In-line monitoring of solvent and CO2 properties: Preliminary assessment using design of experiment

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ABSTRACT
Removing acid gases such as CO_2 and H_2S from a gas mixture is nowadays often done using an absorption process. Two essential operating variables of such a process are the amount of active absorbent present in the solvent mixture and the amount of absorbed acid gas. Normally, the solvent concentration and the acid gas loading are measured by means of regular sample withdrawals and subsequent analysis in a laboratory. This procedure is both laborious as well as time consuming. In addition, the measurement results are not suitable for direct operational purposes; they can only be used for long term solvent and process monitoring.
To enable the real-time measurement of both the solvent concentration and acid gas loading, attempts have been made to use Fourier transform infrared (FTIR) spectroscopy in combination with a multivariate analysis method, also known as chemometrics [1][2]. The use of FTIR spectroscopy showed promising results with respect to predicted solvent concentration and acid gas loading. However, some clear disadvantages exist related to the cost of the apparatus, the requirement for the apparatus to be located within a few meters of the measurement location, and the sensitivity for mixture components that the method is not (properly) calibrated for.
The goal of this work is to assess whether (combinations of) other simpler analysis techniques exist that can overcome these disadvantages, for example pH or density measurements.
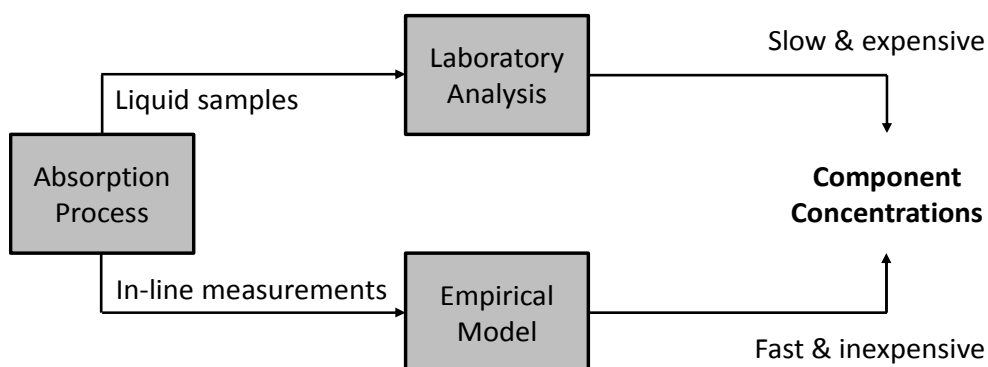
A preliminary assessment of analysis techniques is done based on a Design Of Experiment (DOE) approach, using six varied parameters and five measurement techniques. Varied parameters are the temperature and the concentrations of mono-ethanolamine (MEA), CO_2, HNO_3, H_2SO_4, and a 'pollutant mix' containing ammonia, formaldehyde, formic acid, acetic acid, and oxalic acid. These pollutants are typical solvent degradation products. Measurements are done of the conductivity, pH, density, refractive index, and five selected wavelengths of the ultraviolet–visible (UV–vis) light spectrum (220, 225, 228, 242, and 301 nm).

Using the DOE approach, it is possible to characterize the relations and cross-relations between multiple parameters in a relatively fast and easy way. First, representative low and high values of the involved parameters have to be selected; the chosen values are listed in Table 1. Next, the properties of interest for specific combinations of the low and high values are measured; 17 combinations were used in this work. Based on these measurements, the magnitude of the effect that each of the parameters has on each of the measured quantities is subsequently determined. If these calculated effects are finally divided by the standard deviation of the corresponding measured variable, a list of sensitivities is obtained that can be used to identify the measured variables that are most sensitive to changes in a specific parameter. The resulting list of sensitivities is shown in Table 1.

Table 1. Minimum and maximum input values and first order sensitivity results of the DOE.

	MEA	CO_2	HNO_3	H_2SO_4	Pollutants	Temperature
Low value	25 wt%	0 wt%	0 wt%	0 wt%	0 wt%	20 °C
High value	35 wt%	9.7 wt%	1.0 wt%	1.0 wt%	2.5 wt%	60 °C
Conductivity	-0.24	0.75	0.13	0.03	0.21	0.47
pH	0.29	-0.81	-0.13	-0.20	-0.22	-0.26
Density	0.12	0.96	0.10	0.14	0.08	-0.30
Refractive index	0.56	0.78	0.05	0.06	0.25	-0.02
UV–vis 220	-0.14	0.13	0.93	0.07	0.14	0.00
UV–vis 225	-0.17	0.06	0.91	0.03	0.23	-0.01
UV–vis 228	-0.07	-0.03	0.62	-0.03	0.38	-0.02
UV–vis 242	-0.10	0.10	0.99	0.07	0.02	-0.05
UV–vis 301	-0.09	0.13	0.99	0.04	0.00	-0.05

The results show that the density is very sensitive to the CO_2 concentration and not to any other components, suggesting that it might be suitable for determining the CO_2 concentration. Similarly, seem the UV–vis measurements to be good candidates for measuring the HNO_3 concentration. Combining density and refractive index could allow for characterization of the MEA concentration. The effects of conductivity and pH are for all components similar in magnitude but opposite in direction, except for H_2SO_4. So this combination of measurements might be suitable for determining the H_2SO_4 concentration. The components present in the 'pollutant mix' seem to have limited influence on the measured quantities, making possible prediction more robust. Temperature is a quantity that does influence some measured properties, but it is very easy to measure in-line and is usually known.

Overall, it seems possible to characterize the main components of an absorption process using a combination of readily available and relatively cheap in-line analyses techniques. Future efforts will focus on the characterization of real-plant samples instead of lab-prepared ones, on performing in-line measurements instead of off-line ones, on the evaluation of additional analyses techniques, and on the development of a predictive empirical multivariate model. The current work is an important first step towards a cheap and robust method for real-time determination of the solvent concentration and acid gas loading of absorption processes.

REFERENCES

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