

## Suggested Answers to Homework 3

**General Comment:** These are suggested example answers to the exercises. There are other ways to think about and tackle the different problems, and there is always space for discussion on how different aspects are weighted or sorted.

### Question 3.1

This is a classical chemical engineering plant commissioning risk problem where there are many stakeholders (sugarcane farmers, transport companies, public, plant finance, government, utility companies, and electricity companies are involved). Based on brainstorming (ideally, one should discuss potential risk with the stakeholders), the following risks are highlighted:

1. Biomass has seasonal variation due to the intrinsic nature of biomass growth cycle. The probability for this is high (0.9) given the intrinsic nature of biomass production. The consequence of this is potential shutting down of the plant (0.9).
2. Biomass fails or has significantly lower production due to multiple factors, including drought, insects, forest fire, etc. While this has a high consequence, the probability of this is quite low (0.05), based on historical data.
3. Biomass production is localized, and transportation is required from far-off sites, increasing the transportation cost significantly. This is again due to the intrinsic nature of biomass production, so the probability for this is high (0.6). Its consequence on the plant is significant, in terms of high transportation cost (0.5).
4. Biomass quality differs significantly from farm to farm (depending on farm practices), including the presence of non-valorizable materials such as soils, pebbles, etc. The probability for this is low (0.01), given the modernization of the agricultural practices.
5. Biomass gasification requires water, and the water supply may run into shortages. The probability for this is low but finite (0.2) given that the water table may be affected by future shortages, and climate change. The consequence is high (0.9) given that lack of water will stop the operation of the plant.
6. Public policy changes and imposes a high penalty for the use of food materials (sugarcane) to provide electricity. The probability for this is low, given that sugarcane production is incentivized with better payback to the farmers.
7. Flue gas cleaning technology is too expensive, making the profit negligible. This risk is significant (P of 0.5) given the existing regulations to prevent acid rain (SO<sub>x</sub> and NO<sub>x</sub> emitted from flue gas). Flue gas treatment requires the removal of SO<sub>x</sub> and NO<sub>x</sub>, so the consequence for additional cost is real (0.5).
8. Environmental regulations block the plant operation if it pollutes a nearby high-population city. This is another major risk but given the concern for risk number 3, we will likely not place the plant near high population area (probability of 0.1, consequence of 0.9).

Among these, risks #1, 3, 5, 7, and 8 are most relevant. Risk 2 on biomass failure is a manageable risk based on insurance policies. Risk #4 can be managed by training the farmers and adopting a uniform agricultural protocols. Below is the risk table for this:

Risk type	Probability (P)	Consequence (C)	Risk amount
1. Seasonal variation	0.9	0.9	0.81

3. Local production	0.6	0.5	0.30
5. Water supply	0.2	0.9	0.18
7. Flue gas cleaning tech cost	0.5	0.5	0.25
8. Environment regulation	0.1	0.9	0.09

In the above analysis, the largest impact is from the seasonal variation in the biomass production. This can be managed by developing a sufficient biomass storage facility to buffer the needs for continuous electricity production. The next biggest risk is local production, which in turn affects shipping costs. This should be managed by careful positioning of the plant (somewhere in the middle of the supply-chain network, e.g., in the heavily agricultural zone) where the shipping cost is balanced. Other risks are quite manageable.

### Question 3.2

Here, we are tasked to evaluate the two potential technologies to extract and recycle gold from electronic waste. The first option is to use aqua regia, and the other is to use the recently discovered chemistry involving the combination of thionyl chloride ( $\text{SOCl}_2$ ) and pyridine.

In both cases, we need to remove the majority of the metals, such as copper and aluminum, by dissolving them in concentrated nitric acid, requiring a large-scale hazardous operation. The second issue is the handling of the toxic waste (dissolved copper in nitric acid) and its disposal, including the cost of the disposal. Again, in both methods, one has to extract the dissolved gold by reducing the gold and then by high-temperature calcination. Both steps release toxic vapors and need specialized equipment.

The risk associated with aqua regia is well visualized in the YouTube video, i.e., toxic fumes of hydrochloric acid and nitric acid, a risk that is further increased by the need to work at elevated temperatures to speed up the reaction.

The risk associated with thionyl chloride chemistry is slightly different than that of the chemistry of aqua regia. While we are not working with concentrated acids, we are working with highly dangerous chemicals. Thionyl chloride is a controlled substance under the Chemical Weapons Convention, because it is used to synthesize highly dangerous nerve agents, which can be misused for chemical warfare. It is also a very unstable compound and undergoes violent chemical reactions upon exposure to water or alcohol, releasing fumes of hydrochloric acid and sulfur dioxide. Finally, it is one of the most toxic compounds, with a short exposure leading to death or irreparable major injury.

Overall, the risk of these two chemistries can be categorized into

1. Risk to the operator (accidental exposure): The consequence for thionyl chloride is severe, with fatality. It is also much more difficult to engineer safely on a large scale, given that the organic solvents are involved with an unstable reagent. Aqua regia, while corrosive and toxic, is a mature technology with known engineering controls (acid-resistant materials, fume scrubbing, neutralization). Thionyl chloride, in contrast, presents extreme acute toxicity, unstable reactivity with moisture, and flammability from organic solvents.
2. Risk to the community (in case of a large-scale accident): The consequence for thionyl chloride is severe, with mass fatality. It is also much more difficult to engineer safely on a large scale, given that the organic solvents are involved with an unstable reagent.
3. High cost of handling hazardous waste (dissolved copper in concentrated nitric acid).

4. High cost (equipment/operation) of separation of gold, which can exceed the cost of purchasing mined gold. ]
5. Risk related to the approval of the technology for setting up a plant. Given that the major risk exists for potential misuse of restricted thionyl chloride, the regulatory clearance seems challenging.

The risks for the two methods are compared below

Risk type	Aqua Regia			Thionyl chloride		
	P	C	Risk	P	C	Risk
1. Operator	0.5	0.5	0.25	0.5	1	0.45
2. Community	0.5	0.5	0.25	0.5	1	0.5
3. Cost waste	0.5	0.5	0.25	0.5	0.5	0.25
4. Cost separation	0.5	0.9	0.45	0.5	0.9	0.45
5. Technology approval	0.5	0.5	0.25	0.9	0.5	0.45

Overall, both technologies are highly risky. The main risk for thionyl chloride is its potential impact on the community, the operator, and its approval, given the sensitive nature of this chemical. Having said this, it is used at scale for various chemical processes involving pharmaceuticals, pesticides, and dyes. So, a systematic design of reaction with layers of safety around the processes could eventually work. However, it may further increase the capital and operating costs of the separation process.

### Question 3.3

The gill will likely be made of a polymeric membrane that is selective for air dissolved in the water to the diver. The membrane can optionally concentrate O<sub>2</sub> in the air from its original concentration of 21% to further facilitate the activities of the diver. The average requirement for O<sub>2</sub> near the surface of water is about 20 liters/minute. This means that the membrane must be able to process

$$20/0.21 = 95.2 \text{ liter/min of air}$$

The next aspect is the design of the membrane. The membrane should allow the passage of air but not liquid water. This means that the membrane should have hydrophobic channels that allow desorbed air to flow through the channels to the divers but block liquid water from entering through the channels. One such hydrophobic material is polytetrafluoroethylene or PTFE. Porous PTFE membranes are, in fact, used for removing vaporized water from saline water (a process known as membrane distillation).

The pore size of the material should be small enough that the capillary pressure rejects infiltration of water. For a cylindrical pore, the breakthrough (capillary entry) pressure,  $P_c$ , can be obtained from the Young–Laplace relation:

$$P_c = \frac{2\gamma|\cos\theta|}{r}$$

where  $\gamma$  is surface tension (0.072 Nm<sup>-1</sup> at 20 °C),  $\theta$  is the contact angle (typically around 120°), and  $r$  is the pore radius. We are interested in pressure of ~1 bar (assuming diving is not too deep). Based on this,  $r$  is ~0.7  $\mu\text{m}$ . This indicates that we are interested in pore diameters that are approximately 1.4  $\mu\text{m}$  or smaller in size. Luckily, such PTFE membranes are commercially available.

Next is the needed membrane area. For this, we need to know the air permeance of porous PTFE membrane, and the mass transfer of air from dissolved air in the liquid to the gaseous air in the PTFE membrane. The mass transfer rate from dissolved air to the PTFE depends on the mass transfer coefficient and the concentration of air:

Concentration of dissolved air in water =  $C_o = 23 \text{ mg/L}$  ([https://www.engineeringtoolbox.com/air-solubility-water-d\\_639.html](https://www.engineeringtoolbox.com/air-solubility-water-d_639.html))

In the units of  $\text{mol/m}^3$ ,  $C_o = 0.8 \text{ mol/m}^3$  (using the molecular weight of air to be  $29 \text{ g/mole}$ ).

Diffusivity of air in water is  $2 \times 10^{-5} \text{ cm}^2/\text{s}$  ([https://en.wikipedia.org/wiki/Mass\\_diffusivity](https://en.wikipedia.org/wiki/Mass_diffusivity))

Mass transfer coefficient of air in water =  $k = D/\delta$ , where  $\delta$  is the thickness of the boundary layer (typically  $100 \mu\text{m}$ ), based on the film theory of mass transfer.

Therefore,  $k = 2 \times 10^{-5} \text{ m/s}$

Flux from dissolved air to the membrane =  $k(C_o - C_m)$  where  $C_m$  is the concentration of air inside the membrane.

One can maximize this flux by pulling air using vacuum ( $C_m$ ) inside the membrane, setting  $C_m$  to be 0.

Therefore, flux =  $1.6 \times 10^{-5} \text{ mole/m}^2/\text{s}$

Now given that I need to move  $95.2 \text{ liter/min}$  of air ( $\sim 0.07 \text{ mol/s}$ ) through the membrane, I need the following area of the membrane (flux \* area = flow rate)

Area = flow rate/flux =  $0.07 / (1.6 \times 10^{-5}) \text{ m}^2 = 4375 \text{ m}^2$

This area is huge. One way to reduce the needed membrane area is to increase the mass transfer coefficient by forced convection or by increasing mass transfer in channeled contactors (where  $\delta$  can decrease from  $100$  to  $1 \mu\text{m}$ ).

Overall, such a device will be impractical.

Note: some students looked at flux within the membranes to estimate membrane area. However, in this case, the rate-limiting step is the transfer of dissolved air (in liquid water) to the gaseous air (inside the porous membrane).