Process Design And Development Kai Ruth

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Introduction

Gross Profit Calculation:
$GP = PR - CRM$
GP : Gross Profit
PR : Potential Revenues from Products and By − Prod.
CRM : Cost Of Raw Materials

Heuristics I

Reaction Operations:

- Select raw materials and chemical reactions to avoid, or reduce, the handling and storage of hazardous and toxic chemicals.

Chemical Distribution:

- Use an excess of one chemical reactant in a reaction operation to completely consume a second valuable, toxic, or hazardous chemical reactant.
- For competing series or parallel reactions, adjust the temperature, pressure, and catalyst to obtain high yields of the desired products. Initially obtain kinetics data and check this assumption before developing a base-case design.
- When nearly pure products are required, eliminate inert species **before** reaction operations:
  - When the separations are easily accomplished.
  - When the catalyst is adversely affected by the inerts.
  - **Do not remove inerts before the reaction** if a large exothermic heat of reaction must be removed.
- Introduce purge streams to provide exits for species that:
  - Enter the process as impurities in the feed.
  - Are produced by irreversible side-reactions.

  when species are in trace quantities (and/or) are difficult to separate from the other chemicals.

Heuristics I

Chemical Distribution - continued:

- **Do not purge** valuable species or species that are toxic and hazardous, even in small concentrations:
  - Add separators to recover valuable species.
  - Add reactors to eliminate toxic and hazardous species.
- By-products produced in reversible reactions, in small quantities, are usually not recovered in separators or purged but recycled to extinction.
- Especially for reversible reactions consider conducting them in a separation device capable of removing the products, and hence, driving the reactions to the right.

Separation Operations:

- Separate liquid mixtures using distillation and stripping towers, liquid-liquid extractors, and crystallization, among similar operations.
- Attempt to condense vapor mixtures with cooling water, then separate liquid mixtures.
- Separate vapor mixtures using partial condensers, cryogenic distillation, absorption towers, adsorbers, and/or membranes.

Heuristics II

Heat Removal And Addition:

- To remove a highly-exothermic heat of reaction, consider the use of excess reactant, an inert diluent, and cold shots.
- For less exothermic heats of reaction, circulate reactor fluid to an external cooler, or use a jacketed vessel or cooling coils. Also, consider the use of intercoolers.

Heuristics II

Heat Removal And Addition - continued:

- To control temperature for a highly-endothermic heat of reaction, consider the use of excess reactant an inert diluent, and hot shots.
- For less endothermic heats of reaction, circulate reactor fluid to an external heater, or use a jacketed vessel or heating coils. Also, consider the use of inter-heaters.

Pumping, compression and pressure reduction:

- To increase the pressure of a stream, pump a liquid rather than compress a gas; that is, condense a vapour, as long as refrigeration (and compression) is not needed, before pumping.

$$\text{Reactor Conv.} = \frac{\text{Reactant consumed in reactor}}{\text{Reactant fed to the reactor}}$$
$$\text{Reactor Selec.} = \frac{\text{Desired product produced}}{\text{Reactant consumed in reactor}} \cdot \text{SF}$$
$$\text{Reactor Yield} = \frac{\text{Desired product produced}}{\text{Reactant fed to the reactor}} \cdot \text{SF} = \text{Reactor Conv.} \cdot \text{Reactor Selec.}$$
$$\text{Process Yield} = \frac{\text{Desired product obt. in process}}{\text{Reactant fed to the process}} \cdot \text{SF}$$

SF (Stoichiometric Factor): Stoichiometric moles of reactant required per mole of product.
Single Reactions: Feed → Product, $r = kc^a_{\text{Feed}}$
For single reactions, an ideal-batch or plug-flow reactor is preferred.
Multiple Reactions (Parallel):

$$\text{Feed} \rightarrow \text{Product} \,\&\, \text{Feed} \rightarrow \text{ByProduct}$$
$$r_1 = k_1 c^{a1}_{\text{Feed}} \,\&\, r_2 = k_2 c^{a2}_{\text{Feed}}$$
$$\implies \frac{r_2}{r_1} = \frac{k_2}{k_1} c^{a_2 - a_1}_{\text{Feed}}$$

$a_1 > a_2$: use **Batch** or **PFR**
$a_1 < a_2$: use **mixed-flow** reactor

Heuristics II

Multiple reactions in series producing byproducts:

$$\text{Feed} \rightarrow \text{Product} \rightarrow \text{ByProduct}$$
$$r_1 = k_1 c_{\text{Feed}}^{a1} \,\&\, r_2 = k_2 c_{\text{Product}}^{a2}$$

A mixed-flow model would be expected to give a poorer selectivity or yield than a batch or plug-flow reactor for a given conversion. A **Batch** or **PFR** should be used for multiple reactions in series.

Mixed parallel and series reactions producing byproducts:

$$\begin{cases} \text{Feed} \xrightarrow{r_1} \text{Product} \xrightarrow{r_3} \text{ByProduct} \\ \text{Feed} \xrightarrow{r_2} \text{ByProduct} \end{cases}$$

$r_1 = k_1 c_{\text{Feed}}^{a_1}$
$r_2 = k_2 c_{\text{Feed}}^{a_2}$
$r_3 = k_3 c_{\text{Product}}^{a_3}$

As far as the parallel byproduct reaction is concerned, for high selectivity, if:

- $a_1 > a_2$: use **Batch** or **PFR**
- $a_1 < a_2$: use **mixed-flow reactor**

The series byproduct reaction requires a PFR. Thus, for the mixed parallel and series system above, if:

- $a_1 > a_2$: use a **Batch** or **PFR**
- $a_1 < a_2$: **Conflict** (Parallel needs mixed flow reactor, Series needs PFR). The optimal reactor is likely in between:
  - series of mixed-flow reactors *or*
  - plug-flow reactor with a recycle *or*
  - series combination of plug-flow and mixed-flow reactors

Polymerization Reactions:

- Without termination step: Choose **Batch** or **PFR**(Growth to approximately equal lengths and narrow distribution of molar masses.)
- With termination step: (Mechanisms involving free radicals) Choose **CSTR** (Uniform concentration of monomer and constant termination rate results in narrow distribution of chemicals.)

Heuristics II

Biochemical Reactions — Microorganisms:
$\text{A} \overset{\text{Cells}}{\rightarrow} \text{R} + \text{C}$
Depending on the concentration range, mixed-flow, plug-flow, a combination of mixed- flow and plug-flow or mixed-flow with separation and recycle might be appropriate.

Biochemical Reactions — Enzymes:
$\text{A} \overset{\text{Enzyme}}{\rightarrow} \text{R}$
This means that a plug-flow or ideal batch reactor is favoured if both the feed material and enzymes are to be fed to the reactor.

Open System (Steady Flow) Work: *(derived from Steady-Flow-Energy-Equation)*
$\dot{W} = \int_{p1}^{p2} \dot{V}\, \mathrm{d}p$
(Not the same as for closed system: $W = -\int_{V_1}^{V_2} p\, \mathrm{d}V$)
As a consequence it requires less work to first increase pressure of a liquid and subsequently vaporize compared to vice versa.

Intro to Optimization

Feasible Region (FR):
$\text{FR} = \{x | h(x) = 0, g(x) \leq 0; x \in \mathbb{R}^n\}$
Local minimum (@ $\hat{x}$):
$\exists(\delta \in \mathbb{R}) > 0 : (\forall x \in \text{FR}) \in (|\hat{x} - x| \leq \delta), f(x) \geq f(\hat{x})$
Global minimum (@ $\hat{x}$):
$f(x) \geq f(\hat{x}) \forall x \in \text{FR}$
Convexity: FR is convex $\iff$
$\forall x_1, x_2 \in \text{FR}, \forall \alpha \in [0,1], x_1 + \alpha(x_2 - x_1) \in \text{FR}$
Convex function f:
$f(x_1 + \alpha(x_2 - x_1)) \leq f(x_1) + \alpha(f(x_2) - f(x_1))$
$\forall \alpha \in [0,1]$
Concave function: f
$f(x_1 + \alpha(x_2 - x_1)) \geq f(x_1) + \alpha(f(x_2) - f(x_1))$
$\forall \alpha \in [0,1]$
Convex Minimization Problem: (always has unique minimum)

- All equality constraints ($h(x) = 0$) are linear
- All inequality constraints ($g(x) \leq 0$) are convex
- Objective function (min $f(x)$) is convex

Note: $\max f(x)$ is equivalent to $\min -f(x)$.

Intro to Optimization

Linear Programming (LP):

- Linear objective function
- Linear equality and inequality constraints
- Only continuous variables (no discrete var.)
- Always a convex problem

Nonlinear Programming (NLP):

- At least one nonlinear term (obj. function or equality or inequality constraint)
- Only continuous variables (no discrete var.)
- Either convex or non-convex

Mixed Integer Linear Programming (MILP):

- LP with integer variables
- (Without continuous var. it would be an IP)

Mixed Integer Nonlinear Programming (MINLP):

- At least one nonlinear term (obj. function or equality or inequality constraint)
- Both continuous and discrete *(i.e. integer)* variables

For modeling with discrete variables *e.g. integer cuts*, see the PSF Formulary.

Sizing Costing Financial Metrics

Estimation based on plant capacity and fundamental process factors (Bridgewater's method):

$$C_{\text{IBL}} = \begin{cases} 3200N\left(\frac{S}{Y}\right)^{0.675}, & \text{if } S \geq 60000\,\text{ton/year}, \\ 280000N\left(\frac{S}{Y}\right)^{0.3}, & \text{if } S < 60000\,\text{ton/year}. \end{cases}$$

C_{IBL}: IBL cost in 10^6 \$ USGC 2010, N: Number of unit operations in process, S: Capacity of the plant estimated (in $\mathrm{t\,yr^{-1}}$), Y: Reactor yield in $\mathrm{kg_{Product}} / \mathrm{kg_{Input}}$

Sizing Costing Financial Metrics

Estimating purchased equipment cost:
$C_e = a + bS^n$
C_e: Purchasing Cost of the unit (in $USGC 2010), a: constant cost factor, b: proportional size-cost factor, n: cost exponent, S: unit's capacity. Find values in Table 1 at the end.

Lang Installation Factors F_I:
Add cost of setting up equipment.

Equipment	F_I
Compressor	2.5
Distillation Column	4
Fired Heaters	2
Heat Exchangers	3.5
Instruments	4
Pressure Vessels	4
Pumps	4
Other Equipment	2.5

$$C_{\mathrm{IBL}} = \sum_{e \in \mathrm{Equipment}} \left[C_e \left((1 + F_{PP}) F_{M,e} + (F_{IC} + F_E + F_{CE} + F_B + F_{PC} + F_{EE}) \right) \right]$$

Expanded Lang Factors:

Name (Symbol)	Value
Piping (F_{PP})	0.8
Instrumentation and Control (F_{IC})	0.3
Electrical Infrastructure (F_E)	0.2
Civil Engineering (F_{CE})	0.3
Additional Buildings (F_B)	0.2
Painting and Coating (F_{PC})	0.1
Equipment Edification (F_{EE})	0.3

Material Factors

Material	F_M
Carbon Steel	1
Aluminum	1.07
Bronze	1.07
Cast Steel	1.1
SS304	1.3
SS316	1.3
SS321	1.5
Hastelloy C	1.55
Monel	1.65

Sizing Costing Financial Metrics

Fixed Capital Cost (FCC):
$FCC = C_{\mathrm{IBL}}(1 + F_{\mathrm{OBL}})(1 + F_{\mathrm{ED}} + F_{\mathrm{Con}})$

Name (Symbol)	Value
Outside Battery Limits (F_{OBL})	0.3
Design and Engineering (F_{ED})	0.3
Contingency Charges (F_{Con})	0.1

Geographic Factors (Location of Plant):
$C_{L2} = C_{L1} \frac{F_{L2}}{F_{L1}}$

Location Factors: (F_L)

Location	F_L
US, Gulf Coast (USGC)	1.00
US, East Coast (USEC)	1.04
Canada	1.00
Mexico	1.03
Brazil	1.14
China, Imported Products	1.12
China, Local Production	0.61
Southeast Asia	1.12
Australia	1.21
India	1.02
Middle East	1.07
Germany	1.11
Italy	1.14
Russia	1.53

Temporal Escalation:
$C_{T2} = C_{T1} \frac{\mathrm{CEPCI}_{T_2}}{\mathrm{CEPCI}_{T_1}}$

Year	CEPCI	Year	CEPCI
2001	394.3	2011	585.7
2002	395.6	2012	584.6
2003	402.0	2013	567.3
2004	444.2	2014	576.1
2005	468.2	2015	556.8
2006	499.6	2016	541.7
2007	525.4	2017	572.8
2008	575.4	2018	603.1
2009	521.9	2019	607.5
2010	550.8	2020	596.2

Operating Labor:
$C_{\mathrm{OL}} = 50000 \left\lceil \sqrt{6.29 + 31.7\, PSS^2 + 0.23\, FS} \right\rceil$
PSS: Number of steps involving particulate solids
FS: Number of steps involving fluids (gas, liquids or mixtures)

Sizing Costing Financial Metrics

Operational Fixed Cost:
$OC_{\mathrm{Fix}} = C_{OL}\,(1 + F_{MS}) + C_{IBL}\,(F_{MC} + F_{PL})$

Name (Symbol)	Value
Management and Salary Overhead (F_{MS})	2.13
Maintenance Costs (F_{MC})	0.05
Property and Land Costs (F_{PL})	0.03

More variable costs, which need to be evaluated individually:
Raw materials, heating and cooling utilities, consumables, waste and effluent disposal, packing and shipping.

Cash Flow for time period n:
$CF_n = P_n - (P_{n-1} - D_{n-1})t - \mathrm{investment}_n$
(investment determined from CAPEX)

Profit:
$P_n = Rev_n - OC_{\mathrm{Fix},n} - OC_{\mathrm{Var},n}$
Rev: Revenue, OC: Operational costs

Tax Rate: (t)
Fraction of the taxable capital to be paid to the authorities. Values are often applied to the profits and depreciation obtained in the previous period. Taxes are paid only if profits are positive.

Straight-Line Depreciation:
$D_n = \frac{FCC}{DP}$
DP: Depreciation Period

Declining-Balance Depreciation:
$D_n = FCC \cdot F_D \cdot (1 - F_D)^{n-1}$
F_D: Depreciation factor (usually $\leq \frac{2}{DP}$),
FCC: Fixed Capital Cost (initial investment)
n: Operating year (not absolute year)

Net Present Value: (NPV)
$NPV = \sum_{n=1}^{N} \frac{CF_n}{(1+i)^n}$

Interest Rate Of Return: (IRR)
$0 \stackrel{!}{=} \sum_{n=1}^{N} \frac{CF_n}{(1+IRR)^n}$
(interest rate at which the NPV is zero, easiest to solve numerically)

Sizing Costing Financial Metrics

Pay-back Time: (PB, in years)
$PB = \frac{\text{total investment}}{\text{annual average cash flow}}$
Time required (after the completion of the initial investment) to recover the initial investment. Annual average cash flow starting from first positive cashflow.

Return on Investment: (ROI, in %)
$ROI(\%) = \frac{\text{annual average cash flow}}{\text{total investment}} \cdot 100$
Estimated as the inverse of the pay-back time. Represents efficiency (i.e., profitability) of the investment.

Total Annualized Costs: (TAC)
$TAC = ACC + OC_{\text{Fix}} + OC_{\text{Var}}$
Combination of annualized capital costs and operational costs (fixed and variable).

Annualized Capital Costs: (ACC)
$ACC = FCC \cdot \frac{i(1+i)^n}{(1+i)^n - 1}$
FCC: Fixed Capital Cost (initial investment),
i: Interest rate, n: Number of years. Derivation see section 0.1.

Economic Potential: (EP)
$EP = \text{Revenues} - (ACC + OPEX)$
Appeared in Exercise 5.

Batch Processes

Makespan:
Time that elapses from the starting time of the first task of the batch until the end time of the last task of the batch.

Cycle time:
Time that elapses between starting time of the first task of one batch and the starting time of the first task of the next batch.

Non-Overlapping Operation:
$$CT = \sum_{j=1}^{M} \tau_j$$
τ_j: Operating time of stage j
M: Number of stages

Batch Processes

Overlapping Operation + Zero Wait:
$$CT = \max_{j=1,\dots,M} \{\tau_j\}$$

B: Batch size, amount of product produced in a batch (kg of main product produced in a batch)

Multi Product Batch Plant With Mixed Product Campaigns And Unlimited Storage:
$$CT = \max_{j=1,\dots,M} \left\{ \sum_{i=1}^{N} n_i \tau_{ij} \right\}$$
j: stages, i: products, n_i: number of batches of product i in each campaign, τ_{ij}: operating time of stage j when producing product i.

Productivity: ($prod$)
$prod = \frac{(\#\text{Batches}) \cdot B}{makespan} \approx \frac{(\#\text{Batches}) \cdot B}{(\#\text{Batches}) \cdot CT} = \frac{B}{CT}$

$makespan \approx CT \cdot (\#\text{Batches})$

Batches: Number of batches

Flowshop plant: All the products follow same sequence of tasks.
Jobshop plant: Products can follow different sequences of tasks.

Zero-wait policy: Starting time of a task is equal to the finishing time of the previous task.

No-intermediate storage policy: , Task of a batch is started as soon as both two conditions are satisfied:

- Previous task in the batch has been completed
- Equipment unit where the new task will be carried out is available.

(The content of a vessel is stored in the same vessel until it can be transferred to the next unit.)

Batch Processes

Unlimited Intermediate Storage Policy: A task is started as soon as the following two conditions are satisfied:

- Previous task in the batch has been completed
- Equipment unit where the new task will be carried out becomes available.

The content of a vessel is transferred and stored in a storage tank after the task is completed (and then transferred again to the unit where the new task will take place once the unit becomes available). With this strategy, the new task of the batch (that is executed in another unit) and the new task of the following batch (executed in the same unit) can both start earlier, leading to a more compact schedule.

Sizing Of Vessels In Batch Plants:
$V_j = B \cdot S_j$
V_j: Required vessel volume
S_j: Vessel volume to produce 1 kg of main product

$S_j = \alpha_j \cdot \frac{1}{\rho_j} = \frac{\text{total kg}}{\text{kg main product}} \cdot \frac{1}{\text{total kg}} = \frac{1}{\text{kg main product}}$

$\alpha_j = \frac{\text{total kg}}{\text{kg main product}}$

ρ_j: density ($\text{kg}\,\text{L}^{-1}$)
j: Stages (e.g.: {Mixer, Reactor, Flash})

Retrofit Strategies:

- Increase batch size B
- Reduce cycle time CT
- De-Bottleneck the unit with lowest batch size B or that which limits the cycle time most. (Only improve until the unit stops being a bottleneck!)
- Add parallel equipment units
- Combine the above

In a well-designed plant all units act as bottlenecks simultaneously!

Tables

Equipment	**Capacity unit S**	**Capacity validity**		**a**	**b**	**n**
		Lower	**Upper**			
Boiler	Steam production, kg/h	20000	800000	130000	53	0.9
Compressor	Driver power, kW	75	30000	580000	20000	0.6
U-tube shell and tube heat exchanger	Exchange area, m^2	10	1000	28000	54	1.2
Kettle reboiler	Exchange area, m^2	10	500	29000	400	0.9
Pressure vessel	Shell mass, kg	160	250000	11600	34	0.85
Centrifugal pump	Flow, L/s	0.2	126	8000	240	0.9
Jacketed agitated reactor	Volume, m^3	0.5	100	61500	32500	0.8

Table 1: Capacity, parameters, and scaling factors for different equipment types.

0.1 Annual Capital Charge Ratio

The annual capital charge ratio is given by the following expression,

$$\text{acc} = \frac{i \cdot (1+i)^n}{(1+i)^n - 1}, \tag{1}$$

where i is the annual interest rate and n the total number of years for which annuities are to be paid. In a case where the number of years $n = 20\,\text{yr}$, and the interest rate is assumed to be $i = 20\,\%$ it thus follows,

$$\text{acc} = \frac{0.2 \cdot (1+0.2)^{20}}{(1+0.2)^{20} - 1} = 0.205. \tag{2}$$

The above formula can be derived using the expression for the present value of an annuity, which is given by,

$$p = \sum_{k=1}^{n} \frac{R}{(1+i)^k} = R\left(\frac{1-(1+i)^{-n}}{i}\right), \tag{3}$$

where the second equality assumes a constant value of the recurring annuity payment R and follows from considerations of the properties of a geometric series. This expression can then be rearranged for R, as shown below.

$$R = p\frac{i}{1-(1+i)^{-n}} = p\frac{i(1+i)^n}{(1+i)^n - 1} = p \cdot \text{acc}.$$

Thus, under the assumptions made, the annual cost can be obtained from the total cost via the annual capital charge ratio. The interest rate is chosen quite high however, suggesting that there are other good investment alternatives present or inflation rates are high. This may not always be the case, and if i would be lower, then the annual contribution by CAPEX to the objective cost would be lower.

0.2 Net Present Value (NPV)

The net present value presents the sum of the present values in a given year n, PV_n over the years,

$$CF_n = PV_n(1+i)^n \quad ; \quad PV_n = \frac{CF_n}{(1+i)^n} \tag{4}$$

$$NPV = \sum_{n=1}^{N} PV_n = \sum_{n=1}^{N} \frac{CF_n}{(1+i)^n} \tag{5}$$