Calculation of the Optimal Economic Costs by Enzymatic Hydrolysis of Biomaterial Waste with MAPLE

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Abstract—The paper deals with the use of mathematical software in the control and automation of real technological processes of biomaterials treatment. It describes programming tools of software MAPLE presented on the example of calculation of operating costs in processing of biomaterial waste to protein hydrolysate. For this purpose were prepared mathematical models describing the studied process as in the case of kinetic mechanism, as with the diffusion mechanism. On this basis and using the mass balance were formulated cost functions for both cases studied. The calculation was subsequently programmed in Standard Worksheet user interface and in Maplet user interface. Computed data allow to determine the optimum process to the purpose of saving energy and raw materials.

Keywords—Mathematical model, biomaterial waste treatment, MAPLE, cost curve calculation.

I. Introduction

PROCESSING of raw hides is a sequence of many operations, which produce a number of liquid and solid waste. As a result of using different chemicals may be the waste often harmful. Therefore, it is necessary to find methods that lead to the minimization of waste and also find ways to remove unwanted substances from tanning waste for subsequent use [1], [2].

One of the possible methods of separation of undesirable substances from solid biomaterials is the use enzymatic hydrolysis. To make this process economically feasible, it is necessary to minimize operating costs [3]. In the subsequent text will be described the calculation, which we proposed to calculate the main operating costs during enzymatic hydrolysis by using MAPLE software.

The calculation is based on the solution of a mathematical model describing the dependence of the quantity of a protein hydrolysate on time of process. The application allows the user to compute cost functions for the required input conditions and can be used to determine the optimum process for purpose of saving energy and raw materials.

II. Mathematical background of the studied process

By enzymatic hydrolysis of biomaterials, solid phase reacts with liquid phase in the reactor. The reaction is catalyzed by protheolytic enzymes. Products of reaction are other solid and liquid phases. General description of heterogeneous reactions can be described by equations (1) – (3) [3], [4], [5]:

$$D_{ij}\nabla^2 c_i = \frac{Dc_i}{D\tau} + r_i \tag{1}$$

where

$$\frac{Dc_i}{D\tau} = \frac{\partial c_i}{\partial \tau} + \frac{\partial c_i}{\partial x}v_x + \frac{\partial c_i}{\partial y}v_y + \frac{\partial c_i}{\partial z}v_z\,, \tag{2}$$

$$\nabla^2 c_i = \frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} + \frac{\partial^2 c_i}{\partial z^2}\,. \tag{3}$$

The reaction rate is a function of the concentration of reactants:

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$$r_i = f\left(c_i, c_j \ldots\right). \quad (4)$$

The specific form of the function depends on the mechanism of chemical reactions. If the concentration gradients are negligible, i.e. when the chemical reaction is slow, or the solid phase particles are very small, it is possible to neglect the concentration gradients and thus equation (4) simplifies to (5):

$$r_i = \frac{\partial c_i}{\partial \tau}. \quad (5)$$

The reaction rate is determined by the kinetics of enzymatic reaction. The second limiting case occurs when a chemical reaction is very fast, or solid phase particles are large. In this case, the chemical reaction can be neglected and the velocity is determined by diffusion of reactants into the internal volume of the solid phase. In the following model we consider that hydrolyzed biomaterial particle is in a form of "infinite plate" of larger thickness. Therefore the rate of hydrolysis depends on the diffusion of alkali to the internal volume of hydrolyzed particles. Under these assumptions, the process takes a very long time.

To determine the dependence of the total process time on costs (cost function) is needed to determine the concentration of soluble protein product $c_{s,D}$ on the time of hydrolysis. Diffusion of alkali in biomaterial can be described by Flick's second law (6). The initial and boundary conditions of process are described by equations (7) – (10):

$$\frac{\partial c}{\partial \tau}\left(x,\tau\right) = \frac{D}{1+K}\frac{\partial^2 c}{\partial x^2}\left(x,\tau\right), \quad \left(0 \le x \le b, \tau > 0\right). \quad (6)$$

We suppose symmetrical effect of alkali in biomaterials. It is given by equation (7):

$$\frac{\partial c}{\partial x}\left(0,\tau\right) = 0. \quad (7)$$

The initial concentration of alkali in biomaterial is described equation by (8):

$$c\left(x,0\right) = 0. \quad (8)$$

Condition (9) describes perfectly mixing of liquid phase in reactor:

$$c\left(b,0\right) = \varepsilon \cdot c_{s,D}. \quad (9)$$

Equality of the diffusion flux at the boundary between the solid and the liquid phases with the speed of accumulation of the diffusing element in the surroundings is given by balance equation (10):

$$-DS\frac{\partial c}{\partial x}\left(b,\tau\right) = V_0\frac{dc_0\left(\tau\right)}{d\tau}. \quad (10)$$

The analytical solution of model (6) – (10) we obtained by Laplace transformation. Then concentration of soluble protein product $c_{s,D}$ on the time of hydrolysis is given by equation (11):

$$c_{s,D} = \frac{\varepsilon \cdot c_{s,C}}{\varepsilon + Na} - 2\frac{Na \cdot c_{s,OP}}{\varepsilon}\sum_{n=1}^{\infty}\frac{e^{-Fo \cdot q_n^2}}{\varepsilon + Na + \frac{q_n^2 Na^2}{\varepsilon}}, \quad (11)$$

where Na is ratio of volume of liquid phase V_0 in reactor to volume of hydrolyzed biomaterial V_B (12):

$$Na = \frac{V_0}{V_B}, \quad (12)$$

Fo is Fourier number (dimensionless time of hydrolysis) (13):

$$Fo = \frac{D \cdot \tau}{b^2}. \quad (13)$$

Roots q_n are computed from transcendental equation (14):

$$-\frac{Na \cdot q}{\varepsilon} = \tan\left(q\right). \quad (14)$$

During hydrolysis of very small particles, the internal diffusion can be neglected. Then it holds:

$$\frac{dc}{d\tau} = k_1\left(1 - \frac{c_{s,D}}{c_{s,o}}\right). \quad (15)$$

After integration:

$$c_{s,D} = c_{s,o}\left(1 - e^{-k_1\tau}\right), \quad (16)$$

where k_1 is a rate constant of hydrolysis reaction. The equilibrium concentration $c_{s,o}$ can be determined from the mass balance (17):

$$c_{s,o} = \frac{c_{s,D}m_B}{m_1 + m_{AB}}. \quad (17)$$

Concentration fields of alkali in the solid material during dechromation are shown in Fig. 1, Fig.2.

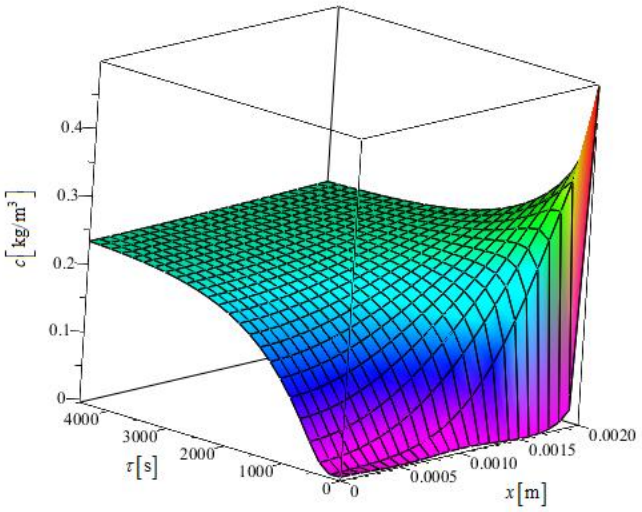

Fig. 1 Concentration field of alkali in the solid phase

$Na = 5$, $A = 10$, $b = 0.002$ m; $D = 2 .10^{-8}$ m^{2}s^{-1}; $V = 1$m^3; $\varepsilon = 0.5$, $V_0 = 5$ m^3.

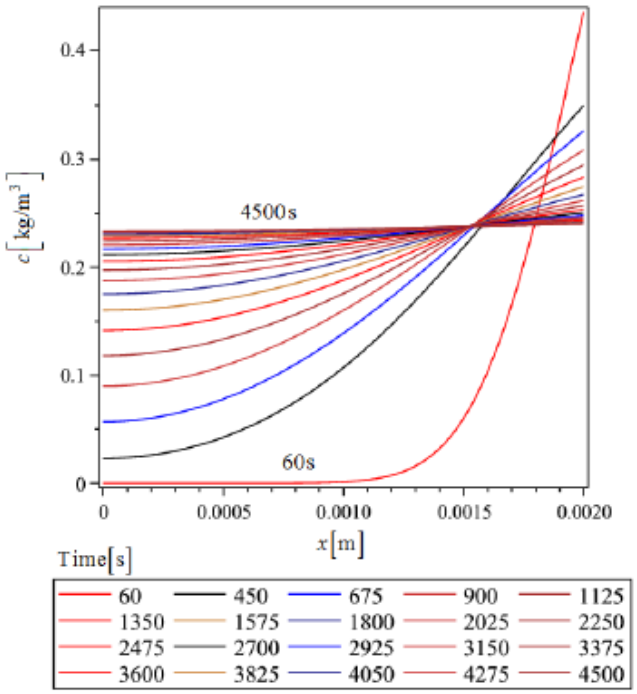

Fig. 2 Concentration fields of alkali in specific time of dechromatization

$Na = 5$, $A = 10$, $b = 0.002$ m; $D = 2 .10^{-8}$ m^{2}s^{-1}; $V = 1$m^3; $\varepsilon = 0.5$, $V_0 = 5$ m^3.

III. Determination of Operating Costs for Enzymatic Hydrolysis

For the calculation of the major operating costs we used the manufacturing scheme given in Fig. 3. It includes the pretreatment of the waste biomaterial before hydrolysis (maceration, denaturation and filtration) and operations after the hydrolysis, by which is obtained pure product (filtration and isolation), [6], [7], [8].

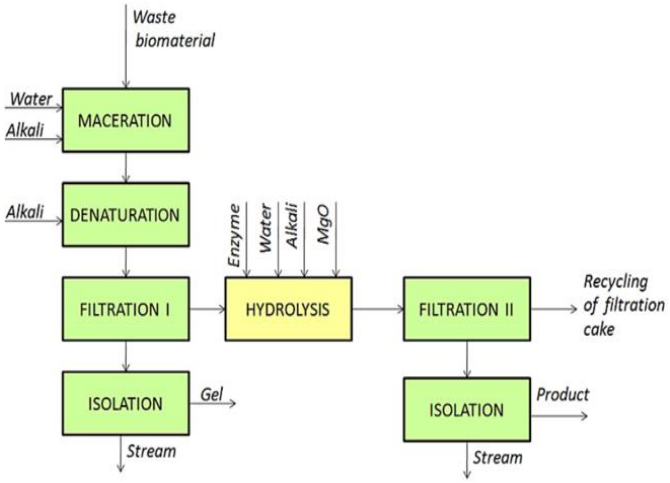

Fig. 3 Enzymatic hydrolysis - manufacturing scheme

The total unit operating costs N_T mainly include the unit costs of hydrolysis N_H and the unit costs of concentration of protein hydrolysate after separation of the heterogeneous reaction mixture N_C. Other unit costs include the price of chemicals, water and heat loss from the reactor into the environment N_O. Then it holds:

$$N_T = N_H + N_C + N_O, \tag{18}$$

where unit price of hydrolysis depends on energy consumption for propulsion of reactor, time of hydrolysis to weight of the product:

$$N_H = \frac{P \cdot K_E \cdot \tau}{m_p}. \tag{19}$$

Unit price of protein hydrolysate concentration is given by consumption on heat energy for evaporation of water:

$$N_H = \frac{P \cdot K_E \cdot \tau}{m_p}, \tag{20}$$

where weight of evaporated water m_{EW} and weight of product m_P are computed from mass balance of the process (21), (22):

$$m_{EW} = \frac{m_p c_{s,P}}{c_{s,D}} - 1, \qquad (21)$$

$$m_p = \frac{c_{s,D}\left\lfloor m_B\left(c_{s,C} - c_{s,FK}\right) - c_{s,FK}\left(m_A + m_{WR}\right) + m_{MgO}\right\rfloor}{c_{s,P}\left(c_{s,D} - c_{s,FK}\right)}. \qquad (22)$$

The other unit operating costs can be computed according to equation (23):

$$N_0 = \frac{c_{s,P}\left(c_{s,D} - c_{s,FK}\right)\left\lfloor m_B\left(c_C.K_{Mgo} + c_{s,B}.K_{SB} + c_v.K_v\right) + k_P.\Delta t.S\tau.K_s + n.K_L.\tau\right\rfloor}{c_{s,D}\left[m_B\left(c_{s,C} - c_{s,FK}\right) - \left(m_A + m_{VR}\right)c_{s,FK} + m_{MgO}\right]}. \qquad (23)$$

In the Fig. 4 is shown the cost function in the case of diffusion mechanism. Its minimum indicates an optimal time of the process.

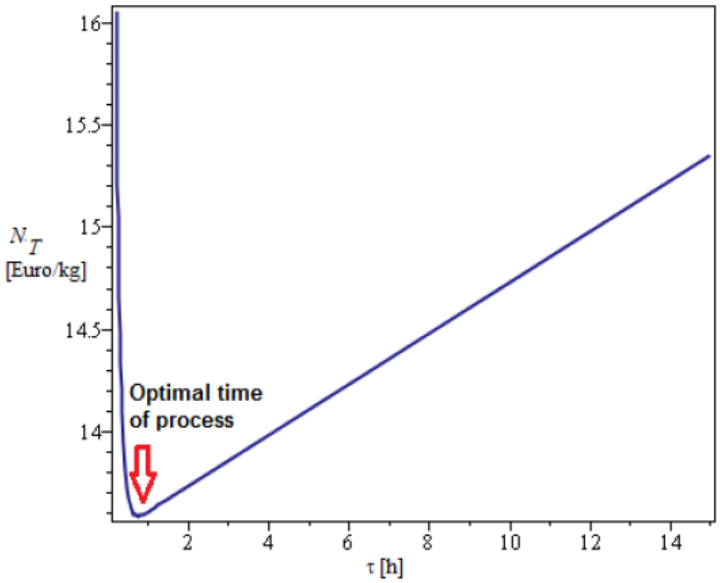

Fig. 4 Cost function for enzymatic hydrolysis

b = 1 mm; ε = 0.5; $D = 3.6 \cdot 10^{-6}$ m^2 · h^{-1}; V_B = 1 m^3; V_0 = 10 m^3; $c_{s,FK}$ = 0.17; $c_{s,C}$ = 0.5; c_C = 0.02; c_V = 5; $c_{s,B}$ = 0.03; $c_{s.OP}$ = 0.05; m_B = 800 kg; Δt = 48 °C;r = 2600 kJ · kg^{-1}; P = 10 kW; k_p = 60 W·m^{-2} ·K^{-1}; K_L = 2.5 Euro·h^{-1}; K_S = 1.8·10^{-7} Euro·J^{-1};K_E = 0.3 Euro·kWh^{-1}; K_V = 1:5 Euro·kg^{-1}; K_{MgO} = 0.76 Euro·kg^{-1}.

IV. OMPUTER CALCULATION OF COST CURVES BY MAPLE

For automatic control of enzymatic hydrolysis is necessary to determine the optimal time of process on the base of suggested deterministic mathematic model. For programming of this algorithm MAPLE offers four types of user interfaces.

The Classic Worksheet which provides a worksheet environment for older computers with limited memory. The Standard Worksheet that contains the full-featured interface. The Maplet user interface allows you to create windows, dialogs, and other visual interfaces that interact with a user to provide the power of MAPLE.

A. Computing of the cost curves in the Standard Worksheet interface

In the following text we show main parts of source code for computing of the cost curves in the case of diffusion mechanism (i.e. when the dependence of weight ratio of dry matter in diluted filtrate on time of hydrolysis can by described according equation (11)).

First, all the necessary mathematical relationships and parameters described in previous section are defined:

```
> NT:=NH+NC+NO;
```

$$NT := NH + NC + NO$$

```
> NH:=(P*KE*tau)/mp;
```

$$NH := \frac{P\,KE\,\tau}{mp}$$

```
> NC:=(mEW*r*KS)/mp;
```

$$NC := \frac{mEW\,r\,KS}{mp}$$

```
> NO:=csP*(mB*(cC*KMgO+csB*KsB+cV*
KV+kp*3600*deltat*S*tau*KS+n*KL*
tau)*(csD-csFK)/((mB*(csC-csFK)-
(mA+mVR)*csFK+mMgO)*csD);
```

$$NO := \left(csP\left(mB\left(cC\,KMgO + csB\,KsB + cV\,KV\right) + 3600\,kp\,deltat\,S\,\tau\,KS + n\,KL\,\tau\right)\left(csD - csFK\right)\right) \Big/ \left(\left(mB\left(csC - csFK\right) - \left(mA + mVR\right)csFK + mMgO\right)csD\right)$$

$$\vdots$$

After them, roots of the transcendental equation (14) are calculated:

```
> for i from 1 to 100 do
> q[i]:=fsolve(tan(q)+Na*q/(epsilon)=0,q=(
i-0.5)*Pi..i*Pi):
> od;
```

$$q_1 := 1.601997238$$

$$q_2 := 4.722975132$$

$$\vdots$$

Then dependency of weight ratio of dry matter in diluted filtrate on time is calculated and displayed (Fig.5):

```
> plot(csD,tau=taumin..taumax,axes=box,
labels=["tau(h)","csD (1)"]);
```

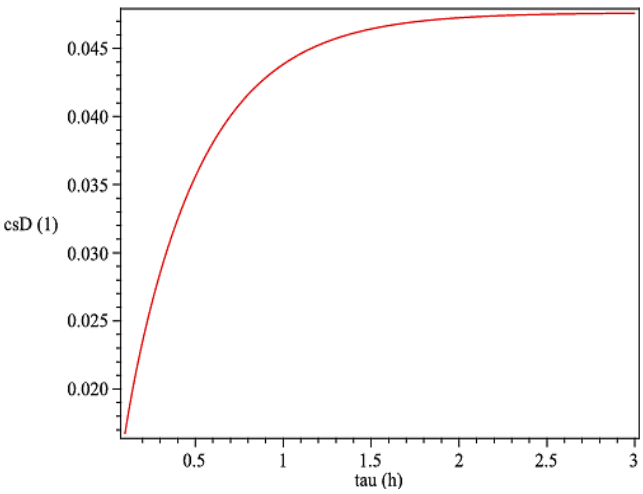

Fig. 5 Dependence of weight ratio of dry matter in diluted filtrate on time of hydrolysis computed by MAPLE

b = 2 mm, ε = 0.5, D = 3.6·10^{-6} m^2.h^{-1}, V_B = 1 m^3, V_0 = 10 m^3, $c_{s,FK}$ = 0.17, $c_{s,c}$ = 0.5, c_C = 0.02, c_v = 5, c_{sB} = 0.03, $c_{s,0P}$ = 0.05, m_B = 800 kg, Δt = 48 °C, K_L = 50 Euro.h^{-1}, r = 2260 kJ.kg^{-1}, P = 10 kW, k_p = 60 W.m^{-2}.K^{-1}.

Finally, the cost curve is calculated and displayed (Fig. 6):

```
> plot(NT,tau=0.1..8,axes=box,
labels=["tau(h)","NT (Euro/kg)"]);
```

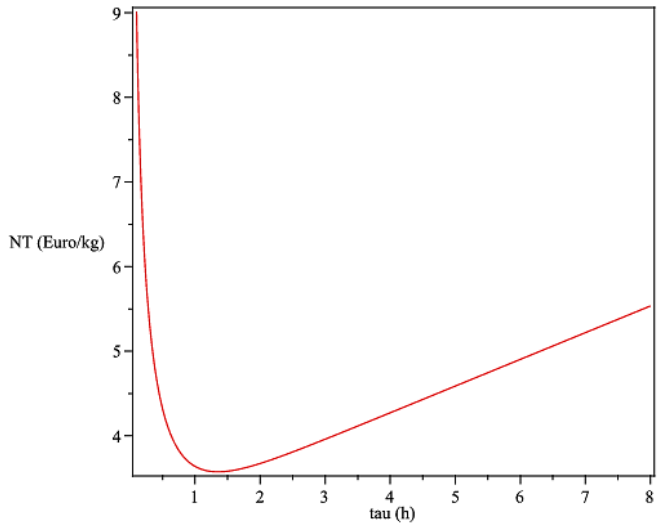

Fig. 6 Cost function computed by MAPLE

b = 2 mm, ε = 0.5, D = 3.6·10^{-6} m^2.h^{-1}, V_B = 1 m^3, V_0 = 10 m^3, $c_{s,FK}$ = 0.17, $c_{s,c}$ = 0.5, c_C = 0.02, c_v = 5, c_{sB} = 0.03, $c_{s,0P}$ = 0.05, m_B = 800 kg, Δt = 48 °C, K_L = 50 Euro.h^{-1}, , r = 2260 kJ.kg^{-1}, P = 10 kW, k_p = 60 W.m^{-2}.K^{-1}, K_S = 1.8·10^{-7} Euro.J^{-1}, K_E = 4 Euro.kWh^{-1}, K_V = 0.05 Euro.kg^{-1}, K_{MgO} = 0.76 Euro.kg^{-1}

The computed data are displayed in the table (spreadsheet), as is shown in Fig. 7.

Computed costs

	A	B	C	D	E
1	"Time (h)"	"NT (Euro/kg)"			
2	0.1000	9.0148			
3	0.8900	3.6994			
4	1.6800	3.6060			
5	2.4700	3.8008			

Fig. 7 Table with computed data

V. Computing of the Cost Curves in the Maplet User Interface

This interface we used for calculating of cost curves in the case of the kinetic mechanism. In this case, the dependence of weight ratio of dry matter in diluted filtrate on time of hydrolysis can by described according equation (17). The advantage of this interface over the source code in the Standard Worksheet user interfaces clarity insertion of input values and comfortable displaying of the results through defined text fields, buttons, and graphics tools in the programmed windows. The Maplet structure can be defined by commands:

```
> use Maplets:-Elements
> maplet := Maplet( onstartup =
RunWindow( W1 ),
> Window[W1](...),
> Window[W2](...),
> Window[W3](...),
      ...
Window[W10](...),
);
end use:
Maplets:-Display( maplet);
```

The programmed application for computing the costs curves in case of kinetic mechanism has these main parts:

- Initial window with text fields for insertion input parameters (see Fig. 8).
- Calculation of dependence of concentration of soluble product cs,D on time of the process (Fig. 9).
- Calculation of the cost curve (Fig. 9).
- Calculation of the total operating costs for required time of hydrolysis (Fig. 9).

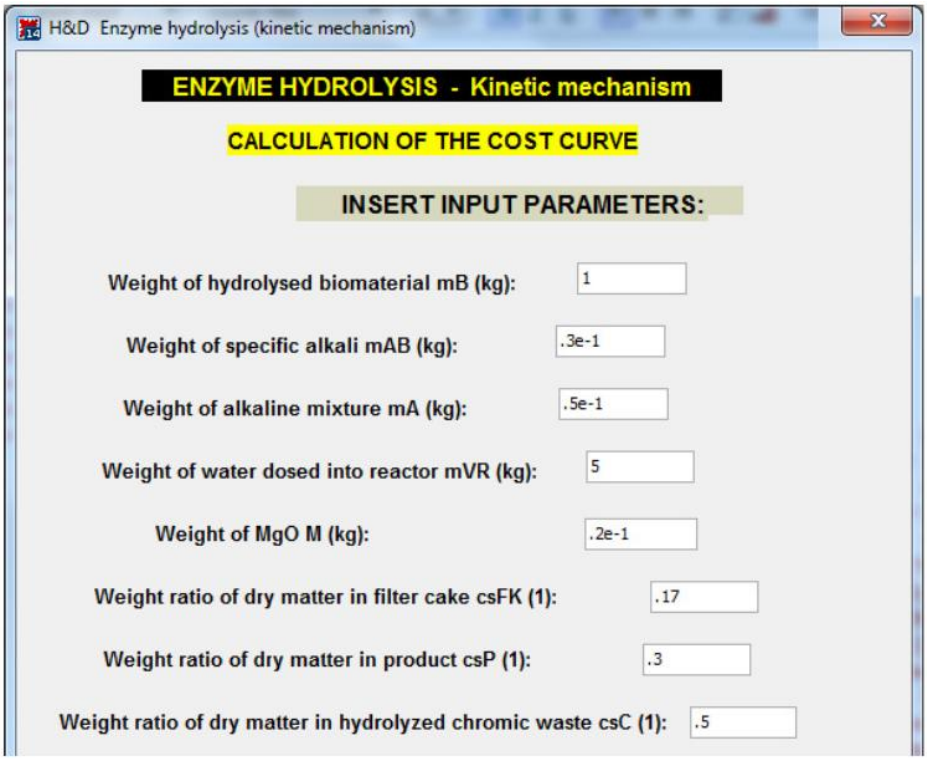

Fig. 8 User interface of software application for computing the cost curves by enzymatic hydrolysis - window for insertion input parameters

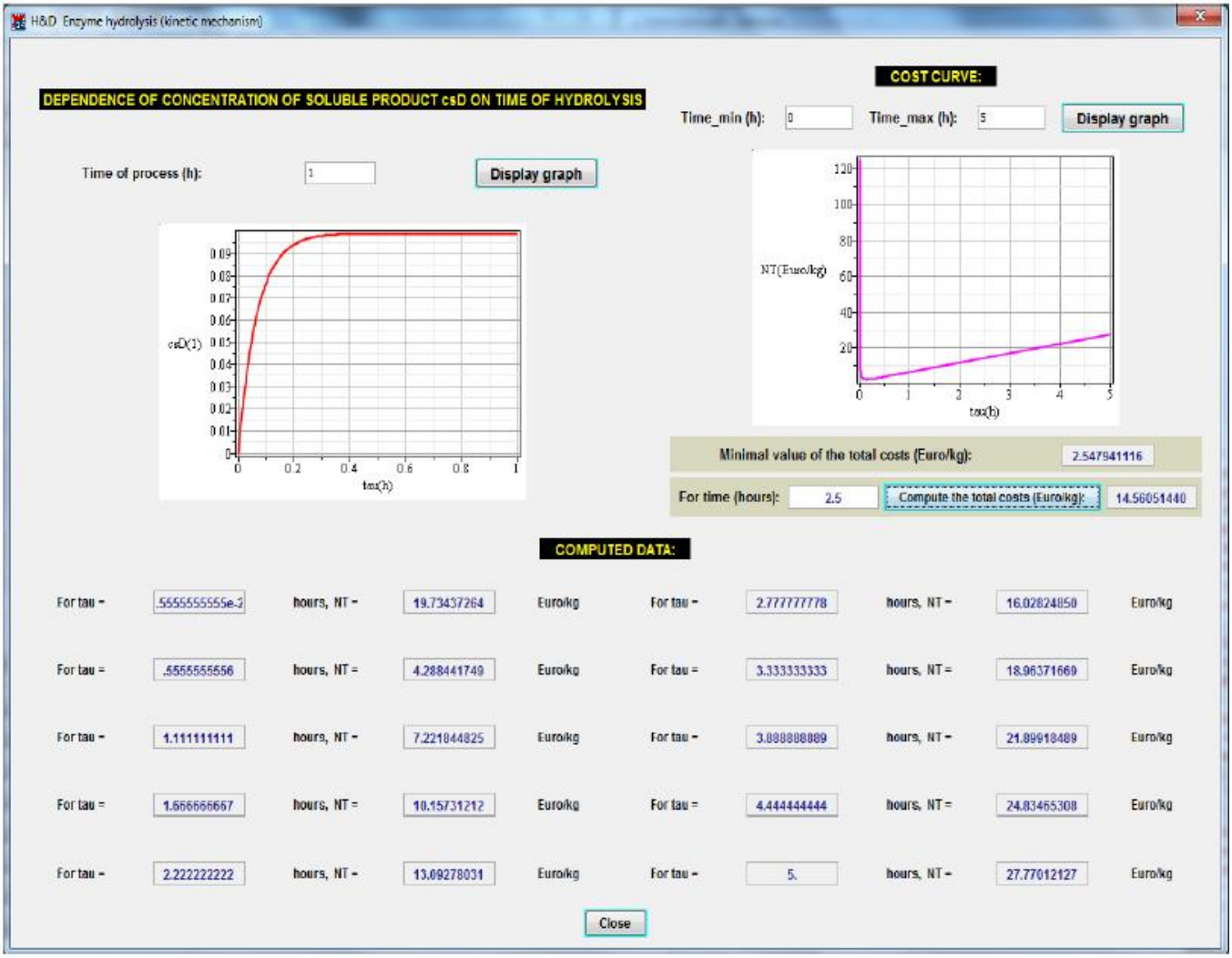

Fig. 9 User interface of software application for computing the cost curves by enzymatic hydrolysis - window for computing the cost curves

VI. Conclusion

The formulated mathematical model describing the dependence of the quantity of a protein hydrolysate on time of hydrolysis enabled us to programme algorithms for computing of operating costs by the processing of biomaterial waste to protein hydrolysates as in the case of kinetic mechanism, as with the diffusion mechanism. Data computed as in the case of kinetic mechanism, as with the diffusion mechanism allow to determine the optimum process to the purpose of saving energy and raw materials. In case of diffusion mechanism, the calculation was programmed in Standard Worksheet user interface.

In case of kinetic mechanism the calculation was programmed in Maplet user interface. The advantage of this interface over the source code in the Standard Worksheet user interface is clarity insertion of input values and comfortable displaying of the results. Therefore we will also prepare application for computing of operating costs by diffusion mechanism in Maplet user interface.

VII. List of Symbols

c - concentration of alkali in biomaterial, [kg·m^{-3}];
c_0 - concentration of alkali in reactive mixture, [kg·m^{-3}];
$c_{s,O}$ - equilibrium concentration of alkali in reactive mixture, [kg·m^{-3}];
$c_{s,P}$ - weight ratio of dry matter in product, [1];
$c_{s,D}$ - weight ratio of dry matter in diluted filtrate, [1];
$c_{s,OP}$ - weight ratio of dry matter in macerated mixture, [1];
$c_{s,FK}$ - weight ratio of dry matter in filter cake, [1];
$c_{s,C}$ - weight ratio of dry matter in hydrolyzed chromic waste, [1];
c_c - weight ratio of MgO to weight of hydrolyzed biomaterial, [1];
$c_{c,B}$ - weight ratio of alkali to weight of hydrolyzed biomaterial, [1];
c_V - weight ratio of water to weight of hydrolyzed biomaterial, [1];
b - half thickness of hydrolyzed biomaterial, [m];
D - effective diffusion coefficient, [m^2·s^{-1}];

Fo - Fourier number (dimensionless time), [1];
K - sorption capacity of hydrolyzed biomaterial, [1];
k_1 - rate constant of hydrolysis reaction, [h^{-1}];
k_p - heat passage coefficient, [$W \cdot m^{-2} \cdot K^{-1}$];
K_A - unit price of alkali, [$Euro \cdot kg^{-1}$];
K_E - unit price of the absorbed electrical power, [$Euro \cdot kg^{-1}$];
K_{MgO} - unit price of MgO, [$Euro \cdot kg^{-1}$];
K_V - unit price of water, [$Euro \cdot kg^{-1}$];
K_S - unit price of heat energy, [$Euro \cdot J^{-1}$];
K_L - time rate, [$Euro \cdot h^{-1}$];
m_A - weight of alkaline mixture, [kg];
m_B - weight of hydrolyzed biomaterial, [kg];
m_{EW} - weight of evaporated water, [kg];
m_{MgO} - weight of MgO, [kg];
m_P - weight of product, [kg];
m_{WR} - weight of water dosed into reactor, [kg];
n - number of degrees of hydrolysis, [-];
N_T - total processing costs, [$Euro \cdot kg^{-1}$];
N_H - costs of hydrolysis, [$Euro \cdot kg^{-1}$];
N_C - costs of the protein solution concentrate, [$Euro \cdot kg^{-1}$];
N_O - other costs, [$Euro \cdot kg^{-1}$];
Na - ratio of volume of liquid reactive mixture to volume of dry matter of hydrolyzed biomaterial, [1];
P - power requirement of the pump electrical engine, [kW];
q - roots of transcendental equation, [-];
r - vaporization heat of water, [$J \cdot kg^{-1}$];
t - temperature, [°C];
V_0 - volume of liquid reactive mixture, [m^3];
V_B - volume of dry matter of hydrolyzed biomaterial, [m^3];
x - space coordinate, [m];
X - dimensionless space coordinate, [1];
ε - porosity of biomaterial, [1];
τ - time, [s].

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