

Mixing of The Production of Bulk Chemicals

Overview

Bulk chemicals or "commodity chemicals" are a broad chemical category including polymers, petrochemicals, other derivatives and basic industrials, inorganic chemicals, and fertilizers. Typical growth rates for basic chemicals are about 0.5 to 0.7 times a country's GDP and product prices are generally less than fifty cents per pound. Mixing and chemical reaction are closely related topics as chemicals need to be agitated in order to make contact and react with one another.^{1,2,3} Insufficient mixing and mass transfer could influence reaction rate and product distribution. In 1989, the cost of poor mixing was estimated at \$1 billion to \$10 billion in the U.S. chemical industry alone.³ In one multinational chemical company, lost value due to poor mixing was estimated at \$100 million per year in 1993.³ Yield losses of 5% due to poor mixing are typical.³



Figure 1. An industrial-size stirred reactor with multiple impellers and baffle⁴

Examples of industrial applications of mixing in the chemical industry³ include:

- Mixing miscible/dispersing immiscible reactants
- Dissolving gases (e.g., chlorination processes)
- Providing plug flow and controlled-reaction conditions in tubular reactors with low or high viscous fluids
- Dispersing liquids in extraction and washing processes
- Mixing gases in front of catalytic reactors (e.g., the production of styrene, nitric acid, maleic anhydride)
- Vaporizing liquids in front of oxidation reactors (e.g., xylene in phthalic anhydride plants)
- Co-current scrubbing acid process gas components
- Homogenizing process and product streams for representative sampling
- Neutralizing or pH adjustment/control of process streams with caustic or acid

The mixing issues of the following four chemical reactions plus a crystallization process, which a chemical engineer named Marco came across in a chemical plant, are vivid real life problems for mixing of bulk chemicals. These cases also serve as an overview to the subentries below.^{3,5,6}

Competitive-consecutive reaction. Bromination of an aromatic ring was the intended reaction, but due to overreaction, a second bromine was being added. This reduced selectivity could be caused by differences in micro-mixing and meso-mixing on scale-up. However, testing at two extreme stirring conditions did not show a difference in overbromination. A reversed addition of reactant to brominating reagent reveals overreaction. Therefore, insufficient mixing will result in lower selectivity due to competitive or consecutive side reactions.

Gas-liquid reaction. A hydrogenation reaction required 8 hours of reaction time, which was inherently slow according to the chemist. Upon careful inspection of the autoclave, it was revealed that surface reincorporation was not achieved due to high z/T ratio and full baffles. After Marco cut the baffles in order to create a vortex to the top of the pitched blade turbine, the reaction finished within half an hour. Reactor design is an important factor to improve the mixing for this type of reaction. Liquid viscosity determines the basic mixing mechanics and types of equipment to use in practice.

Solid-liquid reaction. An alkylation using powdered potassium carbonate to react with an organic acid in solution was scaled up to the pilot plant. The reaction was slower than expected and clogging happened at the bottom outlet of the reactor. Solid dissolving issues and inadequate mixing for the off-bottom suspension were solved by using a pitched blade turbine impeller and full baffles. The sensitivity of reaction rate to both particle size and impeller speed was readily established.

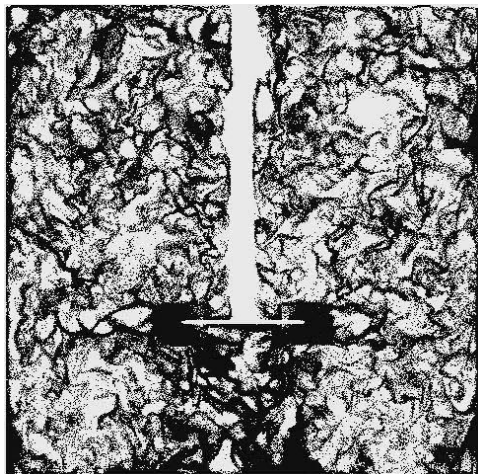
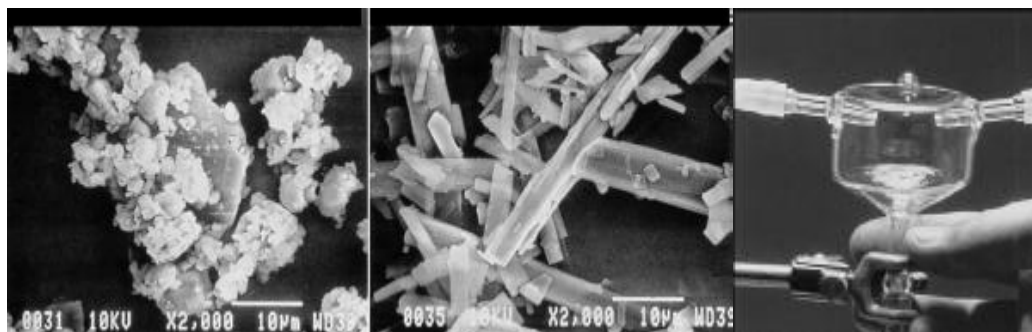


Figure 2. Example of a solid-liquid reaction within an agitated vessel.⁷

Liquid-liquid reaction. A change of reaction vessel and impeller caused a drop in conversion rate and selectivity. Liquid-liquid complex reactions were considered the most difficult reaction scale-up mixing problem. Drop formation and coalescence change with scale, while location in a vessel has a very subtle change in fluids compositions. A quick “fix” is to increase impeller speed. In the meanwhile, overmixing could improve rate while reducing selectivity by exposing the product in droplet film to a higher concentration of reagent in the aqueous phase.⁸

Reactive crystallization. Reactive crystallization presents critical mixing issues because mixing affects both the reaction and crystallization step. Marco's group had always had difficulty with reactive crystallization scale-up due to:

- 1) The need to balance the requirements to achieve a growth-dominated process
- 2) Choose a mixing system fast enough to micro-mix effectively for the fast reaction
- 3) Ensure mixing is not too powerful that it will cause crystal fracture.



Milled from larger crystals Impinging jet crystallization An impinging jet crystallizer

Figure 3. Equal surface area products obtained by milling larger crystals and by impinging jet crystallization (with improved product stability as well)⁹

The above issues will be addressed in four subentries: reactor design, heterogeneous reactions, scale-up of reactors and crystallization. In summary, reaction type dictates the reactor design and scale-up of reactors. Mixing is very important in heterogeneous reactions to avoid mass transfer limitation and in crystallization processes to control crystal size and minimize impurity-uptake.

Principles of Reactor Design and Mixing for the Chemical Industry

In the chemical industry, proper reactor design is crucial because this is where both mixing and reaction occur. For a mixing sensitive reaction, the rate of mixing affects both the yield and selectivity of the reaction.¹⁰ Poor mixing can lead to side reactions and undesirable by-products in competitive reactions. A common industrial example of this is acid/base neutralization in the presence of organic substrates. Rapid, highly turbulent mixing is needed to promote the fast reacting neutralization reaction and inhibit the slower, unwanted side reactions such as hydrolysis.

There are many reactor geometries used in the chemical industry, but discussion will be limited to four geometries: pipeline, Tee mixer, static mixer, and stirred tank as shown in Figure 4. Additionally, the effect of feed point location will be discussed.

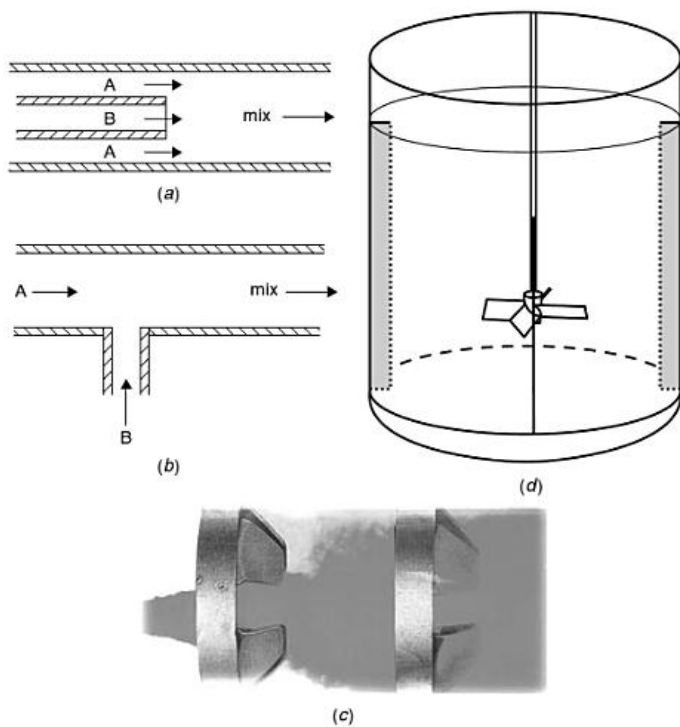


Figure 4. Various mixing geometries used for chemical reactors: (a) co-axial jet pipeline mixer, (b) Tee mixer, (c) static mixer, and (d) stirred tank.³

A pipe, or tubular reactor, is the simplest chemical reactor. Reactants are injected in one end and allowed to mix as they flow towards the outlet. Often injection is done with a co-axial jet in the center of the pipe. Turbulent flow requires approximately 50 to 100 pipe diameters to achieve 95% uniformity within the pipeline.³ This option is often used successfully in highly turbulent flow where mixing length and time are not important.

The Tee Mixer is a variation of the pipe mixer where one of the reactants is injected as a side stream jet into the flow of the other reactant. This promotes rapid mixing within the turbulent core of the pipeline. A Tee mixer can shorten the blending to 95% uniformity to between three and five pipe diameters.¹¹ It is important to design a Tee mixer with the proper jet to pipe velocity and diameter ratios to promote optimal mixing. This option is used when short mixing distances are required and the additive is available at adequate pressure energy.

Static mixers are placed within pipes to divert the internal flow by creating obstructions that promote mixing.¹² Static mixers are the most versatile motionless mixer and have a wide variety of designs and applications. The most economical type of static mixer chosen depends primarily on the flow regime of the system, the viscosity ratio of the feeds to the mixer and the ratio of feed flow rates. Static mixers are ideal for laminar mixing, but also work well in turbulent flow for both single and multiphase flows.³

The stirred tank consists of a vessel and mixing device. They have a wide variety of uses due to their great operating flexibility. Stirred tanks can be operated in both laminar and highly turbulent mixing regimes, and come in a wide selection of sizes. They can be used for a liquid phase mixture, a liquid-gas

mixture, a liquid with suspended solids mixture or a three phase mixture. Precipitation, polymerization and hydrometallurgical processes are usually conducted in stirred vessels.² Important design criteria for a stirred vessel include impeller type, size and speed and baffle design.

Along with reactor geometry, the position of the feed point can also affect reaction yield and selectivity because there can be a wide range of turbulent length scales and intensities within a reactor. Generally, the ideal location for a feed point to promote rapid blending is in the region with the shortest local mixing time constant or the most intense turbulence.³ For example, in a stirred tank, optimal mixing occurs if feed is injected close to the tip of the impeller. Multiple injections points are another option to consider if the rate of injection is important. By increasing the number of feed points, the feed flow rate can be decreased without decreasing productivity.²

Heterogeneous reactions and reactors

Three main types of reactors are classified based on their feeding mode, batch, semi batch and continuous flow. In a pure batch reactor, there is no flow in or out of the reactor while the reaction occurs. Semi batch reactors are also known as fed-batch reactors because feeds can be added at different stages of the reaction. Continuous flow reactors have both inlet and outlet flows while the reaction takes place. Regardless of the reactor type, it is imperative to understand the reactions taking place within the mixing vessel.

When a chemical reaction occurs within a reactor, many complex problems arise. Two of the biggest problems can be categorized into whether the reaction is governed by mass transfer or reaction rate. In general, if a reaction is very fast the reaction is mass transfer controlled and if the reaction is very slow, the chemical kinetics are the controlling factor.

In very slow reactions, the chemical kinetics has a very small impact with respect to the mass transfer rate. This indicates that no molar ratio change for reactants within the mixer is necessary and that strenuous mixing would have no effect on the reaction. When slow reactions occur, the reaction rate is increased when mixing occurs but selectivity is usually unaffected. For fast reactions and very fast reactions, mixing has more of an impact on the reaction. Both conversion and selectivity need to be carefully accessed in these cases. Figure 5 represents a possible industrial reaction with different reaction rates.

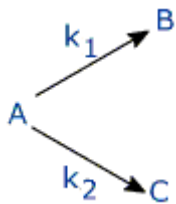


Figure 5. A parallel reaction with two different reaction rates.¹³

For heterogeneous reactions, mass transfer limitations at chemical compound boundaries have a direct impact on reaction. The reasoning for this is that in heterogeneous reactions, the molar ratios can't be maintained. The impact of mass transfer limitations has a direct impact on selectivity; it is one of the main distinct reasons why selectivity for homogeneous and heterogeneous reactions differs.

The intensity of mixing and the time spent in the mixing vessel have a direct impact on mass transfer and kinetic rates. In homogenous reactions, local molar ratios and chemical kinetics are most affected by the degree and intensity of mixing while for heterogeneous reactions; global molar ratios, mass transfer rates and chemical kinetics are most affected. The extent of mixing has a direct impact on reactions as mentioned earlier. In most heterogeneous reactions there is a mass transfer boundary between reactants and depending on the intensity of mixing, this boundary can shift and different products can form. Along with the intensity of mixing, the time spent inside of the reactor has a large impact on selectivity.

Scale-up in the Chemical Industry

A pilot size vessel is scaled up with the intentions of maintaining similar characteristics. However this isn't easy and in order to achieve a successful scale up, it is important to consider the key points related to reaction and mixing. Therefore it is important to analyze information obtained from pilot size reactions so they can be used in the implementation of commercial size reactors.

Some factors affecting scale up include: the range of shear rate and energy dissipation in the vessel widen as volume of vessel is increased. Heat transfer surface area per unit volume will decrease and this could lead to hot spots which are bad because it could lead to unwanted chemical reactions.¹⁴ The manner in which chemicals (feed) are added is critical because the conditions will change between pilot size and scale up and can have an effect by factor > 10. At some critical concentration of chemicals, the chemical reaction becomes faster than mixing and this affects conversion and yield.^{15,16} Therefore chemicals need to be added in such a way little or no reaction takes place before mixing is done.

To address these concerns several methods need to be practiced such as using the same concentration of chemicals in both pilot and scale up. Also the time for addition of chemicals increases on scale-up because of heat transfer limitations and to maintain expected molar ratio at the feed point. If the feed time is small, then the yield may be small. Even though mixing varies depending on size of vessel, the Damkohler numbers stays the same for different vessel size, impeller rotation rate, feed location and concentration. Therefore it is a useful parameter when considering scale up because it tells us about the mixing effects that need to be considered. It is given by equation 1.

$$Da_M = \tau_M/\tau_R = \text{mixing time/reaction time} \quad (1)$$

$Da_M < 0.001$	Reaction rate is slower than mixing rate and chemical kinetics determine selectivity
$Da_M > 1000$	Reaction rate is much faster than mixing rate
$0.001 < Da_M < 1000$	when reaction rate and mixing rate compete and both micromixing and chemical kinetics must be considered

Feed pipe backmixing lowers yield by causing a slower overall mixing rate of the reactants. To avoid this, one must have sufficient feed pipe exit velocity/impeller tip speed (v_f/v_t).¹⁷

Several points need to be discussed for two-phase reaction scale up:

Liquid-Liquid Reaction. There are many uncertainties with this system when scaling up. Testing over a wide range of operating conditions in the pilot phase is required to determine interfacial differences which will help predict sensitivity of each system to changes in dispersion characteristics.^{18,19,20} The range of operating conditions should include mixing configurations, impeller speeds and system compositions. To predict scale-up characteristics, use constant power per unit volume but look out for differences in densities for the reactants. Mass transfer limitation may be present.

Liquid-Solid Reactions. The properties of these reactions are also system dependent and at the pilot scale, these reactions need to be operated under extreme conditions to determine if there is a sensitivity to mixing. Solid suspension is required so sufficient power and speed should be applied but there is the possibility of overmixing. It's important to maintain a good mass transfer rate to get good mixing between solids and liquid in order to achieve the expected reaction rate. The mass transfer rate can be affected when the solid is covered by another solid or liquid. This unwanted film slows mass transfer rate and needs to be removed by either chemical means (addition of surfactant) or physical means (varying mixing intensity).

Crystallization in Chemical Industry

Contrary to many people's beliefs, mixing and crystallization have a strong interaction. A study of calcium oxalate crystallization showed that the particle size distribution was affected significantly by impeller speed and other mixing variables.²¹ Mixing affects crystal nucleation, growth and slurry maintenance in different ways, which makes crystallization the most difficult operation to scale-up successfully.^{3,9,22}

General problems are:

- control of crystal size to ease filtration wash and drying.
- excess nucleation and/or crystal fracture.
- occlusion of impurities and unacceptable physical properties.

Equipment. The crystallizers employed in the fine chemical and pharmaceutical industries are generally multipurpose vessels with a pitched blade turbine, which have good circulation and relatively low shear to reduce secondary nucleation and crystal breakage. Another good impeller choice in some crystallization processes is Internig by Ekato. Baffles are necessary to prevent poor mixing. Other crystallization vessels could also be a batch crystallizer, fluidized bed crystallizer or draft tube baffle (DTB) crystallizer.²² Fluidized beds are optimized for crystal growth by providing low shear, low energy and minimum impact between crystals, while impinging jets do the opposite by promoting nucleation with extreme mixing, high shear and large energy input.

Mixing and Crystal Growth. Mixing minimizes the supersaturation gradient in the film around a growing crystal by maintaining high mass transfer rates. Additionally, mixing improves heat transfer, bulk turnover, dispersion of additives like an antisolvent, uniformity of crystal suspension, avoidance of settling, minimization of wall scale and reduction of impurity concentration at the crystallizing surface. Over-mixing results in crystal breakage and shredding of nuclei promoting secondary nucleation.

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