PNNL-30788

Radiation-Induced Catalysis of Chemical Reactions

December 2020

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Prepared for the U.S. Department of Energy
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Report

Nuclear energy is a process which achieves zero-carbon energy and heat generation that can provide a consistent electricity load to supply the grid when renewables are not available. However, on a cost per kilowatt-hour comparison, nuclear energy is more expensive than many of the renewable energy generation technologies such as wind and solar.[1] In order to increase the economic viability of next generation nuclear reactors for energy production, generation of a secondary product such as a chemical feedstock would increase the economic viability of nuclear energy, particularly for new installations of next-generation nuclear reactors for power production.[2, 3] Currently, commercial nuclear reactors are primarily used for their heat to generate steam for electricity production. There is a large amount of unused energy in the form of photon and neutron radiation that could be exploited to drive chemical processes to produce feedstock materials as a secondary product of a nuclear plant.[4] Chemical processing with radiation is not a new concept. In fact, gamma radiation is an excellent source of high energy photons to drive photochemical reactions. Dow chemical produced commercial quantities of ethyl bromide using gamma irradiation from a ^{60}Co source in the 1960s and 1970s because it was the most cost-effective means of production to meet the demand.[5, 6] Due to the potential economic advantages, there is a new emphasis on studying feedstock production which can be enhanced by excess gamma and neutron radiation, particularly if the reaction could be monitored in real-time which is advantageous for process optimization. A model system of lignocellulose degradation under γ- radiation was chosen for this study while following the degradation products with Raman spectroscopy in real-time.

Lignocellulose has the potential to be a renewable source of chemical precursors for fuels and other feedstocks. Lignocellulose is made up of three main components: (1) cellulose, a polymer chain of cellobiose, a D-glucopyranose dimer, (2) hemicellulose, a macropolymer consisting of C5 and C6 sugars, and (3) lignin, an aromatic polymeric material. The radiation-induced degradation of this type of material has been studied previously on many types of lignocellulosic biomass.[7] The feasibility of the inclusion of ionizing radiation into a wood-based biorefinery has also been discussed.[8]

Online monitoring of changing chemical systems allows for the quantification of complex solution chemistry in real time. Optical spectroscopy provides a powerful route for online monitoring. Optical spectroscopy is sensitive to a wide variety of analytes and can provide low limits of detection for many analytes. Raman spectroscopy is particularly well suited to online monitoring applications. Raman probes are very physically robust, resisting harsh chemical and radiation conditions where other optical spectroscopy such as UV-visible spectroscopy may suffer from effects such as the radiation-induced discoloration of quartz and glass. Raman systems also require infrequent calibration, reducing the interruption to experiments or exposure of workers to harsh conditions.

In this LDRD project, the degradation of lignin and cellulose under gamma irradiation were examined. Over the course of this work, several irradiations were conducted, examining different potential chemical conditions. Initially, the materials were irradiated and grab samples were taken for analysis by high pressure liquid chromatograph (HPLC), gas chromatography-mass spectrometry (GC-MS) and Raman spectroscopy to: (1.) Determine the degradation of the materials and (2.) Determine the feasibility of Raman spectroscopy for potential real-time monitoring of the reaction. Briefly, 10%(w/w) solutions or suspensions in 5% hydrogen peroxide were prepared with cellobiose, pine sawdust, diphenyl ether and Kraft lignin. Cellobiose is the repeating dimer of cellulose, while diphenyl ether represents a readily available dimer of phenol, a model compound surrogate of lignin. Irradiations were conducted in the high exposure facility (HEF) in PNNL's 318 building while another irradiation of cable stacks was ongoing (see Figure 1). The total accumulated dose was between 2 and 6 MRad. From these studies, the peroxide and cellobiose components were focused on for real-time monitoring. Partial Least Squares (PLS) chemometric models were built using Raman spectra for the measurement of these species in solution. The final irradiation was conducted with a Raman probe in place and a secondary sample beside it for periodic grab samples for HPLC and GC-MS analyses. Figure 2 shows the Raman Probe in place in the reaction vessel. The decrease in peroxide and cellobiose concentrations were successfully followed in real-time during gamma irradiation. Figure 3 shows surface plots of the change in spectra over time for both species. Figure 4 shows the data fits to the PLS model for both species as well as the fits to the HPLC grab sample concentrations for the cellobiose.

Figure 1 -Lignocellulose material mixtures in 5% hydrogen peroxide (stainless steel tubes), placed in the

Figure 2 - Raman probe in the stainless-steel reaction vessel for

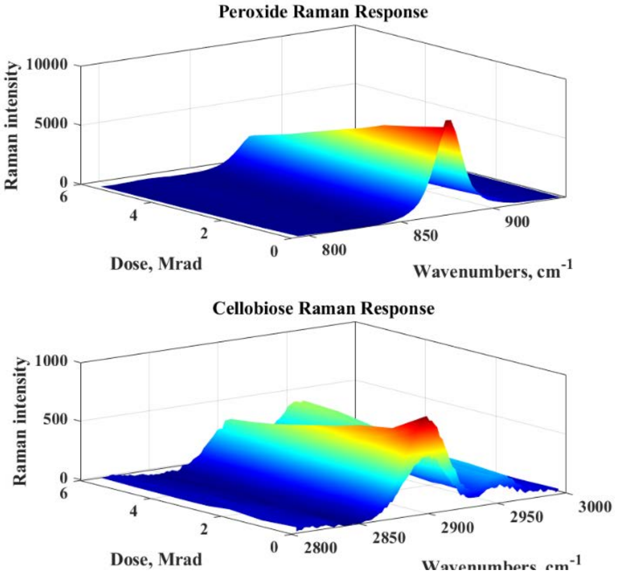
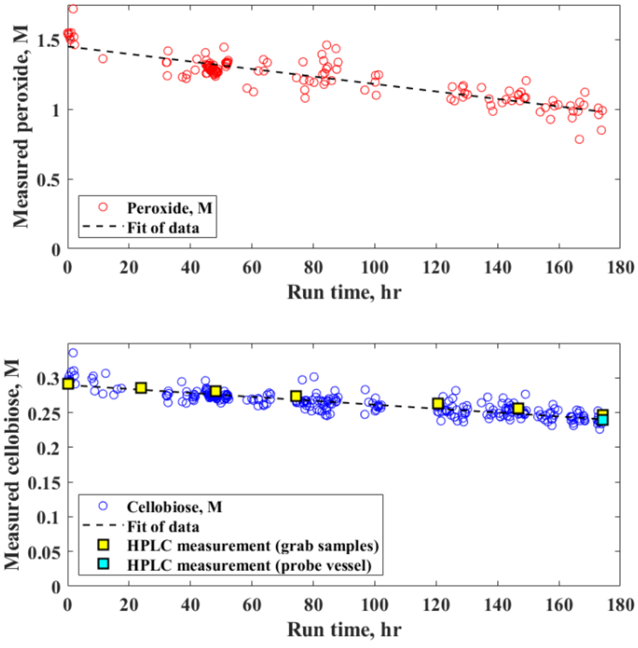


Figure 3 Surface plots of the Raman spectra for hydrogen peroxide (top) and cellobiose with accumulated dose (MRad)

during gamma irradiation.



online monitoring of cellobiose degradation

Figure 4 – Experimental data compared to the PLS model fit for peroxide (top) and cellobiose (bottom). Also shown in the cellobiose plot is the fit to the grab sample HPLC data.

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