Industrial Wastewater Treatment in GREET® Model: Energy Intensity, Water Loss, Direct Greenhouse Gas Emissions, and Biogas Generation Potential

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1. Introduction

Industrial wastewater is a byproduct of industrial activities, such as refinery industry, chemical industry, and food industry. The wastewater must be treated by mechanisms and bioprocesses before it can be reused or discharged. The wastewater treatment has grown during the last 20-30 years and will continue to grow in both developed and developing world (Pabi et al., 2013). To give a broader perspective on waste water treatments, life cycle analysis (LCA) is one of the best model, which can quantify the impacts associated with cradle-to-grave stages of wastewater processes. The Greenhouse gases, Regulated Emissions, and Energy use in Transportation (GREET®) model, which was developed by Argonne National Labs and sponsored by the U.S. Department of Energy (DOE), has been widely used to estimate life cycle energy consumption and air emissions from vehicle-fuel pathways (Argonne National Laboratory, 2016). Recently, the GREET model has expanded water consumption of fuel production and waste to energy (Argonne National Laboratory, 2016). To further improve the ability of the GREET model, we incorporated literature data and engineering calculation to estimate energy use, water loss, greenhouse gas emissions, and biogas generation potential from industrial wastewater treatment.

This memo documented our efforts to calculate energy use intensity, water loss, greenhouse gas emissions, and biogas generation potential from industrial wastewater treatment, with main focus on refinery wastewater treatment.

2. Overall Refinery Water Balance and Refinery Wastewater Treatment

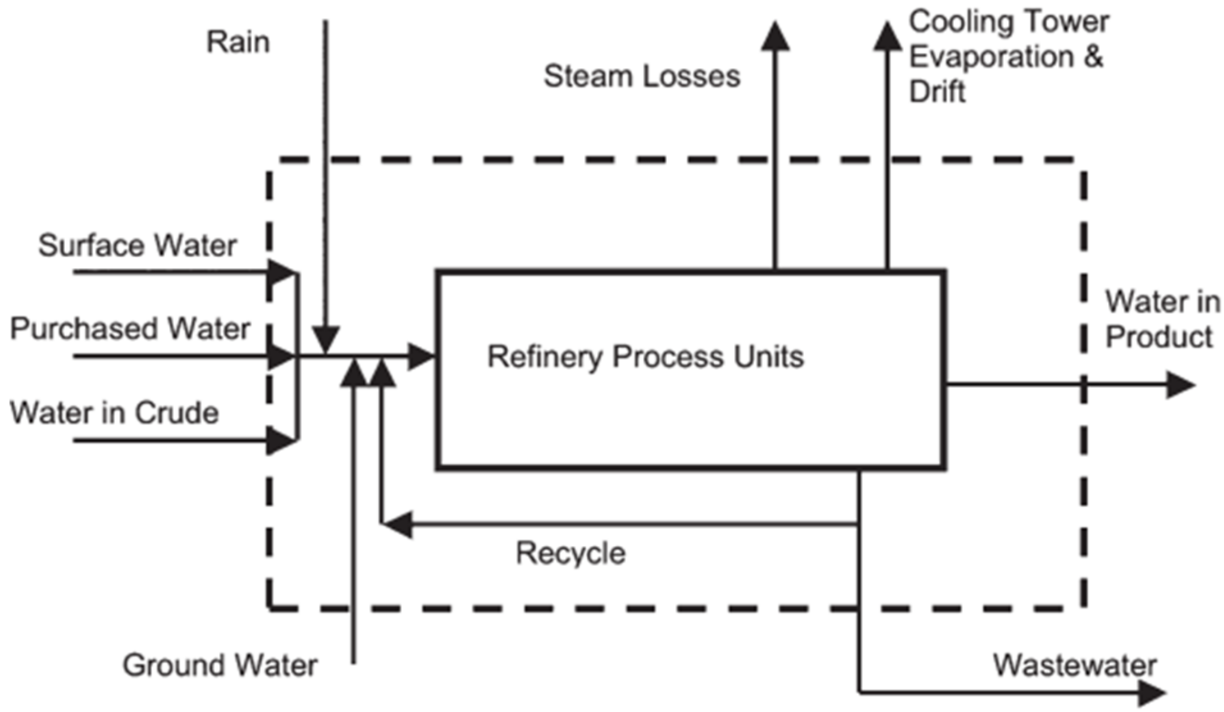

Figure 1. A schematic example of the petroleum refinery water balance (IPIECA, 2010)

As shown in Figure 1, the sources of water to the refinery include surface water, ground water, purchased water, water in crude, and rain. Water leaving the refinery includes wastewater, water in product, cooling tower losses, and steam losses. While the volume of water in product is minimal due to product specification, the volume of cooling tower losses and steam losses are estimated at 0.3-0.6 and 0.07-0.15 times that of the crude oil processed (Jacobs Consultancy, 2016). Compared to the other water sinks, the volume of wastewater is substantial, estimated at 0.4-1.6 times the amount of the crude oil processed (Coelho et al., 2006). Table 1 summarizes the major wastewater streams in refineries. Among them, desalter water, sour water, tank bottom draws and spent caustic have been in contact with hydrocarbon, which makes petroleum refinery wastewaters contain high concentration of hazardous compounds, thus, these wastewater has to be treated before discharging.

Figure 2 depicts a typical refinery wastewater treatment process. The first stage of treatment includes mechanical and physicochemical treatments, and the second stage includes advanced treatment. The treated water could be reused internally, injected to deep wells, discharged to water sources, or treated further in publicly owned treatment works (POTWs).

Table 1. Major wastewater streams (EPA, 2016)

Wastewater	Description
Desalter water	Water produced from washing the raw crude prior to topping operations.
Sour water	Wastewater from steam stripping & fractionating operations that comes into contact with the crude being processed.
Other process water	Wastewater from product washing, catalyst regeneration, and dehydrogenation reactions.
Spent caustic	Formed in extraction of acidic compounds from product streams.
Tank bottoms	Bottom sediment and water settles to the bottom of tanks used to store raw crude.
Cooling tower	Once-through cooling tower water and cooling tower blowdown to prevent buildup of dissolved solids in closed-loop cooling systems.
Condensate blowdown	Blowdown from boilers and steam generators to control buildup of dissolved solids.
Source water treatment system	Source water must be treated prior to use in the refinery. Waste streams may include water from sludge dewatering if lime softening is used; ion exchange regeneration water; or reverse osmosis wastewater.
Stormwater	Process area and non-process area runoff from storm events.
Ballast water	Ballast water from product tankers.

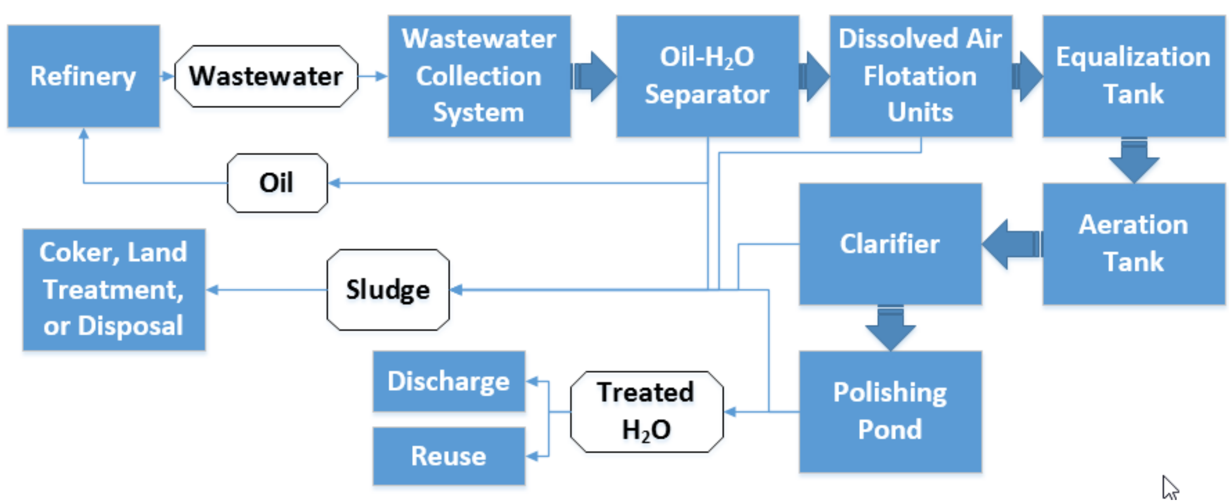

Figure 2. Typical refinery wastewater treatment

3. Wastewater Treatment Energy Intensity Estimation

Effective wastewater treatment is vital for public health. New regulations, expanded service and advanced treatment increase the use of electricity for wastewater treatment. Table 3 lists the overall flow rate for municipal and industrial wastewater from EPA (2012) and electrical energy intensity from Pabi et al. (2013). Primary, secondary and advanced treatment had the electrical energy intensity of 0.75, 2.08 and 2.69 MWh/MG, respectively. Flow rate weighted electricity energy intensity was 2.42 MWh/MG.

Table 2. Wastewater treatment energy intensity

	Flow Rate (MGD)[a]				Electrical Energy Intensity (MWh/MG)[b]
	Municipal		Industrial		
Treatment	w/o reuse	w/ reuse	w/o reuse	w/ reuse	
Primary (MGD)	229	166	11	18	0.75
Secondary (MGD)	6,437	133	758	3	2.08
Tertiary/Advanced (MGD)	9,476	1,249	1,317	116	2.69
Total	16,142	1,548	2,086	137	**2.42**

[a]EPA (2012), [b]Pabi et al. (2013), MG=Million gallons, and MGD=Million gallons per day

4. Wastewater Treatment Water Loss Estimation

Studies on water loss from refinery wastewater treatment operations are very limited. Two main water loss pathways in wastewater treatment include sludge water and evaporation losses. The water losses due to evaporation was less than 0.001% for a WWTP with an average of 10 MGD and a maximum design capacity of 30 MGD (Demirtas, 2016). For sludge water loss, we estimated the loss based on a water balance estimation of 10 MGD municipal wastewater treatment plants (WWTPs) by Qasim (1999) as shown in Figure 3. The plant reused water include dilution water (1,133 m^3/d) and belt and chemicals dilution water (167 m^3/d). The sludge flow rate is 18 m^3/d with 25% of solid. The water loss by sludge is calculated as follows:

$$\frac{18\ m^3/d \times (1-25\%)}{(38{,}016 m^3/d + 4.7 m^3/d)} = 0.04\% \ .$$

So overall water loss from wastewater treatment was estimated at 0.04%, which was considered negligible.

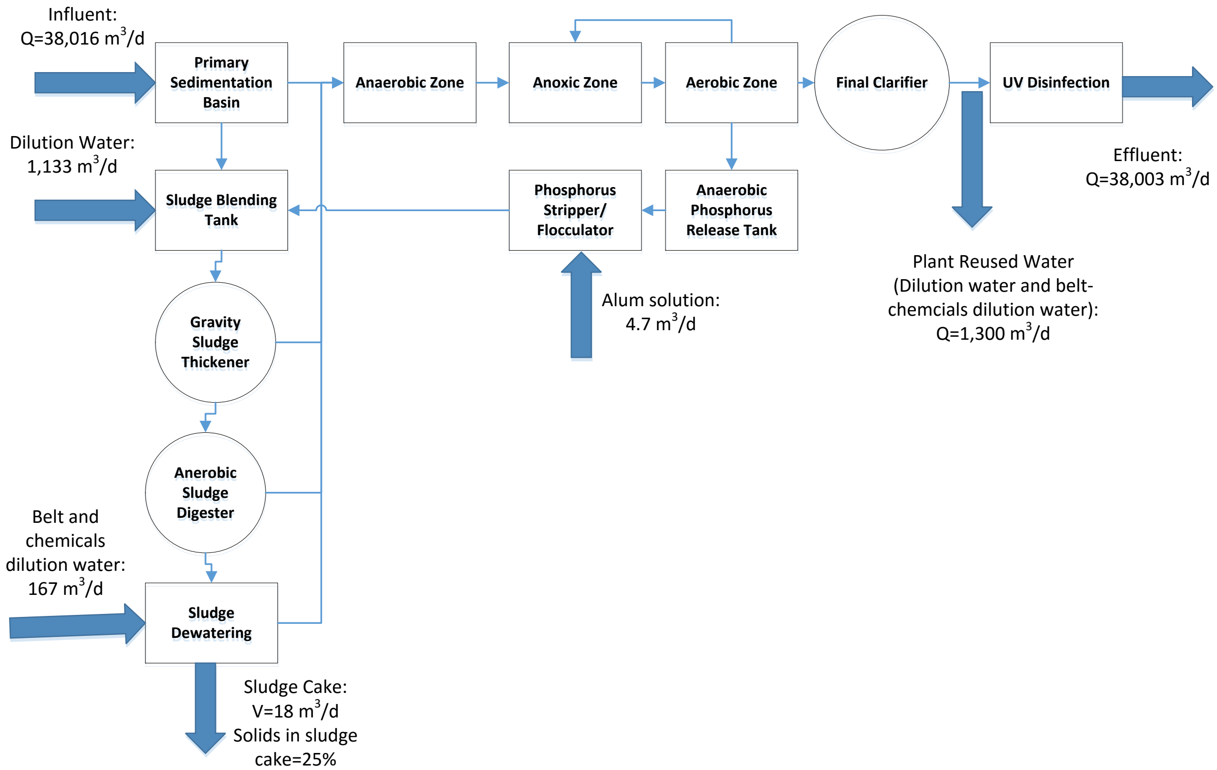

Figure 3. Material mass balance analysis (Qasim, 1999)

5. Greenhouse Gas (GHG) Emissions from Petroleum Refining Wastewater Treatment Plants Estimation

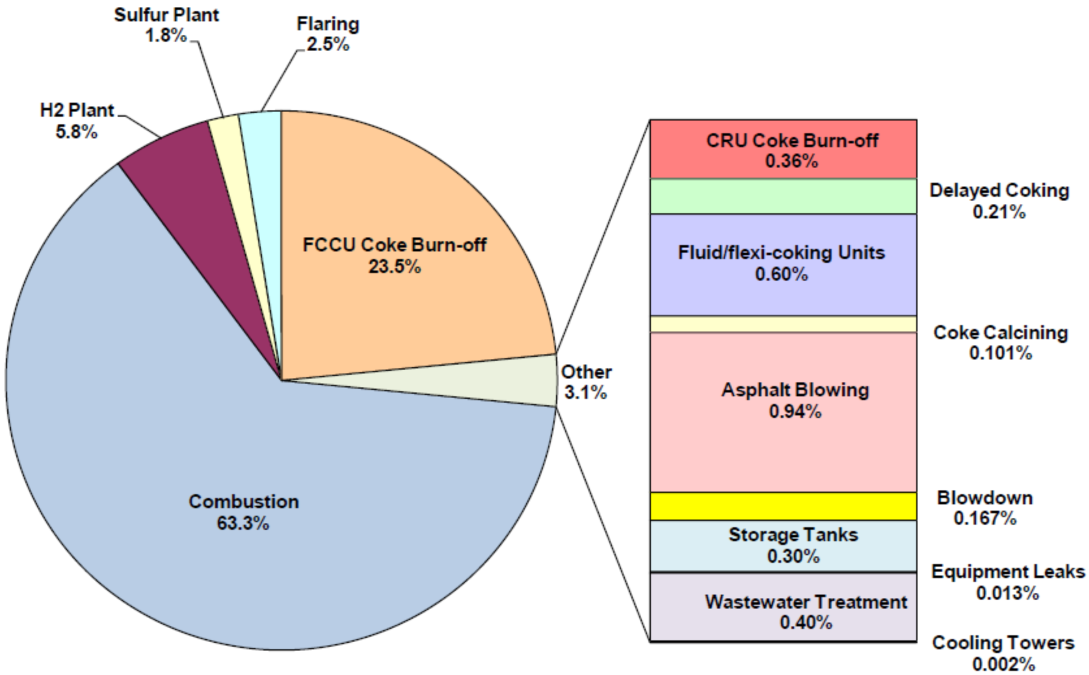

Figure 4. Contribution of different emission source to the nationwide CO_2 equivalent GHG emissions from petroleum refineries (EPA, 2010)

Figure 4 depicts a breakdown of nationwide CO_2 equivalent GHG emissions from petroleum refineries. Fossil fuel combustion is a significant source of GHG emissions (63.3%), and fluid catalytic cracking units (FCCU) also have significant GHG emissions (23.5%). Wastewater treatment accounts for only 0.40% of GHG emissions, which was negligible.

6. Biogas Production from Petroleum Refining Wastewater through Anaerobic Digestion Estimation

Table 3 lists the major processes, wastewater, and COD concentrations. Based on stoichiometric relationship between COD and CH_4 in anaerobic digestion (AD) process, at 35 ºC, the potential efficiency is 5.6 ft^3/lb COD (32 F, 1 atm) (Speece, 1996). Theoretical biogas production calculated for petroleum refinery wastewater is 0.77 ft^3/barrel of crude petroleum. Keep in mind that the COD in petroleum wastewater might not be converted into CH_4 in AD. Anaerobic digestion (AD) efficiency will vary with feedstock, possible co-existing pollutants, as well as with digester.

Table 3. Process wastewater and chemical oxygen demand (COD) concentration at petroleum refineries

Process	**Wastewater description (possible pollutants)**	**COD (mg/l)[a]**	**Wastewater (gal/barrel)[b]**	**Percentage (%)[b]**	**CH_4 (ft^3/barrel)**
Distillation	Sour water (hydrogen sulfide, ammonia, suspended solids, chlorides, mercaptans, and phenol)	600-1,200	26.0	44%	1.23
Fluid catalytic cracking	Sour water (hydrogen sulfide, ammonia, suspended solids, oil, phenols, and cyanides)	600-1,200	15.0	26.0	0.71
Catalytic reforming	Sour water (hydrogen sulfide, ammonia, suspended solids, mercaptans, oil)1	600-1,200	6.0	10%	0.28
Alkylation	Spent potassium hydroxide stream (hydrofluoric acid)	400-1,000	2.6	4%	0.12
Crude desalting	Desalting wastewater (salts, metals, solids, hydrogen sulfide, ammonia, and phenol)	400-1,000	2.1	4%	0.10
Thermal cracking/ Visbreaking	Sour water (hydrogen sulfide, ammonia, suspended solids, dissolved solids, and phenol)	600-1,200	2.0	3%	0.09
Catalytic hydrocracking	Sour water (hydrogen sulfide, ammonia, and suspended solids)	600-1,200	2.0	3%	0.09
Coking	Sour water (hydrogen sulfide, ammonia, and suspended solids)	600-1,200	1.0	2%	0.05

Isomerization	Sour water (hydrogen sulfide and ammonia) and caustic wash water (calcium chloride or other chloride salts)	600-1,200	1.0	2%	0.05
Catalytic hydrotreating	Sour water (hydrogen sulfide, ammonia, suspended solids, and phenol)	600-1,200	1.0	2%	0.05
Total			58.7	100%	0.77[c]

Data sources: [a]IPIECA (2010),[b]Leavitt et al. (2004), and [c]weighted average.

7. Conclusions

The study examined energy intensity, water loss, GHG emissions, and biogas generation potential from industrial wastewater treatment plants. Weighted electricity energy intensity was 2.42 MWh/MG, and overall water loss was considered negligible (0.04%). Wastewater treatment accounted for only 0.40% of GHG emissions, which was negligible. Theoretical biogas production was 0.77 ft^3/barrel of crude petroleum from refinery wastewater.

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