Summer School
Biological and Thermal Treatment of Municipal Solid Waste
Napoli, Italy, 2-6 May 2011

Modelling of Anaerobic Co-Digestion of Organic Solid Waste

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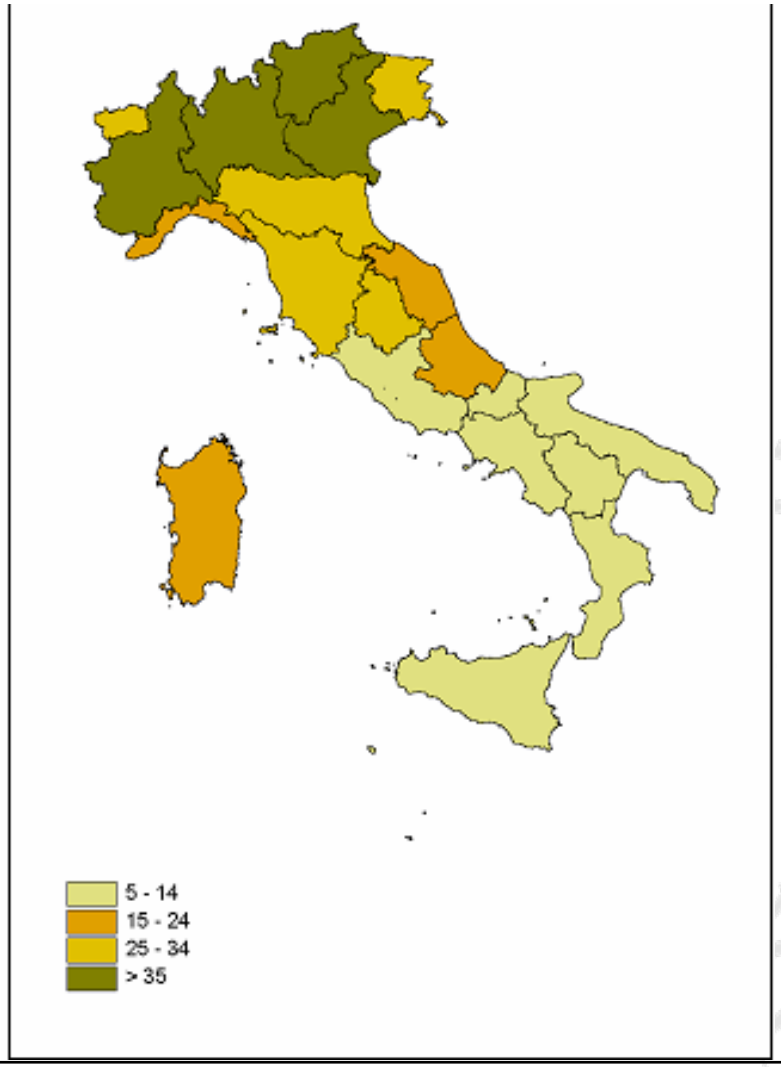
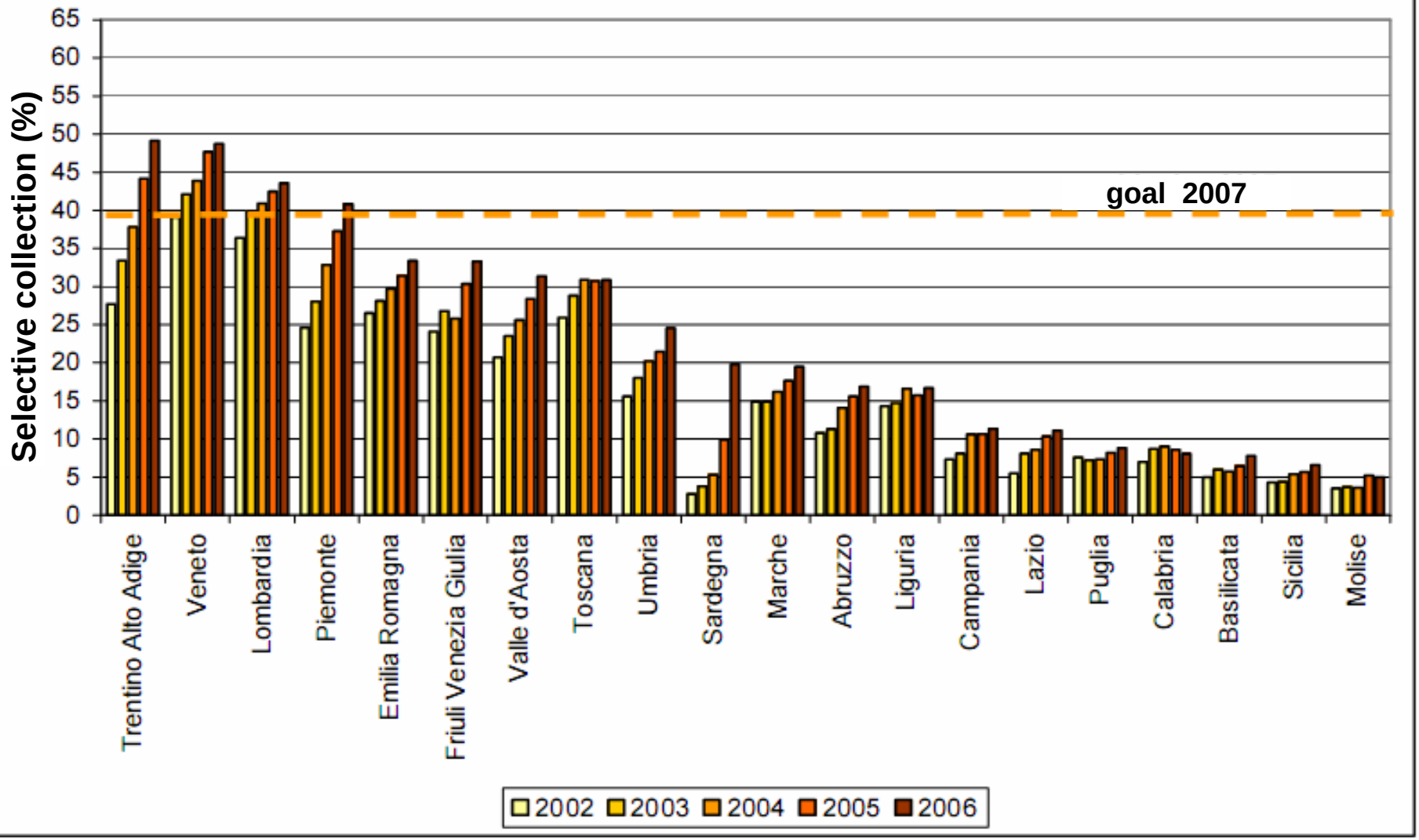
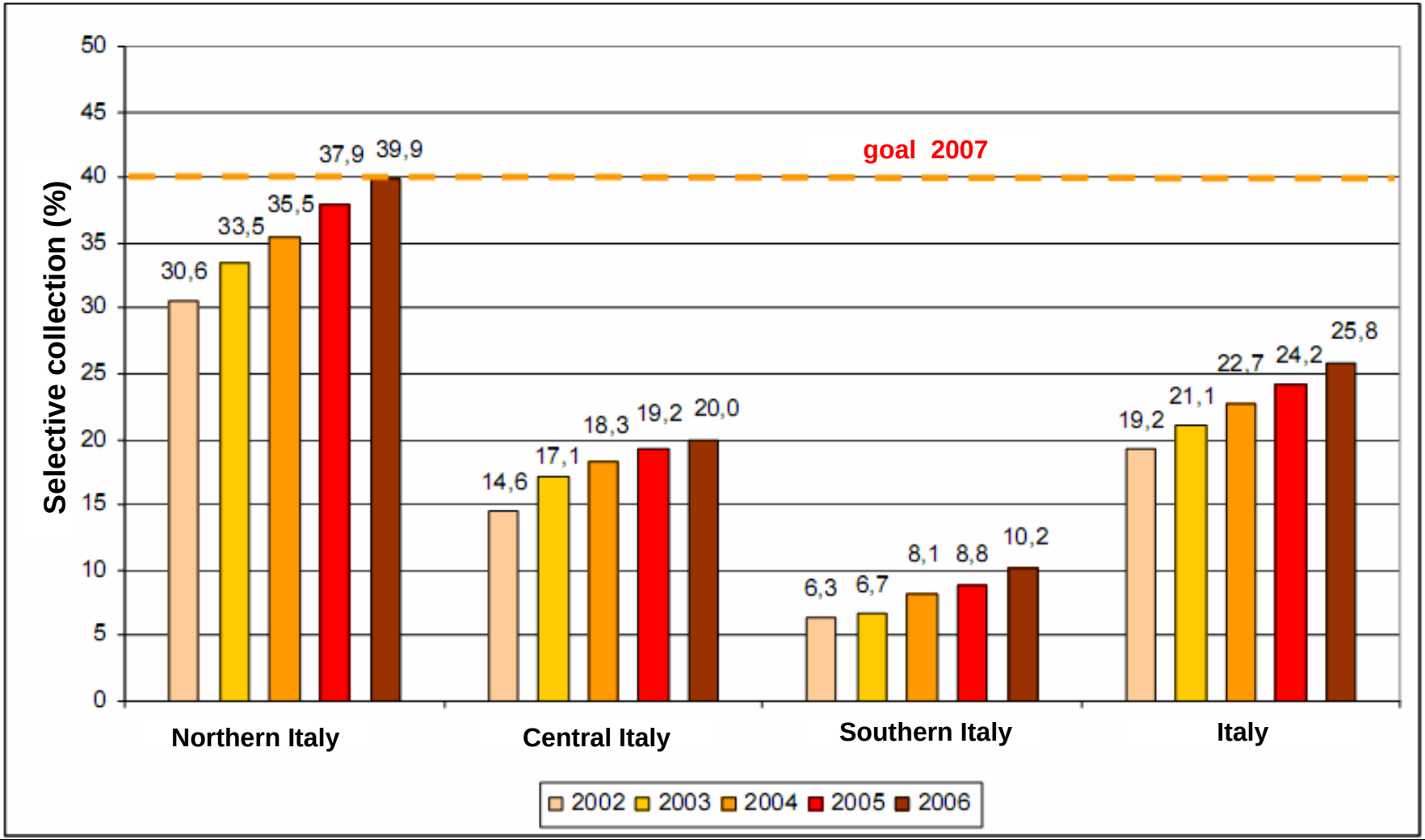
Introduction
(MSW Selective Collection in Italy)



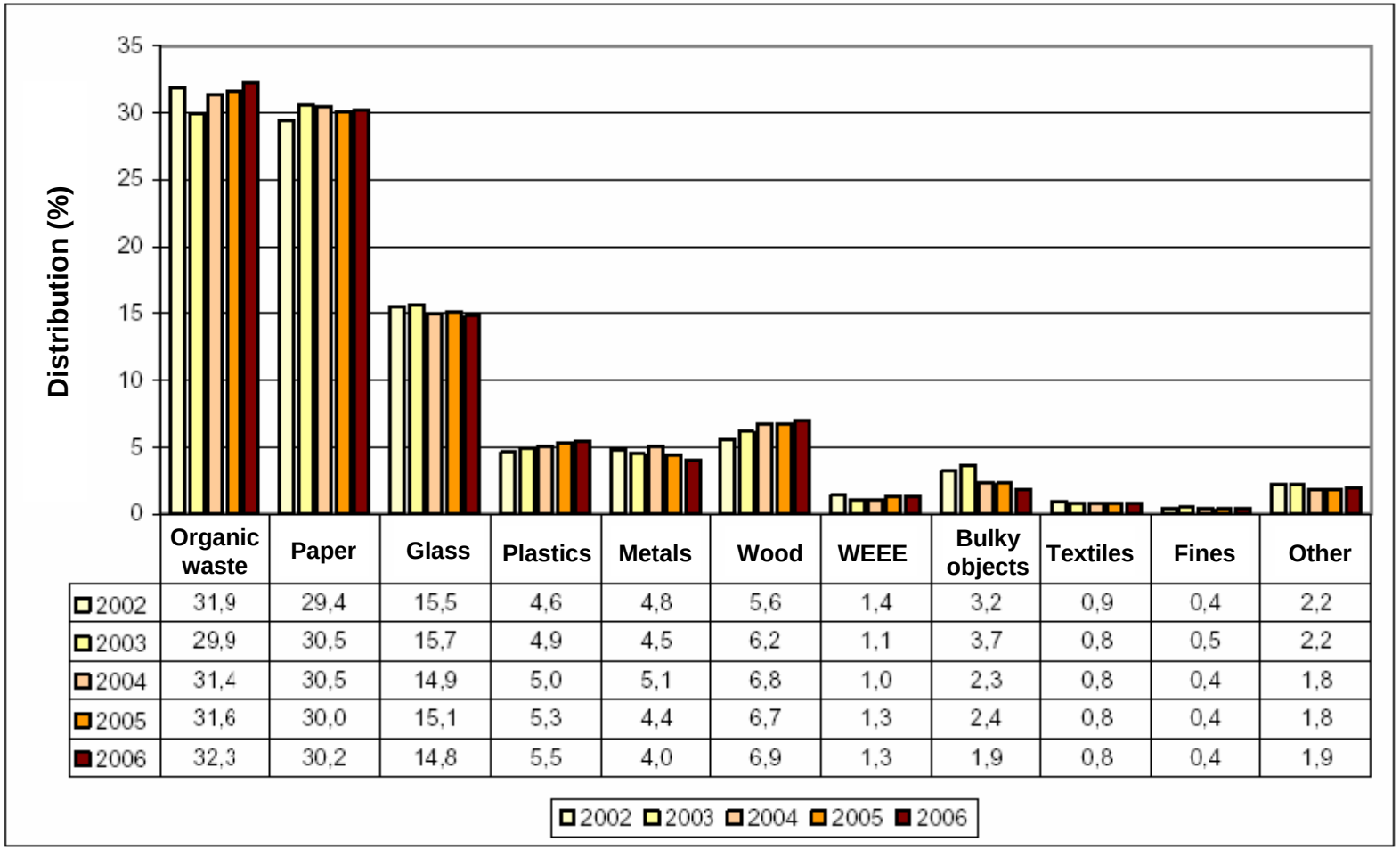
MSW Selective Collection in Italian Regions



MSW Selective Collection in Italian Macro-Regions

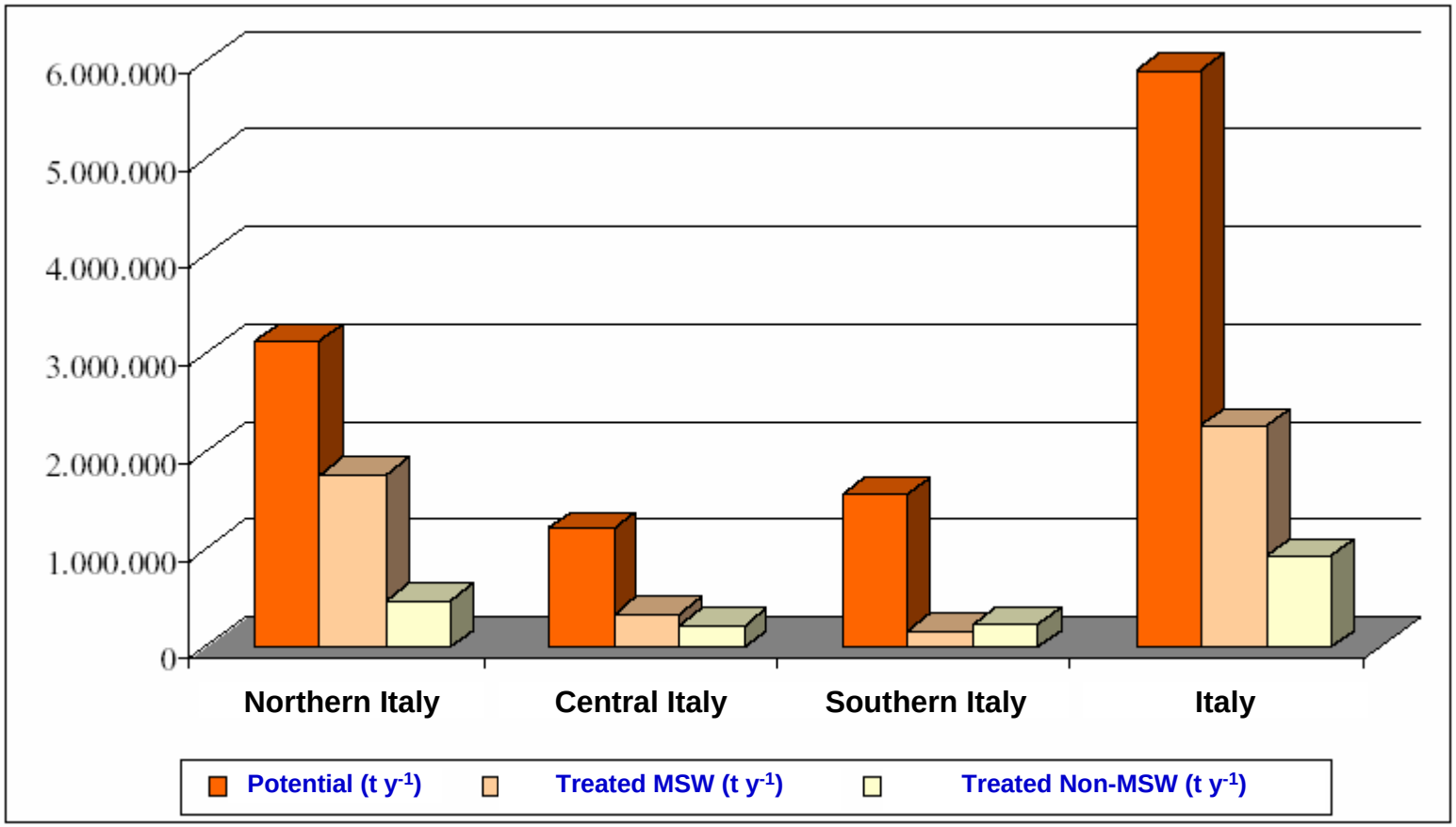


MSW Selective Collection in Italy (Selected Fractions)

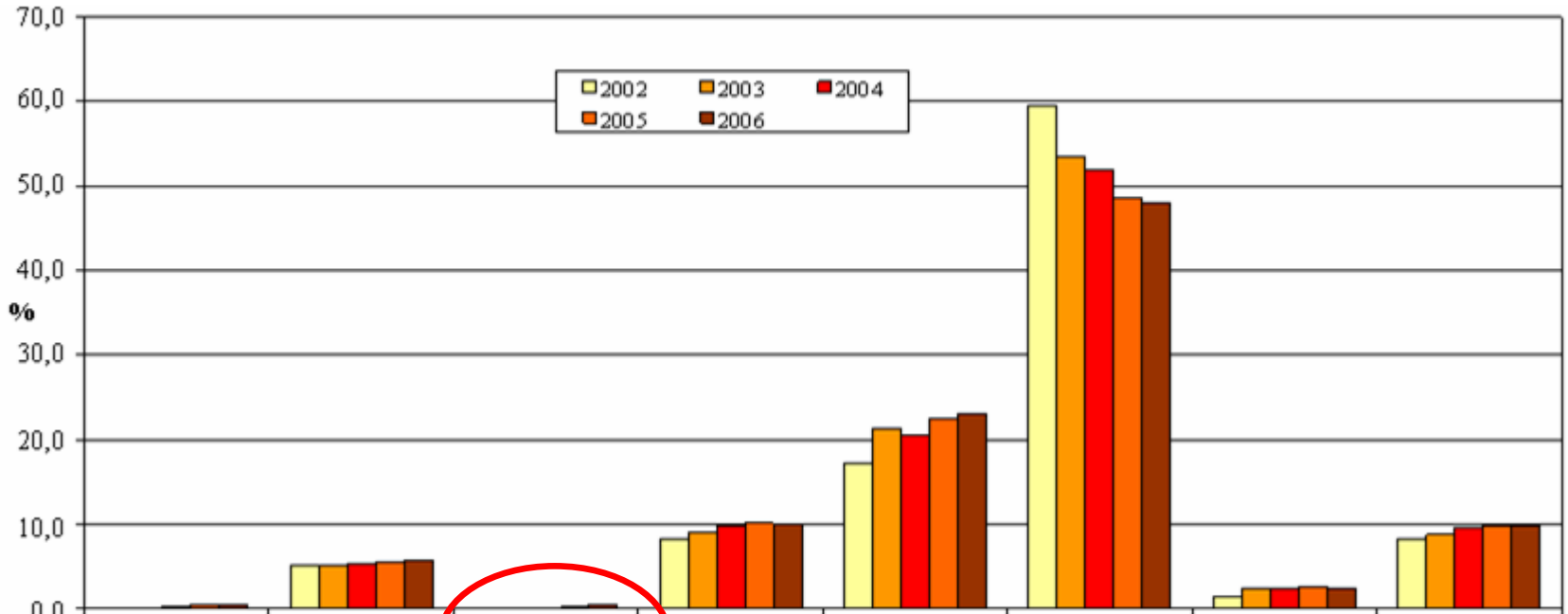


	Organic waste	Paper	Glass	Plastics	Metals	Wood	WEEE	Bulky objects	Textiles	Fines	Other
2002	31,9	29,4	15,5	4,6	4,8	5,6	1,4	3,2	0,9	0,4	2,2
2003	29,9	30,5	15,7	4,9	4,5	6,2	1,1	3,7	0,8	0,5	2,2
2004	31,4	30,5	14,9	5,0	5,1	6,8	1,0	2,3	0,8	0,4	1,8
2005	31,6	30,0	15,1	5,3	4,4	6,7	1,3	2,4	0,8	0,4	1,8
2006	32,3	30,2	14,8	5,5	4,0	6,9	1,3	1,9	0,8	0,4	1,9

Composting Plants: SW Treated vs Potential



MSW Management in Italy



	Energetic source	Compost	Anaerobic digestion	Incineration	Mechanical biological treatment	Landfill	Campania RDF	Other recovery systems
2002	0,1	5,2	0,0	8,3	17,1	59,5	1,5	8,3
2003	0,1	5,1	0,0	8,9	21,2	53,4	2,4	8,8
2004	0,3	5,4	0,0	9,8	20,4	51,8	2,5	9,7
2005	0,5	5,6	0,2	10,2	22,5	48,6	2,6	9,8
2006	0,5	5,8	0,4	10,1	23,1	47,9	2,4	9,7

ADVANCED TREATMENTS FOR ORGANIC WASTE REUSE AND ENERGY RECOVERY

(National Research Project of the Italian Ministry for Research and University)

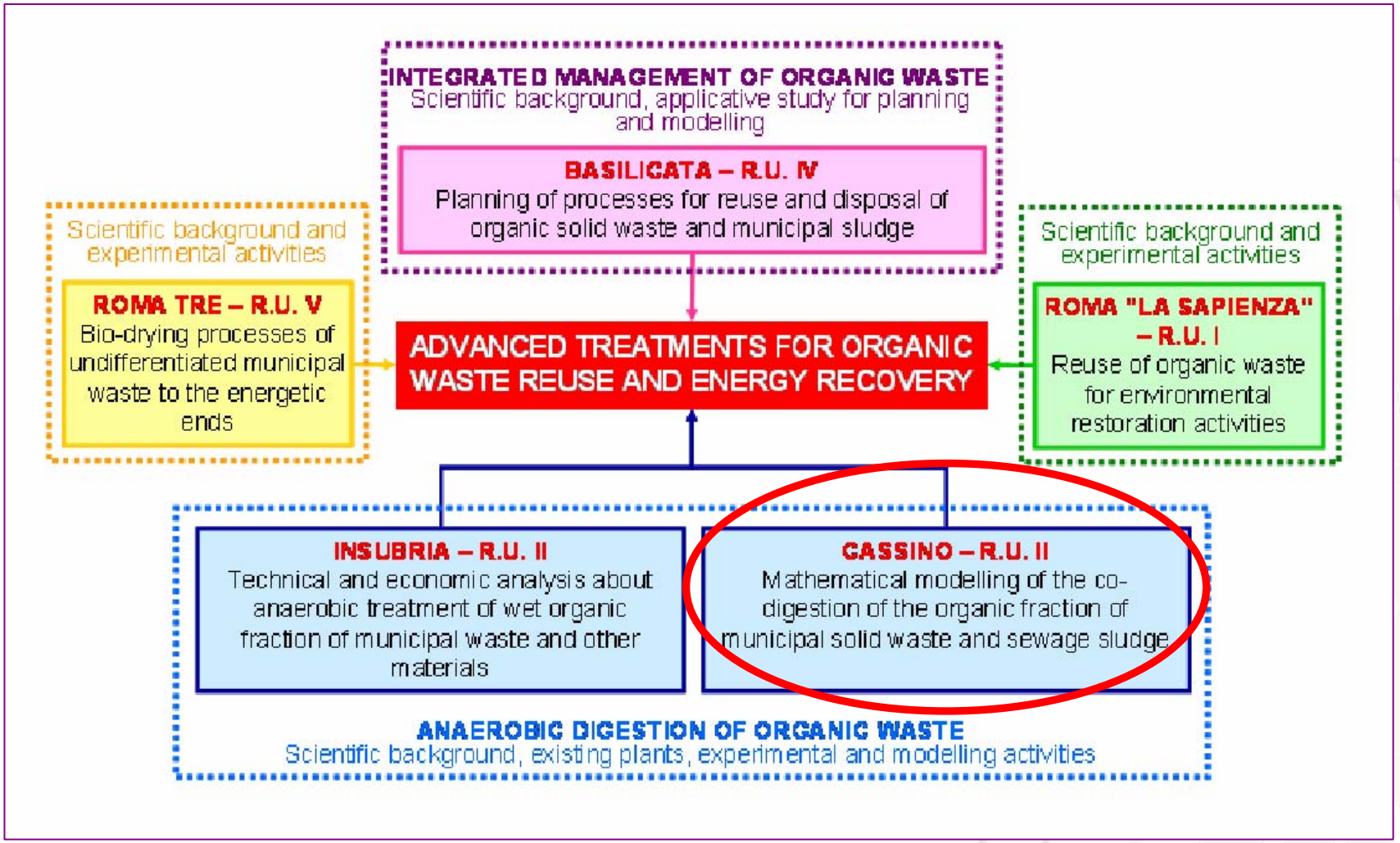
Subject:

- Energy recovery ⟶ biogas production
- Material reuse ⟶ land restoration

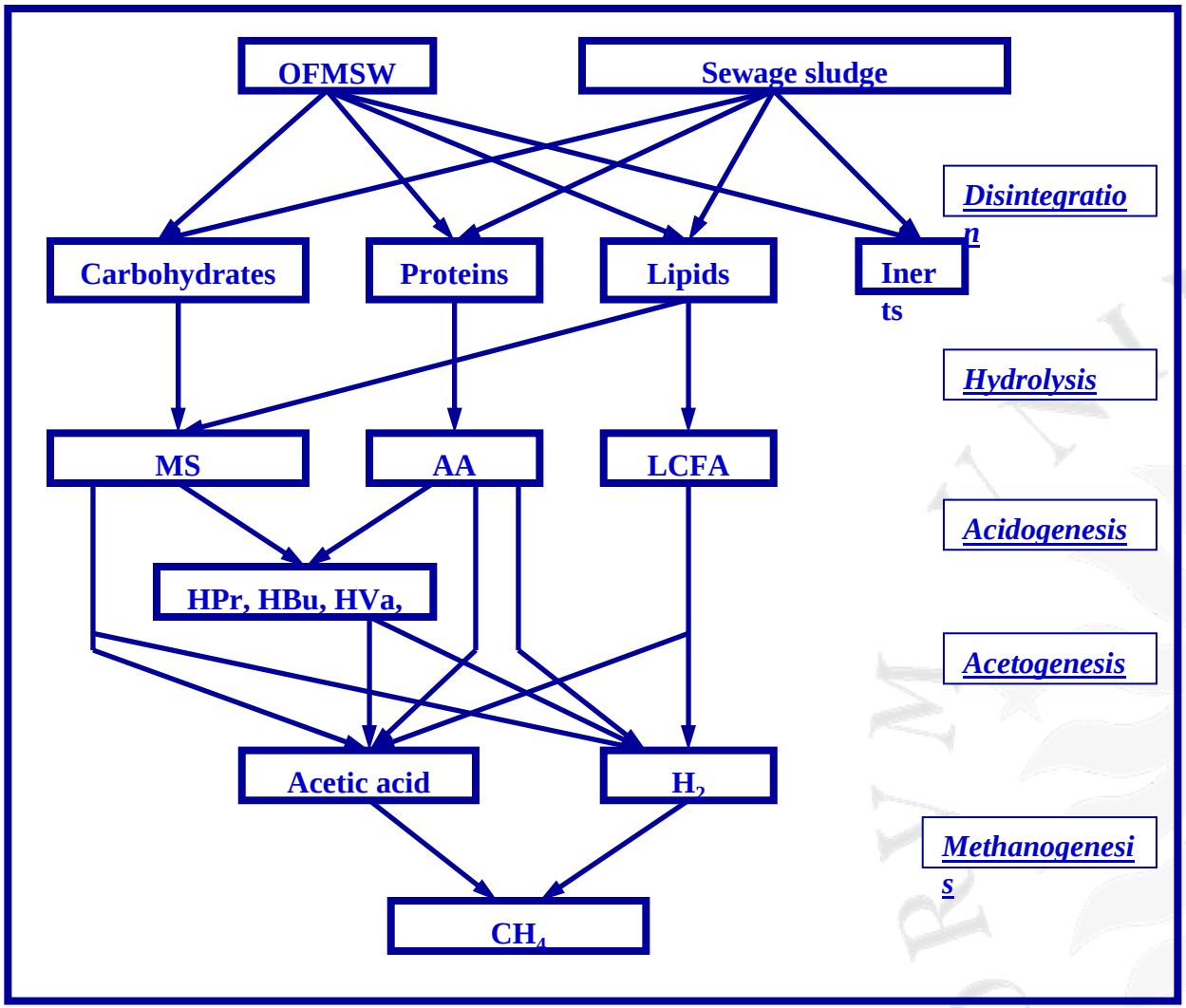
Tasks/Objectives:

- Planning, management and optimization of sewage sludge and OFMSW Co-digestion in Italy
- Technical-economical assessment
- Mathematical modelling
- Environmental restoration

Research Project Structure



Conversion Pathways in the Model



Mass Balance Equations

$$\frac{dS}{dt} = \frac{q}{V_{liq}}\left(S_{in} - S\right) + \sum_{j=1..N} \rho_j \nu_j$$

$$\frac{d[S]_{(g)}}{dt} = \frac{V_{liq}}{V_{gas}} k_{La}\left([S]_{(l)} - [S*]_{(l)}\right) - \frac{Q_{out,g}}{V_{gas}}[S]_{(g)}$$

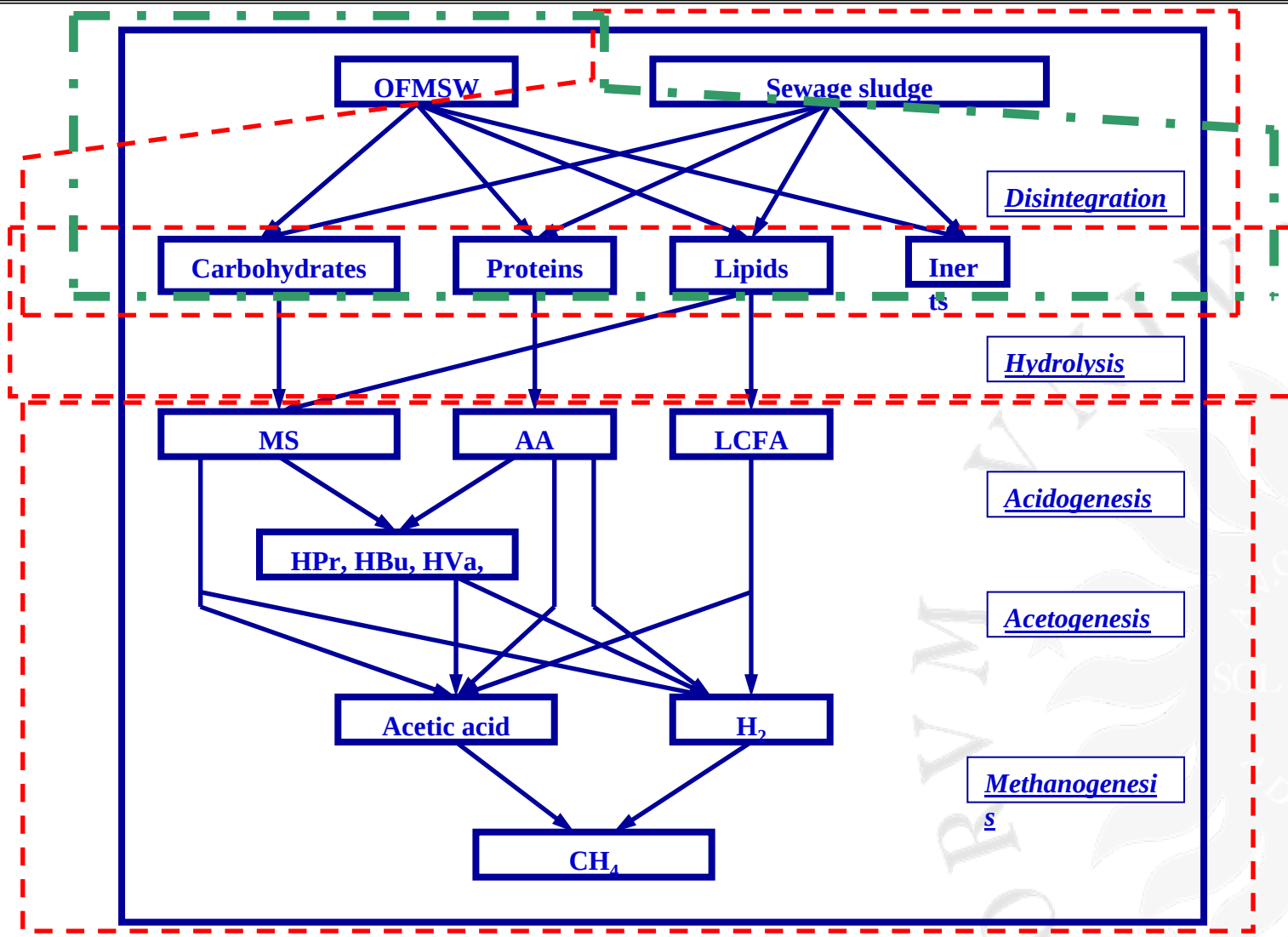
Matrix of model equations – Part 1

	Component →	1	2	3	4	5	6	7	8	9	10	11	12	$rate \rho_j [kgCOD \cdot m^{-3} \cdot d^{-1}]$
	Process ↓	S_{su}	S_{aa}	S_{fa}	S_{va}	S_{bu}	S_{pro}	S_{ac}	S_{h2}	S_{CH4}	S_{IC}	S_{IN}	S_I	
1	Disintegration of OFMSW												f_{sI_Xc}	$K_{sbk} \cdot C \cdot a^*$
2	Disintegration of Sludge													$K_{dis\_Slu} \cdot X_{Slu}$
3	Hydrolysis of Carbohydrates (readily)	1												$K_{hyd\_ch\_R} \cdot X_{ch\_R}$
4	Hydrolysis of Carbohydrates (slowly)	1												$K_{hyd\_ch\_S} \cdot X_{ch\_S}$
5	Hydrolysis of Proteins (readily)		1											$K_{hyd\_pr\_R} \cdot X_{pr\_R}$
6	Hydrolysis of Proteins (slowly)		1											$K_{hyd\_pr\_S} \cdot X_{pr\_S}$
7	Hydrolysis of Lipids (readily)	$1-f_{fa,li}$		$f_{fa,li}$										$K_{hyd\_li\_R} \cdot X_{li\_R}$
8	Hydrolysis of Lipids (slowly)	$1-f_{fa,li}$		$f_{fa,li}$										$K_{hyd\_li\_S} \cdot X_{li\_S}$
9	Uptake of Sugars	−1				$(1-Y_{su})f_{bu,su}$	$(1-Y_{su})f_{pro,su}$	$(1-Y_{su})f_{ac,su}$	$(1-Y_{su})f_{h2,su}$		$-\sum_{i=1,9-11,28} C_i \nu_{i,9}$	$-(Y_{su})N_{bac}$		$K_{m,su} \cdot \frac{S_{su}}{K_s + S_{su}} \cdot X_{su} \cdot I_1$
10	Uptake of Amino Acids		−1		$(1-Y_{aa})f_{va,aa}$	$(1-Y_{aa})f_{bu,aa}$	$(1-Y_{aa})f_{pro,aa}$	$(1-Y_{aa})f_{ac,aa}$	$(1-Y_{aa})f_{h2,aa}$		$-\sum_{i=1,9-11,28} C_i \nu_{i,10}$	$N_{aa}-(Y_{aa})N_{bac}$		$K_{m,aa} \cdot \frac{S_{aa}}{K_s + S_{aa}} \cdot X_{aa} \cdot I_1$
11	Uptake of LCFA			−1				$(1-Y_{fa})0.7$	$(1-Y_{fa})0.3$			$-(Y_{fa})N_{bac}$		$K_{m,fa} \cdot \frac{S_{fa}}{K_s + S_{fa}} \cdot X_{fa} \cdot I_2$
12	Uptake of Valerate				−1		$(1-Y_{C4})0.54$	$(1-Y_{C4})0.31$	$(1-Y_{C4})0.15$			$-(Y_{C4})N_{bac}$		$K_{m,C4} \cdot \frac{S_{va}}{K_s + S_{va}} \cdot X_{C4} \cdot \frac{1}{1+S_{bu}/S_{va}} \cdot I_2$
13	Uptake of Butyrate					−1		$(1-Y_{C4})0.8$	$(1-Y_{C4})0.2$			$-(Y_{C4})N_{bac}$		$K_{m,C4} \cdot \frac{S_{bu}}{K_s + S_{bu}} \cdot X_{C4} \cdot \frac{1}{1+S_{va}/S_{bu}} \cdot I_2$
14	Uptake of Propionate						−1	$(1-Y_{pro})0.57$	$(1-Y_{pro})0.43$		$-\sum_{i=1,9-11,28} C_i \nu_{i,14}$	$-(Y_{pro})N_{bac}$		$K_{m,pro} \cdot \frac{S_{pro}}{K_s + S_{pro}} \cdot X_{pro} \cdot I_2$
15	Uptake of Acetate							−1		$(1-Y_{ac})$	$-\sum_{i=1,9-11,28} C_i \nu_{i,15}$	$-(Y_{ac})N_{bac}$		$K_{m,ac} \cdot \frac{S_{ac}}{K_s + S_{ac}} \cdot X_{ac} \cdot I_3$
16	Uptake of Hydrogen								−1	$(1-Y_{h2})$	$-\sum_{i=1,9-11,28} C_i \nu_{i,16}$	$-(Y_{h2})N_{bac}$		$K_{m,h2} \cdot \frac{S_{h2}}{K_s + S_{h2}} \cdot X_{h2} \cdot I_1$
17	Decay of X_{su}										$-\sum_{i=13-20,26} C_i \nu_{i,17}$	$-\sum_{i=13-20,26} N_i \nu_{i,17}$		$K_{dec,Xsu} \cdot X_{su}$
18	Decay of X_{aa}										$-\sum_{i=13-20,26} C_i \nu_{i,18}$	$-\sum_{i=13-20,26} N_i \nu_{i,18}$		$K_{dec,Xaa} \cdot X_{aa}$
19	Decay of X_{fa}										$-\sum_{i=13-20,26} C_i \nu_{i,19}$	$-\sum_{i=13-20,26} N_i \nu_{i,19}$		$K_{dec,Xfa} \cdot X_{fa}$
20	Decay of X_{C4}										$-\sum_{i=13-20,26} C_i \nu_{i,20}$	$-\sum_{i=13-20,26} N_i \nu_{i,20}$		$K_{dec,Xc4} \cdot X_{c4}$
21	Decay of X_{pro}										$-\sum_{i=13-20,26} C_i \nu_{i,21}$	$-\sum_{i=13-20,26} N_i \nu_{i,21}$		$K_{dec,Xpro} \cdot X_{pro}$
22	Decay of X_{ac}										$-\sum_{i=13-20,26} C_i \nu_{i,22}$	$-\sum_{i=13-20,26} N_i \nu_{i,22}$		$K_{dec,Xac} \cdot X_{ac}$
23	Decay of X_{h2}										$-\sum_{i=13-20,26} C_i \nu_{i,23}$	$-\sum_{i=13-20,26} N_i \nu_{i,23}$		$K_{dec,Xh2} \cdot X_{h2}$

Matrix of model equations – Part 2

	Component →	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	$rate \rho_j [kgCOD \cdot m^{-3} \cdot d^{-1}]$
	Process ↓	C	X_{Ch_R}	X_{Ch_S}	X_{Pr_R}	X_{Pr_S}	X_{Li_R}	X_{Li_S}	X_{su}	X_{aa}	X_{fa}	X_{C4}	X_{pro}	X_{ac}	X_{h2}	X_I	X_{Slu}	
1	Disintegration of OFMSW	-1	$f_{Ch,Xc} \cdot f_r$	$f_{Ch,Xc} \cdot f_s$	$f_{Pr,Xc} \cdot f_r$	$f_{Pr,Xc} \cdot f_s$	$f_{Li,Xc} \cdot f_r$	$f_{Li,Xc} \cdot f_s$								$f_{X_I,Xc}$		$K_{sbk} \cdot C \cdot a^*$
2	Disintegration of Sludge		$f_{Ch,Xslu} \cdot f_r$	$f_{Ch,Xslu} \cdot f_s$	$f_{Pr,Xslu} \cdot f_r$	$f_{Pr,Xc} \cdot f_s$	$f_{Li,Xslu} \cdot f_r$	$f_{Li,Xslu} \cdot f_s$									-1	$K_{dis\_Slu} \cdot X_{Slu}$
3	Hydrolysis of Carbohydrates (readily)		-1															$K_{hyd\_ch\_R} \cdot X_{ch\_R}$
4	Hydrolysis of Carbohydrates (slowly)			-1														$K_{hyd\_ch\_S} \cdot X_{ch\_S}$
5	Hydrolysis of Proteins (readily)				-1													$K_{hyd\_pr\_R} \cdot X_{pr\_R}$
6	Hydrolysis of Proteins (slowly)					-1												$K_{hyd\_pr\_S} \cdot X_{pr\_S}$
7	Hydrolysis of Lipids (readily)						-1											$K_{hyd\_li\_R} \cdot X_{li\_R}$
8	Hydrolysis of Lipids (slowly)							-1										$K_{hyd\_li\_S} \cdot X_{li\_S}$
9	Uptake of Sugars								Y_{su}									$K_{m,su} \cdot \frac{S_{su}}{K_s + S_{su}} \cdot X_{su} \cdot I_1$
10	Uptake of Amino Acids									Y_{aa}								$K_{m,aa} \cdot \frac{S_{aa}}{K_s + S_{aa}} \cdot X_{aa} \cdot I_1$
11	Uptake of LCFA										Y_{fa}							$K_{m,fa} \cdot \frac{S_{fa}}{K_s + S_{fa}} \cdot X_{fa} \cdot I_2$
12	Uptake of Valerate											Y_{C4}						$K_{m,C4} \cdot \frac{S_{va}}{K_s + S_{va}} \cdot X_{C4} \cdot \frac{1}{1 + S_{va}/S_{bu}} \cdot I_2$
13	Uptake of Butyrate											Y_{C4}						$K_{m,C4} \cdot \frac{S_{bu}}{K_s + S_{bu}} \cdot X_{C4} \cdot \frac{1}{1 + S_{va}/S_{bu}} \cdot I_2$
14	Uptake of Propionate												Y_{pro}					$K_{m,pro} \cdot \frac{S_{pro}}{K_s + S_{pro}} \cdot X_{pro} \cdot I_2$
15	Uptake of Acetate													Y_{ac}				$K_{m,ac} \cdot \frac{S_{ac}}{K_s + S_{ac}} \cdot X_{ac} \cdot I$
16	Uptake of Hydrogen														Y_{h2}			$K_{m,h2} \cdot \frac{S_{h2}}{K_s + S_{h2}} \cdot X_{h2} \cdot I_1$
17	Decay of X_{su}	1							-1									$K_{dec,Xsu} \cdot X_{su}$
18	Decay of X_{aa}	1								-1								$K_{dec,Xaa} \cdot X_{aa}$
19	Decay of X_{fa}	1									-1							$K_{dec,Xfa} \cdot X_{fa}$
20	Decay of X_{C4}	1										-1						$K_{dec,Xc4} \cdot X_{c4}$
21	Decay of X_{pro}	1											-1					$K_{dec,Xpro} \cdot X_{pro}$
22	Decay of X_{ac}	1												-1				$K_{dec,Xac} \cdot X_{ac}$
23	Decay of X_{h2}	1													-1			$K_{dec,Xh2} \cdot X_{h2}$

Conversion Pathways in the Model



Disintegration Modelling

1° Order:

$$\frac{dC}{dt} = -K_H C$$

$K_H = K_H$ (substrate type, PSD)

Surface Based:

$K_{sbk} = K_{sbk}$ (substrate type)

$$\frac{dM}{dt} = -K_{sbk} A$$

$a = \frac{A}{V}$ Volume specific Area [L^{-1}]

$a^* = \frac{A}{M}$ Mass specific Area [$L^2 M^{-1}$]

$$a = C \cdot a^*$$

$$\frac{dC}{dt} = -K_{sbk} \cdot C \cdot a^*$$

Acid-base equilibria modelling

Aimed at estimating pH at any time

pH affects bacteria activities

Inhibition modelling according to ADM1:

$$I = \frac{1 + 2 \cdot 10^{0.5(pH_{ll} - pH_{ul})}}{1 + 10^{(pH^* - pH_{ul})} + 10^{(pH_{ll} - pH^*)}}$$

pH_{ll} = pH lower limit

pH_{ul} = pH upper limit

pH^* = pH actual value

Substrate degradation rates:

$$\frac{dS}{dt} = k \frac{S}{K_s + S} X \cdot I$$

S = substrate concentration

t = time

k = Monod maximum specific degradation rate

Ks = half saturation constant

X = biomass concentration

Acid-base equilibria modelling

Chemical species involved:

i) Sodium carbonate;

ii) Propionic, butyric, valeric and acetic acids;

iii) Ammonia;

iv) Carbonic acid.

Model assumptions:

i) Completely stirred tank reactor at any time;

ii) All chemical species completely soluble;

iii) All reactions instantaneous and isothermal;

iv) No complex ion formation or precipitation.

Acid-base equilibria modelling

The following equations have been considered for all the chemical species involved:

i) Chemical equilibrium → $k_{eq} = \frac{[H_3O^+]\cdot[A^-]}{[HA]_{undis}}$ x 8

ii) Mass balance → $[HA] = [HA]_{undis} + [A^-]$ x 6

iii) Electro-neutrality → $\sum_{i}^{N}[cat^+] = \sum_{j}^{M}[an^-]$ x 1

They form an equation system, which results in a 9-order polynomial equation with $[H_3O^+]$ as unknown

Solved by *roots* function of MATLAB®

Acid-base equilibria modelling

Unknowns (15):

H_3O^+, OH^-, HPr, Pr^-, HBu, Bu^-, HVa, Va^-, HAc, Ac^-, NH_3, NH_4^+, H_2CO_3, HCO_3^-, CO_3^{2-}

Chemical equilibrium equations (8):

$$k_w = [H_3O^+]\cdot[OH^-] \qquad k_{Pr} = \frac{[H_3O^+]\cdot[Pr^-]}{[HPr]_{undis}} \qquad k_{Bu} = \frac{[H_3O^+]\cdot[Bu^-]}{[HBu]_{undis}} \qquad k_{Va} = \frac{[H_3O^+]\cdot[Va^-]}{[HVa]_{undis}}$$

$$k_{Ac} = \frac{[H_3O^+]\cdot[Ac^-]}{[HAc]_{undis}} \qquad k_b = \frac{[NH_4^+]\cdot[OH^-]}{[NH_3]_{undis}} \qquad k_{a1} = \frac{[H_3O^+]\cdot[HCO_3^-]}{[H_2CO_3]_{undis}} \qquad k_{a2} = \frac{[H_3O^+]\cdot[CO_3^{2-}]}{[HCO_3^-]}$$

Mass balance equations (6):

$$[HPr] = [HPr]_{undis} + [Pr^-] \qquad [HBu] = [HBu]_{undis} + [Bu^-] \qquad [HVa] = [HVa]_{undis} + [Va^-]$$

$$[HAc] = [HAc]_{undis} + [Ac^-] \qquad [NH_3] = [NH_3]_{undis} + [NH_4^+] \qquad [H_2CO_3] = [H_2CO_3]_{undis} + [HCO_3^-] + [CO_3^{2-}]$$

Electro-neutrality equation (1):

$$[Na^+] + [H_3O^+] + [NH_4^+] = [OH^-] + [Pr^-] + [Bu^-] + [Va^-] + [Ac^-] + [HCO_3^-] + [CO_3^{2-}]$$

Model Peculiarities

- **The proposed model differs from ADM1 for:**
  - **including 2 different influent substrates: OFMSW and Sewage Sludge**
  - **the OFMSW disintegration is modelled with surface based kinetics**
  - **Fractioning the OFMSW in readily and slowly biodegradable fractions**

- **Follows the ADM1 approach for:**
  - **The acidogenesis, acetogenesis and methanogenesis modelling**

Model Implementation

- IMPLEMENTATION
  - MATLAB
  - INTEGRATION OF THE DIFFERENTIAL EQUATIONS WITH *ODE15S*
- CALIBRATION AND VALIDATION
  - LAB SCALE EXPERIMENTS

Model Calibration (substrate selection)

- ~~REAL OFMSW~~

SYNTHETICAL OFMSW (prepared in the lab)

- PASTA
- CHEESE

Why?

Because known composition in terms of carbohydrates, proteins and lipids

MIXTURES WITH DIFFERENT PRECENTAGES

Model Calibration (Reactors set-up)

Reactor

Mixture (pasta + cheese)

Inoculum

Na_2CO_3 buffer solution

Water

Pasta

Hard wheat

-1 mm
-3 mm
-5 mm

Model Calibration
(Preparation of substrates and inoculum)

Cheese

Same size as pasta

SIEVE VERIFICATION

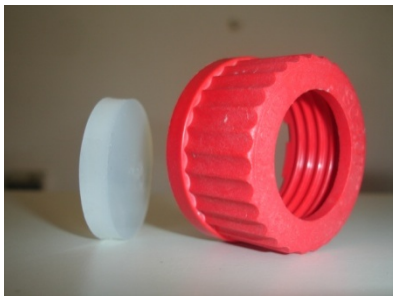
Inoculum

- Mesophilic granular sludge
- from UASB reactor

Model Calibration (BMP Tests)

- **Reactors are located in a water bath T = 37°C**

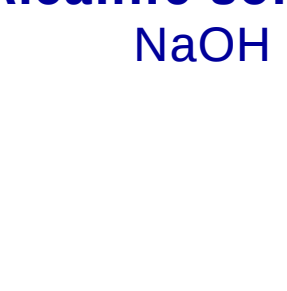
TEST LENGHT **101 DAYS**



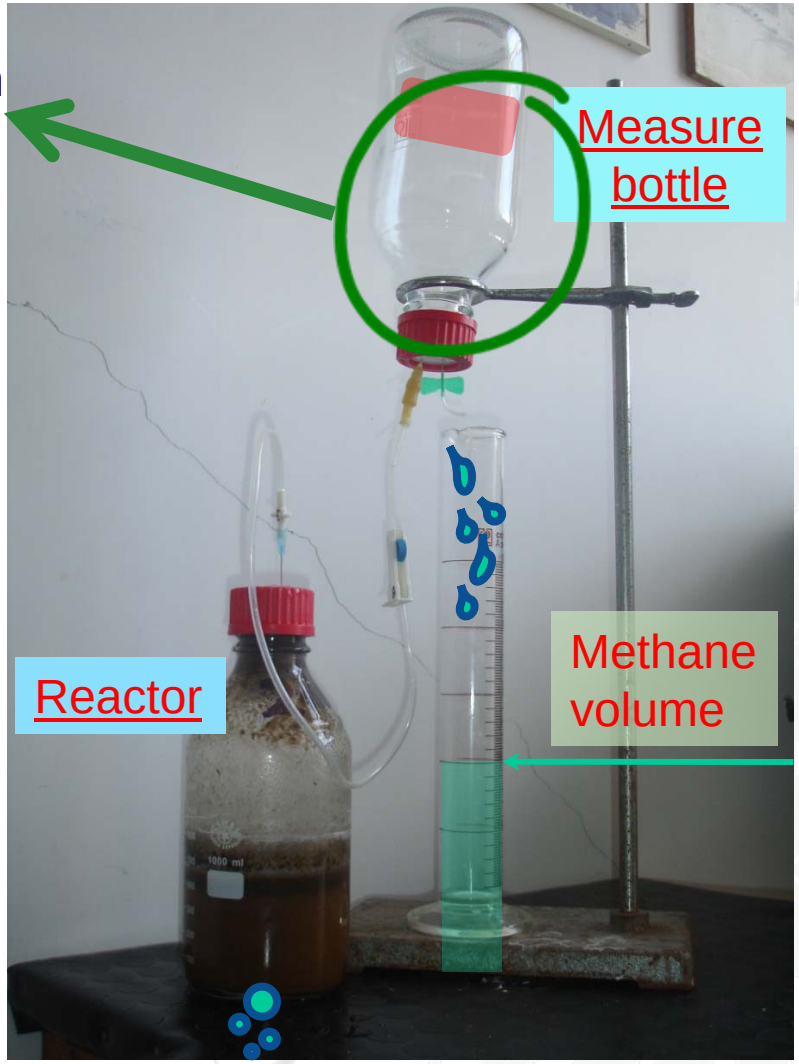
Model Calibration
(Methane Production Measure)

Alcaline solution
NaOH 2%

Volumetric Method



METHANE (L)



Model Calibration

$$\frac{dC}{dt} = -K_{sbk} \cdot C \cdot a^*$$

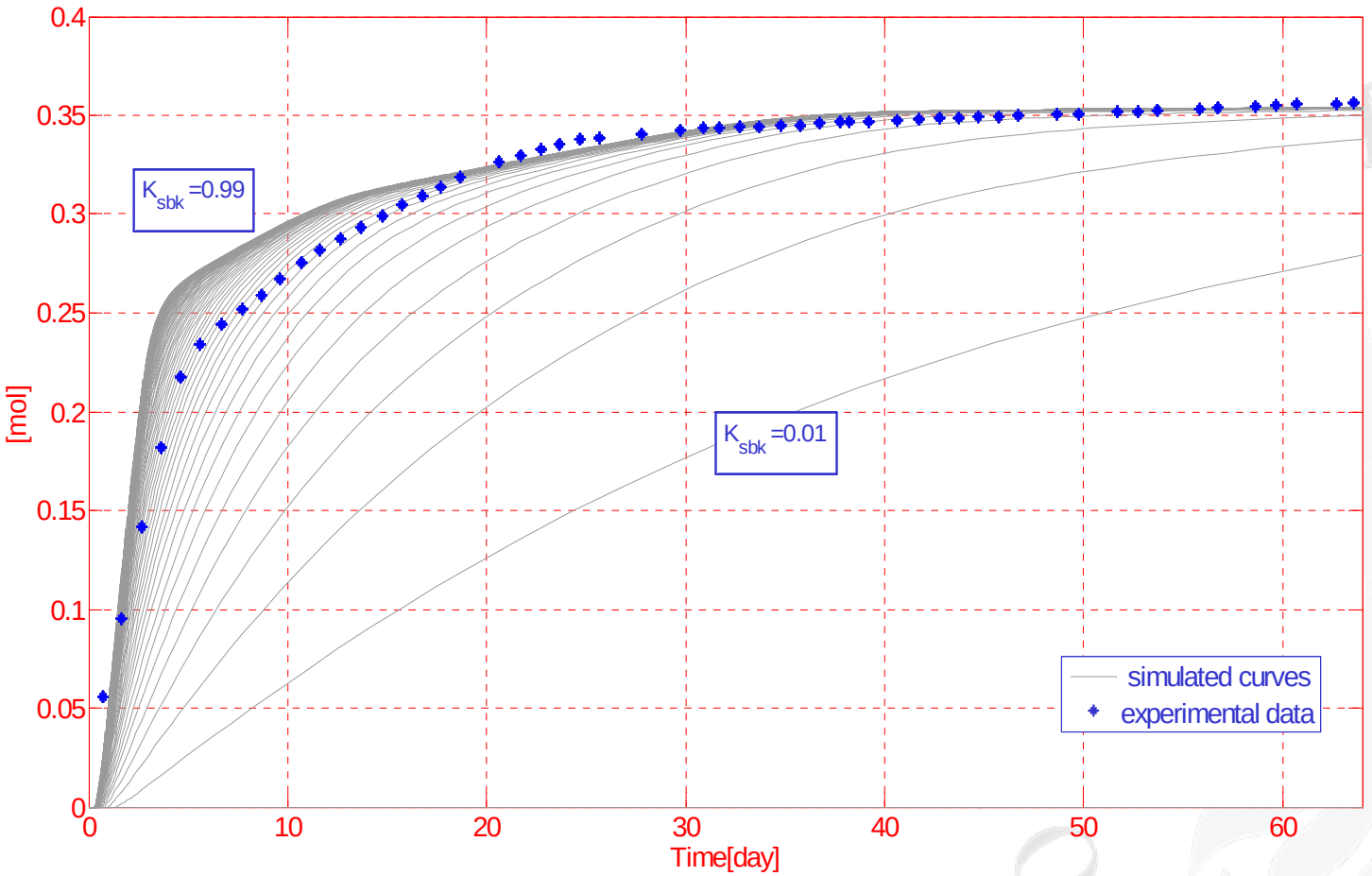
PSD → a*

Best fitting of model results and experimental observations

CALIBRATION → K_{SBK}

Model Calibration (best fitting)

Particle diameter = 1 mm ⟹ a* = 4.55



Model Calibration (best fitting methods)

Modelling Efficiency →

$$ME = 1 - \frac{\sum_{i=1}^{K} (y_i - y'_i)^2}{\sum_{i=1}^{K} (y_i - y_M)^2}$$

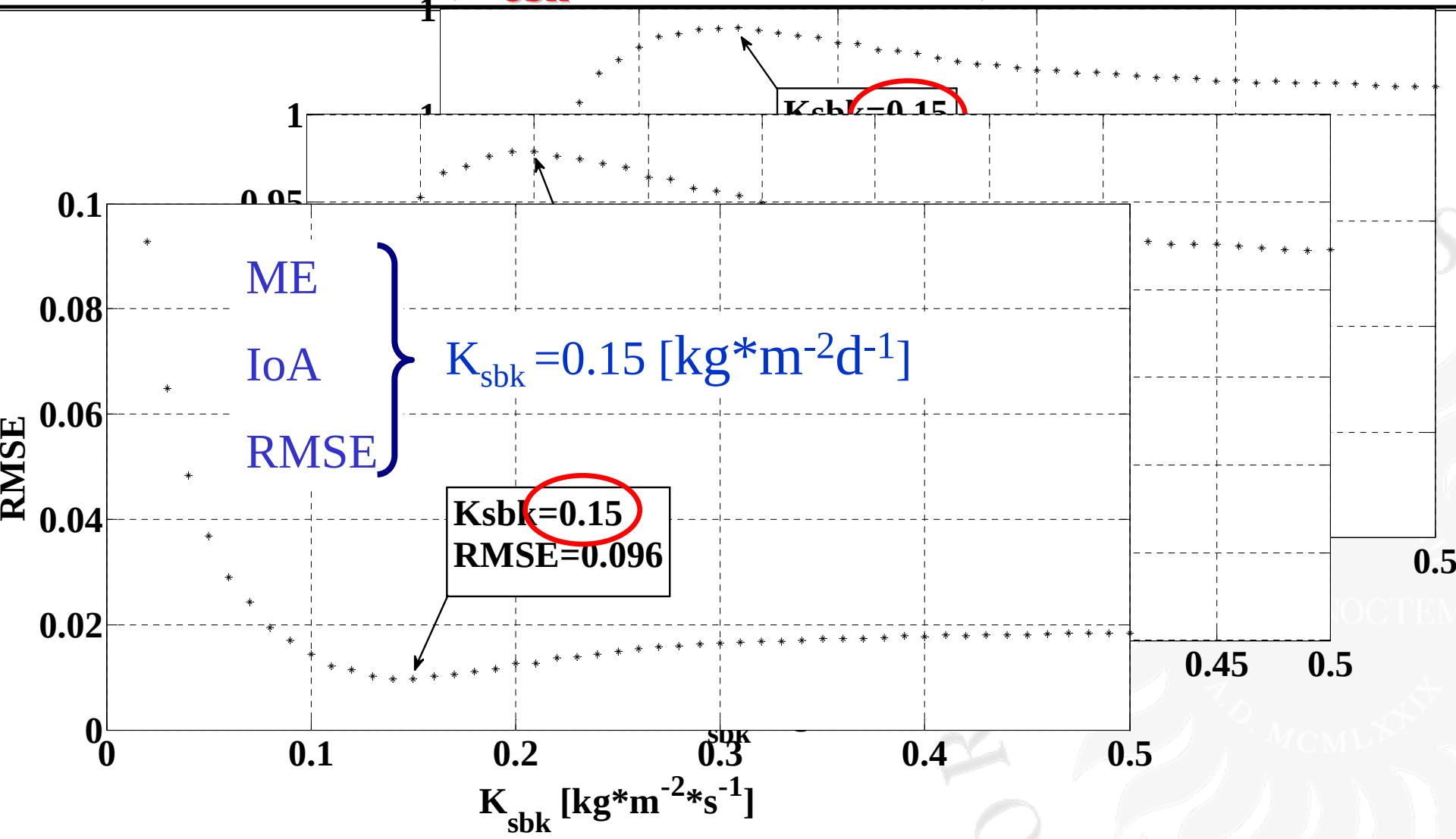
Index of Agreement →

$$IoA = 1 - \frac{\sum_{i=1}^{K} (y_i - y'_i)^2}{\sum_{i=1}^{K} (|y'_i - y_M| + |y_i - y_M|)^2}$$

Root Main Square Error →

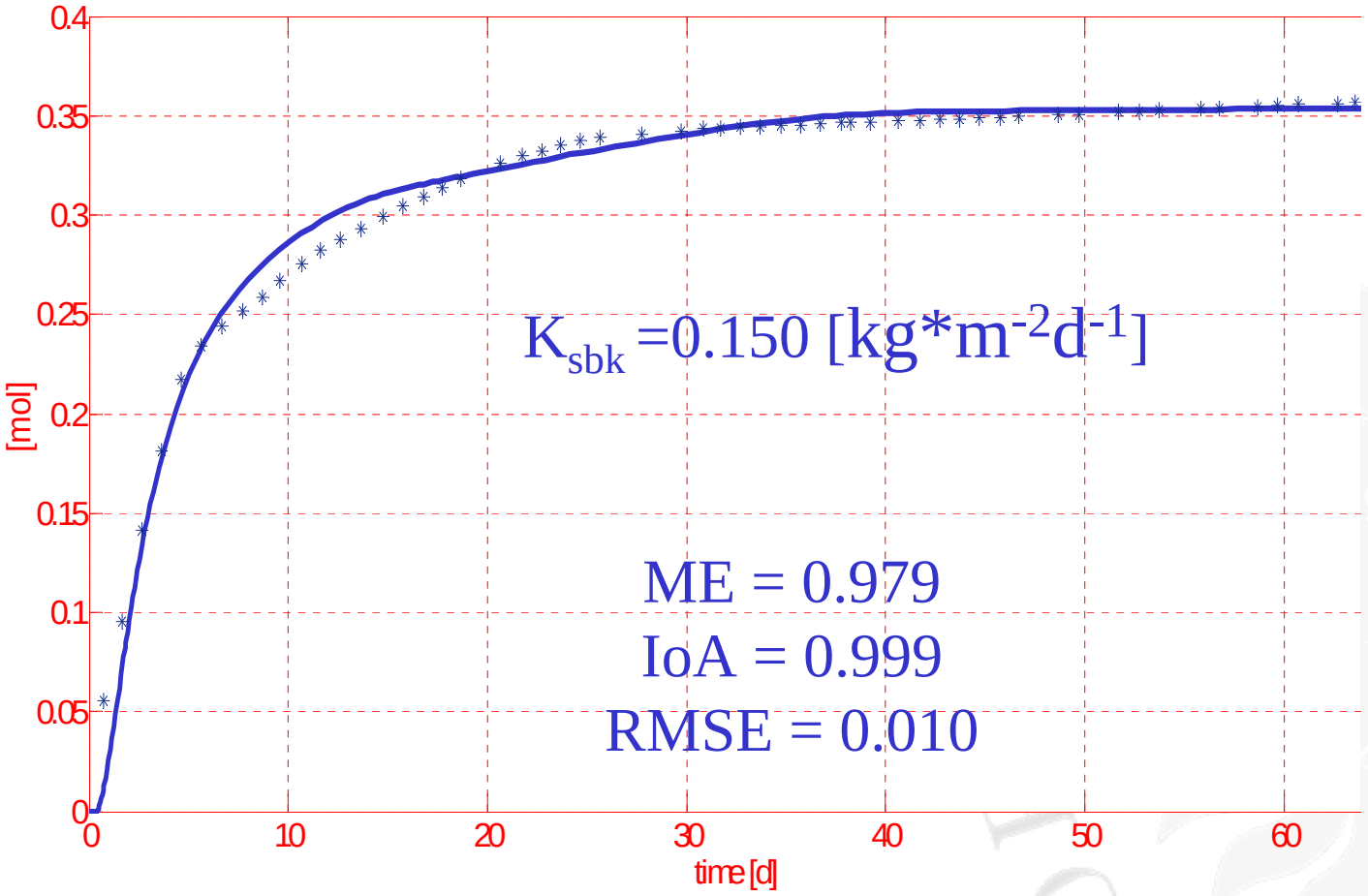
$$RMSE = \sqrt{\frac{\sum_{i=1}^{K} (y_i - y'_i)^2}{K}}$$

Model Calibration (K_{sbk} determination)



Model Calibration (Ksbk determination)

Particle diameter = 1 mm → **$a^* = 4.55\ m^2\ kg^{-1}$**



Model Validation (3 mm)

Particle diameter = 3 mm → **$a^* = 1.52\ m^2\ kg^{-1}$**

Validation data:

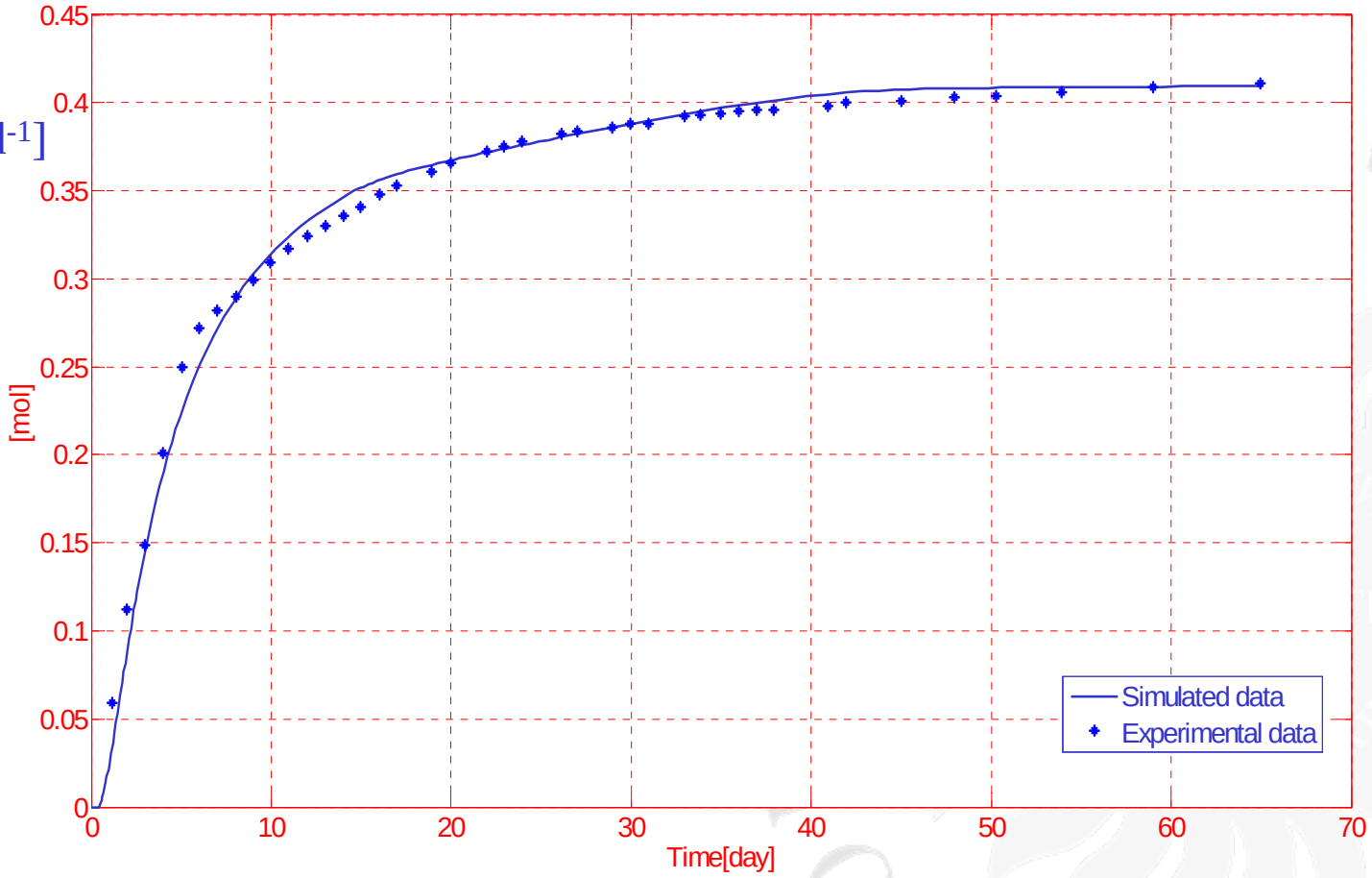
$K_{SBK} = 0.15$ [Kg m^{-2} d^{-1}]

Validation results:

ME = 0.979

IoA = 0.999

RMSE = 0.011



Model Validation (5 mm)

Particle diameter = 5 mm → **a^* = 0.91 m^2 kg^{-1}**

Validation data:

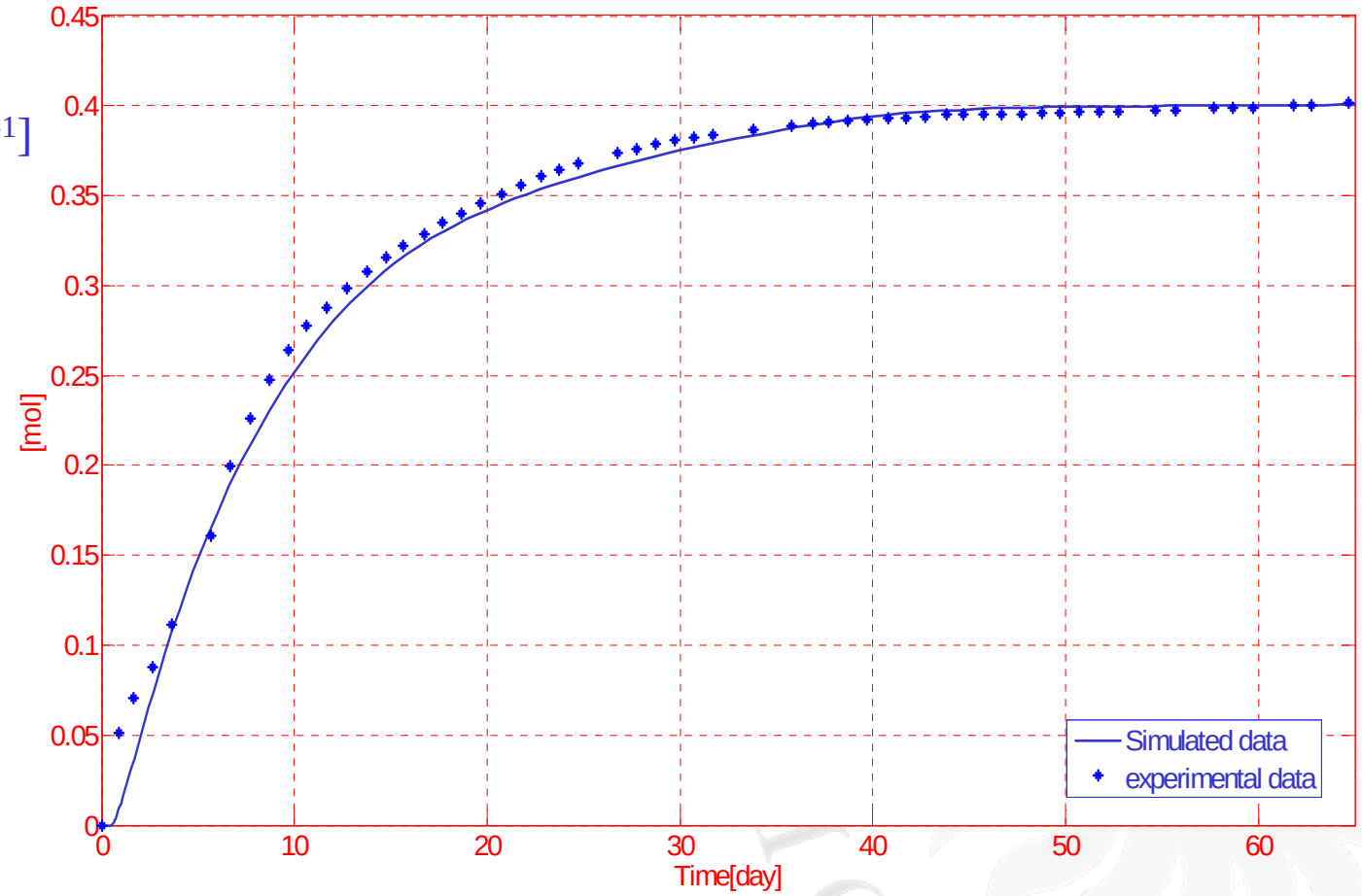
K_{SBK} = 0.15 [Kg m^{-2} d^{-1}]

Validation results:

ME = 0.988

IoA = 0.999

RMSE = 0.010



Model calibration and validation: Conclusions

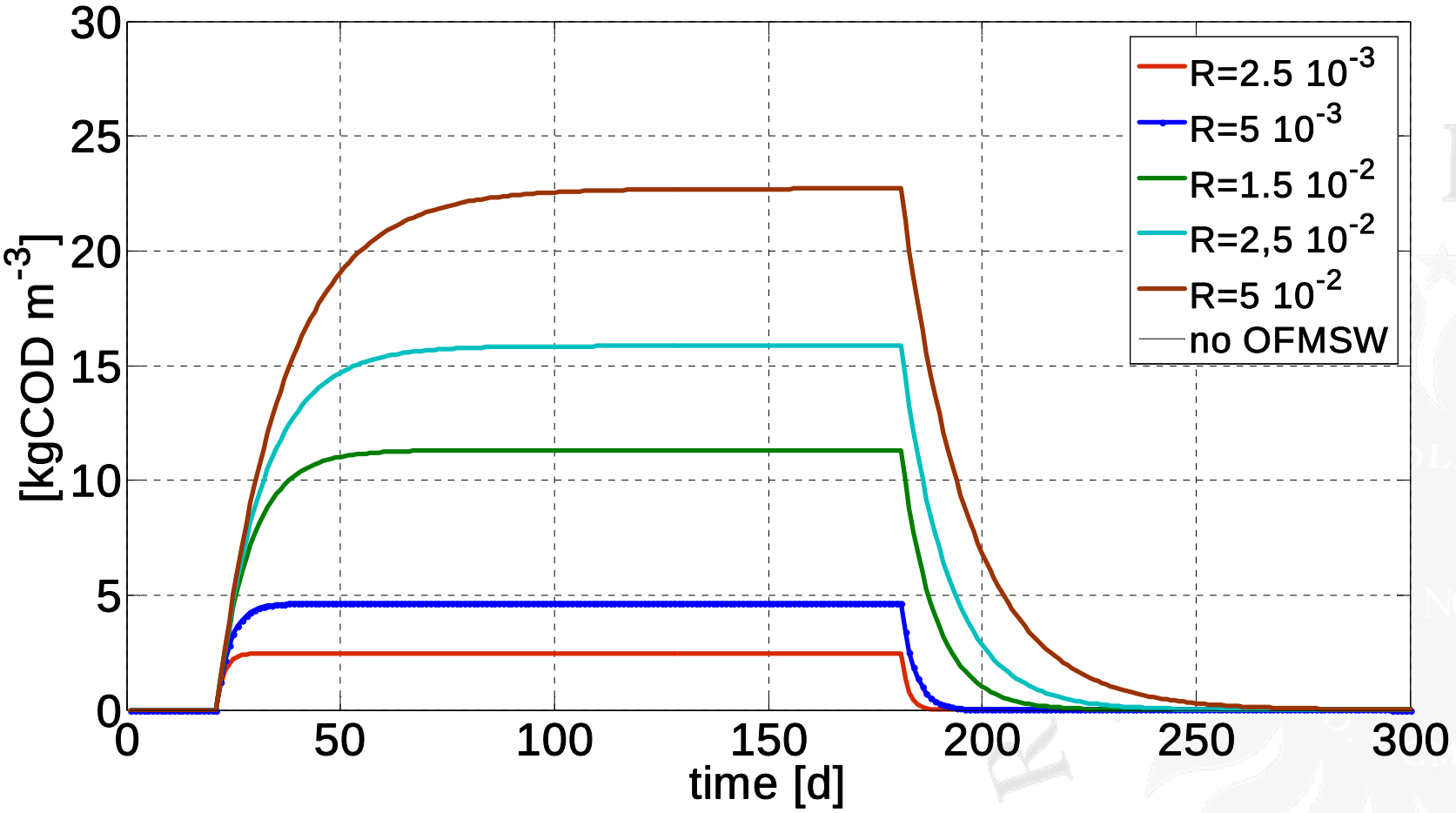
✓ These experiments demonstrate that *Ksbk* only depends on the nature and composition of the organic waste, while it is independent on the PSD of the OFMSW.

✓ This implies that model calibration can be performed on organic waste of any PSD and a PSD variation (e.g. if the OFMSW is pre-triturated) does not effect the calibrated *Ksbk* value.

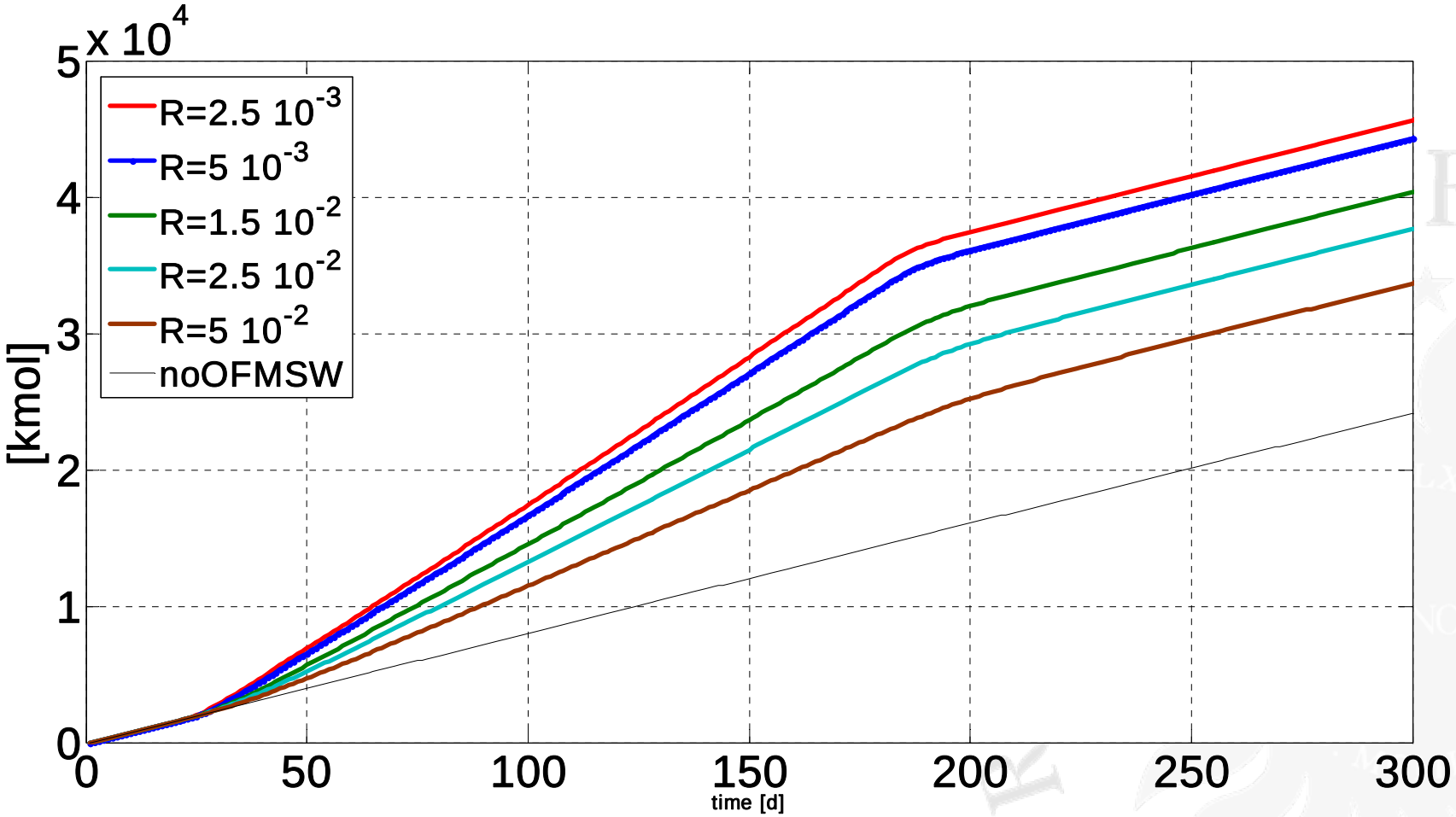
Examples of Model Simulations (effect of OFMSW particle size on AD performances)

Parameter	Unit	Value
Digester volume	m^3	12000
Sewage sludge carbohydrates content	%	20
Sewage sludge OLR	KgCOD d^{-1} m^{-3}	1.43
Sewage sludge lipids content	%	25
Sewage sludge inerts content	%	35
OFMSW OLR	KgCOD d^{-1} m^{-3}	1.43
OFMSW proteins content	%	10
OFMSW lipids content	%	15
OFMSW particle initial diameter	mm	5 ÷ 100
Gas pressure in the digester headspace	bar	1.25
Temperature	°C	35

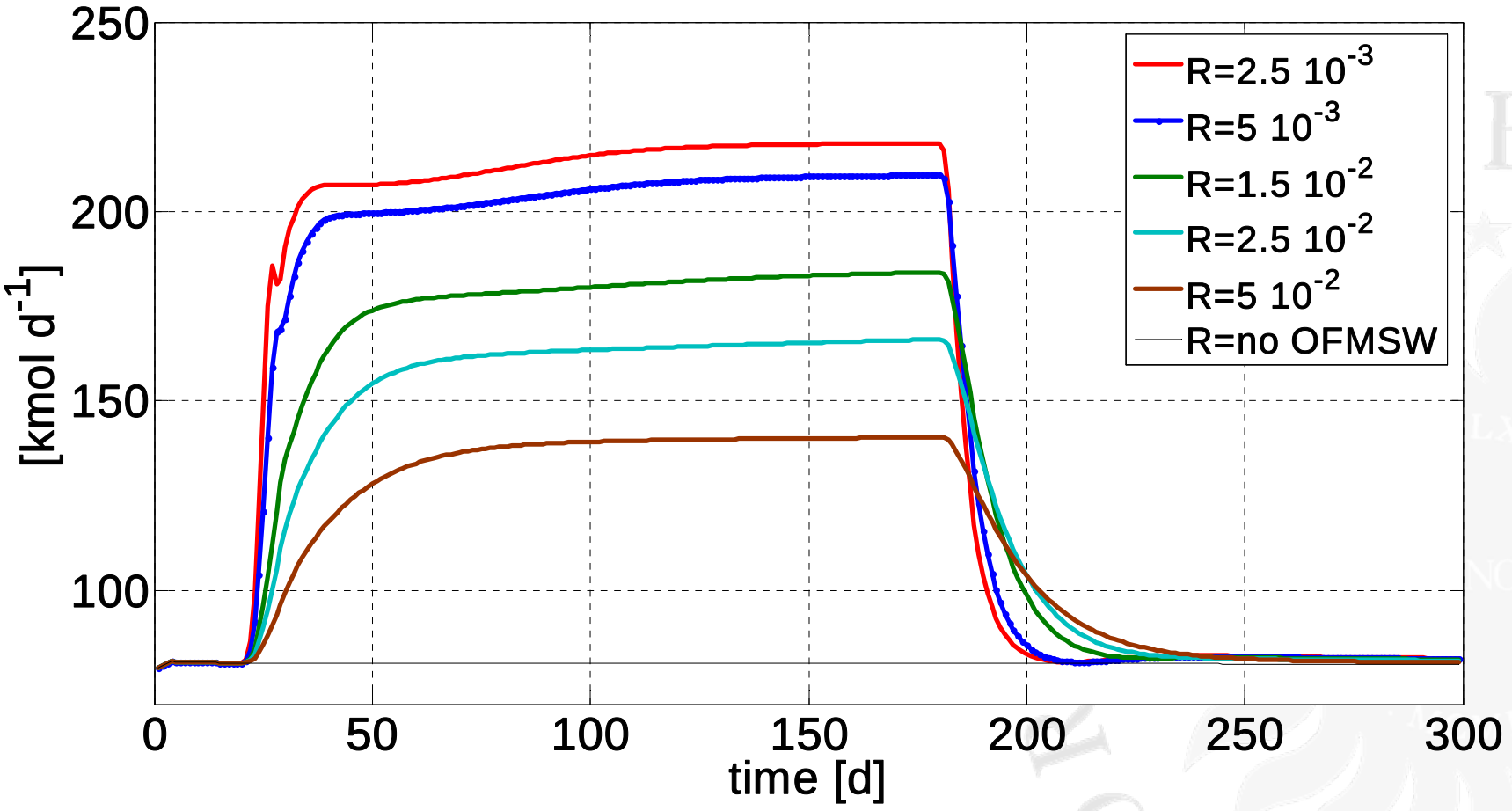
Effect of the OFMSW particle size on the effluent COD



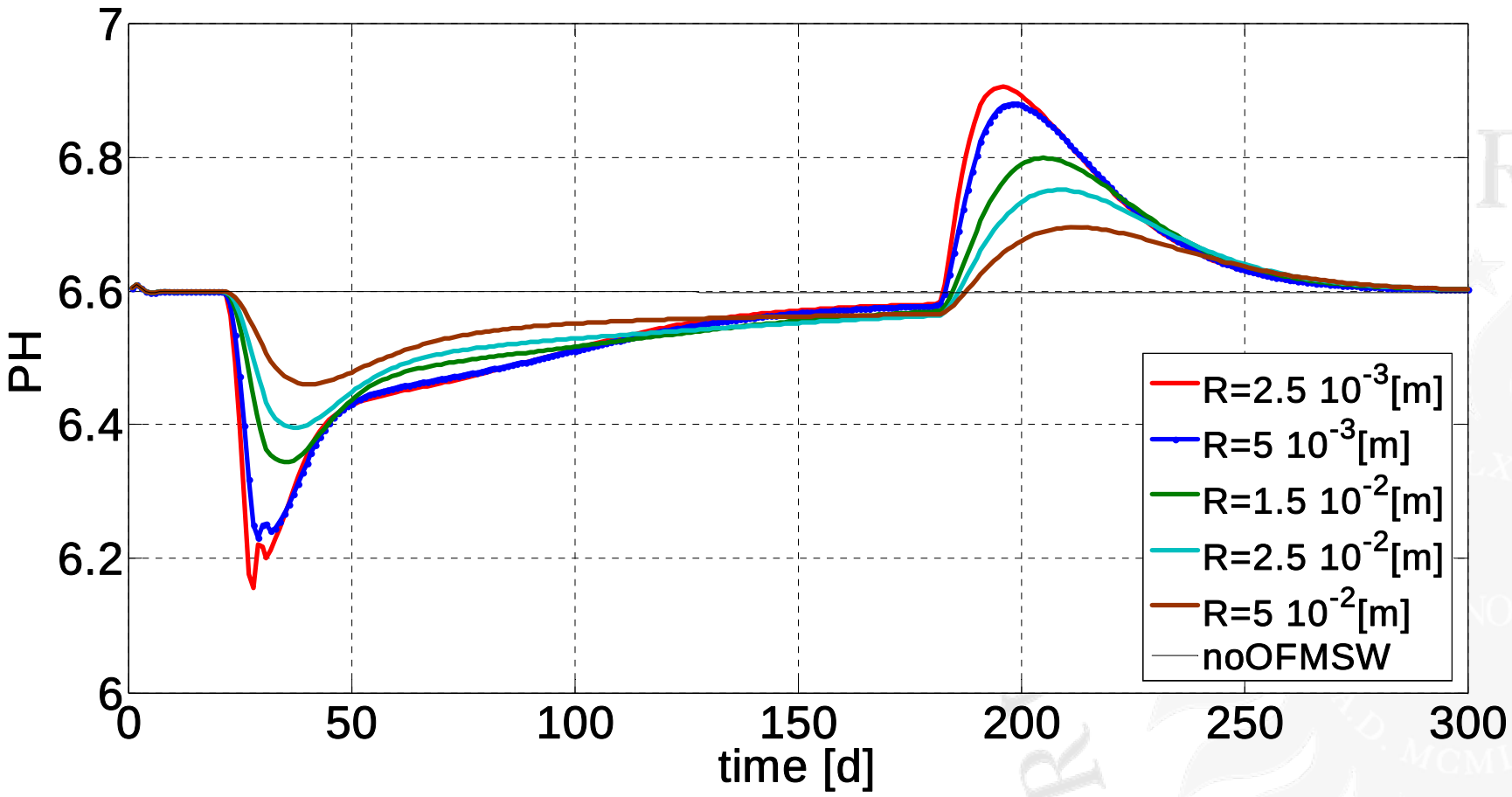
Effect of the OFMSW particle size on the cumulative methane production



Effect of the OFMSW particle size on the methane production rate

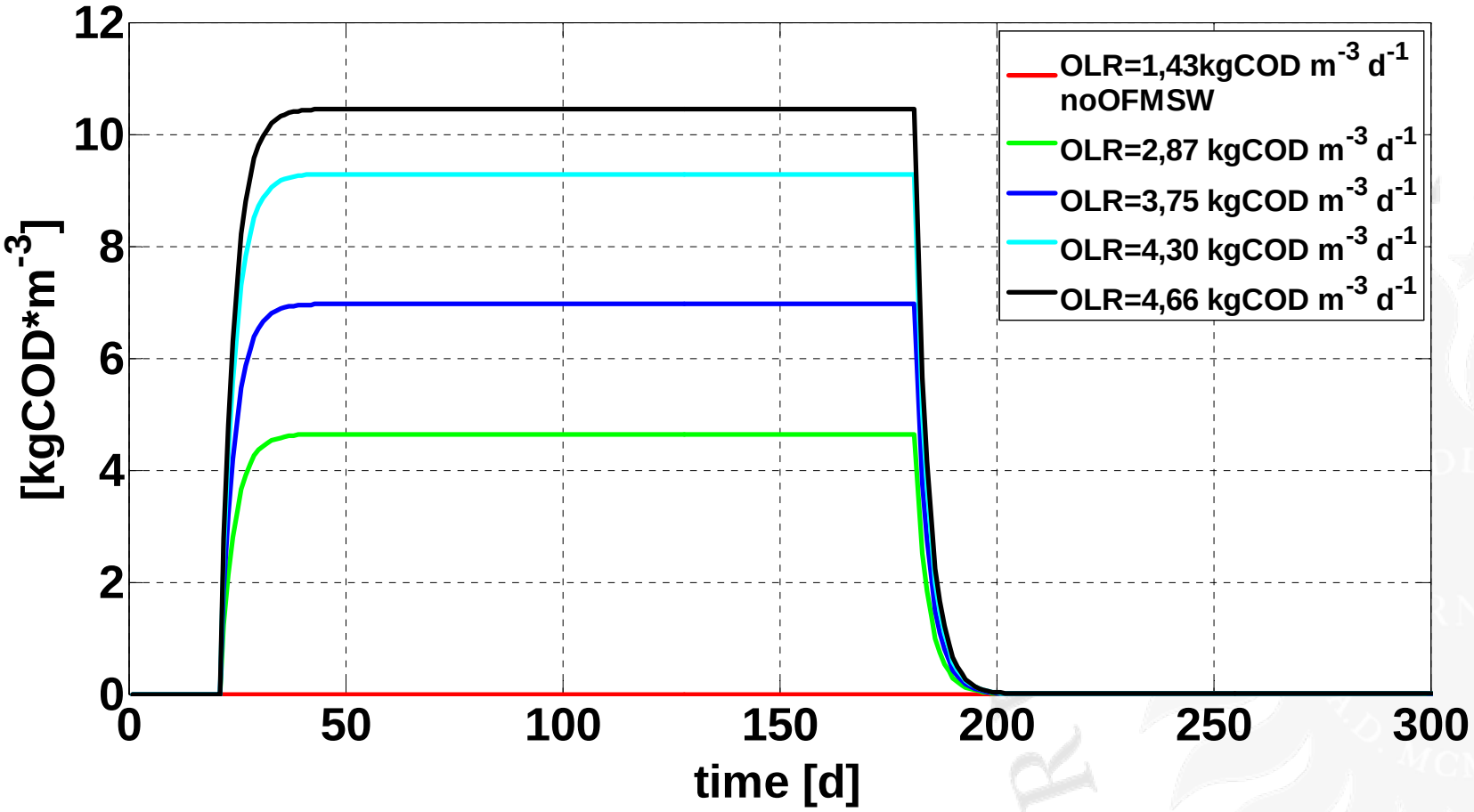


Effect of the OFMSW particle size on pH



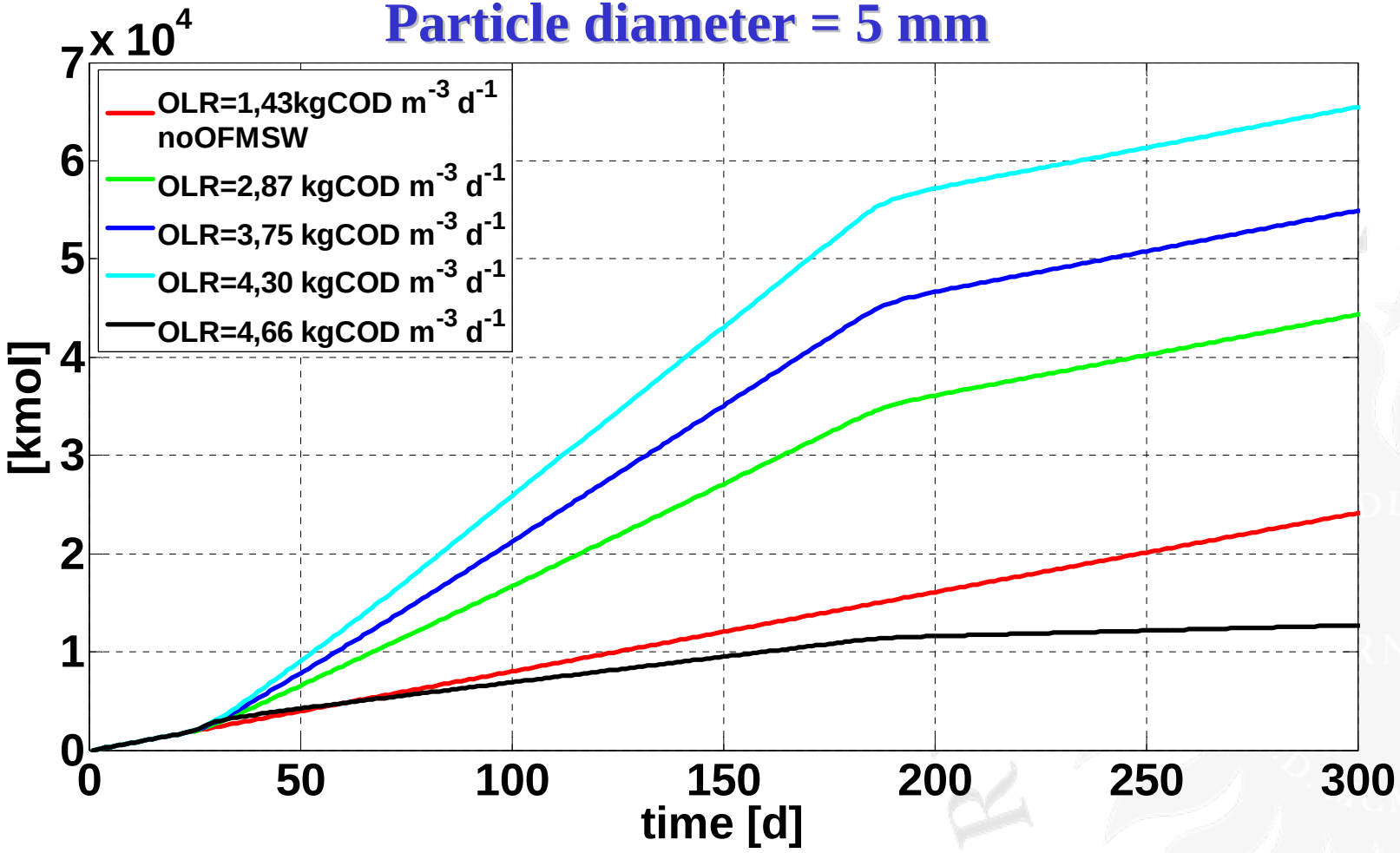
Effect of OFMSW addition on effluent COD

Particle diameter = 5 mm

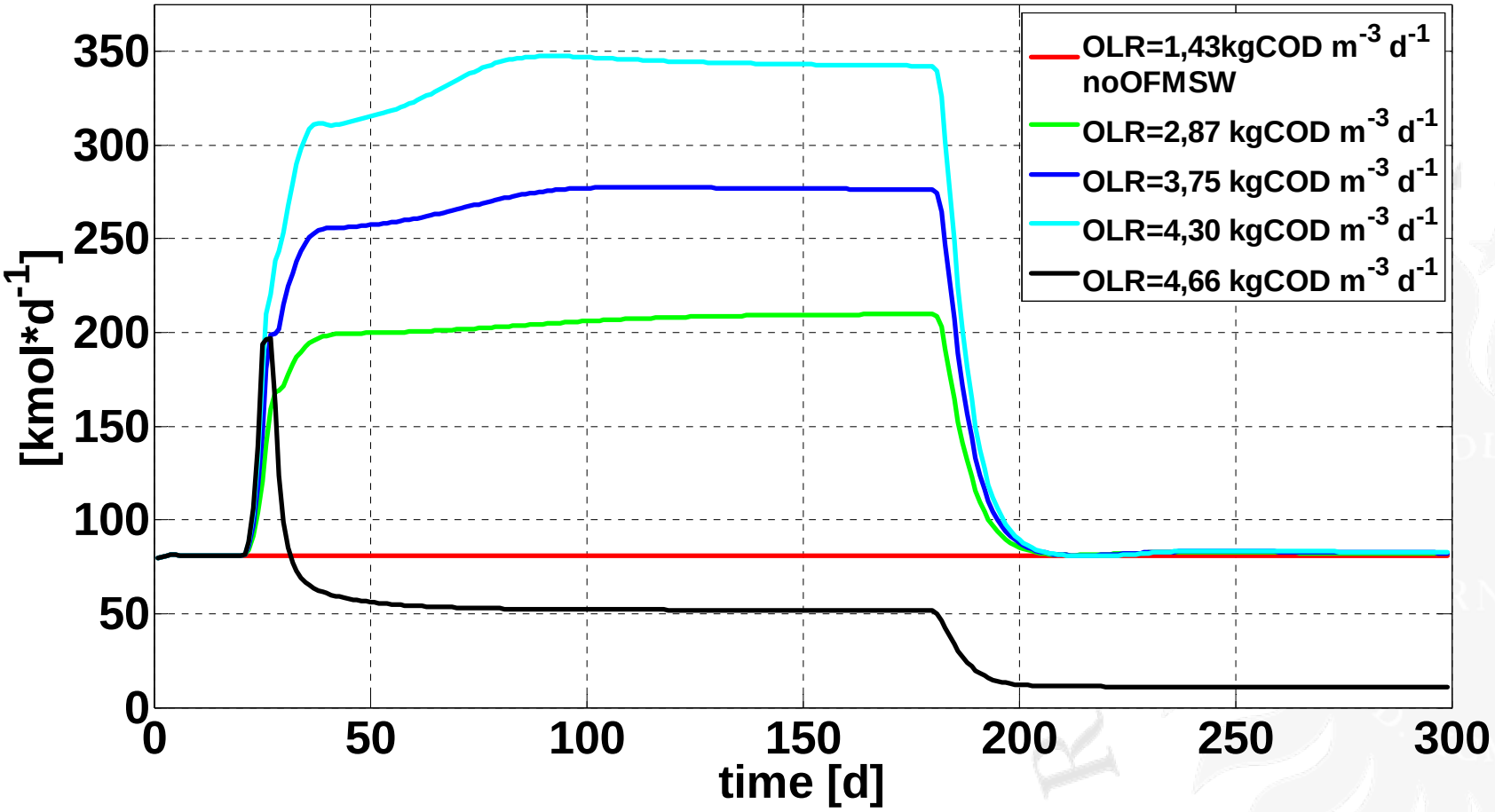


Effect of OFMSW addition on methane cumulative production

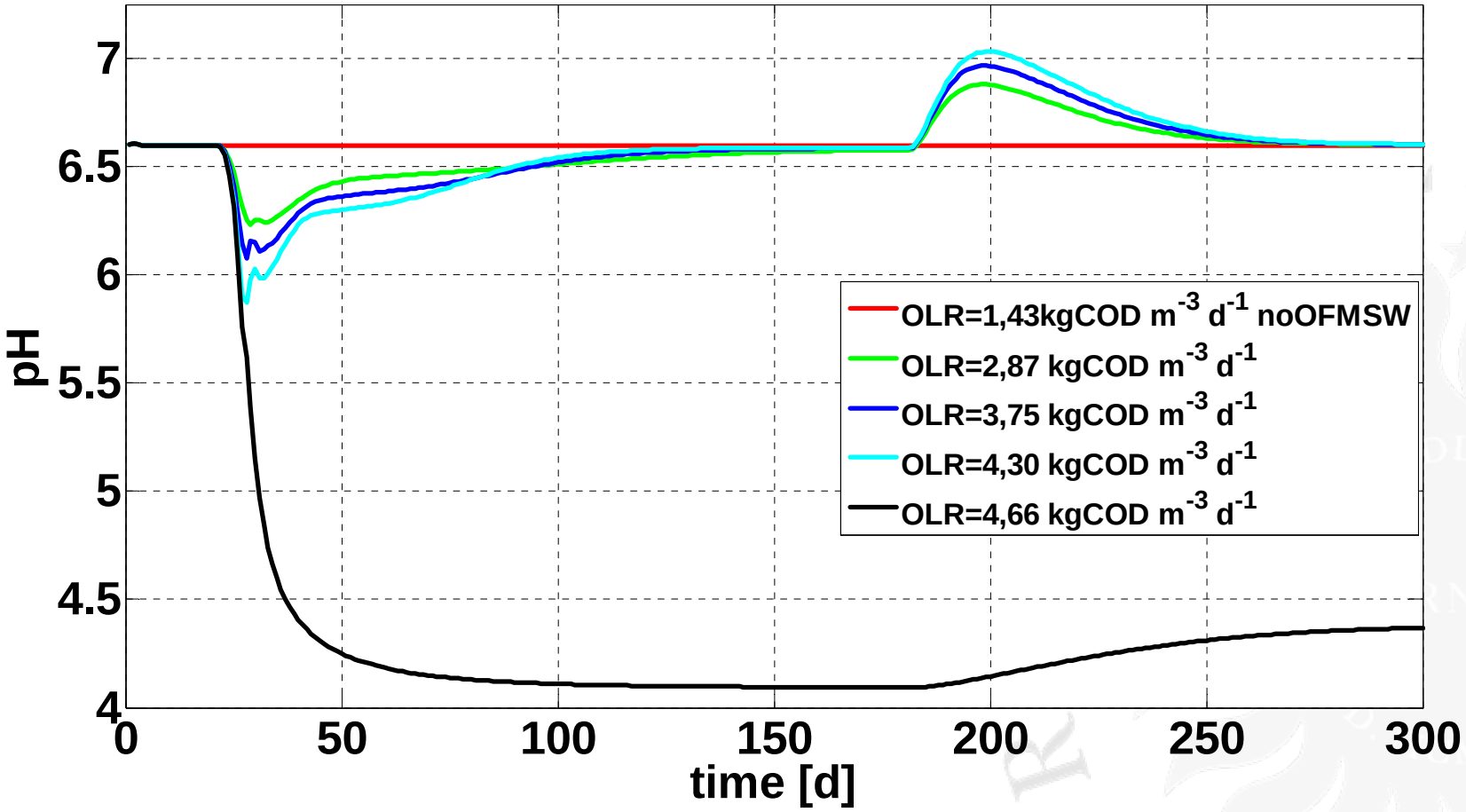
Particle diameter = 5 mm



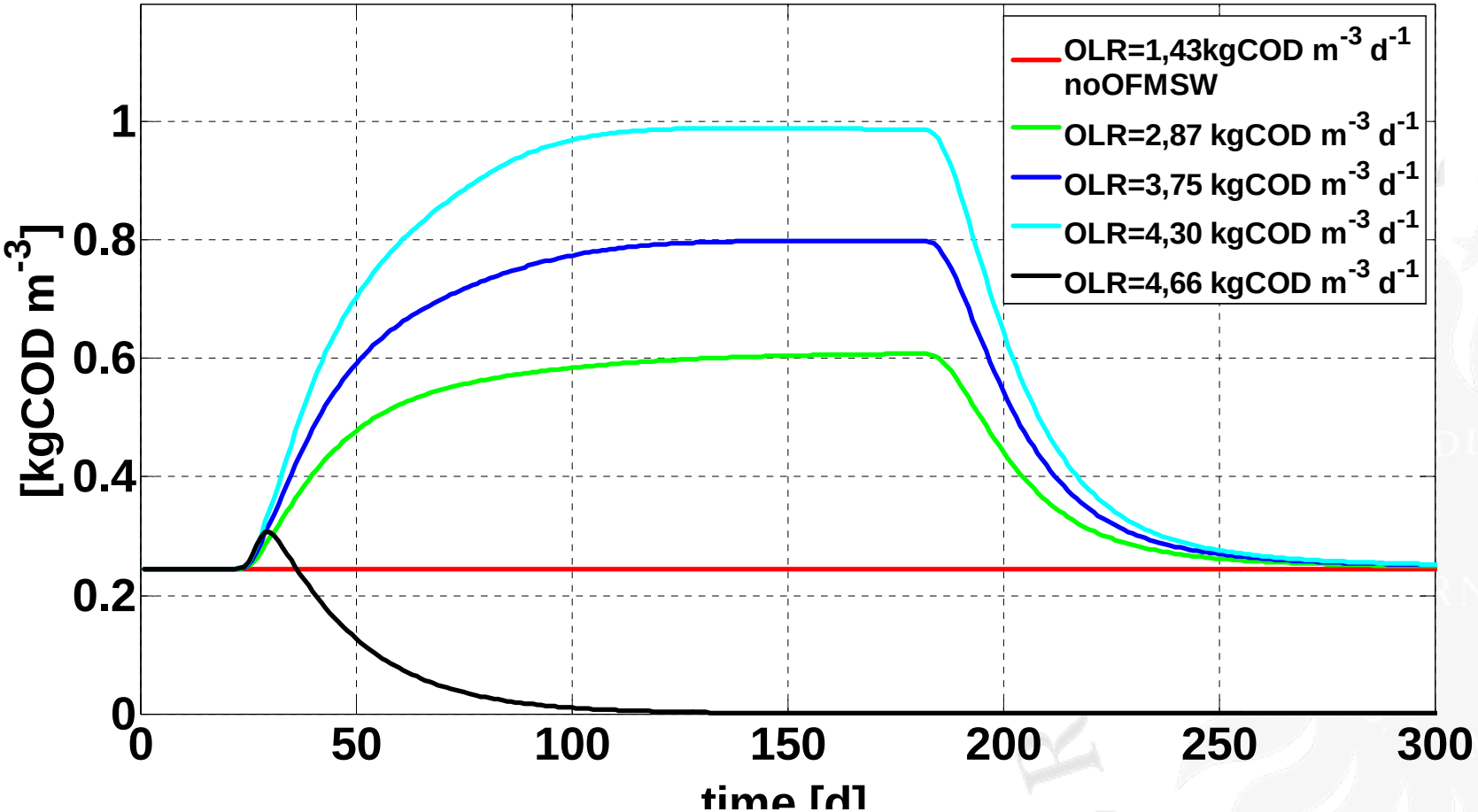
Effect of OFMSW addition on methane PRODUCTION RATE



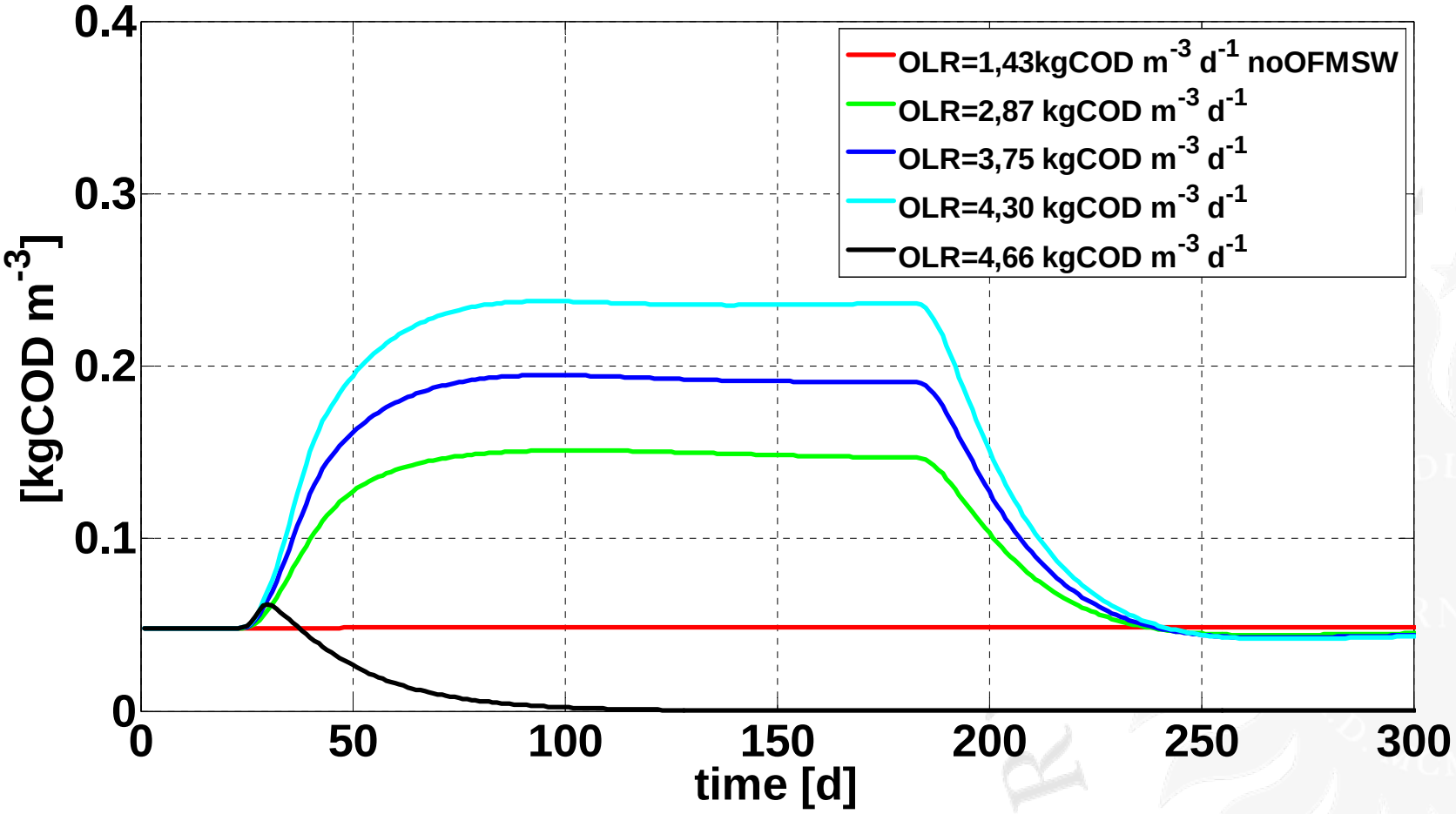
Effect of OFMSW addition on pH



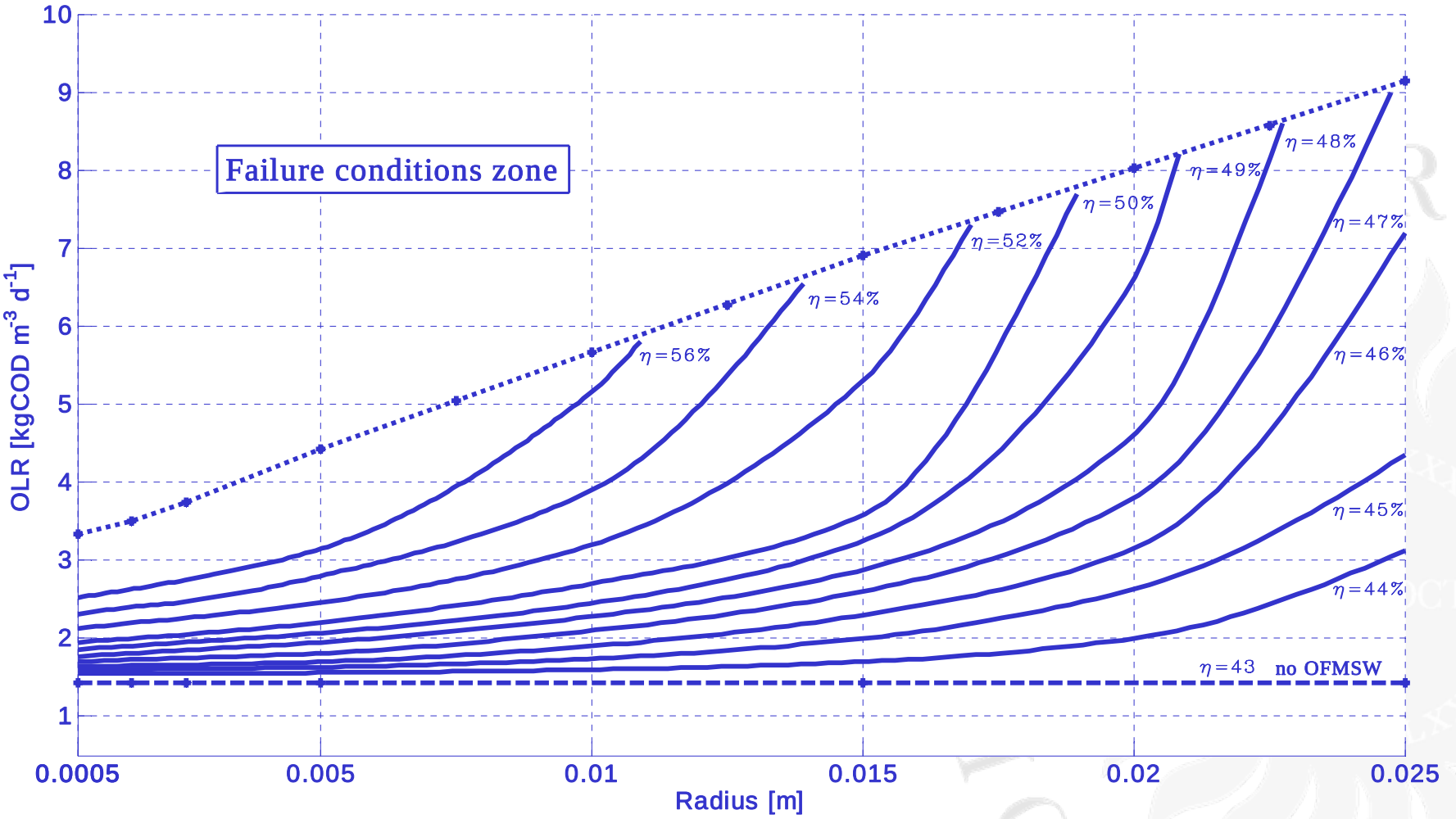
Effect of OFMSW addition on hydrogenotrophic methanogenic archea



Effect of OFMSW addition on acetoclastic methanogenic archea



Combined effect of OFMSW particle size and OLR on digestion performances



Thank You Very Much for Your Attention