

Hazards Assessment of Vegetable Oil Storage and Processing Plants

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A quantitative methodology was developed in order to assess the possible hazards connected with the vegetable oil storage facilities and process plants. The main criticalities in these plants are due to the presence of residual volatile flammable solvents deriving from the extraction processes. The residual solvent may accumulate in the storage tanks generating flammable vapour mixtures. On the same time, the presence of volatile substances in the refining process feed may cause operative problems in the sections operating at high temperature and low pressure. The methodology allowed a preliminary assessment of the possibility of explosion hazard in storage conditions. Moreover, the implementation of the refining process model, allowed simulating undesired process deviations, and determining the effective control measures able to restore the operations.

1. Introduction

The major part of the global vegetable oil production derives from extraction processes which has been extensively used in the food industry from the beginning of last century (Bockisch 1998, Shahidi 2005). The process is based on the selective oil extraction usually carried out with a volatile organic solvent, typically hexane. After separation from solvent the oil phase is processed in chemical refining, in order to remove minor components such as phospholipids, free fatty acids, pigments, proteins and oxidation products. The vegetable crude oil usually presents a low content of residual solvent, which might result in safety and operational issues during storage and processing. In particular, due to the low vapour pressure the residual solvent may cause a loss of efficiency in high temperature vacuum operations (such as the drying and bleaching). In storage operations, since no inertization system is usually present on the tanks, 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. This work focuses on the development of an approach able to quantitatively evaluate the hazards due to the residual solvent on the storage and processing of vegetable oils. A thermodynamic model was then applied for the estimation of vapour phase composition in oil storage tanks and among the oil refining process as a function of operating condition. The refining process was schematized in

order to identify the main operations and the operative conditions in each piece of equipment of the plant. The application of the model allowed on one side the identification of potential hazards due to formation of flammable mixtures inside the storage tanks; on the other side the more significant nodes of solvent accumulation were identified among the plant process operations.

2. Modeling of the oil-hexane system

2.1 Model set up

The modeling of vegetable oil-hexane system is the necessary basis for both the evaluation of the explosion hazards in the vegetable oil storage facilities, related to the potential formation of flammable mixtures inside the storage tanks, and for determining the accumulation of hexane in the process nodes. 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 vapor phase composition is carried out with a thermodynamic model, which describes the vapour-liquid equilibrium using the following relationship:

$$y_i P = \gamma_i x_i \phi_i^{SAT}(T) P_i^{SAT}(T) \quad i = 1, \dots, N_c \quad (1)$$

Where y_i is the molar fraction of the i -th component in vapour phase, P operative pressure (Pa), γ_i the activity coefficient of the i -th component, x_i the molar fraction of the i -th component in liquid phase; ϕ_i^{SAT} the fugacity coefficient of the pure i -th component, P_i^{SAT} the vapour pressure of the pure i -th component, T the operative temperature (K) and N_c the total number of components. The crucial step in the set up of the thermodynamic model is the evaluation of the activity coefficient γ_i . A modified version of the UNIFAC (UNIversal Functional Activity Coefficient) model was applied in this work (Fredenslund et al. 1975, Fredenslund et al. 1977, Sandler 1998, Smith et al. 2001). Given a fixed operative temperature and a composition, the UNIFAC model is then able to predict with good accuracy the activity coefficient, allowing the application of the equation to estimate the partial pressure of residual solvent in the vapour phase.

2.2 Model validation

In order to test the validity of the model, a comparison with available experimental data was carried out. The only available data for diluted solutions, which are significant in the present case, are reported by Smith and Wechter (1951). Data are referred to the soybean oil/n-hexane solutions with a residual solvent content in the range 0.2% - 1.32% by weight. The vapour pressure of the hexane is measured in the experiments as a function of the temperature. Figure 1 reports the results of the model validation.

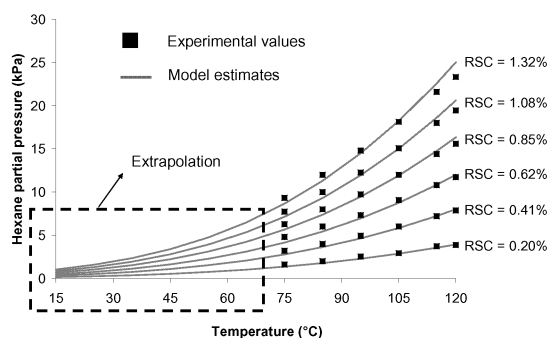


Figure 1 : Results of the model validation. RSC = residual solvent content in liquid phase, expressed in weight percent. The dashed region represents the extrapolated values.

The calculated vapour pressure shows a good agreement with the experimental data, thus allowing a reliable prediction of the vapour phase behaviour. Even if the experimental data are available in a limited range, e.g., between 75 and 120°C, the curve of the predicted data features a regular behaviour, and it can be extrapolated for lower temperatures, which are more significant in the case of oil storage (see Figure 1).

3. Analysis of vegetable oil storage

Once validated, the model was applied to the analysis of an industrial storage plant. In particular, the vegetable oil refinery of SALOV S.p.A., located in Massarosa (Italy), was considered in the analysis. The tank farm of the plant comprises 28 vessels with volumes ranging between 85 and 750 m³, with a total capacity of about 8500 tons. The refinery processes sunflower, olive, peanut and corn oil. In particular, a maximum residual solvent content of 0.1% by weight was taken into account in the analysis, according to the indications directly provided by SALOV. In order to provide a more comprehensive picture of the tank farm, also higher RSC values were taken into account (e.g., 0.38% and 0.75% by weight). The tank farm is equipped with a heating system which prevents the vessel cooling to temperatures lower than about 18°C in presence of cold weather. For temperatures higher than 18°C the operative temperature can be assumed equal to the average ambient temperature. An example is reported in Figure 2 for the typical weather conditions of the zone of the oil refinery. The lower flammability limit of the hexane corresponds to a volumetric fraction of 0.011 and is indicated in the figure as a dashed line. As clearly appears from the figure, the evaluated concentrations are essentially below this limit in the case of SALOV ordinary operative conditions. Thus, the possibility of the formation of flammable mixtures inside crude vegetable oils is avoided in this case. Nevertheless, for higher RSC, high summer temperatures (in particular a maximum temperature of 32°C was registered in the zone) may cause the possibility entering in the flammable field, thus evidencing potential explosion hazards connected to the storage of crude vegetable oils in presence of accidental ignition.

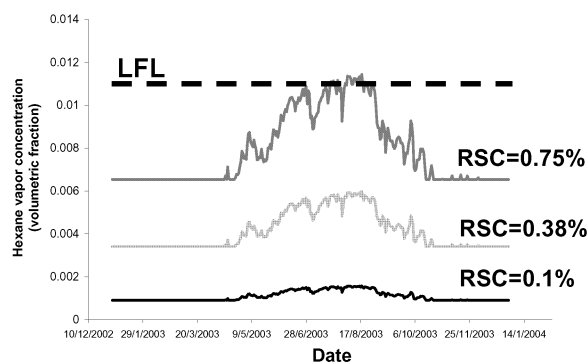


Figure 2 : Results of the case studies: vapor phase hexane concentration (volumetric fraction) for different residual solvent contents (RSC, weight %) in the liquid phase as a function of the daily averaged ambient temperature ($^{\circ}\text{C}$). The dashed line indicates the lower flammability limit (LFL) of hexane in air (1.1.% by vol.)

4. Analysis of vegetable oil refining

4.1 Process description

In order to consider the typical refining process conditions, the purification of a typical sunflower oil was simulated assuming a free fatty acid content (FFAC) of 4 %wt. to be reduced up to 0.04 %wt. A schematization of the process is reported in the PFD shown in Figure 3. The oil is first neutralized by adding sodium hydroxide to an intermediate grade of acidity. Next, the oil is degummed by adding phosphoric acid and subsequently it is sent to centrifugal separation to split the oil fraction from the solid waste. During this step, the oil is washed with water and consequently it is dehydrated in a flash separator under vacuum conditions. Next the oil is discolored using bleaching earth and activated carbon in a stirred vessel in vacuum conditions, filtered and sent to the deodorization treatment. This section consists in a “physical” neutralization with water steam at high temperature under vacuum conditions. The FFAC is stripped and condensed in a direct contact condenser, while steam with non condensable vapor are sent to the ejectors section. Table 1 provides the detailed operative conditions used in each section of the refining process.

Table 1: Operative conditions of the main sections of the refining process

Process section	Operative temperature ($^{\circ}\text{C}$)	Operative pressure (mbar)
Neutralization	20	1000
Degumming	20	1000
Washing	90	1000
Dehydration	90	50
Discoloration	95	60
Deodorization	230	2

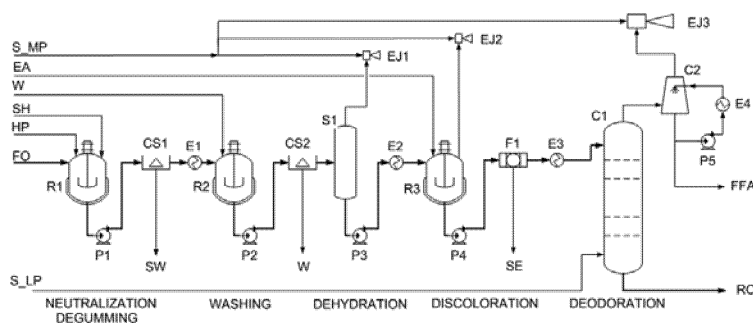


Figure 3 : Process flow diagram (PFD) of the refining process. Equipment: R: reactor; P: pump; CS: centrifugal separator; E: heat exchanger; S: flash separator; EJ : steam ejector; F: filter; C: column. Material streams : S_MP: medium pressure steam; S_LP: low pressure steam; EA: earths & activated carbons; W: water; SH: sodium hydroxide; HP: phosphoric acid; FO: feedstock oil; SW: soaps & waxes; SE: spent earths; FFA: free fatty acids; RO: refined oil.

4.2 Process simulation

Process simulations were performed using HYSYS V7.1 (by ASPEN Tech, Cambridge MA) simulation software. The crude vegetable oil, including FFAC and hexane, was schematized according to the model described in Section 2 already applied for the assessment of storage tanks (Section 3). A residual hexane content of 0.1%wt. was considered as process input. The same oil refinery considered in Section 3 was used as reference case study in order to simulate typical industrial opening conditions. The aim of the process simulation was to “trace” the hexane flow through each part of the process, with particular attention to units working at high temperature and low pressure, in which hexane vaporization is favored. Figure 4a shows a Sankey diagram reporting the more critical nodes in which the accumulation of hexane is predicted. In particular, the analysis evidenced the need to focus on the operative problems related to dehydration, discoloration and deodorization, in which the major part of hexane is accumulated. Since the vacuum conditions are kept in these units by steam ejectors (see Figure 3), the modeling of these devices has strong importance in the simulation process. The steam ejector model was set up on the basis of actual plant field data, based on typical operative conditions reported in Table 1. A sensitivity analysis was performed to determine the effect of the variation of a process variable to the refining process performance. In particular, the increasing content of hexane in feedstock oil was analyzed, considering an increasing input hexane concentration up to 0.5%. As mentioned before, the more critical effect is related to the ejector system aimed at keeping low pressures in high temperature units. The process performance was analyzed through the dehydration efficiency of the critical stages evidenced in Figure 4a, in particular dehydration, discoloration and deodorization. Figure 4b shows a potential decrease of 30% in process efficiency related to ejectors, thus evidencing the criticality of the residual solvent content in input feedstock.

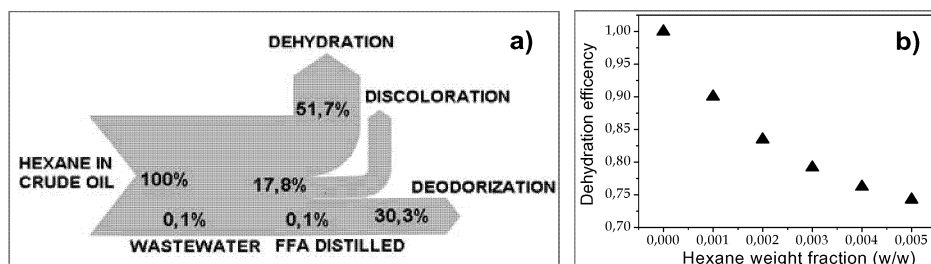


Figure 4: a) Sankey diagram evidencing the main hexane accumulation nodes; b) dehydration efficiency calculated for different hexane input concentrations.

5. Conclusions

In the present work a quantitative methodology was developed for the evaluation of residual volatile solvent content effect on storage and processing of edible extracted oils. 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 on one side the identification of potential hazards due to formation of flammable mixtures inside the storage tanks; on the other side the critical nodes of solvent accumulation were identified among the process, evaluating the influence on the global efficiency.

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References

- Bockisch, M., 1998, Fats and oils handbook. AOCS Press, Champaign (IL), USA
- Fornari T., Bottini S. and Brignole A.E., 1994, Application of UNIFAC to vegetable oil-alkane mixture, Journal of the American oil chemists' society, 71(4), 391-395.
- Fredenslund, A., Gmehling, J. and Rasmussen, P., 1977, Vapor-Liquid Equilibria Using UNIFAC: a group contribution method. Elsevier, Amsterdam, the Netherlands
- Fredenslund, A., Jones, R.L., and Prausnitz J.M., 1975, Group Contribution Estimation of Activity Coefficients in Non-ideal Solutions. AIChE Journal, 21, 1086-1099.
- Sandler, S.I., 1998, Chemical and Engineering Thermodynamics, 2nd Ed., Wiley & Sons, New York.
- Shahidi, F., 2005, Edible Oil and Fat Products: Edible Oils, Bailey's industrial oil and fat products, Vol. 2, 6th Ed., Wiley & Sons, New York.
- Smith, J.M., Van Ness, H.C., and Abbott, M.M., 2001, Introduction to chemical engineering thermodynamics, 6th Ed., McGraw Hill, New York.
- Smith, A.S., and Wechter, F.J., 1951, Vapor pressure of hexane-soybean oil solutions at low solvent concentrations. Journal of the American Oil Chemists' Society, 28, 381-382.