

8. INNOVATIVE PROCESSES AND TECHNOLOGIES FOR MATERIAL RECYCLING

8.1 Introduction

The project allowed developing formal relationships with recycling and recovery industries in particular in the fields of lead from end-life batteries and of plastics and to perform research activities, achieving promising results from the point of view of the industrial application of the processes with relative patents. The activities are characterized by high strategic validity, due to the problem of the recycling/recovery/valorization of industrial wastes and of end-life components, taking into account the maximum respect for the environment. They have a significant innovative share too, due to research and development. Moreover it is an important element that the activities for the best use and valorization of the materials meet a more than mature requirement.

A further beneficial aspect for the ENEA is the possibility to use its experimental laboratories and infrastructures, in particular those located in Saluggia and Casaccia Research Centres, sites with the possibility to value and to develop the relative competences in synergy with those of outside University laboratories.

It is also necessary to keep in mind that the demonstration of the processes on a pilot scale and of prototypic plants (up to the preindustrial scale) needs the primary involvement of field industries and the finding of particularly high funds for each of the projects proposed.

The following project activities are underway or presented for financing procedure:

- Verification on a preindustrial scale of an integrated system for the recovery of the lead from exhausted batteries with the new hydrometallurgic process and for the recovery treatment of the related refuse plastics. The "Ecolead" ("Ecopiombo") research project will be presented to the MIUR (Ministero dell'Istruzione dell'Università e della Ricerca) Italian Ministry by ESI (Milazzo-ME) and Piombifera Bresciana S.p.A. (Macclodio-BS). Total cost of the projects ~ 14 ML € and ENEA consultancy costs are ~ 1 ML € [8.1-1], [8.1-2].
- Construction of the pyrolysis pilot plant, thermally self-sustained according to the FN supply contract. Total cost of the plants is ~ 0.2 ML €.
- Study and verification of processes for recycling and recovery of end-life thermosetting polymer matrix composites and electronic cards with presentation, together with C.S.M. S.p.A. and an industry of the sector (Rotamfer or ESO), of one project to MIUR, concerning the application of pyrolytic and hydrometallurgic processes (foreseen project cost is of ~ 5 ML € and ENEA costs of are ~ 0.5 ML €).
- Study and verification of the technology for recovery of precious metals from exhausted catalytic convertors. The technology proposed is concerned with an integrated process between the pyrometallurgic and hydrometallurgic ones up to the final refining. A proper project on this subject can be proposed. Up to now Chimet and A.D.A. (Car Demolishing Italian Association) have been contacted. Other possible industrial interests can be checked (Rotamfer) [8.1-3].
- Study and verification of the treatment for recovery of oil mill waste waters (OMWW). The project "Oliwa" was proposed as Craft/Growth, concerning an innovative technology (studied by ENEL-Hydro for sea water desalination), which is able to obtain very highly concentrated oil mill waste waters at reduced energy consumption. The technology is based on the principle of the barometric distillation (see Figure 8.1-1). The industrial proposers are O.M.T. (Grassina-FI) and a Greek oil mill company. Step 1 of the project has been already

approved. Step 2 foresees total costs of about ~ 1 ML €.

A different innovative technology, based on reverse osmosis, can be studied, in order to propose the research project.

- In the frame of National Research Council (CNR) fundings (within strategic and/or coordinated projects) activities of study and development of the industrial applications of the microwaves are foreseen, with particular reference to the transesterification reactions of triglycerides (in order to obtain biodiesel, or products of the cosmetic or pharmaceutical industry, etc.) and to the inertization of dangerous wastes (asbestos).
- Study and development of the treatment of liquid wastes, coming from tanneries, based on processes of separation and recovery of chromium (in the reduced form Cr III), in the frame of a wider search project, that SICIT-Chemitech S.p.A. (Vicenza), as representative of the Venetian tanneries, has already been presented to MIUR.

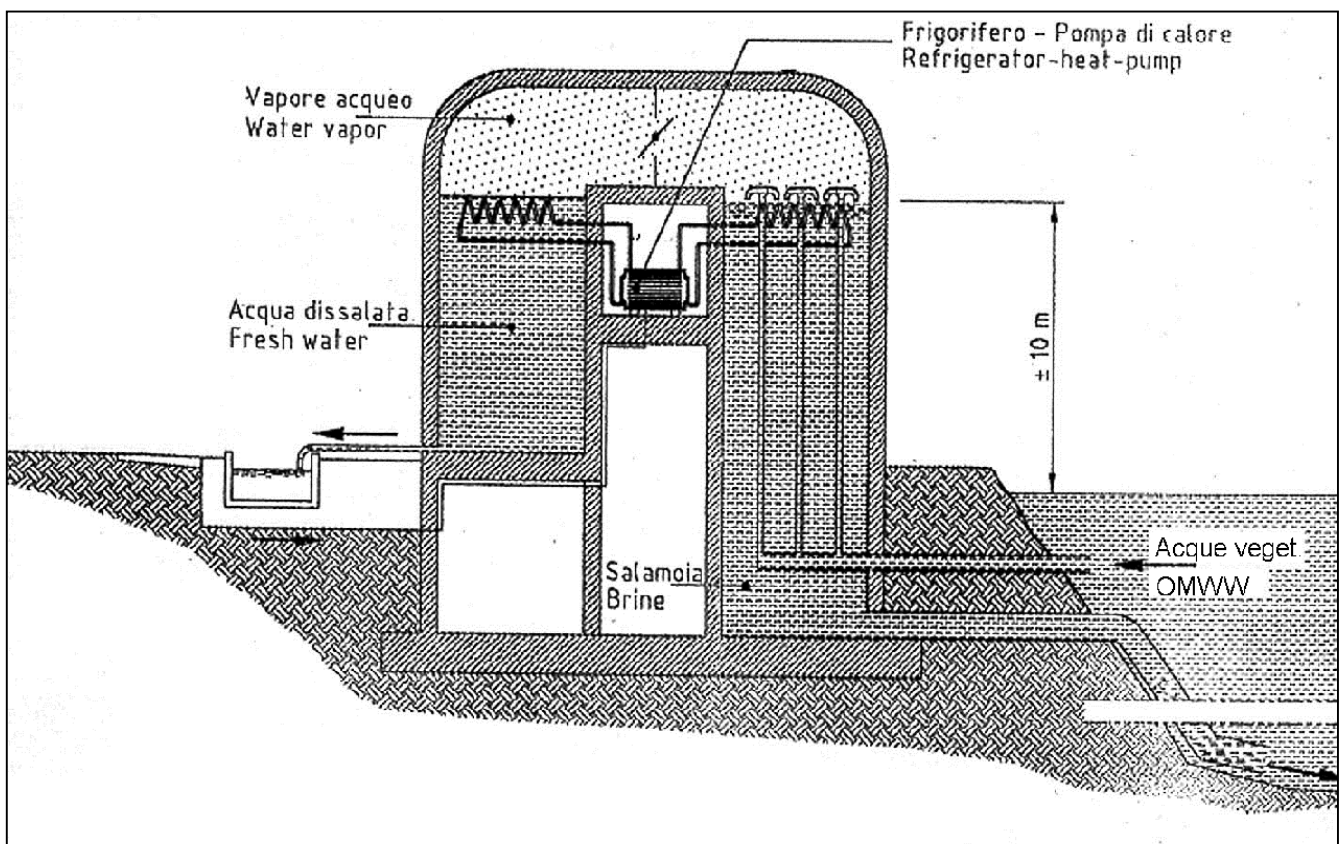


Figure 8.1-1 Barometric Distillator.

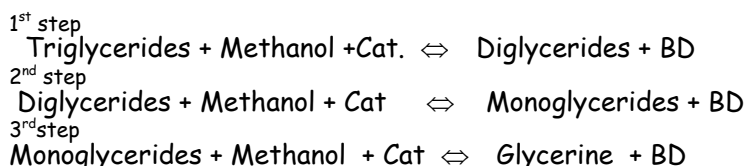
8.2 Industrial Applications of Microwaves

Concerning the activities performed in 2001 on industrial applications of microwaves (within CNR funds) we want to point out what follows.

8.2.1 Biodiesel and Mono/Di-Glycerides Production from Oils

Microwaves (MW) effect is mainly developed on the molecules polar groups, which undergo a continuous orientation induced by the electromagnetic field of the microwaves. The result is to have a localized energy concentration, which is released in the form of heat and causes an increase in the reciprocal solubility of scarcely soluble products (oil and alcohol) with very high acceleration of the reaction rate.

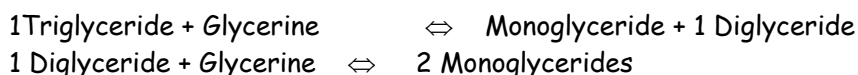
The alcoholysis reaction (transesterification) of oils to obtain methyl esters, whose mixture represents the basis for BioDiesel production, progresses by subsequent reaction steps:



BD = Mixture of methyl esters of fatty acids (BIODIESEL)
Cat = Catalyst

All these reactions are reversible and practically "athermic" (about $\Delta H=0$). The result is that the equilibrium positions is a function of the molar ratio of reagents and products.

The glycerol reactions of oils to produce mono- and di-glycerides are the following:



Also these reactions are practically "athermic" and the temperature influences the reaction rate, but does not influence the equilibrium positions. The reaction occurs at the interphase between reciprocally scarcely soluble phases (triglycerides-glycerine).

In order to increase the reciprocal solubility, in the traditional industrial processes a temperature increase up to 220-240°C and time-periods up to 20-24 hours are needed.

The treatment by means of MW allows obtaining higher quality Biodiesel, which has a lower glycerine and glycerides content. Besides a lower energy consumption, this method of activation allows a reduction of the reaction temperature and time and also avoids the degradation of the products. It has been found that during MW treatment mono- and di-glycerides (which are very good emulsifying agents of oils with polar substances like alcohols) are practically absent, as they capture MW and rapidly react with methanol. The reactions performed by traditional heating need 48 to 100 hours to reach a good phase stratification, while the same result can be obtained by MW in 12 hours only [8.2-1], [8.2-2].

8.2.2 Nuclear Waste Vitrification

The research program was set up to inspect the feasibility of using microwaves heating for the vitrification of nuclear waste in alternative to conventional treatment [8.2-3], [8.2-4].

As a matter of fact, a volumetric heating, like that introduced by means of an electromagnetic field, is expected to introduce a minor level of stress in the glass, and consequently a lesser amount of cracks in the vitreous structure.

Following the preliminary tests carried out in 2000, a larger experimental work was performed. Three kinds of glasses were tested, and many oxides were added in order to simulate the real composition of a nuclear waste. The glasses were both ground or used "as received" (1 mm

balls).

The glass/oxides mixtures were heated in a microwave multimode cavity (Radatherm), and the temperature was measured by an optical fibre system.

The use of optical fibre in the bulk of the glass was very important to appreciate the probe heating behaviour. As the optical fibre just works over 400°C, the probe showed a very little initial thermal gradient, followed by an extremely high heating rate.

That means that a dual heating system, conventional and microwaves, should be used in order to obtain very high heating efficiency.

The best results were obtained using the following, glass and oxides composition.

GLASS (%)		OXIDES (% on global)			
SiO ₂	58	TeO ₂	0,23	NiO	0,33
B ₂ O ₃	20	SrO	0,33	BaO	0,60
Na ₂ O	13	ZrO ₂	1,65	La ₂ O ₃	0,90
Al ₂ O ₃	2	MoO ₂	1,70	CeO ₂	0,93
MgO	5	MnO ₂	0,72	Nd ₂ O ₃	1,59
LiO ₂	2	CoO	0,12	Pr ₆ O ₁₁	0,44

Table 8.2-1 Selected glass/oxides mixture composition.

Regarding quality tests, the results obtained up to now have shown high homogeneity of melted glasses and almost total absence of crystalline phase; but feeble resistance to water-corrosion. Other glass composition need to be tested in the future.

8.2.3 Asbestos Treatment

In 1999 a research program was carried out, with financial contribution of CNR, to verify the feasibility of using microwave heating to convert pure serpentine asbestos into forsterite. The results obtained led to the patenting of the process [8.2-5].

In 2001 a new research program was started, with financial contribution of Environment and Health Protection Agency, to study the application of the technology previously developed to in-field treatment of large amount of asbestos containing waste.

The goal of the program is to modify the microwaves facility at Trisaia Research Centre and to carry out a series of tests in which both probe temperature and energy yield will be measured.

The new technique developed for high temperature measure by optical fibre system will be utilized.

The results of this research program could allow regarding this technology as a very interesting one in order to propose a completely new solution for asbestos waste management.

8.3 References

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