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Review

Optimal Control in Reactive Processing for Fine Chemicals and Polymers in Stirred Jacketed Batch and Semi-Batch Reactors: A Bibliography

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Abstract: After World War II, scientific investigations for processing in chemical batch reactors had been started, for its "most adopted" application in the industrial sector. Taken from the industrial perspective, serious instances, unable to be endured, happen; hence, the process must be in control of, which impedes the realization of batch reactor objectives. Therewithal, with the evolution of large-scale optimization software packages, the "ease" to convert novel optimal control policies into industrial environment strategies, becomes realistic. In this work, a detailed bibliography on the optimal control functioning for reactor configuration named "stirred jacketed", waged in batch/semi-batch processing of fine chemicals and polymers, along with methods according to this definition, is presented. To the author's knowledge, all the existing schemes are discussed, focusing on their strong points.

***Keywords*:** optimal control, batch reactor, polymerization reactor, pontryagin's maximum principle

Nomenclature

ADP	Average Degree of Polymerization
AIBN	Azobisisobutyronitrile
Ann.	Annealing
AZN	α-α 'azobisisobutyronitrile
BANN	Bootstrap Aggregate Neural Network
BMA	Butyl methacrylate
BPO	Benzoyl-peroxide
Calc. Var.	Calculus of Variations
CVP	Control Vector Parametrization
CCD	Copolymer Composition Distribution
Coll.	Collocation
Config.	Configuration
Conj.	Conjugated
Conc.	Concentration

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Cons.	Consumption
Conv.	Conversion
Dev.	Deviation
DE-DO	Differential Evolution-Dynamic Optimization
Det.	Deterministic
DMP	Discrete Maximum Principle
DP	Dynamic Programming
D-RTO	Dynamic Real-Time Optimization
DYNOPT	Dynamic optimization code for MATLAB
EA	Evolutionary Algorithm
ES	Evolutionary Strategy (Classical)
F	Feed rate
Fin. El. Coll.	Finite Element Collocation Method
FP	Fixed Pivot technique
GA	Genetic Algorithm
GAMS	General Algebraic Modeling Solver
GOO	Geometric Optimal Control
GMC	Generic Model Control System
Grad.	Gradient
HEA	2-Hydroxyethyl acrilate
HJB	Hamilton-Jacobi-Bellman theory
HSA	Hybrid Simmulated Annealing Method
HSRNN	Hybrid Stacked Recurrent Neural Network
IDP	Itterative Dynamic Programming
IICP	Initial Initiator Concentration Policy
IMBC	Inverse-Model-Based Control
IOIAP	Initial Optimal Initiator Addition Policy
IVP	Initial Value Problem
Kin.	Kinetic
Lagran.	Lagrangian
MA	Methacrylate
MMA	Methyl Methacrylate
MAUT	Multiattribute Utility Theory
MACBETH	Measuring Attractiveness by a Cathegorical Based Evaluation Technique
Meth.	Method
MM	Moment Model
Mol.	Molar
MOO	Multiobjective Optimization
Multip.	Multiplier
M_{wd}	Weight average molecular weight distribution
M_n	Number average molecular weight distribution
NN.	Neural Network
NPSOL	Nonlinear Constrained Problems Solver
NSGA-II	Nondominated Sorting Genetic Algorithm
Obj.	Objective
OCFE	Orthogonal collocation on finite elements
Opt.	Optimization
Orth.	Orthogonal
Param.	Parametrization
Patt. Sear.	Pattern Search Optimization Method

Part. Swar.	Particle Swarm Opitmization Method
Perf.	Performance
PET	Polyethylene Terephtalate
PI	Performance Index
P_n	Monomer distribution
P_d	Polymer distribution
PM	Pontryagin Maximum Principle
PMMA	Poly(Methyl Methacrylate)
Polym.	Polymeric
Prod.	Productivity
PVA	Poly(vinyl acetate)
PVC	Poly(vinyl chloride)
PSO-SNN	Particle Swarm Optimization with Stacked Neural Network Models
QLP	Quazi-linearization technique
React.	Reactive
Reccur.	Reccurent
Red.	Reduced
Reg.	Regular
Resp.	Respectively
SA	Simmulated Annealing
SCGRA	Sequential Conjugate Gradient Restoration Algorithm
SNOPT	SQP algorithm for large-scale constrained optimization
SMP	Stochastic Maximum Principle
St	Styrene restoration algorithm
Shoot.	Shooting
Seq.	Sequentional
Sim.	Simulated
SOCOLL	Simultaneous Optimization and Collocation Method
SQP	Sequential Quadratic Programming
TBPA	*terc*-butyl peracetate
Tech.	Technique
Therm.	Thermodinamique
Trans.	Transition
Var.	Variation
V	Volume of a reaction mixture
Y	Yield

1. Introduction

The optimal control has precedence over the classical control owing to the fact that not linearized with respect to a nominal state as a case with the latter one. As a more advanced option, optimal control supposes a unique control signal originated in periods of futurity, from there, the cost is defined to be further optimized. It is with the design that the optimal control is comprehended closely, oppositely to classical control which is comprehended with realization.

On that account, from the preamble of the research in the Mid-1940s and with the newcomings in recovering superfluous outputs in the oil & gas industry, unto this date, the motive force for the usage of the optimal control in the industrial batch reactive processing, nevermore halts.[1-4]

Regardless of the foregoing research in the field of reactive processing in batch reactors, Park and Levenspiel[5,6] were the first to use the term “optimal control” in the context of the fine chemicals batch reactors, whereas it was related to the polymerization reactors, in particular.[7] Alike for batch distillation,[8] different optimal control problems definitions were researched by many authors, however, established by Levenspiel,[9] and Bonvin[10] grounded the definitions for mathematical models:

- Maximum conversion.
- Minimum time.
- Maximum profit.

However, it is to note that the list above is not exhaustive, since the formulation is also related to the "type of chemicals" to be produced, consequently, different pathways.

The complexity of optimal controlling for (co)polymerization batch reactors lies in the fact that, in terms of the problem definitions, even more choices compared against fine chemicals, can be stated, adding the options as follows:

- Degree of (co)polymerization minimization.
- Polymer composition distribution maximization.
- Overall monomer conversion maximization.

Importantly, the second and third mentioned above are often combined simultaneously with a possible choice of the other optimal control problems such as energy consumption minimization, number and/or weight average molecular weight distribution(s).

To this end, this article aims to review the advances made in optimal control for different modes of batch processing: batch and semi-batch, with/without vapor recompression, along with the different types of mixtures: fine chemicals and polymers. The distinction of this review from the others on similar topics, is in its specific scope focused only on the "optimal control": the supremacy of the optimal control over all the classical control techniques builds its foundation on open-loop control instead of closed-loop controls since later are established by system models linearized with respect to a nominal state. In consequence, batch and semi-batch processes in the reactors are not "easily controlled" by conventional control techniques due to their strong nonlinearity. Alternatively, optimal control predicts a unique control signal generated over a period of future times, hereof the cost is defined to be further optimized. With a clear distinction from classical control, which is about the realization, the optimal control is about the design.

Considering the vastness of studies on optimal control of fine chemical and polymer production in stirred jacketed batch and semi-batch reactors, it would be impossible to cover all interesting topics, therefore, certaine phenomena following these processes are excluded: such as modeling and control of batch crystal growth and hydraulic fracturing.

The last review on optimal control of stirred jacketed batch reactors for fine chemicals processing was done by Terwiesch et al.[11] and Le Lann et al.,[12] where a long list of papers was reviewed (~115), whereas for polymers processing the authors named Ramteke and Gupta,[13] covered an even more comprehensive list of papers (~160).

2. Optimal control strategies for production in batch and semi-batch stirred jacketed chemical reactors

2.1 *Theoretical background*

In Figure 1, a step-by-step scheme for solving the optimal control problems of batch processing in chemical reactors is given: two widely used theoretical approaches, ie. Pontryagin's Maximum Principle and Dynamic Programming, are detailed.[14,15] Accordingly, if the approach of Pontryagin's Maximum Principle is followed, then it the objective function can be expressed in two different forms: 1) Lagrange, 2) Mayer. Further, taking a path of the Lagrange, Lagrangian multipliers should be defined, so as to form the ‟Augmented Function", from which the extremal arcs should be reached, with the concern that they must satisfy all the conditions numbered: 1) boundary, 2) transversality, 3) Legendre-Clebsch. Otherwise, taking the path of Mayer form, lead to the choice of taking the 1) direct (time discretization) or, 2) indirect methods (no time discretization), to be used for solving the optimal control problem. If taking the direct methods, solvers such as dynamic optimization point optimizer (DYNOPT)/interior point optimize (IPOPT)/sparse nonlinear optimizer (SNOPT), depending on the nature of the process (for example, SNOPT is for polymerization), whereas, the optimal control problem is approximated by a finite-dimensional optimization problem (NLP-nonlinear programming), resulting from the time discretization of the dynamics of the system by an appropriate discretization scheme, Crank-Nicolson, Euler (implicit/explicit), Middle Point, Runge-Cutta, Gauss, Lobatto, Heune, and others going from 1st to 12th order. Even not pointed on Figure 1, a special technique of multiobjective function optimization needs to be mentioned since it provides a great opportunity when two objective functions are conflicting in their nature: model equations can be integrated for any specified set of input variables using specified programs from code libraries, i.e. subroutines, which in case of stiff differential algebraic equations systems, use Gear's method and provides values for the output and the state variables at any time, this model forms an initial value problem IVP, and is then used for solving a multiobjective optimization problem. An initial value IVP problem integrated using specified subroutine available at NAG FORTRANE library, for any given decision variable and initial values of state variables, this subroutine combined with improved versions of NSGA (NSGA-I, NSGA-II, Elitist, etc) provides several feasible solutions which satisfy end-point constraints within specified values of tolerances, and, this set is named, Pareto set.

Otherwise, the indirect method pathway, assumes definition of the Hamiltonian function and/or Boundary Value Problem (BVP), which leads to formation of "shooting equations", which, again must satisfy all the three conditions: 1) Boundary, 2) Transversality, 3) Legendre-Clebsch. The other approach, ie. Dynamic Programming, ie. Bellman theory, requires performance index problem definition, afterwards, the conversion from continuous to piecewise constant control. In the next step, time is 'normalized' and integrated over stages, by backward and upward integration. It is to note, that for both theoretical approaches, the 'conversion' from infinite to finite-dimensional problem is possible, as stated in the Scheme, in the beginning, after the performance index problem definition (Bellman) or after the Mayer problem definition issued from Pontryagin's Maximum Principle (PMP) theory, conversion to NLP.

Finally, the scheme does not consider "data-driven" models, due to the reason that these models does not require computational efforts, since they are obtained from industrial process data, which makes them difficult to be understood/presented.

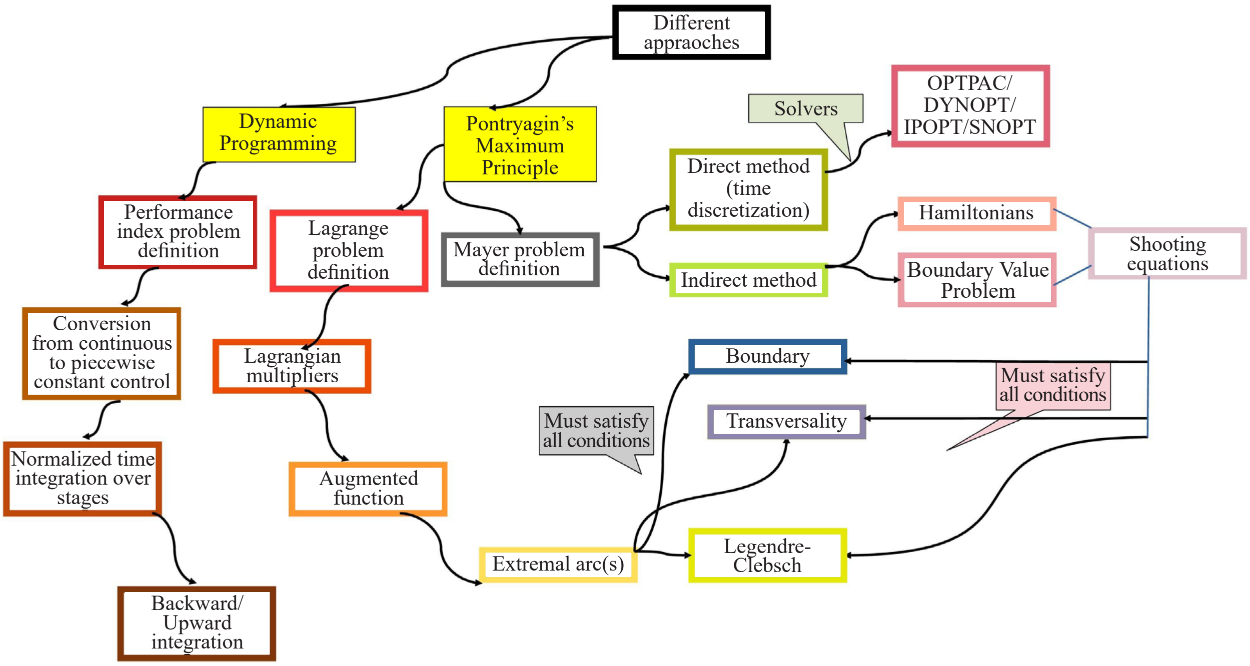

Figure 1. Theoretical steps in optimal control of processing in batch reactors

2.2 *Optimal control strategies for fine chemical processing in discontinuous and semi-continuous mode*

Aris,[16] by the means of dynamic programming, was the first to propose the optimal control of batch reactor train, through the control of the reaction by the addition of cold reagents: as the most optimal found was the bang-bang policy, for which according to the switching functions areas distinguished showed when adding the cold reactant at its upmost rate or its avoidance is recommended.

Szépe and Levenspiel,[17] were the first to define the optimal temperature policies for a class of batch reactors with respect to the specific phenomena, i.e. of catalyst deactivation: if the upper-temperature limit is set, and under the specified conditions, if catalyst decay activation energy is greater than the reaction activation energy - single period function is increasing or constant (maximum isotherm), however, if inverse then the function is double period, i.e. alike "truncated S-shape" (will be used further in the text as confirmed late by the others). In Figure 2, a general scheme to underline the possible reactive processing routes for discontinuous/semicontinuous mode is illustrated.

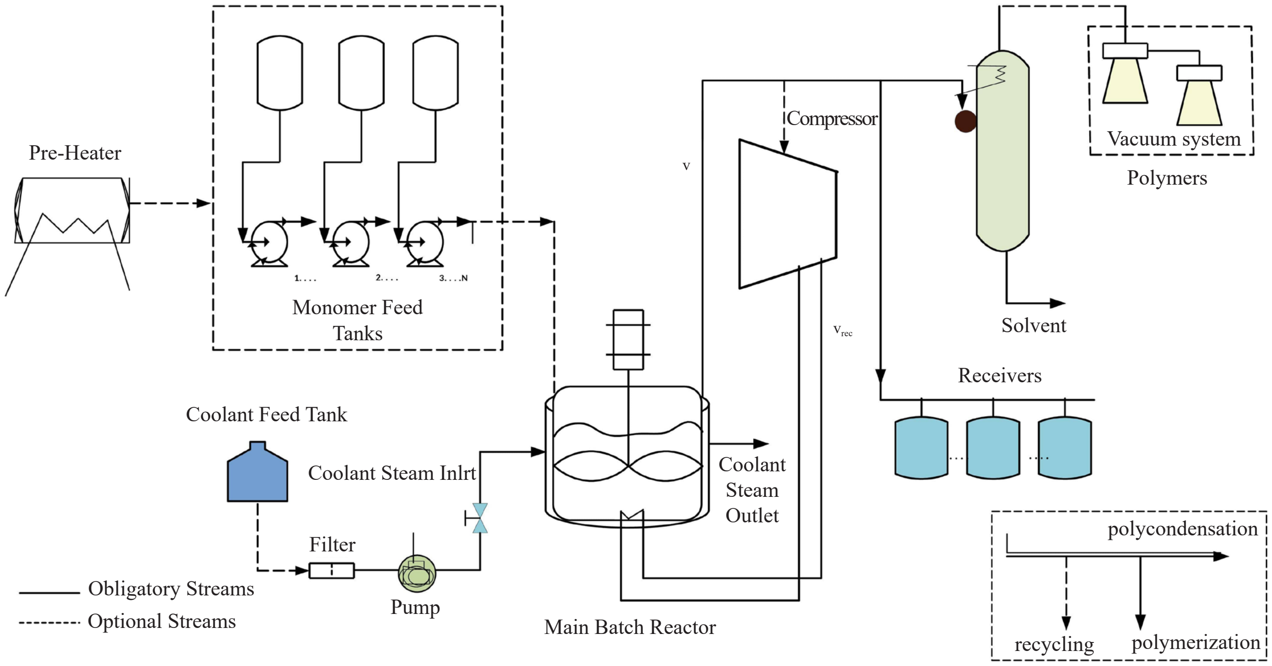

Figure 2. A general scheme for a chemical reactor in a batch or semi-batch mode

Crescitelli and Nicoletti,[18] proposed the "optimal piecewise constant policy" comprised of three periods characterized by the constancy of temperature for each. The authors concluded the optimal strategy should be described by descending temperature and (with) ascending interval lengths progression. In all of the works of the authors cited previously, the singular controls form the core of the optimal solution, whereas, in future research, the "bang" arcs start to come into play. Pommersheim and Chandra,[19] extended the results of the previously mentioned authors, for higher reaction rates, as the temperature decay parameter was shown to affect the optimal process temperature by passing longer periods before reaching a maximum ("-bang") when striving closer to the independency from catalyst decay, ie. dependency from catalyst decay is forgone over prolonged time intervals.

Farhadpour and Gibilaro[20] studied various forms of objectives: 1) ratio-integral, 2) integral, and 3) integral objective with integral side constraint. Despite the fact that optimal control switches only once for all cases, it is the first one that achieves the lowest value for both - variable and constant temperature policy (i.e. 47.13%/53.79% more against the first/third, respectively). Wagmare and Lim,[21] stressed the outperformance of the singular unbounded strategy over the bang-bang control for batch operation with recycling. Again, like the previously mentioned works, singular trajectories have three periods: 1) maximum till desired purity is achieved, 2) exponential mode to keep it constant, and 3) the optimal residual volume to be achieved with maximal feed outlet. The authors, however, stressed the rule for singular control: rate expression to have an inflection point with a negative slope and a feed concentration to be greater than the concentration calculated by the intersection of the tangent at the inflection point with the axis. Through the comparison of the effects of kinetic parameters, it is noticed, productivity uprises from 4.5% to 30% depending on the rate expression used.

Filippi et al.,[22] identified three mathematical models in a hierarchy with their complexity, to detail their conclusions through the optimal evolutions of desired product compositions with time depending on temperature: for an increase in the isothermal set point of 6.27%, second period duration increase from 11.12% to 44.45%, depending on the case studied.

Levien,[23] researched feed addition policies using two feed charges to end with: 1) optimal operations to minimize the overall yield based on the amount of reactant - for almost the equimolar mixture, the maximum yield achieved is 0.25/0.37 for higher/lower-order reaction, resp., 2) optimal operations to maximize the overall yield based on the amount of reactant consumed (B) - working linear trajectory connecting the previous with the byproduct. As they all worked on the Trombouze scheme, Vassiliadis et al.,[24] compared results against continuous mode case researched by Kokossis and Floudas,[25] for the optimal strategies for 1) reactions stage duration: difference per charge lies within the interval [2.70-52.84 (%)] per batch; 2) charge levels: the gap is even broader since it lies within an interval [9.86-94.83 (%)]. Moreover, the final time achieved compared to Kokossis and Floudas[26] resulted in an increase of 9.94%. Vassiliadis et al.[26,27] discussed a particular problem (of industrial interest) without path constraints, having provided a fresh feed of reactant (in charge) to be added throughout the mixing step (constrained) in continuity, whereas the first optimal temperature decay shown as the most significant [from 329.5 K to 316.5 K (almost 4% in the first tenth)]. (alike the "bang" sequence).

Garcia et al.,[28] studied two schemes: 1) consecutive-competitive reaction scheme: it is only by double (T + F)/ triple (T + F + t) optimization that temperature achieved its maximum in the second period, after 55%/65% of the time. The authors stressed that the "optimal amount of added reactant" is lower than the fixed one for both reactive systems, 7.37/3.46 times, even being, lower for consecutive-competitive/parallel, respectively.

Toulouse et al.,[29] imposed a safety constraint on the thermal flux: both the optimal evolution for reaction extent/ heat generation reached a real "bang-sequence", approx. ~34% after the beginning.

Bonnard et al.,[30] Bonnard and Launay,[31] for a case of the consecutive reaction network, studied in-depth minimum time problems with the goal of reaching a predefined concentration of desired product: the authors well-described the switching rule as a function of all concentrations, whereas, after a certain level of the product reached both become linearly increasing.

Luus,[32] examined a "piecewise optimal control policy", two periods can be distinguished, only for the simple reversible reaction, if the total number of stages is reduced to 22, the zero-bang structure initially appeared as, the first switching occurs after 34~35% of the time, whereas if the performance index increase by at least 30%, then the perceived zero-bang structure occurs only after 40% of total time, Industrially relevant, the final case of pyrolytic bitumen, depending on a total number of stages applied: after the first 12.5%/15% of total time, respectively, a final "bang alike" instantaneous increase up to more than 94% of the possible maximum, appeared.

Bojkov and Luus,[32] reworked the reactional scheme of Luus,[33] ie. Denbigh reactional system, last but not least, by adding the last reaction concerning the rate of waste synthesized from desired product: as expected, if the greatest value of penalty imposed (2×10^{-6}), the optimal reactor temperature evolution becomes closer to the "zero-bang-bang" as it starts with zero period lasting for almost 1/6 of total time, followed by a very steep stepwise increase to the "quasi-bang-bang" structure, ended up with an instantaneous decline to ~89% of maximum at the end of the process. Otherwise, the authors witnessed a severe influence of the penalty function on the optimum total time: if increased by 200 times, the time increase is 14.35%, calculated for a maximum number of steps of 50.

Luus and Okongwu,[34] proposed an optimal evolution of the flow rate of coolant for a predefined heat transfer coefficient: the initial "quasi zero-bang structure" that occurs even before one-sixth of total time, It is noted that, with the increase of a total number of steps greater than 30%, the characteristic structure is to disappear since only 50%/22.23%, resp., of the attainable maximums achieved. Furthermore, the phenomenon is even more exaggerated if the power is variated since the least decrease of 13.20% invokes only 30% of the attainable maximum to be reached.

Shin et al.,[35] discussed the optimal temperature evolutions gained from the minimum reaction time policy, with the respect to the undesired side product concentration predefined: for an increase of set-point of concentration constraint by 21.05% and/or 34.79%, the second time cycle elongates up to 28%. Also, characterized by the structure of "quasi bang-zero".

It is noteworthy, that one of the previously mentioned optimal functioning of fine chemicals is motivated by the problem of industrial solvent production in stirred batch reactors, which was accompanied by an industrial study considering heating/cooling jackets, Figure 3.

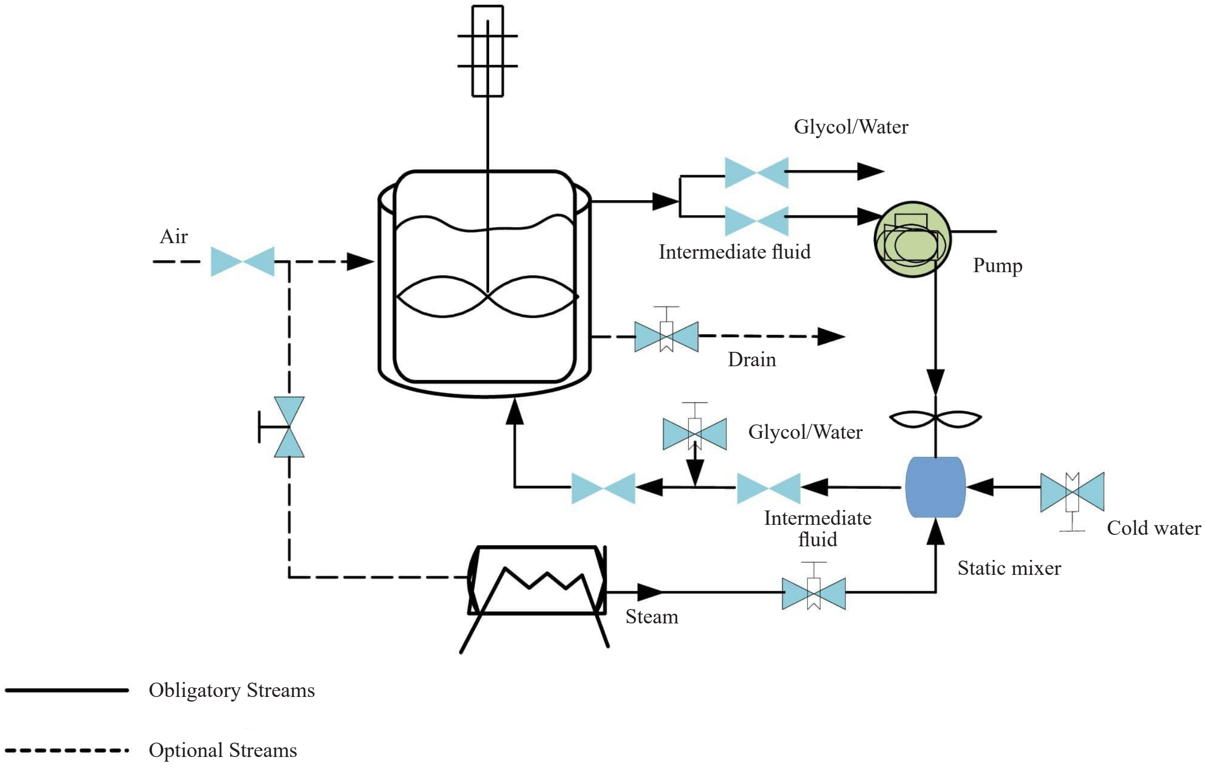

Figure 3. Batch reactor pilot plant scheme fitted out with the hybrid heating-cooling system

Aziz and Mujtaba,[36] are among very few authors to stress the importance of the profit to achieve: to take into the objective, the profit along with time and conversion, brought some improvements in the yield as 3.08%/1.49% but significantly more in time as 25.60%/19.42%.

Grau et al.,[37] proposed both, results for flow predefined/undefined at respective periods of time: 1) if the flow at the intermediate period of time is increased by 1.23 times, then the optimal strategy shows the final period of constancy for approximately 100 s longer (ie. for 1/12 of total time), compared against the undefined case for both optimal flow and temperature time evolution; 2) results in form of “flow combinations” obtained by optimization with a genetic algorithm, clearly shows that the optimal control structure for the initial(s) period(s) is much more complex then predicted previously, as at least three consecutive “pique(s)” needed to reach final time/temperature.

Aziz et al.,[38] searched for the optimal temperature that would maximize the product and minimize the byproduct for the examined reactional system, considering total batch time for both: 1) single, and 2) three-time intervals. In terms of the response structure, the neural network inverse-model-based controller gave very similar outputs for both set points fixed, ie. constant/dynamics, since starting with a “quasi bang-zero” sequence for jacket temperature, and/or ending with a real bang sequence for a reactor temperature.

Zhang and Smith,[39] however, took a step further, by including “the effect of mixing”, ie. considering the existence of the “mixing compartment” analog to the plug-flow reactors (Figure 4). Hereby, the significant results can be noted in particular cases: 1) semi-batch mode with the parallel reactional system - for batch cycle duration elongation by 1/3 the optimal feeding evolution brought gain in yield by 3.1%, whereas, in the case of longer total duration, its optimal evolution follows linear kinetics; 2) semi-batch mode with the multiphase reactional system - whereas the fractional yield of intermediate product, calculated with respect to the reactant in excess, proven to reach almost total purity (99.80%) if addition rate optimized along with reactor temperature, i.e. even 14% more than in the case for constant addition rate optimized along with constant reactor temperature. Rani and Patwardhan,[40] suggested two model-based optimizations: exact and artificial neural network, however, the latter one resulted in less than 5% of improvement in terms of conversion (product B).

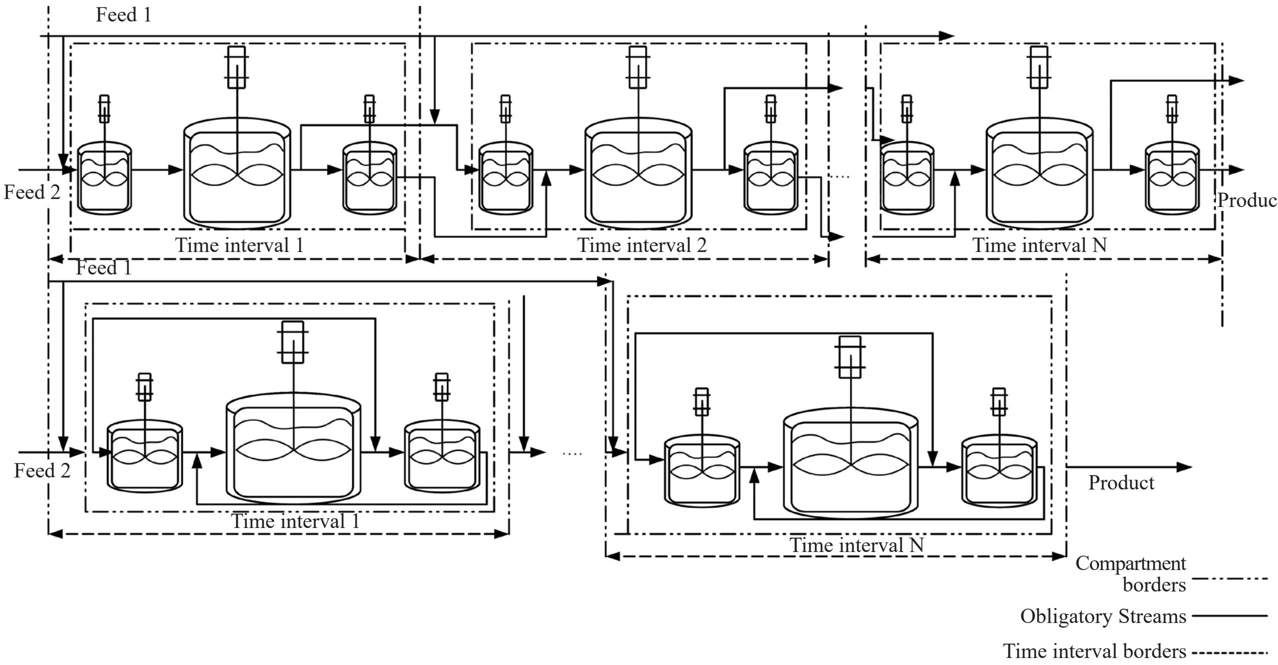

Figure 4. Superstructure of a batch reactor: (a) non-ideal adapting mixing compartment networks; (b) ideal adapting mixing compartment networks

Hirmajer and Fikar,[41,42] reworked the study given by Vassiliadis et al.,[26,27] to prove a better policy for temperature by varying the total number of discretization intervals and/or initial charge temperature, however, concluding that intermediate to give the best performance in terms of process time, ie. both, product and time, but still less than 2%. Sun et al.[43] reported a system of consecutive-competitive reactions: 1) for the maximum yield problem: the optimal coolant flowrate evolutions with different operating constraints, experienced a "quasi-bang" final period (the last 1/7), 2) for minimum time problem: the greater number of discretization stages brought "quasi zero-bang" structure, whereas it switches after more than 60% of process time. Most obviously, these results show the great importance of correctly selecting the temperature constrained/unconstrained, respectively.

Erdirik-Dogan and Grossmann[44] gave significant contributions towards the implementation of batch reactor "network" into industrial usage. In Figure 5, the parallel scheme of two reactors, with five reactions, resulted in all, except B as an intermediate, products in a single stage. Furthermore, four optimal scheduling strategies were "tested", whereas, equal profit reductions were obtained by Detailed Planning (DP) and Rolling Horizon (RH) over a six-week working period, whereas they outperformed Relaxed Planning (RP) by 34.74%. The same figure shows a parallel scheme for three reactors involved in eight reactions, here, the Rolling Horizon (RH) strategy was the best among all and outperformed the Relaxed Planning (RP) by 15.48% over the same period. Even more, complex parallel schemes was presented in Figure 6. The left one, ie. four parallel reactors involved in ten reactions, whereas only product A is intermediate, again Rolling Horizon (RH) and Detailed Planning (DP) strategies equaled by outperforming the Rolling Horizon (RH) by 28.7% over the same production period. Finally, in the previously mentioned figure, the most complex scheme can be perceived: six parallel reactors involved in fifteen reactions, with three intermediate products (A, D, F), but not included by the previous study. In particular, the optimal profit variations with respect to total production times, variated between 6 and 48 weeks, showing, the opposite situation, since Relaxed Planning (RP) against Rolling Horizon (RH) strategy leads over by a "function" of a steeper slope: showing that after 48 weeks, outperformed the RP by even approx. 20%.

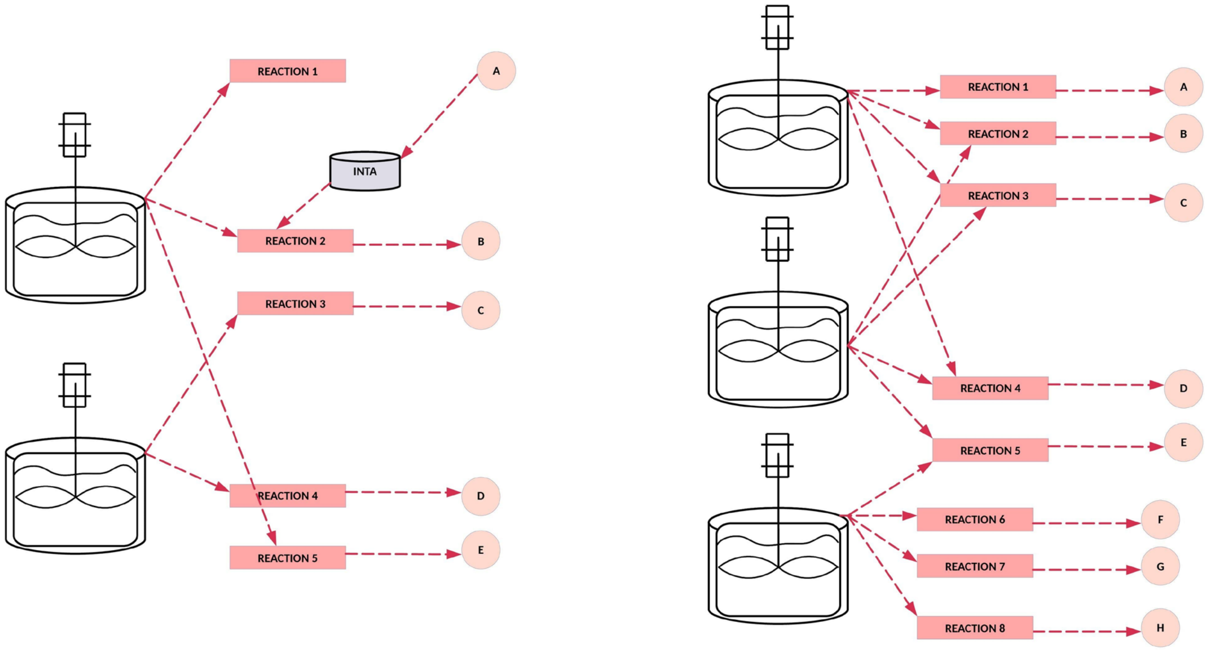

Figure 5. Parallel sequencing: (a) two reactors connected; (b) three reactors connected network

Rapaport et al.,[45] from the theoretical point of view, compared two strategies: 1) single arc strategy, and 2) the immediate one impulse strategy. Further, the first one proved to be better since the concentrations interval [$(10^{-2}$-$10^{-4})$] gave improvements for 7-11%. Varga et al.,[46] invented Covariance Matrix Adaptation Algorithm, to employ it in a real-plant process usage through Hazard and Operability Analysis (HAZOP) of process simulation. Simon et al.,[47] included the liquid hydrodynamics into their process model to propose two scenarios: 1) optimal reactor temperature evolution: stepwise function within 12/20 time intervals shown reaching a maximum after almost 58%/55% of the time, 2) the pressure optimization: normalized pressure evolution, starting with a "quasi-bang", lasting around 37.5% of total time. However compared to industrial cases where it doubled, and, ended with a "quasi bang-bang" sequence of less than 50% of the maximum achieved.

Benavides and Diwekar,[48] considered stochastic optimal control problems for biodiesel production, and finally compared them: 1) the maximum concentration optimal policy: brought only 7.81%/1.79% resp., of improvement in the concentration of methyl-ester compared to minimum time/maximum profit policies, resp., and 2) minimum time policy brought the improvement in time, even by 69.5%/39%, resp., compared to maximum concentration/maximum profit policy, 3) maximum profit policy contributed significantly by 78.05%/31.19% , resp., compared to minimum time/maximum concentration policy, resp. Finally, the authors stressed the difference between stochastic and deterministic approaches related to profit: stochastic brought 7.15% over deterministic approaches, however, the "smooth curve stochastic approach" invented, brought less than 1%.

Gajardo and Rapaport,[49] discussed theoretically the case of batch reactor: applying Hamiltonian-Jacobi-Bellman theory, they ended up finding that considering the feed flow rate as a manipulated variable during the filling phase, consequently influenced the total duration of a cycle. Ivanov et al.,[50] tempted to control the external heater to maintain the overall minimum energy requirement for the coupled reactors. Logist et al.,[51] founded the ACADO optimal control solver, based on GA coupled with direct optimization methods: studying in particular, the Williams-Otto batch reactor, to show: 1) jacket temperature optimal evolution to follow a ‘‘quasi zero-bang” policy, as more than 70% of trajectory shown to be of “on-off ” form, 2) feed rate: also shown “quasi bang-zero” policy, since very short interval switched between them.

Maidi and Corriou[52] however, followed Pontryagin’s Maximum Principle, to solve the problem of the batch reactor in Maple and MATLAB: taking into consideration, a parallel reaction mechanism, tended to maximize a yield of the intermediate product, over a fixed period of time. The manipulation of temperature was enabled by a choice of control variable - the reaction constant of the first reaction, to obtain an optimal control trajectory: “two periods alike”, wheres, ended with a “quasi zero-bang” sequence of short duration (~5% of the time).

Drag and Styczen,[53] for a combined system of reactions (consecutive-parallel), reported the optimal pressure evolution composed from almost linear parts, whereas the increase noticed in the starting period (less than 20% of the time) and steep decrease till the end of the process (3.32 to 3.08). Patel and Padhyar,[54] introducing a novel box-complex assisted method implemented into genetic programming algorithm, tempted to point out for the bibliographic order of works, a difference in methods efficiency for a specific number of discretization intervals used in past works. Bakir et al.,[55] discussed thoroughly batch mode cases applying Bellman theory and were the first to use the term geometric optimal control in this context.

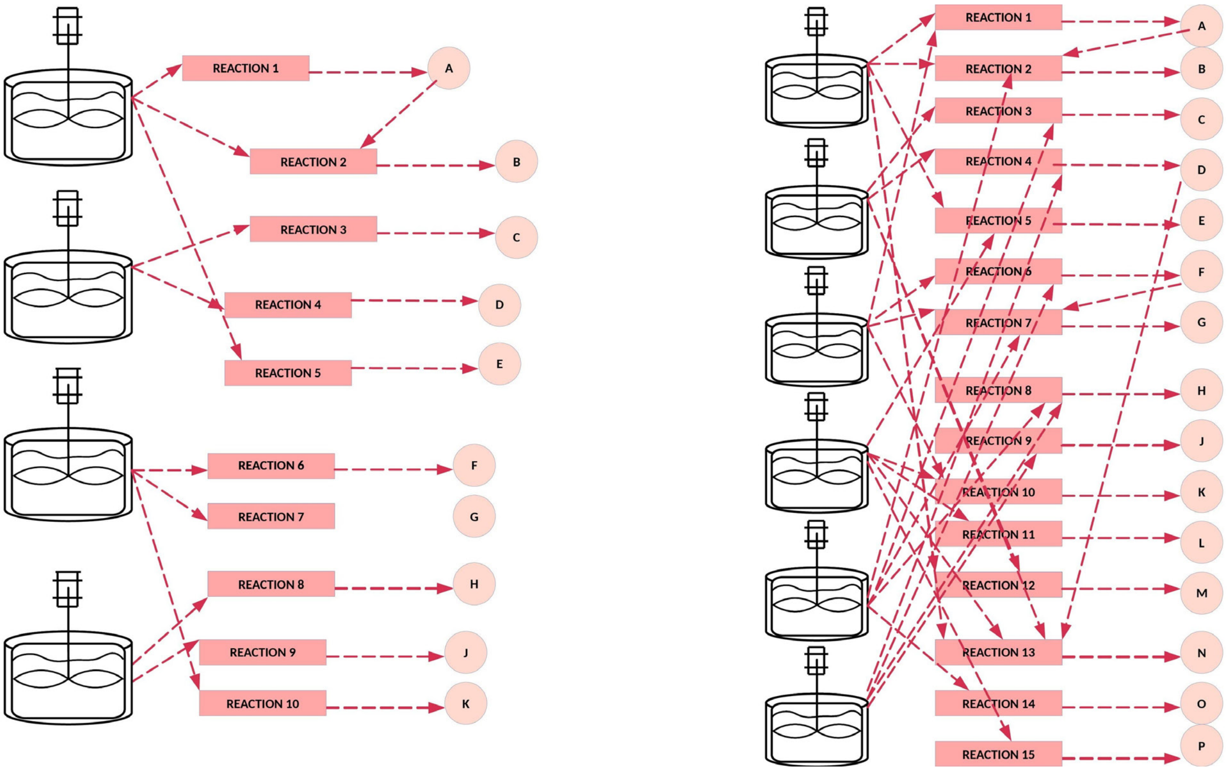

Figure 6. Parallel sequencing: (a) four reactors connected; (b) six reactors connected network

Fenila and Shastry,[56] were the first to study “enzymatic hydrolysis”, in particular, for a batch mode of operation, two optimal control problems with uniform/top/bottom/side initial fed distribution consequently brought different profit gains: 1) maximization of glucose, for a case of total time-limited to 24 h, bottom brought improvement by 11.58% against uniform; 2) maximization of profit, in same total time, bottom brought improvement by 38.51%/15.44% against top/uniform, respectively. A year after, the same authors,[57] offered stochastic and deterministic approaches to solve the problem of maximization of glucose for different cases, whereas deterministic and stochastic approaches are applied. Hereby, the optimal glucose concentration obtained for three different cases based on predefined temperature (case 1) and concentration profiles, the latter considered two cases where the final concentration augmented by 6.80/2.03 times compared to the initial case (case 2a/2b, resp.), achieved optimal concentrations: within 12 h, (case 1) gained 13.06%/13.35% against case 2a/2b respectively.

Woinaroschy,[58] for a specified reactional system(s), studied: 1) batch reactor: optimal evolution of reactor temperature follow the stepwise declining function till followed by final uprisal to 11.12% of initial value; concentrations of desired products simply consisted of linear periods; 2) semi-batch reactor constrained case: as for optimal feed rate evolution, the stepwise function shown initial drop half of the total time, notice to switch to jump in point of 5%/15%/25% of total time finished by a sequence alike to a "quasi bang-zero", whereas, 75% of maximum reached. Amin et al.,[59] tried to reconcile two conflicting objectives working on the following ("combined objectives") optimal control problems: 1) minimization of end-points of formaldehyde and butanol (desired products), 2) minimization of the endpoint of butanol concentration and final time, 3) maximization of the endpoint of formaldehyde and final time, 4) maximization of the endpoint of concentration of X-condensates and minimization of butanol. In the first-mentioned case, non-isothermal conditions brought gains over isothermal: at most 8.49% gain in formaldehyde reduction, For the second and third case, gives close final times, however, optimal endpoint butanol concentration is even 73.90%/69.45% reduced in the third case against the second/fourth, respectively. In their subsequent work, Amin et al.,[60] distinguished between the optimal evolutions for the number average molecular weight and weight average molecular weight, for low and high pH levels to summarize their optimal ratio: after the starting period of uprisal lasting for 38.89% of total time, but with a slope greater for low pH, the evolution follows the trajectory shifted up by ~around equally to the single/double initial point value, respectively. It is worth mentioning that, De et al.,[61] for a jacketed batch reactor, differed the optimal temperature evolutions whereas, inside the reactor/coal, resp., ending with a real bang sequence lasting for even 50%/75% of the total time. However, the optimal coolant flow rate shows that the best strategy is to switch down instantaneously at the very beginning, by 5.2%, but to continue the operation by releasing the valve "progressively" faster at the beginning and within 12.5%, finally to the maximum at almost half of the time. The latter, only confirmed that a real bang-zero-bang sequence could be implemented instead.

Bonvin[10] grounded the definitions for mathematical models, which will be followed in this paper. In a similar way, the classification of mathematical models for polymer processing, grounded by Dubé et al.,[62] will be followed. Last but not the least, the latterly invented models of compartmental mixing (Vivaldo-Lima et al.[63]), and the moments model (Nie et al.[64]), are added. But the list is not exhaustive, a reader can find more about the mathematical models in Broadhead et al.,[65] Aris,[66] Hamielec et al.,[67] Richards and Congalidis,[68] Tobita and Hamielec,[69] Zaldivar et al.,[70] Zaldivar et al.,[71] Hernandez et al.,[72] O'Donnell and Kaler,[73] Jung et al.,[74] Johnson et al.,[75] Varshouee et al.,[76] etc.

In Table 1, a summary is given of all studies done, according to the author's knowledge, on the subject of optimal control for stirred jacketed chemical reactors for both fine chemicals and polymers processing in discontinuous/semicontinuous mode. In particular, a shortlist of reactional systems studied in vessel batch chemical reactors is given in Table 2, whereas a shortlist of polymers produced in polymerization reactors, is in Table 3.

Table 1. A list of different studies on the optimal control for fixed-bed non-tubular batch/semi-batch chemical reactors

author(s)	year	Obj. function	Math. Method or solver	Math. model	Process	Mode	Periods
Aris	1961	Conc./Conv.	PM	Simple	general	batch	single
Szepé and Levenspiel	1968	Conv.	DP	Mechanistic	general	batch	single/double
Hicks et al.	1969	time/cost	PM	Correlation	polymerization	batch	double
Osakada and Fan	1970	ADP + M_{wd} P_n/DP	PM	Multigrain	polymerization	batch	single

Sacks et al.	1972	time	PM	Expansion	polymerization	batch	single
Crescitelli and Nicoletti	1973	yield	DMP	Multigrain	general	batch	three/six
Pommersheim and Chandra	1975	Conv./act.	DP	Mechanistic	general	batch	single
Farhadpour and Gibilaro	1975	yield	PM	Solid core	general	batch	double
Chen et al.	1980	time	PM	Multigrain	polymerization	batch	double
Chen et al.	1981	time	PM	Multigrain	polymerization	batch	double
Wagmare and Lim	1981	Prod.	PM	Solid core	general	batch/rec.	three
Tsoukas et al.	1982	CCD/M_{wd}	GA	Expansion	polymerization	both	single
Wu et al.	1982	time	PM	Multigrain	polymerization	batch	double
Biegler	1984	yield	PM/SQP/Socoll	Mechanistic	general	both	single
Chen et al.	1984	time	PM	Multigrain	polymerization	batch	double
Thomas and Kiparissides	1984	Conv. + M_{wd}	PM	Multigrain	polymerization	batch	single/double
Chen et al.	1985	time	PM	Multigrain	polymerization	batch	double
Louie and Soong	1985a	PD	PM	Polym. flow	polymerization	batch	double/three
Louie and Soong	1985b	PD	PM	Polym. flow	polymerization	batch	double/three
Farber and Laurence	1986	time	PM	Solid core	polymerization	batch	double
Filippi et al.	1986	Conc.	Gray Box	Tendency	general	semi	double
Chen et al.	1987	time	PM	Multigrain	polymerization	both	double
Ponnuswamy et al.	1987	Perf./PD	PM	Solid core	polymerization	batch	single
Butala et al.	1988	time	CONSOLE	Solid core	polymerization	semi	double
Jang and Yang	1989	time	Orth. Coll.	Polym. flow	polymerization	batch	single/double/three
O'Driscoll et al.	1989	time	PM	Polym. flow	polymerization	batch	double
O'Driscoll et al.	1990	time + initiator cost	PM	Polym. flow	polymerization	batch	double

Secchi et al.	1990	Conv. + MWD + M_n	PM/Grad. Meth.	Expansion	polymerization	semi	single/double/three
Jang and Lin	1991	time	Fin. El. Coll.	Polym Multilayer	polymerization	batch	sinle/double
Vaid and Gupta	1991	time	PM + Lagran. Multip.	Combined*	polymerization	batch	double
Butala et al.	1992	time	MOO	Expansion	polymerization	semi	double
Chang and Lai	1992	Conv. + PD + P_n	Fin. El. Coll.	Solid core	polymerization	batch	double
Levien	1992	yield	SQP	Solid core	general	both	double/ten
Maschio et al.	1992	time	PM	Two-step	polymerization	batch	three
Jang et al.	1993	time	Orth. Coll.	Solid core	polymerization	semi	three
Canu et al.	1994	time/rate	GIP	Solid core	polymerization	semi	double/three/four
Luus	1994	Perf.	IDP	Mechanistic	general	batch	double
Tieu et al.	1994	Perf.	OPTPAC	Polym core	polymerization	batch	single
Vassiliadis et al.	1994a	Frac./tot. yield	SQP	Tendency	polymerization	semi	double/five/ten
Vassiliadis et al.	1994b	yield	DAEOPT/SRQPD	Tendency	general	batch	double/five
Vssiliadis et al.	1994c	Product	DAEOPT	Tendency	general	batch	five/ten
Wajge and Gupta	1994	Conc./time	GA	Combined*	polymerization	batch	double/three
Garcia et al.	1995	Conc./yield.	PM	Tendency	general	both	double/five/ten
Bojkov and Luus	1996	Time	IDP	Mechanistic	general	batch	single/five/nine/ten/fifteen
Hinsberger et al.	1996	Dev. of reactor temp.	NPSOL + Multim. Shoot. Meth.	Tendency	Polymerization Chylla-Hasse	semi	five
Toulouse et al.	1996	time	SQP	Mechanistic	general	both	four/three
Hirmajer and Fikar	1996	yield	LSODAR/NLPQR	Rigorous	general	batch	six/ten/twenty
Crowley and Choi	1997	WCLD	Fin. El. Coll.	Polym flow	polymerization	batch	three
Ahn et al.	1998	Conv. + M_{wd} + M_n	PM	Expansion	polymerization	batch	three
Bonnard and Launay	1998	time	PM	Rigorous	general	batch	single

Oliveira et al.	1998	Conv. + M_n + PD	PM	Polym core	polymerization	semi	four
Garg and Gupta	1999	time	GA/NSGA	Combineed*	polymerization	both	three
Luus and Okongwu	1999	yield	IDP	Tendency	general	batch	multiple
Shin et al.	1999	time/side pr.	SQP	Tendency	polymerization	semi	double/three
Abel et al.	2000	time	DYNOPT	Tendency	polymerization	semi	three
Aziz et al.	2001	Conv./time/profit	CVP/SQP	Two-step	general	batch	four
Grau et al.	2001	time	GA	Two-step	general	semi	1. three 2. single
Merquior et al.	2001	MWD + M_n, Conc.	MOO	Combined*	polymerization	batch	single
Pinto and Giudici	2001	time	NLP	Polym flow	polymerization	batch	single
Tian et al.	2001	Conv. + PD + time	HSRNN	NN	polymerization	batch	three
Weitao et al.	2001	time	SQP	Tendency	polycondensation	batch	three
Nougés et al.	2002	time	GA	Two-step	general	semi	three
Zeaiter et al.	2002	yield	gPROMS	Expansion	polymerization	semi	
Aziz et al.	2003	yield	NN-IMBC	Two-step	general	batch	1. single 2. three
Silva and Biscaia	2003	Conv./conc.	GA	Multigrain	polymerization	batch	multiple
Joly and Pinto	2004	Prod.	GA/CONOPT	Russell et al.*	polymerization	batch	single
Rani and Patwardhan	2004	Conv.	ANN	Black-box	polymerization	semibatch	single/multiple
Nayak and Gupta	2004	Conv. + PD/ Conv. + PD + mol. r.	GA	Combined**	polymerization	semi	multiple
Salhi et al.	2004	time	CVP	Polym. flow	polymerization	batch	Seven and more
Zhang	2004	Conv. + M_{wd} + M_n	BANN	NN	polymerization	batch	three
Zhang and Smith	2004	Perf.	SA	Comp.-Mix.	general	both	Multiple [5-40]
Rantow et al.	2005	Conv.		Mechanistic	polymerization	semibatch	single
Kachap and Guria	2005	impurity + pol. comp.	GA	Multigrain	polymerization	batch	multiple

Sundaram and Upreti et al.	2005	Conv./time	GA	Multigrain	polymerization	batch	five
Upreti et al.	2005	Conv./time/ conv. + M_n/ conv. + M_w	GA	Multigrain	polymerization	batch	single/four/five
Xiong and Zhang	2005	quality	Recur. NN	NN-model	polymerization	batch	ten
Zavala et al.	2005	M_{wd}	SDO/AMPL	Polymflow	polymerization	both	three
Hirmajer and Fikar	2006	Conv.	CVP/LSODAR/ NLPQL	Rigorous	general	batch	double/five/ten/twenty
Apostolos et al.	2006	Conv.	OCFE/FP	Multigrain	polymerization	batch	double
Sun et al.	2007	1.yield 2.time	CVP/SA	Rigorous	general	batch	1. ten/twenty/thirty 2. single/three/five/eight/ ten
Lemoine-Naval et al.	2006	Conv. + PD + V	DP	Polymflow	polymerization	semi	multiple
Sun et al.	2007	time + yield	GA	Rigorous	general	batch	three/five/ten
Rapaport et al.	2007	time	PM	Mechanistic	general	batch	single
Varga et al.	2007	purity + conv.	SQP/ES	Stat. Corr.	general	semi	three
Mukherjee and Zhang	2008	Conc. + V	BANN	NN-model	general	semi	ten
Simon et al.	2008	Conc./P	CVP	Expansion	general	batch	double/three/twelve/ twenty
Zhang	2008	yield	NN	NN-model	polymerization	batch	double
Chen et al.	2009	Conv. + M_{wd} + M_n	DP	Expansion	polymerization	batch	double/three/four
Herrera and Zhang	2009	yield	PSO-SNN	NN-model	general	semi	single
Okorafo et al.	2009	time + Comp. + M_{wd}	DYNOPT	Tendency	polymerization	semi	double
Sadi et al.	2009	Conc. + M_{wd}	GA	Polym core	polymerization	batch	multiple
Benyahia et al.	2010	T + rate	GA/EA/MAUT	Solid core	polymerization	both	four
Ivanov et al.	2010	heat	MINLP	Simple	general	batch	single/double/
Perea et al.	2010	M_{wd} + Comp.	NLP	Expansion	polymerization	semi	single
Camargo et al.	2011	M_{wd} + w_{ams}	MOO, GA	Probabilistic	polymerization	batch	multiple
Ibrahim et al.	2011	M_n	gPROMS	Two-step	polymerization	both	three
Wang et al.	2011	Conc.	SAH-NN	NN-model	general	batch	single/five/ten/ twenty

Anand et al.	2012	Comp. dev. + M_{wd}	DE-DO	Multigrain	polymerization	semi	single
Benavides and Diwekar	2012	Conc.	SMP	Two-step	biodiesel	batch	single
Logist et al.	2012	all	ACADO	Rigorous	general	batch	multiple
Drag and Styczen	2013	Conc.	SQP/multiple-shooting	Rigorous	general	batch	eleven
Maidi and Corriou	2013	yield/conc.	PM	Mechanistic	general	batch	single
Paulen et al.	2013	yield/conv.	CVP	Solid core	polymerization	semi	
Nie et al.	2014	time	GAMS	Polym flow	polymerization	both	double/three
Palacios et al.	2014	Conv. + en.cons.	EA/MACBETH	Polym core	polymerization	batch	double
Tijam and Gomes	2014	Conv./M_{wd}	DASOLV/SRQPD	Solid core	polymerization	both	multiple
Patel and Padhiyar	2015	time	Box-complex assited GA	Black box	general	batch	single
Mahajan et al.	2015	Av. Cop. Comp. + M_{wd}	MOO/GA	Combined*	polymerization	batch	single
Herrera et al.	2019	time	CVP	Polym multilayer	polymerization	semi	
Bakir et al.	2019	time	PM/GOO	Mechanistic	general	batch	single
Bousbia-Salah et al.	2019	time	SQP/D-RTO	Two-step	polymerization	batch	five
Fenila and Shastry	2019	profit + quality	SQP/fmincon/MATLAB	Two-step	hydrolysis	both	single
Kong and Chen	2019	time/conv.	DASPK/SNOPT	Expansion	polymerization	batch	double
Woinaroschy	2019	M_n	GA	Set-membership	general	both	multiple
Amin et al.	2020a	yields/yields + time	GA	Two-step	synthesis	batch	1. double 2. multiple
Amin et al.	2020b	Undesired yields	GA	Two-step	synthesis	both	1. batch: 3 2. semi-batch: 4
De Riju et al.	2020	Conc.	SQP/fmincon/MATLAB	Two-step	transesterification	batch	three
Fenila and Shastry	2020	yield/profit	SQP/fmincon/MATLAB	Two-step	hydrolysis	both	single
Bangi and Kwon	2020	Leak off rate	Deep NN, finite difference method	Grey box	polymerization	batch	single
Nasresfahani et al.	2021	time	Kin. Monte Carlo + Patt. Sear./Part. Sw.	Two-step	polymerization	semi	three

*Russell et al. (1998): invented their own model, by modeling each phase separately, whereas, vaporization mass transfer and energy balances included

**Combined: a mathematical model combined from polymeric flow model and multigrain model

Table 2. Shortlist of reactional systems studied and achievements in vessel batch chemical reactors for the aforementioned optimal control strategies

Author(s) (year)	Reactional scheme
Szépe and Levenspiel (1968)	$A \rightarrow B$
Crescitelli and Nicoletti (1973)	$R \rightarrow P \rightarrow Q$
Farhadpour and Gibilaro (1975)	Complex theoretical
Wagmare and Lim (1981)	$A \rightarrow B$
Biegler (1984)	$A \rightarrow B$ $A \rightarrow C$
Filippi et al. (1986)	$A + 2G_1 \rightarrow X + 2G_2$ $X \rightarrow A_5 + 2G_2$ $A_1 + A_5 + 2G_1 \rightarrow 2X + 2G_2$ $A_1 + 2G_1 \rightarrow X + 2G_2$ $X \leftrightarrow A_5 + 2G_2$
Luus (1994)	$A \rightarrow B \rightarrow C$ $A \leftrightarrow B$
Garcia et al. (1995)	$A + B \rightarrow R$ $R + B \rightarrow S$ $A + B \rightarrow C$ $2B \rightarrow D$
Toulouse et al. (1996)	$2B \rightarrow C + D$ $A + B + C \rightarrow E + D$
Luus and Okongwu (1999), Bojkov and Luus (1996)	$A \rightarrow B \rightarrow C$ $A + B \rightarrow X$ $A + B \rightarrow P$ $X \rightarrow Y$ $X \rightarrow Q$ $Y \rightarrow Z$
Aziz et al. (2003), Wang et al. (2011)	$A + B \rightarrow C$ $A + C \rightarrow D$
Aziz et al. (2001)	$2A \rightarrow B \rightarrow C$ $B \rightarrow D$ $B \rightarrow E$ $2B \rightarrow F$
Grau et al. (2001), Nougués et al. (2002)	$Na_2S_2O_3 + 2H_2O_2$
Zhang and Smith (2004)	$A + B \rightarrow R$ $R + B \rightarrow S$ $A + B \rightarrow C$ $2B + D \rightarrow E$
Varga et al. (2007)	$A + B \rightarrow 2P + B$ $P + B \rightarrow \mathrm{X}$

Mukharjee and Zhang (2008), Herrera and Zhang (2019)	$A + B \rightarrow C$ $B + B \rightarrow D$
Simon et al. (2008)	$A_S \leftrightarrow A_I$ $A_I + B \leftrightarrow C + D$ $B + C \leftrightarrow E + D$ $B + E \leftrightarrow F + D$ $B + F \leftrightarrow P + D$
Fenila and Shastry (2019)	Enzymatic hydrolysis of lignocelulose
Fenila and Shastry (2020)	Enzymatic hydrolysis of lignocelulose
Bakir et al. (2019)	$A \leftrightarrow B \rightarrow C$
Woinaroschy (2019)	$2A \rightarrow B \rightarrow C$ $A + B \rightarrow C$ $B + B \rightarrow D$ $A + B \rightarrow C \rightarrow D$
Amin et al. (2020a, b)	Butylation reactions
De Riju et al. (2020)	Transesterification reactions

*Conc. and Conv. correspond the yielded product of interest

Table 3. Shortlist of reactional products synthesized in polymerization batch reactors for the aforementioned optimal control strategies

Author(s) (year)	Reaction type/Product
Hicks et al. (1969)	Theoretical Polycondensation Theoretical Free-radical polymerizattion
Osakada and Fan (1970) Jang and Lin (1991) Sadi et al. (2008) Herrera et al. (2019)	Poly(Vinyl acetate) (α-α ‘azobisisobutyronitrile (AZN))
Sacks et al. (1972) Chen et al. (1980) Chen et al. (1981) Wu et al. (1982) Farber and Laurence (1986) Tieu et al. (1994) Merquior et al. (2001)	Styrene polymerization (*no other compunds reported)
Tsoukas et al. (1982) Nayak and Gupta (2004) Mahajan et al. (2015)	Styrene-Acrylonitrile (*no other compounds reported)
Chen and Hsu (1984)	Styrene polymerization St/AIBN/Toluene/Lauril-Mercaptan
Thomas and Kiparissides (1984)	Poly(Methyl methacrylate) (PMMA)
Chen et al. (1985)	Styrene-acrylonitrile (in toluene with initiator BPO (benzoyl-peroxide))

Sacks et al. (1972) Louie and Soong (1985a) Louie and Soong (1985b) Ponnuswamy et al. (1987) O'Driscoll et al. (1989) O'Driscoll et al. (1990) Secchi et al. (1990) Chang and Lai (1992) Maschio et al. (1992) Tieu et al. (1994) Crowley and Choi (1997) Ahn et al. (1998) Garg and Gupta (1999) Zhang (2004) Sundaram and Upreti (2005) Upreti et al. (2005) Apostolos et al. (2006) Zhang (2008) Kong and Chen (2019)	PMMA (Poly(Methyl Methacrylate))
Chen et al. (1987)	Styrene (co)Polymerization
Butala et al. (1988)	Styrene-acrylonitrile (xylene/AIBN)
Jang and Yang (1988)	Styrene polymerization in toluene Styrene polymerization in toluene with AIBN Styrene polymerization in toluene with lauryl-mercaptan
Vaid and Gupta (1991) Anand et al. (2012)	Styrene-acrylonitrile (AIBN)
Butala et al. (1992)	Polymerization of styrene (in BPO and terc-butyl-perbenzoate (TBPA))
Jang et al. (1993)	Polyacrylamide
Canu et al. (1994)	Styrene/MA MMA-ethyl acrilate MA-vinyl acetate
Wajge and Gupta (1994)	Nylon-6 (polycondensation)
Hinsberger et al. (1996)	Specialty emulsion polymers
Oliveira et al. (1998)	Styrene polymerization (in toluene)
Shin et al. (1999) Weitao et al. (2001)	PET (polyethylene terephtalate)
Abel et al. (2000)	Theoretical polymerization
Pinto and Giudici (2001)	PVC (Poly(vinyl chloride))
Zeaiter et al. (2002)	Emulsion polymerization
Salhi et al. (2004) Chen et al. (2009) Camargo et al. (2011)	Styrene with α-methylstyrene
Kachap and Guria (2005)	Copoly(ethylene-polyethylene terephtalate)
Zavala et al. (2005)	Polyurethane
Lemoine-Naval et al. (2006)	Styrene polymerization (nitroxides)
Ekpo and Mujtaba (2007)	
Okorafo et al. (2008)	Styrene with butyl methacrylate

Benyahia et al. (2010)	Styrene with butyl acrylate (n-C12 mercaptan)
Perea et al. (2010)	
Ibrahim et al. (2011)	Styrene with MMA
Paulen et al. (2013)	Styrene with butyl acrylate (n-C12 mercaptan)
Nie et al. (2014)	Block copolymers
Palacios et al. (2014)	Phtalate-free PVC
Bousbia-Salah et al. (2019)	Styrene with Ground Tire Rubber Particles
Nasresfahani et al. (2021)	Butyl methacrylate with 2-hydroxymethyl methacrylate

2.3 *Optimal control strategies for polymers processing in discontinuous and semi-continuous mode*

In Table 1, a list of studies in optimal control for polymerization reactors is given as well, and scheme in Figure 7. Hicks et al.,[7] brought a study of a polycondensation reactor under two different controls, whereas 1) Optimal temperature evolution - the “suboptimal policy” allows the control/the number average chain length to reach its maximum before 20%/25%, resp., of total time in the initial period, to finally switch to a real bang at 5%/60% of the theoretic maximums, for the rest of more than 60% of the total time, respectively. Whereas “quasi-bang-bang” policy, allowed the control to reach 75% of the attainable maximum, but on a time interval reduced by 20% compared to the previous policy; 2) Optimal flowrate evolution - again, “suboptimal policy” proposes a “quasi bang-bang-zero” scenario since allows a maximum for the control/the number average chain length after less than 5% of total time, leading to the constant policy after 10%/40% of the time, resp. It is mentioned that the authors defined a “steady-state policy” for starting-up free radical reactor under temperature control: polydispersity index drops to its final and/or minimal value followed by constant policy only after 70% of total time, i.e. 10-30% longer than other two policies. Osakada and Fan,[77] proposed the optimal control trajectories for the, 1) molecular weight distribution: double control policy, where both temperature and catalyst feed controlled, outperformed the single control one with more than a hundred thousand times, 2) instantaneous average degree of polymerization: temperature outperformed catalyst feed by even few thousand times. Sacks et al.,[78] discovered the optimal final time/dispersion index increase by almost 2.4%/17.4%, resp., if “the gel effect” is taken into the consideration for variable temperature policy. Therefore, the authors recognized the temperature policy as the most optimal one only if simultaneously achieves reaction time and molecular weight distribution.

Chen and Jeng,[79] started their study for bulk polymerization optimal temperature policies for the thermally-initiated process of styrene production constraining the problem for predetermined initial/final average molecular weight and monomer conversion: the evolution was “truncated S-shape functions”. Whereas with the increase of the final average molecular weight and optimal total time (Table 4), the initial temperature is to be shifted down by 60 °C.

Chen and Lin[80] disclosed different factors influence minimum-time policies for the two-stage process: 1) a decrease in predetermined monomer conversion at the end of the first stage caused the total time for each stage to decrease, 2) a steep decrease in the predetermined number average chain length, caused the second stage will make it up by producing larger molecular weight polymers which will result in a lower temperature, further, lower conversion, and finally larger the total time for the second stage. In Table 4, the influence of the temperature of initialization on the optimal outcome of decision variables and objective (ie. final time), is tabulated.

Chen and Huang,[81] among the policies proposed in Table 4, the outcomes of the simultaneous optimal control of initiator addition with temperature, for constrained/unconstrained, for a change in predetermined monomer conversion at the end of the first stage, are tabulated. Moreover, the additional change in the rate of initiation is observed as (16.79%/14.19%), resp. by Chen and Hsu,[82] the same effect could be perceived as by authors,[81] in Table 4, the data is tabulated for the infinite/finite ratio of monomer and solvent. By analogy, the data for the “best” optimal control of isothermal initial initiator concentration/addition, resp., (IICP/IOIAP), and are tabulated as well (Table 4) for Chen and

Hsu[82] Chen and Lee,[83] succeeded to combine again two optimal policies: optimal initiator addition isothermal policy and constant copolymer composition policy, for predetermined weight average chain length/conversion, the achievements are presented in Table 4, with the distinction made for different polymers fed.

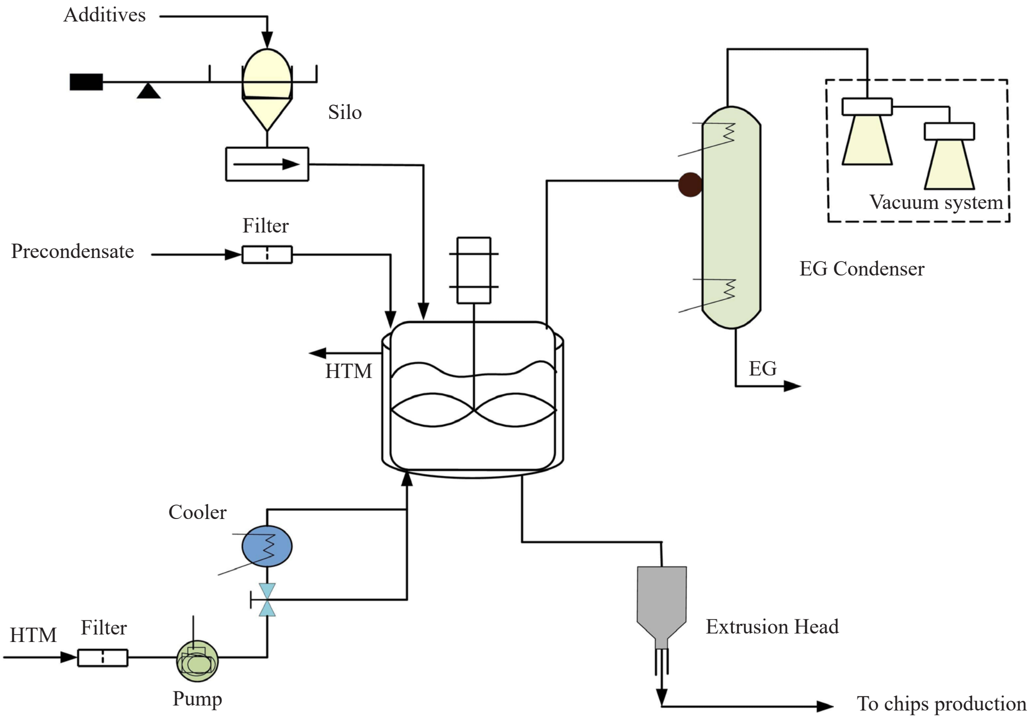

Figure 7. A general scheme for polymers processing in the chemical reactor in a batch or semi-batch mode

Hsu and Chen,[84] likewise, proposed two optimal policies based on the type of polymerization, whereas variated initiators charged within an interval [1.487-0.466]: 1) Bulk polymerization policy under the best isothermal temperature (Chen and Jeng,[79] Chen and Huang,[81] for predetermined chain length and monomer conversion, 2) Solution polymerization under the best isothermal temperature,[81] whereas for the later the data are tabulated (Table 4) with regard to the presence of the chain transfer agent,

Tsoukas et al.,[85] provided studies for 1) temperature control, as to maximize the composition, and/or minimize molecular drift; 2) monomer addition control - as to minimize molecular weight drift and/or copolymer composition, whereas, the optimal increase is in the variables of decision, are detailed in Table 4, final copolymer composition/total number average molecular weight/polydispersity index.

Wu et al.,[86] envisaged the optimal reaction time-temperature policies: difference in temperature of initialization, 150/160 °C, resp., comprised from two distinctive parts, ie. starting linear and "truncated S-shape function". The starting period duration is taken, 27.78%/21.42%, resp., from the total batch time, whereas, the optimal total batch time is reduced by ~35.72%, for the higher initialization temperature case.

Thomas and Kiparissides[87] discussed "near-optimal" temperature policies for single control: 1) Variation of weight average molecular weight - period of temperature constancy tends to reduce, by even almost 10%, with the increase of polydispersity index by 52.28%. Rate of polymerization, however, by 57.14%; 2) Varying number average molecular weight - period of temperature constancy tends to reduce by 63.63% with the increase of polydispersity index by 33.59%. Otherwise, the double-control policy (controlled both temperature and feed flow) gave clear differences in their two-period trajectories: initiator concentration constancy period time is 3.44% longer while its maximum improved by 60%, in favor of the double-control policy.

Table 4. A list of the works done by Chen and co-workers

Authors	Year		Monomer conversion	Average molecular weight (number/weight)	Initiator concentration	Optimal total time
Chen and Jeng	1978		-	5.5 times	-	4 times
Chen and Lin	1980		1.5 times	4 times	6.02 times	3.38 times
Chen and Huang	1981		28.58%	-	-	(40.16%/38.08%)*
Chen and Hsu	1984		57.15%	-	-	(68.29%/78.63)**
Chen and Lee	1985		IICP	5 times	-80.42%	85.42%
			IOIAP	2.26%	-	57.03%
Chen and Lee	1987	St	-22.23%	-40%	-	-25.11%
		AN	-22.23%	-40%	-	-20.10%
Hsu and Chen	1988		1. bulk		68.67%	21.49%
			2. solution polymer	without	52.95%	53.45%
				with chain transfer agent	48.20%.	47.31%

- decrease; * (unconstrained/constrained) operation; ** (infinite/specified) ratio of monomer and solvent

Louie and Song[88,89] compared different policies, conversion vs. time: 1) optimum isothermal photoinitiation, 2) isothermal bulk, 3) constant reaction rate, 4) constant number average molecular weight, and distribution policies. The last proposed policy, ie. "optimal isothermal solvent addition", is shown to be influenced by: 1) initiator loading: varied within an interval [0.05160-0.00645], a "quasi bang sequence" durations elongates as 42.85%/57.14%/78.57%/100% of the total time, respectively; 2) temperature set: ie. with the greatest applied temperature a real "zero-bang" sequence exists, lasting less than 1h, whereas, a "quasi-bang sequence" still appeared, however, ending shifted to the left due to the reason that more time needed than otherwise would have been the case. ie. for an increase of 45%, it is shifted by ~7 times.

Same as previously, heat transfer coefficients affect the "optimal non-isothermal solvent addition policy": varied in an interval [10-60 (kJ/kmol)], whereas, if the heat transfer coefficient doubled, then switching to a real "bang sequence" shifted to the left for at least one-seventh of the total time. More about the influence of "the gel effects" on optimum evolutions (optimum isothermal solvent addition policy/bulk polymerization) a reader can find in Louie and Soong[88] were who detailed the comparison with the other authors (Friis and Hamielec,[90] Cardenas and O'Driscoll,[91] etc).

Farber and Laurence,[92] defined a minimum time to reach conversion, for pure monomer reaction and a target of 85%, to propose the optimal temperature trajectories vs time, for initial temperature interval: a modified truncated S-function(s) ended with a real "bang" sequence, depending on the temperature interval switching point occurred and at a final time are tabulated (Table 5).

Table 5. The temperature interval vs. switching points for the optimal temperature trajectories work by Farber and Laurence, 1986

Temperature interval, [K]	Switching point
360-380	70%/42.5%/25%/15%
380-400	10%/7.5%/5%/2.5%

However, the optimal evolution of temperature via conversion, shows again a modified S-function ended with a real "bang sequence", whereas his period depends strongly on the number of interactions, i.e. If iterations increase only by ~12%, time savings are almost 40%. Ponnyswamy et al.,[93] proposed a minimum polydispersity temperature policy, where depending on the total number of average molecular weight chosen as 40/50, conversion reaches its maximum around 48-49%/45%, respectively, within a total time 2.34 times greater for the latter case (Table 6).

Butala et al.,[94] proposed optimal control policies for both: 1) batch - optimal evolution of conversion for non-isothermal reaction with fixed final time: is "demi-U" shape function, with a tendency to be shifted left for increase (reaching max at 100%/76%, resp., for batch/semi-bach, resp.). Butala et al.,[95] continued their study, using hereby the mixed initiators in three specific cases: 1) predetermined initiator concentration and composition, optimal evolution for conversion showing a "quasi-bang" sequence only after 90% of the time passed, having a tendency to be shifted left if the temperature increased, 2) predetermined initiator concentration only: the optimal evolution for conversion shown, here, the ending period is shortened to 75% of the final time, 3) optimally chosen initial initiator concentration, composition, and, also residual initiator concentration, whereas the optimal conversion evolution is shortened to 45% of the total time.

O'Driscoll et al.,[96] noted the effect of the heat of polymerization to be as, i.e. if varied [64-54 (kJ/mol)], 1) isothermal policy: a successive increase in temperature set (by 20 °C), resulted in even 3/6 times, resp., increase in the total time; 2) non-isothermal policy: for an increase in energy of activation by 30 [kJ/h], almost doubled both, the duration of the process and final monomer conversion. O'Driscoll et al.[97,98] proposed "optimal isothermal and initial initiator policies": for fixed final conversion 90% but number average molecular weight not controlled, the effect of initiator cost on optimal temperature and initial initiator concentration policies found on an initiator cost and concentration interval predefined, the outcomes of the optimal control strategy applied is tabulated in Table 6.

Jang and Yang,[99] worked on the "minimum end-time initiator addition policy", in particular, the "one-charged policy" showed that if reactor temperature increased successively (by 10 °C), the maximum reached approx. doubled each time for reaction rate, all within less than 10% of the total time, respectively. Furthermore, the authors discussed the effect of constraints imposed: for an increase in the value of constraint by 50%, the reaction rate maximum is empowered by almost six times and achieved later. Secchi et al.,[100] noted for the last strategy applied ie. both temperature and initial initiator concentration controlled and constrained, the optimal evolution for initiator feed: "an irregular function" since starting with the "quasi-bang" sequence whereas switching to a "quasi-bang-zero" sequence occurs only after the middle of the total batch time.

Jang and Lin[101] presented optimal control strategies for different schemes, ie. continuous/discontinuous/discontinuous plus temperature scheme, resp.: 1) desired (max.) conversion - reached it within 92.8%/88.6%/78.6% of the time, respectively, 2) for a successive increase in monomer composition, it is perceived for maximums to drift by at least 9%/20%, resp. within time, for optimal reactive rate/conversion policy, resp. Chang and Lai[102] recognized three types of optimal control strategies issued from the "accurate tracking function" of rate constants and moment of the concentration of polymer radicals. But, it is to note that, it is only for the bulk polymerization policy based on the tracking type function obtained for the greatest initiator concentration predetermined, that the optimal temperature evolution starting with a real "bang-zero" sequence lasting for approx. 27% of the batch time, end ending with the "quasi-bang" sequence of extremely short duration (1/100).

Maschio et al.,[103] used monomer initiator ratio to examine the evolutions for optimal: 1) conversions vs time for specified monomer to initiator ratios, gave desired maximums of 90%, whereas, perceived that if the ratio doubled it is at the expense of time (~28.6%). For the same index fixed, parametric sensitivity test with temperature, showing the most rapid achievement of maximum, perceived at the lowest temperature applied (within less than 20% of the time).

Jang et al.,[104] three periods trajectory proposed for optimal monomer/initiator concentration, after the constraints imposed on both, number- and weight-average molecular weight, showed a "quasi bang-zero-bang-zero" sequence. It is to note, however, that the pre-dominant is a quasi-zero sequence taking over more than 90% of the period whereas a quasi-zero maximum reaches not more than 30% of the theoretic value. Canu et al.,[105] the optimal policies were the monomer feed flowrate evolutions vs dependence on the overall amount of polymer produced depending on solubility parameter: whereas a real "bang-zero sequence"/"zero-bang sequence", resp., with a switching after the only a fifth of the time, observed for monomer A/B, resp., for the difference in solubilities of thousand(s) times and/or weight fraction of respected monomer lower than 50%.

Table 6. Results from the most significant works

Tsoukas et al. (1982)

Temperature control	Copolymer composition	Total number average molecular weight	Polydispersity index
Composition maximization	29.10%	43.75%	21.06%
Molecular weight drift minimization	19.61%	-	9.52%

Monomer addition control	Instantaneous average molecular weight	Polydispersion index
Molecular weight drift minimization	24.38%	4.79%
Copolymer composition minimization	3.34%	7.70%

Ponnyswamy et al. (1987)

	Total number average molecular weight	Conversion	Total time
Minimum polidispersity temperature policy	40	48-49%	x
	50	45%	2.34x

O’Driscoll et al. (1990)

Optimal policy	Initiator cost	Initial initiator concentration	Temperature	Total time
Optimal isothermal and initial initiator policies	10^{-6} times	-15.92 times	7.84%	13.29%
Optimal initial initiator and time policy	10^{-6} times	-1.72 times	12.65%	63.21%

Xiong and Zhang (2005)

Model		Number average molecular weight	Performance index
Recurrent network model	With reactive impurities	0.07 (7%)	0.22 (22%)
	Without reactive impurities	0.31 (31%)	0.23 (23%)

Sadi et al. (2009)

Initial concentration of monomer/volume of solvent (ratio)	Optimal initiator residue
25.38%	66.67%
Initial concetration of monomer	Conversion
2.67 times	20%

Ibrahim et al. (2011)

	Initial initiator concentration	Optimal molecular weight	Conversion
Maximization of number average molecular weight	-42.6%	25.8%	-1.28%

Tieu et al.,[106] proposed, 1) time minimization by isothermal policy: highest possible conversion against lowest (ie. 99% vs 90%), for fixed number average molecular weight (of 10^{-4}), achieved with initial initiator concentration/temperature/polydispersity index increase by 21.82%/6.17%/45.57%, respectively; 2) performance index, including number average chain length, minimization by isothermal policy: only lowest possible conversion achieved but initial initiator concentration is by 90.88% lower compared to the same case of previous policy. Wajge et al.,[107] researched the caprolactam and cyclic dimer optimal concentrations: with the increase of 5.56% of the specified number average chain length, the summary of concentration drops by 14.18%. Hinsberger[108] performed the Numerically stable method for quadratic programming (uses a sequential quadratic programming algorithm method introduced by [4]), to show the optimal mass of monomer/polymer, resp., evolution for products A/B, resp., achieved maximum within less than (9.5%/9%)/(52%/73%), resp, of the total time, whereas the latter one ended up with a "quasi bang sequence". For the (optimal) average jacket temperature-time evolution for product A, a "real zero-bang sequence" was observed 52.5% of the time. Crowley and Choi,[109] an optimal control trajectory issued from methods applied Weight Length Chain Distribution (WCLD), respectively, the optimal temperature policy showed a "quasi bang-zero sequence", since temperature falls down to the minimum allowed, and switched after 5% of total time.

Oliveira et al.[110] examined two cases where exist four periods to distinguish for differently defined objectives and operating conditions: 1) without a main transfer agent - an increase in batch time does not affect much the existence of the ending real bang period as lasting at most one-sixth period. But, it is mostly affected by both the predetermined number average molecular weight distribution and initial initiator concentration, since their simultaneous decrease/increase, resp., by a half, provokes its elongation to almost 35% of total time. 2) with the main transfer agent - the ending real bang sequence appeared only in the case if the transfer agent was used and predefined molecular weight increased by 6.4%, elongated to the extent of even 20% of the batch time.

Ahn et al.,[111] having variated number average weight and weight distribution together, the optimal temperatures evolutions for if the difference between number average weight and weight distribution is greater than 10^5, it seemed that after 50% of total time consecutive periods of increase/decrease start to switch.

Garg and Gupta,[112] first compared two genetic algorithms: sorted and non-sorted, establishing firstly the optimal evolution for the temperature. Secondly, the authors proposed the optimal evolution for monomer conversion, number average chain length, and polydispersity index, all based on the previous optimal evolution of temperature. In particular, for polydispersity index optimal evolution, a "quasi zero-bang" sequence is perceived at the total batch time, whereas, switching occurred after 83.34%/88.89% of the time, esp. for the NSGA/SGA algorithm.

Abel et al.,[113] with respect to the minimum adiabatic end temperature of the conventional operation, defined the maximum temperature allowed, in order to work on the isothermal and non-isothermal operation. For isothermal operation: the decision variable is chosen as feed rate, with both initial feed rate and variation coefficient decrease, total time increase significantly ie. even 20.67% if feed rate/variation coefficient is reduced by 21%/9.48% respectively, cases for $\beta = 0.94$ and 0.85. For the non-isothermal operation, however, the duration of the optimal feed flow rate, evolution decreased by almost 23.6% for the cases mentioned previously. Moreover, the piecewise constant temperature profile showed an initial period of longer duration at least 76% for coefficients tested less than infinity. Merquior et al.,[114] for a particular case examined, made the close relationship between the optimal values for the conversion rate and the number average molecular weight: the optimal isothermal policy brought the number average molecular weight/conversion, resp., augmentation/decrease, resp., by only 6.57%/4%, respectively.

Pinto et al.[115] examined the influence of different initiator concentrations on the rate of conversion/heat flow, respectively: 1) if the total initial initiator concentration is risen by more than 30 times, scaled between 2-5 × 10^{-3}, the heat flow variation shows a stable function, as able to keep on maximum for longer and longer periods, with the increase of later. Moreover, the authors proposed, mixing different concentrations; which outcomes in the optimal conversion rate as a linearly increasing function for most of the total time. However, the optimal differential rate of heat flow, only, recognized a quasi-bang sequence, taking most out of the process. Tian et al.,[116] first, searched for optimal temperature evolution, comparing two models: 1) hybrid stack neural network, 2) full mechanistic, whereas the strategy obtained by the first-mentioned model ended with "quasi bang sequence" (ie. ~99% of the attainable maximum achieved). Consequently, the optimal policy resulted from the hybrid best single network model, as it achieved +42.86% more. It is noted these policies differed in their objectives by 7.17%. Weitao et al.,[117] studied the polycondensation process: 1) optimal temperature profiles - shown three characteristic periods, ie. ended with the maximal temperature maintained at the longest period of constancy ie. 56.25% of total time. Acid end group concentration/amount of products optimally showed a rapid steep decrease within almost one-quarter of the total time, the second period of very flattened decrease till the end of the third quarter, finally to end up the period of constancy. Vaid and Gupta,[118] in their parametric sensitivity study on the optimal temperature policy for fixed initial initiator concentrations, revealed a "quasi-zero-bang' sequence for number average chain length and/or monomer conversion.

Nougués et al.,[119] performed genetic algorithm programming, to conclude: the optimal temperature, a real bang sequence characterized by the intermediate period, prevailing over almost half of the total time. Zeaiter et al.,[120] first compared theoretical predictions with experimental observations to conclude the choice of control variable: 1) monomer feed rate: in the case of control for particle size distribution; 2) reaction temperature: to control the molecular weight distribution. Furthermore, the authors performed the optimal control of product size distribution to show for monomer feed optimal trajectory to start with "quasi zero-bang sequence" lasting for more than 22% of the total time.

Silva and Biscaia,[121] ended up with conclusions: if initiator residue/initiator feed concentration is augmented by 1.89×10^{-3}/1.4 times, resp., conversion is risen by 14.8%, and, polydispersity index/molecular weight decreased by 6.89%/14.69%, respectively. Furthermore, authors varied genetic algorithm operators to conclude about their influence on the objective: 1) main operators: for the initiator residue concentration and conversion deviation, least influence if altogether operators used; 2) associated operators: elitism proven to be the best. Nayak and Gupta,[122] Kachap and Guria,[123] and Camargo et al.,[124] applied the Multiobjective Optimization (MOO) method, incorporated within particular (un)sorting genetic algorithms, that will not be discussed thoroughly, however, details can be found in Table 1.

Joly and Pinto,[125] applied both classes of direct methods: control parametrization and collocation strategy, whereas the first-mentioned approach brought somewhat better achievement in the objective at the expense of the desired quality of ammonia (NH_3), whereas the initial guess technique incorporated allowed for further degradation in objective and specifications altogether.

Rantow et al.[126] allowing for the maximum allowable change in reactor temperature over two consecutive periods, the authors reported four optimal feed policies with corresponding profiles in temperature: varying the charge composition, overall time horizon, solvent, and initiator composition, the optimal temperature policy shown to be a gradually decreasing/increasing, resp., by not more than five degrees, whereas the decrease/increase, resp., occurred in Terminal Double Bond (TDBH)/Chain Branching (CB) resp. per 100 monomer units.

Salhi et al.,[127] applying "time-varying optimal control", remarked the influence of the number of the control segments on the performance index, if divided into 7 or more intervals, the total time reduced by 16.44%. It is noted that the optimal function of jacket inlet temperature obtained if variated as both decision and/or control variable shows a "quasi bang-zero sequence" Finally, the final number-average molecular weight also affects the structure of the optimal control trajectory: if augmented 3 times, final times also ie. 2.96 times augmented.

Zhang,[128] included the vector of standard prediction errors in the number average weight, weight average weight distribution, and conversions, along with the weighting factor for process duration, in order to minimize the total time and maximize a monomer conversion. In the first case, in particular, considering the previously mentioned predicted distributions increase, the optimal total time is to increase as well. For example, if doubled, then the optimal total time is to increase by 27.31%. Otherwise, in a second case, having gradually decreased weighting factor data in the vector set ie. 2.98/2.47/2.25 times, the number average weight/conversion decrease/increase, resp. by 12.44%/6%, for the neural network model applied, however, the mechanistic model showed even greater variations. From the last, the author concluded that as greater the difference between models is, as harder would be to "use" the invented model in the "real" process.

Zhang and Smith,[39] however, took a step further, by including "the effect of mixing", ie. considering the existence of the "mixing compartment" similar to the plug-flow reactors. Hereby, the significant results can be noted in particular cases: 1) semi-batch mode with the parallel reactional system - for batch cycle duration elongation by 1/3 the optimal feeding evolution brought gain in yield by 3.1%, whereas, in the case of longer total duration, its optimal evolution follows linear kinetics; 2) semi-batch mode with a multiphase reactional system - whereas the fractional yield of an intermediate product, calculated with respect to the reactant in excess, proven to reach almost total purity (99.80%) if addition rate (of the reactant in the excess) optimized along with reactor temperature ie. even 14% more than in the case for constant addition rate optimized along with constant reactor temperature.

Xiong and Zhang,[129] took three cases into examination: 1) mechanistic model, 2) recurrent neural network model,

3) recurrent neural network model batch-to-batch iterative. In the last optimization approach (invented), the authors re-worked the approach suggested by Lee et al.,[130] ie. quadratic objective comprised of the vector of tracking errors added to the input sequence vector, stressing the importance to penalize only the errors at the end of a batch since only predefined product quality variables are of interest. The "discrepancies" between methods, were evident, furthermore tabulated in Table 6.

Sundaram et al.,[131] tested four objectives: monomer conversion for a predefined performance index, the total time for a predefined performance index, monomer conversion for a predefined number average molecular weight, and monomer conversion for a predefined weight-average molecular weight. The third case found the "best" objective, as even 48.60%/1.50% higher than the last case/first case, respectively. Same as for the last case, the optimal evolution of number-average molecular weight, is shown in four intervals, however, the latter one shows a "zero-bang" structure, starting the period with the switching time point of 7th mins, after 7% of the total time where almost 50% of maximum already have reached.

Zavala et al.,[132] studied both: 1) batch reactor: for optimal reactor temperature evolution it starts with a sequence of a real bang-zero, whereas ending with a "quasi-bang" sequence of similar length; however, inlet jacket temperature, only begins with a real bang-zero sequence, 2) semi-batch reactor: the optimal water flow rate, changes to a real "zero-bang-zero", whereas, steam flowrate keep almost the same structure. Furthermore, the adding dynamics of the polymers to the initial batch does not affect the structure of the pattern.

Upreti et al.,[133] tempted to achieve different objectives: 1) maximum conversion, 2) minimum time, 3) maximum conversion and normal average molecular weight, and, 4) maximum conversion and weight average molecular weight. Accordingly, in the latter two strategies, degradation of conversion happens, for 17.7%/35.9%, respectively.

Apostolos et al.,[134] focused on linear free-radical polymerization system only, shaped the "total optimal molecular weight distribution" as a bimodal curve: four intervals can be distinguished for an isothermal operation, whereas a real bang sequence observed only for a case of the greatest initial total mass assumed, as ending of an optimal chain weight, for more than 70% of total time. Lemoine-Naval et al.,[135] discussed thoroughly policies under 1) batch scheme: number average molecular weight optimal evolution consists of a real bang sequence lasting initial interval (more than 30% of total time), tending to presume even a complete "quasi bang zero", and, optimal polydispersity evolution consisted of the initial real bang-zero-bang sequence at switching points (0.3 [h]; 2.4 [h]), and finally a cooling jacket inlet temperature profile consisted of a "quasi zero-bang-zero" sequence throughout most of the time. Similarly, for the other flowrates, as well, ie. renewal cooling water/steam, a "quasi bang-zero-bang"/"bang-zero sequence", resp. could be noted. 2) semi-batch scheme proved even more sequences than previous: weight average molecular weight beginning with a sequence of "quasi bang-zero", polydispersity described as a real bang-zero-bang, for 25% of the time, and, cooling jacket inlet temperature shown a "quasi zero-bang-zero-bang" sequence throughout most of the time.

Zhang,[136] using a similar neural-network-based model as Mukherjee et al.,[137] proposed four optimal control strategies for reactor temperature evolution two-period policies: comprised from the period of decline till the 11th batch and increase to the value close to the initial. Chen et al.,[138] offered the optimal evolutions for both: 1) pure isothermal operation: if temperature constrained against unconstrained cases, whereas, the initial temperature variated by more than 30% and/or initial time by more than twelve times, both, the optimal average molecular weigh distribution and conversion ended with a real bang sequence of long durations, ie. 64%/84%, resp., 2) piecewise constant temperature operation: If predefined first/second-period duration halved and conversion constrained, then, all together temperature/conversion/average molecular weight shown the same structure for the optimal control, but drifted. Whereas the temperature inside the reactor, is a real bang-zero sequence, but latter both ended with a real bang sequence, occurring after only 10% of the time. It is to note that the latter optimal control policy proposed second-period time duration to increase by even 24 times.

Herrera and Zhang,[139] compared optimal results obtained by different neural network approaches ie. single and stacked to conclude: the difference varies between 24.25%-26.4%. Okorafo et al.,[140] adopted a "conventional starved feed strategy", comparing real-time optimization with a nominal fed-batch strategy through the optimal mass of polymer evolution: they follow the same trajectory of linear uprisal during the starting period, almost 25% of total time, reaching the same, afterward, both are to reach the same maximum at the end just in different times ie. time for optimized to reach is reduced by 40%; same applied for rector content mass, time reduced by 31.72%. Sadi et al.,[141] worked on a case of vinyl-acetate polymerization and presented the results of genetic algorithm programming: if the initiator initial concentrations/volume ratio of monomer to solvent in a feed, is risen (by step) by 25.38%/3.51%, respectively, at most, then the optimal initiator residue/weight average molecular weight, drop/increase by 66.67%/3.80%, respectively. The authors stressed also the influence of initial initiator concentration on the final conversion: conversion arise by 20% if the initial initiator concentration increases by 2.67 times.

Benyahia et al.,[142] provided optimal evolutions for 1) feed: a multiperiod stepwise function started and ended with a period of "quasi zero-sequence" over the greatest part of the total time (more than 51%), whereas a "quasi bang-sequence" occurred only once in between, 2) overall conversion, an initial "quasi zero-bang" connecting closely to the final maximum.

Perea et al.,[143] compared number-average molecular weight optimal evolutions issued by online dynamic optimization technique, calculated by different models: 1) off-line case: shown steepest linear increase till 75% of predefined value reached within 10% of total time, 2) on-line model: less steep till 62.6% of max. reached within 15% of the total time. Ibrahim et al.,[144] worked on two optimal control problems: 1) maximization of number average molecular weight, 2) maximization of conversion, to study further in-depth various sub-cases for each. For example, studying the sub-case of maximization of number average molecular weight for a different number of control intervals without pre-batch time, the authors proved again that double-interval brings improvements in 22.46% (for M_n), however, further divisions into more than two intervals do not influence much. Even more, the sub-case of maximization of the number average molecular weight for a different initial initiator concentration showed that if the initial initiator concentration decreased by 42.67% then improvements by 25.8% (M_n), at the expense of conversion decrease by 1.28%. Wang et al.,[145] developed "structure approaching hybrid neural networks", applying a particle swarm optimization method combined with successive quadratic programming. Same as the previously mentioned authors, they examined the influence of the total number of time intervals on the structure of optimal temperature evolution: 1) single time intervals give constancy overall time, 2) five/ten-twenty intervals, respectively, shown: starting period drop, to at most 40% of the time, followed by gradual increase till the end, however, an overall change in temperature during a process finally is not more than 5.3%, which does not leave a space for the energy integration.

Nie et al.,[146] defined a "moment model" to derive the: 1) scaled optimal temperature evolution: almost constant function over half of the batch time, leading to "bang alike" (last 8.5-9% of the time), 2) scaled optimal feed rate: after 5% (of evolution) function "stabilizes" into constant longest lasting one since it shortly drops after half of the total time, for product A, followed by almost "zero-bang-bang-zero" sequence as it uprises shortly, less than 5%, into an instantaneous jump to a maximum. Palacios et al.,[147] invented a "Measuring Attractiveness by a Categorical Based Evolution Technique" (MACBETH), based on a genetic algorithm combined with the use of predefined functions for all four criteria: 1) preference vs. conversion gave "two-periods" increase function, ie. linear in the first 20% of time reaching 85% of conversion, and the second one, the steeper, till the end, 2) preference vs. acid excess: "three periods" of decline, where the longest one is the starting linear steep within 60% of total time, 3) preference vs. temperature; "two periods" of linear decline, firstly for 70% afterward steeper for the rest. Tiam and Gomes,[148] succeeded in "keeping" the optimal conversion rate on its high levels throughout a considerably long period of operation whereas, maximum conversion/minimum total number average molecular weight, resp., brought 75%/40%, respectively.

Mahajan et al.,[149] revealed two-time optimal control policies, accordingly, 1) with a predetermined conversion and mole fraction of monomer of interest in copolymer (couple (0.94; 0.597)): if number average molecular weight varied, decreased by 29.5%, it affects the optimal total time reduction with 78.98% (~79%), 2) with a predetermined number average molecular weight and mole fraction of monomer of interest in the copolymer, but the conversion rate varied, if increased by 9.58%, it affects the optimal total time with the reduction by 16.61%. Rodrigues et al.,[150] derived the switching law to be further used to be combined with the adaptive laws, for the particular process studied.

Herrera et al.,[151] discussed a two-feed polymerization batch case, comparing different coolants added: water alone and a water-ethylene glycol mixture. The latter case shows the optimal time reduction by 14.49%, therewithal, lower polymer viscosity, the effects explained by the decline of the probability of the reaction between monomer particles which implies polymer chain increase. Further, due to the difference in viscosities characteristic for coolants, heat transfer occurring within the reactor area will differ, and consequently the optimal temperature evolutions. Kong and Chen[152] variated initiator feed along with maximization of conversion: smooth strategy over direct optimization brought time reduction by even 79.36%, However, if constant temperature variated together, too, the situation is inverse, as direct strategy brought an 11.20% of time reduction. However, if constant temperature variation together, the situation is inverse, as the direct strategy brought an 11.20% of time reduction. Bangi and Kwon,[153] treated the problem of hydraulic fracturing, whereas, the model applied was a sort of "grey box model" (ie. a combination of the first principle or "white box model" and "black box model" per definition data-driven models obtained by using process data). An estimator of the unmeasured process data was the deep neural network, as it is processed in a training algorithm using data from the "first principle model". Moreover, it is initialized by assigning some values for the number of layers, type of activated function (Sigmoid, Hyperbolic tangent, Rectified Linear Unit, Leaky rectified Linear Unit), and the initial values of weights and biases, to enter the training algorithm to approximate the unknown parameter where finite difference method is used to calculate the gradient.

Nasresfahani et al.,[154] brought a novel "starved-interval feeding policy": input monomer concentration verging to the minimal monomer accumulation polymerization rate, whereas the monomer(s) and initiator are input into a fixed amount of solvent with the independent constant flowrates. Indeed, the optimal initiator output concentrations, follow a three-periodic function, reaching a maximum, after 35% of total time, here "quasi zero-bang structure" could be assumed, with a clear difference with respect to the base case, where a two-periodic function. Moreover, according to the latter policy, Butyl Methacrilate (BMA)/2-Hydroxyethyl Acrylate (HEA) feed rates mount to the optimal total amount, by 14.64/99.47 times, respectively.

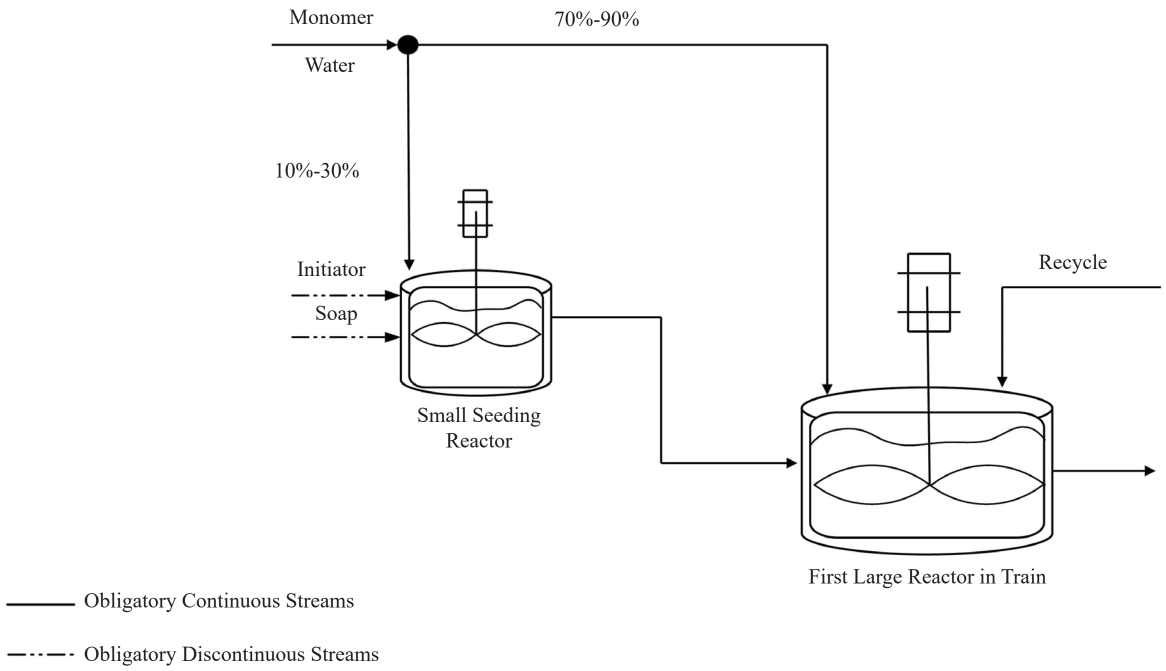

Figure 8. Split-feed reactor system in a semi-batch mode

3. Conclusions

For a particular group of batch reactors entitled "stirred jacketed", a variety of definitions of the objective function "enlarges" with the enhancement of the molecular mass of aggregates formed in the mixture. Being that, required events, configurations, modes, and even start-up procedures become more complex. Nonetheless, a variety of schemes have not been considered in this work: combined/replaced with other than chemical reactions (Luus and Hennessy,[155] Al Mers et al.,[156] Tsang et al.,[157] Lima et al.,[158] Li et al.,[159] Talaghat et al.,[160] Badescu[161]), Moreover, "combined" control, was not included as well (Cott and Macchietto,[162] Cabassud et al.,[163] Uhlemann et al.,[164] Rahman and Palanki,[165] Clarke-Pringle and Mac Gregor ,[166] Aydin et al.,[167] Yoo et al.[168]); batch crystallization growth control (Nayhouse et al.,[169] Kwon et al.,[170] Kwon et al.,[171] Kwon et al.[172]); even not recently developed microstructured chemical reactors (Ozkan et al.,[173] Zarei,[174] Blauth et al.[175]). But this is only due o the scarcity of scientific literature on a specific subject.

Therewithal, based on the continuous mode background, according to Costandy et al.[176] who explained the methodology of "continuous mode transformation into the batch", one can project the ideas toward the novel configurations. For example, in Figure 8, a split-feed reactors system in semi-batch mode, based on a continuous process discussed by Pollock et al.,[177] is presented, with the purpose to give the idea of the simple stirred jacketed reactors, still "unresearched" from the aspect of optimal control. In the same way, in Figure 9, "batch reactors in series" are presented, with an idea of a back mixing process and recycling process, based on the works of Szépe and Levenspiel , Levenspiel and Bishof ,[178] Levenspiel,[179] Miertschin and Jackson,[180] and Liu et al.[181]

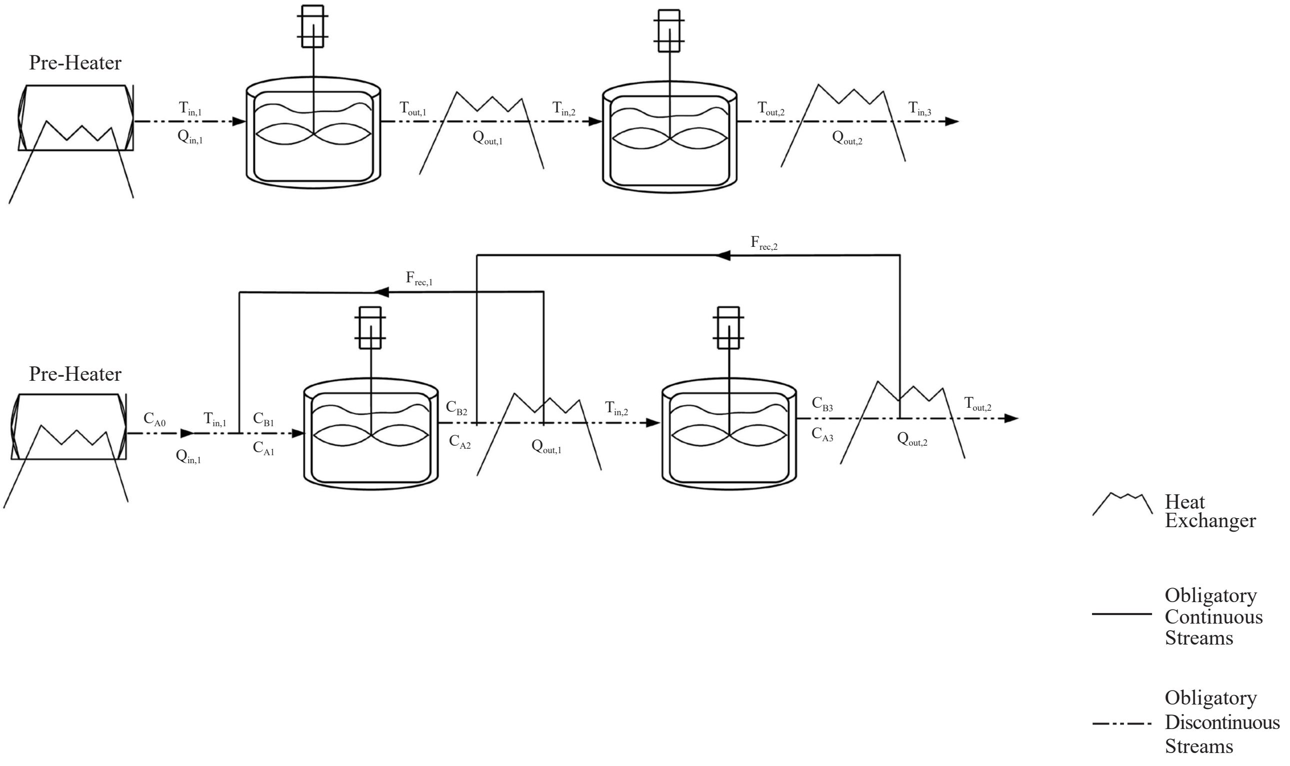

Figure 9. Batch reactors in series: (a) backmixing; (b) recycling

Last but not least, configurations other than stirred could be considered as candidates: plug-flow reactor (Venkateswaran et al.,[182] Wang et al.,[183,184] in terms of reactive process, studied, variety of schemes also, high-pressure reactions (Khazraei and Dhib,[185] Kong et al.,[186] etc.), pyrolysis (Mazloum et al.,[187] Pan et al.,[188] etc.), the Stern-Volmer reaction and moving-bed reactors (Fogler[189]).

Conflict of interest

I declare no conflict of interest, and the responsibility for the published data is up to the author.

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