Brazilian Journal
of Chemical
Engineering

ISSN 0104-6632
Printed in Brazil
www.abeq.org.br/bjche

Vol. 29, No. 03, pp. 677 - 682, July - September, 2012

SAFETY STUDY OF AN EXPERIMENTAL APPARATUS FOR EXTRACTION WITH SUPERCRITICAL CO_2

V. B. Soares and G. L. V. Coelho*

Laboratory of Separation Process, Department of Chemical Engineering,
University Federal Rural do Rio de Janeiro, (UFRRJ),
Phone: + (55) (21) 3787-3742, Fax: + (55) (21) 3787-3750,
BR 465, Km 7, 23890-000, Seropédica, Rio de Janeiro - RJ, Brazil.
E-mail: vsoares@peq.coppe.ufrj.br
*E-mail: coelho@ufrrj.br

(Submitted: May 6, 2011 ; Revised: February 19, 2012 ; Accepted: March 1, 2012)

Abstract - During the process of supercritical CO_2 extraction it is necessary to use high pressures in the procedure. The explosion of a pressure vessel can be harmful to people and cause serious damage to the environment. The aim of this study is to investigate the probability of death and injury in a laboratory unit for supercritical fluid extraction in the case of an explosion of the extractor vessel. The procedure is explained via a case study involving fatty acid extraction from vegetable oils with carbon dioxide above its supercritical conditions and under optimum operating conditions. According to the results, more importance should be given to the use of a protective headset because the probability of eardrum injury is superior to the probability of death from lung injury.

Keywords: Safety Analysis; Pressure Vessel; Probit method; BLEVE.

INTRODUCTION

Over the last few decades, the word “security” has been substituted by the expression “loss prevention” to include new questions about the safety of the environment, materials and businesses (Hendershot, 2006). This is partially due to a large number of accidents involving pressure vessels in the decade between 1970 and 1980, affecting the image and the profits of organizations. In a chemical manufacturing plant, the sudden release of pressurized material is a negative event, especially when it involves the release of toxic materials or flammables. In these cases, fire, explosions and contamination can also occur (Perry *et al.*, 2008). Obviously, the type of substance, its quantity and the operating conditions will determine the intensity of the impact of an accident. In a supercritical extraction plant, the presence of pressure vessels and other devices is necessary due to the high pressures involved in the process. These devices have a variety of functions in the process such as an extraction vessel, a separator, a heater, a condenser and also as a storage tank for volatiles substances (McHugh and Krukonis, 1986).

The challenge for the equipment manufacturer lies in finding technical solutions which are economically feasible and safe. In recent years, also in Brazil, groups of University laboratories have shown an increasing interest in high pressure technology. On the other hand, generating and containing pressures up to hundreds of bars from gases at room temperature are not routine in Research and Development Labs and require special training. These include an adequate level of shielding, training personnel in operation and

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*To whom correspondence should be addressed preventive maintenance and, more importantly, working within the rated pressures and requiring the use of personal protective equipment such as a respirator, gloves, lab coat, safety glasses etc.

Supercritical Fluid Extraction (SFE) is a process that is growing in importance as an alternative to conventional separation processes. The application of supercritical fluid (SCF) solvents is based on the experimental observation that many gases exhibit enhanced solvating power when compressed to conditions above the critical point. The high selectivity, the speed of the process and the possibility to substitute organic solvents by other less aggressive solvents are some of the characteristics of supercritical technology (Carlès, 2010; Cavalcante *et al*., 2005; McHugh and Krukonis, 1986; Schneider, 1983; Velasco *et al*., 2007).

Supercritical carbon dioxide ($SCCO_2$) has been intensively used because of its relatively low critical pressure (73 bar), its low critical temperature (304 K), its non-dangerous character and low cost. Carbon dioxide is considered to be a GRAS solvent with a TLV-TWA value of 5000 ppm (TLV-TWA is the threshold limit value time-weighted average concentration for a normal 8 h workday or 40 h workweek, to which all healthy workers may be repeatedly exposed, day after day, without adverse effect).

As high pressure equipment is installed and operated worldwide, safety rules are internationalized. Regulations for overpressure protection are provided in API RP 520 (American Petroleum Institute), which presents guidance for determining the requirements for the installation, maintenance, and decommissioning of pressure vessels and autoclaves. The pressure relief devices, covered in this recommended practice (RP), are intended to protect unfired pressure vessels and related equipment against overpressure from operating and fire contingencies. The rules for overpressure protection of fired vessels are provided in ASME Section I and ASME B31.1. Also relevant standards for Boiler and Pressure Vessel Code are provided by the Canadian Standards Association (CSA) and the American National Standards Institute/American Society of Mechanical Engineers (ANSI/ASME). In the Federal Republic of Germany, laboratories are required by law to comply with accident-prevention rules of the appropriate professional association and, consequently, are subject to technical regulations published in newsheets of the Pressure Vessel Study Group (AD-Merkblätter, Arbeitsgemeinschaft Druckbehälter). In Brazil, the regulations are provided by the Ministry of Labor and Employment in NR-13 (NR – Norma Regulamentadora).

In this process, the extractor vessel (pressure vessel) is the most important equipment, where the supercritical conditions are established and the extraction occur.

The definitive advantage of supercritical fluids over classical liquid solvents has long been known: the solvent-extract separation is easy and requires very low energy consumption. In fact, this separation is based on the drastic decrease of the solvent power when its specific gravity is decreased: decompression at constant temperature or heating at constant pressure are both used, as explained on Mollier’s diagram.

The designer´s priority task should be to ensure full safety of operation in the process. Therefore, to achieve this goal, the assessment of the amount of energy stored in the system and the prediction of the scenario of a possible breakdown are essential to protect the environment. Normally the measure of the hazard of a gas working fluid is expressed as the product of the pressure and the volume in the pressure vessel (Radomski and Ros, 1992). Due to the high pressure involved in a supercritical extraction plant, any rupture in the structure of the pressure vessel can cause significant damage in the process area in the case of an explosion.

SCF extraction operations not only require the use of hardware rated for high pressures, but also the employment of multiple pressure-relief mechanisms and safety practices. The most common method of overpressure protection is through the use of safety relief valves and/or rupture disks with discharge directly into the atmosphere and are placed on the SCF pump, pressure vessels and at additional positions containing high pressure. In summary, safety is an important factor while dealing with supercritical extraction systems and the design of such equipment should take all the factors into account.

The aim of this study is to examine the probability of the occurrence of deaths and injuries in a laboratory unit for supercritical extraction in the case of an explosion of the extractor vessel.

The procedure is explained via a case study involving the explosion of an extractor vessel with subsequence formation of overpressure. The optimum conditions (P,T) for the extraction of fatty acids present in vegetable oils using carbon dioxide in supercritical conditions were determined in a previous study, as well as the minimum energy necessary to execute this operation continuously on an industrial scale (Penedo and Coelho, 1997). In order to get the thermodynamics data for a given step of the process, it is particularly useful to have a phase diagram for the solvent used in the extraction. Many diagrams are available for CO_2, but they are not always adequate (Eggers, 1980). Temperature-entropy (T,s) diagrams are particularly appropriate because, in these diagrams, the heat energy supplied and removed in reversible processes is represented by areas. The calculation of the energy released at the moment of the vessel explosion was determined by assuming ideal behavior of the gas and adiabatic expansion (Prugh, 1991). The probability of deaths and injuries was determined using a statistical vulnerability model, the probit method (Lucas *et al*., 2003; Sierra, 1991).

SAFETY ANALYSIS OF THE USE OF A SUPERCRITICAL EXTRACTION DEVICE

The safety analysis aims to identify, assess and prevent the possible threats involved in the use of a process or device inside or outside an organization. Although the exact nature of the threats and their resulting consequences are difficult to determine, the benefits of a safety analysis are clearly perceived since the prevention of accidents is less costly than to repair the damages afterward (Perry *et al*., 2008).

Identification of the Threats in a Supercritical Extraction Plant

The analysis of threats is used to identify the sources and types of hazards (Bajpai and Gupta, 2005). Many sources of hazards can be present in a supercritical extraction plant and affect people, the environment, equipment, constructions and business. Some examples of these hazards are a failure in the control of the process, mechanical failure of the equipment, damage to the infrastructure, inappropriate maintenance, electrical damage, undue operation of the safety valve, dust explosion, explosion, boiling liquid expanding vapor explosions (BLEVE), fires (Crowl and Louvar, 2002; Perry *et al*., 2008; Sklet, 2006), floods, tornadoes, storms, hurricanes, earthquakes (Lucas *et al*., 2003), terrorist attacks, vandalism, cyber-attacks, sabotage (Bajpai and Gupta, 2005), etc. All of these threats can affect the extraction vessel and compromise its structure. Beside these, excessive elastic deformation, excessive plastic deformation, high temperature, fracture, fatigue and corrosion are also typical problems involved in the use of a pressure vessel that is built following regulation codes.

Consequence Analysis

To estimate the losses and costs caused by an accident is not a trivial task. The damage to equipment, piping, utilities and installations, the effects on the local population, environment, image reputation and loss of profit, and the indemnities among others, must be accounted for in the construction of a safety analysis model (Medina *et al*., 2009). The prediction of such effects for a specific accident is based on the assessment of vulnerability models already prepared.

Among the statistical vulnerability models, the probit function is commonly used to determinate the damages to people and constructions. The probit method is based on experiments carried out with laboratory animals and on studies of the damages caused by previous accidents (Lucas *et al*., 2003). These vulnerability models allow the determination of the probability of deaths and injuries to people when exposed to fires, explosions and toxic substances release (Sierra, 1991).

In the particular case of explosion of the pressure vessel, the first expected effects on people are eardrum fracture and deaths from lung injury. Secondly, deaths due to body impact, injuries due to body impact, first degree to fatal burns and intoxication are predicted (Lucas *et al*., 2003; Salzano and Cozzani, 2006; Sierra, 1991). Obviously, these effects depend on the quantity and type of materials, the characteristics of the people involved and the exposure time. The present study will focus only on the estimation of the probability of deaths from lung damage and injury due to eardrum rupture, using Equations (1) and (2), respectively (Lucas *et al*., 2003; Sierra, 1991).

$$\mathrm{Pr} = -\,77.1 + 6.91\ln(\mathrm{P}) \tag{1}$$

$$\mathrm{Pr} = -\,15.6 + 1.96\ln(\mathrm{P}) \tag{2}$$

Where: Pr is the probit value; P is the maximum overpressure [Pa]. Table 1 can be used to convert the probit value to its respective probability value.

RELEASE OF ENERGY IN THE CASE OF AN EXTRACTOR VESSEL EXPLOSION

The intensity of overpressure is closely related to the amount of energy available to generate it. To determine the released energy it is necessary to know the type of equipment, the mechanism of failure, the quantity of material present and the operating conditions. As discussed earlier, boiling liquid expanding vapor explosions or BLEVE can cause the explosion of an extractor vessel in a supercritical extraction plant. This physical phenomenon is characterized by sudden release (Salzano and Cozzani, 2006) and its most common causes are mechanical damage, overfilling, runaway reactions, overheating, vapor space contamination and mechanical failure (Abbasi and Abbasi, 2007).

Table 1: Equivalence of the probit values and percentage of population affected

Pr	%	Pr	%	Pr	%	Pr	%	Pr	%
0.00	0	4.19	21	4.8	42	5.33	63	5.99	84
2.67	1	4.23	22	4.82	43	5.36	64	6.04	85
2.95	2	4.26	23	4.85	44	5.39	65	6.08	86
3.12	3	4.29	24	4.87	45	5.41	66	6.13	87
3.25	4	4.33	25	4.9	46	5.44	67	6.18	88
3.35	5	4.36	26	4.92	47	5.47	68	6.23	89
3.45	6	4.39	27	4.95	48	5.5	69	6.28	90
3.52	7	4.42	28	4.97	49	5.52	70	6.34	91
3.59	8	4.45	29	5	50	5.55	71	6.41	92
3.66	9	4.48	30	5.03	51	5.58	72	6.48	93
3.72	10	4.5	31	5.05	52	5.61	73	6.55	94
3.77	11	4.53	32	5.08	53	5.64	74	6.64	95
3.82	12	4.56	33	5.1	54	5.67	75	6.75	96
3.87	13	4.59	34	5.13	55	5.71	76	6.88	97
3.92	14	4.61	35	5.15	56	5.74	77	7.05	98
3.96	15	4.64	36	5.18	57	5.77	78	7.33	99
4.01	16	4.67	37	5.2	58	5.81	79	7.41	99.2
4.05	17	4.69	38	5.23	59	5.84	80	7.51	99.4
4.08	18	4.72	39	5.25	60	5.88	81	7.65	99.6
4.12	19	4.75	40	5.28	61	5.92	82	7.88	99.8
4.16	20	4.77	41	5.31	62	5.95	83	8.09	99.9

During the BLEVE process, an instantaneous increase in volume of the substance confined in the vessel occurs due to the expansion of the vapor phase already existing in the vessel. This expanded material releases a high amount of energy converted into overpressure, thermal radiation and missile ejection. Some particular conditions at the moment of the event define the ways in which this energy is distributed. For example, most of the vessels are built with ductile materials and, in this case, 40% of the energy released in a BLEVE is converted into overpressure. The rest of the energy is used to break the equipment, to project the fragments and to generate heat in the environment (Ronza *et al.*, 2007). This rapid deterioration of the tank and tremendous release of energy can propel the tank and the whole equipment to great distances.

There are many ways to estimate the energy released in a BLEVE (Abbasi and Abbasi, 2007; Planas-Cuchi *et al.*, 2004). One possibility is to assume that the vapor behaves as an ideal gas and that the vapor expansion is adiabatic and reversible (Prugh, 1991). In this case, the energy released is obtained from Equation (3).

$$\mathrm{Ev} = 10^2 \left(\frac{\mathrm{PV}}{\gamma - 1} \right) \left(1 - \left(\frac{\mathrm{Pa}}{\mathrm{P}} \right)^{\left(\frac{\gamma - 1}{\gamma} \right)} \right) \tag{3}$$

Where: Ev is the energy released (kJ), Pa is the atmospheric pressure (bar), V is the initial volume of vapor (m^3), P is the pressure (bar) in the vessel just before the explosion, γ is the ratio of specific heats.

CASE STUDY

The present case study consists in investigating the probability of deaths and injury in a high pressure experimental supercritical extraction apparatus in the case of explosion of the extractor vessel.

Because high pressure systems like experimental apparatus for extraction with supercritical CO_2 are now commonly used in many Research Centers and Universities, safety rules have been defined to assure that the pressure vessels, as well as the main components of a high pressure unit, are perfectly safe for continuous operation.

In a previous study, the optimal conditions and the minimum energy required for the deacidification of vegetable oils using carbon dioxide above its supercritical conditions were investigated (Penedo and Coelho, 1997). Figure 1 shows the Temperature-entropy (T,s) diagram, which summarizes both situations using typical thermodynamic data. The arrows indicate the path of the carbon dioxide in the process cycle. The extraction process involves an isentropic compression step in P_1 (1 – 2), an isobaric heating step in W_1 (2 – 3), an isenthalpic adiabatic expansion step (3 – 4), a vaporization step of the liquid phase (4 – 5) and a condensation step in W_2 that allows the use of a pump (5 – 1).

The energy involved in the extraction step that occurs at 353 K and 140 bar is 3.57 kJ and was read directly from the diagram, which is particularly appropriate since heat energies supplied or removed in reversible processes can be read off as areas. Assuming that 40% of this released energy is converted into overpressure and that 1.28 is the ratio of the specific heat of carbon dioxide at the critical temperature (Smith *et al.*, 2005), 1.01325 bar is the atmospheric pressure and 0.1 m^3 is the initial volume of vapor present at the moment of the collapse of the vessel, then the overpressure generated is 1.1820 bar. The value of the overpressure was obtained using a numerical method together with Equation (3).

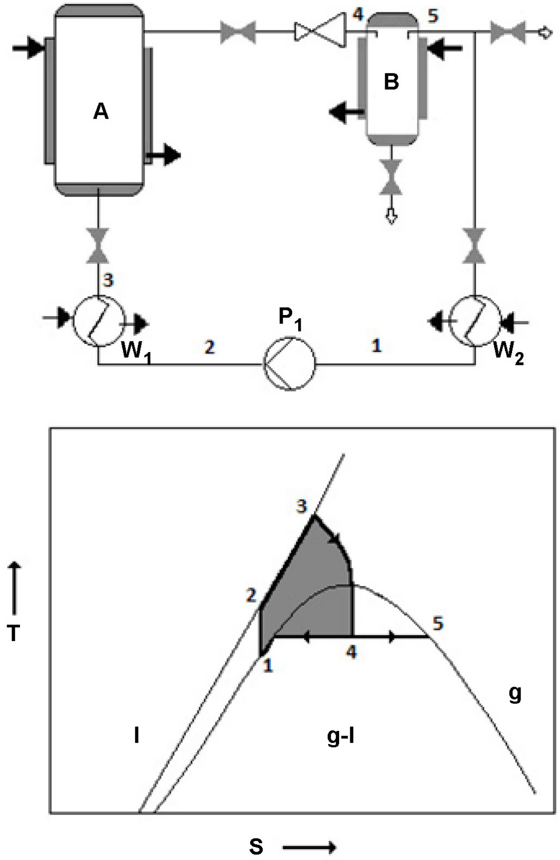

Figure 1: Flow diagram of an experimental apparatus for extraction and the temperature-entropy diagram for carbon dioxide. A and B, pressure vessel; W1 and W_2, heat exchanger

If the pressure term (P) in Equations (1) and (2) is isolated and the probit values (Pr) in Table 1 are employed, it is possible to construct a graph that associates the overpressure with the probability of death from lung injury and injury from eardrum rupture. The probit method results for explosion vulnerability are shown in Fig. 2.

According to Figure 2, when 0.1 m^3 of vapor is present in the extractor vessel in the moment of collapse of the equipment, an overpressure of 118.20 KPa (1.1820 bar) is generated. The probability that this pressure wave could cause death from lung injury is less than 1%. However, the probability that one person could have an eardrum rupture is approximately 95%, which indicates that more attention must be given to the use of protective headsets by operators of the extractor vessel under the conditions addressed in this study.

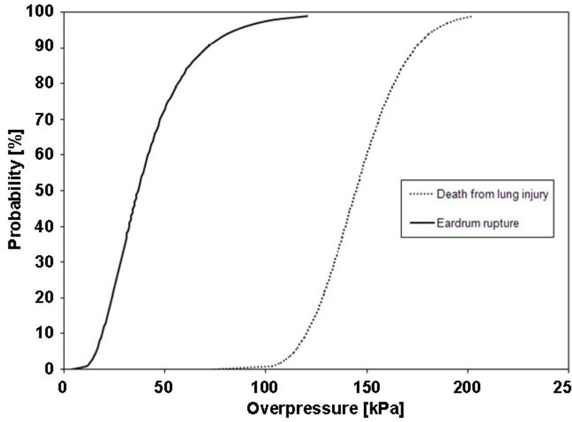

Figure 2: Relationship between probability of affected people and overpressure

The methodology discussed in this paper can also be extended to a larger scale (pilot or industrial) by making the appropriate substitutions of the variables in the models presented. It is recommended that more accurate calculations be made for the determination of the volume of the vapor phase, as well as for the process of expansion of the gases and their actual behavior. Other effects such as thermal radiation and the projection of fragments should also be further studied. Although this case study was related to a supercritical extraction device, this methodology can be applied to any process that uses pressure vessels.

CONCLUSION

If pressurized gases impose extreme safety codes, due to their high compressibility, in liquids it is possible to reach high pressure values without great difficulties. In each situation it is necessary to adjust the design of the equipment and the alloy composition to the specific application. The behavior of materials under high pressure and the compressibility of liquids and gases are known in more and more detail, which allows one to design and build equipment for higher pressures and temperatures.

A safety analysis is very important in a supercritical extraction plant on an industrial, pilot or laboratory scale since high pressure is involved in the process and implies the use of pressure vessels. The explosion of an extractor vessel (pressure vessel) in a supercritical facility can cause a large release of energy, converted into overpressure, thermal radiation and kinetic energy of fragments, harming people and damaging buildings and the environment. The present study investigated the probability of deaths and injuries in a laboratory supercritical extraction unit in the case of explosion of the extractor vessel. According to the results presented, more attention should be given to the use of protective headsets because the probability of eardrum injury is superior to that of death from lung injury.

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