

## REMOVAL OF SOLVENTS FROM INDUSTRIAL WASTE WATERS

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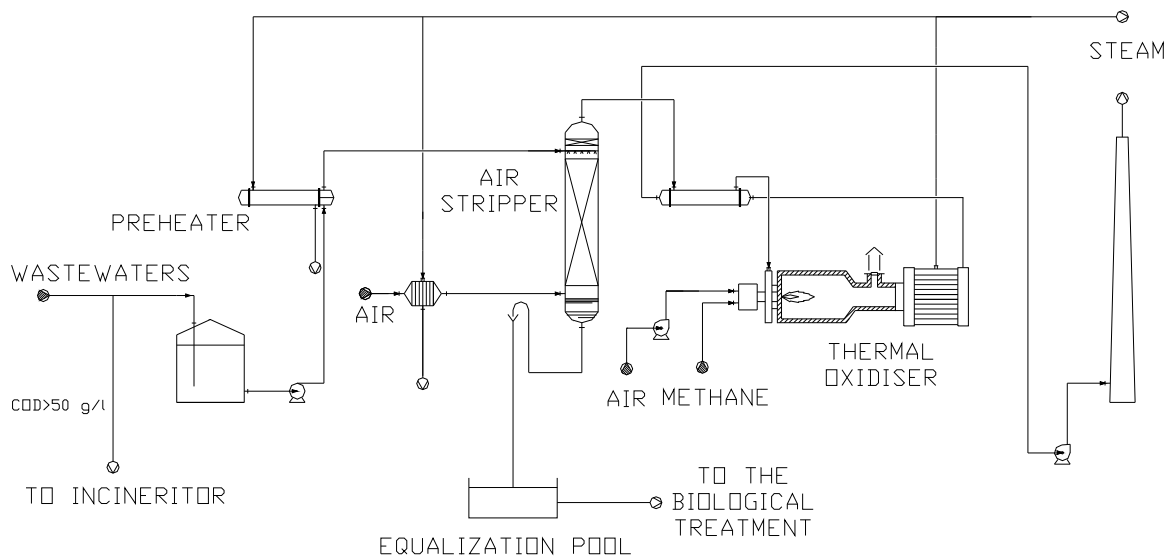
### Abstract

Some processes of the pharmaceutical, textile, paint-making industries produce wastewaters highly polluted by solvents (sometimes with tenor of 20% wt or higher) which are mainly low molecular weight alcohols and ketons. The high value of solvent concentration impedes feeding these contaminated liquids directly to the treatment systems commonly adopted for wastewaters with low tenors of solvents. So these wastewaters are today burned just the same in special type of incinerators. The present work reports the results of laboratory scale experiments carried out with the objective to identify and develop a wastewater upgrading scheme that fits well into an existing treatment configuration. The proposed scheme is then compared with the incineration solution to verify its economical convenience.

### Introduction

Many industrial processes produce wastewaters highly polluted by organic compounds, which may also contain solid particles. The trend is to equip the modern wastewaters treatment plants with a multipurpose treatment platform, composed of a variety of treatment units, which should allow treating every kind of wastewaters. The present work considers the case of wastewaters deriving from pharmaceutical, textile and paint-making industries and containing soluble pollutants, mostly low molecular weight alcohols and ketons, without solid particles. Wastewaters containing low tenors of solvents (up to 5% wt) are today usually fed to an air stripper, and eventually a biological system as in Figure 1. The outgoing air from the stripper, rich in VOC, is usually sent to a thermal oxidiser. Part of the generated steam is generally used to preheat the wastewaters stream and the clean air feeding the stripping tower.

But, if solvents concentration in wastewaters is too high, safety problems related to the explosivity of the mixtures formed in the stripping tower arise. This means an upper limit to the solvents concentration allowed in the wastewater, which correspond to a COD of about 50 g/l for the kind of organic compounds considered in the present work. The wastewaters examined come from pharmaceutical, textile, paint-making processes and their solvents content is so high that the COD can be 200 g/l or higher. Therefore, today these wastewaters are burned. The idea examined in this paper is to insert, upstream the air stripper, a thermal separation unit with the aim to obtain two streams from the wastewater: one stream rich in solvents and the other one constituted by partially purified waters. The COD value of the latter stream should meet the limit COD value that allows feeding it to the air stripper avoiding safety issues. The former stream, rich in solvents, could have a high heating value, which make it desirable as a fuel or it could be thought to perform a solvent recovery. This would be quite appealing since the solvent mixture might have a good market value.



**Figure 1-** Sketch of a treatment plant for wastewaters containing solvents.

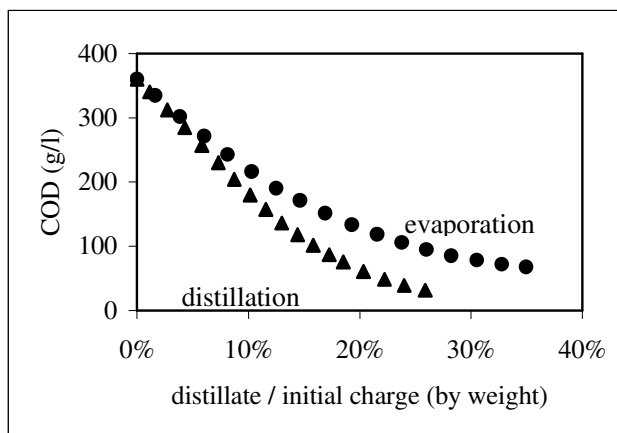
### Experimental apparatus

Wastewaters are multicomponent mixtures and due to their non ideal behaviour in terms of vapour-liquid equilibrium, experiments are required. The vapour-liquid equilibrium data may be also not available. Therefore, lab-scale experiments were carried out with the aim to measure some properties of streams obtainable by the thermal separation unit. The attention was mainly focused on the COD of partially purified waters and the heating value of the rich in solvents stream. On the basis of wastewaters laboratory analysis, typical organic compounds were pointed out. These were essentially acetone, methanol and ethanol. Accordingly wastewaters were reproduced as water-solvents mixtures. Experiments have been carried out on two ternary mixtures (acetone-methanol-water and acetone-ethanol-water) and a quaternary mixture (acetone-methanol-ethanol-water). Mixtures have been prepared in such a way to reach the total solvents concentration of 20% wt. Single compounds concentrations reproduced a wastewater analysis taken as model.

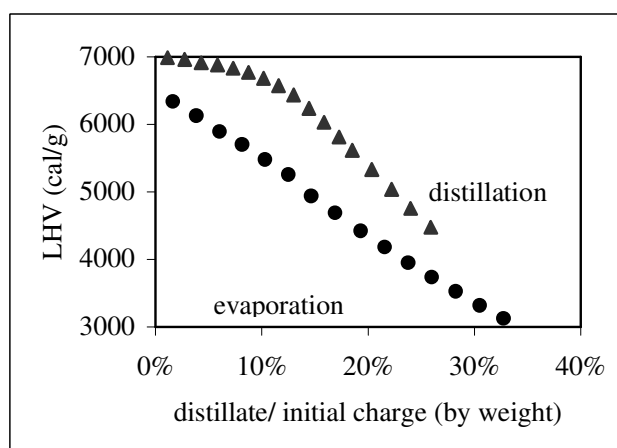
Experiments have been performed as batch operations at atmospheric pressure. First simple distillation ("evaporation") has been carried out. A simple evaporator has been employed: the still pot had a capacity of 500 ml and it has been provided with an heating mantle of 200 W power. Then, distillation experiments have been performed. A 500 ml still pot has been employed, provided with the same heating mantle as the previous one. The reflux system consisted an electromagnetic valve and a timing device which allows regulate the period of distillate take-off and the period of reflux return. Three types of Pyrex-glass distillation columns of 30 mm outer diameter have been used. They consisted of two Vigreux type columns, differing one from the other for the number of indentations, and a column packed with stainless steel Dixon rings arranged to give an overall packed height of 600 mm. To avoid heat losses, the apparatus was insulated with glass wool. Analysis of distillate samples were carried out by gas-chromatography in a Carlo Erba HRGC 5300 Mega Series chromatograph equipped with a 2 m length and 6 mm diameter Chromosorb 102 packed column. The detector was HWD type. The oven temperature is maintained at 100°C for 8 min, then is increased constantly up to 200°C with a rate of 5°C/min. The experimental apparatus has been checked previously by test mixtures to obtain the equivalent number of theoretical stage (N). Cyclohexane-toluene and trichloroethylene-eptane have been used as test mixtures: they were recommended for the operating temperature range and their samples could easily be analysed by refractometer.

## Experimental results

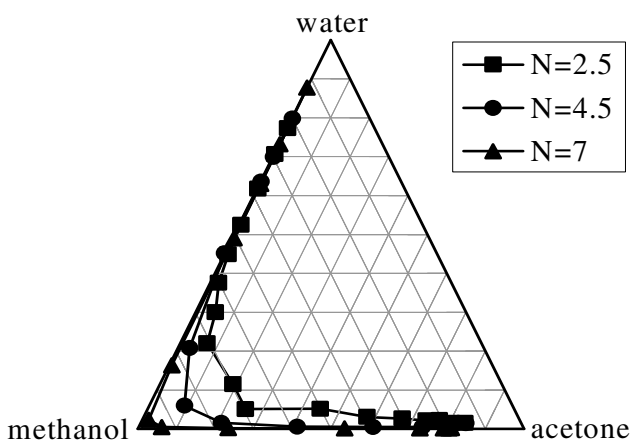
The results reported in the following figures are referred to experiments carried out on the acetone-methanol-water system. The charge composition was: water 80 %, methanol 11.5 % and acetone 8.5 % by weight. In Figure 2 "evaporation" and distillation operations are compared by reporting the COD of the remaining liquid in the still versus the amount of distillate to initial charge. In the distillation operation the reflux ratio was 3 and a column which is equivalent to 2.5 theoretical plates of separations has been used. The experimental results show that these few plates are enough to reach 50 g/l of COD by distilling about 22 % wt of initial charge, instead of evaporating over 40 % wt. In Figure 3 distillation and evaporation are compared by the point of view of the distillate low heating value (LHV). The heating value refers to the total amount of distillate collected up to that point. By comparing results, the convenience of employing distillation stands out. Thus, having assessed that the separation unit must be a distillation, experiments have been carried out to evaluate the influence of parameters either reflux ratio or number of distillation column plates on the desired separation rate. Logically, an increase of reflux ratio or plates number allows a better components separation. However, it has a negligible effect on the residue COD and on the distillate heating value. These two parameters are more affected by the total amount of solvents in the water than by the single compounds separation yield. Experimental results also showed low water concentrations in the initial distillate fractions: this detail suggests that a mixture of solvents with low water content can be easily obtained. Then effects of changing the reflux ratio or the plates number on components separation were investigated. The interest has been focused on the water tenor in distillate samples. Experimental results proved the efficacy and energetic convenience of increasing plates number over reflux ratio. Figure 4 shows ternary diagram referred to the acetone-methanol-water system. Distillation curves relative to different plate numbers (N) have been reported. A reflux ratio of 3 has been used. It can be noticed that the



**Figure 2** - Residue COD against total amount of distillate to initial charge.

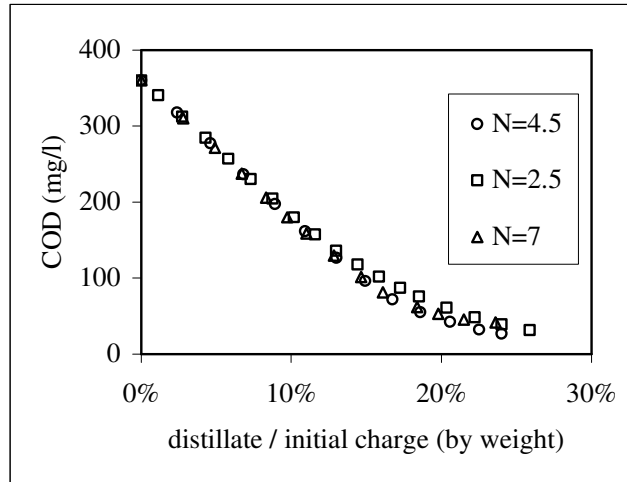


**Figure 3** - Cumulative distillate heating value against total amount of distillate to initial charge.



**Figure 4** - Distillation curves referred to different plates numbers (N). Concentrations are expressed as weight ratios.

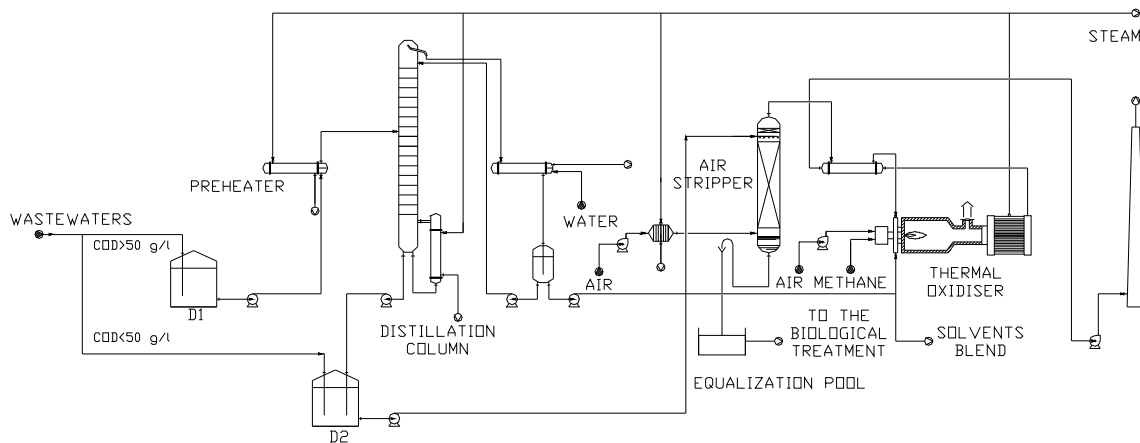
first distillation samples are constituted by the low-boiling acetone-methanol binary azeotrope (12% wt of methanol). The experimental results show that the acetone can be easily removed and that increasing plates numbers means improving separation, thus distillation curves shift to methanol vertex. With about 7 theoretical plates almost complete components separation is reached. Figure 5 shows the corresponding residue COD values obtained by working with different plates number and using a reflux ratio of 3. The figure evidences that varying plates number has negligible effects on the residue COD. Then, distillation operations has been carried out using different reflux ratios and same distillation columns. The reflux ratio has been changed from 3 to 9, that means to increase consistently the energetic expenses. By the effects on compounds separation it was noticed that operating on the reflux ratio is less convenient than working on the plates number. The experiments performed on the other ternary mixture (acetone-ethanol-water system) and the quaternary mixture lead to the same qualitative results. In conclusion, the experimental works showed that is possible to achieve the desired wastewaters COD of 50 g/l and also that solvent recovery is feasible, due to low water concentrations obtained in distillate fractions. Laboratory experimental results have been examined by referring to techniques based on residue curve maps and distillation curves. These methods are particularly useful to describe non ideal and azeotropic mixture distillation behaviour and to assess separation feasibility (Doherty and Perkins (1979), Van Dogen and Doherty (1985) et al.).



**Figure 5**– Residue COD against total amount of distillate to initial charge referred to different plates numbers (N).

### The new scheme and economical aspects

Based on laboratory experiments results, a distillation column was designed to insert in existing treatment plants like the one shown in Figure 1. The new arrangement is illustrated Figure 6.

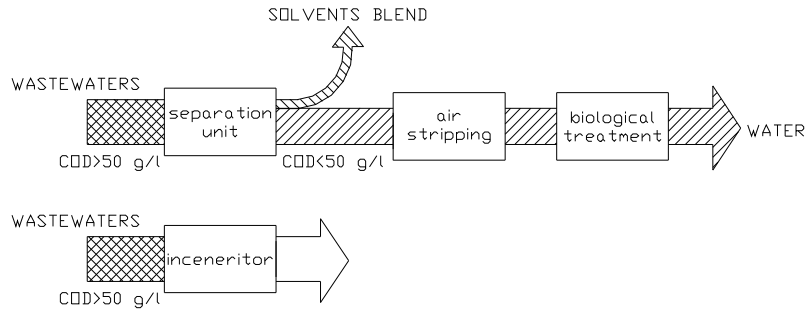


**Figure 6**- Sketch of a treatment plant with separation unit.

Incoming wastewaters with COD values higher than 50 g/l are stored in tank D1 and fed from this to the distillation column. The column overhead stream is a solvents blend and it can either be recovered, if

the water tenor is quite low, or sent to the thermal oxidiser. Logically the former choice is more appealing. The bottoms stream, has a COD value lower than 50 g/l and is fed to the storage tank D2. Wastewaters with low solvents tenors are directly fed to tank D2, by-passing the thermal separation unit.

Due to the large variety of feeding wastewaters, it is quite difficult to develop a comprehensive economic analysis. However, some preliminary considerations can be made to establish when adopting the new scheme is more



**Figure 7-** Flow rates alternatives.

convenient than wastewaters burning. In Figure 7 these two alternatives are illustrated. The innovation in the new arrangement is the opportunity of revaluing solvents, by recovering them as a blend. This has a certain market value which is related to the water tenor as shown in Table 1. First income derives from the wastewater treatment price, which depends on the solvents concentration and the presence of solid particles in the feeding stream. Table 2 relates the treatment price to the solvents tenor for different solid particles contents.

water concentration (% wt)	solvents blend value (€/kg)
0-1	0.335
1-2.5	0.260
2.5-5	0.130

**Table 1** – Solvents blend value against the water tenor.

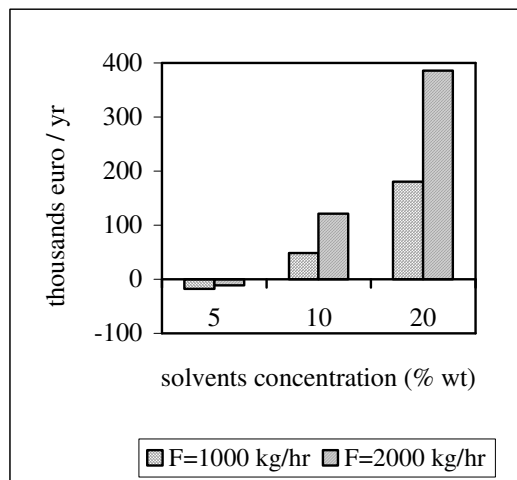
solvents concentration (% wt)	wastewaters treatment price (€/kg)		
	solid particles / (solvents+solid particles)		
	0% wt	5% wt	10% wt
0	0.150	0.150	0.150
10	0.143	0.144	0.146
20	0.135	0.139	0.142

**Table 2** – Wastewaters treatment price against the solvents concentration and the solid particles tenor.

An example of economical estimation is reported, referring to a “base case” of the plant fed with 2 m<sup>3</sup>/hr of wastewaters. By inserting the distillation column two streams are obtained from wastewaters as indicated in Figure 6. Partially purified waters from the bottom of the column are fed to the air stripper, then to an equalization pool and to the biological system: treatment expenses are quite cheap and can be estimated as 0.005 €/kg.

The stream outgoing from the top of the column, could either be recovered, if its water content is quite low, or fed to the thermal oxidiser. In the economical analysis, a total solvent recovery has been assumed and it is considered the case of a solvents blend containing up to 2.5 % wt of water, which means a blend value of 0.26 €/kg. It has been assumed that the plant works continuously 24 hours per day, 220 days per year. Energetic expenses have been evaluated as 0.015 kWh/kg of wastewaters.

Maintenance costs have been evaluated as 10 % of capital costs. Capital costs were available for a



**Figure 8–** Profits increase by introducing separation unit instead of burning wastewaters.

design flow rate of 2 m<sup>3</sup>/hr and they have been arranged in agreement with new flow rates. They have been scaled-up on feed flow rates by using the “six tenths rule”. It has been considered a project life of 5 years. Interest rate of 5% has been assumed. Burning wastewaters has been compared with the new scheme: estimations has been made for different solvent concentrations in the feed wastewater and for different flow rates (F). The treatment price by incinerators is about 0.14 €/kg of feeding wastewaters. Figure 8 shows, for different solvents concentrations and feed flow rates, the profit increase obtained by adopting the modified scheme instead of burning wastewater in incinerators. The new scheme implementation is convenient for flow rates of about 1-2 m<sup>3</sup>/hr, with a solvents tenor of about 10% wt or higher.

## Conclusion

In this paper an alternative scheme has been implemented by inserting a thermal separation unit in existing plants to permit to treat highly polluted liquids instead of their burning. By lab-scale experiments it appeared that the separation unit required to be performed as a distillation column and that it was possible to achieve a good organic compounds separation rate, enough to perform a solvent recovery. Then the new arrangement was compared by economical point of view with wastewaters burning in incinerators for a “base case” and it was assessed when modifying existing scheme is more convenient than burning polluted liquids. A preliminary economic estimation has been made.

## References

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