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Analysis of Maintenance and Storage Operations in Edible Oil Plants: Formation of Flammable Mixtures

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Recent severe accidents occurred among the vegetable oil refining industry evidenced the hazards connected with extracted edible oils due to high residual solvent content (RSC), typically hexane, a high flammable volatile substance. The present study provides a methodology for the analysis of hazards related to the RSC in normal and maintenance operations for crude edible oil storage tanks. A thermodynamic model allowed the analysis of possible operative conditions leading to the formation of flammable mixtures inside the vessels. A specific experimental analysis was devoted to the characterization of the bottom sludge evidencing the potential formation of flammable mixtures in maintenance operations. The analysis provided a quantitative tool for the preliminary screening of the hazards connected to the storage of crude vegetable oils.

1. Introduction

Processing of edible oils obtained by seed extraction presents relevant hazards due to the potential formation of flammable mixtures and consequent fires and explosions. Several accidents occurred in the past presented these features (Landucci et al., 2011) since the solvents used for the extraction are typically volatile and flammable, such as the technical hexane (mainly pure n-hexane), which is the more commonly used among the edible oil supply chain (Shahidi, 2005).

Besides the extraction process, a relevant residual hazard is also connected to the “down-stream” operations, which are aimed at processing the crude vegetable oil in chemical refining before the distribution to the final user. In storage operations, since no inertization system is usually present on the tanks (Shahidi, 2005), the residual solvent may thus accumulate in the vapour phase, mixing with air and forming flammable mixtures which could result in the confined explosion of the storage vessel in presence of ignition.

As a matter of fact, two severe accidents with the same features happened in vegetable oil refineries probably due to the residual solvent content: the first in Italy in 2006 with 4 fatalities (La Repubblica, 2006); the second in Spain in 2007 with 1 fatality and 1 injured (El Economista, 2007). Moreover, the problem of flammable mixtures formation is also crucial in the framework of maintenance operations, which are typically carried out when the tanks are empty and a residual sludge accumulates on the bottom of the tank. In these situation the presence of ignition sources is increased (welding/cut operations, engines of maintenance contractors vehicles, etc.). Therefore, in order to provide quantitative evaluations for the provisional safety of storage and maintenance operations an approach was developed combining experimental and modelling studies on the crude vegetable oil – hexane system.

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A thermodynamic model, validated against experimental results, was used to evaluate hazard indexes related to storage operations. A specific analysis based on thermo-gravimetric techniques (TGA) and gas chromatography was carried out on the bottom sludge, aimed at investigating the potential accumulation of free hexane due to adsorption on the porous solid residual of the crude oil. The analysis allowed determining the potential temperature and hexane residual concentrations able to lead to the formation of flammable mixtures in the storage tanks both during normal operations and maintenance operations.

2. Materials and methods

2.1 Approach for the hazard assessment

The present study is addressed to both the analysis of normal processing and maintenance operations carried out in crude edible oil vessels. Therefore, two different approaches were needed for the analysis: the first is based on modelling the storage system with a thermodynamic analysis discussed in Section 2.2; the second is based on an experimental analysis described in Section 2.3.
Figure 1 reports a scheme representing the possible operations carried out in a vegetable oil storage facility.

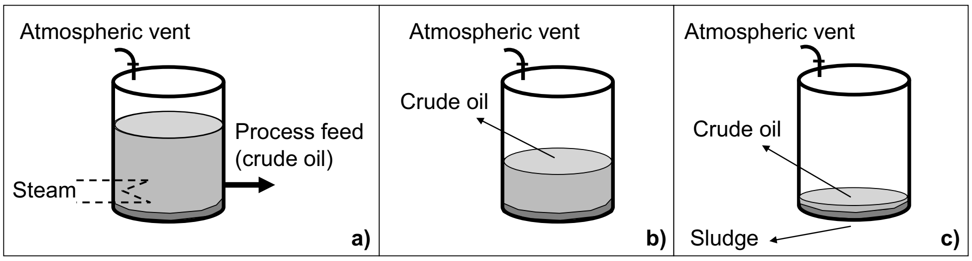


Figure 1: Schematization of the crude vegetable oil storage tank under a) process conditions; b) maintenance operations with high filling level; c) maintenance operations for tank emptying and cleaning

In Figure 1a the ordinary process conditions are schematized. In this case, the indications reported by Landucci et al. (2011) were used to derive specific hazard indexes based on the thermodynamic analysis of the crude oil – hexane equilibrium, thus deriving the potential vaporization of solvent in the top space of the vessel, typically provided with a direct vent to the atmosphere. As remarked in Figure 1a, a high-filling level operation is supposed, hence neglecting the possible effects due to the accumulation of the residual solvent in the sludge. A steam heating coil prevents temperature decrement below an imposed set point (typically 15-20 °C) (SALOV, 2009).
A similar situation is shown in Figure 1b, where the tank is subjected to minor maintenance operations hence a high filling level is kept to continue the operation after a quick intervention. In the case of more complex maintenance operations for tank cleaning or other relevant interventions, being the tank emptied, only a thin layer of residual oil is present in the vessel and eventual hexane accumulated in the residual sludge on the bottom part of the vessel may be released (see Figure 1c). Hence the experimental analysis of the sludge was carried out in order to characterize the eventual hexane accumulation in the residual bottom solid to the hazard assessment of complex maintenance operations.

2.2 Thermodynamic modelling of the storage vessels

In order to investigate the process conditions (Figure 1a) and the short maintenance operations (Figure 1b) the modelling of vegetable oil-hexane system was carried out for the evaluation of the explosion hazards in the vessel, related to the potential formation of flammable mixtures in the top space. The first step of the model implementation is the estimation of the liquid phase composition. In order to obtain a characterization of the oil phase valid for the more common types of crude vegetable oils, a reference triglyceride was selected (LLP composed by two linoleic groups and one palmitic group) coupled with a free fatty acid (oleic acid). The residual solvent content was assimilated to pure n-hexane following the indication of previous studies (Fornari et al., 1994). Once the liquid phase is schematized, the estimation of the vapour phase composition is carried out with a thermodynamic model, which describes the vapour-liquid equilibrium. The main equations and assumptions are summarized in Table 1. The activity coefficient γ_{hex} was estimated with a modified version of the UNIFAC (UNIversal Functional Activity Coefficient) model (Fredenslund et al., 1977) proposed by Sandler (1998) and Smith et al. (2001). The model allowed predicting the potential formation of flammable mixture inside vegetable storage vessels as a function of environmental conditions and residual hexane concentration in the storage tanks. The model was validated against available experimental data reported by (Smith and Wechter, 1951) showing a maximum absolute error of 5 % (Landucci et al., 2011) and thus was used for the present analysis.

Table 1: Main equations and variables of interest for the thermodynamic analysis of storage vessels

ID	Equation	Description and nomenclature
(1)	$y_{hex}P=\gamma_{hex}x_{hex}\phi_{hex}^{SAT}(T)P_{hex}^{SAT}(T)$	Equilibrium equation (Landucci et al., 2011) for the estimation of y_{hex} (molar fraction of hexane in vapour phase) as function of operative pressure and temperature P (Pa) T (K), activity coefficient γ_{hex}, hexane molar fraction in liquid phase x_{hex}, ϕ_i^{SAT} fugacity coefficient of pure hexane, P_i^{SAT} vapour pressure of the pure hexane.
(2)	$ln\,P_{hex}^{SAT}=\left(104.65-\frac{6995.5}{T}-12.702\,ln\,T+1.2381\cdot 10^{-5}T^{2}\right)$	Vapour pressure correlation for pure hexane (Liley, 1999)
(3)	$\phi_{hex}^{SAT}=\exp\left[\left(\frac{P_r}{T_r}\left(B^{(0)}+\omega B^{(1)}\right)\right)\right]$	Virial correlation for fugacity estimation (Reid et al., 1987)
(4)	$B^{(0)}=0.1445-\frac{0.33}{T_r}-\frac{0.1385}{T_r^{2}}-\frac{0.0121}{T_r^{3}}-\frac{0.000607}{T_r^{8}}$	First and second virial coefficients for Eq. (3). T_r = T/T_c; P_r = P/P_c where T_c and P_c are the critical temperature and pressure; ω is the acentric factor (Tsonopoulos, 1974)
(5)	$B^{(1)}=0.0637-\frac{0.331}{T_r}-\frac{0.424}{T_r^{2}}-\frac{0.008}{T_r^{8}}$	

2.3 Experimental set up for sludge characterization

In order to characterize the residual bottom solid, thus evidencing problems related to potential volatile substance accumulation, a combined thermogravimetric analysis (TGA) with Fourier transform infrared spectroscopy (FTIR) was first applied. Next the composition of the volatile compounds in equilibrium with the sludge was determined with chromatographic analysis mass spectrometry (GC-MS). The experimental analysis was carried out on sunflower seed oil sludge.

Table 2: Thermal programs applied in the TGA

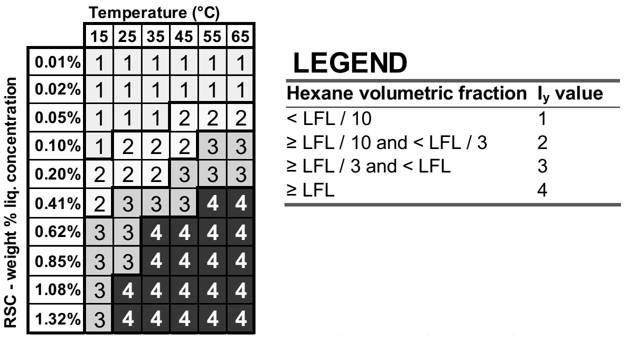
Step	Program 1	Program 2
1	Heating at constant rate (20 °C/min) up to 110 °C	Heating at constant rate (20 °C/min) up to 70 °C
2	Isothermal profile at 110 °C for 10 min	Isothermal profile at 70 °C for 10 min
3	Heating at constant rate (20 °C/min) up to 650 °C	Heating at constant rate (20 °C/min) up to 90 °C
4	Isothermal profile at 650 °C for 5 min	Isothermal profile at 90 °C for 10 min
5	Purge with air and isothermal profile for 5 min	Heating at constant rate (20 °C/min) up to 110 °C
6	-	Isothermal profile at 110 °C for 10 min
7	-	Heating at constant rate (20 °C/min) up to 650 °C
8	-	Isothermal profile at 650 °C for 5 min
9	-	Purge with air and isothermal profile for 5 min

The analysis consisted in exposing a small sample of sludge (10 mg) to progressively increasing temperature at regular intervals, thus evidencing the weight loss and the derivative weight loss (e.g., the amount of material lost per unit time in each step). The TGA was carried out with the analyzer TA Instruments TGA Q500. On the same time, the coupling with the FTIR Bruker Equinox 55 allowed analyzing the developed gas during the heating, in order to screen the composition of the decomposed substances. Table 2 reports the considered thermal programs set up for the analysis. As it can be seen the first program allows a general screening of the sludge (proximate analysis, steps 1 to 5 in Table 2). The second one was applied for the deeper characterization of the more volatile compounds, featuring several “low” temperature steps (1 to 6 in Table 2).
Moreover, the volatile fraction in equilibrium with the sludge was investigated with a further set of trials, in particular applying gas chromatographic analysis and mass spectrometry to evidence top space vapour composition. In particular, a small portion of sludge (500 ml) was mixed in order to get an homogeneous suspension and then conditioned in a closed vessel at 80 °C for 60 min. Next the top space resultant gas phase was analyzed with a gas chromatograph Fisons GC 9060 with a mass spectrometer Fisons MD 800 (GC-MS technique).

3. Results and discussion

3.1 Evaluation of thermodynamic equilibrium in storage vessels

The thermodynamic model described in Section 2.2 was applied to the analysis of the more common storage vessels in vegetable oil refineries. The model allowed estimating the possible combinations of storage temperature and residual solvent concentration (RSC) potentially leading to the formation of flammable mixtures inside the tanks, neglecting the eventual presence of the residual sludge (thus only for the storage conditions described in Figure 1a and 1b).
An example of results representation is shown in Figure 2.



RSC - weight % liq. concentration	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

Hexane volumetric fraction	I_y value
< LFL / 10	1
≥ LFL / 10 and < LFL / 3	2
≥ LFL / 3 and < LFL	3
≥ LFL	4

Figure 2: Determination of vapour hexane concentration and I_y index based on the application of the thermodynamic model as a function of storage temperature (°C) and residual solvent concentration (RSC) in weight %

In the chart shown in Figure 2, for each combination temperature-RSC a quantitative index I_y is given as a function of the evaluated hexane vapour concentration. As it can be seen from the legend, the hexane vapour concentration is expressed in the figure as fraction of its lower flammability limit LFL (= 0.011 volume fraction), thus leading to higher values of I_y if flammable mixtures can be formed in the vessel top space. The chart evidences that RSC exceeding only 0.2 % in the inlet crude oil has the potential to generate hazardous conditions, but only in the case of high temperature conditions in the vessels (due to prolonged and intense solar exposure). Thus the control of inlet feedstock’s is crucial to enhance the safety of the whole refinery.

3.2 Experimental characterization of crude vegetable oil sludge

The results of the thermogravimetric analysis (TGA) on the sludge are reported in Figure 3.
Figure 3a shows the weight loss and derivative weight loss obtained in the case of proximity analysis (Program 1). As it can be seen, three peculiar zones were indentified in the correspondence of the

major weight loss rates. The first peak is the more consistent and occurs at about 100 °C, due to the presence of water and residual volatile organics. The second peak occurs at about 280 °C and it 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 is 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 at about 420 °C and it is due to the oily phase of the bottom sludge, mainly triglycerides. As a matter of fact, the same peak is experienced carrying out the same experiment with commercial refined sunflower oil (Dweck and Sampaio, 2004).

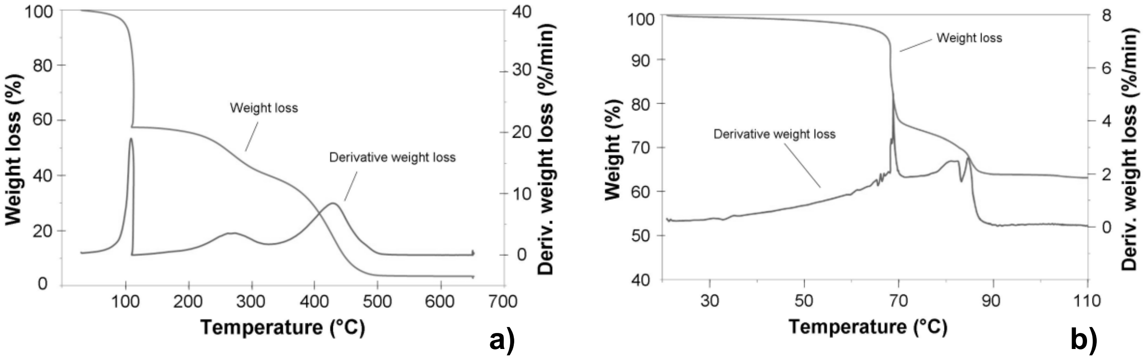


Figure 3: Results of TGA analysis: a) Program 1 results in the full temperature range; b) program 2 results only at low temperatures (see Table 2 for thermal analysis definition).

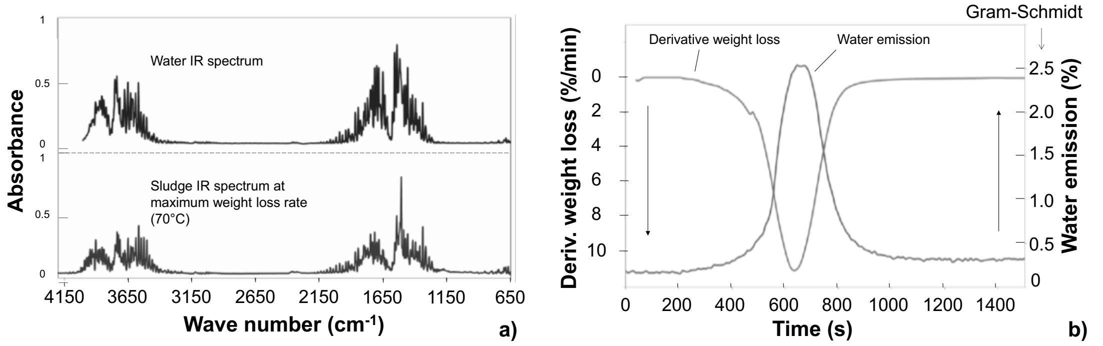


Figure 4: a) Comparison between the water IR spectrum and the sludge spectrum at maximum weight loss rate (at 70 °C, see Figure 3b).

In order to have a deeper characterization of the more volatile compounds of the sludge, the TGA program 2 (see Table 2 for details) was applied. Figure 3b shows the results obtained for a limited temperature range (only up to 110 °C), in order to better specify the temperature at which the maximum weight loss rate occurs. As it can be seen, a peak in the derivative weight loss is experienced at about 70 °C. The gases and vapours developed at that temperature were analyzed with the FTIR technique obtaining the absorbance spectrum shown in Figure 4a. The comparison with the available database allowed identifying that mainly water is released at the peak weight loss, thus evidencing that poor flammable vapour emission should be expected from the sludge phase. In particular, Figure 4b shows the dynamic water development which occurs during sludge decomposition in correspondence of the peak of derivative weight loss. After the characterization of the sludge phase, thus evidencing that mostly water is accumulated in the solid residual, the second part of the experimental set up allowed determining the vapour space composition with chromatographic techniques. Thus, sampling the vapour phase as described in Section 2.3, the CG-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, can occur and thus a higher risk condition due to the potential formation of flammable mixtures is posed to the workers during this type of operations.

4. Conclusion

In the present work a methodology was developed for the analysis of safety issues related to the storage of crude extracted edible oils, both during normal operations and maintenance. The methodology was based on modeling and experimental activities. A thermodynamic model was implemented in order to reproduce the liquid-vapor equilibrium of crude vegetable oil - residual solvent system. The model, validated against experimental data, allowed predicting the operative conditions during normal operations or short maintenance leading to the formation of flammable mixtures inside the tanks. The experimental analysis, in particular TGA-FTIR and gas chromatography techniques, allowed the characterization of the bottom residual. The potential development of flammable products from the bottom sludge was experienced, thus evidencing hazards also for long maintenance operations, in which the tanks need to be emptied or hot work is performed.

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