2 Chemical production processes

This chapter provides an overview on basic definitions, terms, concepts, and techniques to describe and model chemical production processes. This allows modelling of the core components in chemical production networks. Figure 2.1 shows an exemplary chemical production network where the production plants are highlighted.

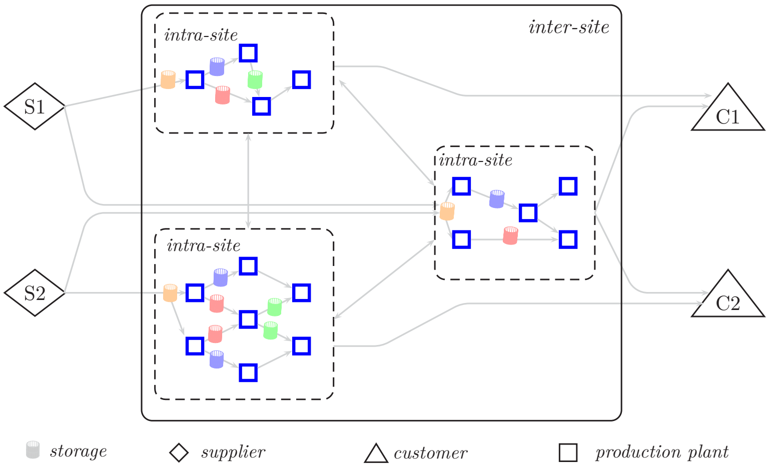

Figure 2.1: Chemical SC scheme with highlighted production plants

From Figure 2.1, it becomes obvious that modelling the production plants provides the basic data to describe the material flows within the whole network. Before the chemical production processes are described in detail, some characteristics and key figures about chemical products are provided.

Basically, two major groups of chemicals can be distinguished: inorganic and organic chemicals. The latter subsumes all chemicals containing at least one bond of a hydrogen and carbon atom. The former group encompasses all chemicals without such a bond.[1]

This work primarily focuses on organic chemicals which are produced by the (basic) chemical industry. For the industrial production of organic chemicals, three basic natural resources are available: natural gas, coal, and crude oil. Of these three materials crude oil

[1]In particular, pure carbon, e.g. in the form of diamonds is handled as an inorganic chemical. See e.g. Seager and Slabaugh (2007) for more details.

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is the exceedingly most important raw material for the production of organic chemicals. The (basic) chemical industry is an intermediary who transforms these raw materials into basic and intermediate (organic) chemicals. Three main production phases can be distinguished:

1. raw substance splitting: raw materials are split into (short-chained) *basic chemicals*

2. re-composition: basic chemicals are re-composed into *intermediate chemicals*

3. final composition: basic and intermediate chemicals react to *final chemicals*.

The category of basic chemicals comprises about 20-30 chemical substances building the basis for all subsequent substances. This class summarizes basic organic substances as well as basic gases and inorganic basic substances (such as Chlorine or Ammonia).[2] These substances are purely intermediate and not sold to consumer markets.

Intermediate chemicals are usually simply structured chemicals most often composed by basic chemicals that are only exceptionally made for (private) consumer markets. This class comprises, e.g., alcohols and many kinds of acids.[3] Examples for marketable intermediate chemicals are ammonia compounds used as basic fertilizers in agriculture.

The classes of basic and intermediate chemicals consist of a fairly small number of substances which are mainly fluids or gases. But these substances are used in vast quantities to produce final chemical products. To give an impression, Figure 2.2 shows the produced quantities of basic and intermediate chemicals in 2008-2010 for Germany (grouped as stated above).[4]

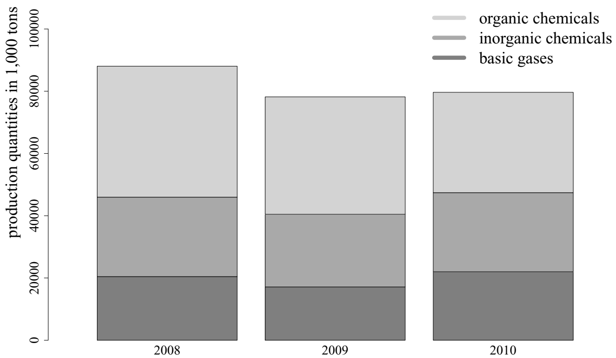

Figure 2.2: Production quantities of basic chemicals in 2008-2010

[2]See e.g. Behr et al. (2010, p. 10 ff.) or Baerns et al. (2006, ch. 16).
[3]See e.g. Behr et al. (2010, p. 10 ff.) or Baerns et al. (2006, ch. 17).
[4]These production statistics are calculated based on the European goods classification scheme NACE. The three classes "basic gases", "inorganic chemicals", and "organic chemicals" correspond to the NACE classes 20.11, 20.13, and 20.14, see Eurostat (2011).

The group of organic chemicals represents about 50% of the total quantity of produced chemicals with a total quantity of about 40 million tons per year in Germany. These products are typically crude oil derivatives. Thereof, approximately 20 million tons account for organic basic chemicals such as alkenes or aromatic compounds where the remaining 20 million tons comprise organic intermediate chemicals such as alcohols or chlorine derivatives.[5]

Final products in chemical industry are produced by chemical reactions of intermediate and basic chemicals. These final products are widely used in almost all other industries.[6] Final chemicals can be categorized into

1. polymers/plastics
2. agrochemicals (fertilizers, pesticides, etc.)
3. body care products (detergents, soaps, cosmetics, etc.)
4. speciality chemicals (coatings etc.)
5. pharmaceuticals.

Among these categories, pharmaceuticals and body care products set up own sub-industries due to the special characters of their products and production processes. These companies directly serve (private) consumer markets. The remaining three categories comprise "classic" chemical companies mainly providing intermediate products for other industries such as mechanical engineering industry, building industry, textile industry, and plastics industry.

In the next section chemical production processes are characterized and categorized. The theoretical modelling of the underlying chemical reactions is described subsequently. Chemical production processes realise chemical reactions in industrial scale in chemical plants. Based on models of chemical reactions, methods are provided to describe the behaviour of chemical production processes.

2.1 Characterization of chemical production processes

Production in chemical industry is in many aspects different from common industries. In most industries final products are produced by mechanical transformation processes such as assembling or machining. In contrast, in chemical industry the chemical and/or physical properties of substances are altered. Most chemical production processes rely on chemical reactions aiming at the transformation of reactants into substances of interest. The term *chemical reactions* refers to changes of the reactants' molecular structures.[7] Be-

[5]See Eurostat (2011).

[6]However, especially in the last two decades a trend towards a deeper vertical integration and specialization is visible in chemical industry. This aims at product portfolios containing a higher share of consumer goods which promise higher contribution margins and less market risks.

[7]See e.g. Baerns et al. (2006, p. 24 ff.).

side chemical reactions, also physical transformation processes (so-called *basic operations*) are used to alter specific properties of the reactants.

Usually, chemical reactions require an initiation, i.e. they only take place under specific circumstances. The list of reaction parameters is vast. Basic physical parameters are pressure, temperature, electricity, or light. Specific constellations of these parameters influence the *reaction rate*, i.e. how fast or slow a reaction takes place.[8] If a reaction can only take place by means of auxiliary chemicals, it is called *catalytic* and such an auxiliary reactant is called *catalyst*.[9] Another important measure of chemical reactions is the *conversion rate* of a reaction, i.e. how many percent of the input reactants' mass is transformed into the substances of interest.[10] This measure is important to decide whether a reaction can be realized in an economically profitable way.

The molecular structure of reactants can be changed in numerous ways:[11] First the reactants' molecules can be combined which is called *synthesis*. A prominent example is the hydrogenation of carbon dioxide to produce methanol.[12]

Second, a molecule or molecular fragment can also be split which is called *decomposition*. To recycle bottles made of polyethylene terephthalate (PET) catalytic depolymerization is used to split the PET in valuable components.[13]

In a *substitution*, a molecular fragment of a reactant is replaced by a fragment of another reactant. A prominent example is the alkylation where an alkyl group is transferred from one molecule to another. E.g., the production of Ethylbenzene from Benzene and Ethylene by the so-called Friedel-Crafts alkylation is a standard process in chemical industry.[14]

If more than one molecular fragment is substituted, this is categorized as a *metathesis*. A recent industrial application is the olefin metathesis to produce e.g. Propene from Ethene and 2-Butene.[15]

The types of reactions presented above can be combined with the ordinary classification of production processes in convergent, divergent, and transformation processes. Depending on the number of input and output products this process classification can be enhanced as Table 2.1 shows.

A SISO process is a single input-single output process and corresponds to transformation processes or substitution reactions. MISO processes (multiple inputs-single output) comprise convergent processes and SIMO processes (single inputs-multiple output) comprise divergent processes similar to decomposition and synthesis, respectively. MIMO

[8] E.g. see Baerns et al. (2006, p. 32).

[9] The catalyst is not part of the molecular reorganization, i.e. no part of the catalyst is part of the resulting chemicals. See Behr et al. (2010, ch. 12) for more information.

[10] E.g. see Baerns et al. (2006, ch. 11.2) for more details.

[11] A similar classification scheme particularly addressing organic reactions can be found in Jones and Bunnett (1989).

[12] See Bill (1997).

[13] The resulting components depend on the specific depolymerization process applied, see e.g. Mishra et al. (2002) or Paszun and Spychaj (1997).

[14] E.g. see Degnan et al. (2001).

[15] See Mol (2004).

# outputs / # inputs	single	multiple
single	SISO	SIMO
multiple	MISO	MIMO

Table 2.1: Typology of production processes

processes (multiple inputs-multiple output) may include transformations as well as convergent and divergent parts. They correspond to metatheses or coupled decomposition reactions.

Based on this classification of chemical reactions, corresponding characteristics of the production systems can be deduced. The production of basic chemicals is in almost all cases a split of long-chained raw materials (crude oil, coal, natural gas) into short-chained substances (such as alkenes). These production processes are primarily divergent and can be categorized as SIMO processes. The cracking of mixtures of long-chained substances into their short-chained components is usually performed by thermal chemical reactions (such as steam-cracking). The resulting mixture of short-chained substances is usually separated by distillation processes. Such processes are in general continuous and hardly interruptible. Typically, they are *single-purpose* assets i.e. assets designed to produce a fixed set of chemicals.[16] Depending on the raw materials' composition and the operating parameters (temperature, pressure, reaction time, etc.) the production coefficients can be controlled under certain restrictions. The set-up and control of the production coefficients depends on the precedence relation of the produced products. Not in all cases a focal main product exists.[17]

The production of intermediate chemicals requires more manifold types of production processes. Similar to the production of basic chemicals, chemical reactions are typically accompanied by separation processes such that most of these reactions can be categorized as SIMO or MIMO processes. Because intermediate chemicals are required for the production of final chemical products in huge quantities, they are usually produced by continuously operated plants. Typically, the production plants are specialized to perform a specific reaction and, hence, are single-purpose plants.

Final chemical products are typically produced on *multi-purpose* plants which are designed for a specific product family. Such production processes are usually convergent. The composition of raw materials to produce a final chemical is called a *recipe*. Multi-purpose plants are capable to handle multiple recipes, i.e. reactants and products handled vary in both type and quantity. These processes can be mainly categorized as MISO or MIMO processes.

[16] However, the production coefficients may vary.

[17] This depends primarily on the further use of the output products and/or their market prices. For example steam crackers are usually optimized for Ethylene production because Ethylene is used in a wide variety of final products.

Depending on the product portfolio as well as the structure of product demand, multi-purpose plants are operated either in batch mode or continuously. There are plenty of definitions about both terms.[18] Here, a technological point of view is used, i.e. batch processes are characterized by a fixed production capacity which is defined as the quantity of produced chemicals after which a process interruption is required. In contrast, continuous processes are characterized by a production rate, which is defined as the quantity of goods produced in a given time. The time between process interruptions is not technically limited. The former especially occurs for specialty chemicals and pharmaceuticals, where the latter is typical for polymers/plastics and some agrochemicals.[19] For body care products the production technology is mixed depending on the product variety. Low-volume products with many product variations and often changing recipes, such as cosmetics, are usually produced in batch mode, whereas high-volume products with few product variations, such as detergents, are usually produced continuously. In both cases, the production processes are interruptible. Table 2.2 summarizes the above-mentioned characteristics.[20]

	basic chemicals	**intermed. chemicals**	**final chemicals**	
			commodity	speciality
mode	continuous	continuous	continuous	batch
vergence	divergent	di-/convergent	convergent/transform.	
purpose	single	single	multiple	

Table 2.2: Characteristics of production processes in chemical industry

The production of basic and intermediate chemicals is typically organized in a network of continuously processed plants. This principally leads to an advantage for horizontally coupled production processes and, hence, horizontally integrated chemical companies. To exploit these economies of scope, locally concentrated production sites are necessary to avoid logistical efforts. These integrated production sites comprise a great variety of production plants which are interconnected by product and energy flows.[21] A typical flow sheet example for sites based on cracking of Naphtha is depicted in Figure 2.3. Main products are the simple alkenes Ethylene, Propylene, and Butadiene. Beside these pure alkenes, a fraction called pyrolysis gasoline (Pygas) is extracted which is a mixture of acyclic and, mainly, cyclic hydrocarbons (aromatics) such as Xylene, Toluene, and Benzene. Benzene is the most important cyclic hydrocarbon and raw material for

[18] See e.g. Loos (1997, p. 48 ff.) and references therein.

[19] Low-volume products such as specialized pesticides are often produced in batch mode, see e.g. Loos (1997, p. 70 ff.).

[20] Far more typical characteristics of production processes could be included, see e.g. Loos (1997, sec. 3.1). However, the chosen characteristics are the most important with respect to logistical implications.

[21] The head sites of BASF in Ludwigshafen and Dow Chemical in Midland are popular, large-scaled examples of such integrated production sites.

e.g. Ethylbenzene which in turn can be de-hydrogenated to Styrene. Styrene can then be used as raw material for Styrene-Butadiene rubber which is an important raw material e.g. for the production of tires. Other branches of Benzene application are the production of Aniline (which is widely used in polyurethane production) and Cumene which is a composition of Benzene and Propylene and is mainly processed to resins.[22]

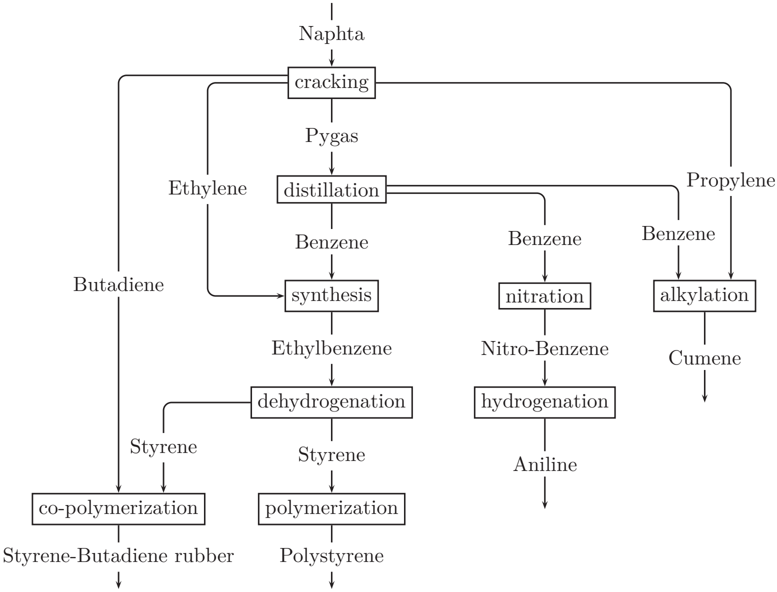

Figure 2.3: Exemplary production network of Naphtha derivatives

Note that the provided final products depicted in Figure 2.3 rather represent a set of sub-products than a uniform substance. These sub-products have the same basic molecular structure but can differ e.g. in certain physical characteristics or colour.[23]

The vessels containing chemical reactions are called (chemical) *reactors*. Their design and size depends on the intended reaction. The performance of a reactor is measured in terms of the conversion rate, the purity of the substances of interest, and economic aspects such as resistance, energy consumption etc. Basic types of reactors can be categorized by different characteristics.[24] The vessel design is a first category. Roughly, one can distinguish between (stirred-)tank reactors and pipe reactors.

To effectively execute chemical reactions, the involved reactants have to be provided in sufficient purity. Moreover, many chemical reactions result not only in one pure output product but in a mixture of output products. Thus, preparation and post-production

[22]See e.g. Baerns et al. (2006, ch. 16) for details.
[23]This can be obtained e.g. by various additives or process settings, see Behr et al. (2010).
[24]E.g. see Baerns et al. (2006) or Trambouze and Euzen (2004) for more detailed classification schemes.

processes have to be carried out to provide valuable reactants for subsequent chemical reactions. These operations are called *basic operations* and can be categorized in thermic and mechanic operations.[25]

The most prominent thermic basic operation is the rectification or distillation to separate individual components from a mixture.[26] For separation, the mixture is evaporated completely and successively cooled down. The components can be effectively separated if they have different boiling points or dew points, respectively. In the case of close boiling points for the components in the feed mixture, distillation is still applicable if an auxiliary chemical (so-called *solvent*) is available changing the boiling or dew points of at least one component (so-called *fractional distillation*).[27]

A distillation column is a metal tube which is separated in compartments by so-called trays or plates. The mixture to be separated is fed into the middle of the column. Inside the column temperature and pressure are variable depending on the height. At the column's top temperature is maximal and pressure minimal. Conversely, at the bottom temperature is minimal and pressure maximal. Depending on the boiling points of the mixture's components, the composition of liquids and gases differs in each compartment and at each tray, respectively. Ideally, at each tray a single fraction/component of the feed mixture can be obtained.[28] To guarantee constant conditions regarding pressure and temperature, a surplus of residue liquids at the bottom of the column is (re-)boiled and fed back into the column (so-called *reflux*). Similarly, a surplus of gases at the top of column is condensed and fed back. Figure 2.4 shows a schematic overview of a prototypical column.[29]

Separation processes are designed and optimized for a specific mixture to be separated which determines e.g. the number and position of trays as well as the atmospheric conditions. Such processes are single-purpose plants for SIMO or SISO[30] processes. The production rate often can be varied in certain ranges without causing serious variations of the separation accuracy.

The distinction in reactions and basic operations to prepare and post-process chemical reactions is valid in most cases. However, there is a principal advantage to integrate both chemical process steps. Despite organizational and technical drawbacks, such an integration is physically and chemically advantageous due to more favourable energy balances. One example is the reactive distillation where chemical reactions take place inside the

[25] E.g. see Baerns et al. (2006) for details.

[26] For a more general overview on (thermal) separation processes see e.g. Seader et al. (2011) or Baerns et al. (2006, ch. 9).

[27] E.g. see Behr et al. (2010, p. 88-89),Hoffman (1977) or Seader et al. (2011) for details.

[28] Regarding the determination of the maximal or optimal number of trays a large body of literature has been expanded and is still growing, e.g. see Seader et al. (2011) for an overview and Yeomans and Grossmann (2000) or Viswanathan and Grossmann (1993) for more detailed insights.

[29] In practice many adaptations and subtypes of this basic form have been derived depending on the specific processes and circumstances the distillation column is intended for. See e.g. Smith (2005, ch. 11 and 12) for an overview.

[30] If only one component is considered as valuable.

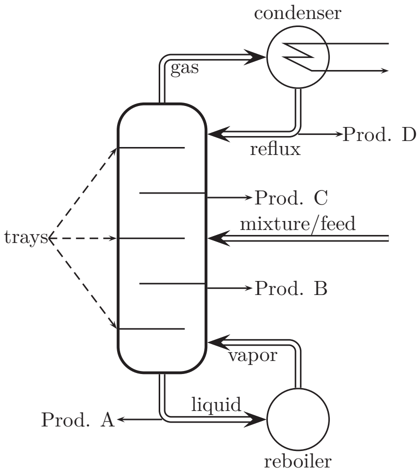

Figure 2.4: Scheme of a distillation column

distillation column.[31] With the exception of such special techniques, chemical operations can be categorized as displayed in Figure 2.5.

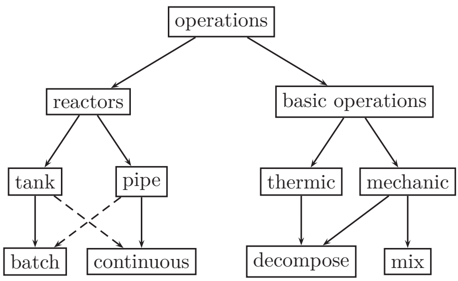

Figure 2.5: Overview on chemical operations

Chemical production processes can be divided in chemical reactions and basic operations (i.e. physical transformations). In chemical production plants, multiple processes from both classes are combined and take place in sub-plants which are closely interconnected. The planning and configuration of such plants is very complex and expensive. Hence, a detailed modelling of the underlying chemical and physical processes is necessary to avoid misinvestments. The next section outlines an overview on the steps necessary to

[31] For an overview on reactive distillation see e.g. Baerns et al. (2006, p. 322 ff.) and for details see e.g. Taylor and Krishna (2000).

model and control a chemical production plant beginning with a brief introduction into the mathematical modelling of chemical reactions.

2.2 Modelling chemical production processes

A chemical production process is a combination of physical and chemical transformation processes. The behaviour of such a transformation system can be described in mathematical terms. To describe the behaviour of a chemical reaction system two general questions have to be answered:

- What are the requirements and outcomes of the intended reaction(s) regarding energy and reactants?
- How can these requirements be maintained over time by technical systems?

Roughly spoken, the first question can be answered by *thermodynamical* analyses of the intended reaction, whereas the answers to the second question are typically subsumed under the term (chemical) *kinetics*.

Based on thermodynamical and kinetic descriptions of the individual process steps, a meta-model can be developed which is able to describe and predict the behaviour of a whole chemical production process. Such a process model can be developed for different purposes and at different levels of detail: To design a chemical production process, a detailed model of the potential plant(s) necessarily includes the description of the system's dynamics. In contrast, once the production process is designed, a model is necessary to describe the dependency of the system's output w.r.t. certain control parameters. Figure 2.6 depicts a prototypical procedure in chemical process modelling.

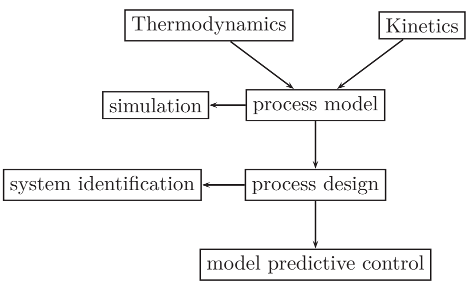

Figure 2.6: Steps in chemical process modelling & control

In the next subsection, kinetic definitions and concepts are introduced. Subsequently, relevant properties of chemical operations w.r.t their modelling are outlined. Special

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