"POLY METHANOL" REACTION SYSTEM

(PolyMth1, PolyMth2, PolyMth 3)

Our first batch modeling example is a polymer model I recently tackled in ChemCAD III. We will hypothetically polymerize methanol to a "polymethanol" in a combination of batch and continuous operations.

Basic polymerization is a relatively straight-forward process: Charge a reactor with 20,000 gallons of monomer, allow about four hours for complete reaction, and transfer the reactor contents into a blow down tank. Then pump the polymer solution into a stripper to remove any remaining unreacted monomer.

This example allows us to examine two distinct processes in a single, basic model. It begins with batch processing within the reactor and blow down tank, then switches to continuous process as the solution enters the stripper. You will be interested to know that ChemCAD III can incorporate both of these process types onto a single flowsheet, and automatically convert from batch to continuous operation! We will start by establishing the parameters needed to allow the software to achieve an accurate heat and material balance.

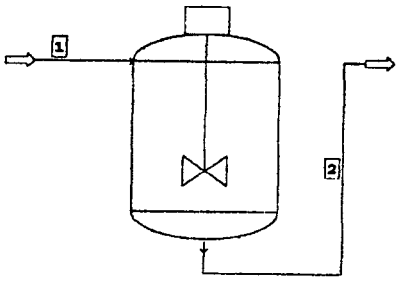
Creating the Polymer

First, we will add the polymer to the database by creating a new component, "polymethanol". Make its average molecular weight 3200 (or 100 times the molecular weight of methanol). Assign the normal BP at 1000° F and the specific gravity at 0.8. These numbers will soon be insignificant when we declare this component a solid.

Establishing an Accurate Heat Capacity Value

When it creates a new component, ChemCAD III bases the heat capacity on the input parameters. This value is often way off the mark, which can create heat balance problems in both the reactor and the stripping functions. Here is how you can achieve a more accurate value. Start by using the LATENT HEAT option in the ENTHALPY menu to change the heat capacity of the new component. You will find that SRK will not accept this change due to factors within the SRK option. There is a simple solution. Go to the UTILITIES screen and select PURE REGRESSION. Within that screen, proceed to the LIQUID HEAT CAPACITY function and enter the appropriate numbers, including the molecular weight of the new component. Follow the on-screen instructions and perform the regression. Once you have completed the regression, the program will accept and store the correct heat capacity.

Estabilishing Heat of Reaction



BATCH POLYMER REACTOR

Stream No.	1	2
Name		
- - Overall - -		
Mass flow lb/batch	146000.0000	146000.2500
Temp F	150.0000	150.0000
Pres psia	150.0000	150.0000
Vapor mole fraction	0.0000	0.0000
Flowrates in lb/batch		
Water	83000.0000	83000.0000
Methanol	63000.0000	10710.0000
POLYMETHANOL	0.0000	52290.2461

Calculating the Heat of Reaction

Next, ChemCAD III will calculate the heat of reaction for the polymer reaction set up on the Stoihiometric Reactor Module. Again, this value is likely to be way off base, and you will need to set up the correct heat of reaction in the reactor. In our example, this will be 460 BTU per pound of methanol reacted.

Start with 1000 pounds of methanol in the feed. Since 100 pound moles of methanol yield on mole of the polymer, the stoichiometric coefficients are 100 and 1. Enter these numbers into the module, and run it isothermally at the feed temperature of the methanol (which in our case is 150° F at 150 psia). Look at the heat duty and divide the methanol feed rate by 1000. Change the heat of reaction until this divided number equals the 460 BTU per pound you designated earlier. Now you will be working with an accurate heat of reaction.

Comp ID 8074 Liq. Heat Capacity Parameters

Max. iterations 1000
Relative error 1e-008
Absolute error 1e-008

	Initial Value	Lower Bound	Upper Bound
LCP_A		-2.0000e+005	2.0000e+012
LCP_B		-5.0000e+003	2.0000e+012
LCP_C		-1.0000e+001	2.0000e+012
LCP_D			
LCP_E			

Required Parameters:
Molecular weight 3.2000e+003

Liquid Heat Capacity Data

Temp F	Lcp Btu/lb-F	Weight factor
1.0000E+002	4.0000E-001	1.0000E+001
0.0000E+000	0.0000E+000	0.0000E+000
0.0000E+000	0.0000E+000	0.0000E+000
0.0000E+000	0.0000E+000	0.0000E+000
0.0000E+000	0.0000E+000	0.0000E+000
0.0000E+000	0.0000E+000	0.0000E+000
0.0000E+000	0.0000E+000	0.0000E+000
0.0000E+000	0.0000E+000	0.0000E+000
0.0000E+000	0.0000E+000	0.0000E+000
0.0000E+000	0.0000E+000	0.0000E+000
0.0000E+000	0.0000E+000	0.0000E+000
0.0000E+000	0.0000E+000	0.0000E+000
0.0000E+000	0.0000E+000	0.0000E+000
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0.0000E+000	0.0000E+000	0.0000E+000
0.0000E+000	0.0000E+000	0.0000E+000
0.0000E+000	0.0000E+000	0.0000E+000
0.0000E+000	0.0000E+000	0.0000E+000
0.0000E+000	0.0000E+000	0.0000E+000
0.0000E+000	0.0000E+000	0.0000E+000

Unit 1 Stoichiometric Reactor

Specify thermal mode:
( ) Adiabatic
(*) Isothermal T --> 150.0000 F
( ) Heat Duty --> -23.94 MMBtu/batch

Key Component 2
Frac. Conversion 0.8300
Heat of Reaction -3e+004 Btu/lbmol
Reactor Pressure psia

Stoichiometric Coefficients:

Comp 1		Comp 4		Comp 7	
Comp 2	-100.0000	Comp 5		Comp 8	
Comp 3	1.0000	Comp 6		Comp 9	

(more comp. coeffs. next page)

PgDn to page 2:

Charging the Batch Reactants

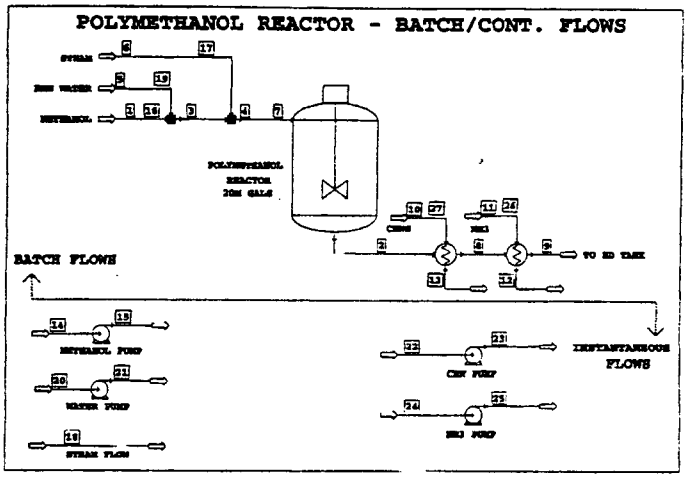
The next step is to charge the batch reactants. Determine the amount of polymer produced per 20,000 gallons reacted, divide by the conversion, and you will know how much monomer to charge to the polymer. In our case, this is 63,000 pounds. You can make up the balance of the 20,000 gallons by filling the reactor with water (83,000 pounds). At this stage, you might find it interesting to have ChemCAD III check the result by calculating the total combined stream. Multiply by 60 if the flowrate is expressed in gpm.

Designating Appropriate Flow Units

Because ChemCAD III is a steady state simulator, all the flow units have a time element. You can, however designate "Batch" as a time unit in the UNITS screen. If you select this option, the first reactor flow diagram will list all streams in pounds per batch. This is appropriate for this screen. As the problem progresses, however, we will see that you will not be able to use this unit for all batch flow sheets.

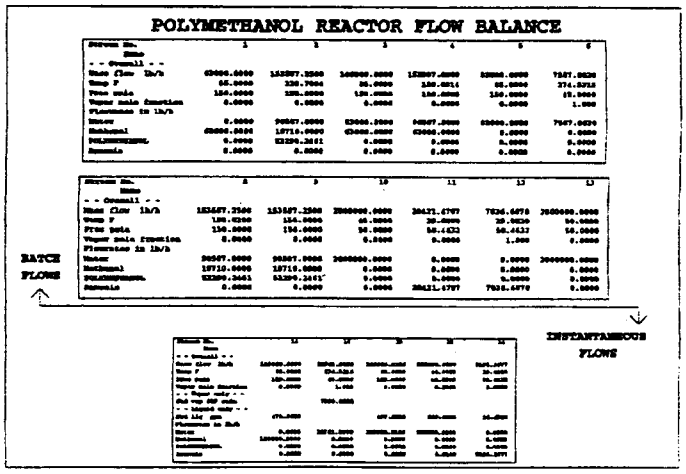
Generating the Batch/Instantaneous Model

Now you have established the basic thermodynamics - heat of reaction and reactor batch flows - you can begin the overall model for this section. We will be using two basic types of flow in this section. One is the total batch flow or pounds per batch required in and around the reactor. Design engineers will also need to know the instantaneous flows in order to size charge pumps, cooling water pumps and other components. You can use the overall batch rates to determine these numbers. For example, there are 83,000 pounds per batch of demineralized water charged to the reactor. But how long does it take to charge this amount into the reactor? How long do you want it to take? As this number affects the overall cycle time per reactor, accuracy is imperative. This is equally true for the monomer charging value. Furthermore, suppose we want to heat the reactor contents to a pre-reaction temperature. How much steam will it take to heat up the reactor contents? What is this quantity on an instantaneous basis? Are there other ways to size this steam line?



Using the Stream Reference Module

The STREAM REFERENCE module is the key to converting batch numbers to instantaneous flow for use by the other modules in this section. Let us take as an example SREF # 8. This converts the methanol charge flow from Stream One to instantaneous flow in Stream 14. It indicates a conversion factor of three, which makes it simple to calculate the transfer rate. If you take the pounds per hour flow rate in Stream One and multiply it by three, you can transfer it in twenty minutes (sixty divided by three equals twenty). Thus, if you run the pump for 20 minutes you will pump in 189000/3, or 63,000 pounds per batch. Is that slick, or what?




```
Unit 8                  STREAM REFERENCE (SREF)

Select mode:
 1 Reference from stream to stream

Select option:
 1 Transfer all stream properties

Destination stream no.        14

If mode = 1:              If mode = 2, 4 or 5:    If mode = 3 or 4:
Source str no      1      TOWR/BATC no            HTXR or PA no
                          Stage no
                          Phase option

Enter flow scale or fixed flow rate:

Scale          3.0000     or     Fixed flow rate
                                 Flow unit
                                  0 Lbmol/hr
```

Removing Heat of Reaction

In the second flow diagram, you will see two heat exchangers installed in series on the outlet side of the reactor. These exchangers actually represent the cooling surfaces of the reactor's two cooling jackets. One uses chilled water, the other uses vaporizing ammonia to maintain a constant reaction temperature. Exchanger values represent batch flows. They also assume an average spread of the heat of reaction over the entire four-hour reaction period. This is not the norm for many polymer reactions, which often display a "heat kick" somewhere during the reaction cycle. Unfortunately, we are not able to model this heat kick

within the present framework, but if you know what heat kick to expect, you can work it into the instantaneous flow value. I would recommend, however, that you use average flows when converting to the instantaneous number. Again, you can accomplish this with the SREF module. Example SREF 15 converts the batch chilled water flow from Stream 22 to the instantaneous flow of Stream 10. The conversion factor indicates a four-hour reaction with ¼, or .25, as the conversion value.

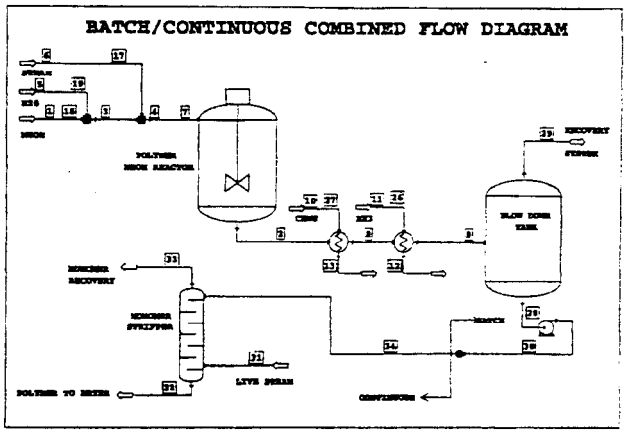
Numbering the Flow Units

Now it becomes a little trickier. As before, you could designate the time units for this flowsheet as "BATCH", and keep the flowrate in GPM. Using this method could, however, produce misleading instantaneous flows as ChemCAD III does not yet allow a mixture of time units on the same flowsheet. It is simpler to keep the units in pounds per hour and designate flows as either batch or instantaneous on the drawing itself. (See the numbered flow rates on the flow diagram).

```
  Unit 15                STREAM REFERENCE (SREF)

Select mode:
 1 Reference from stream to stream

Select option:
 1 Transfer all stream properties

Destination stream no.          22

If mode = 1:              If mode = 2, 4 or 5:    If mode = 3 or 4:
Source str no     10      TOWR/BATC no            HTXR or PA no
                          Stage no
                          Phase option

Enter flow scale or fixed flow rate:

Scale           0.2500    or      Fixed flow rate
                                  Flow unit
                                   0 Lbmol/hr
```

Batch Continuous Combined Model

The next step of the polymer process sends the reactor product to a batch blow down tank where unreacted methanol is removed and sent to recovery. Liquid flow from this tank, consisting of polymethanol and water, is then continuously pumped to a stripping operation. Live steam stripping removes the remainder of the monomer.



Moving from Batch to Continuous

You can accomplish this process, too, within the SREF module. If you look at SREF # 19 you will see how it transfers to the batch flow of Stream 30 to the continuous flow of Stream 34. The polymer process itself determines the factor required to convert batch to continuous flow. Pumping rates must be sufficient to keep the tank at a constant level over a 24-hour period. For example, if the blow down tank receives eighteen batches a day, the factor required to convert the process from batch to continuous is eighteen divided by 24, or 0.75. This calculation assumes that the flow units in the batch area remained in pounds per hour, even though they represent pounds per batch. You can use the same concept to calculate the vapor flow to the recovery compressor in Stream 29. Again, this is a continuous flow to the recovery system and you can place an additional SREF on that stream utilizing the 18/24 conversion factor.

```
  Unit 19                STREAM REFERENCE (SREF)

Select mode:
 1 Reference from stream to stream

Select option:
 1 Transfer all stream properties

Destination stream no.          34

If mode = 1:              If mode = 2, 4 or 5:    If mode = 3 or 4:
Source str no     30      TOWR/BATC no            HTXR or PA no
                          Stage no
                          Phase option

Enter flow scale or fixed flow rate:

Scale           0.7500    or      Fixed flow rate
                                  Flow unit
                                   0 Lbmol/hr
```

And Back to Batch

In some processes you may have flows that are recycled back to the batch side of the plant from the continuous side. As before, you would use the SREF to calculate the flow, but in this case you would reverse the conversion factor to 24/18.

```
/*
   File CALC2.TXT
   Calculator program for HC valve

   Flow rate is 1 kg/hr as defined in feed stream 1.
   If the liquid level in the vessel reaches 70 percent, close the
   valve.

*/

ChemCAD_Link CALC2
{
   int   nc, i;

   float in_flow[200];
   float tin, pin, vin, hin;

   float out_flow[200];
   float tout, pout, vout, hout;

   float vessel_out[200];
   float tvesl, pvesl, vvesl, hvesl;

   float dvsl_uspec[300];
   float liq_level, vessel_height, sum_flow;

   // Get input stream
   CC_Get_Input_Stream(1, in_flow, tin, pin, vin, hin);

   // Get equipment parameters of the vessel
   CC_Get_Equip_Parameters(1, dvsl_uspec);

   // Liquid level for DVSL is parameter no = 43, See VARDVSL.SF in CC3
   liq_level = dvsl_uspec[43];

   // Vessel height for DVSL is parameter no = 17, See VARDVSL.SF in CC3
   vessel_height = dvsl_uspec[17];

   // Check output flow rate of the vessel, the output stream no
   // of the vessel is 4
   CC_Get_Process_Stream(4, vessel_out, tvesl, pvesl, vvesl, hvesl);

   // No of components in flowsheet
   nc = CC_No_Of_Components();

   // Calc total output flow of the vessel
   sum_flow = 0.;
   for( i = 0; i < nc; i++)
   {
      sum_flow = sum_flow + vessel_out[i];
   }

   // HC valve is open only if liquid_level < 70 percent of the height  AND
   // the vessel outlet valve is closed (sum_flow <= 0.)
```

```
/*
   File CALC2.TXT
   Calculator program for HC valve

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ChemCAD_Link CALC2
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   float tout, pout, vout, hout;

   float vessel_out[200];
   float tvesl, pvesl, vvesl, hvesl;

   float dvsl_uspec[300];
   float liq_level, vessel_height, sum_flow;

   // Get input stream
   CC_Get_Input_Stream(1, in_flow, tin, pin, vin, hin);

   // Get equipment parameters of the vessel
   CC_Get_Equip_Parameters(1, dvsl_uspec);

   // Liquid level for DVSL is parameter no = 43, See VARDVSL.SF in CC3
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   // Vessel height for DVSL is parameter no = 17, See VARDVSL.SF in CC3
   vessel_height = dvsl_uspec[17];

   // Check output flow rate of the vessel, the output stream no
   // of the vessel is 4
   CC_Get_Process_Stream(4, vessel_out, tvesl, pvesl, vvesl, hvesl);

   // No of components in flowsheet
   nc = CC_No_Of_Components();

   // Calc total output flow of the vessel
   sum_flow = 0.;
   for( i = 0; i < nc; i++)
   {
      sum_flow = sum_flow + vessel_out[i];
   }

   // HC valve is open only if liquid_level < 70 percent of the height  AND
   // the vessel outlet valve is closed (sum_flow <= 0.)
```
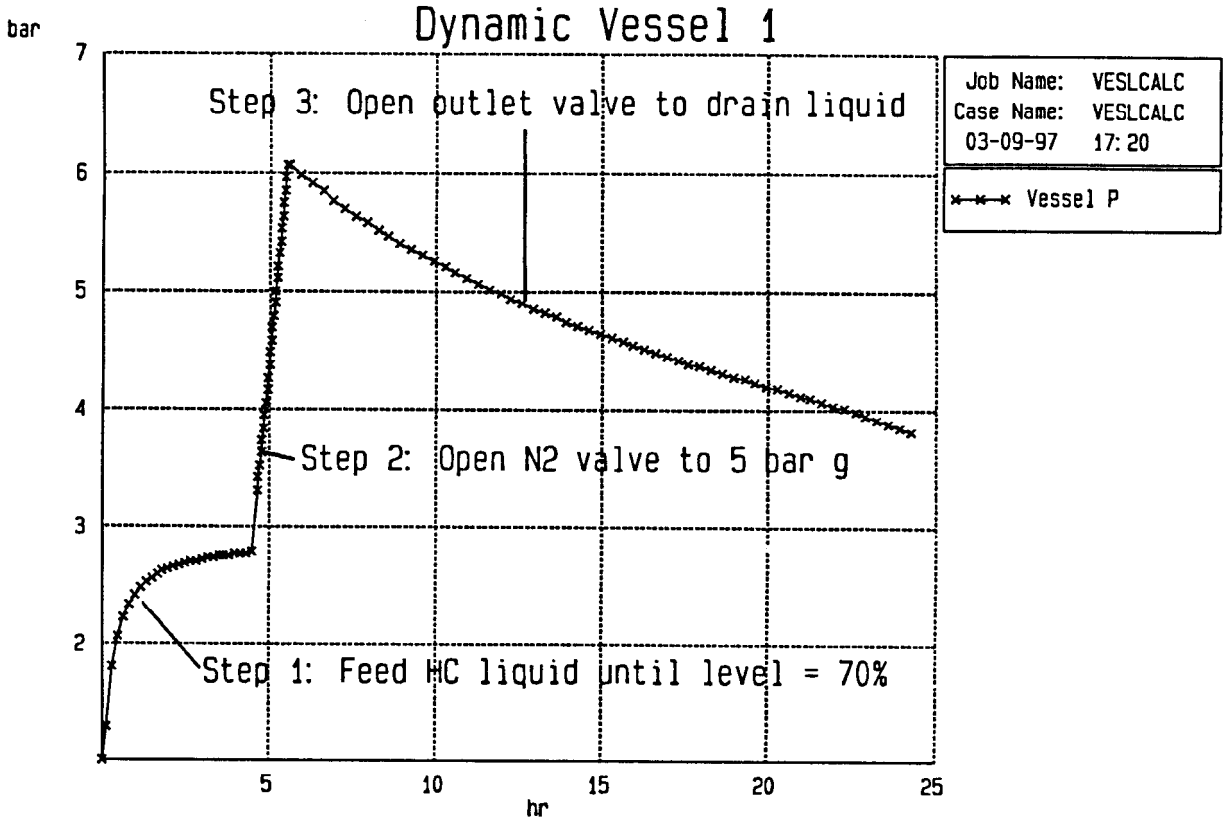
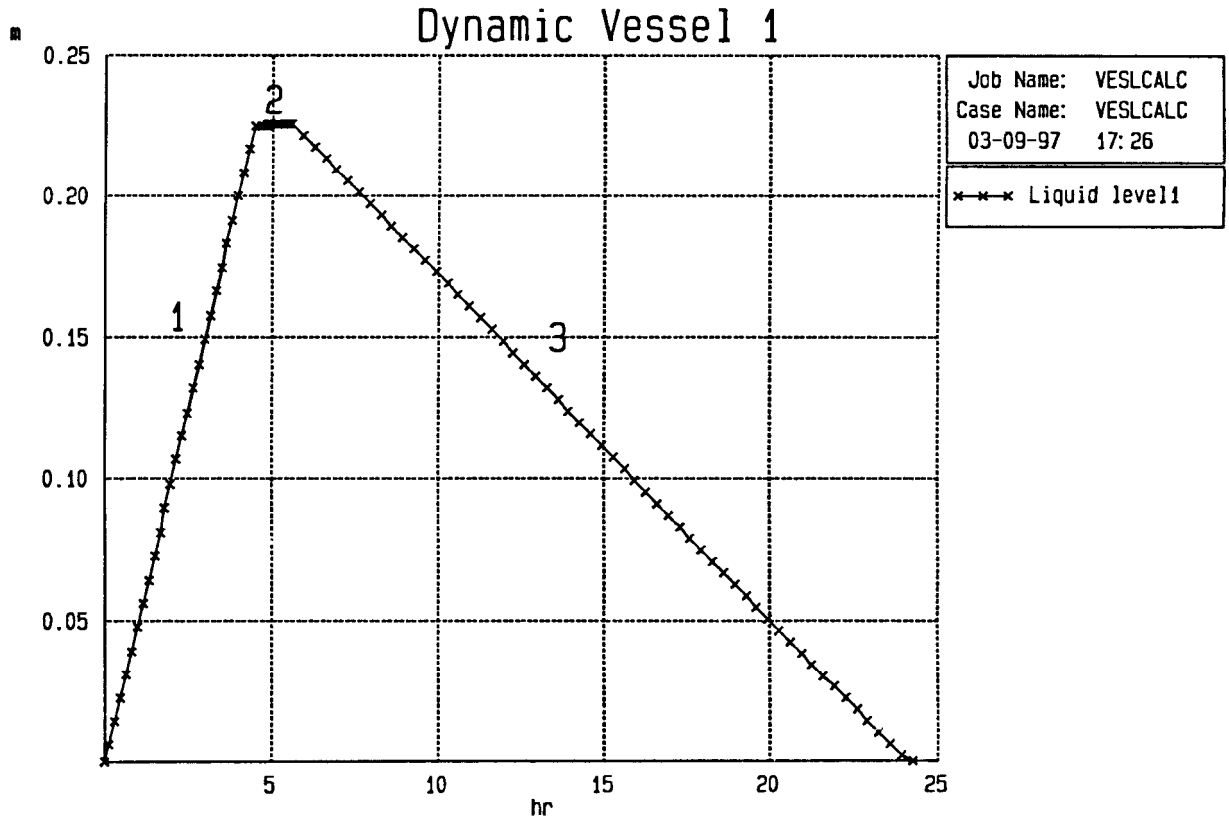
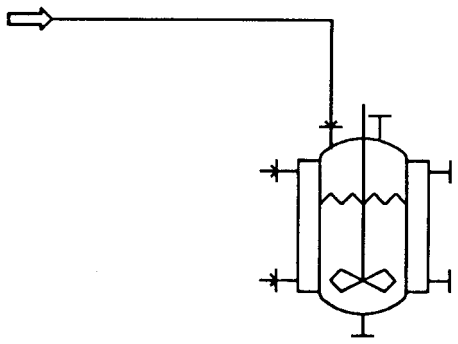
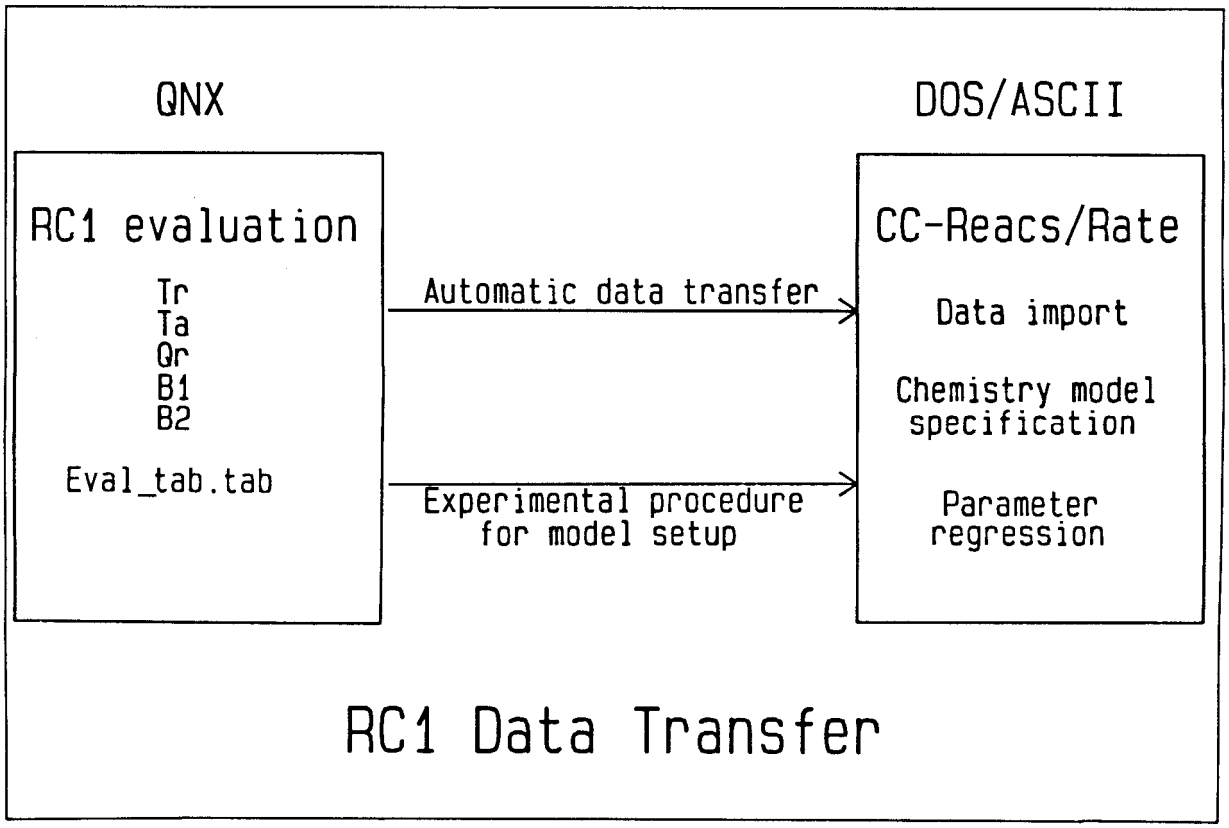

```
    if( liq_level < 0.7 * vessel_height && sum_flow < 1.e-6)
    {
       printf("HC valve open\n");
       for( i = 0; i < nc; i++)
       {
          out_flow[i] = in_flow[i];
       }
       tout = tin;
       pout = pin;
       vout = vin;
       hout = hin;

       CC_Put_Output_Stream(1, out_flow, tout, pout, vout, hout);
    }
    else
    {
       printf("HC valve closed\n");

       // Set output flow and enthalpy to zero to simulate valve close
       for( i = 0; i < nc; i++)
       {
          out_flow[i] = 0.;
       }
       tout = tin;
       pout = pin;
       vout = vin;
       hout = 0.;
       CC_Put_Output_Stream(1, out_flow, tout, pout, vout, hout);
    }

}
```


Dynamic Vessel 1
bar
Step 3: Open outlet valve to drain liquid
Step 2: Open N2 valve to 5 bar g
Step 1: Feed HC liquid until level = 70%
Job Name: VESLCALC
Case Name: VESLCALC
03-09-97 17:20
Vessel P
hr


Dynamic Vessel 1
m
1
2
3
Job Name: VESLCALC
Case Name: VESLCALC
03-09-97 17:26
Liquid level1
hr

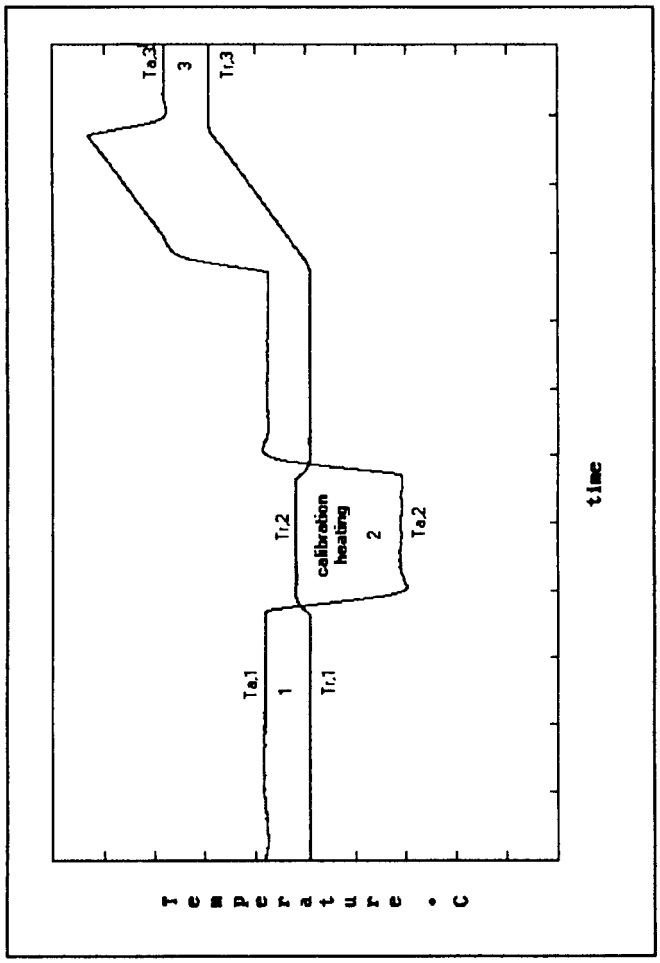


Reaction Calorimetry
Mettler RC1 Calorimeter
Acetic Anhydride + Water => Acetic Acid



RC1 Data Transfer

RC1 Calibration Run



RC1 EVAL_TAB.TAB Output

METTLER RC1 EVALUATION 20 Nov-90 11:06-am
Trial with New Dosing Accessories
Pump Delivery of Acetic Anhydride

INITIALISATION PARAMETERS

Reactor Configuration:

Type of reactor: 0
Type of inserts: 0
Type of lid : 0
2.0 l AP01 glass reactor
with AP01 anchor stirrer,Pt100, calibration heater (all glass)
and AP01 Glass cover

Reactor Parameters for Heat Transfer Calculations:

Capacity : 2.0 l
Diameter : 0.115 m
Min Area : 0.0113 m2 at min virtual volume of 0.124 l
Max Area : 0.0747 m2
Virtual Volume : 1.022 l
Heat Transfer Coeff.: 180.0 W/m2 K
Heat Capacity of Inserts: 69.0 J/K at 1.0 l
: 106.0 J/K at 2.0 l

First Fill into Reactor:

Amount : 1.022 kg water
Volume : 1.022 l
Density : 1000.0 kg/m3
Temperature : 20.0 °C
Cp : 4200.0 J/kg K

RD10 Configuration:

	Control Loop 1	Control Loop 2
Input	B1	none
Mode	DOS	DOS
Output	C1	none

Sensor Symbol	Units	Type	Name
A1	°C	T	Anhydride Temp
A2	bar	P	Reflux Delta T
A3	°C	T	Top T
pH	pH		

SUMMARY OF ACTIONS

Pos	Mode	Start	End	Start Value	Set Value
1	Tr	0:00:50	0:10:50	20.03 °C	30.00 °C
2	Tr	0:58:14	1:08:14	29.92 °C	32.00 °C
3	Tr	3:11:06	3:21:06	31.93 °C	30.00 °C
1	Stirrer	0:01:00	0:01:01	100 rpm	175 rpm
1	Calibration	0:33:08	0:43:08		
2	Calibration	2:47:40	2:57:40		
1	Emergency G		0:00:00	0:00:00	
2	Emergency C		0:00:00	0:00:00	

		Start	Set Point	End	Set Value	Mass from
1	Dosing B1	1:28:04	1:30:04	1:51:08	0.051 kg	B1
2	Dosing B1	1:51:08	1:56:08	2:19:34	0.051 kg	B1
3	Dosing B1	2:19:34	2:22:34	3:39:52	0.051 kg	B1