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In-line characterization of ground oilseeds concentration in solid-liquid dispersions in the food industry

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ABSTRACT

Near infrared spectroscopy is proposed as a method for continuous characterization of ground oilseed concentration in diluted solid liquid dispersions. The effect of operational parameters, such as flow rate and temperature on the stability and reliability of the in-line measurement was investigated. Moreover, in order to widen the applicability of the approach to different materials, the variety of oilseed, the particle size distribution, and the chemistry of the suspending liquid carrier were all changed, and their influence assessed through principal component analysis. Simple multivariate techniques were efficiently used to regress spectral features against known values of dispersed solids concentration. The calibration, obtained after internal cross validation, proved to give values of coefficient of determination always higher than 0.95, ratio of performance to deviation higher than 4, and comparably reduced root mean squared error of cross validation. Instantaneous concentration prediction were characterized by oscillations much dependent on the dispersed solids particle size, being their amplitude lower in the case of finer particles. Those oscillations were characterized through the coefficient of variation that, at steady state, gave values small enough to constitute an effective parameter to tackle mixing end-point, hence constituting a novel way to assess homogeneity during powder incorporation in liquids.

1. Introduction

Seeds constitute a common, affordable, and nutrient food whose consumption has been steadily increasing over the past decades (Day, 2013). This represents a significant opportunity for the development of new methods capable of efficiently extracting and delivering the most important nutrients of human diet from oilseeds, cereals, grains, and legumes. Mechanical and chemical extraction of lipid fraction is a non-trivial operation whose yield has to be carefully monitored. Depending on the kind of seed, after initial mechanical pressing, solid contain in raw vegetable oil is typically in the range of 0.02 ÷ 0.05 kg_{SOLIDS}/kg_{OIL}, but can reach values up to 0.15 (Williams, 2010). Residual sediments can negatively impact on further production steps or have a detrimental effect on taste and body of the final product (Hamm, Hamilton, & Calliauw, 2013, pp. 127–152; Johnson, 2008), therefore solid-liquid separations steps such as sedimentation, filtration or centrifugation are required to purify the raw pressed oil (Mohos, 2010, pp. 449–455). During soluble coffee production, for instance, effective and fast filtering techniques have to be employed to avoid over extraction, keeping dispersed solids weight fraction always below a few percents (Clarke, 1985). Other than extraction selected ground oilseeds, in particular nuts, can also be directly incorporated into the final product stream in food industry to improve taste, texture, and appearance: examples include almonds, hazelnuts, cocoa and coffee seeds (Manley, 2011). In these cases, precise powder dosing and dispersion homogeneity achievement deeply impact on the quality of the final product and often represent key parameters to match customer expectancies. In chocolate confectionery, for instance, cocoa powder agglomeration, caused by oil capillary bridges, can be used to adjust the texture of the product

Abbreviations: CoV, coefficient of variation; CV, cross validation; DoE, design of experiment; LV, latent variable; MSECV, mean squared error of cross validation; NIR, near infrared; PC, principal component; PCA, principal component analysis; PSD, particle size distribution; RMSECV, root mean squared error of cross validation; RPD, ratio of performance to deviation; SG, Savitzky-Golay; SNV, standard normal variate; SSE, summation of squared errors; STD, standard deviation.

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(Wollgarten, Yuce, Koos, & Willenbacher, 2016).

All considered, the need for the development of new, fast, and reliable in-line concentration measuring techniques is well justified. Several technologies have been industrialized and are today available to characterize solid-liquid dispersions, examples including ultrasonic cells, photometric analyzers, mass flow meters, viscometers and conductimeters. Nonetheless, not many in-line analytical techniques proved to be fully adequate in real time monitoring the dispersed powder weight fraction, as most technologies are affected by variations in the physical conditions of the analyte, such as changes in the suspended particle size distribution (PSD) (Fagan, Cullen, & O'Donnel, 2009). By virtue of that, chemical analytical tools seem more suitable to correlate variations in suspended solids concentration and, over the past years, a new generation of in-line near-infrared (NIR) diffuse-reflectance probes has gained much attention (Huang, Yu, Xu, & Ying, 2008).

NIR spectroscopy applied to food industry has an extensive background (Lohumi, Lee, Lee, & Cho, 2015; Porep, Kammerer, & Carle, 2015) and it has become a popular tool for off-line analysis of both granular materials and clear liquids (Agelet & Hurburgh, 2014). Conversely, characterization of diluted dispersions appear to be the subject of a limited number of studies: spectroscopic analysis in those conditions presents some unique challenges, which include probe fouling and nonlinear scattering phenomena caused by the presence of bubbles, agglomerates and powder lumps (Brimmer, DeThomas, & Hall, 2001). Nonetheless, some works have been published concerning spectroscopic analysis on suspensions and emulsions, focusing, in particular, on crystallization processes, determination of mixing end-point and liquid aeration (Abebe, Wang, Li, Roberts, & Lai, 2008; Kaddour, Morel, & Cuq, 2008; Tamburini, Marchetti, & Pedrini, 2014). Additionally, a number of papers deal with the use of in-line spectroscopy to assess dough properties and track flour wet agglomeration (Jirsa, Hruskova, & Svec, 2008; Mandato, Taliani, Aït-Kaddour, Ruiz, & Cuq, 2013). In view of this, the present study proposes a development in the direction of assessing whether in-line measurement of suspended ground oilseeds can be inferred through NIR spectroscopy. Moreover, the research aims at including also the role of temperature and flow rate, which represent key operational variables in any industrial environment, yet are seldom considered in literature.

2. Materials & methods

2.1. Materials

In order to increase the effectiveness of the study and widen the base of its possible applications, two different water-based suspending liquid carriers, together with two varieties of the same oilseed, namely variety V_1 and variety V_2, were used in the experiments. The particular oilseed species tested is not deemed relevant for the applicability of the experimental approach to other types of oilseeds. The lipid fraction of both varieties accounts for less than 0.25 kg/kg of the seeds dry weight, and is mainly composed of triacylglycerols, sterols and tocopherols, which represent typical compounds found in most edible vegetable oils (Pomeranz, 1991, pp. 248–298). The main difference between the two varieties tested is found in the lipid fraction: seed variety V_1 has double oil content compared to seed variety V_2. Proteins and organic acids, account for less than 0.15 kg/kg of the seeds dry mass, while the remaining portion is given by carbohydrates (0.40 kg/kg), minerals, and other minor components.

The two seed varieties were finely ground to similar values of particle mean diameter with an industrial mill. The investigation of PSD effect on NIR measurements was possible varying the level of comminution of seed variety V_2. The grounds were characterized through a laser diffraction analysis (Mastersizer 3000E, Malvern Instruments Ltd, Malvern, UK) repeated twice, mean values being reported in Table 1.

Concerning the liquid phase, it was decided to firstly run the experiments using distilled water (liquid A) in order to ensure consistency among the experiments, as variations in the liquid phase composition and ionic strength have reported to affect NIR spectra (Hashimoto, Sugimoto, Suehara, & Kameoka, 2011). Next, the experiments were run in a more complex liquid matrix (liquid B) consisting of water containing a significant quantity of soluble solids (0.55 ± 2 kg/kg). Liquid B is both denser and much thicker than liquid A ($\rho = 1250 \pm 60$ kg/m^3, $\mu_0 = 0.80 \pm 0.01$ Pa s at 25 °C) and is deemed representative, in terms of viscosity, of some processing conditions such as soaking of soybean during soy milk production or preparation of linseed mucilage (Golbitz, 1992; Khatib, Herald, & Boyer, 2002). The choice of using this complex liquid matrix, characterized by a slightly variable soluble solids content was intended to assess the effectiveness of NIR spectroscopy in coping with real production batches for which slightly variations in composition can be expected. This constituted an additional degree of freedom to assess the extent of probe sensitiveness to changes in liquid media properties. For consistency, the investigated range of dispersed powder weight fraction in the solid liquid dispersions spanned values between 0 and 0.075 kg/kg, with increments of 0.015 kg/kg, in both liquids A and B. Values in this range are of relevant importance in oilseed processing, examples being found in the production of soymilk and tofu (Golbitz, 1992).

2.2. Equipment

Spectroscopic measurements were taken in diffuse reflectance mode using a fixed diode array near infrared spectrometer, model SentroPAT FO, coupled with a SentroProbe DR LS probe tip (Sentronic GmbH, Dresden, Germany). Wavelengths used in the regression (1200 ÷ 2100 nm) are acquired with a resolution of 2 nm and an absolute wavelength accuracy of ±1 nm. The sample

Table 1
Two varieties, V_1 and V_2, of the same oilseed genus, characterized by different lipid content, were crushed using an industrial mill and incorporated into two water-based liquid carriers. Samples from each ground were characterized by laser diffraction (Mastersizer 3000E, Malvern Instruments Ltd, Malvern, UK) the level of comminution of seed variety V_2 was changed so that the effect of particle size distribution (PSD) in the near infrared measurement could be inferred. The laser diffraction analysis was repeated twice per each batch of powder. Average and absolute error of 10th, 50th, and 90th percentiles are reported below.

Powder Variety	PSD[a]	10th percentile[b] (μm)	50th percentile[b] (μm)	90th percentile[b] (μm)
V_1	Fine	3 ± 1	35 ± 5	151 ± 8
V_2	Fine	8 ± 1	45 ± 7	173 ± 11
	Medium	19 ± 3	337 ± 12	730 ± 28
	Coarse	27 ± 6	597 ± 31	1251 ± 43

[a] PSD, particle size distribution.
[b] Volume-based values.