ANAEROBIC DIGESTION OF TWO - PHASE OLIVE MILL SOLID WASTES

Rafael Borja, Francisco Raposo & Bárbara Rincón
Instituto de la Grasa (C.S.I.C.),
Avda. Padre García Tejero, 4,
41012-Sevilla, Spain

CSIC

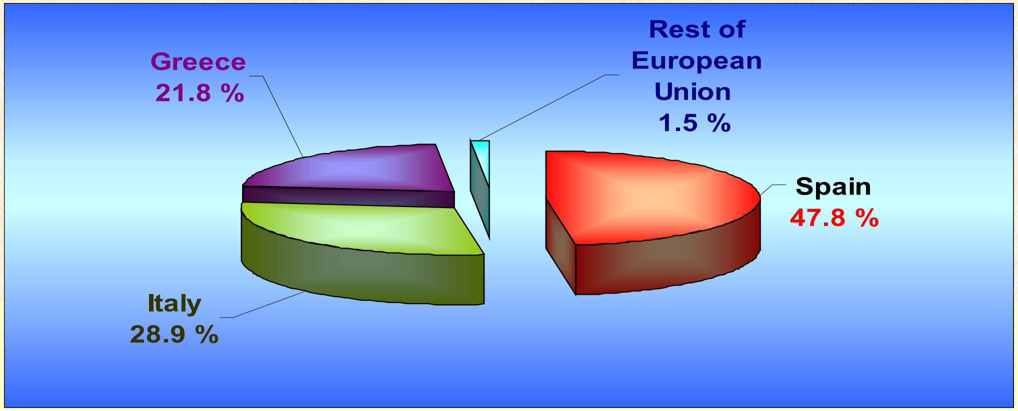
cropgen

MINISTERIO DE EDUCACIÓN Y CIENCIA

Tulln, Austria (6 February 2006)

Olives are one of main crops in terms of cultivation surfaces across the Mediterranean basin. There are approximately 750 million productive olive trees worldwide, which occupy a surface of 7 million ha.

- The annual worldwide production of olive oil has been estimated at 1.75 million metric tons, from **25,000 olive-mills**.
- The largest olive oil producers are Spain, Italy, Greece, Turkey and Tunisia and to a lesser extent Portugal, Morocco and Algeria. **Spain is the leader** as regards the total culture surface (2,121,181 ha) and the number of productive trees (180,000,000).



The evolution of modern technology for olive oil extraction has affected the industrial sector depending directly on the by-products obtained.

- The **traditional three-phase continuous centrifugation process** usually yields:
  - an oily phase (20%),
  - a solid residue (30%) and
  - an **aqueous phase** (50%), the latter coming from the water content of the fruit.
- Such water, combined with that used to wash and process the olives, make up the so-called **"olive mill wastewater" (OMW).** This process generates a total volume of traditional OMW of around **1.25 litres/kg of olives processed**.

The OMW composition is not constant either qualitatively and quantitatively and it varies according to: cultivation soil; harvesting time; the degree of ripening; olive variety; climatic conditions; etc.

The three-phase OMW is characterized by the following special features:

- Intensive violet-dark brown to black in colour.
- High degree of organic pollution (chemical oxygen demand - COD – values up to 220 g/L).
- pH between 3 and 6 (slightly acid).
- High electrical conductivity.
- High content of polyphenols (0.5-24 g/L).
- High content of solid matter.

cropgen

ENVIRONMENTAL PROBLEMS OF OMW

The average total OMW production amounts approximately to 10-12x10^6 m^3/year and occurs over a brief period of the year (November-March). Spain produced 20% of the OMW of the Mediterranean basin (2-3x10^6 m^3/year) before the implantation of the two-phase extraction process.

cropgen

THE TWO-PHASE OLIVE OIL MANUFACTURING PROCESS

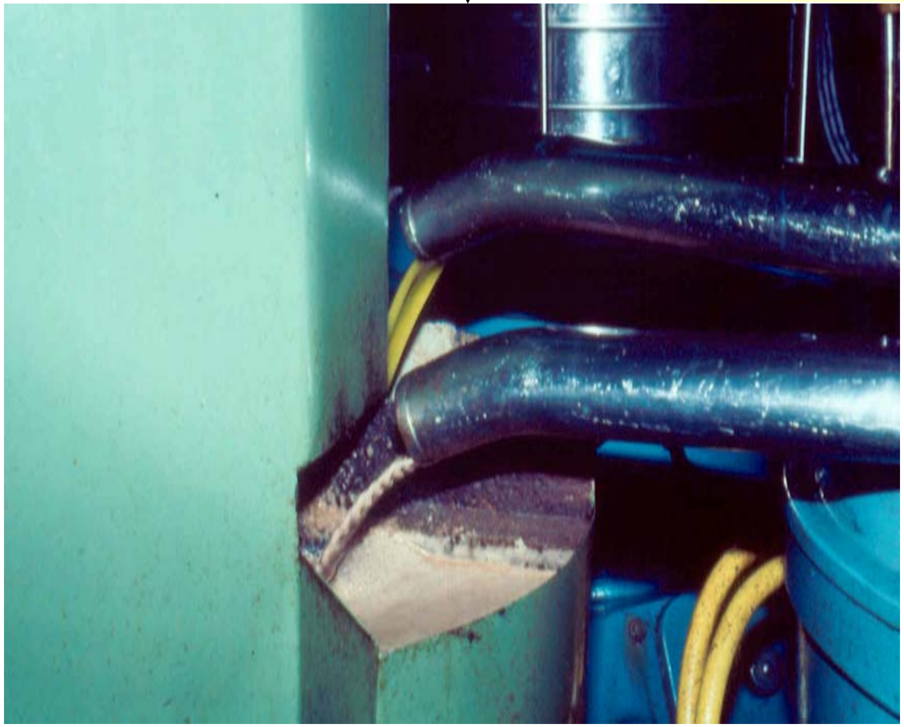
The failure to develop a suitable and economical effluent wastewater treatment technology for OMW has lead manufacturers of technology to develop the "ecological" two-phase process, which uses no process water, and delivers oil as the liquid phase and a very wet olive cake (two-phase olive mill solid waste, OMSW) as the solid residue.

In the two-phase process a **horizontally mounted centrifuge** is used for primary separation of the olive oil fraction from the **vegetable solid material and vegetation water**. Therefore, **the two-phase olive mills produce three identifiable and separate waste streams:**

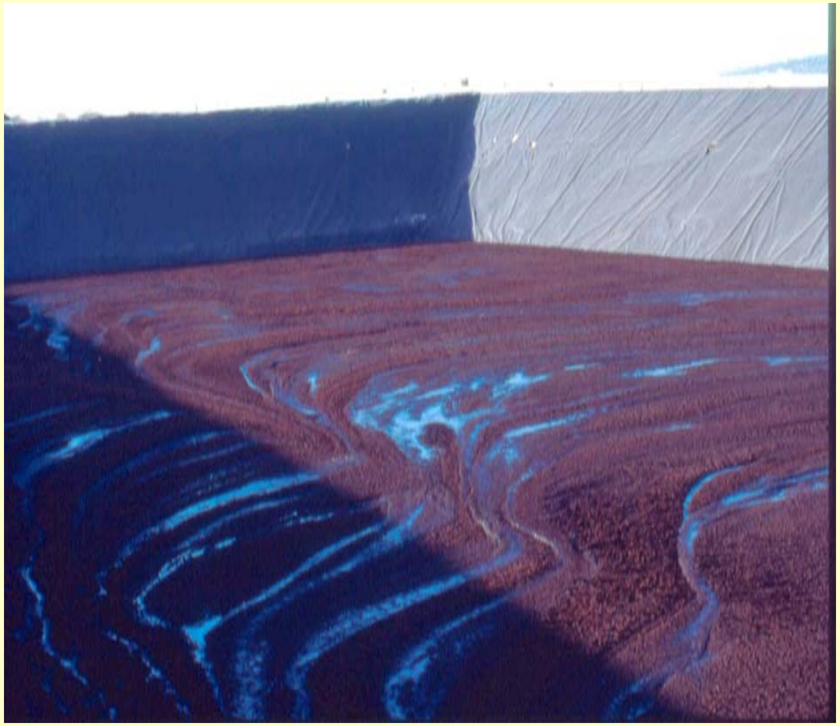
1) The wash waters generated during the initial cleansing of the fruit.
2) The wash waters from the secondary centrifuge generated during the washing and purification of virgin olive oil.
3) **The aqueous solid residues generated during the primary centrifugation (OMSW).**

1) Wash waters generated during the initial cleansing of the fruit

2) Wash waters from the secondary centrifuge generated during the washing and purification of virgin olive oil



3) **The aqueous solid residues generated during the primary centrifugation: two-phase olive mill solid wastes (OMSW).**



The introduction of this technology was carried out in **90% of Spanish olive oil factories**. This new manufacturing process generates a **SOLID RESIDUE (two-phase olive mill solid waste, OMSW)** with a high organic matter concentration giving an elevated polluting load.

The average composition of the two-phase OMSW is: water (60-70%), lignine (13-15%), cellulose and hemicellulose (18-20%), olive oil retained in the pulp (2.5-3%) and mineral solids (2.5%).

Among their organic components, the major ingredients are as follows: sugars (3%), volatile fatty acids (C2-C7) (1%), poly-alcohols (0.2 %), proteins (1.5%), poly-phenols (0.2%) and other pigments (0.5%).

The high polluting power and large volumes of solid wastes generated (around 2-4 millions of tons per year in Spain) can pose large-scale environmental problems, taking into account the 2,000 Spanish olive oil factories, most of them located in the Andalusia Community.

Two-phase decanting has the following main advantages over three-phase decanting:

- **The construction of the two-phase centrifuge is less complicated** and thus is more reliable in operation and less expensive than the three-phase decanter.

- **The throughput of the two-phase centrifuge in relation to the oil quantity is higher because no additional water is required. Energy consumption is also reduced**.

- **Oil produced by the two-phase centrifuge is of higher quality**; in particular, **it has higher oxidation stability and better organoleptic characteristics.**

- **The operating costs are lower**.

The **disadvantages of two-phase decanting** are:

- The two-phase process produces a **semi-solid residue** that combines the olive vegetation water that is generated with the solid fraction of olives. **This doubles the amount of "solid" waste (OMSW or "alperujo")** requiring disposal.

- **Two-phase OMSW has a moisture content in the range of 55%-70%,** while traditional three-phase cake has only around 40%-45% humidity. This increased amount of moisture, together with the sugars and fine solids give new residue a **doughy consistency and makes transport, storage and handling difficult**.

- OMSW, **prior to oil solvent extraction, must be dried with considerably higher energy requirements** than in the three-phase process, making the industrial recovery of the residual oil difficult and expensive.

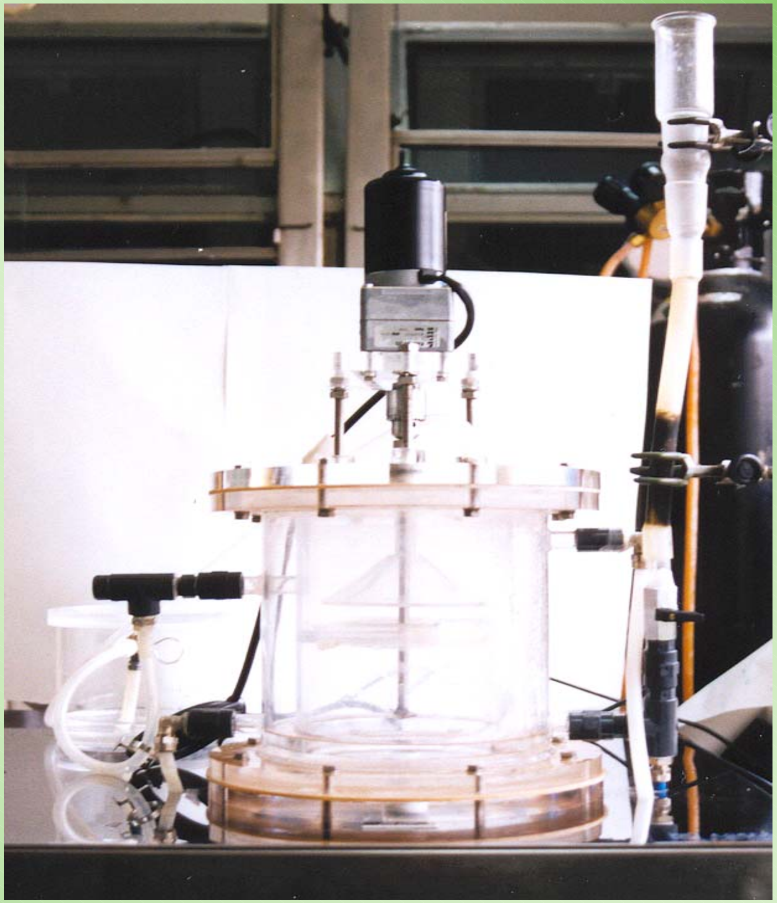
ANAEROBIC BIODEGRADATION OF TWO-PHASE OMSW

Anaerobic treatment of high strength wastes with high biodegradable content presents a number of **advantages** in comparison to the classical aerobic processes:

- **quite a high degree of purification with high-organic load feeds can be achieved;**
- **low nutrient requirements are necessary;**
- **small quantities of excess sludge are usually produced and finally,**
- **a combustible biogas is generated (31 m^3 methane/100 kg COD, with a maximum energetic value equivalent to 78 kwh in electric energy or 195 kwh in heat). The production of biogas enables the process to generate or recover energy instead of just energy-saving.**

Anaerobic Biodegradation of Two-phase OMSW: Equipment and Experimental procedure

- **Laboratory-scale completely stirred tank reactors at mesophilic temperature (35 ºC) were used.**
- **Four influent substrate concentrations (OMSW 20%, 40%, 60% and 80%) were used as feed.**
- **Experiments were carried out using progressive influent substrate concentrations:** those corresponding to the OMSW 20% being the first ones



Composition and features of the four two-phase OMSW used as influent

Parameters	*20 %*	*40 %*	*60 %*	*80 %*
pH	**5,6**	**4,8**	**5,1**	**5,8**
COD	**34,5**	**81,1**	**113,1**	**150,3**
SCOD	**14,5**	**37,5**	**49,8**	**66,5**
VFA	**0,70**	**1,53**	**2,20**	**2,90**
Alkalinity	**0,735**	**1,220**	**0,960**	**2,20**
TS	**40,2**	**84,8**	**124,0**	**165,3**
MS	**5,6**	**9,9**	**15,8**	**21,1**
VS	**34,6**	**74,9**	**108,2**	**144,2**
Total phenolic compounds	**0,61**	**1,22**	**1,83**	**2,44**

*COD: total chemical oxygen demand; SCOD: soluble chemical oxygen demand; VFA: total volatile fatty acids (as acetic acid); alkalinity (as $CaCO_3$); total phenolic compounds (as caffeic acid). All amounts, except pH, are expressed in g/L. Values are averages of five determinations, there was virtually no variation (less than 3%) between analyses.

[illegible]c loading rates (OLR) and hydraulic retention times (HRT) corresponding to the different influent substrate concentrations used as influent

Two-phase OMSW 20 %

OLR (g COD/L·d)	HRT (d)
0,86	40,0
1,21	28,6
1,38	25,0
1,72	20,0
2,08	16,6
2,76	12,5
3,45	10,0
4,14	8,3

Two-phase OMSW 40 %

OLR (g COD/L·d)	HRT (d)
1,62	50,0
3,24	25,0
4,89	16,6
6,49	12,5
8,11	10,0

Two-phase OMSW 60 %

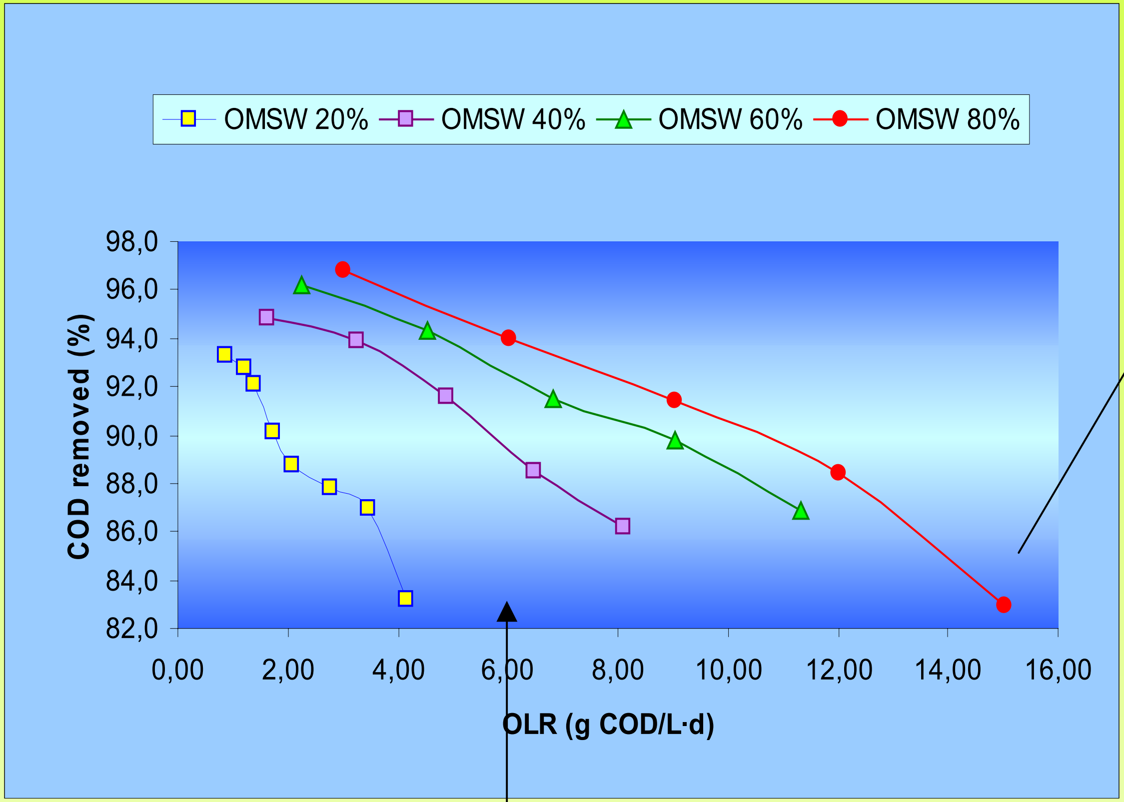
OLR (g COD/L·d)	HRT (d)
2,26	50,0
4,52	25,0
6,81	16,6
9,05	12,5
11,31	10,0

Two-phase OMSW 80 %

OLR (g COD/L·d)	HRT (d)
3,00	50,0
6,01	25,0
9,05	16,6
12,02	12,5
15,03	10,0

Results and discussion: steady-state operating results

Variation in the percentage of COD removal with the organic loading rate (OLR)(g COD/L·d) for the four influent substrate concentrations used

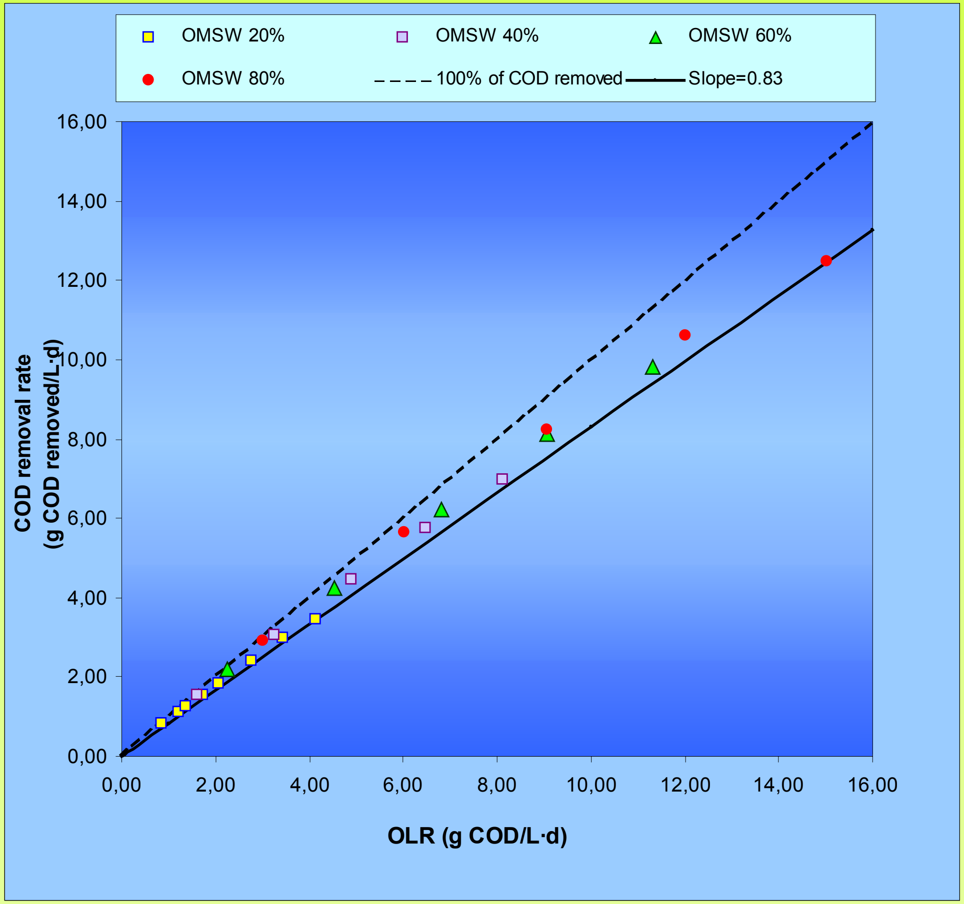


* In general, the percentage of COD removed decreased with increased OLR for the four influent concentrations studied.

- **For the most concentrated influent (OMSW 80%)** a COD removal efficiency of 82% was obtained at an OLR of 15 g COD/L d (HRT = 10 d).

- It can be observed that the percentage of COD removed increased when the influent substrate concentration increased for a fixed OLR value. This fact clearly demonstrates the progressive adaptation of the biomass to an increase in substrate concentration.

Variation of the COD removal rate (g COD removed/L·d) with the OLR (g COD/L·d), for the four influent substrate concentrations

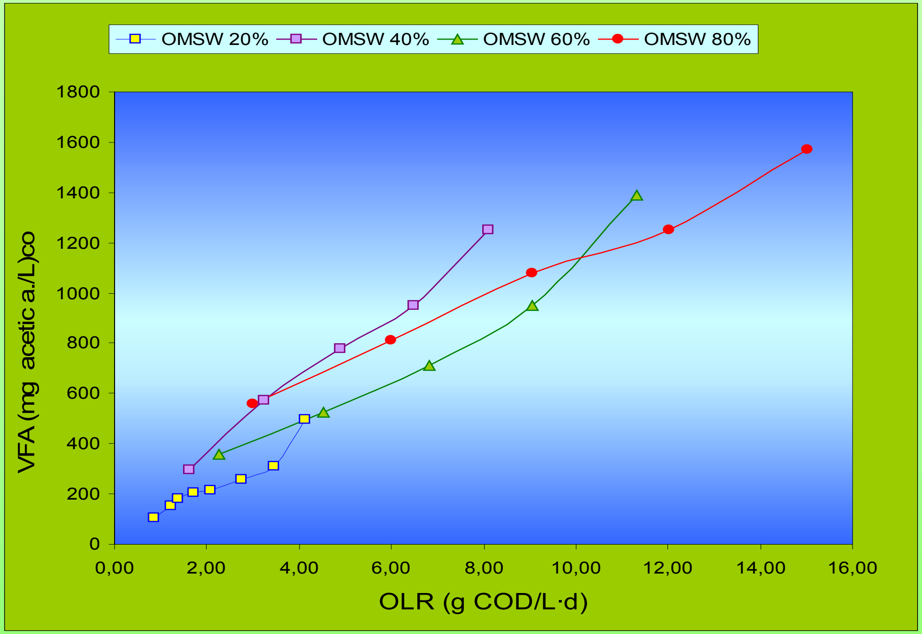


- The rate of COD removal increased linearly with OLR up to OLR values of 4, 8, 11 and 15 for the substrates OMSW 20%, 40%, 60% and 80%, respectively.

- The slope of this plot ($R^2 = 0.99$) indicates that an average of 83% of the organic matter added to the reactor is degraded during the anaerobic digestion of two-phase OMSW at mesophilic temperature.

cropgen

Variation of the total volatile fatty acids VFA (mg acetic acid/L) concentration with the OLR (g COD/L·d), for the four influent substrate concentrations used.



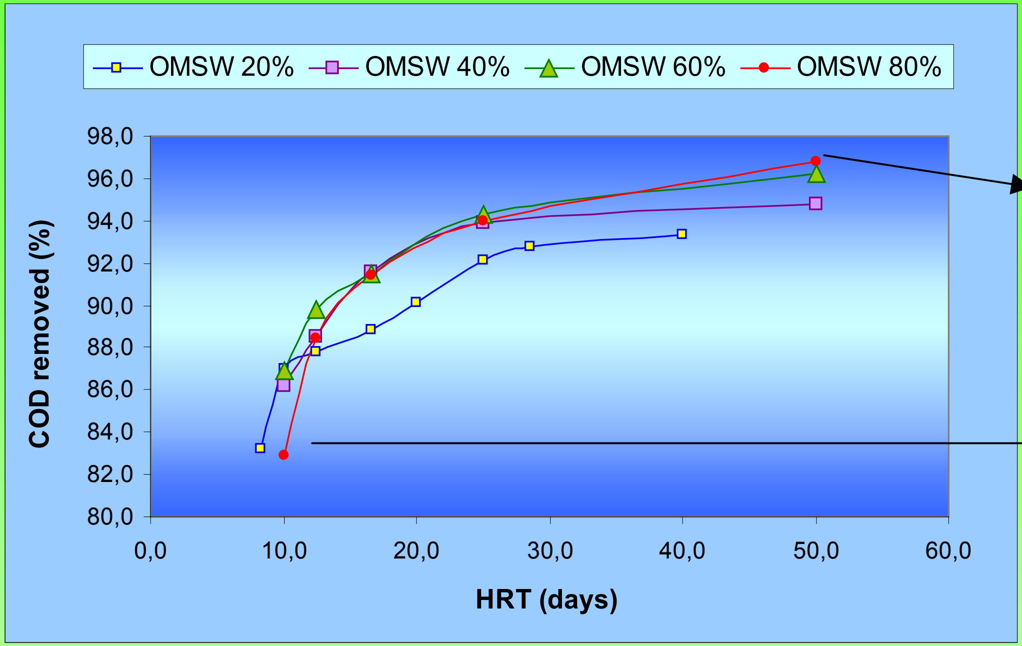
- WHEN OMSW 80% was processed:
- A total alkalinity of 1700 mg $CaCO_3$/L was sufficient to prevent the pH from dropping to below 7.0 at OLR of 12 g COD/L d .
- This high stability can be attributed to carbonate / bicarbonate buffering.

•The VFA increased with increased OLR for the four influent substrate concentrations.

For OMSW 80%, between HRTs of 50.0 and 16.6 d (OLR lower than 9 g COD/L d) the VFA/Alkalinity ratio was always lower than the failure limit value (0.3-0.4) and the process is considered to be operating favourably without acidification risk.

cropgen

Effect of HRT on the percentages of COD and VS removals for the different feed COD concentrations used

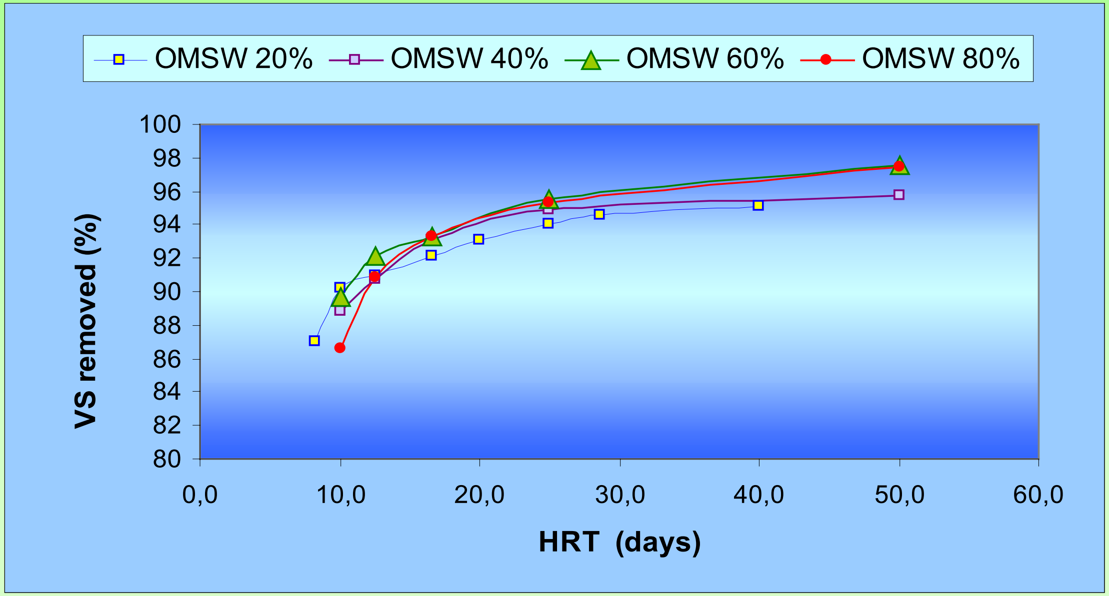


FOR OMSW 80%:

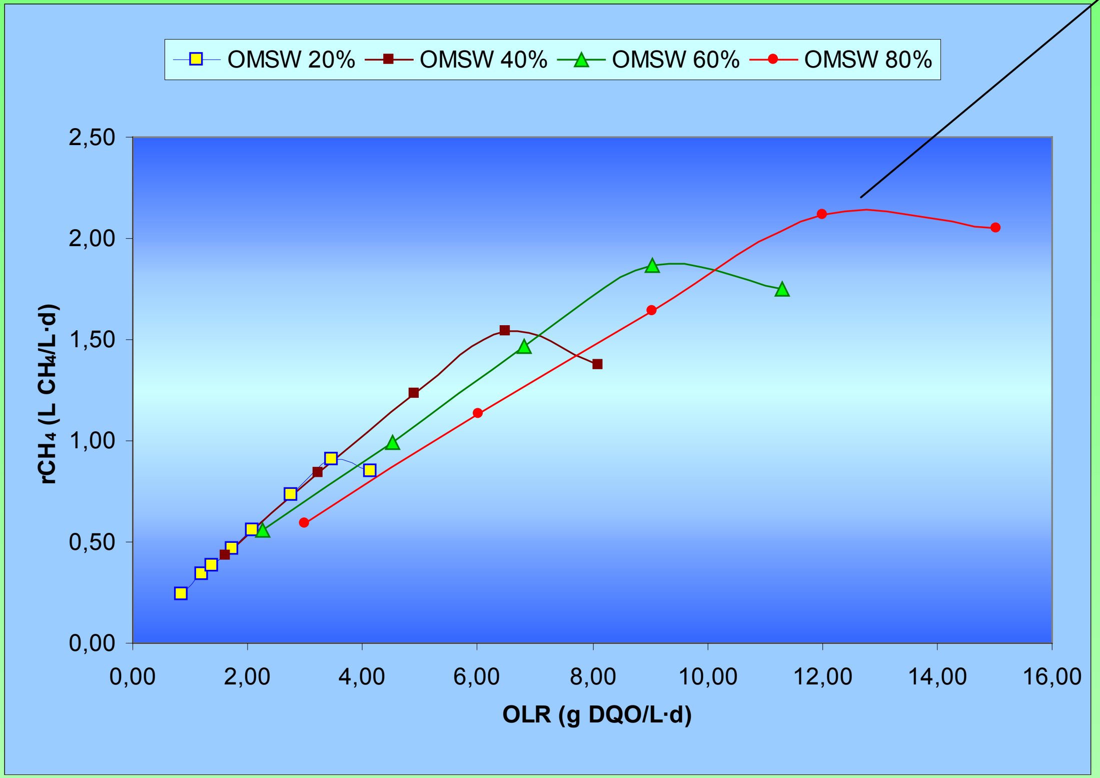
* COD removal decreased from 96 to 91% when the HRT decreased from 50.0 to 16.6 days.

• At an HRT of 10 days a marked decrease in efficiency was observed.

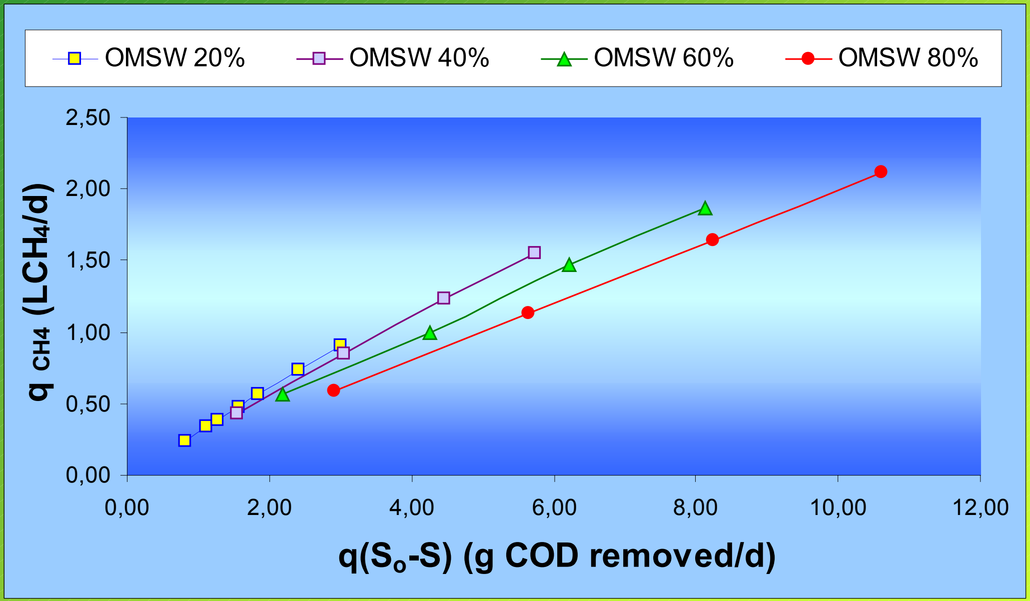
At HRTs higher than 16.6 days, the performance of the reactor is virtually independent of the feed COD concentration.



Variation of the methane production rate (L CH_4/L·d) with the OLR (g COD/L·d), for the different feed COD concentrations used



- The methane production rate increased linearly with increased OLR up to OLR values of 12 g COD/L d **(OMSW 80%).** After this value a slight decrease was observed.
- This decrease in the methane production at the highest OLR values might be attributed to an inhibition of the methanogenic bacteria, which caused an increase in effluent VFA contents and VFA/Alkalinity ratio.



METHANE YIELD COEFFICIENT(Y_p)

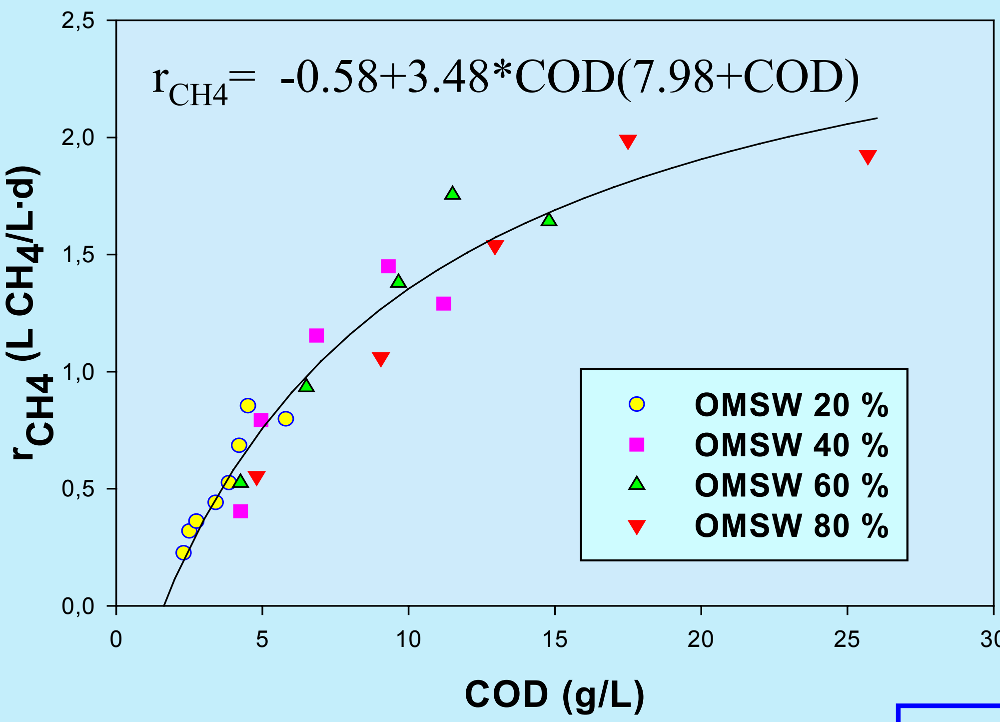
As the volume of methane produced per day, q_{CH4}, is proportional to the amount of substrate consumed ($q\ (S_o-S)$), then equation (1) allows the determination of Y_p:

$$q_{CH4} = Y_p\, q\, (S_o - S) \quad (1)$$

Where q is the feed flow-rate and S_0 and S are the substrate concentration (g COD/L or g VS/L) at the digeter inlet and effluent, respectively.

Influent substrate concentration (%)	*Yp* (L methane STP/g VS removed)
OMSW 20%	**0,290 ± 0,001**
OMSW 40%	**0,280 ± 0,005**
OMSW 60%	**0,230 ± 0,005**
OMSW 80%	**0,200 ± 0,001**

Influent substrate concentration (%)	*Yp* (L met hane STP/g COD removed)
OMSW 20%	0,300 ± 0,001
OMSW 40%	0,270 ± 0,003
OMSW 60%	0,230 ± 0,005
OMSW 80%	0,200 ± 0,006

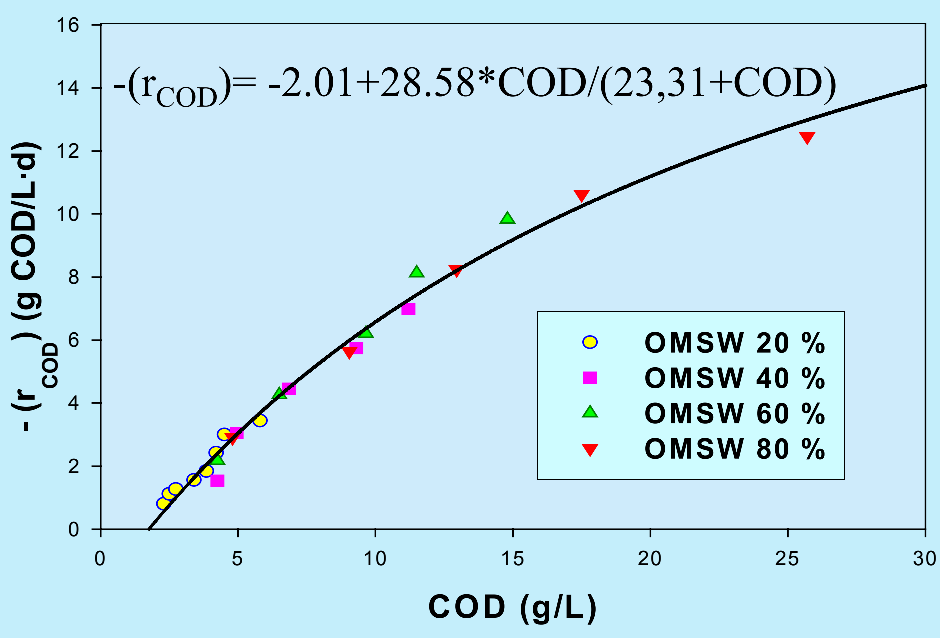


KINETIC STUDY

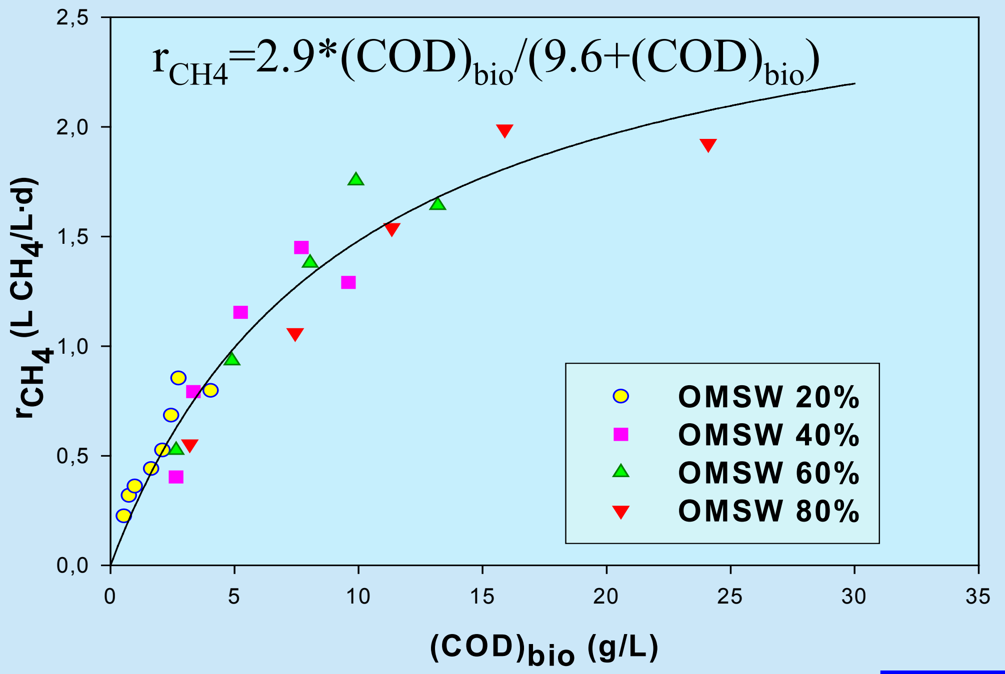
Variation of the methane production rate, r_{CH4} , and substrate removal rate, r_{COD}, as a function of the effluent total COD concentration (g/l) for the four influent substrate concentrations used.

Hyperbolic curves, whose intercepts on the x-axis are not equal to zero, were obtained. This fact shows that a fraction of substrate is not biodegradable.

Therefore, the experimental values of total COD were corrected by substracting the **fraction of non-biodegradable substrate (<u>1.69 g COD/L</u>).**



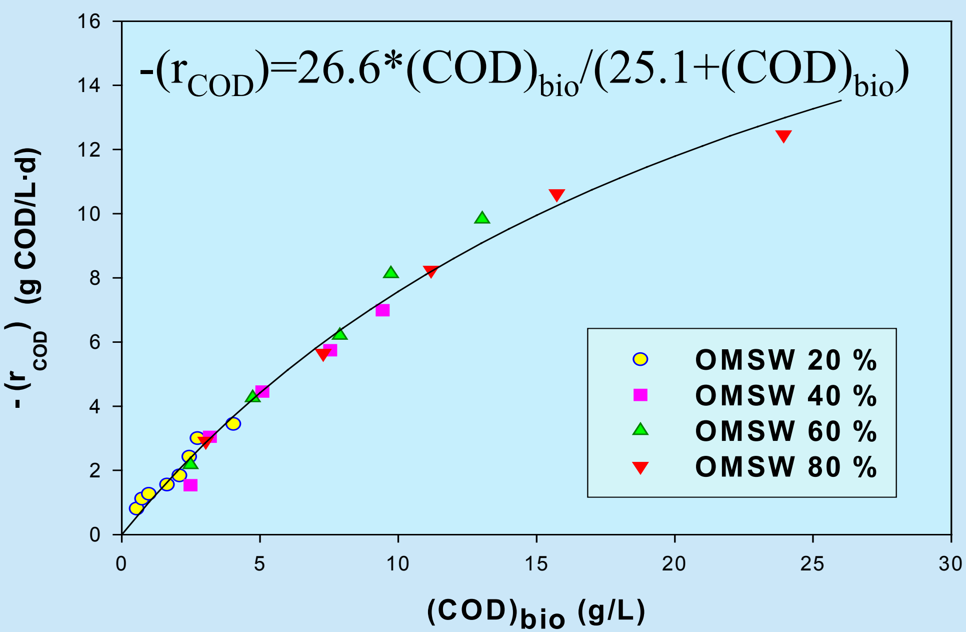
cropgen



Variation of the methane production rate, r_{CH4}, and substrate removal rate, r_{COD}, as a function of the biodegradable total COD (COD_{bio}) concentration in the reactor effluents for all the experiments carried out.

Both methane production and substrate utilization rates fit the Michaelis-Menten kinetic model, which is a hyperbolic function, quite well

cropgen



Comparative study of one and two-stages anaerobic digestion of two-phase OMSW

Characteristics of the OMSW:

COD = 162 g/L

SCOD = 58 g/L

TS = 143 g/L

VS = 126 g/L

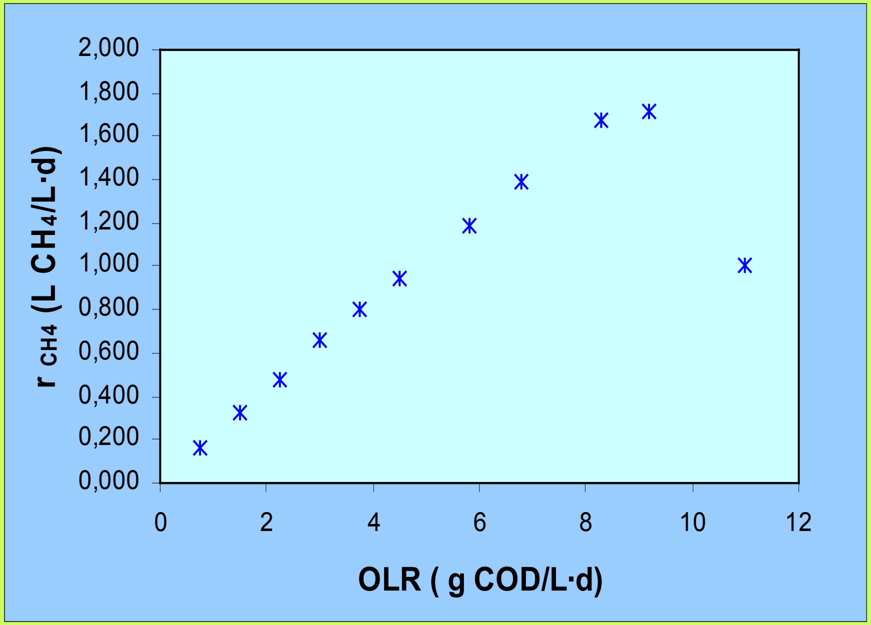
pH = 5.3

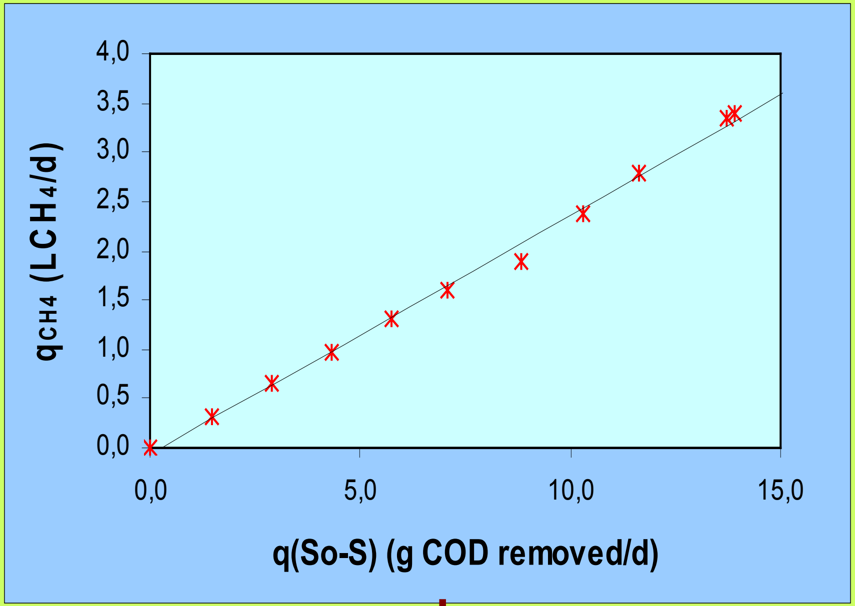
One-stage anaerobic digestion

Range of OLR tested: 0.75-11.0 g COD/L d

One-stage anaerobic digestion

cropgen





r_{CH4} max = 1.7 L CH_4/L d

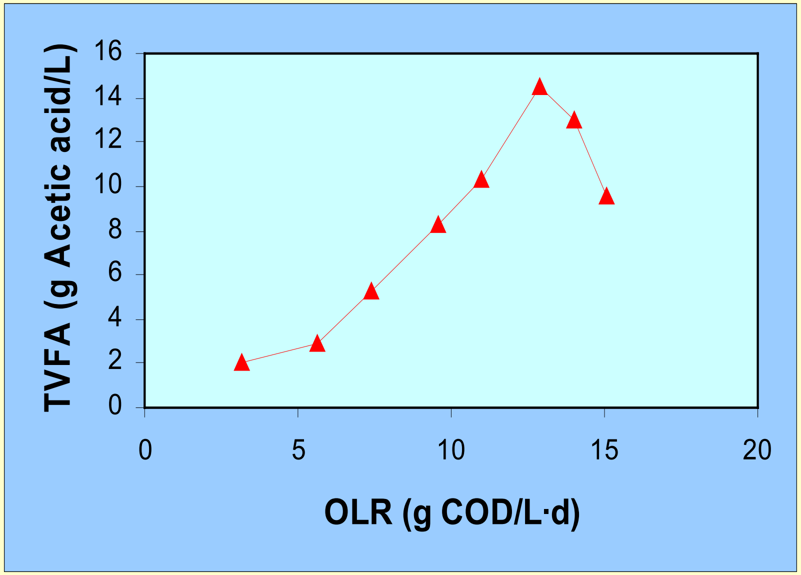
(OLR = 9.2 g COD/L d; HRT = 17.8 d)

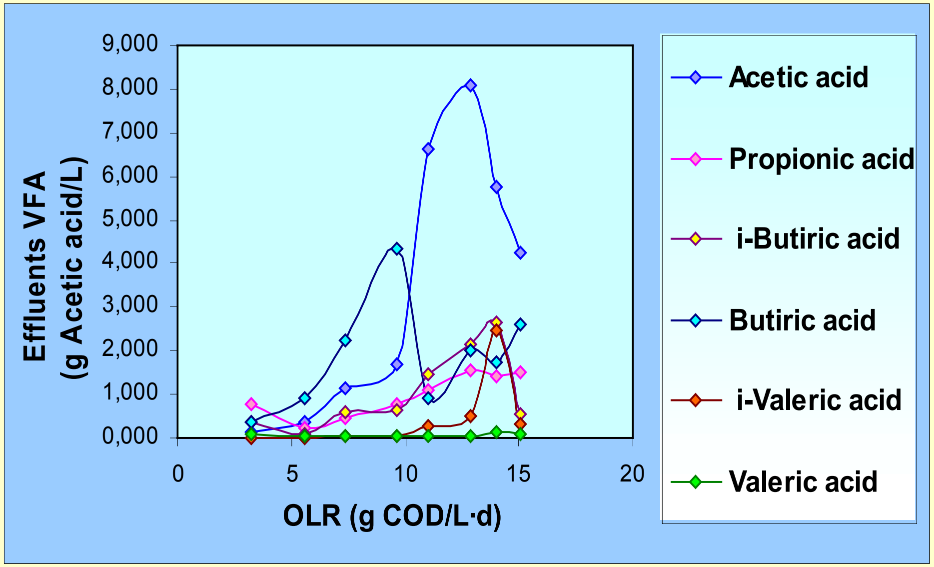
Yp = 0.244 ± 0.005 L CH4/g COD $_{removed}$

Two-stages anaerobic digestion

a) HIDROLITIC-ACIDOGENIC STAGE

(OLR range tested = 3.2 - 15.1 g COD/L d)





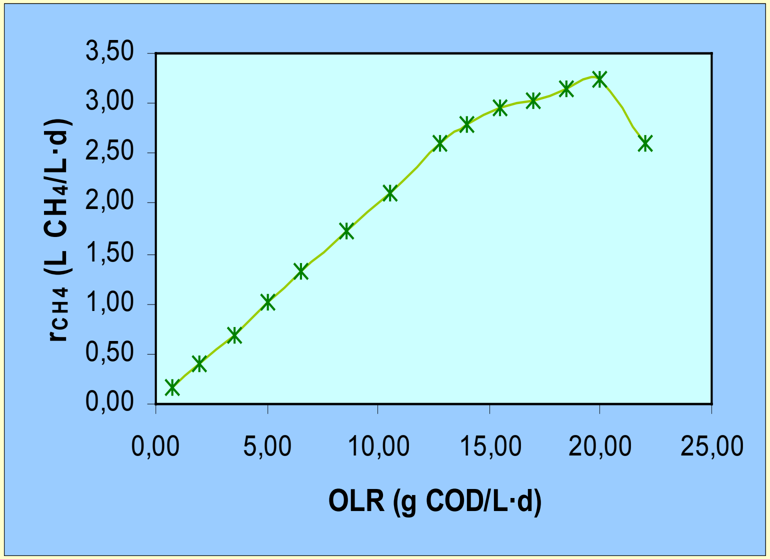
Maximum TVFA production = 14.5 g/L

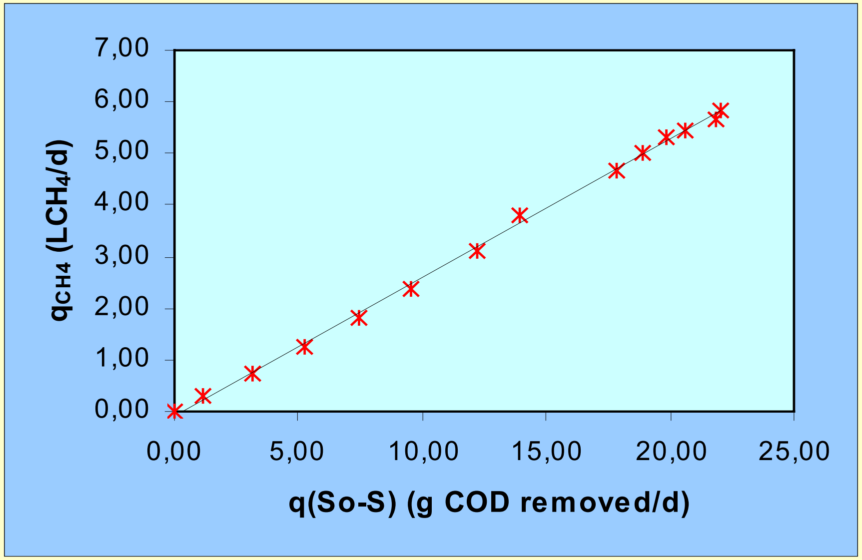
(OLR = 12.9 g COD/L d;   HRT = 12.4 d)

Two-stages anaerobic digestion

b) METHANOGENIC STAGE

(OLR range tested: 0.75 – 22 g COD/L d)





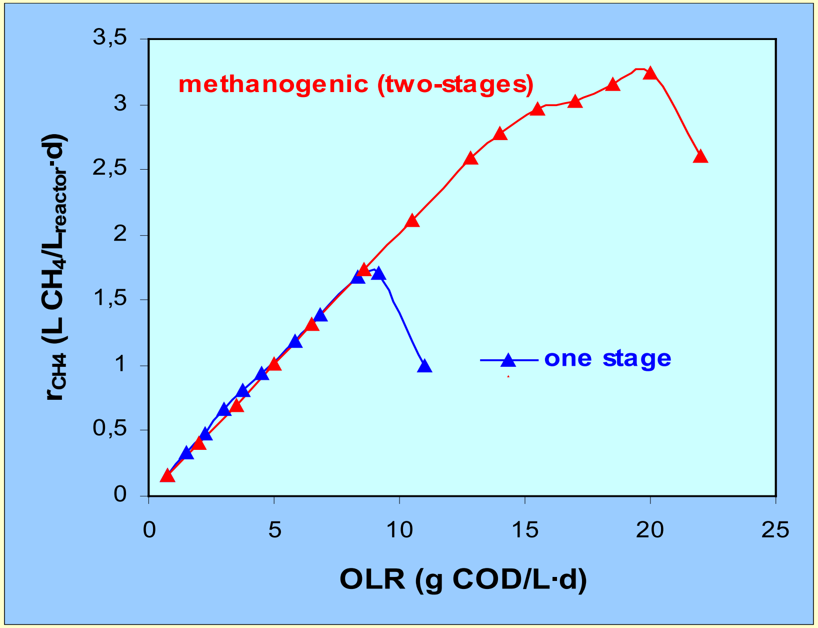
r_{CH4} max = 3.2 L CH4/L d

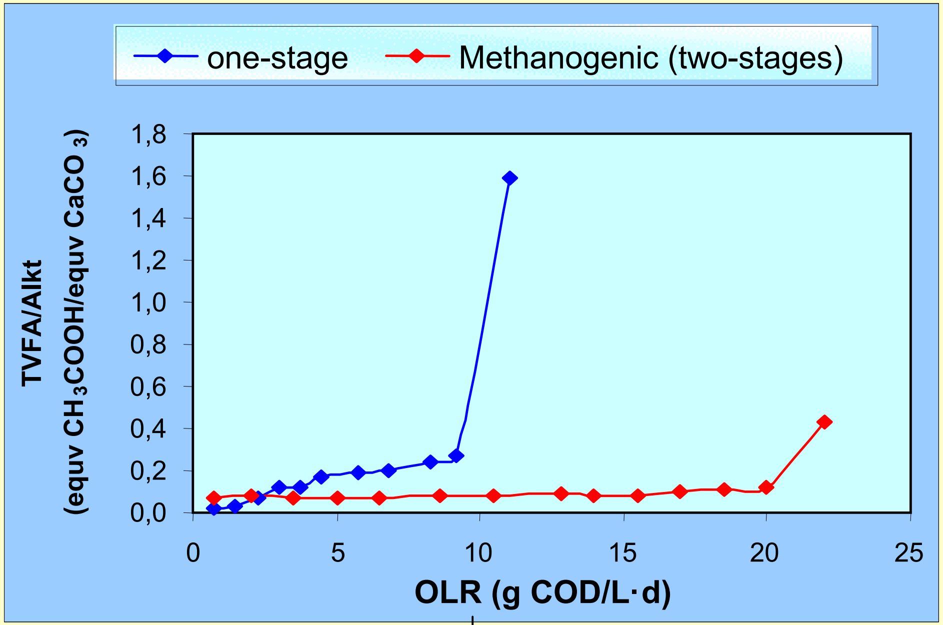
(OLR = 18.5 g COD/L d; HRT = 5.2 d)

Yp = 0.268 ± 0.003 LCH4/gCOD$_{removed}$

This value was 10% higher than that obtained in the one-stage anaerobic digestion experiment

By comparing one and two-stages anaerobic digestion processes





The maximum methane production rate (r_{CH4} max) for methanogenic step of two-stages digestion was **88% higher** than that obtained in the one-stage process

The stability of the methanogenic step of two-stage process was higher than that observed in the one-stage process: TVFA/Alkalinity ratios < 0.3-0.4 (failure limit value) were found at OLR of up to 20 g COD/L d

Therefore, the two-stages anaerobic digestion of this solid waste is more favourable than the one-stage process in terms of:

- **substrate removal efficiency,**
- **maximum methane production rate,**
- **methane yield coefficient, and**
- **process stability.**

cropgen

Thank you very much for your attention