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1 **A life cycle assessment of options for producing synthetic fuel via**

2 **pyrolysis**

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10 **Abstract**

11 The aim of this study was to investigate the sustainability of producing synthetic fuels from

12 biomass using thermochemical processing and different upgrading pathways. Life cycle

13 assessment (LCA) models consisting of biomass collection, transportation, pre-treatment,

14 pyrolysis and upgrading stages were developed. To reveal the environmental impacts

15 associated with greater post-processing to achieve higher quality fuels, six different bio-oil

16 upgrading scenarios were analysed and included esterification, ketonisation, hydrotreating

17 and hydrocracking. Furthermore, to take into account the possible ranges in LCA inventory

18 data, expected, optimistic and pessimistic values for producing and upgrading pyrolysis oils

19 were evaluated. We found that the expected carbon dioxide equivalent emissions could be as

20 high 6000 gCO_{2e}/kg of upgraded fuel, which is greater than the emissions arising from the

21 use of diesel fuel. Other environmental impacts occurring from the fuel production process

22 are outlined, such as resource depletion, acidification and eutrophication.

25

1.   Introduction

27   Approximately 5% of the global transportation demand is met by biofuels, and biomass is set

28   to play an increasingly important role in reducing transport related CO_2 emissions. Currently,

29   the majority of biofuels used for transportation are derived from food crops; this has raised

30   fears of increasing food prices and causing food shortages. There are also concerns with the

31   environmental impacts of using large quantities of fertilizers and pesticides to cultivate

32   certain energy crops (IEA, 2011).

33   Biofuels can be obtained from fast-growing non-food crops, agricultural residues and other

34   waste feedstock. These fuels are often referred to as second-generation biofuels, and they are

35   generally considered more sustainable and environmentally friendly. However, producing

36   second-generation biofuels involves more complex and energy intensive conversion

37   processes. Whilst a significant amount of research has been carried out on the use of first-

38   generation biofuels for transportation, research on second-generation fuels is more limited.

39   There is a range of biochemical and thermochemical processes for converting waste biomass

40   into second-generation biofuels. The thermochemical conversion methods include pyrolysis,

41   liquefaction and gasification, and products from these processes require significant amounts

42   of upgrading to improve their quality. Pyrolysis involves the thermal degradation of matter in

43   the absence of oxygen to produce bio-oil, non-condensable gases and a solid char residue. It

44   has gathered much interest as a promising option for producing synthetic transportation fuels.

45   However, bio-oil from pyrolysis is highly oxygenated, unstable and acidic. This means that

46   the bio-oil quality has to be improved before it can be used as a transportation fuel (Ringer,

47 Putsche and Scahill, 2006). There are a number of upgrading methods, which are being

48 investigated to improve pyrolysis oils. Yet, even if a perfect transportation fuel from

49 pyrolysis can be obtained, it has to offer environmental benefits in comparison to

50 conventional fossil fuels.

51 The environmental impacts of obtaining transportation fuels from a pyrolysis process can be

52 analysed by conducting life cycle assessment (LCA). LCA enables comparisons to be made

53 with fossil fuels and other technological options for producing biofuels. A number of LCA

54 studies on fuels obtained from pyrolysis and other thermochemical conversion processes have

55 been carried out. Iribarren et al. (2012) conducted a life cycle assessment of pyrolysis

56 coupled with hydrotreating. They concluded that the highest impacts were associated with the

57 use of electricity for feedstock processing and natural gas for obtaining hydrogen through

58 steam reforming. Snowden-Swan and Male (2012) conducted a study on pyrolysis with

59 hydrotreating of poplar residues and found the carbon dioxide equivalent (CO_{2e}) emissions to

60 be 32.5 gCO_{2e}/MJ. Peters et al. (2015) simulated a pyrolysis plant and biorefinery for fast

61 pyrolysis of hybrid poplar. An LCA analysis was conducted to see if hydrotreating,

62 hydrocracking, distillation or steam reforming had a more negative impact on the

63 environment. They found that the key contributors to greenhouse gas (GHG) emissions were

64 the pyrolysis plant and the biorefinery, suggesting that the environmental impact could be

65 improved by seeking ways to reduce the electricity consumption. Dang et al. (2014) and Zang

66 et al. (2014) investigated alternative sources of hydrogen for upgrading pyrolysis oils. For

67 conventional natural gas reforming, their results indicated that the GHG emissions would be

68 in the region of 30–40 gCO_{2e}/MJ. In comparison, GHG emissions associated with the use of

69 conventional transportation fuels is around 94 CO_{2e}/MJ.

70 The majority of LCA studies on biofuels obtained from pyrolysis have focused on

71 considering pyrolysis with hydroprocessing (Peters, Iribarren and Dufour, 2015; Dang, Yu

3

72 and Luo, 2014; Zhang, 2014; Iribarren, Peters and Dufour, 2012; Snowden-Swan and Male,

73 2012). However, the structural complexity of bio-oil makes it difficult to find a single

74 comprehensive upgrading method; therefore, there is a rising interest in using a synergy of

75 technologies. There are many upgrading options and additional processing stages, which

76 must be considered if fuels of a comparable quality to fossil fuels are to be obtained. It is also

77 difficult to compare LCA studies that have considered different upgrading methods. The

78 assumptions made among studies vary, such as the feedstock type, pyrolysis technology and

79 processing conditions (e.g. slow, intermediate and fast pyrolysis). LCA results are also highly

80 subjective and variable, and there is often a lack of transparency with the data used.

81 This study aims to analyse the environmental impacts of the main emerging bio-oil upgrading

82 technologies, so that a more informed comparison can be made to guide future R&D on

83 obtaining synthetic fuel from pyrolysis. Moreover, the possible range in LCA data needs to

84 be investigated to highlight the sensitivity of the results. This will enable a combination of

85 pyrolysis and upgrading methods to be identified, which give good fuel yields and quality,

86 whilst still offering environmental benefits in comparison to fossil fuels.

87 In the following section, the method adopted for this study is outlined and the pyrolysis

88 upgrading scenarios are defined. Gathered LCA inventory data, including possible ranges in

89 values, are presented in Section 2.2. The LCA results are outlined and discussed in Section 3.

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95   **2.   Materials and methods**

96   Different bio-oil upgrading methods are initially reviewed to identify the most promising

97   combination of processes to pursue. An outcome from this is six scenarios to be analysed and

98   compared in terms of their environmental impact.

99   A life cycle assessment of each scenario is performed using GaBi Professional with the

100   integrated Ecoinvent database. A well-to-wheel analysis is adopted to consider all the

101   resource inputs and outputs from biomass cultivation to fuel combustion in a vehicle. The

102   LCA system boundary also includes biomass transportation, biomass preparation, an

103   integrated bio-oil production and upgrading plant, and fuel transportation (see Figure 1). The

104   functional unit used to compare the alternative scenarios is one kilogram of upgraded fuel.

105   One mega joule of energy content of the upgraded fuel is not used due to the uncertainties of

106   fuel quality in certain scenarios, but conversions are made where data is available.

107   To enable the alternative upgrading scenarios to be compared, a fixed feedstock and pyrolysis

108   processing technology is used throughout. Corn stover is analysed as it has been considered

109   as a suitable waste feedstock for pyrolysis in a range of studies (Dang, Yu and Luo, 2014;

110   Zhang, 2014). The fluidised bed reactor operating under fast pyrolysis conditions is assumed

111   as it is a popular option due to its ease of operation, high stability under pyrolysis conditions

112   and high oil yields (Ringer, Putsche and Scahill, 2006).

113   Assessing the environmental impacts of obtaining fuel from residual stover waste is

114   challenging as different allocation methods can have a significant impact on the LCA results.

115   Previous researches on corn stover have had a tendency to use subdivision to avoid allocation

116   to corn grain and subsequent co-products (Murphy and Kendall, 2013). This study assumes

117   changes to an existing continuous corn production system and assigns additional processes

118   for the collection and nutrient replacement of partially gathered stover, which would have

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119 otherwise been left unharvested. Subdivision of the co-products arising in each scenario is

120 difficult due to the lack of data and established practices with using pyrolysis products and

121 synthetic fuels. Methods adopted in previous studies include no allocation to the by-

122 products—due to the large uncertainties—and mass-, energy- and value- based approaches

123 (Kendall and Chang, 2009; Larson, 2006). In this study, the total energy and material inputs

124 consumed in the production of by-products are included. Where possible, the by-products are

125 used within the system (e.g. heat generation from the pyrolysis gases). Displacement of

126 energy had the production of the by-products been made via other routes and their market

127 worth are not considered.

128 Due to model uncertainties, where possible, minimum, expected and maximum values have

129 been obtained for each stage of the LCA analysis from the literature, GaBi Professional

130 databases and Ecoinvent 3.3. This allows the most likely values and possible ranges to be

131 obtained in terms of the environmental impacts of each upgrading stage. The sensitivity of

132 the results based on fertiliser and hydrogen usage are further examined. The global warming

133 potential (GWP) of each processing stage and utilised resource is investigated and other

134 environmental impact categories are evaluated based on the CML2001 impact assessment

135 method (Guinée, 2002).

136

137 **2.1   Definition of the bio-oil upgrading scenarios**

138 To upgrade bio-oil obtained through the pyrolysis of biomass, there are a number of physical

139 (filtration, solvent addition and emulsification) and catalytic and chemical methods

140 (hydrotreating, hydrocracking, esterification, ketonisation, and gasification to syngas

141 followed by Fischer-Tropsch). This study focuses on the pyrolysis process and catalytic and

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142 chemical upgrading methods. Gasification with Fischer-Tropsch is considered to be beyond

143 the scope of the study.

144 The process of hydrotreating and hydrocracking is often referred to as hydroprocessing.

145 Hydrotreating involves the use of hydrogen and catalysts to reduce levels of sulphur, nitrogen

146 and oxygen. The process takes place at relatively modest temperatures (150°C–400°C)

147 (Gandarias and Arias, 2013) and is also known as hydrodeoxygenation. Depending on the

148 amount of hydrotreating performed, different degrees of deoxygenation can be achieved.

149 Two-stage hydrotreating can also be carried out which has the potential to achieve higher

150 degrees of deoxygenation, reduce hydrogen consumption and overcome bio-oil instability

151 issues. The first stage, takes place at a relatively low temperature (270ºC) and hydrotreating

152 is performed at a higher temperature (350ºC) in the second stage (Elliott, 2007). Once bio-oil

153 has been hydrotreated, it can be hydrocracked to break carbon-carbon bonds and converted

154 into shorter-chain hydrocarbons, which are more suitable as transportation fuels.

155 A promising option for improving bio-oil quality prior to hydrotreating is esterification

156 (Ciddor et al., 2015). Bio-oil produced from biomass normally has a high oxygen content

157 (20–50wt %) and acidity (pH=2.5–3), resulting in a low heating value (16–18MJ/kg), high

158 viscosity and corrosiveness. Esterification reduces acidity by neutralising carboxylic acids in

159 the bio-oil; this improves stability and reduces catalyst deactivation and hydrogen

160 consumption during hydrotreating. Another pre-hydrotreating method is ketonisation, which

161 is a condensation reaction that enables the partial reduction of oxygen in the form of water

162 (Milina, Mitchell and Pérez-Ramírez, 2014). Ketonisation is a reaction that transforms two

163 carboxylic acids into a ketone, carbon dioxide and water (Pham et al., 2013). Ketonisation

164 also removes highly reactive shorter carboxylic acids, by converting acetic acid into acetone,

165 and increases the size of carbon chains, which improves product stability. Furthermore,

166 acetone can be converted, along with other bio-oil components, into longer chain

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167 hydrocarbons through aldol condensation and subsequent hydrogenation; this prevents small

168 molecules being lost in the form of light gases (Pham et al., 2013; Pham et al., 2012).

169 Ketonisation can be performed on pyrolysis vapours, but conducting ketonisation on the

170 liquid phase minimises decomposition and re-polymerisation of the bio-oil. Phase separation

171 is required to obtain light oxygenates for the ketonisation process, and this can be followed

172 by aldol condensation (Pham et al., 2012). The sugar and lignin derived components can then

173 undergo esterification.

174 Based on the reviewed upgrading methods, six alternative scenarios are developed: i)

175 hydrotreating and hydrocracking; ii) esterification, hydrotreating and hydrocracking; iii)

176 esterification/ketonisation, hydrotreating and hydrocracking; iv) two-stage hydrotreating and

177 hydrocracking; v) esterification, two-stage hydrotreating and hydrocracking, and vi)

178 esterification/ketonisation, two-stage hydrotreating and hydrocracking. Scenarios 1 and 4

179 have been outlined in numerous studies and several LCA studies of scenario 1 have been

180 performed by other researchers (Peters, Iribarren and Dufour, 2015; Dang, Yu and Luo, 2014;

181 Zhang, 2014; Iribarren, Peters and Dufour, 2012; Snowden-Swan and Male, 2012). A few

182 authors have considered introducing esterification into the upgrading process (scenarios 2 and

183 5), but the environmental impacts were not evaluated (Ciddor et al., 2015; Milina, Mitchell

184 and Pérez-Ramírez, 2014). More recently, ketonisation and aldol condensation have been

185 suggested (Milina, Mitchell and Pérez-Ramírez, 2014), and scenarios 3 and 6 are extensions

186 of a process proposed by Pham et al. (2014). The bio-oil production process and the six

187 upgrading scenarios to be analysed are outlined in Figure 2, and their main differences are

188 summarised in Table 1.

189 **2.2   Inventory data**

190 The inventory data gathered and used for modelling each stage of the system is now outlined.

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191   2.2.1 Feedstock cultivation, collection and transport

192   The inventory data associated with corn cultivation depends on the assumed soil conditions

193   and anticipated crop yields. The majority of corn fields are treated with fertiliser to meet the

194   high demand of nitrogen, phosphate and potassium in corn cultivation, and additional

195   requirements are needed when corn stover is removed. Crop rotation is not considered, which

196   could reduce these requirements. Most LCA studies on corn stover use an allocation approach

197   based on nutrient replacement, with stover comprising 0.8% N, 0.2% P_2O_5, and 1.45% K_2O.

198   For a crop yield of 147 bushels/acre, 1.6 dry tonnes/acre of stover can be sustainably

199   gathered, as a stover collection rate of 40% is considered suitable to avoid soil quality

200   degradation (Murphy and Kendall, 2013). Annual fertiliser application rates are determined

201   based on common fertiliser nutrient composition: ammonium phosphate nitrate (8% N, 52%

202   P_2O_5), ammonium nitrate (35% N) and potassium chloride (60% K_2O). Field emissions

203   arising from the denitrification process by soil micro-organisms are taken as 1.25% g N_2O/ g

204   N: all the emissions allocated to K, N and P are provided in Nemecek et al. (2007).

205   Direct land use change emissions depend on soil characteristic baseline assumptions. Carbon

206   stored in soil can be released during field preparations or sequestered in degraded soils;

207   however, stover removal is expected to reduce potential carbon sequestration. Most studies

208   do not include land change emissions, assuming existing corn cropland would be used for

209   gathering stover (Larson, 2006); however, land emissions could have a significant impact and

210   should be considered in specific site evaluations.

211   The energy requirement for cutting, baling, field transport and on-site storage of the stover

212   has been reported to range from 0.22 (Dang, Yu and Luo, 2014) to 0.83 MJ/kg of stover

213   (Murphy and Kendall, 2013). This study assumes that this demand would be met with diesel

214   fuel. The grain is not considered within the system boundary and therefore the additional

215   fertiliser and energy requirements for gathering corn grain are not included.

216   Subsequent transportation would be required to take the raw feedstock from a collection point

217   to the bio-oil production plant. The transportation distance is assumed to range from 50–100

218   km, with 75 km being the most likely value. A 9.3 t payload truck from the GaBi Professional

219   database has been used to meet this transportation requirement, which is equivalent to

220   minimum, expected and maximum diesel usages of 0.05, 0.075 and 0.1 MJ/kg of delivered

221   corn stover, respectively (GaBi, 2017).

222   2.2.2 Pre-treatment

223   Pre-treatment of the feedstock prior to pyrolysis involves grinding and drying to reduce

224   particle size and moisture content. Mechanical feedstock size reduction is required because

225   fluidized bed reactors are designed to use small particles ranging from 2-3 mm. The expected

226   energy for grinding and chopping is expected to range from 0.011–0.057 kWh/kg (Mani,

227   Tabil and Sokhansanj, 2004; Zhang, 2014). To improve reactor temperature stability and

228   reduce pyrolysis processing energy requirements, the moisture content needs to be reduced to

229   less than 10% (Bridgwater and Peacocke, 2000), and this can be achieved using steam and a

230   trommel. Zhang (2014) assumes a steam requirement of 0.085 kg/kg of pre-treated corn

231   stover and Dang et al. (2014) state an energy requirement of 0.148 kWh/kg of pre-treated

232   corn stover. The pyrolysis non-condensable gases (NCG) are expected to have an HHV of 6

233   MJ/kg and yields of 10-20% are typical (Mullen et al., 2010); thus there would be sufficient

234   gas to combust to meet this demand. For higher pyrolysis oil yields, both the gas and char

235   may need to be used. Using the pyrolysis gases for drying has been assumed in other studies

236   (Peters, Iribarren and Dufour, 2015; Han et al., 2011), and therefore the energy requirement is

237   often neglected.

238   2.2.3 Pyrolysis process

239 The pyrolysis plant is assumed to process 2000 metric tons per day of prepared corn stover at

240 500 °C (Wright et al., 2010; Zhang, 2014). Electricity is typically used as the energy input to

241 a pyrolysis system, with power requirements ranging from 0.14–0.487 kWh/kg of bio-oil

242 produced (Dang, Yu and Luo, 2014; Zhang, 2014). A value of 0.417 is suggested in (Zhang,

243 2014), which has been chosen as the expected value. The yield of bio-oil from the fast

244 pyrolysis of corn stover is typically around 62-75 wt% (Dang, Yu and Luo, 2014; Zhang,

245 2014; Han et al., 2011), although yields as high as 80% have been suggested (Bulushev and

246 Ross, 2011).

247 2.2.4 Esterification

248 Esterification is performed within a temperature range of 70–170°C (Gunawan et al., 2012).

249 The yield of upgraded bio-oil in conventional conditions (100 ^{o}C) when using a zeolite

250 catalyst is approx. 62 wt% (Peng et al., 2009). Ideal ethanol to oil ratios of 3:1 (Bulushev and

251 Ross, 2011) and 5:1 (Zhang et al., 2014) have been reported for the esterification process.

252 However, similar yields of upgraded bio-oil (approx. 60%) have been obtained using 2 wt.%

253 sulphuric acid and lower ethanol to oil ratios ranging from 1:1 to 3:1 (Abdul Aziz et al.,

254 2017). Sugar cane, maize and sugar beet are suitable sources for producing bioethanol

255 (Muñoz et al., 2014). For the purposes of this study, bioethanol produced from maize, as

256 given by the Ecoinvent database, has been used. Esterification of the bio-oil in super-critical

257 conditions (250–300°C) has not been considered as it can affect bio-oil composition (Peng et

258 al., 2009). Based on a specific heat capacity of 2.435 kJ/kg of bio-oil, neglected heat losses,

259 an initial bio-oil temperature of 30 °C and the possible operating temperature values, the

260 energy requirement is expected to range from 0.027–0.095 kWh/kg.

261 2.2.5 Ketonisation

262   Ketonisation can be performed on the light oxygenates fraction of the pyrolysis oil at around

263   400 $^{\circ}$C (Snell et al., 2013). The quantity of electricity required in the process is calculated to

264   be 0.25 kWh/kg of light oxygenates. The acetone yield obtained through ketonisation depend

265   on the catalyst, temperature and reaction time, but it is expected to be around 46% using a

266   Ru/TiO$_2$/C catalyst at 5 wt% (Pham et al., 2012); 349g CO_2 would be formed based on the

267   reaction stoichiometry.

268   Phase separation of bio-oil into light oxygenate, sugar derived and lignin derived components

269   can be achieved by processing biomass at 300°C to get acetic acid and acetol. This is

270   followed by heating at 400°C to obtain furfurals, and finally processing at 550°C to get

271   phenolics (Pham, Shi and Resasco, 2014). The additional energy requirements at the

272   pyrolysis stage to achieve phase separation have not been included. Separation is expected to

273   obtain 10% light oxygenate, 30% sugar derived and 60% lignin derived components (Pham et

274   al., 2013; Zhang et al., 2007).

275   2.2.6 Aldol condensation

276   Aldol condensation takes place at 120°C; 5 wt% Pd/MgO–ZrO2 catalyst is used to process

277   acetone from ketonisation of the light oxygenates and sugar derived oils having undergone

278   esterification (Barrett et al., 2006). The yield from aldol condensation is expected to be

279   51.4% (Pham, Shi and Resasco, 2014).

280   2.2.7 Hydrotreating and hydrocracking

281   Single-stage hydrotreating is usually conducted for 4 hours using noble metal catalysts (Ru/C

282   and Pd/C) and pressures and temperature of up to 200 bar and 400°C (Wildschut, 2009).

283   Hydrotreating of fast pyrolysis oils at 180–250°C and pressures of 130-142 bar using

284   ruthenium have been found to reduce oxygen content from around 40 to 18–27 wt%

285   (Wildschut, 2009; Wang, Male and Wang, 2013). Upgraded bio-oil yields reported for

286 hydrotreating are more variable and range from 30–65% (Wright et al., 2010; Wildschut,

287 2009; Holmgren et al., 2008) with the highest yields being obtained when using 5 wt% Ru/C.

288 Hydrotreating pyrolysis oils obtained from corn stover using an Ru/C catalyst can achieve a

289 25–26 wt% oxygenated product and yields between 54–67% (Capunitan and Capareda,

290 2014). Hydrogen consumption for corn stover has been reported to range between 69 and

291 128 litres per litre of feed; higher values of 205 and 252 litres of hydrogen per litre of feed

292 have been reported for mixed wood and poplar (Dang, Yu and Luo, 2014; Elliott et al., 2009).

293 Two-stage hydrotreating involves performing mild hydrotreating at 150-270°C/80-100 bar,

294 followed by moderate processing at 350–425°C/140–200 bar (Jones et al., 2013). The total

295 residence times for two-stage hydrotreating range from 2 to 4 hours (Jones et al., 2013;

296 Wildschut, 2009). In the first stage, Ru/C is used, whereas a Pt/C or NiMo catalyst is

297 normally used in the second stage. Catalyst quantities are normally around 3–5 wt%

298 (Wildschut et al., 2009; Wildschut, Melián-Cabrera and Heeres, 2010) with lifetimes of 700

299 to 1752 hours (Snowden-Swan et al., 2016). Therefore, the expected catalyst requirement is

300 0.1–0.3 g/kg of bio-oil, based on a 4 hour residence time. Reports have claimed that two-

301 stage hydrotreating enables a 13% reduction in hydrogen to be achieved (Gandarias and

302 Arias, 2013), whereas other studies have found the hydrogen consumption to remain

303 proportional to the level of deoxygenation (Boscagli et al., 2015). The amount of

304 deoxygenation can be as low as 2 wt% (Han et al., 2011), but 6–11 wt% is more likely

305 (Wang, Male and Wang, 2013; Wildschut et al., 2009). Hydrogen consumption is expected to

306 range from 58 g/kg (Jones et al., 2013) to 112 g/kg of hydrotreated biofuel (Jones et al.,

307 2009). Other authors have reported 69 g/kg (Dang, Yu and Luo, 2014). The assumption is

308 made that hydrogen is obtained from conventional steam reforming of natural gas; however,

309 make-up hydrogen could be obtained from the off-gases from the pyrolysis and

310 hydroprocessing stages. The overall yield of deoxygenated bio-oil for two-stage

13

311   hydrotreating is expected to range from 30–44% (Jones et al., 2009; Zheng, Chang and Fu,

312   2015).

313   Hydrocracking is performed at temperatures between 400–450°C and at 100–140 bar (Wright

314   et al., 2010). The catalysts used in the process are 3–5 wt% Ni-HZSM-5 zeolites (Weng et al.,

315   2015). Hydrogen consumption can fluctuate between 1.5 wt% to 4.0 wt% (JSC SIE

316   Neftehim, 2015). Output bio-oil yields of 75% are expected (Sayles and Romero, 2011). The

317   amount of deoxygenation after hydrocracking is expected to range from 0.3–5 wt%

318   (Wildschut et al., 2009; Elliott and Neuenschwander, 1997; Elliott et al., 2009).

319   The electricity requirement largely depends on the assumptions made regarding processing

320   temperatures, times and heat losses, pressurisation and pumping. Electricity requirements for

321   hydrotreating and hydrocracking have been reported to be 0.23 kWh/kg (Dang, Yu and Luo,

322   2014) and 0.22 kWh/kg of produced biofuel (Zhang, 2014). Electric energy requirements are

323   very low where the exothermic hydrotreating reactions are considered and values of only

324   0.034 kWh/kg and 0.054 kWh/kg have been asserted for two-stage hydrotreating and

325   hydrocracking respectively (Iribarren, Peters and Dufour, 2012).

326   2.2.8 Transportation and distribution of biofuel

327   The biofuel transportation and distribution was assumed to be via a 9.3t payload

328   truck travelling a total distance of 150 km. Minimum and maximum values of 100 km and

329   200 km are used to account for the possible range in travelled distance.

330   A summary of the inventory data is given in Table 2.

331   **3.   Results and discussion**

332   The expected carbon dioxide equivalent emissions associated with the production (well-to-

333   tank) and use (tank-to-wheel) of synthetic fuel from pyrolysis are shown for each upgrading

334   scenario in Figure 3; the CO_2 absorbed during biomass growth is shown separately and based

335   on corn stover absorbing 0.83 kgCO$_2$/kg (Zan et al., 2001). For comparison, the emissions

336   associated with fossil fuel are provided. Error bars indicate the most optimistic results based

337   on a combination of the most favourable inventory data values.

338   For synthetic fuel obtained from hydrotreating and hydrocracking pyrolysis oil (scenario 1),

339   the expected production emissions of 2240 gCO$_{2e}$/kg of upgraded fuel are around 50% of the

340   well-to-wheel CO$_{2e}$ emissions associated with diesel or petrol fuel. The well-to-tank

341   emissions are relatively low for fossil fuel at around 307–659 gCO$_{2e}$/kg, but the tank-to-

342   wheel emissions are significantly higher at approximately 3387–3571 gCO$_2$/kg (Eriksson and

343   Ahlgren, 2013). The CO$_2$ emissions released during the combustion of synthetic fuel depends

344   on carbon content and they can be considered carbon neutral; carbon contents of 77-89%

345   have been reported for various degrees of hydrodeoxygenation (Mante et al., 2016) and tank-

346   to-wheel emissions are expected to range from 2850-3200 gCO$_2$/kg of fuel (Zhang, 2014;

347   Han et al., 2011).

348   Scenario 1 is the most commonly considered pyrolysis oil upgrading pathway in the

349   literature. The upgraded fuel from scenario 1 is expected to have a lower heating value of 42

350   MJ/kg (Peters, Iribarren and Dufour, 2015), which would suggest an impact of 53.6

351   gCO$_{2e}$/MJ. This finding is comparable with values reported for similar systems: 39.4–55

352   gCO$_{2e}$/MJ has been suggested by other researchers for biofuel from corn stover (Zhang,

353   2014; Dang, Yu and Luo, 2014). Peters et al. (2015) use a well-to-wheel approach to

354   determine the net emissions from synthetic fuels to be 40 gCO$_{2e}$/MJ. Other studies provide

355   values of 38.9 gCO$_{2e}$/MJ when using hybrid poplar (Snowden-Swan and Male, 2012) and

356   33.3gCO$_{2e}$/MJ for southern pine (Jones et al., 2013). However, this study reveals the

357   additional CO$_{2e}$ emissions that will arise from further upgrading to improve fuel quality.

358   The additional upgrading steps in scenarios 2-6, make the CO_{2e} emissions comparable or

359   greater than those associated with using fossil fuel. For example, the emissions caused by

360   producing biofuel in scenario 6 are 43% higher than the total CO_{2e} emissions from diesel

361   fuel. The potential to reduce the CO_{2e} emissions is significant though, as evidenced by the

362   large errors bars. Under more optimistic conditions, the different scenario production

363   emissions range from 1160 to 2930 gCO_{2e}/ kg, which represent a potential decrease of 47%

364   to 52%. However, scenario 6 appears favourable when considering a well-to-wheels analysis

365   including the CO_2 absorbed, as 12.2 kg of corn stover is required to produce 1 kg of biofuel

366   in scenario 6, whereas, in scenario 1, only 3.8 kg of corn stover is required.

367   Further details on the downstream use of the various by-products from the different

368   processing stages are required to give a more accurate representation of the net emissions.

369   When the non-condensable gases are flared or used for heat recovery, up to 17% of the

370   feedstock carbon could be released back into the atmosphere (Mullen et al., 2010), and these

371   emissions are not included in the production emissions. Biochar can act as a long-term carbon

372   sink enabling as much as 20% of the carbon to be recovered during fast pyrolysis (ibid). If the

373   char were combusted to meet the thermal energy requirement in the pyrolysis reactor, credits

374   can be applied to account for the offset fossil fuel requirement; however, the use of electricity

375   is more practical.

376   Figure 4 shows the CO_{2e} emission contributions from the use of electricity, hydrogen,

377   transport, fertilisers, catalysts, ethanol and natural gas. Minimum, expected and maximum

378   values are shown for each scenario. Electricity is the largest contributor with a 50–63%

379   expected share of the total emissions. However, for optimistic conditions, the emissions

380   associated with the use of electricity are reduced by around 70%. At 17-33%, the second

381   largest CO_{2e} contribution comes from the use of hydrogen. These CO_{2e} emissions could be

382   reduced by around 25–29% based on the range of hydrogen consumption values reported in

383   the literature. Fertilisers, transport and catalysts contribute respectively 14–17%, 2.2% and

384   1.2–3% of the total CO_{2e} emissions. Net CO_{2e} emissions from using ethanol obtained from

385   maize in the US are slightly carbon negative (-20 to -70 gCO_{2e}/kg) and the source of ethanol

386   can influence the results significantly.

387   The total CO_{2e} emissions from each stage of the system are shown in Figure 5. The expected

388   CO_{2e} emissions prior to bio-oil upgrading are significant with cultivation, pre-treating and

389   pyrolysis accounting for around 54-64% of the emissions. In an optimistic scenario, e.g.

390   where energy recovery or alternative energy sources to electricity can be used, the share of

391   emissions from pyrolysis are reduced by approximately 74%.

392   The high proportion of CO_{2e} emissions associated with hydrogen and electricity highlight the

393   importance of using more sustainable alternatives, which could also reduce operating costs.

394   Moreover, as the pyrolysis and hydroprocessing stages made the most significant contribution

395   to the total CO_{2e} emissions, this identifies that these stages would benefit the most from R&D

396   to achieve gains in environmental and technical performance. The average EU27 electricity

397   grid mix has been used in this study; however, alternative sources such as natural gas,

398   pyrolysis gases and other renewables can be considered.

399   The pessimistic inventory data provided in this study reveals that the emissions for scenarios

400   1–6 are around 1.5 to 3 times higher than fossil fuel, which is a major concern if facilities and

401   supply chains conduct inefficient practices. This result also highlights the large uncertainty

402   that remains in this field with determining the environmental benefits of using synthetic fuels

403   obtained from the thermochemical conversion of waste feedstocks, and the need for better

404   quality primary data on bio-oil upgrading system performance.

405   Other environmental impacts occurring from the production of fuels (well-to-tank) according

406   to the CML 2001 impact assessment method are summarised in Table 3. Minimum and

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407   expected impacts for scenarios 1-6 are shown in comparison to low sulphur diesel fuel from

408   the Ecoinvent database. Whereas scenario 1 provides environmental advantages over diesel,

409   scenarios 2-6 increase several negative environmental impacts. For scenarios 2-6, the

410   expected eutrophication and acidification potentials range respectively from 0.0026–0.005 kg

411   PO_4^{3-} eq. and 0.0098–0.027 kg SO_2 eq., which are higher than the impacts associated with

412   diesel fuel (0.00167 kg PO_4^{3-} eq and 0.0058 kg SO_2 eq.). In all scenarios, the expected human

413   and eco toxicity potentials are also higher than diesel fuel. These results are to be expected

414   due to the high quantities of fertiliser and other material and energy resources used in

415   scenarios 2-6.

416   Different farming practices can heavily influence the fertiliser requirements. The sensitivity

417   of the GWP and eutrophication result based on ammonium nitrate usage in scenario 1 is

418   further examined in Figure 6a. It shows that the eutrophication potential would be reduced to

419   0.00061 kg PO_4^{3-} eq if ammonium nitrate fertiliser were avoided. The element abiotic

420   depletion potential (ADP) is also high in all scenarios as a result of fertiliser usage.

421   Interestingly, the fossil ADP value is also higher than diesel fuel in scenarios 2-6, which is

422   caused by the increased hydrogen consumption in the more advanced upgrading processes.

423   However, the minimum values reveal that savings could be achieved with the exception of

424   scenario 6. The sensitivity of the GWP and fossil ADP values based on the hydrogen

425   consumption in scenario 1 is shown in Figure 6b. An increase in hydrogen consumption from

426   50 to 168 g/kg of upgraded fuel doubles the fossil ADP and increases the GWP from around

427   1.9 to 2.8 kg $CO_{2e.}$ Whilst conventional externally sourced hydrogen from natural gas has

428   been considered in this study, other authors have suggested that internal steam reforming of

429   by-products to produce hydrogen is a more promising option (Dang, Yu and Luo, 2014).

430   Future LCA studies on synthetic fuels must consider the wide range of environmental

431   impacts that occur during the production of synthetic fuels, as many negative environmental

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432 impacts increase in comparison to the diesel and petrol production processes. In further work,

433 the materials used in system construction could also be taken into account. Different

434 allocation methods for stover and pyrolysis by-products need to be investigated to see if

435 environmental benefits can be gained. For example, economic and energy-based allocation

436 methods have been compared for corn and stover production (Murphy and Kendall, 2013). A

437 displacement approach could also be considered as corn stover would likely be used

438 elsewhere (e.g. as cattle feed). As more and more companies seek to commercialise the

439 production of synthetic fuel via pyrolysis, great care must be taken to ensure that

440 environmental gains over conventional fossil fuels are being achieved and a trade-off

441 between environmental impact, cost and product quality has to be made.

442 **4.   Conclusion**

443 This study identifies that favourable CO_{2e} emission reductions can be achieved by using

444 synthetic fuel from pyrolysis in comparison to conventional diesel fuel. However, if

445 inefficient practices are followed, a low quality synthetic fuel that nearly triples CO_{2e}

446 emissions in comparison to fossil fuel will be produced. High quality fuels obtained via

447 esterification, two-stage hydrotreating and hydrocracking, or esterification, ketonisation, adol

448 condensation, two-stage hydrotreating and hydrocracking, are expected to increase a range of

449 other environmental impact indicators. Esterification and single-stage hydrotreating (scenario

450 2) or two-stage hydrotreating (scenario 4) can provide a reasonable trade-off between product

451 quality and achievable environmental gains.

452

453 **Figures and Tables**

454 **Figure 1:** Life cycle system boundaries for the production and use of synthetic fuels from

455 fast pyrolysis and fossil fuel.

19

456   **Figure 2:** Six alternative bio-oil upgrading scenarios to produce liquid fuels from pyrolysis.

457   **Figure 3:** The CO_{2e} emissions associated with the production and use of synthetic fuel for six

458   different upgrading scenarios. Error bars are used to show the minimum CO_{2e} emissions

459   possible and, under these conditions, less feedstock is required to produce a kilogram of

460   biofuel.

461   **Figure 4:** Minimum, expected and maximum CO_{2e} emissions associated with the use of

462   electricity, hydrogen, transport, fertilisers, catalysts, ethanol and natural gas during the

463   production of synthetic fuel from pyrolysis oil.

464   **Figure 5:** Minimum, expected and maximum CO_{2e} emissions associated with each

465   processing stage during the production of synthetic fuel from pyrolysis oil.

466   **Figure 6a-b:** Sensitivity of the environmental impacts arising from scenario 1 based on

467   ammonium nitrate (a) and hydrogen (b) usage.

468   **Table 1:** Summary of the six different bio-oil upgrading scenarios.

469   **Table 2:** LCA inventory data for the production of synthetic fuels via fast pyrolysis and

470   upgrading.

471   **Table 3:** Environmental impacts conforming to the CML 2001 assessment method for the

472   production of synthetic and diesel fuel.

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474   **References**

475   1. Abdul Aziz, S.M., Wahi, R., Ngaini, Z., Hamdan, S., Yahaya, S.A., 2017.

476   Esterification of Microwave Pyrolytic Oil from Palm Oil Kernel Shell, Journal of

477   Chemistry. Vol. 2017.

478   2. Barrett, C., Chheda, J., Huber, G., Dumesic, J., 2006. Single-reactor process for

479   sequential aldol-condensation and hydrogenation of biomass-derived compounds in

480   water, Applied catalysis B: environmental. 66, 111-118.

481   3. Boscagli, C., Raffelt, K., Zevaco, T.A., Olbrich, W., Otto, T.N., Sauer, J., Grunwaldt,

482   J., 2015. Mild hydrotreatment of the light fraction of fast-pyrolysis oil produced from

483   straw over nickel-based catalysts, Biomass Bioenergy. 83, 525-538.

484   4. Bridgwater, A.V., Peacocke, G.V.C., 2000. Fast pyrolysis processes for biomass,

485   Renewable and Sustainable Energy Reviews. 4, 1-73.

486   5. Bulushev, D.A., Ross, J.R., 2011. Catalysis for conversion of biomass to fuels via

487   pyrolysis and gasification: a review, Catalysis Today. 171, 1-13.

488   6. Capunitan, J.A., Capareda, S.C., 2014. Hydrotreatment of corn stover bio-oil using

489   noble metal catalysts, Fuel Process Technol. 125, 190-199.

490   7. Ciddor, L., Bennett, J.A., Hunns, J.A., Wilson, K., Lee, A.F., 2015. Catalytic

491   upgrading of bio-oils by esterification, Journal of Chemical Technology and

492   Biotechnology. 90, 780-795.

493   8. Dang, Q., Yu, C., Luo, Z., 2014. Environmental life cycle assessment of bio-fuel

494   production via fast pyrolysis of corn stover and hydroprocessing, Fuel. 131, 36-42.

495   9. Elliott, D., Neuenschwander, G., 1997. Liquid fuels by low-severity hydrotreating of

496   biocrude, Anonymous Developments in thermochemical biomass conversion.

497   Springer, pp. 611-621.

498   10. Elliott, D.C., 2007. Historical developments in hydroprocessing bio-oils, Energy

499   Fuels. 21, 1792-1815.

500   11. Elliott, D.C., Hart, T.R., Neuenschwander, G.G., Rotness, L.J., Zacher, A.H., 2009.

501   Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon

502   products, Environmental Progress & Sustainable Energy. 28, 441-449.

503   12. Eriksson, M., Ahlgren, S., 2013. LCAs of petrol and diesel - a literature review, 058,

504   ISSN 1654-9406.

505   13. GaBi, 2017. Process data set: Truck, Euro 3, 12-14t gross weight / 9,3t payload

506   capacity; http://gabi-documentation-2017.gabi-software.com/xml-

507   data/processes/5c4768b3-6b63-44a9-8c67-ef6504f75a52.xml.

508   14. Gandarias, I., Arias, P.L., 2013. Hydrotreating catalytic processes for oxygen removal

509   in the upgrading of bio-oils and bio-chemicals. INTECH Open Access Publisher.

510   15. Guinée, J., 2002. Handbook on Life Cycle Assessment - Operational Guide to the ISO

511   Standards, 1st ed. Springer, Netherlands.

512   16. Gunawan, R., Li, X., Larcher, A., Hu, X., Mourant, D., Chaiwat, W., Wu, H., Li, C.,

513   2012. Hydrolysis and glycosidation of sugars during the esterification of fast pyrolysis

514   bio-oil, Fuel. 95, 146-151.

515   17. Han, J., Elgowainy, A., Palou-Rivera, I., Dunn, J.B., Wang, M.Q., 2011. Well-to-

516   wheels analysis of fast pyrolysis pathways with the GREET model.

517   18. Holmgren, J., Nair, P.N., Elliott, D.C., Bain, R., Marinangelli, R., 2008. Converting

518   pyrolysis oils to renewable transport fuels: processing challenges & opportunities.

519   19. IEA, 2011. Biofuels for Transport Roadmap.

520   https://www.iea.org/publications/freepublications/publication/Biofuels_foldout.pdf,.

521   20. Iribarren, D., Peters, J.F., Dufour, J., 2012. Lyfe cycle assessment of transportation

522   fuels from biomass pyrolysis, Fuel. 812-821.

523   21. ISO, 2006. Environmental management–life cycle assessment–principles and

524   framework. London: British Standards Institution. ISO 14040.

525   22. Jones, S.B., Valkenburg, C., Walton, C.W., Elliott, D.C., Holladay, J.E., Stevens,

526   D.J., Kinchin, C., Czernik, S., 2009. Production of gasoline and diesel from biomass

527   via fast pyrolysis, hydrotreating and hydrocracking: a design case. Pacific Northwest

528   National Laboratory Richland, WA.

529   23. Jones, S., Meyer, P., Snowden-Swan, L., Padmaperuma, A., Tan, E., Dutta, A.,

530   Jacobson, J., Cafferty, K., 2013. Process design and economics for the conversion of

531   lignocellulosic biomass to hydrocarbon fuels: fast pyrolysis and hydrotreating bio-oil

532   pathway.

533   24. JSC SIE Neftehim, 2015. Heavy Residues Hydrocracking.

534   http://nefthim.com/manual/heavy-residues-hydrocracking/.

535   25. Kendall, A., Chang, B., 2009. Estimating life cycle greenhouse gas emissions from

536   corn–ethanol: a critical review of current U.S. practices, Journal of Cleaner

537   Production. 17, 1175-1182.

538   26. Larson, E.D., 2006. A review of life-cycle analysis studies on liquid biofuel systems

539   for the transport sector, Energy for Sustainable Development. 10, 109-126.

540   27. Mani, S., Tabil, L.G., Sokhansanj, S., 2004. Grinding performance and physical

541   properties of wheat and barley straws, corn stover and switchgrass, Biomass

542   Bioenergy. 27, 339-352.

543   28. Mante, O.D., Dayton, D.C., Gabrielsen, J., Ammitzboll, N.L., Barbee, D., Verdier, S.,

544   Wang, K., 2016. Integration of catalytic fast pyrolysis and hydroprocessing: a

545   pathway to refinery intermediates and "drop-in" fuels from biomass, Green Chem. 18,

546   6123-6135.

547   29. Milina, M., Mitchell, S., Pérez-Ramírez, J., 2014. Prospectives for bio-oil upgrading

548   via esterification over zeolite catalysts, Catalysis Today. 235, 176-183.

549   30. Mullen, C.A., Boateng, A.A., Goldberg, N.M., Lima, I.M., Laird, D.A., Hicks, K.B.,

550   2010. Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis,

551   Biomass Bioenergy. 34, 67-74.

552   31. Muñoz, I., Flury, K., Jungbluth, N., Rigarlsford, G., i Canals, L.M., King, H., 2014.

553   Life cycle assessment of bio-based ethanol produced from different agricultural

554   feedstocks, The International Journal of Life Cycle Assessment. 19, 109-119.

555   32. Murphy, C.W., Kendall, A., 2013. Life cycle inventory development for corn and

556   stover production systems under different allocation methods, Biomass Bioenergy. 58,

557   67-75.

558   33. Nemecek, T., Kägi, T., Blaser, S., 2007. Life cycle inventories of agricultural

559   production systems, Final report ecoinvent v2.0 No. 15.

560   34. Peng, J., Chen, P., Lou, H., Zheng, X., 2009. Catalytic upgrading of bio-oil by

561   HZSM-5 in sub-and super-critical ethanol, Bioresour. Technol. 100, 3415-3418.

562   35. Peters, J.F., Iribarren, D., Dufour, J., 2015. Simulation and life cycle assessment of

563   biofuel production via fast pyrolysis and hydroupgrading, Fuel. 139, 441-456.

564   36. Pham, T.N., Sooknoi, T., Crossley, S.P., Resasco, D.E., 2013. Ketonization of

565   carboxylic acids: mechanisms, catalysts, and implications for biomass conversion,

566   ACS Catalysis. 3, 2456-2473.

567   37. Pham, T.N., Shi, D., Resasco, D.E., 2014. Evaluating strategies for catalytic

568   upgrading of pyrolysis oil in liquid phase, Applied Catalysis B: Environmental. 145,

569   10-23.

570   38. Pham, T.N., Shi, D., Sooknoi, T., Resasco, D.E., 2012. Aqueous-phase ketonization

571   of acetic acid over Ru/TiO 2/carbon catalysts, Journal of Catalysis. 295, 169-178.

572   39. Ringer, M., Putsche, V., Scahill, J., 2006. Large-Scale Pyrolysis Oil, Assessment.

573   National Renewable Energy Laboratory. Colorado. NREL/TP-510-37779.

574   40. Sayles, S., Romero, S., 2011. Comparison of thermal cracking and hydrocracking

575   yield distributions, Digital Refining.

576   41. Snell, R.W., Hakim, S.H., Dumesic, J.A., Shanks, B.H., 2013. Catalysis with ceria

577   nanocrystals: Bio-oil model compound ketonization, Applied Catalysis A: General.

578   464, 288-295.

579   42. Snowden-Swan, L.J., Male, J.L., 2012. Summary of Fast Pyrolysis and Upgrading

580   GHG Analyses. Pacific Northwest National Laboratory (PNNL), Richland, WA (US).

581   PNNL-22175.

582   43. Snowden-Swan, L.J., Spies, K.A., Lee, G., Zhu, Y., 2016. Life cycle greenhouse gas

583   emissions analysis of catalysts for hydrotreating of fast pyrolysis bio-oil, Biomass

584   Bioenergy. 86, 136-145.

585   44. Wang, H., Male, J., Wang, Y., 2013. Recent advances in hydrotreating of pyrolysis

586   bio-oil and its oxygen-containing model compounds, ACS Catalysis. 3, 1047-1070.

587   45. Weng, Y., Qiu, S., Ma, L., Liu, Q., Ding, M., Zhang, Q., Zhang, Q., Wang, T., 2015.

588   Jet-Fuel Range Hydrocarbons from Biomass-Derived Sorbitol over Ni-HZSM-

589   5/SBA-15 Catalyst, Catalysts. 5, 2147-2160.

590   46. Wildschut, J., Melián-Cabrera, I., Heeres, H., 2010. Catalyst studies on the

591   hydrotreatment of fast pyrolysis oil, Applied Catalysis B: Environmental. 99, 298-

592   306.

593   47. Wildschut, J., 2009. Pyrolysis oil upgrading to transportation fuels by catalytic

594   hydrotreatment. University Library Groningen.

595   48. Wildschut, J., Mahfud, F.H., Venderbosch, R.H., Heeres, H.J., 2009. Hydrotreatment

596   of fast pyrolysis oil using heterogeneous noble-metal catalysts, Ind Eng Chem Res.

597   48, 10324-10334.

598   49. Wright, M.M., Daugaard, D.E., Satrio, J.A., Brown, R.C., 2010. Techno-economic

599   analysis of biomass fast pyrolysis to transportation fuels, Fuel. 89, S2-S10.

50. Zan, C.S., Fyles, J.W., Girouard, P., Samson, R.A., 2001. Carbon sequestration in perennial bioenergy, annual corn and uncultivated systems in southern Quebec, Agric. , Ecosyst. Environ. 86, 135-144.

51. Zhang, Q., Chang, J., Wang, T., Xu, Y., 2007. Review of biomass pyrolysis oil properties and upgrading research, Energy conversion and management. 48, 87-92.

52. Zhang, Q., Zhang, L., Wang, T., Xu, Y., Zhang, Q., Ma, L., He, M., Li, K., 2014. Upgrading of bio-oil by removing carboxylic acids in supercritical ethanol, Energy Procedia. 61, 1033-1036.

53. Zhang, Y., 2014. Development of integrated assessment platform for biofuels production via fast pyrolysis and upgrading pathway.

54. Zheng, X., Chang, J., Fu, Y., 2015. Catalytic Hydrotreatment of Light Distillates Obtained from Bio-Oil for Use in Oxygenated Liquid Fuels, BioResources. 10, 4854-4866.

Figure 1

Figure 2

Figure 3

Figure 4

(a)   ◆ GWP   ■ EP   (b)   ◆ GWP   ■ ADP fossil
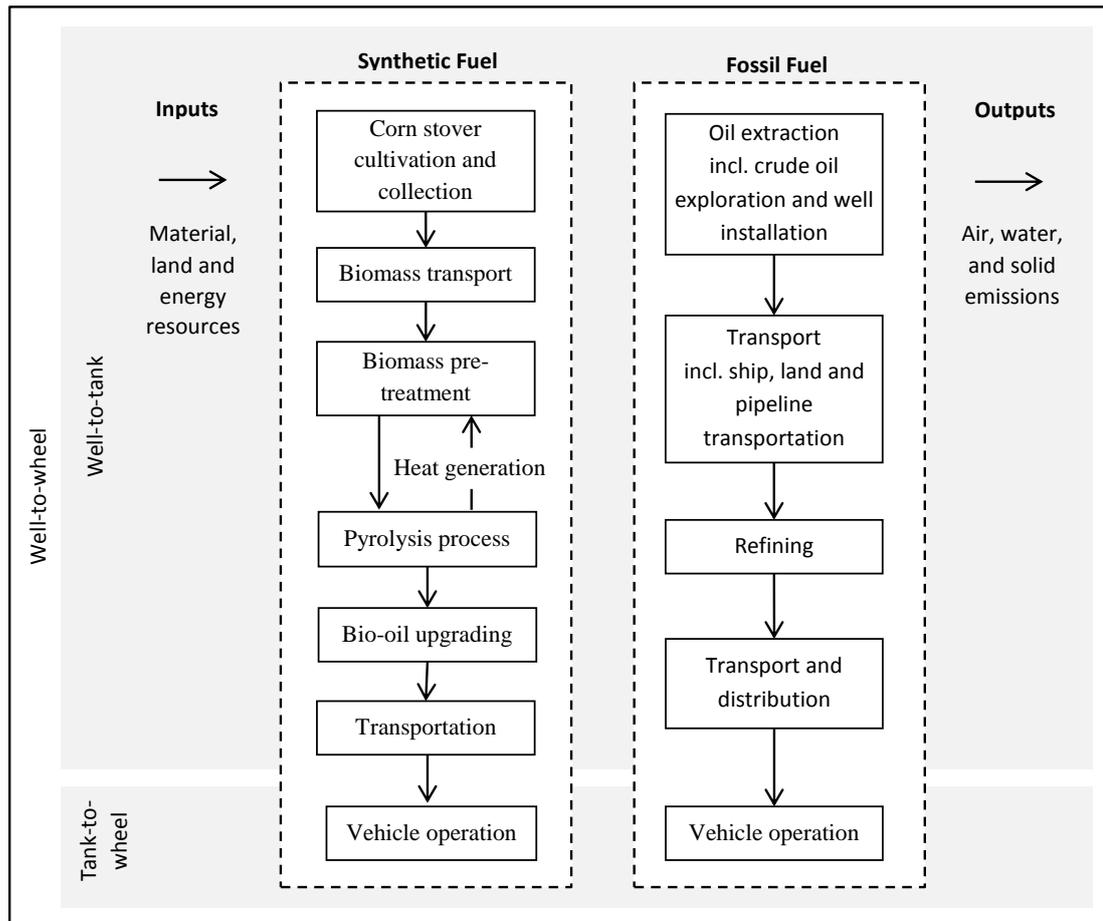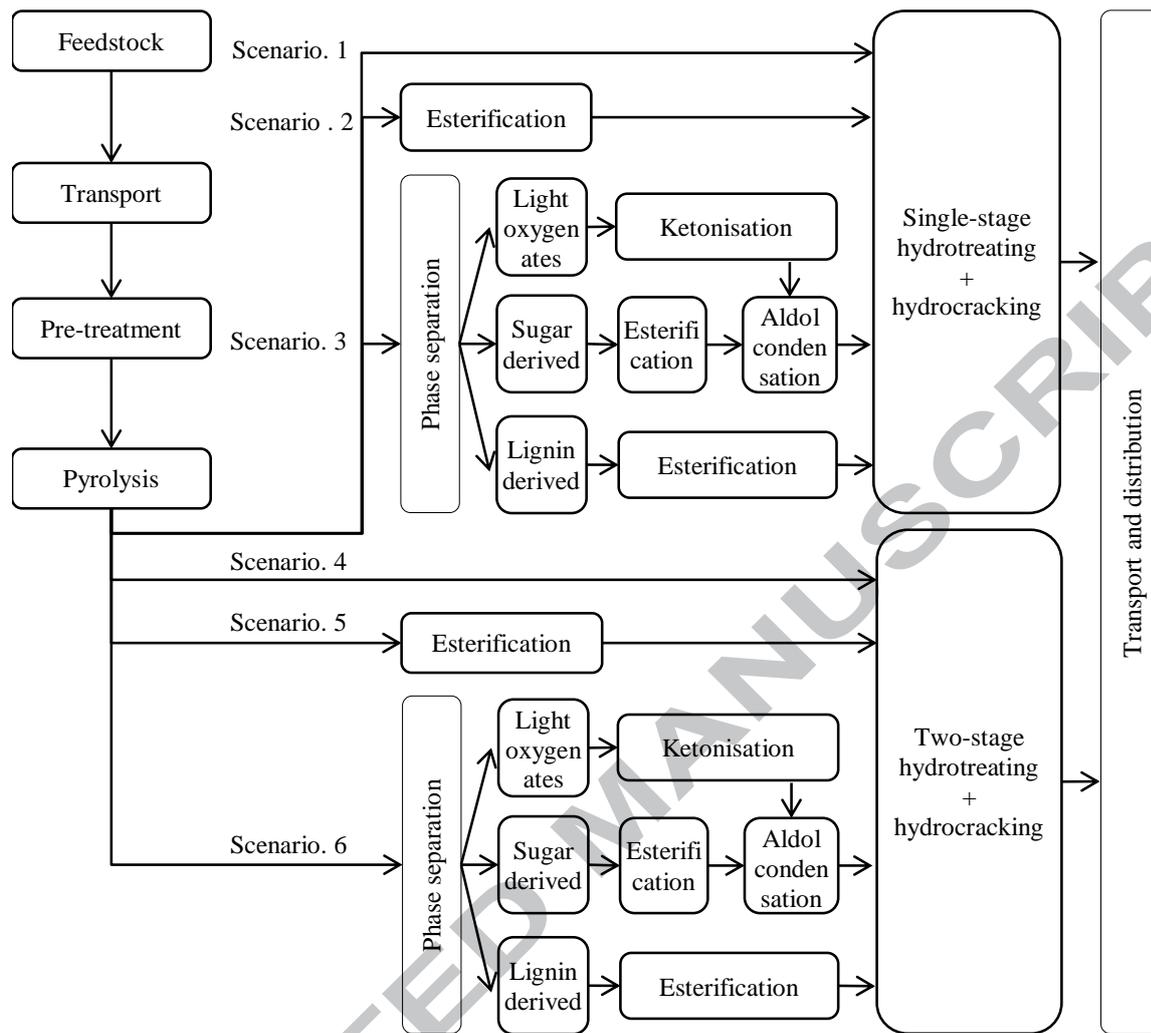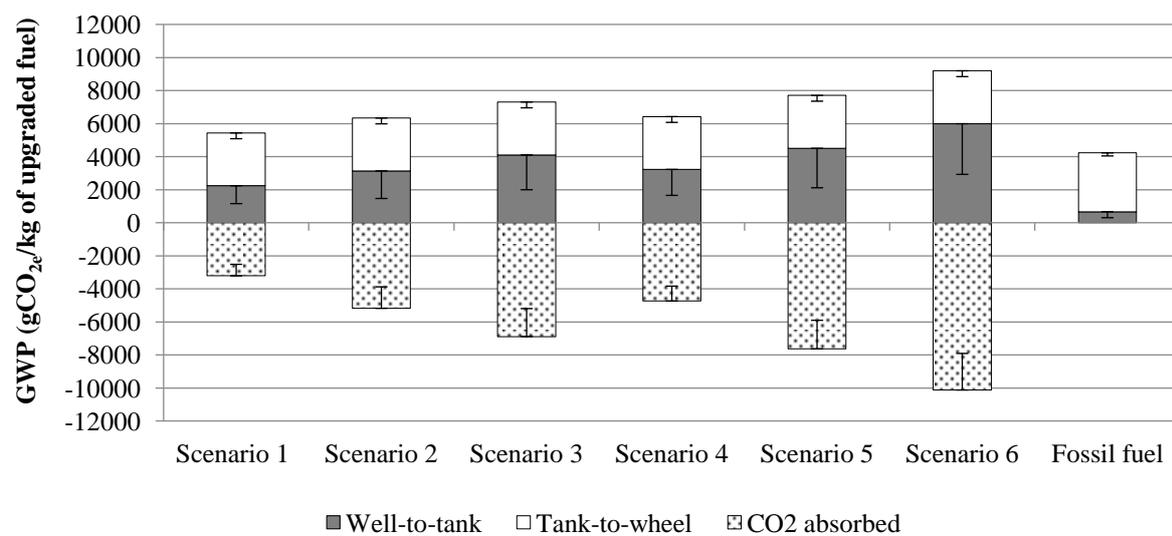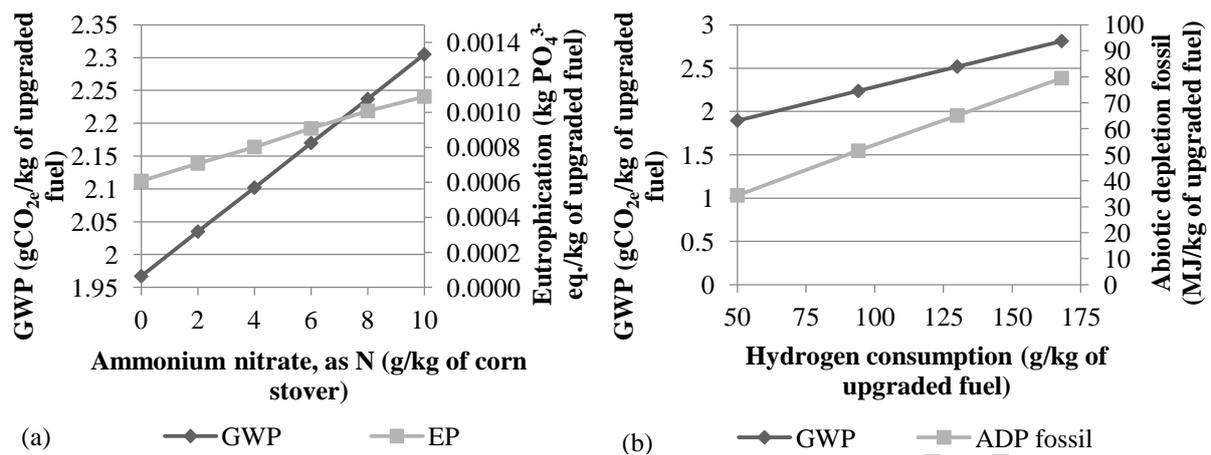
Upgrading scenario	Summary
1. Hydrotreating and hydrocracking	The minimum amount of processing required to obtain a transportation fuel; however, oxygen content is high.
2. Esterification, hydrotreating and hydrocracking	Using esterification prior to hydrotreating and hydrocracking can improve stability and reduce catalytic deactivation and acidification.
3. Esterification, ketonisation, hydrotreating and hydrocracking	Esterification and ketonisation improve stability and neutralise carboxylic acids.
4. Two-stage hydrotreating and hydrocracking	Two-stage hydrotreating can further reduce bio-oil oxygen content.
5. Esterification, two-stage hydrotreating and hydrocracking	Reducing acidity and improving stability of a bio-oil prior to hydrotreating will improve reliability and potentially reduce hydrogen consumption.
6. Esterification, ketonisation, two-stage hydrotreating and hydrocracking	The most comprehensive combination of upgrading processes to produce a stable biofuel with a low oxygen and acidic component content.

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Feedstock cultivation and collection	Min	Expected	Max	Unit	Ref.
Fossil energy	0.22	0.53	0.83	MJ/kg of corn stover	[8, 32]
Ammonium nitrate phosphate, as P_2O_5	-	2	-	g/kg of corn stover	[32, 33]
Potassium chloride, as K_2O	-	14.5	-	g/kg of corn stover	[32, 33]
Ammonium nitrate, as N	-	8	-	g/kg of corn stover	[32, 33]
Biomass transportation	**Min**	**Expected**	**Max**	**Unit**	
Diesel	0.05	0.075	0.1	MJ/kg of delivered corn stover	[13]
Pre-treatment	**Min**	**Expected**	**Max**	**Unit**	
Electricity for grinding	0.011	0.034	0.057	kWh/kg of pre-treated corn stover	[27, 53]
Steam from natural gas boiler	0	0	0.085	kg/kg of pre-treated corn stover	[53]
Prepared feedstock yield	-	82	-	%	[8, 49]
Pyrolysis process	**Min**	**Expected**	**Max**	**Unit**	
Electricity	0.14	0.417	0.487	kWh/kg of produced bio-oil	[8, 53]
Pyrolysis oil yield	62	75	80	%	[5, 8, 17]
Esterification	**Min**	**Expected**	**Max**	**Unit**	
Electricity	0.027	0.061	0.095	kWh/kg of raw bio-oil	-
Sulphuric acid	-	2	-	wt%	[1]
Ethanol	1	2	3	kg/kg of raw bio-oil	[1]
Biofuel yield	55	62	65	%	[1, 34]
Ketonisation	**Min**	**Expected**	**Max**	**Unit**	
Electricity	-	0.25	-	kWh/kg of light oxygenates	-
$Ru/TiO_2/C$ Catalyst	-	5	-	wt%	[38]
Acetone yield	-	46	-	%	[38]
Hydroprocessing	**Min**	**Expected**	**Max**	**Units**	
Single-stage HT hydrogen consumption	69	74	128	g/kg of HT biofuel	[8, 11]
Ru/C Catalyst (first-stage)	0.1	0.2	0.3	g/kg of HT biofuel	[47]
Single-stage HT yield of 18-27 wt% deoxygenated biofuel	36	56	67	%	[6, 18, 47, 49]
Two-stage HT hydrogen consumption	58	69	112	g/kg of HT biofuel	[22, 23]
Pt/C/ Pd/C Catalyst (second-stage)	0.1	0.2	0.3	g/kg of HT biofuel	[46, 48]
Two-stage HT yield of 2-11 wt% deoxygenated biofuel	30	38	44	%	[22, 54]
HC hydrogen consumption	15	20	40	g/kg of HC biofuel	[24]
Zeolite powder for HC	3	5	5	wt%	[45]
HC biofuel yield	-	0.75	-	kg/kg of HC biofuel	[40]
Total electricity for hydroprocessing	0.088	0.16	0.23	kWh/kg of biofuel	[8, 20, 53]
Fuel transportation	**Min**	**Expected**	**Max**	**Unit**	
Diesel	0.1	0.15	0.2	MJ/kg of delivered biofuel	[13]

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Impact Categories	Scenario 1		Scenario 2		Scenario 3		Scenario 4		Scenario 5		Scenario 6		Diesel
	Min	Exp.	Min	Exp.	Min	Exp.	Min	Exp.	Min	Exp.	Min	Exp.	
Acidification Potential (kg SO_2 eq.)	2.80E-03	4.95E-03	4.88E-03	9.78E-03	1.20E-02	1.80E-02	4.04E-03	7.18E-03	7.22E-03	1.40E-02	1.70E-02	2.70E-02	5.82E-03
Eutrophication Potential (kg PO_4^{3-} eq.)	6.18E-04	1.01E-03	1.26E-03	2.61E-03	1.84E-03	3.34E-03	9.16E-04	1.47E-03	1.90E-03	3.57E-03	2.78E-03	4.91E-03	1.67E-03
Ozone layer depletion potential (kg R11 eq.) [a]	1.91E-08	2.70E-08	4.17E-08	7.56E-08	6.01E-08	9.58E-08	2.91E-08	3.99E-08	6.35E-08	1.03E-07	9.24E-08	1.41E-07	6.90E-07
Abiotic depletion element (kg Sb eq.)	1.68E-06	2.65E-06	2.87E-06	5.00E-06	4.78E-06	7.51E-06	2.52E-06	3.90E-06	4.33E-06	7.15E-06	7.25E-06	1.10E-05	4.74E-07
Abiotic depletion fossil (MJ)	3.26E+01	5.16E+01	3.73E+01	6.52E+01	4.14E+01	7.41E+01	4.44E+01	7.31E+01	5.15E+01	9.25E+01	5.77E+01	1.07E+02	5.36E+01
Freshwater aquatic ecotoxicity potential (kg DCB eq.) [b]	6.20E-02	9.50E-02	1.24E-01	2.39E-01	2.15E-01	3.45E-01	9.30E-02	1.40E-01	1.89E-01	3.28E-01	3.27E-01	5.09E-01	8.60E-02
Human toxicity Potential (kg DCB eq.)	1.81E-01	2.75E-01	3.15E-01	5.51E-01	4.37E-01	7.10E-01	2.70E-01	4.03E-01	4.75E-01	7.79E-01	6.61E-01	1.04E+00	2.71E-01
Marine aquatic ecotoxicity potential (kg DCB eq.)	2.27E+02	3.96E+02	4.11E+02	8.46E+02	6.09E+02	1.01E+03	3.43E+02	5.82E+02	6.23E+02	1.15E+03	9.24E+02	1.60E+03	2.79E+02
Photochemical oxidant creation potential (kg C_2H_4 eq.)	2.01E-04	3.45E-04	3.01E-04	5.87E-04	7.51E-04	1.16E-03	2.97E-04	5.06E-04	4.46E-04	8.34E-04	1.012E-03	1.71E-03	5.72E-04
Terrestric ecotoxicity potential (kg DCB eq.)	2.55E-03	3.92E-03	5.16E-03	9.98E-03	7.02E-03	1.20E-02	3.87E-03	5.75E-03	7.84E-03	1.40E-02	1.10E-02	1.80E-02	3.43E-03

620   [a] Trichlorofluoromethane equivalent (R11 eq.)

621   [b] Dichlorobenzene equivalent (DCB eq.)

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623   Highlights

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625   •   The environmental impacts of six different bio-oil upgrading scenarios are analysed
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627   •   Expected, optimistic, and pessimistic values are evaluated
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629   • CO_2 equivalent emissions are expected to range from 2240–6000 gCO_{2e}/kg of biofuel
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631   •   A worst-case scenario leads to CO_{2e} emissions tripling in comparison to fossil fuel
632