www.elsevier.com/locate/fuproc

Resolution of near-infrared spectral data from distillation of binary mixtures and calculation of band boundaries of feasible solutions for species profiles

*Mohsen Kompany-Zareh**, *Mahdi Vasighi*

Institute for Advanced Studies in Basic Sciences, Zanjan — Iran

ARTICLE INFO

Article history:
Received 3 March 2007
Received in revised form
3 September 2007
Accepted 17 September 2007

Keywords:
Distillation
Near-infrared spectroscopy
Rank annihilation
Mean centering

ABSTRACT

In this work, mean centering, ordinary and incomplete rank annihilation based methods were applied to estimate concentration profiles (g/mL) and pure spectra of components from an evolutionary near infrared spectral data for successive condensates from distillation process of binary mixtures. Constraints such as non-negativity, selectivity of some spectral regions and density of condensates were applied during the resolution of some series of data. Fixed size moving window evolving factor analysis (FSMWEFA) and orthogonal projection analysis (OPA) were the applied chemometrics methods for assigning the selective regions. No pure spectrum from any of components or calibration samples was necessary for performing the analysis. Three binary mixtures containing toluene:n-hexane, toluene:cyclohexene and toluene:ethanol were investigated using the proposed method. Band boundaries of feasible solutions for pure absorption spectra and species concentration profiles for the mixture of components were successfully estimated in presence of high spectral overlap. In the first case the solution was unique, but in the second and third distillations a number of acceptable solutions were obtained as band boundaries.

1. Introduction

Distillation is among the most popular separation techniques in industry and laboratory activities. It is particularly useful for quality monitoring in petroleum industrial processes [1,2]. Routinely, distillation is employed to purify or to specify a fraction of constituents of a mixture based on the distinct boiling points of substances. Particularly, batch distillations provide flexibility and involve simplicity and much lower cost than that of continuous distillation. Batch distillation is the subject of many recent studies [3–5], even in the simplest case which is the distillation of the binary mixtures [4,6,7].

Proper operation of a process, such as a batch distillation column, requires a comprehensive knowledge about the composition of products (condensates) during the experiment. In this way, near infrared (NIR) spectroscopy has gained wide acceptance within petroleum, pharmaceutical, and food industries. This is because of NIR capability to exploit information on hydrocarbon content and physical conditions (such as temperature) of considered samples. Applications of NIR for monitoring and optimization of refining and petrochemical process are described by Lambert et al. [8]. Van den Berg et al. [9] used dispersive near-infrared spectroscopy to analyze thirty alcoholic beverage samples for ethanol. Real time monitoring of the distillation of a solvent switch process by near-infrared spectroscopy has been developed by Ge et al. using multivariate statistical methods for quantitative determination of the total alcohol concentrations in the distillate samples [10].

Gas chromatography is also a popular method for following the composition changes in separation processes and determining the feasibility of proposed separations [8,11,12]. But in

* *Corresponding author*. Tel.: +98 241 4153123; fax: +98 241 4153232.
E-mail address: kompanym@iasbs.ac.ir (M. Kompany-Zareh).

0378-3820/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.fuproc.2007.09.005

the present work, as in many of other recent reports, NIR spectroscopy was utilized in place of GC. The reason is that NIR is less time consuming than GC (on-line or off-line), and sampling error which is the main problem in off-line GC does not appear in NIR on-line monitoring. Certainly, temperature measurement is also common in monitoring the distillation processes [13], but it is not informative enough as NIR spectroscopy for estimation of true concentration profiles during distillation process.

Chemometrics is a powerful tool in all branches of chemistry, especially in analytical chemistry. For investigation of distillation, this tool has found a number of valuable applications too. Oisiovici et al. [14] proposed an inferential control system for high purity multi-component batch distillation columns to control the condensate composition using an extended Kalman filter. In their research, univariate physical variables such as temperature or pressure were under consideration which did not result in estimated concentration profile of components in the product. Oliveira et al. [15] employed data on evaporated fraction temperatures obtained from the distillation curves of Brazilian gasolines to identify adulterated samples by applying the soft independent modeling of class analogy (SIMCA) model. Zhang proposed a control strategy for distillation composition control using principal component regression (PCR) and partial least squares (PLS) models so that the top and bottom product compositions could be estimated from multiple tray temperature measurements [16]. In a report, principal component analysis (PCA) was employed to exploit most sensitive variables as soft sensor inputs in process monitoring [3]. These variables were used as input variables for the development of a regression model suitable for on-line batch distillation monitoring. An efficient model reduction technique for the distillation columns is applied to account for the detail dynamics by Lee and Yang [17]. This technique utilizes the orthogonal and cubic spline method. Then the extended Kalman filter is applied to identify the model parameters and the feed composition from the measurements of the column. Many other studies in distillation include chemometrics techniques such as PLS and similar methods [5,12,18].

Employment of NIR spectroscopy combined with recent chemometrics techniques in investigation of processes like distillation is among the recent studies [19]. In a study, principal component analysis (PCA) and some related techniques have been performed on the NIR spectra for monitoring of distillation process [2]. As a result, interpretation of such systems is more effective, rapid, and without great difficulties or efforts [2]. Ge et al. [20] developed an on-line fiber-optic near-infrared spectroscopic method for real-time monitoring of distillate composition using multivariate statistical methods such as multiple linear regression (MLR) and partial least squares (PLS) and incorporating temperature variance into the calibration set. PLS, polynomial-PLS, locally weighted regression (LWR) and genetic inside neural network (GINN) algorithms were used by Andrade et al. [21] to develop models for predicting motor octane number (MON) from non-leaded and catalytically reformed gasolines using medium infrared mid-infrared (MIR) spectroscopy. Obtained predictive model used for routine industrial quality monitoring.

Rank annihilation factor analysis (RAFA) [22] is an efficient chemometric technique based on rank analysis for two-way data. It can be employed with different purposes to analyze the unknown background system quantitatively [23]. RAFA was originally developed by Ho et al. [24] as an iterative procedure and modified by Lorber [25,26] who proposed a direct solution of standard eigenvalue problem.

Burns et al. [27] proposed a new method of rank annihilation with incomplete information in which only one of the vectors is known for the pure component. It is shown that specifications of one of the vectors of a component define a set of possible linear combinations of the eigenvectors for the other dimension decreasing the rank of the residual matrix by one. Minimum fraction of negative values in the residual matrix and minimum overlap between the residual matrix and the derived component are used as constraints.

Present work is the first application of rank annihilation factor analysis for resolution of NIR spectral data from distillation process for several binary mixtures of organic solvents. RAFA, as a soft resolution method, was applied for estimation of concentration profiles for constituents (fraction of each constituent in the condensates gathered in constant time intervals) during a simple distillation process, in addition to spectra of pure components. There are limited numbers of distillation studies in which the concentration profiles of the components are estimated. Tapp et al. [11] presented a simple experimental method for obtaining distillation column profiles at finite reflux and guidelines on how they can be used to determine feasible columns. Distillation of azeotropic mixtures is among the considered subjects for studying [28]. One azeotropic and two normal binary mixtures were considered in this investigation.

2. Theory

2.1. *Rank annihilation factor analysis*

Suppose simple distillation of a mixture of organic solvents. Because of difference in boiling points, fraction variation of species in condensates take place and evolutionary spectral variation of condensate can be observed during distillation process. Each condensate spectrum constitutes one row of data matrix, $\mathbf{X}$, with dimensions $m \times n$, where m denotes the number of condensates and n the number of wavelengths at which absorbances were measured. $\mathbf{X}$ can be written as the product of pure spectral profiles and concentration profiles:

$$\mathbf{X} = \mathbf{C}\mathbf{S}^T \tag{1}$$

Concentration profiles matrix $\mathbf{C}$ is $m \times p$, where p denotes the number of components in mixture and the pure spectral matrix $\mathbf{S}$ is $n \times p$.

When sufficient information is available for one component in mixtures (condensates), the method of rank annihilation has shown good success for completely subtracting the contribution of that component from the spectral data of mixtures [24]. The complete information for a component includes the vector of pure spectrum of the component and the vector of concentration profile of the component in the