Cyclone processing of green liquor dregs (GLD) with results measured and interpreted by ICP-OES and NIR spectroscopy

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HIGHLIGHTS

- A novel type pilot scale cyclone dryer for waste and energy products was employed.
- NIR spectra analysis was proven useful for process modeling and monitoring.
- ICP determined elemental contents were visually displayed for result interpretation.
- Through cyclone processing, metal trace elements were separated from main elements.

GRAPHICAL ABSTRACT

Cyclone processing of green liquor dregs provides a separation of toxic metal elements from the main material stream.
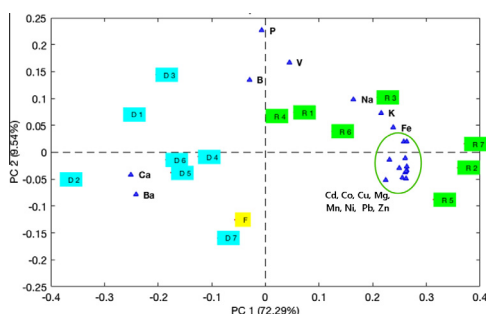
ABSTRACT

An experimental design in cyclone drying parameters for green liquor sludge led to an efficient drying of the material and an interpretation of optimal cyclone parameters. The obtained dried materials were analyzed by ICP-OES and NIR spectroscopy. The inorganic analysis showed that a partial separation of toxic chemicals is possible and the NIR results could be used as an extra way of interpreting the results of the experimental design. The conclusion is that besides drying, also a change in chemical composition occurs as an effect of cyclone treatment. The NIR method is fast and requires little sample preparation while the ICP-OES method gives more direct inorganic results but is more demanding in time for sample handling and measurement.

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1. Introduction

Pulp and paper mills generate a wide variety of organic and inorganic production residues. The characteristics of these residues are mainly dependent on used raw materials, applied processing alternatives and desired paper properties [1]. In general, wood can be converted into cellulose by a selection of mechanical, chemical or semi-chemical pulping methods. In chemical pulping cellulose is obtained by dissolving lignin with alkaline cooking chemicals, such as sodium hydroxide and disodium sulphide. The dissolved lignin is concentrated and incinerated in a recovery

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boiler and the produced smelt is further used for regenerating the cooking chemicals. Non-reactive metals and insoluble materials are precipitated as green liquor dregs and subsequently removed from the chemical recovery circuit.

Green liquor dregs mainly consist of insoluble species from wood and potential make-up chemicals, which do not play an active role in pulping. In addition to dead load, insoluble materials are detrimental to the fibre line and chemical recovery potentially causing operational problems within the mill [2]. Non-process elements (NPEs), such as barium, chlorine, chromium, copper, iron, manganese, nickel, phosphorus, potassium and zinc can generate scale on washers, cause plugging of equipment and increase peroxide decomposition in bleaching plants [3,4]. Although landfill deposition of pulp and paper mill residues has steadily decreased during the recent decades [1], suitable applications for green liquor dregs still remain limited. The Swedish pulp and paper industry generates approximately 110,000 dry metric tonnes of green liquor dregs every year, 76% of which were landfilled or used in landfill construction during 2011 [5].

Previous research on green liquor dregs has involved a wide range of potential applications. As an example, Cabral, Ribeiro, Hilário, Machado and Vasconcelos [6] investigated the use of dregs and other residues for application on acidic soils. Although the dregs had the highest concentrations of metals, respective application lead to pH increases comparable to the use of commercial agricultural limestone. Manskinen, Nurmesniemi and Pöykiö [7] found that a majority of heavy metals in green liquor dregs were recovered during a sequential extraction step which generally corresponds to the oxidation of organic material or sample sulphides. Dregs have also been used as a potential raw material in cement clinker production, but based on the results respective additions should be kept low to control potential sulphur emissions from the kiln [8]. Recently, Pasandin, Perez, Ramirez and Cano [9] reported that utilization of green liquor dregs as mineral filler in asphalt led to poor water resistance and worsened workability compared to unmixed asphalt. In addition, use of green liquor dregs in neutralizing acidic pulp mill wastewater [4] and controlling acid mine drainage [10,11] have been reported.

Current mechanical dewatering alternatives at pulp and paper mills are unable to sufficiently increase the solid content of dregs, which increases respective costs of handling, storage and transport. In previous work [12,13], we have successfully used this pilot equipment for drying of organic sludge residuals from pulp and paper mills. As a natural continuation to earlier work, possible further benefits with the cyclone technology are now investigated. Novel processing methods should be developed for separating non-beneficial components and to enable suitable utilization of green liquor dregs. This work reports pilot-scale experiments on green liquor dregs to simultaneously dry and separate element components from the main material stream. Individual experiments were first performed according to an experimental design, and the obtained samples analyzed by acid digestion followed by elemental quantification. In addition, a near infrared (NIR) spectrometer was used for sample analysis to evaluate the potential of NIR for future process monitoring.

2. Materials and methods

2.1. Green liquor dregs and the dryer setup

Green liquor dregs were provided by a chemical pulp mill located in Sweden. Received 1 m³ containers were sampled, the samples combined and divided [14] to provide a representative sample for feed characterization. The determined dry solids content of the dregs was approx. 34% (1.9 kg H_2O kg^{-1} d.b.). The experiments were performed with a pilot dryer illustrated in Fig. 1. The dryer is centered around a 4 m convective cyclone where sludge can be processed at low temperatures enabled by a high-capacity electrical fan run by an electric motor. The inlet air stream can be heated to approx. ⩽90 °C through the combustion of pellets in a 500 kW heating unit.

The feeding system consisted of a dosing unit coupled to a scale, a small-scale rotating crusher, a belt conveyor and a cell feeder. The processed dregs were recovered from the bottom of the cyclone through a cell feeder coupled to a screw conveyor. Separated fine particles were recovered as a reject fraction and sampled from the bag house filter unit at the end of each experiment. Real-time data logging of relevant fan power input, temperature, relative humidity, and absolute and differential pressure values ensured the acquisition of relevant process data.

2.2. Experiments

The individual experiments were performed according to a two-factor composite design (Table 1). The design included inlet air temperature (15–85 °C) and material feeding (200–700 kg h^{-1}) as controlled factors. Ambient relative humidity (%) was included as an uncontrolled factor but did not prove to be statistically significant and was thus not included in the final models. The actual experiments were performed during representative five minute intervals after the equipment had been stabilized for each inlet air temperature and feeding rate. Processed dregs (D) were sampled three times during each experiment and the feed (F) and
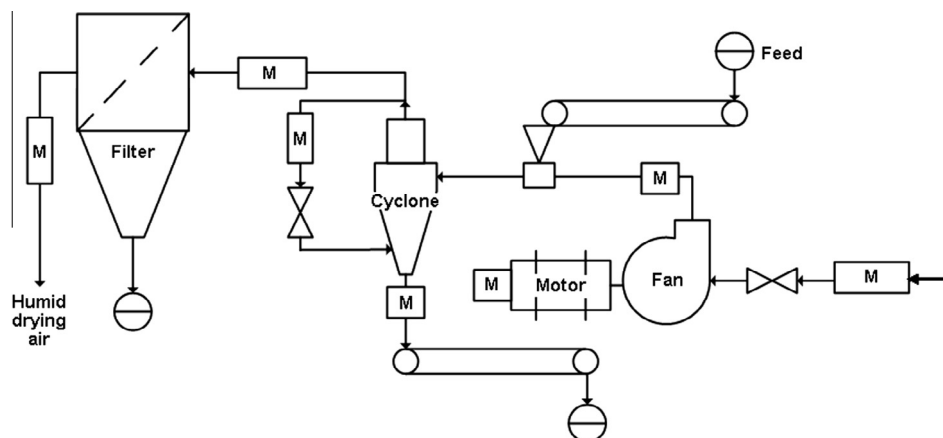

Fig. 1. The pilot-scale cyclone processing setup (M = Measurement point).

Table 1
The experimental design.

Experiment	Inlet air temperature (°C)	Material feeding rate (kg h^{-1})
1	15	200
2	85	200
3	15	700
4	85	700
5	50	450
6	50	450
7	50	450

reject (R) samples were gathered at the end of each experiment. The mass of R was theoretically calculated based on the mass of F and D and respective dry solids contents. Mean values of relevant process parameters (i.e. fan electricity input, temperature, relative humidity, absolute and differential pressure) were used for further calculations.

2.3. Samples

In total 15 samples were collected for analysis. One was the feed (F), seven were processed dregs (D) and seven were from the reject (R) (see Fig. 1). The samples were analyzed for dry solids content by weighing ⩾100 g to stainless steel plates and measuring the mass loss at 105 °C overnight according to the European standard for solid biofuels [15].

2.4. Analyses

Elemental concentrations in dried samples were determined according to US EPA method 3051A [16]. Approximately 0.5 g of each sample was digested in 9 mL HNO$_3$ and 3 mL HCl in a microwave at 175 °C for 10 min. The cooled mixtures were filtered, acidified with 200 μL 54% Suprapure® HNO$_3$ to minimize precipitation and diluted to volume with 100 mL ultrapure water. Elemental concentrations in the eluates were quantified with an inductively coupled plasma-optical emission spectrometer (ICP-OES, iCAP6500 Duo, Thermo Fisher Scientific Inc.). Calibration standards for the ICP-OES were generated by serial dilution of relevant Accustandard (Accustandard Corp., Accutrace®) multielement stock solutions.

Dried samples were also measured by near infrared (NIR) spectroscopy. A NIR spectrometer (Foss 6500, Foss) equipped with a scanning grating as a monochromator and Si and PbS based detectors provided a wavelength range of 400–2498 nm. Only the true NIR part above 800 nm was used. The material was presented in standard 30 mm diameter spinning sampling cups. All measurements were done in four replicates and the spectra were collected in absorbance mode. In total 60 spectra were measured; 7 experiments with 4 replicate measurements provided 28 spectra for the processed dregs, 28 spectra for the reject, and four for the feed material. The resulting data matrix was hence comprised of 60 objects on 850 wavelengths.

2.5. Energy calculations

The specific electricity consumption for drying (kWh kg^{-1} H$_2$O, Eq. (1)) was calculated as:

$$E_{fan} = \frac{W_{fan}}{R_f(X_{feed} - X_{dried})}$$ (1)

where W_{fan} denotes the power input to the fan motor (kW), R_f the sludge feeding rate (kg h^{-1}, d.w.) and X the moisture content of feed or dried sludge (kg H$_2$O kg^{-1} d.w.). In addition, the total energy consumption including the electricity input of the fan motor and inlet air heating was calculated as:

$$E_{tot} = \frac{W_{fan} + Q_{sh}}{R_f(X_{feed} - X_{dried})}$$ (2)

where Q_{sh} denotes the sensible heat in drying air (MJ h^{-1}) prior the fan transformed to kilowatts. Q_{sh} was calculated based on the temperature difference of ambient and heated air. Further details on the use of raw process data can be found from [13].

2.6. Multivariate data analysis

Elemental concentrations and acquired NIR data were interpreted by multivariate methods using principal component analysis (PCA) and partial least squares for regression (PLS) [17,18]. The following principal component model was used:

$$\mathbf{X} = \mathbf{TP^T} + \mathbf{E}$$ (3)

where $\mathbf{X}$ denotes a matrix of pretreated raw data consisting of individual samples or replicates as row objects and elemental concentrations or NIR spectra as the respective columns, $\mathbf{T}$ a matrix of principal component scores, $\mathbf{P}$ a matrix of orthogonal variable loadings and $\mathbf{E}$ a residual matrix. PLS regression models were also constructed based on the NIR spectra:

$$\mathbf{y} = \mathbf{Xb} + \mathbf{f}$$ (4)

where $\mathbf{y}$ denotes a vector of experimental conditions or measured response variables, $\mathbf{X}$ a matrix of NIR spectra with individual samples or replicates as row variables and wavelengths as the corresponding columns, $\mathbf{b}$ a vector of regression coefficients and $\mathbf{f}$ a residual vector. All process variables vectors $\mathbf{y}$ and the NIR spectra in $\mathbf{X}$ were preprocessed by mean-centering. The R^2 parameter was used for evaluating the performance of constructed regression models:

$$R^2 = 1 - \frac{SS_{res}}{SS_{tot}}$$ (5)

where SS_{res} denotes the sum of squares of model residuals $\mathbf{f}$ and SS_{tot} the total sum of squares of variables $\mathbf{y}$ corrected for the mean.

3. Results and discussion

The dry solids contents of processed dregs (D) were in the range 41–65% during the experiments compared with 34% in the feed. The dry solids contents of the D were mainly correlated with material feeding rate (correlation coefficient −0.81, p < 0.05). The specific energy consumption values calculated only based on the electricity consumption of the fan motor were within 0.76–1.35 kW h kg^{-1} H$_2$O and correlated mainly with inlet air temperature (correlation coefficient −0.68, p < 0.10). The total energy consumption values, which included both the electricity consumption of the fan motor and sensible heat in the inlet air, were in the range 1.6–3.2 kW h kg^{-1} H$_2$O and were also mainly dictated by inlet air temperature (correlation coefficient 0.70, p < 0.10).

An example of NIR spectra of untreated green liquor dregs is illustrated in Fig. 2. By PLS modeling of the NIR spectra measured on D samples, good models could be made for material feeding rate, dry solids content of processed dregs, and total energy consumption (Table 2). A reasonable model could also be made for inlet temperature. Determined R^2 values of the final models indicated that 70–97% of total variation in the response values could be explained by the NIR measurements. For NIR-measurements on R samples, the models were worse. The cross validation standard deviation was also higher for R than for D models. The obtained results indicate that a fast process monitoring tool for cyclone treatment, built on NIR spectroscopy, would be possible to develop, but a new design with a higher number of runs is required for this purpose.
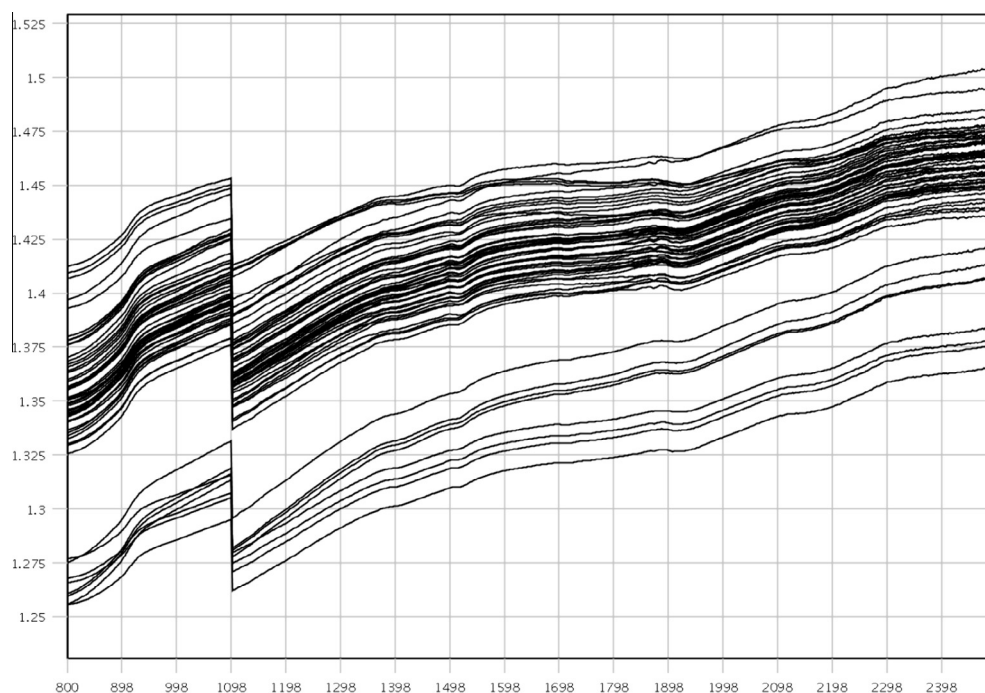
Fig. 2. NIR spectra of non-treated green liquor dregs feed material.

Table 2
Characteristics of determined PLS models based on NIR measurements.

Model	Unit	R^2 value
Inlet air temperature	°C	0.78
Material feeding rate	kg h^{-1}	0.85
Dry solids content of processed dregs	%	0.94
Specific energy consumption (E_{fan})	kW h kg^{-1} H$_2$O	0.70
Total energy consumption (E_{tot})	kW h kg^{-1} H$_2$O	0.97

Table 3
Elemental composition (mg kg^{-1}, d.b.) of untreated green liquor dregs, i.e. process feed material.

Element	Concentration mg kg^{-1}	Concentration molality
Al	25,500	**0.945**
Ba	960	0.007
B	14	0.0013
Ca	175,000	**4.37**
Cd	11	<0.001
Co	19	<0.001
Cr	160	0.003
Cu	330	0.005
Fe	8010	**0.143**
K	1400	0.036
Mg	95,900	**3.95**
Mn	35,100	**0.638**
Na	19,800	**0.861**
Ni	80	0.0014
P	200	0.0065
Pb	52	<0.001
S	31,200	**0.973**
Ti	420	0.048
V	3.4	<0.001
Zn	6490	**0.1**

Bold: major constituents.

Results on the elemental composition of untreated green liquor dregs, i.e. the feed (F) material, are illustrated in Table 3. Based on the data, the dregs were mainly composed of Ca, Mg, S, Mn, Al and Na. In addition, lower concentrations of Fe, Zn, K and some trace elements were detected. For technical, paper mill related, reasons

the major elements are the most important. For environmental concerns, the trace elements may be of special interest.

A principal component model for elemental compositions of feed material (F), processed dregs (D), and reject (R) samples was calculated. The first three principal components explained 91% of variation in the original data and were chosen for the final model. No meaningful structure was found from the model residuals suggesting that the rest of the data were mainly composed of experimental and measurement uncertainties. Principal components scores and loadings based on the first two components are illustrated in Fig. 3a and b.

The t1-t2 score plot in Fig. 3a shows a separation between processed dregs (D) and reject (R) samples along the t1 dimension. Center points D5 and D6 are close together but the third center point D7 is close to that of the starting material, indicating errors in measurement or process performance. For the R samples, all center points (R5-R7) are far away from each other, indicating poor reproducibility in R sample content for which individual measurements should be treated with caution.

To explain the behavior in the score plot, a study of the loading plot (Fig. 3b) is needed. The separation found along the t1 axis in Fig. 1 for D and R samples corresponds to a separation of Ca (with Ba) from other elements along the p1 axis in Fig. 3b. D samples are separated from R samples according to their higher content of Ca while many other elements, including the metals cluster are more present in the R samples. D samples, as the major material stream, are thus reduced in metal content through cyclone treatment.

In the t2 dimension, D1 and D3 are located high up and far away from the starting material. Elements high up along p2 seem to be the more volatile ones, and thus, D1 and D3 have a higher concentration of volatile elements compared to other samples. According to Table 1, runs 1 and 3 were performed at the lowest temperature (set point: 15 °C), which strengthens a hypothesis of volatile off-gassing at higher temperature settings.

The third component showed no clear pattern and therefore figures are not shown. A separate analysis with the five lowest molality elements left out showed similar pattern and there was no need to show it.
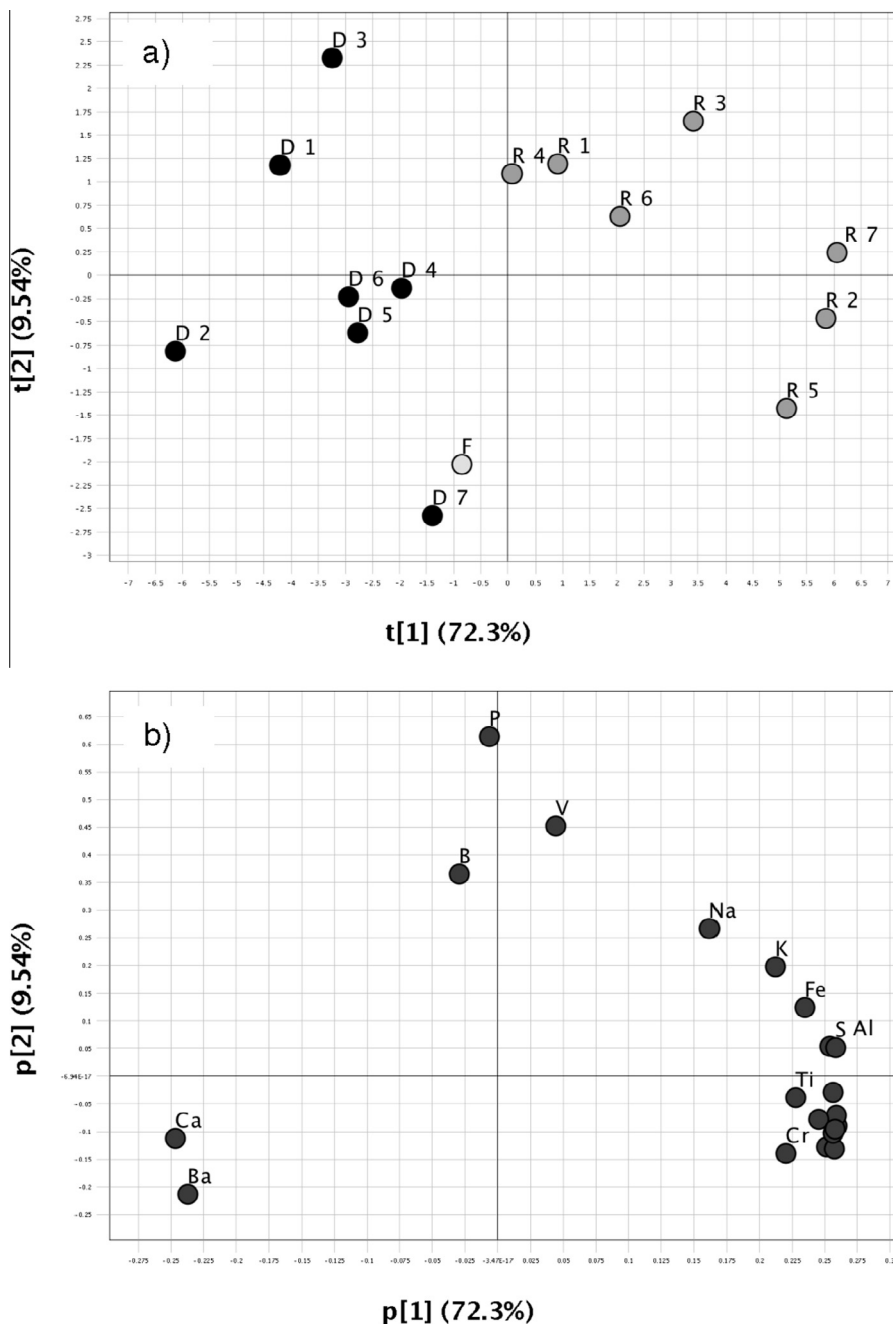
Fig. 3. Principal component a) score plot for elemental content of individual samples according to ICP-OES analysis. F = non-treated feed material, D = processed dregs, R = reject, and b) loading plot for analyzed elements. The metal cluster in the SE corner consists of Cd, Co, Cu, Mg, Mn, Ni, Pb, and Zn.

4. Conclusions

Cyclone processing increased dry solids content of green liquor dregs from 34% to 41–65%. Feeding rate was the most influential factor for the obtained dry solids content. Under the assumption that low-temperature waste heat could be used for drying, specific energy consumption based on the electricity consumption of the fan motor was within 0.76–1.35 kW h kg^{-1} H$_2$O. NIR spectroscopy was found to be a feasible for development of a process monitoring tool, since good models could be built for material feeding rate, dry solids content of processed dregs, and total energy consumption from measurements on processed dregs.

Cyclone treatment was shown to be able to separate metals from the dried dregs to the reject fraction. Processed dregs had higher contents of Ca and Ba, compared to the more metal-rich reject fractions. In conclusion, cyclone processing offers a novel and promising technology for reduction of the heavy metal content in GLD and the presented methodology can thus be part of the solution for one of the major forest industrial disposal problems.

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