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Quickly Estimate Reagent Addition Time

A simple equation suffices in many situations involving batch reactors

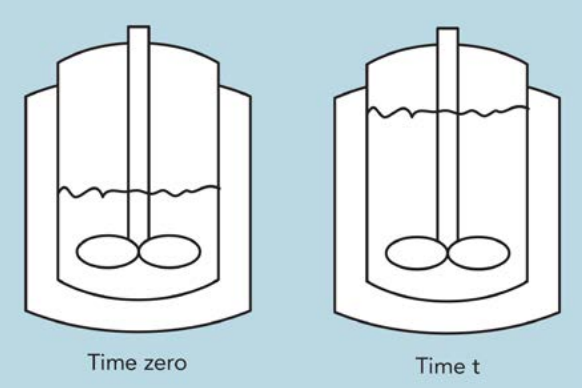
By Michael J. Gentilcore, Mallinckrodt Pharmaceutical, and Luigi Grippa, Libero Professionista

Batches often have a step in which a reagent chemical is added to a mixture being stirred and reacts immediately (with little accumulation) — with the rate of addition controlled by the ability to remove heat. A maximum temperature is specified with full cooling applied to the reactor's jacket. If the reagent chemical is dilute enough to cause a significant level change, then the wetted area for heat transfer will not remain constant.

When the reaction rate is much faster than the feed rate, the added reagent is immediately converted to product by spontaneous reaction with the substrate previously charged to the reactor. A negligible buildup of the reagent occurs in the reactor during the addition. The heat production rate is directly proportional to the feed rate of the reagent as limited by the heat transfer of the jacket. The reagent feed rate can be raised as the volume increases and provides more wetted area for heat transfer.

DERIVING THE EQUATION

For simplification, let's assume the liquid mixture in the reactor prior to addition



JACKETED REACTOR
Figure 1. Equation assumes that batch always is on the straight wall of vessel.

is on the straight wall as shown in Figure 1. For purposes of integration, let's also assume the heat of reaction (ΔH), liquid density (ρ), overall heat transfer coefficient (U) and temperature differential (ΔT) between the utility (jacket) and process (tank) remain constant.

This situation is the reverse of a batch distillation — for which the equations and their derivation have been published previously [1]. The solution is:

$A_t/A_0 = e{-}t/\Theta$ (1)
where $\Theta = \rho \times D \times \Delta H/(4U \times \Delta T)$ (2)

The differences versus batch distillation are in the definition of the terms ρ, ΔH and ΔT. Let's discuss each of these.

Liquid density. In batch distillation, ρ is the density of the liquid in the vessel. For reagent addition, this term is the net weight added during the addition versus the observed volume change of the reaction mix. For the special case where the reagent and reaction mixture mix ideally with a zero volume change, the density equals that of the reagent.

Enthalpy change. In batch distillation, ΔH is the heat of vaporization of the evaporated solvent. For reagent addition, it is the heat of reaction expressed as unit of heat versus the net weight added. The heat of reaction must be calculated at the temperature of reaction and must include all enthalpy effects such as the sensible heat from a reagent below reaction temperature, heat of dilution, evaporative cooling when there is a byproduct off-gas and, of course, the chemical heat of reaction.

Temperature difference. The ΔT term is the same and constant for both batch distillation and reagent addition. Typically in batch distillation, steam is the heating medium and calculation of this term is straightforward because both the process and jacket are isothermal. In reagent addition, a liquid commonly is the coolant and the jacket supply and outlet temperature are unequal. In this case, the difference is determined by a log mean temperature calculation.

For a simple case of water flowing once through a jacket, the following relationships apply:

$T_O = T_P + (T_S - T_P)/K$ (3)
where $K = \exp[(UA)/(WC_p)]$ (4)

Eq. 4 includes the wetted area (A). Under a rigorous analysis, the temperature difference is not constant. However, as an approximation, the log mean temperature difference can be calculated at both the lowest level (A0) and highest level (At) in the integration. For practical problems,

NOMENCLATURE

A	area, ft^2, m^2
Cp	Coolant heat capacity, BTU/(lb×°F), J/(Kg×-°C)
D	Tank i nside diameter, ft, m
ΔH	Heat of reaction, BTU/lb, J/kg
K	Flow rate correction per Eq. 4, dimensionless
t	Temperature, °F, °C
ΔT	Temperature difference (jacket - process), °F, °C
T	Time, hr
U	Overall heat transfer coefficient, BTU/($hr \times ft^2 \times °F$), W/($m^2 \times$-°C)
W	Coolant flow rate, lb/hr, kg/s
ρ	Liquid density, lb/ft^3, kg/m^3
Θ	Time constant per Eq. 2, hr

Subscripts

0	Time zero
f	Formation
t	Time t
S	Coolant supply (jacket inlet temperature)
O	Coolant return temperature (jacket outlet temperature)
P	Process temperature (reaction temperature)

the observed disparity in temperature difference will be slight and the lower value can be used to provide a conservative estimate of addition time. An example will illustrate this.

Many reactors have heat/cool modules that enable the jacket inlet temperature to differ from the coolant supply temperature. In such cases, substitute equations that are available in Reference 2 for Eq. 3 and Eq. 4.

AN EXAMPLE

Molten sodium metal is added to water to make a sodium hydroxide solution — with the temperature controlled isothermally at 77°F during the addition. The reaction chemistry is:

$Na\text{ (liq.)} + H_2O\text{ (liq.)} \rightarrow NaOH\text{ (aq.)} + \frac{1}{2}H_2\text{ (gas)}$

The reaction occurs in a vessel with a 5-ft outer diameter and a $\frac{1}{4}$-in.-thick shell, equipped with a bottom ASME F&D head. The straight wall holds 144.5 gal/ft of liquid height. The bottom head holds 73.9 gal. The straight side has a wetted area of 15.7 ft^2/ft of liquid height. The outside surface area of the bottom head is 23.2 ft^2. Table 1 presents a heat and material balance for this reaction.

Let's now estimate the addition time, assuming an overall heat transfer coefficient of 80 BTU/hr/ft^2/°F and 25,000 lb/hr of 41°F chilled water flow (Cp = 1) to the jacket.

	Before Reaction		After Reaction			
	Liquid to be added	Liquid in reactor	Offgases		Reactor Contents	
	Sodium	Water	No. 1 (H_2)	No. 2 (Water)	Solute (NaOH)	Solvent (Water)
Weight, lb	1,683.5	6,610.3	73.8	14.2	2,928.9	5,276.9
Moles, lb-moles	73.2	366.9	36.6	0.8	73.2	292.9
Volume, gal	219.9	795.9			712.0	
T, °F	260.3	77.0	77.0	77.0	77.0	77.0
ΔH_f@ T, kcal/mole	1.357	-68.315	0.00	-57.796	-110.219	-68.315
ΔH_f @ T, BTU/lb	106.3	-6,831.7	0.0	-5,579.8	-4,964.6	-6,831.7
Enthalpy, kBTU	179.0	-45,159.4	0.0	-82.0	-14,540.7	-36,050.0
Density, lb/gal	7.66	8.31			11.53	
MW, lb/lb-mole	22.9898	18.01528	2.0158	18.01528	39.997	18.01528

HEAT AND MATERIAL BALANCE
Table 1. Sodium added to vessel causes an immediate reaction.

Step 1. Calculate the liquid density, ρ.

Per Table 1, the change in volume is 712.0 - 795.9 = -83.9 gal = -11.2 ft^3. The change in weight is 2,928.9 + 5,276.9 - 6,610.3 = 1,595.5 lb. The liquid density for this reaction is 1,595.5 lb/(-11.2 ft^3) = -142.5 lb/ft^3. (Surprise! The density is a negative number because the total volume shrinks after the addition.)

Step 2. Calculate the heat of reaction.

Per Table 1, the heat liberated is the sum of the product enthalpies minus the sum of the reactant enthalpies, i.e., [0.0 + (-82.0) + (-14,540.7) + (-36,050.0)] - [179.0 + (-45,159.4)] = -5,692.3 kBTU. The net weight added to the reactor is 1,595.5 lb. (Surprise! It doesn't equal the weight of the sodium metal because of the evolution of hydrogen gas.) The heat of reaction is then -5,692.3 kBTU/1,595.5 lb = -3.568 kBTU/lb or -3,568 BTU/lb.

Step 3. Calculate the height on the straight wall.

Start of reaction: (795.9 - 73.9)/144.5 = 5.00 ft

End of reaction: (712.0 - 73.9)/144.5 = 4.42 ft

Step 4. Calculate wetted areas.

Start of reaction: 5.00×15.7 + 23.2 = 101.7 ft^2

End of reaction: 4.42×15.7 + 23.2 = 92.6 ft^2

Step 5. Calculate K factors. (See Eq. 4.)

Start of reaction: K = exp (80×101.7)/(25,000×1) = 1.385

End of reaction: K = exp (80×92.6)/(25,000×1) = 1.345

Step 6. Calculate jacket outlet temperatures. (See Eq 3.)

Start of reaction: T_O = 77 + (41 - 77)/1.385 = 51.0°F

End of reaction: T_O = 77 + (41 - 77)/1.345 = 50.2 °F

Step 7. Calculate ΔT.

Start of reaction: [(77 - 41) - (77 - 51.0)]/ln [(77 - 41)/(77 - 51.0)] = 30.7°F

End of reaction: [(77 - 41) - (77 - 50.2)]/ln [(77 - 41)/(77 - 50.2)] = 31.2°F

The two values differ by less than 2%. Per the integration assumptions, the temperature will be treated as constant — using the lower value, 30.7°F, in subsequent calculations to give a conservative estimate of the addition time.

Step 8. Calculate Φ. (See Eq 2.)

First, calculate the tank's inside diameter:

$5 - 2\times \frac{1}{4}\times \frac{1}{12} = 4.9583$ ft

$\Phi = [(-142.5)\times 4.9583\times (-3{,}568)]/(4\times 80\times 30.7) = 256.6$ hr

Step 9. Rearrange Eq. 1 to solve for time.

$t = -\Phi \ln(A_t/A_0)$

Step 10. Plug in values and calculate addition time.

-256.6×ln(92.6/101.7) = 24.1 hr ●

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REFERENCES

1. Gentilcore, M. J., "Quickly Estimate Batch Distillation Time," *Chemical Processing* (April, 2013)
2. Gentilcore, M. J., "Estimating Heating and Cooling Times for Batch Reactors," *Chemical Engineering Progress* (March 2000).


We’re on board.

Bridge Batch and Continuous Operations Better

Developing an accurate timeline can lead to important insights

By Dirk Willard, contributing editor

"Don't waste your time," bellowed the sales engineer at the engineering procurement construction (EPC) firm. I was working as a contractor for the firm and had just explained the need for a timeline. The plant design consisted of a dryer fed by commercial fermenters that got seed from a battery of seed fermenters. To run the dryers smoothly, i.e., without interruption, required having seed in storage tanks between the dryer and the commercial fermenters.

The statement sounded like a command; so I thought carefully but then developed a spreadsheet for the seed and commercial fermenters anyway. I absolutely needed the timeline to do my job. That's why EPC firms hire contractors: to do what's necessary without concern for advancement or office politics. Once the managers saw the timeline, they realized why I had risked my job to create it.

What makes a timeline so valuable? It allowed me to connect batch production from the fermenter trains to the continuously operated dryer tanks. Using the information on the timeline, I could: 1) check the number of fermenters in each train against the continuous need; 2) estimate utilities like steam, chilled water, water and air — although equipment often is sized based on maximum instantaneous need, tank storage should be checked against hourly demand; 3) evaluate what happens when a batch fails and must go to the sewer; 4) gauge overall loading for feed to the batch systems; and 5) test storage capacities such as for the dryer tanks. My analysis allowed us to identify the need for additional dryer feed storage for lot control. In addition, it enabled more-accurate assessment of utilities like cooling water by knowing how many fermenters were running every hour; assuming all batches are running continuously grossly over-estimates the utility rates required.

I absolutely needed the timeline to do my job.

You must test the model created against reality. The model must effectively answer questions like: What happens when you shut down the dryer — can you store batch product or is it lost to waste? How many batches must be run to keep the dryer going? If a power failure terminates some of the batches, what dryer rate is needed for a period to avoid complete shutdown of the continuous process? How long is that period?

To develop a useful timeline, you'll need the following: 1) the batch cycle time, i.e., the time required for filling, production, emptying and cleaning; 2) the feed rate curves for the ingredients — in fermentation, the accumulated mash (sugars) will take up more than half of the fermenter volume; fermentation starts slowly, builds to a peak and then drops to almost zero at the end; 3) the cleaning time in the event a batch goes to the sewer — this sometimes differs from the time for normal cleaning; 4) the rate curves for steam, cooling water and other utilities; 5) times to complete sampling and testing — bacterial growth vials can take 2–3 days; 6) maintenance cycle information such as the time to arrange for a crane to remove an agitator, the time to dismount the old agitator and gearbox and then mount the new agitator, and the time to certify and test the replacement; 7) outage information — necessary production rates for the continuous and batch sections to maintain customer supply; and 8) the turndown rates for the continuous section.

After you've completed your spreadsheet model, take a hard look at it. For example, did you make the common mistake of forgetting about high cooling-tower temperature when planning for the cooling water flows to reactor jackets? Maybe a 15°F rise is too much? Can you really count on pumping out a pseudo-plastic at 1,000 gpm when the viscosity rises 10 cP every few minutes? Sure you can add 200 gpm of an ingredient to a reactor, but can you blend it effectively? These are just some of the questions you must ask of your model before it can be useful in developing a bridge between your batch operations and continuous ones. ●

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EXPANDING THE POSSIBILITIES FOR SIZE REDUCTION™

Improve Energy Efficiency of Batch Processes

Such processes often offer substantial opportunities for savings

By Riyaz Papar, Hudson Technologies Company

About six years ago, Gary Faagau wrote in his Energy Saver column that being a batch operator doesn't mean you must have inefficient operations (See, "Improve Batch Processing," http://goo.gl/rtxZob). I'm going to expand on the lessons learned from Faagau's column and discuss some of my experiences with batch operations and ways to analyze and improve their energy efficiency.

Generally, chemical plant operations are continuous and most analyzing and quantifying methodologies are very robust when we have "steady state, steady flow" conditions. We, as energy engineers, also neglect startup and shutdown conditions during an energy assessment because usually they occur for a negligible fraction of the time compared to the total operating hours in a year. However, this fundamental assumption breaks down when working with batch operations. Hence, all analyses must pay close attention to cycle time and understand ramp up and ramp down of the utility and feed streams. An engineer should understand every step of the process, its utility requirements and the corresponding time associated with that step. Drawing a temporal cycle plot is an excellent tool to visualize the process. You can use temperature versus time or load (heat duty) versus time profiles to understand the batch process (See "Bridge Batch and Continuous Steps Better," p. 10).

On the electrical side, pumps, fans and other mechanical motor-driven operations

> Batch processes have been neglected from an energy efficiency perspective.

are relatively simple. Apart from a spike in electrical demand when these operations are started, the analysis methodology is straightforward when you take into account the time of operation. However, analysis for compressed air and batch operations can get complex. For batch operations, using storage effectively is the simplest solution to meet peak air demand. It also ensures extra compressors aren't running continuously and eliminates short-cycling of air compressors. Using a master controller on the compressed air generation can be vital to maintaining the highest level of system efficiency.

Most processes require heat for the feed reactants. Reaction temperature is controlled for a certain amount of time and the product removed appropriately. Heat can come from several different sources but the most common are direct-firing (heaters), steam and oil (or a heat transfer fluid).

A fired heater cycles on and off on demand. If multiple heaters are used for multiple batch processes, opportunity exists for substantial energy gains. Turning a heater on and off leads to significant energy loss while purging and short-cycling. Instead, staging different batch trains, if possible, may provide sustained firing on one common heater, allowing tight excess air controls, almost steady-state operations, high energy efficiency and increased system redundancy because the other non-operating heaters can serve as 100% backup.

Steam is a distributed commodity in a plant; a boiler goes to low-fire or hot-standby as steam demand decreases. With the sophisticated controls and turn-down capabilities now available on the market, managing steam demand isn't an issue. Nevertheless, you can optimize steam generation based on load cycles. In some plants, I have seen steam accumulators used effectively to overcome peak steam demands and maintain steady steam generation.

Heating with oil loops (or a heat transfer fluid) may require more innovative strategies such as cascading heat exchangers and thermal storage. The oil heater may still cycle on and off depending on batch process demand. But the circulating oil loop has a lot of thermal energy and will cool down, eventually losing all thermal energy. Thermal storage may be a good option if the holding tanks are conveniently located, rated for the high temperatures and well insulated. It may also save pumping energy because the loop can be turned off. In multiple-batch operation, the excess heat from one batch could be used to pre-heat another batch. However, this would require a creative network of oil piping and heat exchangers and might not be feasible.

In summary, batch processes have been neglected from an energy efficiency perspective and they offer significant opportunities. I have tried to scratch the surface in this column, and hope to provide some targeted case studies in the future of such opportunities. ●

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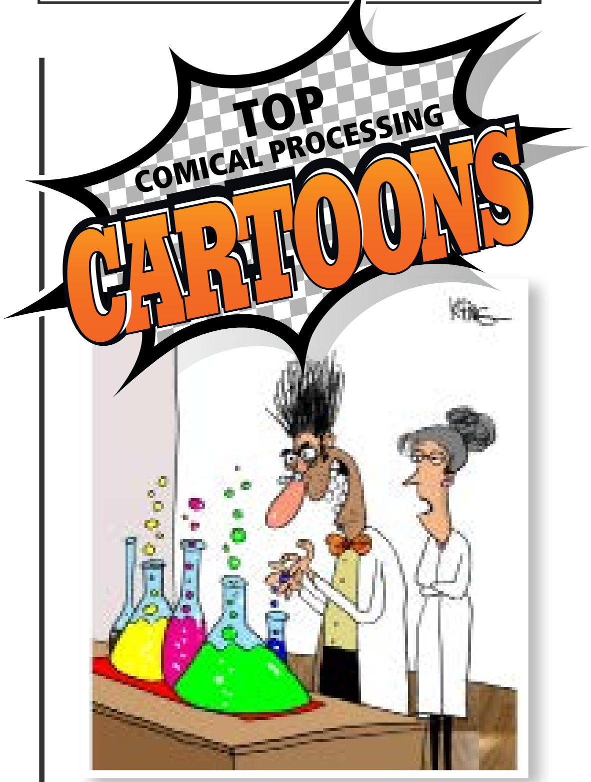

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