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Hazards and Safety Issues Associated to the Residual Solid Content in Crude Edible Oil Processing

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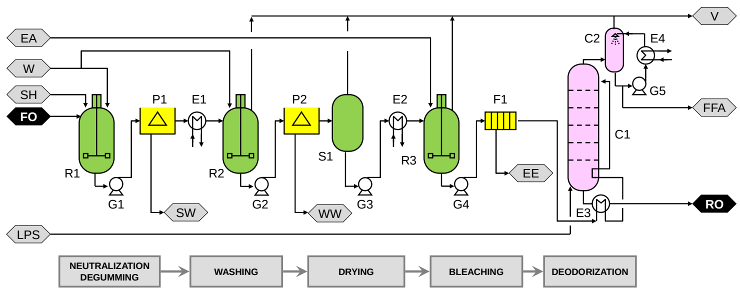
The present work focuses on the hazards connected with edible oil refining during process and maintenance operations. A specific experimental protocol was set up in order to verify the possibility of having fire hazards connected with the unwanted residual solids which might accumulate on the bottom of storage tanks, due to sedimentation, or in process equipment, due to progressive fouling. The analysis of residual solid samples taken from an actual edible oil refinery allowed evaluating the possible formation of flammable mixtures or products during maintenance operations. Specific hazard indexes were defined in order to analyse two case studies which provided indications for the safety enhancement of process and maintenance operations.

1. Introduction

The major part of the global edible oil production is obtained by seed extraction (FAO, 2011). The extracted crude edible oil is processed in chemical and physical refining, based on operations aimed at removing residual solvent, impurities and minor components (Shahidi, 2005). Figure 1 reports a schematization of the vegetable oil refining process.



Equipment items: C: column; E: heat exchanger/condenser; EJ : steam ejector; F: filter; G: pump; P: centrifugal separator; R: reactor; S: flash separator. **Material streams** : EA: bleaching earths & activated carbons; EE: exhausted earths; FFA: free fatty acids; FO: feedstock oil; LPS: low pressure steam; RO: refined oil; SH: sodium hydroxide; SW: soaps & waxes; V: vents; WW: Waste water; W: Water.

Figure 1: Process flow diagram (PFD) of the refining process (adapted from (Landucci et al., 2013)).

Numerous experimental and modelling studies are addressed on one side to the optimisation of the oily phase recovery (Calliauw et al., 2008) and to the quality enhancement of the final product (Carmona et al., 2010); on the other, the valorisation of the process by-products (e.g., olein purification, biodiesel production) is also extensively studied (Franca et al., 2011). Nevertheless, the study of residual solid content on process equipment performance, both considering process and safety aspects, is an emerging issue (Landucci et al., 2011).
The present work focuses on the different sections of the crude edible oil refinery in order to evidence potential hazards and criticalities, investigating two key aspects in detail.

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The first aspect is related to the solid sedimentation which occurs in the ordinary storage phase of the crude oil. During maintenance and cleaning operations, the sludge is drained with potential formation of flammable mixtures due to the release of entrained extraction solvent vapours. Two recent accidents (occurred in Italy in 2006 and in Spain in 2007) happened during this type of phase with multiple fatalities among the workers and consequent environmental contamination (Landucci et al., 2011). Therefore, this emerging issue was investigated with the experimental characterization of different sludge refinery residuals in order to evidence criticalities for maintenance operations.
The second aspect is connected to fouling and solid stratification in the units which only process the liquid phase. In particular, the example of deodorization was considered. This operation, as shown in Figure 1, is aimed at removing free fatty acids from the oil in packed columns, in which the residual of upstream filtrations might accumulate and stratify in the packing. Since the residuals typically contain high carbon content, the possibility of unwanted combustion on the packing surface was investigated by analysing samples taken from an actual deodorization column packing.
The outcomes of the study supported the definition of hazard indexes aimed at the safety assessment of process and maintenance operations of vegetable oil refineries. The methodology was applied to case studies considering an actual vegetable oil refinery.

2. Materials and methods

2.1 Overview of the methodology

The methodology is based on three main steps described in the following sections: 1) identification of potentially hazardous solid residuals and sampling from an actual industrial site; 2) experimental characterization of the considered samples in order to determine eventual hazardous conditions; 3) implementation of the results obtained in specific hazard indexes aimed at synthetically represent the hazard profile of vegetable oil refineries.

2.2 Description of the analysed samples

Two types of residual solid samples were identified as potentially critical and were obtained from SALOV refinery (Massarosa, Italy): 1) Sludge, e.g. a slurry containing crude vegetable oil and solid residuals, taken from the bottom of crude oil tanks (type 1); 2) Residual fouling material taken from the structured packing of process equipment (type 2).
Table 1 shows the summary of the analysed samples with the relevant features. Both samples types allowed determining the potential maintenance hazards in different process and storage units. Type 1 samples were collected before cleaning operations in several crude oil storage tanks. The sludge was stirred in order to have a homogenous slurry before carrying out the experimental analysis. Moreover, the associated oily liquid phase was analysed. The sample was obtained from the sludge sedimentation.
Type 2 samples were obtained after the removal of the structured packing from a deodorization column which was put out of service and replaced by other equipment units in April 2013.

Table 1: List of the analysed samples.

ID sample	Type	Description and source
A	1	Sludge taken from sunflower oil storage tank T1
B	1	Sludge taken from sunflower oil storage tank T2
C	1	Sludge taken from sunflower oil storage tank T3
D	1	Sludge taken from sunflower oil storage tank T4
E	2	Residual solid taken from deodorization column C1

2.3 Experimental set up for residual solids characterization

In order to characterize the residual tank sludge (samples type 1, see Table 1), thus evidencing problems related to potential volatile substance accumulation, a combined thermogravimetric analysis (TGA) with Fourier transform infrared spectroscopy (FTIR) of the evolved gases was first applied. Next the characterization of the sludge volatile fraction was performed with headspace gas chromatography - mass spectrometry analysis (GC-MS).
The TGA consisted in exposing a small sample of sludge (20 - 50 mg) to progressively increasing temperature, thus evidencing the weight loss and the derivative weight loss. The TGA was carried out with the TA Instruments TGA Q500 analyser. The samples were heated at a constant heating rate (20 °C/min) up to a final temperature of 900 °C; an isothermal stage of 10 min at the final temperature was performed. A 100 mL/min purge gas flow of pure nitrogen was employed, switched to air in the isothermal step at 900

°C. A TG-FTIR equipment formed by a Bruker Equinox 55 FTIR spectrometer coupled with a Netzsch STA 409/C thermoanalyser was used for the characterization of the volatile compounds released during the heating of the samples.

The composition of the sludge volatile fraction was investigated with a further set of trials, in particular applying headspace GC-MS analysis. A small portion of sludge (1-5 g) was conditioned in a closed vessel at 80 °C for 60 minutes. Next the headspace gas phase was analysed with a Fisons GC 9060 gas chromatograph interfaced to a Fisons MD 800 mass spectrometer.

For the characterization of type 2 sample (e.g., sample E, see Table 1) a scanning electron microscope model JEOL JSM 5600 LV was used for morphological analysis of the materials and Energy-dispersive X-ray (EDX) spectroscopy was applied in order to identify the potentiality of hazardous substances accumulation.

2.4 Definition of hazard indexes for edible oil refineries

The experimental analysis was aimed at determining potential hazards connected with maintenance operations on process and storage equipment. In fact, due to the presence of flammable materials, some types of operations, such as cutting or welding in confined spaces, may constitute a hazard for workers with potential accident escalation. Hence, depending on the type of maintenance intervention, an hazard score was defined according to the classification reported in Figure 2 (panel a). The hazard score scale range was established between 1 and 4. In order to penalise maintenance interventions, any type of operation during maintenance periods was associated to a minimum value of 3 (see Figure 2, panel a), thus with an intermediate or high severity class.

In previous works, specific hazard indexes were defined for the analysis of process hazards related to flammable mixtures formation in storage tanks during normal operations (Landucci et al., 2011). Those indexes were based on the evaluation of flammable vapours concentration in the top space of storage tanks trough a thermodynamic model, function of the residual solvent content and environmental temperature. In the present work, those indexes were integrated in the hazard assessment methodology, in order to provide a synthetic evaluation of the vegetable oil refinery safety issues, depending on the type of operations and environmental conditions. For this purpose, Figure 2 (panel b) shows the hazard ranking associated to the residual solvent concentration in the top space of the vessel, which can be estimated on the basis of the chart reported in panel c, obtained by the model developed by Landucci et al. (2011).

The analysis of case studies discussed in Section 3.3 will deal with the application of hazard indexes to the safety assessment of vegetable oil refineries.

Type of maintenance operation	Hazard ranking
Simple maintenance (instrument set up, pump start up, etc.)	3
Cutting, welding, hot work	4

a)

Top space solvent concentration (Ψ)	Hazard ranking
Ψ < LFL/10	1
LFL/10 ≤ Ψ <LFL/3	2
LFL/3 ≤ Ψ <LFL	3
Ψ > LFL	4

b)

c)

Solvent liq. concentration (% wt) \ Temperature (°C)	15	25	35	45	55	65
0.01%	1	1	1	1	1	1
0.02%	1	1	1	1	1	1
0.05%	1	1	1	2	2	2
0.10%	1	2	2	2	3	3
0.20%	2	2	2	3	3	3
0.41%	2	3	3	3	4	4
0.62%	3	3	4	4	4	4
0.85%	3	3	4	4	4	4
1.08%	3	4	4	4	4	4
1.32%	3	4	4	4	4	4

Safe operation
«ALARP» zone
Hazard zone

Figure 2: Definition of hazard indexes associated to process and maintenance operations in crude edible oil refineries: a) maintenance operations; b) hazard ranking related to crude vegetable oil storage tanks; c) chart for the evaluation of storage tanks hazard indexes. "ALARP" stands for "as low as reasonably practicable", indicating an intermediate hazard level. LFL = Lower Flammability Limit.

3. Results and discussion

3.1 Hazards during maintenance operations on storage tanks

The results of the thermogravimetric analysis (TGA) on the different types of sludge residuals are reported in Figure 3a. As it can be seen, three peculiar zones were identified in correspondence of the major weight loss rates. The first peak occurs between ambient temperature and 200°C, due to the presence of water and residual organics. This peak is more pronounced for sample type D (about 40% weight loss), while is less apparent for the other type 1 samples. The combined FTIR analysis allowed confirming that mainly water is released at low temperatures. Hence, even by changing the type of stored product and equipment, none of the considered cases presented significant amounts of organic volatile residuals.

The second peak occurs between 220 and 370 °C for all the considered samples, but the associated weight loss strongly differs according to the sludge type (ranging between 10 and about 30%). This peak was associated to the impurities and other products which are removed from the extracted oil in the core of the refining process, mainly free fatty acids. Besides, comparing the present analysis with the typical profile obtained with the same program for wood and cellulose (Haykiri-Acma and Yaman, 2007), the same peak was experienced, thus also associating the weight loss to the thermal decomposition of the solids contained in the sludge (e.g., seeds hulls).
Finally, the third peak occurs in the range 380 – 500 °C and it was due to the oily phase of the bottom sludge, mainly triglycerides. As a matter of fact, the same peak was experienced carrying out the same experiment with commercial refined sunflower oil (Dweck and Sampaio, 2004).

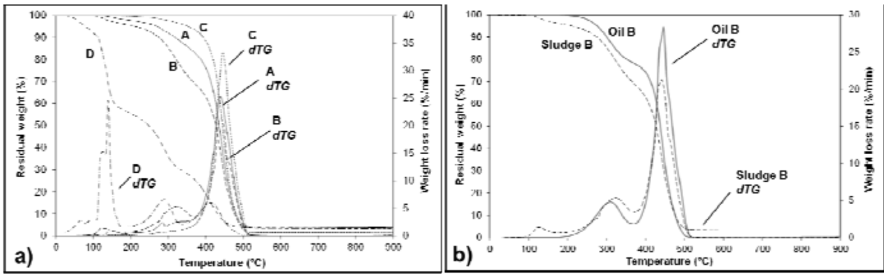


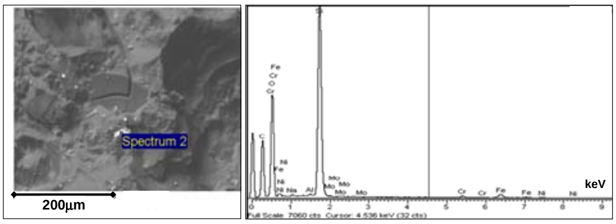
Figure 3: Results of the TG analysis on vegetable oil tanks residuals (100% nitrogen atmosphere): a) comparison among different type of residuals (see Table 1 for sample ID); b) comparison between sludge type B (Sludge B) and the associated liquid phase (Oil B). Curves labelled with the sample letters (A, B, C and D) represent the weight loss; curves labelled with "dTG" represent the weight loss rate for the corresponding sample.

In order to complete the sludge characterization, the comparison with the associated oil phase was carried out. The results are shown in Figure 3b for the residual of tank T2. As expected, the oil phase presented some differences in the weight loss behaviour. The more relevant is related to the absence of a low temperature peak, hence no volatile content was present in the considered sample, which was instead found in the sludge. The other two peaks, previously discussed, were also found in the oil phase. As expected, the peak associated to triglycerides decomposition was more pronounced, with negligible fixed residual quantities. It may be concluded that residual sludge has the potential to entrain volatile compounds but mostly water was accumulated.
The second part of the experimental set up allowed the characterization of the volatile fraction of the sludge with chromatographic techniques. In particular, for sample D, e.g. the one featuring the highest volatile content (see Figure 3a), the GC-MS technique allowed identifying the following substances: pentane, 3-methylpentane, hexane, cyclohexane, 2,4-dimethylpentane.
The experimental analysis demonstrated that in case of maintenance, the presence of flammable substances in the top space of the vessel only with the sludge phase, may occur and thus hazards related to the potential formation of flammable mixtures are posed to the workers during this type of operations.

3.2 Hazards during maintenance operations on process equipment

In order to characterize the hazards related to maintenance operations on process equipment, sample E was analysed. As mentioned in Section 2.2, this residual was taken from the structured packing of a deodorization column. This unit is aimed at removing acid content from the vegetable oil at high temperature (210-240°C) and under strong vacuum conditions (2 kPa).
This may cause the oil thermal decomposition, forming the mentioned residual. Moreover, since the treated vegetable oil is fed from a filtration stage (Landucci et al., 2013), some solid residuals might be also present due to possible filter inefficiencies. In this latter case, the residuals are associated to the spent bleaching earths, containing activate carbons used for the oil bleaching. More details on the vegetable oil refining process are extensively discussed elsewhere (Santori et al., 2012).
For the characterization of the residual extracted from the structured packing, the SEM-EDX analysis was conducted, obtaining the results shown in Figure 4.
The analysis confirmed the presence of silicates corresponding to the bleaching earths (elements such as Si, O and other elements that may be contained in these substances) and traces of Fe, Cr, Ni and Mo, typically part of the AISI 316 steel composition, i.e. the structured packing construction material. Moreover,

due to the bleaching earths presence, a high carbon content was supposed, due to the entrainment of activated carbons.



Element	Weight %
C	37.7
O	46.6
Na	0.2
Si	13.8
Cr	0.3
Fe	1.0
Ni	0.2
Mo	0.2
TOTAL	100

(a) (b) (c)

Figure 4: Results of the SEM analysis carried out on sample E: a) SEM micrograph of the sample; b) EDX spectrum c) composition for the analysed sample.

This evidenced the potential hazards related to the combustion of the residual solid during maintenance of the equipment in absence of nitrogen blanketing which is not normally carried out in some food processing equipment.

3.3 Analysis of two case studies

The experimental analysis confirmed the possibility of accident potential related to maintenance operations both on storage and process equipment. Moreover, as outlined in Section 2.4, a residual hazard is related to the operative conditions of crude vegetable oil. Therefore, in order to show how the operative conditions and maintenance might impact on the hazard profile of a vegetable oil refinery, two case studies were defined:

- Case study 1: analysis of the refinery storage during one year without controlling the quality of input crude oil and, thus, allowing high residual solvent content in the feedstock (Table 2 shows the supposed distribution of residual solvent content during the analysed period);
- Case study 2: analysis of the refinery storage considering the implementation of feedstock quality management, with maximum residual solvent content lower than 0.1 % by weight.

The SALOV refinery was selected to define the process conditions, maintenance service and ambient temperature distribution over a reference period (in particular, the year 2003 was chosen), the same for both the case studies. On the basis of the residual solvent concentration, Figure 2 (panels b and c) allowed estimating the hazard indexes related to storage. Moreover, the following frequencies for maintenance operations were assumed:

- "Simple maintenance" operations: one each two months;
- "Hot work" operations: two each year.

Table 2: Distribution of residual solvent content in the storage of crude vegetable oil used as input for case study 1.

Month	Residual solvent weight %	Month	Residual solvent weight %
January	0.5	July	0.2
February	0.2	August	0.2
March	0.1	September	0.1
April	0.4	October	0.7
May	0.7	November	1.3
June	1.5	December	0.6

The hazard index and the classification of maintenance operations is shown in Figure 2 (panel a).
The maximum hazard index between the one induced by residual solvent content and the one due to the maintenance operation was associated to the facility under analysis. This allowed obtaining a daily hazard profile for the period of interest.
Figure 5 shows the results obtained in the assessment of the case studies, both reporting the numerical value of the estimated hazard index (represented by dark vertical lines in the histograms) and the correspondent hazard ranking, according to the legend. Clearly enough, the hazard index value changes according to both storage and environmental conditions and/or depending on the type of maintenance operations. Figure 5a shows the hazard profile for case study 1, in which no quality management of the inlet crude oil was supposed. Hence, in some periods, high residual extraction solvent concentrations were

considered for the storage tank, resulting in hazardous operations (hazard index = 4) for several days, especially in June, when high ambient temperatures were coupled with high values of residual solvent content (1.5% by weight). Figure 5b shows the results obtained for case study 2, in which the management of feedstock was carried out, thus avoiding the presence of high fractions of residual solvent content. This resulted in limiting the hazardous conditions and the estimated hazard indexes. Nevertheless, even in this case, “hot work” maintenance (cutting or welding) penalized the hazard profile. Therefore, the adoption of the systematic use of nitrogen or steam blanketing before the operations and/or of specific access procedures (equipment full drainage, ventilation etc.) were recognized of fundamental importance to the enhancement of the refinery safety of operations.

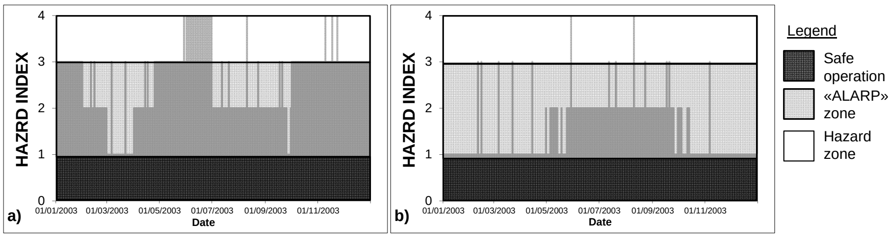


Figure 5: Case studies results: hazard index evaluation (dark histogram lines) and hazard ranking for case study 1 (a) and case study 2 (b).

4. Conclusions

In the present work a methodology was developed for the analysis of hazards and safety issues associated to the residual solid content in crude edible oil processing, both considering normal and maintenance operations. The methodology was based on experimental activities (TGA-FTIR, GC-MS, SEM-EDX) which outcomes supported the definition of specific hazard indexes. Residual solids samples, e.g. sludge (sedimentation residuals) formed in some crude vegetable oil tanks and structured packing fouling, were taken from SALOV refinery and analysed. In both cases, the potential of unwanted combustion hazard was experienced. On the basis of the experimental outcomes, some specific hazard indexes were defined and evaluated for two case studies, which highlighted the hazard potential of hot work operations and the need of adequate maintenance procedures.

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