DOE-ID NEPA CX DETERMINATION
Idaho National Laboratory

CX Posting No.: DOE-ID-INL-21-006

SECTION A. Project Title: Up-cycling Process Feasibility for Coupled Radiolytic and Biochemical Conversion of Polyethylene

SECTION B. Project Description and Purpose:

This Seed LDRD research proposes to test an innovative approach to accelerate the degradation of polyethylene – the most common everyday plastic and subsequent major contributor to waste plastic accumulation. There are currently no sustainable industrial scale processing routes for the recovery and conversion of 'low value' plastics such as PE, and as such they accumulate in landfill waste and/or as contamination in the environment. Due to the absence of sustainable recycling methods, the demand for virgin plastic synthetic feedstocks from petrochemical sources continues to increase and is expected to become a significant energy drain by 2050. This unsustainability, from both an energy and environmental standpoint, has prompted the U.S. Department of Energy (DOE) to encourage the development of sustainable plastic recycling methods, as the billions of tons of waste plastic are potential sources of cost-effective synthetic feedstocks. However, unlike several other types of plastic (e.g., polystyrenes, polyamides, and polyesters), PE does not contain any chemical functionality beyond its carbon-hydrogen backbone, essentially making it chemically and biologically inert unless extreme conditions and/or exotic processes are employed. Consequently, the proposed research will investigate the proof of concept of using gamma irradiation capabilities at Idaho National Laboratory (INL) – an underutilized nuclear asset – to initiate the chemical functionalization and depolymerization of PE blended into aqueous solutions, followed by biochemical conversion at Valparaiso University (VU) to yield synthetic feedstocks. These irradiation experiments will leverage existing analytical techniques at both institutions for the measurement of PE depolymerization, and have the potential to establish a new field of fundamental research, offset the energetic and economic burden associated with current plastic production and recycling technologies, and dramatically reduce the environmental impact of plastic waste.

Significance

Plastics (synthetic organic polymer products) have become an essential component of society due to their wide variety of applications. This versatility has resulted in the manufacturing of over 8 billion metric tons (MTs) of plastic in the last century, with annual production expected to exceed 700 million MTs by 2030. As plastics are predominantly synthesized from petrochemical feedstocks, the burden of plastic production on the world's oil resources is expected to reach 20% by 2050. Consequently, plastics are rapidly becoming an energy problem in addition to an environmental one. The solution should be the offsetting of petrochemical feedstock consumption and plastic waste accumulation by recycling. Unfortunately, 75% of plastic material in the United States is sent to landfill, as current recycling technologies are inadequate due to a combination of scientific, technological, and economic challenges. For example, polyethylene (PE) is predominantly recycled by pyrolysis, which is inherently energy-intensive (>200°C), disincentivizing its adoption. Thus, there is significant interest in the development of alternative methods for the transformation of waste plastics into materials of greater value, so-called up-cycling. In response to this challenge, we propose to test the feasibility of up-cycling PE by coupling radiation-induced functionalization (i.e., grafting) and depolymerization with biochemical conversion using microbes and/or fungus.

Due to its prevalence in packaging materials, low- and high-density PE makes up 36% of total global plastic production, but only a 15% recycling rate in the United States. Consequently, PE is a large, untapped source of up-cycling feedstocks. However, the recycling challenge with PE lies in its absence of chemical functionality, as it is composed entirely of C-C and C-H bonds. This is the main reason why pyrolysis is most widely used for PE recycling, despite the associated energy penalty and lack of product specificity. If PE can be cost-effectively functionalized, it can be more easily recycled using other processes. Hence, our strategy is to employ ionizing radiation to functionalize PE to make it more amendable to biochemical conversion.

The application of ionizing radiation – an underutilized nuclear asset – for the degradation of large organic molecules is not a foreign concept, as high energy ultra-violet light is commonly used in Advanced Oxidation Processes (AOP) for water purification, and fast electrons are the key driving force for up-coming electron beam technologies. In water, polymeric materials have been shown to undergo radical reactions in a similar manner to other carbon-based compounds. Water radiolysis (Eq. 1) leads to the formation of one of the most powerful chemical oxidants, the hydroxyl radical (•OH, Eo = 2.7 V):

$$H_2O \rightsquigarrow [0.27]e_{aq}^-, [0.07]H^\bullet, [0.28]\ ^\bullet OH, [0.07]H_2O_2, [0.05]H_2, [0.27]H_{aq}^+, \quad (1)$$

where the numbers in brackets are the gamma radiolytic yields (μmol J–1) of each produced species for neutral pH water. The formed •OH will extract hydrogen atoms from polyolefins such as PE (Eq. 2), creating carbon-centered radicals (•[Polymer]):

$$^\bullet OH + Polymer_{(aq)} \rightarrow H_2O + {}^\bullet[Polymer]_{(aq)}, \quad (2)$$

which in aerated aqueous solutions [~0.25 mM O_2] are expected to rapidly react with dissolved oxygen (O_2) to form peroxyl radicals (Polymer-$O_2^\bullet$, Eq. 3):

$$^\bullet[Polymer](aq) + O_2 \rightarrow Polymer\text{-}O_2^\bullet{}_{(aq)}. \quad (3)$$

The capping of the carbon-centered radicals formed in the polymer by O_2 addition ensures that cross-linking of the polymer to create higher-molecular-weight species does not occur, which is an age-old stigma for polymer radiolysis. The resulting peroxyl radicals are expected to undergo second-order recombination according to the three well-established (Russell, Alkoxy, and Bennett) mechanisms:

$$Polymer\text{-}O_2^\bullet{}_{(aq)} + Polymer\text{-}O_2^\bullet{}_{(aq)} \rightarrow Polymer\text{-}O\text{-}O\text{-}O\text{-}O\text{-}Polymer \quad \text{(tetroxide intermediate)} \quad (4)$$

$$Polymer\text{-}O\text{-}O\text{-}O\text{-}O\text{-}Polymer \rightarrow O_2 + Polymer\text{-}OH + Polymer{=}O \quad \text{(Russell mechanism)} \quad (5)$$

$$\rightarrow O_2 + Polymer\text{-}O^\bullet + Polymer\text{-}O^\bullet \quad \text{(Alkoxy formation mechanism)} \quad (6)$$

$$\rightarrow H_2O_2 + Polymer{=}O + Polymer{=}O \quad \text{(Bennett mechanism)}, \quad (7)$$

resulting in a mixture of activated, oxygen-containing, polymer fragment ketones, aldehydes, and alcohols. Many of these chemicals are already useful and easily separable feedstocks prior to biochemical conversion. Overall, we expect for the radiolysis of PE in water to yield a variety of functionalized materials that are easily accessible to biochemical conversion.

With regards to biochemical conversion, there is a growing demand for more sustainable plastic recycling processes. Although there are several organisms that have demonstrated the ability to digest plastics, their rates of plastic depolymerization in the environment are currently too slow for feasible conversion of polymers. To overcome this temporal barrier, biomass (naturally occurring polymers) deconstruction processes employ a thermochemical pretreatment step (100-200°C) to accelerate biochemical conversion. Although these pretreatment temperatures are less severe than pyrolysis, there is still an energetic penalty and thus economic consequences. However, pretreatment with ionizing radiation may provide a means to functionalize PE and break it down into smaller molecular units at ambient temperature so as to be more readily digested by living organisms.

In summary, the unique innovation of the proof of concept to pair radiolytic and biochemical processes to deconstruct PE into potential synthetic feedstocks could potentially establish a new field of fundamental research, offset the energetic and economic burden associated with current plastic production and recycling technologies, and dramatically reduce the environmental impact of plastic waste.

Research Plan

The goal of this proposal is to establish the feasibility for coupled radiolytic and biochemical conversion of PE in aqueous solutions to yield synthetic feed stocks that could be used for the synthesis of new materials. To achieve this goal two research objectives will be initiated:

1. *Gamma Radiolytic Functionalization and depolymerization of PE in Aqueous Solutions*. The proposed hypothesis is that irradiation of PE in aqueous solutions will: (i) populate the inert polymeric hydrocarbon backbone with chemical functionality that is amenable to subsequent biochemical conversion; and (ii) yield smaller organic molecules that are either synthetic feedstocks in their own right or are also more susceptible to biochemical conversion. To evaluate this hypothesis, commercially sourced high and low density PE will be procured and suspended in aqueous solutions of various headspace gas composition (aerated, O_2, and argon) and pH (acidic, neutral, and alkaline). These PE loaded solutions will be irradiated at various doses using either of the INL Center for Radiation Chemistry Research's ^{60}Co-irradiators: a Nordion Gammacell located in the Fuels and Applied Science Building (FASB) at INL's Materials and Fuels Complex (MFC); and/or a Foss Therapy Model 812 located in the Energy Innovation Laboratory (EIL). Post irradiation, samples will be partitioned for analysis and follow-up biochemical conversion.
2. *Biochemical Conversion of Gamma Irradiated PE*. Post irradiation, PE samples will be independently exposed to a bank of known microbes as well as to selected populations of mixed microbes from plastic-contaminated environments (e.g., landfills and waste-water streams). These suspensions will be incubated in the dark for up to 9 months and periodically sampled for analysis of PE conversion and microbial growth. Aqueous solutions and insoluble particles will be analyzed for evidence of chemical depolymerization products.

For both research objectives a variety of analytical techniques will be employed to evaluate the extent of PE depolymerization and product distribution by radiolytic, biochemical, and radiolytic and biochemical conversion. The analysis of the aqueous solutions will be performed using liquid chromatography-mass spectrometry (LCMS) methods to determine the formation of small molecules. For volatile and low water solubility products, gas chromatography (GC) will be used in conjunction with mass spectrometry (GC-MS): volatiles will be analyzed by direct injection of the headspace gas into the GC-MS; and whole solids/precipitates via solid phase microextraction (SPME-GC-MS). The radical-induced addition of O_2 and the formation of carbonyl or hydroxyl groups on the polymer surface can be identified with infra-red (IR) spectroscopy, especially for olefin polymers that do not originally possess these IR absorptions. Complementary structural data will also be obtained using nuclear magnetic resonance (NMR) spectroscopy, which will aid in the determination of depolymerization products that form over time in the irradiated aqueous systems. Samples of the PE solids post-irradiation will also be dissolved in organic solvents and subjected to diffusion-ordered NMR spectroscopy (DOSY), which will provide estimates on the size of the polymer as a means of determining to what extent the molecular weight of the original material has changed.

No equipment purchases are planned. Valparaiso University will be doing both the analytical work and biochemical conversion component of the project. All other work will be performed at INL facilities.

SECTION C. Environmental Aspects or Potential Sources of Impact:

Air Emissions

Minor amounts of oxygen and argon may be released from experimental apparatus.

Discharging to Surface-, Storm-, or Ground Water

N/A

Disturbing Cultural or Biological Resources

The Fuels and Advanced Sciences Building (MFC-787) is over 50 years old. Modifications to the structure or appearance of the building are not planned.

Generating and Managing Waste

Aqueous solutions (predominantly just water) with suspended polyethylene plastic powders. No wastewater will be released to the drain.

Releasing Contaminants

Although not anticipated spills or releases of chemicals are possible.

Using, Reusing, and Conserving Natural Resources

All material will be reused and/or recycled where economically practicable. All applicable waste would be diverted from disposal in the landfill when possible.

SECTION D. Determine Recommended Level of Environmental Review, Identify Reference(s), and State Justification: Identify the applicable categorical exclusion from 10 Code of Federal Regulation (CFR) 1021, Appendix B, give the appropriate justification, and the approval date.

For Categorical Exclusions (CXs), the proposed action must not: (1) threaten a violation of applicable statutory, regulatory, or permit requirements for environmental, safety, and health, or similar requirements of Department of Energy (DOE) or Executive Orders; (2) require siting and construction or major expansion of waste storage, disposal, recovery, or treatment or facilities; (3) disturb hazardous substances, pollutants, contaminants, or Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)-excluded petroleum and natural gas products that pre-exist in the environment such that there would be uncontrolled or unpermitted releases; (4) have the potential to cause significant impacts on environmentally sensitive resources (see 10 CFR 1021). In addition, no extraordinary circumstances related to the proposal exist that would affect the significance of the action. In addition, the action is not “connected” to other action actions (40 CFR 1508.25(a)(1) and is not related to other actions with individually insignificant but cumulatively significant impacts (40 CFR 1608.27(b)(7)).

References: 10 CFR 1021, Appendix B to subpart D, items B3.6, "Small-scale research and development, laboratory operations, and pilot projects"

Justification: Project activities are consistent with 10 CFR 1021, Appendix B, B3.6, "Siting, construction, modification, operation, and decommissioning of facilities for small-scale research and development projects; conventional laboratory operations (such as preparation of chemical standards and sample analysis); and small-scale pilot projects (generally less than 2 years) frequently conducted to verify a concept before demonstration actions provided that construction or modification would be within or contiguous to a previously disturbed or developed area (where active utilities and currently used roads are readily accessible). Not included in this category are demonstration actions, meaning actions that are undertaken at a scale to show whether a technology would be viable on a larger scale and suitable for commercial deployment."

Is the project funded by the American Recovery and Reinvestment Act of 2009 (Recovery Act) ☐ Yes ☒ No

Approved by Jason Sturm, DOE-ID NEPA Compliance Officer on:02/02/2021