

## The impact of using hydrogen to upgrade pyrolysis oils

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### Abstract

This study aimed to investigate the hydrogen requirements and environmental impacts for producing synthetic transportation fuels via pyrolysis and different upgrading pathways. Several life cycle assessment (LCA) models consisting of biomass collection, transportation, pre-treatment, processing and upgrading were defined and analysed in GaBi ecoinvent<sup>®</sup>. The pyrolysis oil upgrading methods included esterification, ketonisation, single-stage hydrotreating, two-stage hydrotreating and hydrocracking. Furthermore, the most optimistic scenarios were evaluated, and alternative sources of hydrogen were considered: hydrogen obtained from an external source, through steam reforming 50% of the bio-oil aqueous phase and steam reforming 100% of the bio-oil aqueous phase. Single-stage hydrotreating and two-stage hydrotreating contributed between 18.8-32.2% and 28.3-45.5%, respectively, to the total CO<sub>2</sub> equivalent emissions. However, two-stage hydrotreating reduced the oxygen content by a further 18-25%. The hydrocracking process contributed 6-15% to the total CO<sub>2</sub> emissions. For the entire pyrolysis oil upgrading process, 12-24% of the total environmental impact resulted from the use of hydrogen. It was found that the hydrogen GWP emissions ranged from 840 to 1110 gCO<sub>2</sub>/kg of upgraded pyrolysis oil produced. In the most optimistic scenario, the CO<sub>2</sub> emissions caused by hydrotreating were decreased by up to 26.5% for single-stage processing and up to 36.6% for a two-stage process. In terms of different hydrogen sources, it was found that the energy requirement for producing hydrogen internally from the aqueous phase of the pyrolysis oil through steam reforming was between 33.7% to 40.1% higher. Total CO<sub>2</sub> emissions were 19.9-27.8% higher when producing hydrogen only for the upgrading process, and over 50% higher when co-producing hydrogen. To obtain synthetic transportation fuels from upgrading pyrolysis oils, the total CO<sub>2</sub> emissions are expected to range from 3510 - 9650 gCO<sub>2</sub>/kg of biofuel. In comparison, the emissions for producing diesel are 4230 gCO<sub>2</sub>/kg. Therefore, as more and more companies seek to commercialise the production of synthetic transportation fuel, great care must be taken to ensure that environmental gains over convention fossil fuels are being achieved. Determining a trade-off between GHG emissions, cost and product quality has to be carried out in further work.

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### 1. Introduction

Most biofuels currently used for the transportation industry are derived from food crops or crops that require vast

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expanses of land; this has raised fears of increasing food prices and causing food shortages. The second-generation of biofuels are obtained from agricultural residues, grasses and other waste feedstock, and are considered to be more sustainable and environmentally friendly. However, producing second-generation biofuels can be challenging as it involves complex and energy intensive conversion processes. The research in producing sustainable transportation fuels from second-generation biofuels is rather limited. A significant number of studies research the thermochemical process for converting waste biomass bio-oil via pyrolysis, but just a few researches the upgrading pathway of pyrolysis bio-oils into viable transportation fuels. Highly oxygenated, unstable and acidic bio-oils have to be improved before they can be used as transportation fuels. There are various upgrading methods which are being investigated to improve pyrolysis oils, but in order to be sustainable it has to offer environmental benefits in comparison to conventional fossil fuels. The environmental impact of converting waste biomass into bio-oil from the pyrolysis process, and obtaining biofuels from different upgrading pathways, can be analysed by conducting life cycle assessments (LCA).

Several authors have used LCA to investigate the environmental impacts of producing fuels from pyrolysis. Irribaren et al. [1] conducted a life cycle assessment of pyrolysis of poplar followed by hydrotreating, and found that over 40% of the total CO<sub>2</sub> emissions result from using steam reforming to obtain hydrogen. Peters et al. [2] simulated a pyrolysis plant and biorefinery (hydrotreating, hydrocracking, distillation and steam reforming) for fast pyrolysis of hybrid poplar and hydrougrading. It was found that the energy demand from steam reforming natural gas was 30% from the total energy demand of producing an upgraded biofuels. Reducing electricity consumption was considered one of the key factors in reducing the overall environmental impact. Swan et al. [3] looked into biomass conversion to biofuels through pyrolysis and upgrading (hydrotreatment and hydrocracking) where hydrogen was produced through steam reforming; the conversion accounted for 63% from the total CO<sub>2</sub> emissions for hybrid poplar and 72% for forest residue. Electricity was considered the main contributor to the conversion process, so the study focused on reducing the electricity consumption. Hsu et al. [4] conducted a life cycle assessment of gasoline and diesel produced through fast pyrolysis and hydroprocessing; it showed that hydroprocessing highly contributed to the total CO<sub>2</sub> emissions: around 55% in diesel production and 60% in gasoline production. Dang et al. [5] carried out a life cycle assessment of bio-fuel production from corn stover feedstock focusing on the GWP impact, but the study did not consider the contribution of each process to the total environmental impact. These studies show that there has been a tendency to focus on considering pyrolysis with hydrotreating [1-5]. Only a few take into consideration hydrocracking or other upgrading methods [2,3]. However, the structural complexity of lignocellulosic bio-oil requires a synergy of technologies to upgrade bio-oils into synthetic fuels. Therefore, this study, aims to analyse the environmental impacts of the main emerging combinations of pyrolysis and upgrading methods to obtaining sustainable transportation fuels from pyrolysis. This will enable a combination of upgrading methods which give good fuel yields and quality, whilst offering sustainable environmental impacts in comparison to fossil fuels.

## 2. Materials and methods

Various bio-oil upgrading methods were reviewed to identify the most promising combination of processes, resulting in six possible scenarios to be analysed and compared in terms of their environmental impact. Life cycle assessment of each scenario was conducted conforming to ISO14040 and ISO14044 standards [6]. GaBi Professional software and Ecoinvent database were used to perform the LCA analysis. The study considers the inputs of materials, energy and resources at each stage from collection of the waste feedstock to biofuel production and distribution.

The inventory data for each stage is outlined and any assumptions are explicitly stated. Where possible, along with the most commonly reported values, optimistic values have been obtained from the literature. The impacts associated with electricity and transport have been taken from Ecoinvent and GaBi databases, and correlated with inventory data. This enabled the most likely values to be obtained in terms of the global warming potential (GWP) for each stage.

To enable the different upgrading scenarios to be compared, the same feedstock (corn stover) was taken into consideration, and the pyrolysis processing technology has been considered throughout. Corn stover was used in this study, as it has been considered as a suitable waste feedstock in a range of life cycle assessment studies [5,7]. For the pyrolysis process, the fluidised bed reactor was considered as it is a popular option due to its ease of operation, stability and high oil yields [8]. To investigate the alternative options for sourcing hydrogen, each scenario was modelled for hydrogen obtained from steam reforming of methane, 50% of the bio-oil aqueous phase. Steam reforming of 100% of the bio-oil aqueous phase which resulted in hydrogen co-production was not considered for this study.

### 3. Definition of the bio-oil upgrading case scenarios

Pyrolysis bio-oil can be upgraded into biofuels using a number of physical and chemical methods [9]. However, this study focuses on the pyrolysis process and catalytic and chemical upgrading methods: hydrotreating, hydrocracking, esterification and ketonisation; the physical upgrading is assumed to be incorporated in the pyrolysis process, and gasification with Fischer-Tropsch is considered beyond the scope of this study. Hydrotreating involves the use of hydrogen and catalysts to reduce levels of oxygen, sulphur and nitrogen. The oxygen level is reduced by rejecting it as water through a catalytic reaction with hydrogen, and the process takes place at relatively low temperatures (150°C – 400°C). This process is also referred to as hydrodeoxygenation. Hydrotreated oil can be hydrocracked to break carbon-carbon bonds to produce shorter-chain hydrocarbons, which are more suitable as fuels [10]. To obtain higher degrees of hydrodeoxygenation, two-stage hydrotreating processes can be used. In two-stage hydrotreatment, mild hydrotreating is followed by a more severe hydrotreating step. Single stage-hydrotreating can generate a tar-like product, but two-stage processing overcomes the reactivity of the bio-oil. A promising process for improving bio-oil quality prior to hydrotreating, is esterification. This process reduces acidity and oxygen content of the bio-oil, thus improving the stability. Esterification reduces the acid concentration through neutralising the carboxylic acids in bio-oil [11]. Another upgrading method is ketonisation, which is a condensation reaction that enables the partial reduction of oxygen in form of water [11]. Ketonisation transforms two carboxylic acids into ketone, carbon dioxide and water [12]. Ketonisation also increases the size of the carbon chain, resulting in a more stable product with higher energy content, and prevents the smaller molecules to be eliminated in the form of light gases [13].

Based on the different upgrading methods, six upgrading scenarios are considered in this study: i) hydrotreating and hydrocracking – considered to be the minimum requirement to obtain transportation fuels [10,14]; ii) esterification, hydrotreating and hydrocracking [10,11,14,15]; iii) esterification, ketonisation, hydrotreating and hydrocracking [10,11,14-16]; iv) two-stage hydrotreating and hydrocracking [10,17]; v) esterification, two-stage hydrotreating and hydrocracking [10,11,14,15,17]; and vi) esterification, ketonisation, two-stage hydrotreating and hydrocracking [10,11,14-17]. The bio-oil upgrading scenarios to be analysed are outlined in Figure 1.

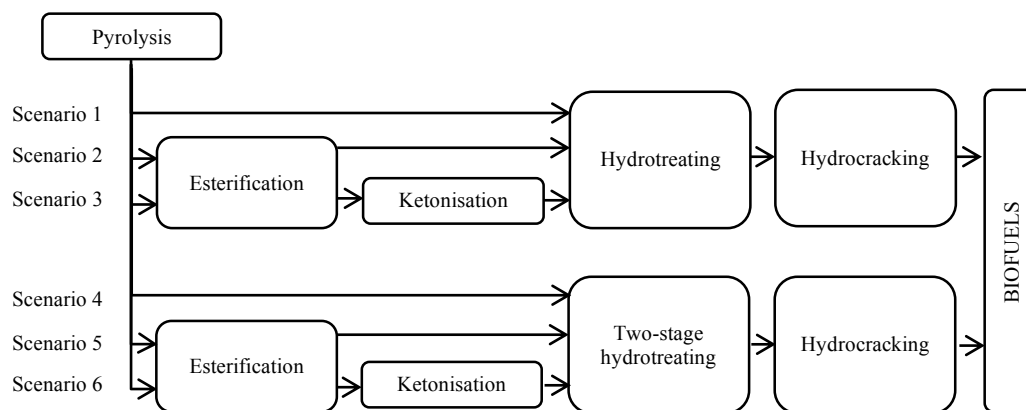


Figure 1: Alternative bio-oil upgrading scenarios to produce upgraded liquid fuels from pyrolysis

### 4. Inventory data

#### 4.1. Pyrolysis oil production: Biomass production, Feedstock transport, Feedstock pre-treatment, Pyrolysis process

The LCA biomass production stage consists of biomass collection. It also includes fertilisers as phosphate, potassium oxide and nitrogen are used in cultivation. The assumption is made that the corn stover will be transported from the biomass collection point to the bio-oil production plant. A 9.3t heavy-duty truck from the ecoinvent database has been used. Pre-treatment of the feedstock prior to pyrolysis is required, and involves grinding and drying. Feedstock particle size reduction is necessary because pyrolysis Bubbling fluidized bed reactors are designed to use very small particle sizes - from 2-3 mm [18]. Grinded corn stover with a moisture of 25% is dried to a moisture of 7% [19,20]. Pyrolysis plant capacity was assumed to be of 2000 metric tons / day of dry corn stover [7,20]. Corn stover average

LHV was considered to be 15.6 MJ/kg [5]. Pyrolysis was performed at 500°C and bio-oil yields through fast pyrolysis of corn stover ranged from 62 – 75 wt% [5,18], and up to 80% under optimised conditions [21].

#### **4.2. Pyrolysis oil upgrading to biofuels: Esterification, Ketonisation, Hydrotreating, Hydrocracking, Transportation and distribution of biofuel**

Esterification is required to reduce the bio-oil high oxygen content (20-50wt %) and acidity (pH=2.5-3). This improves the lower heating value and other proprieties, such as viscosity and corrosiveness [11,15]. Esterification was performed at temperature values between 70 - 170°C [15]. Zeolite catalyst was assumed to be used for 12 hours (2 hours and then reused for 10 hours) [11,22], and the yield of upgraded bio-oil was found to be up to 63wt% [23]. The optimum ethanol to oil ratio was assumed to be 5:1 [24]. The optimistic ethanol to oil ratio was assumed to be 3:1 [21]. Ketonisation can be performed at around 400°C [25] and the quantity of electricity required in the process was assumed to be 0.44 kWh/kg. Through ketonisation, yields of 75 - 98% [12] have been reported and an average conversion rate of 90% was assumed [26].

Hydrotreatment is required to reduce the high content of oxygen in pyrolysis oils (around 40wt%) [27] in order to upgrade them to synthetic transportation fuels. Hydrotreating can be performed either in one or two stages, and different degrees of deoxygenation can be achieved. Hydrotreatment of corn stover bio-oil can be performed using noble metal catalysts (Ru/C and Pd/C) at 125bar, 200°C or 300°C and 4 hour reaction time in a batch catalytic reactor. Results show that ruthenium can accomplish 25–26wt% deoxygenation and yields between 54–67 wt% [28]. It was also found that Ru/C for the hydrotreatment of fast pyrolysis oils at 180-240 °C and hydrogen pressures of 133-142 bar resulted in a reduction of the oxygen content from 41.3 %-wt. down to 20 - 27wt% [29]. Bio-oil yields of 30% [20], 55.6% (PNNL) [30], 40.8% (UOP) and 42% [31] have been reported. Through mild hydrotreating under Ru/C catalyst (5 wt%) at 250°C and a hydrogen pressure of 130bar for 4 h, the oxygen content is significantly decreased to 20 – 26wt% [14]. For temperatures of 250-350°C and hydrogen pressure of 100 – 200 bar, Ru/C was found to be superior to common catalysts in yield (60%wt) and deoxygenation (90wt%) [9]. The highest oil yield (65%wt) was obtained after 4h, using 5 wt% catalyst to bio-oil ratio, a temperature of 350°C and 200 bar [29]. The two-stage hydrotreating involves performing mild hydrotreating at 150-270°C, 80-100 bar, followed by moderate processing at 350-425°C, 140-200 bar [32]. Brown et al. assumed that the first-stage hydrotreatment was performed at 125°C and 100 bar pressure, by using Ru/C catalysts, while the second-stage hydrotreatment was carried out at 250°C and 100 bar pressure, by using Pt/C catalysts [10]. The total residence time for the two-stage hydrotreating ranges from 2-4 hours [32], [29]. The levels of deoxygenation for the two-stage hydrotreating tend to be 2% oxygen or less [17]. In stage one a Ru/C is used, whereas a Pt/C or NiMo catalyst is normally used in stage two. Catalyst quantities are normally around 3 - 5wt% of bio-oil, with a better performance of the catalyst loaded with 5wt% [29], and with lifetimes of around 700 - 1752 hours (Ru/C) catalyst lifetime is of one year with a value of 5 wt% [33]. The overall yield of deoxygenated bio-oil for two stage hydrotreating is expected to range from 30% [34] to 38-44% [35], and the yield of upgraded oil is assumed to be up to 90% of first-stage hydrotreatment [34].

Hydrocracking involves cracking bio-oil into short-chain hydrocarbons in the presence of a catalyst and H<sub>2</sub>. Hydrocracking is performed at more severe condition than hydrotreating: at temperatures between 400-450°C and pressures of 100-140 bar [20]. The catalysts used in the hydrocracking process to obtain transportation biofuels were assumed to be Ni-HZSM-5 zeolites [36]. Hydrocracking is expected to produce a liquid yield up to 75% [37]; the average was assumed to be 70%.

The liquid biofuel transportation was assumed to be via trucks travelling a distance of 100-150 km/kg of biofuel. Heavy-duty truck transportation and heavy-duty truck distribution were found to be between 55 – 80 km/kg and respectively 48 - 53 km/kg [5,7].

The inventory data is summarised in Table 1.

**Table 1: Inventory data for each stage of the life cycle assessment processes, including references and calculated values.**

Inputs	Average	Optimistic	Unit	REF
<b>Biomass production</b>				
Diesel used in the production of corn stover	0.22	0.219	MJ/kg of corn stover	[5] [7] [38]
Phosphate	2.21		g/kg of corn stover	[5] [7] [38]
Potassium oxide	13.23		g/kg of corn stover	[5] [7] [38]
Nitrogen	8.5		g/kg of corn stover	[5] [7] [38]
<b>Biomass Transportation</b>				
Diesel	0.20		MJ/kg of biofuel	[5]
Heavy-duty truck	75	50	km/kg of biofuel	Calc.
<b>Biomass pre-treatment</b>				
Electricity used for grinding	0.057	0.011	kWh/kg of corn stover	[5] [7] [19]
Electricity used for drying	0.176	0.046	kWh/kg of corn stover	[5] [7] [20]
<b>Biomass pyrolysis</b>				
Electricity used in pyrolysis	0.487	0.252	kWh/kg of corn stover	[5] [7]
<b>Esterification</b>				
Electricity used by heater	0.259	0.217	kWh/kg of bio-oil	[15] Calc.
Zeolite powder	5wt%	3wt%	Kg of bio-oil	[11] [11,22] [23]
Ethanol	5	3	kg/kg of bio-oil	[24] [21]
<b>Ketonisation</b>				
Electricity used by heater	0.440		kWh/kg of bio-oil	Calc.
Ru/TiO <sub>2</sub> /C Catalyst	5wt%		kg of bio-oil	[13,39]
Pd/ZrOx – ZrO <sub>2</sub>	0.25wt%		kg of bio-oil	[26]
<b>One stage hydrotreating</b>				
Hydrogen consumption	74	69	g/kg of bio-oil	[5,40]
Electricity consumption	0.255	0.23	kWh/kg of bio-oil	[5] [7] Calc.
Ru/C (Pd/C) Catalyst	0.3	0.1	g/kg of bio-oil	[14] [9] [29] [33]
<b>Two-stage hydrotreating (mild+moderate)</b>				
Overall hydrogen consumption	69	58	g/kg of bio-oil	[32] [5] [35]
Overall Electricity consumption	0.75	0.569	kWh/kg of bio-oil	[1] Calc.
Ru/C Catalyst (mild stage)	0.3	0.1	g/kg of bio-oil	[14] [9] [29] [33]
Pt/C/ Pd/C	0.3	0.1	g/kg of bio-oil	[29] [33]
<b>Hydrocracking</b>				
Electricity used by heater	0.451		kWh/kg of bio-oil	[20]
Hydrogen	0.02	0.015	kg/kg of bio-oil	[41]
Zeolite powder	5wt%		kg of bio-oil	Calc.
<b>Transportation and distribution of biofuel</b>				
Diesel	0.28		MJ/kg of biofuel	[5]
Heavy-duty truck	150	100	km/kg of biofuel	Calc.

## 5. Environmental results

Figure 2 shows the results obtained for scenario 1 making use of: an outside source of H<sub>2</sub>; hydrogen produced in the plant through steam reforming by using 50% of the aqueous phase bio-oil (based on [5] and H<sub>2</sub> ratios of hydrotreating and hydrocracking); hydrogen produced through steam reforming all the aqueous phase bio-oil, in which case it also produced H<sub>2</sub> as a co-product. To calculate the real amount of CO<sub>2</sub> emissions from the GaBi results, the life span absorption of the corn stover was deducted. It was assumed that 1kg of corn stover can uptake during its lifespan 0.57 kgCO<sub>2</sub> [7], and this was considered to evaluate the overall environmental impact of biofuel production from corn stover.

The results show that making use of an outside source of H<sub>2</sub>, where conventional steam reforming of methane has been performed, the CO<sub>2</sub> emissions were lower than by using hydrogen produced in the plant through steam reforming using 50% (based on [5] and H<sub>2</sub> ratios of hydrotreating and hydrocracking) of the aqueous phase bio-oil (Figure 2). Steam reforming of 100% of the bio-oil aqueous phase which resulted in hydrogen co-production showed a high increase in CO<sub>2</sub> emissions and therefore was not considered for this study.

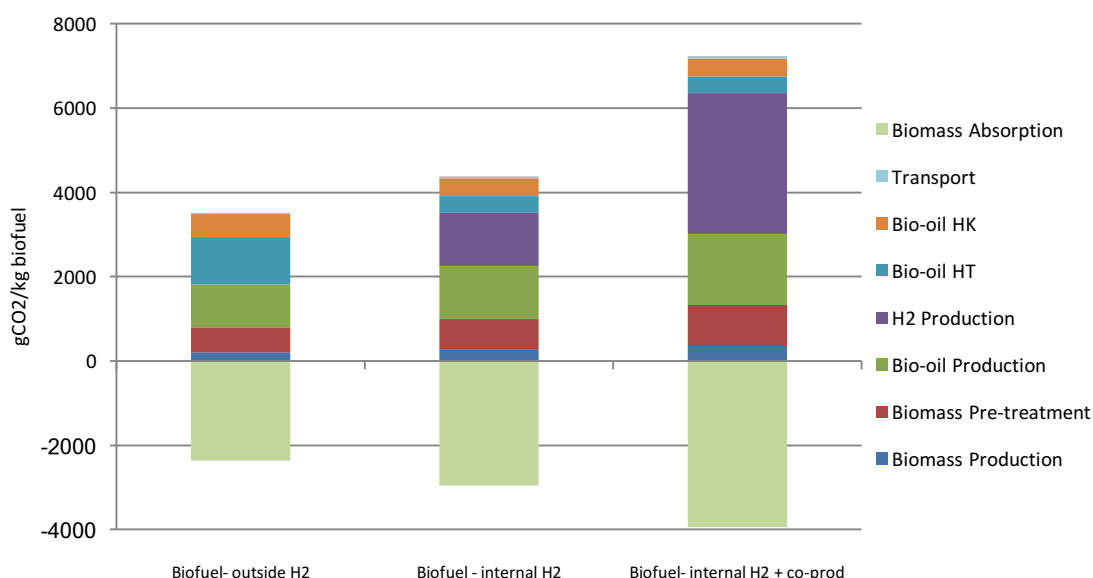


Figure 2 – Scenario 1 with different H<sub>2</sub> sources, showing feedstock biomass, and H<sub>2</sub> produced life span absorption

The six scenarios were simulated using the inventory data, and the results for both average and optimistic data are illustrated in Figure 3. The LCA results show that the CO<sub>2</sub> emissions could be as high as three times more than the CO<sub>2</sub> emissions associated with convention transportation fuels; however, favourable net emissions are achieved when considering the CO<sub>2</sub> absorbed during plant growth. The most likely net CO<sub>2</sub> emissions based on average values from the inventory data provide only small environmental gains (1130 – 3494 gCO<sub>2</sub>/kg) in comparison to diesel fuels; however, in the most optimistic scenario, CO<sub>2</sub> reduction is significant ranging from 78 - 121% for scenarios 6 and 2 respectively. In all six scenarios, the mass of corn stover used for obtaining 1 kg of biofuel with internal hydrogen is approximately 20% higher than if external hydrogen was used. Also, the emissions of average scenarios increased with 19.9-27.8% when external hydrogen was used and the emissions of optimistic scenarios increased with 25-33% in optimistic scenarios when external hydrogen was used. In Average scenarios biofuel showed the overall emissions between of 3510 gCO<sub>2</sub>/ kg and 9650 gCO<sub>2</sub>/ kg of biofuel produced (Figure 3). In the optimistic Scenarios the CO<sub>2</sub> emissions decreased by up to 48%, but the life span absorption also decreased by up to 31%. Different transportation fossil fuels can vary with 3% of the total emissions.

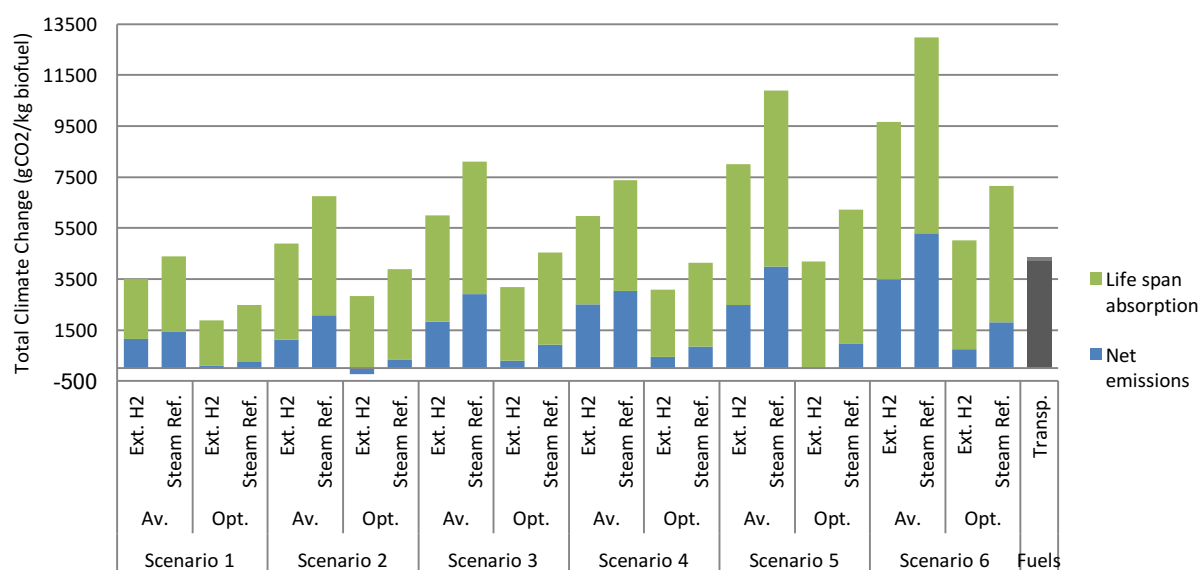


Figure 3 – Average and Optimistic GWP gross and net emissions for all six scenarios (with internal and external H<sub>2</sub> sources)

Unlike previous studies, this study took into consideration the catalysts and solvents involved in the upgrading processes. The result showed that the electricity and hydrogen have the main impact on the CO<sub>2</sub> emissions (68-87% respectively 12-24%), and catalysts contribute up to 3% to the total CO<sub>2</sub> emissions. Bio-solvents showed a reduction in CO<sub>2</sub> emissions of 8-9 %, and synthetic solvents showed an increase in CO<sub>2</sub> emissions of 9-11%.

The ratios of hydrogen to the total CO<sub>2</sub> emissions were evaluated to analyse the contribution to the total CO<sub>2</sub> emissions of each process, as shown in Figure 4. Bio-oil Hydrotreating process had a share of 19-46% of the total CO<sub>2</sub> emissions with single-stage hydrotreating and two-stage hydrotreating contributed between 18.8-32.2% and 28.3-45.5%, respectively, to the total CO<sub>2</sub> equivalent emissions. In the optimistic scenarios, bio-oil hydrotreating and hydrocracking decreased by 26-37% and 33-37% respectively.

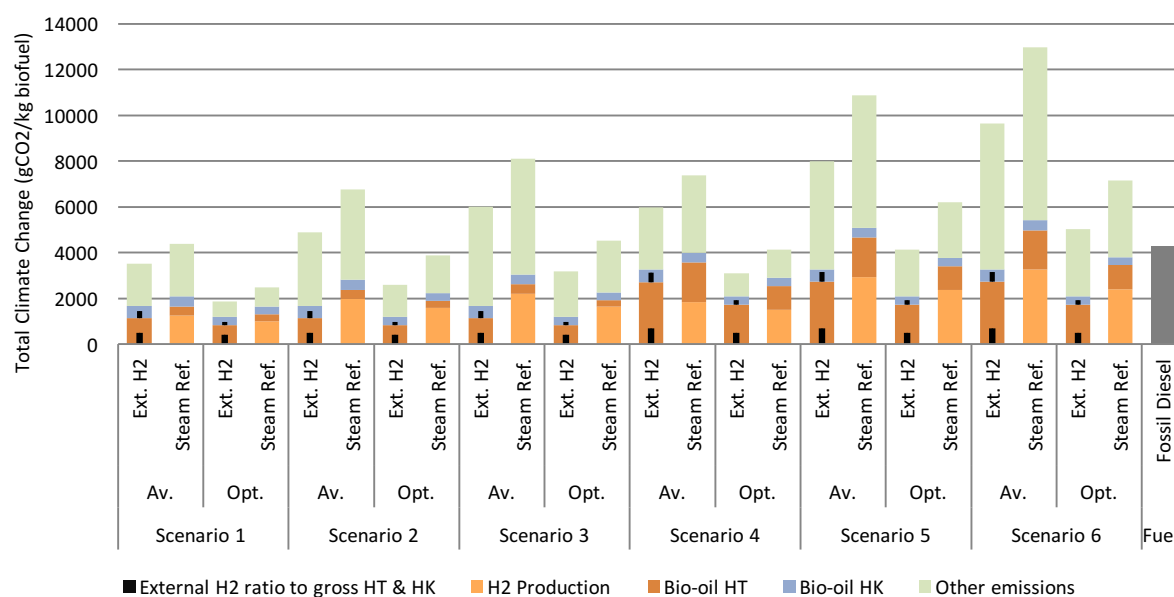


Figure 4 – Hydrogen impact on total GWP



## 6. Discussion

This study aimed to investigate the hydrogen requirements and environmental impacts for producing synthetic transportation fuels via pyrolysis and different upgrading pathways. Several LCA models with upgrading processes such as esterification, ketonisation, single-stage hydrotreating, two-stage hydrotreating and hydrocracking were defined and analysed. However, to draw a comparison with other LCA studies in the literature, upgrading corn stover into a fuel using only pyrolysis and hydrotreating was also considered. Using pyrolysis and hydrotreating to turn corn stover into a fuel was found to release 54.74 gCO<sub>2</sub>/MJ. This is comparable with other studies with values ranging from 39.1–55 gCO<sub>2</sub>/MJ [5,7]. Similar values of 39, 54 and 34 gCO<sub>2</sub>/MJ have been obtained for hybrid poplar [2,3], wood [4] and southern pine [32]. Hydrotreating alone is not sufficient to upgrade pyrolysis oils into high quality fuels, so this study modelled six additional upgrading scenarios. The fuels obtained through pyrolysis, hydrotreating and hydrocracking (Scenario 1) showed an environmental impact was 41% higher than pyrolysis and hydrotreating.

For the six different scenarios, the total CO<sub>2</sub> emissions ranged from 3510 to 9650 gCO<sub>2</sub>/kg of biofuel (2365 – 6156 gCO<sub>2</sub>/kg absorbed during feedstock life span). In comparison, the emissions for producing diesel are 4230 gCO<sub>2</sub>/kg. When taking into account the CO<sub>2</sub> absorption, the gross carbon emissions were reduced by 57-109% (Figure 3). Similar findings are presented by Zhan's [7], Iribarren *et al.* [1], Peters *et al.* [2] and Hsu [4], where the total effect of the CO<sub>2</sub> emissions were reduced by 100 to 200% amount when considering the carbon dioxide absorbed during the feedstock's total lifespan. In comparison with obtaining hydrogen from an external source, producing hydrogen internally was found to increase the CO<sub>2</sub> emissions by 20% when using a steam reforming process and 53% when hydrogen was produced for both upgrading and co-production processes. Specifically, the emissions increased to 4380 - 12980 gCO<sub>2</sub>/kg (2958 – 7695 gCO<sub>2</sub>/kg considering feedstock life span). The increase in emissions can be attributed to the high energy demand for the production of hydrogen through steam reforming, as it was found that the energy requirement for producing hydrogen internally from the aqueous phase of the pyrolysis oil through steam reforming was between 33.7% to 40.1% higher than obtaining hydrogen from steam reforming of methane. Another reason for the increase in emissions is the decreased biofuel yield due to the process of producing internal hydrogen.

Figure 4 shows that that hydrogen usage (hydrotreating and hydrocracking) contributed between 45-66% of the total CO<sub>2</sub> emissions (1670 gCO<sub>2</sub>/ kg of biofuel to 3270 gCO<sub>2</sub>/ kg of biofuel). When the hydrogen was produced internally through steam reforming, the emissions increased by up to 40% (2080 gCO<sub>2</sub>/ kg of biofuel to 5410 gCO<sub>2</sub>/ kg of biofuel) due to hydrogen production and usage (hydrotreating and hydrocracking). In the optimistic scenarios the hydrogen usage decreased with up to 37% (1190 gCO<sub>2</sub>/ kg of biofuel to 2090 gCO<sub>2</sub>/ kg of biofuel) when external hydrogen was used, and increased with up to 26% (1640 gCO<sub>2</sub>/ kg of biofuel to 3810 gCO<sub>2</sub>/ kg of biofuel) when internal produced hydrogen was used. Single-stage hydrotreating and two-stage hydrotreating contributed between 18.8-32.2% and 28.3-45.5%, respectively, to the total CO<sub>2</sub> equivalent emissions. This is due the lower amount of hydrogen required for two-stage hydrotreatment, but also because the yields reported for two-stage hydrotreatment were also lower (see Table1). The mass of biomass required to get 1 kg of biofuel through two stage hydrotreating was 32% higher compared with single-stage hydrotreating. However, two-stage hydrotreating reduced the oxygen content by a further 18-25%. The hydrocracking process contributed 6-15% to the total CO<sub>2</sub> emissions. It could be also noticed that the environmental impact resulted from the usage of hydrogen was between 12-24% (840 to 1110 gCO<sub>2</sub>/kg). From the total hydrogen up to 63% of the hydrogen used in the process was used in the hydrotreating process and the rest for hydrocracking.

## 7. Conclusions

This study investigated the global warming potential of upgrading pyrolysis oils in synthetic transportation fuels. Six alternative upgrading scenarios were considered and depending on the amount of upgrading performed, the gross GHG emissions were found to range from 3510 to 9650 gCO<sub>2</sub>/kg of upgraded bio-oil; 12-24% of the CO<sub>2</sub> equivalent emissions were associated with the use of hydrogen. The processing stages that had the highest impact on the environment were found to be bio-oil production (up to 33%) and hydrotreating (up to 46%). Overall net emissions, which take into account CO<sub>2</sub> absorption during feedstock lifespan, were significantly lower at 1130 to 3494 gCO<sub>2</sub>/kg. This suggests favourable CO<sub>2</sub> emission reductions can be achieved in comparison to conventional diesel fossil fuels, which emit approximately 4300 gCO<sub>2</sub>/kg. A combination of esterification, ketonisation, two-stage hydrotreating and hydrocracking processes to upgrade pyrolysis oil's, can still reduce CO<sub>2</sub> emissions by as much as 82%. This value is



highly dependent on the efficiency of the individual upgrading stages and R&D needs to focus on reducing the use of electricity and hydrogen to upgrade pyrolysis oils. One option to be pursued is to use hydrogen produced internally through steam reforming; however, this could actually result in the emissions being increased by up to 26%. Further research on techno-economics will reveal if two-stage hydrotreatment, esterification and ketonisation can be sustainable in terms of costs.

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