CHEMICAL ENGINEERING TRANSACTIONS
VOL. 104, 2023
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Sabrina Copelli, Ernesto Salzano

ISBN 979-12-81206-06-9; **ISSN** 2283-9216
DOI: 10.3303/CET23104026

Inherent Safety Development Applied to Green Processes and Energy Transition

Maria Bolla*, Margherita Pettinato, Bruno Fabiano

Department of Civil Chemical and Environmental Engineering University of Genoa, via Opera Pia 15, 16145, Genoa, Italy.
maria.bolla01@edu.unige.it

Agri-food wastes are annually generated in huge amounts along the whole supply chain and are distinguished for their high moisture content, biological instability, organic load, and potential environmental impact, contributing to climate changes. For these reasons, agri-food waste reuse and recycle are highlighted by EU within a broader biorefinery concept. In this context, spent coffee grounds (SCGs) represent a promising source of high-added value compounds due to their appreciable amounts of polyphenols, caffeine, and lipids, which can be recovered to find applications in several industrial fields. Nevertheless, the unit operation of solid-liquid extraction, can be carried out by several alternative methods and solvents under different operating conditions. Green extraction processes can be seen as an alternative to conventional solvent extraction, but may entail new threats that require further investigation, since the equivalence between green and safer must not be taken for granted. Each option inevitably comprises several hazards, including fire and explosion to be “aprioristically” considered at the initial design stages. This work focuses on the implementation of specific inherent safety indexes to compare SCGs treatments alternatives for designing intrinsically safer plants and contributing to a more aware transition to green processes.

1. Introduction

During the last decade, many efforts have been expended to counteract improper disposal of waste, which is related to remarkable environmental pollution. Thus, policies and legislations have become more restrictive in terms of their handling and end-of-life procedures, including agri-food by-products. According to the Food Waste Hierarchy (FWH) framework, the best recommended practice is to prevent waste generation, in favour of reuse and recycle, up to the production of energy in a biorefinery layout (Nayak & Bhushan, 2019) and within the broader context of energy transition. Together with climate change, the last one implies challenges for new technologies and processes entailing new process and personal hazards, with much effort spent into renewal but limited safety analyses (Pasman et al., 2023). Within this broad context, spent coffee grounds (SCGs) are a potential source of chemicals and energy, but commonly disposed in landfill as solid wastes, incinerated, or used as fertilizers. Due to their large amount of compounds they still contain, such as caffeine, tannins, and polyphenols, their disposal can exert a negative effect on the environment, which can be reduced through their conversion into high-added value compounds. On the other hand, the same compounds can be recovered and employed for different purposes, including the production of active food packaging and biopolymers (Pettinato, 2021). Several methods can be exploited for this purpose, including both the traditional solid-liquid extraction (SLE) and the non-conventional techniques, the last providing higher extraction yields with lower energy demand, reduced volumes of equipment, and higher extract quality, like high pressure and temperature extraction (HPTE), microwave-assisted extraction (MAE), and ultrasound-assisted extraction (UAE). The different process alternatives can involve the use of organic solvents under mild operating conditions, or environmental-friendly solvents, but entailing different hazards due to stricter operational states (Frosi et al., 2021). Each treatment alternative inevitably comprises several hazards, including fire and explosion (F&E), that should be taken into account at the process design stage. A safe process relies on a four-layer strategy, including procedural, active, passive, and inherently safe design. The minimization of process risk can be attained by modifying and identifying the best materials, operative conditions, and equipment, rather than

Paper Received: 22 April 2023; Revised: 12 June 2023; Accepted: 22 August 2023
Please cite this article as: Bolla M., Pettinato M., Fabiano B., 2023, Inherent Safety Development Applied to Green Processes and Energy Transition, Chemical Engineering Transactions, 104, 151-156 DOI:10.3303/CET23104026

placing additional and expensive safety measures and devices (Fabiano et al., 2019). Seveso II and III directives implementation in different Countries (Laurent et al., 2021) explicitly consider inherent safety (IS) design as the best approach to avoid accidents, by stating that “hazards should be possibly avoided or reduced at source through the application of inherently safe practices” (Athar et al., 2019). The application in the early design stages of the guidewords “intensification”, “substitution”, “attenuation”, “simplification” offers more flexibility, both from a decision making and economic point of view, even if some difficulties arise from little information available (Park et al., 2020). The advantages and disadvantages of any alternative should be compared for each case, as a function of the involved process, materials, and equipment by the implementation of new and reproducible IS methods (Heikkilä, 1999). An aprioristic approach based on targeted risk indexes (e.g., Dow F&E Indexes) allows for a quantitative comparison of different conceptual design solutions that embed the process and risk analysis, including easiness of calculation, ranking capability according to different features of the investigated process, and generalizability (Bassani et al., 2022). This preliminary work focuses on the development of safety indexes applied to the design of extraction processes of antioxidant and lipidic compounds from SCGs. The safest alternatives were individuated accounting for chemicals, operating conditions, and equipment. Special attention was paid to the F&E hazards of the investigated systems, as well as those associated with the toxicity levels and conditions potentially harmful for human health.

2. Theoretical

In this study, an inherent safety (IS) approach was applied to the selection of the extraction method to be applied for the recovery of antioxidant compounds and lipids from SCGs. The inherent safety of the selected process routes was evaluated by applying the inherent safety index (ISI) methodology (Heikkilä, 1999), ad-hoc properly modified and expanded. According to a cautious assumption, the index was evaluated in the most severe conditions. Ad-hoc indexes were developed to account for the different hazards connected with the application of SLE, MAE, UAE, and HPTE. Data collected by preliminary experimental runs were used to establish the technical feasibility and to compare chemical and process hazards. The overall inherent safety index (I_{TI}) was evaluated basing on two subindexes, i.e., the chemical safety index (I_{CI}) and the process safety index (I_{PI}), as reported in Eq(1).

$$I_{TI} = I_{CI} + I_{PI} \quad (1)$$

I_{CI} is associated to chemical hazards triggered by the intrinsic properties of the solvent, representing one of the main actors of the extraction process (Eq(2)).

$$I_{CI} = I_{FL,max} + I_{EX,max} + I_{TOX,max} + I_{COR,max} \quad (2)$$

I_{CI} was defined as the summary of the contributions of flammability, explosiveness, toxicity, and corrosiveness of chemicals. The flashpoints, the lower and upper explosivity limits (LEL and UEL), the toxicity levels, and the corrosiveness attitude of each solvent involved in the process were used to give a relative score to $I_{FL,max}$, $I_{EX,max}$, $I_{TOX,max}$, and $I_{COR,max}$, respectively. Flashpoints of pure compounds were obtained from OSHA (Occupational Safety and Health Administration, 2023), while those for hydroalcoholic mixtures were evaluated by the empirical

$$FP = 40.2 - 86.1x + 122x^2 - 63x^3 \quad (3)$$

where FP (°C) is the ethanol-water mixture flashpoint and x is the molar fraction of ethanol.
LEL and UEL at atmospheric conditions for pure compounds were collected from OSHA (Occupational Safety and Health Administration, 2023). The method reported by Zabetakis (1965) was used to determine the Mixture Lower Explosivity Limit (MLEL) [vol%] and the Mixture Upper Explosivity Limit (MUEL) [vol%], as follows in Eq(4) and Eq(5):

$$MLEL = \frac{1}{\sum \frac{x_i}{LEL_i}} \quad (4)$$

$$MUEL = \frac{1}{\sum \frac{x_i}{UEL_i}} \quad (5)$$

where LEL_i and UEL_i [vol%] are the LEL and UEL of a single component of the mixture and x_i is the molar fraction. The Burgess-Wheeler method (Zabetakis, 1965) were used to account for temperature difference, according to Eq(6) and Eq(7), respectively.

$$\frac{LEL(T)}{LEL(T_0)} = 1 - 0.000721(T - 25°C) \quad (6)$$

$$\frac{UEL(T)}{UEL(T_0)} = 1 + 0.000721(T - 25°C) \quad (7)$$

where LEL(T) and UEL(T) [vol%] are LEL and UEL at the working temperature T (°C) and LEL(T_0) and UEL(T_0) [vol%] are LEL and UEL [vol%] at 25°C. The effect of pressure was considered by applying Eq(8) and Eq(9) (Zabetakis, 1965):

$$LEL(P) = LEL(P_0) - 0.71 log \Delta P \quad (8)$$

$$UEL(P) = UEL(P_0) + 0.71 log \Delta P \quad (9)$$

where LEL(P) and UEL(P) [vol%] are LEL and UEL at the working pressure P (bar) and LEL(P_0) and UEL(P_0) [vol%] are LEL and UEL at 1 bar.The toxicity ($I_{TOX,max}$) was evaluated by accounting for the ACGIH Threshold Limit Value – Short-Term Exposure Limit (TLV – STEL) and the OSHA Permissible Exposure Limit – 8-hour Time-Weighted Average (PEL – 8 hour TWA) for methanol, ethanol and n-hexane, petroleum ether, respectively (OSHA, 2023). The overall process safety index (I_{PI}) provided by Eq.(10) is strictly related to the process equipment and the adopted operating conditions.

$$I_{PI} = I_{I,max} + I_{T,max} + I_{P,max} + I_{EQ} \quad (10)$$

$I_{I,max}$, the inventory subindex, was defined as a function of the total feed flow rate, consisting of the sum of solvent and biomass flow rates. Process stream calculation was based on batch experimental runs, by fixing the compounds of interest flow rate equal to the highest experimentally obtained among the tested extraction techniques and process variables. The liquid and the solid flow rates were normalized to a maximum TP flow rate as a product. The input and the output flow rates were defined as the cumulative quantities needed to perform a defined number of extractions in 24 hours. The maximum number of feasible batches per day for each extraction process was evaluated considering both the extraction and dead times, the latter including the heating, cooling, material loading, and discharging phases. $I_{T,max}$ and $I_{P,max}$ consider the maximum process temperatures and pressures, respectively. I_{EQ} was associated to equipment complexity, in agreement with “simplification” principle of inherent safety design. Index values were assigned according to the checklist reported in Table 1. Answers to the proposed questions were provided by expert elicitation, on the basis of specific numerical parameters (LEL, UEL, TLV, etc.), experience, and targeted literature review, for both chemicals and process factors.

Table 1: Checklist to qualitatively evaluate the inherent safety of chemicals, process, and equipment involved in the process alternatives under study.

Question number	Question
Chemicals	
1	What is the hazard level of the boiling temperature of the chemicals involved in the reaction?
2	What is the flashpoint of each component of the mixture?
3	What are the explosivity limits of each component of the mixture?
4	Are the chemicals involved in the process stable at the chosen operating condition?
5	What is the toxicity level of the chemicals involved in the extraction?
6	What is the corrosiveness level of the chemicals involved in the extraction?
Process and equipment	
1	Does the inlet mass flow to the process constitute a relevant hazard?
2	What is the volume level of the chemicals in the process tanks and extractors?
3	How many process control devices are needed?
4	What is the maximum achievable temperature?
5	What is the maximum achievable pressure?
6	How is the equipment layout organized?
7	What is the level of complexity of the system?
8	Does the equipment in the onsite area work in hazardous conditions?
9	What is the integrity level of the process structures?
10	Which operations are involved in the process and how are they connected together?

Scores were assigned to each subindex through the use of specific values associated to the process features, according to Table 2. Consequently, the lower the total score, the higher the relative safety associated to the

index under investigation. Values of weights were set according to the methodology outlined by Heikkilä (1999), properly adapted to the investigated case study.

Table 2: Values associated to chemicals and process conditions.

Index	Score
$I_{FL,max}$	Non-flammable: 0; Combustible (flash point >328 K): 1; Flammable (flash point ≤ 328 K): 2; Easily flammable (flash point <294 K): 3; Very flammable (flash point <273 K & boiling point ≤ 308 K): 4
$I_{EX,max}$	Non explosive: 0; (UEL-LEL) vol% = 0–20: 1; (UEL-LEL) vol% = 20–45: 2; (UEL-LEL) vol% = 45–70: 3; (UEL-LEL) vol% = 70–100: 4
$I_{TOX,max}$	TLV or PEL > 10000 ppm: 0; TLV or PEL ≤ 10000 ppm: 1; TLV or PEL ≤ 1000 ppm: 2; TLV or PEL ≤ 100 ppm: 3; TLV or PEL ≤ 10 ppm: 4; TLV or PEL ≤ 1 ppm: 5; TLV or PEL ≤ 0.1 ppm: 6
$I_{COR,max}$	Carbon steel: 0; Stainless steel:1; Special materials: 2
$I_{I,max}$	$(L+S)_{in}/(L+S)_{min}$ < 1.5: 0; $(L+S)_{in}/(L+S)_{min}$ = 1.5–3: 1; $(L+S)_{in}/(L+S)_{min}$ = 3–5: 2; $(L+S)_{in}/(L+S)_{min}$ = 5–8: 3; $(L+S)_{in}/(L+S)_{min}$ = 8–10: 4; $(L+S)_{in}/(L+S)_{min}$ ≥ 10: 5
$I_{T,max}$	T = 273–343 K: 0; T < 273 K or T = 343–423 K: 1; T = 423–573 K: 2; T = 573–873 K: 3; T > 873 K: 4
$I_{P,max}$	P = 0.05–0.5 MPa: 0; P = 0–0.05 or P = 0.5–2.5 MPa: 1; P = 2.5–5.0 MPa: 2; P = 5.0–20.0 MPa: 3; P = 20.0–100.0 MPa: 4
I_{EQ}	Stirred vessel: 0; Stirred vessel with heating jacket: 1; Stirred vessel with ultrasounds: 2; Stirred vessel with heating jacket and under pressure: 3; Stirred vessel with heating jacket and condenser: 4; Stirred vessel with heating jacket and microwaves, under pressure: 5

3. Materials and methods

Table 3: Experimental extraction conditions.

Extraction technique	Solvent type	L/S (10^{-3} m^3/kg)	Solvent (*10^{-6} m^3)	T_{max} (K)	P_{max} (MPa)	t (h)
SLE	Methanol	10	30	298	0.10	24
	Ethanol	10	30	298	0.10	24
	Water	10	30	298	0.10	24
	Ethanol 50% (v/v)	10	30	298	0.10	24
HPTE	Methanol	10	40	453	2.50	1.5
	Ethanol	10	40	453	2.00	1.5
	Water	10	40	453	1.30	1.5
	Ethanol 50% (v/v)	10	40	453	1.60	1.5
	Methanol	10	40	423	1.40	1.5
	Ethanol	10	40	423	0.96	1.5
	Water	10	40	423	0.48	1.5
	Ethanol 50% (v/v)	10	40	423	0.72	1.5
	Methanol	10	40	393	0.64	1.5
	Ethanol	10	40	393	0.42	1.5
	Water	10	40	393	0.20	1.5
	Ethanol 50% (v/v)	10	40	393	0.31	1.5
	Ethanol 54% (v/v)	10	40	453	0.72	1
MAE Maximum radiation power: 500 W	Methanol	10	20	383	0.48	1.5
	Ethanol	10	20	383	0.30	1.5
	Water	10	20	383	0.14	1.5
	Ethanol 50% (v/v)	10	20	383	0.36	1.5
	Ethanol 54% (v/v)	10	20	453	0.36	1
UAE Ultrasound amplitude: 40%,On/off pulsed ratio: 30 s/ 30 s	Ethanol 54% (v/v)	10	30	298	0.10	1
	Water	10	30	298	0.10	1
RE	n-hexane	10	200	342	0.10	2
	Petroleum ether	25	50	333	0.10	4

Antioxidant compounds were extracted from dried SCGs by testing four different techniques: SLE, HPTE, MAE, and UAE. SLE was performed in a stirred extractor working at room temperature, while for HPTE a stainless-steel extractor equipped with a heating jacket was used. The system worked at temperature higher than the solvent boiling point temperature (1 atm), so under pressure (*f(T)*), and in the closed vessel an inert atmosphere was created by fluxing N_2 before vessel sealing and heating, to reduce antioxidants' degradation reactions. MAE was carried out in a closed PTFE vessel, posed under agitation in a microwave laboratory oven, composed by a stirred vessel, equipped with a heating jacket and a microwave generator. A vessel working at room temperature and atmospheric pressure was employed for UAE, where a submerged ultrasound probe delivered the mechanical energy to the extraction medium. Reflux extraction (RE) was, instead, the selected technique aimed at recovering the coffee oil (lipidic fractions of SCG). The reflux extractor, working at the solution boiling point, is composed of an extraction vessel, heated by an external jacket, and of a condenser at the top, to avoid internal pressure raising. Operating conditions adopted for each extraction technique are shown in Table 3. Optimal operating conditions were chosen after a critical literature review and previous sets of experiments (Pettinato 2019, 2021).The obtained extracts were analyzed in terms of total polyphenol yields (TPY, Eq(11)) through Folin-Ciocalteu's assay, according to the protocol reported in Pettinato et al., (2019) and lipid fraction (Eq(12)), determined gravimetrically.

$$TPY = Total\ polyphenol\ concentration\ in\ the\ extract \cdot \frac{Solvent\ volume}{mass_{dried\ SCG}} \tag{11}$$

$$L_f = \frac{mass_{lipids}}{mass_{dried\ SCG}} \tag{12}$$

4. Results

4.1 Extractions yields and comparison

The highest TP yield (71.8 ± 4.9 mg_{CAE}/g_{SCG}) was obtained by HPTE at 453 K and 1.6 MPa and with ethanol 50% (v/v) as solvent, so this performance was used as reference for calculations. Approximately, the same results were obtained for RE under both the explored extraction conditions: 8.13 ± 0.21% and 8.42 ± 1.58% for *n*-hexane and petroleum ether, respectively.

4.2 Inherent safety assessment

The checklist procedure was carried out for each extraction alternative to qualitatively identify the weakest points to focus on during the score assignment step. Methanol was the most hazardous solvent in terms of flammability, explosiveness, toxicity, and corrosiveness, due to its lower boiling point and flashpoint and its broader explosive range. At more severe conditions, the hazards of the chemicals mainly increased using HPTE, which exploits higher pressures and temperatures. MAE and UAE present additional hazards related to thermal, non-thermal, and acoustic impacts in the surrounding environment. For each proposed antioxidant extraction technology, water was the safest solvent, since it led to a lower I_{CI} and, consequently, I_{TI}. However, solvent separation required an increased energy consumption, if compared to the use of other more volatile solvents, like methanol. The last one demonstrated to be the most hazardous extraction solvent (Figure 1), as verified by the calculous of I_{CI}. It also presented the highest score for I_{TI}, if used in combination with HPTE at 453 K and 2.5 MPa. In fact, the severe operating conditions had a significant impact on I_{PI}, as well as the equipment complexity, affecting I_{EQ}. Significant lower I_T and I_P scores were obtained by applying the inherent safety guideword "attenuation": Lower temperatures and pressures than HPTE were selected as optimal ones in MAE. However, it should be remarked that the equipment complexity increased, due to the microwaves application. SLE was applied as a further alternative by a combination of the "attenuation" and "simplification" principles, leading to less hazardous operating conditions and a simpler equipment. On the other hand, I_I increased, leading to the necessity of storing and handling larger amount of chemicals. This finding is connected to the higher inlet flow rates with respect to those of HPTE, where the guideword "intensification" was fully applied. SLE carried out with water, as a substitute of methanol and ethanol, was finally individuated as the safest alternative, but not the most economic and technical solution due to the low extraction yield, the large volume of equipment requires, and the lower volatility of the solvent to be separated from the compounds of interest. Once the antioxidants were recovered, the obtained solid residues were further treated to extract. Extraction of lipids were carried out by using the same process equipment at similar operating conditions with petroleum ether and n-hexane as solvents. The final I_{TI} were affected only in terms of inventory, since petroleum ether required a higher inlet flow rate.

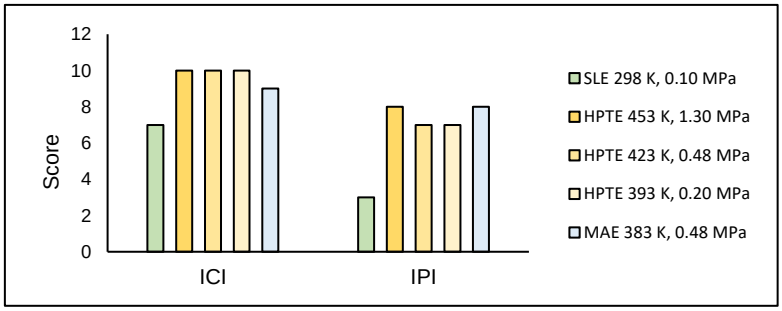

Figure 1: I_{CI} and I_{PI} for SLE, HPTE, and MAE with methanol as solvent.

5. Conclusions

Within the broad context of energy transition, in this study, SCGs were valorised by recovering antioxidants and lipids. Starting from experimental data, an inherent safety index was developed to compare different extraction techniques in terms of chemicals, process conditions, and equipment. Solvent selection and operating conditions are the aspects mainly impacting the IS index value. Further steps include extending the approach to occupational safety indices, e.g., to evaluate the non-thermal effect of cavitation and the ultrasonically induced heating, as well as investigating the trade-off between the safety level and the costs connected to the process.

Acknowledgments

The authors gratefully acknowledge partial funding by INAIL, within the framework of the call BRIC/2021/ID3 (Project DRIVERS- Approccio combinato data-driven ed experience-driven all'analisi del rischio sistemico).

References

Athar M., Shariff A.M., Buang A., Hermansyah H., 2019, Equipment-based route index of inherent safety, Process Safety Progress, 39.

Bassani A., Vianello C., Mocellin P., Dell'Angelo A., Spigno G., Fabiano B., Maschio G., Manenti F, 2023. Aprioristic integration of process operations and risk analysis: Definition of the weighted F&EI-based concept and application to AG2S technology, Ind. Eng. Chem. Res., 62, 500-510.

Fabiano B., Reverberi A.P., Verbanov P.S., 2019, Safety opportunities for the synthesis of metal nanoparticles and short-cut approach to workplace risk evaluation, Journal of Cleaner Production, 209, 297-308.

Frosi I., Montagna I., Colombo R., Milanese C., Papetti A., 2021, Recovery of Chlorogenic Acids from Agri-Food Wastes: Updates on Green Extraction Techniques, 26.

Heikkilä A.M., 1999, Inherent safety in process plant design. An index-based approach, VTT Publ. Hollnagel.

Hristova M., Damgaliev D., Hristov J., 2011, Practical data correlation of flashpoints of binary mixtures by a reciprocal function: the concept and numerical examples, Thermal Science, 15, 905-910.

Laurent A., Pey A., Gurtel P., Fabiano B. 2021, A critical perspective on the implementation of the EU Council Seveso Directives in France, Germany, Italy and Spain, Process Safety and Environmental Protection,148, 47–74.

Nayak A., Bhushan B., 2019, An overview of the recent trends on the waste valorization techniques for food wastes, Journal of Environmental Management, 233, 352-370.

OSHA, 2023, Occupational Safety and Health Administration, United States Department of Labor, <osha.gov> accessed 28.06.2023.

Pettinato M., Casazza A.A., Ferrari P.F., Palombo D., Perego P., 2019, Eco-sustainable recovery of antioxidants from spent coffee grounds by microwave-assisted extraction: Process optimization, kinetic modeling and biological validation, Food and Bioproducts Processing, 114, 31-42.

Pettinato M., Drago E., Campardelli R., Perego P., 2021, Spent coffee grounds extract for active packaging production, Chemical Engineering Transactions, 87, 583–588.

Park S., Xu S., Rogers W., Pasman H., El-Halwagi M.M., 2020, Incorporating inherent safety during the conceptual process design stage: A literature review, J Loss Prev Process Ind. , 63, 104040.

Pasman H., Sripaul E., Khan F., Fabiano, B., 2023, Energy transition technology comes with new process safety challenges and risks, Process Safety and Environmental Protection,177, 765-794.

Zabetakis M.G., 1965, Flammability characteristics of combustible gases and vapors. Bureau of Mines Bulletin 627, Washington, USA.