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

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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/Al₂O₃ and Ru/C, and integrated into the conversion-stage GHG analysis. Life cycle GHGs are estimated at 5.5 kg CO₂-e/kg catalyst for NiMo/Al₂O₃. 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 CO₂-e/kg catalyst using economic allocation and 13.7 kg CO₂-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/Al₂O₃ 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.

Keywords: biofuel; catalyst; bio-oil; hydrotreating; life cycle analysis; greenhouse gas

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 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.

¹ As determined by the US Environmental Protection Agency, the 2005 baseline GHGs for petroleum gasoline and diesel are 93.08 gCO₂-e/MJ and 91.94 gCO₂-e/MJ, respectively [4].

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/Al₂O₃ 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 CO₂-equivalents (CO₂-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 Al₂O₃ 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 MoS₂/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 (IMOIA) [19]. The inventory was determined from [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 $\text{CO}_2\text{-e/kg MoO}_3$ 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 $\text{CO}_2\text{-eq/kg NiO}$ [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 than nickel or other common metals and they exist in very small concentrations. Related to this, PGMs are regarded as “critical” materials, meaning that they are crucially important for society, yet are associated with a high supply risk [22]. While ruthenium has less commercial use than other PGMs, it has applications in catalysts for chemical synthesis and for electrode coatings [23].

Information specific to energy use and GHG emissions of ruthenium mining and processing is extremely limited in the literature. To overcome this data gap, the life cycle inventory for ruthenium ore was estimated based on PGM production inventories developed by Ecoinvent [10] for Russia and South Africa. The updated Ecoinvent Version 3 dataset [11] was chosen for estimating PGM inventory because it includes an important update to the electricity mix used for the South African operations. For consistency, the Version 3 dataset for Russia was also used. The dataset for primary PGMs² covers production of virgin Pt, Pd, Rh, with Ni, and Cu co-products and is aggregated to include all upstream processes leading up to and including the final PGM refining process (mining, beneficiation, metallurgy, separation, and refining). Two alternative methods of allocation were considered: economic and mass. In economic allocation, the portion of the life cycle emissions inventory allocated to each PGM is based on the revenue generated from each PGM relative to the total product ore from the process [23]. This form of impact allocation is an approach commonly applied to the mining/metals industry [24]-[29] and is recommended for consideration in cases where the prices of co-products differ widely [30] as in the case

² “Platinum group metal production, primary, ZA (South Africa)” ; “Platinum group metal production, primary, RU (Russia).”

of PGM production. The rationale for using economic allocation is that industrial operations are driven by revenue generation, and in this type of situation mass allocation fails to adequately capture the main purpose of processing [29]. As shown in Fig. 2, PGM prices can fluctuate significantly, making it necessary to update economically allocated analyses periodically with more recent market prices. Results using mass allocation, where energy and emissions burdens are allocated based on the composition of the ore, are also presented for comparison.

For estimating emissions associated with Ru, the Ecoinvent 3.1 primary PGM processes for South African and Russian production were modified to include Ru in the PGM mix, with the remainder of PGM components (Pt, Pd, and Rh) normalized using the same relative proportions of Pt, Pd and Rh as are in the original Ecoinvent 3.1 process. The concentration of Ru in the ore is assumed to be 0.44 ppm for South African ore [23] and 0.3 ppm for Russian ore [17]. In addition, the process economic allocations were updated with the 5-year average prices (shown in Fig. 2) to reflect more current prices. The resulting PGM product mix, co-product allocations, and GHG estimates per kilogram of metal (using the IPCC GWP 100a v1.02 method) are given in Tables 1 and 2. Using economic allocation, the resulting total PGM GHG intensities for production in South Africa and Russia are 26,100 kg CO₂-e/kg PGM and 11,800 kg CO₂-e/kg PGM, respectively. Using mass allocation, the resulting total PGM GHG intensities are 112 kg CO₂-e/kg PGM for South Africa and 7 kg CO₂-e/kg PGM for Russia. South African production is high relative to Russian production, due primarily to the prevalence of inefficient coal-fired power plants in South Africa [26]. It is assumed that the source mix of Ru used in catalyst precursor production (RuCl₃) is the same as that for primary Rh included in the global Rh market in Ecoinvent 3.1. [11]: 78% from South Africa and 22% from Russia. Secondary (recycled) Ru is not considered in the analysis.

Table 1 - Primary PGM product composition, allocation and GHGs, South Africa.

Metal	Ecoinvent (v3.1)				This Analysis				
	tonne/ tonne PGM ^a	\$/troy oz ^b	Economic Allocation (%)	kg CO ₂ -e/kg metal ^c	tonne/ tonne PGM	\$/troy oz ^d	Economic Allocation (%)	kg CO ₂ - e/kg metal ^c (with econ. allocation)	Mass Allocation (%)
Nickel	147	0.39	8	16.2	147	0.49	5.4	10.3	58.3
Copper	104	0.09	1	3.41	104	0.24	1.9	5.07	41.3
Palladium	0.29	210	9	8,776	0.27	658	13.5	13,898	0.11
Platinum	0.68	762	77	32,055	0.64	1561	75.2	32,978	0.26
Rhodium	0.03	885	4	37,035	0.03	1652	3.5	35,335	0.01
Ruthenium	-	-	-	-	0.06	127	0.5	2,665	0.02

^a Classen et al. [23].

^b Ecoinvent Version 3, 2014 (ecoquery.ecoinvent.org).

^c Using IPCC GWP 100a v1.02 method in SimPro 8.0.

^d Average price for 9-1-2009 through 9-1-2014 (Johnson Matthey PGM Price Tables 2014 [31]).

Table 2 - Primary PGM product composition, allocation and GHGs, Russia.

Metal	Ecoinvent (v3.1)				This Analysis				
	tonne/ tonne PGM ^a	\$/troy oz ^b	Economic Allocation (%)	kg CO ₂ -e/kg metal ^c	tonne/ tonne PGM	\$/troy oz ^d	Economic Allocation (%)	kg CO ₂ - e/kg metal ^c (with econ. allocation)	Mass Allocation (%)
Nickel	2310	0.39	59	9.49	2310	0.49	40.5	6.52	41.9
Copper	3200	0.09	17	2	3200	0.24	27.7	3.23	58.1
Palladium	0.73	210	10	5,148	0.71	658	16.8	8,842	12.8e-3
Platinum	0.25	762	13	18,805	0.24	1561	13.7	20,983	4.4e-3
Rhodium	0.02	885	1	21,726	0.02	1652	1.2	22,257	3.5e-4
Ruthenium	-	-	-	-	0.03	127	0.1	1,737	5.4e-4

^a Classen et al. [23].

^b Ecoinvent Version 3, 2014 (ecoquery.ecoinvent.org).

^c Using IPCC GWP 100a v1.02 method in SimPro 8.0.

^d Average price for 9-1-2009 through 9-1-2014 (Johnson Matthey PGM Price Tables 2014 [31]).

Ru catalyst can be made with various precursors such as RuCl₃, Ru(NO₃)(NO₃), and Ru(acac)₃.

RuCl₃ was selected as the precursor material, as it has been shown to result in a high activity and a low

rate of reduction in metal dispersion and pore volume [32]. Ruthenium is purified by reacting it with

chlorine gas to form RuCl₃, and it is typically sold in that form. Inventory for chlorine gas used in RuCl₃

production was used without modification from the Ecoinvent Version 2.2 database [10]. As the process

energy for production of RuCl_3 is not available in the literature, an estimate was made based on enthalpy.

The heat required to overcome system losses to the environment was not considered in the estimate.

The process for synthesis of RuCl_3 is assumed to occur via the reaction [33]:

Using thermodynamic information from Bell et al. [34], the heat of reaction was estimated to be 181.8 kJ/mol of RuCl_3 product. Assuming a 50% heating efficiency, this results in a heating load of 0.101 kWh/mol or 0.487 kWh/kg. This energy requirement was assumed to be provided by the average US grid mix used in the Ecoinvent Version 2.2 database, as listed in Table 3.

Table 3 - Assumed US electricity grid mix (Ecoinvent 2.2).

Resource	%
Coal	50
Nuclear	20
Natural Gas	17
Renewables	10
Oil/Industrial Gas	3

The carbon support traditionally used for Ru/C catalyst is likely generated from a biomass source such as coconut shells due to its high crush strength and high surface area. However, as data for coconut-shell-based carbon could not be found in the literature, coal-based carbon was used as a proxy, the GHG emissions for which are taken from Bayer et al. [35]. This activated carbon is produced by grinding coal, mixing with binding agent, briquette production, drying, carbonization, activation, crushing, sieving, and packaging, resulting in a GWP of 11.0 kg $\text{CO}_2\text{-e/kg}$ virgin granulated activated carbon [35].

2.3.2 Catalyst synthesis and preparation

The most likely catalysts for hydrotreating bio-oil are produced commonly by incipient wetness impregnation [36]-[38]. The active metal and ligand precursor is dissolved in an aqueous or non-aqueous solvent and is added to a porous support. Capillary action from the pores draws the metal solution into the pores. After the solution is applied, the catalyst is dried to remove the solvent. The desired loading is

achieved by multiple solution and drying steps and by concentrating the metal solution. After the final drying, the catalyst is calcined at high temperature to remove the ligand from the metal atoms. Some hydrotreating catalysts must also be sulfidated.

2.3.2.1 *MoS₂/NiS on Al₂O₃*

Life cycle inventory data for synthesis of MoS₂/NiS on Al₂O₃ was developed based on steps described in a Shell Oil Company patent [18] and is shown in Fig. 3. The catalyst modeled in this process is 13.6 wt% MoS₂ and 9.1 wt% NiS on Al₂O₃. The process material and energy balance is scaled from a batch-wise process operating at bench scale, so it may be significantly different from an actual manufacturing setting (e.g., with continuous production, heat integration, and different primary energy sources). However, where available, the best information for process data was used. The product is sulfided ex-situ and therefore pre-sulfiding is not necessary at the refinery. Ex-situ sulfiding is indicated as the preferred choice in the Shell patent [18]. The use of pre-sulfided hydroprocessing catalysts has gained increasing favor in the refining industry, due to reduced start-up time and higher catalyst activity [39]-[41]. The actiCAT® process is used for ex-situ sulfiding, which consists of treating the catalyst with elemental sulfur and then heating in the presence of liquid olefinic hydrocarbon (assumed to be diesel) and hydrogen to produce metal sulfides. High-temperature calcination is not needed with this process.

In addition to metal and support, there are several system inputs for the production of the final catalyst. The diesel used in the sulfiding and activation steps is assumed to be completely recycled with no makeup required (start-up diesel is ignored). Hydrogen used in the activation step is assumed to be purchased. GHGs associated with hydrogen use are estimated from the GREET model [42]. All other raw materials and energy needed for catalyst production (H₃PO₄, sulfur, natural gas, electricity, steam) come from the Ecoinvent Version 3.1 database [11].

The catalyst production process was modeled using the commercial process flow simulation software Aspen Plus (Version 8.4 [43]) and energy consumption was estimated from the results of the model. The assumptions for the catalyst preparation stage, including energy estimations from the Aspen

model, are given in Table 4. Industrially relevant energy sources for heating steps were chosen for the model. For example, for heating processes below about 100C, low quality steam is most often used. Above about 250C, natural gas is the most appropriate choice. The average US grid mix is assumed for the electricity usage in the analysis[10] (see Table 3). Sensitivity analysis is conducted for cases where all manufacturing energy in Table 4 is assumed to be electricity and the electricity grid mix is varied according to different regions of the U.S.

Table 4 - Primary assumptions for manufacture of MoS₂/NiS on Al₂O₃ catalyst.

Process Energy Step	Energy Use (kJ per kg catalyst)	Energy Type	LCI/GHG Source
Al ₂ O ₃ drying/calcination	416.8	natural gas	Natural gas, burned in industrial furnace > 100 kW/RER with US Electricity U (US-EI 2.2)
Overall cooling water	-3358.0	160.8 kg 20 °C cooling water fed, 5 °C gain	Water, process, unspecified natural origin/m ³
Dissolution	206.0	steam	Process steam from natural gas, heat plant, consumption mix, at plant, MJ EU-27 S (ELCD)
Precursor drying	1656.9	steam	Process steam from natural gas, heat plant, consumption mix, at plant, MJ EU-27 S (ELCD)
Sulfiding and activation	485.6	natural gas	Natural gas, burned in industrial furnace > 100 kW/RER with US Electricity U (US-EI 2.2)
Solvent recycle	14.9	electricity	Electricity, medium voltage, at grid/US with US Electricity U (US-EI 2.2)
Final catalyst drying	1266.9	natural gas	Natural gas, burned in industrial furnace > 100kW/RER with US Electricity U (US-EI 2.2)
Material Input	Mass (g/kg catalyst)	Comment	LCI/GHG Source
Al ₂ O ₃	772.2	1.2 mm trilobe extrudate; 100% yield	Alumina, at plant NREL/US (US EI 2.2)
Water	617.7		Water, deionized, at plant/CH with US electricity U
H ₃ PO ₄	34.9	14.8 molar phosphoric acid	Phosphoric acid, industrial grade, 85% in H ₂ O, at plant/RER with US electricity U (US-EI 2.2)
MoO ₃	136.0	90% yield	IMOA [19]
NiO	83.4	90% yield	Nickel Institute [13]
Sulfur	97.3	Elemental sulfur	Secondary sulphur, at refinery/RER with US electricity U (US EI 2.2)
Hydrogen	8.8	Pressurized gas, 900 psi	REET [42](13,655 g CO ₂ -e/kg H ₂)
Diesel	1301.0	Assumed to be 100% recycled	

2.3.2.2 *Ru/C*

The catalyst modeled in this analysis contains a 2.8 wt% loading of ruthenium on a carbon support. Life cycle inventory for synthesis of Ru/C catalyst was developed based on steps described by Wildschut et al. [32]. Similar methods of preparation (with slightly different conditions) are found in [44]-[46]. A model of the catalyst synthesis process was developed with Aspen Plus and is shown in Fig. 4. The design includes six general unit operations. Activated carbon is dried in B1 at 110 °C for 2 hours to drive off any volatiles present in the source material. The carbon is cooled by H-101 and combined with the RuCl₃ and water and mixed in a slurry for 24 hours at 20 °C and 1 atm. The water is driven from the sample by evaporation at 40 °C and 30 mbar of pressure in B5 for 8 hours. After evaporation, the sample is dried at 100 °C and 35 mbar of pressure for 12 hours to completely remove any residual solvent. The catalyst is activated by heating under nitrogen atmosphere at 250 °C for 2 hours. The overall mass balance of the system is shown in Table 5. Energy consumption for each stage of catalyst production was estimated from the results of the model, also listed in Table 5. The average US electricity grid mix from the EcoInvent database is assumed (see Table 3).

Table 5. Primary assumptions for manufacture of Ru/C catalyst.

Process Energy Step	Energy Use (kJ per kg catalyst)	Energy Type	LCI Source
Carbon drying	147.0	steam	Process steam from natural gas, heat plant, consumption mix, at plant, MJ EU-27 S (ELCD)
Overall cooling water	-122.2	5.85 kg 20 °C cooling water fed, 5 °C gain	Water, process, unspecified natural origin/m3
Solvent Evaporation	87.3	electricity	Electricity, medium voltage, at grid/US with US Electricity U (US-EI 2.2)
Drying/Separation	2370.4	steam	Process steam from natural gas, heat plant, consumption mix, at plant, MJ EU-27 S (ELCD)
Activation	312.0	natural gas	Natural gas, burned in industrial furnace > 100kW/RER with US Electricity U (US-EI 2.2)
Material Input	Mass (g/kg catalyst)	Comment	LCI/GHG Source
Activated carbon	941.8	Coal based as proxy; 100% yield	Granular activated carbon (Bayer et al. [35])
Water	945.4		Water, deionized, at plant/CH with US electricity U
RuCl ₃	58.2	100% yield	Enthalpy calculation (0.487 kWh/kg electrical heat)
Nitrogen	2.59	Separated from air, low pressure	Nitrogen, via cryogenic air separation, production mix, at plant, gaseous EU-27 S

242 3. Results and discussion

243 3.1 Catalyst LC GHGs

244 Shown in Fig. 5, the LC GHGs for the MoS₂/NiS catalyst are estimated to be 5.5 kg CO₂-e/kg
 245 catalyst. Production of the precursor materials, alumina, NiO, and MoO₃, contributes the majority of
 246 GHGs to the total catalyst carbon footprint. There are very few catalyst GHG studies in the literature with
 247 which to compare this estimate. Johnson Matthey estimates the LC GHGs for their nickel-based
 248 hydrotreating catalyst at 7 kg CO₂/kg and 8-10 kg CO₂/kg for their copper-zinc-based catalysts [47]. The
 249 value estimated in this analysis is in the general range of the Johnson Matthey estimate for nickel-based
 250 catalyst. Lavery et al. [48] estimates GHGs for sponge nickel catalyst at 25-37 kg CO₂-e/kg sponge
 251 nickel; however, the process used for sponge nickel catalyst production is significantly different from the
 252 process used here. To investigate the sensitivity of catalyst GHGs to the energy mix used in the catalyst
 253 manufacturing step, additional cases were run for an all-electricity case using the base case mix and

varying the grid mix corresponding to the North American Electric Reliability Corporation (NERC) regions (in the 48 contiguous states). A map of the NERC regions and their respective mixes are given in Figure 6 and Table 6, respectively [49]. Figure 7 shows the results of the sensitivity analysis. As shown, if electricity is used exclusively at the catalyst production plant, GHGs are 3-13% higher than the base case energy mix. The case with the lowest GHGs is for the NPCC region, which has the lowest portion of fossil derived power of all the NERC regions. The case with the highest GHGs is for the SPP region, where coal and gas derived power make up ~85% of the grid mix.

Table 6. Electricity generation resource mix for U.S. NERC regions [49].

Resource, % of Grid Mix	WECC	MRO	SPP	TRE	RFC	SERC	FRCC	NPCC
Coal	26.19	61.26	55.37	30.51	48.72	41.11	19.42	3.11
Oil	0.38	0.24	0.56	0.95	0.48	0.47	0.64	0.38
Gas	30.26	5.35	30.15	49.05	18.02	28.26	68.06	48.55
Other fossil	0.08	0.15	0.15	0.12	0.67	0.22	0.66	1.13
Nuclear	8.12	11.44	3.73	10.67	28.77	25.50	8.46	29.52
Hydro	25.79	5.87	1.41	0.11	0.70	2.27	0.07	11.98
Biomass	1.32	1.60	1.06	0.20	0.90	1.84	1.76	3.63
Wind	5.20	13.84	7.52	8.29	1.66	0.24	---	1.64
Solar	0.43	---	0.05	0.03	0.04	0.01	0.09	0.03
Other	0.12	0.24	0.01	0.08	0.04	0.08	0.83	0.03

The estimated LC GHGs for the Ru/C catalyst are shown in Fig. 8. When economic allocation is used, LC GHGs are estimated at 80.4 kg CO₂-e/kg catalyst. A large majority of the carbon footprint is due to the production of RuCl₃, GHG emissions for which are almost completely attributable to the production of Ru. When mass allocation is used, the estimated LC GHGs are 13.7 kg CO₂-e/kg Ru/C, much lower than that estimated using economic allocation. Other than Ru production, a significant contributor to total GHGs is the carbon support, which is assumed to be coal-based for this analysis. Biomass based supports, such as coconut shell carbon, would likely reduce this impact, and GHG analysis of these types of supports is needed. When economic allocation is used, the Ru/C catalyst has a carbon footprint that is over 10-fold higher than the MoS₂/NiS catalyst, primarily due to the high value of Ru (resulting in higher economic allocation of emissions per kilogram of metal) compared to more abundant metals like Ni and Mo. Using mass allocation, the Ru/C is over twice as GHG intensive as MoS₂/NiS, primarily due to the high GHG-intensity of the activated carbon compared to that of the alumina. It is important to note that

these estimates do not consider secondary Ru sources, in particular from metals reclamation of spent catalyst. This could substantially decrease the carbon footprint of the Ru/C catalyst.

3.2 Potential impact of metals reclamation

Energy usage data for catalyst recycling and metals reclamation processes is extremely limited in the open literature and therefore secondary metals sourcing was not considered in the analysis. It is useful, however, to consider the qualitative aspects of catalyst recycling and the potential impact on the catalyst carbon footprint. In the petroleum industry, it is estimated that approximately 45,000 tons of spent hydrotreatment catalyst are processed for metals recovery each year [50]. Recovery of Ni, Co, Mo, and W is accomplished, while alumina is disposed of as an inert slag [50]. The refiner's decision of whether to send catalyst off for metals reclamation depends primarily on the catalyst type (value of metals) and whether the spent catalyst is considered hazardous [51]. Based on the metal values alone, it is anticipated that in the case of ruthenium, spent catalyst would enter the secondary materials processing chain after leaving the refinery, as the cost to replace with virgin material would significantly outweigh the cost to recover. Even with catalysts made from more abundant metals like Ni and Mo, there may be significant savings associated with recovery over disposal, depending on the hazardous nature of the waste.

Catalysts made from secondary metals reclaimed from spent materials are likely to be less energy-intensive than catalysts made from primary metals extraction and refining processes. One study estimates that the GHG emissions associated with catalytic converter metal recovery of secondary PGMs is more than ten-fold lower than those associated with primary PGMs [26]. Therefore, the GHG values presented here likely provide a conservative estimate compared with scenarios that incorporate recycled metals.

3.3 Catalyst impact on biofuel production GHGs

The ultimate goal of this study is to ascertain the relative contribution of hydrotreating catalyst consumption to the fuel production stage GHGs for the fast pyrolysis and bio-oil upgrading process. Using reactor space velocities and catalyst lifetimes from Jones et al. [5], catalyst consumption per gallon of fuel was estimated. Catalyst consumption along with GHG estimates presented in Section 3.1 were

then incorporated into the conversion stage life cycle for the US Department of Energy's Bioenergy Technologies Office (BETO) fast pyrolysis and upgrading pathway design case [5]. The detailed GHG LCA for the design case conversion process can be found in [5].

Fig. 9 shows the fossil GHGs associated with the conversion pathway for both the economic and mass allocation results for Ru/C. Because the focus of this analysis is the biomass-to-fuel conversion process (see Fig. 1), other stages of the fuel life cycle (e.g., feedstock production, transportation, fuel distribution) are not included here. Furthermore, conversion inputs other than catalyst (see [5] for details) are aggregated to focus only on the catalyst impacts and their relative importance to the total conversion-related GHGs. Note that these results include both direct fossil GHG emissions from the plant and emissions associated with the production of energy and materials used at the plant (e.g., natural gas and electricity). Two cases of hydrotreating catalyst lifetime are included in the analysis to represent the current state of technology and the target maximum thought to be achievable through experimental research. Hydrotreating catalyst lifetime is highly dependent on the quality of the oil being processed. Fast pyrolysis bio-oil contains certain species that cause coking of the catalyst, in particular at the more severe conditions of the 2nd and 3rd stage reactors (after stabilizer). Lifetimes of about 0.2 year are currently being achieved in the laboratory for the Ru/C and the MoS₂/NiS used in these reactors [52]. A target lifetime of 1 year (or equivalent consumption through combined strategies) has been set to help reach BETO's programmatic 2017 cost target of \$3/gasoline gallon equivalent for the pyrolysis pathway [5]. Research to meet the target is focused on reducing catalyst consumption through a combination of strategies including increasing lifetime, increasing reactor space velocities, reducing Ru loading, and extending time between regenerations [52]. Also shown for comparison in Fig. 9 is the conversion GHGs estimated in the design report [5], for which catalyst was approximated with a zeolite process from the Ecoinvent Version 2.2 database [10]. For the hydrocracking catalyst and steam reforming catalyst, a zeolite process from the Ecoinvent database is still used as a proxy (as in the design case) for lack of more specific data on these catalysts. The GHG intensity of the Ecoinvent zeolite process ("zeolite, powder, at

plant/RER with US Electricity U”) is 4.19 kg CO₂-e/kg. Transportation of catalyst to the refinery is not included in the analysis.

As shown in Fig. 9, in the case where economic allocation is used for Ru/C, overall conversion GHGs for pyrolysis and upgrading are estimated at 19.9 g CO₂-e/MJ at the target catalyst lifetime of 1 year. This is an increase of 5% over the 2013 design case estimate. The shorter lifetime of 0.2 year for the state of technology case results in 14% higher GHGs compared to the 1 year case. The effect of lifetime is not as evident when mass allocation is used, as the catalyst related GHGs are lower compared to the economic allocation case. For the 1-year base case (using economic allocation), catalyst consumption contributes approximately 6% to the total conversion GHGs (1% using mass allocation), with the Ru/C catalyst accounting for the majority of this, as shown in Table 7. For the 0.2-year case (using economic allocation), catalyst contribution is much higher at 17% of the total conversion GHGs (6% using mass allocation). The catalyst contribution is less significant when considering the entire fuel life cycle (including feedstock production, transportation, and fuel distribution), GHGs for which are in the range of 28.3-33.3 g CO₂-e/MJ gasoline for forest residue feedstock [5].

Table 7. Catalyst consumption and contribution to conversion GHGs

Catalyst	Consumption at 1 yr Life (lb/gge fuel produced) ^a	GHGs, gCO ₂ -e/MJ fuel (% of total conversion GHGs) Economic Allocation for Ru/C	GHGs, gCO ₂ -e/MJ fuel (% of total conversion GHGs) Mass Allocation for Ru/C
Ru/C (stabilizer and first stage)	0.004	1.04 (5.2%)	0.18 (0.9%)
Ni-Mo (second stage)	0.005	0.10 (0.5%)	0.10 (0.5%)
Hydrocracking (proxy of zeolite, [10])	0.00009	0.001 (0.005%)	0.001 (0.007%)
SMR (proxy of zeolite, [10])	0.0002 ^b	0.003 (0.01%)	0.003 (0.02%)
Total	0.009	1.15 (5.8%)	0.28 (1.2%)

^a Jones et al. [21]
^b SMR catalyst lifetime not specified in [5].

Based on the results of this analysis, it can be concluded that at the target 1 year catalyst lifetimes, the consumption of Ni-Mo catalyst in the pyrolysis bio-oil upgrading process does not significantly contribute to the conversion stage GHGs, while the contribution of virgin Ru catalyst is more significant

and should be considered in the analysis when possible, especially when economic allocation is chosen for determining Ru/C GHGs.

3.4 Data quality considerations

While a quantitative uncertainty analysis is not within the study scope, it is useful to consider the source of the data and qualitatively discuss the relative uncertainty of data sets to aide with the interpretation of the results. The data used in this analysis are taken from a variety of sources, including studies by trade industry organizations, the Ecoinvent database, and the open literature. As the most significant processes contributing to catalyst GHGs are metal precursor production; these are the focus of this discussion.

Data for NiO come from a 2000 LCA study of several nickel products, commissioned by the Nickel Institute [15]. For this study, data were collected from nickel production facilities around the world via questionnaires for all inputs and outputs of each facility. A data quality evaluation was conducted as part of this study, per ISO 14041 guidance [53], and showed that the data were representative of 85% of western world production. Data for MoO₃ are from a study commissioned by the IMOA [19], and similar to the NiO, rely on site data collected via questionnaires sent to processing facilities around the world. These data were deemed to be representative of 90% of western world production of MoO₃. Because the NiO and MoO₃ studies are based primarily on first-hand data collected from multiple facilities from multiple countries, the data for these precursors are expected to be highly reliable.

Data for ruthenium production is based on Ecoinvent data for PGM production, which is developed primarily from a 1997 German LCA study by C. Hochfeld that is based mainly on two major PGM mining sites in Bushveld (South Africa) and Noril'sk (Russia). Hochfeld is not available in English and therefore could not be directly accessed for this study. The data were determined to be representative of 63% of South African production and 23% of Russian production [23], comparatively low with respect to the NiO and MoO₃ studies. However, for comparison, the Ecoinvent data give results similar to those from Saurat and Bringezu [26]. Based on environmental report data published in 2005 by three PGM

mining companies in South Africa, Russia, and Canada, Saurat and Bringezu estimate GHG emissions for global primary PGMs (65% South Africa, 27% Russia, and 8% Canada) at 23,451 kg CO₂-e/kg PGMs. This is comparable to the GHGs allocated to the global PGM mix assumed in this study from Ecoinvent data (23,000 kg CO₂-e/kg PGMs for a 78% South African and 22% Russian mix).

Because the data set for Ni and Mo was collected via direct survey of many industrial facilities, it may be generally more reliable than the Ecoinvent PGM data, which are derived primarily from a seemingly more limited data set. For this reason, GHG results for the Ru/C catalyst may have a higher related degree of uncertainty than the NiMo catalyst results. However, the general difference in magnitudes of results seen between the NiMo and Ru catalysts is to be expected, due to the heavy burdens of precious metals compared to more common metals like Ni and Mo. Further, the impact of catalyst consumption on overall fuel GHGs is expected to be in the same approximate range as determined from this study. A more detailed analysis employing a survey-based data collection procedure would help strengthen the Ru/C catalyst results. In addition, process data is needed on Ru reclamation from spent catalyst recycling to quantify the impact of secondary sourcing on Ru/C LC GHGs.

4. Conclusions

Life cycle GHGs were estimated for two representative examples of potential bio-oil hydrotreating catalysts to determine the impact of catalyst consumption on the GHGs associated with fast pyrolysis and bio-oil upgrading biomass conversion. The GHGs for the NiMo/Al₂O₃ catalyst are estimated to be 5.5 kg CO₂-e/kg catalyst. Sensitivity analysis shows that if the catalyst manufacturing energy comes from only electricity, GHGs for the catalyst are 3-13% higher, depending on the grid mix assumed. At a catalyst lifetime of 1 year, NiMo/Al₂O₃ contributes approximately 0.5% of the total fuel conversion stage GHGs, a relatively insignificant impact. The Ru/C catalyst GHGs are estimated to be 80.4 kg CO₂-e/kg when using economic allocation and 13.7 kg CO₂-e/kg when using mass allocation. Ru/C has a significant impact on overall conversion GHGs, contributing 5% of the total conversion stage GHGs when economic allocation is used for Ru/C. When mass allocation is used for Ru/C, catalyst contribution is less

significant (1.2%). At lifetimes currently being achieved (0.2 yr), conversion stage GHGs are 14% higher than the 1 year target case (5% higher for Ru/C mass allocation). This analysis considers only virgin ruthenium in the production of Ru/C catalyst and as such provides a conservative GHG estimate. The inclusion of reclaimed metal from spent catalyst recycling is expected to reduce the ruthenium impact. In general, fuel processing catalysts that contain virgin precious metals will have a higher GHG impact than those containing more common metals, especially when economic allocation is used. However, the ultimate GHG contribution of catalysts will depend on the specifics of each application, most importantly a combination of composition, lifetime, and whether metals can be recovered efficiently from spent catalyst. A more detailed assessment involving direct survey and data collection of the PGM industry, including spent catalyst recycling process information, would help to build upon this study.

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Fig. 1. Pyrolysis oil hydrotreating catalyst life cycle.

Fig. 2. Five-year daily price history for PGMs (Johnson Matthey PGM Price Tables 2014 [31]).

Fig. 3. Preparation of MoS₂/NiS on Al₂O₃ with ex-situ sulfiding (Gabrielov and Bhan [18]).

Fig. 4. Preparation of Ru/C (Wildschut [32]).

Fig. 5. Life cycle GHGs for MoS₂/NiS on Al₂O₃.

Figure 6. NERC regions for electricity grid mix sensitivity [49].

Fig. 7. Sensitivity of MoS₂/NiS GHGs to energy mix used for catalyst manufacturing.

Fig. 8. Life cycle GHGs for Ru/C catalyst.

*Original conversion GHGs were estimated in the design case using a zeolite as a proxy for all catalysts (Ecoinvent [10])

Fig. 9. Catalyst contribution to biomass-to-fuel conversion GHGs for fast pyrolysis and upgrading