INTRODUCTION

Over the last decade, global transportation-related CO₂ emissions rose by 97 million metric tons, an increase of 5.4%, with motor gasoline accounting for 58% of emissions (U.S. Energy Information Administration, 2015). At the same time, research has shown that to mitigate climate change and stabilize global temperature rise to a safe limit of 2°C, atmospheric greenhouse gas (GHG) concentrations should fall in the range of 445–490 ppm CO₂ equivalents (CO₂ eq.). This means that by 2050, GHG emissions will need to decrease by 50%–85% below year 2000 levels (Arvizu et al., 2011; ...
Barros et al., 2014). To reach this target, there is a need for an aggressive shift from fossil fuels to low-carbon fuels, among which biofuels are a promising option (Creutzig et al., 2015; Daystar et al., 2013) and one requiring the advancement of biomass conversion technology. The commercial viability of biofuels depends on achieving competitive production costs, improving product yield, and having access to an abundant and sustainable supply of biomass (Huber, Iborra, & Corma, 2006; Liu, Wang, Karim, Sun, & Wang, 2014). Using select technologies, biomass can be converted into an energy dense fuel that can fit into existing infrastructure and meet energy policies on renewable and low carbon fuels (Liu et al., 2014; Richard, 2010). Current federal energy policy in the United States requires decarbonizing transportation fuels by 2022 (U. S. Congress, 2007). First-generation biofuels in commercial production (Elliott et al., 1990; Guzzi & Erdöhelyi, 2012) rely on food crops such as corn, sugarcane, and soybeans, which interfere with food and feed markets (Manchoio, Andrade, Rodriguez, & Moraes, 2017). This constraint has motivated an interest in developing second-generation biofuels, produced from non-food biomass resources such as sustainable forms of crop, animal, and forest residues (Kimes, 2007; Sims, Mabee, Saddler, & Taylor, 2010).

Second-generation biofuels rely on lignocellulose (biomass) as feedstock that can be converted through biochemical (pretreatment, enzymatic hydrolysis, and fermentation; Sims, Taylor, Saddler, & Mabee, 2008) and thermochemical (torrefaction, pyrolysis, and gasification) processes. To date, life cycle assessment (LCA) methods (Agusdinata, Zhao, Ileleji, & DeLaurentis, 2011; Emery et al., 2017; Iribarren, Peters, & Dufour, 2012; Spatarli, Zhang, & MacLean, 2005; Wiloso, Heijungs, & Snoo, 2012; Zaimes, Soratana, Harden, Landis, & Khanna, 2015; Zhang, Hu, & Brown, 2013) and techno-economic analysis (TEA; Beckman et al., 1990; Brown, 2015; Brown, Thilakaratne, Brown, & Hu, 2013; Crawford et al., 2016; Dutta, Schaidle, Humbird, Baddour, & Sahir, 2016; Jong et al., 2015; Pearlson, Wollersheim, & Hileman, 2013; Sorumnu et al., 2017; Swanson, Platon, Satrio, & Wright, 2010; Thilakaratne, Brown, Li, Hu, & Brown, 2014; Wright, Daugaard, Satrio, & Brown, 2010; Zhang, Brown, Hu, & Brown, 2013) have been used to estimate the environmental and economic performance of not-yet-commercial second-generation biofuels. Such evaluations fall under the general rubric of prospective or ex-ante LCA/TEA (Arvidsson et al., 2018; Damartzis & Zabaniotou, 2011; Elangovan et al., 2015; Shonnard et al., 2015; Shonnard, Williams, & Kalnes, 2010). Select literature has reviewed the environmental and economic performance of multiple products derived from thermochemical conversion (Patel et al., 2016) and the technology readiness level (TRL), a measure of the maturity of new technology (Mankins, 2009), of potentially scalable biofuels and bioproducts derived from both thermochemical and biochemical conversion (Dunn et al., 2018). Knowledge of the latter, TRL, is required to judge the maturity of the development
The primary purpose of bio-oil upgrading is to remove oxygen from bio-oil compounds and then fractionate or refine its constituents to renewable fuels and chemicals. Figure 1 summarizes alternative means of bio-oil upgrading; while some of the upgrading pathways are catalytic, others are non-catalytic.

### 2.1 Fast pyrolysis conversion with catalytic upgrading using hydrodeoxygenation with external hydrogen supply

Predominantly, hydrodeoxygenation (HDO) reacts hydrogen and bio-oil over a catalyst to remove oxygen, forming water. HDO uses catalysts typically used for hydrodesulfurization (HDS), such as nickel-molybdenum supported on aluminum oxide (NiMo/Al₂O₃) or cobalt-molybdenum supported on aluminum oxide (CoMo/Al₂O₃), and hydrogen at moderate temperatures (300–600°C) to remove oxygen from bio-oil (Bu et al., 2012). Precious metal catalysts, like platinum, ruthenium, and rhodium, can be used and have demonstrated higher catalytic activities compared to sulfide catalysts (Horáček, Šťávová, Kelbichová, & Kubička, 2013). One HDO study that used a precious metal catalyst specifically used platinum-loaded HY zeolites (Pt/HY) with different Si/Al molar ratios to deoxygenate lignin monomers such as guaiacol, anisole, veratrole, and phenol to a range of hydrocarbons, such as cyclohexane (Lee et al., 2016).

Previously, bio-oil upgrading work focused on heterogeneous catalytic hydroprocessing (Elliott, 2007), particularly concentrating on a hydrothermal, alkali catalyzed process based on high pressure liquefaction to create a product more deoxygenated than fast pyrolysis bio-oil. In that process, hydrogen consumption is reduced by HDO targeting only oxygen containing compounds and not aromatic compounds as that would only saturate the aromatic compounds. Nevertheless, a recurring concern with this process is the maintenance of the aromatic character of the bio-oil in order to produce a high-octane gasoline and value-added co-products. Moreover, this single-stage hydrotreating process produces a heavy tar-like product that weakens its stability. To combat problems of instability, a two-stage hydrotreatment process initiated by Pacific Northwest National Laboratory (PNNL; Jones et al., 2009) was developed comprising mild hydrotreating followed by more severe hydrotreating (Elliott 2007; Jones et al., 2009) at temperatures between 240°C in the first hydrotreater and 370°C in the second hydrotreater (Beckman et al., 1990) with either Ni or sulfided CoMo catalyst. The first mild hydrotreating stage is over a CoMo catalyst at lower temperatures of about 300°C producing a partially deoxygenated oil. The product is further deoxygenated in the second severe hydrotreating stage,

| Table 1 | Comparison of properties of catalytic and non-catalytic pyrolysis oils without co-reactants |
|---------|---------------------------------|
|          | Non-catalytic                  | Catalytic                     |
| Catalyst | Ahmad, Hamidin, and Md Ali (2013) | Ahmad et al. (2013)            |
| Feedstock | Rice straw                | Zeolite                       |
|          | Corn cob                   | Dolomite                      |
|          | Oak wood                   | HZSM-5                        |
| Temperature (°C) | 450                  | 550                           |
| Carbon (wt.%) | 21                          | 52                            |
| Hydrogen (wt.%) | 9                           | 7                             |
| Nitrogen (wt.%) | 0.6                        | 0.8                           |
| Sulfur (wt.%) | 0.4                         | 0.08                          |
| Oxygen (wt.%) | 69                          | 40                            |
| pH         | 2.8                         | 2                             |
| Total acid number | 68                         | 2                             |
| HHV (MJ/kg) | 18.8                       | 34.6                          |

Abbreviations: HHV, higher heating value.

and the modeling approaches taken (computational, experimental or pilot data, ex post or ex ante) to assess environmental and economic performance. It thus affects the certainty levels of the assessment, as well as the degrees of freedom available for future optimization. To our knowledge, no one specific study has quantitatively integrated LCA, TEA, and TRL metrics. Thus, our objective is to review specific literature on pyrolysis bio-oil upgrading methods from studies that applied environmental LCA, TEA, and TRL metrics in order to evaluate their benefits, trade-offs, and potential for commercialization.
which operates at a higher temperature and a lower space velocity while using CoMo catalyst. The product of the second hydrotreater is subsequently separated into product oil, off-gas streams, and wastewater. The off-gas is used to produce hydrogen gas that can be recycled and used for HDO of the bio-oil while a smaller portion of the off-gas is used to preheat the feed for the second stage hydrotreater. HDO has been tested at laboratory scale and simulated with Aspen Plus. Although the HDO process is very similar to HDS, which has been commercialized in the petroleum industry, HDO of bio-oil is not currently commercial.

2.2 Fast pyrolysis conversion with catalytic upgrading using HDO with hydrogen production from off gas

One of the limitations of upgrading bio-oil using HDO is its heavy consumption of external hydrogen in order to produce high quality fuel products, which raises operating costs given the high market price of hydrogen ($1.98 kg\(^{-1}\); Energy.gov, 2015). To address hydrogen supply, Carrasco et al. (2017) demonstrate how to maximize the potential of the HDO process with minimal hydrogen consumption. The authors evaluate alternative methods of hydrogen production without using fossil fuels. Their proposed process, similar to that of PNNL, uses steam gasification of the bio char generated from fast pyrolysis in a high temperature (850°C) bubbling fluidized bed reactor to generate syngas and steam reforming of the syngas to produce hydrogen. The hydrogen produced is purified and used to deoxygenate the bio-oil reducing the need for external hydrogen supply.

2.3 Tail gas reactive pyrolysis conversion with extraction upgrading

Similar to fast pyrolysis, tail gas reactive pyrolysis (TGRP) is a thermochemical process that converts biomass to bio-oil under high temperatures in the absence of oxygen producing TGRP oil, bio char, and noncondensable gases (NCG; Elkasabi, Mullen, & Boateng, 2014; Elkasabi, Mullen, et al., 2015). The main difference between the two processes is that TGRP recycles the NCG into the pyrolyzer. TGRP yields a bio-oil with improved thermal stability and a high concentration of valuable compounds like phenols that can easily be extracted (Sorunmu et al., 2017). As a result of the reductive TGRP environment, the TGRP oil contains less oxygen than bio-oils made from traditional fast pyrolysis. The TGRP oil can be distilled to separate a top hydrocarbon layer from coke in the bottom layer. The coke from the distillation process can be further refined and sold as green coke for use as bio-bitumen (Elkasabi, Boateng, & Jackson, 2015; Elkasabi, Darmstadt, & Boateng, 2018; Elkasabi, Mullen, Boateng, Brown, & Timko, 2019), while the distillates undergo phenol extraction. The latter is done using sodium hydroxide, water, and hydrogen chloride for neutralization. After the extraction of phenol from the distillates, oxygen-free hydrocarbons are formed and hydrogenated with a sponge nickel catalyst to form fuels. While the TGRP process has been tested on a mobile 2 MTPD process development unit (Boateng, Schaffer, Mullen, & Goldberg, 2019), upgrading of the bio-oil product has been carried out at laboratory scale.

2.4 In situ and ex situ catalytic pyrolysis

The primary goal of catalytic pyrolysis is to reduce oxygenated species and increase the relative quantity of hydrocarbons in the bio-oil, which should result in a product that is stable and less corrosive compared to fast pyrolysis bio-oil. In order to improve the stability of bio-oil compounds such as alkanes, hydrogen breaks the C–O bond in the presence of a catalyst; hence, the aim for deoxygenation of the pyrolysis
vapor is to remove oxygen while preventing the loss of carbon and hydrogen (Corma et al., 2007; Huber & Corma, 2007).

Where in situ catalytic pyrolysis embeds the catalyst within the pyrolysis reactor, ex situ catalytic pyrolysis applies the catalytic step on the pyrolysis vapors prior to quenching (Iisa et al., 2016). Therefore, in situ catalytic pyrolysis is a process whereby the catalyst is mixed directly with the feedstock in the pyrolysis reactor (Liu et al., 2014) whereas ex situ catalytic pyrolysis upgrades the pyrolysis vapors (Diebold & Schahill, 1988; Horne & Williams, 1995; Williams & Nugranad, 2000). Hence, ex situ catalytic pyrolysis can also be described as a two-stage process that comprises the thermal decomposition of biomass into pyrolysis vapor making the pyrolysis vapor compounds available for secondary reactions over the process catalyst (Mullen, Boateng, Mihalcik, & Goldberg, 2011). Catalytic pyrolysis partially deoxygenates the biomass during pyrolysis conversion thereby decreasing the concentration of reactive oxygenated compounds, increasing the concentration of hydrocarbons, and producing a stable, noncorrosive oil that can be stored (Corma et al., 2007; Huber & Corma, 2007). The advantage of both in situ and ex situ catalytic pyrolysis is that the bio-oil is upgraded prior to condensing the pyrolysis vapors, which avoids condensation and re-evaporation of the pyrolysis oil (Liu et al., 2014). In situ catalytic pyrolysis removes the oxygen to form CO₂, CO, and H₂O. The stability of catalytic fast pyrolysis oil avoids or reduces the formation of coke in the reaction and requires less hydrogen in subsequent hydrotreating processes.

2.5 | Ex situ catalytic pyrolysis with electricity (EDOx)

Another form of upgrading that produces a stable bio-oil uses electricity to remove oxygen. A few studies (Lessard, 2014; Li et al., 2014; Moutet, 1992; Wang, Lee, Olarte, & Zacher, 2016; Zhang, Zhang, & Zhong, 2018) have explored the use of electrocatalytic hydrogenation (ECH) as an approach to stabilize and upgrade biomass pyrolysis liquids to form chemicals and fuels. Herein, we review a fast pyrolysis process with electrochemical deoxygenation, wherein the biomass undergoes fast pyrolysis forming char and bio-vapor, which are separated via a cyclone to isolate the vapor and pass it through a solid oxide membrane reactor (EDOx; Milobar, Hartvigsen, & Elangovan, 2015). The EDOx unit is connected to the cyclone to facilitate passing the bio-vapor through at high temperature. The EDOx contains membrane cells attached directly into the vapor stream of the pyrolysis unit before the condenser improving its overall oxygen removal efficiency (Elangovan et al., 2015). The EDOx unit consists of a nickel-catalyst cathode and an oxygen ion conducting ceramic membrane. When the bio-vapor goes through the EDOx unit, an electric potential is applied across the ceramic membrane under high temperatures causing to be oxygen liberated from either the bio-vapor or the electrolysis of water to be ionized. The oxygen ions travel through the ceramic membrane to the anode releasing oxygen gas. Consequently, hydrogen produced from steam electrolysis reacts with the remaining hydrocarbon radical forming deoxygenated hydrocarbon or water. The extent of reduction depends on the catalytic properties of the cathode, which are the oxygenated bio-oil, and the temperature of the hydrogen. The deoxygenated bio-vapor goes through the condenser where it is condensed to form partially deoxygenated oil. The deoxygenated oil is stable enough to be transported to a petroleum refinery for complete deoxygenation through hydrotreating, after which it goes through hydrocracking and product separation forming renewable diesel and gasoline.

Similar to EDOx, ECH uses an electrocatalyst (ruthenium supported on activated carbon cloth) as a catalytic cathode deoxygenating water-soluble bio-oil to produce a stabilized partially deoxygenated bio-oil, diols, and hydrogen. (Li et al., 2014). The process converts most of the aldehydes and ketones present in the bio-oil to their corresponding alcohols stabilizing bio-oil against polymerization.

3 | PRODUCT CHARACTERIZATION

The features of alternative bio-oil upgrading processes coupled with different forms of pyrolysis are summarized in Table 2. Among the processes reviewed, yields and compositions vary depending on the feedstock and the technological process used (Table 2). These include the conversion of corn stover to gasoline, diesel, and polyol fuels using hydrocracking and hydrotreating or esterification and catalytic hydrogenation; horse manure to biojet fuel through fast pyrolysis with extraction; pine to renewable fuels through torrefaction pretreatment and fast pyrolysis; poplar to renewable fuels through pyrolysis and HDO with external hydrogen supply; hog fuel chips to renewable fuels through pyrolysis and HDO; woody biomass to renewable fuels through in situ and ex situ catalytic pyrolysis; and short rotation woody biomass with multiple combinations of hydrolysis and oxidation, ketonization, hydrogenation, alkylation, and HDO upgrading methods. While prospects for commercialization depend on many factors, including the energy density, GHG intensity, and minimum selling price of the fuel product, a major factor is the oxygen content of the upgraded fuel produced. Fuel oxygen contents of pathways summarized in Table 2 range from less than 0.1% in the TGRP with extraction process to 18% in the fast (catalytic) pyrolysis followed by a
| Reference                        | Biomass conversion       | Upgrade method                                      | Thermochemical conversion scale (tonnes/day) | Feedstock         | Intermediate product     | Final products                     | Co-products     | Oxygen (wt.%) in fuel |
|---------------------------------|--------------------------|---------------------------------------------------|---------------------------------------------|-------------------|---------------------------|------------------------------------|----------------|----------------------|
| Zhang, Hu, et al. (2013)        | Fast (non-catalytic) pyrolysis | Hydrocracking and hydrotreating                    | Corn stover                                | Bio-oil           | Gasoline and diesel      | Hydrogen                          |                |                      |
| Heng et al. (2018)              | Fast (non-catalytic) pyrolysis | Esterification and Catalytic hydrotreatment       | 25                                          | Corn stover       | Bio-oil                   | Polyol fuel                       | Hydrogen gas   |                      |
| Thilakaratne et al. (2014)      | Fast (catalytic) pyrolysis | Two-stage hydrotreating                            | 2,000                                       | Hybrid poplar     | Bio-oil                   | Gasoline and diesel               | Biochar        |                      |
| Sorunmu et al. (2017)           | Fast (non-catalytic) pyrolysis | Distillation, Extraction, and Hydrogenation       | 200                                         | Horse manure      | Bio-oil                   | Jet fuel                          | Phenols and coke | <0.1                |
| Hsu (2012), Jones et al. (2009) | Fast (non-catalytic) pyrolysis | Hydrodeoxygenation with external hydrogen         | 2,000                                       | Forest residue    | Bio-oil                   | Gasoline and diesel               | Biochar        | 1.4                  |
| Carrasco et al. (2017)          | Fast (non-catalytic) pyrolysis | Hydrodeoxygenation without external hydrogen      | 2,000                                       | Forest residue    | Bio-oil                   | Gasoline and diesel               | Biochar        | <2                   |
| Vasalos et al. (2016)           | Fast (catalytic) pyrolysis | Condensation                                       | 500                                         | Beechwood         | Bio-vapor                | Catalytic pyrolysis oil           |                | 18                   |
| Dutta et al. (2015)             | Fast (catalytic) pyrolysis | Catalytic hydrodeoxygenation                       | 2,000                                       | Woody biomass     | Bio-oil                   | Gasoline, diesel, and jet fuel    | Biochar        | 0.5                  |
| Dutta et al. (2015)             | Fast (catalytic) pyrolysis | Ex situ catalytic pyrolysis vapor phase upgrading  | 2,000                                       | Woody biomass     | Bio-vapor                | Gasoline and diesel               | Biochar        | 0.4                  |
| Sorunmu et al. (2018)           | Fast (non-catalytic) pyrolysis | Ex situ catalytic pyrolysis vapor phase upgrading with electricity | 300                                         | Forest residue    | Bio-vapor                | Gasoline                          | Oxygen         | <5                   |
| Winjobi, Shonnard, et al. (2017), Winjobi, Zhou et al. (2017) | Fast (non-catalytic) pyrolysis | Catalytic hydrodeoxygenation                       | 1,000                                       | Pine              | Bio-oil                   | Gasoline and diesel               | Char and Torrefaction condensed liquid |                      |
| Winjobi, Shonnard, et al. (2017), Winjobi, Zhou et al. (2017) | Torrefaction pre-treatment and fast pyrolysis | Catalytic hydrodeoxygenation                       | 1,000                                       | Pine              | Bio-oil                   | Gasoline and diesel               | Char and Torrefaction condensed liquid |                      |
| Zaimes et al. (2017)            | Pretreatment, multistage torrefaction, and pyrolysis | Three upgrading combinations of: hydrolysis and oxidation, ketonization, hydrogenation, alkylation, and HDO | 2,000                                       | Short rotation woody crops | Bio-oil                   | Gasoline and diesel               | Electricity, heat, and biochar |                      |
| Brown et al. (2013)             | Fast (catalytic) pyrolysis | Hydroprocessing                                     | Corn stover                                | Bio-oil           | Gasoline and diesel      |                                   |                |                      |
| Zhu, Biddy, Jones, Elliott, and Schmidt (2014) | Hydrothermal liquefaction | Hydrotreating and Hydrocracking                    | 2,000                                       | Hybrid poplar     | HTL bio-oil               | Gasoline, diesel, and heavy oil   |                |                      |

*All processes are modeled and not operational plants.
condensation process. Most of the processes except one fall within or are less than the maximum allowable 3.7 wt.% oxygen mandated by the federal trade commission (Yanowitz, Christensen, & McCormick, 2011).

4 | LIFE CYCLE ASSESSMENT

Life cycle assessment provides a standardized framework for assessing and quantifying the environmental impacts of products, processes, and activities. Life cycle GHG emissions are the sum of direct and indirect GHG emissions that occur over all stages of life of a product. We review prior literature from Table 2 that quantified GHG emissions using the 100 year global warming potential (GWP) over the lifetime (cradle-to-grave) as an indicator of sustainability for alternative upgraded fast pyrolysis bio-oil products. Most processes include coproducts, the treatment of which, vary among previous LCA studies reviewed (Hsu, 2012; Hsu et al., 2010; Winjobi, Shonnard, & Zhou, 2017; Winjobi, Zhou, Kulas, Nowicki, & Shonnard, 2017). Coproducts in studies that employed full and partial HDO (Hsu, 2012; Zaimes et al., 2017), distillation and extraction (Sorunmu et al., 2017), and vapor phase electrochemical deoxygenation (Sorunmu, Billen, Elangovan, Santos, & Spatari, 2018) were treated using the product displacement method (Wang, Huo, & Arora, 2011) otherwise known as system expansion. System expansion is a rule applied to coproducts in LCA that are assumed to displace existing products on the market, whose impacts are assumed displaced and therefore credited. Comparing the GHG emissions among studies on the basis of 1 MJ of fuel ranked from lowest to highest and benchmarked against the GWP of gasoline and diesel (Figure 2), the two-step torrefaction and fast pyrolysis of pine has the lowest GWP while the one-step torrefaction and fast pyrolysis of pine (Winjobi, Zhou, et al., 2017) has the highest compared to conventional petroleum-based fuels. A reason for this significant difference in GHG emissions between the highest and lowest processes is that the increase in temperature in the torrefaction process combined with it being a two-step process (Winjobi, Zhou, et al., 2017) increases the quantity of coproduct (char), which is credited using system expansion and thereby significantly reduces the net GHG emissions compared to the one-step lower temperature torrefaction process.

Furthermore, comparing the fast pyrolysis HDO process that requires external hydrogen (Hsu, 2012; Jones et al., 2009) to the HDO process that does not (Carrasco et al., 2017), the former (Hsu, 2012; Jones et al., 2009) results in almost double GHG emissions compared to the latter (Carrasco et al., 2017). Except for one torrefaction/fast pyrolysis/HDO scenario examined by Winjobi, Shonnard, et al. (2017) and Winjobi, Zhou, et al. (2017), all pathways meet the US RFS2 for advanced biofuels. Processes with a GWP reduction potential in the >90% and 71%–90% range could be competitive in meeting fuel standards such as California’s Low Carbon Fuel Standard that reward incremental reductions (Gao et al., 2018).

5 | TECHNO-ECONOMIC ANALYSIS

The technological and economic performance of the alternative pathways was evaluated based on published literature. We use the minimum fuel selling price (MFSP) as an indicator of economic feasibility toward commercialization of the fuel pathway. On average, conventional diesel and gasoline are sold at $0.48 and $0.51 L⁻¹, respectively (U.S. Department Of

FIGURE 2 Survey of global warming potential (GWP) estimates of fuel pathways from alternative processes (Carrasco et al., 2017; Dutta et al., 2015, 2016; Heng et al., 2018; Hsu, 2012; Jones et al., 2009; Sorunmu et al., 2018, 2017; Winjobi, Zhou, et al., 2017; Zaimes et al., 2017; Zhang, Brown, et al., 2013). Greenhouse gas emissions per 1 MJ of fuel used with GWP reduction shown in yellow (<50%), orange (50%–70%), green (71%–90%), and blue (>90%) bars. Studies are benchmarked against the GWP of diesel and gasoline, which are assumed to be 93 g CO₂ eq./MJ
Energy, 2017) in the United States, and the average MFSP of the renewable fuels falls within the range between $0.54 and $1.8 L$^{-1}$, represented in Figure 3a ranked from lowest to highest. All fuel pathways studied are estimated to exceed the average price of gasoline and diesel; however, few are optimized to approach that price (Figure 3a). The fuel produced from fast pyrolysis with HDO upgrading without external hydrogen has the highest MFSP (Carrasco et al., 2017) while the fuel produced from fast pyrolysis with HDO upgrading requiring external hydrogen has the lowest MFSP (Jones et al., 2009).

Select studies undertook both LCA on GHG emissions and sensitivity analyses to test alternative operating conditions that optimize the MFSP. We further apply a social cost of carbon to those studies to estimate whether pricing their performance in reducing GHG emissions relative to gasoline sufficiently reduces the MFSP, and with that provide a first integration of LCA and TEA into a more complete sustainability view. Results suggest that a modestly set tax ($36 metric ton$^{-1}$) on carbon is insufficient in bringing most of the technologies to commercial competitiveness (Figure 3b). Only the HDO upgrading process by Jones et al. (2009), which is scaled and optimized to meet an MFSP of $0.50 L^{-1}$, attains a modest further reduction to $0.40–0.50 with a social cost of carbon (SCC) of $36 metric ton$^{-1}$. Except for the TGRP-extraction upgrading process that uses animal waste (horse manure) as feedstock (Sorunmu et al., 2017), all studies assumed use of forest resource or residue as feedstock, which incurs a cost.

**FIGURE 3** (a) Survey of minimum fuel selling price (MFSP) estimates of fuel pathways from alternative fast pyrolysis and upgrading processes from literature. Color schemes show the global warming potential (GWP) reduction relative to gasoline (93 g CO$_2$ eq./MJ) in yellow (<50%), orange (50%–70%), green (71%–90%), and blue (>90%) bars. Black striped bars represent studies that have not reported GWP. Reviewed MFSPs from literature are benchmarked against the average market price of gasoline ($0.51 L^{-1}$) and diesel ($0.48 L^{-1}$). (b) Social cost of carbon ($36 metric ton$^{-1}$) applied to the studies that reported MFSP and GWP.
of ~$60 metric ton\(^{-1}\). Waste resources can have negative costs if the unit disposal cost is assumed to replace the cost of the feedstock. Sorunmu et al. (2017) assumes a conservative $0 feedstock cost, which brings their jet fuel MFSP to $0.66 \pm 0.13$ L\(^{-1}\), close to the market price of a fossil fuel ($0.57 \pm 0.14$ L\(^{-1}\) jet fuel). Overall, all fast pyrolysis bio-oil upgrading technologies require further testing to bring down the costs to conventional fossil fuel levels. Our review further underscores the need for market prices that reflect external costs on carbon to begin to compete with petroleum-based fuels. In parallel, the review demonstrates that a more holistic analysis, applying the various upgrading technologies on identical feedstocks and identical products, is desired in order to rank their techno-economic potential.

### 6 TECHNOLOGY READINESS

The technological readiness of a process is the term used to describe the maturity of the technology. The TRL is a number assigned to the technology that embodies qualities such as efficiency, field conditions, level of commercialization, and technical and economic performance (Figure 4). TRL can be combined with the position of a technology on its developmental life cycle, and may relate to the precision and accuracy of sustainability predictions made, depending on the assessment methodology used. Often, from TRL 2–3 onwards, both environmental and economic performance may be underestimated because of unrevealed deviation from ideal conditions, whereby in scaling various efficiency losses may appear due to, for example, increasingly difficult mass and energy transfer. From TRL 6–7 onwards, environmental impact and costs may be reduced again because of beneficial scale effects and identified synergies with adjacent processes, and technological learning effects during commercialization. However, it must be stressed that no generic trend relating the environmental and economic performance to TRL exists to date, yet it is quite clear that the predictive uncertainty drops strongly with increasing TRL. In commercial technologies, the TRL space above 9 relates to learning curves, the concept that a technology’s performance improves as experience with the technology accumulates (Argote & Epple, 1990; McDonald & Schrattenholzer, 2002), typically bringing production costs further down. The alternative processes reviewed (Table 1) differ in their stage of maturity. When a technology has achieved TRL 4, all individual components or processes have been demonstrated to work together as a system. Studies at this stage (Elkasabi et al., 2014; Elkasabi, Mullen, et al., 2015; Sorunmu et al., 2017) have been published based on the success of laboratory scale experiments of the technology with readiness set to move to the TRL 5.

### 7 INTEGRATION OF TECHNOLOGICAL, ECONOMIC, AND ENVIRONMENTAL CRITERIA: LIMITATIONS AND SOLUTIONS

The upgrading technologies reviewed herein are not currently commercial, owing largely to limitations or barriers related to the technology (e.g., catalyst deactivation), uncertainties in projecting their scalability, and cost competitiveness with existing technologies and products on the market. We use Figure 5 to compare the thermochemical pathways side by side using TRL, LCA, and TEA metrics applied herein.

Beginning with studies listed under TRL 5 and 6, this review shows that only the TGRP with extraction study by Sorunmu et al. (2017) estimates all three metrics. It has the lowest GHG emission, lowest oxygen content in its final product (Table 2), but highest MFSP among the upgrading technologies at TRL 6 and overall (Figure 5). However, the case of catalytic fast pyrolysis with condensation by Vasalos, Lappas, Kopalidou, and Kalogiannis (2016) and hydroprocessing by Brown et al. (2013) both estimate promising MFSP at TRL 6,

![Figure 4](image-url)  
**Figure 4** Technological readiness of the fast pyrolysis upgrading processes (Engel, Dalton, Anderson, Sivaramakrishnan, & Lansing, 2012; Sanchez, 2011). The stars symbolize the number of technologies reviewed herein at a given technology readiness level (TRL) level.
without having computed the GHG metric. Potentially both pathways could yield low GHG intensities if using sustainably harvested forest and agricultural residues. At TRL 5, Zaimes et al. (2017) and Heng, Zhang, Xiao, and Xiao (2018) estimate GHG emissions that meet policy goals for advanced fuels, but they do not include MFSP. Although the TGRP with extraction study by Sorunmu et al. (2017) has commercial worthy qualities and reports all three metrics, its variable and high MFSP ($0.66–$2.38 L⁻¹, Figure 3b) is a major limitation owing to high costs in the pyrolysis step. The fact that the pathway uses a waste feedstock (horse manure), with very low GHG emissions and a zero or negative feedstock cost, suggests that if other bio-oil upgrading technologies investigated herein used waste feedstocks as well, they may also meet low GWP and competitive MFSP. At TRL 6 and more so at TRL 5, there are many unknowns for all upgrade technologies, even when MFSP estimates from process models (TEA) predict near-competitive market prices, much testing and learning remains for first-of-a-kind and nth (full scale at mature technology) plant performance (Worley & Yale, 2012).

Studies by Winjobi, Shonnard, et al. (2017), Winjobi, Zhou, et al. (2017), at TRL 3, excluding their high GHG scenario, and Jones et al. (2009) combined with Hsu (2012; TRL 4) make projections of all three metrics and both assume HDO with woody biomass (Table 2), suggesting an opportunity to exploit features of each technology to minimize GHG emissions and MFSP. The majority of published studies (Gollakota, Reddy, Subramanyam, & Kishore, 2016; Graca, Lopes, Cerqueira, & Ribeiro, 2012; Han, Elgowainy, Dunn, & Wang, 2013; Hsu, 2012; Sorunmu et al., 2017, 2018; Zacher, Olarte, Santos, Elliott, & Jones, 2014) on bio-oil upgrading TEA and LCA assume use of HDO, including two studies we review (Figure 5) at TRL 3 (Winjobi, Zhou, et al., 2017) and 4 (Hsu, 2012; Jones et al., 2009). Furthermore, multiple studies (Carrasco et al., 2017; Hsu, 2012; Jones et al., 2009) have been published based on the results of experiments and estimates have been made on how the experimental components and results differ from the projected system performance. HDO has several limitations, particularly its need for large quantities of external hydrogen and biomass supply that can accommodate an economic scale of 2,000 MTPD. Carrasco et al. (2017; TRL 3) proposed in situ hydrogen generation with feedstock residuals, and other studies propose small/distributed scale pyrolysis operation (e.g., 200–500 MTPD) to overcome feedstock supply barriers (Fan et al., 2011; Fan, Shonnard, Kalnes, Streff, & Hopkins, 2013; Pourhashem, Spatari, Boateng, McAloon, & Mullen, 2013; Sorunmu et al., 2018). While supplying hydrogen from renewable sources as proposed by Carrasco et al. (2017) could lower GHG emissions while keeping all other HDO factors constant, it could raise the MFSP, which would affect its commercial attractiveness.

Active research and development has been carried out at laboratory scale and through chemical process models, TEA and LCA for in situ and ex situ catalytic pyrolysis processes, as described by Dutta et al. (2015). For in situ and ex situ catalytic pyrolysis, scale, MFSP, GHG emissions, oxygen content, and TRL are very similar, but catalyst deactivation is faster in ex situ catalytic pyrolysis. One of the limitations that presents a considerable barrier to commercialization of the technology is the low oil yields in catalytic pyrolysis due to coking and light gas losses; hence, more research on ways to increase the oil yield is essential to deliver an economically competitive technology (Lisa et al., 2016). The EDOx process described by Sorunmu et al. (2018), having been integrated with a fast pyrolysis unit, tested, and patented (Elango, & Karanjikar, 2015), can be situated between TRL 3 and TRL 4. While the process has a comparatively low GHG intensity (4.9 g CO₂ eq. of diesel and 7.4 g CO₂ eq./MJ of gasoline), MFSP and other TEA metrics have not been published and its development beyond TRL 3–4 depends on achieving greater deoxygenation to reduce external hydrogen costs.

Although TRL presents a decision metric that can guide investment decisions based on current development state (e.g., assuming higher levels are the closest approximation of
commercialization), this does not preclude technologies with low TRL from consideration to invest in their further development. In fact, the inclusion of TRL in the side-by-side comparison of technological alternatives is in this respect imperative, as the differences in developmental stage should affect decision makers given that assessment results are based either on different scale data or projections to a commercial stage via distinct methods. Decision rules are greatly needed to advance promising technologies that have only been tested at laboratory scale (e.g., low TRL between 3 and 4) in order to assess their prospects of advancing to a higher TRL. While many of the studies we reviewed on upgrading technology for fast pyrolysis bio-oil are currently at low TRL (3–5), and many of these are missing either MFSP or GWP estimates (Figure 5), this lack of information does not warrant their exclusion from R&D investment. For some technologies at low TRL with high estimated MFSP or GWP based on lab-scale results, proper projections toward commercial stage production could mean a decrease of both, because of learning and scaling effects (Thomassen et al., 2019). Merely including TRL information in the integrated comparative assessment of technologies under development at least provides some additional information about uncaptured uncertainties. Yet, as outlined recently by Buyle, Audenaert, Billen, Boonen, and Passel (2019), equally important in ex ante sustainability assessment is developing or using standardized methods to project the environmental impact and cost to a future commercial stage. How data are gathered, by experimental or in silico methods, as well as how technological scaling is measured, strongly affects the outcome of assessments, and subsequently the comparative base for decision-making. Buyle et al. (2019) thus call for formalized methods that render technological projections reproducible and comparable in ex-ante sustainability assessment.

Once common ex-ante sustainability projection methods are established, comparable results of TEA and LCA at the same TRL could be integrated to support decision-making. Possible methods to evaluate a set of technologies that reach, for instance, TRL 6, include multi-criteria decision-making (MCDM) with expert judgment, among which Delphi methods and analytical hierarchy process have been applied to support life cycle sustainability assessments for bio-based products and engineering infrastructure (de la Fuente, Armengou, Pons, & Aguado, 2017; Opher, Friedler, & Shapira, 2019; Van Schoubroeck, Springael, Dael, Malina, & Passel, 2019). A multi-objective optimization could be used as input to the MCDM, by which the decision-making mainly refers to the resulting set of Pareto-optimal scenarios related to environmental and economic criteria (Thomassen et al., 2019). If using MCDM, it would be worthwhile expanding TEA and LCA metrics to gather judgment on top priorities for investment.

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