Fields Industrial Optimization Seminar

Modeling Successes in a Polymer Production Process

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SOME THEMES FOR MATHEMATICAL MODELS

The Importance of Data

Application of Theory-Experimental Mix

Choice of approaches:
Fundamental or Statistical

Use of a simulation in place of
a direct analytical method

OPTIMIZATION GOALS OF MATHEMATICAL MODELING OF A CHEMICAL PROCESS

Maximize Capacity

Maximize Yield from Raw Materials

Improve Process Control

Minimize Operating Costs, including
Labour and Environmental Compliance

Minimize Capital Cost of Capacity Increase

PLAN

1. Primer on Chemical Engineering Equations

2. Data Gathering on a Batch Polymerization Process

3. Construction of a General-Purpose Model

4. Product Prediction via On-Line Simulation

5. Process Control Strategy via Unsteady-State Simulation

1.

THE EQUATIONS OF ENGINEERING

Electrical: Maxwell's four equations
of Electricity and Magnetism

Mechanical: Newton's Three Laws of Motion

Civil: Newton's Third Law

Chemical: Balance Equations for Momentum,
Energy, and Mass (of Components)

CHEMICAL ENGINEERING
BALANCE EQUATIONS

Carried out on one or more defined finite or infinitesimal parts of the universe

d(Momentum) / d(time) = Sum of momenta of material entering and leaving, forces due to pressure differences, to gravity, to friction, to mechanical action

d(Energy) / d(time) = Sum of energy content of materials entering and leaving, heat diffusing from the boundaries, heat generation by mechanical dissipation and by chemical reaction

d(Component Mass) / d(time) = Sum of component flows entering and leaving,
component diffusion across boundaries,
generation or consumption by chemical reaction

CHEMICAL REACTION

$$A + B \longrightarrow C$$

$H_3C - C = O \quad + \quad H_2N - CH_2 - CH_3$

\

OH

↓

O

||

$H_3C - C - N - CH_2 - CH_3 \quad + \quad H_2O$

H

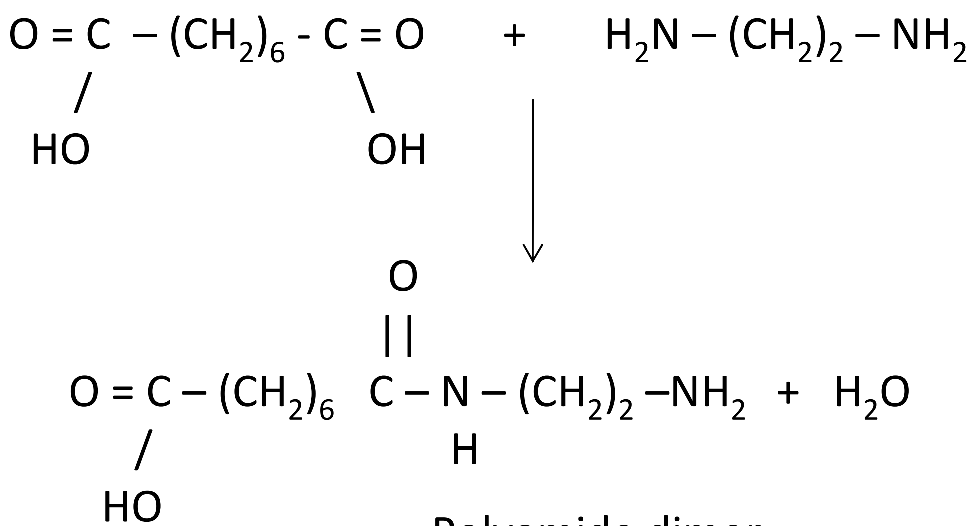
Bifunctional ingredients

$O = C - (CH_2)_6 - C = O \quad + \quad H_2N - (CH_2)_2 - NH_2$

/ \

HO OH

STEP-GROWTH POLYMERIZATION



Polyamide dimer

AA + BB ALB + water

ALB + AA ALLA + water

BB + ALB BLLB + water

ALB + ALB ALLLB + water

. . . .

ALLL ...... LLLLB

ALLL ......LLLA

BLLL .... LLLLB

2.

PREPARATION OF A SPECIFIC POLYAMIDE

Pre-mix components in approximately
equal proportions, along with water

Bring to a boil

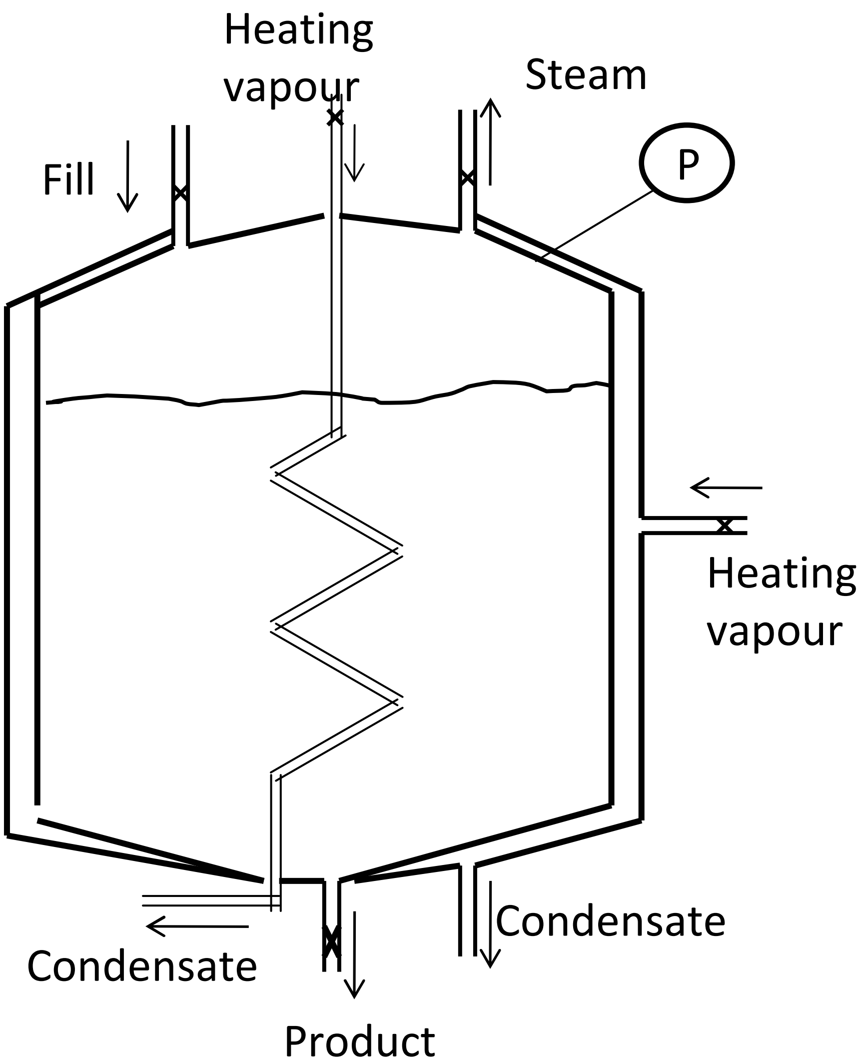
Concentrate and maintain at sufficient
temperature to promote reaction

When done, expel the polymer into
desired shape and allow to solidify

May be done in a batch or continuous manner

See “Polyamides – Still Strong After Seventy Years”
Macromolecular Reaction Engineering **2011**, *5* (1), 22-54

THE BATCH PROCESS



BATCH PROCESS STUDY

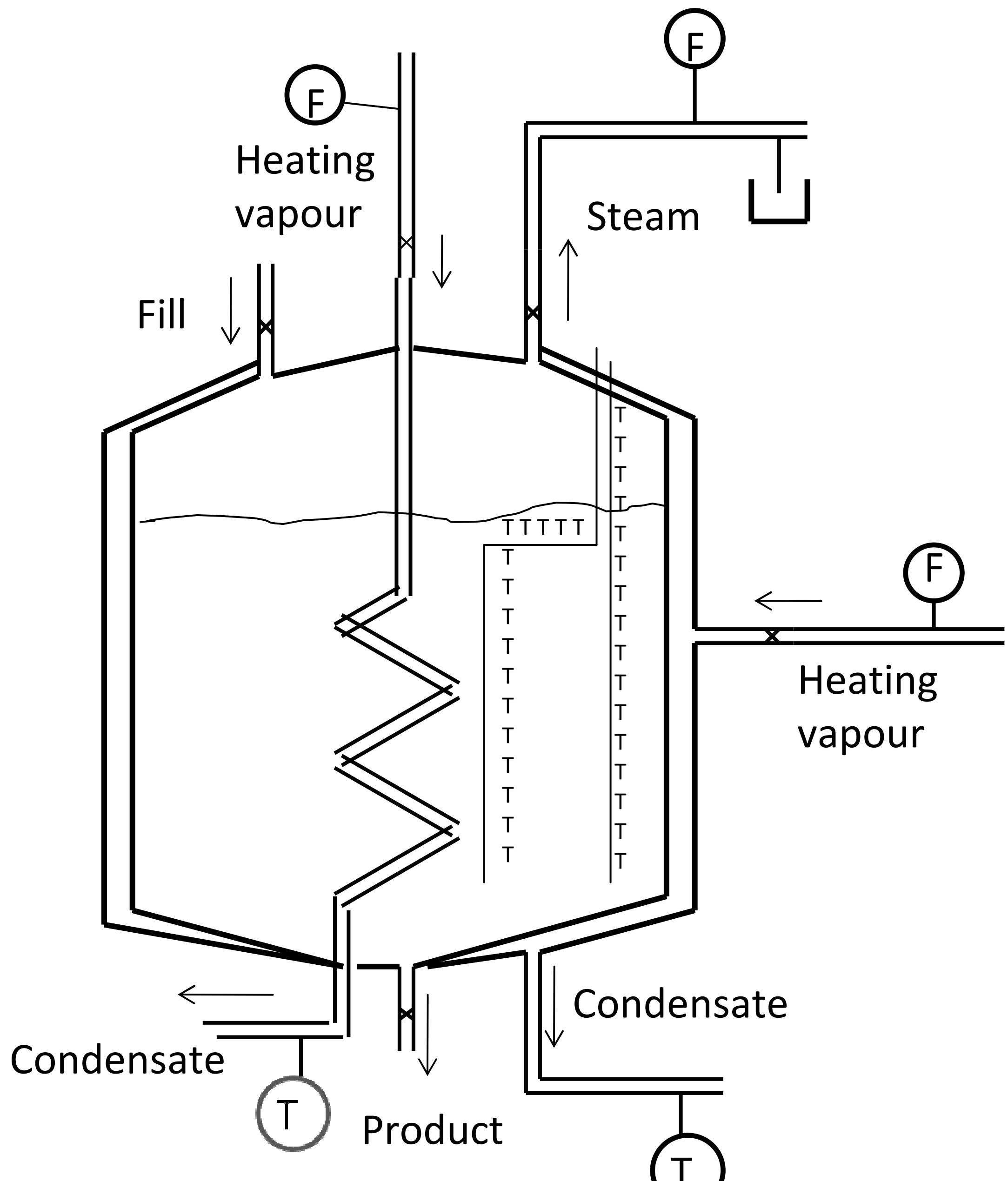
Program of in-depth measurements proposed
for the batch operation.

Reasons:
(1) learn more about this specific process

(2) learn more about the fundamentals of the
polymerization in general

Proposed time-wise measurements:
- temperature distribution within the polymerizing mass
- flow rate of steam from the vessel
- flow rate of heating media
- content of slightly volatile monomer BB in the steam

Challenges:
- being allowed to do this study
- introducing multiple temperature devices into a pressure vessel
- accurately measuring steam rate over a wide range of flows


F
Heating
vapour
F
Steam
Fill
F
Heating
vapour
Condensate
Condensate
T
Product
T

RESULTS OF BATCH PROCESS STUDY

(in terms of the Chemical Engineering Balances)

Momentum

Coil was up to 50% flooded in lower part,
hence ineffective for heat transfer

Batch temperature was uniform laterally but significantly
non-uniform vertically in the early stages

Energy

Unflooded part of coil was more effective (heat/area) than jacket

** Heat rate was twice the expected value **

Component (mass)

** Loss of component BB in vapour was much lower than
predicted from its volatility **

BENEFITS OF THE BATCH STUDY

Guide to future capacity increases via study and exploitation of heating-medium flow and heat transfer

Understanding of process complexity and construction of a realistic mathematical model

Explanation of measurement anomalies in terms of an ionization mechanism:

$$AA + BB \leftrightarrows AA^- + BB^+$$

- which is highly energetic and
- which impedes the vaporization of BB

This reaction closed the heat balance to within 5% and also explained the observed vaporization of BB.

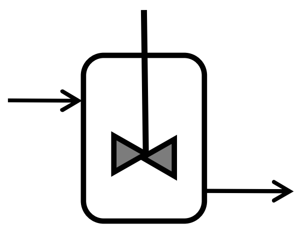
Further study led to more soundly-based calculation of ionic effects and inclusion of these effects in the math models for ALL of the processes.

3.

GENERAL-PURPOSE MATHEMATICAL MODEL FOR A SPECIFIC *AABB* POLYAMIDE

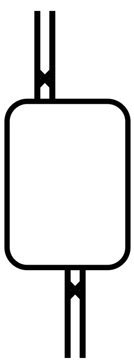
A Comprehensive Model

Built to describe all of the company's processes for this polymer. These processes comprise some or more Of the following elements.



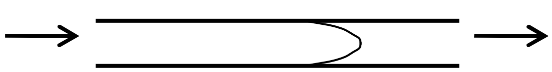
Continuous
Back-Mixed

Plug-flow



Batch

Two-Phase
(Gas-Liquid)
Flow



Viscous,Parabolic-Profile Flow

A Fundamental Model:

Based on the three chemical engineering balance equations

with transfer terms and generation terms incorporating well-founded theoretical or experimental relationships

An Integrated Model:

Simulations for individual processes and equipment draw on a common set of property relationships and of mathematical methods

A Sequential Model:

Allowing output from one process step to be the input for the next step

A "Natural-Simulation" Type of Model:

The inputs are those of the real process:-
feed-material characteristics, operating conditions, geometry.

The outputs are what would be observed in the real process:-
product characteristics, heating rates, rate and composition of evolved vapour, power consumption

Time Treatment:

Continuous flow at steady state

Batch

Continuous flow at unsteady-state (limited)

APPLICATIONS OF THE MODEL

Design of polymer piping systems –
frequently required and highly constraint-bound

Provision of parameters for empirical
matching with performance

Guide to best or new operating conditions

Design of process equipment

Identification of bottlenecks to capacity increase

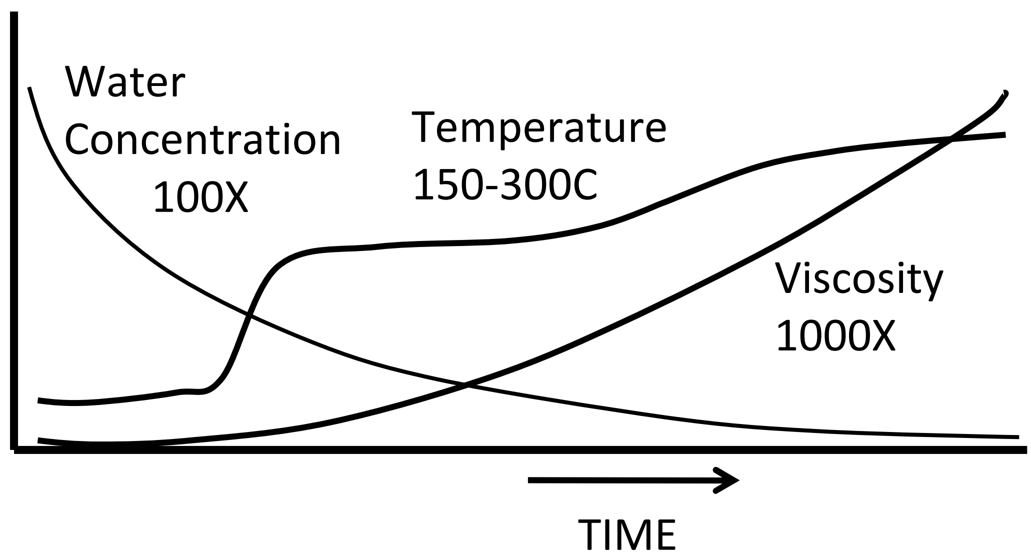
Generation of estimates for environmental
Certificate-of-Approval applications

Training of new employees

Indicator of requirements for improved property data

PROPERTY EXPERIMENTAL STUDIES

Reaction mixture undergoes large changes with time



Challenges:

- gather data for reaction mixtures over all these conditions

- devise equation forms to provide a seamless description
  the full range

MAJOR IN-HOUSE STUDIES OVER THE YEARS

Polymerization Kinetics
- Rate of forward reaction under conditions of
• initial low temperature, high water concentration,
  low viscosity
• final high temperature, low water, high viscosity

- Rate of hydrolysis under same conditions

Viscosity
Under conditions of initial process and of final process

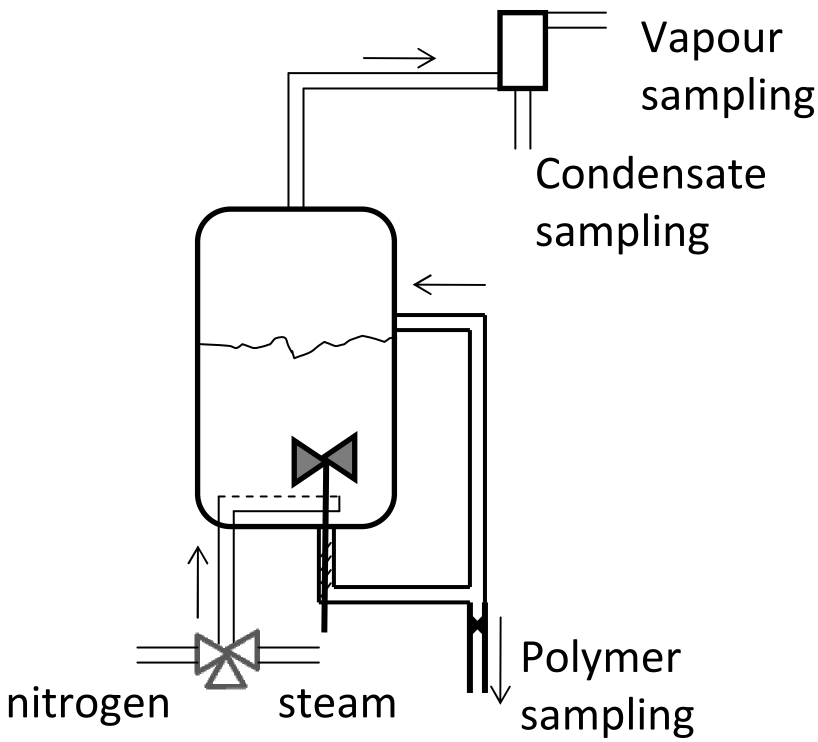
Thermal Degradation (mainly under final conditions)
Changes in balance of reactive species and in viscosity with time and temperature

"Bad" reactions

.... LLB + BLLL ... . LLBLLL .... leading to branching

.... LLA .... L- ⬠
also leading to 3-way branches

POLYMERIZATION AND THERMAL DEGRADATION STUDY AT QUEEN'S



Complete accounting for all substances entering and leaving the polymer mass: the most complete study ever of thermal degradation. Amidation kinetics as well.

Confirmation of species. Rigorous quantification of reaction rates, including uncertainties in the constants

See for instance

Schaffer et al., *Macromol. React. Eng.* **2007**, *1*, 563

Zheng et al., *Ind. Eng. Chem. Res.* **2005**, *44*, 2675.

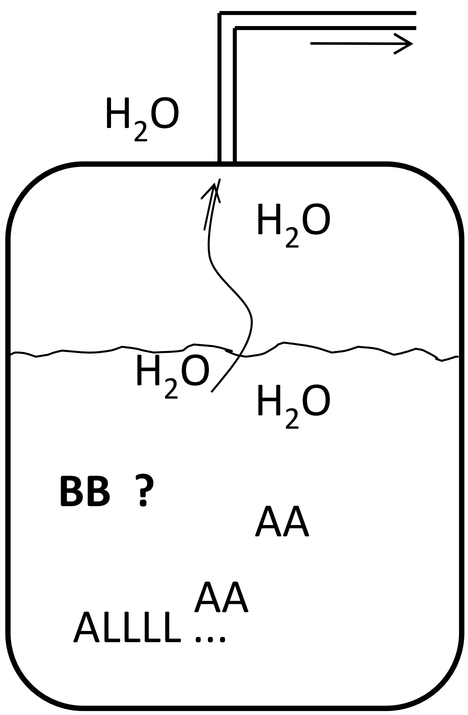
4.

REAL-TIME RELEASE OF BATCH POLYMER

Most of this polymer ends up as fibre, often in carpets.

The fibre is dyed and some common dyes are sensitive to the concentration of residual [**BLLL ...**] groups in the polymer.

This concentration is affected by how much **BB** escapes with the steam in the early stages of the polymerization.



Major influence on BB loss: processing speed – i.e., rate of heat addition

Requirement for Real-Time Release:
prediction of relative concentrations in the final polymer of

[BLLL ....] and [ALLL ...]

Statistical approach:

- choose observable during-process indicators of events likely to affect [BLLL ...] final concentration
- carry out multi-batch study, correlating product [BLLL ...] concentrations with these indicators
- create a set of predictive equations for product pedigree

Simulation approach:

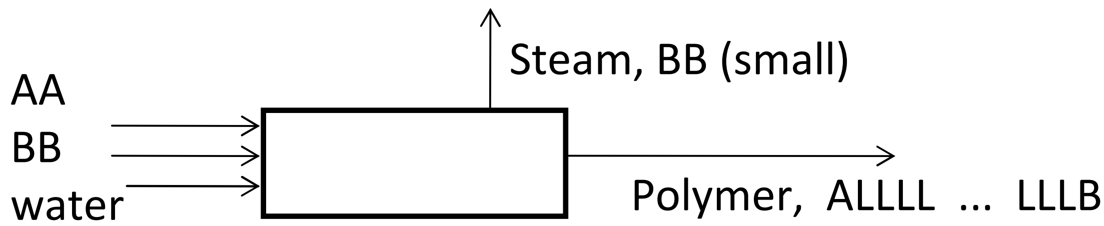
use selected parts of the full off-line mathematical model to create an on-line predictor model of minute-to minute changes in concentrations of BB and BLLL ...

The on-line predictor model makes use of the continuous measurement of temperature and steam rate.

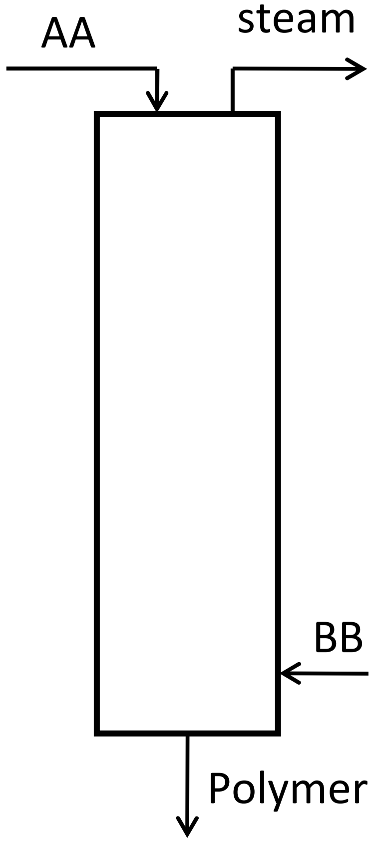
This is the chosen and very successful approach.

5.

SOLUTION OF A PROBLEM IN PROCESS CONTROL USING AN UNSTEADY-STATE MATHEMATICAL MODEL



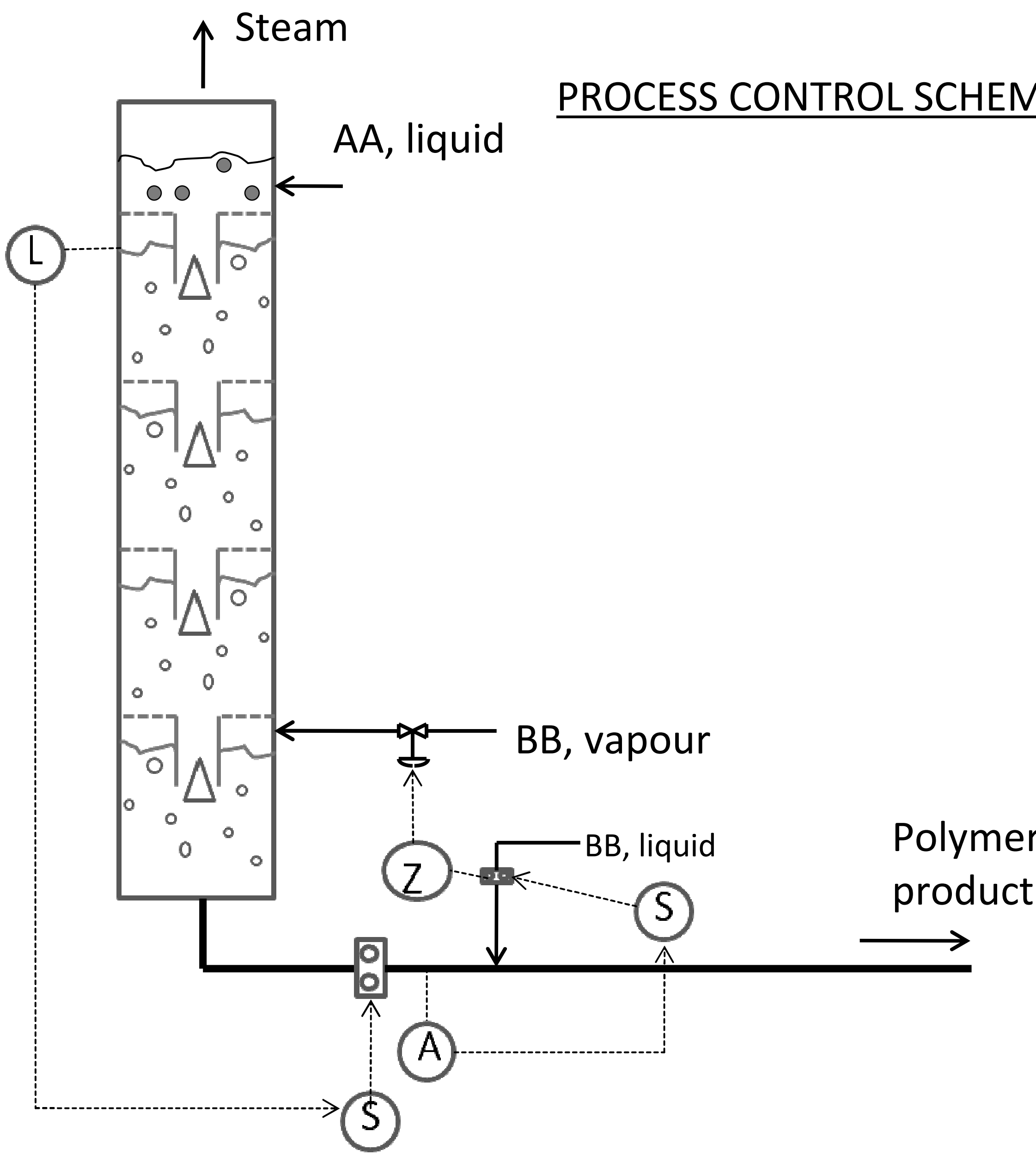
Traditional Generic Polymerization Process



Novel, Column-Reactor Process

US patent 5,416,189

PROCESS CONTROL SCHEME



BRINGING THE PROCESS UNDER CONTROL

Polymer molecule types:
ALLL .... LLLA   ALLL .... LLLB   BLLL .... LLLB

Requirement: [A] – [B] = ± 1 in customary units

Initially: [A] – [B] was ± 500 due to gross instability

After level control was switched to bottom flow:
[A] – [B] ± 50 improving to [A] – [B] ± 15

Problem: determine the optimum settings for the controllers

Control action = Gain x [Error + $(1/\tau_{reset}) \int$ Error d(time)]

<u>OPTIMIZATION OF THE CONTROL SYSTEM</u>

STEPS THAT WERE TAKEN

1. Construct an unsteady-state mathematical model of the process, including the action of controllers
2. Introduce into the model a sinusoidal perturbation in the value of [A] - [B] entering a lower stage
3. Note the amplitude of the predicted variation of [A] - [B] leaving the bottom stage
4. In the simulation, try various combinations of controller settings to minimize the latter variation.
5. Test the optimum settings in the actual process

Three Results:

1.Variation of [A] - [B] in the product was reduced to ± 1.5

2.Confidence that this is a way to solve ANY control problem

3.Conclusion that brute force sometimes beats brains

REVIEW OF
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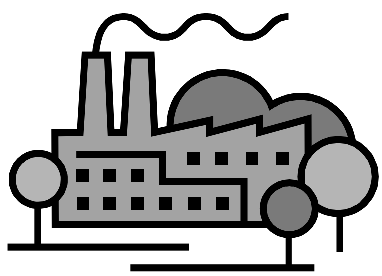

THANK YOU