Anaerobic digestion of residues from production and refining of vegetable oils as an alternative to conventional solutions

M. Torrijos, Arun Kumar Thalla, P. Sousbie, F. Bosque and J. P. Delgenès

ABSTRACT

The purpose of this work was to study the anaerobic digestion of by-products generated during the production and refining of oil with the objective of proposing an alternative solution (methanisation) to the conventional solutions while reducing the energy consumption of fossil origin on refinery sites. The production of sunflower oil was taken as example. Glycerine from the production of biodiesel was also included in this study. The results show that glycerine has a high potential for methanisation because of its high methane potential (465 ml CH_4/g VS) and high metabolization rates (0.42 g VS/g VSS.d). The use of oil cake as substrate for anaerobic digestion is not interesting because it has a low methane potential of 215 ml CH_4/g VS only and because it is easily recovered in animal feed. Six residues have quite a high methane potential (465 to 850 ml CH_4/g VS) indicating a good potential for anaerobic digestion. However, they contain a mixture of rapidly and slowly biodegradable organic matter and the loading rates must remain quite low (0.03 to 0.09 g VS/g VSS.d) to prevent any accumulation of slowly biodegradable solids in the digesters.

Key words | anaerobic digestion, fatty solid wastes, fed-batch, glycerine, oil production, oil refining

M. Torrijos (corresponding author)
Arun Kumar Thalla
P. Sousbie
J. P. Delgenès
INRA, UR50, Laboratoire de Biotechnologie de l'Environnement, Avenue des Etangs, Narbonne F-11100, France
E-mail: *torrijos@supagro.inra.fr*

Arun Kumar Thalla
Department of Civil Engineering, Indian Institute of Technology, Roorkee 247 667, Uttrangal, India

F. Bosque
ITERG, 11, Rue Gaspard Monge, Parc industriel Bersol 2, Pessac F-33600, France

CONTEXT

The fat sector includes the industries producing vegetable oils (crushing, refining, packaging), the industries producing fats of animal origin, the lipochemistry industry, …

Fourth in Europe, the French crushing rose over the past decade, reaching 3.4 million tonnes of grains in 2005 (rapeseed, sunflower, soybean,…). Crushing and refining factories are reaching today high production capacities. In crushing, a dozen sites have a production capacity ranging from 50,000 to 800,000 tonnes of seeds per year. In refining, 6 sites have a production capacity ranging from 25,000 to 250,000 tonnes of crude oil. The current amount of oil refined in France is estimated to be about 800,000 t/y. It is also necessary to take into account the quantity of "semi-refined" oil for the production of vegetable oil methyl ester. Considering the development of biofuels in France, ester production is expected to exceed 800,000 tonnes in 2008. The whole French sites is approved for the production of around 2.4 million tonnes of vegetable oil methyl ester by 2010.

According to various surveys carried out in recent years among industrialists on the management of their wastes, by-products and effluents, and in the light of the changes in the regulation, there is a willingness to reconsider the current recovering for some types of by-products and anaerobic digestion is one possible solution. Furthermore, the refining process involves the use of steam and the energy consumption is quite significant. Indeed in 1995, the refining industry consumed 25,394 TOE/year (27% of electric energy; 73% of thermal energy) and the average consumption was 425 kWh/tonne of refined oil. In an international context of rising costs of fossil fuels and of reduction in the

doi: 10.2166/wst.2008.505

emissions of greenhouse gases, manufacturers want to reduce the energy consumption of fossil fuels and biogas recovery can respond to this desire.

THE BY-PRODUCTS FROM THE REFINING OF VEGETABLE OILS

Refining of oils is intended to produce a product with a given quality, corresponding to the consumer expectations and to the needs of the industries and the quality of the refined oils must meet very comprehensive specifications.

The refining of vegetable oils involves several chemical or physical steps which generate different residues (see Figure 1).

Tank sediments

The storage of crude oils (before refining) leads to sedimentation of solid particles from the oil. These solids are called "tank sediments" and are, most of the time, incinerated.

Neutralization pastes

The First Step of the refining of oils is an acid-conditioning followed by neutralization, generating a by-product called "neutralization pastes". The goal is to eliminate the free fatty acids from the oil. The neutralization pastes generated contain soaps, phospholipids, various impurities, oxidation products and neutral oil in the form of an emulsion. For their elimination, neutralization pastes can undergo: (i) an on-site acid treatment at high temperature called "paste breaking" in a special workshop resulting in the production of "acid oils" which are used in animal feed; (ii) or can be shipped to undergo treatment in outside firms. These 2 solutions are unsatisfactory for several reasons. First, "Paste breaking" has several drawbacks such as risks to staff related to the projection of hot acid and to the production of sulfuric fumes, energy consumption, generation of a liquid waste with a high organic load in significant amount. Second, sustainability of the recovery path of the acid oils, or of the neutralization paste if they are not processed at the site before shipping, is threatened due to increased demands of the animal feed sector on the quality of raw materials. The amount of neutralization paste is not accurately known, but production is estimated to be in the range of 20 to 130 kg per ton of refined oil that is to say up to 160,000 t/y in 2008 (1,132,000 t/y in Europe).

Used clays

Discoloration, aimed at eliminating pigments from the oil, requires the use of clay as an agent of discoloration added in the range 0.1% for sunflower to 0.8% for rapeseed. This step generates a residue called "Used Discoloration Clay" (UDC).

Waxes present in some vegetable oils (sunflower and corn in particular) are removed in the winterisation step which requires the use of an adjuvant (clay), added in the range 0.05 to 1%. This step generates a residue called "Used Winterisation Clay" (UWC). The UDC and the UWC constitute the "Used Clay" (UC).

After use, the UC is in the form of a solid waste more or less pasty, depending on the moisture content, dark yellow to black for UDC and white for UWC. Apart from inorganic compounds, the UDC contains mainly oil and water. The UWC contains mainly waxes. The quantity of UC produced in France in 2001 was estimated to be 10,000 t/y approximately. Currently, the majority of the UC is sent to Denmark for anaerobic digestion and recovered by energy production.

Water from dewaxing

It is the wastewater produced when the dewaxing of the oil is achieved with a process which do not require the addition of clay. Waxes are fatty acid esters and long chain fatty alcohols naturally found in sunflower, cotton, … When pure, theses substances have a melting point higher than 70°C (158°F) but when dissolved in oil, they start to precipitate at 40°C (104°F) which turns the oil turbid and flaky.

Deodorizing condensates

For deodorization, the oil is heated at high temperature with steam stripping under vacuum. The condensate obtained after the washing of the vapors from the deodorization contains various constituents of the oil: sterols, tocopherols, oxydation products,… There are no precise studies, but the amount of condensates of deodorization in France is estimated to be about 1,500 t/y. They are generally sold with the acid oils.

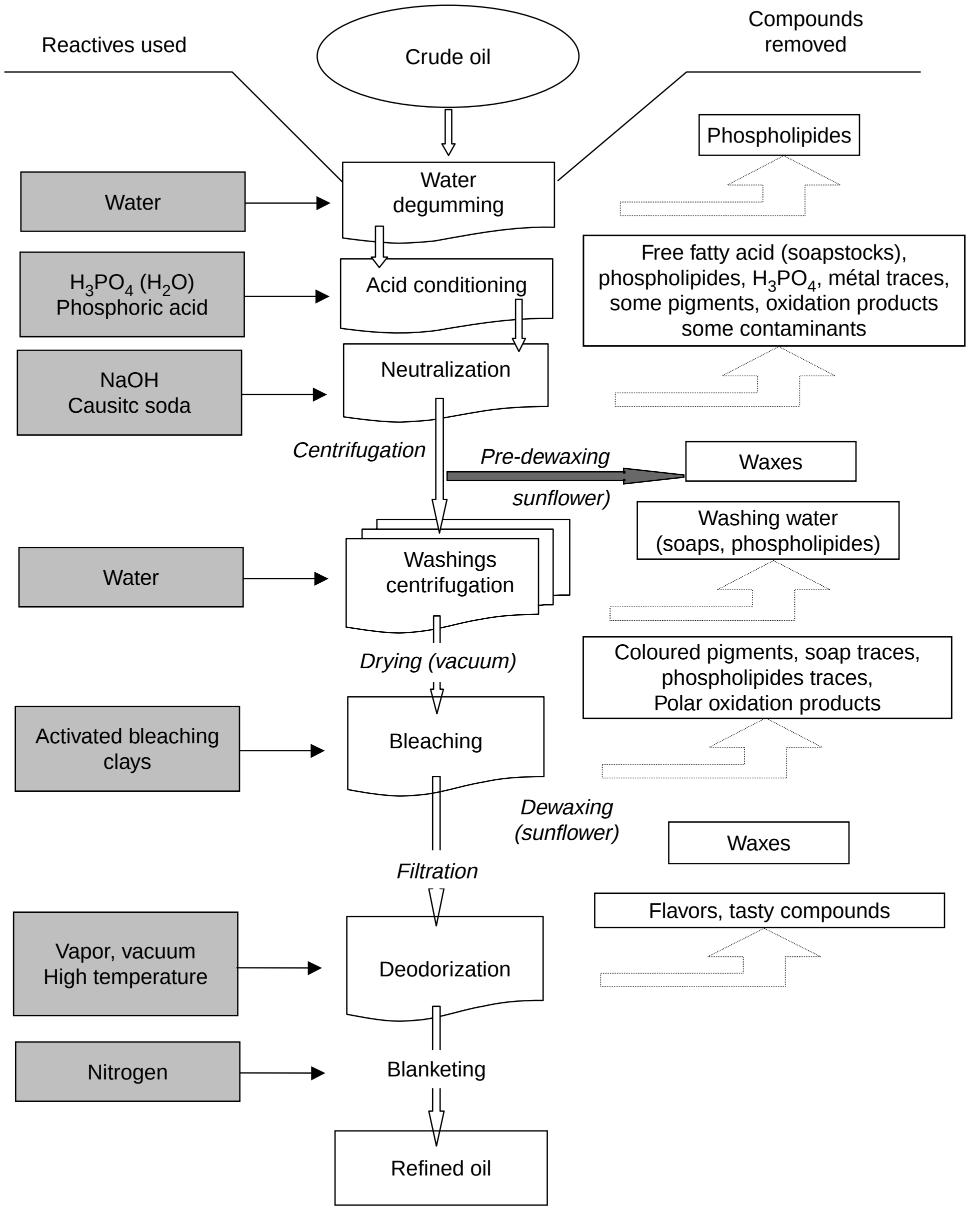

Figure 1 | Classical vegetable oil refining Steps.

OTHER BY-PRODUCTS FROM UPSTREAM AND DOWNSTREAM PROCESSES

Two by-products are generated by upstream and downstream oil refining processes: oil cake and glycerine.

Oil cake

The oils before refining are called "crude oils" and are produced by trituration of oilseeds. This process generates a by-product, the "oil cake", generally recovered in animal feed. The selling price of oil cake is currently quite high and the recovery of the oil cake in animal feed is not questioned in the short term.

Glycerine

Production of biodiesel from vegetable oils generates a co-product: the glycerine which contains mainly glycerol (Propane-1,2,3-triol, $C_3H_5(OH)_3$). World production of glycerine was 1 Mt in 2005, including 270,000 t from biodiesel production. The world production of glycerine from the production of biodiesel is expected to reach 600,000 t in 2008. That year, the supply may exceed demand in the order of 400,000 t. It is therefore necessary to find new ways of recovery, taking into account the increase in biodiesel production.

AIM OF THE STUDY

The purpose of this work was to study the anaerobic digestion of the by-products generated during the production and refining of oil in order to evaluate the potential of anaerobic digestion as an alternative to the conventional solutions while reducing the energy consumption of fossil origin on refinery sites. The production of sunflower oil was taken as example.

MATERIALS AND METHODS

Fatty solid waste

7 wastes from the production and refining of sunflower oil were used in this study: neutralization paste, Used Discoloration Clay (UDC), Used Winterisation Clay (UWC), deodorizing condensates, tank sediments, water from dewaxing and oil cake. Glycerine from the production of biodiesel was also studied.

Reactors

The experiments were carried out in double-walled reactors of 5 L effective volume, maintained at 35°C by a regulated water bath. Mixing in the reactors was done by a system of magnetic stirring. The biogas production was measured online by Milligascounter MGC-1 flow meters (Ritter gas meters) fitted with a 4–20 mA output. The software "Modular SPC", developed at the INRA laboratory, was used to acquire the data (gas output and pH).

Inoculum

The reactors were seeded with anaerobic sludge taken from the outlet of an anaerobic reactor treating distillery vinasse. The volatile suspended solid concentration (VSS) at the start-up of the reactors was around 12 g VSS/L. After seeding and before starting the addition of the waste, the reactors were fed 3 times with 2 mL of ethanol as sole source of carbon and energy to check the activity of the sludge.

Operation of the reactors

The reactors were fed manually with the raw wastes and were operated by batches without withdrawal (fed-batch mode). The reactors were fed with 1 to 2 g VS/l of reactor at the beginning of each batch (Table 1). The S_0/X_0 ratio was in the range 0.083 to 0.17 g of VS_{added}/g $VSS_{reactor}$. Each batch was carried on until the biogaz production rate was less than 5 mL/h. The experiments lasted between 1 and 2 months for each waste, according to the length of the batches.

Sampling and analysis

Gas composition was measured using a chromatograph Shimadzu GC 8 associated with an integrator Shimadzu GC 3A. The vector gas was argon. Other parameters were measured following *Standard Methods* (APHA 1992).

Table 1 | Operating conditions of the reactors

	Neutralisation paste	UDC	UWC	Deodorizing condensates	Tank sediments	Water from dewaxing	Oil cake	Glycerine
Qty added	1 gVS/L	1 gVS/L	1 gVS/L	1 gVS/L	1 gVS/L	1 gVS/L	1 gVS/L	1 or 2 gVS/L
Number of batches	12	7	6	5	10	7	7	4 at 1 gVS/L 12 at 2 gVS/L

RESULTS

The wastes studied

The solid and volatil solid concentrations of each waste are presented in Table 2. Two wastes (water from dewaxing and glycerine) were liquid and the others in solid form. The water from dewaxing was the less concentrated residue with 35 g TS/kg. All the other wastes had a high total solid content with values around 525 g TS/kg for neutralisation paste and tank sediments and more than 800 g TS/kg for the 5 other wastes. The organic fraction of the total solids was high (85% or more) except for the 2 residues containing clay for which the organic content was much lower with 48% for Used Discoloration Clay (UDC) and 61% for Used Winterisation Clay (UWC).

Biogas production

To evaluate the anaerobic biodegradability of the wastes, 5 L anaerobic reactors were operated with successive batches (fed-batch mode). All residues were added at 1 g of VS/L.batch, except glycerine which was added at 1 g of VS/L.batch for the first 4 batches and then at 2 g of VS/L.batch (Table 1). The volume of biogas produced was monitored online and the results obtained are presented in Figure 2 which represents the evolution of the volume of biogas produced with time for each waste during a typical batch.

The curves in Figure 2 show that towards the end of each batch, the biogas production rate was very low (<5 mL/h). For such low gas flow rates, it was not possible to differentiate between the biogas production from the endogenous metabolism and the biogas production linked to the degradation of the very slowly biodegradable organic matter. It was then considered that, in the operating conditions used in this study, the reaction was finished when biogas production was less than 5 mL/h which corresponded to the degradation of only about 1.7 mg of COD/L reactor.h. The arrow on each curve indicates the end of the reaction phase.

For neutralisation paste, biogas production was still 8.7 mL/h after 7 days indicating that the reaction phase was not completely finished. For this waste, the volume of biogas, the volume of methane and the methane potential were then slightly under-estimated and the organic rates slightly over-estimated as the reaction was not completely finished when the experiment was stopped.

Methane potential

The total volume of biogas produced during a batch was collected in a bag to analyse its average composition, to calculate the methane potential of each waste (Figure 3).

For the 8 residues, the % of methane in the biogas was in the range 62 to 74%, depending on the waste. High methane potentials (590 to 850 ml of methane/g VS, Figure 3) were measured for 5 wastes (UDC, Tank sediments, UWC, water from dewaxing, Neutralization pastes), indicating that theses residues are highly biodegradable and contain compounds with a high COD/VS ratio which can explain the high quantity of methane produced per g of VS.

Two residues (Deodorizing condensates, glycerine) had the same methane potential of 465 ml of methane/g VS.

Table 2 | Composition of the different wastes

	Appearance	Total solids (g/kg)	Volatile solids (g/kg)	VS/TS
Water from dewaxing	Thick and white liquid	35	31	89%
Neutralization paste	Light brown solid	520	440	85%
Tank sediments	Very thick and brownish paste	530	490	93%
UDC	Black powder	840	400	48%
Oil cake	Dry and dark granules	890	830	93%
UWC	Whitish powder	900	550	61%
Glycerine	Viscous, thick and light brown liquid	920	870	95%
Deodorizing condensates	Thick and dark brown paste	990	990	100%

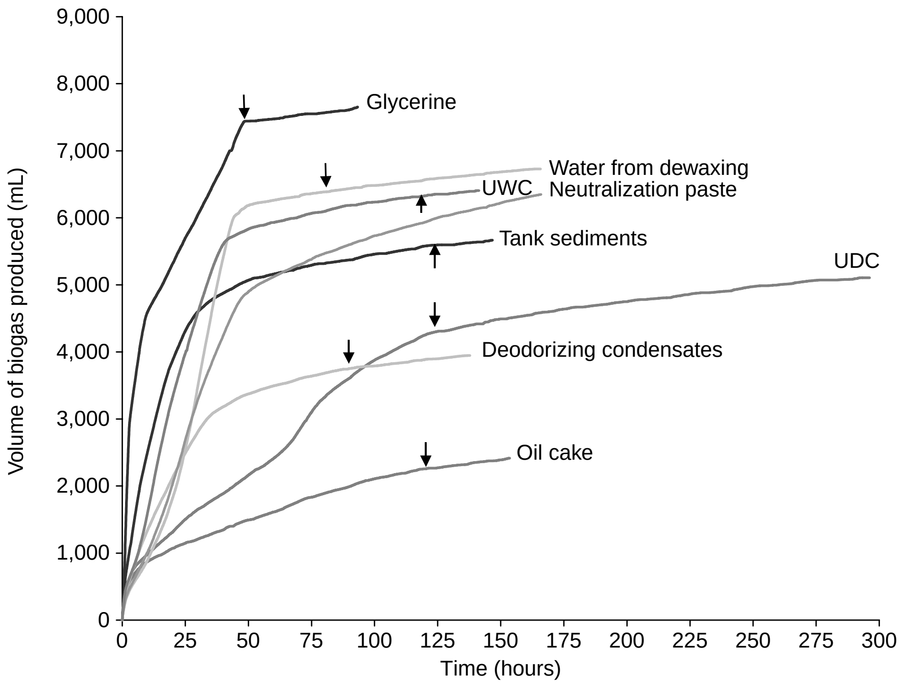

Figure 2 | Biogas production with time for the 8 wastes.

The methane potential of glycerine, which has a COD/VS ratio of 1.22, was very close to the theoretical value showing that this substrate was completely eliminated. For the deodorizing condensates, the organic matter added was not fully eliminated as small pellets were found in the reactor at the end of the experiment. Indeed, 4.8 g of dried solids and 4.4 g of volatile solids were accumulated which represented about 12.6% of the VS introduced with the feeds.

Oil cake, which was in the form of dry pellets, had the lowest methane potential with only 215 ml of methane/g VS

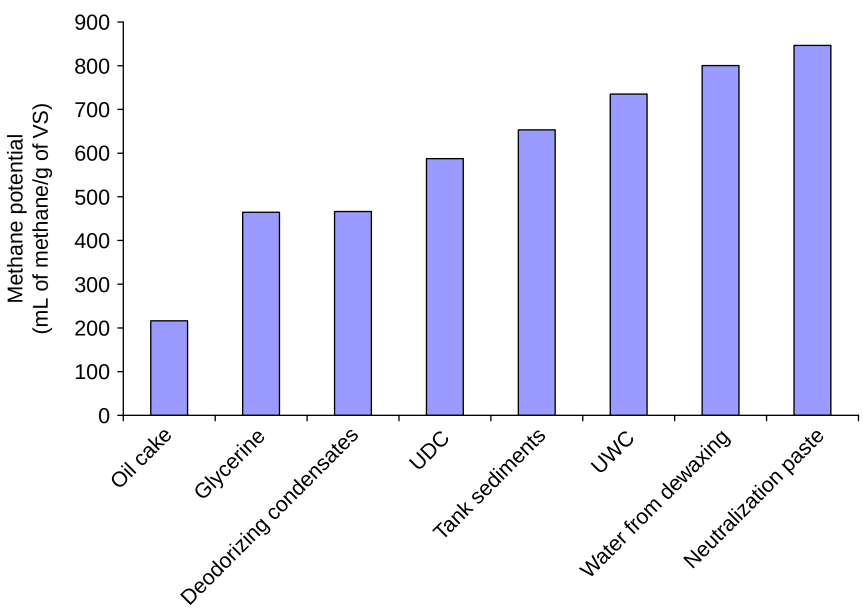

Figure 3 | Methane potential of the 8 wastes.

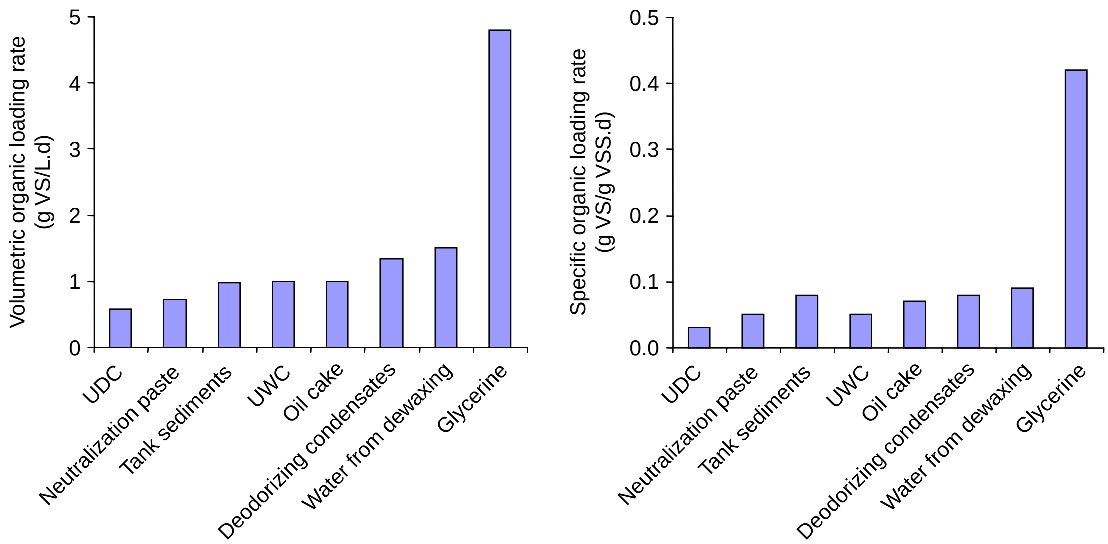

Figure 4 | Average volumetric loading rates and specific loading rates for the 8 wastes.

indicating that the anaerobic biodegradability of this substrate is low in the operating conditions used in this study.

The organic matter of 2 residues (oil cake and UDC) was slowly biodegradable and the rates of biogas production were slow for the entire batch and UDC for example had a specific loading rate 10 times lower than that of glycerine.

Loading rates

Figure 4 shows that glycerine was metabolized at high rates indicating that it is an easily biodegradable substrate. Indeed, the 2 g of VS/L added at the beginning of the batches were eliminated in 50 hours at average loading rates of 4.80 g of VS/L.d and 0.42 g of VS/g of VSS.d which is in the range of the data reported by Ruiz (2001, 2002) for different effluents. The other substrates were metabolized at much lower rates with volumetric loading rates in the range 0.57 to 1.50 VS/L.d and specific loading rates in the range 0.05 to 0.09 g of VS/g of VSS.d.

For 5 substrates (neutralization paste, UWC, deodorizing condensates, tank sediments, water from dewaxing) biogas production occurred at a high rate during the first 30 to 50 hours of the reaction phase (Figure 2) linked to the degradation of both rapidly and slowly biodegradable organic matter and then at a much lower rate during the following 30 to 80 hours indicating the degradation of the remaining slowly biodegradable compounds. Due to the presence of this slowly biodegradable organic matter, the overall loading rates were quite low.

CONCLUSION

The potentialities of 8 residues as substrates for anaerobic digestion have been investigated in this study, in 5 L reactors operated in fed-batch mode. The 8 residues were wastes generated during the production of sunflower oil (oil cake), the refining of sunflower oil (neutralization pastes, used clays, tank sediments, deodorizing condensates, water from dewaxing) and during the production of biodiesel (glycerine).

The potential of oil cake for anaerobic digestion is low. Indeed, the methane potential and the volumetric and specific reaction rates are low with respectively 215 ml CH_4/g VS, 1 g VS/L.d and 0.07 g VS/g VSS.d. At present, oil cake is recovered in animal feed and, according to the results of this study, it seems that anaerobic digestion of the oil cake is not really an interesting option which cannot compete with the current solutions of recovery.

Glycerine has a high potential for methanisation. Indeed, it is 100% biodegradable, it has a high methane potential (465 ml CH_4/g VS) and is metabolized at high rates (0.42 g VS/g VSS.d).

The 6 other residue are quite interesting for an utilisation as substrates for anaerobic digestion as they have quite high methane potentials ranging from 465 to 850 ml CH_4/g VS. However, they contain a mixture of rapidly and slowly biodegradable organic matter and the loading rates must remain quite low (0.03 to 0.09 g VS/g VSS.d) to prevent any accumulation of slowly biodegradable solids in the digesters.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the ADEME (French environment and energy management agency), ITERG (French Institute for Fats and Oils) and the following companies: Daudruy Van Cauwenberghe, Desmet Ballestra, Lesieur, Provence Huiles and Saipol, for Providing Financial support.

REFERENCES

APHA (American Public Health Association) 1992 American Water Works Association, Water Pollution Control Federation). Clesceri, L. S., Greenberg, A. E. & Trussell, R. R. (eds) *Standard Methods for the Examination of Water and Wastewater*. 18th edition.

Ruiz, C., Torrijos, M., Sousbie, P., Martinez, J. L. & Moletta, R. 2001 The anaerobic SBR process: basic principles for design and automation. *Water Sci. Technol.* **43**(3), 201–208.

Ruíz, C., Torrijos, M., Sousbie, P., Lebrato Martinez, J., Moletta, R. & Delgenès, J. P. 2002 Treatment of winery wastewater by an anaerobic sequencing batch reactor. *Water Sci. Technol.* **45**(10), 219–224.