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Catalysis Today 34 (1997) 429–446

CATALYSIS TODAY

Chapter 13

Approach to the industrial process

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1. Introduction to process design

The major feature that distinguishes design problems from other types of engineering problems is that they are underdefined: only a very small fraction of the information needed is available from the problem statement.

If the research department discovers a new reaction or a new catalyst to make an existing product, the process department will have to translate these discoveries into a new process: thus, engineers start with a knowledge of the reaction, transferred by the researchers, and with some information about available raw materials and product specifications, and must supply everything else is needed to define the design problem.

Assumptions must be made about which types of process units should be used, how those process units will be interconnected and what temperatures, pressures and process flow rates will be required: this activity is named ''conceptual design''.

Conceptual design can be approached at different levels during the development of a chemical process.

The first approach must be done while research is in the exploratory phase, and must be followed by the first economical evaluations.

This is very important because the critical points of the process can be defined, and goals for the researchers set from the beginning.

There is a very large number of ways that might be considered to accomplish the same goal.

The first aim is to find the process alternative that gives the lowest production cost, but it also must be ensured that the process is safe, it will satisfy environmental constraints, and the plant is easy to start-up and operate.

In the following paragraphs a correct approach to the problem of designing a new process is described, by first developing very simple solutions and then adding successive layers of detail: this will result in a series of always more accurate economic estimates.

It is very important to conceptually define every single operation to be performed, dividing the process in stages: every stage corresponds to a single operation.

The main key to the successful design of a new process is the continuous transfer of information between researchers and engineers, particularly the feedback of engineers to researchers, identifying critical points and addressing further research to clarify them.

At the moment in which process development begins, the reaction has been tested in laboratory reactors, a catalyst is available, even if it will not be the final one, possible by-prod-

PII S0920-5861(96)00065-X

ucts and a plausible stoichiometry have been determined.

A range of possible operating variables (temperature, pressure, space velocity) and the reaction phase have been determined, too.

The information that is normally available at the initial stages of a new design is summarized herebelow:

1. The stoichiometry of the reactions that take place (at least the main reaction).
2. The range of temperatures, pressures and concentrations for the reactions
3. The phases of the reacting system.
4. Every available information about conversion and selectivities versus operating variables, including thermodynamic equilibrium limitations, if possible.
5. Rate of catalyst deactivation, regenerability of the catalyst, method of regeneration, catalyst poisons.
6. A range of desired production rates.
7. The desired product purity and the quality of possible feeds.
8. Any processing constraints, as explosive mixtures, unstable or fouling components, highly corrosive components, etc.
9. Physical properties of at least the main components.
10. Some information concerning safety, toxicity, and environmental impact of the components involved in the process.

It is necessary to write down any side reactions that might take place. Even if only a trace amount of by-product is produced in a laboratory experiment, it may build up to very large levels in a recycle loop: it almost always leads to paying large economic penalties.

Many process developers worldwide have experienced from ppm of by-products, neglected at laboratory level, and building up in the prototype in such way to make critical some unit operations.

The condition of maximum conversion does not necessarily correspond to the optimum economic conditions.

As an example, let us consider an hypothetical reaction system: $A \rightarrow B \rightarrow C$, where B is the desired product, and C an undesired by-product.

The maximum conversion of A can coincide with a considerable amount of C, while different operating conditions might lead to a lesser A conversion and maximize B formation.

So, it must be decided if it is more economical to operate with larger recycle flows (and higher recycle costs), or to lose more raw material A.

Again, establishing a close relationship with the researchers and providing them with the feedback about the optimum process conditions early in the experimental program, will lead to more profitable processes.

It would be highly desirable to have a detailed kinetic model, but it can be available at this stage only in case of very simple reactions: it will be developed later, if necessary and possible.

At the moment, an empirical model, to have conversion and selectivities versus operating variables will satisfy us.

Even thermodynamic data are not available, if nobody has studied the same reaction before: in case, some experiment will be directed to their achievement, if they cannot be obtained theoretically.

The choice of reaction conditions can be influenced by factors unrelated to the reaction itself.

For example, methanol is produced from syngas (a mixture of CO and hydrogen) that in turn is produced from natural gas through the following reaction:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$

This reaction is thermodynamically favoured at low pressure, taking place with increase of number of moles, but is done in industrial plants at the highest possible pressure.

The reason is that methanol synthesis takes place at high pressure (70–80 atm), and compressing natural gas is much less expensive than compressing syngas because of its higher volume and of the presence of hydrogen, that requires particular types of compressors.

The general lay-out of the process must be kept in mind since the first development phases.

Researchers use very pure chemical reagents in their studies, whereas natural or purchased raw materials always contain some impurities: it is important to understand if the impurities in raw materials are inert or will affect the reactions, and also examine their effect on the separation system to decide whether to include a purification facility as part of the scheme.

Conceptual designs often focus on attempts to make new materials, so that in many cases physical property data are not available in the literature.

Estimation procedures based on group contribution methods are an area of active research: the book of Reid et al. cited in the references is an excellent collection of techniques for estimating physical properties, even if in some cases errors remain large.

Anyway, data and methods found in the literature must be used very carefully, as far as possible with the aid of an expert in the field.

2. Batch vs. continuous

The first decision to take is whether the process will be batch or continuous: continuous processes are designed so that every unit will operate 24 h/day for close to a year at almost constant conditions before the plant is shut down for maintenance or catalyst replacement.

In contrast, batch processes normally contain several units that are designed to be started and stopped frequently.

Large petrochemical and refinery plants are normally continuous: the development of the process scheme must try to approach as close as possible a continuous process to improve overall economics.

Batch processes become economical in case of small productions of fine chemicals where many different products can be made, or operations be performed, in the same vessel.

In our field of interest, we assume that our process will be continuous.

3. The input–output structure

Now we consider the whole process as one single block, as reported in Fig. 1a and b.

It must be introduced here the concept that most industrial processes have some internal recycle streams: as conversion of at least one reactant is not total, the unreacted feed must be recycled to the reactor to avoid diseconomies, if it cannot be used in other parts of the plant.

The recycle stream is mixed with the fresh feed somewhere before the reactor, so that the composition at the reactor inlet is different from that of the fresh feed: this is an important information for researchers, that must study the reaction in the real inlet conditions.

A typical example is methanol synthesis:

$CO + 2H_2 \leftrightarrow CH_3OH$

In the fresh feed the molar ratio H_2/CO is usually equal to 4, while it becomes 10 or more at the entrance of the reactor after mixing with the recycle.

If a kinetic is developed on the fresh feed composition, it could not be applied to model the industrial reactor.

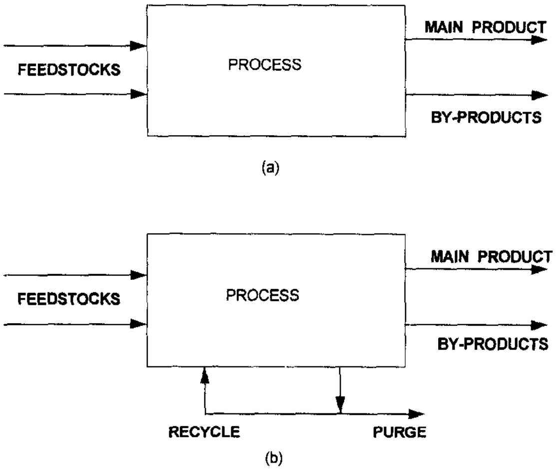

Fig. 1. General process scheme.

Thus, almost every process scheme has one of these two structures: unreacted feed is recovered and recycled (a), or, if some gaseous feed impurities or by-products cannot be easily separated, a stream must be purged from the process, so that they do not continue to build-up in the recycle-loop (b).

The concept of recycle of the main reactant is always associated to the principle of feed purification and/or build-up and purge.

A decision to purify the feeds before they enter the process is important because it adds a section to the process itself.

The economic trade-off is between building a pre-process separation system and increasing the cost of the process to handle the impurities.

As a guideline, an impurity will be removed if it is a catalyst poison, if it is separated more easily from the feed than from the products, if it is not inert and its by-products cannot be easily separated, or if it is inert, but can build-up in the recycle loop.

Unfortunately, these guidelines are not quantitative: if we are not certain that our decision is correct, we list the opposite decision as a process alternative.

This is a systematic way of generating process alternatives.

The necessary decisions to fix the input–output structure of the process are summarized below:

1. Removal or recycle of reversible by-products.
2. Necessity of purge.
3. Number of product streams.

Let us consider the following reaction system, where the second is an equilibrium reaction:

$A \rightarrow B \rightleftharpoons C$

B is the desired product: if C is recycled back to the reactor, it builds up in the recycle loop until it reaches its equilibrium level and its net production falls to zero.

In this case the decision is between oversizing all equipment in the recycle loop and avoiding production of a less valuable by-product.

If a feed impurity or a by-product is not easily separable from a reactant that must be recycled, it is common practice to "purge" the recycle stream, i.e. to withdraw a small fraction of the recycle stream to prevent build-up of inerts or of undesired by-products: for instance, C could decompose to not easily separable products.

The purge stream can make environmental problems, otherwise can be vented or used as fuel.

The number of product streams is determined listing all the components that must leave the process with their destination (primary product, valuable by-product, vent, fuel or waste).

Components are then ordered according to their boiling points and neighbouring components with the same destination are grouped together.

The number of groups formed in this way is the number of product streams, unless there are problems of separation by distillation (e.g. azeotropes, as will be explained later) or of immiscible phases.

At each stage of the development of a process it is essential to make sure that all products, by-products and impurities leave the process: if even a trace amount of a component is fed to a recycle loop and is not removed, the process will be inoperable.

Once defined the input–output structure of the process, it is possible to perform the first overall mass balance: starting with the specified production rate the by-product flows and reactant requirements can be found and the impurity inlet and outlet flows can be calculated.

The internal recycle streams are not yet defined and this is the next target in the development of the scheme.

4. The recycle structure

Now that the input–output structure of the conceptual process scheme has been decided, we want to add the next level of detail.

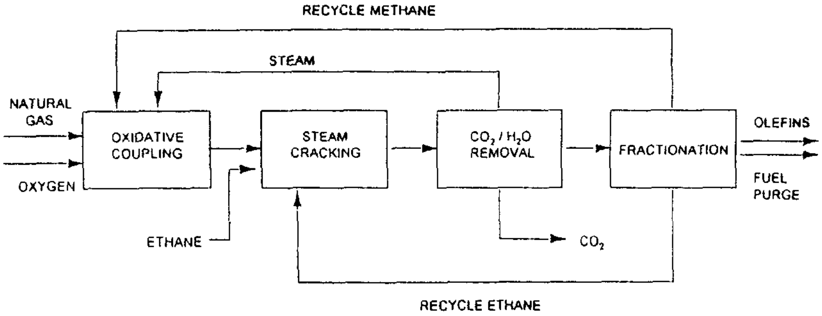

Fig. 2. An example: oxidative coupling of methane.

We break our single process block identifying the fundamental sections of the process, as exemplified in Fig. 2, where four sections can be recognized:

- First reaction (oxidative coupling of methane).
- Second reaction (steam cracking of ethane).
- Separation of water and carbon dioxide.
- Purification of the product (olefins, mainly ethylene).

By the way, this is an example, that will be recalled later, of an innovative process widely studied all over the world in the last years.

Oxidative coupling is the reaction of methane with oxygen to give mainly ethane and ethylene.

Since olefins are the most valuable product, the effluent from oxidative coupling reactor is fed to a steam cracking reactor to convert ethane completely into ethylene and propylene.

In the third section water and carbon dioxide are removed: carbon dioxide is a by-product (probably with no market), while steam is recycled to oxidative coupling where it acts as inert to moderate the temperature increase caused by the strongly exothermic reactions.

In the final separation section, unconverted methane is recycled to the coupling reactor, unconverted ethane is recycled to steam cracking, ethylene and propylene are the main products, while some light gases to be used as fuel are purged to avoid build-up in the cycles.

In almost every chemical process, four sections can be identified:

- Purification of the feed.
- Reaction.
- Separation.
- Purification of the product.

Discussing the input–output structure we had already examined the possibility of a feed purification section.

Then there will be one or more reaction sections, with separation systems in between, if necessary and one final separation section.

There will also be compressions or expansions if different sections of the process operate at different pressures.

The decisions that fix the recycle structure of the process scheme are summarized below:

1. Number of reaction sections required and necessity of separation between the reactors.
2. Number of recycle streams.
3. Excess of reactants
4. Necessity of gas compressors.
5. Types of reactors required.
6. Concentration of reactants, products and by-products.
7. Possibilities of separations in the reactor effluent.

If sets of reactions take place at different temperatures or pressures, or if they require different catalysts, then different reactor systems must be used for these reaction sets.

In case of equilibrium limitations, it can be useful to perform a single reaction in many consecutive stages with intermediate separation of the product.

The number of recycle streams is determined in the same way than the number of product streams: all the excess reactants to be recycled are identified and grouped by neighbouring boiling points if they have the same reactor destination.

Then the number of recycle streams is merely the number of groups.

In some cases the use of an excess reactant can shift the product distribution improving selectivity to the desired product.

If we consider the following set of reactions:

$$A + B \rightarrow C$$

$$A + C \rightarrow D$$

where C is the desired product, the use of an excess of B maximizes selectivity because no A is left to react with C, but leads to larger costs to recover and recycle B: an optimum amount of excess must be determined from an economic analysis.

An excess component can also be used to force another reactant to complete conversion.

For example, in the production of phosgene:

$$CO + Cl_2 \rightarrow COCl_2$$

an excess of CO is used to have a product free from chlorine.

Similarly, an excess reactant can be used to shift the equilibrium conversion.

It must be remembered that whenever a gas-recycle stream is present, a gas compressor is needed: gas compressors are very expensive items that can greatly affect the cost of a chemical plant.

To have a quick estimate of the recycle flow, we make a balance on the limiting reactant, i.e. the reactant present in sub-stoichiometric quantity.

Referring to Fig. 3, representing a process with one liquid recycle stream, and one gaseous recycle with purge, we let the flow of the limiting liquid reactant A entering the reactor be F.

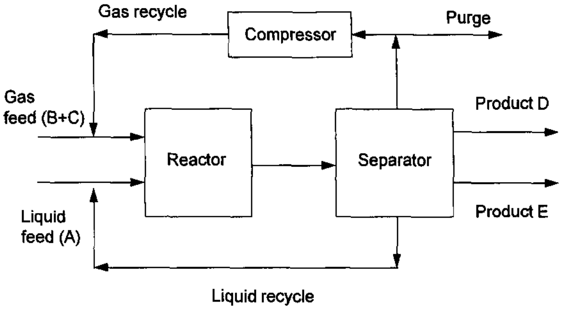

Fig. 3. Process scheme with recycles.

Then, for a conversion x, the amount of A leaving the reactor will be $F(1-x)$.

For complete recovery in the separation system, the flow leaving the reactor will be equal to the recycle flow.

If we make a balance at the mixing point before the reactor, the sum of the fresh feed (FF) plus the recycle A will be equal to the flow of A into the reactor, or:

$$\mathrm{FF} + F(1-x) = F$$

Thus, the feed to the reactor is:

$$F = \mathrm{FF}/x$$

This material balance is always valid for the limiting reactant when the same is completely recovered and recycled.

We assume now that the gaseous reactant B has a 1% impurity of C, making necessary a purge on the gas recycle.

The quantity to be purged is determined by two opposite demands: not to purge too much losing reactants and not to build-up excessive quantities of inert, overdesigning piping, vessels and recycle compressor.

The calculation procedure is iterative by trial-and-error: an impurity concentration in the recycle is assumed, calculations are performed and the final check is on the purge stream flowrate.

If an excessive amount of reactant is purged, a higher concentration in the recycle is assumed.

Assuming a 5% impurity concentration in the recycle, the procedure is the following:

– The fresh feed gas flowrate (F_G) and the molar ratio B/A at the rector inlet (MR) are fixed.

– A mass balance on B at the mixing point at the reactor inlet is performed:

$$\mathrm{MR}(\mathrm{FF}/x) = 0.99F_G + .95R_G$$

where R_G is the recycle stream flowrate that is calculated solving the equation.

– The flowrate of B at the reactor outlet is calculated subtracting the reacted quantity from the reactor inlet flowrate.

– A mass balance is performed around the splitting point between recycle and purge, determining the purge flowrate.

As the number of recycle streams increases and recycle loops are nested one inside another, as in the process reported in Fig. 2, the difficulty of calculations increases and systems of ordinary equations must be solved.

Nowadays these calculations are performed with the aid of specialized software, as detailed later.

5. The choice of the reactor

The first items to be defined in a very detailed way are the chemical reactors: in our block flow diagram, the ''black box'' named reactor must be substituted by the conceptual type of reactor to be used.

Herebelow are reported some useful guidelines to the choice of industrial reactors.

Our analysis will be limited to the case of heterogeneous reactions with solid catalyst.

First, it must be decided if it is desirable to approach more closely an ideal plug-flow reactor or a continuous stirred tank reactor (CSTR).

In case of single reactions, either reversible or irreversible, plug flow is preferred, because it allows to reach a higher average concentration of the reactants than a CSTR in which concentrations are constant and equal to the final ones.

Being usually the reaction kinetics a function of the concentration of reactants, a lower catalyst volume is required in case of plug flow.

In case of parallel reactions:

$$A \rightarrow R$$

$$A \rightarrow S$$

where R is the desired product and S a waste product, if a high reactant concentration favours the desired reaction, a plug flow is indicated.

On the contrary, if the high concentration of reactant favours the undesired reaction, a CSTR is preferred.

For more complicated systems of parallel reactions:

$$A + B \rightarrow R$$

$$A + B \rightarrow S$$

the choice is a little more difficult, depending on A and B concentrations, and a detailed discussion can be found in the book by Levenspiel cited in the references.

In case of consecutive reactions, a plug flow should be chosen in any case.

The thermal effects of the reactions must be considered to select an adequate type of reactor: from this viewpoint, the choice is between an isothermal and an adiabatic reactor.

Let us now consider reactors with solid catalyst and one fluid (gas or liquid) phase.

In case of exothermic reactions the problem is how to handle the heat generated by the reaction.

The cheapest alternative is the packed (or fixed) bed reactor: here reaction takes place almost adiabatically because heat losses are negligible in industrial reactors with large diameters, and the reaction heat raises the temperature of the reacting fluid.

Because temperature has a positive effect on reaction kinetics, in case of irreversible reactions the danger of adiabaticity is an uncontrollable temperature increase (run-away): it can also happen in limited zones of the catalytic bed, known as ''hot spots'', caused by maldistribution of the catalyst or of the reacting fluid.

When the main reaction is equilibrium limited, reaction runaway could be unlike, however secondary irreversible reactions can be present and must be taken in due account.

To decide whether an adiabatic reactor can be chosen, a good model of reaction kinetics, or an expensive experimentation performed on a size homologous to the industrial one are needed (the concept of homology will be explained later): if the temperature profile obtained simulating the industrial reactor is concave upward (Fig. 4), the reaction cannot be performed adiabatically, unless operating conditions are found that allow the profile to be concave downward, as shown in the graph: to do so, it can even be thought to use a less active catalyst, or to dilute the feed with some inerts, or to increase the recycle flowrate.

For exothermic reactions, equilibrium conversion decreases as temperature raises: the diagram of Fig. 5 reports conversion vs. temperature for the methanol synthesis reaction: the equilibrium curve is shown together with adiabatic and isothermal reactor profiles along the reactor starting from the same point.

It is possible to see that the highest conversion can be reached operating isothermally.

Isothermal reactions are performed industrially using multi-tubular reactors where catalyst is placed inside small tubes (even thousands) with a thermostatic fluid flowing around the tubes themselves (for instance saturated water, diathermic oil or molten salts).

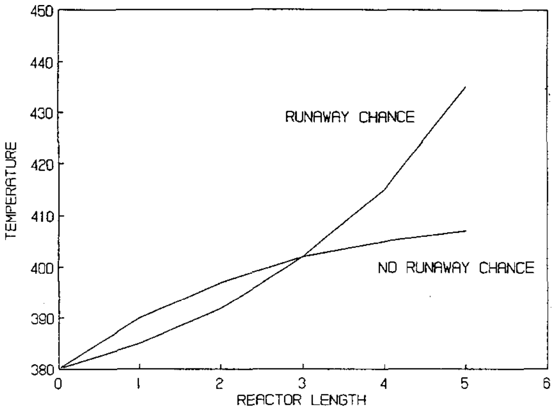

Fig. 4. Runaway conditions.

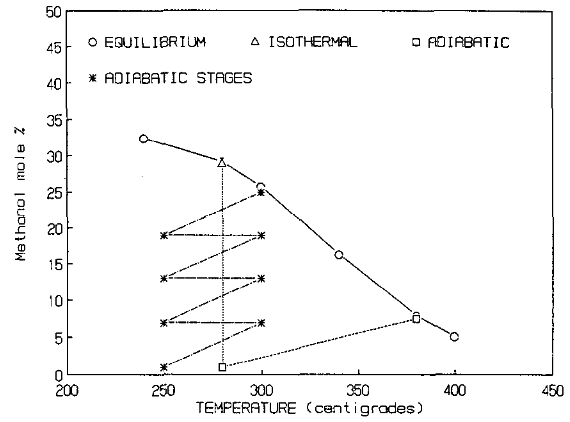

Fig. 5. Different types of temperature profiles.

This type of reactor is very effective in keeping reaction temperature constant, but it is very expensive and its maximum size is limited by mechanical considerations.

Anyway, even a multitubular reactor is not perfectly isothermal: there is always a peak of temperature at the beginning of the tubes, where the reaction rate is the fastest.

When multitubular reactors cannot be employed, isothermal operation can be approximated alternating some smaller fixed beds (usually 3–5) and intermediate cooling (multistage reactors): in Fig. 5 is reported the temperature-conversion profile that can be obtained with this type of operation, that allows to reach conversions closer to the isothermal path.

Intermediate cooling can also be obtained by "quenching" with cold reactants.

Typical industrial examples of this type of reactor are methanol or ammonia synthesis and SO_2 oxidation in sulphuric acid manufacture.

In case of severe equilibrium limitations, an intermediate separation of the product between two consecutive fixed beds can be considered: a further extension of this concept is the reactive-distillation column in which liquid and gas phases are simultaneously present and normal distillative trays are alternated with catalytic beds.

In case of endothermal reactions, the problem is opposite: how to supply the heat necessary to the reaction.

An adiabatic fixed bed can be used, preheating the feed at the maximum reaction temperature: this is an expensive operation with the risk to start unwanted homogeneous reactions, like for instance thermal cracking.

In case of athermal reactions, heat must be anyway given to the feed, to bring it to the reaction temperature.

Another common way to give heat to a reaction is to put the catalyst in tubes installed inside a furnace (a typical application is the steam reforming of methane to CO and hydrogen): if the reaction requires high temperatures, special and very expensive materials must be used for the tubes, and, in any case, the thermal efficiency of a furnace is normally quite low.

This is the way to approach isothermal operation with endothermal reactions.

The third chance is to give the reaction heat to the catalyst.

If this is done in a fixed bed, it is impossible to perform the reaction in a continuous mode: at least two reactors in parallel must be present: one under reaction and the other one under heating phase.

When a reactor becomes too cold for reaction, because the catalyst has lost its stored heat, valves are switched and the second reactor comes into operation: these reactor systems are known as ''swing reactors''.

Operation can be made continuous using the technology of fluidized beds: if the catalyst is a very fine powder (usually particles with average diameter around 100 μm), there is a wide range of gas velocities at which the solid remains suspended in the gas phase, forming a gas–solid emulsion that behaves like a liquid.

A fluidized solid can be easily continuously transported through pipes between two vessels in very large flow rates.

So, catalyst can be continuously withdrawn from the reactor, sent to another vessel where it is heated in some way and then transferred back to the reactor.

A very important problem to be considered in the choice of the reactor is the life of the catalyst: large industrial plant are usually stopped (shut-down) once a year or every two years for ordinary maintenance (turn-around).

If catalyst useful life is at least one year, ordinary maintenance can include its replacement.

Usually in fixed beds, feed temperature is raised during catalyst life to maintain its activity, until an upper limit is reached, where selectivity is too low, or catalyst begins to sinter: after that catalyst must be replaced.

If catalyst life is less than one year, some way must be found to prevent catalyst decay (e.g. eliminating poisons from the feed), or to restore its activity without stopping the plant.

This last operation is called regeneration: for instance, catalysts working in presence of hydrocarbons generally deactivate by deposition of coke on their surface.

Coke is produced by thermal cracking side reactions and catalyst deactivation can be very fast (even a few minutes).

Fluidized beds are particularly advantageous in such cases: deactivated catalyst is withdrawn continuously from the reactor, transported to a regenerator where coke is burnt with air restoring its activity, and then sent back to the reactor.

If the main reaction is endothermal, this is a way to give heat to the reaction itself, because coke combustion is highly exothermal.

There are very important petrochemical processes operating in this way: fluid catalytic cracking (FCC), where a naphtha feedstock is cracked to gasoline on a zeolite catalyst, or fluid bed dehydrogenation (FBD) of paraffins to olefins.

In case of endothermal reactions, a fluidized bed reactor with countercurrent movement of gas and solid allows a better approach to thermodynamic equilibrium: examining Fig. 6, where curve a represents the growing equilibrium conversion vs. temperature, and keeping in mind that at the top of the catalytic bed, where

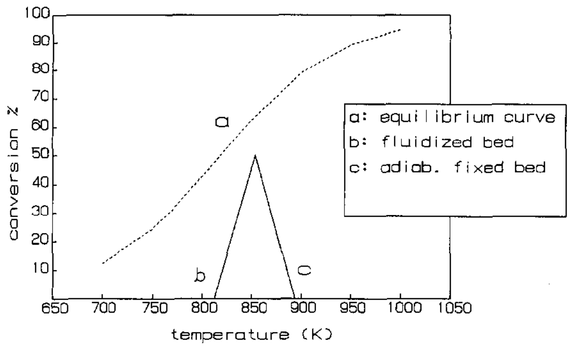

Fig. 6. Approach to equilibrium in different types of reactors.

hot regenerated catalyst arrives the temperature is higher than at the bottom, the temperature-conversion path of the gas phase along the reactor is b.

If we want to reach the same equilibrium conversion in a fixed bed with feed preheating, remembering that in this case there will be a reversal temperature profile, decreasing toward the gas outlet, the feed itself should be preheated at a very high temperature to reach the same equilibrium conversion than before (path c).

Another feature of fluidized beds is that the irregular movement of gas and solid inside the reactor brings about a high degree of back-mixing, taking the system away from plug-flow, and approaching CSTR conditions: this feature can be controlled adding baffles inside the beds, hindering the free movement of solids in the reactor.

An alternative to fluidized bed is mobile bed in which catalyst, in form of small spheres (normally 1 mm diameter), drops down slowly by gravity, in countercurrent with the gas and then is pneumatically transported to the regenerator.

This technology can be used if catalyst deactivation is not too fast or if the reaction does not need much heat, because the attainable solid flow rates are much lower than with fluidized beds.

When a fluid flows through a solid bed of catalyst, it loses energy in form of pressure, undergoing what is called ''pressure drop''.

In fixed beds with axial movement of the fluid phase which must pass through thick beds of solid (even many meters), pressure drop can become a major concern, for gas compression is very expensive, or because the operating pressure may change significantly throughout the catalyst bed.

Pressure drop in fixed beds can be much reduced placing the catalyst in an annular zone inside the reactor, and imposing a radial movement to the gas (Fig. 6): these are called ''radial reactors''.

By doing so, catalyst can be put in a thin layer, without enlarging too much the reactor: of course, it becomes very important (and difficult) to have a good distribution of the gas on the bed.

The same basic concepts apply in the case of triphasic systems: gas, liquid and solid catalyst.

The fixed bed becomes a ''trickle bed'' in which the gas can flow upward or downward, and the liquid flows downward by gravity.

The main problem with trickle beds is to achieve a correct distribution of gas and liquid flows on the catalyst: it is very important that solid particles are well wetted by a uniform liquid film.

The fluidized bed becomes a ''slurry reactor'' where catalyst in form of a fine powder is dispersed in the liquid phase: slurry reactors are usually stirred to favour intimate contact between the phases and thus approach very closely CSTR reactors.

6. The separation section

The choice of the reactor is the first step in the transformation of the block flow diagram in the flow-sheet diagram where every single item of the process is identified.

An important effort must be devoted to the optimization of the separation section, identifying every single unit operation (distillation, absorption, liquid extraction, etc.), and their sequence.

Since this is a subject for specialists, we will not go into detail, but just try to give a quick overview.

The first type of separation that everybody thinks of is distillation.

Distillation is indeed the most common method to separate the components of a mixture, based on their difference in boiling points (or, better, relative volatilities): it is performed stagewise, with gas and liquid phase flowing countercurrently and coming into intimate contact on trays or on particular packing.

The tower is heated at the bottom by a reboiler, and a temperature profile is established with the lowest temperature at the top.

Going upwards the gas is always richer in the more volatile component, while going downwards, the liquid is always richer in the heavier component.

The feed is introduced some (optimal) way along the path.

The liquid product (residue) is withdrawn from the bottom, while the gas (distillate) is withdrawn from the top.

At least part of the distillate is condensed and then refluxed to the top of the tower to provide a good quantity of liquid phase in the section above the feed, so that liquid–vapor equilibrium can take place.

To allow the use of distillation, all components to be separated must be present in both phases in the operating conditions chosen.

Another hindrance to the use of distillation is the presence of ''azeotropes''.

Azeotropism is the consequence of a deviation from ideality in the behaviour of a mixture at gas–liquid equilibrium: there is a temperature at which gas and liquid in equilibrium have the same composition: such temperature can be a minimum (Fig. 7) or a maximum, and azeotropism can be associated with immiscibility of the components in the liquid phase.

When this temperature is reached, it is not possible to push further separation by distillation.

The temperature/composition diagram of a system forming a minimum boiling azeotrope (point L) is reported in Fig. 7. A zone of liquid immiscibility is also present.

There are many alternatives to distillation,

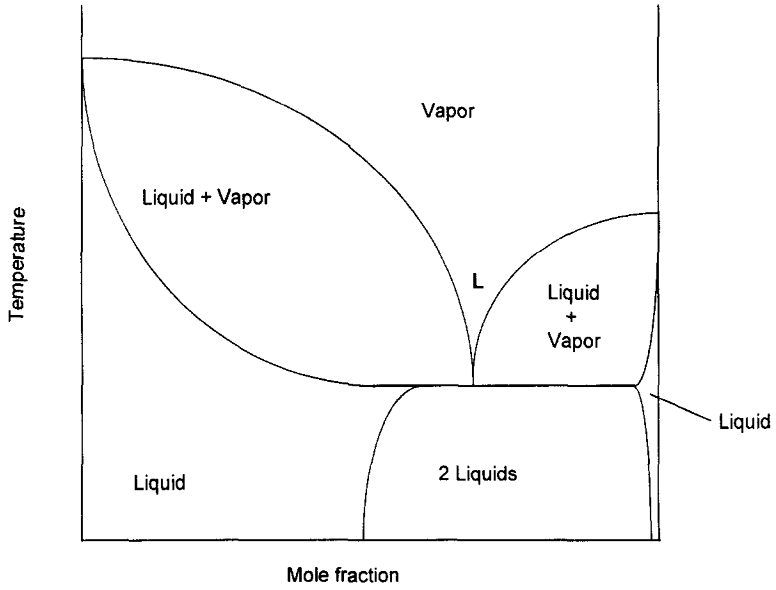

Fig. 7. Phase diagram for an azeotropic mixture.

often requiring the use of an external component:

– Gas absorption is an operation in which a gas mixture is contacted with a liquid for the purpose of preferentially dissolving one or more components of the gas.

When mass transfer occurs in the opposite direction, i.e. from the liquid to the gas, the operation is called desorption or stripping.

A general principle to be remembered for separations in which an external component is added is that a new mixture to be further separated is formed: the external component must be recovered and reused, while the absorbed or stripped component must follow its path in the process.

This means that in this case one more unit operation is added to the process scheme.

– Liquid extraction is the separation of the constituents of a liquid solution by contact with another insoluble liquid: if the substances of the original solution distribute themselves differently between the two liquid phases, a certain degree of separation is achieved, and this can be enhanced by the use of stagewise operation.

– If the energy involved in the liquid–solid transition is lower than that involved in gas–liquid transition, two or more components can be separated by crystallization.

Separations involving solids are usually quite expensive because it is more difficult to move a solid than a gas or a liquid.

– A rapidly increasing field is that of membrane separations, exploiting the different diffusivities of fluids through microporous membranes.

– Two immiscible liquid phases can be quickly separated by gravity settling or centrifugation.

7. The concept of homology

When the main unit operations involved in the process have been defined, it is possible to perform a first technical-economical feasibility study, that, even if approximate, gives important indications about the opportunity to pass to a phase of intensive research.

The areas of uncertainty still existing are defined, and research is addressed toward these areas.

It is important to determine at this stage the minimum necessary experimental equipment size to obtain useful data to develop the process.

When reliable mathematical models are available for scale-up, the size can be very small, even the same that in the exploratory phase.

Otherwise, the minimum size will be chosen to operate in ''homology'' with the industrial plant: homology means same fluid-dynamical, chemical and mechanical behaviour.

A conceptual ''scale-down'' must be performed, to design an experimental unit able to work in ''homology'' with the industrial operation: for instance, the homologous for a multitubular reactor is not a single tube, but a bundle of tubes, because otherwise thermal effects caused by close tubes are ignored.

An experimentation performed in this way can be very expensive, because it means pilot plants of conspicuous dimensions.

8. Energy optimization

Once data from this phase are available, the elaboration of detailed mass and energy balances is performed culminating in the formalization of the flowsheet.

The results of mass and energy balances are of primary importance for the following evaluations of technical-economical feasibility: they constitute the input for the experts of this discipline.

For economical evaluations of material and energy consumption, the process scheme can be reduced again to a single ''black box'' block again, reporting all the results.

Referring for instance to the oxidative coupling process of Fig. 2, the following material inputs and outputs can be identified:

Input
Methane: 11598.2 lb mol/h
Oxygen: 6392.0 lb mol/h

Output
Ethylene: 4464.3 lb mol/h
Propylene: 128.1 lb mol/h
Fuel gas: 7386.9 lb mol/h
CO_2: 1985.0 lb mol/h
Water: 8306.1 lb mol/h

The cost of raw materials methane and oxygen and the value of the various products contribute to the determination of the economical feasibility of the process.

There are also inputs and outputs of energetic nature: the overall process of transformation of the reactants into products can require energy in various forms and can produce energy in various forms that can be exported from the plant and sold.

In the process of Fig. 2, the following energy per pound of ethylene produced is required:

– Electrical power:	0.00902 KWH
– Fuel gas:	0.00757 MM Btu
– Cooling water:	0.02438 M Gal
– Boiler feedwater:	0.00001 M Gal

It is worth spending some words about the optimization of the process from the energetic point of view.

The cost of production of a chemical product, other conditions (for instance yield) being equal, is a function of the overall money spent to build the plant (investment cost) and of the energy consumed in the production cycle (consumption).

In the design and optimization phase, reducing the consumption always leads to increased investment costs: for instance, we could release to the atmosphere a hot waste gas at 300°C, or recover its heat producing steam to be used in the plant or exported; to recover the heat additional equipment must be added to the plant.

Another typical example are distillation towers in which the same degree of purification can be reached increasing the number of trays or increasing the reflux flowrate at the top: the first alternative means increased investment costs, while the second means mainly increased consumption (it can also mean increased investment if reflux flowrate becomes so large to make it necessary to increase the diameter of the tower).

As it is shown in Fig. 8, there is an optimal pair number of trays-reflux flowrate that minimizes overall costs.

Optimization means finding the best compromise between investment and consumption: in times of high costs of energy, the trend is to go toward low consumption, while if energy is cheap, it is preferable to decrease the investment.

In any chemical process, a number of streams must be heated, while other streams must be cooled, energy is produced in some sections of the plant and is required in other sections.

Decisions to be taken involve how to exchange heat between hot and cold streams, how to use the energy produced in the plant and if it is better to maximize energy production or to import energy from external sources.

This kind of optimization has been traditionally left to the experience of process engineers.

Only in the last decade mathematical methods have been developed to perform this task, but they have not yet entered in common practice.

Once the number of streams to be cooled and the number of streams to be heated, their starting temperatures and their desired final temperatures have been determined, it is possible to establish the way to pair them off, so to minimize the overall heat exchange surface.

During this optimization, the importance of the fluid phase in the efficiency of heat exchange must be remembered: a gas stream is much worse than a liquid stream, that in turn is worse than a phase transient stream (condensing vapour or vaporizing liquid).

It must also be remembered that in a chemi-

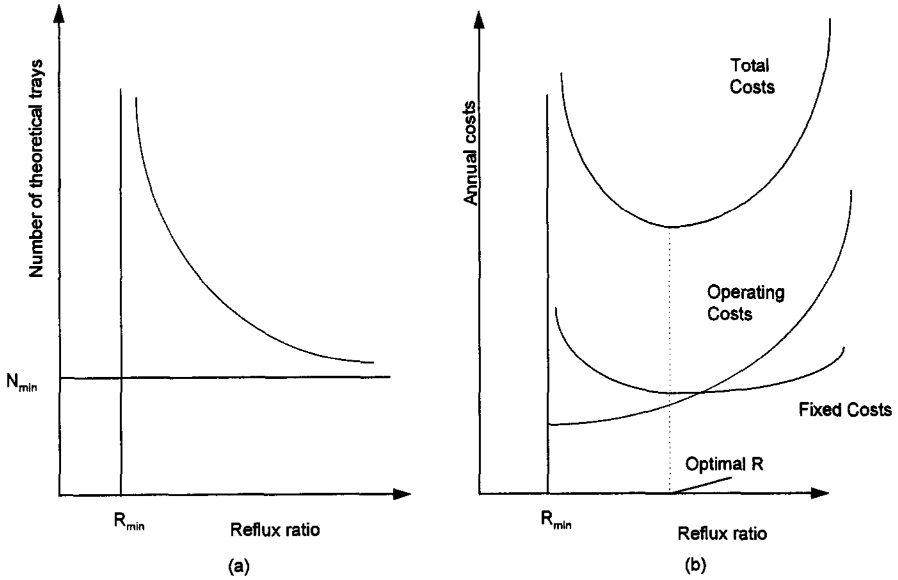

Fig. 8. Determination of optimum reflux ratio.

cal plant, some fluid streams are always available, even if not always at the same price: water, steam (usually at different pressures), air.

These are called "utilities" and can be used as hot or cold streams in the heat exchange network.

It is possible to reach temperatures lower than ambient using refrigerant media as utilities in refrigeration cycles, but this is very expensive and it is done only in absence of viable alternatives.

In this phase it is important to begin to consider materials of construction: if to recover heat from a very hot stream, a heat exchanger must be built with very expensive materials, the recovery may not be convenient.

The sections of a process that require more energy generally are:

1. The separation system
2. Compressors and pumps
3. Endothermic reactions

Almost every separation needs energy.

For example, in a distillation part of the feed is vaporized: the necessary energy is given by a reboiler on the bottom of the column, usually operated by condensing steam.

The latent heat of condensation of the steam is transferred to the gas–liquid mixture inside the column.

In every process some fluids must be brought from a lower to a higher pressure.

Pumping of a liquid does nor require much energy, unless very particular cases, and small electric motors are used.

Compressing a gas, on the contrary, involves enormous quantities of energy: electrical energy is usually quite expensive, and therefore gas compressors are often mechanically moved by steam turbines or by expanding some high pressure process stream (turbo-expanders).

In last paragraphs we have been mentioning steam quite often.

In every large chemical plant a complete cycle of steam is present: steam is generated at high temperature and pressure; its energy is used in the turbines that move turbogenerators, then, at medium or low pressure, it is condensed in the reboilers or it is used to heat some cold streams, and when it has all been transformed into water, the cycle starts again.

In case of exothermal reactions, steam can be generated by the reaction heat (waste steam boilers): directly in a multi-tubular reactor or by heat exchange of the hot effluent stream in a fixed bed reactor.

9. Process simulation software

In the past, the enormous amount of trial-and-error calculations necessary to the optimization and design of a chemical process was performed by engineers with the help of only a slide-rule.

Nowadays, sophisticated simulation software is available, performing detailed mass and energy balances and solve almost every type of unit operation in few minutes, thanks to hardware evolution that allows interactive working.

Such software is very expensive (they are usually rent by producers) and people by the dozens continuously work to their updating in specialized software houses.

All of them have essentially the same components:

- An executive system
- A physical properties data bank
- A thermodynamic methods package
- A collection of design (and sometimes cost) subroutines for a variety of process units.

The current trend is to add optimization routines, process dynamic capabilities and friendlier user interfaces with always more sophisticated graphics.

This software must anyway be used by expert people.

Physical properties for the components of interest must be carefully evaluated and if the user has more reliable data, he must substitute them to the default data.

The aid of an expert in thermodynamics is necessary to choose, among the myriad of thermodynamic methods proposed, the one that fits at the best to the type of components and operating conditions: a bad choice leads inevitably to big errors.

Errors are always present in process design: it is important to know their amplitude.

There are often convergence problems on some single units or on the whole scheme and it is not always easy to understand the reasons and to insert the right corrections.

The main problem with this software remains reactor simulation: it is possible to simulate by default only reactions going to thermodynamic equilibrium (if thermodynamic data are available) and thus it is not possible to design a reactor.

It is usually possible to add Fortran subroutines to the program (''user added subroutines''): for example, the kinetics of a reacting system and a reactor model can be added and thus implemented in the overall process scheme.

Some of these software packages allow to make approximate economical evaluations of the process: this is very useful in the phase of process development to compare different process alternatives.

In this phase absolute costing values do not matter much, but just the comparison.

10. The flowsheet

This phase of the work culminates with the issue of the process flowsheet diagram (PFD).

In the flowsheet, the exact type of equipment is specified for every process operation, and every equipment is identified by an acronym.

All the process streams are shown as lines connecting the process units, numbered and their temperature and pressure are reported.

To the flowsheet are attached the stream tables, in which complete composition, temperature and pressure are indicated for every process stream.

On the flowsheet, the main control loops are conceptually indicated: for instance, how can the outlet reactor temperature be kept constant during operation?

In a multitubular reactor, for instance, by varying the temperature of the coolant, while in

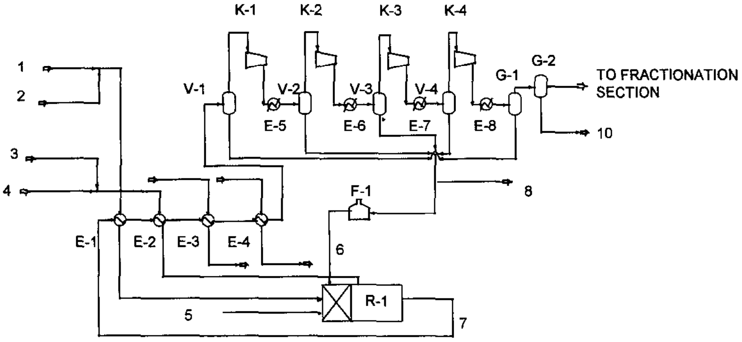

Fig. 9. Simplified process flowsheet.

an adiabatic reactor the controlled variable could be the temperature of the feed.

Fluid flow rates are controlled by valves operated by flow transmitters, while pressures are controlled by pressure transmitters and valves.

A simplified flowsheet, without temperatures, pressures and instruments is reported in Fig. 9, and the attached stream tables in Fig. 10.

The design is now going to pass from conceptual to practical: the first approximate design of the main process equipment allows a preliminary evaluation of their mechanical and thermal problems.

The so-called "battery limits" conditions have also been fixed: process streams exiting or entering the process unit, purity of products and reactants, definition of effluents from the environmental view-point.

Type and quality of utilities and construction materials have also been defined.

Up to this point alternative schemes can be studied and compared, to reach a preliminary process optimization.

11. Process design and further work

The next step is process design, a phase of maximum engagement for process engineers.

Now the goal is the issue of the P and I diagram and the process specifications of the single pieces of equipment.

Stream n°		1	2	3	4	5	6	7	8	10	11	12	13
Name		Methane Feed	Recycle Methane	Ethane Feed	Recycle Ethane	Oxygen Feed	Recycle Water	Reactor Effluent	Wasle Water	Carbon Dioxide	Fuel Purge	Ethylene Product	Propylene Product
Mole Flow	Kmol/hr												
Methane		5260.86	12732.34					14174.83			1437.57		
Oxygen						2899.36							
Hydrogen			279.41					2058.5			1782.66		
Carbon Monoxide			201.85					329.17			127.32		
Carbon Dioxide								899.51		898.61	0.90		
Ethylene			0.73		23.13			2046.53			2.86	2023.75	
Ethane				720.17	596.02			600.80			0.18	1.22	
Propylene								54.32					0.59
Propane								3.26					54.25
Water							7197.28	11062.27	3864.99				3.22
Total Flow	Kmol/hr	5260.86	13214.32	720.17	619.15	2899.36	7197.28	31229.19	3864.99		3351.49	2024.97	58.06
Total Flow	Kg/hr	84384.11	2.11E+06	185170.00	18571.31	928000.00	1.30E+05	557880.00	69627.9		30306.74	56811.04	2442.63

Fig. 10. Stream tables.

P and I diagrams (Piping and Instruments) are detailed schemes, in which are normally reported:

- Every piece of equipment.
- Every pipe and valve with their size and materials of construction.
- The complete instrumentation system, including the definition of safety systems.

By the way, process engineers must be able to foresee the consequences of every possible malfunctioning of the process, and design safety procedures to avoid any risk of damage to persons, environment and equipment: from alarms to automatized procedures for rapid shut-down.

The process specifications are sheets of paper: one or more sheets for every piece of equipment, in which all the necessary features to mechanical design are reported; design and operating temperatures and pressures, types of materials handled, construction suggested materials, vessel dimensions, and any necessary information to allow the correct design.

Process schemes and specifications are the systematic ways through which the process engineers tell the colleagues working on detailed design how the plant must be built to meet the requirements of the process.

Just as researchers have transferred their knowledge to process engineers, now knowledge is transferred to the men who will build the plant: the success of these transfers of information is the key-point to achieve the final success.

The issue of P and I and specifications has the following consequences:

- Further requests to research (at increasing specificity).
- Issue of a detailed lay-out by the specialists involved.
- Technical-economical feasibility study made by specialists with uncertainty reduced to 10%.
- Issue of a detailed safety study (HAZOP – Hazard operation study, HAZAN – Hazard analysis), with an important feedback on instrumentation schemes and safety systems.
- Definition of operating and analytical manuals: the sacred books for people who will operate the process.
- Definition of process guarantees (yield, purity, consumption, etc.)
- Possibility to offer LSTK (Lump Sum Turn Key)

Everything enters the technological package that allows the construction of the plant, but work is not yet over: a strong control is necessary during the construction to be sure that everything is realized as desired.

A very important moment comes at the start-up of the plant: all the components that have taken part in the process development are engaged to reach easily steady operating conditions, to verify the consistency of experimental data with design values, to understand the reason of possible differences and to solve unexpected problems.

Experiences and data collected in this period and in the following runs of the plant will give an important feedback to the design of new plants and to further research in the field.

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