to a design with more flow passes)
- b) cascade the active area

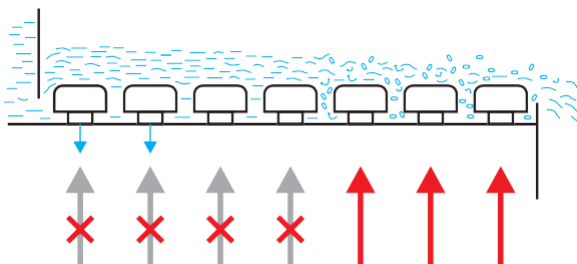


Fig. 5: Maldistribution

The maximum liquid throughput of a down-comer is limited by the liquid velocity and the effect of overload (so called *Choke Flood*). The maximum allowable liquid velocity in the down-comer depends on the density ratio of gas to liquid, the tray spacing and the system factor. (The system factor describes the difficulty of phase separation. For common applications it is 1.0.) The most popular downcomer choke flooding calculation was published by GLITSCH 1993.

Another effect of Choke Flood at center and off-center downcomers is initiated by the mutual interference of the two liquid flows into the downcomer.

To prevent downcomer Choke Flood you have to

- a) enlarge the downcomer area
- b) implement more flow passes (with in sum an overall higher downcomer area)
- c) enlarge the tray spacing (if limiting)
- d) install anti-jump baffles for center / off-center downcomers

Maximum Weir Load

The maximum liquid flow handled by a down-comer can also be limited by the weir.

If the weir crest exceeds 37mm or the weir load $120 \text{ m}^3/\text{m/h}$, the liquid will not enter the downcomer properly.

To prevent overload of the weir, you have to extend the weir length by

- a) larger downcomers with longer weirs (or multichordal downcomers)
- b) more flow passes
- c) swept back weirs at the side downcomers

Conclusion

There are multiple limiting effects that have to be considered at the design and operation of bubble cap trays. Among the “standard” limits there are bubble-cap-individual limits as pulsating, gas maldistribution and cap overload.

Even if bubble caps are sometimes considered as dinosaurs, they are still in use and often the only solution (among all types of internals!) for low liquid loads.

Author

Volker Engel studied process engineering at the Technical University of Munich and did his Ph.D. thesis on packed columns with Prof. Johann G. Stichlmair. Since 1998 he has been the managing director of WelChem Process Technology GmbH and head of the TrayHeart software. TrayHeart has developed into a state-of-the-art design tool for trays and internals in process technology.

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Operational Optimization of HDS Feed Pre-heat Exchangers through Targeted Ammonium Salt Deposition Mitigation:

A Case Study in Fuel Gas Savings

Shahzeb Hassan, Adnan Masood, Arsalan Saleem

Abstract:

This research paper addresses a heat recovery inefficiency in the feed pre-heat exchange trains of a Gas Oil Hydrodesulphurization (HDS) unit that ultimately effects the Fuel gas consumption for unit furnaces in an evident manner as well increases the duty on furnaces & downstream fin fan coolers exiting the preheat exchangers. A significant temperature difference (ΔT) of up to $\sim 120^{\circ}\text{C}$ developed between two parallel banks of exchangers shell side outlets which is the reactor feed, indicating a poor & unbalanced heat transfer in each bank and increased load on the downstream reaction furnaces, costing fuel gas. Process data analysis identified the root cause as uneven flow distribution of reactor effluent due to the deposition of ammonium bisulfide (NH_4HS) salts in the comparatively cooler tubes of one exchanger bank. An operational intervention was implemented, involving the periodic injection of Boiler Feed Water (BFW) upstream of the affected exchangers to dissolve the salt deposits, which are the product of hydrogen sulfide & Ammonia.

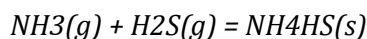
Post-implementation, the temperature difference (ΔT) between the exchanger banks was reduced to just 12°C , and the outlet temperature of the underperforming bank increased from 234°C to 324°C (shell side), showing evidently the recovery from tube side effluent stream. This improvement in heat recovery led to a 40% reduction in reaction furnaces fuel gas consumption, resulting in annual savings of approximately 4.0 MM USD. This study demonstrates a simple but cost-effective method for maintaining heat exchanger efficiency and optimizing energy usage in hydro-processing units & can be referenced for similar process methodologies with salt deposits in exchanger tubes.

1. Introduction

HDS is widely used as a provocative hydro-processing technology to clean the fuel by removing the impurities associated in form of sulfur, nitrogen & oxygen. It's an energy intensive methodology that uses catalysts mainly Co-Mo on Alumina/Silica base to perform rigorous exothermic reactions to break the complex chain of sulfides, oxides & Nitrites into their derivatives that can be removed from strippers & stabilizers columns downstream, depending on process technologies used.

The exchanger train (often termed as combine feed exchangers) cool the hot reactor effluent while pre-heating the cold feed, thereby reducing the heating duty required from the fired furnace. This is a key aspect of process energy efficiency that is used universally to efficiently conserve heat energy

The issue of fouling in these effluent/feed exchangers have a long history. Specifically, with ammonium bisulfide (NH_4HS) salts, which form from the NH_3 and H_2S produced in the HDS/HDN reactions and can deposit into inner walls of exchanger tubes at temperatures around 130°C , leading to fouling, under-deposit corrosion, and reduced heat transfer.



Problem Statement:

As observed in the Hydro Desulfurization unit of a refinery, after a debottlenecking study to increase throughput, the unit experienced a gradual decline in heat recovery, evidenced by a large temperature difference between two parallel banks of exchangers in both processing trains. This led to increased furnace duty, higher fuel gas consumption & load increment for downstream air coolers.

Objective of the Paper:

- a) To Identify the root cause of the heat recovery loss & analyze the effects
- b) To describe the troubleshooting methodology & compare them
- c) Studying the outcome of the implemented mitigation strategy & prioritize them
- d) To quantify the significant energy savings achieved

2. Process Methodology Description:

The objective of the HDS Unit is the catalytic hydrogenation of a Gas Oil (GO) blend (Light Gasoil LGO from the Crude Distillation-CDU unit and up to 37% Light Vacuum Gasoil LVGO from the Vacuum Distillation Unit-VDU) to remove impurities from GO blend. Major impurities are sulfur, oxygen, and nitrogen compounds. These impurities affect the quality of the GO. HDS unit main feed is a blend of LGO from CDU and LVGO from VDU. Both streams are blended before entering feed surge drum. The reaction section consists of two identical reactors (R01/R101) termed as Train 1 & 2, using heat, pressure, hydrogen, and a hydro-treating catalyst (cobalt molybdenum Co-Mo) to remove sulfur from GO as H_2S . GO feed pre-heated in combine feed charge heat exchangers (E02/102) by hot reactor effluents. Each train is equipped with 12 combine feed pre-heat exchangers, these 12 exchangers are further divided into two banks of six exchangers, and downstream of these exchangers is a furnace for each train (F02/102) to increase the feed temperature to reaction temperature before entering the reactors. This process converts sulfur, oxygen, and nitrogen to hydrogen sulfide, water, and ammonia. Reactor effluents are cooled in feed charger exchangers E02/102 tube side and fin fan cooler before entering to HP separator where gas goes back to recycle gas compressor and GO goes to the stripping section. Stripping section consists of HP Stripper and LP Stripper. HP stripping operation utilizes MP steam to remove H_2S , NH_3 , water and some traces of gas from the process stream. The product of HP stripper goes to LP stripper where lighter components and traces of H_2S removed to meet the target flash point of the product.

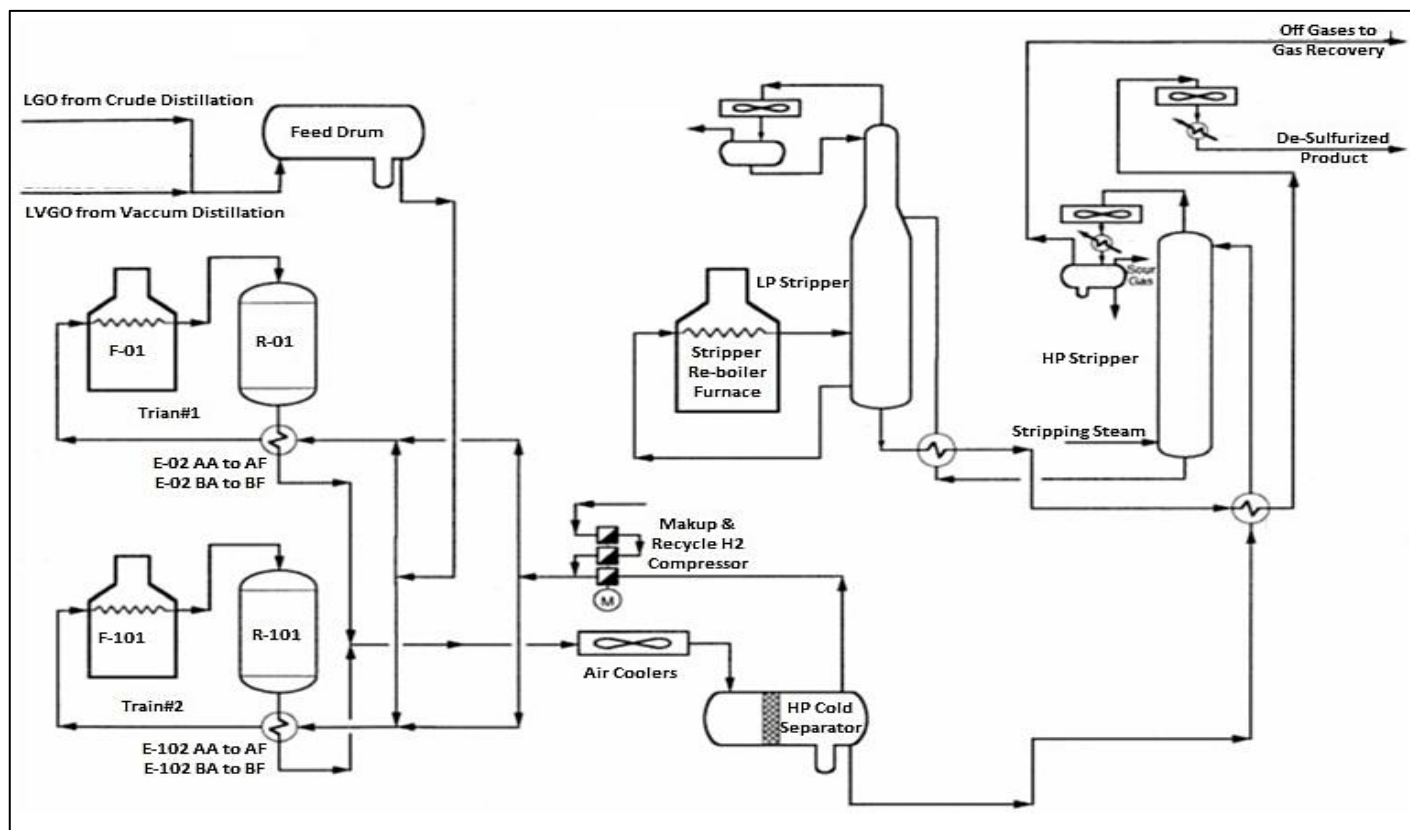


Figure 1 Process Flow Diagram of the Unit

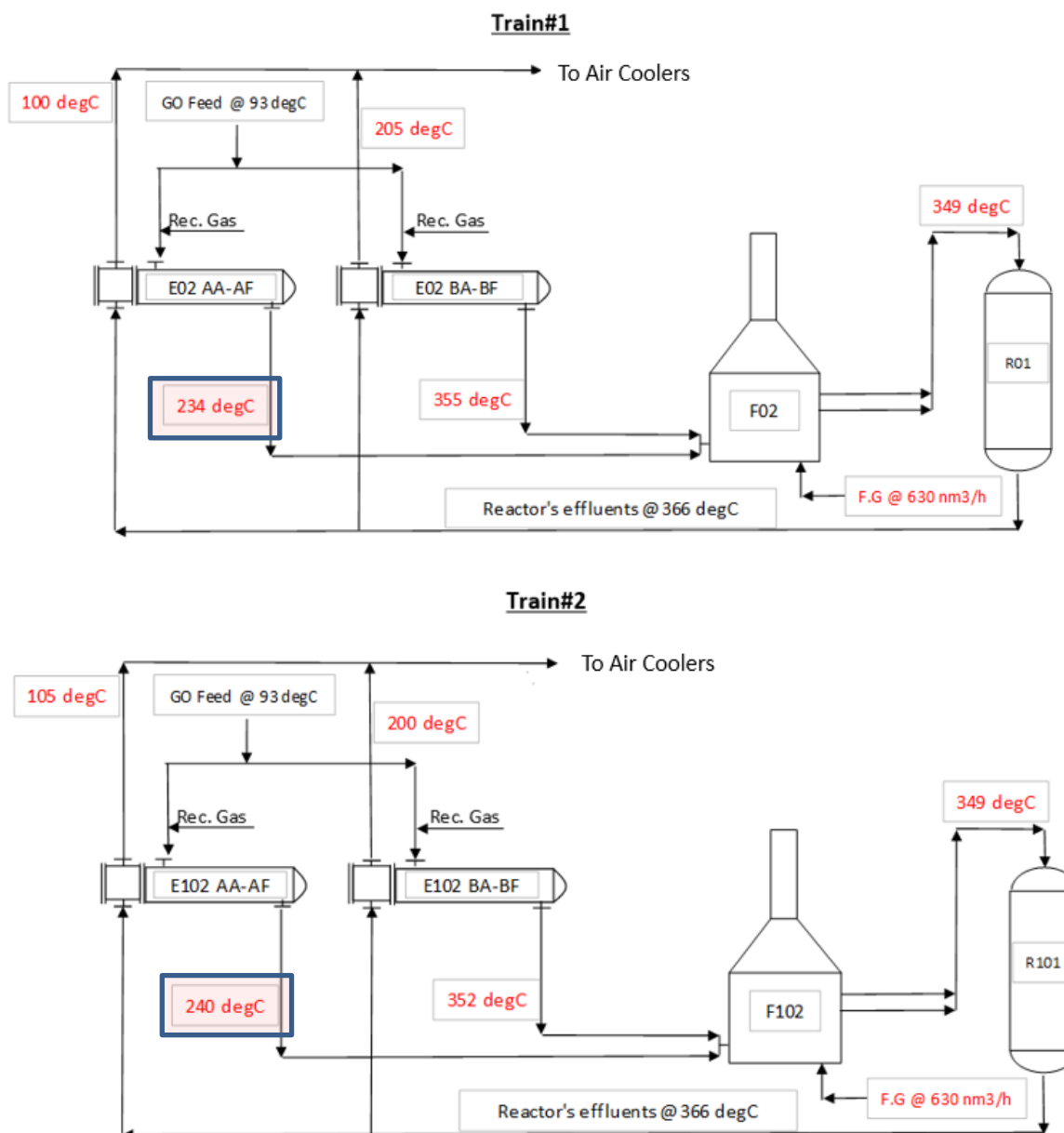
Pre-heat Exchangers Purpose:

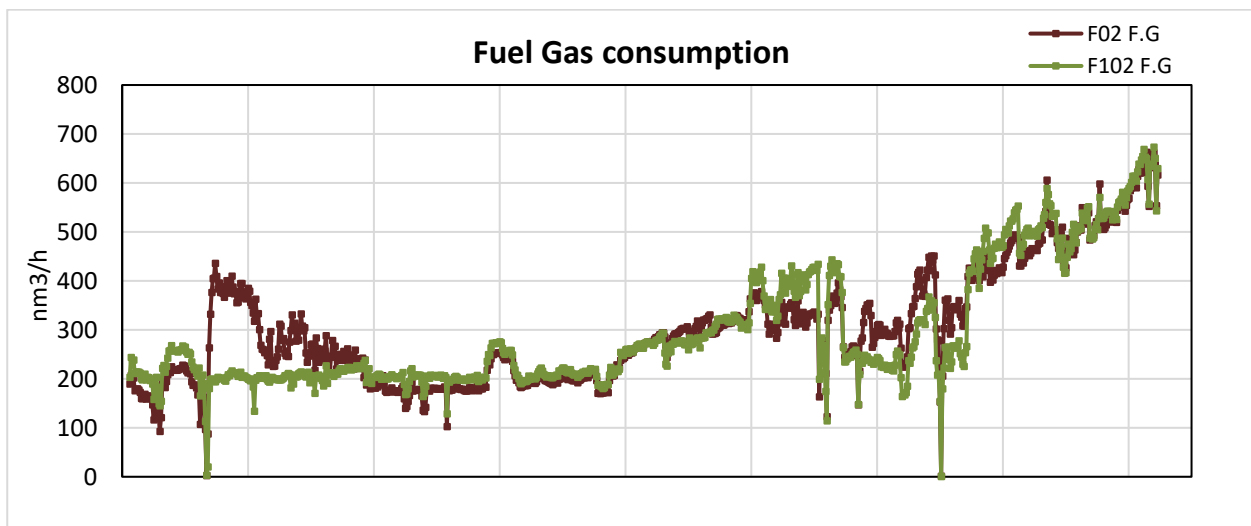
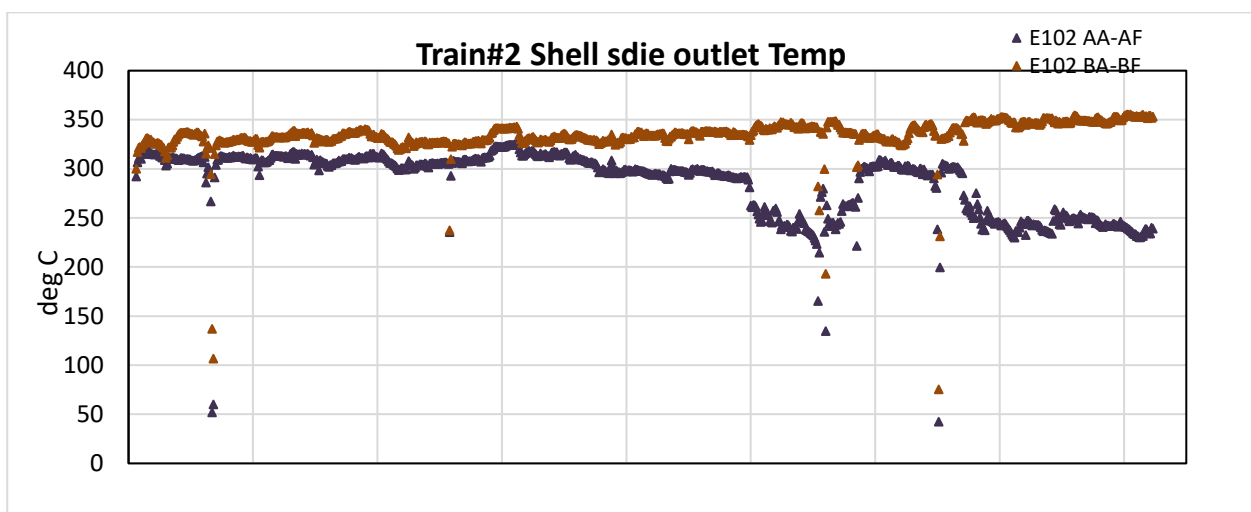
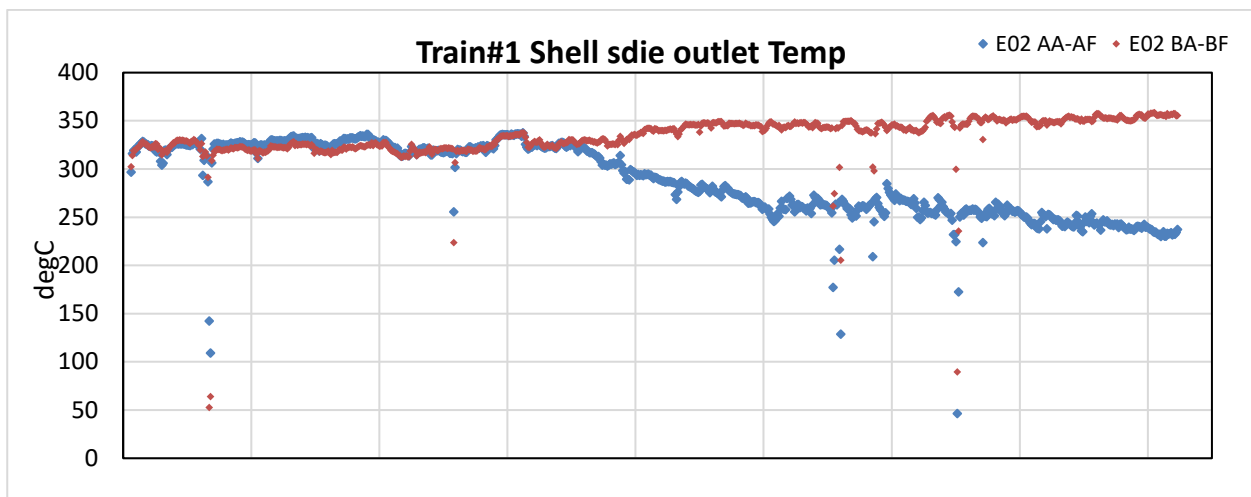
GO feed charge pumps route GO from feed surge drum to HDS reactors through combine feed charge heat exchangers E02/102 and reaction furnaces F02/102. Before entering to feed exchangers, H2 enriched recycle gas from recycle & makeup H2 gas compressors injected in the GO for hydro-treating reactions. HDS unit has feed heat exchangers divided in two trains. Each train has equal number of shell & tube type heat exchangers and these exchangers are further divided into two banks of heat exchangers in series. These two banks are parallel to each other. GO & Recycle Gas mixed stream splits into two streams, one for each train. Both streams further splits into two, one for each bank of exchangers. Each bank has identical heat exchangers in series with countercurrent flow arrangement.

Reactor's effluents from both trains are cooled in tube side of -E2/102 by pre-heating the feed in shell side. The temperature of this pre-heated feed is further increased to reaction temperature by two furnaces F2/102, one for each train. From furnaces, GO/R.G stream enters in the HDS reactors R01/101. Due exothermic nature of the reaction, outlet temperature of reactor effluents increases. Effluents from both trains are cooled in E2/102 tube side and fin fan coolers before entering to High pressure cold separator.

3. Problem Identification & Analysis:

The standard mitigation for NH_4HS fouling downstream of the exchangers was continuous BFW injection upstream of the air coolers. However, it was hypothesized that a similar approach could be used to clean the existing deposits within the affected feed-effluent exchangers. The unit had existing available nozzle connections upstream of the last two exchangers (AE and AF) in each bank. The proposed solution was to temporarily inject BFW at 85-90 °C into these connections to dissolve the accumulated ammonium bisulfide salts in the tube side of the E02/102 (AA-AF) banks that amplified two ideological & favorable conditions.





a) Effectiveness

The BFW dissolves the water-soluble ammonium bisulfide salts, clearing the flow path. Ammonium salts are generally readily soluble in water, and targeted water washing is a prominent recognized method to remove them.

b) Operational Significance:

It reduced the cooling load on the downstream air coolers for the effluent stream. This prevented unit extra load handling during hot summer months when the air coolers outlet temperature would have otherwise been too high.

4. Comparison with Alternative Mitigation Strategies:

It is valuable to contrast the simple BFW injection method with other, more complex solutions adopted in past & their economic significance

a) Chemical Dispersants:

Some refineries use oil-soluble salt dispersant additives to prevent deposition. However, these can be surface-active and may stabilize emulsions or leave salts to be carried over to downstream processes that can be deposited in downstream elbows, fittings or narrow necks.

b) Advanced Chemical Programs:

Kurita's ACF (a strong organic base), offer a different approach. These chemicals react preferentially with HCl and ammonium salts to form a liquid, non-corrosive salt that is easily removed with water. A case study on a naphtha hydrotreater showed that ACF injection successfully stopped corrosion in feed/effluent exchangers. This represents a more advanced but also more costly chemical treatment option.

For severe blockages, mechanical methods like high-pressure water jetting or steam flushing using lancers may be required. A proven case study described using specialized 55,000 psi jetting to clear heavily fouled, 25m-long tubes in a vertical exchanger. This method is effective but requires a plant shutdown and is far more intrusive than an online chemical clean, involving a downtime is never favorable from economic perspective

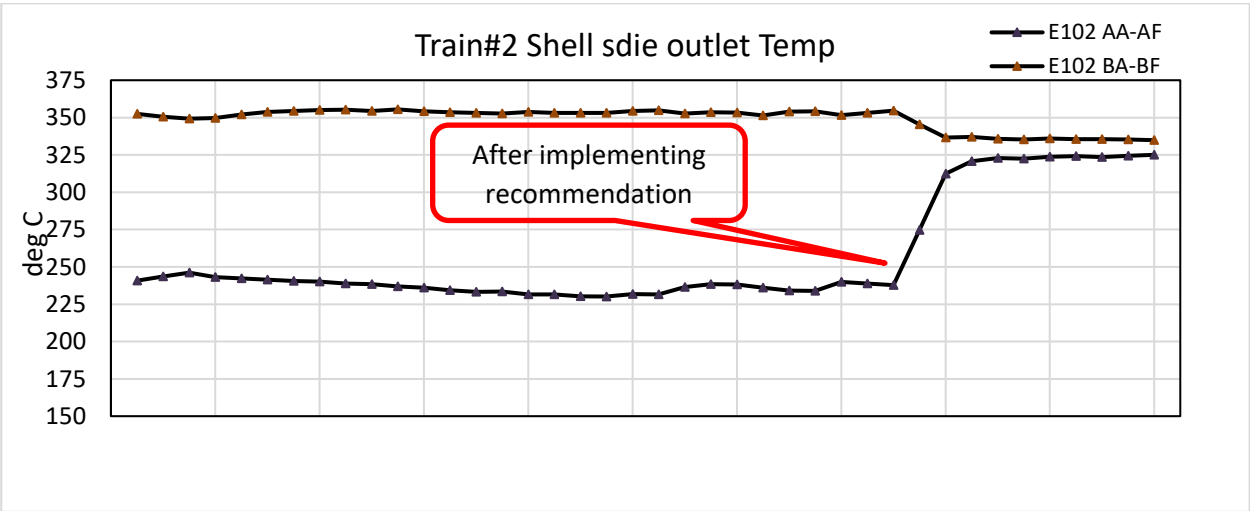
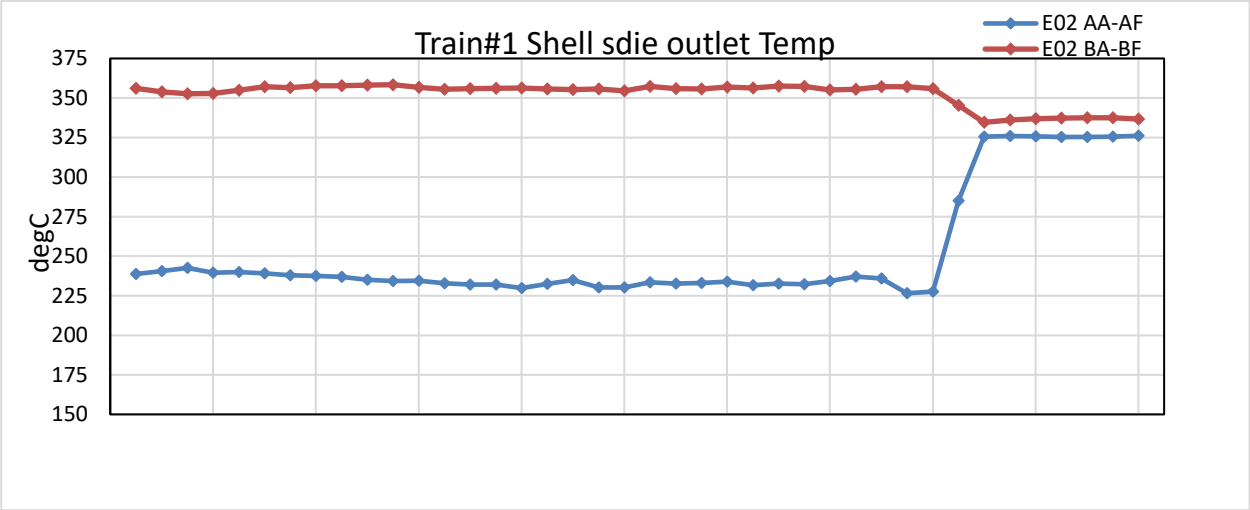
Alignment with Industry Best Practices & Regulations:

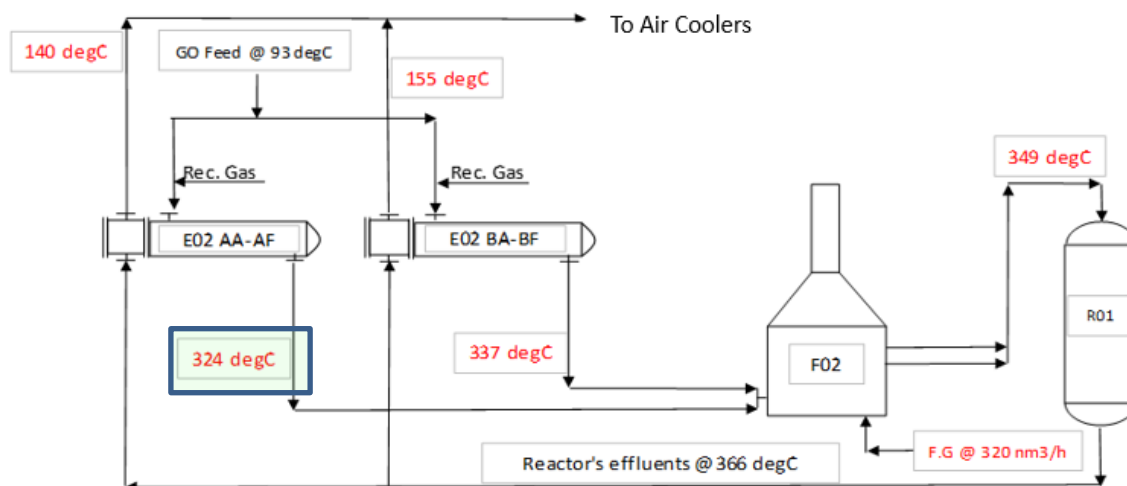
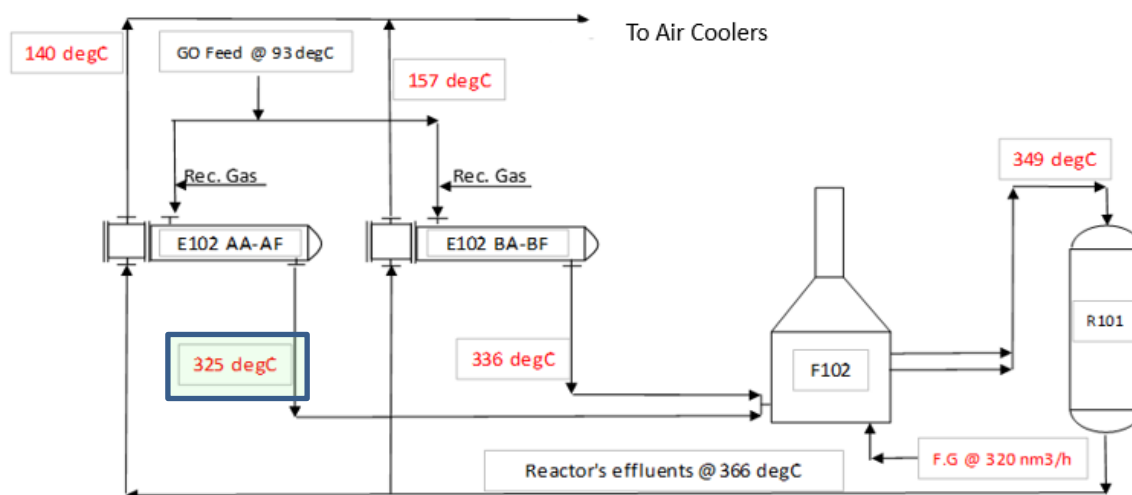
The success of this intervention reinforces the guidance provided in industry standards like API RP 932-B, which provides comprehensive guidelines for managing corrosion and fouling from ammonium salts in hydro-processing & hydrotreating reactor effluent systems. By proactively injecting water at the point of salt deposition, the operation effectively manages the fouling risk, avoiding the more severe consequences of under-deposit corrosion and unplanned outages.

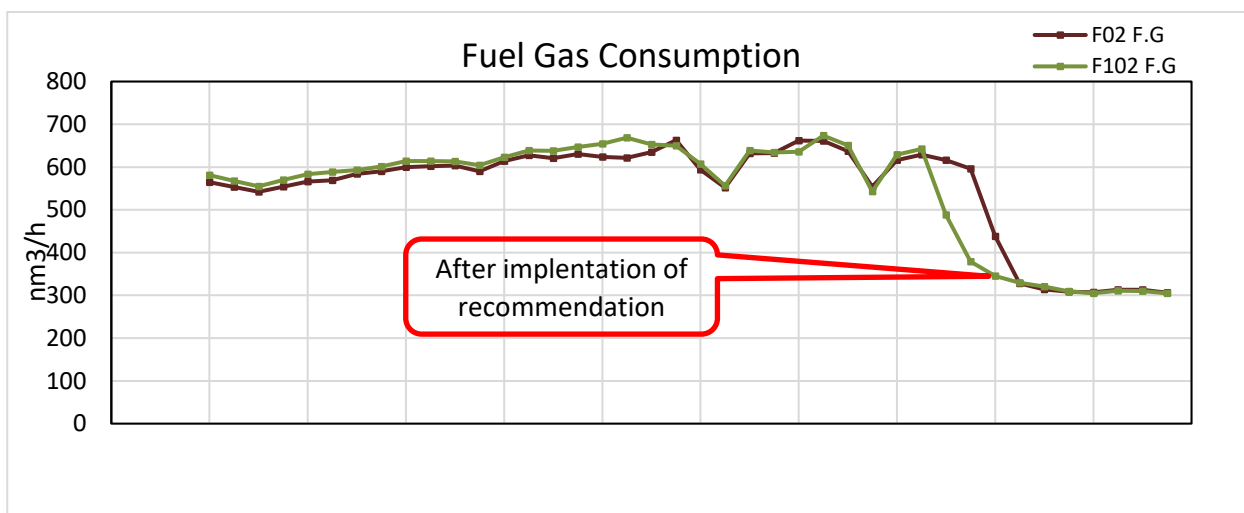
Immediate Impact on Heat Recovery:

The BFW injection yielded an immediate and significant improvement in heat transfer. Following the procedure, the shell-side outlet temperature of the previously fouled bank (E02-AA-AF) in Train #1 rose

from 234°C to 324°C. The ΔT between the two parallel banks collapsed from 119°C to just 13°C. Similar results were achieved in Train #2, where the ΔT was reduced to 11°C. This confirmed that the salt deposits had been effectively removed, restoring balanced flow and proper heat transfer across both banks, whereas the load on air coolers downstream is significantly reduced because of effective heat transfer towards shell side by effluent stream.



Train#1Train#2



Digital twin Strategies (A real time synchronization for timely monitoring)

The virtual model of exchanger train is connected to plant's Historian data allowing the model to reflect current operating conditions rather than designed steady state specifications.

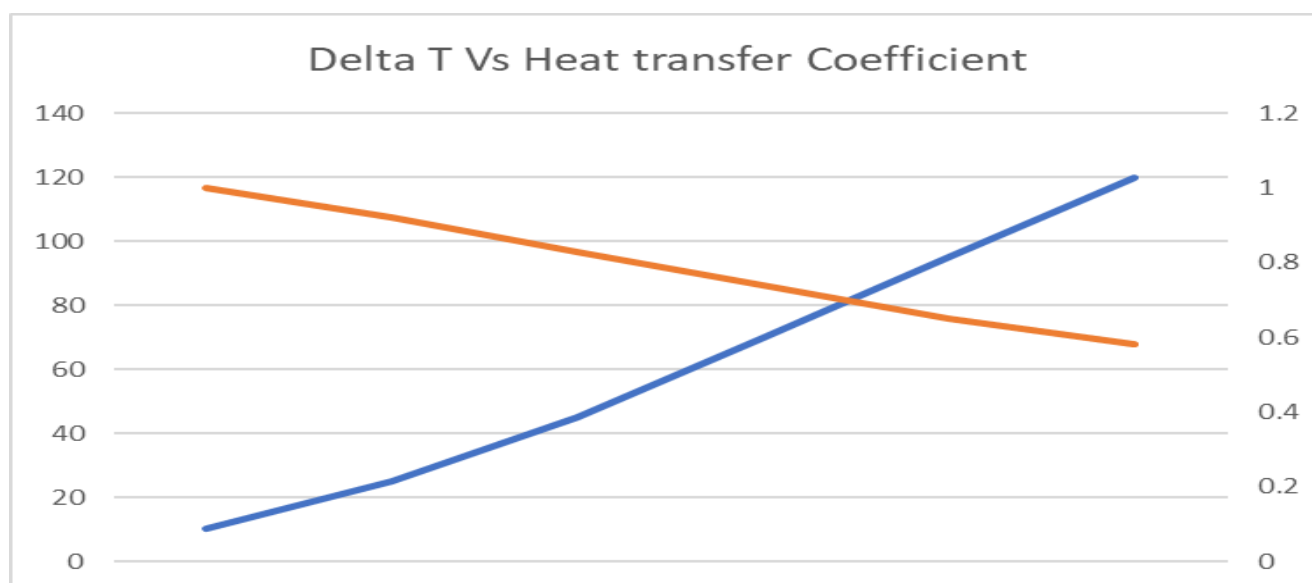
It helped in monitoring the gaps between ideal & actual heat transfer that ultimately predicts, when the exchanger needs to be cleaned.

A real time parameter from DCS to Excel via plant data historian & translating these values to Hysys streams using ASW then getting the output & comparing those with the actual temperatures predicts the fouling of your exchangers well in advance that allows you to plan & precisely know the fouling areas for example the last 2 exchangers mostly because of temperatures reaching salt points.

A relative chart has been shown below to evaluate the effect of ΔT 's between two parallel exchanger trains & their impact on heat transfer coefficient, while an impact on fouling resistance is also being put for understanding the real rate of changing being observed while exchanger was in service.

Month	ΔT Between Trains (°C)	Heat Coefficient (Relative value)	Fouling Resistance ($m^2 \cdot K/W$)
0 (initial cleaned stage)	10	1.00	0.0000
3	25	0.92	0.0012

Month	ΔT Between Trains ($^{\circ}\text{C}$)	Heat Coefficient (Relative value)	Fouling Resistance ($\text{m}^2\cdot\text{K}/\text{W}$)
6	45	0.83	0.0028
9	70	0.74	0.0049
12	95	0.65	0.0075
15 (Before Injection)	120	0.58	0.0085



5. Quantification of Energy Savings:

It's an economical concern to translate the optimization in value added to the business, with the heat recovery restored, the duty on the downstream reaction furnaces (F02/102) decreased substantially. The fuel gas (LPG) consumption per train dropped from 630-640 Nm^3/h to 315-320 Nm^3/h . This represents a 40% reduction in furnace firing.

Based on an average fuel gas (LPG) cost of 516 USD/ton, these savings are valued at approximately 4.0 MM USD per year. The simple payback on this operational adjustment is immediate.

Condition	Fuel Gas Consumption (Nm ³ /h)	Reduction (%)
Before BFW Injection	635	Baseline (reference taken as 0% for understanding)
After BFW Injection	315	50.4%

a) Detailed Economic Impact Analysis

The economic benefits of this operational adjustment extend far beyond the immediate 4.0 MM USD/year in fuel savings. A comprehensive analysis reveals additional significant financial advantages when benchmarked against industry alternatives and avoided costs that could have resulted in multiple of this

I. Bench marking Against Alternative Mitigation Strategies

The BFW injection method proved to be exceptionally cost-effective compared to other fouling mitigation approaches.

i. Chemical Antifoulant Programs:

A case study of a naphtha hydrotreater experiencing severe feed-effluent exchanger fouling implemented an antifoulant additive treatment program. While successful, the economic analysis showed that even with a "yearly economic return of over 500%," the program still required ongoing chemical procurement and injection infrastructure. In contrast, the BFW injection method utilizes an existing utility stream (boiler feed water) already available on-site, eliminating recurring chemical procurement costs.

ii. Filtration System Upgrades:

Another refinery case addressing HDS unit fouling implemented custom-engineered filtration to protect downstream reactors from contaminants. This solution delivered extended run times and reduced maintenance frequency, with documented savings of approximately \$2,000,000 per year in maintenance costs alone, plus an additional roughly \$5,000,000 in avoided catalyst replacement costs. While effective, such filtration systems require significant capital investment and ongoing element replacement, whereas the BFW method required zero capital expenditure.

iii. Process Integration Projects:

A U.S. Department of Energy-sponsored study evaluated passive heat integration options for HDS units, specifically increasing process-to-process heat exchanger area by 3,426 square feet. This project achieved combined savings of approximately \$245,000/year with a 1.3-year payback period. The BFW injection method achieved 16 times greater annual savings (\$4.0 MM vs. \$245,000) with zero capital cost and immediate payback. Although it has certain complications & liability issues for particularly exchanger applications.

II. Avoided Production Loss and Unit Derating

The operational issue created two distinct production risks that were eliminated by the intervention:

i. Summer Derating Avoidance:

As found, prior to the intervention, the fin fan cooler outlet temperature reached 70°C during high ambient temperature periods, exceeding the desired 63°C maximum for HP separator operation as per general operating pressure manual. This forced the unit to reduce throughput to maintain separator conditions. With heat recovery restored, the cooling load on air coolers decreased sufficiently to maintain target temperatures year-round, eliminating approximately 5-8% of potential summer production capacity loss. At 100% throughput and typical refining margins, this avoided derating represents an additional economic benefit of \$2-3 MM annually during peak demand seasons roughly.

ii. Unplanned Shutdown Avoidance:

The progressive fouling trend (reaching 120°C ΔT) would inevitably have necessitated a shutdown for mechanical cleaning. Industry experience with similar fouling in hydrotreater feed-effluent exchangers confirms that mechanical cleaning becomes unavoidable when ΔT exceeds design limits, requiring unit shutdown and significant maintenance expenditure. To explain the magnitude of asset & time involved in the activity, A typical Hydro-treatin unit shutdown for exchanger cleaning involves:

- 7-10 days of lost production (448,000-640,000 barrels at 64000 barrels/day throughput)
- Mechanical cleaning costs (\$200,000-500,000 for specialized high-pressure jetting as documented in cases previously, as rough estimate)
- Catalyst deactivation risks during startup/shutdown cycles
- The BFW intervention completely avoided these costs and production losses.

b) Maintenance Cost Reduction

The periodic BFW injection program provides sustained maintenance benefits:

I. Reduced Frequency of Mechanical Cleaning:

Prior to the intervention, mechanical cleaning would have been required every 12-18 months based on the observed fouling rate. The proactive BFW program extends this interval indefinitely, saving \$150,000-300,000 per year in avoided maintenance expenses.

II. Extended Equipment Life:

By preventing ammonium salt accumulation, under-deposit corrosion is minimized. Ammonium bisulfide deposits create highly corrosive local environments that can accelerate tube thinning and premature exchanger failure. The water washing program preserves asset integrity, extending the remaining useful life of 24 high-pressure heat exchangers.

c) Environmental and Carbon Emission Benefits

The 50% reduction in furnace fuel gas consumption as shown above directly correlates with reduced CO₂ emissions. At 640 Nm³/h baseline consumption per train (two trains total) and typical natural gas emission factors, the annual CO₂ reduction is approximately:

CO₂ emission considering GHG protocol: F.G used x Heating Value of F.G x Emission factor

Assumption on basis of Natural gas fuel

- Fuel gas reduction: 320 Nm³/h × 2 trains × 8,400 operating hours = 5.38 million Nm³/year
- 10,200-10,800** metric tons CO₂ equivalent per year.

This emission reduction also aligns with industry goals for greenhouse gas mitigation and may qualify for carbon credits or emissions trading benefits in applicable jurisdictions. Furthermore, The European chemical and refining industry recognizes such energy efficiency improvements as critical to achieving SPIRE 2030 objectives of reducing fossil energy intensity by up to 30%.

Significant Outcomes

Heat Exchanger Outlet Temperature Imbalance Before and After BFW Injection

Condition	Bank AA-AF (°C)	Bank BA-BF (°C)	ΔT (°C)
Before BFW Injection	234	355	121

Condition	Bank AA-AF (°C)	Bank BA-BF (°C)	ΔT (°C)
After BFW Injection	324	337	~ 13

Table : Real time temperature values as per ste data

Table above shows the dramatic temperature imbalance between the two parallel exchanger banks prior to intervention. The 121°C differential indicates severe fouling in Bank AA-AF, forcing 85% of the thermal duty onto Bank BA-BF. Post-injection, the temperatures nearly equalize, demonstrating restored flow distribution and heat transfer.

Heat Recovery Efficiency Comparison

The table below demonstrates the improvement in approach temperature to the reactor. Pre-fouling, the pre-heated feed was 132°C below reactor temperature, requiring significant furnace firing. Post-cleaning, this approach temperature reduced to 42°C, indicating that the feed is now 88.5% of the way to reaction temperature before entering the furnace, putting less load & asking for low duty hence low fuel gas consumption

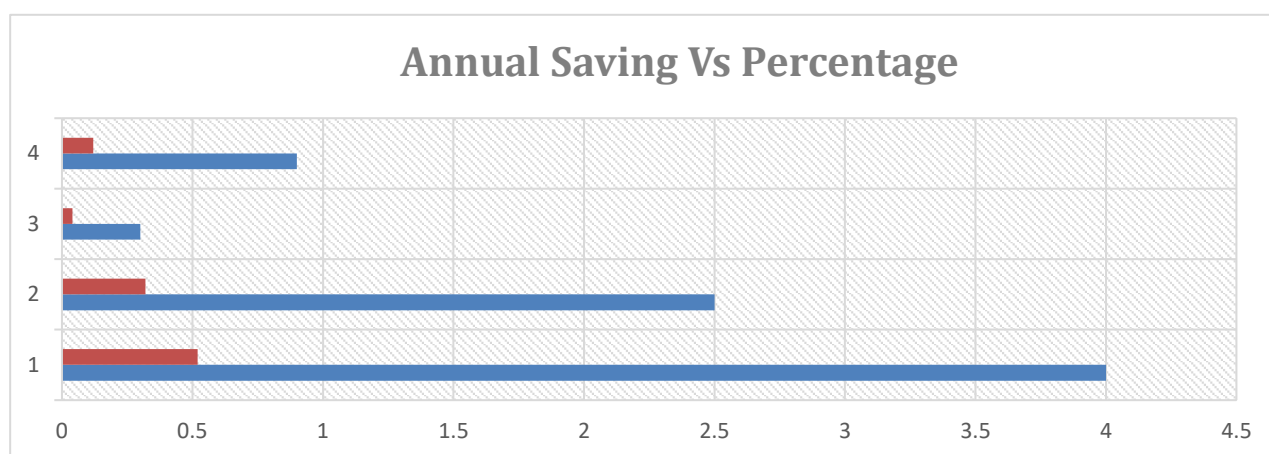
Parameter	Before BFW	After BFW	Improvement
Reactor Inlet Temp (°C)	366	366	Desired
Shell Side Outlet - Bank AA-AF (°C)	234	324	+90°C
Approach to Reactor Temp (°C)	132	42	90°C closer
Heat Recovery Efficiency (%)	64%	88.5%	+24.5%

Economic Benefit Breakdown

The chart below illustrates another stream of benefit & decomposes the total annual economic benefit of \$7.7 MM. While direct fuel savings represent the largest component (52%), the avoided production losses during summer months (32%) and extended catalyst life (12%) contribute substantially to the overall value proposition.

Using the temperature data before and after cleaning, & keeping mass flow & active surface area constant, the calculated fouling resistance at the time of intervention was approximately $0.0085 \text{ m}^2\cdot\text{K}/\text{W}$ (as mentioned). This corresponds to a 42% reduction in heat transfer coefficient compared to clean conditions, consistent with severe ammonium salt fouling reported in literature for similar services in past as studied.

Benefit Category	Annual Value (MM USD)	Percentage
Direct Fuel Gas Savings	4.0 (experimental)	52%
Avoided Summer Derating	2.5 ~	32%
Avoided Mechanical Cleaning	0.3 (experienced)	4%
Avoided Catalyst Change-out (annualized)	0.9 (Alternative)	12%
Total	7.7	100%



Summary of Economic Benefits

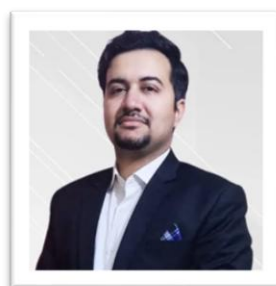
Benefit Category	Annual Value (MM USD)	Notes
Direct Fuel Gas Savings	4.0	40% reduction in furnace firing
Avoided Summer Derating	2.0-3.0	5-8% throughput preservation during peak demand
Avoided Mechanical Cleaning	0.15-0.30	Extended intervals between shutdowns
Avoided Catalyst Change-out	0.5-1.0 (periodic)	Based on industry benchmark of \$5M per event
Total Annual Economic Benefit	6.65-8.3	Carbon credit values are not added; it's additional benefit to contribute towards Environmental aspects

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His accomplishments as a Chartered Chemical Engineer have also been featured in a case study by the Engineering Council UK, available on their official website. Beyond his engineering practice, He has also delivered knowledge-sharing sessions as a guest speaker to young engineers.

In addition, Shahzeb supports the development of fellow engineers as an Initial Professional Development (IPD) Assessor for IChemE, where he evaluates the professional growth of both new and experienced engineers. He was also selected as judge two time for oil & gas ICheme global awards & currently acting as professional reviewer for CEng Applications. His expertise over 13 years of experience Covers Oil refinery & petrochemical plants Process engineering. He has completed 5 turnarounds in his career in different companies and countries.

Adnan Masood holds a Chemical Engineering from COMSATS University and a Registered Engineer with both the Pakistan Engineering Council (PEC) and the Saudi Council of Engineers (SCE), with credentials certified by Engineer Australia, working as Process Engineer in one of the leading Oil & Gas company in Saudi Arabia, contributing to the process optimization, energy index improvement and environment conservation by reducing greenhouse gases.



Adnan brings over 15 years of international Oil & Gas refinery experience specializing in basic & detail design, commissioning, and operational troubleshooting, especially in hydroprocessing technologies. An

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Arsalan brings over 9 years of international Oil & Gas refinery experience specializing in basic engineering, detail design, commissioning, and operational troubleshooting. An expert in distillation, hydro treating, reforming, and Aspen HYSYS simulation, he also provides elite global engineering advisory services.

Integrated Biorefinery of Agricultural Waste Biomass:

Sustainable Production of Bioethanol, Biochar, and Bioactive Compounds for Decarbonization and Circular Bioeconomy in a Biorefinery Model

Hamid Reza Seyed Jafari

Abstract

The global transition toward decarbonization and renewable energy has positioned agricultural waste biomass (AWB) as a promising feedstock for sustainable biorefinery operations. Annually, over 998 million tons of agricultural residues—including rice husk, wheat straw, corn stover, and sugarcane bagasse—are generated worldwide, presenting both environmental challenges and immense opportunities for valorization. This review presents an integrated biorefinery framework for the sustainable conversion of AWB into three high-value product streams: bioethanol (second-generation biofuel), biochar (carbonaceous material), and bioactive compounds (polyphenols and antioxidants). The lignocellulosic composition of AWB—comprising cellulose (35–52%), hemicellulose (20–35%), and lignin (10–25%)—provides the structural basis for bioethanol production through pretreatment, enzymatic hydrolysis, and fermentation. Concurrently, thermochemical conversion via pyrolysis transforms the residual biomass into biochar, a versatile material with applications in soil remediation, wastewater treatment, catalysis, and carbon sequestration. Furthermore, AWB, particularly tea processing waste, contains significant quantities of polyphenolic compounds (9.7–16.6% dry weight) that can be extracted as bioactive products for pharmaceutical, nutraceutical, and food applications. This integrated biorefinery approach not only mitigates greenhouse gas emissions—with life-cycle assessments reporting up to 90% reduction compared to fossil-based alternatives—but also generates multiple revenue streams, supporting the principles of circular bioeconomy and contributing to global decarbonization efforts. The global second-generation biofuel market, valued at USD 6.98 billion in 2023, is projected to reach USD 51.96 billion by 2030, reflecting the growing economic viability of AWB valorization.

Keywords: Agricultural waste biomass, biorefinery, bioethanol, biochar, bioactive compounds, lignocellulose, circular bioeconomy, decarbonization, pyrolysis, polyphenols, petrochemical complex, petroleum refinery

1. Introduction

1.1 Global Challenge of Agricultural Waste Biomass

The intensification of agricultural activities to meet growing global food demand has resulted in the generation of vast quantities of agricultural waste biomass (AWB). Globally, over 998 million tons of agricultural residues are produced annually, including rice husk (~101.8 million tons), wheat straw (~350 million tons), corn stover (~170 million tons), and sugarcane bagasse (~279–300 million tons). More recent estimates suggest that agricultural waste generation exceeds 5.5 billion tons annually, presenting major environmental challenges. These residues, if improperly disposed of through incineration, landfilling, or open dumping, contribute significantly to greenhouse gas (GHG) emissions—AWB is reported as the second-largest (19.9%) contributor to environmental GHGs. The agricultural sector alone contributes approximately 21–37% of global GHG emissions.

However, these agricultural residues are not merely waste; they represent a rich source of lignocellulosic biomass (LCB) with high potential for conversion into valuable bioproducts. For example, the typical LCB composition of major agricultural biomasses includes cellulose (35–52%), hemicellulose (20–35%), and lignin (10–25%). This chemical composition makes AWB an ideal feedstock for second-generation (2G) biofuel & biopolymers production in a biorefinery model. Also, there are valuable soluble bioactive compounds included in LCB for other applications in food, pharmaceutical cosmetic sectors and etc.

1.2 The Biorefinery Concept

The biorefinery concept, analogous to petroleum refineries, involves the integrated conversion of biomass feedstocks into multiple value-added products, including biofuels, biochemicals, biomaterials, and bioenergy. In the context of AWB, a biorefinery can simultaneously produce bioethanol (for energy consumption as a biofuel), biochar (for environmental remediation and catalysis in science material), and bioactive compounds (for pharmaceutical and nutraceutical applications). This integrated approach maximizes resource utilization, minimizes waste generation, and creates diverse revenue streams, thereby enhancing economic viability while reducing environmental impact.

1.3 Decarbonization and Circular Bioeconomy

The global imperative to decarbonize energy systems has accelerated interest in renewable alternatives to fossil fuels. Biofuels produced from AWB have been recognized as sustainable alternatives that can reduce dependence on non-renewable resources and mitigate the negative environmental effects of fossil fuel consumption. Life-cycle assessments report up to 90% reduction in GHG emissions when replacing fossil fuels with biofuels derived from agricultural sources.

The circular bioeconomy framework—which emphasizes resource efficiency, waste minimization, and the continuous cycling of materials—provides the conceptual foundation for AWB valorization. By converting agricultural waste into valuable products, this approach addresses both waste management challenges and resource scarcity, contributing to the transition from a linear "take-make-dispose" economy to a circular, sustainable model.

1.4 Scope and Objectives of This Review

This review presents an integrated biorefinery framework for the valorization of AWB into three major product streams:

1. **Bioethanol(biofuel)** – produced via biochemical conversion (pretreatment, enzymatic hydrolysis, fermentation)
2. **Biochar** – produced via thermochemical conversion (pyrolysis, gasification)
3. **Bioactive compounds** – extracted for pharmaceutical, nutraceutical, and food applications

The review focuses on agricultural residues including tea waste, wheat straw, corn stover, rice husk, and sugarcane bagasse, examining their composition, conversion technologies, and application in energy, pharmaceutical, healthcare, food, catalysis, wastewater treatment, and polymer industries.

2. Materials and Methods

2.1 Agricultural Waste Biomass Feedstocks

Agricultural waste biomass encompasses a wide range of residues generated during crop cultivation and agro-industrial processing. Table 1 presents the lignocellulosic composition of major agricultural biomasses.

Table 1: Composition of Lignocellulosic Constituents of Major Agricultural Biomass

Agricultural Waste Biomass (Crop Type)	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Black tea processing waste biomass (BTPWB)	14.6	5.7	13.6
Rice straw	39.04	20.91	5.71
Rice hull	33.47	21.03	18.08
Wheat straw	43.2	34.1	22.0
Maize (corn straw)	42.6	21.3	8.2
Sorghum straw	32	24	13
Barley straw	40	30	15
Coconut husk	24.7	12.26	40.10
Rapeseed straw	32	16	18
Soybean straw	35	17	21
Sunflower straw	32	18	22
Peanut shell	40.5	14.7	26.4
Sugarcane bagasse	65.0	—	18.4

Source: Adapted from multiple studies in references.

The variation in composition across different biomass types influences their suitability for specific conversion pathways and product yields. Biomasses with higher cellulose content (e.g., sugarcane bagasse, wheat straw) are generally more suitable for bioethanol production, while those with higher lignin content (e.g., coconut husk) may be better suited for biochar production.

2.2 Biorefinery Conversion Technologies

2.2.1 Bioethanol Production Pathway

The production of bioethanol (as a biofuel) from AWB follows a three-step biochemical conversion process:

Step 1: Pretreatment

Pretreatment is a critical step that disrupts the lignocellulosic matrix, breaking down the complex structure of AWB to separate cellulose, hemicellulose, and lignin. Various pretreatment methods have been developed, including:

- **Physical methods:** Grinding, milling, steam explosion
- **Chemical methods:** Acid pretreatment (dilute acid), alkaline pretreatment (NaOH, CaO)
- **Physicochemical methods:** Steam explosion, ammonia fiber expansion (AFEX)
- **Biological methods:** Microbial and enzymatic delignification
- **Nanotechnology-based methods:** Nanoparticle-assisted pretreatment

Alkaline pretreatment has demonstrated particular efficacy, with studies reporting lignin removal rates of up to 56.15% and subsequent enzymatic hydrolysis efficiency improvements from 20.32% to 70.9%. Advanced pretreatment strategies, including recyclable alkaline pretreatment under high-solid conditions, have achieved up to 41% water savings while maintaining high conversion efficiency. Emerging technologies such as natural deep eutectic solvents (NADES) and microwave-assisted methods have significantly enhanced enzymatic digestibility.

Step 2: Enzymatic Hydrolysis (Saccharification)

Following pretreatment, enzymatic hydrolysis using enzymes (cellulase, amylase, xylanase) converts polysaccharides (cellulose, hemicellulose) into fermentable simple sugars (glucose, xylose, galactose, arabinose). The efficiency of this step directly determines the yield of reducing sugars available for fermentation.

Step 3: Fermentation

Microorganisms, primarily *Saccharomyces cerevisiae* yeast, convert the simple sugars into bioethanol. The stoichiometric reaction is:



The distinction between "total sugar" and "reducing sugar" is fundamental to understanding bioethanol production. Reducing sugars—measured by the 3,5-dinitrosalicylic acid (DNS) method—are simple monosaccharides (glucose, xylose) that yeast can directly ferment. Total sugars—measured by the phenol-sulfuric acid method—include both reducing sugars and non-fermentable oligosaccharides. Effective pretreatment must maximize the conversion of total carbohydrates into fermentable reducing sugars.

2.2.2 Biochar Production Pathway

Biochar is produced through thermochemical conversion of AWB under oxygen-limited conditions. The primary production methods include:

- **Pyrolysis:** Thermal decomposition at 300–700°C
- **Gasification:** Partial oxidation at high temperatures (700–1500°C)
- **Torrefaction:** Mild pyrolysis at 200–300°C
- **Hydrothermal carbonization:** Wet biomass conversion at 180–250°C

Pyrolysis is the most widely studied method for biochar production from agricultural residues. The pyrolysis temperature significantly influences biochar properties:

- **Low temperature (300–400°C):** Higher biochar yield, lower surface area
- **Medium temperature (400–600°C):** Optimal balance of yield and porosity
- **High temperature (>600°C):** Higher surface area but potential pore collapse

The Brunauer-Emmett-Teller (BET) surface area is a key parameter determining biochar performance. Activation methods (chemical with phosphoric acid, KOH; physical with steam) can dramatically increase BET surface area. For example, activation of tea waste biochar with phosphoric acid coupled with ultrasound increased the BET surface area from approximately 942 to 1984 m²/g.

2.2.3 Bioactive Compound Extraction

Agricultural waste, particularly tea processing waste, contains significant quantities of bioactive compounds, primarily polyphenols. There are a few extraction methods to produce polyphenol groups such as:

- **Conventional solvent extraction (CSE):** Using ethanol, methanol, or acetone
- **Microwave-assisted extraction (MAE):** Rapid heating under microwave radiation
- **Ultrasound-assisted extraction (UAE):** Using ultrasonic waves to enhance mass transfer
- **Natural deep eutectic solvent (NADES) extraction:** Using green, biodegradable solvents

Comparative studies have shown that MAE yields the highest total polyphenol content compared to CSE and UAE. NADES-based extraction has demonstrated enhanced stability of extracted compounds and superior antioxidant activity.

3. Results and Discussion

3.1 Bioethanol Production from Agricultural Waste Biomass

3.1.1 Pretreatment Efficiency and Sugar Yields

The efficiency of pretreatment directly influences the subsequent enzymatic hydrolysis and fermentation steps. Table 2 summarizes bioethanol yields from various agricultural residues.

Table 2: Bioethanol Production from Different Agricultural Waste Biomass

Feedstock	Pretreatment	Reducing Sugars (g/L)	Ethanol Yield (g/L)
Corn stover	Recyclable alkaline	—	20.19
Corn stalks	Acid hydrolysis	84.625	158.59
Tobacco stalks	Enzymatic hydrolysis	5.43	75.74
Sorghum stalk	CaO alkaline	—	—
Sugar beet pomace	Fermentation	—	0.703 g/g
Spent coffee grounds	Fermentation	—	18.9 ± 0.3

Studies have demonstrated that optimized pretreatment strategies can significantly enhance bioethanol yields. Recyclable alkaline pretreatment of corn stover improved cellulose enzymatic hydrolysis efficiency from 20.32% to 70.9% with a lignin removal rate of 56.15%. The highest reported ethanol yield from corn stalks reached 158.59 g/L at 120 hours of fermentation.

The relationship between sugar type and bioethanol yield is critical. Total sugar concentration represents the maximum potential for bioethanol production, whereas reducing sugar concentration reveals the immediately available fermentable carbon source. Yeast can only ferment reducing sugars (monosaccharides); therefore, pretreatment must maximize the conversion of total sugars to reducing sugars.

3.1.2 Techno-Economic Considerations

The global second-generation biofuel market, valued at USD 6.98 billion in 2023, is projected to reach USD 51.96 billion by 2030 at a CAGR of 25.6%. This growth reflects increasing demand for sustainable alternatives to fossil fuels and the improving economic viability of biofuel production from agricultural residues.

Conversion efficiencies through optimized pretreatment methods such as ammonia fiber expansion, steam explosion, and microwave-assisted hydrolysis can yield up to 90% fermentable sugars and 223–358 L ethanol per ton of dry biomass. Life-cycle assessments report up to 86% reduction in GHG emissions when replacing fossil fuels with biofuels derived from agricultural sources.

3.1.3 Applications of Bioethanol

Bioethanol produced from AWB has diverse applications across multiple sectors:

- **Energy sector:** Transportation fuel (blended with gasoline), fuel additive
- **Chemical industry:** Feedstock for ethylene, ethyl acetate, and other chemicals
- **Pharmaceutical industry:** Solvent and disinfectant
- **Food and beverage industry:** Food-grade ethanol for beverages and food processing

3.2 Biochar Production from Agricultural Waste Biomass

3.2.1 Biochar Properties and Production Optimization

Biochar is a porous, carbon-rich material produced through thermochemical conversion of AWB. The properties of biochar—including surface area, pore structure, surface functional groups, and elemental composition—are influenced by feedstock type, pyrolysis temperature, heating rate, and activation methods.

Table 3: Biochar Properties from Different Agricultural Wastes

Feedstock	Pyrolysis Temp (°C)	BET Surface Area (m ² /g)	Carbon Content (%)	Applications
Tea waste	400–600	942–1984 (activated)	—	Adsorption, catalysis
Rice husk	500–700	200–400	50–70	Soil amendment, remediation
Wheat straw	450–650	150–350	45–65	Wastewater treatment
Corn stover	400–600	100–300	40–60	Carbon sequestration

The BET surface area is a critical parameter determining biochar's adsorption performance and catalytic activity. Higher pyrolysis temperatures generally increase porosity, but an optimal temperature range exists beyond which pore collapse may occur. Activation methods can drastically increase BET surface area by degrading the lignocellulosic structure and removing volatile compounds, thereby opening micropores within the biochar matrix.

3.2.2 Applications of Biochar

Biochar produced from AWB has versatile applications across multiple sectors:

Agriculture and Soil Management

Biochar as a soil conditioner improves soil quality, water holding capacity, pH buffering capacity, fertility, nutrient cycling, and microbial activity. Its application enhances crop productivity while reducing the need for synthetic fertilizers.

Environmental Remediation

Biochar is recognized as one of the most efficient adsorbents for removing contaminants from wastewater, including heavy metals (Cu^{2+} , Cd^{2+}), organic matter, pathogens, and microplastics. Removal efficiencies of up to 85.87% have been reported for various contaminants.

Catalysis and Catalyst Support

Due to its high specific surface area, porous structure, and surface functional groups (hydroxyl, carboxyl, carbonyl), biochar can catalyze important reactions including transesterification for biodiesel production and conversion of glycerol into glycerol carbonate. Doping with small amounts of metals (Ni, Fe, Co) creates efficient, cost-effective catalysts that can replace conventional expensive noble-metal or zeolite catalysts.

Bioenergy Production Enhancement

When added to anaerobic digesters, biochar acts as a microbial support, enhances electron transfer between microorganisms, prevents pH drops, and adsorbs inhibitory compounds, significantly increasing methane yield from biogas production.

Carbon Sequestration and Climate Change Mitigation

The aromatic carbon structure of biochar makes it an excellent carbon sink, strongly reducing GHG emissions (CO_2 , CH_4 , N_2O) in farming practices. This application directly supports global decarbonization efforts.

3.3 Bioactive Compound Extraction from Agricultural Waste Biomass

3.3.1 Polyphenol Content and Extraction Efficiency

Agricultural waste, particularly tea processing waste, contains significant quantities of bioactive compounds. Table 4 summarizes the total phenolic content (TPC) found in different types of agricultural waste biomass and by-products.

Table 4: Polyphenol Content in Agricultural Wastes

Agricultural Waste Biomass/ By-Product	Total Phenolic Content (TPC)	Extraction / Assay Method
Grape Marc	4.5% (w/w) 4,480.5 ± 886.58 mg TAE/100g	Chemical extraction Folin-Ciocalteu assay
Olive Leaves / Pomace	0.7% (w/w)	Chemical extraction
Tea Waste stalks	16.57%	Folin-Ciocalteu assay
Sunflower Cake	1,441.46 ± 0.09 mg GAE/100g DW	Folin-Ciocalteu assay
Local Brew Waste	1,265.04 ± 0.90 mg GAE/100g DW	Folin-Ciocalteu assay
Cotton Seed Cake	976.22 ± 0.56 mg GAE/100g DW	Folin-Ciocalteu assay
Pineapple Peel	847.94 ± 0.42 mg GAE/100g DW	Folin-Ciocalteu assay
Banana Peel	514.83 ± 0.35 mg GAE/100g DW 0.15 - 55.5 mg/g	Folin-Ciocalteu assay
Soybean Hull Meal	376.16 ± 0.10 mg GAE/100g DW	Folin-Ciocalteu assay

Agricultural Waste Biomass/ By-Product	Total Phenolic Content (TPC)	Extraction / Assay Method
Dry Maize Cob	306.41 ± 0.04 mg GAE/100g DW	Folin-Ciocalteu assay
Pumpkin Peel	238.84 ± 0.06 mg GAE/100g DW	Folin-Ciocalteu assay
Maize Stover	216.65 ± 15.1 mg GAE/100g	Folin-Ciocalteu assay
Rice Straw	211.75 ± 7.6 mg GAE/100g	Folin-Ciocalteu assay
Cassava Peel	186.64 ± 0.04 mg GAE/100g DW	Folin-Ciocalteu assay
Soybean Residue	174.15 ± 4.6 mg GAE/100g	Folin-Ciocalteu assay
Blackgram Residue	165.93 ± 7.6 mg GAE/100g	Folin-Ciocalteu assay
Greengram Residue	153.20 ± 7.0 mg GAE/100g	Folin-Ciocalteu assay
Pumpkin Pulp	122.37 ± 0.07 mg GAE/100g DW	Folin-Ciocalteu assay
Sunhemp Residue	103.73 ± 4.7 mg GAE/100g	Folin-Ciocalteu assay
Fruit & Vegetable Waste (FVW)	238.0 - 1,583.0 mg TAE/100g	Chemical extraction (methanol)
Banana Pseudostem	26.04 mg GAE/g DM	Folin-Ciocalteu assay

Note on Units: GAE = Gallic Acid Equivalents; TAE = Tannic Acid Equivalents; DW = Dry Weight; DM = Dry Matter.

3.3.2 Applications of Bioactive Compounds

Bioactive compounds extracted from AWB have diverse applications:

Pharmaceutical and Healthcare

Polyphenols exhibit potent antioxidant, anti-inflammatory, and antimicrobial properties, with applications in preventing chronic diseases including cardiovascular disorders, diabetes, and certain cancers.

Nutraceutical and Functional Foods

Polyphenolic compounds are incorporated into functional foods and nutraceuticals due to their health-promoting properties.

Cosmetics and Personal Care

The antioxidant properties of polyphenols make them valuable ingredients in skincare and cosmetic products.

Food Preservation

Polyphenols serve as natural preservatives, extending the shelf life of food products.

3.4 Integrated Biorefinery: A Synergistic Approach

The integration of bioethanol, biochar, and bioactive compound production within a single biorefinery framework maximizes resource utilization and economic viability. Figure 1 presents a conceptual integrated biorefinery for AWB valorization.

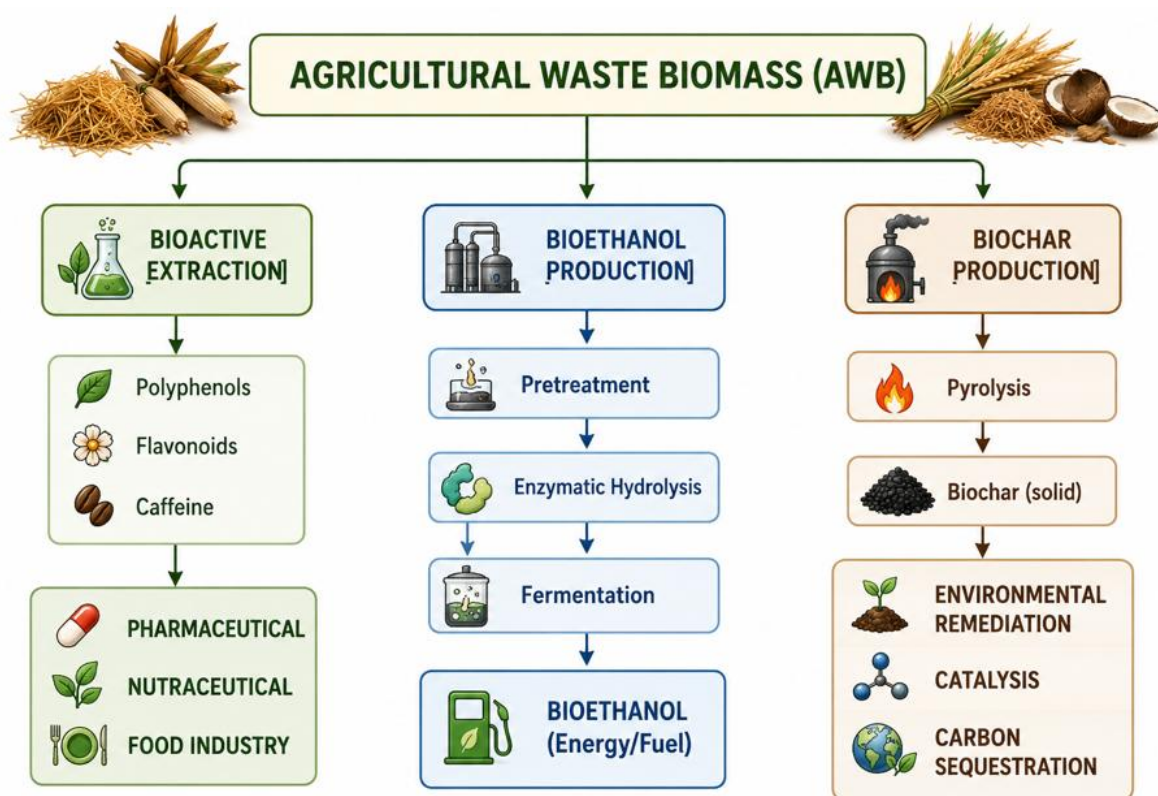


Figure 1: Conceptual Integrated Biorefinery for Agricultural Waste Biomass Valorization

This integrated approach offers several synergistic benefits:

- 1. Resource Efficiency:** Each conversion pathway utilizes different components of the biomass. Bioactive extraction removes valuable compounds without significantly altering the lignocellulosic structure, which can then be used for bioethanol production. The residual lignin-rich stream can be converted to biochar.
- 2. Waste Minimization:** The biorefinery approach achieves near-zero waste by converting all biomass fractions into valuable products.
- 3. Economic Viability:** Multiple revenue streams enhance the economic feasibility of the biorefinery, making it more attractive for commercial investment.
- 4. Environmental Benefits:** Life-cycle assessments indicate that integrated biorefinery systems can reduce GHG emissions by up to 90% compared to fossil-based alternatives.
- 5. Decarbonization Support:** The co-production of bioethanol (renewable fuel), biochar (carbon sequestration), and bioactive compounds (replacing synthetic chemicals) contributes to multiple decarbonization pathways.

4. Conclusion

Agricultural waste biomass represents a vast, underutilized resource with immense potential for sustainable biorefinery operations. This review has demonstrated that AWB can be effectively converted into three high-value product streams:

- 1. Bioethanol:** Through biochemical conversion involving pretreatment, enzymatic hydrolysis, and fermentation, bioethanol (as a biofuel) yields of up to 158.59 g/L can be achieved from agricultural residues. Optimized pretreatment strategies can improve enzymatic hydrolysis efficiency from 20.32% to

70.9%, with up to 86% reduction in GHG emissions compared to fossil fuels. The global second-generation biofuel market, projected to reach USD 51.96 billion by 2030, reflects the growing economic viability of this pathway.

2. Biochar: Thermochemical conversion via pyrolysis produces biochar with BET surface areas up to 1984 m²/g (activated). Biochar applications span soil fertility enhancement, heavy metal adsorption (up to 85.87% removal efficiency), wastewater purification, catalysis (including transesterification for biodiesel production), biogas production enhancement, and carbon sequestration. Its aromatic carbon structure makes it an effective carbon sink for GHG reduction.

3. Bioactive Compounds: Agricultural waste contains significant polyphenolic compounds. So green technologies like microwave-assisted ultrasonic-assisted extraction yield the highest polyphenol content, with applications in pharmaceutical, nutraceutical, food, and cosmetic industries.

The integrated biorefinery approach offers synergistic benefits including resource efficiency, waste minimization, economic viability, and environmental sustainability. Life-cycle assessments confirm up to 90% reduction in GHG emissions compared to fossil and hydrocarbon-based alternatives, supporting global decarbonization goals and the transition from non-renewable to renewable energy sources.

Future research directions should focus on:

- Developing cost-effective, scalable biofuel technologies for all abundant AWB
- Optimizing pyrolysis conditions for tailored biochar properties
- Enhancing extraction efficiency of bioactive compounds using green solvents
- Integrating artificial intelligence and machine learning for process optimization
- Conducting comprehensive techno-economic and life-cycle assessments
- Establishing policy frameworks to support biorefinery commercialization

By converting agricultural waste biomass (AWB), once considered an environmental burden, into valuable bioproducts for energy, pharmaceutical, healthcare, food, catalysis, wastewater treatment, and polymer industries, the integrated biorefinery approach represents a significant step toward a circular bioeconomy and a sustainable, decarbonized future next to petroleum refinery and petrochemical complex in energy transition to net zero carbon emission target.

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