Spectroscopic Measurements in Oil Sands Industry-From Laboratories to Real-time Applications

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Abstract: This article presents an overview of the principle, engineering implementation and applications of spectroscopic measurements technology, such as NIR (near infrared), FTIR (Fourier transform infrared), Raman and NMR (nuclear magnetic resonance). The discussions are focused on oil sands industry in which the process majorly consists of the mining, slurry hydro-transport, extraction, froth treatment and upgrading plants.

Keywords: Spectroscope, NIR, NMR, oil sands, measurement, chemometrics

1. INTRODUCTION

Oil sands in Alberta, Canada, are formed in the earth age when the land was covered by the tropical sea. Through the combined effects of pressure, heat and time, the bodies of marine creatures were squished and became tar type oil-rich material, i.e. Athabasca oil sands as called today. Oil sands are a mixture of bitumen, quartz, fine clays, solids, salts and water. Because of its high viscosity and heavy hydrogencarbon components it must be mined or heated underground before it can be processed.

1.1 Overview of oil sands process

The original process for extraction of bitumen from the sands was developed by Dr. Karl Clark, working with the Alberta Research Council in the 1920s (Clark K. 1929). Today, all of the producers doing surface mining, such as Suncor Energy, Syncrude Canada, etc., use similar processes based on Clark's hot water extraction technology. For open-pit mining oil sands plants, the mined ore is crushed for size reduction. Hot water at 50-80 °C is added to the ore and the formed slurry is transported using hydro-transport line to a primary separation vessel (PSV) where bitumen is recovered by flotation as bitumen froth. The recovered bitumen froth consists of 60% bitumen, 30% water and 10% solids by weight (Gu, G., Xu, Z., Nandakumar, K., Masliyah, J.H., 2002).

The recovered bitumen froth needs to be cleaned to reject the contained solids and water to meet the requirement of downstream upgrading processes. Depending on the bitumen content in the ore, 90% to 100% of the bitumen can be recovered using modern hot water extraction techniques (Mikula, R. J., Omotoso, and Friesen, W. I., 2007). After oil extraction, the displaced sand is reclaimed.

The simplified flow diagram of Clark hot water extraction process is as shown in Fig.1.



Fig. 1. Simplified Diagram of Clark Hot Water Extraction

1.2 Challenges of measurement and control for oil sands

The measurements and process control becomes the more and more critical as government and industry are keen to reduce environmental and health risks caused by large-scale oil sands operations. Actually the objective discussion of the environmental impacts has often been clouded by polarized arguments from industry and from advocacy groups. The oil sands industry has spent huge investment to develop more accuracy and effective measurement and control technologies in order to improve the bitumen recovery efficiency, water treatment and greenhouse gas emission.

Until even today, the online applications of effective chemical and physical properties measurement, such as bitumen, water, clays, chloride, viscosity, density, etc. are still far away from to achieving the same level of successes as in conventional refinery or petrochemical industry. The major technical challenges are listed below

- Probe erosion and corrosion for slurry streams: There is a lot of quartz type of solids in the slurry hydro-transport pipeline, tailings water streams and even in froth transportation pipelines. Any in-situ probes contacting with fluid will be worn out in a short period of time, for instance, in a few days or as long as a couple of weeks. The maintenance and replacement will require huge engineering time, outage of operation and capital input.
- The non-consistent phased material flow in the 2) equipment and pipeline: The multi-phase flows and levels can be found almost everywhere in oil sands process. For example, the interface of PSV (primary separation vessel) is generated by sticky froth, water, air bubbles, clay and solid in the middle of the large vessel. The interface looks fuzzy from the glass window mounted on the vessel. Furthermore, the froth produced from the overflow stream of the PSV becomes a bitumen continuous-phase flow from a water continuous-phase in the vessel. The interface control is a critical performance index for bitumen recovery efficiency required by process operating departments. However the reliable and accurate measurement of the interface is still a challengeable and questionable problem.
- 3) The complex compositions in the streams: The oil sands plants consist of mining, slurry transportation, extraction, tailings water treatment and bitumen upgrading facilities. It is necessary to measure as much as possible information of the ores feed, tailings components, bitumen quality and process status either from environmental or economic perspectives. The tailings water released, for instance, must be strictly controlled within environmental regulations. The current sampling and lab analysis is very labour intensive and with significant accuracy and repeatability challenges. The oil sands streams includes much more complex components compared to other conventional petrochemical processes, such as clay, fines, particle size distribution (PSD), chlorides, heavy bitumen as well as lighter hydrogen carbons. The amount varies in wide ranges even in a single stream. For example, the bitumen average value in tailings water is controlled under 0.1% in normal operation, but the peak values during process upset time may reach as high as 3% in a short period of time, see 10 to 30 minutes. It is impossible to capture the dynamic changes using an auto-sampler with 6 to12 hours composite samples or grab samples by operators.
- 4) Difficult controlled sampling and lab procedures: Unlike conventional refineries and chemical plants, the oil sands plants generally use Dean-Stark lab analysis and other non-standard methods. Naturally the human factor has huge impact on the results and repeatability. Take into the account of non-

consistent and multi-phase samples, the subsampling by different lab technicians may obtain totally different conclusion about the process operations. Another issue is the timing of the lab analysis. Some lab work may need 24 hours and sometimes even longer. This type of lab data can only be adopted for statistical purpose but not for real-time process control and optimization.

The issues above are part of current challenges and also there are great opportunities to improve and better control oil sands process. The measurement technology based on spectroscopic devices, such as NIR (near infrared), FTIR (Fourier transform infrared), UV(ultraviolet), Vis(visible), MIR(mid-infrared) Raman and NMR (nuclear magnetic resonance) spectrometers have been widely utilized in polymer and pharmaceutical industry since early-1990s with introduction of light-fibre optics and development of the monochromatic detector (Butler, L. R. P., Laqua, K., 1995). Until only recent years, oil sands industry just started to employ the spectroscopic instruments for online measurement (Friesen, W. I., 1996; Long, Y., and etc. 2004.) and process control (Kadali, R. Feng, E, 2013).

2. PRINCIPLES OF PHOTONIC SPECTROMETERS

2.1 Molecular Vibrational Based Measurement

The principle to measure the properties of the matter is to "look" into the structure of the molecular. The interactions of various types of electromagnetic with matter provide the information of the molecular bands and movement behaviours. The electromagnetic wave in different range of wavelengths from gamma rays to radio waves can be used to excite the molecular. It can be collected amount of absorbance and reflectance signals to estimate the structures of samples. Each range of wavelengths or frequencies reacts with matter in a different way. For examples, the higher energy ultraviolet and visible (UV and Vis) wavelengths affect the energy levels of the outer electrons; infrared (IR) light is absorbed by matter resulting in rotation and vibration of molecules; the radiation waves used in nuclear magnetic resonance (NMR) affect the spin of nuclei in a magnetic field.



Fig.2 Wavelength Range of Radiation

Vibrational states of molecules are associated with absorbance and emission or changes of energy. A molecule generally has many different vibrational levels and styles. There are also a number of rotational states for each of the vibrational states which are often hindered in liquid or solid samples to the extent that these small energies are not ordinarily detected. Many compounds can absorb visible (Vis) (380-780nm) or ultraviolet (UV) light (10-380nm). The most commonly used UV spectrum is from 200-380nm because air absorbs the UV light below 200nm. The instruments must be operated under a vacuum which is not always practical for industrial applications. Some chemical solvents and inorganic species also absorb the energy in the UV and Vis region of the spectrum. The radiation chart is shown in Fig.2.

Infrared spectrometers are primarily for the identification and structural analysis of organic materials. The spectrum of an unknown sample is collected to compare with the samples of known materials. Reference charts displaying the absorption wavenumbers of chemical groups are often used for identification purpose. However this work strongly relies on the human experience and the type of samples, such as purity, complexity, prior-knowledge of the chemical groups, etc.

Near infrared region (NIR) between 800-1500nm are used in industrial NIR analyser. Absorption bands in this region are weak, but sensitivity of the instruments has been significantly improved since last decade by adopting innovated incident light sources and the detectors. The application of NIR for quantitative analysis is more complicated than in the midinfrared region, therefore Fourier transform infrared (FT-IR) was developed to overcome these difficulties. Usually chemometric software packages and a set of known samples with primary data are required to build multivariate statistical models in order to identify the unknown samples. The NIR spectra can be obtained by using transmission or reflectance probes which is highly dependent on the physical status and characteristics of the samples chemical and the manufacturing process. The important feature of infrared light is that it has good response to the hydrogen-carbon bands which is the most useful region in oil industry.

Raman spectrometers are used to observe vibrational, rotational, and other low-frequency modes of matter. It is made based on signal of inelastic scattering (i.e. Raman scattering) of monochromatic light, usually generated from a laser in the visible, near infrared, or near ultraviolet range. Raman analyzer is complementary to NIR and Mid-IR but with different intensities and selectivity.

2.2 Fundamental Setup of the Spectrometers

In the spectroscopic system the incident light beam targets to the samples required to be analysed. The response light or energy loss in other words, can be collected in very different ways, such as reflection, transmission and scattering light as shown in Fig 3. The practical decision to use which parts of response strongly relies on the purpose of analyser and the sample characteristics. Two most common kinds of setup are transmittance and reflectance which are shown in Fig.4. For examples, the transmittance setup is usually used for transparent and clean liquid samples and the reflectance setup for dark and solid samples.

In general it is not required to carry out sample preprocessing for spectrometer analysis if the samples are in consistent phase or homogenous mixed. However, for online measurement applications extreme attention must be exercised in order to keep the status of off-line samples as close as possible to the real time status in the process equipment. Sometimes an online testing in a pilot plant may be necessary before implementing the project engineering work.



Fig.3 Response Collection in Different Ways



Fig.4 Different Setup of Spectrometric Systems

3. APPLICATIONS IN OIL SANDS

As previously discussed, the measurements in oil sands plants are not as easy and standard as in conventional petrochemical plants and refineries. The major difficulties are caused by inconsistent material flow, high viscosity and probe erosion, such as ores on conveyor belt, long slurry pipeline, dark froth with water, and so on. The major properties for process and operation control are shown in Fig.5.

As the first step of oil sands process, mining is a labour intensive and environmental impacting action. The mobile analyser can allow geologists to make better and timely decision for shovel arrangement and shift schedule. The NIR, FTIR and Raman portable analysers are powered by a pile of batteries and the tablets are connected to commercial data services. The ores analytic information can be sent back to control centre through wireless communication for truck scheduling and ores blending.

The NIR applications for ores feed on conveyor belt was tested in several companies such as Syncrude Canada and Suncor Energy (Speta, M., Rivard, B., Feng, J. and Gingras, M, 2013.). Basically it combines image processing techniques and chemometric models to predict ores bitumen and clays concentrations. The most recent innovation is on the image devices, the 2-dementional NIR signal can be collected to increase the signal/noise ratio. This kind of image NIR applications is still in the experimental stage for more reliable and weather insensitive results.

The tailings is probably the most difficult stream for obtaining measurements due to the partly stratified heterogeneous process flow and low concentration of bitumen and diluents which need to be measured accurately. Any in-situ probe is easily eroded and cannot last even a few weeks. The only online measurement is to use nuclear densitometer mounted around the pipeline. The analysis of chemical compounds like bitumen etc. totally relies on offline or at-line lab work. This situation has not been changed until Suncor Energy published its patented technology recently (Kadali, R. and Feng, E. 2013). This technology may bring a revolution in measurement and real time control of oil sands industry.



Fig.5 Measurement Requirement of Oil Sands Process

Other important measurements are in froth treatment unit in which pilot NIR online experiment was reported for analysis of solvent/bitumen ratio of diluted bitumen product. The online applications are implemented at Suncor Oil Sand plant, which claims successful measurement of almost all required properties such as bitumen, diluents, mineral, water, density, chlorides, sulphur and even particle size distribution. This implementation makes it possible for real-time quality control and optimization.

4. IMPLEMENTATION OF MEASUREMNT PROJECTS

4.1 Feasibility Study and Vendors Selection Criteria

The feasibility is extremely important before starting the major engineering design and implementation capital arrangement. In general the feasibility study includes process requirement meeting, initial samples preparation, initial chemometric modelling, primary data quality test and initial installation location and networking layout field inspection.

First of all, the feasibility can create an opportunity to allow all people, including project team, and final users, to get more understandings about the new technology, new instruments, limitations and process characteristics. Secondly, the initial chemometric modelling work has to be conducted to check the correlation between spectrometric signal or spectrum and primary data. Thirdly, the expectations from the new instruments should be built based on the primary data quality and precision. It may be needed to carry out a two-blind repeatability study with current lab quality and procedures. Very often, lab instruments or procedures issues could be unveiled which might never be looked at before. The initial modelling work can also identify the best spectrum range for each particular application and most suitable spectrometric vendors.

Instruments and vendors selection requires a rigorous evaluation of the different functions and capabilities, which may be listed as below:

- 1) Measurements required: physical properties or chemical properties.
- 2) Process status: main process pipeline or sample fast loop; solid or liquid, slurry or clean flow.
- 3) Field installation limitation: fire-class of field, weather-proof requirement, etc.
- 4) Vendors: products reputation and service.
- 5) Spectrometric techniques: hardware wavelength ranges, resolutions, probe types and fibre; software reliability, modelling capability and online functions.

4.2 Chemometric Modelling and Maintenance

The key core of spectrometric projects and applications is the chemometric models. Advanced process control engineers should be responsible for building the models. This is due to the special multivariate statistical skills requirement in order to develop and maintain the models.

The four main stages in model development are:

- Pre-calibration: This phase is to determine that the model to be created for a stream conforms to the operating requirements and all modelling requirements are in place. This stage also provides valuable information such as how much laboratory work will be required for the final model calibration and if the spectra ranges and type of probe are suitable to model the properties and correlations are strong.
- 2) Calibration: Once the pre-calibration is completed and the required stream properties have been identified and confirmed, the models generated can be used for process analysis. The primary laboratory analyses carried out during this phase are done to ensure that models cover the complete operating

envelopes for all streams. After the laboratory data validation process is complete, process spectra representing the same samples are used to generate the calibration models that will be later used for plant operations.

- 3) Online validation: The objective of validation or cross-verification is to ensure that the models are suitable for their intended purpose for online applications. Generally speaking, the initial models based on the spectra of off-line samples are not exactly the same as the one from online probe due to the different conditions inside and outside pipelines. The initial models should ensure all major chemometric features are captured except for minor uncontrollable features. This type of uncontrolled features can often explain the bias and dynamic variance ranges between lab analysis data and online predictions. The trends should not be impacted by the minor features if the initial models are developed correctly. The grab samples are collected with properly time recording. The online spectra which match exactly time of the grab samples are added into the pre-calibrated models for a Principal Component Analysis (PCA) in order to investigate any major features missed. The online validation process may not always quick work due to availability of lab data with good repeatability. The alternative method, i.e. cross-verification, is to conduct a material balance calculation based on existing online measurements such as flow rates, densitometers and composed lab data. It is important to keep it in mind that the crossverification needs to carefully deal with the data set and understand the details of the process flow sheet.
- 4) Model maintenance: Model maintenance is based on routine performance evaluations. This process requires the periodic collection of online samples analysed by both the chemometric method and the primary laboratory method. Depending on the stream, this may take place weekly or monthly, or at some other frequency. The models may require further development if spectra features change due to process stream composition change or coverage of a wider range of the process characteristics is required.

All model maintenance work should be clearly documented by the modeller in a way that is traceable and transparent.

There are two key differences between spectrometric and conventional analysers, from the point of view of skills required. First, the models development and maintenance require skills in multivariate statistical methods that are most often found among advanced control engineers. Secondly, spectrometric analysers are more dependent on solid state electronics and computers than most conventional analysers, so "maintenance" of the analysers mostly means software maintenance such as signal verification, spectrum patterns inspection, model updating, and so on. The hardware maintenance, such as probe inspection and light source replacement, is relatively much less than conventional analysers. For this reason, it may make sense to rather coordinate the maintenance by advanced process control group. The applications of online monitoring and recursive modelling algorithm could be used to reduce the model maintenance work load (Chen M. Khare S. and others, 2013).

4.3 Engineering Considerations

The spectrometric instrument installation should be designed for an appropriate level of reliability that minimizes the cost of the installation while maximizing its benefits. Due to the relatively low cost per property analysis of a spectrometer installation it is recommended that the installation be designed for reliability and quick recovery following a failure of a component of the sampling system, the fibre optic cable, or the analyser itself.

For some cases, the fibre optic cable can be of significant length, so the location of the spectrometric analyser should take advantage of the fibre length to connect multiple streams to the same analyser. The location and allocation of samples to individual analysers need to align with plant operational boundaries and physical constraints such as power distribution.

The fibre length affects the signal to noise ratio and cut-off wavelength of spectra, and fibre degrades slowly over the life of the installation, so the design needs to consider the eventual fibre performance, not just the initial performance. Whether a probe or cell is used, the design needs to consider isolation requirements to protect the cell from special operating conditions, e.g. caustic washes. Also, flow past the sensor should be upward, and, if it is located immediately after a bend, the location must consider swirl and turndown in order to avoid recirculation cells and ensure fresh process fluid continuously flows past the sensor. Well-mixed flow is the objective. Horizontal runs should be avoided wherever possible.

Servers for online instruments should be accessed through the plant information network. This is driven by security policy: since the analysers communicate directly with the DCS they are part of the plant control system, and must be treated as such. The servers should be maintained just like other DCS servers. Servers in a production environment should be set up in a manner that is consistent with the other servers on the network, including user authorization/authentication and backup protocols. At least three different user roles should be defined as system administrator, modeller and maintenance user.

5. CONCLUSIONS

The spectrometric analysers bring different methodology for oil sands process measurement, control and optimization. The key considerations for implementing spectrometric projects and engineering design are discussed including technical evaluation, chemometric modelling, and maintenance plan. All of these require a close collaboration among process engineering, process control and design group. The opportunities and possibilities to employ this innovative spectroscopic technology could be found everywhere in oil sands industry. A revolution in measurement of oil sands is on the way coming with big data technology, new photonic devices and emerging computing technology.

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