2 Systems modeling

2.1 Importance of systems modeling in renewable energy

Energy is deeply embedded in every aspect of our society and daily activities. Our consumption of energy is often one of our major expenses outside of rent (i.e. land use, another important concept for sustainability). Because energy use is so ubiquitous and massive, the installations used for energy production are often complex, highly optimized systems consisting of several integrated units. As engineers, some of you will probably be asked to help design these systems. Due to their complexity, the era at which it was possible to understand a system just by being clever and thinking about it with a pencil and paper has long passed. Nowadays, you still have to be smart enough to be able to comprehend and model a single unit (a turbine, a burner, a heat pump, etc.). However, depending on the level of detail (combustions can involve thousands of parallel and consecutive reactions), even such unit operations can be too complicated to model with a pencil and paper. The problem becomes even more complex when you consider the effect of a given technology on our planet. For example, replacing a coal-fired power plant with a wood-fired plant will reduce its efficiency, increase the price of electricity, consume trees, change the nature of the soil, reduce the total amount of CO_2 emissions, change consumer behavior… I could go on forever.

The only way to understand an energy production system or its effect on our environment is to use **systems modeling**. In theory, an infinitely complex systems model can give you any answer you want. However, infinite complexity is impractical in all cases, so precise questions have to be posed. In the case of a gas turbine, if the production of electricity from a well-known fuel is to be determined within 5% error, a simple model using mass and energy balances along with an equation describing a standard turbine efficiency can be used. If, in a given situation, a precise composition of NO_x gases must be determined for a specific gas quality and turbine blade, a complex computational fluid dynamics model might be required.

Scientists are trying to determine the potential increase in global temperature due to different energy policy decisions. Global temperature increases then give policy makers an indication of the severity of consequences that could result from their policy decisions. This is an extremely complex question and requires an extremely complex model (see Fig. 2.1).

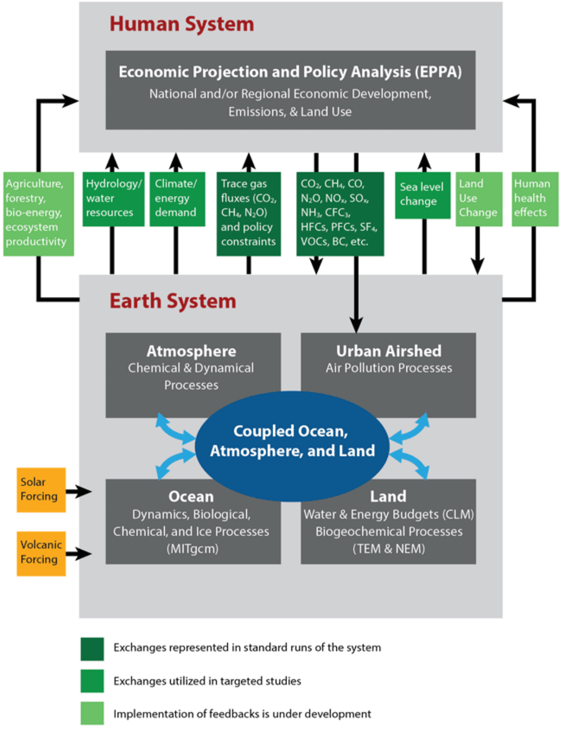


Fig. 2.1 A schematic of the MIT Global Change Model

This systems model involves the coupling of several units and sub-units, including an atmospheric model and ocean models that are themselves divided into multiple sub-units with various volumes and chemical processes. The system is complex enough that it cannot give an exact answer, and so the results of different scenarios are reported as a series of probabilistic outcomes (see Fig. 2.2). The model shows that a more proactive environmental stance buys us a better chance at good outcomes (or as they represent it, as a better “wheel of fortune”, see Fig. 2.2).

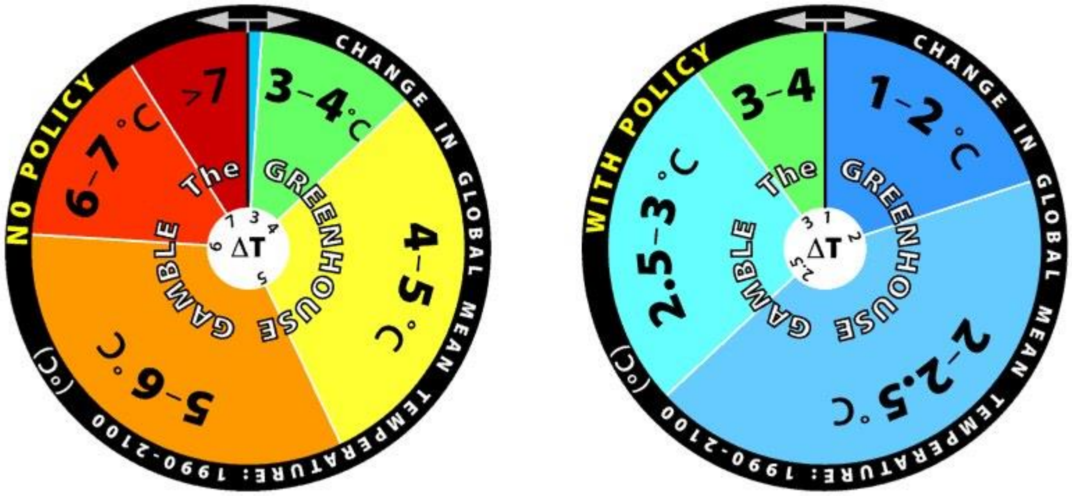


Fig. 2.2 The “greenhouse gamble”. Probabilistic global mean temperature increase between 1990 and 2100 as predicted by the MIT Global Change Model without policy change (*left*) and with mitigation policies put in place (*right*).

As a chemical engineer, you will probably be mostly involved in designing process models that might one day become small parts of such a global model. In this part of the course, we will briefly introduce the following methods (their interaction is detailed in Fig. 2.3):

- **Process systems modeling**. This will be briefly introduced, as it will likely be explored much more in detail during a future process design course.
- **Heat integration and pinch analysis**. This plays a key role in renewable energy processes and must be done in tandem with process modeling.
- **Life cycle assessment**. To understand the environmental impact of a process, the process systems model can be used as the core of a larger life cycle inventory and assessment model.
- **Uncertainty analysis**. As illustrated by the “wheel of fortune” concept shown above, it is important to understand that what you are modeling is inherently subject to uncertainty and we will describe methods to estimate the inherent uncertainty in the model’s predictions.

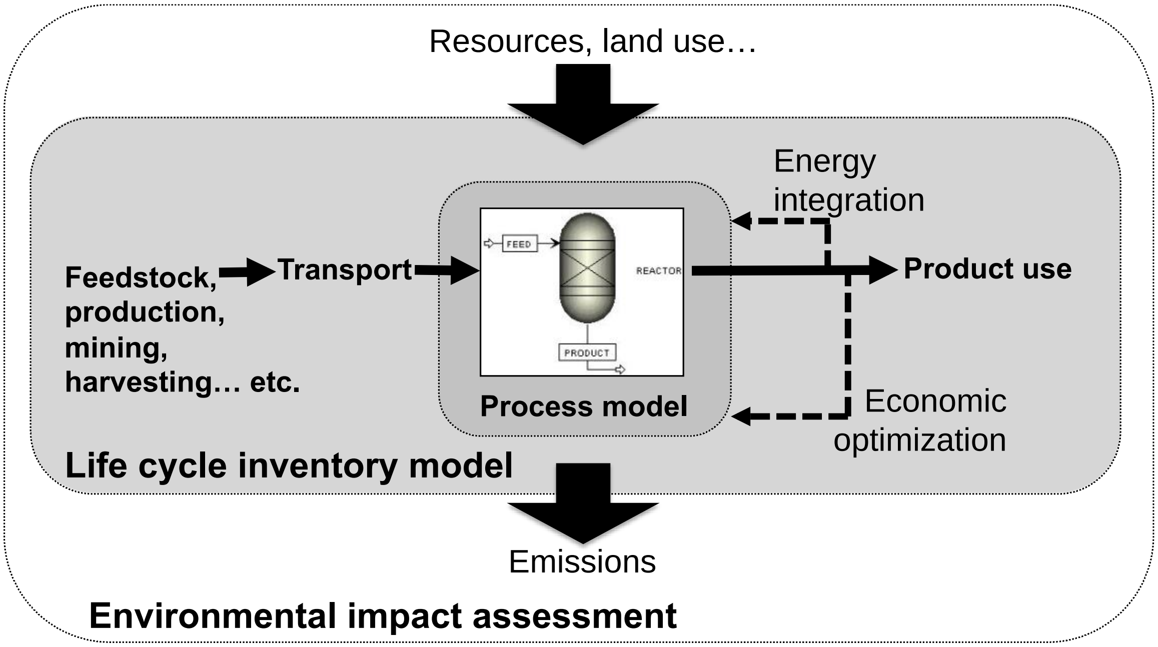


Fig. 2.3 Overall process design approach coupled with heat integration, techno-economic modeling and life cycle assessment.

2.2 Modeling Systems

Models, at least for material transformation processes, are generally assemblies of interconnected units. They can be represented graphically as flowsheets (see example in Fig. 2.4).

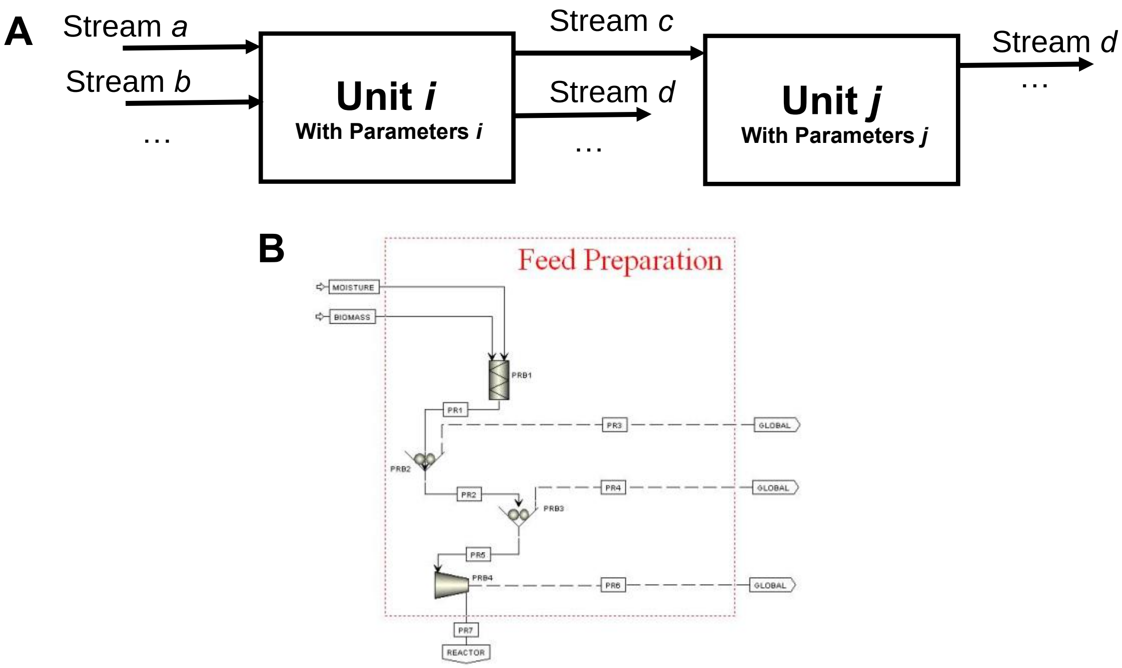


Fig. 2.4 Flowsheet examples. **(A)** A simple generic flowsheet. **(B)** A flowsheet generated using the Aspen Plus software modeling the Grinding and pressurization of a biomass slurry.

Despite the graphical representation, it is important to remember that these models remain just a series of equations, which describe the following three types of relations:

i. Streams properties. Streams can be:

- Heat streams, which are characterized by there energetic flux (energy/time). In the case where heat integration is performed it is important to know the temperature at which they are generated.

- Other energetic streams (mechanical and electrical), which are characterized by their power (energy/time) and, in the case of mechanical work, the rotation speed of the shaft.
- Material streams, which are characterized by intensive (properties that are independent of the streams size/quantity, e.g. T, P…) and extensive properties (properties that are dependent on a streams size). A material stream is completely characterized when:

  $$N_{S.P.}=(N_{S.P.I.} + N_{S.P.E.})= 2 + N_c \quad \text{with } N_{S.P.E.} \geq 1 \qquad (2.1)$$

  With:

  $N_{S.P}$: Number of required specified properties

  $N_{S.P.I}$: Number of specified intensive properties

  $N_{S.P.E}$: Number of specified extensive properties

  N_C: Number of components in the stream

The number of extensive properties must be greater than 1 so at least one indication of the size/quantity of the stream is given (typically, this will be a volume, mass or energy flow rate). The other variables must be independent in order to completely specify the material stream. Variable independence can depend on the stream properties. This is a consequence of the Gibbs phase rule, which allows you to determine how many intensive degrees of freedom a system has (e.g. "how many intensive variables can I specify independently of each other?"):

$$F_{int.}= 2 + N_c - N_P \qquad (2.2)$$

With:

$F_{int.}$: Degree of freedom of intensive properties

N_C: Number of components in the stream

N_P: Number of phases in the stream

Therefore, for a single-phase system (e.g. liquid water at 25°C) you have $F_{int.}$= 2+1-1=2, which means you can specify T and P independently. For a two-phase system, e.g. boiling water, you cannot ($F_{int.}$=1), so you have to specify an extra extensive property such as quantity of vapor.

For material streams, we will have to specify $N_{S.P.}$=2 + N_c properties. This leads the total number of specifications to be:

$$N_{specifications} = N_{streams,Q} + N_{streams,W_{el}} + 2N_{streams,W_{mech}} + N_{streams,material}(2 + N_c) \qquad (2.3)$$

However, they must not necessarily be specified for every stream as some connections/units might pre-determine the state of one or several streams (e.g. a mass and/or energy balance on a give unit). The specification of stream properties will constitute a set of equation denoted by the following matrix for stream a:

$$\boldsymbol{S_a}\big(\overbrace{m_a, P_a, h_{a,\alpha}, x_{\alpha,a}, x_{\beta,a} \ldots}^{stream\ variables:}\big) = 0 \qquad (2.4)$$

with:

$\boldsymbol{S_a}$: the stream specification matrix of stream a

m_a: mass flow of stream a

P_a: Pressure of stream a

$h_{a,\alpha}$: Molar (or mass) enthalpy of component α in stream a

$x_{\alpha,a}$: Molar (or mass) fraction of component α in stream a

$x_{\beta,a}$: Molar (or mass) fraction of component β in stream a

The stream variables shown here is one possible set of variables that will completely define a two-component stream, but it is not necessarily the ones you can or want to specify. For example, you probably don’t know the enthalpy of your fluid but only the temperature or the vapor fraction. In addition, you probably need to know other dependent thermodynamic properties based on these specifications. For example, you might need the volumetric flow rate of your stream at the specified conditions to be able to size the equipment properly. Therefore, you need another set of equations, which are the second major type of equations:

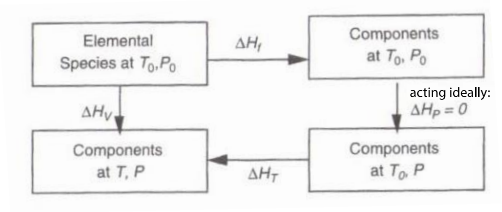
ii. Thermodynamic relationships. Calculating the thermodynamic relationships in a model is not simple, and typical process design software has many different models that vary in complexity to choose from, making this entire subject extremely complicated. You could teach several advanced courses on how these calculations are performed. In this course, the goal will be to briefly summarize the basic sequence of thermodynamic calculations so that you understand the different steps:

Step 1: calculating pure component properties in ideal conditions. Models for pure components are generally used to calculate the necessary properties of single components in a mixture. Typical process modeling software will generally contain a set of pure component relationships that allow the calculation of heat capacity, viscosity, enthalpies, etc. For the principal thermodynamic properties (e.g. enthalpy or Cp) we assume at this stage that components behave ideally, i.e. with no pressure or mixing effects.

Again, there are many possible calculations depending on which property is chosen. Let's go through the calculation of enthalpy to get an idea of the process.

Enthalpy is always calculated from a reference state (where $\Delta H_0=0$). The reference state that is generally chosen is elemental species in the ideal gas state at $T_0=298$ K and $P_0= 1$ bar. To get from this state to the enthalpy at the desired conditions, two paths are possible, which depend on whether the stream is in the vapor or liquid state (Fig. 2.5).

Enthalpy calculation in the gas phase



Enthalpy calculation in the liquid phase

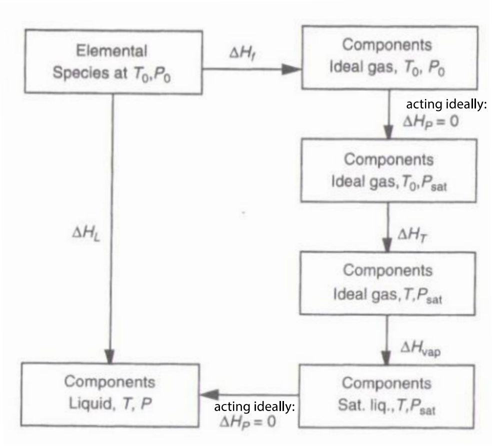


Fig. 2.5 Pathways for calculating enthalpy of a component in the vapor phase (ΔH_V) or in the liquid phase (ΔH_L) using ideal assumptions

In both cases, we need the enthalpy of formation of our compounds ($\Delta H^0_{f,\alpha}$). This can be found in various databases, including NIST's chemistry webbook: http://webbook.nist.gov or the CRC handbook of chemistry and physics.

To determine if you are in a vapor or liquid state (depending on the mixture's T or P) we can use Antoine's law:

$$log_{10}(P_{sat,\alpha}) = A_\alpha - (B_\alpha / (T_{sat,\alpha} + C_\alpha)) \tag{2.5}$$

where:

$P_{sat,\alpha}$: Saturation pressure of component α

$T_{sat,\alpha}$: Saturation temperature of component α

A_α, B_α and C_α: Antoine parameters for component α (you can find them for given components in several references including again NIST's chemistry webbook: http://webbook.nist.gov or Perry's Chemical Engineering Handbook).

For a component in the vapor phase, we then have to calculate the ideal gas change to our target temperature T from T_0. In the ideal gas state this can be done with Cp_α. Therefore:

$$\Delta H_{v,\alpha}(T) = \Delta H^0_{f,\alpha} + \int_{T_0}^{T} Cp_\alpha(T')dT' \tag{2.6}$$

with:

$$Cp_\alpha(T) = A_\alpha + B_\alpha T + C_\alpha T^2 + D_\alpha T^3 + E_\alpha/T^2 \tag{2.7}$$

where:

A_α, B_α, C_α, D_α and E_α: are *Cp* parameters for component α (**NOT the same as Antoine parameters!!!**).

For a compound in the liquid state we need to add the vaporization enthalpy at the desired temperature ($\Delta H_{vap,\alpha}(T)$), yielding the following expression:

$$\Delta H_{L,\alpha}(T) = \Delta H_{f,\alpha}^{0} + \int_{T_0}^{T} Cp_{\alpha}(T')dT' - \Delta H_{vap,\alpha}(T) \tag{2.8}$$

The Watson correlation can be used to calculate $\Delta H_{vap,\alpha}(T)$:

$$\Delta H_{vap,\alpha}(T) = \Delta H_{vap,\alpha}(T_{\alpha,b})\left[(T_{\alpha,c} - T)/(T_{\alpha,c} - T_{\alpha,b})\right]^{\eta\approx 0.38} \tag{2.9}$$

with:

$\Delta H_{vap,\alpha}(T_{\alpha,b})$: the enthalpy of vaporization at $T_{\alpha,b}$

$T_{\alpha,b}$: the temperature of saturation at atmospheric pressure

$T_{\alpha,c}$: the critical temperature of component α

All of these parameters can be found in the same databases/reference books mentioned above.

The approach is very similar for entropy except that standard entropies are used as a basis and they have absolute values (entropy only equals 0 for a perfect crystal at 0 K). The analogous scheme for entropy is shown in fig. 2.6.

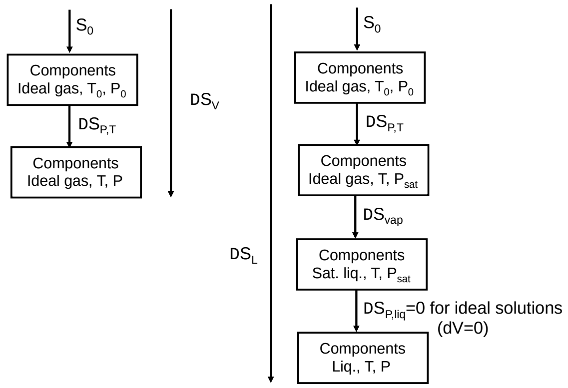


Fig. 2.6. Pathways for calculating entropy of a component in the vapor phase (ΔS_V) or in the liquid phase (ΔS_L) using ideal assumptions

The overall entropy calculation leads to:

$$\Delta S_{v,\alpha}(T,P) \ = S_\alpha^0 + \int_{T_0}^{T} \frac{Cp_\alpha(T\prime)}{T\prime} dT' - Rln\frac{P}{P_0} \tag{2.10}$$

$$\Delta S_{L,\alpha}(T,P) = S_\alpha^0 + \int_{T_0}^{T} \frac{Cp_\alpha(T')}{T'} dT' - Rln\frac{P_{sat}}{P_0} - \Delta S_{vap,\alpha}(T) \tag{2.11}$$

Because at phase change, we are at equilibrium *(*$\Delta G=\Delta H\text{-}T\Delta S=0$), we have:

$$\Delta S_{vap,\alpha}(T) = \Delta H_{vap,\alpha}(T)/T \tag{2.12}$$

Once you know H and S, you can easily calculate other state functions such as G or U.

Step 2: calculating mixture properties in ideal conditions. Once properties are established for pure compounds in ideal conditions, the next step is to model the behavior of the resulting ideal mixture. In ideal mixtures, the state variables such as U and H are additive (you just add the properties to get the property of the total mixture), while S requires calculating the entropy of mixing:

$$U_{L\ or\ V,tot} = \sum_\alpha U_{L\ or\ V,\alpha} \qquad H_{L\ or\ V,tot} = \sum_\alpha H_{L\ or\ V,\alpha} \qquad S_{L\ or\ V,tot} = \sum_\alpha S_{L\ or\ V,\alpha} - \sum_\alpha n_\alpha R \ln x_\alpha \tag{2.13}$$

with:

n_α: is the number of moles of component α.

G can be easily calculated form S and H ($\Delta G=\Delta H\text{-}T\Delta S$).

With mixtures, the other important stage is to calculate vapor-liquid-liquid-equilibriums (VLLE). VLLEs are important in countless modeling operations including distillations or extractions in chemical plants, but also in atmospheric and oceans modeling. In the ideal case (ideal gases/ideal solutions), this is fairly straightforward. Recall that for a component α to be at equilibrium across phases, the free energy of the overall system (G) must be at its minimum ($dG=0$). For phase equilibrium at a specific T and P, the only thing that can change is composition. The general expression for dG of a system with α components p phases can be written as:

$$dG = -SdT + VdP + \sum_P \sum_\alpha \mu_{p,\alpha} dn_{p,\alpha} = \sum_P \sum_\alpha \mu_{p,\alpha} dn_{p,\alpha} = 0 \text{ (Constant T and P)} \qquad (2.14)$$

If components are independent of each other, we have:

$$\left(\frac{\partial G}{\partial n_\alpha}\right)_{T,P,n_{\alpha\neq\beta}} = 0 = \sum_P \mu_{p,\alpha} \quad \rightarrow \quad \mu_{1,\alpha}=\mu_{2,\alpha} = \mu_{3,\alpha} \,.... \qquad (2.15)$$

For component α in a vapor liquid equilibrium (VLE), we have:

$$\mu_{L,\alpha} = \mu_{V,\alpha} \rightarrow \mu_{L,\alpha} = \mu_{L,\alpha}^0 + RTln\frac{f_{\alpha,L}}{f_{\alpha,L}^0} = \mu_{V,\alpha} = \mu_{V,\alpha}^0 + RTln\frac{f_{\alpha,V}}{f_{\alpha,V}^0} \qquad (2.16)$$

with:

$\mu_{L,\alpha}$: Partial molar Gibbs free energy / chemical potential of component α in the liquid phase (at the systems T and P). These two components are equivalent even though they are referred to with either name depending on the context.

$\mu_{V,\alpha}$: Partial molar Gibbs free energy / chemical potential of component α in the vapor phase (at the systems T and P). These two components are equivalent even though they are referred to with either name depending on the context.

$\mu_{L,\alpha}^0$ and $\mu_{V,\alpha}^0$: Chemical potential at a reference state in the liquid and vapor phase, respectively.

$f_{\alpha,L\, or\, V}$ and $f_{\alpha,L\, or\, V}^0$: fugacity of component □ in for the liquid or vapor phase and their corresponding reference fugacity.

Fixing either μ_α^0 or f_α^0 is arbitrary as the choice of the reference state is arbitrary. However, you cannot choose them *independently* of each other. Let's assume a reference state where the two phases are equilibrium (e.g. : $P_{sat,\alpha}$ and $T_{sat,\alpha}$):

$$\mu_{L,\alpha}^0 = \mu_{V,\alpha}^0 \rightarrow RTlnf_{\alpha,L}^0 = RTlnf_{\alpha,V}^0 \rightarrow f_{\alpha,L}^0 = f_{\alpha,V}^0 \qquad (2.17)$$

Substituting this into Equation 2.15, we have:

$$f_{\alpha,L} = f_{\alpha,V} \tag{2.18}$$

As you will see in a minute, this is a key law governing vapor liquid equilibria or vapor liquid, liquid equilibria. However, let's look at the case where the two phases are not at equilibrium at the reference state (e.g. a random T and P). There we have:

$$\mu^0_{L,\alpha} - \mu^0_{V,\alpha} = \frac{RTlnf^0_{\alpha,L}}{RTlnf^0_{\alpha,V}} \tag{2.19}$$

Again, substituting this into Equation 2.16 gives us

$$f_{\alpha,L} = f_{\alpha,V} \tag{2.20}$$

Now, let's define fugacity further by saying that:

$$f_{\alpha,L} = \varphi_{\alpha,L} x_\alpha P = \gamma_\alpha x_\alpha \, f^0_{\alpha,L} \tag{2.21}$$

$$f_{\alpha,V} = \varphi_{\alpha,V} y_\alpha P \tag{2.22}$$

where:
γ and φ are the activity and fugacity coefficients, respectively. Using $\varphi_L$or □ depends on the situation (as we will see).

γ and φ can depend on T, P and x_α or y_α (x or y depending on whether they are in the liquid or vapor phase, respectively). Therefore, we have not gained much. We can just show x_α or y_α explicitly. This gives us the general expression (applicable to all mixtures at any T and P):

$$\varphi_{\alpha,V} y_\alpha P = x_\alpha \gamma_\alpha \, f^0_{\alpha,L} \tag{2.23}$$

Let's define $f^0_{\alpha,L}$, by setting the reference state as the state where we have pure □ at T and P:

$$f^0_{\alpha,L} = f_{\alpha,L}(T, P, x_\alpha = 1) = \varphi_{\alpha,L} P = \varphi^{sat}_{\alpha,L} P_{sat} \frac{\varphi_{\alpha,L} P}{\varphi^{sat}_{\alpha,L} P_{sat}} \tag{2.24}$$

where:
P_{sat}: is the saturation pressure for α at T
φ^{sat}_α: is the fugacity coefficient for α at T and P_{sat}

By manipulating Maxwell relations, you can show that φ_α depends on the partial molar volume of α ($\bar{v}_\alpha$):

$$\varphi_\alpha = exp\left[\int_0^P \frac{\bar{v}_\alpha}{RT} - \frac{1}{P}\, dP\right] \tag{2.25}$$

Therefore:

$$\frac{\varphi_\alpha}{\varphi_\alpha^{sat}} = exp\left[\int_0^P \frac{\bar{v}_\alpha}{RT} - \frac{1}{P}\, dP - \int_0^{P_{sat}} \frac{\bar{v}_\alpha}{RT} - \frac{1}{P}\, dP\right] = \frac{P_{sat}}{P} exp\left[\int_{P_{sat}}^P \frac{\bar{v}_\alpha}{RT}\, dP\right] \tag{2.26}$$

Combining equations 2.26 and 2.24:

$$f_{\alpha,L}^0 = \varphi_{\alpha,L}^{sat} P_{sat} exp\left[\int_{P_{sat}}^P \frac{\bar{v}_\alpha}{RT}\, dP\right] \tag{2.27}$$

The exponential of the volume integral is known as the *Poynting Factor*. Our general equation then becomes (using Equation 2.23):

$$\varphi_{\alpha,V}\, y_\alpha P = x_\alpha \gamma_\alpha\, \varphi_{\alpha,L}^{sat}\, P_{sat}\, exp\left[\int_{P_{sat}}^P \frac{\bar{v}_\alpha}{RT}\, dP\right] \tag{2.28}$$

There are several approximations that can be made:

- For an ideal solution γ=1 (Assumption 1).
- For an ideal gas φ=1 (Assumption 2).
- For negligible changes in molar volumes (incompressible liquids) and/or low pressures, the *Poynting Factor* is close to 1. This is of course the case for ideal solutions (Assumption 3).

If all three apply (i.e. in ideal conditions), we get Raoult's law:

$$y_\alpha P = x_\alpha\, P_{sat} \tag{2.29}$$

This can be used to fully calculate VLEs in ideal conditions.

Step 3: calculating mixture properties in real conditions.

The methods used to calculate the properties of real solutions are especially complicated and we will only provide an overview of the two main approaches. Equation 2.28 applies to all real solutions and thus is used as a starting point. Of the three assumptions described above, assumption 1 is almost never true, assumption 2 is valid for most chemical systems at moderate pressures, and assumption 3 is often true except for very high pressures (especially near the critical point).

Therefore, the most important parameter to determine is □ as it will be needed for most situations. This has led to the development of a series of models called activity coefficient models (1st approach). These models function based on the estimate of the excess molar Gibbs free energy ($\bar{G}_E$), which is the deviation of the molar Gibbs energy from ideality:

$$\bar{G} = \bar{G}_{Id} + \bar{G}_E \tag{2.30}$$

These quantities are generally estimated based on the concentration of each component (as well as T in most cases):

$$\bar{G}_E = f(x_\alpha, x_\beta, \dots, T) \tag{2.31}$$

The next step is then simply to relate this to activity. From Equation 2.14 we can see that, since μ_i is the partial molar gibbs free energy ($\overline{G_\imath}$) for component *i*, then we have:

$$RTln\gamma_\alpha = \bar{G}_\alpha^E = \frac{\partial}{\partial n_\alpha}[(\textstyle\sum_k n_k)(\bar{G}_E)] = \frac{\partial}{\partial n_\alpha}\left[(\textstyle\sum_k n_k)\big(f(x_\alpha, x_\beta, \dots, T)\big)\right] \tag{2.32}$$

With this relation, we can define various functions $f(x_\alpha, x_\beta, \dots, T)$ to calculate γ_α, and several of these semi-empirical exist and are used extensively. A famous relation is called NRTL (Non-Random Two-Liquid) and functions on a series of binary parameters that have been measured experimentally for two component mixtures. Another model is called UNIQUAC (Universal Quasi Chemical) which is also based on semi-empirical parameters but these parameters are based on functional groups and therefore do not require experiments with every set of molecules.

Having excess Gibbs free energies allows us to calculate other thermodynamic properties that deviate from ideality in solution:

$$\bar{V}_{E,L} = \left(\frac{\partial\, \bar{G}_{E,L}}{\partial P}\right)_T \tag{2.33}$$

$$\Delta\, \bar{S}_{E,L} = -\left(\frac{\partial\, \bar{G}_{E,L}}{\partial T}\right)_P \tag{2.34}$$

$$\Delta\, \bar{H}_{E,L} = \Delta\, \bar{G}_{E,L} + T\Delta\, \bar{S}_{E,L} \tag{2.35}$$

So this covers Assumption 1, but what if Assumptions 2 and 3 do not hold? If this is the case, we need a generalized set of equations that can model *both* the behavior in the liquid and gas phase. These equations are known as Equations of State (EOS, recall part 2 of this course). This is the second approach. In activity coefficient model approaches, we started from excess thermodynamic state properties. With EOS, we start with volumetric properties and arrive at excess properties. The general EOS structure is:

$$P = f(R, T, V, z_\alpha, z_\beta, \ldots) \tag{2.36}$$

with:

$z_i, z_j, \ldots$: molar fractions of components $i, j, \ldots$ for the total mixture.

Once we have this, we can use Equation 2.25 to obtain fugacity coefficients:

$$\varphi_{\alpha,L} = exp\left[\int_0^P \frac{\bar{v}_{\alpha,L}}{RT} - \frac{1}{P}\, dP\right] \tag{2.37}$$

$$\varphi_{\alpha,V} = exp\left[\int_0^P \frac{\bar{v}_{\alpha,V}}{RT} - \frac{1}{P}\, dP\right] \tag{2.38}$$

Where:

$$\bar{v}_{\alpha,L\,or\,V} = \left(\frac{\partial V_{L\,or\,V}}{\partial n_\alpha}\right)_{T,P,n_{\beta\neq\alpha}} \tag{2.39}$$

Since some most EOS do not give *V=f(P,T…)* but *P=f(V,T…)*, Maxwell's relations can once again be manipulated to give these more convenient expressions:

$$RT\ ln\varphi_{\alpha,L\,or\,V} = \int_{V_{L\,or\,V}}^{\infty}\left[\left(\frac{\partial P}{\partial n_\alpha}\right)_{T,P,n_{\beta\neq\alpha}} - RT/V_{L\,or\,V}\right]dV - RT\ ln\frac{PV_{L\,or\,V}}{NRT} \tag{2.40}$$

How do you choose between the two approaches (activity coefficient models and EOS)? Well, there are some basic rules. Apolar mixtures (e.g. hydrocarbons) and those close to their critical point are better modeled by EOS models. In other cases, it is preferable to model the system using an activity coefficient model. However, in the end it always depends on how reliable the available model and parameters are for your given mixture.

We are **finally** done with VLE calculations and with the overview of thermodynamic properties. All these thermodynamic relations form another series of equations that we can add to all those we have to solve. They can be represented by the matrix (for stream a):

$$\boldsymbol{Th_a}\left(T_a, P_a, C_{p,a}, h_a, z_{\alpha,a}, z_{\beta,a}\,\ldots\right) = 0 \tag{2.41}$$

iii. Unit models. The equations governing a given unit i (see Fig. 2.4A) can be divided into 4 categories:

- Mass balances
- Energy balances
- Momentum balances
- Unit equations

Mass and energy balances are defined by the basic structure of such balances:

$$In - Out = Accumulation + Source \tag{2.42}$$

In a continuous system there is never accumulation, so that term disappears. For mass and energy balances, there is no source, so the equation becomes:

$$In - Out = 0 \tag{2.43}$$

Momentum balances are only used in very specialized units (usually involving computation fluid dynamics), which we won't address here.

As their name indicates, unit equations are equations that are specific to each unit. They almost always introduce extra variables, which are referred to as unit parameters. One example could be the introduction of an equation describing energy losses in a pump (as dissipated heat). Such an equation would involve an efficiency term (the parameter, for this example) describing the deviation in reversible needed and actual electrical work needed.

$$W_{rev} = \eta \, W_{el.} \tag{2.44}$$

With:

η: the efficiency

W_{rev} and $W_{el.}$: The reversible and electrical work, respectively.

Overall, these equations lead to another set of equations, which we will refer to with the Matrix $\boldsymbol{U}_{\text{i}}$ (for unit i), which depends on the relevant stream variables and the associated unit parameters:

$$\boldsymbol{U_i}\big(\overbrace{T_a, P_a, h_a, \dots,}^{\text{Relevant stream variables}} \underbrace{P_{i,1}, P_{i,2} \dots}_{\text{Unit parameters}}\big) = 0 \tag{2.45}$$

With all of these categories of equations defined, this leads us to being able to build an overall set of equations into a final matrix **F**:

$$\boldsymbol{F}\begin{bmatrix} \boldsymbol{S_a}\big(m_a, P_a, h_{a,\alpha}, x_{\alpha,a}, x_{\beta,a} \dots\big) \\ \boldsymbol{S_b}\big(m_b, P_b, h_{b,\alpha}, x_{\alpha,b}, x_{\beta,b} \dots\big) \\ \dots \\ \boldsymbol{Th_a}\big(T_a, P_a, C_{p,a}, h_a, z_{\alpha,a}, z_{\beta,a} \dots\big) \\ \boldsymbol{Th_b}\big(T_b, P_b, C_{p,b}, h_b, z_{\alpha,b}, z_{\beta,b} \dots\big) \\ \dots \\ \boldsymbol{U_i}\big(T_a, P_a, h_a, \dots, P_{i,1}, P_{i,2} \dots\big) \\ \boldsymbol{U_j}\big(T_b, P_b, h_b, \dots, P_{j,1}, P_{j,2} \dots\big) \\ \dots \end{bmatrix} = 0 \tag{2.46}$$

In **F**, the number of lines is the total number of equations, and the number of columns is the total number of variables. The system can be solved if:

1. The matrix is square (the number of equations equals the number of variables).
2. The equations are independent (i.e. you must be able to permute the lines and columns of the matrix to place a nonzero element on each of the diagonal positions).

If you have too many equations, the system is over-specified. If you don’t have enough or have included dependent equations, you need to add specification equations to make the system solvable.

2.3 Heat integration and renewable energy

Often times, an energy system cannot be properly understood unless some form of heat recovery has been performed. In fact, without heat recovery, most of our refineries (which are still one of our principal primary sources of energy) would be much less efficient than they are now, and the cost of liquid fuels and commodity chemicals would be much higher. Heat recovery is important because without it, several heat production systems would seem incredibly inefficient and un-exploitable, when in fact they are attractive solutions used today.

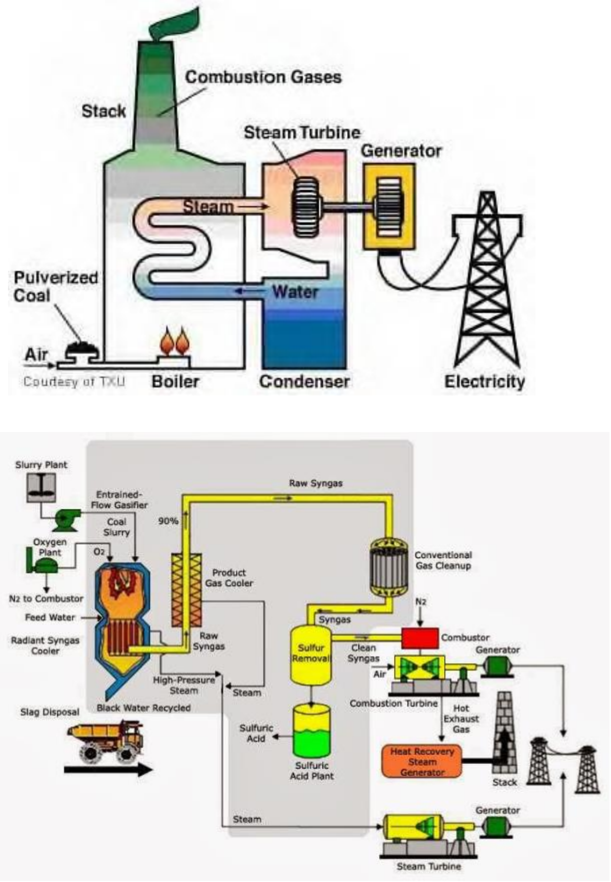


Fig. 2.7 Conversion of coal to electricity: **(A)** in a pulerized coal plant and **(B)** in a an integrated gasificiation combined cycle (IGCC) plant.

One example is coal gasification, where coal is converted to methane at high temperatures. Without heat recovery, this step would make the process much too energy intensive. With heat recovery, converting coal to syngas leads to an overall process that is more efficient. This is because gas can be more efficiently converted to electricity than solid coal, because gas is converted to electricity directly in a gas turbine, whereas pulverized coal has to be burned and used to heat steam for a steam turbine. Typically, a conventional coal plant can reach efficiencies of around 35-38%. An integrated gasification combined cycle plant (IGCC) can reach 40-45%[1]. This may not seem like much, but it is huge when you consider the amount of coal that is burned each day in the world. To reach this efficiency, several heat recovery strategies are used including transferring the heat of the hot syngas to steam and using this steam in a Rankine steam cycle to produce electricity. These recovery strategies introduce several pieces of equipment that are the main tools of heat integration: heat exchangers and Rankine steam cycles. Of course, introducing these extra unit operations and extra pieces of equipment into a process lead to additional costs making the plant usually about 30% more expensive.

This illustrates the typical tradeoff in heat integration. It is often present in modern complex processes and can introduce significant improvements in energy efficiency but it often leads to increases in capital costs. Regardless of this tradeoff, heat integration effects must be accounted for to accurately compare sustainable energy systems. To do so, we will introduce a systematic method to calculate the *minimum* heating and cooling requirements for a system that is optimally integrated. We will also be able to estimate

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[1] http://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/compare

the *minimum* size of the heat exchanger network that is needed to support this integration. The method is called “pinch analysis”.

2.4 Pinch analysis

As explained above, in this chapter, we will introduce the *pinch analysis*, which allows us to quickly calculate the minimum cooling and heating requirements of any process assuming perfect heat integration.

A simple example

The easiest way to introduce this method is to take you through an example using a given process. Let's begin with a very simple process that includes a feed stream that is heated, reacts in a reactor and is cooled:

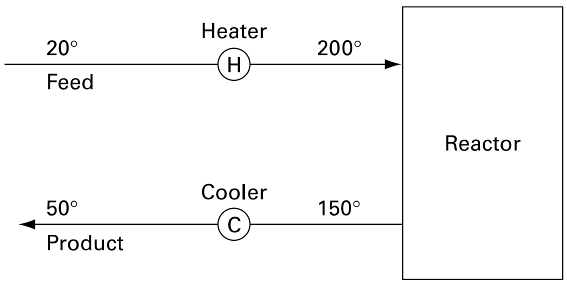

Fig. 2.8. A simple process flowsheet.

The streams have the following thermodynamic properties (for simplicity, we assume that the Cp is constant):

	Mass flowrate W *(kg/s)*	*Specific heat capacity* C_P *(kJ/kgK)*	*Heat capacity flowrate* CP *(kW/K)*	*Initial (supply) temperature* T_S *(°C)*	*Final (target) temperature* T_T *(°C)*	*Heat load* H *(kW)*
Cold stream	0.25	4	1.0	20	200	−180
Hot stream	0.4	4.5	1.8	150	50	+180

Table 2.1. Data associated with our process.

It is pretty obvious that in the process above, we can lower some of the heat needs by introducing a heat exchanger:

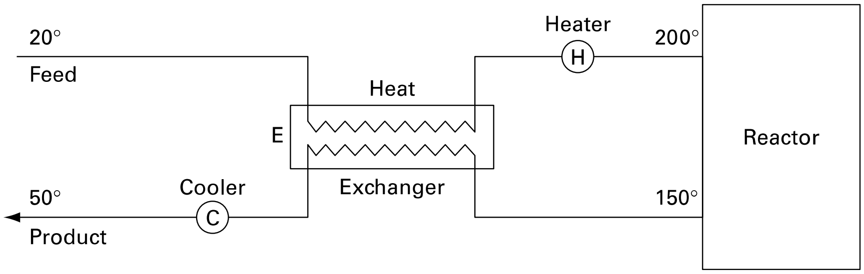

Fig. 2.9. Our simple process with a heat exchanger.

The question here is: how much heat can we recover? Intuitively, you probably realize that this is limited by temperature and heat load. You cannot heat a stream from 90 to 100°C with a stream that needs to cooled from 80°C to 60°C. Also, you cannot heat 1 kg of water at 100°C with 1 g of water at 200°C. The heat loads have to match. As you will see, a good way to represent and solve this problem is to construct a Temperature (T) vs. heat load (Q) diagram. As you recall, the best way to calculate heat load for streams in a continuous system is to use enthalpy changes. As you recall, enthalpy can be related to temperature with *Cp*:

$$Q = \Delta H = \int_{T_1}^{T_2} Cp\, dT = Cp(T_2 - T_1) \text{ (for a constant Cp)} \qquad (2.47)$$

Let's place our two streams from Fig. 2.8 and 2.9 on a T-Q diagram. But how can we do this? Though their temperature is fixed, only their *change* in enthalpy matters. Their absolute enthalpy does not (enthalpy is always calculated with respect to a reference anyway). Therefore, enthalpy changes can be plotted anywhere on the T-Q diagram (Fig. 2.10) provided that the change in enthalpy remains the same and that it runs between the same supply and target temperatures.

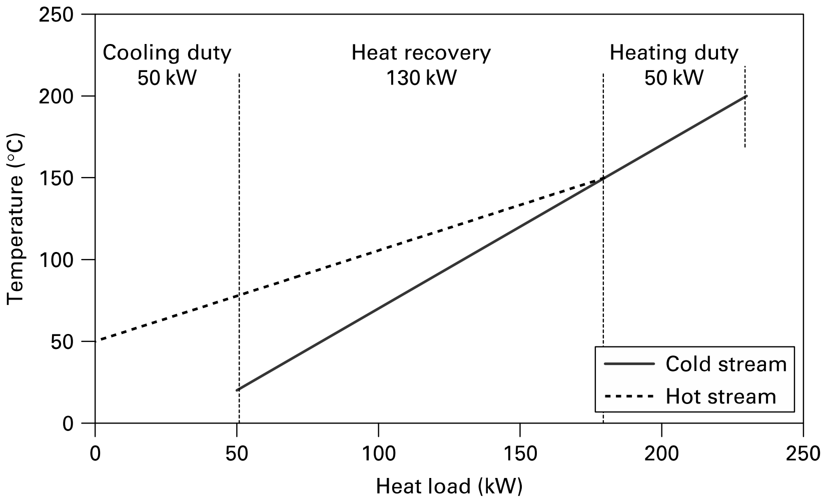

Fig. 2.10. A T-Q diagram for our simple process.

In practice, this means you can freely "slide" your T-Q curve horizontally on the graph. Let's slide both curves horizontally so that they touch each other without crossing (Fig. 2.10). What we have just done is represent heat exchange. The section where the two curves overlap represents the potential for heat recovery. The stream that needs to be cooled (the hot stream) has a higher temperature than the stream that needs to be heated (the cold stream). In addition, within this zone of overlap, the same heat is required to heat the cold stream and cool the hot stream. Therefore, heat exchange can occur. Outside of the overlapping area, you have the cold stream that is not covered by the hot stream, which means that, for this part of the process, an external source of heat will have to be found at temperatures above that of the cold stream. This heating load is referred to as the *heating duty*. Conversely, there is an area, in which the hot stream is not above the cold stream. Therefore, you will require an external cooling source at a temperature below the hot stream in this zone. This is referred to as the *cooling duty.*

You can see that if you slid the two streams further so that they crossed, you would reduce the cooling and heating duties. You would also create zones where heat exchange was supposed to occur, from a stream at a colder temperature to a stream at a hotter temperature, which is physically impossible. Furthermore, even the heat exchange represented by Fig. 2.10 is actually a limiting case that is not possible in practice. Though most of the heat exchange occurs with a sufficient difference in temperature, heat exchange where the two curves join is occurring at ΔT=0. This is only possible given an infinitely long time for heat exchange (or an infinitely large heat exchanger). In practice, there has to be a minimum temperature difference (ΔT_{min}) at the place where the hot and cold streams are the closest to each other; the spot that is referred to as the *pinch point*. Setting ΔT_{min}=20°C, a reasonable value, leads to the T-Q diagram shown in Fig. 2.11.

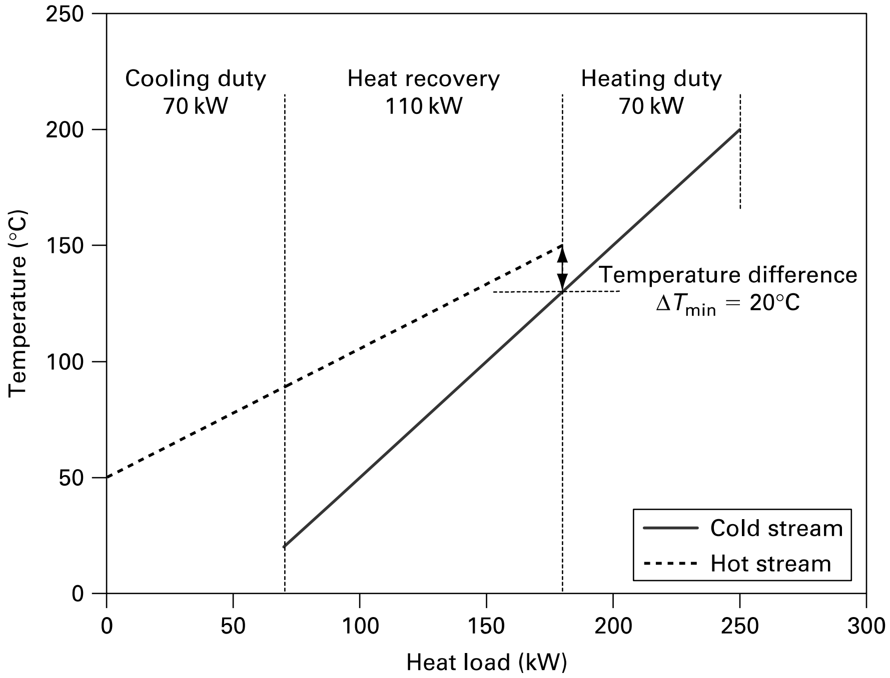

Fig. 2.11. A T-Q diagram for our simple process with ΔT_{min}=20°C.

Complex systems: composite curves

You might think that this was only feasible because it was a simple system. However, the exact same strategy can be used if you have dozens or even hundreds of streams by producing hot and cold *composite curves*. To handle multiple streams, we simply add together the heat loads (or Cp flows) over relevant temperature intervals. This approach is demonstrated graphically in Fig. 2.12 for the hot composite curve. These relevant temperature intervals are defined by areas that have a unique overlap of streams. For example, in Fig. 2.12, starting with T_1, we see that until we reach T_2 we have a single stream (with Cp=B). This is our first T-interval. From T_2, we have streams with Cp=A, Cp=B and Cp=C and this remains the case until we reach T_3. This is our second temperature interval, and so on.

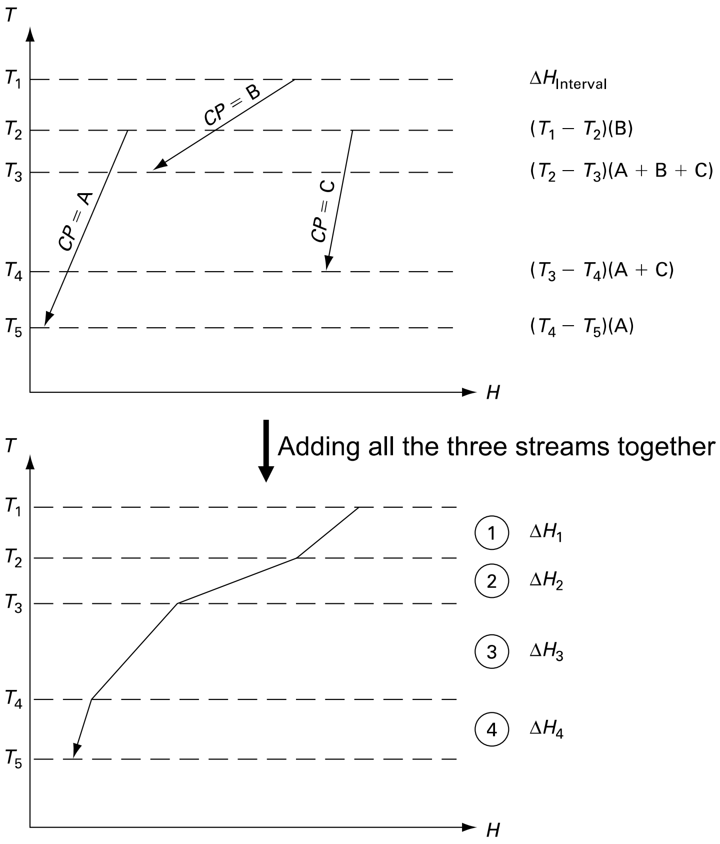

Fig. 2.12. Construction of the hot composite curve.

Once added up, we have produced a unique composite curve for all hot streams. Of course, we can do the same for cold streams as well. An example of the resulting composite curve system is shown in Fig. 2.6.

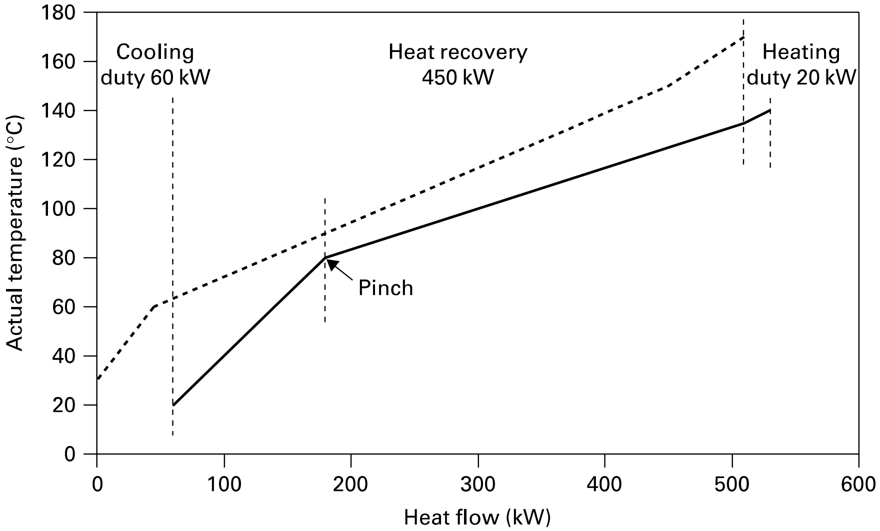

Fig. 2.13 Hot and cold composite curves for a multi-stream system.

The heat cascade and the grand composite curve

The method that we just went through works very well graphically, but ideally, we would like to be able to do this computationally using a systematic method. This approach is called *solving the heat cascade*. The basic assumption is that you have the following information in the form of a thermal stream (***Ts***) matrix resulting from your systems analysis:

$$\boldsymbol{Ts} = \begin{bmatrix} T_{i,in} & T_{i,out} & Q_i \\ T_{j,in} & T_{j,out} & Q_j \\ \dots & \dots & \dots \end{bmatrix} \tag{2.48}$$

Where:

$T_{i,in}$ and $T_{i,out}$ are the inlet and outlet temperatures of unit *i*.

Q_i is the heat received (positive) or removed (negative) from unit *i*. For a continuous process, it can be computed with the enthalpy difference ($Q_i = H_{i,out} - H_{i,in}$).

Hot and *cold* streams can be identified by whether or not Q_i is negative or positive. For computing the heat cascade, the procedure is simplified by correcting the stream temperatures by $\frac{\Delta T_{min}}{2}$:

$$T_i^* = T_i + \frac{\Delta T_{min}}{2} \quad \text{for } Q_i > 0 \text{ (cold streams)} \tag{2.49}$$

$$T_i^* = T_i - \frac{\Delta T_{min}}{2} \quad \text{for } Q_i < 0 \text{ (hot streams)} \tag{2.50}$$

ΔT_{min} can be a different value for each stream, and can be optimized to both maximize heat recovery and minimize cost. For an initial estimate, you can use values for ΔT_{min} of 8°C for gaseous streams, 4°C for liquid streams, 2°C for evaporating or condensing streams and 25°C for reacting streams.

The corrected version of Fig. 2.14 (with the new temperatures) would be:

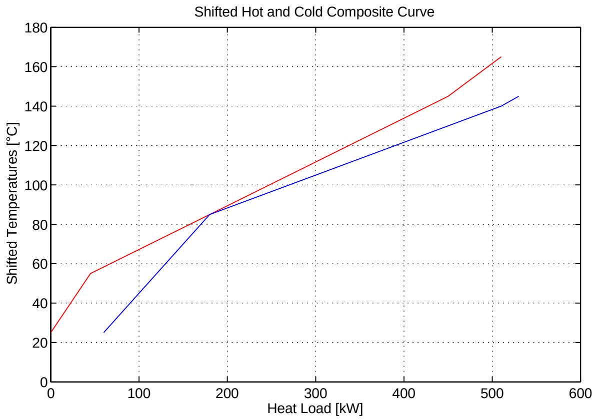

Fig. 2.14. T-shifted hot and cold composite curves for the multi-stream system shown in Fig. 2.13.

As we assumed in Equation 2.47, we will continue to assume constant *Cp* values. These values can be calculated from Q_i:

$$Cp_i = \frac{|Q_i|}{|T_{i,in} - T_{i,out}|} \tag{2.51}$$ [2]

At this point, you can use the following matrix to describe the system:

$$\boldsymbol{Ts'} = \begin{bmatrix} T^*_{i,in} & T^*_{i,out} & Cp_i \\ T^*_{j,in} & T^*_{j,out} & Cp_j \\ \dots & \dots & \dots \end{bmatrix} \tag{2.52}$$

We can then define the temperature intervals that we will use. These are found by identifying all the unique inlet and outlet temperatures in our system. These unique temperatures will then be the basis for forming the temperature intervals used in the heat cascade (listed in matrix $\boldsymbol{T_{int}}$):

$$\boldsymbol{T_{int}} = \begin{bmatrix} T^*_1 & T^*_2 \\ T^*_2 & T^*_3 \\ \dots & \dots \end{bmatrix} \text{ with } T^*_1, T^*_2, T^*_3 \dots = \text{all unique inlet or outlet temperatures} \tag{2.53}$$

Now, we are ready to calculate the heat cascade. We will start with the highest temperature and *cascade* down. First, we have to identify all units *i* that operate within each temperature increment. For temperature interval *k*, we can set the following rule for identifying relevant units (or in this case relevant "lines" in $\boldsymbol{Ts'}$, which we will call $\boldsymbol{T_{rel,k}}$):

$$\boldsymbol{T_{rel,k}} = \boldsymbol{Ts'} \text{ for which } \boldsymbol{Ts'}(i, high) > \boldsymbol{T_{int}}(k,2) \;\&\; \boldsymbol{Ts'}(i, low) < \boldsymbol{T_{int}}(k,1) \tag{2.54}$$

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[2] At this point, there can be a number of problems if you have a phase change, because for this operation, $T_{in} = T_{out}$. To address this, there are several options when constructing a heat cascading code. The first would be to specifically detect and treat phase changes separately throughout the computational process. The second option (which is easier), is to similarly detect phase changes and change the outlet temperature by a vary small increment (e.g. $T^*_{i,out} = T^*_{i,out} + \Delta T_{min}/1000$). Using these values to calculate *Cp* and $\boldsymbol{Ts'}$ will approximate a phase change quite accurately and allow you to identify this as a regular temperature increment.

Where $\boldsymbol{Ts}'(i, high\ or\ low)$ designates the high or low temperature of line i in $\boldsymbol{Ts}'$.

Then, we can sum up all *Cp* values in $\boldsymbol{T_{rel,k}}$, to calculate the relevant heat for interval *k*: (Q_k):

$$Q_k = \sum_i \left[\boldsymbol{T_{rel,k}}(i,3)\left(-\frac{Q_i}{|Q_i|}\right)\right](\boldsymbol{T_{int}}(1,k) - \boldsymbol{T_{int}}(2,k)) \qquad (2.55)$$

This heat is the surplus for interval k and thus it can be *cascaded* down to the following intervals. To do this we calculate the cumulative heat $Q_{c,k}$ as we move down in temperature intervals (i.e. we *cascade* the heat):

$$Q_{c,k} = \sum_1^k Q_k \qquad (2.56)$$

The lowest value of $Q_{c,k}$ is the pinch point. We only cascade positive heat (heat flows from high to low temperature not the opposite), so we need all the cascaded heat (i.e. cumulative heat) to be positive at all time. Of course, since only the difference in heat matters, we can add a constant to all heat. We will add the value corresponding so that the lowest cascaded heat is zero:

$$Q'_{c,k} = Q_{c,k} + \left|\min(Q_{c,k})\right| \qquad (2.57)$$

As you may have guessed, the value at which $Q'_{c,k}$= 0 is the pinch. What this mean is that no heat cascades through the pinch. This is *the* golden rule of pinch analysis. A poorly integrated process usually has heat transferring through the pinch. In other words, they are using parts of the process that require heating to heat parts of the process that require cooling. This increases both the heating and cooling duties of the process.

The grand composite curve $\boldsymbol{GCC}$ is defined as:

$$\boldsymbol{GCC} = \begin{bmatrix} \boldsymbol{T_{int}}(1,1) & \left|\min\left(Q_{c,k}\right)\right| \\ \boldsymbol{T_{int}}(1,2) & Q'_{c,1} \\ \boldsymbol{T_{int}}(2,2) & Q'_{c,2} \\ \dots & \dots \\ \boldsymbol{T_{int}}(n,2) & Q'_{c,n} \end{bmatrix} \quad \text{for } n \text{ T intervals} \qquad (2.58)$$

The minimum heating duty is defined as:

$$MER = \left|\min\left(Q_{c,k}\right)\right| \tag{2.59}$$

This is the heating duty often called the minimum energy requirement or *MER*. The minimum cooling duty (*MCR*) is:

$$MCR = Q'_{n,2} \tag{2.60}$$

The grand composite curve that would result from the process shown in Fig. 2.13 and 2.14 is shown in Fig. 2.15.

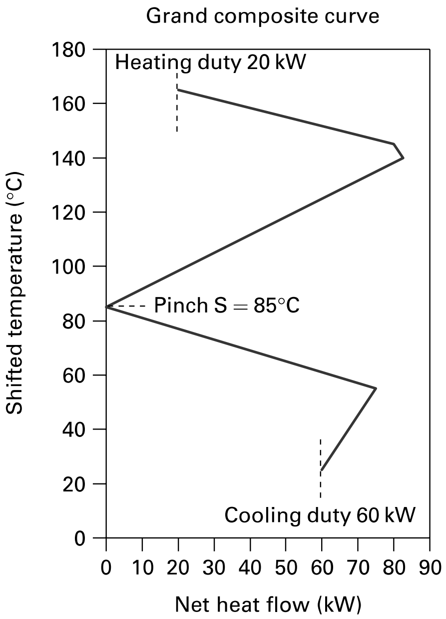

Fig. 2.15 Grand composite curve for the previously shown multi-stream system (see Fig. 2.13).

To fulfill the hot utility, you need to provide one or more streams that can fit above the GCC and above the pinch. Similarly, you need to provide one or more streams that can fit under the GCC below the pinch to fulfill a cold utility. As an example, let's assume we use a stream of gas coming from a burner at 400°C (assuming a linear Cp is accurate even over a large change in temperature) that needs to be cooled to 60°C before it is released in the atmosphere. To provide the cold utility, let's assume we have a stream of cooling water that is provided at 15°C and can be released at a temperature no higher than 25°C. The resulting curves can be added to the GCC:

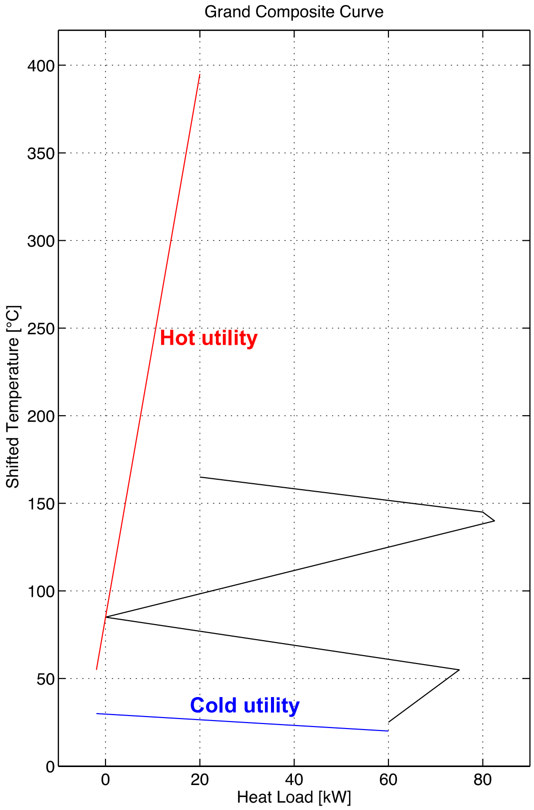

Fig. 2.16 Grand composite curve for the previously shown multi-stream system with hot and cold utilities.

You may have noticed that the hot and cold utilities extend the heat load negatively. This is because the cooling requirement of the hot utility (which, in this case, cannot be avoided) extends below the pinch and therefore requires a slight increase in the cooling utility. You might also notice that both of these curves have been temperature-shifted. This is the case because once they are added to the process, the hot and cold utilities can be considered part of the hot and cold streams, respectively. In fact, they can be integrated into the process and into the GCC, which can be represented in the following way:

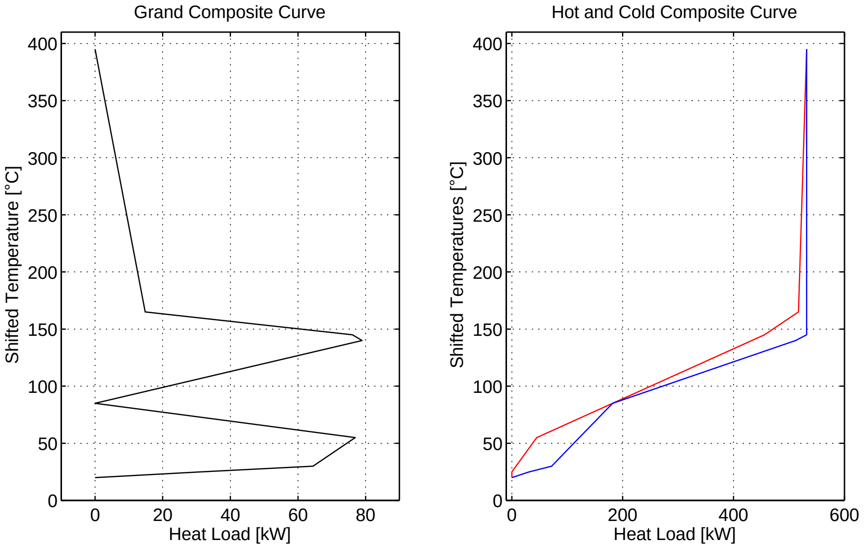

Fig. 2.17 Grand composite curve and composite curves with integrated hot and cold utilities.

Unsurprisingly, we have successfully removed any heating and cooling requirement and now have a fully self-sufficient set of streams!

These newly formed composite curves can be used to calculate the minimum heat exchanger area by assuming that each composite curve is one long single stream that can exchange with the other composite curve. It can be divided into segments that correspond to constant *Cp* (Fig. 2.18).

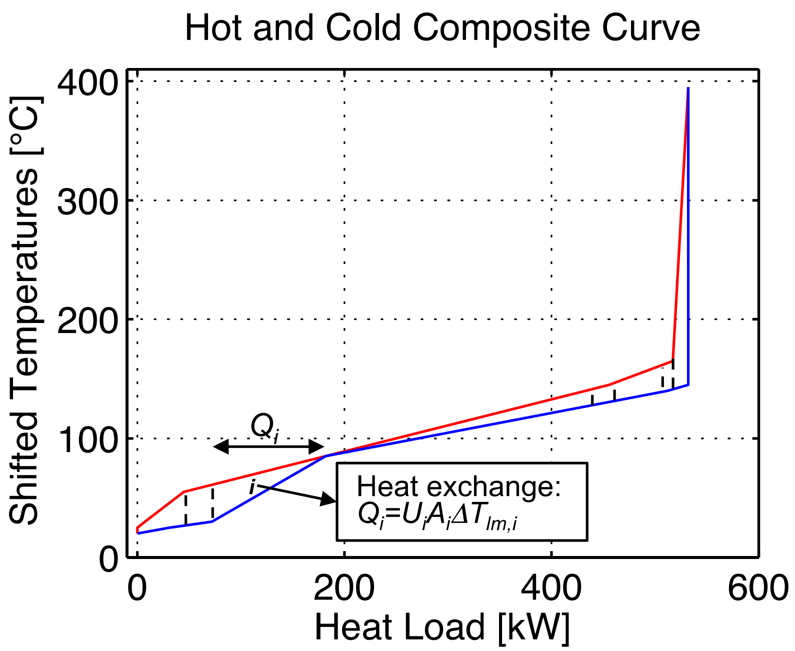

Fig. 2.18. Cutting the composite curves into segments to calculate the minimum heat exchanger area (8 segments in this example). The heat exchanged in a segment *i* is shown as a function of heat transfer coefficient (U_i), heat exchanger area (A_i) and the logarithmic mean temperature difference ($\Delta T_{lm,i}$).

Once the segments are defined, the minimum heat exchanger area (A_{min}) for the whole system can be estimated:

$$A_{min} = \sum_i^{n_{seg.}} A_i = \sum_i^{n_{seg.}} \frac{Q_i}{U_i \Delta T_{lm,i}} \tag{2.61}$$

where:

A_i : the heat exchanger area for segment *i*

Q_i: the heat exchanged

U_i : heat transfer coefficient for segment *i*

$\Delta T_{lm,i}$: Log mean temperature difference $\Delta T_{lm,i} = \frac{(T_{in,hot} - T_{out,cold} + \Delta T_{min}) - (T_{out,hot} - T_{in,cold} + \Delta T_{min})}{\ln\left(\frac{T_{in,hot} - T_{out,cold} + \Delta T_{min}}{T_{out,hot} - T_{in,cold} + \Delta T_{min}}\right)}$

2.5 Life Cycle Assessment

Modeling a process or other forms of production or conversion often gives you an idea about the economics, energetic efficiency or even sustainability of that particular process. However, this is often an incomplete picture for truly evaluating different product and process choices in terms of sustainability. Whether or not a process is sustainable is often a complex question, which cannot be answered by focusing too narrowly on a single product or process. For example, driving an electric car might seem more sustainable than driving a gasoline powered car but what if all the electricity used to charge that car is produced in a coal-fired power plant? Electric production using solar power might seem sustainable, but what if it is used to replace a hydropower plant, and it requires transporting solar panels by truck over long distances to a remote location every two years due to the panels short lifetime. To answer these questions, a method called *Life Cycle Assessment* (LCA) was developed. This method looks at the entire life cycle of a product. There are two forms of LCA, the first is called *Cradle To Grave*, which deals with a product's life cycle all the way to its disposal. This is important if you are comparing two different alternatives. For example, if you are comparing electric and gasoline vehicles, LCA is useful as the battery disposal costs can lower the sustainability of the electric vehicle. The second form is called *Cradle To Gate*, which deals with a product up to its delivery. This is less broad, but can be useful for comparing two production processes for identical products e.g., two bioethanol plants). In such cases, the use and disposal phase will be identical, and therefore not add anything to the analysis.

LCA is generally described as having three phases: Goal and Scope Definition, Life Cycle Inventory (LCI), Life Cycle Impact Assessment (LCIA).

Goal and Scope Definition. During this phase, the *functional unit* is defined. This is the quantity of product or action that will be the basis for and will be used to normalize all the numbers produced. Examples of functional units could include: *1 MW of* CH_4 *produced*, *1 km driven*, *1 car used for its entire lifetime*, etc. This phase will also be used to set the scope and boundaries of the study (e.g. whether the study is limited geographically, whether it will go to the product's grave or gate, what the assumptions are, etc.). At this stage, allocation methods are also defined. This refers to the procedure of allocating the impact of a given unit that is only partially used by the product. An example could be the impact of mining ruthenium in a catalyst, which is mined simultaneously with other platinum group metals such as platinum, palladium, rhodium, etc. Allocation rules answer the question: how do you allocate the mining effects between the three metals?

Life Cycle Inventory (LCI). This phase is the one that would include the earlier described systems modeling (Section 2.2). Here you are basically building a model or inventory[3] that accounts for all inputs and outputs (in LCA, these are sometimes referred to as *exchanges*). Inputs or outputs can include quantities that will link to other inventories, which are usually referred to as *activities* or, if they are basic enough, as *intermediate exchanges* in LCI. An example of such an activity could be *130 kg of*

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[3] The word inventory used here designates a simple model where all inputs and outputs are linearly correlated

aluminum at the production site (Fig. 2.19). You will need to link this input to two intermediate exchanges: a transportation activity and an activity describing the production of aluminum (or aluminum at the foundry). Each of these activities has a functional unit that you use to link it to your global process. For transportation, the functional unit could be something like *1 kg transported freight by a medium truck over 1 km*. For aluminum production, the functional unit would be something like *1 kg of aluminum at foundry (Germany)* (indicating how far it would have to be transported). All these activities will have a list of exchanges that will include some *intermediate* but also some *elementary exchanges*. *Elementary exchanges* are the final exchanges with the environment and can be categorized in three areas: (1) land use, (2) resources consumed and (3) emissions (to land, water or the atmosphere). The LCI is done once you only have a list of these three types of elemental exchanges. Therefore, you keep adding activities, within the boundaries set by your *Goal & Scope,* until you only have a list of elemental exchanges. As you may have guessed, each of these added activities is itself the result of an LCI. Since you are not expected to build an LCI for every single activity or intermediate exchange, you generally use an LCI database that already contains inventories. One such database is Ecoinvent® which is one of the most commonly used databases. The final result of your LCI is an overall inventory of elemental exchanges. This will serve as the starting point for your LCIA.

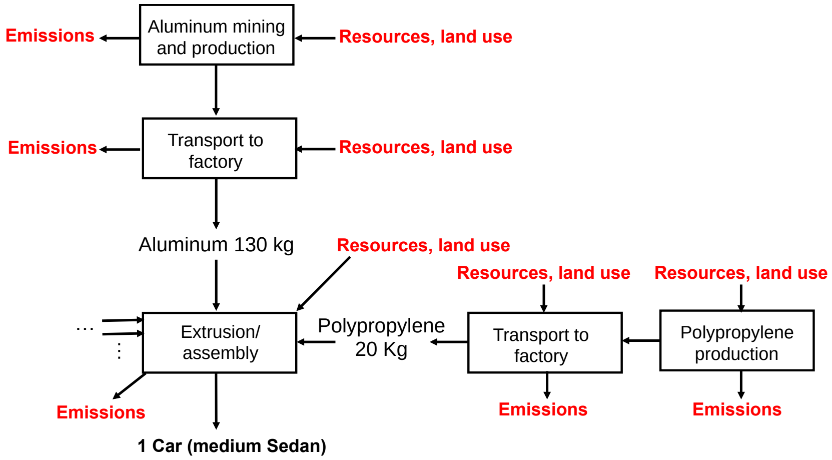


Fig. 2.19. Example of a (grossly incomplete) LCI of a car. Each box represents an activity, and is linked by a functional unit. The result is a list of resource and land use as well as emissions.

Life Cycle Impact Assessment (LCIA). The impact assessment phase's goal is to translate the inventory of elemental exchanges representing various forms of land use, consumed resources and emissions into a single or multiple measures of environmental impact/damages. The main difficulty is comparing very different exchanges with the environment into a single impact. For example, how do you compare 1 kg of ore extraction (resource) with 1 kg of CO_2 emitted to the atmosphere? This is what the LCIA tries to do. The generalized procedure is (see also Fig. 2.20):

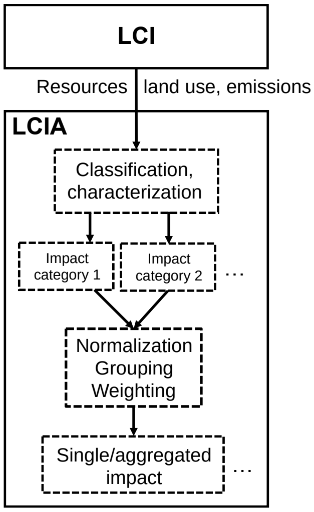


Fig. 2.20. General scheme of the LCIA procedure.

- Classification: The various elemental exchanges are grouped into their impact categories. These categories are generally linked to a particular physical phenomenon such as global warming potential (GWP), ecotoxicity, etc.
- Characterization: The calculation of the overall impact within that category. Here, characterization factors are used to calculate the category’s impact from the exchanges classified as being in that category. Since the categories are based on physical phenomena, the characterization factors are similarly based on physical relations. For example, GWP characterization factors are calculating based on the radiative forcing values of known greenhouse gases.

Note: In practice, these first two steps of LCIA are accomplished at once by using a multiplication vector (or characterization vector ***C****) that contains a characterization factor for elemental exchanges (e.g. that multiplies the LCI vector (****L)*** *containing all exchange values). For example, for calculating global warming potential after 100 years from* ***L****, we use the characterization vector* $\mathbf{C}_{GWP100}$. $\mathbf{C}_{GWP100}$ *contains multiplication* *factors for various global warming gases (for all other exchanges, multiplication factors are set to 0) that represent their global warming potential compared to CO₂. For an **L** vector with methane (which during 100 years is 25 times more potent than CO₂ for global warming on a weight basis), CO₂ and land use, we would have:*

$$GWP_{100} = \boldsymbol{C}\,\boldsymbol{L} = [1 \quad 0 \quad 25 \quad \ldots]\begin{bmatrix} x\ kg\ CO_2\ emitted \\ y\ m^2\ land\ used \\ z\ kg\ CH_4\ emitted \\ \ldots \end{bmatrix} = x + 25z\ kg\ CO_2\ equivalent \qquad (2.62)$$

- Normalization/grouping/weighting: These operations can all occur when aggregating various impacts obtained from characterization into a single impact value. There are various ways of doing this that are more or less rigorous. One of the more rigorous methods is to convert all environmental impacts to economic damages (the amount that it costs to repair/live with the impact that was created). However, this often requires fairly intricate economic modeling. An example of such a result is shown in Fig. 2.21.

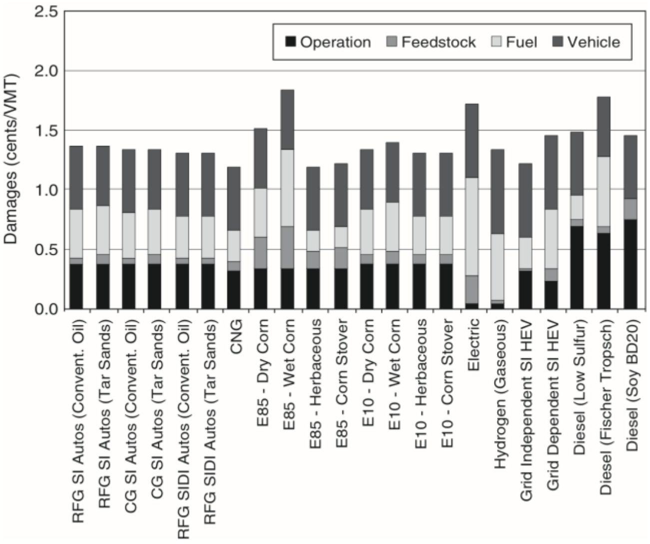


Fig. 2.21. Non-climate damages for different combinations of fuels and cars. Green house gases are <u>not</u> included. Source: NAS, 2010. VMT stands for *vehicle mile traveled*.

2.6 Uncertainty estimation and the Monte Carlo Method

The result of all we have seen until now can be a deterministic model giving us exact inputs and outputs and exact measures of environmental impacts. This is of course highly misleading. There is often uncertainty in all the parameters fed into the model. Furthermore, models themselves often rely heavily on predictive physical property models that are themselves never 100% accurate. Therefore, it is important to realize that the predictions that result from models are associated with uncertainty, and it is important to be able to estimate the extent of this uncertainty. In this section, we will discuss how to calculate estimates of the uncertainty associated with model prediction based on a measure of uncertainty for the input variable. For simple analytical models, with randomly distributed variables that follow Gaussian distributions, you can estimate the cumulative variance of e (σ_e^2) can be estimated from the variance of independent variables x_i with the following formula:

$$\sigma_e^2 = \sum_i \left(\frac{\partial e}{\partial x_i}\right) \sigma_{x_i}^2 \qquad (2.63)$$

In more complicated cases (e.g. highly complex non-linear systems such as the models presented earlier), this formula becomes impossible to use and/or gives imprecise results. With such systems, the *Monte Carlo Method* is particularly useful and is used for most systems models such as those described in previous sections. This method relies on the availability of fairly intensive computing power, which, fortunately, is increasingly available.

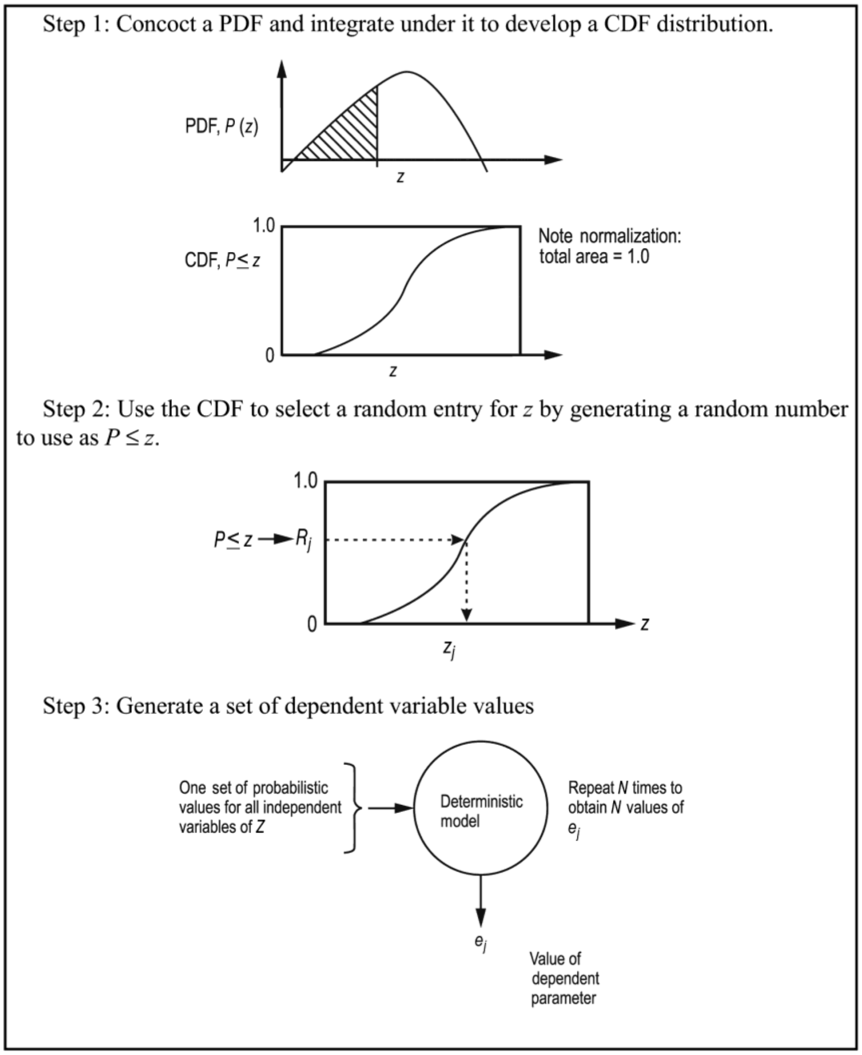


Fig. 2.22. Basic approach to the Monte Carlo Method.

The basic approach (Fig. 2.22) requires sampling various possible values for independent variables based on their probability density function (PDF). Sampling can be done by using a random number generator (which generates a random number between 0 and 1) and applying this to the cumulative distribution function (CDF) of variable z to determine a value z_j (Fig. 2.22). Doing this for all independent variables will lead to a set of probabilistic values for all independent variables (vector $\boldsymbol{Z}$). This can be fed into our deterministic model to obtain our dependent prediction e_j. Repeating this N times will lead to a set of values for e_j.

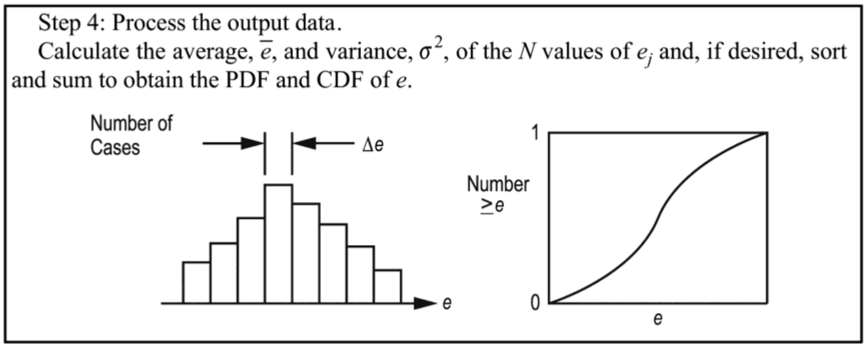
This set of values e_j is a range of possible outcomes for the variable e. Therefore, the analysis of this set of values can be used to estimate the uncertainty of e (Fig. 2.23). For example, the expected value for e ($\bar{e}$) can be calculated as follows:

$$\bar{e} = \frac{\sum_j e_j}{N} \tag{2.64}$$

Similarly, the variance can be estimated by:

$$\sigma^2 = \frac{\sum_j \left(e_j - \bar{e}\right)^2}{N(N-1)} \tag{2.65}$$

These values will only be valid for large N, which requires significant computational power. Fortunately, this has become more and more widespread lately and such a simulation can often be run on a personal computer. Note that in most cases, since the model is highly non-linear, variance might not be the most appropriate measure of uncertainty. Confidence intervals (e.g. 95% confidence intervals) are often more appropriate. Variance can falsely give the impression that error is symmetrically distributed around the estimated mean value, which, in cases where the mean is predicted by a deterministic model that is highly non-linear, is often not the case. On the other hand confidence intervals accurately portray the absence or presence of symmetry in the uncertainty of a predicted value.



Step 4: Process the output data.

Calculate the average, $\overline{e}$, and variance, σ^2, of the N values of e_j and, if desired, sort and sum to obtain the PDF and CDF of e.

Fig. 2.23 Basic approach to the Monte Carlo Method (continued).

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