Bulletin No. 202

LABORATORY REACTION SYSTEMS

System design aspects for batch, semi-batch and continuous-flow mode reactors.

It used to be that our customers were happy to buy the reactor, heater and temperature controller from us and either use it without additional components or incorporate it into their own systems. Today they continue moving towards more complete systems and asking us for a more packaged unit. Parr will be pleased to assist you in meeting these more encompassing needs.

Some vendors offer very complete systems for this type of work; some including sampling and analytical analysis, with prices easily ranging from $150,000 to $500,000. Parr offers alternatives to these vendors, at very attractive prices.

REACTORS

Parr Stirred Reactors

In chemical engineering terms, our stirred reactors are often called **stirred tank reactors**. They are commonly operated in a **batch mode**, where all reactants are charged into the reactor before the reaction is started. Oftentimes, a gaseous reactant is fed to the other reagents at the same rate it is consumed in what is called a **semi-batch mode**. Many times, however, they are operated in a **continuous-flow mode** where reactants are introduced and products are removed from the reactor on a continuous basis. Obviously, the latter mode of operation requires a means of introducing reactants at elevated pressures and of removing product under controlled conditions. Along these lines, note also that our non-stirred vessels can also be considered reactors for systems that do not require agitation. Such reactions are generally gaseous phase or gas-solid phase reactions.

Some modifications of our standard design are required to convert a batch reactor to a continuous-flow reactor. At a minimum, we would typically move the gas inlet from the double valve to a gage adapter and shorten the dip-tube to allow its use as an outlet that can maintain a specific liquid level in the reactor. Other modifications, such as installing a sintered filter on the dip-tube, may be desired to meet the needs of a particular project.

Parr Tubular Reactor

In the realm of continuous-flow reactions, another popular style of reactor is the **tubular flow reactor**. In this style, liquids and gases are introduced to one end of the reactor. Within the reactor, they are heated to the operating temperature and then flow through a fixed bed of packed catalyst where the reaction takes place. The products then leave the reactor through the discharge end, where they are cooled and collected.

Although they are becoming more popular in the pharmaceutical and adsorption industries, the petroleum industry is a principal user of tubular flow reactors. They are generally used for catalytic reactions such as hydro-treating, hydro-cracking, and reforming. Operating temperatures to 500 °C and operating pressures to 5000 psig are common for some of these reactions.

We have furnished a number of tubular flow reactors based upon the concept shown in Figure 1. This exploded view of the vessel shows the type we have most commonly furnished. We have made these units in various lengths up to 33" long. The standard vessel has an inside diameter of approximately 1". These units, when made of stainless steel, are rated for 5000 psig at 500 °C.

Figure 1 Tubular Reactor

The vessel is split into essentially two zones; the pre-heater and the reaction section. The lengths of these zones, as well as the overall length of the reactor, can be adjusted to meet individual requirements. We can also provide spacers that will adjust the length of the lower catalyst bed.

Reactants enter through one or more inlet tubes at the top, side of the reactor and flow through the pre-heater section that provides a spiral path where the

reactants kept in close contact with the outer heated wall to bring them to their initial temperature. Catalyst is packed into the fixed bed area, which can be varied in length by a set of spacers. The temperature in the pre-heater or at various points along the catalyst bed can be monitored by a thermocouple inserted from the top, center of the reactor into the thermowell. The products of the reaction then leave the vessel at the bottom center. In most cases, tubular flow reactors operate in a vertical position with the discharge at the bottom, although up-flow reactors and counter-current flow schemes are also possible.

We provide a split-tube furnace for heating these vessels. Insulation is provided at each end so that the end caps are not heated to the same temperature as the core of the reactor. The heater length is normally divided into two or three separate heating zones, although it can be split into as many zones as required. We can furnish either a fixed internal thermocouple in each zone or a single movable thermocouple that can be used to measure the temperature at any point along the catalyst bed. External thermocouples are typically provided for control of each zone of the heater. Figure 2 shows a typical split-tube furnace.

More complete details on Tubular Reactor systems are available on our website at http://www.parrinst.com/default.cfm?Page_ID=370 or by contacting the Customer Service Department at Parr and requesting Bulletin 5400.

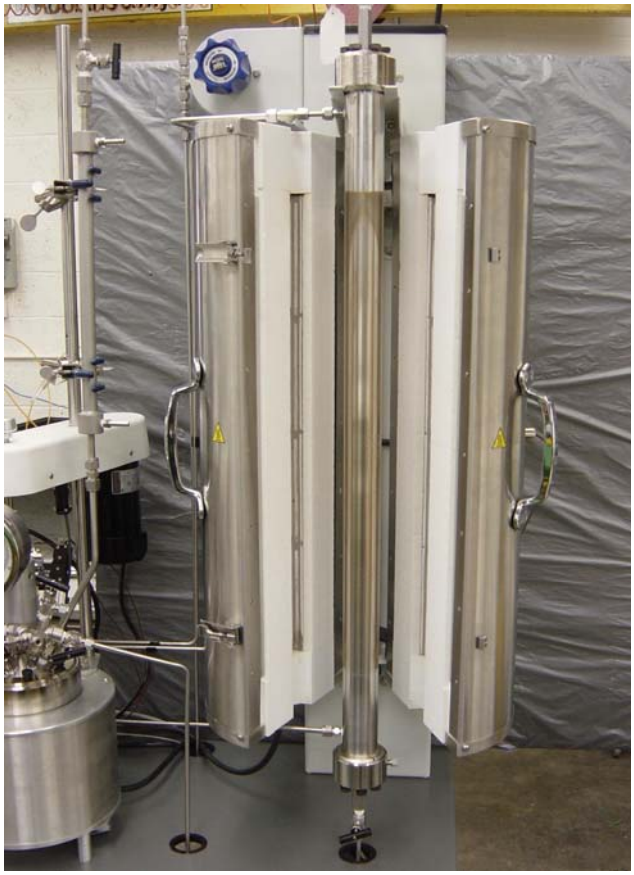


Figure 2 Split Tube Furnace

GAS FEED SYSTEMS

A common requirement for users of our stirred, non-stirred, and tubular reactors is to feed reactants to the reactor. The method of feeding reactants depends on whether they are gases or liquids and whether they are being fed to a reactor operating in a batch, semi-batch, or continuous-flow mode.

Batch Mode Reactions

Catalytic hydrogenations are an excellent example of this type of reaction. Here it is often desired to measure the amount of hydrogen consumed during a reaction. Certainly the easiest way to conduct a reaction of this type is to pressurize the vessel with an excess of gas in the headspace and allow the pressure in the vessel to fall as the reaction occurs. The vessel could be re-pressurized if necessary. When the pressure no longer drops, the reaction is complete or the pressure has fallen below that required to significantly drive the reaction. If the user filled the vessel to the same level each time, they could calibrate the headspace and by combining this with the observed pressure drop, they could determine the amount of gas consumed in the reaction.

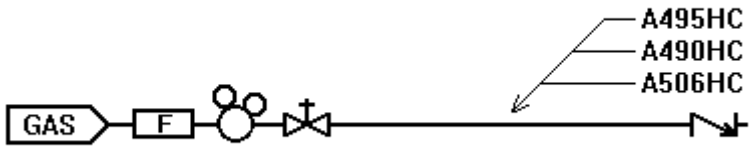


Figure 3 Batch Feed System

Semi-batch Reactions at constant pressure

Many users will find the above method of operation unacceptable for several reasons. First, the operating pressure of the reaction will be continually falling as the reaction takes place. Under different operating conditions and different reaction rates, different ratios of isomers or even different reactions can be produced. Second, it would also be difficult to calibrate the system for different quantities of material and the vessel may not be able to initially hold enough of the reactant gas to complete the reaction without resorting to an inappropriate pressure level. Finally, the reaction rates may be dangerously high in this batch mode and the gas must be fed slowly to control the reaction to prevent thermal run-away and over-pressurization.

To address these needs, a constant pressure regulator, or Forward Pressure Regulator (FPR) regulator, is commonly used. This regulator attaches to the supply tank and can be set to deliver gas whenever the downstream pressure in the reactor falls below the desired operating pressure. With the use of this type of regulator, the pressure in the reactor will remain constant and the reactions

and rates will be much more predictable and repeatable. A schematic of a feed system for introducing gas at a constant pressure to batch-mode reactions is shown in Figure 3 (See last page of this Tech Note for symbol key).

Caution: The gas inlet valve on essentially all Parr reactors leads through a dip tube to the bottom of the reactor. A reverse-flow check valve should always be installed in the gas supply line to prevent back flow of liquid from the reactor into the regulator and gas supply tank if the pressure in the reactor exceeds that of the supply tank.

Many researchers also want to monitor the amount of incoming gas needed to maintain a constant pressure. The amount of gas entering a reactor that is being held at constant pressure is a measure of the amount of gas being consumed by the reaction. Thus monitoring the amount of entering gas gives a measure of the total consumption, indicating the extent to which the reaction has proceeded. Additionally, monitoring the consumption of gas as a function of time gives a direct measurement of the reaction rate. This parameter is important to researchers involved in scale-up and in comparing the relative speed and effectiveness of different catalysts in producing products. There are a number of ways in which this can be accomplished, as described below.

Intermediate Supply Tanks

One method of measuring the amount of gas consumed by a reaction under constant pressure is to use an intermediate supply cylinder, or **reservoir**. The pressure drop in a large gas supply tank will normally not be large enough to give an accurate indication of the amount of gas consumed. There is so much gas in the tank that the small pressure drop during the course of a reaction is difficult to measure. A smaller intermediate reservoir can be filled with gas and used as the supply to the constant pressure regulator. Such reservoirs are available in a variety of sizes to match the expected gas consumption. In sizing this intermediate reservoir remember that the final pressure in the reservoir must still be greater than the reactor operating pressure. The initial pressure in the reservoir, less the final pressure in the reservoir, multiplied by the volume of the reservoir represents the gas consumed by the reaction. An example of this type of feed system, known at Parr as a High Pressure Gas Burette, is shown in Figure 4. Standard bourdon tube gages can be used to make this measurement. Electronic pressure transducers can be added to provide greater resolution and provide a signal that can be fed to a recorder or data logger to develop a rate-of-change signal representing the reaction rate.

Note: For condensable gases, such as carbon dioxide, propane, and ammonia, the intermediate reservoir will need to be weighed since the pressure will remain constant as long as liquid is present in the cylinder.

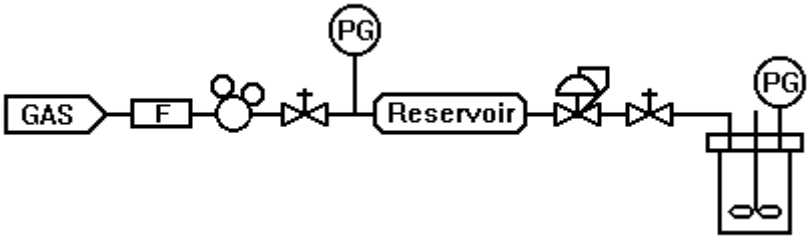


Figure 4 High Pressure Gas Burette System

Electronic Flow Meters

An alternative to the pressure drop approach used in the High Pressure Gas Burette is to use an **electronic flow meter** rated for the operating pressures and flow rates to be encountered in the reaction. The Brooks Instrument Company in the US and the Bronkhorst Company in Europe are leading suppliers of this type of meter. With the appropriate accessories (such as the Parr Model 4846 Data Acquisition System), you can record both rates and accumulated totals. Flow meters must be calibrated for the individual gas. These meters require a power supply and a read-out device. Figure 5 shows a schematic of a typical installation of this type of feed system.

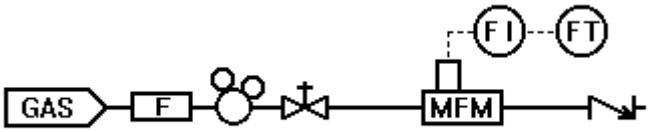


Figure 5 Electronic Flow Meter System

One disadvantage of the Flow Meter approach is that these meters have a 1% full-scale, or at best a 0.5% full-scale, accuracy. Since they must be sized to accommodate the largest expected flow, the relative error in the flow reading will exceed 10% as the flow rate falls below 10% of full scale. This problem is not experienced when measuring the pressure of an intermediate reservoir to follow the consumption of reactant gas.

Continuous-Flow Reactions at Constant Pressure

Electronic Mass Flow Controllers

In order to deliver a constant flow of gas to a reactor, it is necessary to provide gas at a constant pressure to an **electronic mass flow controller**. This instrument will compare the actual flow rate delivered to the set point chosen by the user, and automatically adjust an integral control valve to assure a constant flow. Care must be taken to size these controllers for the specific gas, the flow rate, and the pressure of operation. As with mass flow meters, a mass flow controller needs a power supply and read-out device, and additionally it requires a means of introducing the desired set point and of providing the desired control features.

Note that the **Parr 4871 Process Controller** can also furnish the secondary electronics functions for these flow meters/controllers. The 4871 Controller, when also used for heating, stirring, etc., most often will provide the most economical method for total control of the entire system.

When ordering flow meters and flow controllers, you will need to specify:

1. Type of gas to be metered (e.g. N_2, H_2, CH_4)
2. Operating pressure of the gas
3. Flow range (maximum)
4. Flow rate and pressure for calibration of the instrument (typically 1/2 full scale flow at Standard Temperature and Pressure (0 °C, 0 psig)
5. Inlet and outlet connections.

Mass flow meters and mass flow controllers are available for use to 4500 psi. Considerable savings can be obtained if the mass flow controller is to be used only to 1500 psi.

You will also need to address your requirements for power supplies, indicators, totalizers, interconnecting cables, and any additional accessories. Note that the options include various O-ring materials for chemical compatibility.

Figure 6 schematically depicts the installation of a mass flow controller for the introduction of gas to a continuous-flow reaction system. Such installations can be enhanced with the addition of a by-pass valve for rapid filling. Mass flow controllers are calibrated for use at a constant pressure and with a constant ΔP across the device. Figure 7 shows an enhanced installation schematic.

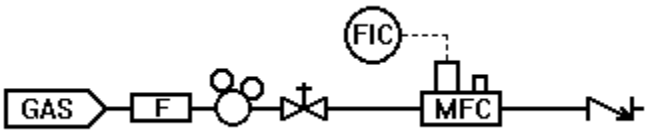


Figure 6

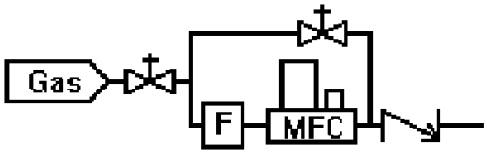


Figure 7

Back Pressure Regulators

In addition to supplying gases to a reaction through electronic mass flow controllers, the reactor is kept at a constant pressure by installing a **Back Pressure Regulator** downstream of the reactor. This style of regulator will release products only when the reactor pressure exceeds a preset value.

A Back Pressure Regulator (BPR) can be spring-loaded, dome-loaded, or electronically controlled. A spring-loaded BPR is adjusted by turning a knob on the front of the regulator, much the same as a typical gas tank regulator, referred to above as a Forward Pressure Regulator (FPR). Dome-loaded regulators use a secondary gas pressure source as a reference to set the operating pressure. An electronic BPR compares the signal from a pressure transducer to the user set-point and automatically adjusts a control valve to maintain the desired pressure.

When a BPR is used in conjunction with mass flow controllers, the user is assured that a constant flow of gas is passing through a reactor, which is being held at a constant pressure. This provides for the highest degree of control and reproducibility in a continuous-flow reactor system.

LIQUID FEED SYSTEMS

Liquid Charging Pipettes

A relatively simple way to add liquid to a pressurized reactor is with the use of a pressure pipette assembly as illustrated and described in our Reactors and Pressure Vessels catalog. In this technique, liquid is added to a small pressure vessel and then blown into the reactor with a high pressure gas.

Sample cylinders are typically used as the liquid charging vessel. They offer a wide variety of volumes, are rated for pressures to 1800 psi, and are constructed of stainless steel. Valves are installed on both ends of these vessels.

After closing the valve at the bottom of the cylinder, the liquid to be added to the reactor is introduced and the cylinder is then pressurized to a pressure higher than the pressure in the reaction vessel. The easiest way to do this is with pressure from a nitrogen supply tank. We generally use a slightly modified version of our 1831 Nitrogen filling connection to connect from the supply tank to top of the pipette.

The final connection is between the pipette and the vessel. A fairly simple needle valve can be used if the pipette will be used simply to add all of the liquid. A fine metering valve might be chosen if an attempt is to be made to add the liquid more slowly over a period of time. This would, of course, require some calibration of the pressure and valve settings. Finally, if the pipette is to be used to add slurries containing catalysts or other solids, a ball valve may be more appropriate. Parr will be please to meet your individual requirements.

Liquid Metering Pumps

Inexpensive transfer pumps, such as peristaltic pumps, can be used to charge a reactor with liquid prior to pressurization and operation in a batch mode.

High pressure piston pumps are most often used to inject liquids into a pressurized reactor operating in a continuous-flow mode. For low flow rates, HPLC pumps, many of which are rated for 5000 psig, are excellent choices. Typical flow rates for pumps of this type range up to 10 or 40 mL per minute. These pumps vary in cost, depending upon the make and model chosen and whether they are manually-controlled from their digital face plate or computer-controlled from a 4871 Process Controller.

High Pressure Syringe Pumps can also be used to feed very low flow rates of liquids into these reactors. Pumps are available that are rated for pressures to 8000 psig and can deliver flow rates as low as 1 micro-liter per minute. This type of pump can be used for liquids that are near their boiling point or that are saturated with gases that would cause a reciprocating piston pump to vapor lock. Syringe pumps deliver nearly pulse less flow.

Chemical feed pumps are our recommendation for continuous feeding of liquids when the desired flow rate is greater than 2 liter per hour. Here we will try to help you find a suitable pump. We will need to know the type of liquid; the minimum, typical, and maximum desired feed rate; the maximum operating pressure; and any special operating considerations such as explosion proof operation or corrosion possibilities.

Product Handling

Cooling Condensers

It is often desired to cool the products of the reaction prior to handling them. For this purpose, tube-and-shell heat exchangers are available to act as the cooling condensers. An adaptation of our standard condensers provides an excellent design. Descriptions and available sizes are found in the 4500 Catalog, Stirred Reactors and Pressure Vessels, and on our web site, www.parrinst.com.

Gas/Liquid Separators

Reactors operating in continuous-flow mode with both gas and liquid products will also require a **Gas/Liquid Separator** for smooth operation. The separator is placed downstream of the reactor, often separated from the reactor by a cooling condenser. In the separator vessel, liquids are condensed and collected in the bottom of the vessel. Gases and non-condensed vapors are allowed to leave the top of the vessel and pass on to the back pressure regulator. It is important to operate the BPR with a single phase of material to prevent oscillation of the reactor pressure.

The gas/liquid separator can be sized large enough to act as a liquid product receiver that can be manually drained periodically. Alternatively, it can be equipped with a level control device and electronic drain valve to allow for automated draining to a low pressure receiver. Many of the non-stirred pressure vessels listed in our catalog are ideally suited for use as gas/liquid separators.

Level Control

Liquid level indicators and controllers are required on automatic gas/liquid separators and have often been requested for use in the reactor itself. Unfortunately, a good, universal solution for this task has yet to be found. While probes are available that are based upon float, capacitance, conductivity, light absorption, pressure differentials, ultra sound, and a variety of other techniques, the makers generally think a 1 inch pipe thread is a miniature mounting and that 60 psi and 80 °C are severe operating conditions.

Siphon Control

An interesting means of providing level control in a continuous-flow stirred reactor is to connect the reactor and gas/liquid separator through both the gas and liquid phases, so that there is a siphon between them. This allows the level in the reactor to be changed by moving the separator vessel up and down.

CONTROL and DATA ACQUISITION SYSTEMS

A variety of solutions exist to meet the needs of system operators. At one end, a table-top control system might consist of a Model 4848 Controller for heating and stirring control. This might be supplemented with an HTM, PDM, and MCM. Multiple controllers or custom packaging of controllers are often required. System accessories such as mass flow controllers, pumps, and pressure controllers can be obtained with individual control chasses to create a distributed control system.

As the number of channels to be controlled increases, economics will often dictate that the distributed system of individual controllers should be replaced with the computer-based Model 4871 Process Controller. This controller is described in detail in our catalog and on the web site.

SYSTEMS HELP AVAILABLE

The staff at Parr Instrument Company is eager to assist you with the various design aspects of system integration, including explosion-proof safety designs. Below are a series of schematic representations of some typical systems, along with a symbols chart to facilitate understanding. The first three systems depict some of the variations possible in the design of batch-reactor systems. They differ mostly in the level of system control, gas monitoring and data collection. The next four schematics show continuous-flow systems. The first two show stirred reactors, modified for continuous-flow operation, with differing feed systems. The next two show tubular reactor systems with various levels of automation and control. A symbol key is shown on the last page.

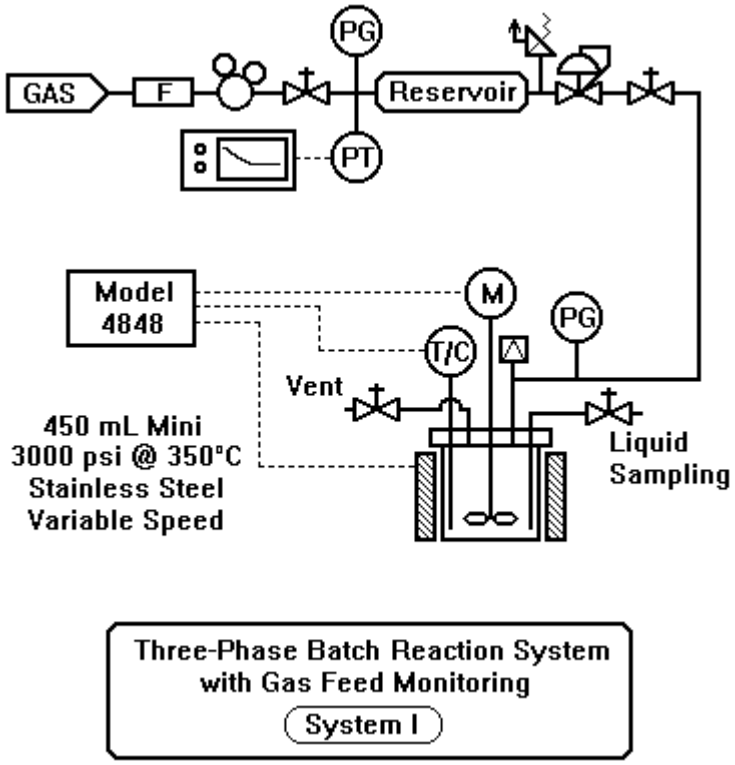


Figure 8

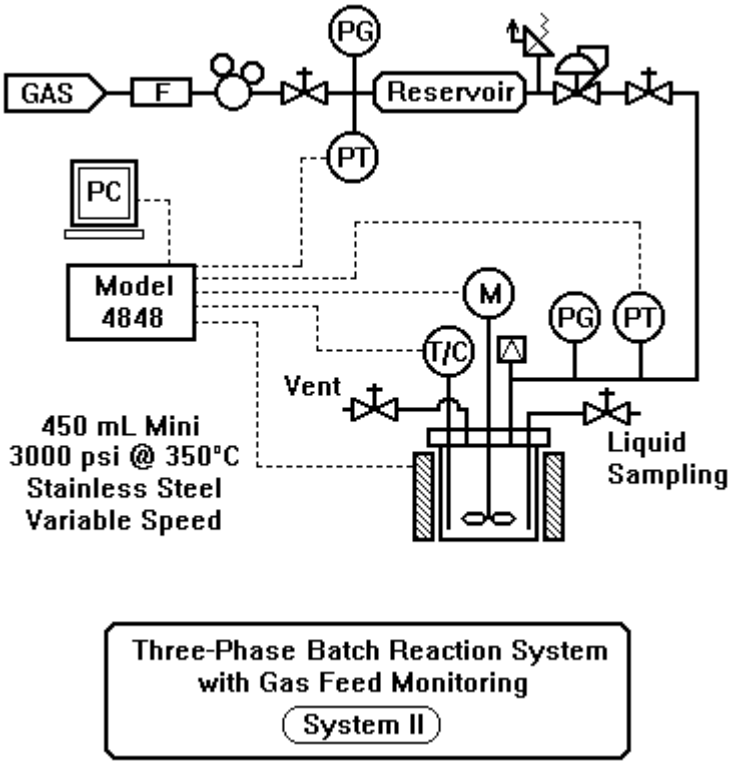


Figure 9

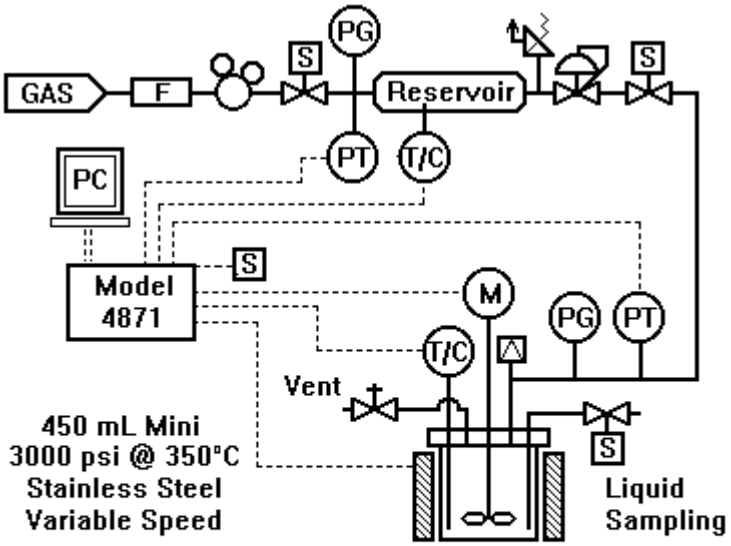


Figure 10

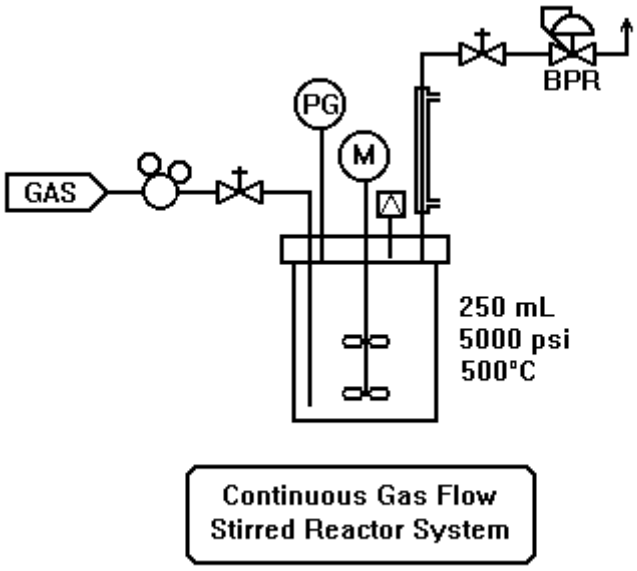


Figure 11

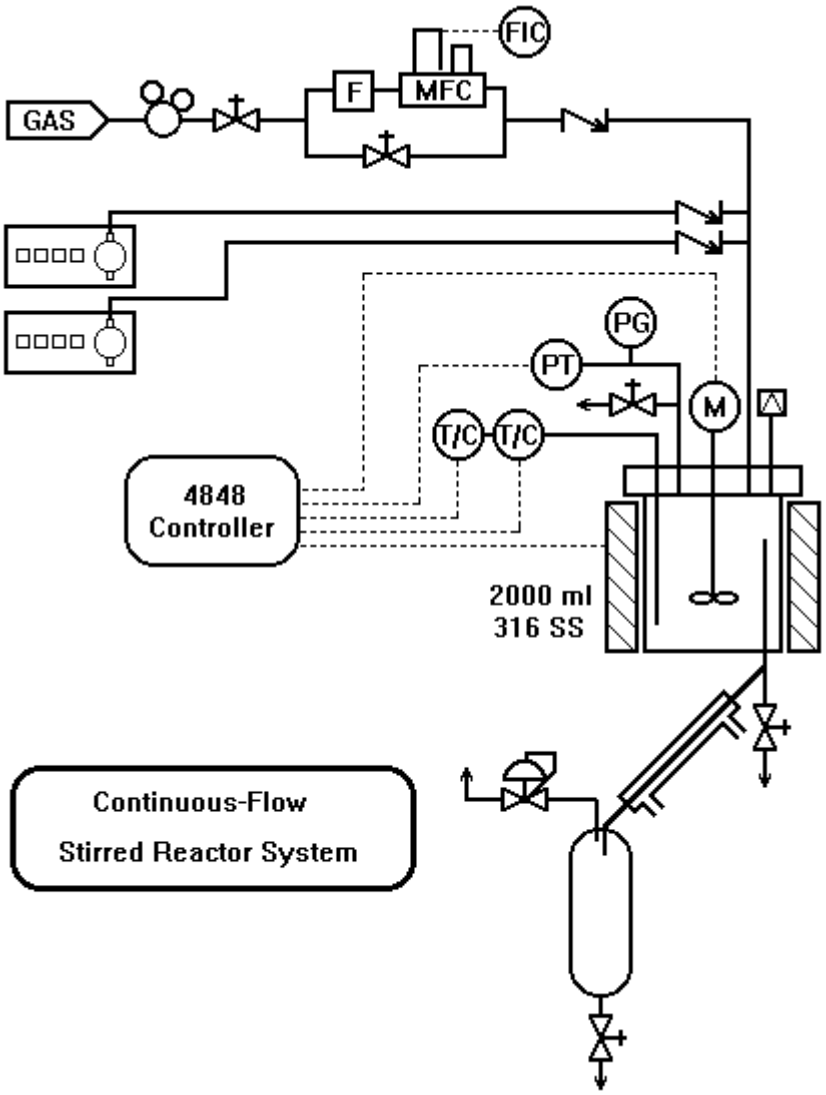
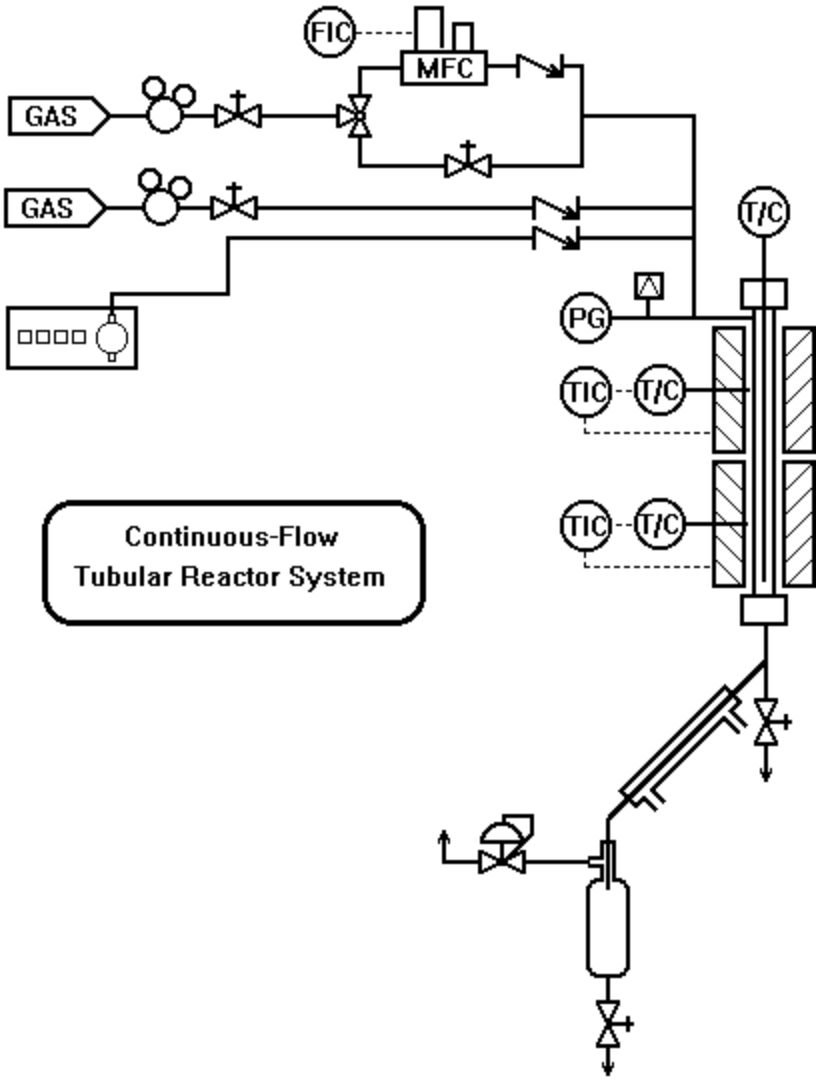

FIC
F
MFC
GAS
PG
PT
M
T/C
T/C
4848
Controller
2000 ml
316 SS
Continuous-Flow
Stirred Reactor System

Figure 12


FIC
MFC
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GAS
T/C
PG
TIC
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TIC
T/C
Continuous-Flow
Tubular Reactor System

Figure 13

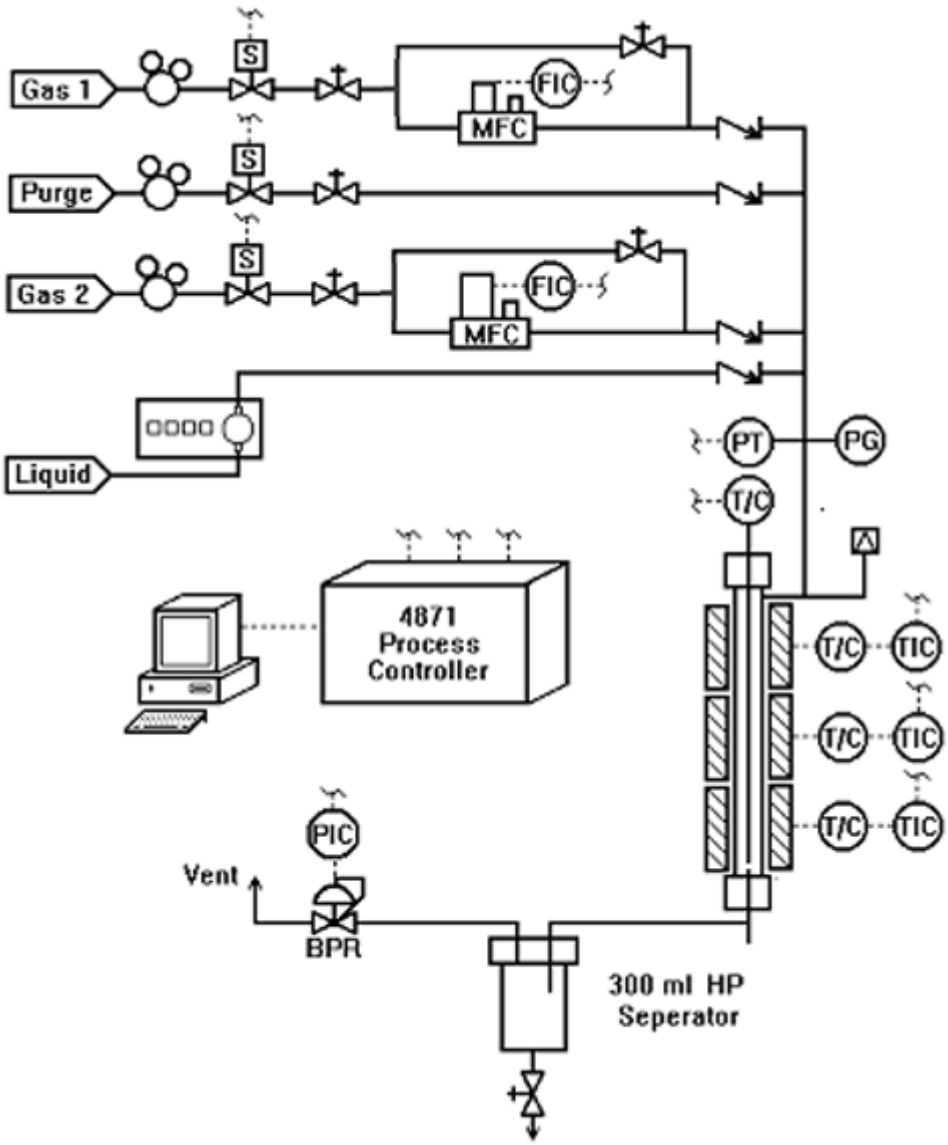
Gas 1
S
FIC
MFC
Purge
S
Gas 2
S
FIC
MFC
Liquid
PT
PG
T/C
4871
Process
Controller
T/C
TIC
T/C
TIC
T/C
TIC
PIC
Vent
BPR
300 ml HP
Seperator

Figure 14

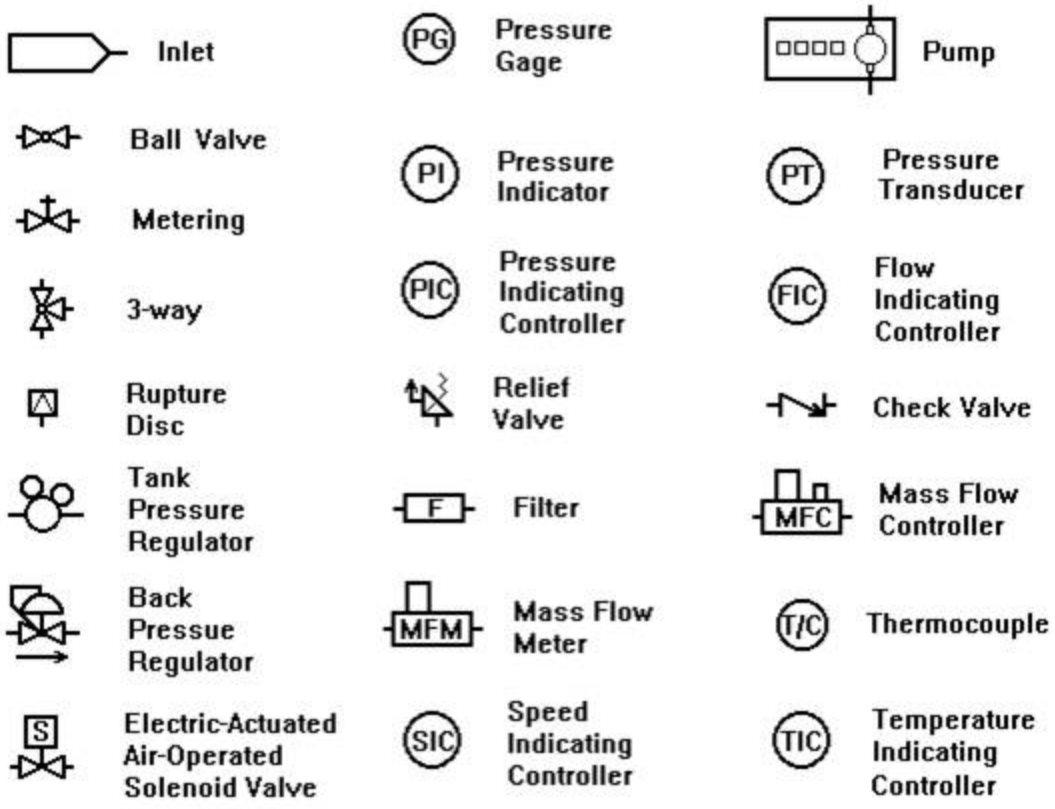

Figure 15

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