Research paper

Life cycle greenhouse gas emissions analysis of catalysts for hydrotreating of fast pyrolysis bio-oil

L.J. Snowden-Swan*, K.A. Spies, G.J. Lee, Y. Zhu

Pacific Northwest National Laboratory, Richland, WA, USA

ARTICLE INFO

ABSTRACT

Bio-oil from fast pyrolysis of biomass requires multi-stage catalytic hydroprocessing to produce hydrocarbon drop-in fuels. One process design currently in development involves fixed beds of ruthenium-based catalyst and conventional petroleum hydrotreating catalyst. As the catalyst is spent over time as a result of coking and other deactivation mechanisms, it must be changed out and replaced with fresh catalyst. A main focus of bio-oil upgrading research is increasing catalyst lifetimes to 1 year. Biofuel life cycle greenhouse gas (GHG) assessments typically ignore the impact of catalyst consumed during fuel conversion as a result of limited lifetime, representing a data gap in the analyses. To help fill this data gap, life cycle GHGs were estimated for two representative examples of fast pyrolysis bio-oil hydrotreating catalyst, $NiMo/Al_2O_3$ and Ru/C, and integrated into the conversion-stage GHG analysis. Life cycle GHGs are estimated at 5.5 kg CO_2-e/kg catalyst for $NiMo/Al_2O_3$. Results vary significantly for Ru/C, depending on whether economic or mass allocation methods are used. Life cycle GHGs for Ru/C are estimated at 80.4 kg CO_2-e/kg catalyst using economic allocation and 13.7 kg CO_2-e/kg catalyst using mass allocation. Contribution of catalyst consumption to total conversion-stage GHGs at 1-year catalyst lifetimes is 0.5% for $NiMo/Al_2O_3$ and 5% for Ru/C when economic allocation is used (1% for mass allocation). This analysis does not consider the use of recovered metals from catalysts and other wastes for catalyst manufacture and therefore these are likely to be conservative estimates compared to applications where a spent catalyst recycler can be used.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Raw pyrolysis oil from biomass is an unsuitable feedstock for direct insertion into a petroleum refinery because it contains excess moisture and high levels of heteroatoms, primarily oxygen, compared to petroleum crude oil. The bio-oil must first be processed via hydrodeoxygenation to produce a hydrocarbon mixture more amenable to fungible transportation fuels production. Years of research at Pacific Northwest National Laboratory (PNNL) and by other entities have led to the development of a general multi-stage catalytic hydrotreating scheme for the successful upgrading of bio-oil into transportation fuels [1]. Several catalysts have been studied for this developing process, including conventional petroleum hydrotreating catalysts such as NiMoS and CoMoS, and newer catalysts such as Ru/C [1], [2]. Research at PNNL on pyrolysis bio-oil upgrading has focused on improving reactor stability and testing

and developing improved catalysts to achieve optimal technical and cost performance.

In addition to the economical production of renewable cellulosic biofuels, a measure of the overall sustainability of these fuel production pathways is of critical importance. To ensure that biofuels are more renewable and less impactful than the fossil fuels they are designed to replace, the Renewable Fuel Standard (RFS2), as legislated by the 2007 Energy Independence and Security Act (EISA 2007) [3], requires a minimum life cycle greenhouse gas (LC GHG) savings that biofuels must achieve over the status quo. The minimum LC GHG savings for fuels made from renewable biomass are a reduction of 50% (advanced) or 60% (cellulosic) compared with the petroleum baseline.[1] Several studies have estimated LC GHGs for fuels from fast pyrolysis and upgrading, but they have overlooked the impact of catalyst consumption by either ignoring it completely

---

* Corresponding author.
 E-mail address: lesley.snowden-swan@pnnl.gov (L.J. Snowden-Swan).

---

[1] As determined by the US Environmental Protection Agency, the 2005 baseline GHGs for petroleum gasoline and diesel are 93.08 gCO_2-e/MJ and 91.94 gCO_2-e/MJ, respectively [4].

or using a proxy [5—7]. This data gap needs to be addressed in order to assess the contribution of catalyst consumption to the overall fuel cycle GHGs for the pathway.

While the catalysts most likely to be used for hydrodeoxygenation are expected to be variants of commercially available hydrotreating catalysts, very little in the way of life cycle analysis of chemical processing catalysts has been published in the open literature. The goal of this study is to quantify the GHG emissions associated with production of two representative examples of bio-oil hydrotreating catalysts, $NiMo/Al_2O_3$ and Ru/C, and to determine the contribution of catalyst consumption to the LC GHGs attributed to the fast pyrolysis and upgrading conversion process.

2. Life cycle assessment methods

Life cycle assessment (LCA) has become the predominant tool for evaluating and comparing the environmental impact of processes and products. If applied early in the design stages and throughout research and development, it can be used to design a "greener" product than otherwise might be produced. LCA accounts for all inflows and outflows of all stages of a product's supply chain, from extraction of natural (raw) materials to the final fate of the product. The methodology in theory includes all aspects of environmental impact, providing a holistic approach to product assessment. As such, a complete LCA evaluates multiple impact categories; some of the more commonly used ones are global warming, ozone depletion, resource depletion, photochemical smog, acidification, human health, terrestrial toxicity, aquatic toxicity, eutrophication, land use, and water use. All of these indicators, along with economic and social implications, need to be evaluated during technology development to facilitate the most sustainable outcome. While LCA is a strong tool for a wide range of sustainability indicators, this study focuses only on global warming potential (GWP) because it is central to determining whether a fuel meets RFS2 fuel definitions. The scope of the LCA for this study is global warming, represented in grams of CO_2-equivalents (CO_2-e) using a 100-year GWP [8].

2.1. Goal and functional unit

The goal of this study is to estimate the LC GHG emissions associated with production of two representative examples of candidate bio-oil hydrotreating catalysts that may be used for pyrolysis oil upgrading: a sulfided Ni/Mo on Al_2O_3 and Ru/C. The study results are intended to inform the LC GHG analysis for biofuels from pyrolysis and upgrading and to determine the relative impact of catalyst consumption for this pathway. Results may also help to inform other, related fuel production routes under development that are based on bio-oil upgrading (e.g., from hydrothermal liquefaction and catalytic fast pyrolysis). The functional unit for this study is 1 kg of fresh catalyst produced at the manufacturing plant ("cradle to gate").

2.2. System boundaries

Fig. 1 shows the complete bio-oil catalyst life cycle and how it contributes to the overall fuel supply chain. For the focus of this study, the catalyst life cycle begins with mining and extraction of metals and raw materials, includes the refining and processing of the raw materials, and ends with the production of the catalyst. A case could be made for including catalyst recycling, regeneration, and metal reclamation; however, due to large variability in the processing of spent catalyst and the lack of current data for those processes, they were excluded from this analysis. The scope of this analysis is limited to estimation of GHGs associated with manufacture of 1 kg of fresh catalyst. The impact of these results on the conversion-stage GHGs for fuels produced from biomass fast pyrolysis and bio-oil upgrading is also presented in the results section. Multi-stage hydrotreating of pyrolysis oil for production of transportation fuels uses increased processing severity (temperature and pressure) with each stage, a design that reduces the overall coking in the system [1]. The first stage (stabilizer) and second stage use a ruthenium-based catalyst and the third stage uses a sulfided molybdenum-based catalyst [5]. Although the exact catalyst compositions for commercial application are still under development, a Ru/C catalyst and a pre-sulfided MoS_2/NiS on alumina were chosen as representative examples with the expectation that the analysis will need to be refined as more becomes known about bio-oil hydrotreating catalysts.

2.3. Modeling and data collection

The LCA software, SimaPro [9], is used to model the catalyst life cycle. The data for the study comes from a variety of sources, including studies from metal industry trade organizations, engineering calculations and process modeling based on literature and patents, and databases included in the SimaPro package (Ecoinvent Versions 2.2 [10] and 3.1 [11], US Life Cycle Inventory (LCI) [12], US-EI [13], and European reference Life Cycle Database (ELCD) [14]).

2.3.1. Metals and precursor production

The production of catalyst-grade metal compounds generally consists of four steps: (1) mining, (2) beneficiation (grinding and crude separation), (3) primary extraction, and (4) refining [15]. The ore mining occurs both underground and in open pits around the world. Typically, the ore occurs in metal concentrations that are too low for direct smelting, so it must undergo beneficiation [16], [17]. The beneficiation process can involve the mechanical pulverization of ores, which are separated by density or magnetic qualities. After beneficiation, the material undergoes primary extraction, which includes smelting, leaching, calcining, and other processes to concentrate the metal. The final refining step separates the desired metal from other metals and impurities.

2.3.1.1. Nickel and molybdenum.
There are three primary raw materials used for the production of nickel/molybdenum catalyst: molybdenum trioxide (MoO_3), nickel oxide (NiO), and alumina (Al_2O_3) [18]. The product overall inventory for MoO_3 was obtained directly from a study by the International Molybdenum Association (IMOA) [19]. The inventory was determined from Ref. [19] and is aggregated to include mining of Mo through the manufacture of MoO_3. From the inventory, an aggregated GHG emissions value of 10.8 kg CO_2-e/kg MoO_3 was calculated using the Intergovernmental Panel on Climate Change (IPCC) 2007 GWP 100a v1.02 method included in the SimaPro package. The GHG emissions value used for the NiO is taken from the Nickel Institute's estimate of 21,547 g CO_2-eq/kg NiO [15]. The majority of the GWP for NiO results from the energy used during primary extraction, which consists of smelting for the nickel ore portion of the feedstock, and solvent extraction followed by calcination for the nickel liquor portion of the feedstock [20].

2.3.1.2. Ruthenium.
The ruthenium catalyst uses a 2.8 wt% loading of ruthenium on a carbon support. Ruthenium is a platinum group metal (PGM) that is produced as a co-product of platinum and palladium production, primarily in South Africa and Russia [21]. PGMs consist of platinum, palladium, rhodium, ruthenium, iridium, and osmium and are often found with nickel (Ni), copper (Cu), and gold (Au). The worldwide supply of PGMs is much more limited