# IMPROVED KINETIC MODELING AND THERMAL CONTROL OF FOOD INDUSTRY BATCH ETHANOL FERMENTATION

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**Abstract** - Mathematical modeling and simulation of ethanol batch fermentation with improved equations was investigated. A multistep calculating algorithm was developed in order to achieve more realistic ethanol fermentation kinetic modeling for more precise heat transfer conditions, for better thermal control of fermentation process. Substituting earlier kinetic model parameters with functions creates new set and more complex ordinary differential equation (ODE) systems, subsequently may calculate reaction mass chemical composition and temperature by generated heat flux, may estimate heat transfer to cooling agent. Of the equation systems tested on laboratory and industrial brewing conditions, results smaller reaction mass concentration and temperature gradients by predictive process control. Present work contain an evolved mathematical approach proposal which may be used successfully in computer aided simulation environments.

**Index Terms** - Batch ethanol fermentation, heat transfer, kinetic modeling, simulation.

## I. INTRODUCTION

In 2018-2023 period, food grade ethanol expected Compound Annual Growth Rate (C.A.G.R.) value is 5.7% [1]. Beer and wine industry are moderately interested in fermentation process improvement, greater interests are present in food-grade and bioethanol production [2]. Food industry batch ethanol fermentation process provide large scale of products, by subsequently distillation and rectification producing food grade ethanol, with wide range of applications in the food, beverage, healthcare and pharmaceutical sectors [3]. Food grade ethanol may be used as preservative, to increase the shelf life of end products, manufacturing colors and flavors for food applications, preparing coating agents, for solid-liquid extraction, as food ingredient and food additive [4]. Fermentation ethanol yield, selectivity and secondary byproducts concentrations are influenced by substrates, yeasts, yeast nutritional conditions, temperature, pressure and many other process parameters [5].

Regular ethanol fermentation by-products are acetic acid and other mono-, di- and tricarboxylic organic acids, methyl alcohol and higher aliphatic alcohols (HAA), phenols, like cis-3-hexenol, secondary and tertiary alcohols, esters (isoamyl acetate, ethyl-hexanoate), aliphatic aldehydes and ketones, 2-methyl-propionaldehyde, glycerol, vicinal diketones (VDK), sulphur-containing organic compounds, dimethyl sulfide (DMS), free fatty acids (FFA), eugenol, benzaldehyde, vanillin and cell-decay products, with significant impact on product quality [6].

According to ethanol fermentation process complexity, is difficult to create a realistic virtualization, by which to achieve predictive control, in order to improve reaction mass chemical composition and product quality [7].

## II. GENERALIZED OBJECTIVES

Kinetic modeling and thermal control improvement major objectives are creating more precise process stoichiometry, earlier kinetic models comparative study, establishing correlations of process parameters with step-by-step identification, identifying determinant and critical process parameters, process parameters effects deeper analysis, elaborating extended mathematical expressions, constructing generalized equation system, approaching dynamic process parameters for industrial environment, selective improvement of mathematical models, improving steady-state simulations, later creating adaptive dynamic simulations to achieve fermentation predictive and dynamic control and better fermentation bioreactor design.

## III. INITIAL REACTION MASS CHARACTERIZATION

In order to proper describe initial reaction mass, have to consider carbohydrate substrates species and their concentrations (carbohydrates), yeast cells concentration and yeast species mass distribution, organic and inorganic nitrogen compounds concentrations, especially amino acids, organic and inorganic phosphorous compounds concentrations, especially phospholipids, inorganic species concentrations (K, Ca, Mg, Na, Se, S, Cr, Li, Fe, Mo and Mn containing compounds), other important organic compounds are fatty acids as triglycerides (TG), free fatty acids (FFA), mono-unsatturated fatty acids (MUFA), polyunsatturated fatty acids (PUFA), vitamins molecular species and their concentrations (pantothenic acid, pyridoxine, thiamine, biotin, niacin, folic acid), additional substrates and other nutrients mass ratios, yeast preparation path (cooled storage

conditions and re-hydrating process parameters), yeast molecular mechanism antagonists or toxic compounds species and their concentrations, hydrophilic-lyophilic balance (HLB), added surface-active compounds profile, other yeast nutrients (polyphenols, anthocyanins, cysteine, calcium lactate), yeast cell growth inhibitors (farnesol, bacterial signaling nucleotides, methionine, copper ions), cell respiratory inhibitors, lag phase duration, previous temperature values history, including temperature variation rate (dT/dt), preparation maximum temperature variation, oxygen partial pressure, pressure variation rates, yeast cells dispersion characteristics, added enzymes, density (ρ), viscosity (η), and of course the water activity [8].

## IV. PARAMETER VARIATIONS DURING FERMENTATION PROCESS

Usually, basic considered process parameters during fermentation are temperature, substrate concentration, yeast cells concentration, actual ethanol concentration, fermentation time, cell and ethanol yields, maximum cell growth rate and substrate affinity constant [9]. To achieve more precise kinetic study, have to consider other process parameters too, like total system pressure and pressure distribution over fermentation time, reaction mass hydrostatic distribution, acidity (pH), $CO_2$ partial pressure in liquid and gaseous phase, redox condition, mixing parameter (Reynolds criteria), reaction mass specific heat, density, viscosity and heat conductivity. These additional parameters varies over fermentation time, influencing the overall process [10]. In addition, reaction mass temperature, pressure, pH, chemical species concentrations, redox condition and liquid phase viscosity variation rates varies during fermentation process. Usually, pH and cell nutrients concentrations are decreasing, redox potential value having a minimum at maximum cell concentration, later increasing to the end of fermentation process [11]. Cell growth inhibitor bioprocess products concentrations are increasing over fermentation time, other parameter like mixing criteria rate will decrease, appearing higher radial and vertical temperature gradients, all over causing lower ethanol yield. During fermentation process may appear less active geometric regions in reaction mass, greater cell sedimentation, flocculation and greater cell death rate. $CO_2$ generation rate in fermentation process have a maximum value at maximum reaction rate, this creates significant gas nucleation, affecting ascending bubble dynamics, improving cell floating and foaming. Frequently, the most important process parameters are temperature, temperature gradients, pressure and pressure dynamics [12].

Process heat generation flux can be expressed as:

$$Q_{gen\max} = v_{r\max} \cdot (\Delta_r H) \cdot V_R = m_{\tau CA} \cdot c_{pCA} \cdot \Delta T_{CA} \quad (1)$$

$$Q_{gen\max} = A_{HT} \cdot K_W \cdot \Delta T_{med} \quad (2)$$

where:

$Q_{gen\max}$ - maximum generated heat flux, W;

$v_{r\max}$ - maximum reaction rate g/L·h;

$\Delta_r H$ - reaction heat, J/mol;

$V_R$ - reaction mass volume, $m^3$;

$m_{\tau CA}$ - cooling agent mass flow rate, $m^3/s$;

$c_{pCA}$ - cooling agent specific heat, J/kg·K;

$\Delta T_{CA}$ - cooling agent temperature variation, K;

$A_{HT}$ - available heat transfer surface, $m^2$;

$K_W$ - overall heat transfer coefficient, $W/m^2 \cdot K$;

$\Delta T_{med}$ - mean temperature gradient, K.

In isothermal operating conditions, bioprocess generated heat flux are transferred to the cooling agent (CA) through wall (W), at maximum reaction rate may occur internal thermal instability or runaway, because reaction rate are increased by the higher temperature. To avoid this phenomenon, is necessary to proper design the cooling region of bioreactor, with better estimation of expected reaction rates and reaction rate maximum. Equation (1) terms varies during fermentation process, becoming necessary to recalculate frequent as possible the generated heat flux over fermentation time. Equation (2) $K_W$ term may have significant lower values due accumulated depositions, needing higher cooling agent mass rates.

## V. FERMENTATION KINETICS AND STOICHIOMETRY

Scientific literature contain many available kinetic equations referring to fermentation processes, regularly as ordinary differential equation (ODE) systems, these equations frequently having low or limited precision.

Considering Groot kinetic model [12], the complete ODE equation system (3) may be used in algorithm state:

$$\begin{aligned}
&t_i : S_i, X_i, P_i \\
&\frac{1}{X}\frac{dX}{dt} = \mu = \mu_{\max}\frac{S}{K_{SX}+S}\left(1-\frac{P}{P_{max}}\right)^m \\
&\frac{1}{X}\frac{dS}{dt} = q_S = q_{S\max}\left(1-\frac{P}{P_{mS}}\right) \\
&\frac{1}{Y_{X/S}} = \frac{1}{Y_{X/S,m}} + \frac{m_{a\,\mathrm{int}\,X}}{\mu} \\
&\frac{1}{X}\frac{dP}{dt} = v_P = q_S Y_{P/S} \\
&Y_{P/S} = 0,43(1-1,3Y_{X/S}) \\
&v_{rX} = \mu X \\
&v_{rS} = q_S X \\
&v_{rP} = v_P X \\
&S_{i+1} = S_i - \Delta S_i \\
&X_{i+1} = X_i + \Delta X_i \\
&P_{i+1} = P_i + \Delta P_i \\
&t_{i+1} : S_{i+1}, X_{i+1}, P_{i+1}
\end{aligned} \quad (3)$$

where:

$t_i : S_i, X_i, P_i$ - substrate, biomass and product concentrations at $t_i$ fermentation time, g/L;

$\mu, \mu_{\max}$ - cell growth and maximum cell growth rates, $h^{-1}$;

$q_S$, $q_{S\max}$ - substrate consumption rates, $h^{-1}$;

$v_P$ - product generation rate, $h^{-1}$;

$m_{a\text{int}X}, m$ - experimental coefficients;

$Y_{X/S}$ - cell yield coefficient consider to substrate, g/g;

$Y_{P/S}$ - product yield coefficient consider to substrate, g/g;

$v_{rX}$ - reaction rate consider to cells, g/L·h;

$v_{rS}$ - reaction rate consider to substrate, g/L·h;

$v_{rP}$ - reaction rate consider to product, g/L·h ;

$t_{i+1} : S_{i+1}, X_{i+1}, P_{i+1}$ - substrate, biomass and product concentrations at $t_{i+1}$ fermentation time.

Considering Damiano kinetic model [12], the complete ODE equation system (4) may be used in algorithm state:

$$
\begin{aligned}
&t_i : S_i, X_i, P_i \\
&\frac{1}{X}\frac{dX}{dt} = \mu = \mu_{\max} \exp(-a_1 P) \\
&\frac{1}{X}\frac{dS}{dt} = q_S = \frac{v_{P\max}}{Y_{P/S}} \\
&v_P = v_{P\max} \quad (P \le P_c) \\
&v_P = v_{P\max} \exp(-a_2 (P / P_c)) \\
&v_{rX} = \mu X \\
&v_{rS} = q_S X \\
&v_{rP} = v_P X \\
&S_{i+1} = S_i - \Delta S_i \\
&X_{i+1} = X_i + \Delta X_i \\
&P_{i+1} = P_i + \Delta P_i \\
&t_{i+1} : S_{i+1}, X_{i+1}, P_{i+1}
\end{aligned}
\tag{4}
$$

where:

$P_c$ - critical product inhibition limiting concentration, g/L.

Considering Damiano kinetic model [12], the complete ODE equation system may be used in algorithm state:

$$
\begin{aligned}
&t_i : S_i, X_i, P_i \\
&\frac{1}{X}\frac{dX}{dt} = \mu = \mu_{\max} \frac{S}{K_{SX} + S}(1 - \frac{P}{P_{max}})^m (1 - \frac{X_t}{X_{\max}}) \\
&\frac{1}{X}\frac{dS}{dt} = q_S = \frac{\mu}{Y_{S/X}} + m_{a\text{int}S} \\
&\frac{1}{X}\frac{dP}{dt} = v_P = v_{P\max} \exp(-a_1 X_t) \\
&K_d = a_2 \mu + a_3 \\
&v_{rX} = \mu X - K_d X \\
&v_{rS} = q_S X \\
&v_{rP} = v_P X \\
&S_{i+1} = S_i - \Delta S_i \\
&X_{i+1} = X_i + \Delta X_i \\
&P_{i+1} = P_i + \Delta P_i \\
&t_{i+1} : S_{i+1}, X_{i+1}, P_{i+1}
\end{aligned}
\tag{5}
$$

where:

$K_{SX}$, $P_{max}$, $X_{\max}$, $m_{a\text{int}S}$, $a_2$, $a_3$ - kinetic parameters.

Solving kinetic models ODE systems by fermentation time offer evolving S, X and P values, usually extending $t_{i+1}$ to obtain the needed substrate conversion or product concentration. The primary challenge in kinetic models is to determine the entire fermentation time and reaction rates as well to establish generated heat flux. Common problem in kinetic models are the differentiated cell affinity to substrates and nutrients, which clearly affects the entire fermentation process, consequently the new kinetic model construction must start reconsidering the whole process stoichiometry, considering an extended description of reaction that take place. Vast majority of previous works use a simplistic yeast cell chemical composition:

$$CH_{1.8}O_{0.5}N_{0.2} \tag{6}$$

More exact chemical composition includes other chemical species [13]:

$$CH_{1.613}O_{0.557}N_{0.158}P_{0.012}S_{0.003}Mg_{0.003}K_{0.022}Ca_{0.001} \tag{7}$$

Modified cell composition require the reconsideration of entire reaction stoichiometry:

$$
\begin{aligned}
&(a_1 S_1 + a_2 S_2 + \ \dots \ + a_n S_i) \ + \ (b_1 N_1 + b_2 N_2 + \ \dots \ + b_n N_i) + \\
&+ (c_1 P_1 + c_2 P_2 + \ \dots \ + c_n P_i) \ + \ \dots \ + \xi O_2 = \\
&= \ CH_{1,613}O_{0,557}N_{0,158}P_{0,012}S_{0,003}Mg_{0,003}K_{0,022}Ca_{0,001} + \\
&+ dCO_2 + eH_2O \ + fEt-OH + gCH_3COOH \ + hIPA + \\
&+ iTBA \ + jG \ + kDA
\end{aligned}
\tag{8}
$$

where:

$a_1, a_2, \ \dots \ , a_n$ - substrates stoichiometric coefficients;

$b_1, b_2, \ \dots \ , b_n$ - N containing compounds stoichiometric coefficients;

$c_1, c_2, \ \dots \ , c_n$ - P containing compounds stoichiometric coefficients;

$\xi$ - oxygen stoichiometric coefficient, fed by air inlet;

$f$ - ethanol stoichiometric coefficient;

$g$ - acetic acid stoichiometric coefficient;

$h$ - isopropanol stoichiometric coefficient;

$i$ - tert-butyl alcohol stoichiometric coefficient;

$j$ - glycerol stoichiometric coefficient;

$k$ - diacetyl stoichiometric coefficient.

In order to find stoichiometric coefficients, we have to create a more complex linear equation system, afterwards solving in dedicated software environments like Polymath, Sequalator, MathCAD or Wolfram Mathematica. Obtained stoichiometric coefficients may be used to achieve mass balance of entire fermentation process by assuming constant value coefficients, more realistic description is

possible with differentiated reaction stoichiometric coefficients to the fermentation period.

## VI. IMPROVING FERMENTATION HEAT BALANCE

To achieve improved process heat balance with equation (1), reaction mass thermal properties have to be cyclic recalculated, because reaction mass chemical composition modifies from the initial state to the end of fermentation process.

Heat balance construction needs estimated thermophysical properties for each major constituents of reaction mass (RM), like water, carbohydrates, ethanol, biomass, proteins and fats. Thermophysical properties of reaction mass constituents that are often required for heat transfer calculations including specific heat capacity, specific enthalpy, and thermal conductivity [14], these properties can be deduced with (9), (10) and (11) equations, using polynomial temperature-dependent mathematical models:

$$\rho_{RM} = \sum(\rho_i \cdot x_i) \quad (9)$$

where:

$\rho_{RM}$ - overall reaction mass density, kg/m$^3$;

$\rho_i$ - reaction mass constituents individual density, kg/m$^3$;

$x_i$ - relative concentrations of reaction mass constituents.

$$c_{pRM} = \sum(c_{pi} \cdot x_i) \quad (10)$$

where:

$c_{pRM}$ - overall reaction mass specific heat, J/kg·K;

$c_{pi}$ - reaction mass constituents individual specific heat, J/kg·K;

$$k_{RM} = \sum(k_i \cdot x_i) \quad (11)$$

where:

$k_{RM}$ - overall reaction mass thermal conductivity, W/m·K;

$k_i$ - reaction mass constituents thermal conductivity, W/m·K;

More recent work in ethanol-water mixtures description [15] contain mathematical expressions included in REFPROP software environment that offer the possibility to calculate mixtures specific heat capacity, liquid phase thermal conductivity, viscosity, liquid enthalpy (h) and surface tension (σ) using polynomial coefficients.

Polynomial Coefficients for Liquid Density and Specific Heat Capacity

| | f(T)=a1*T⁴+a2*T³+a3*T²+a4*T+a5 | | | | |
|---|---|---|---|---|---|
| ρ(T) | a1 | a2 | a3 | a4 | a5 |
| T<78.2 | 0.0 | -8.873x10$^{-6}$ | -2.567x10$^{-4}$ | -0.8158 | 806.08 |
| T≥78.2 | -1.793x10$^{-7}$ | 7.474x10$^{-5}$ | -1.468x10$^{-2}$ | 0.2803 | 775.20 |
| $c_p$(T) | | | | | |
| T<78.2 | 2.707x10$^{-6}$ | -6.118x10$^{-4}$ | 3.051x10$^{-2}$ | 11.78 | 2268.83 |
| T≥78.2 | 8.637x10$^{-6}$ | -3.946x10$^{-3}$ | 0.6675 | -39.65 | 3774.52 |

Polynomial Coefficients for Liquid Thermal Conductivity and Viscosity

| | f(T)=a1*T⁴+a2*T³+a3*T²+a4*T+a5 | | | | |
|---|---|---|---|---|---|
| k(T) | a1 | a2 | a3 | a4 | a5 |
| T<78.2 | 0.0 | -3.545x10$^{-9}$ | 6.713x10$^{-7}$ | -2.629x10$^{-4}$ | 0.1713 |
| T≥78.2 | 2.826x10$^{-11}$ | -1.313x10$^{-8}$ | 2.265x10$^{-6}$ | -3.920x10$^{-4}$ | 0.1752 |
| μ(T) | | | | | |
| T<78.2 | 1.398x10$^{-11}$ | -3.931x10$^{-9}$ | 5.029x10$^{-7}$ | -3.951x10$^{-5}$ | 1.813x10$^{-3}$ |
| T≥78.2 | 6.726x10$^{-13}$ | -4.978x10$^{-10}$ | 1.467x10$^{-7}$ | -2.157x10$^{-5}$ | 1.443x10$^{-3}$ |

Polynomial Coefficients for Liquid Enthalpy and Surface Tension

| | f(T)=a1*T⁴+a2*T³+a3*T²+a4*T+a5 | | | | |
|---|---|---|---|---|---|
| h(T) | a1 | a2 | a3 | a4 | a5 |
| T<78.2 | 0.0 | -4.399x10$^{-3}$ | 6.473 | 2260.17 | 2.000x10$^5$ |
| T≥78.2 | 0.0 | 9.685x10$^{-3}$ | 1.340 | 2851.98 | 1.780x10$^5$ |
| σ(T) | | | | | |
| T<78.2 | 0.0 | 9.954x10$^{-11}$ | 6.917x10$^{-8}$ | -1.308x10$^{-4}$ | 2.500x10$^{-2}$ |
| T≥78.2 | 0.0 | 3.609x10$^{-10}$ | -1.190x10$^{-8}$ | -1.222x10$^{-4}$ | 2.470x10$^{-2}$ |

Reaction mass chemical composition evolution induces significantly higher viscosity values, these states are difficult to calculate because substrates concentrations are lowering, ethanol and biomass concentrations are increasing. In these conditions scientific literature recommends a modified Guzman-Andrade equation [16]:

$$\eta_{RM} = A_0 \cdot \exp(B_0 / T) + \sum_i C_i \cdot A_i \cdot \exp(B_i / T) \quad (15)$$

where: $A_0$, $B_0$, $A_i$ and $B_i$ - experimental coefficients

$$\mu_{\max} = \frac{\nu_{\max N assim} \cdot X^h}{K_{half}^h + X^h}$$

In order to reconsider specific growth rate [17]:

μ = f(T, pH, S)

$$\mu_{\max} = \beta_0 + \beta_1 X_1 + \beta_{11} X_{21} + \beta_2 X_2 + \beta_{22} X_{22} + \\ + \beta_3 X_3 + \beta_{33} X_{33} + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + e \quad (16)$$

where:

$\beta_i$ - coefficients estimated by regression;

$\beta_1$ - coefficient for the linear effect of $X_1$;

$\beta_{11}$ - quadratic effect of $X_1$;

$\beta_{12}$ - interaction between variables $X_1$ and $X_2$;

$X_1, X_2, X_3$ - environmental variables (T, pH and S).

| Regression coefficient | Value | Standard deviation | *p*-value |
|---|---|---|---|
| ***Model for yeast T73*** | $R^2 = 0.812$ | | |
| $\beta_0$ (Mean/Inter) | 0.220 | 0.013 | [a]0.003 |
| $\beta_1$ (linear *T*) | 0.108 | 0.006 | [a]0.003 |
| $\beta_{11}$ (quadratic *T*) | −0.014 | 0.006 | 0.175 |
| $\beta_2$ (linear pH) | 0.025 | 0.006 | 0.054 |
| $\beta_{22}$ (quadratic pH) | 0.013 | 0.007 | 0.180 |
| $\beta_3$ (linear *S*) | −0.040 | 0.006 | [a]0.023 |
| $\beta_{33}$ (quadratic *S*) | 0.032 | 0.007 | [a]0.041 |
| $\beta_{12}$ (interaction *T**pH) | 0.019 | 0.008 | 0.139 |
| $\beta_{13}$ (interaction *T***S*) | 0.010 | 0.008 | 0.325 |
| $\beta_{23}$ (interaction pH**S*) | −0.001 | 0.008 | 0.861 |

## VII. EFFECTS OF GENERATED $CO_2$

Fermentation process generated $CO_2$ may have significant variations over time, function of process parameters [18]. In initial state, RM $CO_2$ concentration is very low, later $CO_2$ accumulates in liquid phase, concentration reaches the solubility limit and generated $CO_2$ excess nucleates with bubbles

formation, which floating induce many effects, like RM mixing and moderate yeast cells soaring.

$CO_2$ concentration evolution in reaction mass:

$$d([\mathrm{DCO_2}])/dt = CER(t) - K_L^{CO_2} \cdot a \cdot ([DCO_2] - pCO_2 / H^{CO_2} - (k_b / K_1) \cdot [H^+] \cdot \{(\mathrm{K_1}/[H^+]) \cdot [DCO_2] - [\mathrm{HCO_3^-}]\} \quad (17)$$

where:

$[\mathrm{DCO_2}]$ - total solved $CO_2$ concentration in liquid phase, g/L;

$t$ - fermentation time, s;

$CER(t)$ - $CO_2$ concentration evolution rate over time, g/L·h;

$K_L^{CO_2}$ - Volumetric mass transfer coefficient for $CO_2$ (L/h);

$a$ - activity coefficient;

$pCO_2$ - $CO_2$ partial pressure;

$H^{CO_2}$ - Henry's Law constant for $CO_2$;

$k_b$ - reaction rate constant;

$K_1$ - equilibrium constant;

$[H^+]$ - concentration of hydrogen ions, mole/L;

$[\mathrm{HCO_3^-}]$ - concentration of bicarbonate ions, mole/L.

RM liquid phase $CO_2$ concentration have impact on cell growth rate [19]:

$$\mu = \mu_{\max} \cdot [\mathrm{DCO_2}] \cdot (a_L + b_L x + c_L x^2)$$

where:

$a_L, b_L, c_L$ - limiting constants;

$x$ - transformed impact coefficient.

## VIII. BATCH FERMENTATION REACTION MASS HEAT TRANSFER TO COOLING AGENT

In order to maintain or achieve desired temperature during fermentation process, have to transfer generated heat flux from reaction mas to the cooling agent (CA) through bioreactor side wall or other involved surface [20]. In first step we have to calculate heat transfer coefficient with Nusselt (Nu) criteria:

$$Nu_{RM} = (\alpha_{RM} \cdot l) / \lambda_{RM} \quad (18)$$

where:

$Nu_{RM}$ - RM side Nu criteria value;

$\alpha_{RM}$ - RM heat transfer coefficient, W/m$^2$·K;

$l$ - heat transfer path length in RM, m;

$\lambda_{RM}$ - RM heat conductivity, W/m·K.

Reaction mass chemical composition and temperature varies during the fermentation process, needing cyclic recalculation of heat conductivity coefficient value.

$$\lambda_{RM}(C_i, T) = A \cdot c_{pC_i,T} \cdot \rho_{C_i,T} \cdot \sqrt{\rho_{C_i,T} / M_{avg}} \quad (19)$$

where:

$\lambda_{RM}(C_i, T)$ - RM liquid phase heat conductivity, function of composition and temperature, W/m·K;

$A$ - molecular association coefficient, f($C_i$, $T_{RM}$);

$c_{pC_i,T}$ - calculated RM density with specified chemical composition and temperature, J/kg·K;

$\rho_{C_i,T}$ - calculated RM specific heat with specified chemical composition and temperature, J/kg·K;

$M_{avg}$ - RM average molar mass, g/mol.

On reaction mass side there are different heat transfer conditions, needing also cyclic recalculations of heat transfer coefficient value:

$$Nu_{RM}(C_i, T_{RM}) = 0.187 \cdot \mathrm{Re}_{ag}^{0.688} \mathrm{Pr}^{0.36} \cdot (\nu_{RM} / \nu_w)^{0.11} \cdot (D_t / D_a)^{0.62} \quad (20)$$

where:

$Nu_{RM}(C_i, T_{RM})$ - RM side Nusselt criteria value, function of concentrations and temperature;

$\mathrm{Re}_{ag}$ - reaction mass Reynolds criteria value, varies during fermentation process;

Pr - reaction mass Prandtl criteria value, varies during fermentation process;

$\nu_{RM}$ - RM calculated viscosity at specified concentrations and temperature, varies during fermentation process, Pa·s;

$\nu_w$ - water viscosity at specified temperature, varies during fermentation process, Pa·s;

$D_t$ - bioreactor inside diameter, m;

$D_a$ - bioreactor mixing element diameter, m.

On cooling agent (CA) side there are also different and evolving heat transfer conditions, needing cyclic recalculations of heat transfer coefficient values:

$$Nu_{CA}(L_{CA}, T_{CA}) = 0.14 \cdot ((\mathrm{Re}_{CA}^{0.688} \cdot \mathrm{d}_{CA}) \cdot \mathrm{Pr}_{CA}^{0.33} \cdot (\mathrm{Pr}_{CA} / \mathrm{Pr}_{wall\ CA})^{0.25} \quad (21)$$

where:

$Nu_{CA}(L_{CA}, T_{CA})$ - CA Nusselt criteria value, calculated at specified cooling path length and temperature;

$L_{CA}$ - CA specified cooling path length, m;

$T_{CA}$ - CA estimated temperature, T;

$\mathrm{Re}_{CA}^{0.688}$ - CA calculated Reynolds criteria value;

$\mathrm{d}_{CA}$ - cooling path equivalent diameter, m;

$\mathrm{Pr}_{CA}$ - CA calculated Prandtl criteria value;

$\mathrm{Pr}_{wall\ CA}$ - CA calculated Prandtl criteria value besides wall.

With previously calculated partial heat transfer coefficients may calculate the overall heat transfer coefficient, function of chemical species concentrations, reaction mass temperature and with calculated cooling agent temperature:

$$K_{bior}(C_i, T_{RM}, T_{CA}) = 1/((1/\alpha_{RM}) + \sum(\delta_i / \lambda_i) + (1/\alpha_{CA})) \quad (22)$$

where:

$K_{bior}(C_i, T_{RM}, T_{CA})$ - overall heat transfer coefficient,

function of chemical species concentrations, reaction mass temperature and calculated cooling agent temperature, W/m$^2$·K;

$\delta_i$ - bioreactor wall layers thickness, m;

$\lambda_i$ - bioreactor wall layers thermal conductivity, W/m·K.

With estimated overall heat transfer coefficient may be calculated bioreactor overall transferred heat flux, taking consider also the cooled reaction mass height:

$$Q_T(C_i, T_{RM}, T_{CA}, H_{bior}) = \\ = K_{bior}(C_i, T_{RM}, T_{CA}) \cdot A_{HT} \cdot \Delta T_{med}(T_{RM}, T_{CA}) \quad (23)$$

where:

$Q_T(C_i, T_{RM}, T_{CA}, H_{bior})$ - overall transferred heat flux in bioreactor, W;

$H_{bior}$ - bioreactor cooled wall height, m;

$A_{HT}$ - available heat transfer area, m$^2$;

$\Delta T_{med}(T_{RM}, T_{CA})$ - available temperature gradient between RM and CA, K.

Reaction mass heat content variation rates can be evaluated at different fermentation periods, in order to identify possible bioreactor thermal unstable states:

$$dQ_{RM} / dt = m_{RM,t_i} \cdot (\sum (C_{i,t_i} \cdot c_{Pi,t_i})) \cdot T_{RM,t_i} - \\ - m_{RM,t_{i+1}} \cdot (\sum (C_{i,t_{i+1}} \cdot c_{Pi,t_{i+1}})) \cdot T_{RM,t_{i+1}} \quad (24)$$

where:

$Q_{RM}$ - RM heat content, J;

$t$ - fermentation time, s;

$t+1$ - incremented fermentation time, s;

$m_{RM,t_i}$ - RM calculated mass value at $t_i$ time, kg;

$C_{i,t_i}$ - RM chemical species concentrations at $t_i$ time, g/L;

$c_{P\,RM,t_i}$ - RM chemical species specific heat at $t_i$ time, g/L;

$m_{RM,t_{i+1}}$ - RM calculated mass value at $t_{i+1}$ time, kg;

$C_{i,t_{i+1}}$ - RM chemical species concentrations at $t_{i+1}$ time, g/L;

$c_{P\,RM,t_{i+1}}$ - RM chemical species concentrations at $t_{i+1}$ time, g/L;

$T_{RM,t_i}$ - RM temperature at $t_i$ time, K;

$T_{RM,t_{i+1}}$ - RM temperature at $t_{i+1}$ time, K.

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