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BL2F

Transforming Black Liquor to Biofuel

Research and Innovation Action

H2020-LC-SC3-2019-NZE-RES-CC

D1.7 - Report on the online analysis of the HTL-oil

WP1 - Task 1.4.2

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Lead Beneficiary: Tampere University

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Abbreviations and acronyms

Acronym	Description
NIR	Near Infrared
UV	Ultraviolet
VIS	Visible
nm	Nanometer
min	Minute
dB	Desibel
ms	Millisecond
WP	Work Package
C	Carbon
H	Hydrogen
TAU	Tampere University

Executive Summary

The aim of this task was to investigate the possibility of providing runtime feedback on the high-pressure processing reactor by means of optical online measurements. Optical transmission at Near Infrared (NIR) and Raman spectroscopy methods were considered for the task. The work was separated into a laboratory phase, where samples were tested at room temperature conditions with standard measurement systems, and a reactor site phase where selected techniques were used at operating reactor. Laboratory test showed that there is low potential for detecting chemical species in the reactor products, as their complicated composition blurs individual features into broad response. The best responses were recorded from aqueous phase of the final product. The reactor measurements were quite limited due to low overall running time of the

reactor, but the recorded NIR transmission measurements did show good potential for online monitoring especially if the optical cell length would be shorter to avoid signal saturation.

Keywords

Black liquor, Fuel, NIR spectroscopy, Raman spectroscopy

1 Introduction

The gal of this work package was to investigate the possibility of providing feedback on the wastewater processing reactor, by means of optical measurements. Optical transmission at Near Infrared (NIR) and Raman spectroscopy methods were considered for the task. The work was separated into laboratory phase where, samples were tested at room conditions with standard measurement systems, and reactor site phase where selected techniques were used on operating reactor.

2 Optical measurements at the laboratory

A series of optical transmission and Raman spectroscopy measurement were performed at the Tampere university laboratories to test possible detection schemes. The laboratory tests were performed at room temperature and pressure, which are significantly different than the supercritical fluid condition expected at the reactor measurements, nevertheless they allowed to study the sample materials while the reactor experiment was in preparation.

2.1 Transmission measurements of the reactor product samples.

Samples of Brine and Top product were tested at the Photonics Laboratory a PerkinElmer Lambda 1050 UV/VIS/NIR spectrophotometer. Transmission spectra from 600 nm to 2000 nm were recorded and are shown on Figure 1. The spectra of both samples are similar and are dominated by water absorption, with signs of potential oil induced absorption at NIR wavelengths around 1200 nm. Unfortunately, no distinct transmission lines were detected, most likely due to complicated chemical composition of the samples, that led to partial overlap of multiple absorption lines.

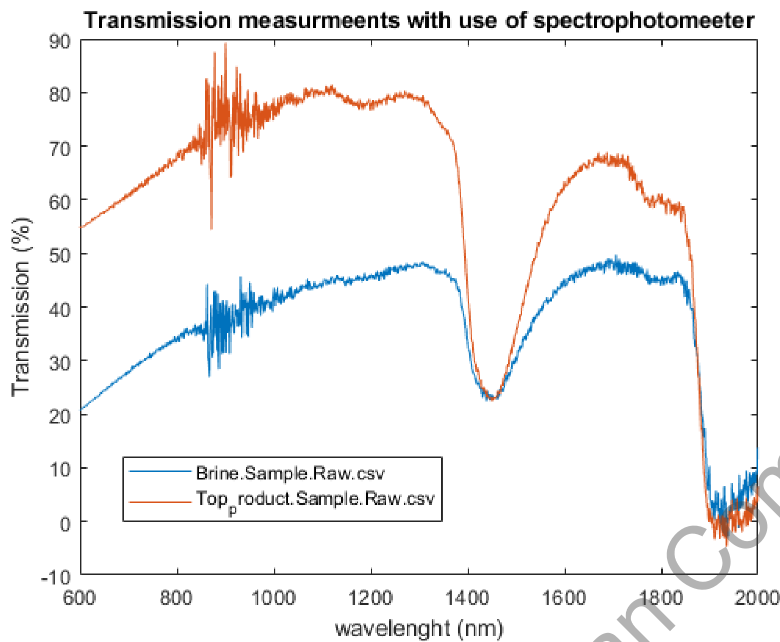


Figure 1 Transmission of Brine and Top product samples measured at TAU laboratories with use of spectrophotometer.

2.2 Initial investigations on Raman measurement of Biocrude oil.

Biocrude oil, believed to be similar to expected reactor product, was tested for possibility of using Raman spectroscopy technique. A comparison of Bio crude and diesel oil Raman spectra are presented on Figure 2. The measurements were performed at Micoscopy Centre of Tampere University with use of Renishaw InVia Qontor Raman microscope. Biocrude oil Raman spectrum showed significant amount of fluorescence at both 532 nm and 785 nm pump wavelenghts which have hidden any Raman scattering spectrum features. On the figure, one can compare the tested Biocrude signal with Raman spectrum of diesel oil, showing distinct carbon-carbon and carbon-hydrogen vibration transitions.

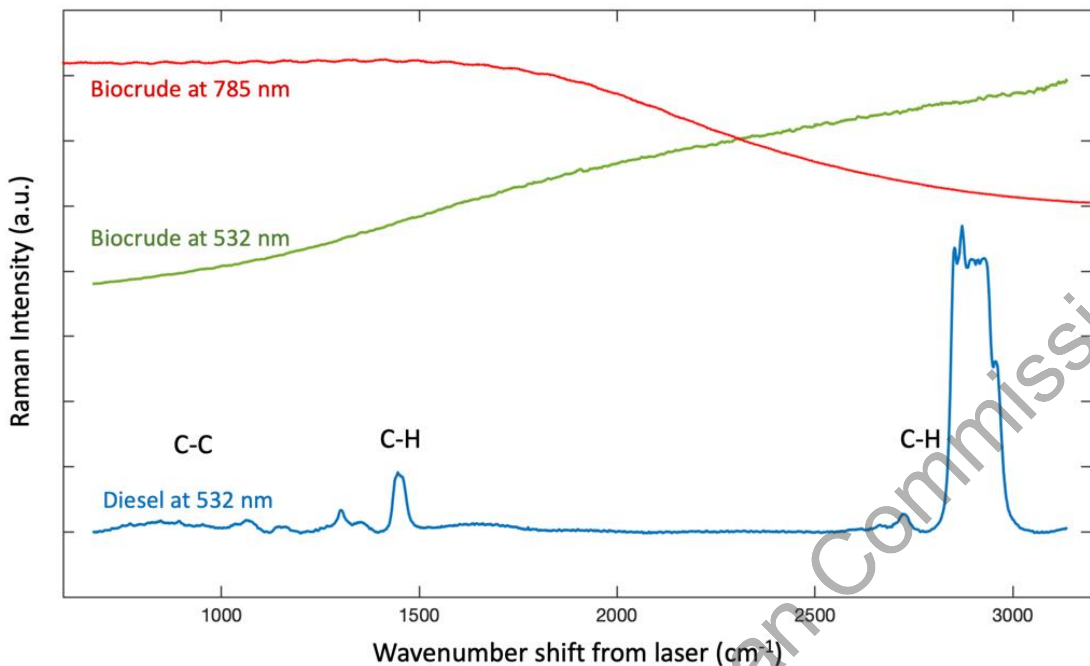


Figure 2 Raman spectra of diesel with 532 nm laser and biocrude oil with 532 nm and 785 nm lasers.

A custom Raman scattering measurement setup was constructed at Optics Laboratory of TAU, that utilized 1032 nm pump laser, at which samples showed significantly lower absorption, in hope of avoiding high fluorescence levels. The Raman scattering signal levels from biocrude oil was too low for existing detection schemes and no valuable data was collected.

2.3 Raman spectra measurements of the reactor product samples.

Raman scattering measurements of Top-product and Brine water samples obtained from the reactor run were performed at the microscopy centre of Tampere University. Two pump wavelengths were tested: 532 nm and 785 nm. Signal collected while pumping with 532 nm light was dominated by fluorescence and thus did not allow for any Raman scattering information retrieval. However, when 785 nm pump was used it was possible to record Raman spectra corresponding to transitions withing carbohydrate chains vibrations in wavenumber range between 1100 cm^{-1} to 2000 cm^{-1}. Exemplar Raman spectra for Top-product and Bine samples are presented on Figure 3. One has to notice that samples were measured few days after they were collected from the reactor test run and they might have degraded form initial state. One of the observed effects was the emergence of microscopic oil droplets in mostly water-based solution. This affected the Raman scattering signal in both sample types, causing high variation of the signal strength depending on sampling position and power.

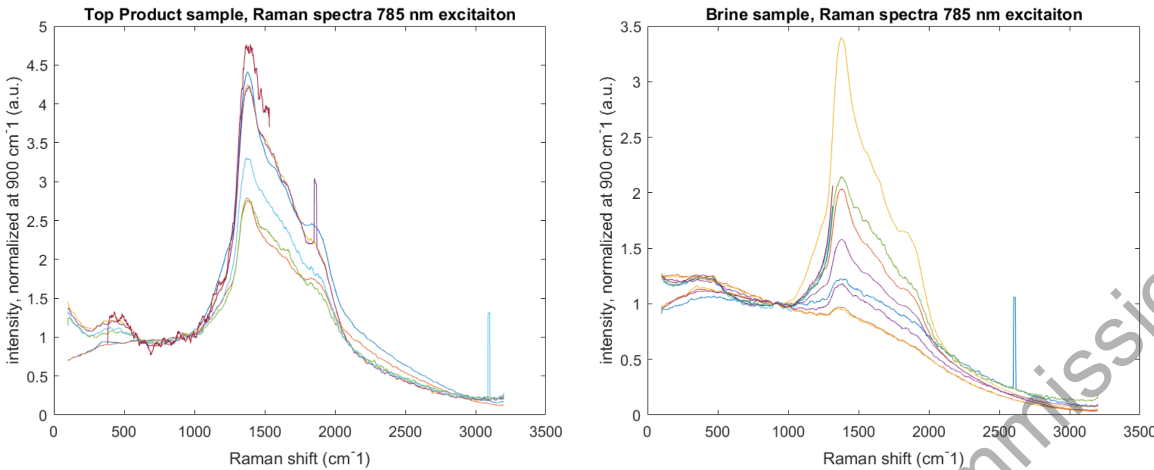


Figure 3 Raman spectrum of a top-product (left) and Brine (right) sample measured at TAU microscopy center at room conditions.

2.4 Laboratory measurement conclusions.

Laboratory test showed that there is low potential for detecting chemical species in the reactor products, as their complicated composition blurs individual features into broad response. The best responses were recorded from aqueous phase of the final product.

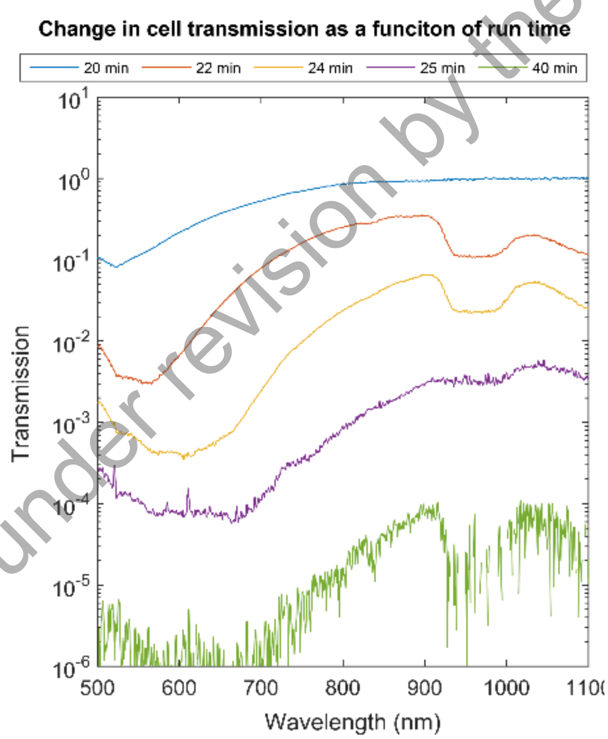
3 Optical measurements at the reactor’s site

Optical measurements at the reactor's site were possible thanks to the installation of see through cell connected to the output of the reactor. The cell is kept at high temperature and pressure, allowing for the reactor product examination while it still exists in supercritical state.

3.1 See-through cell transmission measurements at Vis-NIR wavelengths.

First optical measurements on working reactor involved simple transmission measurements combined with real time video inspection of the cell, as due to the safety restrictions, human presence at the measurement site was restricted. A schematic drawing of the optical measurement setup is presented on Figure 4. The light from incandescent source was directed through the see-through cell containing super critical fluid, after which it was collected and guided to a spectrometer via a multimode fibre.

A sequence of transmission spectra was collected during reactor startup and wastewater feeding phase. Measurement results are presented on Figure 5. The spectrum recorded at time 0 min was used as a baseline for following measurements. About 20 minutes after the reactor start cell transmission started dropping significantly suggesting that the product have reached the cell. Unfortunately, no spectral features allowing for identification chemical species were observed.



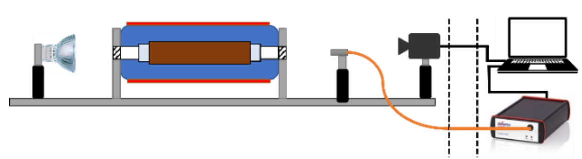


Figure 4 (top) Schematic of the see through cell transmission measurements.

Figure 5 (left) Vis-Nir-IR transmission spectra of the see through cell captured during reactor startup.

This measurement run confired that measurement environment allows for this simple optical setup operation, the vibration level are acceptable for given optical rail desing, othough it was clear that thermal isolation of the rail was necessary to avoid extensive heat transfer from the cell housing to the optical components and their holders.

The reactor run have ended prematurely due to the reactor process controls failure. Unfortunately, the stable condition was not reached, thus samples of the product related to the spectra were not collected.

3.2 See-through cell transmission measurements at Nir-infrared.

The second step was to investigate the reactor product transmission in the near infrared Nir-IR. For that purpose, incandescent light source collimation was improved, and light collecting lens was added before the fibre. A Long-wavelength-pass optical filter was placed in front of collection optics to avoid stray light interference on the measurement. NIR spectra were recorded by StellarNet DwarfStar spectrometer. A simple thermal isolation was implemented to the optical rail mount, which significantly limited the heat transfer to the rail keeping the setup at acceptable temperatures.

Figure 6 shows a series of collected transmission spectra over the approximated reactor run time. The measurements start at time 0 with the test cell filled with water in supercritical state, note that there is a possibility of oil residue being still present. At that time wastewater is fed to the reactor. It takes roughly 20 minutes for the first products of the reactor to reach the test cell which significantly lowers the transmission.

The data was collected over a wide range of integration times which allow to focus on the highly attenuated spectral bands or highly transmitted ones thus increasing effective dynamical range of the measurement series. To accommodate for that data was normalized by integration time effectively providing counts-per-millisecond unit. For better clarity, data is presented in dB scale that better visualizes significant signal fluctuations at multiple orders of intensity values.

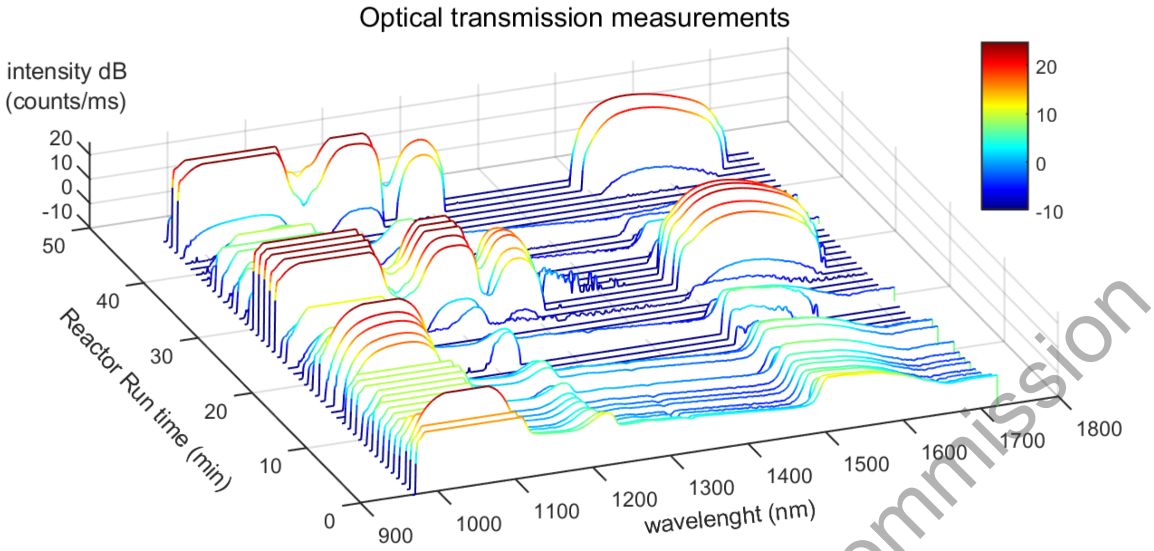


Figure 6 Near-infrared transmission spectra of the see through cell.

At midpoint of the reactor run time, the reactor operation got unstable, which resulted in several, not well-known events of losing and retrieval supercritical conditions in the cell, and possibly significant change of material composition, leading to significant changes of transmission over multiple orders of magnitude. Due to the lack of explicit information of the state of the device it is hard to make detailed conclusions about the measurement outcome.

It is clear however that even this simple optical setup was able to provide feedback on the reactor output conditions, that could potentially be refined over time, if more stable operation had been achieved.

3.3 On site measurements conclusions.

Due to reactor operation problems, it was hard to establish and refine optical measurement technique that would provide adequate feedback on the device operation. Only simple transmission experiments were carried out, results of which could not be fully verified. However, the recorded NIR transmission measurements did show good potential for online monitoring especially if the optical cell length would be shorter to avoid signal saturation.

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